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U.S. GEOLOGICAL SURVEY

Analytical methods manual for the Mineral Resource Surveys Program

U.S. Geological Survey

by

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Table of Contents

Page

Introduction vi

Branch Safety Policy vi

Analytical Method Format vii

Method Validation vii

Definition of Terms viii

- Limit of Detection viii
- Limit of Quantitation viii
- Lower Reporting Limit viii

Analytical Performance Summary viii

- Reference Materials ix
- Duplicate Samples ix
- Method Blank x

Acknowledgments xi

References Cited xi

Analytical Methods

- Rock sample preparation 2
- Stream-sediment sample preparation 7
- Soil sample preparation 11
- Heavy-mineral concentrate preparation by heavy liquid and magnetic separation 15
- Plant material preparation and determination of weight percent ash 20
- Arsenic, antimony, and selenium by flow injection or continuous flow-hydride generation-atomic absorption spectrometry 24
- Gold by flame or graphite furnace atomic absorption spectrometry 31
- Tellurium and thallium by flame atomic absorption spectrometry 37
- Mercury in water, geologic, and plant materials by continuous flow-cold vapor-atomic absorption spectrometry 42
- Mercury in whole coal and biological tissue by continuous flow-cold vapor-atomic absorption spectrometry 51
- Cadmium and silver by flame atomic absorption spectrometry 56
- Carbonate carbon by coulometric titration 60
- Moisture and total water in silicate rocks 67
- Forty elements by inductively coupled plasma-atomic emission spectrometry 77

Twenty-four elements in natural and acid mine waters by inductively coupled plasma-atomic emission spectrometry ... 95
Organometallic halide extraction for 10 elements by inductively coupled plasma-atomic emission spectrometry ... 102
Coal ash by inductively coupled plasma-atomic emission spectrometry and inductively coupled plasma-mass spectrometry ... 109
Niobium, tungsten, and molybdenum by ion exchange/inductively coupled plasma-atomic emission spectrometry ... 126
Direct-current arc emission spectrographic method for the semiquantitative analysis of geologic materials ... 130
Flame photometric determination of K_2O and Na_2O ... 144
Fluoride, chloride, nitrate, and sulfate in aqueous solution by chemically suppressed ion chromatography ... 149
Chlorine in coal by ion chromatography ... 154
Platinum group elements by nickel sulfide fire assay separation and inductively coupled plasma-mass spectrometry ... 158
Rare earth elements by inductively coupled plasma-mass spectrometry ... 166
Total carbon by combustion ... 173
Total sulfur by combustion ... 177
Acid-soluble sulfate, sulfide, and organic sulfur ... 182
Carbon, hydrogen, and nitrogen by a CHN elemental analyzer ... 186
Chloride by ion-selective electrode following $KMnO_4$-H_2SO_4-HF dissolution ... 191
Fluoride in silicates by ion-selective electrode following $LiBO_2$ fusion and HNO_3 dissolution ... 195
Ferrous oxide by potentiometric titration ... 200
Uranium and thorium by delayed neutron counting ... 206
Instrumental neutron activation by abbreviated count ... 211
Instrumental neutron activation by long count ... 218
Twelve selected trace elements by energy-dispersive X-ray fluorescence spectrometry ... 228
Major element analysis by wavelength dispersive X-ray fluorescence spectrometry ... 236

Illustration

Figure 1. The flow-through cell used for the determination of mercury ... 48
Figure 2. Phase separator used in the determination of mercury ... 49
Figure 3. Manifold used for the automated generation of mercury vapor ... 50

Tables

Table 1. Operating conditions for determination of As, Sb, and Se by HG-AAS ... 28
Table 2. Analytical performance summary for As, Sb, and Se by HG-AAS ... 28

Table 3. Operating conditions for determination of Au by FAAS 33

Table 4. Operating conditions for determination of Au by GFAAS 34

Table 5. Analytical performance summary for Au by FAAS 35

Table 6. Analytical performance summary for Au by GFAAS 35

Table 7. Operating conditions for determination of Te and Tl by FAAS 39

Table 8. Analytical performance summary for Te and Tl by FAAS........ 40

Table 9. Operating conditions for determination of Hg by CV-AAS........ 45

Table 10. Analytical performance summary for Hg by CV-AAS........ 46

Table 11. Operating conditions for determination of Hg in coal and biological tissue by CV-AAS...... 54

Table 12. Analytical performance summary for Hg in coal and biological tissue by CV-AAS 54

Table 13. Operating conditions for determination of Cd and Ag by FAAS........ 58

Table 14. Analytical performance summary for Cd and Ag by FAAS 58

Table 15. Analytical performance summary for carbonate carbon as CO_2 65

Table 16. Analytical performance summary for moisture and essential water 75

Table 17. Reporting limits for 40 elements by ICP-AES........ 78

Table 18. Operating conditions for determination of 40 elements by ICP-AES........ 80

Table 19. Analytical performance summary for 40 elements by ICP-AES 81

Table 20. ICP-AES elements, wavelengths, and operating ranges for natural and mine waters 96

Table 21. Operating conditions for determination of 24 elements in waters by ICP-AES 97

Table 22. Analytical performance summary for 24 elements in waters by ICP-AES 98

Table 23. Wavelength and operating range for 10 elements by ICP-AES........ 103

Table 24. Operating conditions for determination of 10 elements by ICP-AES........ 105

Table 25. Analytical performance summary for 10 elements by ICP-AES 105

Table 26. Reporting limits, wavelengths, and decomposition technique for coal ash samples by ICP-AES 110

Table 27. Reporting limits, mass, and decomposition technique for coal ash samples by ICP-MS 111

Table 28. Operating conditions for coal ash determinations by ICP-AES........ 113

Table 29. Operating conditions for coal ash determinations by ICP-MS........ 113

Table 30. Analytical performance summary for elements in coal ash by ICP-AES 115

Table 31. Analytical performance summary for elements in coal ash by ICP-MS........ 120

Table 32. Operating conditions for determination of Nb, W, and Mo by ion exchange/ICP-AES 128

Table 33. Analytical performance summary for Nb, W, and Mo by ion exchange/ICP-AES 129

Table 34. Visual reporting limits for elements determined by the dc arc emission spectrographic method based on a 10-mg sample 130

Table 35. Concentrations of elements in F-3 standards........ 134

Table 36. Concentrations of elements in F-4 standards 135
Table 37. Dilution factor for the base mixtures to yield standard concentrations 135
Table 38. Analytical performance summary of the dc-arc emission spectrographic method 136
Table 39. Analytical performance summary for K_2O and Na_2O by FES 147
Table 40. Operating conditions for determination of selected anions by IC 151
Table 41. Calibration standards for IC using 10 µs scale 151
Table 42. Analytical performance summary for selected anions by IC 152
Table 43. Operating conditions for determination of chlorine in coal by IC 156
Table 44. Analytical performance summary for chlorine in coal by IC 157
Table 45. Problem elements during fusion and digestion of PGE 159
Table 46. Operating conditions for determination of PGE by ICP-MS 162
Table 47. Standard concentrations, dwell times, and masses measured for PGE 162
Table 48. Analytical performance summary for PGE 163
Table 49. Operating conditions for determination of REE by ICP-MS 168
Table 50. Standard concentrations, dwell times, and masses measured for REE 168
Table 51. Analytical performance summary for REE 169
Table 52. Analytical performance summary for total carbon 176
Table 53. Analytical performance summary for total sulfur 180
Table 54. Analytical performance summary for forms of sulfur 184
Table 55. Analytical performance summary for carbon, hydrogen, and nitrogen 189
Table 56. Analytical performance summary for chloride by ISE 194
Table 57. Analytical performance summary for fluoride by ISE 198
Table 58. Weight of potassium dichromate required for water temperature 202
Table 59. Analytical performance summary for FeO 204
Table 60. Analytical performance summary for U and Th by DN 209
Table 61. Analytical performance summary for elements by INAA abbreviated count 213
Table 62. Analytical performance summary for elements by INAA long count 221
Table 63. Lower limit of detection and upper limit of calibration curve for the EDXRF method 229
Table 64. Operating conditions for determination of elements by EDXRF 230
Table 65. Calibration standards used in the EDXRF method 231
Table 66. Analytical performance summary for elements by EDXRF 231
Table 67. Operating conditions for determination of elements by WDXRF 238
Table 68. Analytical performance summary for elements by WDXRF 239

Appendices

Appendix A. Conversion Factors and Equivalents Tables

Table A1. Element to oxide conversion factors 243
Table A2. Weight to ppm to ppb equivalents 243
Table A3. Grain size and sieve equivalents 244
Appendix B. Glossary of Symbols and Terms 245

INTRODUCTION

The analytical methods validated by the Mineral Resource Surveys Program, Geologic Division, is the subject of this manual. This edition replaces the methods portion of Open-File Report 90-668 published in 1990. Newer methods may be used which have been approved by the quality assurance (QA) project and are on file with the QA coordinator.

This manual is intended primarily for use by laboratory scientists; this manual can also assist laboratory users to evaluate the data they receive. The analytical methods are written in a step by step approach so that they may be used as a training tool and provide detailed documentation of the procedures for quality assurance. A "Catalog of Services" is available for customer (submitter) use with brief listings of:

the element(s)/species determined,
method of determination,
reference to cite,
contact person,
summary of the technique,
and analyte concentration range.

For a copy please contact the Branch office at (303) 236-1800 or fax (303) 236-3200.

BRANCH SAFETY POLICY[1]

Due to potentially high hazardous work areas, laboratory safety and health is a top priority. All federal, state, and local regulations concerning worker and community safety are to be strictly followed. Included in this policy is the propagation and distribution of Chemical Hygiene Plans (*CHP*) and Material Safety Data Sheets (*MSDS*) for every laboratory procedure that involves hazardous or toxic chemicals. These regulations affect Branch management, personnel, facilities, and activities. If violated, some of these regulations carry financial and criminal penalties.

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[1] Sutley, 1994

ANALYTICAL METHOD FORMAT

The written analytical method is to reflect the procedure actually being used in the laboratory. Routine methods are written in the following standard format:

TITLE—contains the name(s) of the analyte and the measurement method

PRINCIPLE—brief discussion of the scientific basis

INTERFERENCE—sample matrices, or element concentrations, which may cause chemical, physical, or spectral interferences

SCOPE—the range of analyte concentration and applicable sample matrices for which the method is useful, and an estimate of time required for analysis

APPARATUS—instruments and special equipment required

REAGENTS—chemical name, chemical symbol, purity, method of preparation, and shelf life if stability is a problem

SAFETY PRECAUTIONS—hazards peculiar to the method of analysis and handling procedures

PROCEDURE—describes a strict time sequence and the critical steps in the analysis

CALCULATION—equation(s) necessary to calculate the results of the analysis

ASSIGNMENT OF UNCERTAINTY—statistical summary table of the historical analytical results for selected reference materials, duplicate samples, and method blank. For a detailed discussion please refer to the *Analytical Performance Summary* section.

BIBLIOGRAPHY—references to the literature on which the method is based

METHOD VALIDATION

Before any method is approved to generate analytical data under the QA program, the method is assigned a unique code and must be validated. If a method is provisional, two dashes (--) are entered for the approval date. Method validation includes:

1. A copy of the analytical method in standard written format
2. Research report of analytical data from testing the proposed method using reference materials, duplicate samples, and method blanks
3. Quality assurance review
4. Research section review
5. Operations section review

DEFINITION OF TERMS

Limit of Detection

The limit of detection (LOD) must refer to the entire analytical measurement process and is usually regarded as the lowest concentration level of the analyte that can be determined to be statistically different from the analytical blank.

According to the American Chemical Society (ACS, 1980) a confidence level of 3 sigma above the measured average blank is considered minimum since this implies the risk for 7 percent false positives (concluding the analyte is present when it is absent) and false negatives (the reverse). The 3 sigma value actually corresponds to a confidence level of about 90 percent as "a 99.6 percent confidence level applies only for a strictly one-sided Gaussian distribution. At low concentrations, non-Gaussian distributions are more likely" (International Union of Pure and Applied Chemistry, 1978).

Limit of Quantitation

Ten sigma above the average blank is often suggested for the limit of quantitation (LOQ) or limit of determination. This is the lower limit for quantitative measurements (as opposed to qualitative measurements) and at this level the risk of false positives and negatives is decreased.

Lower Reporting Limit

The term "lower reporting limit" is used in this report for concentrations expected to be at or above five times the standard deviation determined from the method blank or low analyte concentration samples. Given the varied matrices submitted to the laboratory and diverse data quality needs, method-blank and reference material results are included in the analytical performance summary table to assist in appropriate use of laboratory data.

All submitted samples are initially run undiluted unless sample dilutions are required in order to reduce or eliminate known matrix/interference effects. When an analyte concentration exceeds the calibration or linear range, the sample is re-analyzed after appropriate dilution. The analyst will use the least dilution necessary to bring the analyte within range. In both cases, a loss of sensitivity is experienced. All sample dilutions result in an increase in the lower reporting limit by a factor equal to the dilution.

Assuming independent normally distributed measurements, confidence limits may be assigned from the mean and standard deviation (based on a relatively large number of observations, or by use of a significance test). "In order to detect bias equal in magnitude to the standard deviation, one needs at least 12 degrees of freedom (13 replicates)" (Currie, 1988).

ANALYTICAL PERFORMANCE SUMMARY

A table is included under the *Assignment of uncertainty* section in each method write-up and provides an estimate of the analytical method performance. The results of the analytical measurement process are estimates of general performance only, given the sample matrix and analyte concentration. Outliers are not rejected unless reasons are known why the results are unacceptable. Calculated results (i.e. percent recovery) may not appear to match initial numbers due to rounding-off.

The analytical performance summary table is arranged in three sections: (1) reference materials, (2) duplicates, and (3) method blank results.

Reference Materials

Reference material (RM) samples are materials having one or more well established or certified concentrations or physical properties to be used for instrument calibration, method accuracy, or testing. The RM is used for evaluation of the analytical method bias expressed as percent recovery (% R). An attempt is made to test methods (if appropriate reference material is available) at the lower, mid-point, and upper end of the operating range with a number of varied matrices. Solid phase samples are reported on an as received basis. No corrections are made for moisture content unless noted in the method.

The first section of the table lists selected reference materials tested and associated results in rows. The table has column headings as follows:

REFERENCE—sample name of the geochemical reference material

DESCRIPTION—identification of the reference material

n—number of observed measurements or samples in a subgroup

Mean—arithmetic mean. Generally, the result is quoted with all digits which are certain, plus the first uncertain one. In order to compare some laboratory to proposed values and avoid the loss of information, whole numbers may not appear rounded-off. Less than symbol, "<" is used for qualified data below the lower reporting limit

s—standard deviation

pv—proposed value taken from the published reference material compositions of Potts and others (1992). Where the proposed value has an accompanying upper case letter, the corresponding reference is in the headnote. According to Potts the tabulated data are distinguished by:

> **bold typeface** indicates precision better than 10 percent relative (two sigma), normally based on five or more results from two or more independent techniques
>
> certified value from the distributor of reference materials is designated *"cv"*
>
> plain typeface indicates other compiled data; distinguished by a question mark if there is additional uncertainty (for example, fewer than 3 reported results, large disparity in reported results, and/or data derived from only one non-definitive technique)
>
> *italic typeface* indicates data abstracted from individual schemes of analysis fully described in the literature

%RSD—percent relative standard deviation

%R—percent recovery

Duplicate Samples

Duplicate samples are a second aliquot of a submitted sample (taken at the time of sample weighing) selected to evaluate laboratory variance (precision) expressed as percent relative standard deviation (% RSD). The aliquot is treated the same as the original sample through the analytical process. Duplicate samples take into account the analyte concentration and matrix of the sample of interest, i.e. samples submitted by ACSG customers.

The second section of the table deals with duplicate samples. The column headings are as follows:

k—number of subgroups under consideration

n—2, number of samples in the subgroup

Mean—arithmetic mean for duplicate measurements

s—standard deviation for duplicate measurements

%RSD—relative standard deviation

Concentration Range—the minimum and maximum values reported of unqualified data (data that are greater than the lower reporting limit)

No. of "<" (total)—the number of values less than the lower reporting limit

No. of "<" (pairs)—the number of times the duplicates were both reported as less than values

Method Blank

A method blank contains deionized water or other solutions processed through the entire analytical method with submitted samples. It is used as an indicator of possible contamination due to reagents or apparatus and sensitivity of the analytical method. The variability (standard deviation) of the method blank can be used for estimating the lower limits of detection or determination. Pure solutions, however, assume no matrix effects and tend to be normally distributed. In reality, matrix effects occur even in methods considered to be relatively free from interferences.

The last section of the table lists the results for the method blank. The column headings are as follows:

n—number of observed measurements on completely independently prepared blanks

Mean—arithmetic mean

s—standard deviation

3s—three times the standard deviation (limit of detection)

5s—five times the standard deviation (lower reporting limit)

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Sutley, S.J., January 1994, Branch of Geochemistry, Written communication to the editor: U.S. Geological Survey, Denver, Colo.

Analytical Methods

Rock sample preparation

By Cliff D. Taylor and Peter M. Theodorakos

Code: Q010

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Principle

Most samples of naturally occurring material require some kind of physical preparation prior to chemical analysis. Samples require preparation to effect one or more of the following: (1) reduce the sample to a size that is more conveniently transported; (2) increase the sample surface area to enhance the efficiency of subsequent chemical attack; (3) homogenize the sample to ensure that a subsample is representative of the entire sample; and (4) separate the sample into components based on mineralogy, grain size, or physical and morphological criteria. Sample preparation is an important step in the analytical process. Without careful preparation, and attention to inter-sample contamination, the worth of the subsequent analyses is significantly diminished.

Rock samples are reduced to ½-cm fragments in a jaw crusher. The crushed sample is split, if necessary, and fed into an operating and properly adjusted Braun vertical pulverizer equipped with ceramic plates. The sample is pulverized to approximately minus 100-mesh (<150 µm) and mixed to insure homogeneity for subsequent analysis. Mineral samples with distinctive cleavage planes (i.e. mica flakes) can present a problem in pulverizing due to the crystal structure of the sample. In some methods where the quality of pulverization is critical in obtaining accurate results, shatterboxing the sample is required. The sample is placed in either a ceramic or agate shatterbox and ground until 100 percent passes a 100-mesh screen.

Scope

Approximately 50 samples can be processed per day.

Apparatus

- Sample cartons, 3-oz (1⅞" x 2½ ")
- Large sample funnel, plastic
- Compressed-air source, dry air, 40 psi
- Core splitter, if available
- Rock hammer
- Flexible hand pad, 6" x 4" x 1" (15 cm x 10 cm x 2.5 cm)
- Steel plate, approximately 8" x 8" x 1" (20 cm x 20 cm x 2.5 cm)
- "Chipmunk" jaw crusher
- Knife
- Brush, automotive parts cleaning, stiff bristle
- Brush, wire
- Vertical pulverizer with ceramic plates, catch pan, and cover plate
- Silicon carbide, approximately 60- to 80-mesh (250 µm to 180 µm)
- Jones splitter, with ½" riffles (1.25 cm)
- Tube-type revolving mixer, with tube diameter to accommodate sample cartons

- Rectangular aluminum pans to fit under Jones splitter, to serve as catch pans for the crusher, and to hold the samples during various stages of processing
- Grease gun for lubricating equipment
- Kimwipes or paper towels
- Assortment of tools for equipment maintenance

Safety precautions

Eye and ear protection and a dust mask must be worn and it is recommended that a lab coat be worn. Caution must be exercised in operating the equipment, particularly the jaw crusher and the Braun pulverizer, which have the potential of inflicting serious injury if not properly and carefully used. Keep your hands, hair, and clothing away from any moving machinery parts. Remove all jewelry before you begin work. Belts on equipment must be guarded to prevent catching clothing, hands, hair, etc. Power should be turned off prior to dislodging any jammed material from the equipment with a push stick. Power should likewise be turned off prior to making adjustments to the equipment, except when adjusting the grinding plates of the pulverizer. Rock particles and fragments ejected from the crusher and grinder can cause injury, operate grinder behind safety shield. Compressed air, used to clean the equipment and work area, presents a safety hazard, especially to the eyes. Particles of debris propelled by the high velocity air stream present an additional hazard. The compressed-air stream should never be directed toward the face. A fan or hood exhaust should be used to vent dust. See the *CHP* for further information.

Preliminary procedure

Check the Request for Analysis form (RFA) for notes on mineralogy of samples, requests for preparation that vary from standard procedure, and disposition of excess sample.

Verify that the number of samples received and the field numbers on the sample collection/transport bags correspond to the number of samples and field numbers listed on the RFA. If they do not correspond, contact Sample Control.

Properly label the correct number of sample cartons with the laboratory number assigned to each sample. Label both the container tops and sides using permanent ink markers, or premade labels. Affix premade labels to the tops and side of the cartons with clean transparent tape.

Place the labeled sample containers in a cardboard tray labeled with the required information: (1) assigned job number, (2) submitter's last name, and (3) number of samples in the job.

Procedure

Check to see sample-size of chips produced by jaw crusher is adequate. If not, adjustments to the jaw crusher are made by varying the number of metal shims inserted behind the stationary jaw plate. Increasing the number of shims reduces the crushed rock fragment size. The spacing between the sides of the movable jaw and the cheek plates can also be varied with metal shims inserted between the cheek plates and the body of the crusher.

Open the sample bag and place the sample into a loaf pan in preparation for crushing and splitting. Using a core splitter or a rock hammer and steel plate, break all large pieces down to approximately 2½" x 2", a size that readily fits into the crusher. Clean the core splitter, hammer, and plate with a wire brush and compressed air prior to use and between samples.

Place a second loaf pan under the jaws of the crusher to catch the crushed sample and begin feeding the sample into the jaws. Do not overload the jaws. Overloading may cause the crusher to bind. Hold the 6" x 4" x ½" hand pad over the mouth of the crusher to prevent rock chips from flying out of the jaws. Crush the entire sample, using more than one loaf pan if necessary.

Turn the power to the crusher off and thoroughly clean the crusher mouth, jaws, and cheek plates by alternately scrubbing the components with the parts brush and blowing away dust and fragments with compressed air. Lodged rock fragments and buildup of powdered rock material can be removed with a long, thin steel knife blade.

When extreme cleanliness is required to avoid low-level contamination or when ore-grade samples are being prepared, a small quantity of quartzite gravel should be crushed before crushing each sample to clean the apparatus. If such a cleaning gravel is not available, a small amount of the next sample to be prepared should be crushed and discarded with the Jaw crusher scrubbed out prior to preparing the whole sample.

When necessary, split the entire crushed sample by distributing it evenly into a Jones splitter to obtain a representative split of sufficient size to fill the sample carton. Save or discard the remainder of the sample, whichever is noted on the RFA. It is suggested that the bulk material be saved until after all the samples have been pulverized. In the event of sample loss during pulverizing, additional sample is then available. Clean the splitter and splitter pans with compressed air prior to splitting the next sample. Use the knife to dislodge fragments caught in the riffles of the splitter.

Turn on the Braun pulverizer and check the adjustment of the ceramic grinding plates. Plate adjustment is checked visually with the aluminum catch pan removed and by sound. The rotating lower plate should be evenly contacting the stationary upper plate and there should be a slight "skipping" sound. Adjusting the plates closer than this without any sample material present can cause the plates to chatter and bind. If the chattering becomes severe enough, the plates can crack or shatter, rendering them useless.

Adjust the plates by holding the threaded adjustment shaft, at the top of the pulverizer, stationary with a 12" crescent wrench and loosening the two lower adjustment nuts. The upper adjustment nut is then *slowly* turned to raise the shaft. This brings the lower revolving plate closer to the stationary upper plate; the closer the spacing between plates, the finer the size of the ground sample. When the desired spacing is achieved, the lower nuts are screwed tight against the lower side of the topmost, fork-shaped, pulverizer frame piece, locking the adjustment shaft in place. Proper adjustment of the plates is verified by pulverizing several ounces of quartz sand. Sieve the ground material through a series of mesh sizes, bracketing the desired particle size. With experience, the operator can quickly determine the suitability of a grind by visually examining, and by feel of, the ground sample.

Proper adjustment of the ceramic plates extends the useful lifetime of the plates. Even a small improper adjustment of the plates results in uneven plate wear and/or grooves and ridges forming on the plate surfaces. This has obvious implications on grinding efficiency and quality. Minor plate imperfections can be removed by running several ounces of silicon carbide through the operating pulverizer, and with great care, slowly closing the gap between the plates while the carbide is being ground. The process is repeated with the now-used portion of carbide until the desired even spacing and skipping sound of the plates is achieved. Test the adjustment by pulverizing a small amount of quartz sand and check the result as described above.

Caution: The plates can be over-adjusted; plates that are run too close together can easily bind, chip and crack. The used carbide is probably still suitable for at least one more use and should thus be saved in a cardboard container marked "Used SiC". The adjustment procedure is the most critical step in consistently producing acceptably prepared samples. It is also the most difficult step to perform. With increasing experience, the degree of difficulty diminishes.

Carefully place the catch pan under the plates of the running pulverizer, lift and rotate the pan until the two teeth on the upper lip of the pan are firmly engaged in the slots of the hopper. Clean the pulverizer by passing several ounces of approximately 20-mesh quartz sand through the pulverizer. Examine the ground sand for adequate fineness and adjust plates, if necessary, as described above. Discard the sand and thoroughly blow out any excess sand and dust from the pulverizer and pan with compressed air. Replace the catch pan.

Pour the crushed rock from the sample carton into the hopper and place the removable cover plate over the hopper to prevent the sample from flying out of the pulverizer. Keep the catch pan in place until all of the sample is ground, which is readily determined by sound.

Place a mixing card into the sample carton which held the crushed sample and place the powder funnel over the top of the carton. Carefully remove the catch pan containing the completely pulverized sample from the pulverizer by turning the pan in the opposite direction used in placing the pan, and lowering the pan below and away from the revolving plate (and the plate lock nut located below the plate). Examine the fineness and thoroughness of grind. The sample is considered acceptable if 100 percent passes an 80-mesh screen (<180 µm) and at least 80 percent passes a 100-mesh screen (<150 µm). Pour the prepared sample from the pan through the funnel into the carton. Fill the carton ⅔ to ¾ full. Discard or save excess sample according to the submitter's request. If the quality of the grind is not acceptable, the sample should be reground. If this fails to improve the quality, the plates likely need adjusting and/or smoothing, as described above.

Thoroughly clean the pulverizer and catch pan using compressed air. Remount the catch pan on the pulverizer and grind about 1 oz of quartz sand to further clean the plates of the residue from the previously prepared sample. Remove the pan, discard the sand and again thoroughly blow remaining dust and particles from the pan and pulverizer with compressed air. When some "sticky", fibrous, micaceous, or ore-grade samples are prepared, the cleaning process should be repeated two or more times until no visible traces of the sample remain in the pulverized sand.

Pulverize the remaining samples in the same manner.

Secure the lids of the sample-bearing containers with tape if the lids are not snug and place the containers into the tube-type mixer. Turn on the mixer and allow the samples to mix for 15 min. Mix all of the samples in the same way.

This completes the preparation process. Clean the work area and return the completed job to sample control.

Equipment maintenance

All mechanical equipment should be lubricated at least once each week, or more often as may be required by heavy use. Use a grease gun containing metal-free grease (i.e. free of elements of interest in analysis) and make certain the lubricant is injected into all of the grease fittings. Do not over-lubricate and wipe excess grease from the fittings with a Kimwipe or paper towel.

Check and make sure all nuts and bolts are securely tightened, prior to turning on any equipment. Check moving parts, including crusher and pulverizer belts, crusher jaws and arms, grinding plates, and pulverizer bushing for wear. Replace worn parts.

Stream-sediment sample preparation

By Thomas R. Peacock, Cliff D. Taylor, and Peter M. Theodorakos

Code: Q020

Accepted: 6/25/90
Revised: 11/18/93

Principle

Most samples of naturally occurring material require some kind of physical preparation prior to chemical analysis. Samples require preparation to effect one or more of the following: (1) reduce the sample to a size that is more conveniently transported; (2) increase the sample surface area to enhance the efficiency of subsequent chemical attack; (3) homogenize the sample to ensure that a subsample is representative of the entire sample; and (4) separate the sample into components based on mineralogy, grain size, or other physical and morphological criteria. Sample preparation is an important step in the analytical process. Without careful preparation, and attention to inter-sample contamination, the worth of the subsequent analyses is significantly diminished.

The dry stream-sediment samples are disaggregated by hand, as necessary, and as much organic material as possible is removed. The samples are sieved to pass an 80-mesh screen (<180 μm) or the particle size specified on the RFA. The sieved fraction is generally ground in a mechanical pulverizer, placed in a 3-oz container and mixed to ensure homogeneity.

Scope

Approximately 50 samples can be processed per day.

Apparatus and materials

- Ro-Tap table top-mounted sieve shaker
- Sieves with stainless steel screens, with pans and cover
- Sample cartons, 3-oz
- Sieve brush
- Large sample funnel, plastic
- Compressed-air source, 40 psi
- Braun vertical pulverizer with ceramic plates
- Jones splitter with catch pans
- Grease gun for lubricating equipment
- Kimwipes or paper towels
- Assortment of tools for equipment maintenance

Safety precautions

Eye and ear protection and a dust mask must be worn and it is recommended that a lab coat be worn. Caution must be exercised in operating equipment, particularly the Braun pulverizer, which has the potential of inflicting serious injury if not properly, and carefully used. Belts on equipment must be guarded and power should be turned off prior to dislodging any jammed material from the equipment with a push stick. Keep hands, hair, and clothing away from any moving machinery parts. Remove all jewelry before you begin work. Compressed air, used to clean the sieves and equipment, presents a safety hazard, especially to the eyes. The compressed-air stream should never be directed toward the face. A fan or exhaust hood should be used to vent dust. See the *CHP* for further information.

Preliminary procedure

Check the Request for Analysis form (RFA) for notes on mineralogy of samples, requests for preparation that varies from standard procedure, and disposition of excess sample.

Verify that the number of samples received and the field numbers on the sample collection/transport bags correspond to the number of samples and field numbers listed on the RFA. If they do not correspond, contact Sample Control.

Properly label the correct number of sample cartons with the laboratory number assigned to each sample. Label both the container tops and sides using permanent ink-markers, or premade labels. Affix premade labels to the tops and sides of the cartons with clean transparent tape.

Place the labeled sample containers in a cardboard tray labeled with the required information: (1) assigned job number, (2) submitter's last name, and (3) number of samples in the job.

If the samples are wet or damp, place them in a drying oven and dry at 60°C until they are thoroughly dry.

Procedure

Disaggregate the samples, if necessary, by pounding the sample bag with a hammer or mallet on a contaminate free surface that is cleaned between samples.

Arrange five sieves of the specified mesh size on a counter top, placing a sieve pan under the sieve at the bottom of the stack, and sieve separator pans under the other four. If a series of sized fractions of the samples is requested, the sieves are stacked with the largest mesh sieve at the top and progressively smaller mesh sizes to the bottom. The sieve of smallest mesh size is placed at the bottom.

Open the sample bags and pour five samples into the sieves in a sequential order. Remove as much organic material, larger pebbles, and rock fragments as possible, and further disaggregate any small clumps, still present, by hand. The sieves should not be overfilled, but loaded loosely enough so that the material can move freely in them. Samples of large volume should be divided among as many sieves as needed or, if they contain abundant fine material, split with a Jones splitter to a volume that can be suitably placed in one sieve. Excess sample should be saved or discarded, whichever is noted on the RFA.

Place a sieve cover on the sequentially arranged stack of sieves. Place the heavy metal Ro-Tap cover over the top of the stack and lift the stack into the frame of the Ro-Tap. Adjust the Ro-Tap for the height of the stack by loosening the friction lock bolts on either side of the base plate and sliding the stack up or down on the vertical rails as needed. The stack is positioned correctly when the metal cover plate is up against the metal tongs of the top bracket. Flip down the front half of the hinged top bracket and make sure the automatic hammer is in the down position.

Turn on the Ro-Tap sieve shaker and run long enough to allow thorough sieving of the samples. The length of time required depends on sample composition, average grain size, sieve mesh size, and the volume of sample in the sieve. Sieving the samples for 3 minutes is generally adequate.

During the interval that the sieve shaker is running, clean a second set of five sieves in preparation for loading with the next five samples. The sieves should be thoroughly brushed on both sides of the screen with a sieve brush. All particles should be blown from the sieves with compressed air. If the sieves become particularly dirty, or if the grains become trapped in the screens, they can be placed in an ultrasonic bath for more vigorous cleaning.

When sieving is complete and the sieve shaker has been turned off, remove the stack of sieves. Each sample should be removed from the stack in proper sequence. The coarse fraction of each sample is saved in the sample submittal bag or discarded, whichever is noted on the RFA. The fine fraction of each sample is poured into its corresponding, appropriately labeled, sample carton using a large plastic sample funnel. Care must be taken to maintain the proper order in which the samples were placed into the shaker. As added assurance for maintaining correct sample identity, a small piece of paper with the sample's laboratory number written on it may be placed in the sieve with the sample prior to stacking the sieves.

After the samples have been sieved, they must ordinarily be pulverized to the grain size required for the chemical analysis, and then mixed in a tube-type mixing machine. The sample is considered acceptable if 100 percent passes an 80-mesh screen (<180 µm) and at least 80 percent passes a 100-mesh screen (<150 µm). Refer to the section of this manual entitled *Physical preparation of rock samples* for the details regarding the pulverizing and mixing procedure. The nature and small grain size of the sediment samples facilitates pulverizing and pulverizer cleanup. Pour each pulverized sample back into its carton from the pulverizer catch pan with the aid of the sample funnel. Blow away remaining particles from the pulverizer, pan, and counter top. Run approximately 1 oz of quartz sand through the pulverizer, discard the pulverized sand, and again blow away remaining particles. The equipment should now be suitably clean for introduction of the next sample.

Equipment maintenance

All mechanical equipment should be lubricated at least once each week or every 250 samples. Use a grease gun containing metal-free grease (i.e. free of elements of interest in analysis) and make certain the lubricant is injected into all of the grease fittings. Do not over-lubricate and wipe excess grease from the fittings with a Kimwipe or paper towel.

Check and make sure all nuts and bolts are securely tightened, prior to turning on any equipment. Check moving parts, including pulverizer belt and grinding plates, for wear. Replace worn parts.

Soil sample preparation

By Thomas R. Peacock

Code: Q030

Accepted: 6/25/90
Revised: 3/10/93

Principle

Most samples of naturally occurring material require some kind of physical preparation prior to chemical analysis. Samples require preparation to effect one or more of the following: (1) reduce the sample to a size that is more conveniently transported; (2) increase the sample surface area to enhance the efficiency of subsequent chemical attack; (3) homogenize the sample to ensure that a subsample is representative of the entire sample; and (4) separate the sample into components based on mineralogy, grain size, or physical and morphological criteria. Sample preparation is an important step in the analytical process. Without careful preparation, and attention to inter-sample contamination, the worth of the subsequent analyses is significantly diminished.

The dry soil sample is disaggregated, if necessary, in the mechanical, ceramic mortar and pestle (soil grinder). The sample is sieved to the required grain size of 100 percent minus 80-mesh (<180 µm) and at least 80 percent minus 100-mesh (<150 µm) using sieves with stainless-steel screens. The sieved fraction is pulverized if further reduction in grain size is required by the subsequent chemical analysis.

Scope

Fifty samples can normally be processed per person day.

Apparatus

- Drying oven
- Nalgene (or similar) trays for air-drying samples
- Aluminum trays for oven-drying samples
- Soil grinder, Nasco-Asplin
- Stainless-steel sieves, with catch pans and lids
- Sieve brush
- Ro-Tap sieve shaker
- Large plastic powder funnel
- Shatter-box, Angstrom or Spex, for pulverizing samples
- Braun vertical pulverizer with ceramic plates
- Sample cartons, 1-oz through 1-pt
- Compressed air source, 40 psi
- Grease gun packed with metal-free grease
- Kimwipes or paper towels
- Quartz sand

Reagents

- Acetone, C_3H_6O, laboratory grade

Safety precautions

Eye and ear protection and a dust mask must be worn at all times; it is recommended that a lab coat be worn. Caution must be exercised by the technician while operating grinding equipment. Belts on equipment must be guarded. Keep hands, hair, and clothing away from any moving machinery parts. Remove all jewelry before you begin work. Compressed air (40 psi), used to clean sieves and grinding equipment, presents a safety hazard, particularly to the eyes. A fan or exhaust hood should be used to vent excessive dust. The compressed air stream should never be directed toward the face.

Acetone, used to clean the soil grinder, is extremely flammable, and should be handled accordingly, being kept away from sources of ignition. Avoid breathing acetone fumes by wearing an appropriate respirator and having adequate ventilation. Avoid repeated or prolonged skin contact with acetone. Treatment for acetone exposure is to irrigate eyes with water, wash contaminated areas of body with soap and water, gastric lavage if ingested, followed by saline. See the *CHP* and *MSDS* for further information.

Preliminary procedure

Check the Request for Analysis form (RFA) for notes on mineralogy of samples, requests for preparation that varies from standard procedure, and disposition of excess sample (bulk).

Verify that the number of samples received and the field numbers on the sample collection/transport bags correspond to the number of samples and field numbers listed on the RFA. If they do not correspond, contact Sample Control.

Properly label the correct number of sample cartons with the laboratory number assigned to each sample. Label both the container tops and sides using permanent ink-markers, or premade labels. Affix premade labels to the tops and sides of the cartons with clean transparent tape.

Place the labeled sample containers in a cardboard tray labeled with the required information: (1) assigned job number, (2) submitter's last name, and (3) number of samples in the job.

Procedure

Damp samples are dried overnight in a forced-air drying oven in their original containers or on the nalgene trays upon which they have been spread. To insure proper sample identity is maintained, place the sample bag on the tray with the sample and weight it down with some of the sample. Generally no heat is required, the flow of air in the oven being sufficient to dry the sample. Drying of wet samples is facilitated by setting the oven temperature to 30°C.

If the samples contain aggregates of material following drying they should be disaggregated in the soil grinder.

Remove pebbles and larger rock fragments from the sample by hand. The presence of large pebbles and fragments impedes the operation of the soil grinder and may damage it. Fill the bowl of the soil grinder about halfway. Start the auger and lower it gently onto the sample. If additional fragments or pebbles are revealed, raise the auger well out of the way and turn it off before removing them. When the maximum downward travel of the auger has been reached, maintain this position approximately 30 s, then raise the lever and turn the auger off.

Turn on the switch that activates the chain-driven sieve shaker. Pour the sample slowly onto the 10-mesh screen (2.0 mm). Pour the minus 10-mesh fraction, that is the material that passes through the screen, into the previously labeled sample cartons using a large sample funnel. If there is too much material for the sample carton, split the sample using a Jones Splitter to obtain a split of the sample in an amount to fill the sample carton. Discard the plus 10-mesh fraction, which rolls off into a hopper near the base of the grinder, unless otherwise instructed by the sample submitter. Repeat the soil-grinding process with the remainder, if any, of the sample.

Clean the grinder using a stiff bristle brush and compressed air to rid the sieve screen and the grinder of all dust and soil particles. Wipe the auger bit and bowl with a paper towel or large Kimwipe dampened with acetone.

Caution: Acetone is flammable. Used towels/Kimwipes should be disposed of in fire-proof containers. Plastic or rubber gloves should be worn if working with acetone.

If sieving to a finer grain size is required, pour the sample onto the screen of the proper-sized, clean sieve, with the catch pan of the sieve in place, cover with the lid, and agitate, either by hand or in a Ro-Tap Sieve Shaker, for approximately 2 to 3 min or until no more appreciable gain of finer grained material is realized. Pour the fine fraction from the catch pan into the pre-labeled sample carton using a large, plastic powder funnel. Dispose of the coarse fraction unless otherwise instructed by the submitter. Clean both sides of the sieve screen with a sieve brush and compressed air. Clean the catch pan with an acetone-moistened Kimwipe.

If pulverizing of the sieved sample is required, use the shatter-box to pulverize the sample to 100-mesh (<150 μm) or less or the Braun Pulverizer to grind the sample to approximately 100-mesh.

Pour the sample into the grinding chamber of the shatter-box with the agate puck (and ring, on the Angstrom model) in place in the chamber. Fill the chamber about halfway. Clamp the chamber into place and start the machine. Normal soil grinding to 100-mesh or less is accomplished in approximately 1 to 3 min. Suitability of grind is verified by sieving the sample through a 100-mesh sieve.

Transfer the ground sample to the prelabeled sample carton.

Clean the shatter-box by running quartz sand through it in the same manner as a sample. Use compressed air to rid the chamber of dust and particles and then wipe down with acetone.

For sieved samples that require grinding to only an approximate 100-mesh grain size, pour the sample into a running Braun pulverizer, with previously adjusted, and conditioned grinding plates (see section *Rock sample preparation* for procedure on setting up and operating the pulverizer), with the catch pan in place. Usually, one pass of the soil sample through a properly adjusted pulverizer is adequate. Transfer the ground sample to the previously labeled sample carton. Clean the pulverizer by running approximately 1 tablespoon of sand through it, in the same manner as a sample. Use compressed air to rid the pulverizer of remaining dust and particles.

Equipment maintenance

Lubricate all mechanical equipment at least once each week, or every 250 samples. Use a grease gun containing metal-free grease (i.e. free of elements of interest in analysis) and make certain the lubricant is injected into all of the grease fittings. Do not over-lubricate. Wipe excess grease from the fittings with a Kimwipe or paper towel.

Make sure all nuts and bolts are securely tightened prior to turning on any equipment. Check moving parts, including pulverizer belt and grinding plates, for wear. Replace worn parts.

Heavy-mineral concentrate preparation by heavy liquid and magnetic separation

By Cliff D. Taylor and Peter M. Theodorakos

Code: Q040

Accepted: 6/25/90
Revised: 11/18/93

Principle

Most samples of naturally occurring material require some kind of physical preparation prior to chemical analysis. Samples require preparation to effect one or more of the following: (1) reduce sample to a size that is more conveniently transported; (2) increase the sample surface area to enhance the efficiency of subsequent chemical attack; (3) homogenize the sample to ensure that a subsample is representative of the entire sample; and (4) separate the sample into components based on mineralogy, grain size, or other physical and morphological criteria. Sample preparation is an important step in the analytical process. Without careful preparation, and attention to inter-sample contamination, the worth of the subsequent analyses is significantly diminished.

The heavy-mineral concentrates, prepared in the field by panning, are dried and sieved through a 35-mesh screen. The minus 35-mesh (<425 µm) fraction is separated into heavy and light fractions using bromoform, specific gravity 2.8. The heavy fraction (specific gravity >2.8) is further separated magnetically, using a Frantz Isodynamic Separator, into a highly magnetic (ferromagnetic) fraction, a weakly magnetic fraction (paramagnetic), and a nonmagnetic fraction. Depending on the amount of material available, the heavy, nonmagnetic fraction is normally divided into an analytical split and a split used for mineralogical identification by the submitter. The analytical split is pulverized using an agate mortar and pestle after which it is ready for analysis.

Scope

Approximately 50 samples can be prepared per day.

Apparatus

- Sieve, with stainless steel screen and pan, 35-mesh
- Sieve brush
- Source of compressed air, 40 psi, hose and nozzle
- 5-ring stands
- 5, 1-L separatory funnels
- 100-mL glass stoppered graduated cylinder
- 7, 18.5-cm plastic funnels
- 2 or 3 large holding bottles
- 2, 1-L plastic wash bottles
- 100, 250-mL beakers
- 100, 18.5-cm, fast-flow, qualitative filter papers
- 4 or 5, 40-cm, fast-flow, qualitative filter papers
- Stirring rod, glass or Teflon
- Frantz Isodynamic Separator
- Approximately 9" square, mylar-covered plate

- Static-eliminating sample brush
- Cleaning brush
- Microsplitter with $^{1}/_{16}$' riffles, and sample boats
- Sample cartons, 3-oz
- Plastic poly vial, 1-oz
- Agate mortar and pestle

Reagents

- Acetone, C_3H_6O
- Bromoform, $CHBr_3$ (tribromomethane), specific gravity 2.89 at 20°C
- Quartz sand

Safety precautions

Bromoform presents a potentially severe health risk. The heavy liquid separation step must be conducted in a fume hood. Personnel are to be familiar with the properties of bromoform, be able to recognize symptoms of exposure, and be aware of the possible health effects of overexposure. See the *CHP* and *MSDS* for further information.

The heavy liquid bromoform, $CHBr_3$, is a colorless liquid with a sweet, "heavy" odor similar to chloroform. Pure bromoform has a specific gravity of 2.89 at 20°C. Because of its instability, chloroform and ethanol are added to it in minor amounts as preservatives, lowering the specific gravity of the bromoform to 2.85 through 2.88. Bromoform is completely miscible in acetone, alcohol, and benzene. In this procedure, acetone is used exclusively as the diluent. Although sufficient research has not been conducted to determine its long-term effects on the human body, bromoform is a suspected carcinogen. It is thought to be cumulative in the fatty tissue of body organs. Repeated exposure can result in damage to the liver, kidneys, heart, and lungs. The adverse physiological effects of smoking or alcohol consumption are enhanced by exposure to bromoform, and vice versa. Never engage in these activities immediately prior to, during, or immediately after conducting the heavy liquid separation procedure.

Bromoform has a permissible exposure limit, set by OSHA (Occupational Safety and Health Administration), of 0.5 ppm in air per 8-hour day. It can be inhaled, ingested, and absorbed through the eyes and skin. Bromoform causes irritation of the eyes, nose, and throat, tearing, headaches, excessive saliva flow, nausea, reddening of the face, dizziness, drowsiness, or a state of apparent inebriation. With prolonged exposure, it can cause deep narcosis and death. A lethal dose is 2 to 4 oz for a 150-pound man. Review the *MSDS* for further information.

Protective equipment should be worn in a manner indicated by the manufacturer and should include a lab coat or rubber apron, rubber gloves, protective eyewear, and a respirator with suitable organic vapor filters and, preferably, a full face mask. All of the safety equipment should be worn at all times when working with bromoform. If the odor of bromoform is detected in the air, its threshold limit for an 8-hour day may already have been reached. A person subjected to the odor of bromoform may become sensitized to the point where he or she may not be aware of increased exposure until more unpleasant side effects occur.

First-aid treatment for exposure to bromoform involves removing the victim to fresh air and administering artificial respiration and oxygen if needed. Get medical assistance immediately. For skin contact, flush thoroughly with water and wash with soap, as bromoform is absorbed by skin oils. Remove contaminated clothing immediately and wash before reuse.

Acetone presents a two-fold hazard. It is a highly flammable and reactive liquid. It should be kept away from possible sources of combustion and noncompatible chemicals, such as strong oxidizers. The accumulation of acetone vapors in air is potentially explosive. Acetone also poses the physiological hazards common to organic ketones. Using the above-described precautionary measures for bromoform when working with acetone, insures the well being of the person conducting the procedure.

Safety glasses should be worn when cleaning apparatus with compressed air. The compressed air stream should never be directed toward the face.

Preliminary procedure

Carefully read the request for analysis form (RFA) for any special instructions and make sure any such instructions are understood. Label the 3-oz sample cartons, polycons, and sample trays with the information required by Sample Control. Examine all glassware for cleanliness, especially for traces of mineral grains, and clean if necessary. It is recommended that an adequate supply of filter papers be folded for the day's use.

Procedure

Sieving the Sample

Dry the submitted panned-concentrate, if necessary, by placing it in a drying oven at 60°C for the time required. Caution must be used for samples submitted in plastic bags or containers to prevent accidental meltdown.

Prior to handling the samples, remove all jewelry (rings, watches, etc.) to minimize possible contamination. Sieve the dry concentrate through a 35-mesh screen. Remove larger pebbles and fragments (>0.5") by hand to prevent possible damage to the screen.

Transfer the minus 35-mesh fraction to the appropriately labeled (laboratory ID number) cardboard container. Discard the plus 35-mesh fraction unless otherwise requested. Split large sieved samples with a Jones Splitter to a size required to fill the 3-oz container, discard or save the rest (in a second 3-oz container) as requested.

Thoroughly clean the sieve of all dust, grains, and chips using a sieve brush and compressed air between the sieving of each sample.

Heavy liquid separation

The separation must be performed in a fume hood. Pour approximately 250 mL of bromoform into a 1-L separator funnel. More bromoform may be required for large samples, e.g., full 3-oz sample cartons.

With a glass stirring rod, stir the bromoform until a vortex forms and while still stirring, slowly introduce the sample into the vortex and continue stirring for 10 seconds after the entire sample is in the bromoform.

Rinse all mineral grains adhering to the stirring rod into the funnel with bromoform from a squirt bottle.

Allow approximately 2 to 3 min for the heavy minerals (specific gravity >2.8) to settle to the bottom of the funnel. Experience will help determine the actual time required for this settling process. Too long can result in grains of intermediate specific gravity to settle and too little time can result in incomplete separation of heavy minerals, neither is desirable.

After separation, open the stopcock and catch the heavy minerals on a filter paper placed in a plastic filter funnel resting in an Erlenmeyer flask. Close the stopcock immediately after all of the heavy minerals have been drained from the separatory funnel. Carefully avoid drawing off intermediate specific gravity mineral grains.

Allow as much of the bromoform as possible to drain into the Erlenmeyer flask, then remove the filter funnel to another Erlenmeyer flask marked "WASH." Wash the separated "heavies" with acetone twice (in which bromoform is readily soluble) and allow to drain. **Caution**: acetone is a hazardous and extremely flammable substance. Treat accordingly. Save the "WASH" solution to recover bromoform using a hot water bath procedure.

Remove the heavy-mineral-bearing filter paper from the funnel, transfer to a 25-mL beaker (larger if necessary), place in a fumehood and allow the remaining acetone to evaporate.

Filter the remaining bromoform and light-mineral fraction in the separatory funnel through a large (40-cm) fast-flow filter paper into another Erlenmeyer flask or back into the bromoform reagent bottle. Rinse any residual light material from the separatory funnel into the filter with bromoform.

When the large filter paper in step 12 is two-thirds full, remove the filter funnel and place into yet another bottle (or flask) and thoroughly rinse the light material with acetone. The acetone rinse removes a substantial amount of bromoform from the sludge. The specific gravity of the bromoform is obtained from the ratio of the mass of a body to the mass of an equal volume of liquid at a specified temperature. Ten milliliter of bromoform is measured in a graduated cylinder, stoppered, and weighed. A specific gravity above 2.8 is considered acceptable.

Pour the heavy minerals (step 11) back into the appropriate red top. If very little heavy material is present the entire filter paper may be folded and placed into the container, taking care not to lose any material.

Magnetic separation

Remove the highly magnetic fraction (ferromagnetic minerals) from the heavy minerals by pouring large samples through the Frantz separator that has been specifically set up for this purpose (vertical configuration of magnet poles). It may be necessary to repeat this process several times to assure thorough separation of less magnetic minerals. Pour small samples (<5 g) into a rectangular, mylar-covered tray in a uniformly-spread layer (<2 mm thick) and pass the tray ½ to 1 cm below the horizontally configured, mylar-covered poles of the magnet, with the current set at 0.25 A. The highly magnetic minerals will adhere to the magnet. Switch off the current and catch the minerals on a clean paper sheet.

Place the highly magnetic fraction (in general, principally magnetite, Fe_3O_4) into an appropriately labeled polycon also marked "C_1." Discard excess material unless instructed to do otherwise.

Lightly touch the remaining minerals on the tray to the poles of the magnet with the current set at 1.75 A. The weakly magnetic minerals will adhere to the magnet and the nonmagnetic minerals will remain on the tray. Switch the current off and catch the weakly magnetic minerals on the clean paper sheet.

Thoroughly brush all traces of weakly magnetic minerals that may continued to adhere to the face of the magnet with the current switched off onto the paper sheet using an antistatic brush.

Repeat steps 17 and 18, if necessary, to obtain thorough separation of weakly magnetic and nonmagnetic minerals.

Carefully place the nonmagnetic fraction into a polycon marked "C_3-spec" and the weakly magnetic fraction into one marked "C_2." Discard excess material unless otherwise requested.

Grinding

Split the "C_3-spec" fraction in a mini-Jones Splitter, place one half in another polycon marked "C_3-min" and transfer the other half to an agate mortar. (If the quantity of C_3 minerals is judged inadequate for splitting, i.e., less than approximately 20-30 mg, proceed to hand grinding).

Grind the samples in the mortar with an agate pestle to a powder consistency (minus 200-mesh) and return the ground-up sample to the "C_3-spec" polycon.

Fine grind approximately 5 g of previously pulverized quartz in the mortar to remove potentially contaminating mineral remnants. Rinse mortar with acetone and wipe clean with tissue paper.

The end product of this procedure should consist of three separate heavy mineral fractions of concentrate samples: The C_1 highly magnetic fraction; the C_2 weakly magnetic fraction; and the C_3 nonmagnetic fraction.

Plant material preparation and determination of weight percent ash

By Thomas R. Peacock

Code: Q050

Accepted: 3/2/93
Revised: 5/12/94

Principle

The physical preparation of plant material generally consists of washing, drying, milling, and dry ashing an aliquot, or subsplit of the sample (Peacock, 1992). Whenever ashing is required by an analytical technique, a calculation of weight percent ash is reported. The results are converted back to a dry weight basis for comparison with other analytical techniques. Some analytical techniques, such as hydride generation atomic absorption spectroscopy and instrumental neutron activation analysis, do not require plant ash. Others, such as inductively coupled argon plasma atomic emission spectroscopy, need plant ash exclusively.

Interferences

The interferences most commonly encountered are: (1) dust from the sampling site which may coat stems and leaves; (2) loss of volatile elements at ashing temperature; and (3) incomplete ashing of some material species at the prescribed temperature. Most contamination of samples by dust can be eliminated by washing them in deionized water. The ashing temperature of 500°C was chosen because it is the optimum temperature at which most plant materials will lose their organic components. It is maintained for 13 hours to maximize loss of organic material. Volatile elements (i.e., Se, As, Hg, P) are determined in unashed subsplits of the sample. Material that does not ash completely at 500°C is allowed to remain in the furnace for a second attempt. If the sample is still not ashed completely (as observed by weight, texture, color, and appearance), a notation is made on the RFA., the submitter contacted for advice, and/or material forwarded to Sample Control.

Scope

The average time required for preparation and percent ash calculation is 5 days, based on a suite of 40 samples. The minimum measurement of ash content is 0.01 percent. If the sample has been washed or washing is not requested and the sample has been milled, ashing and percent ash calculation can be done in 2 days.

Apparatus

Laboratory equipment consists of the following:

- Thomas/Wiley Mill Standard Model 4, with 2 mm screen
- Mellen Model B-222 muffle furnaces fitted with Cramer 24-hour timers
- Christy-Norris pulverizer, 8"
- Laboratory drying ovens, 0-200°C, 8-10 cu-ft capacity
- Spex 8000 Mixer/Mill
- Box fans (4.5") mounted to ring stands

- Vitreosil evaporating dishes (fused silica, 3.75" id)
- Coors evaporating dishes (porcelain, 3.0" id)
- Glass or plastic beakers, 4-L capacity
- Rotary mixer holding at least 36-pint sample containers
- Mettler AC100 electronic balance
- Scientech 3300 electronic balance

A supply of 0.5-oz polycons (pillboxes), 5-mm solid borosilicate beads and waxed weighing paper is also needed.

Reagents

Acetone, C_3H_6O, laboratory grade, 1 pint (useful as a cleaning aid)

Safety Precautions

As with all machinery, care must be taken while grinding or ashing the sample materials. The Wiley Mill has stationary and rotating razor-edged knives that can easily remove fingertips. The Christy/Norris Mill becomes very hot after just a short period of operation. Both mills must be cleaned between samples. This is usually done with compressed air (40 psi) and a toothbrush. Before cleaning, the mill should be at rest. Occasionally, a sample will leave a resinous buildup on the spinning cutting head, door, or screen. It can often be removed with the careful use of a razor knife and acetone. Due to dust, noise in excess of 80 dB, and heat hazards, the worker should be fully protected with a lab coat or smock, leather work gloves, dust mask, safety glasses, and hearing protectors. Acetone must be handled with care to avoid fumes and possible fire hazards. All work must be done in a dust hood having a face velocity of at least 150 linear feet per minute. A muffle furnace also creates a potential shock and burn hazard. Avoid contact with heating elements and never load or unload a hot furnace (>100°C). Review the *CHP* and *MSDS* for further information.

Procedure

Washing

A plant sample received for preparation, with a request for washing, undergoes a washing process to eliminate contamination from adhering particles such as dust. There are two methods for this: (1) "beaker soak" hand washing in tap or deionized water, and the most common (2) "colander rinse" with tap or deionized water.

When the "beaker soak" method is used, water must be constantly changed since the sample is actually moved from one beaker to another over the course of a few minutes. The sample is rinsed in a colander, and the beakers are rinsed and refilled for the next sample. All samples rinsed manually are transferred to a colander for drying. Drying temperatures are held under 40°C unless specified otherwise. Material having a resinous coating on stems or leaves is dried without heat to minimize the possibility of its loss through liquification. Samples are dried to brittleness; usually 24–48 hours.

Milling

Dry samples can be put directly into the grinder. It has been found that the Wiley Mill is best for young, woody growth up to a thickness of 5 mm. The Christy/Norris Mill is used for all thicker materials such as twigs, roots, and branches up to about 13 mm in diameter, mosses and lichens are ground in a blender. Larger diameter material must be cut to prevent jamming of the mill. This is most easily accomplished with pruning shears or a band saw.

Samples are mixed using a rotary type of tumbling device. The top 2.5 cm of the pint container must remain unfilled to insure proper mixing. The holders are set to accommodate four 8.9-cm diameter sample containers in line. These sample holders form the circumference of the mixer. Samples are held in place by flat plates secured with wing nuts to long threaded bolts mounted in the holder frames. The mixer is driven by a gear reduction motor having an output of 45 rpm (39:1 ratio). A toothed timing belt is linked to a 1/3 hp, single phase, ac 1,725 rpm drive motor. The average weight of a plant sample after grinding is 200 g.

Dry Ashing

Ashing requires only a portion of the sample, but enough to satisfy the analytical need and be representative of the entire sample. The amount of this "aliquot" is also determined by its density, estimated ash yield, and amount of sample available. Sample material is taken from its container with a teaspoon, off the top. An aliquot of 10 g is optimum for a 3.75 in Vitreosil dish, although satisfactory results have been obtained from splits of 1 to 24 g. Using a spatula, the sample is spread evenly along the sides and bottom of each dish to enhance even heat distribution throughout the aliquot. The ashing vessels are arranged in each furnace three across, left to right, upper shelf first (nine per shelf). Any consistent arrangement is appropriate provided it is known which dish holds what sample. There should be some space between each dish and the furnace walls. Breakage can occur from tightly packed arrangements. Shelving material is stainless-steel mesh wrapped over a similar framework forming a flat tray.

Ashing proceeds with the door fully closed. The small amount of oxygen necessary for the process enters through the imperfect seal between door and wall bricks and any hole drilled for thermocouple mounting. The furnaces are programmed to "ramp" up to the ashing temperature of 500°C over a period of 5 hours. Complete ashing is insured by maintaining this temperature for 13 hours. The furnaces are allowed to cool for 8 hours before sample dishes are removed. While cooling, the door should be slightly open but not swung away until the inside temperature dips below 200°C. Sample dishes should remain undisturbed until cooled to 100°C. Ashing vessels are removed using tongs and placed on a metal or insulated surface for further cooling. At least 20 min should be allowed for this. After sample removal, cooling of the furnaces is enhanced by box fans positioned in front of the interior. Due to limitations in the controller and programmer circuitry, the brick temperature must be reduced to 24°C or less before the next ashing cycle can begin. In all, furnace cooling requires about 10 hours to complete.

The ash is transferred to 0.5-oz pillboxes using weighing paper as funnels. The ash must then be mixed and reduced in volume as it tends to be highly charged with static. This is done through the use of a 5-mm solid-borosilicate bead (placed into the polycon prior to addition of the ash), and 10 to 60 s of shaking in a Spex 8000 mixer/mill. The ash is then ready for laboratory analysis.

Calculation

Weight percent ash is determined for all ashed samples. It requires the measurement of the empty vessel, the combined weight of vessel and sample aliquot before ashing, and the weight of the cooled vessel and ashed sample aliquot. All are weighed and recorded to a minimum of four decimal places (0.0001 g). The net weight of the aliquot and resulting ash must be determined by difference, multiplying the result by 100. Rounding gives the reported values in three significant figures. The weight of the vessel is subtracted from both figures and the formula for calculating percent ash is:

$$\%\text{ ash} = \frac{\text{ashed sample wt (g)}}{\text{unashed sample wt (g)}} \times 100$$

Assignment of Uncertainty

Reference materials are included in each batch of samples for control check use by the analyst.

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Arsenic, antimony, and selenium by flow injection or continuous flow-hydride generation-atomic absorption spectrophotometry

By Philip L. Hageman and Eric Welsch

Code: A011

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Principle

Geologic samples are digested using a multiacid procedure in an open Teflon vessel. At the end of the digestion period, arsenic, antimony, and selenium are reduced to oxidation states, +3, +3, and +4, respectively. Sodium borohydride is added to the solution resulting in rapid formation of the hydrides as illustrated by:

$$3\ NaBH_4 + 4H_3AsO_3 \rightarrow 4\ AsH_3(g) + 3\ H_3BO_3 + 3\ NaOH$$
$$3\ NaBH_4 + 4H_3SbO_3 \rightarrow 4\ SbH_3(g) + 3\ H_3BO_3 + 3\ NaOH$$
$$3\ NaBH_4 + 4H_2SeO_3 \rightarrow 4\ H_2Se(g) + 3\ H_3BO_3 + 3\ NaOH$$

The gaseous hydrides are stripped from the analytical stream and transported with inert gas to the atomizer (a heated quartz furnace) of the atomic absorption spectrophotometer. For selenium, the quartz furnace is heated by an air acetylene flame to 2000°C; the arsenic and antimony furnace is electrically heated to 900 and 1,000°C respectively. Concentrations of the elements are determined using calibration standards in solutions of similar matrix.

Interferences

Interferences usually associated with atomic absorption analysis are negligible, but incomplete recoveries of the elements from the digest solution may yield low analytical results. Incomplete recoveries are principally due to:

1. Concentration of certain transition and heavy metals (e.g. Cu, Fe, Ni, and Sn) of more than 500 ppm in the sample compete with As, Sb, and Se, for available $NaBH_4$. This competition may result in insufficient $NaBH_4$ for completion of the hydride-forming reaction.
2. Concentrations of one or more of the hydride forming elements in excess of 1,000 ppm. Competing hydride elements deplete the oxygen supply in the furnace which is needed to convert hydrides to ground state elements.
3. Interference of hydride formation by incompletely digested organic material.
4. Possible volatility losses of the analyte in an organic rich matrix due to organometallic compounds.
5. Coprecipitation of the hydride elements if a metal is reduced to the metallic form, as is seen with Ag or Au.

Problems one and two are generally of minimal concern in environmental samples because the probability of high concentrations of these elements is quite low. More often, interference problems occur in mineral studies, but can be resolved by dilution of the sample solution. This dilution will raise the appropriate detection limits. Special care should be taken to ensure that all the organic material in organic-rich sample is thoroughly and rapidly digested (i.e., oxidized) to enable the reaction to reach completion and to avoid loss through volatilization.

Scope

The hydride generation-atomic absorption spectrophotometric method (HG-AAS) described herein is useful for the determination of As, Sb, and Se, in a variety of geochemical samples. The optimum concentration ranges without sample dilution for these elements in various sample media are as follows:

Matrix	*Concentration range*		
	Selenium	*Arsenic*	*Antimony*
Rock	0.2 to 4 ppm	0.6 to 20 ppm	0.6 to 20 ppm
Coal	0.1 to 10 ppm	0.1 to 50 ppm	--- ---
Plant	0.05 to 1 ppm	0.05 to 12.5 ppm	--- ---
Water	1 to 40 ppb	3 to 50 ppb	--- ---

Above these ranges, the options of sample dilutions versus alternative techniques, e.g. energy dispersive X-ray fluorescence for selenium, should be considered. One day is required to complete digestion of 40 samples. The analyses of 40 samples requires about 1.5 hours of instrument time for each element.

Apparatus

- Standard laboratory hot plate with a 30x60-cm heating surface
- 2.5-cm-thick x 25-cm-wide x 50-cm-long aluminum heating block with 34-mm holes drilled through in a 5x10 matrix
- Thick-walled, 30-mL Teflon bottles, #0201 T from Savillex Corp., Minnetonka, Minnesota
- 125-mL Erlenmeyer flasks with refluxers
- 60 mL plastic bottles with screw tops
- Gilson 212b autosampler
- Perkin Elmer 4100 AA with FIAS 400, AS 90 autosampler, PC controller and printer for arsenic and antimony determinations
- Perkin Elmer 2380 AA with Varian hydride generator Model V6A76 and strip chart recorder, for selenium determination.

Reagents

- Deionized water (DI)
- Nitric acid, HNO_3 'INSTRA-ANALYZED' grade
- Hydrochloric acid, HCl 'INSTRA-ANALYZED' grade
- Perchloric acid, $HClO_4$ 'INSTRA-ANALYZED' grade
- Sulfuric acid, H_2SO_4 'INSTRA-ANALYZED' grade

- Hydrofluoric acid, HF reagent grade
- Ascorbic acid, C_6HO_6 reagent grade
- Potassium iodide, KI reagent grade
- Sodium borohydride, $NaBH_4$ reagent grade
- Sodium hydroxide, NaOH reagent grade

6 N HCl solution: Dilute 'INSTRA-ANALYZED' grade HCL suitable for trace metals analysis, with an equal volume of DI water. The use of the 'INSTRA-ANALYZED' grade or HCl of similar purity is advised throughout the procedure.

Sodium borohydride solution: For As and Sb dissolve 0.5 g NaOH and 2.0 g $NaBH_4$ in DI water and dilute to 1 L in a volumetric flask. For Se dissolve 3.5 g $NaBH_4$ and 5 g NaOH in DI water and dilute to 1 L. All solutions should be made weekly and kept refrigerated between analyses.

Potassium iodide-ascorbic acid solution: Dissolve 100 g KI in DI water. Add 50 g C_6HO_6. Dilute to 1 L with DI water. Stable for at least 2 weeks.

Saturated persulfate: Dissolve sufficient $K_2S_2O_8$ into one liter of DI so that crystals remain and no more will go into solution.

Arsenic and antimony standard solutions: Commercially prepared As and Sb standards are used to make a 10 ppm stock solution in 10 percent HCl. The 10 ppm stock is used to prepare 20, 40, and 80 ppb working standards by transferring 0.2 mL, 0.4 mL, and 0.8 mL aliquots to three 100-mL volumetric flasks. To these add 50 mL of 6 *M* HCl, 20 mL of KI/C_6HO_6 solution, and enough DI water to bring the volume to 100 mL. The working standards are stable for at least 1 week and should be refrigerated between analyses.

Selenium standard solutions: A commercially prepared selenium stock is used to make a 10 ppm standard in 10 percent HCl. From this 0.05, 0.10, and 0.20 mL aliquots are transferred to three 100 mL volumetric flasks and brought to volume with 50 mL 6 *M* HCl, 4 mL H_2SO_4, and DI water. Important note: for water analysis, do not add H_2SO_4 to standard solutions. These standards should be stable for at least 1 week and kept refrigerated between analyses.

Safety precautions

The principal hazards associated with the technique deal primarily with the decomposition of the samples and the use of concentrated acids. Most dangerous is HF which inflicts painful and lasting bone and neural damage. Gloves, goggles or safety glasses, and a laboratory coat should be used whenever handling chemical reagents. Extra care should be taken in the dispensing of this acid and all equipment used in this operation should be rinsed thoroughly afterward. A salve such as calcium gluconate or magnesium sulfate should be prominently located in the laboratory and applied if an HF burn is detected. A chemical exhaust hood should be used for the digestion procedure and over the atomic absorption instrument due to the evolution of toxic hydrides and HCl vapors. There is a danger of H_2 ignition and flashback if the inert carrier gas is not turned on in advance. Review the *CHP* and *MSDS* for further information.

Procedure (rock, soil, and sediment)

1. Weigh 0.25 g sample (<80-mesh) into a 30-mL Teflon vessel, add 9 mL HNO_3 and 0.25 mL of 10 percent HCl. Allow to stand for 3 hours.
2. Add 2 mL $HClO_4$, 2 mL H_2SO_4, 10 mL HF and heat overnight at 125°C.
3. Cool, add 25 mL 6 *N* HCl and let stand for half an hour.
4. Transfer the sample solution to a 60-mL polyethylene bottle and bring up to 55 g with DI water.
5. Approximately 8 mL of the solution is decanted into 13x100-mm test tubes for selenium analysis and another 8 mL is mixed with 2 mL of $KI\text{-}C_6HO_6$ solution in 17x100-mm test tubes and allowed to stand for 1 hour before arsenic or antimony analysis.
6. Arsenic and antimony are determined by means of a Perkin Elmer-4100AA and FIAS-400 hydride system while selenium is determined using a Varian hydride generation system which is joined with a Perkin Elmer-2380AA.
7. Sample peaks are compared to standard peaks recorded on a strip chart recorder for selenium while the 4100 software does the data reduction mathematically for arsenic and antimony.

Procedure (coal and plant)

1. Weigh a 0.1 g sample of coal or a 1.0 g sample of plant material into a 125 mL Erlenmeyer flask.
2. Add 20 mL HNO_3, 2 mL H_2SO_4, and let stand overnight.
3. Then add 3 mL of $HClO_4$, insert refluxers, and heat at about 175°C for 30 min.
4. Remove refluxers and continue to heat to dense white fumes.
5. See step three of the rock procedure.

Procedure (water and extracts)

1. Weigh 10 g liquid sample into a 30-mL Teflon vessel.
2. Add 1 mL of saturated $K_2S_2O_8$ and let stand for 1 hour.
3. Add 1 mL conc HCl and heat at 110°C with watch glass in place.
4. Remove watch glass after 1 hour and continue heating for roughly 2½ to 3 hr or until the volume is reduced to somewhere between 2 and 5 mL.
5. Add another 2 mL conc HCl, replace the watch glass, and heat for another hour.
6. Cool, add 25 mL 6 *N* HCl and let stand for half an hour.
7. Transfer to 60-mL polyethylene bottles with distilled water, and bring to a weight of 20 g.

Operating Conditions

The analyte content of the digest solution is determined using the instrumental operating conditions shown in table 1.

Table 1.—Operating conditions for determination of As, Sb, and Se by HG-AAS

	Arsenic	*Antimony*	*Selenium*
Grating	ultraviolet	ultraviolet	ultraviolet
Wavelength	193.7 to 197.2 nm	217.6 nm	196.0 nm
Slit	0.7 nm	0.2 nm	0.7 nm
Lamp setting	8 W	8 W	6 W
Source	EDL	EDL	EDL
Cell (furnace) temp	900°C	1,000°C	2,000°C
Mode	absorbance	absorbance	absorbance
Strip chart recorder	n/a	n/a	10 mV, 5 mm
Concentration mode, 10 μg	0.45 *A*	0.20 *A*	30 *A*

Assignment of uncertainty

The analytical results for As, Sb, and Se in selected reference materials, duplicate samples, and method blanks are summarized in table 2.

Table 2.—Analytical performance summary for As, Sb, and Se by HG-AAS (solid phase samples in ppm, water samples in ppb)

[A=National Institute of Standards and Technology (NIST), 1992; B=Water Resources Division; C=NIST, 1976; D=Harms, 1988; E=NIST, 1979; F=Wilson, 1994; remaining *pv* from Potts and others, 1992]

Reference	*Description*	*n*	*Mean*	*s*	*pv*		*% RSD*	*% R*
Antimony, Sb								
SDC-1	mica schist	10	0.40	0.05	0.54		12	75
GSD-6	stream sediment	10	1.7	0.1	*1.25*	?	6	134
SRM 2709	soil	10	7.5	0.5	**7.9**	A cv	7	95
Arsenic, As								
T81	water (trace elements)	10	11	1	10.3	B	9	108
T89	water (trace elements)	10	17	2	17.7	B	12	98
SRM 1575	pine needles	10	0.20	0.01	**0.21**	C cv	5	95
SDC-1	mica schist	10	0.29	0.04	0.22		14	132
GSD-6	stream sediment	10	14	0.5	*13.6*		4	106
SRM 2709	soil	10	18	0.8	**17.7**	A cv	4	102
Selenium, Se								
T81	water (trace elements)	10	14	1	12.7	B	7	109
T89	water (trace elements)	20	23	3	17.8	B	13	127

Table 2.—Analytical performance summary for As, Sb, and Se by HG-AAS (solid phase samples in ppm, water samples in ppb)—Continued

Reference	*Description*	*n*	*Mean*	*s*	*pv*		*% RSD*	*% R*
Selenium, Se (Continued)								
ALF	alfalfa leaves	20	0.18	0.02	0.19	D	11	95
SRM 1635	coal fly ash	10	1.0	0.1	0.9	E	10	106
CLB-1	coal	20	2.5	0.2	**2.1**	F	8	119
SRM 2709	soil	20	1.5	0.1	**1.57**	A cv	7	95

Duplicate samples	*k*	*n*	*Mean*	*s*	*% RSD*	*Concentration range*			*No. of < (total)*	*No. of < (pairs)*
Antimony										
Rock	7	2	0.9	0.1	11	0.4	to	1.5	0	0
Arsenic										
Water	--	--	--	--	--	--		--	12	6
Rock	31	2	8.0	0.2	3	0.2	to	22	6	3
Coal	5	2	14.62	0.02	0.1	0.1	to	70	4	2
Plant	7	2	1.03	0.07	7	0.04	to	6.8	0	0
Selenium										
Water	5	2	29	2	8	1.4	to	79	10	5
Rock	44	2	1.33	0.04	3	0.05	to	9.0	5	2
Coal	10	2	2.59	0.08	3	0.4	to	8.4	0	0
Plant	8	2	0.98	0.02	2	0.04	to	5.8	2	1

Method blank	*n*	*Mean*	*s*	*3s*	*5s*
Antimony					
Rock	189	0.008	0.1	0.3	0.6
Arsenic					
Water	14	0.1	0.5	2	3
Rock	43	0.07	0.1	0.3	0.6
Coal	9	0.01	0.01	0.04	0.06
Plant	8	0.03	0.01	0.02	0.04
Selenium					
Water	21	0.002	0.006	0.02	0.03
Rock	39	0.03	0.04	0.1	0.2
Coal	10	0.05	0.02	0.06	0.10
Plant	9	0.01	0.01	0.02	0.04

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Gold by flame or graphite furnace atomic absorption spectrometry

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Principle

Gold is determined in geologic materials by the flame atomic absorption spectrophotometry (FAAS) (Thompson, and others, 1968; Ward and others, 1969; O'Leary and Meier, 1986) or graphite furnace atomic absorption spectrophotometry (GFAAS) (Meier, 1980). The gold in the sample is dissolved with a hydrobromic acid-0.5 percent bromine solution. The gold-bromide complex that is formed is extracted from the acid solution with methyl isobutyl ketone (MIBK). The organic solvent is washed with dilute hydrobromic acid to remove iron which causes interference. The MIBK is atomized into the flame or pipetted into a graphite furnace of an atomic absorption spectrophotometer for estimation of gold content.

Interference

Iron causes interference in the estimation of gold by atomic absorption spectrometry, presumably by light scattering. The iron is effectively eliminated by washing the MIBK extract with 0.1 *M* HBr. Care must be taken to avoid contamination of the graphite furnace by samples containing high concentrations (>0.1 ppm) of gold. All samples should be first analyzed by FASS and then by GFAAS for samples with concentrations of less than 0.05 ppm gold.

Scope

This method is applicable to a wide variety of geologic materials. However, heterogeneous distribution of gold in the sample may result in pronounced imprecision due to sampling error. Also the HBr-Br_2 digestion may not effectively solubilize gold occluded in silicate matrices. These problems can be minimized by extra fine grinding and the use of as large a sample size as possible. The lower reporting unit for 10-gram samples is 0.1 ppm for the FAAS and 0.002 ppm for GFAAS. Upper reporting limit without dilution is 2.0 ppm for FAAS and 0.05 ppm for GFAAS. Approximately 50 samples per day can be analyzed by this method.

Apparatus

- Atomic-absorption spectrophotometer equipped with flame and graphite furnace atomizers
- Centrifuge
- Horizontal tube-shaking machine
- Hot plate
- Metal test tube rack
- Muffle furnace
- Pipette, 5 mL disposable transfer
- Porcelain evaporating dish, 60-mm diameter
- Powder funnel, 65-mm

- Test tubes 25 x 150-mm disposable
- Vortex mixer

Reagents

All chemicals should be of reagent grade and all water deionized (DI)

- Bromine, Br_2
- Hydrobromic acid, HBr
- Methyl isobutyl ketone MIBK: 4-methyl-2-pentanone

Hydrobromic acid—0.5 percent bromine solution: Add 5 mL Br_2 per 1 L of conc HBr.

Hydrobromic acid 0.1 M, MIBK saturated: Dilute 12 mL conc HBr to 1 L with DI water. Add 200 mL MIBK, shake thoroughly, allow phases to separate, and discard MIBK layer.

Gold standard solution, 1,000 µg/mL: Dissolve exactly 1.000 g gold in 100 mL HBr·0.5 percent Br solution in a volumetric flask. Heat gently to expel excess bromine. Cool and dilute to 1 L with conc HBr.

Dilute gold solution, 100 µg/mL: Dilute 10.0 mL of 1,000 µg/mL stock gold solution to 100 mL in a volumetric flask with conc HBr. Make fresh yearly.

Dilute gold solution, 1 µg/mL: Dilute 1.0 mL of 100 µg/mL gold solution to 100 mL in a volumetric flask with conc HBr. Make fresh yearly.

Gold standard solutions in MIBK for FAAS: 0.5, 1.0, and 2.0 µg/mL: Add 1.0, 2.0, and 4.0 mL of 100 µg/mL dilute gold solution to three 200-mL volumetric flasks containing 200 mL MIBK. Shake vigorously. Transfer contents to three 500-mL regent bottles containing 100 mL equilibrated (MIBK-saturated) 0.1 *N* HBr and shake. Make fresh every 3 months.

Gold standard solutions in MIBK for GFAAS: 0.025 and 0.050 µg/mL: Add 0.250 mL and 0.50 mL of 1 µg/mL dilute gold solution to two 25x150-mm disposable test tubes containing 10 mL of MIBK and 40 mL of equilibrated 0.1 *N* HBr. Cap and shake vigorously for 2 minutes. Make fresh weekly.

Blank MIBK solution for FAAS and GFAAS: Shake 200 mL MIBK vigorously in a 500-mL reagent bottle containing 100 mL equilibrated 0.1 *N* HBr.

Safety precautions

All digestions and work with open or uncapped reagents must be done in an operating chemical hood. Protective clothing, eyewear and gloves must be worn. See the *CHP* and *MSDS* for precautions, effects of overexposure, first-aid treatment, and disposal procedures for reagents used in this method. The muffle furnace must be adequately vented.

Procedure

1. Weigh 10 g sample into a porcelain evaporating dish. Turn on the hood exhaust vent for the muffle furnace.

2. Ignite sample at 700°C in a muffle furnace for 1 hour or until sulfides and organic matter are completely oxidized.

3. Transfer sample to a 25x150-mm test tube containing 10 mL HBr-0.5 percent Br_2. Care must be taken when adding a sample containing carbonate materials to the HBr-0.5 percent bromine solution. Rapid effervescence may cause loss of sample from the culture tube and splattering of acid. Add sample slowly, mix, and add extra HBr-0.5 percent bromine solution to insure a high acid concentration. Red to orange color is present if acidity is correct. The 65-mm funnels inserted in the tube will often serve to contain effervescing sample.

4. Mix sample solution thoroughly and heat in a metal rack in a hot plate set on high until the tubes begin to tap. Remove immediately. Do not allow tubes to overheat.

5. Allow to cool, add 10 mL MIBK and 10 mL DI water, cap, and shake in a horizontal shaking machine for 3 min.

6. Centrifuge until layers separate and transfer the MIBK layer using a 5-mL disposable transfer pipette, to a 25x150-mm test tube containing 40 mL equilibrated 0.1 *M* HBr. (The transfer of MIBK need not be quantitative but should consist of at least 4 mL for all subsequent analysis.)

7. Cap, shake for 2 min, and allow phases to separate.

8. Estimate the gold content by atomizing the organic layer into the flame and/or graphite furnace of an atomic absorption spectrophotometer. Calibrate flame or reslope graphite furnace after every 10 samples.

Standardization of Instrument

Table 3 shows the operating conditions for a Perkin-Elmer Model 603 flame atomic absorption spectrophotometer.

Table 3.—Operating conditions for determination of Au by FAAS

Grating	ultraviolet
Wavelength	242.8 nm
Slit	0.7 nm
Lamp current	10 mA
Source	gold (hollow cathode lamp)
Integration time	1 s
Burner	Boling (three slot)
Flame condition	oxidizing (lean blue)
Concentration mode	
1 µg/mL	0.074 *A* (instrument calibration setting = 1.00)
2 µg/mL	0.148 *A* (instrument calibration setting = 2.00)

The following instrumental operating conditions, table 4, are for a Perkin-Elmer 5000 equipped with a graphite furnace with Zeeman background correction.

Table 4.—Operating conditions for determination of Au by GFAAS

Grating	ultraviolet
Wavelength	242.8 nm
Background correction	Zeeman
Slit	0.7 nm, low
Lamp current	10 mA
Graphite tube	Pyrocoated with L'vov platform
Source	gold (hollow cathode lamp)
Purge gas	nitrogen, 35 cc/min
Integration time	6 s
Mode	concentration
Signal	peak area
Dry cycle	
Ramp	10 s
Hold	20 s
Temp	120°C
Char cycle	
Ramp	1 s
Hold	15 s
Temp	500°C
Atomization Cycle	
Ramp	0 s
Hold	5 s
Temp	2000°C
REC	-1 s
Read	-1 s
Baseline	not used
INT FLOW	0
Clean-up cycle	0.05 µg/mL (calibration setting = .050 ppm)
Ramp	1 s
Hold	3 s
Temp	2700°C
Concentration mode	
0.025 µg/mL	0.300 ± 10% *A* (instrument calibration setting = 0.25 ppm)

Calculation

The formula to calculate the gold concentration is:

$$\text{Au (ppm)} = \frac{\text{volume of MIBK (mL)}}{\text{sample wt (g)}} \times \text{AAS sample reading } (\mu\text{g / mL})$$

Assignment of uncertainty

The analytical results for gold, by flame and graphite furnace AAS respectively, in selected reference materials, duplicate samples, and method blanks are summarized in tables 5 and 6.

Table 5.—Analytical performance summary for Au (ppm) by FAAS

[A=Grimes, 1991; B=Nevada Bureau of Mines, 1991; remaining *pv* from Potts and others, 1992]

Reference	*Description*	*n*	*Mean*	*s*	*pv*	*% RSD*	*% R*
GXR-4	coppermill ore	10	0.48	0.06	0.47	13	102
DGPM-1	disseminated gold	10	0.57	0.01	0.72 A	2	79
NBM-1b	andesite	10	1.19	0.02	1.54 B	2	77
GXR-1	jasperoid	30	3.2	0.2	3.4	6	94

Duplicate samples	*k*	*n*	*Mean*	*s*	*% RSD*	*Concentration range*	*No. of < (total)*	*No of < (pairs)*
	8	2	5.31	0.08	1	0.05 to 38	48	23

Method blank	*n*	*Mean*	*s*	*3s*	*5s*
	10	-0.002	0.01	0.03	0.06

Table 6.—Analytical performance summary for Au (ppm) by GFAAS

[A=Nevada Bureau of Mines, 1991; B=Canadian Certified Reference Materials Project, 1992, C=Grimes, 1991; remaining *pv* from Potts and others, 1992]

Reference	*Description*	*n*	*Mean*	*s*	*pv*	*% RSD*	*% R*
NBM-1a	andesite	10	<0.002	--	**0.003** A ?	--	--
GXR-2	soil	25	0.024	0.003	0.036	12	67
UMT-1	ultramafic ore tailings	10	0.045	0.005	**0.0482** B	11	93
GXR-6	soil	131	0.087	0.009	0.095	10	92
DGPM-2	disseminated gold	10	0.24	0.02	0.263 C	8	91

Duplicate samples	*k*	*n*	*Mean*	*s*	*% RSD*	*Concentration range*	*No. of < (total)*	*No. of < (pairs)*
	18	2	0.007	0.001	17	0.001 to 0.028	38	19

Method blank	*n*	*Mean*	*s*	*3s*	*5s*
	38	0.00003	0.0004	0.001	0.002

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Ward, F.N., Nakagawa, H.M., Harms, T.F., and VanSickle, G.H., 1969, Atomic absorption methods useful in geochemical exploration: U.S. Geological Survey Bulletin 1289, 45 p.

Tellurium and thallium by flame atomic absorption spectrometry

By Richard M. O'Leary

Code: A061 Accepted: 1/19/94

Principle

Tellurium and thallium are determined by the modified flame atomic absorption method developed by O'Leary and Viets (1986). The sample is decomposed by hydrofluoric and sulfuric acids and the residue is treated with hydrochloric acid and hydrogen peroxide. Tellurium and thallium are selectively extracted into a 10 percent Aliquat 336-MIBK organic phase in the presence of ascorbic acid and potassium iodide. The organic solution is atomized by flame atomic absorption spectrometry (FAAS) for determination of tellurium and thallium concentrations.

Interferences

Iron is the major interfering element in the determination of tellurium and thallium in geologic materials by atomic absorption spectrometry. However, this interference is eliminated by reducing the iron with ascorbic acid. Addition of the 10 percent Aliquat 336-MIBK in the presence of ascorbic acid and potassium iodide eliminates this interference.

Scope

The lower reporting limit for tellurium and thallium is 0.1 ppm. The upper limit of 10 ppm can be extended by the dilution of an aliquot of the 10 percent Aliquat 336-MIBK layer. Approximately 35 samples can be analyzed per day for both elements.

Apparatus

- Atomic-absorption spectrophotometer equipped with flame atomizer
- Boiling chips
- Centrifuge
- Beakers, 50-mL, Teflon FEP
- Test tubes, 16x150-mm disposable, with caps
- Hot plate
- Horizontal shaking machine
- Vortex mixer

Reagents

All chemicals should be reagent grade, and all water should be metal-free, unless otherwise indicated.

- Deionized water (DI)
- Aliquat 336, tricaprylylmethylammonium chloride (obtainable from Aldrich Chemical Company)
- Hydrochloric acid, HCl conc 36 to 37 percent
- Hydrogen peroxide, H_2O_2 conc 30 percent
- Hydrofluoric acid, HF conc 49 percent

- Methyl isobutyl ketone, MIBK
- Sulfuric acid, H_2SO_4 conc 98 percent

Aliquat 336-MIBK 10 percent (v/v): Pour 100 mL Aliquat 336 into a clean 1-L, graduated cylinder, dilute to 1 L with MIBK, shake to dissolve the Aliquat 336, and pour into brown glass bottle. This solution is stable for at least 1 month.

Ascorbic acid-potassium iodine solution, 30-15 percent (w/v): Weigh 300 g $C_6H_80_6$ (U.S.P. food grade or metal-free equivalent) and 150 g KI into a beaker, dissolve in DI water by stirring, and warming over low heat, then dilute to 1L. Store in brown glass bottle. Prepare fresh weekly.

Tellurium and thallium standard solutions, 1,000 µg/mL: Prepare by accurately weighing 1.000 g pure thallium and 1.250 g tellurium oxide into separate 1,000-mL flasks. Dissolve in 20 mL HCl-10 percent Br solution, heat gently to expel excess of bromine, and make up to volume in 1,000-mL volumetric flask with 10 *M* HCl.

Combined stock solution 2, 5, and 10 µg/mL: Add 0.20, 0.50, and 1.0 mL of each 1,000 µg/mL stock solution to three 100 mL volumetric flasks and dilute to volume with 10 *M* HCl.

Instrument calibration standards 2, 5, and 10 µg/mL: Add 1 mL H_2SO_4 to three 16x150 mm disposable test tubes containing a boiling chip. **Carefully and slowly, with the test tube pointed away from the preparer**, add 3 mL HCl down the inside of the tube to avoid effervescence of the acids out of the tube. Add 2.00 mL of the combined stock solutions containing 2, 5, and 10 µg/mL. Add 0.5 mL H_2O_2 and mix. Allow to set for 10 min and add 0.5 mL H_2O_2 and mix. After 10 min place in a heating block at 110°C and heat until the remaining chlorine and hydrogen peroxide is evolved. Remove from heat and when cool add 4 mL ascorbic acid-potassium iodide solution, mix and allow to set for 20 min. Continue preparation starting at step 6 in the procedure. Calibration standard and method blank should be made for every 20 samples.

Safety precautions

Special care must be taken when preparing the instrument standards. Cautiously and slowly, with the test tube pointed away from the preparer, add the HCl to the tubes containing the sulfuric acid. Rapid addition of the HCl will cause the acids to effervesce from the tube. All work with open or uncapped reagents must be done in a chemical hood. Protective clothing including laboratory coats or aprons, gloves, and eyewear must be worn. Refer to the *CHP* and *MSDS* for further information concerning specific precautions, first-aid treatment and disposal procedures for chemical products used in this method. Calcium gluconate gel should be available in labs where HF is in use.

Procedure

1. Weigh 2.00 g sample into a 50-mL Teflon FEP beaker.

2. Add 2 mL DI water to wet the sample, 1 mL conc H_2SO_4 and 10 mL conc HF, place on the hot plate preset to 140°C overnight. The HF must be consumed and evaporated leaving the H_2SO_4 and sample.

3. Remove from heat and allow to cool. Add 5.0 mL conc HCl followed by 1.0 mL 30 percent H_2O_2 dispensed in 0.25 mL portions, 10 min apart. Mix sample well after each addition of the hydrogen peroxide.

4. After 10 min place beaker on hot plate at 125°C and evolve remaining hydrogen peroxide and chlorine. It is critical to minimize the loss of liquid during this step, therefore, do not over heat.

5. Remove from hot plate and transfer contents to a 16x150-mm disposable test tube. Rinse beaker with 4.0 mL ascorbic acid-potassium iodide solution, transfer to the test tube, mix, and let stand for 20 min.

6. Accurately add 3.0 mL 10 percent Aliquat 336-MIBK solution to each tube. Cap and shake for 5 min.

7. Centrifuge the samples at 1,000 rpm for 10 min to separate the organic layer from the acid layer.

8. Determine the tellurium and thallium content by atomizing the organic layer in a flame atomic absorption spectrophotometer.

Standardization of equipment

Table 7 lists the instrumental operating conditions for determining tellurium and thallium using a Perkin-Elmer 5000 atomic absorption spectrometer.

Table 7.—Operating conditions for determination of Te and Tl by FAAS

	Tellurium	*Thallium*
Grating	ultraviolet	ultraviolet
Source lamp	EDL	EDL
Integration time	1 s	1 s
Flame condition	oxidizing	oxidizing
Wavelength	214.3 nm	276.8 nm
Slit	0.2 nm	0.7 nm
Burner, cm	3-slot	3-slot
Background correction (deuterium)	yes	no
Concentration mode		
2.0 ppm	0.045 *A*	0.045 *A*
5.0 ppm	0.090 *A*	0.090 *A*

Assignment of uncertainty

Table 8 is the analytical results for tellurium and thallium of selected reference materials, duplicates samples, and method blanks.

Table 8.—Analytical performance summary for Te and Tl (ppm) by FAAS

[A=Hubei Geological Research Laboratory, 1990; B=Govindaraju, 1989; C=National Institute of Standards and Technology, 1992; remaining *pv* from Potts and others, 1992]

Reference	*Description*	*n*	*Mean*	*s*	*pv*			*% RSD*	*% R*
Tellurium, Te									
SRM 2709	soil	10	0.04	0.03	--			75	--
GSD-7	stream sediment	10	0.05	0.01	0.065			20	77
GSD-12	stream sediment	10	0.24	0.02	0.29			8	83
GSD-11	stream sediment	10	0.44	0.04	0.38		?	9	116
GSS-6	soil	10	0.42	0.02	0.42		?	5	100
GXR-4	coppermill ore	40	0.73	0.07	0.97			10	75
GBW 07236	lead ore	10	1.03	0.05	1.2	A		5	86
SRM 2711	soil	10	1.28	0.04	--			3	--
GBW 07235	lead ore	10	3.5	0.1	3.9	A		3	90
GSS-5	soil	10	6.2	0.2	4.0		?	3	155
GXR-1	jasperoid	10	11.8	0.9	13		?	8	91
Thallium, Tl									
GXR-1	jasperoid	10	0.42	0.05	0.39	B	?	12	108
GBW 07235	lead ore	10	0.41	0.03	0.43	A		7	95
SRM 2709	soil	10	0.61	0.01	0.74			2	82
GSD-7	stream sediment	10	0.86	0.03	0.93			3	92
GBW 07236	lead ore	10	0.88	0.03	1.0	A		3	88
GSS-5	soil	10	1.71	0.06	1.6			4	107
GSD-12	stream sediment	10	1.62	0.02	1.8			1	90
GSS-6	soil	10	2.38	0.04	2.4			2	99
SRM 2711	soil	10	2.30	0.04	**2.47**	C	*cv*	2	93
GSD-11	stream sediment	10	2.73	0.03	2.9			1	94
GXR-4	coppermill ore	40	3.1	0.1	3.2			3	97

Duplicate samples	*k*	*n*	*Mean*	*s*	*% RSD*	*Concentration range*	*No. of < (total)*	*No. of < (pairs)*
Tellurium	20	2	0.33	0.01	3	0.12 to 0.91	8	4
Thallium	16	2	0.56	0.02	3	0.01 to 1.37	16	8

Method blank	*n*	*Mean*	*s*	*3s*	*5s*
Tellurium	12	0.01	0.02	0.08	0.1
Thallium	12	-0.008	0.02	0.04	0.07

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Mercury in water, geologic, and plant materials by continuous flow-cold vapor-atomic absorption spectrometry

By Richard M. O'Leary, Philip L. Hageman, and James G. Crock

Code: A091

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Principle

To determine mercury in geologic and plant materials, samples are digested with nitric acid and sodium dichromate in a disposable test tube. After digestion, samples are diluted with water to 12 mL. To determine mercury in water, samples must be preserved with a 1 percent sodium dichromate/nitric acid solution. All samples are then mixed with air and a sodium chloride-hydroxylamine hydrochloride-sulfuric acid solution and Hg (II) is reduced to Hg° with stannous chloride in a continuous flow manifold. The mercury vapor is separated and measured using continuous-flow cold vapor-atomic absorption spectrometry (CV-AAS). This method is a variation of Kennedy and Crock (1987).

Interference

Samples containing high concentrations of Ag, Au, Pt, Te, and Se may diminish the extraction efficiency of the Hg in geologic samples (Bartha and Ikrenyi, 1982 and Suddendorf, 1981). Of these, only selenium poses a significant problem for nonmineralized geologic materials. Although a 1 ppm solution of the other elements causes greater than a 90 percent suppression of a 0.01 ppm Hg solution, these elements either will not be dissolved (Au, Pt) or are normally present at low concentrations (Ag, Te). Silver does not become a problem until its concentration exceeds 12 ppm in sample. Samples containing silver above 12 ppm need to be diluted. Concentrations above 25 ppm Se suppress recovery of Hg and should be diluted.

Scope

The method offers a lower reporting limit of 0.02 ppm mercury in solid-phase samples. Samples exceeding the working range of 0.02-1.8 ppm mercury require dilution. For water samples, the method offers a lower reporting limit of 0.1 ppb. Samples exceeding the working range of 0.1-1.5 ppb mercury must be diluted. Approximately 40 samples can be analyzed per person-day.

Apparatus

- Perkin-Elmer 3030B Spectrophotometer
- Perkin-Elmer 56 Strip Chart Recorder

- Technicon AAII Autosampler, modified by replacing the metal sampling probe with a glass sampling probe
- Gilson Medical Electronic (Middleton, Wisconsin) Model Minipulse 2, eight channel, variable-speed peristaltic pump equipped with standard tygon pump tubing
- Standard laboratory hot plate with a 30x60-cm heating surface
- General Electric Chill Chaser Deluxe Infrared Heat Lamp. Position around the flow-through cell and the phase separator
- 7.5-cm-thick x 33-cm-wide x 43-cm-long aluminum heating block, with 18-mm holes drilled through in a 10 by 10 matrix

See figures 1 and 2 for the flow-through cell and phase separator used in this method. These have been described by Skougstad and others (1979). Mixing coils are available from Bran + Luebbe, Inc., Buffalo Grove, IL.

Reagents

Unless otherwise noted, chemicals are reagent grade and water is deionized (DI).

1 percent (w/v) sodium dichromate-nitric acid solution: Dissolve 10 g $Na_2Cr_2O_7{\cdot}2H_2O$ in 1.0 L conc 'INSTRA-ANALYZED' grade HNO_3.

30 percent (w/v) potassium hydroxide solution: Dissolve 30 g KOH in DI water and dilute to 100 mL.

25 percent (w/v) sodium dichromate solution: Dissolve 500 g reagent grade $Na_2Cr_2O_7{\cdot}2H_2O$ in sufficient DI water to bring the volume to 2 L.

Nitric acid wash: Dilute 40 mL 'INSTRA-ANALYZED' grade HNO_3 (16 *M*) to 4 L with DI water.

Stannous chloride solution: Dissolve 100.0 g $SnCl_2{\cdot}2H_2O$ (suitable for Hg determination grade) in 100 mL conc (12 *M*) 'INSTRA-ANALYZED' grade HCl. Let the solution stand for 20 to 30 min until the $SnCl_2{\cdot}2H_2O$ totally dissolves. Dilute to 1 L with DI water. This solution is stable for about 1 week with refrigeration at 5°C.

Complex-reducing solution: Dissolve 30.0 g hydroxylamine hydrochloride and 30.0 g NaCl in about 500 mL DI water. While mixing, slowly add 100 mL conc (18 *M*) H_2SO_4, 'INSTRA-ANALYZED' grade. When the solution is cool, dilute to 1 L with DI water.

Stock solution: SRM 1641c (1.47 ppm mercury in DI water) available from the National Institute of Standards and Technology.

Mercury calibration standards: 1.47 ppb, 7.35 ppb, and 14.7 ppb: Prepare by diluting with DI water, 0.5 and 2.5, and 5.0 mL of 1.47 ppm mercury solution (SRM 1641c) in three 500 mL volumetric flasks containing 100 mL conc HNO_3 and 10 mL 25 percent sodium dichromate solution.

Safety precautions

Normal laboratory safety procedures should be observed, including the use of protective eyewear, laboratory coat, and gloves. All chemical digestion activities should be performed in a chemical hood. See the *CHP and MSDS* for further information concerning first-aide treatment and disposal procedures etc. for chemical products used in this method. The atomic absorption spectrophotometer should be located under a vent exhaust hood to evacuate the acid gases and mercury vapors that are generated by the continuous flow-cold vapor system.

Procedure for geologic and plant samples

1. Weigh 0.100 g sample into 16x100-mm disposable test tube.
2. Add 2.0 mL 16 *M* HNO_3, and 0.50 mL 25 percent sodium dichromate solution to the sample. Vortex wet the entire sample solution.
3. Place test tube in the aluminum heating block for 2 hours at 110°C. Remove from the heating block and allow to cool completely. (Overnight cooling is acceptable.)
4. Dilute sample solution to 12 mL with DI water, cap and shake for 2 min.
5. If the sample is mineralized or it contains more than 25 ppm Se, 10 ppm Au, 10 ppm Ag; transfer 0.6 mL to a second test tube, add 2 mL HNO_3, 0.5 mL 25 percent dichromate solution, and dilute to 12 mL with DI water.
6. Aqueous standards of 1.47, 7.35, and 14.7 ppb Hg are used for the calibration curve with each day's analysis.
7. Using the manifold illustrated in figure 3, the digested geochemical materials are analyzed along with aqueous calibration standards. The modifications to the manifold include changes to reagent and sample flow rates and reagent composition. These were made to maximize the absorbance signal of a 0.01 ppm Hg solution, and to allow the high dichromate concentration in the sample digest. Samples with Hg concentration greater than the highest standard (14.7 ppb in solution or 1.8 ppm in the sample) must be diluted and reanalyzed. Any sample following a sample that exceeds the concentration of the upper standard, should be reanalyzed due to potential Hg carry over from the previous sample.
8. The calibration curve is checked at the beginning and end of every job (approximately 40 samples).

Procedure for water samples

Water samples should arrive at laboratory preserved with a 1 percent sodium dichromate/conc HNO_3 solution in a ratio of 1:19 (one part sodium dichromate/HNO_3 solution to 19 parts DI water sample).

1. Upon arrival at laboratory, water samples are shaken and transferred into 16 x 100 mm disposable test tubes.
2. Aqueous calibration standards of 0.37, 0.74, and 1.47 ppb are used for water analysis. They are obtained by dilution of the calibration standards used for geologic and plant samples, using the dilution technique previously described.

3. Water samples are then analyzed using the same reagents and equipment used for geologic and plant samples with the exception of increasing sensitivity of the strip chart recorder from 5mV to 2mV. Any sample exceeding the working range (0.20-1.47 ppb) must be diluted and reanalyzed.
4. The calibration curve is checked at the beginning and end of every job.

Standardization of Instrument

Instrument settings used for a Perkin-Elmer 3030B AAS Spectrometer and a Perkin-Elmer 56 Recorder are outlined in table 9.

Table 9.—Operating conditions for determination of Hg by CV-AAS

Lamp	Hg hollow cathode, 4 mA
Slit	0.7 nm
Wavelength	253.7 nm, no background correction
Recorder	5 mV full-scale response, 5 mm/min; 2mV for water samples
1.47 µg/L	9 mm on recorder paper

Calculation

Measure peak height to the nearest division and calculate the mercury concentration in the sample with the following formula:

$$\text{Hg (ppm)} = \frac{\text{standard conc } (\mu\text{g / mL})}{\text{recorder reading of standard (divisions or mm)}} \times \frac{\text{total sample solution volume (mL)}}{\text{sample wt (g)}} \times \text{recorder reading of sample (divisions or mm)}$$

Assignment of Uncertainty

The reporting limit can be lowered by using a larger sample (up to 0.5 g) or a smaller dilution volume (as little as 8.0 mL due to the requirements of the manifold). Table 10 shows the analytical results of selected reference materials, duplicate samples, and method blanks obtained by this method.

Table 10.—Analytical performance summary for Hg by CV-AAS (water samples in ppb, solid phase samples in ppm)

[A=Erdmann, 1994; B=National Institute of Standards and Technology (NIST), 1993; C=National Bureau of Standards, 1983; D=Govindaraju, 1989; E=NIST, 1992; remaining *pv* from Potts and others, 1992]

Reference	*Description*	*n*	*Mean*	*s*	*pv*		*% RSD*	*% R*
HG 5	water	9	0.23	0.01	0.30	A	6	77
HG 4	water	9	0.58	0.04	0.60	A	6	97
HG 1	water	9	0.92	0.03	0.98	A	3	94

Reference	*Description*	*n*	*Mean*	*s*	*pv*		*% RSD*	*% R*
SRM 1515	apple leaves	9	0.04	0.01	**0.044**	B *cv*	27	83
G-2	granite	10	0.07	0.01	0.049		13	135
GSD-12	stream sediment	68	0.10	0.04	0.056		40	179
SRM 1572	citrus leaves	9	0.07	0.02	0.08	C *cv*	26	88
SRM 1575	pine needles	9	0.14	0.01	0.15	B *cv*	7	95
GXR-5	soil	77	0.19	0.02	0.167		10	112
MESS-1	marine sediment	10	0.22	0.01	0.171	D	6	131
SGR-1	shale	20	0.18	0.01	*0.254*		8	69
GXR-3	hot spring deposit	63	0.32	0.02	0.33		5	97
SRM 2709	soil	28	1.4	0.1	**1.40**	E *cv*	6	99
GXR-2	soil	145	3.1	0.2	2.9		8	107
GXR-1	jasperoid	10	4.0	0.3	3.9		8	103
SRM 2711	soil	11	5.9	0.5	**6.25**	E *cv*	8	94

Duplicate samples	*k*	*n*	*Mean*	*s*	*% RSD*	*Concentration range*	*No. of < (total)*	*No. of < (pairs)*
Solid phase	46	2	0.06	0.01	15	0.02 to 0.18	82	36
No duplicate data available for water samples at this time								

Method blank	*n*	*Mean*	*s*	*3s*	*5s*
Water	15	0.01	0.02	0.04	0.08
Solid phase	15	0.001	0.001	0.004	0.006

Each daily run of samples is preceded by three aqueous calibration standards, a reference sample taken through the digestion procedure, and a digested reagent blank. The three aqueous standards establish the sensitivity; the reference sample is a check of digestion and the blank establishes if there is any contamination. Low values for the aqueous standards and/or high values for the reference sample suggest the apparatus needs to be disassembled and cleaned with 30 percent KOH. Upon heating this removes any residual mercury or organic carbon buildup.

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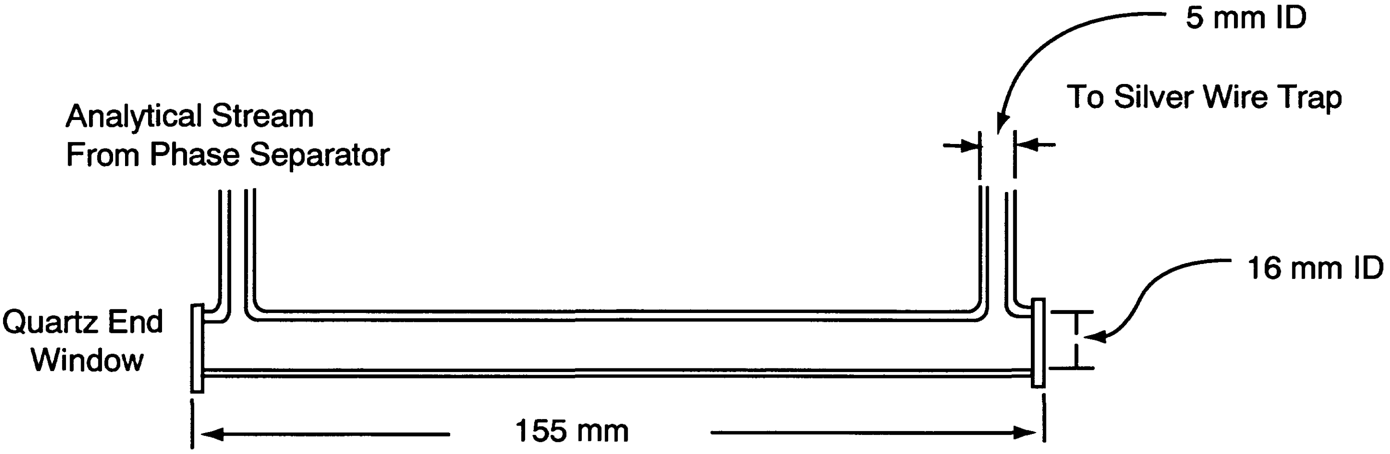

Figure 1. The flow-through cell used for the determination of mercury. The two 16-mm end windows of this cell are quartz and the remainder of the cell is Pyrex glass. J.G. Crock and others, 1987, U.S. Geological Survey Open-File Report 87-84, 16 p.

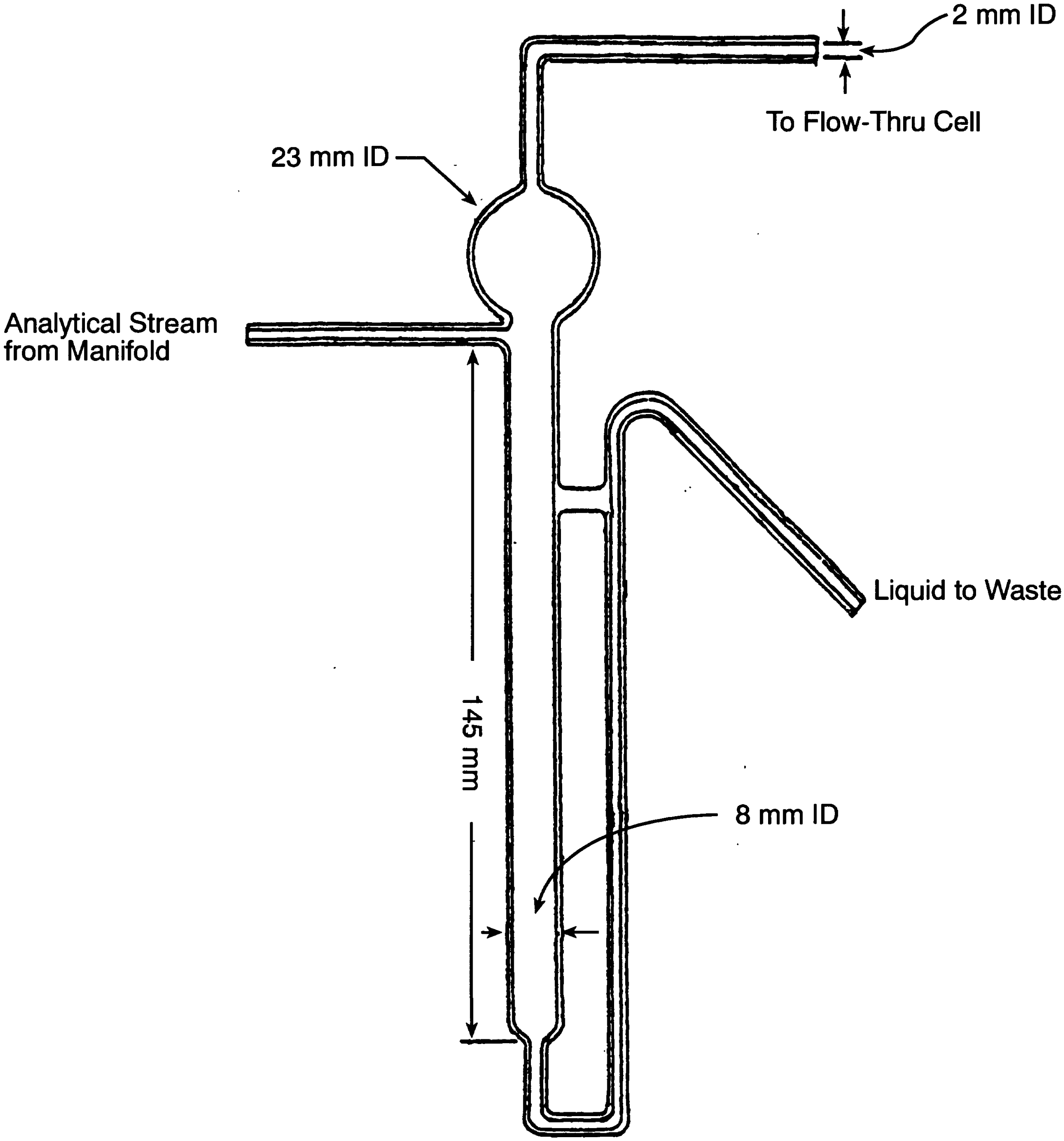

Figure 2. Phase separator used in the determination of mercury. The separator is made from Pyrex glass. J.G. Crock and others, 1987, U.S. Geological Survey Open-File Report 87-84, p. 17.

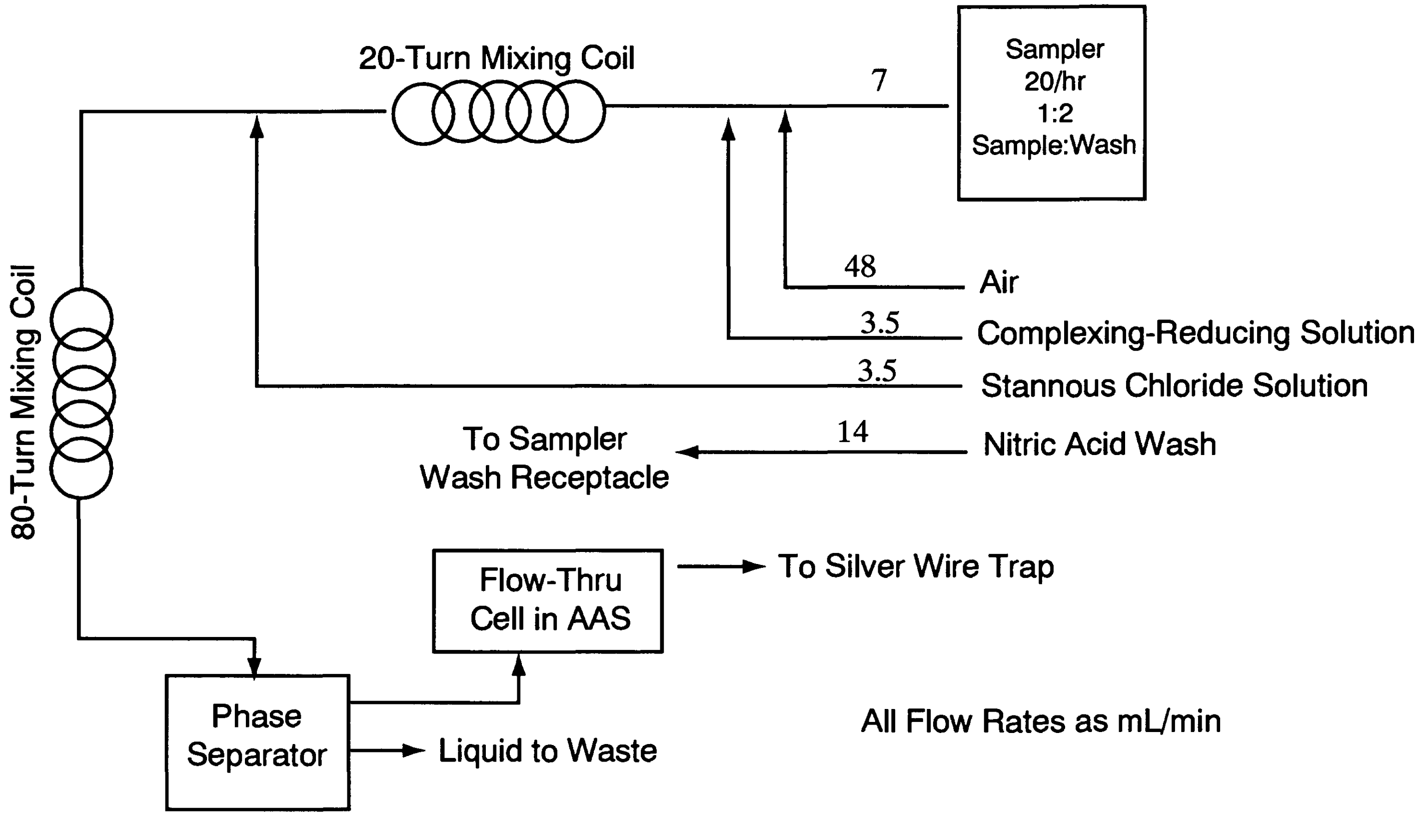

Figure 3. Manifold used for the automated generation of mercury vapor. J.G. Crock and others, 1987, U.S. Geological Survey Open-File Report 87-84, p. 19.

Mercury in whole coal and biological tissue by continuous flow-cold vapor-atomic absorption spectrometry

By Richard M. O'Leary

Code: A200 Accepted: 6/6/94

Principle

To determine mercury in whole coal and biological tissue, samples are digested with nitric acid, sulfuric acid, and vanadium pentoxide in a disposable glass test tube. After digestion, samples are diluted with water to a constant volume. All samples are then mixed with air and a solution of sodium chloride, hydroxylamine hydrochloride, and sulfuric acid and then Hg (II) is reduced to Hg° with stannous chloride solution in a continuous flow manifold. The elemental mercury vapor is separated and measured using cold vapor-atomic absorption spectrometry (CV-AAS).

Interference

Sample solutions containing elevated concentrations of Ag, Au, Pt, Te, and Se may diminish the recovery of the Hg, as has been noted by previous investigators (Bartha and Ikrenyi, 1982 and Suddendorf, 1981). Of these, only Se poses a significant problem for nonmineralized geologic materials. Although a 1 ppm solution of the other elements causes greater than a 90 percent suppression of a 0.01 ppm Hg solution, these elements either will not be dissolved (Au, Pt) or are normally present at lower concentrations (Ag, Te). Silver does not become a problem until its concentration exceeds 12 ppm in the sample. Samples containing silver above 12 ppm need to be diluted. Selenium concentrations above 25 ppm suppresses recovery of mercury and the sample should be diluted.

Scope

The method offers a lower reporting limit of 0.02 ppm mercury in whole coal and biological samples. Samples exceeding the working range of 0.02–1.5 ppm mercury require dilution. Approximately 40 samples can be analyzed per person-day.

Apparatus

- Perkin-Elmer 272 Spectrophotometer
- Perkin-Elmer 056 Strip Chart Recorder
- Technicon AAII Autosampler, modified by replacing the metal sampling probe with a glass tube
- Gilson Medical Electronic (Middleton, Wisconsin) Model Minipulse 2, eight channel, variable-speed peristaltic pump equipped with standard tygon pump tubing
- Standard laboratory hot plate with a 30x60-cm heating surface
- General Electric Chill Chaser Deluxe Infrared Heat Lamp. Position around the flow-through cell and the phase separator
- 7.5-cm-thick x 33-cm-wide x 43-cm-long aluminum heating block, with 18-mm holes drilled through in a 10 by 10 matrix (100 holes)
- Watch glass, 25-mm diameter

See figures 1 and 2 (pages 48 and 49) for the flow-through cell and phase separator used in this method. These have been described by Skougstad and others (1979). Mixing coils are available from Bran + Luebbe, Inc., Buffalo Grove, IL.

Reagents

Unless otherwise noted, chemicals are reagent grade and water is deionized (DI).

- Hydrochloric acid, 12 *M* conc 'BAKER INSTRA-ANALYZED'
- Sulfuric acid, 18 *M* conc 'BAKER INSTRA-ANALYZED'
- Vanadium Pentoxide, V_2O_5: Some brands of V_2O_5 contain detectable amounts of mercury. All V_2O_5 should be roasted prior to use in a chemical hood. Roast in a porcelain dish using a muffle furnace or a fisher burner, at a temperature below 690° C, the melting point of V_2O_5. Do not breath V_2O_5 dust as it is highly toxic, an irritant, and a possible mutagen.
- Nitric acid, 16 *M* conc 'BAKER INSTRA-ANALYZED'

Nitric acid wash: Dilute 40 mL 'BAKER INSTRA-ANALYZED' grade HNO_3 to 4.0 L with DI water

30 percent potassium hydroxide solution: Dissolve 30 g KOH in DI water and dilute to 100 mL

Stannous chloride solution: Dissolve 100.0 g $SnCl_2 \cdot 2H_2O$ (Baker, suitable for Hg determination grade) in 100 mL conc. 'BAKER INSTRA-ANALYZED' grade HCl. Let the solution stand for 20 to 30 minutes until the $SnCl_2 \cdot 2H_2O$ totally dissolves. Dilute to 1.0 L with DI water. This solution is stable for about 1 week with refrigeration.

Complex-reducing solution: Dissolve 30 g hydroxylamine hydrochloride and 30 g NaCl in about 500 mL DI water. Add very slowly 100 mL conc H_2SO_4. When the solution is cool, dilute to 1 L with DI water.

Sodium dichromate, 25 percent (w/v) solution: Dissolve 25 g $Na_2Cr_2O_7 \cdot 2H_20$ in DI water and dilute to 100 mL.

Mercury standard solution: SRM 1641c (1.47 ppm mercury in DI water) available from the: National Institute of Standards and Technology

Mercury calibration standards, 0.00147, 0.00735, and 0.0147 ppm: Prepare by diluting in DI water, 0.5, 2.5, and 5.0 mL of 1.47 ppm mercury solution (SRM 1641c) in three 500 mL volumetric flasks containing 115 mL conc HNO_3, 50 mL conc H_2SO_4 and 10 mL of 25 percent (w/v) sodium dichromate. These standards correspond to 0.147, 0.735, and 1.47 ppm Hg in the whole coal sample. Make fresh every 3 months.

Safety precautions

Normal laboratory safety procedures should be observed, including the use of protective eyewear, laboratory coat, and gloves. All chemical digestion activities should be performed in a chemical hood. See the *CHP and MSDS* for further information concerning first-aid treatment and disposal procedures, etc. for chemical products used in this method. The atomic absorption spectrophotometer should be located under a vent exhaust hood to evacuate the acidic gases and mercury vapors that are generated by the continuous flow-cold vapor system.

Procedure

1. Weigh 0.150 g of whole coal or dried biological tissue (0.75 to 1.5 g undried biological tissue) into 16x150-mm disposable test tube.
2. Add approximately (scooped) 0.1 g V_2O_5, 3.5 mL conc HNO_3, and 1.50 mL conc H_2SO_4 to the sample. Vortex to wet the entire sample solution.
3. Place test tube in the aluminum heating block, cover with watch glass, and ramp gradually to 150°C over a 2-hour period. Heat overnight at this temperature.
4. Remove the tube, allow to cool and dilute sample solution to 15 mL with DI water, cap and shake for 5 min.
5. Centrifuge at 1,000 rpm for 5 min and transfer approximately 12 mL sample solution to a 16x100 mm disposable tube.
6. Calibrate the instrument for each day's analyses against the aqueous standards of 0.00147, 0.0075, and 0.0147 ppm Hg.
7. Using the manifold illustrated in figure 3 (page 50), modified from Koirtyohann and Khalil (1976) and Kennedy and Crock (1987), the digested geochemical materials are analyzed along with aqueous calibration standards. The modifications to the manifold include changes to reagent and sample flow rates and reagent composition. These were made to maximize the absorbance signal of a 0.00147 ppm mercury solution. Samples with mercury concentration greater than the highest standard (1.47 ppm in the sample) must be diluted and reanalyzed. Also, any sample following a sample that exceeds the concentration of the upper standard, should be reanalyzed due to the possibility of mercury carry over from the previous sample.
8. The calibration curve is checked at the beginning and after every 20 samples.

Standardization of Instrument

Instrument settings used for a Perkin-Elmer 272 AAS Spectrometer and a Perkin-Elmer 56 Recorder are outlined in table 11.

Table 11.—Operating conditions for determination of Hg in coal and biological tissue by CV-AAS

Lamp	Hg hollow cathode
Slit	0.7 nm
Wavelength	253.7 nm
Recorder	2 mV full-scale response, 5 mm/min
AA recorder mode	TC3
0.00147 µg/mL	approximately 28 mm on recorder paper

Calculation

Measure peak height to the nearest mm with a ruler and calculate the mercury concentration in the sample with the following formula:

$$\text{Hg (ppm)} = \frac{\text{calibration std. } (\mu\text{g / mL})}{\text{std. peak height (mm)}} \times \frac{\text{final sample volume (mL)}}{\text{sample wt (g)}} \times \text{sample peak height (mm)}$$

Assignment of Uncertainty

Low values for the aqueous standards and/or high values for reference materials suggest the apparatus needs to be disassembled and cleaned with 30 percent KOH. Upon heating this removes any residual mercury or organic carbon buildup. Each daily set of analyses is preceded by three aqueous calibration standards. Table 12 shows the analytical results of selected reference materials, duplicate samples, and method blanks obtained by this method.

Table 12.— Analytical performance summary for Hg (ppm) in coal and biological tissue by CV-AAS

[A=National Institute of Standards and Technology, 1983; B=Lengyel and others, 1994; C=National Bureau of Standards (NBS), 1974; D=Wilson, 1994; E=NBS, 1978; F=Govindaraju, 1989; G=Potts and others, 1992; H=National Research Council of Canada, 1983]

Reference	*Description*	*n*	*Mean*	*s*	*pv*			*% RSD*	*% R*
SRM 1566a	oyster tissue	10	0.060	0.009	0.0642	A	*cv*	15	93
SRM 1632b	coal (bituminous)	15	0.068	0.005	0.077	B		7	88
SRM 1632	coal	11	0.09	0.01	0.12	C	*cv*	12	75
CLB-1	coal	20	0.15	0.01	0.12	D	?	8	125
SRM 1632a	coal fly ash	14	0.119	0.007	0.13	E	*cv*	6	92
SRM 1633b	coal fly ash	20	0.12	0.01	**0.141**	D		11	87
MESS-1	marine sediment	20	0.18	0.02	0.171	F		11	102
SDO-1	shale	20	0.18	0.01	0.19	G		6	95
TORT-1	lobster	10	0.32	0.02	0.33	H	*cv*	6	97

Duplicate samples	*k*	*n*	*Mean*	*s*	*% RSD*	*Concentration range*	*No. of < (total)*	*No. of < (pairs)*
Whole coal	34	2	0.103	0.008	8	0.01 to 0.51	0	0
Biological tissue	16	2	0.55	0.04	8	0.02 to 2.3	0	0

Table 12.—Analytical performance summary for Hg (ppm) in coal and biological tissue by CV-AAS—Continued

Method blank	*n*	*Mean*	*s*	*3s*	*5s*
	37	0.001	0.003	0.009	0.02

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Cadmium and silver by flame atomic absorption spectrometry

By Richard M. O'Leary

Code: A100 Accepted: 3/2/93

Principle

Cadmium and silver are determined by a modified flame atomic absorption method developed by O'Leary and Viets (1986). The sample is decomposed by hydrofluoric acid and the residue is treated with hydrochloric acid and hydrogen peroxide. Cadmium and silver are selectively extracted into a 10 percent Aliquat 336-MIBK organic phase in the presence of ascorbic acid and potassium iodide. The organic solution is atomized by flame atomic absorption spectrometry (FAAS) for determination of silver and cadmium concentrations.

Interferences

Calcium and iron are major interfering elements in the determination of cadmium and silver in geologic material by atomic absorption spectrometry. However, these interferences are eliminated by the use of the 10 percent Aliquat 336-MIBK which will not extract calcium, and will not extract iron in the presence of ascorbic acid and potassium iodide.

Scope

The lower reporting limit for cadmium is 0.1 ppm and silver 0.2 ppm. The upper limit of 10 ppm can be extended by the dilution of an aliquot of the 10 percent Aliquat 336-MIBK layer with 10 percent Aliquat 336-MIBK. Approximately 35 samples can be analyzed per day.

Apparatus

- Atomic absorption spectrophotometer equipped with flame atomizer
- Aluminum block with holes to accommodate 16-mm digestion tubes
- Boiling chips
- Centrifuge
- Beakers, 50-mL, Teflon FEP
- Test tubes, 16x150-mm disposable, w/caps
- Hot plate
- Horizontal shaking machine
- Vortex mixer

Reagents

All chemicals should be reagent grade, and all water should be metal free, unless otherwise indicated.

- Deionized water (DI)
- Aliquat 336, tricaprylylmethylammonium chloride (obtainable from Aldrich Chemical Company)
- Hydrochloric acid, HCl, conc
- Hydrogen peroxide, H_2O_2, 30 percent

- Hydrofluoric acid, HF, conc
- Methyl isobutyl ketone, MIBK

Aliquat 336-MIBK 10 percent (v/v): Pour 100 mL Aliquat 336 into a clean 1-L, graduated cylinder, dilute to 1 L with MIBK, shake to dissolve the Aliquat 336, and pour into brown glass bottle. This solution is stable for at least 1 month.

Ascorbic acid-potassium iodine solution, 30 to 15 percent (w/v): Weigh 300 g $C_6H_8O_6$ (U.S.P. food grade or metal-free equivalent) and 150 g KI into a beaker, dissolve in DI water by stirring, and warming over low heat, then dilute to 1 L. Prepare fresh weekly. Note: Some KI has been found to contain cadmium and silver contaminants. Check for contamination before using. If the reagent is contaminated, try another manufacturer or lot number of the potassium iodide.

10 M hydrochloric acid solution: Dilute 833 mL of conc HCl to 1L with DI water

Stock cadmium and silver solutions, 1,000 µg/mL: Prepare by accurately weighing 0.1142 g CdO and 0.1074 g Ag_2O into separate 100-mL flasks. Dissolve and dilute the CdO to volume with 10 *M* HCl. Add 25 mL 10 *M* HCl and 2 mL H_2O_2 to the flask containing the Ag_2O, heat at 95°C until dissolved. Additional amounts of H_2O_2 may be necessary. Add H_2O_2 in 1 mL increments 10 min apart until totally dissolved. Dilute to volume with 10 *M* HCl.

Stock solutions 2, 5, and 10 µg/mL: Add 0.20, 0.50, and 1.0 mL of each 1,000 µg/mL stock solution to three 100 mL volumetric flasks and dilute to volume with 10 *M* HCl.

Instrument calibration standards 2, 5, and 10 µg/mL: Add 0.50 mL of the combined stock solutions containing 2, 5, and 10 µg/mL to three 16x150 mm disposable test tubes containing a boiling chip. Add 4.5 mL conc HCl and 0.5 mL H_2O_2 and mix. Allow to set for 10 min, add 0.5 mL H_2O_2 and mix. After 10 min place in a heating block at 110°C and heat until the remaining chlorine and hydrogen peroxide is evolved. Remove from heat and when cool add 4 mL ascorbic acid-potassium iodide solution, mix and allow to set for 20 min. Continue preparation starting at step six in the procedure. One set of calibration standards and blank should be made for every 20 samples.

Safety precautions

All work with open or uncapped reagents must be done in a chemical hood. Protective clothing, including laboratory coats or aprons, gloves, and eyewear must be worn. See the *CHP* and *MSDS* for further information concerning first-aid treatment and disposal procedures for chemical products used in this method.

Procedure

1. Weigh 0.50 g sample into a 50-mL Teflon FEP beaker.
2. Add 5 mL conc HF, place on the hot plate and evaporate to dryness at 110°C.
3. Remove from heat and add 5.0 mL conc HCl followed by 1.0 mL 30 percent H_2O_2 dispensed in 0.5 mL portions, 10 min apart. Mix sample solution well after each addition of the hydrogen peroxide.
4. After 10 min place beaker on hot plate and evolve remaining hydrogen peroxide and chlorine. It is critical to minimize the loss of liquid during this step, therefore do not over heat.

5. Remove from hot plate and transfer contents to a 16x150-mm disposable test tube. Rinse beaker with 4.0 mL ascorbic acid-potassium iodide solution, transfer to the test tube, mix, and let stand for 20 min.
6. Accurately add 3.0 mL 10 percent Aliquat 336-MIBK solution to each tube. Cap and shake for 5 min.
7. Centrifuge the sample solution to separate the organic layer from the acid layer.
8. Determine the cadmium and silver content by atomizing the organic layer in a flame atomic absorption spectrophotometer.

Standardization of equipment

The following table lists the instrument operating conditions using a Perkin-Elmer 5000 atomic absorption spectrophotometer.

Table 13.—Operating conditions for determination of Cd and Ag by FAAS

	Silver	*Cadmium*
Grating	ultraviolet	ultraviolet
Source Lamp	hollow cathode	hollow cathode
Integration time	1 s	1 s
Flame	Air-acetyline	Air-acetyline
Flame condition	oxidizing	oxidizing
Wavelength	328.1 nm	228.8 nm
Slit	0.7 nm	0.7 nm
Burner	10 cm	10 cm
Background correction	no	no
Concentration mode		
2.0 ppm	0.080 *A*	0.140 *A*
5.0 ppm	0.160 *A*	0.280 *A*

Assignment of uncertainty

Table 14 is the analytical results for cadmium and silver of selected reference materials, duplicates samples and method blanks.

Table 14.—Analytical performance summary for Cd and Ag (ppm) by FAAS

[Proposed values from Potts and others, 1992]

Reference	*Description*	*n*	*Mean*	*s*	*pv*	*% RSD*	*% R*
Cadmium, Cd							
GSD-3	stream sediment	10	0.07	0.02	0.10	29	70
SCo-1	shale	13	0.13	0.02	0.140	15	93
MAG-1	marine mud	11	0.22	0.03	0.202	14	109

Table 14.—Analytical performance summary for Cd and Ag (ppm) by FAAS—Continued

Reference	*Description*	*n*	*Mean*	*s*	*pv*	*% RSD*	*% R*
Cadmium (Continued)							
GSD-6	stream sediment	12	0.36	0.03	0.43	8	84
MESS-1	marine sediment	10	0.66	0.03	0.59 *cv*	5	112
SGR-1	shale	10	0.97	0.06	0.93	6	104
GSD-7	stream sediment	11	0.92	0.09	1.05	10	88
GXR-1	jasperoid	12	2.7	0.2	3.3 ?	7	82
GSD-12	sediment	10	3.9	0.2	4	5	98
GXR-2	soil	31	3.8	0.2	4.1	5	93
Silver, Ag							
MAG-1	marine mud	10	0.08	0.01	0.08	13	100
SCo-1	shale	10	0.14	0.02	0.134	14	104
SGR-1	shale	10	0.25	0.03	**0.184**	12	136
GSD-6	stream sediment	10	0.34	0.02	**0.36**	6	94
GSD-3	stream sediment	10	0.61	0.05	**0.59**	8	103
GSD-7	stream sediment	10	1.06	0.08	**1.05**	8	101
GSD-12	sediment	10	1.06	0.06	1.15	6	92
GXR-2	soil	31	16.4	0.6	17	4	96
GXR-1	jasperoid	10	33	2	31	5	105

Duplicate samples	*k*	*n*	*Mean*	*s*	*% RSD*	*Concentration range*	*No. of < (total)*	*No. of < (pairs)*
Cadmium	31	2	0.64	0.03	4	0.2 to 3.2	6	2
Silver	32	2	0.50	0.04	8	0.1 to 2.8	2	0

Method blank	*n*	*Mean*	*s*	*3s*	*5s*
Cadmium	13	-0.01	0.01	0.03	0.05
Silver	13	0.01	0.03	0.08	0.2

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Carbonate carbon by coulometric titration

By Clara Papp, Elaine Brandt, and Phillip Aruscavage

Code: C011 Accepted: 2/16/93

Principle

Carbonate carbon in geologic material is determined as carbon dioxide, CO_2, by coulometric titration. The sample is treated with hot 2 *N* perchloric acid and the evolved CO_2 is passed into a cell containing a solution of monoethanolamine. The CO_2, quantitatively absorbed by the monoethanolamine, is coulometrically titrated using platinum and silver/potassium iodide electrodes (Jackson and others, 1987).

Interference

Processing samples containing high concentrations of sulfur quickly exhausts the sample prescrubber. The analyst must give close attention to the build-up of black sulfide precipitate in the prescrubber solution.

Scope

The lower reporting limit is 0.01 percent CO_2 and samples containing up to 50 percent CO_2 may be analyzed. Sample size is adjusted from 0.5 g for the range 0.01 to 5 percent CO_2, 0.1 g for the range 5 to 10 percent CO_2, and 0.02 g for greater than 10 percent CO_2. Generally, 20 to 30 samples can be analyzed per day. The analysis of shales often requires 30 to 40 minutes for complete liberation of carbon dioxide.

Apparatus

Carbonate Carbon Apparatus Model 5030 with Carbon Dioxide Coulometer Model 5010 (U.I.C. Inc.), HP85 Computer with "COUL" program, or if available, programmable calculator.

Reagents

- Deionized water (DI)
- Ammonium hydroxide NH_4OH, conc
- Acetone, C_3H_6O
- Potassium hydroxide, KOH, 45 percent solution, Coulometrics
- Hydrogen peroxide, H_2O_2, 30 percent solution, Baker reagent grade
- Sulfuric acid, H_2SO_4, conc

Perchloric acid, 2 N solution: Dilute 170.3 mL $HClO_4$ (70 percent) to 1 L; store in a plastic bottle

Potassium iodide saturated solution: Add 2.0 g KI to 100 mL DI water and stir for 2 hours on a magnetic stirrer

Coulometer solution: Proprietary solution of monoethanolamine and thymolphthalein indicator, available from Coulometrics, Inc.

Silver sulfate solution: Add 1.5 g Ag_2SO_4, to 100 mL DI water and stir for 2 hours on a magnetic stirrer. Add 2.0 mL conc H_2SO_4 and mix. Store in a glass bottle.

Safety precautions

The instrument should be operated in a fume hood. Lab coat, proper gloves, and safety glasses must be worn. Preparation of reagents and handling of acids and bases shall be done under an operating chemical hood. Use perchloric hood for all analytical procedures involving $HClO_4$ and clean at end of each days use. Ammonia fumes from concentrated NH_4OH are extremely irritating to eyes and lungs. See the *CHP* and *MSDS* for precautions, effects of overexposure, first-aid treatment, and disposal for chemical products used in this method.

Procedure

Additional details of the procedure and internal calibration are in the on-site instruction manuals by Coulometrics Incorporated (1978). Reference materials used for the analysis include USGS standards PCC-1, STM-1, and MAG-1 and reagent grade $CaCO_3$. One or more of these are used at the beginning of the days run, depending on the amount of carbonate expected in the samples.

1. Weigh approximately (e.g. 0.4912 or 0.5076) half a gram of ground geological material to four significant figures and transfer to a clean, dry sample tube. Reduce the amount of sample to 0.1 or 0.02 g if the subsequent analysis indicates concentrations of CO_2 in excess of 5 and 10 percent respectively.

2. Place a small, magnetic stirring bar in the clean coulometer cell beaker. Add 80 mL coulometer solution.

3. With a small spatula, add 0.1 g KI to the bottom of the anode cell compartment, covering the bottom frit.

4. Place the electrode cell assembly in the beaker containing the coulometer solution so that it is tilted towards the printing on the beaker. Tilting the assembly towards the printing keeps the light path unobstructed when the beaker is placed into the coulometer apparatus. The platinum electrode should be curved in a horizontal position around the anode compartment.

5. Insert the silver electrode into the anode compartment, then lift slightly so anode solution may be added by a dropper. The level of the solution inside the compartment should be the same as the level of the solution in the beaker when the electrode is immersed. The tip of the silver electrode should be slightly above (approximately ¼") the potassium iodide crystals covering the frit. As the anode wears away through usage, the holder must be readjusted.

6. Clamp the cell and beaker in place on the coulometer apparatus, making sure the electrodes and air jet are to the back of the cell holder and not in the path of the light beam.

7. For a blank solution, connect a clean sample tube to the condenser with small rubber bands and add 4 mL 2 *N* $HClO_4$ from a Repipet bottle to the sample tube. The ground glass connection on the condenser must be lightly greased with special stopcock grease (Lubriseal) to provide an air-tight connection.

8. Connect the Teflon air tube from the cell assembly to the Teflon air tube from the sample tube apparatus.

9. Connect wires from the electrodes to proper color-coded receptacles (red to red, black to black).

10. In exact sequence:

    a. Turn on the heating element on the sample digestion compartment of the apparatus. Turn it up to six on the dial.

    b. Open the air valve and set air flow to read 100 cc/min on the gauge. Check for leaks.

    c. Turn on the coulometer power switch and adjust the transmission control so that it reads 100 percent T. Once the transmission control is set initially for the days run, it should not be changed. If it cannot be set to 100 percent T, check to see if something is obstructing the light beam.

    d. Turn on the electrolysis current switch to begin the titration. The color of the liquid in the cell will turn to blue.

11. Turn on the HP 85 computer and load tape, then load the "COUL" program. When the digital display becomes stable, run the blank.

12. Move the tube assembly to the heater position and allow the system to run for 5 min as a blank determination. This time is in the program. After 5 min, the microgram count for the blank should be no more than 5 µg. If it is much higher than this, e.g., 50 µg, suspect something wrong with the anode compartment.

13. Remove the blank tube and save. Wipe the Teflon intake tubing and the inner portion of the condenser dry. If there is acid left on the tubing or condenser, it may release CO_2 prematurely when the sample tube is connected.

14. Enter the sample number into the computer. Connect the sample tube to the condenser and make sure of an air-tight seal. Allow air to flow through the system for 2 to 3 min to purge any atmospheric CO_2 introduced. If there is a leak, values could be low and/or carrier air will not flow through the system. After the purge, the microgram count should not exceed 16 to 24. If it does, the excess should be added to the sample count because CO_2 is being released prematurely. This sometimes happens with certain samples with high carbonate concentrations.

15. Press "R" on the computer to start titration. Slowly add a few milliliters of acid to the sample tube from the Repipet and shake the tube gently to wet the sample evenly. Add the remainder of the 4 mL acid.

16. Place the tube assembly into the heater position and allow the reaction to proceed. Maintain incipient boiling and flow rate of 100 cc/min during the evolution of CO_2. Adjust heat as needed to prevent bumping and possible ejection of sample into the condenser tube.

17. Completion of CO_2 release and titration, is indicated by the stability of readings, (less than 10 µg difference in 2 min). Normal samples usually require 5 to 10 min. As an example, if the count is 20 µg at 6 min, 24 µg at 7 min, and 28 µg at 8 min, it can be assumed equilibrium has been reached. Often there will be duplicate counts on successive minute intervals at equilibrium and usually before 10 min.

18. Remove the sample tube and if there are more samples to be run, repeat the procedure from step 13.

19. For shutdown:

    a. Turn off electrolysis current switch and remove electrode leads;

    b. Turn off power switch;

    c. Turn off computer *after* removing tape.

    This sequence must be followed to avoid damage to electrical system.

20. Remove the last sample tube, clean the inlet tube with a small wire and flush out residue into a plastic beaker using a small amount of acid from the dispenser. Rinse the inside of the condenser with distilled water from a small squeeze bottle. The cleaning procedure should be run between samples if a large amount of residue builds up in the inlet tube and/or if bumping ejects sample into the condenser neck.

21. Place a clean sample tube onto the apparatus and introduce 4 mL 2 N $HC1O_4$ into it and continue shutdown by:

    a. turning off the air gauge;

    b. turning off the heater and pump switch.

    Follow this sequence to prevent any back flow of fluids into the air pump.

22. Disconnect the air tube from cell assembly and remove the beaker promptly from the apparatus, brush off any yellow deposit that forms on the anode and rinse off and dry. Deterioration of the electrode can result if it is left in the used solution for long periods of time.

23. Pour out the solution from the anode compartment and rinse with acetone. Brush gently to dislodge the potassium iodide from the frit and flush out with acetone from a squeeze bottle. Invert the stopper and apply suction to the tube while flushing the frit with small amounts of acetone until it is thoroughly clean. Rinse the stopper with water, dry and put away. Don't rinse the anode compartment with water and be careful about handling acetone. It is extremely flammable!

24. Clean out all the used sample tubes by rinsing and using a brush to remove all sample residue. Rinse with distilled water, dry the outside and store in a rack.

Trouble Shooting

The system should be continually monitored to see if any conditions requiring troubleshooting are necessary.

1. The presence of large amounts of sulfide precipitate indicates that the scrubbing effect of the solution may be becoming depleted, which if not corrected means future sample runs may be in error. The precipitate may also clog the scrubber frit.
2. When sulfide precipitate (black) is detected in the prescrubber at the back of the apparatus or in the Teflon tubing, separate the prescrubber from the system, along with the Teflon tubing. Flush out with conc HCl and then thoroughly with water. Rinse with DI water. Add silver sulfate solution (saturated) to the mark (4 mL) and add nine drops 30 percent H_2O_2. Reconnect the system. NOTE: Traces of HCl, a result of insufficient rinsing with water, will react with silver sulfate to form a white precipitate of silver chloride.
3. Periodically check the platinum electrode wire for dirt or film. Wipe clean with tissue or clean with dilute HNO_3 and rinse with DI water.
4. If there is excessive frothing in the 45 percent KOH scrubber, if it becomes cloudy, or when the air-flow rate through the sintered glass plug cannot be corrected by the addition of a little DI water, remove the tube from the system. Clean the sintered glass plug by passing DI water through it. Add 12 mL 45 percent KOH to the cleaned scrubber tube and re-assemble in the apparatus. Addition of a little DI water to the scrubber will usually correct the condition. After this has been done ten times or so, it will be necessary to replace the KOH.
5. To clean the sintered glass frit in the silver sulfate sample scrubber, drain sample scrubber and rinse with DI water. Fill the scrubber with ammonium hydroxide and warm in a water bath to clean the frit. Rinse thoroughly with DI water. When the disk is clean, the tube may be refilled with silver sulfate solution.
6. Clean a dirty and clogged frit in the anode cell compartment with saturated potassium iodide solution. Use an aspirator to draw the solution through the frit and then flush with DI water.
7. If a run is interrupted for 1 hour or more, continue operating the system with the last determined sample in place.
8. Replace the cell solution if over 350,000 µg CO_2 is exceeded in a day.

Calculation

If a programmed computer is hooked up to the titration instrumentation (coulometer), a printout for µg values for CO_2 can be generated. By entering the sample weights and corresponding µg CO_2 values; the percent CO_2, or carbonate results are calculated automatically. If calculations are made by hand use the following formulas:

a. To determine percent CO_2

$$\%\ CO_2 = \frac{CO_2(\mu g)}{\text{sample}\ (\mu g)} \times 100$$

b. To determine percent carbonate carbon

$$\%\ \text{carbonate carbon} = \frac{C(\mu g)}{\text{sample}\ (\mu g)} \times 100$$

Assignment of uncertainty

Table 15 shows the carbonate carbon (quoted as CO_2) results for reference materials, duplicate samples, and method blanks by coulometric titration.

Table 15.—Analytical performance summary for carbonate carbon (percent) as CO_2

[Proposed values from Potts and others, 1992]

Reference	*Description*	*n*	*Mean*	*s*	*pv*	*% RSD*	*% R*
STM-1	syenite	10	0.019	0.002	0.026 ?	11	73
BHVO-1	basalt	14	0.013	0.002	0.036	15	36
G-2	granite	16	0.073	0.001	0.08	1	91
GXR-2	soil	114	0.020	0.007	0.09	35	22
SDC-1	schist	10	0.093	0.001	0.099	1	94
GSP-1	granodiorite	30	0.104	0.006	0.11	10	95
PCC-1	peridotite	78	0.171	0.007	0.15	4	114
GSD-12	stream sediment	68	0.04	0.01	0.18 ?	25	22
MAG-1	marine mud	20	0.459	0.005	0.47 ?	1	98
GSD-6	stream sediment	10	1.96	0.01	2.01 ?	0.5	97
SRM 88b	dolomite limestone	10	47.0	0.3	**46.37** *cv*	1	101

Duplicate samples	*k*	*n*	*Mean*	*s*	*% RSD*	*Concentration range*	*No. of < (total)*	*No. of < (pairs)*
	91	2	5.59	0.07	1	0.01 to 46	36	17

Method blank	*n*	*Mean*	*s*	*3s*	*5s*
	29	0.002	0.001	0.003	0.004

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Moisture and total water in silicate rocks

By Daniel R. Norton and Clara S.E. Papp

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Principle

The evolved total water in silicate rocks is determined by coulometry using the Karl Fischer titration method (Norton, 1982). The total water is released with the aid of a flux at 900°C. Dry nitrogen is used as a carrier gas to drive the water from the ground rock material into the Karl Fischer reagent contained in the titration cell. In the presence of the reagent, water reacts quantitatively with coulometrically generated iodine. The instrumentation allows for the rapid and accurate determination of total water through an automated titration system using controlled electrolysis current and blank compensation. The moisture (H_2O-), or non-essential water, is determined by weight loss after heating the sample at 110°C. Essential water (H_2O+) is determined by calculation using the total water and moisture concentrations.

Interferences

Usually, high temperature and a flux are required to effect complete release of water from the sample (Jackson, and others, 1987). The flux not only breaks down the mineral structure, but retains other volatile elements such as sulfur, fluorine, and chlorine that may interfere with the determination. The presence of organic matter in the sample affects the accuracy of determinations. The loss of volatile organic species at 110°C yields high results for H_2O-. High results also are obtained for total water or H_2O+ content due to combustion of the organic matter yielding water and carbon dioxide (Jackson, and others, 1987). Determination of water in samples of high organic content should be forsaken entirely. Sample preparation, i.e., grinding, may also affect the water content of the sample. Increased surface area of the finely-ground sample, particularly of naturally hygroscopic minerals, may cause increased absorption of moisture. Grinding may rupture fluid inclusions in various mineral phases in the sample. Introduction of atmospheric water through an improperly sealed instrumental system will cause erroneous results.

Scope

The lower reporting limit is 0.05 percent for all three forms of water. Approximately 25 samples can be analyzed in a day. The method is most applicable to the analysis of water in silicate rocks. The total water, moisture (H_2O-), and essential water (H_2O+) are reported as weight percent.

Apparatus

- Coulometric titrator with microprocessor control unit, electrolytic cell, and printer: Mitsubishi Chemical Industries (MCI) Model CA-05
- Vaporizer, zero to 1000°C: MCI Model VA-21
- Analytical balance, electronic: Mettler Model AC-100
- Boat, quartz, MCI part no. VAHSB
- Sample cup, Pyrex, 11-mm od by 11-mm height

Reagents

- Anode reagent solution: Aquamicron A (available from MCI)
- Calcium carbonate, $CaCO_3$
- Cathode reagent solution: Aquamicron C (available from MCI)
- Check solution U: water content 3.8 to 4.1 mg H_2O mL (available from MCI)
- Ethyl alcohol, C_2H_6O, reagent grade, anhydrous
- Desiccant, 8 mesh indicating
- Molecular sieves: grade 513, 4-8 mesh beads, effective pore size 4Å (base:alumina-silicate, cation:sodium). Available from Fisher Scientific Co. as Davison® molecular sieves
- Nitrogen gas, Linde, prepurified grade
- Lead oxide, PbO (litharge)
- Lead chromate, $PbCrO_4$, "Baker Analyzed" reagent powder

The flux is prepared according to the instructions of Peck (1964). In this procedure 200 g PbO and 100 g $PbCrO_4$ are heated 1 hour at 800°C in separate platinum crucibles. After cooling, the constituents are hand-ground in a mortar to just pass a 20-mesh sieve, mixed on a paper with 50 g dry $CaCO_3$ and stored in a bottle having a tight seal cap.

Safety precautions

All work with open or uncapped reagents should be done in an exhaust hood. In use, instrumentation should be vented into an exhaust hood. In this procedure, it is of utmost importance to maintain proper setting of the stopcocks on the titration devise. It is of even greater importance to **never** turn off the furnace or gas flow while the titration device is connected to the furnace. Resulting negative pressure can draw the reagent back into the furnace which is hot enough to create an explosion. Caution must be exercised in handling bottled, compressed gases. Protective clothing, safety glasses, and gloves must be worn. Safety precautions are re-iterated in the section, *Discussion of procedure*. Effects of overexposure, first-aid treatment, and disposal procedures for reagents used in this method are discussed in the *CHP and MSDS*.

Procedure

Additional details of the procedure are in the on-site instruction manuals by Mitsubishi Chemical Industries (1986).

Steps 1-12 are done before attaching titration devices to heating devices.

1. Remove the glass rod with adapter joint from the heating tube of the furnace unit, clean the rod with a tissue containing some absolute ethyl alcohol, dry with another tissue, replace in the heating tube, and move the boat into the heating zone.

2. Turn on the hood.

3. Turn on the main valve of the nitrogen gas cylinder, set the diaphragm valve to 5 psi and open the outlet valve.

4. Turn the nitrogen inlet stopcock to direct the flow of gas through the heating tubes of the furnace and adjust the flow of gas to 100 mL /min with the needle valve.

5. Check all joints in the titration cells to determine that they move freely. If any of the joints move with difficulty, clean and regrease these joints.

6. Check the desiccants contained in the drying tubes on the cathode and anode cell compartments of both electrolytic cells. Discard spent desiccant and replace as required.

7. Check the level of the reagent solutions in both electrolytic cells. When the level has dropped to 100 mL, introduce 5 mL of the Cathode Solution and enough Anode Solution to bring its level to that of the Cathode Solution.

8. With the furnace temperature control set to 900°C turn on the power switch to the furnace.

9. Turn on the CA-05 titrator.

10. If a negative voltage is registered, introduce approximately 100 µL of the Check Solution with a syringe. If a negative voltage persists, introduce additional 100 µL aliquots of the Check Solution until a positive voltage is obtained.

11. When a positive voltage is registered, turn on the titration switch and allow the water to be titrated automatically to the end point. Allow the background to attain a value of less than 0.1 µg/s before proceeding.

12. Turn the gas outlet stopcock of the electyrolytic cell to direct the flow of gas through the exit tube to the hood duct. Attach the cell inlet tube to the furnace outlet tube.

13. Adjust the nitrogen gas flow rate to 100 mL/min. Allow the background to reach a low level, less than 0.07 µg/s, before proceeding with blank and sample determinations.

14. Check the operation of the balance under the approximate load utilized for the determinations with a calibration weight equivalent to the sample weight employed.

15. Analyze 300 mg of flux as a blank approximately five times. Weigh a 50-mg sample of the ground rock material into a Pyrex sample cup on the electronic balance and add 300 mg of the flux.

16. Mix the contents of the cup with a small metal rod and brush the latter to transfer adhering particles to the cup. Enter weight of sample into CA-05 titrator.

17. Pull out the glass rod in the heating tube of the furnace unit to align the quartz boat with the glass stoppered sample port. Transfer the cup with the sample-flux mixture onto the Fiberfrax liner of the boat, and move the boat into the heating zone.

18. Press the start button on the CA-05 titrator and allow the coulometric titration to proceed automatically to the electronically displayed end point.

19. Pull out the glass rod in the heating tube of the furnace unit to align the quartz boat with the glass stoppered sample port. Remove the cup with fluxed sample. Repeat steps 15 through 19 until all of the samples, standards, and blanks have been processed. The average blank value has to be entered into the CA-05 titrator at the start of each day.

20. To close down the operation of the entire system perform the following:

    a. Disconnect the gas inlet tube of the electrolytic cell from the gas outlet tube of the heating unit and immediately attach the ball joint stopper to the inlet tube with the metal clamp.

    b. Turn off the heating unit.

    c. Turn the stopcock on the drying tube of the electrolytic cell to close the gas exhaust vent and open the drying tube vent.

    d. Turn off the CA-05 titrator.

    e. Move the boat into the heating zone.

    f. Turn off the main gas valve of the nitrogen cylinder and allow the system to reach atmospheric pressure.

    g. Turn off the diaphragm and shut-off valves of the pressure regulator.

    h. Turn the stopcock on the gas inlet of the heating tube to close the connection to the gas drying manifold.

    i. Turn off the hood.

Moisture or nonessential water (H_2O-) is determined by weight loss after heating the sample at 110°C. Weigh 1 g sample into porcelain crucibles. Heat the crucibles in an oven set at 110°C. After 4 hours take the crucibles out of the oven. Cool samples in a dissector. Weigh samples again. The difference in weight is the loss of moisture.

Discussion of procedure

1. A discussion of each step in the procedure is given below to familiarize the analyst with the details of the operations and the safety precautions to be followed. Metal springs are used to secure the adapter joint in place and to prevent leaks. It is important that the hole in the adapter joint not be aligned with the hole in the heating tube. If the holes are aligned, nitrogen gas will escape through these ports. Loss of gas pressure at this point prevents gas from flowing through the anode solution contained in the electrolytic cell. To prevent grease from entering the heating tube, the ground glass joints of the adapter and the glass rod are not lubricated. Precision fit of these joints and a positive pressure of gas inside the heating tube prevents moisture laden atmosphere from entering the tube in any significant amount. When replacing the glass rod, insert the hook on the end of the rod into the ring of the boat to control its movement in and out of the heating zone of the furnace.

2. Reagents solutions and the Check Solution contain components that are injurious to health and must be handled according to recognized safety practices. To prevent inhalation of these harmful constituents the operation is carried out under an

operating chemical exhaust hood. The composition of the volatile reagents contained in the solutions are given below.

Component	*Anode solution Aquamicron A*	*Cathode solution Aquamicron C*	*Check solution*
Chloroform	34	--	--
Carbon tetrachloride	3	26	--
Methanol	22	35	99[b]
Pyridine	--[a]	--[a]	--
Sulfur dioxide	--[a]	--	--

[a] percentage composition not disclosed
[b] minimum value

3. Standard safety practices are followed for handling gas cylinders under high pressure. It is required that the cylinder be secured to the bench at all times.

4. Incorrect setting of these three-way stopcocks can be avoided by following the instructions below for operating and closing down the furnace.

Unit	*System*	*Arrow*	*Gas flow*
Furnace	Operational	Forward	Through heating tube
Furnace	Closed down	Up	Drying train closed

5. With the furnace temperature control set to 900°C and its reset dial control set to +5, the temperature of the central zone of the heating tube will control at 900°±10°C. Furnace temperature calibration should be checked periodically with a potentiometer using a chromel-alumel thermocouple to confirm that the proper temperatures are being maintained.

6. There are eight joints to check for proper lubrication in each of the electrolytic cells. These are identified as the drain stopcock, check solution port, inlet tube, detection electrode, cathode cell assembly with its drying tube, and the anode cell drying tube with its stopcock. Wearing disposable plastic gloves, remove defective joints, wipe with a tissue, and regrease. Avoid eye contact with grease as it is an eye irritant, and may have absorbed some of the reagent solution from the electrolytic cell. Used tissues are placed in a regular chemical hood until the vapors have evaporated before disposing of them in the trash container. The drain stopcock cannot be cleaned and regreased when the electrolytic cell contains the reagent solutions. It is cleaned and regreased when the spent reagent solutions are removed from the cell.

7. The fresh silica gel desiccant is the indicating type which is blue. It turns pink when exhausted. The spent material is stored in a waste jar with a tight cover in a regular hood and later disposed of through the services of a waste disposal company. Use a plastic funnel to facilitate refilling of the drying tubes. When the drying capacity of the silica gel has been exhausted, moisture enters both cells and is absorbed on the glass surfaces as well as in the reagent solutions. This results in high and unstable blank values and a resultant decrease in accuracy and precision. The silica gel desiccant in the gas drying mainfolds of the heating units should also be checked and replenished when exhausted. Since the prepurified nitrogen has a low water content, it is not required to change the desiccant frequently.

8. Using disposable plastic gloves, remove the drying tube for the anode compartment, wipe the ground glass joint of the tube with a tissue, and leave it on the bench with the gas exit tube attached. Stopper the hole in the anode compartment with a cork stopper covered with Parafilm. Remove the electrode pin contacts from the magnetic stirrer stand and transfer the electrolytic cell to a regular chemical hood. Use a plastic funnel to add 5 mL of the cathode solution (Aquamicron C) to the cathode compartment. Introduce anode solution (Aquamicron A) to the anode compartment filling it to the level of the solution in the cathode compartment. The ground glass joints are conveniently cleaned with a tissue and regreased at this time. Replace the electrolytic cell on the Fiberfrax insulating mat on the magnetic stirrer stand and attach the electrode pin contacts. The electrode wire from the cathode compartment contains both the cathode and anode wire connections and must be attached to the pin contact labeled "Titr." on the magnetic stirrer stand. The electrode wire from the detector electrode must be attached to the pin contact labeled "Det." on the magnetic stirrer stand. Remove the cork stopper from the anode compartment, clean the port with a tissue, regrease the joint, and replace the drying tube with the gas exit tube attached.

9. Maintain a setting of 5 on the rheostat control of the magnetic stirrer. A higher setting of the control can result in breakage of the cathode cell, the detection electrode, and the gas inlet tube. Turning on the power and start switches before the magnetic stirrer switch results in the generation of iodine in the cathode reagent solution and a corresponding negative voltage of the cell.

10. A negative voltage indicates that some iodine has been formed. The Check Solution contains water which reacts quantitatively with iodine according to the Karl Fischer reaction, and when in excess results in a positive voltage.

11. The end point is indicated automatically by the digital display of micrograms of water and a buzzer. The detector electrode measures voltage which is proportioned to the amount of excess water in the electrolytic cell at any instant during the time of the titration. The titrant iodine is generated at the platinum anode located just below and attached to the cathode compartment. Iodine is generated at a rate controlled electronically in proportion to the amount of water present at any instant. The maximum rate of electrolysis for this circuit is 300 mA, reducing to lower rates as the end point is approached. The titrant iodine is generated in direct proportion to the quantity of electricity according to Faraday's Law for the half reaction, $2I^- + 2e \rightarrow I_2$. In the Karl Fischer reaction, 1 mole of iodine reacts with 1 mole of water, and 1 milligram of water is the equivalent of 10.71 coulombs. These are the relationships on which the internal electronic calibration of the instrument is based.

If a low background (<0.1 µg/s) is not reached within 5 minutes, it indicates spent reagents or leaks in the system. In the case of spent reagents, replace the reagent solutions following the guidelines in step 8 of this section, with the following exceptions. Turn off the magnetic stirrer, start, and power switches. Drain all of the anode solution into a glass beaker through the draincock and remove all of the cathode solution using a plastic tube with rubber suction bulb. The drain stopcocks can be cleaned with a tissue and regreased at this time. Using a plastic funnel introduce 10 mL of the cathode solution (Aquamicron C) into the cathode compartment. Then introduce enough of the anode solution (Aquamicron A) into the anode compartment to fill it to the level of the solution in the cathode compartment. Continue with step 8 of this section replacing the electrolytic cell on the magnetic stirrer and proceeding again through steps 9-11 in the section titled *Procedure*.

Absolute ethyl alcohol contained in a plastic wash bottle is used for rinsing the plastic funnel and the plastic suction tube. The empty ampoules that contained Aquamicron C reagent solution are also rinsed with this solvent. Spent reagent and rinsing solvent are stored in tightly stoppered heavy glass bottles. Large amounts are stored in the chemical storage facility for organic solvents prior to their submittal to a hazardous waste disposal company.

The capacity of 10 mL of Aquamicron C and 150 mL of Aquamicron A reagent solutions is reported to be approximately 1.5 g of water. The reagent solutions should serve for the titration of 1,000 samples averaging 1,500 µL water content each. In actual practice the loss of reagent solution out of the vent and the mixing of the two reagent solutions through pressure differentials in the anode and cathodes compartments result in more frequent changing of the solutions than the theoretical capacity implies.

12. Failure to correctly turn the three-way stopcocks for the electrolytic cells results in destroying the capacity of the silica gel in the drying tubes. It also can result in the removal of volatiles from the anode reagent solution at a position directly over the electrolytic cells instead of into the duct of the hood.

    A small amount of lubricant is used on the joints connecting the inlet tubes of the electrolytic cells to the outlet heating tubes.

13. The procedure is for routine analysis using a 50 ± 0.5 mg sample and 300 ± 20 mg flux which are weighed successively into the Pyrex sample cups. Sample weight can be varied from 20 to 100 mg depending on a number of factors. The lower the percentage of moisture and combined water in the samples, and the smaller the sample weight, the less time is required for the titration. The greater the percentage of water in the samples, and the larger the sample weight, the more time is required for the titration. Sample and flux are weighed, and water determined soon after opening the sample container. The sample is not allowed to remain in the open atmosphere nor is it stored in a desiccator. Either one of these alternatives could lead to a change in the water content from that of the original sample in its container. The flux is relatively free of moisture and remains anhydrous if stored in a desiccator. It is not hygroscopic and can be exposed for fairly long times in a relatively dry laboratory atmosphere without absorbing appreciable moisture. While the determination of a blank on the flux is used to correct for this contingency, the flux is kept in a closed storage weighing bottle between weightings, and only enough flux for 1 day's run is used in the weighing bottle.

In this procedure flux is added to all samples prior to the determinations of total water. The purpose of the flux is to release total water quantitatively from certain types of samples (biotites, hornblende's, micas, etc.). Although many types of samples do not require flux for determination of total water, flux is added to all samples for convenience.

The sample containers are constructed of 11-mm od Pyrex tubing of standard wall thickness. One end of the tube is sealed flat and the other end cut off with a silicon carbide saw to result in a sample cup 11-mm od and 11-mm height. The cups are deformed by melting during the determination of combined water. The cup with the fluxed sample is stored in metal cans prior to their submittal to a hazardous waste disposal company.

14. Any rigid metal rod can be used for mixing the sample and flux. A glass rod may present a problem in electrostatic attraction of sample particles.

15. All parts of the furnace heating tube are constructed of quartz. A quartz boat with Fiberfrax liner is used for containing the Pyrex sample cups with their contents. The quartz boat supplied by Mitsubishi is constructed from 24-mm od quartz tubing with a 2-mm wall thickness, and a ring at one end to attach to the hook of the quartz rod for transferring the boat into and out of the heating zone. The boat is 55-mm in length, 24-mm in width and 15-mm in height. Fiberfrax is a Union Carbide product used as insulator material to replace asbestos.

    The liner is made from 1/32-in Fiberfrax paper cut to dimensions of 26-mm width and 55-mm length, and prefired 2 hours at 1100°C. Liners are stored in a desiccator.

    Differential heating of the quartz rod and adapter joint, and deposits formed on the rod, may cause a vibration which results in the sample cup moving out of its proper position in the center of the boat as it is transferred into the heating tube. To prevent the sample cup from moving out of position, a second liner with a 13-mm hole cut in its center, can be used. The hole in the top liner maintains the cup in its proper position.

    Since the position of the boat in the furnace can be seen only when the furnace is open, a pencil mark is made on the ground glass surface of the quartz rod near the adapter joint to serve as a guide to position the boat in the center of the furnace.

16. Evolution of total water usually commences within 40 s and is complete within 5 to 10 min depending on the sample type, combined water content, and size of the sample. Determinations of total water in the flux (blank), and in samples containing less than 0.5 percent total water are usually complete within 6 min.

17. It is imperative from a safety viewpoint to follow these instructions explicitly in the sequence outlined. If the nitrogen gas flow were inadvertently stopped while the heating tube was cooling, and while it was still connected to the electrolytic cell, the resultant negative pressure could draw the cathode solution up into the heating zone. A serious explosion and fire could occur with the escape of toxic fumes. This procedure for closing down the system eliminates this hazard by opening the heating tube to atmospheric pressure and immediately closing the electrolytic cell by stoppering the gas inlet tube to the cell before the furnace is turned off and the flow of nitrogen is stopped.

To temporarily place the system on standby during working hours while the instrument is unattended, reduce the gas flow to 50 mL/min, and follow the close-down procedure under steps a, c, d, and e. To commence operations increase the gas flow to 100 mL/min, and restore the parameters changed under a, c, and d in the temporary shut-down.

If the operation of the equipment is suspended for 1 week, the reagent solutions can be maintained relatively free of moisture by changing the silica gel in the drying tubes when it is indicated that the drying agent is exhausted. If it is planned to suspend operations for longer than 1 week, drain the reagent solutions by following the instructions in step 11 of the section titled *Discussion of Procedure*. Rinse all parts of the electrolytic cell with anhydrous ethyl alcohol, then with acetone, allow to dry and store the parts. After a 1-week period excessive hydrogen evolution from the cathode may be observed with the solution turning reddish brown. This is generally associated with an increase in the blank, an increase in the time required for the determination, and a reduced accuracy and precisions.

Calculation

The general equation for the calculation of the percentage composition of H_2O- is shown below:

$$\% H_2O- = \frac{wt\ of\ water\ released\ from\ heating\ the\ sample\ (g)}{sample\ wt\ (g)} \times 100$$

The percent total water is calculated and printed out by the MCI-CA-05 titrator, taking into consideration the average daily method blank value and the weights. The percent H_2O+ is calculated as the difference between the percent total water and the percent H_2O-.

Assignment of uncertainty

Table 16 shows the analytical results for reference materials, duplicate samples, and method blanks by coulometric titration. Accuracy may vary for moisture determinations as samples absorb variable amounts of water.

Table 16.—Analytical performance summary for moisture and essential water (percent)

[Proposed values from Potts and others, 1992]

Reference	*Description*	*n*	*Mean*	*s*	*pv*	*% RSD*	*% R*
Moisture, H_2O^-							
BIR-1	basalt	9	0.07	0.02	0.07 ?	28	97
STM-1	syenite	10	0.17	0.04	0.19	20	91
GXR-3	hot spring deposit	10	2.4	0.2	2.8	8	86
Essential water, H_2O^+							
BIR-1	basalt	10	0.14	0.04	0.10 ?	25	144
STM-1	syenite	46	1.50	0.05	1.50	3	100
GXR-3	hot spring deposit	10	5.0	0.3	4.81	6	105

Table 16.—Analytical performance summary for moisture and essential water (percent)—Continued

Duplicate samples	*k*	*n*	*Mean*	*s*	*% RSD*	*Concentration range*	*No of < (total)*	*No of < (pairs)*
Essential water	77	2	3.68	0.05	1	0.10 to 17.2	0	0

Method blank	*n*	*Mean*	*s*	*3s*	*5s*
Total water	28	0.09	0.01	0.03	0.05

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Forty elements by inductively coupled plasma-atomic emission spectrometry

By Paul H. Briggs

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Principle

Forty major, minor, and trace elements are determined in geological materials by inductively coupled plasma-atomic emission spectrometry (ICP-AES). The sample is decomposed using a mixture of hydrochloric, nitric, perchloric, and hydrofluoric acids at low temperature (Crock and others, 1983). The digested sample is aspirated into the ICP-AES discharge where the elemental emission signal is measured simultaneously for the forty elements. Calibration is performed by standardizing with digested rock reference materials and a series of multi-element solution standards (Lichte and others, 1987).

Interferences

ICP-AES interferences may result from spectral interferences, background shifts, and matrix effects (Thompson and Walsh, 1983). Interelement correction factors and background corrections are applied using the proprietary data system software (Thermo Jarrell Ash, 1988 or Perkin-Elmer, 1993). Approximately 220 (100 for the Perkin-Elmer) spectral interference corrections are being made on each sample. Further corrections are made when an element influences other elements beyond the "normal correction." It is common to not report an effected element due to the extraordinary interference of the affecting element. Matrix effects can generally be negated by proper matching of standard and sample matrices.

Sample decomposition using this multi-acid digestion technique is suited to dissolve certain rock types, soils, and sediments. As with any technique there are going to be exceptions. The method does not fully dissolve refractory or resistant minerals and some secondary minerals. Examples of incomplete digestion are as follows: Ba in barite, Cr in chromite, Ti in rutile, Sn in cassiterite, Al in corundum, and rare earth elements in a monazite. Samples that contain elements in high concentrations where normally the element is a trace constituent or beyond the linear working range will have to be diluted (i.e., Mg in a dolomite, Pb in a galena, Zn in a sphalerite, Cu in a chalcopyrite). This dilution increases the lower reporting limits.

Scope

Analysis by ICP-AES for major, minor, and trace elements is useful for a variety of geochemical investigations. The lower and upper reporting limits used for this method are shown in table 17. Approximately 150 samples can be analyzed daily by the ICP-AES instrumentation.

Table 17.—Reporting limits for 40 elements by ICP-AES

Element	*Concentration range*		*Element*	*Concentration range*	
Aluminum, Al	0.005	50 %	Gallium, Ga	4	50,000 ppm
Calcium, Ca	0.005	50 %	Holmium, Ho	4	5,000 ppm
Iron, Fe	0.02	25 %	Lanthanum, La	2	50,000 ppm
Potassium, K	0.01	50 %	Lithium, Li	2	50,000 ppm
Magnesium, Mg	0.005	5 %	Manganese, Mn	4	50,000 ppm
Sodium, Na	0.006	50 %	Molybdenum, Mo	2	50,000 ppm
Phosphorous, P	0.005	50 %	Niobium, Nb	4	50,000 ppm
Titanium, Ti	0.005	25 %	Neodymium, Nd	9	50,000 ppm
Silver, Ag	2	10,000 ppm	Nickel, Ni	3	50,000 ppm
Arsenic, As	10	50,000 ppm	Lead, Pb	4	50,000 ppm
Gold, Au	8	50,000 ppm	Scandium, Sc	2	50,000 ppm
Barium, Ba	1	35,000 ppm	Tin, Sn	5	50,000 ppm
Beryllium, Be	1	5,000 ppm	Strontium, Sr	2	15,000 ppm
Bismuth, Bi	10	50,000 ppm	Tantalum, Ta	40	50,000 ppm
Cadmium, Cd	2	25,000 ppm	Thorium, Th	6	50,000 ppm
Cerium, Ce	5	50,000 ppm	Uranium, U	100	100,000 ppm
Cobalt, Co	2	25,000 ppm	Vanadium, V	2	30,000 ppm
Chromium, Cr	2	50,000 ppm	Yttrium, Y	2	25,000 ppm
Copper, Cu	2	15,000 ppm	Ytterbium, Yb	1	5,000 ppm
Europium, Eu	2	5,000 ppm	Zinc, Zn	2	15,000 ppm

Apparatus

- Thermo Jarrell Ash, Model 1160 Plasma Atomcomp simultaneous ICP-AES or Perkin Elmer Optima 3000 simultaneous ICP-AES
- Hot plate with 50-position aluminum heating block
- 30-mL Teflon vessels with caps (Savillex)
- Acid dispensers (Labindustries)
- Repeating pipet (Eppendorf)
- Drying oven set at 95°C
- 13x100 mm disposable polypropylene test tubes with caps

Reagents

Hydrochloric acid, HCl reagent grade, 37 percent
Nitric acid, HNO_3 reagent grade, 70 percent
Hydrofluoric acid, HF reagent grade, 48 percent
Perchloric acid, $HClO_4$ reagent grade, 70 percent
Deionized water (DI)

One percent nitric acid solution: 10 mL 70 percent conc HNO_3 diluted in 1000 mL DI water

Aqua regia: three parts conc HCl and one part conc HNO_3; solution is not stable and must be prepared immediately before use

Lutetium internal standard (Lu): 500 µg Lu/mL, as Lu_2O_3 in 5 percent (v/v) HCl

Safety precautions

All laboratory personnel are required to wear safety glasses, rubber gloves, and lab coats when working in the laboratory. All sample digestions must be performed in a perchloric acid hood; the latter is washed down after each day's use. Refer to the *CHP* and *MSDS* for specific precautions, effects of overexposure, disposal, and first-aid treatment, for reagents used in the digestion procedure and operating the ICP-AES instrumentation. Calcium gluconate gel should be available in labs where HF is in use.

Procedure

Digestion of samples

1. Weigh 0.200 g sample into Teflon vessel.
2. Add 100 µL Lu internal standard to each vessel with repeating pipet.
3. Rinse side walls of Teflon vessel with a minimum amount of DI water.
4. In the fume hood, slowly add 3 mL HCl and allow any reaction to subside.
5. Add 2 mL HNO_3, 1 mL $HClO_4$, and 2 mL HF. Place sample solution vessel on hot plate with aluminum heat block at a controlled temperature of 110°C in a perchloric acid fume hood.
6. Evaporate sample solution to hard dryness on hot plate (usually overnight).
7. Remove from hot plate, cool to touch and add 1 mL $HClO_4$ and 2 to 3 mL DI water.
8. Return to hot plate and evaporate to hard dryness. The temperature of the hot plate is increased to 160°C. This step usually takes a few hours.
9. Remove dried sample from hot plate and cool.
10. Add 1.0 mL *aqua regia* with repeating pipet and let react for 15 min.
11. Add 9.0 mL 1 percent HNO_3 and thread screw cap tightly on vessel. Place vessel in drying oven for 1 hour at a controlled temperature of 95°C.
12. Remove sample solution and cool. Transfer solution into labeled disposable polypropylene test tube and cap with test tube cap.
13. Analyze sample solution by ICP-AES.

ICP-AES analysis

The ICP-AES instrument is calibrated at the start of each day using established geological reference materials (USGS basalt BHVO-1 and Canadian Certified Reference Materials Project syenite SY-3) and four multi-element solutions; nine solutions for the Perkin-Elmer (Lichte and others, 1987). The major and trace elements are determined by comparing the element intensities obtained from the standards to those obtained from the samples. There are three method preparation blanks digested with each sample set. A blank subtraction is performed to negate the effect of the reagents.

Table 18 shows instrumental operating conditions and element wavelengths for this method.

Table 18.—Operating conditions for determination of 40 elements by ICP-AES

[Wavelengths are common to both instruments except those in parentheses which are unique to the Perkin-Elmer instrument]

	Thermo Jarrell ash instrument	*Perkin-Elmer instrument*
RF power to the torch	1250 W	1100 W
Plasma argon flow rate, nebulizer argon flow	18 L/min coolant, 0.5 L/min sample	15 L/min, 1.2 L/min
Sample pump rate	0.7 mL/min	0.75 mL/min
Observation height above load coil	14.5 mm	15 mm
Equilabration time	15 s	15 s
Reciprocal linear dispersion	0.54 mm/mm	-----
Nebulizer	Modified Babington	crossflow
Optics	1:3 magnification at entrance slit	-----
Slits	25 µm x 33 mm, entrance 50 µm x 33 mm, exit	-----

Element	*Wavelength, nm*	*Element*	*Wavelength, nm*
Ag	328.0	Mg	285.2 (279.0)
Al	309.2	Mn	257.6
As	189.0	Mo	202.0
Au	242.7	Na	588.9
Ba	455.4	Nb	309.4
Be	313.0	Nd	430.3
Bi	223.0	Ni	231.6
Ca	317.9	P	213.6
Cd	226.5	Pb	220.3
Ce	418.6 (413.7)	Sc	424.6
Co	228.6	Sn	189.9
Cr	267.7	Sr	421.5
Cu	324.7	Ta	240.0
Eu	381.9	Th	401.9
Fe	271.4 (273.9)	Ti	334.9
Ga	294.3	U	409.0
Ho	345.6	V	292.4
K	766.4	Y	321.6 (371.0)
La	298.8 (408.6)	Yb	328.9
Li	670.7	Zn	213.8

Most elements in each sample data set are normalized (i.e. standardized) using well defined in-house reference materials (RM) that have undergone the sample digestion process. The normalized sample set is quality control checked by an independent, established RM that has undergone the sample digestion process also. The RM QC check is accepted if the recovery is within the upper and lower control limits of three times the standard deviation of the certified value, if the concentrations of the elements are >10 times the lower reporting limit. If the standardization is not accepted the sample set and in-house standards are redigested and reanalyzed.

Calculation

Element concentration = IRU/IRS x CONSTD x WT SOLN/WT SAMPLE +IEC

where

IRU = intensity of element/intensity of Lu
IRS = intensity of calibration standard/intensity of Lu
CONSTD = conc of calibration standard
WT SOLN = weight of final solution
WT SAMPLE = weight of sample
IEC = interelement corrections

Assignment of Uncertainty

The analytical results for the selected reference materials, duplicate samples, and method blanks are summarized in table 19. Please note: Some *pv* data has been converted from the oxide using the conversion factors in appendix A, table A1.

Table 19.—Analytical performance summary for 40 elements by ICP-AES

[A=National Institute of Standards and Technology, 1992; B=National Bureau of Standards, 1979; C=Govindaraju, 1989; remaining *pv* from Potts and others, 1992; in-house laboratory data from the Thermo Jarrell Ash instrument]

Reference	*Description*	*n*	*Mean*	*s*	*pv*	*% RSD*	*% R*
Aluminum, Al	**(percent)**						
IF-G	iron formation	10	0.08	0.01	0.079	13	97
GSD-12	stream sediment	68	4.7	0.1	**4.92**	2	95
SRM 2711	soil	7	6.5	0.3	**6.53** A *cv*	5	99
RGM-1	rhyolite	10	7.2	0.1	**7.26**	1	98
GSD-6	stream sediment	20	7.5	0.2	**7.49**	3	100
SRM 278	obsidian	9	7.78	0.08	**7.49** *cv*	1	104
SRM 688	basalt	9	9.04	0.05	**9.19** *cv*	0.6	98
MA-N	granite	10	8.3	0.5	**9.32**	6	89
DNC-1	diabase	10	9.9	0.2	**9.68**	2	103
FK-N	K-feldspar	10	9.4	0.1	**9.85**	1	95
SRM 1633a	coal fly-ash	10	13.4	0.5	**14.30** B *cv*	4	94
GXR-2	soil	114	6.6	0.3	**16.46**	5	40

Table 19.—Analytical performance summary for 40 elements by ICP-AES—Continued

Reference	*Description*	*n*	*Mean*	*s*	*pv*		*% RSD*	*% R*
Arsenic, As (ppm)								
MA-N	granite	10	17	8	13		46	131
SRM 2711	soil	7	94	7	105	A	8	90
SRM 1633a	coal fly-ash	10	141	10	145	B	7	97
Barium, Ba (ppm)								
MA-N	granite	10	40	2	42		5	95
SRM 688	basalt	9	178	2	*200*		1	89
FK-N	K-feldspar	10	195	5	200		3	98
GSD-12	stream sediment	68	193	7	206		3	94
GSD-6	stream sediment	20	310	11	*330*		4	94
SRM 2711	soil	7	709	13	**726**	A *cv*	2	98
RGM-1	rhyolite	10	827	22	807		3	102
SRM 278	obsidian	9	928	9	*1,100*		1	84
SRM 1633a	coal fly-ash	10	1,310	74	1,500	B	6	87
GXR-2	soil	114	2,120	80	**2,240**		4	95
Beryllium, Be (ppm)								
DNC-1	diabase	10	<1	---	1	?	---	---
GXR-2	soil	114	2.0	0.2	1.7		10	118
GSD-6	stream sediment	20	2	0	1.7		0	118
SRM 278	obsidian	9	2.4	0.1	*2*	?	4	120
RGM-1	rhyolite	10	2	0	2.37		0	84
IF-G	iron formation	10	4	0	4.7		0	85
GSD-12	stream sediment	68	6.8	0.4	8.2		6	83
SRM 1633a	coal fly-ash	10	12	1	12	B	8	100
MA-N	granite	10	341	23	280		7	122
Bismuth, Bi (ppm)								
GSD-12	stream sediment	68	10	1	10.9		14	94
Cadmium, Cd (ppm)								
MA-N	granite	7	2	0	2		0	100
GSD-12	stream sediment	68	3.8	0.3	4		8	95
GXR-2	soil	114	3.4	0.5	4.1		15	83
SRM 2711	soil	7	38	2	41.7	A *cv*	5	91

Table 19.—Analytical performance summary for 40 elements by ICP-AES—Continued

Reference	*Description*	*n*	*Mean*	*s*	*pv*		*% RSD*	*% R*
Calcium, Ca (percent)								
FK-N	K-feldspar	10	0.076	0.005	0.079		7	96
MA-N	granite	10	0.51	0.03	0.42		6	121
SRM 278	obsidian	9	0.72	0.01	**0.70**	*cv*	1	103
RGM-1	rhyolite	10	0.9	0.2	0.82		22	110
GSD-12	stream sediment	98	0.85	0.03	**0.83**		4	102
GXR-2	soil	114	0.91	0.02	0.93		2	98
SRM 1633a	coal fly-ash	10	1.1	0	**1.11**	B *cv*	0	99
IF-G	iron formation	10	1.1	0	1.11		0	99
GSD-6	stream sediment	20	2.8	0.1	**2.76**		4	102
SRM 2711	soil	7	2.92	0.08	**2.88**	A *cv*	3	101
DNC-1	diabase	10	7.9	0.2	**8.05**		2	98
SRM 688	basalt	9	8.82	0.02	8.70	?	0.2	101
Cerium, Ce (ppm)								
DNC-1	diabase	10	8.2	0.9	10.6		11	77
SRM 688	basalt	9	11.3	0.4	*13*		4	87
RGM-1	rhyolite	10	47	2	47		3	99
GXR-2	soil	114	51	2	**51.4**		4	99
SRM 278	obsidian	9	61	1	*60*		2	102
GSD-12	stream sediment	68	54	4	61		8	89
GSD-6	stream sediment	20	64	2	*68*		3	94
SRM 2711	soil	7	72	2	69	A	3	104
SRM 1633a	coal fly-ash	10	152	13	180	B	9	84
Chromium, Cr (ppm)								
MA-N	granite	10	3	2	3	?	70	90
RGM-1	rhyolite	10	2.5	0.7	3.7		28	68
FK-N	K-feldspar	9	1.1	0.3	5		27	22
SRM 278	obsidian	9	5	0.5	*6.4*		10	78
IF-G	iron formation	10	3	1	10	?	33	30
GSD-12	stream sediment	68	38	3	35		7	109
GXR-2	soil	114	36	3	36		8	101
SRM 2711	soil	7	46	2	47	A	4	98
GSD-6	stream sediment	20	199	12	*190*		6	105
SRM 1633a	coal fly-ash	10	201	10	**196**	B *cv*	5	103
DNC-1	diabase	10	260	25	285		9	91
SRM 688	basalt	9	260	20	332	*cv*	8	78

Table 19.—Analytical performance summary for 40 elements by ICP-AES—Continued

Reference	*Description*	*n*	*Mean*	*s*	*pv*		*% RSD*	*% R*
Cobalt, Co (ppm)								
RGM-1	rhyolite	10	2.9	0.3	2.0		10	145
SRM 278	obsidian	9	2	1	*2.1*		50	95
GXR-2	soil	114	11.1	0.5	**8.6**		5	129
GSD-12	stream sediment	68	9.0	0.4	8.8		4	102
SRM 2711	soil	7	10.8	0.4	10	A	4	108
FK-N	K-feldspar	10	17.2	0.4	16		2	108
GSD-6	stream sediment	20	26	1	*24.4*		5	106
IF-G	iron formation	10	36	1	29		4	124
SRM 1633a	coal fly-ash	10	46	3	46	B	5	101
SRM 688	basalt	9	47	1	*49*		2	95
DNC-1	diabase	10	60	2	54.7		3	109
Copper, Cu (ppm)								
FK-N	K-feldspar	6	<1	---	2		---	---
SRM 278	obsidian	9	<5	---	**5.9**	*cv*	---	---
RGM-1	rhyolite	10	11	1	11.6		9	95
IF-G	iron formation	10	6	1	13	?	17	46
GXR-2	soil	114	79	4	76		5	104
DNC-1	diabase	10	104	5	96		5	108
SRM 688	basalt	9	90	1	96	?	1	94
SRM 2711	soil	7	115	5	**114**	A *cv*	5	101
SRM 1633a	coal fly-ash	10	113	5	**118**	B *cv*	4	96
MA-N	granite	10	174	8	140		5	124
GSD-6	stream sediment	20	395	15	383		4	103
GSD-12	stream sediment	68	1,240	62	**1,230**		5	101
Europium, Eu (ppm)								
SRM 278	obsidian	9	0.77	0.03	*0.8*		4	96
SRM 688	basalt	9	1.01	0.02	*1.01*		2	100
SRM 2711	soil	7	<2	---	1.1	A	---	---
SRM 1633a	coal fly-ash	10	3	0	4	B	0	75
Gallium, Ga (ppm)								
SRM 278	obsidian	9	22	4	*11*		18	200
GSD-12	stream sediment	68	13.8	0.7	14.1		5	98
DNC-1	diabase	10	14.0	0.5	15		3	93
RGM-1	rhyolite	10	16	1	15		8	108
SRM 2711	soil	7	16.1	0.7	15	A	4	107
GSD-6	stream sediment	20	17.1	0.9	*16.7*		5	102
SRM 688	basalt	9	17	7	*17*		41	100
FK-N	K-feldspar	10	23.1	0.7	19		3	122
GXR-2	soil	114	18	1	37		7	49
SRM 1633a	coal fly-ash	10	55	2	58	B	3	95
MA-N	granite	10	70	4	59		5	119
Gold, Au (ppm)								
No reference material data available at this time								

Table 19.—Analytical performance summary for 40 elements by ICP-AES—Continued

Reference	*Description*	*n*	*Mean*	*s*	*pv*		*% RSD*	*% R*
Holmium, Ho (ppm)								
SRM 688	basalt	9	0.80	0.05	*0.81*		6	99
RGM-1	rhyolite	10	<4	---	*0.95*		---	---
SRM 278	obsidian	9	1.5	0.1	*1.3*		7	115
Iron, Fe (percent)								
FK-N	K-feldspar	10	0.054	0.007	**0.063**	?	13	86
MA-N	granite	10	0.36	0.02	0.33		6	109
RGM-1	rhyolite	10	1.35	0.05	**1.30**		4	104
SRM 278	obsidian	9	1.47	0.01	**1.43**	*cv*	0.7	103
GXR-2	soil	114	1.90	0.06	1.86		3	102
SRM 2711	soil	7	2.87	0.05	**2.89**	A *cv*	2	99
GSD-12	stream sediment	68	3.40	0.08	**3.41**		2	100
GSD-6	stream sediment	20	4.0	0.1	**4.11**		3	98
DNC-1	diabase	10	6.9	0.2	**6.66**		3	104
SRM 688	basalt	9	7.34	0.03	**7.24**	*cv*	0.4	101
SRM 1633a	coal fly-ash	10	9.3	0.5	**9.40**	B *cv*	5	99
IF-G	iron formation	10	40	1	**39.1**		2	102
Lanthanum, La (ppm)								
DNC-1	diabase	10	4	0	3.8		0	105
SRM 688	basalt	9	5.3	0.1	*5.3*		2	100
RGM-1	rhyolite	10	25.4	0.5	**24.0**		2	106
GXR-2	soil	114	27	1	25.6		4	104
GSD-12	stream sediment	68	29	3	32.7		9	88
SRM 278	obsidian	9	31	1	*33*		3	94
GSD-6	stream sediment	20	34	2	39		5	87
SRM 2711	soil	7	41	2	40	A	4	101
SRM 1633a	coal fly-ash	10	78	7	84	C	9	93
Lead, Pb (ppm)								
DNC-1	diabase	10	<4	---	6.3		---	---
IF-G	iron formation	6	<8	---	6.5		---	---
SRM 278	obsidian	9	18	3	**16.4**	*cv*	17	110
RGM-1	rhyolite	10	25	1	24		5	103
GSD-6	stream sediment	20	28	3	27		9	105
MA-N	granite	10	36	6	29		17	124
SRM 1633a	coal fly-ash	10	60	6	**72.4**	B *cv*	9	82
FK-N	K-feldspar	10	213	12	240		5	89
GSD-12	stream sediment	68	292	22	285		8	102
GXR-2	soil	114	696	57	690		8	101
SRM 2711	soil	7	1,120	102	**1,162**	A *cv*	9	97

Table 19.—Analytical performance summary for 40 elements by ICP-AES—Continued

Reference	*Description*	*n*	*Mean*	*s*	*pv*		*% RSD*	*% R*
Lithium, Li (ppm)								
DNC-1	diabase	10	5.6	0.5	5.1		9	110
SRM 688	basalt	9	7	1	*7*	?	14	100
FK-N	K-feldspar	10	7.3	0.5	8.5		7	86
GSD-12	stream sediment	68	40	1	39		3	101
GSD-6	stream sediment	20	43	2	**40**		5	107
SRM 278	obsidian	9	47	1	*47*		2	100
GXR-2	soil	114	61	2	**54**		4	113
RGM-1	rhyolite	10	58	2	57		3	102
SRM 1633a	coal fly-ash	10	195	11	**165**	C	6	118
MA-N	granite	10	5,150	381	4,900		7	105
Magnesium, Mg (percent)								
FK-N	K-feldspar	7	<.005	---	0.006	?	---	---
MA-N	granite	10	0.03	0.01	0.02		33	150
SRM 278	obsidian	9	0.14	0.002	0.14	*cv*	1	100
RGM-1	rhyolite	10	0.18	0.004	0.17		2	106
GSD-12	stream sediment	68	0.25	0.01	**0.28**		4	89
SRM 1633a	coal fly-ash	10	0.46	0.01	**0.455**	B *cv*	2	101
GXR-2	soil	114	0.82	0.03	0.85		4	96
SRM 2711	soil	7	1.07	0.05	**1.05**	A *cv*	4	102
IF-G	iron formation	10	1.22	0.04	1.14		3	107
GSD-6	stream sediment	20	1.80	0.05	**1.81**		3	99
SRM 688	basalt	9	5.08	0.02	5.07	?	0.4	100
DNC-1	diabase	10	5.2	0.2	**6.06**		3	86
Manganese, Mn (ppm)								
FK-N	K-feldspar	10	18	2	39	?	11	46
SRM 1633a	coal fly-ash	10	170	8	**179**	B *cv*	5	95
RGM-1	rhyolite	10	278	19	279		7	100
MA-N	granite	10	344	25	310		7	111
IF-G	iron formation	10	314	16	325		5	97
SRM 278	obsidian	9	373	3	**403**	*cv*	1	93
GSD-6	stream sediment	20	959	23	**1,007**		2	95
GXR-2	soil	114	1,020	41	1,007		4	101
DNC-1	diabase	10	1,110	32	**1,154**		3	96
SRM 688	basalt	9	1,240	20	**1,293**	*cv*	2	96
GSD-12	stream sediment	68	1,420	41	**1,394**		3	102
Molybdenum, Mo (ppm)								
RGM-1	rhyolite	8	<2	---	2.3		---	---
SRM 278	obsidian	9	2	1	*3*	?	50	67
GSD-6	stream sediment	20	6.0	0.7	7.7		12	78
GSD-12	stream sediment	68	6.6	0.9	8.4		14	79
SRM 1633a	coal fly-ash	10	29	1	29	B	5	100

Table 19.—Analytical performance summary for 40 elements by ICP-AES—Continued

Reference	*Description*	*n*	*Mean*	*s*	*pv*		*% RSD*	*% R*
Neodymium, Nd (ppm)								
DNC-1	diabase	10	7	2	**4.9**		22	143
SRM 688	basalt	9	10.4	0.5	*9.6*		5	108
GXR-2	soil	114	22	1	19	?	7	113
RGM-1	rhyolite	10	20	2	19		10	104
GSD-12	stream sediment	68	23	2	25.6		8	89
SRM 278	obsidian	9	29	1	*29*		3	99
SRM 2711	soil	7	31	1	31	A	4	100
GSD-6	stream sediment	20	31	2	*33*		6	93
SRM 1633a	coal fly-ash	10	75	4	74	C	6	101
Nickel, Ni (ppm)								
MA-N	granite	10	5	1	3	?	20	170
FK-N	K-feldspar	10	<2	---	3		---	---
SRM 278	obsidian	9	4	2	3.6	*cv*	50	110
RGM-1	rhyolite	8	<2	---	4.4	?	---	---
GSD-12	stream sediment	68	12.0	0.6	12.8		5	94
SRM 2711	soil	7	19.4	0.8	**20.6**	A *cv*	4	94
GXR-2	soil	114	17	1	21		6	81
IF-G	iron formation	10	22	1	22.5	?	7	96
GSD-6	stream sediment	20	75	3	*78*		3	96
SRM 1633a	coal fly-ash	10	123	5	**127**	B *cv*	4	97
SRM 688	basalt	9	143	2	*158*		1	91
DNC-1	diabase	10	267	7	247		3	108
Niobium, Nb (ppm)								
DNC-1	diabase	9	5	1	3.0		25	170
IF-G	iron formation	10	<8	---	4	?	---	---
SRM 688	basalt	9	5	1	5		20	100
RGM-1	rhyolite	10	8	2	8.9		21	92
GXR-2	soil	114	7	2	11.0		21	65
GSD-6	stream sediment	20	6	2	12	?	36	49
GSD-12	stream sediment	68	8	2	15.4		22	51
SRM 278	obsidian	9	13	1	*16*		8	81
MA-N	granite	10	84	66	173		79	49
Phosphorus, P (percent)								
FK-N	K-feldspar	10	0.006	0.001	0.010	?	17	60
SRM 278	obsidian	9	0.017	0.001	0.016	*cv*	6	106
RGM-1	rhyolite	10	0.02	0	0.021		0	96
GSD-12	stream sediment	68	0.02	0.002	0.024		10	83
IF-G	iron formation	10	0.027	0.005	0.027		19	100
DNC-1	diabase	10	0.03	0	0.037		0	81
SRM 688	basalt	9	0.056	0.002	**0.058**	*cv*	4	97
GXR-2	soil	114	0.07	0.004	0.06		6	117
SRM 2711	soil	7	0.087	0.005	**0.086**	A *cv*	6	101
GSD-6	stream sediment	20	0.10	0.006	**0.10**		6	100

Table 19.— Analytical performance summary for 40 elements by ICP-AES—Continued

Reference	*Description*	*n*	*Mean*	*s*	*pv*		*% RSD*	*% R*
Phosphorus (Continued)								
SRM 1633a	coal fly-ash	10	0.182	0.006	0.17	C	3	106
MA-N	granite	10	0.80	0.03	0.61		4	130
Potassium, K (percent)								
SRM 688	basalt	9	0.16	0.003	**0.16**	*cv*	2	100
DNC-1	diabase	10	0.22	0.02	**0.19**		10	116
GXR-2	soil	114	1.35	0.06	1.37		4	98
SRM 1633a	coal fly-ash	10	1.79	0.09	**1.88**	B *cv*	5	95
GSD-6	stream sediment	20	2.02	0.08	**2.02**		4	100
GSD-12	stream sediment	68	2.3	0.1	**2.42**		4	95
SRM 2711	soil	7	2.32	0.08	**2.45**	A *cv*	3	95
MA-N	granite	10	3.0	0.2	**2.64**		7	115
SRM 278	obsidian	9	3.34	0.03	**3.45**	*cv*	0.9	97
RGM-1	rhyolite	10	3.6	0.1	**3.57**		3	99
FK-N	K-feldspar	10	9.6	0.5	**10.63**		5	100
Scandium, Sc (ppm)								
RGM-1	rhyolite	10	4.9	0.3	4.4		7	111
SRM 278	obsidian	9	6	0.5	*5.1*		8	118
GSD-12	stream sediment	68	4.9	0.3	5.1		6	96
GXR-2	soil	114	6.1	0.3	6.88		5	89
SRM 2711	soil	7	9.6	0.5	9	A	5	107
GSD-6	stream sediment	20	16.1	0.7	*17*		4	95
DNC-1	diabase	10	32.2	0.8	31.0		2	104
SRM 688	basalt	9	43	1	*38*		2	114
SRM 1633a	coal fly-ash	10	37	2	40	B	6	92
Silver, Ag (ppm)								
MA-N	granite	9	<2	---	2	?	---	---
SRM 2711	soil	7	3.4	0.5	4.63	A *cv*	15	73
GXR-2	soil	114	19	1	17		5	112
Sodium, Na (percent)								
IF-G	iron formation	10	0.023	0.007	0.024		30	96
SRM 1633a	coal fly-ash	10	0.18	0.01	**0.17**	B *cv*	6	106
GSD-12	stream sediment	68	0.31	0.01	**0.33**		3	94
GXR-2	soil	114	0.57	0.02	**0.56**		4	102
SRM 2711	soil	7	1.2	0	**1.14**	A *cv*	0	105
DNC-1	diabase	10	1.6	0	**1.39**		0	115
SRM 688	basalt	9	1.63	0.05	1.59	*cv*	3	102
GSD-6	stream sediment	20	1.8	0.1	**1.71**		6	104
FK-N	K-feldspar	10	1.76	0.05	1.91		3	92
RGM-1	rhyolite	10	2.9	0.1	**3.02**		4	97
SRM 278	obsidian	9	3.44	0.02	**3.59**	*cv*	0.6	96
MA-N	granite	10	4.9	0.4	**4.33**		7	113

Table 19.—Analytical performance summary for 40 elements by ICP-AES—Continued

Reference	*Description*	*n*	*Mean*	*s*	*pv*			*% RSD*	*% R*
Strontium, Sr (ppm)									
IF-G	iron formation	10	5	1	3 ?			21	160
GSD-12	stream sediment	68	23.7	0.7	24.4			3	97
FK-N	K-feldspar	10	39	1	39			3	100
SRM 278	obsidian	9	60	3	**63.5**		*cv*	5	94
MA-N	granite	10	85	5	84			6	101
RGM-1	rhyolite	10	107	5	108			5	99
DNC-1	diabase	10	152	4	**145**			3	105
GXR-2	soil	114	160	6	160			4	100
SRM 688	basalt	9	170	10	**169.2**		*cv*	6	100
SRM 2711	soil	7	251	7	**245.3**	A	*cv*	3	102
GSD-6	stream sediment	20	280	8	*266*			3	105
SRM 1633a	coal fly-ash	10	808	28	**830**	B	*cv*	3	97
Tantalum, Ta (ppm)									
MA-N	granite	7	181	116	306		?	64	59
Thorium, Th (ppm)									
GXR-2	soil	114	8	1	8.8			12	94
GSD-6	stream sediment	20	8.2	0.9	9.0			11	91
SRM 278	obsidian	9	13	3	**12.4**		*cv*	23	105
SRM 2711	soil	7	13	1	14	A		8	93
RGM-1	rhyolite	10	15	2	15.1			11	99
GSD-12	stream sediment	68	21	1	21.4			6	97
SRM 1633a	coal fly-ash	10	23	2	**24.7**	B	*cv*	9	95
Tin, Sn (ppm)									
SRM 1633a	coal fly-ash	10	<5	---	10	C		---	---
GSD-12	stream sediment	68	21	3	**54**			14	39
MA-N	granite	10	89	52	1,050			59	8
Titanium, Ti (percent)									
MA-N	granite	10	0.007	0.002	0.006			29	117
IF-G	iron formation	10	<.01	---	0.008			---	---
FK-N	K-feldspar	9	<.005	---	0.01		?	---	---
SRM 278	obsidian	9	0.148	0.001	**0.147**		*cv*	0.7	100
GSD-12	stream sediment	68	0.13	0.01	**0.15**			8	87
RGM-1	rhyolite	10	0.17	0.01	0.16			6	106
DNC-1	diabase	10	0.32	0.01	**0.29**			4	110
GXR-2	soil	114	0.27	0.01	0.30			4	90
SRM 2711	soil	7	0.28	0.02	**0.306**	A	*cv*	7	92
GSD-6	stream sediment	20	0.41	0.02	**0.47**			5	87
SRM 688	basalt	9	0.74	0.01	**0.70**		*cv*	1	106
SRM 1633a	coal fly-ash	10	0.84	0.05	0.80	B		6	105

Table 19.—Analytical performance summary for 40 elements by ICP-AES—Continued

Reference	*Description*	*n*	*Mean*	*s*	*pv*		*% RSD*	*% R*
Uranium, U (ppm)								
SRM 278	obsidian	9	<80	---	**4.58**	*cv*	---	---
Vanadium, V (ppm)								
FK-N	K-feldspar	10	<2	---	3		---	---
IF-G	iron formation	7	<4	---	4	?	---	---
MA-N	granite	10	<2	---	4.6	?	---	---
RGM-1	rhyolite	10	11	1	13		9	85
SRM 278	obsidian	9	8	1	*15*		13	53
GSD-12	stream sediment	68	42	2	46.6		5	91
GXR-2	soil	114	48	2	52		4	92
SRM 2711	soil	7	78	2	**81.6**	A *cv*	3	96
GSD-6	stream sediment	20	137	5	142		4	96
DNC-1	diabase	10	152	4	148		3	103
SRM 688	basalt	9	248	1	*242*		0.4	102
SRM 1633a	coal fly-ash	10	284	16	**297**	B *cv*	6	96
Ytterbium, Yb (ppm)								
DNC-1	diabase	10	2	0	**2.01**		0	100
SRM 688	basalt	9	2.2	0.03	*2.05*		1	105
RGM-1	rhyolite	10	3	0	2.6		0	115
SRM 2711	soil	7	2.6	0.5	2.7	A	19	96
SRM 278	obsidian	9	4.7	0.1	*4.5*		2	104
SRM 1633a	coal fly-ash	10	7.8	0.4	7.4	C	5	105
Yttrium, Y (ppm)								
IF-G	iron formation	10	5.2	0.4	**9**		8	58
GXR-2	soil	114	14.3	0.5	17		3	84
DNC-1	diabase	10	16	0	18		0	89
GSD-6	stream sediment	20	16	1	20.2		6	81
RGM-1	rhyolite	10	23	1	25		4	92
SRM 2711	soil	7	25	1	25	A	4	100
GSD-12	stream sediment	68	20	1	29.3		5	68
SRM 1633a	coal fly-ash	10	80	5	82	C	6	98

Table 19.—Analytical performance summary for 40 elements by ICP-AES—Continued

Reference	*Description*	*n*	*Mean*	*s*	*pv*		*% RSD*	*% R*
Zinc, Zn (ppm)								
FK-N	K-feldspar	10	8	1	10	?	13	80
IF-G	iron formation	10	19	3	**27**	?	16	70
RGM-1	rhyolite	10	33	1	32		3	102
SRM 278	obsidian	9	48	0.4	*54*		0.8	89
SRM 688	basalt	9	79	1	58		1	136
DNC-1	diabase	10	62	1	66		2	94
GSD-6	stream sediment	20	137	7	144		5	95
SRM 1633a	coal fly-ash	10	210	8	**220**	B *cv*	4	95
MA-N	granite	10	277	17	220		6	126
SRM 2711	soil	7	336	10	**350.4**	A *cv*	3	96
GSD-12	stream sediment	68	508	21	498		4	102
GXR-2	soil	114	545	22	530		4	103

Duplicate samples	*k*	*n*	*Mean*	*s*	*% RSD*	*Concentration range*			*No. of < (total)*	*No. of < (pairs)*
Ag ppm	6	2	15.6	0.7	4	4	to	32	50	25
Al %	31	2	5.31	0.03	0.6	0.4	to	11	0	0
As ppm	19	2	1,200	43	4	3	to	14,000	23	11
Au ppm	2	2	14	1	10	8	to	22	58	29
Ba ppm	31	2	1,310	155	12	40	to	9,500	0	0
Be ppm	19	2	11.2	0.5	4	1	to	160	24	12
Bi ppm	1	2	22.5	0.7	3	22	to	23	60	30
Ca %	30	2	4.61	0.04	0.9	0.05	to	21	2	1
Cd ppm	2	2	14.8	0.4	2	11	to	19	58	29
Ce ppm	30	2	50	1	2	4	to	500	2	1
Co ppm	30	2	21.4	0.4	2	1	to	198	2	1
Cr ppm	30	2	19	1	6	1	to	66	1	0
Cu ppm	28	2	109	1	0.9	2	to	1,700	3	0
Eu ppm	6	2	3.0	0.2	7	2	to	7	54	27
Fe %	31	2	5.08	0.06	1	0.3	to	30	0	0
Ga ppm	28	2	17.1	0.7	4	4	to	34	6	3
Ho ppm	1	2	14	0	0	14	to	14	60	30
K %	29	2	1.34	0.02	1	0.07	to	4.4	4	2
La ppm	30	2	30.2	0.6	2	4	to	310	1	1
Li ppm	31	2	24.4	0.3	1	2	to	162	0	0
Mg %	27	2	1.30	0.02	1	0.06	to	4.5	8	4
Mn ppm	31	2	904	16	2	3	to	10,400	0	0
Mo ppm	11	2	306	5	1	6	to	2,730	38	18

Table 19.—Analytical performance summary for 40 elements by ICP-AES—Continued

Duplicate samples	*k*	*n*	*Mean*	*s*	*% RSD*	*Concentration range*	*No. of < (total)*	*No. of < (pairs)*
Na %	31	2	1.00	0.01	1	0.01 to 4.2	0	0
Nb ppm	10	2	18	1	6	5 to 93	37	16
Nd ppm	27	2	32.0	0.5	2	8 to 280	7	3
Ni ppm	23	2	2,443	106	4	4 to 55,500	14	6
P %	30	2	0.393	0.002	0.5	0.01 to 9.7	1	0
Pb ppm	25	2	107	1	1	1 to 4	11	5
Sc ppm	24	2	12.4	0.2	2	3 to 40	14	7
Sn ppm	1	2	48.5	0.7	1	48 to 49	60	30
Sr ppm	31	2	501	14	3	33 to 3,300	0	0
Ta ppm	--	--	--	--	--	---	62	31
Th ppm	17	2	11.4	0.6	5	4 to 72	28	14
Ti %	30	2	0.274	0.007	3	0.01 to 1.7	1	0
U ppm	--	--	--	--	--	---	62	31
V ppm	30	2	129	1	0.9	2 to 480	2	1
Y ppm	28	2	31.2	0.5	2	4 to 430	6	3
Yb ppm	23	2	6.3	0.4	6	1 to 31	18	9
Zn ppm	30	2	195	4	2	6 to 1,970	2	1

Method blank	*n*	*Mean*	*s*	*3s*	*5s*
Ag ppm	30	-0.07	0.1	0.3	0.6
Al %	30	-0.00003	0.0001	0.0004	0.0005
As ppm	30	-0.4	0.8	2	4
Au ppm	30	0.3	0.6	2	3
Ba ppm	30	0.003	0.03	0.03	0.2
Be ppm	30	-0.01	0.007	0.02	0.04
Bi ppm	30	0.2	0.9	3	4
Ca %	30	-0.0001	0.0002	0.0007	0.001
Cd ppm	30	-0.02	0.07	0.2	0.4
Ce ppm	30	-0.5	0.5	2	3
Co ppm	30	-0.01	0.2	0.5	0.9
Cr ppm	30	0.05	0.1	0.3	0.6
Cu ppm	30	-0.2	0.3	0.8	1
Eu ppm	30	-0.01	0.02	0.06	0.1
Fe %	30	-0.001	0.002	0.006	0.01
Ga ppm	30	-0.2	0.3	1	2
Ho ppm	30	0.006	0.07	0.2	0.4
K %	30	-0.002	0.0002	0.0005	0.001
La ppm	30	-0.1	0.1	0.4	0.7
Li ppm	30	-0.3	0.2	0.5	0.8

Table 19.—Analytical performance summary for 40 elements by ICP-AES—Continued

Method blank	*n*	*Mean*	*s*	*3s*	*5s*
Mg %	30	0.00007	0.00005	0.0002	0.0003
Mn ppm	30	-0.04	0.08	0.2	0.4
Mo ppm	30	-0.1	0.2	0.7	1
Na %	30	0.0006	0.0006	0.002	0.003
Nb ppm	30	0.004	0.09	0.3	0.5
Nd ppm	30	-0.2	0.9	3	5
Ni ppm	30	0.1	0.3	0.9	2
P %	30	0	0.0002	0.0005	0.001
Pb ppm	30	-0.4	0.5	1	2
Sc ppm	30	-0.05	0.08	0.2	0.4
Sn ppm	30	0.1	0.2	0.4	0.8
Sr ppm	30	0.009	0.01	0.04	0.05
Ta ppm	30	-0.2	0.7	2	3
Th ppm	30	0.6	0.6	2	3
Ti %	30	-0.0001	0.00003	0.00009	0.0002
U ppm	30	-3	3	6	16
V ppm	30	0.03	0.1	0.4	0.6
Y ppm	30	-0.01	0.09	0.3	0.5
Yb ppm	30	-0.1	0.1	0.4	0.7
Zn ppm	30	-0.09	0.06	0.2	0.3

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Twenty-four elements in natural and acid mine waters by inductively coupled plasma-atomic emission spectrometry

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Principle

Twenty-four elements are determined in natural and acid mine waters by inductively coupled plasma-atomic emission spectrometry (ICP-AES). In order to detect the trace constituents in water a preconcentration by evaporation (Thompson and Walsh, 1989) is necessary. Only samples with specific conductivities less than 2,000 microsiemens per centimeter (µS/cm) will be preconcentrated. Each sample is analyzed twice in order to report the required elements. A split of the original solution is made for the analysis of Si. A second split is made by preconcentrating the sample 20:1 for the remaining elements. If the specific conductivity is greater than 2,000 µS/cm the sample is analyzed as received with no preconcentration. The solution is analyzed by ICP-AES (Lichte and others, 1987).

Multielement standards are used to calibrate the instrument for each element. Two blanks, four reference standards and one duplicate are included with every set of samples analyzed.

Interferences

ICP-AES interferences may result from spectral interferences, background shifts and matrix effects. Interelement correction factors and background corrections are applied using proprietary data system software (Thermo Jarrell Ash, 1988). Matrix effects can generally be negated by proper matching of standard and sample matrices.

Scope

This method is applicable to the analysis of a variety of waters. All samples must have a specific conductivity measurement, and be filtered and acidified prior to submission for analysis. Samples with specific conductivities less than 2,000 µS/cm are generally preconcentrated. In order to be preconcentrated, a minimum of 100 mL of solution is required. Samples with specific conductivities greater than 2,000 µS/cm are analyzed as received and require a minimum of 10 mL of solution. The elements determined, wavelengths used, and operating ranges for this method are shown in table 20. Approximately 100 sample solutions can be analyzed daily by the ICP-AES system. Higher concentrations may be obtained by dilution of the sample.

Table 20.—ICP-AES elements, wavelengths, and operating ranges for natural and mine waters

[Range #1 dilution factor = 1 (no preconcentration); Range #2 dilution factor = 0.05 (preconcentrated)]

Element	*Wavelength, nm*	*Range #1*		*Range #2*	
Aluminum, Al	309.2	0.5	1,000 ppm	0.025	1,000 ppm
Barium, Ba	455.4	20	10,000 ppb	1	10,000 ppb
Beryllium, Be	313.0	20	10,000 ppb	1	10,000 ppb
Boron, B	249.7	50	10,000 ppb	2.5	10,000 ppb
Cadmium, Cd	226.5	20	10,000 ppb	1	10,000 ppb
Calcium, Ca	317.9	1	1,000 ppm	0.05	1,000 ppm
Chromium, Cr	267.7	40	10,000 ppb	2	10,000 ppb
Cobalt, Co	228.6	40	10,000 ppb	2	10,000 ppb
Copper, Cu	324.7	80	10,000 ppb	4	10,000 ppb
Iron, Fe	259.9	0.5	1,000 ppm	0.025	1,000 ppm
Lead, Pb	220.3	100	10,000 ppb	5	10,000 ppb
Lithium, Li	670.7	100	10,000 ppb	5	10,000 ppb
Magnesium, Mg	285.2	1	1,000 ppm	0.05	1,000 ppm
Manganese, Mn	257.6	40	10,000 ppb	2	10,000 ppb
Molybdenum, Mo	202.0	80	10,000 ppb	4	10,000 ppb
Nickel, Ni	231.6	80	10,000 ppb	4	10,000 ppb
Sodium, Na	588.9	1	1,000 ppm	0.05	1,000 ppm
Phosphorous,P	213.6	0.5	1,000 ppm	0.025	1,000 ppm
Potassium, K	766.4	1	1,000 ppm	0.05	1,000 ppm
Silicon, Si	251.6	1	1,000 ppm	--	--
Strontium, Sr	421.5	20	10,000 ppb	1	10,000 ppb
Titanium, Ti	334.9	200	10,000 ppb	10	10,000 ppb
Vanadium, V	292.4	40	10,000 ppb	2	10,000 ppb
Zinc, Zn	213.8	40	10,000 ppb	2	10,000 ppb

Apparatus

- ICP-AES, Thermo Jarrell Ash, Model 1160 Plasma Atomcomp
- 250 mL Teflon beakers
- Hotplate
- Vortex mixer
- Transfer pipet
- Repeating pipet (Eppendorf)

Reagents

- Deionized water (DI)
- Hydrochloric acid, HCl, reagent grade 37 percent
- Nitric acid, HNO_3 reagent grade 70 percent

5 percent hydrochloric acid solution (v/v): 50 mL conc HCl diluted to 1 L with DI water

50 percent nitric acid solution (v/v): 500 mL conc HNO_3 diluted to 1 L with DI water

15 percent nitric acid solution (v/v): 150 mL conc HNO_3 diluted to 1 L with DI water

Lutetium internal standard (Lu): 500 µg Lu/mL, as Lu_2O_3 in 5 percent HCl

Safety precautions

All laboratory personnel are required to wear safety glasses, rubber gloves, and lab coats when working in the laboratory. All sample preconcentrations are performed in a hood. Refer to the *CHP* and *MSDS* for specific precautions, effects of overexposure, and first-aid treatment for reagents used in the preparation procedure and operation of the ICP-AES system.

Procedure

No preconcentration

1. Using a transfer pipet weigh 4.00 g sample into a 13X100 mm polypropylene test tube.
2. Add 40 µL Lu as the internal standard with the repeating pipet.
3. Cap sample to store and vortex to mix.
4. Analyze for 24 elements by ICP-AES. (Table 21 shows instrumental operating conditions for the ICP-AES system)

Preconcentration

1. Into a 250-mL Teflon beaker, weigh 80.00 g sample.
2. Evaporate to dryness on a hot plate set at 100°C.
3. Dissolve residue in beaker with 2 mL 50 percent HNO_3 and mix by swirling solution in beaker.
4. Add 2 mL 15 percent HNO_3 and mix by swirling solution in beaker.
5. Add 40 µL Lu as the internal standard with the repeating pipet and swirl solution to mix.
6. Transfer solution in beaker to a 13X100-mm polypropylene test tube and cap to store.
7. Analyze for 24 elements by ICP-AES.

Table 21.—Operating conditions for determination of 24 elements in waters by ICP-AES

Power	1,250 W
Sample argon flow rate	0.5 L/min
Coolant argon flow rate	18 L/min
Sample pump rate	0.7 mL/min
Observation height	14.5 mm above load
Nebulizer	Modified Babington

Calculations

Concentration (ppm or ppb) = Sample volume / sample wt(g) × ICP reading (ppm or ppb)

Preconcentration dilution factor = 0.05 (80 g sample is concentrated to 4 mL)

Assignment of uncertainty

Table 22 is the analytical results of 24 elements for selected water reference materials and method blanks. Method blank data for a dilution factor of one represents a conservative estimate of instrument performance. In order to achieve reporting limits for the preconcentration procedure a twenty fold preconcentration is performed. By dividing the reporting limit at 1:1 by twenty (the preconcentration factor), reporting limits at 1:0.05 are achieved. Therefore, blank data for the preconcentration procedure can not be achieved instrumentally for all the elements.

Table 22.—Analytical performance summary for 24 elements in waters by ICP-AES

[a=0.05 dilution factor; b=1 dilution factor; *pv* from Water Resources Division, 1992 and 1993]

Reference	*Description*	*n*	*Mean*	*s*	*pv*	*% RSD*	*% R*
Aluminum, Al (ppm)							
T-125	trace constituents	30a	0.030	0.008	0.024	27	125
AMW-2	acid mine water	30b	20.6	0.2	19.0	0.7	108
Barium, Ba (ppb)							
AMW-2	acid mine water	30b	<20	---	5.0	---	---
T-125	trace constituents	30a	16.7	0.3	16.9	2	99
M-124	major constituents	30b	60	2	---	3	---
Beryllium, Be (ppb)							
AMW-2	acid mine water	30b	<20	---	13	---	---
T-125	trace constituents	30a	14.9	0.3	15.0	2	99
Boron, B (ppb)							
T-125	trace constituents	30a	19.6	0.4	19.4	2	101
M-124	major constituents	30b	297	8	294	3	101
AMW-2	acid mine water	30b	745	22	---	3	---
Cadmium, Cd (ppb)							
T-125	trace constituents	30a	7.2	0.1	7.20	1	100
AMW-2	acid mine water	30b	130	4	130	3	100

Table 22.—Analytical performance summary for 24 elements in waters by ICP-AES—Continued

Reference	*Description*	*n*	*Mean*	*s*	*pv*	*% RSD*	*% R*
Calcium, Ca (ppm)							
T-125	trace constituents	30a	9.26	0.06	9.34	0.6	99
T-125	trace constituents	30b	9.2	0.1	9.34	1	98
M-124	major constituents	30b	156	1	154	0.5	101
AMW-2	acid mine water	30b	327	3	320	0.8	102
Chromium, Cr (ppb)							
T-125	trace constituents	30a	4.0	0.2	3.99	5	100
AMW-2	acid mine water	30b	<80	---	10	---	---
Cobalt, Co (ppb)							
T-125	trace constituents	30a	9.8	0.2	9.45	2	104
AMW-2	acid mine water	30b	156	4	190	3	82
Copper, Cu (ppb)							
T-125	trace constituents	30a	18	1	17.4	6	103
AMW-2	acid mine water	30b	5,280	37	4,900	0.7	108
Iron, Fe (ppm)							
T-125	trace constituents	30a	0.101	0.005	0.0979	5	103
AMW-2	acid mine water	30b	98.3	0.6	94.0	0.7	105
Lead, Pb (ppb)							
T-125	trace constituents	30a	8.4	0.5	8.11	6	104
AMW-2	acid mine water	30b	<100	---	10	---	---
Lithium, Li (ppb)							
T-125	trace constituents	30a	16.0	0.2	16.2	2	99
AMW-2	acid mine water	30b	<100	---	39	---	---
Magnesium, Mg (ppm)							
T-125	trace constituents	30a	2.03	0.03	2.00	1	101
T-125	trace constituents	30b	1.95	0.03	2.00	2	98
M-124	major constituents	30b	58.4	0.4	58.4	0.6	100
AMW-2	acid mine water	30b	114	1	---	0.7	---
Manganese, Mn (ppb)							
T-125	trace constituents	30a	17.7	0.2	18.0	1	98
AMW-2	acid mine water	30b	91,500	980	92,000	1	99
Molybdenum, Mo (ppb)							
AMW-2	acid mine water	30b	<80	---	10	---	---
T-125	trace constituents	30a	20.2	0.2	20.1	1	100
Nickel, Ni (ppb)							
T-125	trace constituents	30a	10.7	0.9	11.2	9	96
AMW-2	acid mine water	30b	234	7	230	3	102

Table 22.—Analytical performance summary for 24 elements in waters by ICP-AES—Continued

Reference	*Description*	*n*	*Mean*	*s*	*pv*	*% RSD*	*% R*
Phosphorus, P (ppm)							
T-125	trace constituents	30a	0.042	0.002	---	5	---
M-124	major constituents	30b	<0.5	---	0.110	---	---
Potassium, K (ppm)							
T-125	trace constituents	20a	1.04	0.01	1.04	1	100
T-125	trace constituents	20b	0.7	0.2	1.04	29	68
AMW-2	acid mine water	20b	3.8	0.3	---	8	---
M-124	major constituents	20b	13.8	0.4	13.9	3	99
Silicon, Si (ppm)							
T-125	trace constituents	30b	2.42	0.03	2.42	1	100
M-124	major constituents	30b	9.14	0.08	9.07	0.9	101
AMW-2	acid mine water	30b	21.6	0.2	20.6	0.8	105
Sodium, Na (ppm)							
T-125	trace constituents	30a	22.1	0.2	22.3	1	99
T-125	trace constituents	30b	22.4	0.4	22.3	2	100
AMW-2	acid mine water	30b	26.1	0.4	25	2	104
M-124	major constituents	30b	167	1	166	0.7	101
Strontium, Sr (ppb)							
T-125	trace constituents	30a	45.9	0.3	46.0	0.6	100
T-125	trace constituents	30b	45.2	0.9	46.0	2	98
AMW-2	acid mine water	30b	1,520	11	1,400	0.7	109
M-124	major constituents	30b	1,700	14	1,669	0.8	102
Titanium,Ti (ppb)							
No reference material data available at this time							
Vanadium, V (ppb)							
T-125	trace constituents	30a	6.6	0.1	6.56	2	101
M-124	major constituents	30b	<40	---	7.5	---	---
AMW-2	acid mine water	30b	<40	---	10	---	---
Zinc, Zn (ppb)							
T-125	trace constituents	30a	5	2	5.95	40	85
AMW-2	acid mine water	30b	45,700	460	41,000	1	111

No duplicate data available at this time

Table 22.—Analytical performance summary for 24 elements in waters by ICP-AES—Continued

Method blank	*n*	*Mean*	*s*	*3s*	*5s*
Al ppm	30 a	0.0008	0.001	0.004	0.007
B ppb	30 a	0.3	0.3	0.9	2
Ba ppb	30 a	0.01	0.04	0.1	0.2
Be ppb	30 a	-0.01	0.01	0.04	0.07
Cd ppb	30 a	-0.01	0.06	0.2	0.3
Ca ppm	30 a	-0.003	0.004	0.01	0.02
Co ppb	30 a	0.03	0.2	0.6	0.9
Cr ppb	30 a	2	3	10	16
Cu ppb	30 a	-0.5	0.6	2	3
Fe ppm	30 a	0.004	0.02	0.05	0.09
K ppm	20 a	-0.02	0.01	0.04	0.07
Li ppb	30 a	0.2	0.2	0.6	0.9
Mg ppm	30 a	-0.0001	0.0008	0.002	0.004
Mn ppb	30 a	0.2	0.4	1	2
Mo ppb	30 a	0.05	0.2	0.7	1
Na ppm	30 a	0.01	0.03	0.09	0.2
Ni ppb	30 a	1	2	5	8
P ppm	30 a	-0.0003	0.002	0.005	0.008
Pb ppb	30 a	-0.1	0.7	2.1	4
Si ppm	30 a	0.01	0.0006	0.002	0.003
Sr ppb	30 a	0.002	0.03	0.09	0.2
Ti ppb	30 a	-0.06	0.8	2	4
V ppb	30 a	-0.04	0.1	0.4	0.7
Zn ppb	30 a	-0.05	0.09	0.3	0.5

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Organometallic halide extraction for 10 elements by inductively coupled plasma-atomic emission spectrometry

By Jerry Motooka

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Principle

A widely used extraction technique tricaprylmethylammonium chloride/methyl isobutyl ketone (Aliquat/MIBK) (Viets, 1978) has been modified and adapted for use with inductively coupled plasma-atomic emission spectrometry (ICP-AES) for the analysis of geologic materials. A hydrochloric acid-hydrogen peroxide digestion (O'Leary and Viets, 1986) solubilizes metals not tightly bound in the silicate lattice of rocks, soils, and stream sediments. The metals are extracted by a 10 percent aliquat 336-diisobutylketone (Motooka, 1988) solution as organic halides. The separated organic phase is pneumatically aspirated into a multichannel ICP instrument where the concentrations of the extracted metals (Ag, As, Au, Bi, Cd, Cu, Mo, Pb, Sb, Zn) are determined simultaneously. It is important to note that this procedure is a partial digestion and depending on element availability, results may be biased low when compared to other methods of analyses.

Interferences

Organic solvent extraction provides preconcentration of the analyte species and when used in conjunction with ICP-AES virtually eliminates the need for complex interference corrections. There are, however, some spectral interferences that must be considered, particularly where very high concentrations of iron and extracted metals (Cu, Mo, and Pb) are encountered. Correction coefficients are determined and computer calculations made to compensate for these interferences.

Scope

ICP-AES offers the capability of generating analytical data in a relatively short period of time, approximately 120 samples can be analyzed in an 8-hour day. The technique is especially useful in geochemistry and in the environmental sciences where the need to determine trace metals at or near their crustal abundance level is of great importance. The suggested wavelengths and lower reporting limits are listed in table 23. The upper limits extend a minimum of four orders of magnitude beyond.

Table 23.—Wavelength and operating range for 10 elements by ICP-AES

Element	*Wavelength, nm*	*Concentration range, µg/g*	
Ag	328.0	0.08	400
As	193.7	1.0	6,000
Au	242.8	0.10	1,500
Bi	223.0	1.0	6,000
Cd	226.5	0.05	500
Cu	324.7	0.05	500
Mo	202.0	0.10	900
Pb	220.3	1.0	6,000
Sb	217.6	1.0	6,000
Zn	213.8	0.05	500

Apparatus

- Applied Research Laboratories Model 3580 ICP spectrometer
- Standard equipment for acid digestions done in water bath. See procedure for test tubes, etc.
- 25x150 mm disposable glass test tube

Reagents

All chemicals should be reagent grade, and all water should be metal free, unless otherwise indicated.

- Aliquat 336, tricaprylmethylammonium chloride (obtainable from Henkel Chemicals, Minneapolis, Minn.)
- Hydrochloric acid, HCl
- Hydrogen peroxide, H_2O_2, 30 percent
- Diisobutylketone

Aliquat 336-diisobutylketone 10 percent (v/v): Pour 200 mL Aliquat 336 into a clean 1,000 mL graduated cylinder, dilute to 1 L with DIBK (diisobutylketone), shake to dissolve the Aliquat 336, and pour into a brown glass bottle. This solution is stable for up to 1 month.

Ascorbic acid-potassium iodine solution, 30 percent— 15 percent (w/v): Weigh 300 g C_6HO_6 (U.S.P. Food grade or metal-free equivalent) and 150 g KI into a brown glass bottle, add 1 L DI water, stir, and warm over low heat until dissolved. Prepare fresh weekly. Note: Some KI has been found to contain Cd and Ag contaminants. However, if samples, standards, and blanks are prepared using the same bottle of reagents, contamination factors should be accounted for.

Safety precautions

All work with open or uncapped reagents must be done in a chemical hood. Protective clothing, including laboratory coats or aprons, gloves, and eyewear must be worn. A good ventilating system must be employed over samples when analysis is performed even though *MSDS* indicates health hazard for DIBK is only slight. See the *CHP* and *MSDS* for further information concerning first-aid treatment and disposal procedures for chemical products used in this method.

Procedure

1. Weigh 1.5 g sample into a 25x150-mm disposable glass test tube (see below).
2. Add 5.0 mL conc HCl followed by 1.0 mL 30 percent H_2O_2 dispensed in ½-mL portions, 15 min apart. Mix sample well after each addition of the hydrogen peroxide.
3. Allow sample solution to stand for 1 hour, mixing once after 30 min, and then place test tube in boiling water bath for 20 min.
4. After sample solution is cool, add 5.0 mL C_6HO_6-KI solution, mix, and let stand for 20 min.
5. Accurately add 3.0 mL 10 percent Aliquat 336-DIBK solution to each tube. Cap and shake for 5 min.
6. Centrifuge the sample solution to separate the organic layer from the acid layer.
7. Transfer the organic layer to a 13x100-mm disposable test tube. This tube is specific for the Gilson carousel-type auto sampler.
8. Place tubes in carousel and analyze.
9. An exception in the above procedure is with samples that are high in carbonate. Recent studies have shown the normality to be more critical than previously thought. It is imperative that the normality window be maintained between 4.4 and 6. Extractability of all the elements begin to suffer below 4.4. Although the window is wide, it may be maintained by doubling the aqueous reagents in samples that effervesce greatly.

Standardization of equipment

The linearity of ICP-AES concentration curves extend over a minimum of four orders of magnitude with this method primarily set-up to determine metals in the low ppm ranges. Therefore, in order to speed up calibration, the number of standards are kept to a minimum; a blank which is equated to zero concentration, a multi-element standard containing 20 ppm of each of the sought after metals, and a 200 ppm iron standard which is necessary to make inter-elemental corrections since small amounts of iron are extracted. The iron standard is prepared by pipetting 1 mL 50,000 ppm Fe into a 250 mL volumetric flask and bringing to volume with 10 percent Aliquat-DIBK solution. The iron solution is totally absorbed into the DIBK solution.

The following table lists the instrumental operating conditions using an Applied Research Laboratories Model 3580 ICP spectrometer.

Table 24.—Operating conditions for determination of 10 elements by ICP-AES

Nebulizer	Meinhard concentric glass, C type, 1 mL/min
Torch configuration	Standard, three concentric-tube
Coil	Three turn, water cooled
Power	1400 W
Gas, argon	Coolant, 16 L/min Plasma, 1 L/min Carrier, 1.5 L/min
Observation height	16 mm above coil
Integration time	2 periods, 10 s each
Sample introduction rate	1.0 mL/min

Assignment of uncertainty

Table 25 is the analytical results of ten elements for selected reference materials, duplicate samples, and method blanks. Depending on the type of sample, there may be a significant discrepancy between the proposed value and the laboratory value. This is primarily due to the availability of the metal in the sample. Since this is a partial digestion, those metals tightly bound in highly resistant minerals will not be extracted. Results are reported in ppm (mg/L).

Table 25.—Analytical performance summary for 10 elements (ppm) by ICP-AES

[A=National Institute of Standards and Technology, 1992; remaining *pv* from Potts and others, 1992]

Reference	*Description*	*n*	*Mean*	*s*	*pv*		*% RSD*	*% R*
Antimony, Sb								
BHVO-1	basalt	10	<1.0	---	0.159		---	---
GXR-5	soil	10	1.6	0.2	1.63		13	98
SRM 1633a	coal fly-ash	10	3.6	0.3	**6.8**	A *cv*	8	53
SRM 2709	soil	10	5.4	0.4	**7.9**	A *cv*	7	68
SRM 2711	soil	10	19.0	0.7	**19.4**	A *cv*	4	98
GSD-12	stream sediment	10	24.0	0.5	24.3		2	99
GXR-2	soil	10	41	2	49		5	84
GXR-1	jasperoid	10	104	5	116		5	90
Arsenic, As								
BHVO-1	basalt	10	<1.0	---	0.40		---	---
JG-2	granite	10	<1.0	---	0.80		---	---
GXR-5	soil	10	8.5	0.4	11.2		5	76
SRM 2709	soil	10	16	2	**17.7**	A *cv*	13	90
GXR-2	soil	10	13	1	25		8	53
SRM 2711	soil	10	102	4	**105**	A *cv*	4	97
GSD-12	stream sediment	10	114	3	115		3	99
SRM 1633a	coal fly-ash	10	139	4	145	A *cv*	3	96
GXR-1	jasperoid	10	432	18	401		4	108

Table 25.—Analytical performance summary for 10 elements (ppm) by ICP-AES—Continued

Reference	*Description*	*n*	*Mean*	*s*	*pv*		*% RSD*	*% R*
Bismuth, Bi								
GXR-5	soil	10	<1.0	---	0.38		---	---
GXR-2	soil	10	<1.0	---	0.7	?	---	---
SRM 2711	soil	10	1.8	0.2	---		9	---
GSD-12	stream sediment	10	8.8	0.3	10.9		3	81
GXR-1	jasperoid	10	1,600	77	1,380	?	5	116
Cadmium, Cd								
BHVO-1	basalt	10	<0.05	---	0.069		---	---
SRM 2709	soil	10	0.35	0.02	**0.38**	A *cv*	6	92
GXR-5	soil	10	0.10	0.01	0.7	?	10	14
SRM 1633a	coal fly-ash	10	0.49	0.02	1.00	A *cv*	4	49
GXR-1	jasperoid	10	2.6	0.2	3.3	?	8	79
GSD-12	stream sediment	10	4.1	0.1	4		2	103
GXR-2	soil	10	3.8	0.3	4.1		8	93
SRM 2711	soil	10	41	1	**41.70**	A *cv*	2	99
Copper, Cu								
JG-2	granite	10	0.3	0.2	0.4		67	75
SRM 2709	soil	10	34	2	**34.6**	A *cv*	6	99
GXR-2	soil	10	75	4	76		5	99
SRM 2711	soil	10	114	4	**114**	A *cv*	4	100
SRM 1633a	coal fly-ash	10	41	3	**118**	A *cv*	6	34
BHVO-1	basalt	10	103	3	**136**		3	76
GXR-5	soil	10	350`	6	354		2	99
GXR-1	jasperoid	10	1,180	56	1,110		5	106
GSD-12	stream sediment	10	1,180	22	**1,230**		2	96
Gold, Au								
SRM 2711	soil	10	<0.10	---	0.03	A	---	---
GXR-2	soil	10	<0.10	---	0.036		---	---
SRM 2709	soil	10	0.23	0.05	0.3	A	22	77
GXR-1	jasperoid	10	3.7	0.1	3.4		3	109
Lead, Pb								
BHVO-1	basalt	10	1.4	0.2	2.6		14	54
SRM 2709	soil	10	14	1	**18.9**	A *cv*	7	74
GXR-5	soil	10	13.6	0.3	21		2	67
JG-2	granite	10	4.5	0.4	32.8		9	14
SRM 1633a	coal fly-ash	10	19	1	**72.4**	A *cv*	5	27
GSD-12	stream sediment	10	249	3	285		1	87
GXR-2	soil	10	667	52	690		8	97
GXR-1	jasperoid	10	713	45	720		6	99
SRM 2711	soil	10	1,150	34	**1,162**	A *cv*	3	99

Table 25.—Analytical performance summary for 10 elements (ppm) by ICP-AES—Continued

Reference	*Description*	*n*	*Mean*	*s*	*pv*		*% RSD*	*% R*
Molybdenum, Mo								
JG-2	granite	10	0.32	0.04	0.23		13	139
BHVO-1	basalt	10	0.62	0.04	1.02		6	61
SRM 2711	soil	10	1.5	0.1	1.6	A	7	94
SRM 2709	soil	10	1.87	0.06	2.0	A	3	94
GXR-2	soil	10	1.16	0.04	2.1	?	3	57
GSD-12	stream sediment	10	8.1	0.3	8.4		4	96
GXR-1	jasperoid	10	18	1	18	?	6	100
SRM 1633a	coal fly-ash	10	27	2	29	A	7	93
GXR-5	soil	10	35	1	31		3	113
Silver, Ag								
SRM 2709	soil	10	0.36	0.02	**0.41**	A *cv*	6	88
GSD-12	stream sediment	10	1.04	0.03	1.15		3	90
GXR-5	soil	10	0.67	0.01	1.4	?	1	48
SRM 2711	soil	10	4.6	0.2	**4.63**	A *cv*	4	98
GXR-2	soil	10	18	1	17		6	106
GXR-1	jasperoid	10	31	2	31		6	100
Zinc, Zn								
JG-2	granite	10	8.1	0.3	12.7		4	64
GXR-5	soil	10	27	2	49		7	55
BHVO-1	basalt	10	37	1	**105**		3	35
SRM 2709	soil	10	75	14	**106**	A *cv*	18	71
SRM 1633a	coal fly-ash	10	48	6	**220**	A *cv*	13	22
SRM 2711	soil	10	207	11	**350.4**	A *cv*	5	59
GSD-12	stream sediment	10	296	8	498		3	59
GXR-2	soil	10	492	43	530		9	93
GXR-1	jasperoid	10	837	64	760		8	110

Duplicate samples	*k*	*n*	*Mean*	*s*	*% RSD*	*Concentration range*	*No. of < (total)*	*No. of < (pairs)*
Ag	11	2	2.4	0.1	5	0.10 to 8.9	130	65
As	57	2	8	1	13	0.92 to 89	32	18
Cu	74	2	43	1	3	0.72 to 743	0	0

Additional duplicate data not available at this time

Table 25.—Analytical performance summary for 10 elements (ppm) by ICP-AES—Continued

Method blank	*n*	*Mean*	*s*	*3s*	*5s*
Ag	21	-0.01	0.001	0.004	0.005
As	21	-0.16	0.04	0.1	0.2
Au	21	-0.01	0.001	0.003	0.005
Bi	21	-0.12	0.07	0.2	0.4
Cd	21	-0.01	0.004	0.01	0.02
Cu	21	-0.01	0.001	0.004	0.005
Mo	21	-0.01	0.001	0.003	0.005
Pb	21	0.001	0.06	0.2	0.3
Sb	21	-0.02	0.09	0.3	0.5
Zn	21	0.002	0.005	0.02	0.03

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Coal ash by inductively coupled plasma-atomic emission spectrometry and inductively coupled plasma-mass spectrometry

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Principle

In coal ash, 58 major, minor, and trace elements are determined by a combination of inductively coupled plasma-atomic emission spectrometry (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS) using two decomposition techniques. A multi-acid decomposition (a mixture of hydrochloric, nitric, perchloric, and hydrofluoric acids) is used to determine 31 elements (Crock and others, 1983), the remaining elements are determined in coal ash following a sodium peroxide sinter decomposition technique (modification of Borsier and Garcia, 1983). The ICP-AES is standardized with a digested coal ash reference standard and a series of multi-element solution standards (Lichte, Golightly, and Lamothe, 1987). Calibration for each element determined by the ICP-MS is made by using the average intensity of five blanks taken through the entire procedure(s) and the intensities acquired on a solution of a glass standard (PP-93) containing a known concentration of each element (Lichte, Meier, and Crock, 1987).

Interferences

ICP-AES interferences may result from spectral interferences, background shifts, and matrix effects (Thompson and Walsh, 1983). Interelement correction factors and background corrections are applied using the proprietary data system software (Thermo Jarrell Ash, 1988). It is common to not report an affected element due to the extraordinary interference of the affecting element. Matrix effects can generally be negated by proper matching of standard and sample matrices.

ICP-MS interferences come from matrix effects, instrumental drift, and isobaric overlap of some elemental isotopes and molecular ions formed in the plasma resulting in suppression or enhancement of measured ion intensity. A glass standard is used so samples and standards are matrix matched. Internal standards are added to compensate for matrix effects and instrumental drift. The standard solution is run at 15 sample intervals, drift is calculated, and correction applied between standards. The isotopes measured are selected to minimize isobaric overlap from other elements and molecular species that might be present.

Scope

Analysis by ICP-AES and ICP-MS for major, minor, and trace elements is useful for a variety of coal and geochemical investigations. The elements analyzed and their reporting limits are shown in tables 26 and 27. Twelve to twenty samples can be prepared daily for each decomposition technique.

Table 26.—Reporting limits, wavelengths, and decomposition technique for coal ash samples by ICP-AES

[S=sinter, M=multi-acid]

Element	*Wavelength (nm)*	*Concentration range*			*Decomposition technique*
Aluminum, Al	3092	0.05	to	100%	S
Barium, Ba	4554	10	to	100,000 ppm	S
Beryllium, Be	3130	2	to	10,000 ppm	M
Boron, B	2497	20	to	100,000 ppm	S
Calcium, Ca	3179	0.6	to	100%	S
Chromium, Cr	2677	11	to	100,000 ppm	M
Cobalt, Co	2286	2	to	50,000 ppm	M
Copper, Cu	3247	5	to	100,000 ppm	M
Iron, Fe	2714	0.3	to	100%	S
Lithium, Li	6707	4	to	100,000 ppm	M
Magnesium, Mg	2852	0.02	to	50%	S
Manganese, Mn	2576	8	to	100,000 ppm	M
Nickel, Ni	2316	5	to	100,000 ppm	M
Phosphorus, P	2136	0.03	to	100%	S
Potassium, K	1999	0.5	to	100%	S
Scandium, Sc	4246	4	to	100,000 ppm	M
Silicon, Si	2516	0.3	to	100%	S
Sodium, Na	5889	0.04	to	100%	M
Strontium, Sr	4215	4	to	30,000 ppm	M
Thorium, Th	4019	10	to	100,000 ppm	M
Titanium, Ti	3349	0.02	to	50%	S
Vanadium, V	2924	4	to	60,000 ppm	M
Yttrium, Y	3216	4	to	50,000 ppm	M
Zinc, Zn	2138	7	to	100,000 ppm	M
Zirconium, Zr	3391	20	to	100,000 ppm	S

Table 27.—Reporting limits, mass and decomposition technique for coal ash samples by ICP-MS

[S=sinter, M=multi-acid]

Element	*Mass*	*Concentration range*			*Decomposition technique*
Antimony, Sb	121	0.6	to	1,500	M
Arsenic, As	75	1	to	5,000	M
Bismuth, Bi	209	0.5	to	800	M
Cadmium, Cd	114	0.2	to	500	M
Cerium, Ce	140	3	to	6,000	S
Cesium, Cs	133	0.1	to	150	M
Dysprosium, Dy	163	0.2	to	16,000	S
Erbium, Er	168	0.2	to	16,000	S
Europium, Eu	151	0.2	to	10,000	S
Gadolinium, Gd	157	1	to	25,000	S

Table 27.—Reporting limits, mass and decomposition technique for coal ash samples by ICP-MS—Continued

Element	*Mass*	*Concentration range*			*Decomposition technique*
Gallium, Ga	69	0.3	to	300	M
Germanium, Ge	74	0.6	to	1,700	M
Hafnium, Hf	178	1	to	25,000	S
Holmium, Ho	165	0.5	to	4,000	S
Lanthanum, La	139	2	to	6,000	S
Lead, Pb	208	3	to	700	M
Molybdenum, Mo	98	0.5	to	700	M
Neodymium, Nd	143	2	to	30,000	S
Niobium, Nb	93	2	to	200	M
Praseodymium, Pr	141	0.5	to	4,000	S
Rubidium, Rb	85	0.5	to	230	M
Samarium, Sm	147	0.5	to	30,000	S
Tantalum, Ta	181	1	to	8,000	S
Terbium, Tb	159	0.5	to	4,000	S
Thallium, Tl	205	0.5	to	480	M
Thulium, Tm	169	0.5	to	4,000	S
Tin, Sn	118	3	to	1,100	M
Tungsten, W	184	1	to	30,000	S
Uranium, U	238	0.2	to	950	M
Ytterbium, Yb	172	0.5	to	20,000	S

Apparatus

- Thermo Jarrell Ash, Model 1160 Plasma Atomcomp simultaneous Inductively Coupled Plasma Atomic Emission Spectrometer
- Inductively Coupled Plasma Mass Spectrometer, Sciex Elan 250
- Hotplate with aluminum heating block
- 30-mL Teflon vessels with caps (Savillex)
- Muffle furnace
- Graphite crucibles, ACGC-315 (A C Technologies Inc)
- 4-oz plastic disposable specimen jars with screw caps
- 13x100 mm disposable polypropylene test tubes with caps (ICP-AES)
- 17x100 mm disposable polypropylene test tubes with caps (ICP-MS)

Reagents

- Deionized (DI) water
- Hydrochloric acid (HCl), conc reagent grade (37%)
- Nitric acid (HNO_3), conc reagent grade (70 %)
- Perchloric acid ($HClO_4$), conc reagent grade (70%)
- Hydrofluoric acid (HF), conc reagent grade (48%)
- Sodium peroxide (Na_2O_2), ground to minus 80-mesh (<180 µm)
- *1% HNO_3:* Dilute 10 mL conc HNO_3 to 1000 mL with DI water
- *15% HNO_3:* Dilute 150 mL conc HNO_3 to 1000 mL with DI water
- Hydrogen peroxide (H_2O_2), solution (30%)

Internal standards

- *In-Lu internal standard 40/1000 µg/mL solution:* Dissolve 1.1371 g lutetium oxide, Lu_2O_3, in a minimum volume of HNO_3. Add 40 mL 1000 µg/mL commercial Indium standard. Dilute to 1000 mL with 1% HNO_3.

Oxide correction solutions

- *Ba and Ce oxides standard:* Prepare a solution to contain 1 µg/mL of each element, 2.5 µg/mL Lu, and 1.5% sodium peroxide. To a 100 mL volumetric flask, add 1.5 g sodium peroxide, 25 mL DI water, 25 mL 15% HNO_3, 0.625 mL 400 µg/mL Lu solution, 0.1 mL 1000 µg/mL Ba, 0.1 mL 1000 µg/mL Ce, and dilute to volume with 1% HNO_3.
- *Gd and Sm oxides standard:* Prepare a solution to contain 1 µg/mL of each element, 2.5 µg/mL Lu, and 1.5% sodium peroxide. To a 100 mL volumetric flask, add 1.5 g sodium peroxide, 25 mL DI water, 25 mL 15% HNO_3, 0.625 mL 400 µg/mL Lu solution, 0.1 mL 1000 µg/mL Gd, 0.1 mL 1000 µg/mL Sm, and dilute to volume with 1% HNO_3.
- *Eu, Nd, and Pr oxides standard:* Prepare a solution to contain 1 µg/mL of each element, 2.5 µg/mL Lu, and 1.5% sodium peroxide. To a 100 mL volumetric flask, add 1.5 g sodium peroxide, 25 mL DI water, 25 mL 15% HNO_3, 0.625 mL 400 µg/mL Lu solution, 0.1 mL 1000 µg/mL Eu, 0.1 mL 1000 µg/mL Nd, 0.1 mL 1000 µg/mL Pr, and dilute to volume with 1% HNO_3.
- *Ta oxide standard:* Prepare a solution to contain 1 µg/mL Ta and 1.5 µg/mL Lu. To a 100 mL volumetric flask, add 25 mL DI water, 25 mL 15% HNO_3, 0.625 mL 200 µg/mL Lu solution, 0.1 mL 1000 µg/mL Ta, and dilute to volume with 1% HNO_3.
- *Nb and Mo oxides standard:* Prepare a solution to contain 1 µg/mL of each element, and 1.5 µg/mL Lu. To a 100 mL volumetric flask, add 25 mL DI water, 25 mL 15% HNO_3, 0.625 mL 200 µg/mL Lu solution, 0.1 mL 1000 µg/mL Nb, 0.1 mL 1000 µg/mL Mo, and dilute to volume with 1% HNO_3.

Calibration standard

PP-93: In house glass standard material containing all elements used for calibration.

Safety precautions

All laboratory personnel must wear safety glasses, a lab coat or apron, and gloves when working in the laboratory. All digestions and flux (sodium peroxide) preparations must be performed in a chemical fume hood (digestions using perchloric acid are handled in a perchloric acid hood); the latter is washed down after each days use. All personnel must read the *CHP* and *MSDS* for each procedure. Calcium glucaonte gel should be available in labs where HF is in use.

Procedure

The instrument operating parameters are shown in tables 28 and 29.

Table 28.—Operating conditions for coal ash determinations by ICP-AES

Power to the torch	1250 W
Argon flow rate	18 L/min coolant, 0.5 L/min sample
Sample pump rate.	0.7 mL/min
Observation height	14.5 mm above load coil
Reciprocal linear dispersion	0.54 mm/mm
Nebulizer	Modified Babington
Optics	1:3 magnification at entrance slit
Slits	25 µm x 33 mm, entrance 50 µm x 33 mm, exit

Table 29.—Operating conditions for coal ash determinations by ICP-MS

Sweeps/Replicate	50
Number of replicates	1
Points/Peak	1
Resolution	Variable
Calculation frequency	Replicate
Polarity	+
Plasma RF Power	1300 W
Sheath flow	minimum CeO to Tb ratio L/min
Nebulizer flow	1.0 L/min
Plasma flow	16.0 L/min
Nebulizer pressure	60.0 psi
Sample uptake rate	1.8 mL/min
Sample delay time.	50 s
Sampler wash time	30 s
Delivery line temp	10°C
E1 lens	90
P lens	30
S2 lens	02
B lens	max Tb

Multi-acid digestion:

1. Weigh 0.2 g sample into a Teflon vessel. Standard coal ash and duplicates are taken through the procedure as well as two samples of PP-93 (in-house glass standard material used for calibration).
2. Add 0.1 mL Lu internal standard (1000 µg/mL).
3. Rinse sample from side walls of the Teflon vessel with a minimum of DI water.
4. Slowly add 3 mL conc HCl.
5. Add 2 mL conc HNO_3. Allow any reaction to subside.

6. Add 1 mL $HClO_4$ and 2 mL HF.

7. Place Teflon vessels on double aluminum heating block preset at 110°C and heat to incipient dryness. Raise temperature to 160°C for 1 hour. Remove Teflon vessels from hot plate.

8. Add 1 mL $HClO_4$ and take to dryness at 160°C.

9. Remove vessels from hot plate and allow to cool.

10. Add 1 mL HNO_3 and 1 drop H_2O_2 and heat at 110°C for 5 minutes (samples high in Mn may require more H_2O_2).

11. Cool Teflon vessels and add 19 mL 1% HNO_3, cap and allow to sit overnight.

12. Use the sample solution in the Teflon vessel directly for ICP-AES.

13. For ICP-MS, take 2 mL sample solution in the Teflon vessel and dilute to 8 mL with 1% HNO_3.

14. Wash Teflon vessels with soap and water, rinse with DI water and dry at 100°C.

Sinter method:

1. Weigh 0.1 g sample into a graphite crucible. Standard coal ash and duplicates are taken through the procedure as well as two samples of PP-93 (in-house glass standard material used for calibration).

2. Add 0.5 g sodium peroxide (dry Na_2O_2). Mix sample and Na_2O_2 thoroughly (keep under a heat lamp until placed into muffle furnace).

3. Heat in a preheated 450°C muffle furnace for 30 min.

4. Remove crucibles and allow to cool.

5. Place the crucible in a 4 oz specimen jar and add 20 mL DI water. Cap the jar and swirl a few times (process may be halted at this time until ready for analysis).

6. Add 0.2 mL Lu internal standard solution (1000 µg/mL) to each jar.

7. Add 20 mL 15% HNO_3. Let stand until reaction has stopped (approximately 30 min) and then mix thoroughly.

8. Use the solution directly in the specimen jar for both ICP-AES and ICP-MS.

9. Clean the graphite crucibles by soaking in 5% HCl overnight. Remove from the acid, rinse with water, soak for 30 min in 1% sodium hydroxide solution, rinse with water, and soak overnight in 1% HNO_3. Rinse with DI water and dry at 100°C. If a white residue appears on the crucible, repeat cleaning procedure.

Calculations

For the multi-acid decomposition, a 0.200 g sample is diluted to 20 mL.
The dilution factor = 100.

$$\text{Concentration (ppm)} = \frac{\text{sample volume (mL)}}{\text{sample weight (g)}} \times \text{ICP-AES reading (ppm)}$$

For ICP-MS, a 2 mL aliquot is diluted to 8 mL before analysis. The dilution factor = 400.

$$\text{Concentration (ppm)} = \frac{\text{Sample volume (mL)}}{\text{sample weight (g)}} \times \text{ICP-MS reading (ppm)}$$

For the sinter decomposition, a 0.100 g sample is diluted to 40 mL.
The dilution factor = 400.

$$\text{Concentration (ppm)} = \frac{\text{Sample volume (mL)}}{\text{sample weight (g)}} \times \text{ICP-AES reading (ppm)}$$

$$\text{Concentration (ppm)} = \frac{\text{Sample volume (mL)}}{\text{sample weight (g)}} \times \text{ICP-MS reading (ppm)}$$

Assignment of uncertainty

The analytical results for selected reference materials duplicate samples, and method blanks are summarized in tables 30 and 31.

Table 30.—Analytical performance summary for elements in coal ash by ICP-AES

[A=National Institute of Standards and Technology (NIST), 1985; B=NIST, 1993; C=Kane, 1990; S=sinter, M=multi-acid]

Reference	*Description*	*n*	*Mean*	*s*	*pv*		*% RSD*	*% R*	*Decomposition technique*
Aluminum, Al (percent)									
CLB-1	coal	28	12.7	0.5	12.3	C	4	103	S
SRM 1632b	coal (bituminous)	18	12.7	0.5	**12.6**	B *cv*	4	101	S
SRM 1633a	coal fly ash	18	14.3	0.7	**14.3**	A *cv*	5	100	S
Barium, Ba (ppm)									
CLB-1	coal	28	594	36	581	C	6	102	S
SRM 1632b	coal (bituminous)	18	964	56	**993**	B *cv*	6	97	S
SRM 1633a	coal fly ash	18	1,343	71	1,500	A	5	90	S

Table 30.—Analytical performance summary for elements in coal ash by ICP-AES—Continued

Reference	*Description*	*n*	*Mean*	*s*	*pv*			*% RSD*	*% R*	*Decomposition technique*
Beryllium, Be (ppm)										
SRM 1632b	coal (bituminous)	21	9.7	0.6	--			6	---	M
SRM 1633a	coal fly ash	21	13.7	0.7	12	A		5	114	M
CLB-1	coal	29	19.0	0.9	19.4	C		5	98	M
Boron, B (ppm)										
SRM 1633a	coal fly ash	18	74	13	---			17	---	S
CLB-1	coal	28	98	21	60	C	?	21	163	S
SRM 1632b	coal (bituminous)	18	746	159	---			21	---	S
Calcium, Ca (percent)										
SRM 1633a	coal fly ash	18	1.3	0.1	**1.11**	A	*cv*	5	114	S
CLB-1	coal	28	2.5	0.1	2.58	C		4	97	S
SRM 1632b	coal (bituminous)	18	2.9	0.1	**3.00**	B	*cv*	3	97	S
Chromium, Cr (ppm)										
CLB-1	coal	29	164	14	160	C		8	103	M
SRM 1632b	coal (bituminous)	21	166	24	162	B		15	103	M
SRM 16633a	coal fly ash	21	236	22	**196**	A	*cv*	9	121	M
Cobalt, Co (ppm)										
SRM 1632b	coal (bituminous)	21	33	1	**33.7**	B	*cv*	4	98	M
SRM 1633a	coal fly ash	21	51	4	46	A		7	112	M
CLB-1	coal	29	113	3	107	C		3	105	M
Copper, Cu (ppm)										
SRM 1632b	coal (bituminous)	21	86	3	**92.4**	B	*cv*	4	93	M
SRM 1633a	coal fly ash	21	113	9	**118**	A	*cv*	8	96	M
CLB-1	coal	29	176	7	172	C		4	103	M
Iron, Fe (percent)										
SRM 1633a	coal fly ash	18	9.5	0.4	**9.4**	A	*cv*	4	101	S
SRM 1632b	coal (bituminous)	18	11.3	0.4	**11.2**	B	*cv*	4	101	S
CLB-1	coal	28	14.0	0.6	13.6	C		4	103	S
Lithium, Li (ppm)										
CLB-1	coal	29	130	4	131	C		3	99	M
SRM 1632b	coal (bituminous)	21	147	5	147	B		3	100	M
SRM 1633a	coal fly ash	21	200	15	---			8	---	M
Magnesium, Mg (percent)										
SRM 1633a	coal fly ash	18	0.48	0.02	**0.455**	A	*cv*	4	105	S
CLB-1	coal	28	0.44	0.02	0.460	C		5	96	S
SRM 1632b	coal (bituminous)	18	0.57	0.04	**0.563**	B	*cv*	7	102	S

Table 30.—Analytical performance summary for elements in coal ash by ICP-AES—Continued

Reference	*Description*	*n*	*Mean*	*s*	*pv*		*% RSD*	*% R*	*Decomposition technique*
Manganese, Mn (ppm)									
CLB-1	coal	29	144	6	142	C	4	101	M
SRM 1632b	coal (bituminous)	21	147	5	**182**	B *cv*	3	81	M
SRM 1633a	coal fly ash	21	195	12	**179**	A *cv*	6	109	M
Nickel, Ni (ppm)									
SRM 1632b	coal (bituminous)	21	93	3	**90**	B *cv*	4	104	M
SRM 1633a	coal fly ash	21	145	11	**127**	A *cv*	8	114	M
CLB-1	coal	29	306	9	304	C	3	101	M
Phosphorus, P (percent)									
SRM 1632b	coal (bituminous)	18	0.074	0.004	---		9	---	S
SRM 1633a	coal fly ash	18	0.20	0.01	---		5	---	S
CLB-1	coal	28	0.44	0.03	0.513	C	7	86	S
Potassium, K (percent)									
CLB-1	coal	28	0.98	0.06	**1.01**	C	6	97	S
SRM 1632b	coal (bituminous)	18	1.06	0.06	**1.10**	B *cv*	6	96	S
SRM 1633a	coal fly ash	18	2.0	0.2	**1.88**	A *cv*	9	105	S
Scandium, Sc (ppm)									
SRM 1632b	coal (bituminous)	21	29	1	28	B	4	103	M
CLB-1	coal	29	32.4	0.7	30.9	C	2	105	M
SRM 1633a	coal fly ash	21	40	3	40	A	7	101	M
Silicon, Si (percent)									
CLB-1	coal	28	19.2	0.9	**18.9**	C	5	102	S
SRM 1632b	coal (bituminous)	18	20.6	0.9	20.6	B	4	100	S
SRM 1633a	coal fly ash	18	23	1	**22.8**	A *cv*	4	102	S
Sodium, Na (percent)									
SRM 1633a	coal fly ash	21	0.18	0.01	**0.17**	A *cv*	6	106	M
CLB-1	coal	29	0.27	0.01	---		4	---	M
SRM 1632b	coal (bituminous)	21	0.77	0.04	**0.757**	B *cv*	5	102	M
Strontium, Sr (ppm)									
SRM 1633a	coal fly ash	21	870	24	**830**	A *cv*	3	105	M
CLB-1	coal	29	1,095	31	1,156	C	3	95	M
SRM 1632b	coal (bituminous)	21	1,443	40	1,500	B	3	96	M
Thorium, Th (ppm)									
SRM 1632b	coal (bituminous)	21	19	1	**19.74**	B *cv*	8	98	M
CLB-1	coal	29	23	2	**22.7**	C	8	99	M
SRM 1633a	coal fly ash	21	24	3	**24.7**	A *cv*	13	97	M

Table 30.—Analytical performance summary for elements in coal ash by ICP-AES—Continued

Reference	*Description*	*n*	*Mean*	*s*	*pv*		*% RSD*	*% R*	*Decomposition technique*
Titanium, Ti (percent)									
SRM 1632b	coal (bituminous)	18	0.64	0.02	**0.668**	B *cv*	3	96	S
CLB-1	coal	28	0.71	0.04	0.727	C	6	98	S
SRM 1633a	coal fly ash	18	0.88	0.05	0.8	A	6	110	S
Vanadium, V (ppm)									
CLB-1	coal	29	204	6	200	C	3	102	M
SRM 1632b	coal (bituminous)	21	202	7	206	B	4	98	M
SRM 1633a	coal fly ash	21	321	23	**297**	A *cv*	7	108	M
Yttrium, Y (ppm)									
SRM 1632b	coal (bituminous)	21	42	3	---		7	---	M
CLB-1	coal	29	78	4	71.3	C	6	109	M
SRM 1633a	coal fly ash	21	86	10	---		11	---	M
Zinc, Zn (ppm)									
SRM 1632b	coal (bituminous)	21	165	13	**174.9**	B *cv*	8	95	M
SRM 1633a	coal fly ash	21	222	17	**220**	A *cv*	8	101	M
CLB-1	coal	29	820	23	817	C	3	100	M
Zirconium, Zr (ppm)									
CLB-1	coal	28	210	28	195	C	13	108	S
SRM 1632b	coal (bituminous)	18	204	13	---		6	---	S
SRM 1633a	coal fly ash	18	235	16	---		7	---	S

Duplicate samples	*k*	*n*	*Mean*	*s*	*% RSD*	*Concentration range*			*Decomposition technique*
Al %	37	2	21.6	0.8	3	12	to	32	S
B ppm	37	2	513	17	3	22	to	5,180	S
Ba ppm	37	2	1,303	39	3	158	to	9,450	S
Be ppm	46	2	10.4	0.4	4	0.81	to	57	M
Ca %	7	2	4.6	0.1	2	0.14	to	16	S
Co ppm	46	2	43	1	3	2.7	to	373	M
Cr ppm	46	2	110	7	6	7.5	to	646	M
Cu ppm	46	2	120	3	2	19	to	507	M
Fe %	37	2	9.5	0.2	2	1.8	to	43	S
K %	37	2	1.27	0.05	4	0.13	to	3.0	S
Li ppm	46	2	86	1	2	9.6	to	228	M
Mg %	37	2	1.71	0.04	2	0.37	to	4.5	S
Mn ppm	46	2	755	21	3	42	to	7,877	M

Table 30.—Analytical performance summary for elements in coal ash by ICP-AES—Continued

Duplicate samples	*k*	*n*	*Mean*	*s*	*% RSD*	*Concentration range*	*Decomposition technique*
Na %	46	2	1.60	0.05	3	0.13 to 8.6	M
Ni ppm	46	2	103	3	3	6.3 to 1,118	M
P %	37	2	0.49	0.02	4	0.02 to 4.4	S
Sc ppm	46	2	33.7	0.4	1	10 to 97	M
Si %	37	2	49	2	4	17 to 71	S
Sr ppm	46	2	1,508	32	2	72 to 7,021	M
Th ppm	46	2	17.8	0.7	4	3.3 to 64	M
Ti %	37	2	1.97	0.05	3	0.37 to 5.8	S
V ppm	46	2	278	9	3	44 to 1,746	M
Y ppm	46	2	75	3	4	9.8 to 350	M
Zn ppm	46	2	139	3	0.7	21 to 774	M
Zr ppm	37	2	437	19	4	144 to 1,596	S

Method blank	*n*	*Mean*	*s*	*3s*	*5s*	*Decomposition technique*
Al %	30	0.01	0.01	0.03	0.05	S
B ppm	30	2	3	9	15	S
Ba ppm	30	2	2	5	9	S
Be ppm	30	0.01	0.04	0.1	0.2	M
Ca %	30	0.2	0.1	0.3	0.6	S
Co ppm	30	0.1	0.4	1	2	M
Cr ppm	30	3	2	6	11	M
Cu ppm	30	1	1	3	5	M
Fe %	30	0.03	0.06	0.2	0.3	S
K %	30	0.1	0.1	0.3	0.5	S
Li ppm	30	0.1	0.4	1	2	M
Mg %	30	0.001	0.003	0.008	0.01	S
Mn ppm	30	0.3	0.4	1	2	M
Na %	30	-0.008	0.008	0.03	0.04	M
Ni ppm	30	1	1	3	5	M
P %	30	0.005	0.006	0.02	0.03	S
Sc ppm	30	-0.01	0.2	0.5	0.8	M
Si %	30	0.05	0.05	0.2	0.3	S
Sr ppm	30	0.4	0.5	2	3	M
Th ppm	30	3	2	6	10	M
Ti %	30	0.005	0.004	0.01	0.02	S
V ppm	30	0.4	0.3	1	2	M
Y ppm	30	0.1	0.3	0.8	1	M
Zn ppm	30	2	1	4	7	M
Zr ppm	30	2	4	11	18	S

Table 31.—Analytical performance summary for elements (ppm) in coal ash by ICP-MS

[A=National Institute of Standards and Technology (NIST), 1985; B=NIST, 1993; C=Kane, 1990; S=sinter, M=multi-acid]

Reference	*Description*	*n*	*Mean*	*s*	*pv*			*% RSD*	*% R*	*Decomposition technique*
Antimony, Sb										
SRM 1632b	coal (bituminous)	23	3.6	0.3	3.5	B		7	102	M
SRM 1633a	coal fly ash	23	7.3	0.6	**6.8**	A	*cv*	9	108	M
CLB-1	coal	37	25	2	**24**	C		9	106	M
Arsenic, As										
SRM 1632b	coal (bituminous)	23	63	4	**54.7**	B	*cv*	7	115	M
SRM 1633a	coal fly ash	23	172	9	**145**	A	*cv*	5	118	M
CLB-1	coal	37	260	24	**237**	C		9	110	M
Bismuth, Bi										
CLB-1	coal	37	1.3	0.1	1.2	C	?	9	106	M
SRM 1633a	coal fly ash	23	1.3	0.2	---			13	---	M
SRM 1632b	coal (bituminous)	23	1.7	0.2	---			14	---	M
Cadmium, Cd										
SRM 1632b	coal (bituminous)	23	1.1	0.3	**0.843**	B	*cv*	28	127	M
SRM 1633a	coal fly ash	23	1.2	0.2	1.00	A	*cv*	15	117	M
CLB-1	coal	37	1.2	0.2	1.1	C		16	109	M
Cerium, Ce										
SRM 1632b	coal (bituminous)	21	125	7	132	B		6	94	S
SRM 1633a	coal fly ash	21	169	12	180	A		7	94	S
CLB-1	coal	35	174	14	183	C		8	95	S
Cesium, Cs										
CLB-1	coal	37	5.1	0.8	5.7	C		15	89	M
SRM 1632b	coal (bituminous)	23	6	1	6.5	B		24	93	M
SRM 1633a	coal fly ash	23	10	2	11	A		19	93	M
Dysprosium, Dy										
SRM 1632b	coal (bituminous)	21	9.4	0.6	---			6	---	S
CLB-1	coal	35	15	1	15.2	C	?	7	101	S
SRM 1633a	coal fly ash	21	16	1	---			7	---	S
Erbium, Er										
SRM 1632b	coal (bituminous)	21	5.3	0.4	---			7	---	S
SRM 1633a	coal fly ash	21	8.5	0.4	---			5	---	S
CLB-1	coal	35	8.7	0.7	8.7	C	?	8	100	S

Table 31.—Analytical performance summary for elements (ppm) in coal ash by ICP-MS—Continued

Reference	*Description*	*n*	*Mean*	*s*	*pv*			*% RSD*	*% R*	*Decomposition technique*
Europium, Eu										
SRM 1632b	coal (bituminous)	21	2.5	0.2	2.5	B		8	102	S
CLB-1	coal	35	3.9	0.3	**3.8**	C		7	103	S
SRM 1633a	coal fly ash	21	4.0	0.2	4	A		6	99	S
Gadolinium, Gd										
SRM 1632b	coal (bituminous)	21	10.2	0.9	---			8	---	S
SRM 1633a	coal fly ash	21	16	2	---			9	---	S
CLB-1	coal	35	16	1	17	C	?	8	91	S
Gallium, Ga										
SRM 1632b	coal (bituminous)	23	44	3	---			7	---	M
CLB-1	coal	37	55	4	**51.3**	C		6	108	M
SRM 1633a	coal fly ash	23	65	6	58	A		10	112	M
Germanium, Ge										
SRM 1632b	coal (bituminous)	23	33	4	---			13	---	M
SRM 1633a	coal fly ash	23	39	3	---			6	---	M
CLB-1	coal	37	187	21	158	C	?	11	118	M
Hafnium, Hf										
SRM 1632b	coal (bituminous)	21	6.8	0.6	6.3	B		8	108	S
CLB-1	coal	35	7.3	0.6	**6.6**	C		8	110	S
SRM 1633a	coal fly ash	21	8.1	0.8	8	A		10	101	S
Holmium, Ho										
SRM 1632b	coal (bituminous)	21	1.7	0.1	---			6	---	S
SRM 1633a	coal fly ash	21	2.9	0.2	---			6	---	S
CLB-1	coal	35	2.9	0.2	3.1	C	?	7	94	S
Lanthanum, La										
SRM 1632B	coal (bituminous)	21	64	3	75	B		5	86	S
CLB-1	coal	35	91	9	83.8	C		9	109	S
SRM 1633a	coal fly ash	21	88	5	---			6	---	S
Lead, Pb										
SRM 1632b	coal (bituminous)	23	63	8	**54.0**	B	*cv*	13	117	M
SRM 1633a	coal fly ash	23	83	7	**72.4**	A	*cv*	9	115	M
CLB-1	coal	37	95	6	81.9	C		7	116	M
Molybdenum, Mo										
SRM 1632b	coal (bituminous)	23	13.4	0.5	13	B		3	102	M
SRM 1633a	coal fly ash	23	35	1	29	A		3	119	M
CLB-1	coal	37	220	11	162	C	?	5	136	M

Table 31.—Analytical performance summary for elements (ppm) in coal ash by ICP-MS—Continued

Reference	*Description*	*n*	*Mean*	*s*	*pv*			*% RSD*	*% R*	*Decomposition technique*
Neodymium, Nd										
SRM 1632b	coal (bituminous)	21	53	3	---			5	---	S
SRM 1633a	coal fly ash	21	76	5	---			6	---	S
CLB-1	coal	35	77	5	81	C		6	95	S
Niobium, Nb										
CLB-1	coal	37	22	3	18	C		14	122	M
SRM 1632b	coal (bituminous)	23	24	1	---			5	---	M
SRM 1633a	coal fly ash	23	30	3	---			8	---	M
Praseodymium, Pr										
SRM 1632b	coal (bituminous)	21	13.7	0.7	---			5	---	S
CLB-1	coal	35	19	1	15	C	?	8	129	S
SRM 1633a	coal fly ash	21	19	1	---			7	---	S
Rubidium, Rb										
SRM 1632b	coal (bituminous)	23	75	21	**80.9**	B	*cv*	28	92	M
CLB-1	coal	37	91	18	97	C		20	94	M
SRM 1633a	coal fly ash	23	148	31	**131**	A	*cv*	21	113	M
Samarium, Sm										
SRM 1632b	coal (bituminous)	21	10.9	0.7	13	B		6	85	S
CLB-1	coal	35	16	1	16	C		7	102	S
SRM 1633a	coal fly ash	21	16.4	0.8	---			5	---	S
Tantalum, Ta										
SRM 1632b	coal (bituminous)	21	2.0	0.2	---			12	---	S
CLB-1	coal	35	2.0	0.2	**2.1**	C		9	95	S
SRM 1633a	coal fly ash	21	2.1	0.2	---			9	---	S
Terbium, Tb										
SRM 1632b	coal (bituminous)	21	1.5	0.1	---			7	---	S
CLB-1	coal	35	2.4	0.2	2.5	C		8	96	S
SRM 1633a	coal fly ash	21	2.5	0.2	---			7	---	S
Thallium, Tl										
SRM 1632b	coal (bituminous)	23	2.3	0.3	---			12	---	M
SRM 1633a	coal fly ash	23	6.5	0.6	**5.7**	A	*cv*	9	113	M
CLB-1	coal	37	13	0.9	12	C	?	7	107	M
Thulium, Tm										
SRM 1632b	coal (bituminous)	21	0.76	0.07	---			9	---	S
SRM 1633a	coal fly ash	21	1.2	0.08	---			7	---	S
CLB-1	coal	35	1.3	0.1	1.3	C	?	8	96	S

Table 31.—Analytical performance summary for elements (ppm) in coal ash by ICP-MS—Continued

Reference	*Description*	*n*	*Mean*	*s*	*pv*			*% RSD*	*% R*	*Decomposition technique*
Tin, Sn										
SRM 1632b	coal (bituminous)	23	9.5	0.5	---			5	---	M
SRM 1633a	coal fly ash	23	9.2	0.7	---			7	---	M
CLB-1	coal	37	11	1	11	C	?	11	100	M
Tungsten, W										
SRM 1632b	coal (bituminous)	21	6.8	0.5	7.1	B		8	97	S
SRM 1633a	coal fly ash	21	6.1	0.5	---			9	---	S
CLB-1	coal	35	12	1	12	C		9	102	S
Uranium, U										
SRM 1632b	coal (bituminous)	23	6.6	0.6	**6.41**	B	*cv*	9	103	M
CLB-1	coal	37	8.4	0.5	9.9	C		6	84	M
SRM 1633a	coal fly ash	23	12	0.9	**10.2**	A	*cv*	8	115	M
Ytterbium, Yb										
SRM 1632b	coal (bituminous)	21	5.0	0.4	---			8	---	S
SRM 1633a	coal fly ash	21	7.7	0.5	---			6	---	S
CLB-1	coal	35	7.8	0.6	8.5	C		7	91	S

Duplicate samples	*k*	*n*	*Mean*	*s*	*% RSD*	*Concentration range*			*No of < (total)*	*No of < (pairs)*	*Decomposition technique*
As	52	2	91	5	5	0.39	to	1,287	2	1	M
Bi	52	2	0.81	0.05	6	0.02	to	2.96	2	1	M
Cd	53	2	0.92	0.04	4	0.10	to	10	0	0	M
Ce	47	2	126	3	2	29	to	340	0	0	S
Cs	53	2	7.4	0.2	3	0.15	to	26	0	0	M
Dy	47	2	11.9	0.3	3	1.8	to	29	0	0	S
Er	47	2	6.8	0.2	3	1.2	to	21	0	0	S
Eu	47	2	3.4	0.2	6	1.2	to	7.8	0	0	S
Ga	53	2	48	1	2	13	to	283	0	0	M
Gd	47	2	12.4	0.4	3	2.6	to	32	0	0	S
Ge	53	2	34	3	9	0.47	to	905	0	0	M
Hf	47	2	12.1	0.4	3	14	to	45	0	0	S
Ho	47	2	2.23	0.06	3	0.38	to	6.5	0	0	S
La	47	2	66	2	3	13	to	143	0	0	S
Mo	53	2	16.5	0.5	3	0.34	to	126	0	0	M
Nb	53	2	42	3	7	7.5	to	146	0	0	M
Nd	47	2	58	2	3	13	to	183	0	0	S
Pb	53	2	44	2	5	4.4	to	149	0	0	M
Pr	47	2	14.7	0.4	3	3.6	to	44	0	0	S
Rb	53	2	88	6	7	2.0	to	315	0	0	M
Sb	53	2	4.25	0.09	2	0.02	to	34	0	0	M

Table 31.—Analytical performance summary for elements (ppm) in coal ash by ICP-MS—Continued

Duplicate samples	*k*	*n*	*Mean*	*s*	*% RSD*	*Concentration range*	*No of < (total)*	*No of < (pairs)*	*Decomposition technique*
Sm	47	2	12.5	0.3	2	2.9 to 39	0	0	S
Sn	53	2	8.6	0.4	4	2.0 to 29	0	0	M
Ta	47	2	2.9	0.1	3	0.47 to 9.8	0	0	S
Tb	47	2	1.88	0.05	3	0.39 to 4.7	0	0	S
Tl	51	2	3.2	0.1	3	0.07 to 22	4	2	M
Tm	47	2	0.97	0.02	2	0.16 to 3.1	0	0	S
U	53	2	8.1	0.2	2	1.9 to 48	0	0	M
W	47	2	5.6	0.5	9	0.20 to 21	0	0	S
Yb	47	2	6.2	0.2	3	1.1 to 20	0	0	S

Method blank	*n*	*Mean*	*s*	*3s*	*5s*	*Decomposition technique*
As	30	0.03	0.08	0.3	0.4	M
Bi	30	0.05	0.05	0.2	0.3	M
Cd	30	0.10	0.03	0.08	0.1	M
Ce	30	0.06	0.06	0.2	0.3	S
Cs	30	0.005	0.004	0.01	0.02	M
Dy	30	0.03	0.03	0.09	0.2	S
Er	30	0.03	0.03	0.1	0.2	S
Eu	30	0.02	0.02	0.05	0.08	S
Ga	30	0.04	0.01	0.04	0.06	M
Gd	30	0.04	0.04	0.1	0.2	S
Ge	30	0.05	0.04	0.1	0.2	M
Hf	30	0.2	0.1	0.4	0.6	S
Ho	30	0.09	0.01	0.03	0.06	S
La	30	0.04	0.03	0.1	0.2	S
Mo	30	0.08	0.04	0.1	0.2	M
Nb	30	0.1	0.1	0.3	0.5	M
Nd	30	0.11	0.09	0.3	0.4	S
Pb	30	0.5	0.4	1	2	M
Pr	30	0.02	0.02	0.05	0.08	S
Rb	30	0.03	0.02	0.05	0.08	M
Sb	30	0.12	0.07	0.2	0.4	M
Sm	30	0.08	0.05	0.1	0.2	S
Sn	30	0.4	0.3	0.9	1	M
Ta	30	0.19	0.08	0.2	0.4	S
Tb	30	0.02	0.03	0.09	0.2	S
Tl	30	0.05	0.05	0.2	0.3	M
Tm	30	0.01	0.01	0.02	0.04	S
U	30	0.008	0.004	0.01	0.02	M
W	30	0.21	0.09	0.3	0.5	S
Yb	30	0.06	0.03	0.1	0.2	S

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Niobium, tungsten, and molybdenum by ion exchange/inductively coupled plasma-atomic emission spectrometry

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Principle

Niobium, tungsten, and molybdenum are determined in geologic materials by an ion exchange separation followed by inductively coupled plasma-atomic emission spectrometry (ICP-AES). The sample is digested using concentrated HNO_3, $HClO_4$, and HF in a closed Teflon vessel for 4 hours. The vessel is then uncovered and the sample is evaporated to dryness. The residue is dissolved in 14 mL 8 *N* HCl. This solution is eluted through and ion exchange column where Nb, W, and Mo are adsorbed onto the column. Hydrofluoric acid is added to remove iron. Nitric acid is used to strip Nb, W, and Mo from the column. The HNO_3 fraction is collected and evaporated to dryness. The residue is dissolved in 2 mL 2 *N* HCl and 0.050 mL conc HF. This solution is analyzed by ICP-AES (Lichte and others, 1987).

Multielement standard solutions are used to calibrate the instrument for each element. One blank, three to four standard reference materials, and two duplicates are included with every set of samples analyzed.

Interferences

Most interfering elements are removed during the ion exchange separation but some spectral interferences will still be present. Ninety-five percent of titanium and iron are separated from the analytes by the separation procedure but corrections must be made for the remainder. Ti interferes with Nb; Zn interferes with W; and Fe and Nb interfere with Mo (Boumans, 1980). These interferences are corrected by calculating factors for the effect of each interfering element on each analyte.

Scope

This method is most applicable to the analysis of silicate rocks. Geologic materials containing high concentrations of organic matter (i.e. shales, etc.) should be ashed before digestion. The lower reporting limit for Nb, W, and Mo is 1 ppm. The applicable range for this method is 1 to 200 ppm. Higher concentrations may be obtained by diluting the remaining sample. Approximately 75 to 80 samples a week can be analyzed by this method.

Apparatus

- ICP-AES, 63 channel Jarrell-Ash ICP-AES Polychromator, Model 1160 Plasma Atomcomp
- 50-mL Teflon screw cap vessels (Savillex)
- 15-mL Teflon round bottom screw cap vessels (Savillex)
- Hot plate
- Pipettes

- Polypropylene columns (8 mm x 20 cm) with 9 mL reservoir, and outlet adapter with polyethylene bed support

Reagents

- Distilled H_2O
- Hydrochloric acid, HCl, conc reagent grade
- Nitric acid, HNO_3, conc reagent grade
- Hydrofluoric acid, HF conc reagent grade
- Perchloric acid, $HClO_4$, conc reagent grade

8 N HCl solution: 667 mL conc HCl diluted to 1 L with distilled H_2O

20 percent (v/v) HF solution: 200 mL conc HF diluted to 1 L with distilled H_2O

8 N HNO_3-0.05 N HF solution: 500 mL conc HNO_3 and 1.2 mL conc HF diluted to 1 L with distilled H_2O

2 N HCl solution: 167 mL conc HCl diluted to 1 L with distilled H_2O

Anion exchange resin: 50/50 mixture of BioRad AG1-X8 and AG2-X8, 100-200 mesh, chloride form, in water.

Safety precautions

Sample digestion and ion exchange separation are done in a chemical hood. Protective clothing, gloves, and safety glasses must be worn. Calcium gluconate gel should be available in labs where hydrofluoric acid is in use. See the *CHP* and *MSDS* for further information concerning first-aid treatment and disposal procedures for chemical products used in this method.

Procedure

1. 100-mg samples are digested on a hot plate with 5 mL HNO_3, 2 mL $HClO_4$, and 10 mL HF in sealed screw-cap Teflon vessels for 4 hours at 150°C. Samples are removed from hot plate and let cool. Samples are then uncapped and evaporated to dryness overnight at 150°C.

2. Dissolve residue with 14 mL of 8 *N* HCl and cap the vessel. Heat on hot plate at 120°C for 15 min.

3. Sample columns are prepared by filling the column with distilled water and then adding the resin mixture to a mark of 4 in (approximately 3.5 g of resin). Condition the column with 10 mL 8 *N* HCl.

4. Add the sample to the column. Discard fraction.

5. Wash twice with 5 mL of 8 *N* HCl. Discard fraction.

6. Add 14 mL 20 percent (v/v) HF to remove iron. Discard fraction.

7. Place a 15-mL round-bottom Teflon vial under each column.

8. Strip Nb, W, Mo from the column with 14 mL 8 *N* HNO_3-0.05 *N* HF solution. Collect this fraction.

9. Evaporate this fraction on hot plate overnight at 130°C .

10. Remove vials from hot plate and let cool.
11. Dissolve residue by adding 0.050 mL conc HF and 2 mL 2 *N* HCl to samples, capping vials, and heating to 120°C for 15 min.
12. Analyze for Nb, W, Mo by ICP-AES. The following table lists the instrumental operating conditions.

Table 32.—Operating conditions for determination of Nb, W, and Mo by ion exchange/ICP-AES

Power	1.1 kW
Argon flow rate	sample, 0.64 LPM
	coolant, 17 LPM
Sample pump rate	0.8 mL/min
Observation height	12 mm above load coil
Nebulizer	cross flow

Element	*Wavelength, nm*	*Method blank, ppm (2 N HCl)*	*High standard, ppm*
Nb	316.3	0	1
W	207.9	0	1
Mo	202.0	0	1
Ti	334.9	0	1
Fe	259.9	0	100
Zn	213.8	0	20

Calculations

A 0.100 g of sample is diluted to 2 mL. Dilution factor = 20.

$$\text{Concentration (ppm)} = \frac{\text{sample volume}}{\text{sample wt (g)}} \times \text{ICP sample reading (ppm)} - \text{blank}$$

A blank correction is generally made for molybdenum only. The ICP is standardized between 0 and 1 ppm for Nb, W, and Mo. Samples above 1 ppm in solution can be checked by analyzing a 10 ppm standard to insure that they are still within the linear range of the instrument.

Assignment of uncertainty

Table 33 shows the analytical results of selected reference materials, duplicates, and method blank obtained by this method.

Table 33.—Analytical performance summary for Nb, W, and Mo (ppm) by ion exchange/ICP-AES

[Proposed values from Potts and others, 1992]

Reference	*Description*	*n*	*Mean*	*s*	*pv*	*% RSD*	*% R*
Molybdenum, Mo							
GSD-2	stream sediment	40	2.5	0.4	2.0	16	125
RGM-1	rhyolite	14	2.4	0.1	2.3	4	104
STM-1	syenite	10	5.1	0.3	5.2	6	98
SGR-1	shale	35	33.0	0.6	**35.1**	2	94
GSD-3	stream sediment	8	90	2	92	2	98
Niobium, Nb							
SGR-1	shale	35	5.9	0.3	5.2	5	113
RGM-1	rhyolite	14	8.7	0.2	8.9	2	98
GSD-3	stream sediment	8	14.9	0.6	16	4	93
GSD-2	stream sediment	40	103	6	95	6	108
STM-1	syenite	10	259	7	**268**	3	97
Tungsten, W							
RGM-1	rhyolite	33	1.5	0.2	1.50	11	99
SGR-1	shale	35	2.3	0.1	**2.57**	6	90
STM-1	syenite	29	3.3	0.2	3.6	6	92
GSD-3	stream sediment	6	5.5	0.4	*4.9*	7	112
GSD-2	stream sediment	59	25	2	*24.4*	8	101

Duplicate samples	*k*	*n*	*Mean*	*s*	*% RSD*	*Concentration range*	*No. of < (total)*	*No. of < (pairs)*
Mo	18	2	83.0	0.4	0.4	1.1 to 1,100	42	20
Nb	38	2	46	2	5	1.3 to 240	6	3
W	9	2	5.0	0.2	4	1.2 to 15	59	28

Method blank	*n*	*Mean*	*s*	*3s*	*5s*
Mo	40	0.05	0.02	0.05	0.09
Nb	40	0.004	0.004	0.01	0.02
W	40	0.004	0.004	0.01	0.02

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Direct-current arc emission spectrographic method for the semiquantitative analysis of geologic materials

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Principle

Thirty-five elements are determined in rocks, stream-sediment, and soil samples, and 37 elements are determined in heavy-mineral-concentrate samples by the direct-current arc emission spectrographic method (Grimes and Marranzino, 1968; Myers and others, 1961). The powdered sample is mixed with graphite or a graphite-quartz mixture, packed into a preformed graphite electrode, and volatilized in a direct-current (dc) arc. Sample spectra are photographically recorded and concentrations of the elements are determined by visual comparison with standard spectra.

Interferences

Spectral line interferences are common in the analysis of geologic materials by emission spectroscopy. They should be anticipated and verified. Interferences in the analysis of heavy-mineral concentrates can be particularly severe and require astute judgment and care by the analyst for recognition and resolution. Interference on an analytical line by nearby spectral lines is normally checked by reference to wavelength tables (Massachusetts Institute of Technology, 1969). If an analytical line cannot be resolved from an interfering line, an alternate analytical line is used. For most applications of this method, matrix effects due to large variations in chemical composition between samples and standards are minimized by the addition of graphite to both. Silica, as finely ground quartz, is added to the samples only if the samples are silica poor, e.g., heavy-mineral concentrates.

Scope

The semiquantitative spectrographic method provides an overview of the elements, and the concentration of these elements, in the sample (table 34). The method is readily employed in mobile laboratories where analytical results can be quickly provided to help field investigators make decisions regarding further geochemical sampling. The method has an overall production of 40 samples per person-day.

Table 34.—Visual reporting limits for elements determined by the dc arc emission spectrographic method based on a 10-mg sample

[Spectrographic concentration range(s) for heavy-mineral-concentrate samples are based on a 5-mg sample, and are therefore two reporting intervals higher than the limits given for rocks and stream sediments.]

Elements	*Lower limit*	*Upper limit*
	Percent	
Ca	0.05	20
Fe	0.05	20
Mg	0.02	10

Table 34.—Visual reporting limits for elements determined by the dc arc emission spectrographic method based on a 10-mg sample—Continued

Elements	Lower limit	Upper limit
	Parts per million	
Na	0.2	5
P	0.2	10
Ti	0.002	1
	Parts per million	
Ag	0.5	5,000
As	200	10,000
Au	10	500
B	10	2,000
Ba	20	5,000
Be	1	1,000
Bi	10	1,000
Cd	20	500
Co	10	2,000
Cr	10	5,000
Cu	5	20,000
Ga	5	500
Ge	10	100
La	50	1,000
Mn	10	5,000
Mo	5	2,000
Nb	20	2,000
Ni	5	5,000
Pb	10	20,000
Pd*	2	1,000
Pt*	10	1,000
Sb	100	10,000
Sc	5	100
Sn	10	1,000
Sr	100	5,000
Th	100	2,000
V	10	10,000
W	20	10,000
Y	10	2,000
Zn	200	10,000
Zr	10	1,000

*Determined in heavy-mineral-concentrate samples only.

Apparatus and materials

- Optical emission spectrograph with dc-arc source
- Graphite electrodes (preformed cupped electrodes and counter electrodes)
- Analytical balance
- Spectrographically pure graphite and quartz
- Spectrographically pure standards (oxides, carbonates)
- Photographic film or plates
- Photographic developer and fixer
- Photo-Flo (wetting agent)
- Properly equipped darkroom
- Comparator or densitometer

Safety Precautions

The arc stand of the spectrograph shall be properly vented to avoid accumulation of hazardous gases. Eye (UV-filter) protection is recommended depending on light leakage from arc stand. Extreme caution is required in handling the equipment because of high voltages and hot electrodes. Equipment should be serviced only by trained, competent, electrical technicians.

Safety switches on dc-source unit and arc stand electrical circuits must be in working order and properly maintained.

Procedure

Weigh 10 mg sample, add 20 mg pure graphite, and mix in an aluminum weighing pan with a disposable wooden toothpick. For heavy-mineral-concentrate samples, weigh 5 mg sample and add 25 mg 4:1 graphite-quartz mixture. Transfer the mixture into the cavity of a preformed electrode with the aid of an acetyl funnel and pack tightly with a tapered acetyl venting tool. The resulting conical depression in the packed sample-graphite mixture acts as a vent for gases emitted during initial excitation. In the absence of this vent, the sample and graphite should be heated under an infrared lamp prior to arcing. Clean the funnel, venting tool, and weighing pan after each sample. Place the sample-bearing electrode and the counter electrode into the arc stand electrode clamps, initiate a current of 3 A with the arc gap set at 4 to 6 mm. After a few seconds, increase power to 8 to 9 A, and after a few seconds burn the sample to completion at 12 to 15 A. Wait to increase power if sample sputters. Maintain the arc gap at 4 to 6 mm throughout the entire burn time of 2 min and 15 s. Process the spectrographic film or plate with developer for 3 min, rinse in cold water, fix for 3 min; rinse in cold water and Photo-Flo and dry. The same procedure is used to prepare standard spectra only substituting previously prepared standard powders for the sample. Compare the spectra on the processed film with the spectra of the standards using a comparator with a magnified split-view display. The spectral range recorded with instrumentation and spectrographic film commonly used is between 2200 and 4800 Å in the second order. The spectral range is dependent on the type of instrument, filters, and emulsion in use.

The quality of semiquantitative spectrographic data is verified by arcing a reference standard and recording its spectrum on each film. As this method is semi-quantitative, the acceptability is a judgment call by the analyst. The spectra of standards are visually checked for similar sensitivity and gradation. Standard films are prepared once a year or whenever there is a change in standard operating conditions, such as emulsion batch change or instrument realignment.

The principal standards used for the analysis of most geologic materials have been designated F-3 and F-4. The F-3 standards (table 35) contain concentrations of 23 trace elements in a stock matrix that approximates the matrix of average siliceous rocks. The F-4 standards (table 36) contain concentrations of major elements (Fe, Ca, Mg, and Na), the noble metals (Au, Pt, and Pd), and As, Sb, W, Nb, and Th in a matrix of pure quartz.

For the F-3 standards, a base mixture of the elements is prepared by adding a specified amount of each element, usually as the oxide or carbonate, to a predetermined amount of matrix to give the desired concentration of the element (Grimes and Marranzino, 1968). After the base mixture is prepared, standards containing successively lower amounts of the elements are made using the reciprocal of the cube root of 10 (0.464) as a dilution factor. For example, if the base mixture contains an element at a concentration of 100 parts per million (ppm), the succeeding standards would contain the same element at concentrations of 46.4 ppm, 21.5 ppm, 10 ppm, 4.6 ppm, and so forth (table 37). For the semiquantitative procedure, these numbers are rounded to 50, 20, 10, and 5. The logarithmic midpoint between these numbers is calculated to be 68.1, 31.6, 14.7, 6.8 and so forth. For the semiquantitative procedure, these numbers are rounded to 70, 30, 15, 7 etc.

> "The blackness of a line is a logarithmic function of the quantity of the element producing the line, and the voluntary assignment of numbers to the midpoints of the above concentration ranges is not valid; nevertheless, because the differences between the assigned number and the actual value are small, the former numbers are used as convenient approximations in geochemical exploration" (Ward and others, 1963).

Each dilution is transferred to a clean glass vial containing several mixing beads and is shaken or mixed mechanically for 1 hour before further dilution. If thorough mixing is not achieved, the succeeding lower concentrations will be inaccurate. The quantity of each standard should be kept low (2 to 4 g) to insure a good mix. Extreme care must also be taken to prevent contamination.

The F-4 standards consist of two base mixtures, one containing the carbonates of Ca, Mg, and Na, and the other the oxides of Fe, As, Sb, W, Nb, Ge, and Th, and a commercially available noble metal mix. To prepare the F-4 standards, the base mixtures are diluted with pure SiO_2 using the same dilution factor as for the F-3 standards (0.464). A part of each diluted base mixture is further diluted in the same manner as the F-3. A weighed amount of one base mixture is added to a weighed amount of the other base mixture and the combination is mixed with the SiO_2 matrix to give the desired concentrations (table 39). The same precautions are taken as with the F-3 standards to insure a homogeneous mixture.

Geologic material that contains high concentrations of Ca (>10 percent) and Mg (>5 percent) is generally lower in concentrations of Fe (<1 percent). Conversely, material that contains high concentrations of Fe (>5 percent) is usually lower in Ca (<1 percent) and Mg (<1 percent). The F-4 standards are prepared with this generalization in mind.

Table 35.—Concentrations (ppm except as noted) of elements in F-3 standards

Ag	*B*	*Ba*	*Be*	*Bi*	*Cd*	*Co*	*Cr*	*Cu*	*La*	*Mn*	*Mo*	*Ni*	*P* %	*Pb*	*Sc*	*Sn*	*Sr*	*Ti* %	*V*	*Y*	*Zn*	*Zr*
										10								0.002				
5		20								20								0.005				
1		50	1					5		50		5						0.01	10			10
2		100	2				10	10		100	5	10		10			100	0.02	20		200	20
5	10	20	5		20	10	20	20	50	200	10	20		20	5		200	0.05	50	10	500	50
10	20	500	10	10	50	20	50	100	500	20	50	50		500	10	10	500	0.1	100	20	1,000	100
20	50	1,000	20	20	100	50	100	100	200	1,000	50	100		100	20	20	1,000	0.2	200	50	2,000	200
50	100	2,000	50	50	200	100	200	200	500	2,000	100	200		200	50	50	2,000	0.5	500	100	5,000	500
100	200	5,000	100	100	500	200	500	500	1,000	5,000	200	500	0.2	500	100	100	5,000	1	1,000	200	10,000	1,000
200	500		200	200		500	1,000	1,000			500	1,000	0.5	1,000		200			2000	500		
500	1,000		500	500		1,000	2,000	2,000			1,000	2,000	1	2,000		500			5,000	1,000		
1,000	2,000		1,000	1,000		2,000	5,000	5,000			2,000	5,000	2	5,000		1,000			10,000	2,000		
2,000								10,000					5	10,000								
5,000								20,000					10	20,000								

Table 36.—Concentrations (ppm except as noted) of elements in F-4 standards

Ga	*Ge*	*As*	*Au*	*Ca %*	*Fe %*	*Mg %*	*Na %*	*Nb*	*Sb*	*W*	*Th*	*Nd*	*Pd*	*Pt*
				20		10	5					5		
				10		5	2					2		
				5		2	1					1		
				2	0.05	1	0.5			20				
				1	0.1	0.5	0.2			50		0.5	2	
5	10			0.5	0.2	0.2		20	100	100		0.2	10	10
20	50	500	20	0.1	1	0.05		100	500	500	100		20	20
50	100	1,000	50	0.05	2	0.02		200	1,000	1,000	200		50	50
100		2,000	100		5			500	2,000	2,000	500		100	100
200		5,000	200		10			1,000	5,000	5,000	1,000		200	200
500		10,000	500		20			2,000	10,000	10,000	2,000		500	500

Table 37.—Dilution factor for the base mixtures to yield standard concentrations

Mixture number	*Dilution factor*	*Resulting standard, ppm*
1 (base mixture)	*X*g metal oxide+*Y*g SiO_2 matrix=4 g	100
2	1.857 g 100 ppm (mixture #1)+2.143 g SiO_2 matrix =4 g	46.4
3	1.857 g 46.4 ppm (mixture #2)+2.143 g SiO_2 matrix=4 g	21.5
4	1.857 g 21.5 ppm (mixture #3)+2.143 g SiO_2 matrix=4 g	10
5	1.857 g of 10 ppm (mixture #4)+2.143 g SiO_2 matrix=4 g	4.64

Assignment of uncertainty

Disallowing results obtained near the reporting limits and for calcium, the precision of the method has been documented (with respect to the specific sample medium used in the precision study) to generally be within one adjoining reporting interval on each side of the in-house mean, 83 percent of the time, and within two adjoining reporting intervals on each side of the mean 96 percent of the time (Motooka and Grimes, 1976). Ten replicates of graphite electrodes showed no elements detected at the lower concentration range. Table 38 shows the results of selected reference materials and duplicate samples analyzed by this method. Please note some *pv* data has been converted from the oxide using the conversion factors in appendix A, table A1.

Table 38.—Analytical performance summary of the dc arc emission spectrographic method

[A=National Institute of Standards and Technology, 1992; remaining *pv* from Potts and others, 1992]

Reference	*Description*	*n*	*Mean*	*s*	*pv*			*% RSD*	*% R*
Antimony, Sb (ppm)									
SRM 2710	soil	10	120	24	**38.4**	A	*cv*	21	300
Arsenic, As (ppm)									
GXR-6	soil	10	420	140	330			33	127
SRM 2710	soil	10	910	150	**626**	A	*cv*	16	145
Barium, Ba (ppm)									
GSS-6	soil	14	91	52	118			57	77
GSD-11	stream sediment	13	220	97	260			43	86
GSR-1	granite	8	250	71	343			28	73
MAG-1	marine mud	10	840	260	479			31	175
SRM 2710	soil	10	900	260	**707**	A	*cv*	29	127
SRM 2711	soil	10	1,000	160	**726**	A	*cv*	16	145
GXR-6	soil	80	1,200	340	1,300			28	89
GXR-4	coppermill ore	18	1,260	350	**1,640**			28	76
GXR-5	soil	21	1,300	670	2,000			50	67
GXR-2	soil	8	1,800	270	**2,240**			15	78
Beryllium, Be (ppm)									
GXR-5	soil	8	1.1	0.2	1.4		?	18	79
GXR-2	soil	8	1.3	0.3	1.7			23	76
GXR-4	coppermill ore	17	1.6	0.5	1.9			38	84
MAG-1	marine mud	10	2.1	0.4	3.2			19	66
GSS-6	soil	14	4	2	4.4			50	91
GSR-1	granite	8	9	5	12.4			56	73
GSD-11	stream sediment	13	30	15	26			50	115
Bismuth, Bi (ppm)									
GXR-4	coppermill ore	17	25	5	19			20	132
GSS-6	soil	14	58	26	49			44	118
GSD-11	stream sediment	13	75	28	50			38	150
Boron, B (ppm)									
GXR-5	soil	21	29	12	22			41	132
GSR-1	granite	8	33	23	24			68	138
GXR-2	soil	7	67	24	**42**			35	160
GSS-6	soil	14	100	30	57			31	177
GSD-11	stream sediment	13	140	40	68			29	200
MAG-1	marine mud	10	140	44	**136**			31	107
Cadmium, Cd (ppm)									
SRM 2710	soil	7	30	10	**21.8**	A	*cv*	33	138
SRM 2711	soil	10	70	0	**41.7**	A	*cv*	0	168

Table 38.—Analytical performance summary of the dc arc emission spectrographic method—Continued

Reference	*Description*	*n*	*Mean*	*s*	*pv*			*% RSD*	*% R*
Calcium, Ca (percent)									
GSS-6	soil	11	0.07	0.03	**0.16**			43	44
GXR-6	soil	74	0.07	0.02	0.18			29	39
GSD-11	stream sediment	13	0.3	0.2	**0.34**			67	88
GXR-5	soil	21	0.4	0.3	0.84			75	48
GXR-2	soil	8	0.5	0.1	0.93			26	57
MAG-1	marine mud	10	1.1	0.8	0.98			72	112
GXR-4	coppermill ore	18	0.3	0.1	**1.01**			33	30
GSR-1	granite	8	0.6	0.2	**1.11**			33	64
SRM 2710	soil	10	0.8	0.3	**1.25**	A	*cv*	38	64
SRM 2711	soil	10	4	2	**2.88**	A	*cv*	41	139
Chromium, Cr (ppm)									
GXR-2	soil	8	41	16	36			40	114
SRM 2710	soil	10	57	19	39	A		33	146
GSD-11	stream sediment	13	43	11	40			26	108
SRM 2711	soil	10	79	14	47	A		18	168
GXR-4	coppermill ore	18	57	17	64			29	89
GSS-6	soil	14	83	22	75			26	111
GXR-6	soil	80	90	28	96			32	94
MAG-1	marine mud	10	130	26	97			20	134
Cobalt, Co (ppm)									
SRM 2710	soil	10	16	3	10	A		18	160
SRM 2711	soil	10	15	3	10	A		22	150
GXR-4	coppermill ore	18	13	6	14.6			46	89
MAG-1	marine mud	10	27	5	20.4			18	132
GXR-5	soil	21	35	12	30			35	117
Copper, Cu (ppm)									
MAG-1	marine mud	10	30	0	30			0	100
GXR-6	soil	80	74	20	66			28	112
GXR-2	soil	8	70	23	76			33	92
GSD-11	stream sediment	13	75	19	78.6			26	95
SRM 2711	soil	10	110	33	**114**	A	*cv*	30	93
GSS-6	soil	14	390	120	390			31	99
GXR-5	soil	21	270	75	354			28	76
SRM 2710	soil	10	2,300	480	**2,950**	A	*cv*	21	78
GXR-4	coppermill ore	18	6,300	3,100	6,520			49	96
Gallium, Ga (ppm)									
SRM 2711	soil	10	42	15	15	A		37	280
MAG-1	marine mud	10	76	13	20.4			17	373
SRM 2710	soil	10	53	21	34	A		40	156
GXR-6	soil	80	57	23	35			40	163
Germanium, Ge (ppm)									
SRM 2710	soil	10	16	5	--			28	---

Table 38.—Analytical performance summary of the dc arc emission spectrographic method—Continued

Reference	*Description*	*n*	*Mean*	*s*	*pv*			*% RSD*	*% R*
Gold, Au (ppm)									
No reference material data available at this time									

Reference	*Description*	*n*	*Mean*	*s*	*pv*			*% RSD*	*% R*
Iron, Fe (percent)									
GSR-1	granite	8	1.6	0.3	**1.50**			19	107
GXR-2	soil	8	1.8	0.5	**1.86**			28	97
SRM 2711	soil	10	4	1	**2.89**	A	cv	25	138
GSD-11	stream sediment	13	3	1	**3.07**			33	98
GXR-4	coppermill ore	18	3	2	**3.09**			67	97
GXR-5	soil	21	3	2	**3.38**			67	89
SRM 2710	soil	10	3	1	**3.38**	A	cv	33	89
MAG-1	marine mud	10	4	1	**4.76**			25	84
GXR-6	soil	80	6	2	**5.58**			33	108
GSS-6	soil	14	6	3	**5.66**			50	106
Lanthanum, La (ppm)									
SRM 2711	soil	10	50	0	40	A		0	125
MAG-1	marine mud	10	66	8	43			13	153
GSR-1	granite	7	50	16	54			32	93
GXR-4	coppermill ore	18	61	26	**64.5**			43	95
Lead, Pb (ppm)									
GXR-5	soil	19	23	13	21			58	110
MAG-1	marine mud	10	72	17	24			23	300
GSR-1	granite	8	39	12	31			32	126
GXR-4	coppermill-head	18	64	16	52			25	123
GXR-6	soil	80	120	31	101			26	115
GSS-6	soil	13	360	210	314			58	114
GSD-11	stream sediment	13	980	720	636			73	155
GXR-2	soil	8	600	110	690			18	87
SRM 2711	soil	10	2,400	600	**1,162**	A	cv	25	211
SRM 2710	soil	10	6,700	1,800	**5,532**	A	cv	27	121
Magnesium, Mg (percent)									
GSS-6	soil	14	0.2	0.1	**0.20**			50	102
GSR-1	granite	8	0.3	0.2	**0.25**			67	128
GSD-11	stream sediment	13	0.5	0.2	**0.37**			40	127
GXR-6	soil	80	0.8	0.2	0.61			25	131
GXR-2	soil	8	1.0	0.2	0.85			20	118
SRM 2710	soil	10	0.8	0.2	**0.853**	A	cv	25	94
SRM 2711	soil	10	1.2	0.2	**1.05**	A	cv	17	114
GXR-5	soil	20	1.3	0.6	1.19			46	110
GXR-4	coppermill ore	18	1.5	0.7	1.66			47	90
MAG-1	marine mud	10	1.7	0.2	**1.81**			12	94

Table 38.—Analytical performance summary of the dc arc emission spectrographic method—Continued

Reference	*Description*	*n*	*Mean*	*s*	*pv*			*% RSD*	*% R*
Manganese, Mn (ppm)									
GXR-4	coppermill ore	18	130	34	155			26	86
GXR-5	soil	19	280	140	309			50	90
GSR-1	granite	7	430	210	465			49	92
MAG-1	marine mud	10	930	250	759			27	122
GXR-6	soil	80	950	270	1,007			28	94
GXR-2	soil	8	940	360	1,007			38	92
GSS-6	soil	14	1,600	780	**1,471**			49	107
GSD-11	stream sediment	12	2,700	990	**2,478**			37	109
SRM 2710	soil	10	>5,000	---	**10,100**	A	*cv*	---	---
Molybdenum, Mo (ppm)									
GSD-11	stream sediment	13	9	4	5.9			44	152
GSS-6	soil	14	21	11	18			52	117
SRM 2710	soil	10	18	8	19	A		44	95
GXR-5	soil	21	37	16	31			43	119
GXR-4	coppermill ore	18	390	200	310			51	126
Nickel, Ni (ppm)									
SRM 2710	soil	10	19	5	**14.3**	A	*cv*	26	133
GSD-11	stream sediment	13	17	5	**14.4**			29	118
SRM 2711	soil	10	25	5	**20.6**	A	*cv*	20	121
GXR-2	soil	8	19	6	21			32	90
GXR-6	soil	80	22	9	27			41	81
GXR-4	coppermill ore	18	42	20	42			47	100
GSS-6	soil	14	60	18	53			31	113
MAG-1	marine mud	10	44	10	53			22	83
GXR-5	soil	21	73	17	75			23	97
Niobium, Nb (ppm)									
MAG-1	marine mud	8	<20	---	12			---	---
GXR-5	soil	9	28	13	25			47	112
Palladium, Pd (ppm)									
No reference material data available at this time									
Phosphorus, P (percent)									
No reference material data available at this time									
Platinum, Pt (ppm)									
No reference material data available at this time									

Table 38.—Analytical performance summary of the dc arc emission spectrographic method—Continued

Reference	*Description*	*n*	*Mean*	*s*	*pv*			*% RSD*	*% R*
Scandium, Sc (ppm)									
GSR-1	granite	7	5	1	6.1			20	82
GXR-2	soil	8	6	1	6.88			17	87
GSD-11	stream sediment	13	7	3	7.4			43	95
GXR-5	soil	21	7	2	7.4			29	95
GXR-4	coppermill head	17	6	2	7.7			33	78
SRM 2710	soil	10	9	1	8.7	A		11	103
SRM 2711	soil	10	12	3	9	A		25	133
GSS-6	soil	14	14	6	15.5			43	90
MAG-1	marine mud	10	17	3	17.2			18	99
GXR-6	soil	80	19	7	27.6			37	69
Silver, Ag (ppm)									
GXR-5	soil	19	0.8	0.3	1.4		?	38	57
GSD-11	stream sediment	13	4	2	3.2			50	125
GXR-4	coppermill ore	18	4	1	4.0			31	100
SRM 2711	soil	10	7	2	**4.63**	A	*cv*	28	151
GXR-2	soil	8	15	5	17			33	88
SRM 2710	soil	10	51	19	**35.3**	A	*cv*	37	144
Sodium, Na (percent)									
SRM 2710	soil	10	1.7	0.2	**1.14**	A	*cv*	12	149
SRM 2711	soil	10	1.4	0.2	**1.14**	A	*cv*	14	123
MAG-1	marine mud	10	4	2	**2.84**			50	127
Strontium, Sr (ppm)									
GXR-5	soil	8	100	0	110			0	91
MAG-1	marine mud	10	220	63	146			29	147
GXR-2	soil	8	130	26	160			20	82
GXR-4	coppermill-head	18	200	30	221			15	90
SRM 2710	soil	10	420	140	240	A		33	175
SRM 2711	soil	10	420	100	**245.3**	A	*cv*	24	171
Thorium, Th (ppm)									
No reference material data available at this time									
Tin, Sn (ppm)									
GSR-1	granite	8	14	4	12.5			28	112
SRM 2710	soil	10	13	4	---			31	---
GSS-6	soil	14	95	45	72.4			47	131
GSD-11	stream sediment	13	410	230	370			56	111

Table 38.—Analytical performance summary of the dc arc emission spectrographic method—Continued

Reference	*Description*	*n*	*Mean*	*s*	*pv*			*% RSD*	*% R*
Titanium, Ti (percent)									
GSR-1	granite	8	0.16	0.04	**0.17**			25	94
GSD-11	stream sediment	13	0.21	0.05	**0.21**			24	100
GXR-5	soil	21	0.19	0.06	0.22			31	86
SRM 2710	soil	10	0.32	0.06	**0.283**	A	*cv*	19	113
GXR-4	coppermill ore	18	0.26	0.08	0.29			31	90
GXR-2	soil	8	0.26	0.05	0.30			20	87
SRM 2711	soil	10	0.5	0.1	**0.306**	A	*cv*	26	161
GSS-6	soil	14	0.4	0.2	**0.44**			50	91
MAG-1	marine mud	10	0.48	0.06	0.45			13	107
GXR-6	soil	80	0.4	0.2	**0.50**			40	80
Tungsten, W (ppm)									
GSS-6	soil	9	57	10	89.5			18	64
SRM 2710	soil	10	83	19	93	A		23	89
GSD-11	stream sediment	13	220	290	126			132	173
Vanadium, V (ppm)									
GSR-1	granite	8	24	6	24			25	100
GSD-11	stream sediment	13	67	26	46.8			39	143
GXR-2	soil	8	66	17	52			25	127
GXR-5	soil	21	53	23	56			43	95
SRM 2710	soil	10	130	31	**76.6**	A	*cv*	24	166
SRM 2711	soil	10	140	39	**81.6**	A	*cv*	28	172
GXR-4	coppermill head	18	91	27	87			30	105
GSS-6	soil	14	140	58	130			41	105
MAG-1	marine mud	10	180	26	**140**			14	125
GXR-6	soil	80	170	66	186			38	93
Yttrium, Y (ppm)									
GXR-4	coppermill head	17	14	6	14			43	100
GXR-5	soil	21	14	4	16			29	88
GXR-2	soil	8	14	5	17			36	82
GSS-6	soil	14	21	9	18.8			43	112
SRM 2710	soil	10	25	5	23	A		20	109
SRM 2711	soil	10	44	16	25	A		36	176
MAG-1	marine mud	10	31	7	28			23	111
GSD-11	stream sediment	13	44	13	42.7			29	103
GSR-1	granite	8	55	14	62			25	89
Zinc, Zn (ppm)									
MAG-1	marine mud	8	<200	---	**130**			---	---
GSD-11	stream sediment	13	370	140	373			38	99
GXR-2	soil	8	440	270	530			61	82
SRM 2711	soil	10	340	84	**350.4**	A	*cv*	25	97
SRM 2710	soil	10	6,000	1,400	**6,952**	A	*cv*	23	86

Table 38.—Analytical performance summary of the dc arc emission spectrographic method—Continued

Reference	*Description*	*n*	*Mean*	*s*	*pv*		*% RSD*	*% R*
Zirconium, Zr (ppm)								
GXR-6		80	100	19	110	?	19	94
SRM 2710	soil	10	130	35	---		27	---
MAG-1	marine mud	10	110	39	126		35	87
SRM 2711	soil	10	420	140	230	A	33	183

Duplicate samples	*k*	*n*	*Mean*	*s*	*% RSD*	*Concentration range*			*No. of < (total)*	*No. of < (pairs)*
Ag ppm	8	2	59	5	9	0.2	to	300	46	23
As ppm	2	2	1,000	0	0		---		58	29
Au ppm	--	--	--	--	--		---		62	31
B ppm	25	2	110	34	30	10	to	700	9	3
Ba ppm	31	2	560	250	44	20	to	7,000	0	0
Be ppm	11	2	2.9	0.6	21	1	to	7	37	17
Bi ppm	--	--	--	--	--		---		62	31
Ca %	21	2	3	1	33	0.07	to	10	16	6
Cd ppm	--	--	--	--	--		---		62	31
Co ppm	21	2	36	6	17	10	to	70	19	9
Cr ppm	25	2	280	50	18	10	to	2,000	11	5
Cu ppm	23	2	740	34	5	7	to	15,000	11	3
Fe %	31	2	4.9	0.9	18	0.1	to	20	0	0
Ga ppm	23	2	26	6	25	5	to	100	13	5
Ge ppm	--	--	--	--	--		---		62	31
La ppm	7	2	150	24	16	50	to	300	43	19
Mg ppm	31	2	1.4	0.5	33	0.02	to	10	0	0
Mn ppm	25	2	1,700	290	17	10	to	7,000	12	6
Mo ppm	4	2	37	0.4	1	5	to	100	53	26
Na %	23	2	0.8	0.2	26	0.1	to	3	15	7
Nb ppm	11	2	79	18	18	20	to	300	39	19
Ni ppm	28	2	43	6	14	5	to	100	6	3
P %	3	2	0.9	0.1	14	0.5	to	1.5	56	28
Pb ppm	19	2	330	89	27	10	to	3,000	22	10
Pd ppm	--	--	--	--	--		---		26	13
Pt ppm	--	--	--	--	--		---		26	13
Sb ppm	3	2	250	59	24	150	to	500	56	28
Sc ppm	16	2	28	4	15	5	to	70	27	12
Sn ppm	--	--	--	--	--		---		61	30
Sr ppm	13	2	460	140	30	200	to	2,000	33	15
Th ppm	--	--	--	--	--		---		62	31
Ti %	28	2	0.4	0.04	10	0.002	to	2	0	0

Table 38.—Analytical performance summary of the dc arc emission spectrographic method—Continued

Duplicate samples	*k*	*n*	*Mean*	*s*	*% RSD*	*Concentration range*			*No. of <* *(total)*	*No. of <* *(pairs)*
V ppm	29	2	140	20	14	10	to	500	4	2
W ppm	4	2	130	73	55	20	to	500	53	26
Y ppm	20	2	81	15	19	10	to	300	21	10
Zn ppm	11	2	420	89	21	200	to	700	39	19
Zr ppm	27	2	150	29	20	15	to	1,000	7	3

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Flame photometric determination of K_2O and Na_2O

By Terry Fries, Joe Christie, and Sarah Pribble

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Principle

Sodium and potassium in rocks and mineral separates are determined by the method of flame emission spectrometry (FES) and are reported as their oxides (Cremer and others, 1984; Jackson and others, 1987). The samples are fused with lithium metaborate in graphite crucibles and the fusion beads dissolved in 4 percent (v/v) nitric acid. The sample solution is aspirated into a propane-air flame. Filters are used to isolate the light emitted by the analyte atoms and lithium internal standard. Photomultipliers detect the emitted light. The analyte signals are ratioed to the lithium signal. Use of an internal standard compensates for variations in flame characteristics and sample introduction (aspiration).

Interferences

The only known interference is the presence of rubidium (Rb) in high concentration when potassium (K) content is very low. The effect is ignored in routine work as it occurs rarely and only in certain uncommon minerals.

Scope

The method is applicable to all geologic samples compatible with the lithium metaborate fusion digestion. Approximately 2 days are required for 40 determinations. It is routinely applicable to samples containing K_2O concentrations between 0.025 percent and 15 percent and Na_2O concentrations between 0.08 and 10.00 percent in two ranges (less than 2.9 percent and greater than 2.9 percent. The concentration range should be specified by the submitter to avoid re-analysis.

Apparatus

Other than common laboratory equipment, only a multi-channel flame photometer with internal standard compensation (e.g., Instrumentation Laboratories (IL) models 343 and 443) is required for this determination.

Reagents

- Water: Deionized (DI) water with a resistivity of greater than 18 megohms/cm is used throughout this method. A Millipore Milli-Q with a Milli-RO4 attachment water purification system is used to prepare all water used in this method.
- Dehydrated human blood serum.
- Lithium metaborate, $LiBO_2$: Anhydrous lithium metaborate, reagent grade powder, specially prepared for fusions. This material can be obtained in 25-pound lots from Southwestern Analytical Chemicals, Inc., Austin, Texas. Each new lot should be checked for freedom from contamination.

4 percent nitric acid, HNO_3 (v/v): Prepare by adding 4 parts 70-71 percent conc HNO_3 (Baker analyzed reagent grade) to 96 parts DI water.

Safety precautions

All safety precautions normally employed in laboratory handling of acids, hot materials from high temperature furnaces, and devices producing flames from potentially explosive gas mixtures must be followed. Workers should wear protective clothing including, but not limited to, lab coats, protective glasses, and face masks when dealing with powdered materials such as flux and sample; insulated gloves when working with the furnace; and protective gloves when working with chemicals. Furnace work and sample digestion are carried out in a hood and the flame photometer is serviced by a fan-driven exhaust device. See the *CHP and MSDS* for further information concerning first-aid treatment and disposal procedures for chemical products used in this method.

Procedure

1. Based upon rock description, decide whether high or low standards are to be used for the calibration curve. Specific standard materials used include USGS standard rocks, G2, BCR, and AGV. The division between "high" and "low" occurs at approximately 3.0 percent K_2O. Weigh each standard and blank (sierra quartz) in duplicate. To extend the limited supply of standards, 40-50 samples are run at one time. All sodium calibration curves are calculated from the sodium values also present in the chosen K_2O standards. Two quality control samples and one duplicate are included in each run.

2. In a tared, size-00 black porcelain crucible weigh 100 ± 3 mg sample. Add 700 ± 5 mg anhydrous $LiBO_2$. Record both sample weight and total weight. In the same crucible, mix the sample and flux. Samples and standards are weighed on the same day because $LiBO_2$ is somewhat hygroscopic. The purity of each new batch of $LiBO_2$ is checked by emission spectroscopy.

3. Brush out the interior of a high purity graphite crucible and quantitatively transfer the sample-flux mixture to the crucible. Store samples and standards in Lucite trays. The purity of each new batch of graphite crucibles is checked by firing one crucible to disintegration at 1,000°C in a platinum dish. The residue, if any, is weighed and analyzed by emission spectrography. New crucibles must be ignited for 2 hours at 1,000°C before being put into use.

4. Fuse the contents of the first six crucibles at 950°C for 15 min.

5. During the fusion, equip six dry 250-mL polypropylene beakers with dry 1 5/8-in Kel-F magnetic stirring bars. Label six covers. Add 100 mL 4 percent (v/v) HNO_3; begin stirring as the time approaches to remove the crucibles from the muffle furnace.

6. At the end of 15 min, using tongs slightly swirl the red hot crucible and pour the molten bead into its corresponding beaker. Place each emptied crucible in same noted order. Cover beakers tightly. Stir for 10 min while fusing the next lot of six. Inspect the solutions for clarity. Cloudy solutions may contain some reducible element, like MnO_2; a drop of 30 percent H_2O_2 usually causes the solution to clear.

7. Inspect each cool graphite crucible for adhering particles. Adhering particles, if any, must be dug out with a stainless steel spatula and added to the appropriate beaker. If this is not feasible, a new portion must be fused on another day.

8. Repeat the above procedure for all samples and standards.

9. Use the automatic diluter to dilute samples 1:10 with DI water, dispensing into small 15-mL plastic beakers. The dilution need not be exactly 1:10 but it must be the same for all solutions.

10. On flame photometer, turn on both the propane gas and air completely, in that order.

11. Depress POWER button (flame will automatically ignite). Allow 30 min for warm-up. The warm-up should take place during fusion and dilution steps.

12. Continually aspirate DI water during warm-up. For 5 min during the warm-up, aspirate a dilute solution of reconstituted normal human blood serum (1 drop/25 mL DI water). The blood serum protein coats the spray chamber to minimize formation of water droplets on the chamber walls. Undiluted serum is kept refrigerated.

13. Before operating with rock solutions, check that the aspiration rate is approximately 25 s/mL.

14. On the Digital Printer press RESET to set the sequential counter to 001. Depress ADVANCE to position the paper.

15. For K_2O analysis, aspirate the blank (Sierra Quartz). Adjust the signal display on the lithium response meter so that the red needle comes to rest opposite the black triangle between the horizontal black lines. Set the digital concentration display to zero with the ZERO knob.

16. Aspirate the highest K_2O standard. Check the lithium response and adjust if necessary, using the INTERNAL STANDARD dial at the left of the display. Set the digital concentration to <180.0 (high scale) or <18.0 (low scale), whichever is applicable. The RANGE switch selects the high or low scale. The setting chosen for the high standard is arbitrary. The settings suggested allow for instrument drift since the full span is 0 to 200.0 or 0 to 20.0. The decimal point appears between the second and third digit (e.g., 17.00 for 1.70 percent K_2O); on the high scale it appears between the third and fourth digit (017.0).

17. If Na_2O has also been requested, repeat step 15; otherwise go to step #19.

18. Aspirate the highest Na_2O standard and switch to low scale because Na_2O is always run on that scale. Check lithium as before and set the percent Na_2O on the digital display. The decimal point appears between the 3rd and 4th digit.

19. Aspirate standards and unknowns in the following order, depressing DATA when the display no longer changes, usually after 8-10 s.

    All solutions must be read in the same manner.

    Typical aspiration order:

    a. duplicate standards
    b. ten unknowns
    c. duplicate standards
    d. repeat the ten unknowns from step #19b
    e. duplicate standards

Drift response is inherent in the operation of the flame photometer. Frequent aspiration of standards to bracket unknowns minimizes errors introduced by instrumental drift. A set of standards and unknowns should not exceed ten of each.

20. Continue the operation until all unknowns have been run. The data collected from steps #19a and c above are weight corrected and used to prepare a linear regression. From this slope-intercept equation the concentration of the unknowns in step #19b is calculated and weight corrected. Data from steps #19c, d, and e are treated in the same manner. The reported value is the average of the two calculated values.

Calculation

A linear calibration curve is prepared using standard results which have been normalized to a 700-mg flux weight and 100-mg sample weight. The equation of this line is used to calculate unknown concentrations which are then weight corrected.

$$\text{Concentration} = [(\text{slope} \times \text{intensity}) + \text{intercept}] \times \text{unknown wt}/100$$

Assignment of uncertainty

Table 39 is the analytical results of K_2O and Na_2O for selected reference materials, duplicate samples, and method blanks by flame emission spectrometry.

Table 39.—Analytical performance summary for K_2O and Na_2O (percent) by FES

[A=Fries, 1991; remaining *pv* from Potts and others, 1992]

Reference	*Description*	*n*	*Mean*	*s*	*pv*		*% RSD*	*% R*
Potassium as K_2O								
SRM 88	dolomite	10	0.025	0.005	0.03	*cv*	20	83
SRM 88b	dolomitic limestone	10	0.106	0.005	**0.1030**	*cv*	5	103
AL-1	albite	10	0.137	0.008	0.14		6	98
LK-1	glass	30	1.49	0.01	1.50	A	0.7	99
LK-2	phylite	30	2.22	0.01	2.23	A	0.5	100
HK-1	granodiorite	30	5.55	0.05	5.53	A	0.9	100
HK-2	feldspar	30	13.73	0.07	13.62	A	0.5	101
Sodium as Na_2O								
SRM 88b	dolomitic limestone	10	0.050	0.008	**0.029**	*cv*	16	172
SRM 88	dolomite	10	0.051	0.007	0.08		14	62
Na-1	plagioclase	30	2.13	0.03	2.15	A	1	99
HK-1	granodiorite	30	2.78	0.03	2.80	A	1	99
LK-1	glass	30	3.19	0.02	3.17	A	0.6	101
AL-1	albite	10	10.8	0.1	**10.59**		0.9	102

Table 39.—Analytical performance summary for K_2O and Na_2O (percent) by FES—Continued

Duplicate samples	*k*	*n*	*Mean*	*s*	*% RSD*	*Concentration range*			*No of < (total)*	*No of < (pairs)*
K_2O	59	2	3.01	0.05	1	0.31	to	8.78	0	0
Na_2O	36	2	3.31	0.02	0.6	0.14	to	7.40	0	0

Method blank	*n*	*Mean*	*s*	*3s*	*5s*
Low K_2O	30	0.001	0.005	0.02	0.03
High K_2O	30	0.02	0.05	0.1	0.2
Na_2O	36	-0.003	0.02	0.05	0.08

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Fluoride, chloride, nitrate, and sulfate in aqueous solution by chemically suppressed ion chromatography

by W.M. d'Angelo and W.H. Ficklin

Code: I011

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Principle

Four common anions, fluoride, chloride, nitrate, and sulfate are determined in aqueous solution by ion chromatography (IC). In addition bromide, nitrite, and phosphate may be determined at the same time and are available on a research basis. The anions are separated based on their relative affinity for a low capacity, strongly basic anion exchange resin (Small and others, 1975). Each anion elutes from the AS4A column with a characteristic retention time in the order fluoride, chloride, nitrite, nitrate, phosphate, and sulfate when using the conditions described below.

Chemically suppressed IC employs a suppresser that reacts with the carbonate eluent to reduce the background conductivity, thus providing greater sensitivity. The separated anions pass through a semi-permeable membrane bathed in dilute sulfuric acid. Each analyte is converted to the highly conductive acid form, while the eluent is converted to weakly conducting carbonic acid. The liquid phase goes into a conductivity cell for detection.

Interferences

"Interferences can be caused by substances with retention times that are similar to and overlap those of the anion of interest. Large amounts of an anion can interfere with the peak resolution of an adjacent anion. Sample dilution and/or fortification can be used to solve most interference problems.

The water dip or negative peak that elutes near can interfere with the fluoride peak and can usually be eliminated by the addition of the equivalent of 1 mL of concentrated (100×) eluent to 100 mL of each standard and sample.

Method interferences may be caused by contamination in the reagent water, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or elevated baseline in ion chromatograms.

Sample that contain particles larger than 0.45 microns and reagent solutions that contain particles larger than 0.20 microns require filtration to prevent damage to instrument columns and flow systems.

Any anion that is not retained by the column or only slightly retained will elute in the area of fluoride and interfere. Known co-elution is caused by carbonate and other small organic anions. At concentrations of fluoride above 1.5 mg/L this interference may not be significant, however, it is the responsibility of the user to generate precision and accuracy information in each sample matrix.

The acetate anion elutes early during the chromatographic run. The retention times of the anions also seem to differ when large amounts of acetate are present. Therefore, this method is not recommended for leachates of solid samples when acetate is used for pH adjustment." (Pfaff and others, 1991).

Scope

This method is applicable to the analysis of natural waters and leachate solutions. It can be extended (on a research basis) to include the analysis of solid samples that are water soluble. Liquid phase samples should be refrigerated at 4°C and stored no longer than 28 days when sulfate and nitrate are to be analyzed. For fluoride, chloride, and bromide, no refrigeration is required. If nitrite or phosphate are to be analyzed, the samples must be refrigerated and analyzed within 48 hours. In a given sample, the anion that requires the most preservation treatment and the shortest holding time will determine the preservation treatment (Pfaff and others, 1991).

Using this method, an operator can analyze about 25 samples per day. Depending on the detector range used, fluoride can be determined from 0.01 to 5 mg/L, chloride from 0.07 to 10 mg/L nitrate from 0.1 to 30 mg/L, and sulfate from 0.1 to 50 mg/L. Solutions with higher concentrations can be diluted to the appropriate calibration range.

Apparatus

- Ion chromatograph (Dionex Model 2120i or equivalent)
- Guard column (Dionex AG4A or equivalent)
- Separator column (Dionex AS4A or equivalent)
- Anion suppresser (Dionex Anion Fiber Suppresser AFS-1 or Dionex Micromembrane Suppresser AMMS-1)
- Integrator or strip chart recorder

Reagents

- Deionized water (DI)
- Sodium carbonate, Na_2CO_3 ACS reagent grade
- Sodium bicarbonate, $NaHCO_3$ ACS reagent grade
- Sulfuric acid, H_2SO_4 conc 96 percent ACS reagent grade

Eluent: 0.0018 M Na_2CO_3, 0.0017 M $NaHCO_3$. Dissolve 1.1424 g $NaHCO_3$ and 1.5264 g Na_2CO_3 in 8 L DI water.

Regeneration solution: 0.025 N H_2SO_4. Dilute 2.8 mL conc H_2SO_4 to 4 L with DI water.

Safety precautions

Normal laboratory safety procedures should be followed. Protective clothing, gloves, and chemical hood should be used when handling sulfuric acid. The operator should take care when analyzing samples of an unknown nature. Refer to the *CHP* and *MSDS* for specific precautions, effects of overexposures, and first-aid treatment for reagents used in this method.

Procedure

The instrument should be turned on and running at least 30 min prior to any sample or standard injection. The background conductivity should be between 13 and 14 microsiemens (µS) and remain constant for 5 min before analysis. Instrumental operating conditions are summarized in table 40.

Table 40.—Operating conditions for determination of selected anions by IC

Columns	AG4A guard column
	AS4A analytical column
Suppresser	AFS-1 anion fiber suppresser
Eluent	0.0018 *M* Na_2CO_3
	0.0017 *M* $NaHCO_3$
Regenerant	0.025 *M* H_2SO_4
Flow rate	eluent: 2 mL/min
	regenerant: 2-3 mL/min
Detector scale	between 1 and 30 µS
Sample loop	100 µL

Each sample or standard is injected by syringe through the sample injection port. About 3 mL of solution is required to assure that the previous solution has been thoroughly washed through the tubing leading to the sample loop. The first injection of the day should be a standard containing all of the anions desired in order to establish retention times for each. After the last peak has eluted and the conductivity has returned to baseline, another injection may be made.

Calibration is accomplished by injection of mixed standard solutions containing the anions of interest. At least three different concentration levels should be used at or near the suspected concentration of the samples to be analyzed. The concentrations of calibration standards are listed in table 41. Peak height responses are tabulated from the data obtained on the integrator. A calibration curve is prepared for each anion, plotting peak height vs. concentration. Correlation coefficients of "r" value 0.995 or better should be obtained before proceeding with sample analysis. Peak heights for samples are compared to the calibration curve and the concentration of each analyte is so determined.

Table 41.—Calibration standards (ppm) for IC using 10 µS scale

Anion	*Standard 1*	*Standard 2*	*Standard 3*	*Standard 4*	*Standard 5*
F^-	0.10	0.20	0.50	1.0	2.0
Cl^-	0.20	0.40	1.0	2.0	4.0
NO_3^-	0.5	1.0	2.5	5.0	10.0
SO_4^{2-}	1.0	2.0	5.0	10.0	20.0

Calculations

If the response has been determined to be linear, the concentration of an analyte may be determined using the equation:

$$C = (H \times F \times D) - B$$

where:

C=analyte concentration (mg/L)
H=peak height
F=response factor
D=dilution factor for samples requiring dilution
B=method blank calculated in ppm

Alternatively, a curve is prepared from the peak heights of at least three standards.

Assignment of uncertainty

Table 42 is the analytical results of anions for selected reference materials, duplicate samples, and method blanks.

Table 42.—Analytical performance summary for selected anions (ppm) by IC

[Reference materials are water samples with *pv* from Water Resources Division, 1994]

Reference	*Description*	*n*	*Mean*	*s*	*pv*	*% RSD*	*% R*
Fluoride, F^-							
N-39	nonpreserved	10	0.050	0.002	---	4	---
N-38	nonpreserved	10	0.052	0.002	---	4	---
M-122	major constituents	10	0.23	0.01	0.23	4	100
M-120	major constituents	10	0.62	0.03	0.625	5	99
M-126	major constituents	14	0.63	0.03	0.59	5	107
Chloride, Cl^-							
N-38	nonpreserved	10	0.68	0.04	---	6	---
P-18	precipitation	10	0.92	0.05	0.94	5	98
N-39	nonpreserved	10	3.1	0.1	---	3	---
M-120	major constituents	10	7.6	0.4	7.6	5	100
M-126	major constituents	10	21	1	20.7	5	101
M-122	major constituents	10	57	3	56.1	5	102
Nitrate, NO_3^-							
M-122	major constituents	10	0.29	0.06	---	21	---
N-38	nonpreserved	10	0.56	0.08	0.93*	14	60
M-126	major constituents	10	0.89	0.09	---	10	---
M-120	major constituents	10	1.4	0.1	---	7	---
N-39	nonpreserved	10	3.0	0.1	4.03*	3	74

*Values for nitrate include nitrite

Table 42.—Analytical performance summary for selected anions (ppm) by IC—Continued

Reference	*Description*	*n*	*Mean*	*s*	*pv*	*% RSD*	*% R*
Sulfate, SO_4^{2-}							
P-18	precipitation	10	1.44	0.04	1.6	3	90
N-39	nonpreserved	10	3.8	0.1	---	3	---
N-38	nonpreserved	10	3.9	0.1	---	3	---
M-126	major constituents	10	5.9	0.1	6.06	2	98
M-122	major constituents	10	9.8	0.2	9.6	2	102
M-120	major constituents	10	158	3	155	2	102

Duplicate samples	*k*	*n*	*Mean*	*s*	*% RSD*	*Concentration range*	*No. of < (total)*	*No. of < (pairs)*
Fluoride	47	2	0.53	0.02	4	0.05 to 2.5	16	8
Chloride	53	2	10.7	0.6	6	0.1 to 80	7	3
Nitrate	20	2	4.0	0.3	8	0.1 to 53	60	30
Sulfate	55	2	602	47	8	0.29 to 10,700	0	0

Method blank	*n*	*Mean*	*s*	*3s*	*5s*
Chloride	30	0.03	0.01	0.04	0.05
Nitrate	30	0.04	0.02	0.06	0.1
Sulfate	30	0.04	0.01	0.02	0.05
Fluoride*	30	0.007	0.002	0.007	0.01

*Fluoride blank values determined using a low standard (0.005 ppm)

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Chlorine in coal by ion chromatography

by William M. d'Angelo

Code: I020 Accepted: 6/20/94

Principle

Chlorine is determined in coals by ion chromatography after decomposition by sintering with Eschka's mixture. The coals are weighed into porcelain crucibles, mixed with Eschka's mixture and put into a cold furnace (American Society For Testing and Materials, 1991). The temperature of the furnace is step ramped to 200°C then stepped in 15-min increments to 800°C and held there for 2 hours. The sintered sample is removed from the furnace, cooled and dissolved in water. An aliquot is then filtered and diluted for analysis (Gent and Wilson, 1985).

Interferences

There is a possible interference from the nitrite anion which elutes just after chloride. Nitrogen in coal appears to be volatilized during the sintering step (Gent and Wilson, 1985), thereby minimizing this possible interference.

The large peak eluting at approximately 1 min is due to the sodium in the flux. This peak does not interfere, even when using the 1 microsiemen (µS) scale on the detector.

Scope

An operator can analyze approximately 25 samples per day, including blanks, duplicate, and reference samples. The lower reporting limit that can be achieved is 0.015 percent chlorine. Chlorine can be determined at concentration levels up to 0.2 percent. Samples with higher concentrations can be diluted to the appropriate range.

Apparatus

- Ion Chromatograph (Dionex Model 14 or equivalent)
- Guard Column (Dionex AG2 or equivalent)
- Separator Column (Dionex AS2 or equivalent)
- Anion Suppressor (Dionex Anion Fiber Suppressor AFS-1 or Dionex Anion Micro-Membrane Suppressor AMMS-1)
- Integrator or Strip Chart Recorder
- 3-mL and 5-mL syringes
- 0.2- micron or 0.45-micron syringe filters
- Muffle furnace

Reagents

- Deionized water (DI) reagent grade
- Sodium carbonate Na_2CO_3, ACS reagent grade
- Sodium hydroxide NaOH, ACS reagent grade
- Sulfuric acid, conc H_2SO_4, 96 percent ACS reagent grade
- Chloride standard: 1,000 ppm

Eluent: 0.003 *M* Na_2CO_3, 0.002 *M* NaOH. Dissolve 1.272 g sodium carbonate and 0.32 g sodium hydroxide in 4 L DI water.

Eschka's mixture: 2 parts magnesium oxide 1 part sodium carbonate

Regenerant solution: 0.025 *N* sulfuric acid. Dilute 2.8 mL conc H_2SO_4 to 4 L with DI water.

Standard solutions: Prepared daily by diluting 1,000 ppm chloride standard with an aliquot of the blank solution and DI water. The concentrations of calibration solutions used for IC (10 µs detector) scale are as follows:

Standard	*Chlorine (as chloride), ppm*
1	0.50
2	1.00
3	2.00
4	4.00

Safety precautions

Normal laboratory safety procedures should be followed. Protective clothing, gloves, and chemical exhaust hood should be used when handling sulfuric acid.

Procedure

1. Weigh 1.000 g coal sample into 30-mL porcelain crucible.
2. Add 3 g Eschka's mixture. Mix thoroughly. Cover evenly with 2 g Eschka's mixture.
3. Cover crucible and place in cold muffle furnace.
4. Raise temperature to 200°C. When furnace reaches 200°C, raise temperature 100°C every 15 min until temperature reaches 800°C. Hold temperature at 800°C for 2 hours.
5. After 2 hours, turn off furnace and remove crucibles. Allow the crucible to cool to room temperature.
6. Add about 20 mL DI water to partially dissolve the sample. Break up the solid phase (melt) with a glass rod and transfer the sample to a tared 50 mL centrifuge tube.
7. Bring solution to 53.5 g with DI water.
8. Filter about 5 mL sample solution through a 0.45 µm syringe filter (or 0.20 µm syringe filter) into a small beaker. Dilute 1 mL filtrate to 10 mL with DI water.
9. Inject 3 mL diluted sample solution into Ion Chromatograph for analysis. Instrumental operating conditions for the Ion chromatograph (dionex model 14) are summarized in table 43. The Ion Chromatograph should be turned on and running for at least 30 min prior to injection of any standard or sample to allow instrument to stabilize.

Table 43.—Operating conditions for determination of chlorine in coal by IC

Columns	AG2 Guard Column
	AS2 Analytical Column
Suppressor	AFS-1 Anion Fiber Suppressor
Eluent	0.003 *M* Na_2CO_3
	0.002 *M* NaOH
Regenerant	0.025 *M* H_2SO_4
Flow Rates	eluent: 2.0 mL/min
	Regenerant: 2-3 mL/min
Detector Scale	between 1 and 10 µS
Sample Loop	100 µL

Calculations

If the response is determined to be linear, the chlorine concentration may be calculated from the following equation:

$$C = (H \times F \times D) - B$$

where:

C = chlorine (as chloride) concentration
H = peak height from integrator or recorder
F = response factor calculated from standards
D = dilution factor
B=method blank calculated in percent

Alternatively, a curve is prepared from the peak heights of at least three standards.

Assignment of uncertainty

Table 44 is the analytical results of chlorine obtained for selected reference materials, duplicate samples, and method blanks. Certain reference materials were analyzed less than 10 replicates due to insufficient material.

Table 44.—Analytical performance summary for chlorine (ppm) in coal by IC

[A=Alpha Resources, Inc.; B=Gladney and others, 1987; C=Wilson, 1994]

Reference	*Description*	*n*	*Mean*	*s*	*pv*	*% RSD*	*% R*
AR-782	coal	3	172	39	100 A	23	172
AR-771	coke	3	484	69	300 A	14	161
AR-772	coke	4	658	36	400 A	5	165
SRM 1632a	coal fly ash	4	802	36	756 B	4	106
SRM 1632	coal	2	932	81	876 B	9	106
CLB-1	coal	11	1,070	23	1,200 C ?	2	89
SRM 1632b	coal (bituminous)	15	1,200	47	1,260 B	4	95

Duplicate samples	*k*	*n*	*Mean*	*s*	*% RSD*	*Concentration range*	*No of < (total)*	*No. of < (pairs)*
	18	2	1,167	22	2	220 to 2,100	28	14

Method blank	*n*	*Mean*	*s*	*3s*	*5s*
	40	125	25	75	125

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Platinum group elements by nickel sulfide fire assay separation and inductively coupled plasma-mass spectrometry

By Allen L. Meier, Robert R. Carlson, Fred E. Lichte, and John H. Bullock, Jr.

Code: M010 Accepted: 6/1/94

Principle

The platinum group elements (PGE) Pt, Rh, Ir, and Ru, and Pd are determined by inductively coupled plasma-mass spectrometry (ICP-MS) in 10-gram samples of geologic materials (Meier et al. 1988, 1991). Nickel sulfide fire assay procedure described by Robért et al. (1971) is used with modifications, to collect the PGE from the sample. The digestion and separation procedure used is a modification of that reported by Jackson et al. 1987 and 1990 in which the nickel sulfide button is dissolved in hydrochloric acid. Tellurium is added and reduced with stannous chloride to co-precipitate with the insoluble PGE leaving a residue that is collected by filtration. The residue is dissolved in *aqua regia* and presented as a solution to the ICP-MS instrument for determination of the PGE. The useful range, without modification, is from the lower reporting limit of 0.5 ppb to about 5 ppm. Recovery of the PGE is tracked through the collection and separation procedure by isotope dilution using enriched ^{191}Ir. Two internal standards are used to correct for instrument instability, indium for the lower mass PGE and thallium for the higher mass PGE. Calibration for each of the PGE is made by using the average intensity of five blanks taken through the entire procedure and the intensities acquired on a solution containing a known concentration of each PGE. The standard solution is run at 15 sample intervals, drift is calculated, and correction applied between standards. Recovery is calculated by comparing a standard containing the same concentration of enriched ^{191}Ir as that added to the samples.

Interferences

Interferences in ICP-MS come from matrix effects, instrumental drift, and isobaric overlap of some elemental isotopes and molecular ions formed in the plasma resulting in suppression or enhancement of measured ion intensity. Most potential matrix and isobaric interferences are eliminated by separation of the PGE from the matrix materials by fire assay and acid digestion and the collection of the insoluble PGE. The analyzed solution has a consistent matrix to which standards are matched and internal standards are added to minimized matrix effects and instrumental drift. The isotopes measured are selected to minimize isobaric overlap from other elements and molecular species that might be present. In some samples, Ni or Cu is carried over into the solution to be analyzed resulting in a small isobaric interference on ^{99}Ru from $NiCl^+$ and $CuAr^+$ on ^{103}Rh. These interferences are negated by measuring Ni and Cu and subtracting the amount of interference from the measurements. Spectral overlap from ^{107}Ag on ^{106}Pd can also occur, however this interference can also be corrected mathematically or ^{105}Pd can be used if the sample contains little or no Cu. Usually, Ni and Cu are separated better by using a smaller sample, although this raises the detection limits for that sample and increases the probability of sampling error due to nugget effect.

Scope

Samples that contain unusual or high concentrations of some elements can cause difficulty in the fire assay separation and digestion of the NiS button. Some of the problematic elements are listed in table 45. The most problematic samples are those that contain more than 5 ppm total noble metals, 2 percent Cu or greater than 50 ppm Ag. These problem samples can be analyzed by using smaller samples and mathematically correcting the spectral overlap from Cu or Ag species. Using a smaller sample raises the lower reporting limits for that sample and increases the probability of sampling error due to nugget effect.

To maintain normal lower reporting limits of 0.5 ppb for Ir, Rh, and Ru; 1.5 ppb for Pt and Pd, reagents must be selected which contain very low levels of PGE. Reporting limits are estimated with each set of samples analyzed. If the estimated limits for the sample set are higher than 0.5 ppb, the higher limit is reported. Approximately 25 samples per person day can be analyzed using this method.

Table 45.—Problem elements during fusion and digestion of PGE

Problem element	*Effect on procedure*	*Solution(s)*
ΣPGE > 5 ppm	Overload *aqua regia* and ICP-MS	Reduce sample size, increase dilution
S > 10%	Crucible overflow in fusion, digestion imbalance	Reduce sample size
As > 5,000 ppm	Digestion problems, much residue, poor PGE recovery	Reduce sample size
Sb > 1-5%	Digestion problems, precipitate resembling "yogurt"	Reduce sample size, increase dilution
C > 3%	Incomplete fusion and digestion	Reduce sample size
Pb > 5%	$PbCl_2$ crystals—suppressed ICP-MS	Reduce sample size
Bi > 3,000 ppm	Poor digestion	Reduce sample size
Cu > 10%	Digestion problems, Pd and Rh interference	Reduce sample size, correction on ICP-MS
Cr > 5%	Incomplete fusion	Fuse for 3 hours
Au > 30 ppm	Digestion problems for procedures B and C	Reduce sample size
Fe > 50%	Digestion problems	Reduce sample size
Ni > 1%	NiS imbalance—poor digestion	Reduce sample size
CO_3	Crucible overflow in fusion	Reduce sample size

Apparatus

- Inductively Coupled Plasma Mass Spectrometer, Sciex Elan 250
- Denver Fire and Clay (DFC) fire assay furnaces
- Twin shell dry blender ("V" blender)
- DFC 10-g fire clay crucibles
- 4-oz plastic disposable specimen jars with screw caps
- 25x250 mm culture tubes
- Hotplates with solid aluminum heating blocks drilled to hold 50, 25-mm tubes
- Glasseine weighing paper
- 25-mm diameter Nucleopore polycarbonate membrane filters
- Vacuum filter system (Millipore)
- 15-mL disposable polypropylene centrifuge tubes

Reagents

One of the most important factors for this as well as the other procedures is the condition of the reagents. Many reagents contain trace amounts of PGE. Since the method is extremely sensitive, even trace contributions of PGE to the blank level can raise the detection limits of the method. All reagents must be tested for PGE contamination (especially the nickel powder and acids). If a reagent is deemed satisfactory for the procedure (usually by testing blanks on the ICP-MS), it should be purchased in large quantities of the same lot number. In this manner, time is not wasted constantly checking for contaminants, and if problems do arise in the future, chances are good that the reagents are not involved.

- Hydrochloric acid, HCl conc 'BAKER INSTRA-ANALYZED' grade
- Hydrochloric acid, HF conc reagent grade
- Nitric acid, HNO_3 conc 'BAKER INSTRA-ANALYZED' grade
- Nitric acid, HNO_3 conc reagent grade

Silver interference solution: Add 0.02 mL commercial 1,000 µg/mL silver to a tube containing 10 mL 40 percent *aqua regia* solution.

Aqua regia, 40 percent solution: Prepare by slowly adding 75 mL conc HCl 'BAKER INSTRA-ANALYZED' to 25 mL conc HNO_3 'BAKER INSTRA-ANALYZED' to a 250 mL volumetric flask. Allow to stand in fume hood loosely covered with occasional mixing to allow free chlorine gas to dissipate. Carefully bring to volume with water when most of the dissolved chlorine gas is gone (1 week to several weeks). It is helpful to have several flasks prepared in advance so the aqua regia is spent before dilution is needed.

Copper interference solution: Add 0.01 mL commercial 1,000 µg/mL Cu to a tube containing 10 mL 40 percent *aqua regia* solution.

Flux: Fire assay flux is prepared by adding 200 g sulfur powder, 320 g nickel powder, 200 g silicon dioxide (SiO_2) powder, and 1,200 g sodium borate ($Na_2B_4O_7$) powder into each half of a "V" blender. Mix for at least 3 hours. Add 600 g sodium carbonate (Na_2CO_3) powder to each half of the "V" blender containing the first mixture and mix for at least 2 more hours. Store in an airtight container. To aid in homogeneity when preparing the flux, it is imperative that all components are ground as fine as possible. The $NaCO_3$ and the $Na_2B_4O_7$ are sieved to minus 9 mesh (2 mm). The sulfur, nickel, and SiO_2 are mixed in a beaker, with any remaining large clumps being pulverized by a spatula, before being emptied into the "V" blender.

10 percent hydrochloric acid: 100 mL conc reagent grade HCl diluted to 1 L with DI water.

Isotope 100 µg/mL ^{191}Ir solution: Dissolve 0.0100 g ^{191}Ir metal in *aqua regia* and dilute to 1 L with 10 percent HCl.

Ni interference solution: Add 0.02 mL commercial 1,000 µg/mL Ni to a tube containing 10 mL 40 percent *aqua regia* solution.

Recovery spike standard 2 µg/mL ^{191}Ir solution: Dilute 2.00 mL isotope 100 µg/mL ^{191}Ir solution to 100 mL with 10 percent HCl.

Recovery standard solution: Dilute 0.05 mL isotope 100 µg/mL ^{191}Ir and 2.5 mL internal standard solution to 250 mL with 40 percent *aqua regia.*

20 percent stannous chloride solution: Dissolve 20 g $SnCl_2$ in 100 mL conc HCl

Stock calibration standard: From commercial 1,000 µg/mL solutions add 2.5 mL of Ru, Pd, Pt, and 1.0 mL Rh and Ir and 30 mL Tl and 20 mL In to a 500 mL volumetric flask along with 10 mL isotope 100 µg/mL ^{191}Ir and dilute to 500 mL with 10 percent HCl.

1 percent tellurium solution: Dissolve 1 g Te metal in 100 mL conc HCl

Internal standard solution 20 µg/mL In and 60 µg/mL Tl: Add to a 100 mL volumetric flask, 2.00 mL commercial 1,000 µg/mL In and 6.00 mL commercial 1,000 µg/mL Tl and dilute to 100 mL with 40 percent *aqua regia* solution.

Working calibration standard: Dilute 10 mL stock calibration standard to 1.00 L with 40 percent *aqua regia*.

Safety precautions

All laboratory personnel must wear safety glasses, a lab coat or apron, and gloves. Digestion and flux preparations should be done in chemical and dust hoods, respectively. Aluminized apparel must be worn (hood, sleeves, and gloves) when loading and unloading the fire assay furnaces for heat protection. All personnel must read the *CHP* and *MSDS* for each procedure.

Procedure

1. Weigh 10 g sample into a 4 oz plastic disposable specimen jar. Standard rocks and duplicates are also weighed as well as five splits of AGV-2 (USGS reference material) to be used as the blank.
2. Add approximately 50 g (one scoop) flux to each jar.
3. Cap the jar and mix by shaking for 15 s. Discard the cap.
4. Add 100 µL recovery spike standard 2 µg/mL ^{191}Ir solution and allow to dry overnight.
5. Transfer the mixture to a 10-g fire assay clay crucible.
6. Load 25 to 30 crucibles into the preheated 1050°C fire-assay furnaces with crucible tongs.
7. Add seven shielding crucibles (crucibles filled with carbon, used spectrographic dc-arc electrodes work well).
8. Fuse samples for 2 hours at 1,050°C (chromitite samples greater than 20 percent chromium must be fused for 3 hours).
9. Remove crucibles from furnaces with crucible tongs and allow to cool.
10. Break open the crucibles with a hammer and remove NiS button. Place button between two pieces of glasseine weighing paper and break button with a small hammer.
11. Transfer the pieces to a 25x250-mm glass-culture tube.
12. Add to each culture tube containing the pieces of NiS button:
    a. 100 µL 1 percent Te solution
    b. 65 mL conc HCl, reagent grade
    c. 1 mL 20 percent stannous chloride solution
13. Heat tubes:
    a. Put the tubes in the aluminum heating block on a hotplate set at 160 to 220°C .
    b. Cover each tube with a watch glass.
    c. Heat until the button is completely digested (2-7 days).
14. Filter:
    a. After the reaction is completed, filter the warm solution using a vacuum filtration system, to collect the residue on a 25-mm diameter Nucleopore polycarbonate membrane filter (0.45 µm pore size).
    b. Wash the residue from the sides of the funnel onto the filter paper thoroughly with conc HCl followed by DI water.
    c. Transfer the filter paper containing the residue to a 15 mL plastic disposable polypropylene centrifuge tube and cap.
15. Dissolve the residue from the filter paper. To each centrifuge tube add:
    a. 100 µL internal standard solution (20 µg/mL In and 60 µg/mL Tl)
    b. 3 mL conc 'BAKER INSTRA-ANALYZED' HCl
    c. 1 mL conc 'BAKER INSTRA-ANALYZED' HNO_3
16. Cap the tube loosely and allow the reaction to proceed for at least 4 hours.
17. Place the tubes in a boiling water bath for 2 hours.

18. Allow the tubes to cool.
19. Dilute each tube to approximately 10 mL by adding 6 mL 1 percent 'BAKER INSTRA-ANALYZED' HCl.
20. Cap the tubes tightly and mix.
21. Analyze for Ru, Rh, Pd, Ir, and Pt with ICP-MS instrumental operating conditions as indicated in table 46. The standard concentrations, dwell times, and masses measured for the platinum group elements are listed in table 47.

Table 46.—Operating conditions for determination of PGE by ICP-MS

Sweeps/replicate	100
Number of replicates	1
Points/peak	1
Resolution	variable
Calculation frequency	replicate
Polarity	+
Plasma RF power	1300 W
Sheath flow	80 percent of Pb max. L/min
Nebulizer flow	1.0 L/min
Plasma flow	16.0 L/min
Nebulizer pressure	60.0 psi
Sample uptake rate	1.8 mL/min
Sample delay time	50 s
Sampler wash time	20 s
Delivery line temp	10°C
E1 LENS	90
P LENS	30
S2 LENS	02
B LENS	Equal intensity for 1 µg/mL In and 4 µg/mL Pb

Table 47.—Standard concentrations, dwell times, and masses measured for PGE

Element	*Symbol*	*Mass*	*Repetition, ms*	*Dwell, ms*	*Omni*	*Standard, µg/mL*
Nickel	Ni	61	1,000	10	3.80	100
Copper	Cu	65	1,000	10	4.20	10.0
Ruthenium	Ru	99	3,000	30	0.00	0.05
Ruthenium	Ru	101	2,000	20	0.00	0.05
Rhodium	Rh	103	1,000	10	0.00	0.02
Palladium	Pd	105	3,000	30	0.00	0.05
Palladium	Pd	106	2,000	20	0.00	0.05
Silver	Ag	107	1,000	10	4.00	2.0
Indium	In	115	1,000	10	0.00	0.20
Iridium	Ir	191	5,000	50	0.00	0.02
Iridium	Ir	193	5,000	50	0.00	0.02
Platinum	Pt	195	4,000	40	0.00	0.05
Thallium	Tl	203	1,000	10	0.00	0.60
Background	Bg	230	1,000	10	0.0	0.00

Calculation

A 10.000 g sample is diluted to 10 mL. Dilution factor = 1

$$\text{Concentration (ppb)} = \frac{\text{sample volume}}{\text{sample wt (g)}} \times \text{ICP - MS reading (ppb)}$$

Assignment of uncertainty

Table 48 is the platinum group element analytical results for selected reference materials, duplicate samples, and method blanks by ICP-MS.

Table 48.—Analytical performance summary for PGE (ppb)

[A=Barnes, 1991; B=Canadian Certified Reference Materials Project, 1992; C=Ore Research and Exploration Party, 1991; remaining *pv* from Potts and others, 1992]

Reference	*Description*	*n*	*Mean*	*s*	*pv*			*% RSD*	*% R*
Iridium, Ir									
DTS-1	dunite	10	1.0	0.6	0.67			60	150
OREAS-11	metanorite	13	1.5	0.2	--			13	---
AX-90	komatite	10	3.4	0.2	2.8	A		6*	120
UMT-1	ultramafic ore tailings	10	9.2	0.9	8.73	B		11	105
SARM-7	platinum ore	60	77	7	74		*cv*	9	104
Palladium, Pd									
DTS-1	dunite	10	0.3	0.5	3		?	170	10
OREAS-11	metanorite	13	24	3	23	C		13	104
UMT-1	ultramafic ore tailings	10	107	12	104.2	B		11	103
AX-90	komatite	10	319	9	330	A		3*	97
SARM-7	platinum ore	60	1,500	94	**1,530**		*cv*	6	98
Platinum, Pt									
DTS-1	dunite	10	4	2	5.7			50	70
OREAS-11	metanorite	13	53	4	52	C		8	102
UMT-1	ultramafic ore tailings	10	138	18	128.3	B		13	108
AX-90	komatite	10	143	3	135	A		2*	106
SARM-7	platinum ore	60	3,700	243	**3,740**		*cv*	7	99
Rhodium, Rh									
DTS-1	dunite	10	0.9	0.4	0.83			44	108
OREAS-11	metanorite	13	6.7	0.6	--			9	--
UMT-1	ultramafic ore tailings	10	9	1	9.8	B		11	92
AX-90	komatite	10	11.4	0.4	12.5	A		4*	91
SARM-7	platinum ore	60	239	13	**240**		*cv*	5	100

Table 48.—Analytical performance summary for PGE (ppb)—Continued

Reference	*Description*	*n*	*Mean*	*s*	*pv*		*% RSD*	*% R*
Ruthenium, Ru								
DTS-1	dunite	10	2.0	0.7	2.5	?	35	80
OREAS-11	metanorite	13	2.0	0.3	--		15	--
UMT-1	ultramafic ore tailings	10	10	1	--		10	--
AX-90	komatite	10	18.1	0.7	17.7	A	4*	102
SARM-7	platinum ore	60	434	36	430	cv	8	101

*Replicates analyzed on the same day, within batch.

Duplicate samples	*k*	*n*	*Mean*	*s*	*% RSD*	*Concentration range*	*No of <* *(total)*	*No. of <* *(pairs)*
Ir	10	2	36.9	0.5	1	0.5 to 300	156	77
Pd	25	2	73	1	2	0.5 to 1,230	116	52
Pt	54	2	56	6	11	0.5 to 2,110	58	23
Rh	12	2	36	2	4	0.5 to 262	152	75
Ru	22	2	12.2	0.7	6	0.5 to 96	120	54

Method blank	*n*	*Mean*	*s*	*3s*	*5s*
Ir	25	0.12	0.05	0.2	0.2
Pd	25	0.8	0.3	0.8	1
Pt	25	0.4	0.3	0.8	1
Rh	25	0.03	0.02	0.06	0.09
Ru	25	0.12	0.03	0.09	0.2

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Rare earth elements by inductively coupled plasma-mass spectrometry

By Allen L. Meier and Fred Lichte

Code: M020 Accepted: 6/1/94

Principle

The rare earth elements (REE) La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Yb are determined by inductively coupled plasma-mass spectrometry (ICP-MS) in geologic materials (Lichte, et al., 1987). The REE are made soluble in the sample material by sintering with sodium peroxide, leaching with water, and acidifying with nitric acid. Lutetium is added as an internal standard to correct for instrument instability and oxide correction. Calibration for each of the REE is made by using the average intensity of five blanks taken through the entire procedure and the intensities acquired on a solution of a glass standard containing a known concentration of each REE.

Interferences

Interferences in ICP-MS come from matrix effects, instrumental drift, and isobaric overlap of some elemental isotopes and molecular ions formed in the plasma resulting in suppression or enhancement of measured ion intensity. A glass standard is used so samples and standards are matrix matched. An internal standard is added to minimized matrix effects and instrumental drift. The standard solution is run at 15 sample intervals, drift is calculated, and correction applied between standards. The isotopes measured are selected to minimize isobaric overlap from other elements and molecular species that might be present. Oxide overlaps from the lighter REE on the heavier REE are subtracted by measuring the ratio of oxide to element for single element standards in each run and applying this ratio to each sample.

Scope

Rocks and sediments can be analyzed by this method from lower reporting limits of 1.0 La, 2.0 Ce, 0.2 Pr, 1.0 Nd, 0.4 Sm, 0.1 Eu, 0.5 Gd, 0.1 Tb, 0.5 Dy, 0.1 Ho, 0.4 Er, 0.1 Tm, and 0.4 Yb ppm, (Lichte, et al., 1987) to approximately 500 ppm La in the sample. Samples that contain higher concentrations of REE must be diluted before analysis. Approximately 40 samples per person day can be analyzed using this method.

Apparatus

- Inductively coupled plasma-mass spectrometer
- Muffle furnace
- Zirconium crucibles, 5 mL
- Teflon screw capped bottles, thick walled, from Savellex
- 15-mL disposable polypropylene tubes

Reagents

- Deionized water (DI)
- Sodium peroxide, Na_2O_2, reagent grade ground in a shatter box to pass a 80-mesh screen (<180 µm).
- Nitric acid HNO_3, conc reagent grade

Nitric acid 25 percent: Dilute 250 mL conc HNO_3 to 1,000 mL with DI water.

Nitric acid 1 percent: Dilute 10 mL conc HNO_3 to 1,000 mL with DI water.

400 µg/mL Lu internal standard stock solution: Dissolve 0.4548 g lutetium oxide, Lu_2O_3, in a minimum volume of HNO_3. Dilute to 1000 mL with 1 percent HNO_3.

Ba and Ce oxides standard: Prepare a solution to contain 1 µg/mL of each element, 2.5 µg/mL Lu, and 1.5 percent Na_2O_2. To a 100 mL volumetric flask add 1.5 g Na_2O_2, 25 mL DI water, 25 mL 25 percent HNO_3, 0.625 mL 400 µg/mL Lu solution, 0.1 mL 1,000 µg/mL Ba, 0.1 mL 1,000 µg/mL Ce, and dilute to volume with 1 percent HNO_3.

Gd and Sm oxides standard: Prepare a solution to contain 1 µg/mL of each element, 2.5 µg/mL Lu, and 1.5 percent Na_2O_2. To a 100 mL volumetric flask add 1.5 g Na_2O_2, 25 mL DI water, 25 mL 25 percent HNO_3, 0.625 mL 400 µg/mL Lu solution, 0.1 mL 1,000 µg/mL Gd, 0.1 mL 1,000 µg/mL Sm, and dilute to volume with 1 percent HNO_3.

Eu, Nd, and Pr oxides standard: Prepare a solution to contain 1 µg/mL of each element, 2.5 µg/mL Lu, and 1.5 percent Na_2O_2. To a 100 mL volumetric flask add 1.5 g Na_2O_2, 25 mL DI water, 25 mL 25 percent HNO_3, 0.625 mL 400 µg/mL Lu solution, 0.1 mL 1,000 µg/mL Eu, 0.1 mL 1,000 µg/mL Nd, 0.1 mL 1,000 µg/mL Pr, and dilute to volume with 1 percent HNO_3.

Safety precautions

All laboratory personnel must wear safety glasses, a lab coat or apron, and gloves. Digestion and flux preparations should be performed in chemical fume and dust hoods, respectively. All personnel must read the *CHP* and *MSDS* for each procedure.

Procedure

1. Weigh 0.100 g sample into zirconium crucible. Standard rocks and duplicates should be taken through the procedure as well as two samples of PP93 PRIMARY STANDARD (in-house glass standard material used for calibration).
2. Add 0.6 g dry Na_2O_2. Mix sample and peroxide thoroughly. (Keep under a heat lamp until samples and flux are placed into the muffle furnace.)
3. Place crucibles into muffle furnace preheated to 450°C. Heat for 30 min and remove from furnace. Cool the crucibles.
4. Place each crucible into a Teflon bottle (may be stored capped until analysis).
5. Add 10 mL DI water, cap and mix by inverting a few times, let sit overnight or a minimum of 4 hours.
6. Mix and add 0.25 mL Lu Internal Standard Solution (400 µg/mL Lu).
7. Add 10 mL 25 percent HNO_3, let stand until reaction has stopped (about 15 min), and then mix thoroughly.
8. Take a 5 mL aliquot and dilute with 1 percent HNO_3 to 10 mL for ICP-MS analysis.
9. Analyze for REE by ICP-MS using the instrumental operating conditions in table 49. The standard concentrations, dwell times, and masses measured for the rare earth elements are listed in table 50.

Table 49.—Operating conditions for determination of REE by ICP-MS

Sweeps/replicate	50
Number of replicates	1
Points/peak	1
Resolution	variable
Calculation frequency	replicate
Polarity	+
Plasma RF power	1,300 W
Sheath flow	minimum CeO to Tb ratio L/min
Nebulizer flow	1.0 L/min
Plasma flow	16.0 L/min
Nebulizer pressure	60.0 psi
Sample uptake rate	1.8 mL/min
Sample delay time	50 s
Sampler wash time	30 s
Delivery line temp	10°C
E1 LENS	90
P LENS	30
S2 LENS	02
B LENS	MAX Tb

Table 50.—Standard concentrations, dwell times, and masses measured for REE

Element	*Symbol*	*Mass*	*Repetition, ms*	*Dwell, ms*	*PP93 primary standard, µg/g*
Barium	Ba	135	500	10	250
Lanthanum	La	139	1,000	20	41
Cerium	Ce	140	500	10	40
Praseodymium	Pr	141	2,500	50	42
Neodymium	Nd	143	4,000	80	42
Samarium	Sm	147	9,000	180	43
Europium	Eu	151	8,000	160	43
Gadolinium	Gd	157	4,500	90	47
Terbium	Tb	159	5,000	100	44
Dysprosium	Dy	163	3,500	70	47
Holmium	Ho	165	4,000	80	47
Erbium	Er	168	5,000	100	48
Thulium	Tm	169	9,000	180	51
Ytterbium	Yb	172	6,500	130	49
Lutetium	Lu	175	500	10	2.5
Hafnium	Hf	178	500	10	50
Background	Bg	230	500	10	-

Calculation

A 0.100 g sample is diluted to 40 mL. Dilution factor = 400

$$\text{Concentration (ppm)} = \frac{\text{sample volume}}{\text{sample wt (g)}} \times \text{ICP - MS reading (ppm)}$$

Assignment of uncertainty

Table 51 is the rare earth element analytical results for selected reference materials, duplicate samples, and method blanks by ICP-MS.

Table 51.—Analytical performance summary for REE (ppm)

[A=Crock and Briggs, 1991; remaining *pv* from Potts and others, 1992]

Reference	*Description*	*n*	*Mean*	*s*	*pv*		*% RSD*	*% R*
Cerium, Ce								
FK-N	dolomitic limestone	10	0.8	0.2	1		25	80
JGb-1	gabbro	10	8.6	0.8	8		9	108
GSS-3	stream sediment	10	42	3	39		7	108
BHVO-1	basalt	10	40	3	39		8	103
TMB	basalt	46	92	5	84.5	A	5	109
BCR-1	basalt	21	55	5	**53.7**		9	103
SY-3	syenite	10	2,430	171	2,230		7	109
Dysprosium, Dy								
FK-N	dolomitic limestone	10	<0.2	--	0.06		--	--
JGb-1	gabbro	10	1.8	0.2	1.4		11	129
GSS-3	stream sediment	10	2.6	0.4	2.6		15	100
TMB	basalt	46	4.7	0.2	4.3	A	4	109
BHVO-1	basalt	10	5.7	0.6	5.2		11	110
BCR-1	basalt	21	6.5	0.7	**6.34**		11	102
SY-3	syenite	10	132	10	118		8	112
Erbium, Er								
FK-N	dolomitic limestone	10	<0.09	--	0.04		--	--
JGb-1	gabbro	10	1.1	0.1	0.91		9	121
GSS-3	stream sediment	10	1.56	0.04	1.5		3	107
BHVO-1	basalt	10	2.5	0.2	2.4		8	104
TMB	basalt	46	2.6	0.1	2.49	A	4	104
BCR-1	basalt	21	3.7	0.3	**3.63**		7	102
SY-3	syenite	10	82	5	*76.8*		6	107
Europium, Eu								
FK-N	dolomitic limestone	10	0.38	0.08	0.42		21	90
JGb-1	gabbro	10	0.58	0.06	0.61		10	95
GSS-3	stream sediment	10	0.62	0.08	0.72		13	86
TMB	basalt	46	1.71	0.06	1.61	A	4	106
BCR-1	basalt	21	1.9	0.2	**1.95**		11	97
BHVO	basalt	10	2.1	0.2	**2.06**		10	102
SY-3	syenite	10	18	1	17		6	106

Table 51.—Analytical performance summary for REE (ppm)—Continued

Reference	*Description*	*n*	*Mean*	*s*	*pv*	*% RSD*	*% R*
Gadolinium, Gd							
FK-N	dolomitic limestone	10	<0.6	--	0.05	--	--
JGb-1	gabbro	10	1.8	0.4	1.5	22	120
GSS-3	stream sediment	10	2.6	0.2	2.9	8	90
TMB	basalt	46	5.9	0.3	5.4 A	5	109
BHVO-1	basalt	10	6.4	0.4	6.4	6	100
BCR-1	basalt	21	7.0	0.8	**6.68**	11	105
SY-3	syenite	10	116	9	105	8	110
Holmium, Ho							
JGb-1	gabbro	10	0.38	0.04	0.32	11	119
GSS-3	stream sediment	10	0.52	0.04	0.53	8	98
TMB	basalt	46	0.94	0.04	0.94 A	4	100
BHVO-1	basalt	10	1.00	0.04	0.99	4	101
BCR-1	basalt	21	1.3	0.1	1.26	8	105
SY-3	syenite	10	29	2	29.5	7	98
Lanthanum, La							
FK-N	dolomitic limestone	10	0.9	0.1	0.9	11	100
JGb-1	gabbro	10	3.9	0.4	3.95	10	99
BHVO-1	basalt	10	17	1	15.8	6	108
GSS-3	stream sediment	10	22	2	21	9	105
BCR-1	basalt	21	28	2	**24.9**	7	111
TMB	basalt	46	49	3	44.3 A	6	111
SY-3	syenite	10	1,140	117	1,340	10	85
Neodymium, Nd							
FK-N	dolomitic limestone	10	<0.5	--	0.3	--	--
JGb-1	gabbro	10	5.4	0.4	5.7	7	95
GSS-3	stream sediment	10	16	1	18.4	6	87
BHVO-1	basalt	10	26	2	25.2	8	103
BCR-1	basalt	21	29	3	**28.8**	10	100
TMB	basalt	46	40	2	38.9 A	5	103
SY-3	syenite	10	751	57	670	8	112
Praseodymium, Pr							
JGb-1	gabbro	10	1.2	0.1	1.1	8	109
GSS-3	stream sediment	10	4.7	0.3	4.8 7	6	98
BHVO-1	basalt	10	5.4	0.4	5.7	7	95
BCR-1	basalt	21	6.8	0.7	6.8	10	100
TMB	basalt	46	10.8	0.5	10.4 A	5	104
SY-3	syenite	10	238	18	223	7	107

Table 51.—Analytical performance summary for REE (ppm)—Continued

Reference	*Description*	*n*	*Mean*	*s*	*pv*	*% RSD*	*% R*
Samarium, Sm							
FK-N	dolomitic limestone	10	<0.2	--	0.06	--	--
JGb-1	gabbro	10	1.5	0.2	1.5	13	100
GSS-3	stream sediment	10	3.0	0.2	3.3	7	91
BHVO-1	basalt	10	6.1	0.3	**6.2**	5	98
BCR-1	basalt	21	6.6	0.5	**6.59**	8	100
TMB	basalt	46	7.2	0.3	6.9 A	4	104
SY-3	syenite	10	121	9	109	7	111
Terbium, Tb							
FK-N	dolomitic limestone	10	<0.06	--	0.01	--	--
JGb-1	gabbro	10	0.29	0.03	0.30	10	97
GSS-3	stream sediment	10	0.43	0.06	0.49	14	88
BHVO-1	basalt	10	1.02	0.06	0.96	6	106
TMB	basalt	46	0.85	0.04	<1 A	5	--
BCR-1	basalt	21	1.10	0.08	1.05	7	105
SY-3	syenite	10	21	1	18	5	117
Thulium, Tm							
JGb-1	gabbro	10	0.14	0.02	0.17	14	82
GSS-3	stream sediment	10	0.24	0.03	0.28	13	86
BHVO-1	basalt	10	0.33	0.02	0.33	6	100
TMB	basalt	46	0.38	0.02	0.4 A	5	95
BCR-1	basalt	21	0.52	0.05	0.56	10	93
SY-3	syenite	10	12.0	0.7	11.6	6	103
Ytterbium, Yb							
FK-N	dolomitic limestone	10	<0.2	--	0.04	--	--
JGb-1	gabbro	10	0.91	0.08	1.0	9	91
GSS-3	stream sediment	10	1.5	0.2	1.68	13	89
BHVO-1	basalt	10	2.0	0.2	2.02	10	99
TMB	basalt	46	2.5	0.2	2.6 A	8	96
BCR-1	basalt	21	3.2	0.4	**3.38**	13	96
SY-3	syenite	10	63	4	*62*	? 6	102

Duplicate samples	*k*	*n*	*Mean*	*s*	*% RSD*	*Concentration range*	*No of < (total)*	*No of < (pairs)*
Ce	70	2	1,070	270	25	2.1 to 46,500	0	0
Dy	70	2	39	10	25	0.43 to 1,690	0	0
Er	70	2	23	4	16	0.37 to 958	0	0
Eu	70	2	8	2	32	0.08 to 300	0	0
Gd	70	2	40	8	19	0.68 to 1,633	0	0
Ho	70	2	8	2	19	0.10 to 335	0	0
La	70	2	652	184	28	0.64 to 28,000	0	0
Nd	70	2	318	94	29	2.5 to 14,300	0	0
Pr	70	2	103	29	28	0.49 to 4,790	0	0
Sm	70	2	54	13	25	0.51 to 2,380	0	0

Table 51.—Analytical performance summary for REE (ppm)—Continued

Duplicate samples	*k*	*n*	*Mean*	*s*	*% RSD*	*Concentration range*			*No of < (total)*	*No of < (pairs)*
Tb	70	2	7	2	28	0.09	to	292	0	0
Tm	70	2	3.5	0.7	20	0.06	to	150	0	0
Yb	70	2	24	5	22	0.29	to	924	0	0

Method blank	*n*	*Mean*	*s*	*3s*	*5s*
Ce	114	0.08	0.07	0.2	0.3
Dy	114	0.004	0.02	0.05	0.1
Er	114	0.003	0.01	0.04	0.06
Eu	114	0.005	0.01	0.02	0.04
Gd	114	0.008	0.03	0.1	0.2
Ho	114	0.002	0.004	0.01	0.02
La	114	0.03	0.03	0.09	0.2
Nd	114	0.04	0.05	0.2	0.3
Pr	114	0.01	0.01	0.03	0.05
Sm	114	0.03	0.05	0.1	0.2
Tb	114	0.02	0.02	0.06	0.1
Tm	114	0.002	0.003	0.01	0.02
Yb	114	0.02	0.02	0.05	0.09

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Total carbon by combustion

By Kenneth Joe Curry

Code: N011 Accepted: 1/27/93

Principle

Total carbon in geologic materials is determined by the use of an automated carbon analyzer (Jackson and others, 1987). A weighed sample (approximately 0.25 g) is combusted in an oxygen atmosphere at 1370°C to oxidize carbon (C) to carbon dioxide (CO_2). Moisture and dust are removed and the carbon dioxide gas is measured by a solid state infrared detector.

Interferences

High concentrations of fluorine and molybdenum will interfere with the detection of CO_2 by coating the cell walls and the detector of the carbon analyzer. Samples suspected to contain molybdenum in the range of 0.2 to 1 percent are analyzed using a reduced sample weight and a halogen trap is installed in the flow system when high concentrations of fluorine are present in the samples. A problem may be encountered due to abnormally rapid combustion of organic-rich materials. This problem can be corrected by the addition of a retardant (COM-AID) to the sample.

Scope

The operating range for total carbon is from 0.05 percent to about 30 percent. Approximately 40 samples can be analyzed in a day.

Apparatus

- Carbon analyzer, LECO Model CR-12
- Ceramic combustion sample boats
- Tank of high purity oxygen, with regulator

Reagents

- COM-AID, combustion retardant
- Anhydrone, magnesium perchlorate, $Mg(ClO_4)_2$
- Distributing organization and reference material samples are:
  - LECO Corporation: 0.98, 12.0, 42.0, and 47 percent total carbon
  - U.S. Geological Survey: GXR-4, GXR-3, GXR-5, GXR-2, and SDO-1
  - Canadian Certified Reference Materials Project (CCRMP): SY-3, SY-2, MGR-1, SO-4, and SO-2
  - National Institute of Standards and Technology (NIST): SRM 88 and SRM 88a

Safety precautions

The major danger in this procedure is potential thermal burns to the operator due to contact with the very hot sample boats upon their removal from the furnace. Care must be exercised in removing the boats with tongs. Avoid contact of the hot boats with combustible materials. The use of a lab coat, safety glasses, and protective shoes are strongly recommended while operating the instrument. Toxic gases may be produced during sample combustion, therefore, the instrument should be used under a working exhaust hood or vented to one. See the *CHP* and *MSDS* for further information.

Procedure

Additional details of the following procedure are in the on-site instruction manual by LECO Corporation (1982).

A. Oxygen pressure and flows
   1. Turn on fume hood.
   2. Open valve on oxygen cylinder and set second stage regulator to 30 psi.
   3. Press the GAS key on the control console and observe the oxygen pressure on the front of instrument. The oxygen pressure must be greater than 8 psi.
   4. Observe that the PURGE rotometer is adjusted to a flow reading of 4 L/min and the LANCE rotometer is adjusted to a flow reading of 1 L/min.
   5. Press the GAS key again to stop the oxygen flow.

B. Check power supply
   1. Press the MONITOR key on the control console keyboard.
   2. The printer will provide a list showing the current status of the various systems parameters. If any of the power supply voltages are out of range, they will be printed in red with a corresponding alarm message. If this occurs, turn off system power and refer to the *Power supply adjustments* section of the instruction manual.
   3. If no alarm appears, proceed to next section.

C. Calibrate balance
   1. Press the SYSTEM UPDATE key on the control console.
   2. Then press the NO key until the message center displays: "CALIBRATE BALANCE YES/NO."
   3. Press the YES key and the message center will display: "PUT EMPTY CRUCIBLE ON BALANCE THEN TARE."
   4. Place an empty combustion boat on the balance and then push the TARE key.
   5. The message center will display: "PUT 1 GRAM IN CRUC 01 WT=0.000."
   6. Place a 1-g standard weight in the combustion boat.
   7. The message center will display: "AUTO-CALIBRATION 01 WT=1.000."
   8. After the above message is displayed for a few seconds, the system will return to OPERATE MODE. The balance is now calibrated.
   9. Remove the combustion boat and the 1-g standard weight from the balance.

D. Conditioning the instrument for analyses
   1. It is a standard operating practice to change out the right side anhydrone tube daily or if, during a day's operation, visible moisture and discolorization appear more than a third of the way down the tube.
   2. Three to five conditioning analysis should be run at the start of the day. Use the spent combustion boats for this purpose. At the same time, randomly pick a couple of samples from the job of interest and run them as conditioners to obtain an idea as to what carbon concentration range is in the samples.
      NOTE: Anytime the instrument has been idle for a period of time, or where fresh anhydrone has been installed, you must condition the system again.
   3. Select the ID CODE A by pressing the ID CODE key until the letter A appears on the display.
   4. Enter the ID number 1 by moving the cursor to the desired position (pressing the YES key moves the cursor left, pressing the NO key moves the cursor right) and then press the 1 key.
   5. When the last digit is pressed, as shown on the message center, the system returns to Operate mode.
   6. Place five spent combustion boats on the loading tray next to the furnace entrance.
   7. To enter and store in the Weight Stock memory:
      a. Press the MANUAL WEIGHT key

    - b. Press the number 1 key for 1 g
    - c. Press the ENTER key
    - d. Repeat the above five times
8. Place a combustion boat on the balance pan. The balance will automatically tare.
9. Add approximately 0.250 g of one of the samples in the job of interest into the boat.
10. When the weight is stable, press the ENTER key.
11. Remove the boat from the balance and spread the sample evenly in the boat by gently shaking the boat in a back and forth motion.
12. Place the sample boat on the loading tray in order of weighing.
13. Press the ANALYZE key. The PURGE flow will start immediately. The LANCE flow will start later in the analysis cycle.
14. Slide the viewing window to the open position.
15. Wait until the message center displays "LOAD FURNACE" (also the load furnace LED lamp will come on) and then slide the first combustion boat into the furnace until it touches the boat stop.
16. Slide the viewing window to the close position.
17. Immediately press the ANALYZE key again.
    NOTE: Normally the analysis cycle will start automatically as soon as the carbon is detected. But, in low carbon analysis, the amount of carbon released is insufficient to start the analysis, so the ANALYZE key must be pressed again.
18. When the analysis is complete, the CARBON display will indicate the results and the printer will print the value.
19. Remove the spent combustion boat from the furnace.
20. Repeat steps 13 through 19 to run the remaining conditioner samples.

D. Calibration procedure

1. If the calibration channels have already been pre-programmed with a different range of sulfur standards, select the channel to be used by pressing the SELECT key and then the appropriate number key.
2. A wide variety of standards are used for calibration (see *Reagents* section for type of standards). Choose a standard in the percent range and type of material as the samples being analyzed.
3. For the determination of the standards, use the ID CODE B by pushing the ID CODE key until the letter B appears on the message center. The press the ENTER key.
4. Place a combustion sample boat on the balance pan. The balance will automatically tare.
5. Weigh out approximately 0.250 g of standard into the sample boat.
6. When the weight is stable, press the ENTER key.
7. To determine the carbon concentrations for the standards, follow steps 11 through 19 described in Conditioning the instrument for analysis.
   NOTE: While the instrument is in the Analyzed Mode, the balance is freed to weight additional samples, which are then stacked on the loading tray in order of weighing.

E. Sample analysis

1. For the determination of carbon in the samples, use the ID CODE D by pushing the ID CODE key until the letter D appears on the message center. At this time, enter the RASS ID number for the first sample to be analyzed. When the last digit is entered, as shown on the message center, the system will return to Operation mode.
2. Weigh out the samples in the same weight range as used in weighing the standard.
3. Follow the same sequence of analysis (steps 8 through 19) described above in **Conditioning the instrument for analysis.**

Calculation

Calculations are performed by the instrument's microprocessor, and the percent carbon is reported for each sample.

Assignment of uncertainty

Table 52 is the analytical results of total carbon for selected reference materials, duplicate samples, and method blanks by combustion.

Table 52.—Analytical performance summary for total carbon (percent)

[A= Terashima, 1979; B=Govindaraju, 1989; remaining *pv* from Potts and others, 1992; carb=carbonate carbon, org=organic]

Reference	*Description*	*n*	*Mean*	*s*	*pv*			*% RSD*	*% R*
JP-1	peridotite	10	0.068	0.004	0.0764			6	89
GXR-1	jasperoid	10	0.187	0.005	0.15	?	carb	3	125
MRG-1	gabbro	20	0.30	0.01	0.292			4	101
GSD-12	stream sediment	68	0.50	0.03	0.35	?	org	6	143
GSD-6	stream sediment	20	0.97	0.06	0.62	?	org	6	156
STSD-2	stream sediment	24	1.69	0.01	1.60			0.8	106
MAG-1	marine mud	12	2.28	0.01	2.31	A		0.4	99
GXR-2	soil	30	2.87	0.02	2.59		org	0.5	111
SDO-1	shale	32	9.94	0.05	9.95	B		0.5	100
SRM 88b	dolomitic limestone	10	12.69	0.03	12.65	*cv*	carb	0.2	100
SGR-1	shale	14	27.5	0.3	27.03	A		1	102

Duplicate samples	*k*	*n*	*Mean*	*s*	*% RSD*	*Concentration range*	*No. of < (total)*	*No. of < (pairs)*
	66	2	4.84	0.05	1	0.23 to 49.0	0	0

Method blank	*n*	*Mean*	*s*	*3s*	*5s*
	30	-0.02	0.01	0.03	0.05

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Total sulfur by combustion

By Kenneth Joe Curry

Code: N021 Accepted: 1/27/93

Principle

Total sulfur in geologic materials is determined by the use of an automated sulfur analyzer (Jackson and others, 1985, 1987). Approximately 0.25 g sample is weighed and mixed with 1 g vanadium pentoxide flux. The sample is combusted in an oxygen atmosphere at 1370°C where the sulfur oxidizes to sulfur dioxide. Moisture and dust are removed and the sulfur dioxide gas is then measured by a solid state infrared detector. Total sulfur is determined first. If the total S is less than 0.1 percent, S species are not determined. If the total S is greater than 0.1 percent, then methodologically defined S species are determined directly and by difference on separately leached sample splits. The first sample split is leached with 0.1 N hydrochloric acid to remove dilute acid-soluble sulfates. Sulfur is then determined in the leached and washed residue (residue #1). A second sample split is leached sequentially with 0.1 N HCl and then with 0.1 M sodium pyrophosphate to remove acid-soluble sulfates and pyrophosphate soluble organic S. Sulfur is determined in the leached residue (residue #2) and is a direct measure of sulfide S. Acid-soluble sulfate is calculated as the difference between the total S and the S in residue #1. Organic S is calculated as the difference between S in residue #1 and in residue #2.

Interferences

Possible interfering elements are fluorine and molybdenum, both of which can coat the cell walls and the detector. Samples suspected to contain greater than 0.2 percent F or 1 percent Mo should be analyzed by using a reduced sample weight. Also, a halogen trap must be installed in the flow system when higher concentrations of fluorine are present in the samples. A problem may be encountered due to abnormally rapid combustion of organic-rich materials. This problem can usually be corrected by the addition of a retardant (COM-AID) to the sample. It may be necessary to cover some samples completely with vanadium pentoxide to assure complete conversion of the sulfur to the dioxide.

Scope

The reporting range for total sulfur is from 0.05 percent to about 35 percent. Approximately 40 samples can be analyzed in a day.

Apparatus

- Sulfur analyzer, Leco Model SC-132
- Ceramic combustion sample boats
- Tank of high purity oxygen, with regulator

Reagents

- COM-AID, combustion retardant
- Vanadium pentoxide, V_2O_5
- Conditioner, ground coal
- Anhydrone, magnesium perchlorate, $Mg(ClO_4)_2$

- Distributing organization and reference material samples are:
  LECO Corporation coal: 0.33, 0.55, 1.05, 2.96, and 5.10 percent sulfur
  U.S. Geological Survey: SDO-1, GXR-4, SGR-1, GXR-1, and BCR-1
  National Institute of Standards and Technology (NIST): SRM 697, SRM 1633a, SRM 1572, and SRM 113a

Safety precautions

The major potential danger in this procedure is thermal burns to the operator due to contact with the very hot sample boats upon their removal from the furnace. Care must be exercised in removing the boats with tongs. Avoid contact of the hot boats with combustible materials. A lab coat, safety glasses and protective shoes should be worn while operating the instrument. Toxic gases may be produced upon sample combustion, therefore, the instrument should be used under a working exhaust hood, or vented to one. See the *CHP* and *MSDS* for further information.

Procedure

Additional details of the following procedure are in the on-site instruction manual by LECO Corporation (1983).

A. Check power supplies
  1. Press the MONITOR key on the control console keyboard.
  2. The printer will provide a list showing the current status of the various system parameters. If any power supply voltages are out of range, it will be printed in red and an alarm message will be printed. If this occurs, turn off system power and refer to the power supply adjustments section.
  3. If no alarm appears, proceed to next section.

B. Oxygen pressure and flows
  1. Turn on fume hood.
  2. Open valve on oxygen cylinders and set second stage regulator to 30 psi.
  3. Press the GAS key on the control console and observe the oxygen pressure gauge on the front of instrument. The oxygen pressure must be greater than 8 psi.
  4. Observe that the PURGE rotameter is adjusted to a flow reading of 4.0 L/min and the LANCE rotameter is adjusted to a flow reading of 1.0 L/min.
  5. Press the GAS key to stop the oxygen flow.

C. Calibrate balance
  1. Press the SYSTEM UPDATE key on the control console.
  2. Press the 1 key and then the 0 key for quick access to calibrate balance procedure.
  3. Enter the security number and then press the ENTER key.
  4. When the message displays, PUT EMPTY CRUCIBLE ON BALANCE THEN TARE, place an empty crucible on the balance pan and then press the TARE key.
  5. When this message center displays, PUT 1 GRAM IN CRUC, place a standard weight in the crucible.
  6. After a few seconds the balance will be automatically calibrated to the 1-g weight, then the system will return to the operate mode.
  7. Remove the crucible and the 1-g standard weight from the balance.

D. Conditioning the instrument for analysis.
  1. It is a standard operating practice to change out the right side anhydrone tube daily or if during a day's operation when visible moisture and discolorization appear more than a third of the way down the tube.

2. Three to five conditioning analysis should be run at the start of the day. Use a powdered COAL sample for this purpose. At the same time, randomly pick a couple of samples from the job of interest and run them as conditioners (cover with 1 g V_2O_5 pentoxide) to give you an idea as to what range of concentration of sulfur is in the samples.
   NOTE: Any time the instrument has been idle for a period of time or where fresh anhydrone has been installed, you must condition the system again.
3. Select the ID CODE A by pressing the ID CODE key until the letter A appears on the display.
4. Enter the ID number 1 by moving the cursor to the desired position (pressing the YES key moves the cursor left, pressing the NO key moves the cursor right) and then press the 1 key.
5. Press the ENTER key to store in memory.
6. Place a combustion boat on the balance pan. The balance will automatically tare.
7. Add approximately 0.250 g of the COAL CONDITIONER sample into the boat.
8. When the weight is stable, press the ENTER key.
9. Remove the boat from the balance and spread the ground sample evenly in the boat by gently shaking the boat in a back and forth motion.
10. Place the sample boat on the loading tray near the furnace opening.
11. Press the ANALYZE key. The PURGE flow will start immediately. The LANCE flow will start later in the analysis cycle.
12. Slide the viewing window to the open position.
13. Wait until the message center displays LOAD FURNACE (also the load furnace LED lamp will come on and a "beep" will sound) and then slide the combustion boat into the furnace until it touches the boat stop.
14. Slide the viewing window to the close position.
15. Immediately press the ANALYZE key again.
    NOTE: Normally the analysis cycle will start automatically as soon as the sulfur is detected. In very low sulfur analysis, immediately (after inserting the combustion boat) press the ANALYZE key again since the amount of sulfur released will be insufficient to start the analysis automatically.
16. When the analysis is complete, the SULFUR display will indicate the results and the printer will print the value.
17. Remove the spent sample/combustion boat from the furnace.
    NOTE: While the instrument is in the analyzed mode, the balance is freed to weight additional samples, which are then stacked on the loading tray in order of weighing.
18. Repeat steps 6 through 17 to run the remaining conditioner samples.

E. Calibration procedure

1. If the calibration channels have already been preprogrammed with a different range of sulfur standards, select the channel to be used by pressing the SELECT key and then the appropriate number key.
2. Select the form (S, SO_3 or SO_4) of sulfur for calibration (percent sulfur) for total sulfur analysis. A wide variety of standards are used for calibration (see *Reagents* section for type of standards). Choose a standard in the percent range and type of material that is the same as the samples are for analysis.
3. For the determination of the standards, use the ID CODE B by pushing the ID CODE key until the letter B appears on the message center.
4. Analyze three to five samples of the standard in the same procedure as in steps 6 through 17 in the *Conditioning of the instrument for analysis* section.
   NOTE: When using standards other than coal standards, such as ore, rock, or soil standards, add a layer of about 1 g V_2O_5 over the standard after it has been weighed out in the combustion boat. This will help to assure complete conversion of the sulfur to the dioxide.

5. Press the SYSTEM UPDATE key and then the number 1 key.
6. In response to the query 'CALIBRATE SYSTEM' press the YES key. The message center will display CALIBRATE BY STD YES/NO.
7. Press the YES key. Up to the 10 last analyses will be printed from the answer stack and the message center will prompt for entry of the sulfur content of the standard as a percent.
8. Enter the percent of the sulfur in the standard used and then press the ENTER key. The entered value and the old calibration will be printed.
9. Analytical results will be displayed one by one in the message center for selection of calibration calculation. Press the YES key to include and print a result or the NO key to exclude it.
10. When all desired results have responded, the printer will print the new calibration and the last 10 values in the answer stack will be recalculated according to the new calibration value.

F. Sample analysis

1. For the determination of the samples use the ID CODE D by pushing the ID CODE key until the letter D appears on the message center. Then press the ENTER key.
2. Again, follow the same procedure as in steps 6 through 17 in the *Conditioning of the instrument for analysis* section, except add two scoops of vanadium pentoxide (about 1 gram) to cover the sample.

Calculation

Calculations are performed by the instrument's microprocessor, and the percent sulfur is reported for each sample.

Assignment of uncertainty

Table 53 is the analytical results for total sulfur of selected reference materials, duplicate samples, and method blanks by combustion.

Table 53.—Analytical performance summary for total sulfur (percent)

[A=National Bureau of Standards (NBS), 1985; B=NBS, 1982; remaining *pv* from Potts and others, 1992]

Reference	*Description*	*n*	*Mean*	*s*	*pv*			*% RSD*	*% R*
GXR-2	soil	114	0.03	0.008	0.031			27	96
SRM 697	bauxite	10	0.039	0.001	0.052		*cv*	3	75
GSD-6	stream sediment	20	0.07	0.01	0.091			14	77
GSD-12	stream sediment	68	0.09	0.01	0.094		?	11	96
SRM 1633a	coal fly-ash	10	0.195	0.005	0.18	A		3	111
MAG-1	marine mud	10	0.36	0.005	0.39			1	92
SRM 1572	citrus leaves	10	0.406	0.005	**0.407**	B	*cv*	1	100
SRM 1646	estuarine sediment	10	0.98	0.01	0.96			1	102
SDO-1	shale	10	5.44	0.01	**5.35**			0.2	102

Table 53.—Analytical performance summary for total sulfur (percent)—Continued

Duplicate samples	*k*	*n*	*Mean*	*s*	*% RSD*	*Concentration range*	*No. of < (total)*	*No. of < (pairs)*
	52	2	1.82	0.06	3	0.05 to 32	7	2

Method blank	*n*	*Mean*	*s*	*3s*	*5s*
	32	0.0001	0.0001	0.0004	0.0007

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Acid-soluble sulfate, sulfide, and organic sulfur

By K.J. Curry and C.S.E. Papp

Code: N030 Accepted: 8/8/94

Principle

Total sulfur is determined first. If the total S is less than 0.1 percent, sulfur species are not determined. A separately weighed split of the sample is leached with 0.1 *N* hydrochloric acid and the leached sample is analyzed for its sulfur content (residue #1). Another separately weighed split is sequentially extracted with 0.1 *N* hydrochloric acid and 0.1 *M* sodium pyrophosphate to remove the acid-soluble sulfate and the organic sulfur leaving the sulfide behind (residue #2), which is then analyzed for its sulfur content. The acid-soluble sulfate is determined as the difference between the total sulfur and residue #1. The organic sulfur is determined as the difference between residue #1 and residue #2.

Interferences

The method is subjected to the same interferences as the method for the determination of total sulfur, such as fluorine greater than 0.2 percent, or molybdenum greater than 1 percent. These interferences can be minimized by reducing the sample size or by using a halogen trap for the sulfur instrument. High chloride content is deleterious to the instrument and should be noted on the sample submittal form.

Scope

The operating range for this method is from 0.05 percent to about 35.0 percent sulfur. The separation of the sulfur species is operationally defined, dependent on the nature of the extractions used. Due to the complexity of the method, approximately 30 samples can be analyzed per week. This method is applicable to the dissolution of the acid-soluble sulfates but is not suitable for coal-like materials. The acid insoluble sulfates such as barite or alunite will be included with the sulfide fraction.

Laboratory experiments using mixtures of elemental sulfur and quartz, and also standards with known amounts of elemental sulfur, indicate elemental sulfur is not extracted with either the 0.1 *N* HCl or the 0.1 *M* sodium pyrophosphate. If elemental sulfur is present in the sample, it will be included with the sulfide fraction. Laboratory experiments on standards with known amounts of sulfides indicate that the best acid concentration for removing the acid-soluble sulfates with out dissolving monosulfides is the cold 0.1 *N* HCl leach. Higher concentrations of the acid and heat dissolve part or all of the monosulfides. Laboratory experiments on monosulfide minerals show only negligible amounts of monosulfides are dissolved by the 0.1 *M* sodium pyrophosphate.

To make this method more useful to the submitter, it is essential to communicate with the analyst regarding the mineralogy of the sample and the specific needs of the requester.

Apparatus

- LECO SC432 DR Dual Range Sulfur Analyzer
- Lab-line Junior Orbit Shaker
- Gelman Sciences filter Funnel Manifold

- Vacuum line
- Vortex mixer
- Burrell Wrist-Action Shaker
- Orion pH meter
- Millipore membrane cellulose, pH, 47 mm diameter, 0.3 and 0.45 µm pore size filters

Reagents

- Deionized water (DI)
- Hydrochloric acid, HCl reagent grade
- Sodium pyrophosphate, $Na_4P_2O_7 \cdot 10H_2O$ reagent grade
- Vanadium pentoxide, V_2O_5 reagent grade
- LECO Com-Aid (aluminum oxide)

0.1 N hydrochloric acid: 8.3 mL conc HCl diluted to 1 L with DI water

0.1 M sodium pyrophosphate: 44.61 g $Na_4P_2O_7 \cdot 10H_2O$ dissolved in 1 L DI water, which produces a pH 10 solution

Safety Precautions

All acid dilutions are carried out in a chemical hood. Protective clothing, gloves, and safety glasses must be worn. Care must be exercised in removing the hot sample crucibles from the LECO furnace after the combustion of the samples. Toxic gases may be produced upon sample combustion, therefore, the instrument should be used under an exhaust hood. Care must be taken when using V_2O_5 as an accelerator due to the toxicity of the compound. Personnel must read the *CHP* and *MSDS* for each procedure.

Procedure

1. Total S and S in residues #1 and #2 are determined by using a LECO analyzer as described in this manual under "Total sulfur by combustion."
2. Extraction of the acid-soluble sulfate.
   a. Accurately weight out a sample between the range of 0.1500 to 0.1525 g and transfer into a 250-mL glass beaker.
   b. Add 50 mL 0.1 *N* HCl to the beaker, cover it with a watch glass, and place it on the shaker for 3 hours at 100 rpm to leach out the acid-soluble sulfate.
   c. Filter the sample through a vacuum filter apparatus using the 0.3 µm pore size filter.
   d. Wash the residue several times with water to assure that all the acid-soluble sulfate is removed.
   e. Carefully remove the filter containing the residue (residue #1), fold, and place it into a LECO ceramic crucible and allow it to dry (Jackson and others, 1987).
   f. Analyze residue #1 for sulfur on the LECO instrument.
3. Sequential extraction for the removal of acid-soluble sulfate and organic sulfur.
   a. Accurately weigh out a separate split of the sample between the range of 0.1500 to 0.1525 g and transfer into a 250-mL glass beaker.
   b. Leach out the acid-soluble sulfate as in procedure 2, but, place the filter with the residue into a 50-mL centrifuge tube.
   c. Add 20 mL 0.1 *M* sodium pyrophosphate solution, seal the centrifuge tube with its screw cap, and allow it to agitate for 18 hours (overnight) on a wrist-action shaker (Papp and others, 1991).
   d. Remove the sample and filter through a 0.45 µm pore size filter. The filter is rinsed into the filtration apparatus with H_2O and then discarded.
   e. Wash the residue several times with water to assure that the pyrophosphate solution containing the organic sulfur is removed.

f. Carefully remove the filter containing the residue (residue #2), fold, and place it into a LECO ceramic crucible and allow it to dry.
g. Analyze residue #2 for sulfur on the LECO instrument.

A reagent blank is carried through both procedures 2 and 3. The cellulose filter is then analyzed for sulfur on the LECO instrument.

Calculations

The acid-soluble sulfate fraction is reported as the difference between the total sulfur in the sample and in residue #1. Sulfur residue #2 represents the sulfide sulfur fraction. The organic sulfur fraction is reported as the difference between the sulfur in residue #1 and in residue #2.

Based on the weight of each sample, the LECO instrument automatically calculates and prints the sulfur results in percent total sulfur.

Total sulfur - residue #1 = acid-soluble sulfate
Residue #2 = sulfide sulfur
Residue #1 - residue #2 = organic sulfur

Assignment of uncertainty

Table 54 is the analytical results of acid-soluble sulfate, sulfide, and organic sulfur in selected reference materials and method blanks.

Table 54.—Analytical performance summary for forms of sulfur (percent)

[A=Canadian Certified Reference Materials Project, 1991; B=Kane and others, 1990]

Reference	*Description*	*n*	*Mean*	*s*	*pv*	*% RSD*	*% R*
Total sulfur							
LKSD-4	lake sediment	5	1.02	0.02	0.99 A	2	103
LKSD-1	lake sediment	5	1.58	0.01	1.57 A	0.6	101
SDO-1	shale	10	5.35	0.01	5.35 B	0.2	100
RTS-3	sulphide ore tailings	10	9.99	0.08	9.98 A	0.8	100
Sulfate sulfur							
LKSD-1	lake sediment	5	0.11	0.01	--	9	--
LKSD-4	lake sediment	5	0.29	0.01	--	3	--
SDO-1	shale	10	0.74	0.04	--	5	--
RTS-3	sulphide ore tailings	10	1.42	0.04	1.54 A	3	92
Sulfide sulfur							
LKSD-4	lake sediment	5	0.58	0.01	--	2	--
LKSD-1	lake sediment	5	1.28	0.03	--	2	--
SDO-1	shale	10	3.72	0.03	--	0.8	--
RTS-3	sulphide ore tailings	10	8.57*	0.08	8.44 A*	0.9	102

*Sulfide plus elemental sulfur

Table 54.—Analytical performance summary for forms of sulfur (percent)—Continued

Reference	*Description*	*n*	*Mean*	*s*	*pv*	*% RSD*	*% R*
Organic sulfur							
LKSD-4	lake sediment	5	0.15	0.01	--	7	--
LKSD-1	lake sediment	5	0.19	0.02	--	11	--
SDO-1	shale	10	0.89	0.05	--	6	--

No duplicate data available at this time.

Method blank	*n*	*Mean*	*s*	*3s*	*5s*
0.1 *N* HCl	10	0.0004	0.0003	0.0009	0.002
0.1 *M* Na-pyrophosphate	10	0.0004	0.0002	0.0008	0.001

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Carbon, hydrogen, and nitrogen by a CHN elemental analyzer

By Carol J. Skeen

Code N040 Accepted: 11/2/94

Principle

Carbon, hydrogen, and nitrogen are determined in geologic materials by a gas chromatography/thermal conductive analyzer (Culmo and Swanson, 1983). A 1 to 20-mg sample (depending on concentration and/or sample type) is combusted in a pure oxygen environment in the CHN elemental analyzer. Carbon, hydrogen, and nitrogen present in the material are converted to CO_2, H_2O, and N_2 and separated by a frontal gas chromatograph. Concentrations of these gases are determined by thermal conductivity detectors. Acetanilide is used as the calibration standard.

Interferences

The combination of reagents used in the combustion zone provide both efficient oxidative properties and a high-capacity scrubbing efficiency, insuring the complete oxidation of volatile products and the effective removal of common interferences.

Scope

The range of concentration covered is from 0.01 percent for carbon, hydrogen, and nitrogen to an upper limit of a 100 percent for each element; although, concentrations for carbon greater than 90 percent, for hydrogen greater than 10 percent, and for nitrogen greater than 15 percent have not been observed. With the use of the 60-position autosampler and an analysis time of just under 5 minutes per sample, approximately 70 samples can be analyzed in a day with accompanying blanks, duplicates, and controls.

Apparatus

- Perkin-Elmer PE 2400 CHN Elemental Analyzer with autosampler, combustion and reduction tubes, and a microbalance
- Tin vials
- Ultrapure helium and oxygen

Reagents

- Silver vanadate
- Silver tungstate/magnesium oxide
- EA-1000 (chromium oxidizer)
- Copper plus
- Cuprox
- Silver gauze
- Quartz wool
- Combustion standard: acetanilide

Safety precautions

When filling the reaction tubes (combustion or reduction), use a fume hood, safety glasses, gloves, and a lab coat. After using reagents, wash your hands and face thoroughly. When replacing the reaction tubes, always turn off the furnace and allow the tubes to cool to room temperature. To prevent burns, always keep the furnace door closed when the furnace is on. Personnel must read the *CHP* and *MSDS* for each procedure.

Procedure

A. Start-up procedure when the analyzer has been off

1. Turn on the helium (the oxygen may remain on at all times; the helium only needs to be on when the analyzer is on), the printer and the microbalance; then turn on the power switch.
2. Respond to the start-up questions (i.e., time, date, fill pressure and temperatures). Normal operating temperatures are 925°C for the combustion tube and 625°C for the reduction tube. Purge the analyzer with helium (set regulator to 19 psi) for 200 s and oxygen (set regulator to 16 psi) for 60 s; then wait for a warm-up time of 2½ hours to stabilize the detector.
3. After the warm-up time, check the furnace temperatures; purge with helium for 200 s and oxygen for 20 s.
4. Perform a series of blank runs until the runs are reproducible to with ±30 for carbon, ±100 for hydrogen and ±16 for nitrogen.
5. Calibrate the microbalance and prepare all standards and samples by carefully placing the sample in a tared tin vial and recording the weight in a notebook. With micro forceps, seal the vial by flattening and folding in thirds. Recheck the weight to ensure that there are no holes in the vial and place it into instrument via the autosampler or single sample injector.
6. Condition the analyzer by running two samples of acetanilide in a tin vial between blanks with tin.
7. Calibrate the analyzer by first entering the theories for the acetanilide standard by using the parameter key. (Once these are entered, they will remain in memory even when the analyzer is turned off.) Weigh 2 to 4 mg of acetanilide three times, seal in tin vials and enter the weights by using the auto run parameter. The K factors are generated by the auto run parameter. The K factors generated by the acetanilide should reproduce from the mean value to within ±0.15 for carbon, ±3.75 for hydrogen and ±0.16 for nitrogen.
8. Follow operating procedures for analyses (section B).
9. When leaving the analyzer on overnight in standby mode, the helium should be left on and turned down to half pressure to conserve helium consumption. The temperatures may be left at operating levels overnight, or they may be turned down and brought back up with the use of the parameter key for automatic temperature turn-down and wake-up feature.
10. If there is more than 1 day between the operation of the instrument, turn the analyzer off. Before turning the analyzer off, use the diagnostic key to open valve H for a few seconds. The helium should be turned off after the analyzer has been turned off.

B. Operating procedures for the analyses from standby mode

1. Purge the analyzer. (Do this any time the analyzer has been in standby mode). Use the monitor key to observe the sensors for proper operating temperatures and conditions.
2. Set parameters for the analyses via the auto run.
3. Run blanks and calibrate with acetanilide according to the procedures used in start-up.

4. Weigh a 1.8 to 3.2-mg sample on the microbalance and seal in a tin capsule for placement in the autosampler which is coordinated with the auto run parameters which ask for ID number and weight information (any run may be performed singularly by using the single run parameter). If the samples appear to be easily combusted with low carbon content (<30 percent), a 10-mg sample can be used. For very low carbon and nitrogen contents, a sample between 10 and 20 mg should be used. For "difficult to combust" samples, it may be necessary to optimize combustion by the addition of extra oxygen. Follow the Perkin-Elmer instrument manual on pages 6-13 and 6-14 for the parameters to do this.
5. Run a blank, appropriate standard rocks and a duplicate for every 10 samples. After 20 samples, run acetanilide for a calibration check. If necessary, recalibrate the instrument. Monitor blanks for depletion of reaction tubes' chemicals and replace according to manual maintenance direction.
6. Calculations for blanks, K factors, and CHN values are performed by the analyzer and recorded on the printer which is interfaced with the analyzer.

Calculations

A known standard is first analyzed to calibrate the analyzer in micrograms. The calibration factor is then used to determine unknowns. All quantitation is performed on a weight percent basis, using a gravimetric calculation. The system uses a steady state, wave front chromatographic approach to separate the measured gases from the combustion of the geologic material. As the gases elute, each gas separates as a steady state step process, with each subsequent gas added to the previous one. Consequently, each step becomes the reference for the subsequent signal and is in the order outlined as follows:

Nitrogen Signal = Nitrogen Read—Bridge Zero
Carbon Signal = Carbon Read—Nitrogen Read
Hydrogen Signal = Hydrogen Read—Carbon Read

Blank runs are performed by running empty tin vials through the analyzer. Blank values are used to make the necessary correction for the determined element and are determined after a sample run. They need to be within the deviations stated in *Procedure A.5* and are averaged by the system:

Nitrogen Blank (NB) = Nitrogen Read—Nitrogen Zero
Carbon Blank (CB) = Carbon Read—Nitrogen Read
Hydrogen Blank (HB) = Hydrogen Read—Carbon Read

K factors are determined when a known standard (i.e., acetanilide) is analyzed to calibrate the analyzer in terms of micrograms of carbon, hydrogen, or nitrogen. These calibration factors are then used to determine unknowns and should always be within the deviations stated in *Procedure A.10*. The calculation for each element is:

$$\text{K factor} = \text{counts}/\mu\text{g} = \frac{[(\text{read}-\text{zero})-\text{blank}] \times 100}{\text{std. wt.} \times \text{theory wt. \%}}$$

Calculation for a sample run for each element is:

$$\text{\% wt.} = \frac{[(\text{read}-\text{zero})-\text{blank}] \times 100}{\text{sample wt.} \times \text{K factor}}$$

Although the instrument makes all the calculations and prints out the final percent answers for carbon, hydrogen, and nitrogen, the signals and sample weights are also printed. Thus, if necessary, results can be calculated and checked by hand.

Assignment of Uncertainty

In this method, there is selective retention of the gases to produce a steady-state, stepwise signal rather than a peak signal. The stepwise series of gases is then passed through a thermal conductivity detector system. Since measurements are made as stepwise changes from the carrier gas baseline, the variations associated with the quantitation of peak signals in standard chromatography techniques are eliminated. Thus, a broad linear range of operation can be accomplished with the calibration of the analyzer with a single standard material. For analysis of samples with low levels of C, H, or N, sample size can be increased up to 100 mg to produce signal levels comparable to those of a few milligrams of pure organic material. Combustion can be optimized in those cases by adding more oxygen and/or combustion time. The detection limits are thus established by the signal level of the gases and the automatic calculation by the instrument to two significant figures to the right of the decimal point.

The precision obtained in 54 replicate analyses of the calibration standard, acetanilide, expressed as % RSD is 0.45 for carbon, 2.5 for hydrogen and 1.9 for nitrogen. Table 55 shows the analytical results for selected reference materials and duplicate samples by combustion (thermal conductivity). Note that materials SRM 1632b and 1571 were analyzed on an "as received basis" which may explain some oxidation and water absorption of these materials. Some hydrogen *pv* data has been converted from the oxides.

Table 55.—Analytical performance summary for carbon, hydrogen, and nitrogen (percent)

[A=Terashima, 1993 (n=3 to 6); B=Gladney and others, 1987; C=National Institute of Standards and Technology, 1993; remaining *pv* from Potts and others, 1992]

Reference	*Description*	*n*	*Mean*	*s*	*pv*			*% RSD*	*% R*
Carbon, C									
SCo-1	soil	10	0.97	0.02	**0.96**	A	?	2	101
SO-2	soil	10	4.75	0.06	**4.76**	A	?	1	100
SRM 1645	river sediment	11	5.44	0.06	**5.49**	A	?	1	99
SGR-1	shale	10	27.7	0.2	**26.8**	A	?	0.7	103
SRM 1571	orchard leaves	8	46.1	0.4	**46.00**	B		0.9	100
SRM 1632b	coal (bituminous)	4	76.56	0.08	**78.11**	C	*cv*	0.1	98
Hydrogen, H									
SCo-1	soil	10	0.64	0.04	0.65			6	98
SRM 1645	river sediment	11	0.82	0.02	---			2	---
SO-2	soil	10	0.9	0.4	---			**44**	---
SGR-1	shale	10	3.1	0.1	2.22		?	3	141
SRM 1571	orchard leaves	8	6.2	0.1	**5.54**	B		2	112
SRM 1632b	coal (bituminous)	4	5.29	0.08	**5.07**	C	*cv*	2	104

Table 55.—Analytical performance summary for carbon, hydrogen, and nitrogen (percent)—Continued

Reference	*Description*	*n*	*Mean*	*s*	*pv*			*% RSD*	*% R*
Nitrogen, N									
SCo-1	soil	10	0.05	0.01	**0.058**	A	?	20	86
SRM 1645	river sediment	11	0.080	0.006	**0.0797**	B		8	100
SO-2	soil	10	0.19	0.02	**0.22**	A	?	11	86
SGR-1	shale	10	0.83	0.02	**0.82**	A	?	2	101
SRM 1632b	coal (bituminous)	4	1.54	0.03	**1.56**	C	*cv*	2	99
SRM 1571	orchard leaves	8	2.66	0.08	**2.76**	B		3	96

Duplicate samples	*k*	*n*	*Mean*	*s*	*% RSD*	*Concentration range*	*No. of < (total)*	*No. of < (pairs)*
Carbon	14	2	23.2	0.2	0.9	1.7 to 45	0	0
Hydrogen	14	2	3.2	0.1	3	0.54 to 6.2	0	0
Nitrogen	14	2	1.05	0.02	2	0.16 to 3.0	0	0

No method blank information available at this time.

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Chloride by ion-selective electrode following $KMnO_4$-H_2SO_4-HF dissolution

By Phillip Aruscavage

Code: P011 Accepted: 3/2/93

Principle

Chlorine in geologic materials is determined as chloride by the ion-selective electrode (ISE) potentiometric method. The sample is digested in the outer compartment of a sealed Conway diffusion cell with $KMnO_4$, H_2SO_4, and HF. Chlorine is distilled from the outer chamber and reduced to chloride in the inner chamber, which contains Na_2SO_3, and KOH. The chloride is measured directly in the inner chamber with a chloride ion-selective electrode (Aruscavage and Campbell, 1983).

Interferences

High concentrations of ions which form insoluble silver salts could deposit on the membrane surface, causing a malfunction. The diffusion of chloride ions between the outer and inner compartments of the Conway cell separates chloride from this type of interference. Other ions that are potentially problematic to the membrane electrode are bromide, iodide, and hydroxide. The hydroxide molar concentration is constant from sample to sample, iodide is not oxidized in an acidic permanganate solution, and bromide is generally much lower in concentration than chloride for a given sample so that its molar ratio to that of chloride is not a problem. The only other type of interference is caused by high concentrations of sulfur, ferrous iron, or other reducing component which would compete with chloride for the oxidizing power of the rock digestion solution. In such cases the sample size taken for analysis can be reduced to as little as 50 mg. Results are satisfactorily reproducible at this sample level, even with considerable competition from reducing species.

Scope

The operating range for chloride (Cl^-) in geologic materials is 0.01 to 2 percent concentration. Results above 0.01 percent are reported in no more than three significant figures to the nearest 0.01 percent. Analyses are limited by the availability of equipment to approximately 120 samples per week.

Apparatus

- A digital pH/mV meter or specific ion meter (Corning, Orion, etc.)
- A combination chloride ion-selective electrode (Orion)
- Teflon Conway gaseous diffusion cells, a minimum of 40, which are permanently numbered on the top of the lid and on the base
- Large (14x18-inch) oscillating shaker platform
- Digital volumetric pipettes for addition of precise increments of standard chloride solutions
- A microbalance for sample weighings
- An electronic top loading analytical balance for reagent weighings
- Lab ware associated with preparation of all reagents

Reagents

All reagents should be of analytical reagent grade, but it is especially important that they be as chloride free as possible. For example, KOH should contain less than 0.0003 percent Cl, which is not true of all analytical grades of KOH. The use of lab ware should be minimized and the few reusable pieces of plastic lab ware scrupulously cleaned after each use.

Reducing solution: Weigh 22.6 g KOH into a 200-mL plastic or glass container. Add 140 mL distilled water and stir to dissolve. Let stand for 10 minutes while preparing oxidizing solution; then add 1.12 g anhydrous Na_2SO_3. Transfer into a capped plastic bottle and shake well. Make up solutions fresh each day.

Oxidizing solution: Weigh 2.6 g $KMnO_4$ into a 100-mL sterilized plastic or glass container (assuming the determination of 34 samples plus 7 standards). Add 50 mL 15 percent H_2SO_4 or 35 mL DI water and 15 mL 1:1 H_2SO_4 previously mixed. *Previously mix and cool the H_2SO_4. If the conc H_2SO_4 is diluted at the time of the preparation of the oxidizing solution, the heat of reaction will dissipate the digestive and oxidizing strength of the solution.* Stir to dissolve the $KMnO_4$. To 40 mL $KMnO_4$ solution in a plastic container, add 160 mL conc HF from a plastic graduated cylinder and mix. (This should be done after completing reducing solution prep and as the last step).

Safety precautions

The usual precautions, i.e., use of an exhaust hood, protective clothing, safety glasses or safety shield, and gloves, should be observed when handling strong acids, plus added caution in handling the HF solution. See the *CHP and MSDS* for further information. When pipetting from the oxidizing solution is not in progress, the plastic container should be covered.

Procedure

1. Clean and set aside on a lab cart the requisite number of Teflon cells for that day's determinations, including seven cells for a reagent blank and six standard solutions.
2. Weigh 200 mg (less if warranted by the presence of sulfides or other reducing substances) of each sample into a confined area of the outer compartment of the appropriate numbered Teflon cell. Enter weights into a record book or computer.
3. Add the appropriate increments of standard (100 ppm or 1,000 ppm stock solution) to the outer compartment of each of seven cells using digital volumetric pipettes. The specific concentrations added should be 0, 10 or 20, 50, 100, 200, 500, and 700 or 1,000 µg Cl-.
4. Prepare the oxidizing and reducing solutions. Add the standard solution in a manner that precludes premature mixing of the two solutions. Close the cells, tighten the lids, and place on the oscillating platform as described in #6.
5. Pipette 2.5 mL reducing solution into the inner compartment of each of the cells using a 5-mL digital volumetric pipette and cover them with their respective lids.

6. Pipette 3.0 mL oxidizing solution into the outer compartment of each sample- and standard-cell (one cell at a time), again using a 5-mL digital volumetric pipette. Exercise care in adding the solution by holding the pipette in a vertical position at a point 180° opposite the sample location. As necessary, move the tip of the dispensing pipette around the perimeter of the outer chamber to compensate for excessive flow of the liquid in one direction or another. The object of these maneuvers is to prevent the premature mixing of the oxidizing solution with the sample prior to closure of the Teflon cells. With these precautions, there should be no chlorine lost to the atmosphere and no wild scramble to tighten the lid of the cell before such loss might occur. Immediately after completing addition of oxidizing solution to the cell, cap it, and tighten the lid. Rotate the cell very gently to ensure mixing of the sample and solution and place on an oscillating shaker platform.
7. Repeat the process in #6 until all of the solid samples have been mixed with oxidizing solution. One or two cells should be used as reagent blanks. Turn platform on low speed.
8. Allow the samples to mix on the oscillating platform overnight for a total of 14 to 18 hours. By implication this means that the above procedures are initiated in late afternoon. About 2 to 3 hours are required for the preparation of 40 sample cells, depending on the operational skills of the analyst.
9. Store the combination chloride electrode overnight in a 50- to 100-ppm chloride solution.
10. Turn off the oscillating platform after the requisite time. Check filling level of electrode before each reading. Fill if necessary with Cl^- electrode filling solution.
11. Remove the blank cell, unscrew its lid, and slightly immerse the previously rinsed (with Millipore water) and dried (gently wiped with a Kimwipe—Do not rub bottom of electrode) combo chloride electrode into the inner cell compartment. Move the electrode around in the compartment to stir the contents and pick up any droplets on the edge. Observe the highest mV reading (most positive) and allow the electrode to remain immersed in the cell for a period of at least half and hour, but not longer. This is for equilibrating the electrode.
12. Measure the emf in mV of each of the standard solutions by successively removing their lids, rinsing and drying the electrode, immersing and moving the electrode around in the inner cell compartment. Allow the mV reading for each cell to come to equilibrium 5 minutes before recording the value.
13. Repeat the process in #12 for each of the sample cells.

Calibration

For each day's set of determination, a suite of seven synthetic standard solutions are prepared and carried through the same procedure as the samples. A calibration curve is derived from semi-log plot of the mV readings versus the chloride concentration values of the standards in ppm. The concentrations of the unknown samples are read from this concentration plot. A maximum number of analyses can be made if a new set of samples are being prepared while current readings are being made. If several days or more of determinations are being made, it is possible to read the unknown concentrations from a composite plot of the various daily standard values due to the consistency of measurement of the combination chloride electrode, but it is much better to derive a new plot for each suite of samples due to daily differences in temperature and humidity.

Calculation

The calculations are simple, requiring only the division of the concentration value of the sample solution derived from the calibration curve by the weight of the sample in micrograms times 100 percent. This value represents the percent of chloride in the rock, which is then rounded off to the nearest 0.01 percent. If a computer is available, the mV readings for each standard solution are entered into the computer which print out the calibration curve. By entering the weights and the mV readings for each sample, results calculated for each sample are printed out by the computer.

Assignment of uncertainty

Table 56 is the analytical results of chloride for selected reference materials, duplicate samples, and method blanks.

Table 56.—Analytical performance summary for chloride (percent) by ISE

[Proposed values from Potts and others, 1992]

Reference	*Description*	*n*	*Mean*	*s*	*pv*	*% RSD*	*% R*
AGV-1	andesite	57	0.012	0.003	0.012	25	100
RGM 1	rhyolite	10	0.055	0.001	0.051	2	108
SRM 278	obsidian	18	0.060	0.006	*0.0622*	10	96
JR-1	rhyolite	37	0.097	0.008	0.092	8	105
MESS11	marine sediment	10	0.80	0.05	**0.820** *cv*	6	98
MAG-1	marine mud	19	3.35	0.08	**3.1**	2	108

Duplicate samples	*k*	*n*	*Mean*	*s*	*% RSD*	*Concentration range*	*No. of < (total)*	*No. of < (pairs)*
	34	2	0.15	0.007	5	0.002 to 1.00	0	0

Method blank	*n*	*Mean*	*s*	*3s*	*5s*
AGV-1	21	0.01	0.002	0.005	0.008

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Fluoride in silicates by ion-selective electrode following $LiBO_2$ fusion and HNO_3 dissolution

By Sarah Pribble

Code: P021 Accepted: 11/22/93

Principle

Fluorine in silicate rocks and minerals is determined as fluoride by the ion-selective electrode potentiometric method (Bodkin, 1977; Cremer, and others, 1984). Samples are fused with lithium metaborate and dissolved in nitric acid. A complexing buffer is added, and the potential of the solution is determined with a pH meter with an absolute millivolt scale. A known volume of standard fluoride solution is added and the potential is again checked. The concentration of fluoride in the sample is computed using the potential difference and the Nernst equation.

Interferences

1,2-diaminocyclohexane-NNN'N'-tetraacetic acid (DCTA) buffers the solution to pH 5.5. At a pH below five, hydrogen complexes fluoride as the undissociated acid HF and the ion HF_2^-. At a pH greater than seven, hydroxide ion interferes when the level of hydroxide is greater than one-tenth the level of fluoride ion present. DCTA also controls aluminum and iron interference.

Scope

Fluoride can be determined in silicate rocks and minerals with a lower reporting limit of 100 ppm and an upper limit of 2.7 percent without modification of this procedure. If a sample is suspected of having a fluoride concentration greater than 2.7 percent, another fusion should be made and a suitable aliquot diluted with an appropriate volume of DCTA buffer prior to measurement. Approximately 30 samples can be analyzed in a day.

Apparatus

- Beakers, 8-oz (220 mL) polypropylene, with tightly fitting covers
- Magnetic stirrers
- Orion Expandable Ion Analyzer EA 940 or Corning pH Meter 130 or equivalent
- Orion Combination pH Electrode 91-05
- Orion Combination F Electrode 960900
- Stirring bars, Teflon coated, magnetic
- Crucibles, graphite
- Muffle furnace, Lindberg/Hevi-Duty

Reagents

- Lithium metaborate, $LiBO_2$, anhydrous
- Deionized water (DI)

Nitric acid, 4 percent (v/v): Prepare by adding 4 parts 70.71 percent HNO_3 ('BAKER INSTRA-ANALYZED') to 96 parts DI water. Arrange for delivery from a 100-mL Teflon stopcock-type automatic pipet.

Standard fluoride solution: Heat NaF in a platinum crucible at low red heat (640°C) for 1 to 2 hours. Cool, weigh 1.105 g, NaF, dissolve in DI water and dilute to 500 mL. Transfer to a polyethylene bottle for storage (1 mL = 1000 g F).

Complexing buffer solution: To 1.5L DI water add the following:

1. 18.2 g DCTA (1,2-diaminocyclohexane-NNN'N'-tetraacetic acid) (available from Mallinckrodt), also known as DCYTA (1,2-cyclohexylenedinitrilo-tetraacetic acid) (available from Eastman)
2. 300 g sodium citrate dihydrate, $C_6H_5Na_3O_7{\cdot}2H_2O$.
3. 60 g NaCl.

Stir magnetically until dissolved. Adjust the pH to 6.85 with 40 percent (w/v) NaOH and HCl. Dilute to 2L with DI water. Arrange for delivery from a 100 mL Teflon stopcock-type automatic pipet.

Safety precautions

All work with open or uncapped reagents must be done in a chemical hood. Protective clothing, safety glasses, and gloves must be worn. See the *CHP* and *MSDS* for further information concerning first-aid treatment and disposal procedures used in this method.

Procedure

1. Mix 200 mg sample with 1.2 g $LiBO_2$. Transfer the mixture to a graphite crucible and fuse in a muffle furnace at 900°C for 10 min.
2. While the sample is fusing, add to an 8-oz (220 mL) polypropylene container a magnetic stirring bar and 100 mL of 4 percent (v/v) HNO_3 with the automatic pipet. Prepare a reagent blank by dissolving 1.2 g $LiBO_2$ in 100 mL 4 percent HNO_3.
3. Begin stirring the solution magnetically as the fusion nears completion. Remove the crucible from the muffle, swirl it, and then pour the molten bead into the container.
4. Cover the container and continue stirring until the sample is dissolved—usually about 15 minutes.
5. When solution is complete, add 100 mL buffer from the automatic pipet. Stir well, cover, and set aside. Also add 100 mL buffer to the blank solution.
6. From the standard NaF solution prepare 10 and 100 ppm fluoride solutions.
7. Use the blank solution to prepare a calibration curve as follows:
   Add 0.2 mL 10 ppm NaF solution to the blank, stir and immerse the fluoride electrode in the stirring solution. When a constant potential reading is obtained (usually 5 min), record the millivolts (mV). Continue in the same manner with the addition to the same solution of the following increments:

   0.5 mL of 10 ppm
   0.8 mL of 10 ppm
   0.2 mL of 100 ppm
   0.5 mL of 100 ppm
   0.8 mL of 100 ppm
   0.2 mL of 1,000 ppm
   0.5 mL of 1,000 ppm
   0.8 mL of 1,000 ppm

8. Using semi-log paper, plot the concentration in ppm on the vertical or log axis and the mV readings on the horizontal axis. Draw a straight line from the highest concentration to 0.15 ppm. Determine the slope by subtracting mV readings a decade apart in concentration. The theoretical slope varies with temperature, but between 20 and 25°C, it is approximately 58 mV for a univalent electrode. The standards must be run each time fluorine is determined.
9. Immerse the electrode in the sample solution, stirring as before. Record the mV reading after 5 min.
10. Use the foregoing reading with the graph to determine the apparent concentration in ppm of the unknown. Approximately double the apparent concentration; add that amount of standard fluoride to the solution, stir, and again record the potential after 5 min. This procedure should lead to a ΔE of approximately 15 to 30 mV.

Calculation

Calculate the exact concentration of the initial solution using the following form of the Nernst equation:

$$C = \frac{C^{*}\left[Vs/(Vx+Vs)\right]}{(\text{antilog}\ \Delta E/S) - [Vx/(Vx+Vs)]}$$

where

C = Sample concentration, µg/mL
C^{*} = Concentration of addition before adding to sample, µg/mL
Vx = Sample volume
Vs = Volume of addition
ΔE = Potential difference between initial and final mV values with addition of standard
S = mV span of electrode for decade of interest; i.e., the slope.

therefore:

$$\text{percent F} = \frac{[\mu\text{g/mL (i.e. C)}] \times (200\ \text{mL}) \times 100}{1000\ \mu\text{g/mg} \times \text{weight (mg)}}$$

Report the values to two decimal places.

Assignment of uncertainty

Table 57 shows the fluoride analytical results for reference materials, duplicate samples, and method blank by this method in the Menlo Park and Denver laboratories.

Table 57. Analytical performance summary for fluoride (ppm) by ISE

[Proposed values from Potts and others, 1992; note Denver laboratory uses 80 mg sample, 480 mg flux, and a platinum crucible]

Menlo Park, California laboratory data

Reference	*Description*	*n*	*Mean*	*s*	*pv*	*% RSD*	*% R*
JB-2	basalt	6	100	0	101	0	99
W-1	diabase	10	248	18	230	7	108
RGM-1	rhyolite	27	305	33	342	11	89
BHVO-1	basalt	10	390	32	385	8	101
AGV-1	andesite	17	362	57	420	16	86
BCR-1	basalt	10	517	24	490	5	106
STM-1	syenite	27	779	72	910	9	86
GXR-1	jasperoid	10	1,260	52	1,260	4	100
G-2	granite	16	1,270	54	1,260	4	101
GSP-1	granodiorite	19	3,560	214	3,600	6	99
GXR-3	hot spring deposit	10	8.4 %	0.2	8.62 %	2	98

Duplicate samples	*k*	*n*	*Mean*	*s*	*% RSD*	*Concentration range*	*No. of < (total)*	*No. of < (pairs)*
	10	2	247	6	2	236 to 1,835	0	0

Method blank	*n*	*Mean*	*s*	*3s*	*5s*
Quartz	13	20	10	29	48

Denver, Colorado laboratory data

Reference	*Description*	*n*	*Mean*	*s*	*pv*	*% RSD*	*% R*
RGM-1	rhyolite	14	353	11	342	3	103
BHVO-1	basalt	8	425	43	385	10	110
STM-1	syenite	20	926	31	910	3	102
GXR-1	jasperoid	16	1,300	100	1,260	8	103
GSP-1	granodiorite	25	3,740	175	3,600	5	104

Duplicate samples	*k*	*n*	*Mean*	*s*	*% RSD*	*Concentration range*	*No. of < (total)*	*No. of < (pairs)*
	16	2	1,269	35	3	200 to 4,200	0	0

Method blank	*n*	*Mean*	*s*	*3s*	*5s*
Quartz	11	79	8	24	40

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Ferrous oxide by potentiometric titration

By Clara S.E. Papp, Phillip Aruscavage, and Elaine Brandt

Code: P051

Accepted: 2/16/93
Revised: 4/6/96

Principle

Half a gram of sample is digested in a platinum crucible with a boiling mixture of sulfuric and hydrofluoric acids. After digesting, the crucible and the digestate are immersed into a solution of boric, sulfuric, and phosphoric acids. The solution is potentiometrically titrated with potassium dichromate by using a platinum indicator electrode (Peck, 1964; Cremer and others, 1984; Jackson and others, 1987).

Interference

The oxidation of ferrous sulfate in air is strongly catalyzed by hydrofluoric acid (Hillebrand and others, 1953). Air must be excluded during dissolution of the sample. In this procedure, steam generated by the boiling acid mixture displaces much of the air from the reaction vessel. The oxidation of ferrous iron by residual air is negligible. Boric acid prevents the catalytic oxidation effect of hydrofluoric acid by converting it to fluoboric acid (Hillebrand and others, 1953). This conversion serves also to minimize the attack by hydrofluoric acid on the glassware.

Some micas dissolve quickly, and clear solutions of these minerals tend to bump during boiling. The first sign of bumping indicates that dissolution of the mineral is complete, and heating should be discontinued, to avoid a loss of sample. The decomposition of garnet is seldom complete after a single treatment with the mixed acids. Usually the solution must be decanted from the residue and the residue redigested with a new portion of mixed acid (sometimes several times) to obtain complete dissolution. The solutions obtained are titrated separately. Fine grinding, which facilitates dissolution, is not advised because such treatment oxidizes ferrous iron (Hillebrand and others, 1953).

Tramp iron introduced during sample grinding causes high results, not only because of the additional ferrous iron introduced but also because ferric iron in the sample may be reduced by the introduced metal. Mechanical grinding devices equipped with steel plates are to be avoided.

Chromite is not dissolved, and other oxide minerals such as ilmenite and magnetite may be incompletely dissolved if present in large amounts. Complete dissolution of ilmenite and magnetite may be effected by repeated treatments, as with garnet. Because of the uncertain composition of chromite, a correction for its ferrous iron content based on the amount of chromium present is only approximate.

Siderite dissolves slowly in the mixed acids, and a residue generally remains after the normal digestion period. This mineral occurs in many sedimentary or metamorphic rocks containing finely divided carbon, which obscures the presence of a siderite residue. If a sample is known to contain siderite, the residue should be tested.

Certain silicate minerals that contain ferrous oxide, such as staurolite and tourmaline, are insoluble in the mixed acids. Other methods must be used to determine their ferrous iron content. The Mitscherlich method (Hillebrand and others, 1953), in which the sample is decomposed by heating it with sulfuric acid in a sealed tube, is not entirely satisfactory. In another method (Groves, 1951), the sample is decomposed by fusion with sodium metafluoborate in an inert atmosphere. Sulfides interfere in both methods.

Pyrite is not appreciably attacked by the mixed acids and the ferrous iron present in pyrite is not included in the reported value for ferric oxide. If pyrite is the only mineral containing sulfur, a correction can be calculated from the sulfur content of the sample.

The method fails if any constituents in the sample are either oxidizing or reducing agents. Some of these are mentioned in the following paragraph. If corrections cannot be made, the analyst should note in his report that the ratio of ferrous oxide to ferric oxide is unreliable.

Pyrrhotite and a few other sulfide minerals are decomposed by the action of the mixed acids, and hydrogen sulfide released may reduce ferric iron causing a large error in the apparent amount of ferrous iron. Manganese dioxide will oxidize ferrous iron when the sample is dissolved. Vanadium in the trivalent state reduces ferric iron and in the pentavalent state oxides ferrous iron. Tetravalent vanadium does not react with iron in either of its valences nor is it oxidized by potassium dichromate. Many kinds of organic matter reduce potassium dichromate and consequently result in high results for ferrous iron. Potassium permanganate is a less satisfactory oxidant than is potassium dichromate; because of its high oxidation potential, it reacts with an even greater variety of organic compounds. The determination of ferrous iron in the presence of organic matter is discussed by Nicholls (1960).

Scope

The lower reporting limit is 0.01 percent FeO. It takes approximately 15 min to process a sample.

Apparatus

- Brinkmann Metrohm 636 Titroprocessor
- Metrohm Dosimat EJ65
- Pt indicator electrode and calomel reference electrode

Reagents

All reagents are analytical grade except the $K_2Cr_2O_7$ which is G. Frederick Smith Certified primary grade.

- Deionized water (DI)

Saturated potassium chloride, KCl solution: To 100 mL DI water add as much KCl as the water can dissolve at room temperature

- Hydrochloric acid, HCl conc
- Hydrofluoric acid, HF conc
- Sulfuric acid, H_2SO_4 conc
- Phosphoric acid, H_3PO_4 conc
- Boric acid, H_3BO_3 granular

Potassium dichromate solution 0.06262 N: Fill a 2-L storage bottle with DI water the night before preparing the $K_2Cr_2O_7$ solution so it stabilizes at room temperature. From this transfer about 1L to a 2-L volumetric flask. Measure the temperature of the water and use table 58 to determine the amount of $K_2Cr_2O_7$ required for that temperature. Weigh this amount using a Sartorius electronic balance. Transfer the $K_2Cr_2O_7$ to the volumetric flask. Swirl until it dissolves. Dilute the solution to the mark with the rest of the DI water from the bottle and mix.

Table 58.—Weight of potassium dichromate required for water temperature

H_2O, °C	$K_2Cr_2O_7$, g
21	6.147
22	6.146
23	6.144
24	6.143
25	6.141
26	6.140
27	6.138
28	6.137
29	6.135
30	6.134

Dissolving solution, boric acid: Weigh out 50 g boric acid on balance. Transfer to a clean 2-L beaker. Add 1,500 mL DI water, 175 mL conc H_2SO_4, and 200 mL conc H_3PO_4. Stir, cover, and heat on steam bath until boric acid dissolves. Pour carefully while hot into a 2-L polypropylene storage bottle. Dilute to the 2-L mark and mix.

Standard spike solution: Weigh 3.900-g ferrous ammonium sulfate, add to 500 mL DI water in a clean 1-L volumetric flask, add 11 mL conc H_2SO_4, swirl to dissolve, then add DI water to 1-L mark and mix. Store in plastic bottle.

Safety Precautions

Safety glasses, protective gloves, and lab coats must be worn. Dissolution of samples must be done in a vent hood. Wash hands thoroughly each time after handling acids. See the *CHP* and *MSDS* for further information concerning first-aid treatment and disposal procedures for chemical products used in this method. Carbonate-rich samples may splatter and bubble over when adding acid (add acid slowly).

Procedure

USGS Standards are used to check the quality control for the analytical procedure. Each day, three to five ferrous iron "Spikes" are run to calculate the average spike for the day. A small constant spike of ferrous iron is added to each sample after the digestion stage to minimize titrator error for samples with very small amounts of FeO.

Additional details of the procedure are in the on-site instruction manual by Metrohm, 1978.

1. Turn dial on electric heater to 60. It needs at least 15 to 20 min to warm up. Weigh out the number of samples to be analyzed in a day.

2. Turn on Dosimat by pressing red lever on the left which activates the magnetic stirrer. (This *must* be done before turning on Titroprocessor).
3. Turn on Titroprocessor by pressing the red button on left rear. Display should read "88888888...." Fill levers on Dosimat will activate and then the display will read "36 0.000."
4. On console, press in the year, month, day, (i.e.: 921001) then ENTER button.
5. Press RESET button, display will read "Crd". Insert card A in direction of the arrow on the card and withdraw slowly. This is the calculation card. Display will read "13 .4500000."
6. Press RESET button, display will read "Crd". Insert card B in the direction of the arrow on the card and withdraw slowly. This is the program card. Display will read "0". Steps 5 and 6 *cannot* be reversed.
7. Run out any air bubbles from the burette by lifting the red switch lever on the right of the Dosimat and then depressing it to refill the burette.
8. Insert the platinum electrode in the left slot of the holder; place the Ag/AgCl electrode in the right slot. (Be sure the calomel electrode is filled with saturated KCl and the rubber stopper opened).
9. In a clean 250 mL beaker, place a magnetic stirring bar and add 50 mL of *dissolving* solution. Dilute to 150 mL with DI water. This will be the first blank.
10. Lift the electrode holder and set the beaker on the Dosimat stirrer base. Lower the electrodes into the solution but be sure they clear the stirring bar.
11. Shake the bottle of Fe^{++} "Spike" solution and use a pipettor to add 1,000 µL of the standard solution to the beaker. (Be sure there are no air bubbles in the pipette tip). After 10 s, press the GO button on the titroprocessor. (Use a new plastic tip on the pipettor each day or more frequently if necessary).
12. While the titration is proceeding automatically, the second spike-blank solution may be prepared.
13. When the titration has been completed, the titroprocessor will print out the data for mV potential, volume of titrant used and the percent FeO.
14. After the data has been printed out, lift the electrode assembly, wash off the electrodes with DI water, and replace the beaker with the second blank solution. Repeat procedure as in the first blank run (#10-13).
15. Run a third blank. If the range of percent FeO for the three blanks is no greater than 0.0009 percent use the average of the three as the blank value. Run five blanks if there is a greater discrepancy. Type in "14" on the console, then press MOD button. Type in the average blank then press ENTER button. Replace the solution beaker, after rinsing off the electrodes with a small beaker of distilled water.
16. Digest the sample in the following manner:
    a. One-half gram of sample is weighed into a platinum crucible.
    b. A mixture of 5 mL H_2SO_4, 5 mL of HF, and 5 mL H_2O is added to the sample.
    c. The mixture is digested for 10 min on the electric heater.
    d. The crucible is removed from the heater and immersed in a solution containing boric, sulfuric, and phosphoric acids.
    e. The sample is titrated with potassium dichromate.
17. During the titration a second sample can be digested. Enter the weight for each consecutive sample by pressing "12" MOD on the console and typing in appropriate weight.

Manual calculation

$$\% \text{ FeO} = \text{mL } 0.06262\ N\ K_2Cr_2O_7 \times \frac{45}{\text{sample weight}} \times 100$$

Calculations for percent FeO are done automatically on an HP85 computer.

Assignment of uncertainty

Table 59 is the analytical results of ferrous oxide for selected reference materials, duplicate samples, and method blank by potentiometric titration.

Table 59.—Analytical performance summary for FeO (percent)

[Proposed values from Potts and others, 1992]

Reference	*Description*	*n*	*Mean*	*s*	*pv*	*% RSD*	*% R*
FK-N	potash feldspar	10	0.023	0.007	0.06 ?	30	38
SRM 278	obsidian	10	1.31	0.01	**1.36** *cv*	0.8	96
W-2	diabase	42	8.29	0.05	**8.31**	0.6	100
BCR-1	basalt	30	8.77	0.04	**8.88**	0.5	99
SARM-5	pyroxenite	10	8.77	0.05	10.59 *cv*	0.6	83

Duplicate samples	*k*	*n*	*Mean*	*s*	*% RSD*	*Concentration range*	*No. of <* (total)	*No. of <* (pairs)
	73	2	3.58	0.01	0.4	0.06 to 26.6	0	0

Method blank	*n*	*Mean*	*s*	*3s*	*5s*
	31	0.005	0.002	0.007	0.01

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Uranium and thorium by delayed neutron counting

By R.J. Knight and D.M. McKown

Code: R011 Accepted: 10/13/93

Principle

Delayed neutron counting (DN) is a nuclear activation analysis method that is used to measure uranium and thorium in complex geologic sample matrices without chemical processing. Neutron irradiation of thorium and uranium induces nuclear fission reactions yielding fission products that subsequently decay by delayed neutron emission. Most other naturally occurring elements undergo neutron capture reactions yielding radioisotopes which subsequently undergo beta/gamma decay. Delayed neutrons from an irradiated sample can be selectively and quantitatively counted with practically no interference from beta/gamma emitters.

This procedure for the simultaneous determination of uranium and thorium employs two equivalent, sequential irradiation-counting cycles for each sample consisting of individual uranium, thorium, and oxygen standards, and sample aliquots. A custom-built, automated DN facility integrates the irradiation termini, transfer systems, and neutron counters with a computer that provides on-line experiment control and data handling. First a Cd-shield epithermal neutron irradiation cycle is performed to maximize the thorium fission contribution relative to uranium. A thermal neutron irradiation cycle is then performed which yields predominately uranium fission. Using the sensitivity data for each elemental standard measured individually for each irradiation-counting condition, an iterative algorithm is applied to the gross neutron-counting data for a composite sample to resolve individual contributions and compute the concentrations of uranium and thorium. A detailed description of the DN principles, facilities, and procedure has been published by McKown and Millard (1987).

Interferences

There are three types of potential interferences: nonfission delayed neutron emitters, uranium and thorium interelement interference, and anomalous levels of certain elements which affect the standard/sample sensitivity equivalency.

The only direct source of nonfission delayed neutron interference arises from the activation of O-17 and Be-9. These interferences are insignificant in the analyses of most geologic materials because oxygen is accounted for by standardization, and Be is low in abundance and its activation product is very short-lived. Another neutron-counting interference, indistinguishable from the DN signal, may arise from γ (gamma), n (neutron) reactions during the counting cycle caused by extreme levels of very high energy gamma rays emitted from a sample. This interference is insignificant except for samples with highly anomalous concentrations of beryllium and fluorine. Such samples are considered unsuitable for DN analysis.

Even under optimum conditions, thorium and uranium represent a mutual interference to each other. The iterative data reduction algorithm used in this procedure adequately resolves and corrects this interference for all geologic materials that exhibit a thorium-to-uranium ratio greater than three.

Highly anomalous levels of Li, B, Cd, and Gd in a sample can seriously affect the accuracy of DN results because of neutron shielding (flux depression) within the sample. Samples of this type are not suitable for DN analysis. Similarly, the analysis of highly carbonaceous materials, such as coal, and ammonium compounds, may yield erroneously high thorium values due to neutron thermalization within the sample. To minimize this error, samples must be designated as carbonaceous and run with standards of equivalent matrix.

Scope

The method is generally applicable to a wide variety of geologic materials, including most common silicate rocks, soils, and sediments that exhibit a thorium-to-uranium ratio greater than three. Most moderately mineralized materials, except those highly anomalous in F, Be, Li, B, Cd, or Gd, are also generally suitable for DN. The analysis of uranium and thorium ores may exhibit decreased sensitivity and confidence for thorium if the thorium-to-uranium ratio is less than three, and similarly, for uranium if the ratio is greater than 50. Coal matrix samples are suitable for DN analysis if designated as such.

The reporting limits for the analysis of suitable 10 g sample are about 0.1-300 ppm for uranium and 1-900 ppm for thorium.

Apparatus

Custom-built delayed neutron facility (USGS-TRIGA Reactor)

Vial heat-sealer
2-dram polyvials
Pneumatic-transfer capsules

Reagents

None

Safety precautions

This procedure requires on-line access to the USGS TRIGA reactor and thus entails potential radiological hazards. All analysts (DN operators) must be trained and receive authorization as experimenters (DN operators) under the provisions of a valid Reactor Utilization Permit, and Operation Reference Manual (ORM), Section IV (1991).

Procedure

Additional details of the procedure are in the on-site ORM. This manual is regularly updated and used for training. No analyst is allowed to operate the system without this training.

1. Load 2-dram polyvial full (-10 g silicate)
2. Group into experimental run sets consisting of 20 samples, U, Th, O standards, and QC monitor (ORM, Sect. I).
3. Prepare computer sample files corresponding to the run sets using the computer program SFPREP (ORM, Sect. II. A. 1-4).

4. Tare the computer-interfaced Mettler balance using an empty 2-dram polyvial, and weigh each sample using the program SFWGT (ORM, Sect. II. A. 5) to automatically enter sample weights into corresponding sample files.
5. Trim, seal, and place polyvials into rabbits, and stack into DN system magazines.
6. For a group of sample sets (sample files) to be included in a DN analysis run, create and zero corresponding data files on a DN-nn Run Disk using the programs DNOPEN and DNPREP (ORM, Sect. II. B).
7. Prepare for a DN analysis run session by scheduling reactor time and health physics coverage, and check that the DN system electronics are turned on (ORM, Sect. III).
8. Place a blank test rabbit in each DN system changer and initiate a test run using the automatic system control program DN (ORM, Sect. IV., A,B). Confirm that all parts of the DN analysis system are functioning properly.
9. Place a sample set magazine on the DN system changer and initiate the sample set run using the automatic system control program DN (ORM, Sect. IV. D). Repeat for each sample set magazine corresponding to the DN run data disk.
10. After a DN run session is completed, reduce the raw counting data to U and Th concentration values and generate an analysis report using the program DNCALC or DNAUTO, an auto-sequencing version of DNCALC (ORM, Sect. VI).

Standardization of Instrument

Operating conditions:

Instrument Power	ON (Ref. ORM, Sect. III)
Initial Test Run	OK (Ref. ORM, Sect. IV, B)

Calibration is performed automatically during data reduction using the instrument response obtained for U, Th, and O standards run with each experiment set of 20 samples.

Standards:
Uranium standards are prepared by homogeneously doping a low-uranium rock powder (dunite DTS-1, which contains 3 ppb U and 10 ppb Th) with uranium standard solutions prepared from isotopically normal uranium oxide (National Bureau of Standards SRM 950a). Thorium-doped standards are prepared in a similar fashion using solutions prepared from reagent grade thorium nitrate. The undoped DTS-1 (USGS reference material) is used as an oxygen standard. Weighed aliquots of these materials, sealed in 2-dram polyvials, constitute a set of reusable working standards for the DN analysis procedure. The calibration value for each working standard is verified by replicate analyses of a set of at least five reference material samples for which reliable literature values are available (McKown and Millard, 1987).

Calculation

Raw data deconvolution and comparison to standard sensitivities using computer programs DNCALC or DNAUTO (ORM, Sect. VI).

Assignment of uncertainty

From McKown and Millard (1987) and Millard and Keaten (1982), the DN method is inherently more sensitive to the measurement of uranium than to the measurement of thorium. Comparing the 3σ uncertainty of the counter background with the uranium sensitivity yields an absolute detection limit of 1 μg uranium, which corresponds to 0.1 ppm (μg/g) uranium in a 10-g sample. For thorium, the minimum detectable count rate depends on counter background plus uncertainties in correcting the gross counts for oxygen and uranium contributions. For samples having a thorium to uranium ratio greater than three, the 3σ detection limit for thorium is about 10 μg thorium, or 1 μg/g for a 10-g sample. The detection limit for thorium is correspondingly higher if the thorium to uranium ratio is less than three. Thorium is not measured reliably, even at high levels, if the thorium to uranium ratio is less than one.

The data reduction program DNCALC (ORM, Sect. VI) automatically generates and reports an analytical uncertainty estimate (coefficient of variation) for each uranium and thorium value based on appropriate propagation of the counting statistics (measurement uncertainty) associated with each individual sample and standard counting interval.

Table 60 is the analytical results of uranium and thorium for selected reference materials, duplicate samples, and method blank. Please note: duplicate samples of submitted materials are not run routinely due to time and cost constraints.

Table 60.—Analytical performance summary for U and Th (ppm) by DN

[A=National Bureau of Standards, 1981; B=Knight, 1990; remaining *pv* from Potts and others, 1992]

Reference	*Description*	*n*	*Mean*	*s*	*pv*	*% RSD*	*% R*
Thorium, Th							
SRM 688	basalt	10	<2	--	**0.33** A *cv*	--	--
W-2	diabase	5	2.7	0.3	2.2	11	123
BCR-1	basalt	6	5.3	0.8	**5.98**	15	89
AGV-1	andesite	9	7	1	**6.50**	14	107
GXR-2	soil	21	9.6	0.8	8.8	8	109
SRM 1646	estuarine sediment	10	10	1	*10*	10	100
G-2	granite	6	24	1	**24.6**	4	98
PPG	granite	37	31	2	29.2 B	6	106
Uranium, U							
SRM 688	basalt	9	0.45	0.06	0.37 A	13	122
W-2	diabase	10	0.53	0.05	0.53	9	100
BCR-1	basalt	6	1.81	0.06	**1.75**	3	103
AGV-1	andesite	10	2.1	0.1	1.89	5	110
G-2	granite	6	2.15	0.07	2.07	3	104
GXR-2	soil	21	3.12	0.09	**2.90**	3	108
SRM 1646	estuarine sediment	10	3.2	0.1	**2.99**	3	107
TMB	andesite	62	4.3	0.1	4.10 B	2	105
PPG	granite	37	5.8	0.2	5.40 B	3	107

Table 60.—Analytical performance summary for U and Th (ppm) by DN—Continued

Duplicate samples	*k*	*n*	*Mean*	*s*	*% RSD*	*Concentration range*	*No. of < (total)*	*No. of < (pairs)*
Thorium	18	2	13.9	0.6	5	6.84 to 24.4	1	0
Uranium	19	2	4.17	0.04	1	2.37 to 8.4	0	0

Method blank	*n*	*Mean*	*s*	*3s*	*5s*
Counter background					
Thorium	33*	0.8	0.1	0.4	0.6
Uranium	33*	0.21	0.03	0.09	0.1

*same day replicates

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Instrumental neutron activation by abbreviated count

By G.A. Wandless

Code: R021 Accepted: provisional

Principle

Neutron activation analysis selectively measures radioactive nuclide activity produced by nuclear reactions on naturally occurring isotopes The activity of the indicator radionuclide produced during irradiation is directly proportional to the amount of the element in the sample. The analytical determination is made by comparing the induced activity in the sample with well-characterized standards activated under identical conditions of neutron flux. The activities of the samples and standards are measured using gamma-ray spectroscopy. Gamma-ray radiation emitted by a radionuclide is converted to an electrical signal by a semiconductor detector. The electrical signal is analyzed by a multichannel analyzer. Semiconductor detectors, such as high-purity and lithium-drifted germanium detectors, are used to exploit their high resolution. Spectra produced are analyzed by software which locates peaks, identifies peaks, and calculates the area of each peak. Refer to Gordon and others (1968), Baedecker and McKown (1987), and Laul (1979) for more detailed descriptions of the principles of INAA.

Interference

Neutron activation analysis is matrix dependent. Samples with uranium concentrations higher than 100 ppm increases the detection limits for select rare earth elements from the generation of fission products. Detection limits are also effected by samples with high rare earth abundances, and ore-type samples. Ore-type samples require special counting and computer analysis for accurate determinations. Metamorphic marbles/limestones and quartzites also require special handling and analysis. Samples that have low abundances of elements, such as Fe, Co, and Sc, will normally decrease the detection limits for other determined elements. A detailed discussion of other known interferences can be found in Baedecker and McKown (1987).

Scope

Not all of the stated elements will be detectable for all matrixes. Samples having unusual matrixes will require adjustments to the counting protocol. A minimum of 4 months is required for completion of the analysis. The technique is "non-destructive" and sample may, with some restrictions, be analyzed by other methods if sample is limited. Reporting limits are matrix dependent and may be higher for routine analyses. A lower limit on the concentration of an element is calculated by estimating the minimum detectable peak area above the observed background using the peak detection criteria used in the peak fitting algorithm. The minimum detectable peak is determined by 3 sigma.

Element	*Lower limit (ppm)*	*Element*	*Lower limit (ppm)*
Ca	1,000	Ce, Co, Cr, Cs, Sb,	0.1
Ba	100	Sm, Th, U, Yb	
Fe, Na, Ni, Sr	10	Eu, Hf, La, Lu, Sc,	0.01
As, Nd, Rb, Zn	1	Ta, Tb	

Apparatus

- Ge (Li), High-Purity Germanium, and Intrinsic Planar Germanium detectors
- Associated electronics for detector signal processing, i.e. amplifier, high-voltage power supply, analog-to-digital converter
- A multi-channel analyzer (ND6700), with a minimum of 4096 channels

Safety precautions

Samples returning from irradiation in the nuclear reactor are radioactive. Handling precautions are used to minimize exposure to gamma radiation. All personnel are monitored with radiation badges and dosimeters as regulated by the Nuclear Regulatory Commission.

Reagents

None

Procedure

1. For each irradiation at least one USGS reference sample is used as a QC monitor. Spiked Horse Mountain Obsidian (HMS) is used as a multielement standard and is run in triplicate.
2. Samples received for analysis are normally ground to 200 mesh and require no further treatment. Samples, standards, and QC monitor(s) are weighed (0.3 - 1.0 g) into appropriate containers and irradiated for 6.5 to 8 hours in a uniform neutron flux (2.4×10^{12} ns^{-1}cm^{-2}).
3. The detector/data acquisition system is energy calibrated prior to sample counting by a source of known gamma-ray energies.
4. Data acquisition is performed by a multichannel analyzer adjusted for 0.1 keV/channel for low energy detectors and 0.5 keV/channel for high energy detectors.
5. Spectra are acquired for samples, standards, and QC monitor(s) on the same detector, at the same counting geometry for short half-life nuclides, and for intermediate and long half-life nuclides after 23 days on a HGe or Ge(Li) detector. Data is collected at 6 to 9 days after completion of irradiation on a HPGe or Ge(Li) detector. This schedule may be altered as needed for ore-type samples or samples containing high concentrations of interference elements.
6. Spectra for the three HMS standards are collected near the beginning and at the end of each count sequence. The irradiation set is concentration calibrated by averaging the specific activity for each radionuclide. Standard outlier tests are used to reject any anomalous results.
7. Data reduction is performed using the computer program, SPECTRA, Baedecker (1976), Baedecker and Grossman (1989) and Baedecker and Grossman (1994).
8. The precision, σ, is determined by counting statistics. Data for QC monitors are compared with expected result. Results that deviate from expected by more than 3 σ, determined by counting statistics, are checked for experimental error. Long term accuracy is determined by control charts.

Energy calibration of instrument

Detector	Low Energy	High Energy
Multichannel analyzer	2048 channels	4096 channels
	0.1 keV/channel	0.5 keV/channel
Gamma-ray source	^{57}Co, ^{241}Am, ^{182}Ta	^{60}Co, ^{237}Am, ^{88}Y, ^{137}Ba

Calculation

Elemental concentration are determined by calculating comparitor factors for standards (MCF) and for samples (SCF). The equations for those calculations are shown below. For more details of the calculations, refer to Baedecker (1977), Baedecker and Grossman (1989), and Baedecker and Grossman (1994).

$$MCF = \frac{(\textit{peak area}) \cdot \lambda \cdot t_c \cdot e^{\lambda t_d}}{(\textit{standard weight}) \cdot t_l \cdot (1 - e^{-\lambda t_c})}$$

$$SCF = \frac{(\textit{peak area}) \cdot \lambda \cdot t_c \cdot e^{\lambda t_d}}{(\textit{sample weight}) \cdot t_l \cdot (1 - e^{-\lambda t_c})}$$

$$CONCENTRATION = \frac{SCF}{\textit{Average MCF}}$$

where

λ = the decay constant for the indicator radionuclide
t_d = the elapsed time between the start of the first count in the sample set and the start of the count being processed
t_l = live time duration of the count
t_c = clock time duration of the count

Assignment of Uncertainty

Table 61 is the analytical results for selected reference materials by the INAA abbreviated count protocol.

Table 61.—Analytical performance summary for elements by INAA abbreviated count

[Proposed values from Potts and others, 1992]

Reston, VA laboratory data

Reference	*Description*	*n*	*Mean*	*s*	*pv*	*% RSD*	*% R*
Antimony, Sb (ppm)							
G-2	granite	8	0.10	0.02	0.078	20	123
QLO-1	quartz latite	34	2.0	0.4	2.1	18	96
GSP-1	granodiorite	9	3.4	0.1	3.2	4	105
Arsenic, As (ppm)							
G-2	granite	8	<0.9	--	0.27	--	--
QLO-1	quartz latite	31	3.0	0.7	3.5	? 22	85
Barium, Ba (ppm)							
GSP-1	granodiorite	9	1,270	21	**1,310**	2	97
QLO-1	quartz latite	34	1,390	34	1,370	2	102
G-2	granite	8	1,820	33	**1,880**	2	97

Table 61.—Analytical performance summary for elements by INAA abbreviated count—Continued

Reference	*Description*	*n*	*Mean*	*s*	*pv*	*% RSD*	*% R*
Calcium, Ca (wt percent)							
G-2	granite	4	1.8	0.2	**1.41**	13	127
GSP-1	granodiorite	8	1.8	0.6	**1.46**	30	126
QLO-1	quartz latite	31	2.4	0.6	**2.27**	24	105
Cerium, Ce (ppm)							
QLO-1	quartz latite	34	50	1	**54**	2	92
G-2	granite	8	158	3	**159**	2	99
GSP-1	granodiorite	9	422	8	**406**	2	104
Cesium, Cs (ppm)							
GSP-1	granodiorite	9	1.04	0.05	0.95	5	109
G-2	granite	8	1.34	0.04	**1.33**	3	101
QLO-1	quartz latite	34	1.69	0.10	1.75	6	97
Chromium, Cr (ppm)							
QLO-1	quartz latite	18*	2.3	0.5	3.2	20	71
G-2	granite	8	7.4	0.3	9	4	82
GSP-1	granodiorite	9	10.4	0.8	13	8	80
*Additional 16 < values							
Cobalt, Co (ppm)							
G-2	granite	8	4.6	0.3	**4.6**	7	100
GSP-1	granodiorite	9	6.7	0.2	6.5	4	103
QLO-1	quartz latite	34	7.4	0.3	7.2	3	103
Europium, Eu (ppm)							
G-2	granite	8	1.28	0.03	1.41	3	91
QLO-1	quartz latite	34	1.25	0.04	1.43	3	87
GSP-1	granodiorite	9	2.13	0.04	**2.36**	2	90
Hafnium, Hf (ppm)							
QLO-1	quartz latite	34	4.5	0.1	4.6	2	98
G-2	granite	8	7.8	0.2	**7.9**	2	98
GSP-1	granodiorite	9	14.9	0.5	**15.0**	3	99
Iron, Fe (wt percent)							
G-2	granite	8	1.93	0.03	**1.87**	2	103
GSP-1	granodiorite	9	3.11	0.05	**3.01**	2	103
QLO-1	quartz latite	34	3.17	0.06	**3.04**	2	104
Lanthanum, La (ppm)							
QLO-1	quartz latite	34	28	1	27	2	102
G-2	granite	8	90	1	**86**	1	105
GSP-1	granodiorite	9	186	3	**183**	2	102

Table 61.—Analytical performance summary for elements by INAA abbreviated count—Continued

Reference	*Description*	*n*	*Mean*	*s*	*pv*	*% RSD*	*% R*
Lutetium, Lu (ppm)							
G-2	granite	8	0.098	0.008	0.113	8	87
GSP-1	granodiorite	9	0.22	0.01	0.22	5	101
QLO-1	quartz latite	34	0.37	0.01	0.37	3	99
Neodymium, Nd (ppm)							
QLO-1	quartz latite	34	22	1	26	5	84
G-2	granite	8	49	3	53	5	92
GSP-1	granodiorite	9	188	3	**190**	1	99
Nickel, Ni (ppm)							
GSP-1	granodiorite	7	<29	--	9.8	--	--
Rubidium, Rb (ppm)							
QLO-1	quartz latite	34	75	2	74	3	102
G-2	granite	8	171	3	**170**	2	101
GSP-1	granodiorite	9	255	3	**254**	1	100
Samarium, Sm (ppm)							
QLO-1	quartz latite	34	4.9	0.1	**4.88**	2	100
G-2	granite	8	7.5	0.2	**7.2**	2	104
GSP-1	granodiorite	9	27.1	0.7	**26.8**	3	101
Scandium, Sc (ppm)							
G-2	granite	8	3.37	0.04	3.5	1	96
GSP-1	granodiorite	9	5.91	0.07	**6.1**	1	97
QLO-1	quartz latite	34	8.5	0.1	8.9	2	96
Sodium, Na (wt percent)							
GSP-1	granodiorite	9	2.10	0.04	**2.08**	2	101
G-2	granite	8	3.03	0.05	**3.02**	2	100
QLO-1	quartz latite	34	3.16	0.08	**3.12**	3	101
Strontium, Sr (ppm)							
GSP-1	granodiorite	9	248	15	**234**	6	106
QLO-1	quartz latite	34	372	18	**336**	5	111
G-2	granite	8	520	16	**478**	3	109
Tantalum, Ta (ppm)							
QLO-1	quartz latite	34	0.94	0.03	0.82	3	115
G-2	granite	8	0.93	0.03	0.88	3	106
GSP-1	granodiorite	9	1.01	0.03	0.91	3	111

Table 61.—Analytical performance summary for elements by INAA abbreviated count—Continued

Reference	*Description*	*n*	*Mean*	*s*	*pv*	*% RSD*	*% R*
Terbium, Tb (ppm)							
G-2	granite	8	0.46	0.01	0.48	3	96
QLO-1	quartz-latite	34	0.65	0.02	0.71	3	92
GSP-1	granodiorite	9	1.31	0.04	**1.36**	3	96
Thorium, Th (ppm)							
QLO-1	quartz latite	34	4.9	0.1	4.5	2	108
G-2	granite	8	24.8	0.4	**24.6**	2	101
GSP-1	granodiorite	9	108	2	**105**	2	103
Uranium, U (ppm)							
QLO-1	quartz latite	34	1.9	0.3	1.94	16	96
G-2	granite	8	2.0	0.3	**2.04**	17	98
GSP-1	granodiorite	9	2.3	0.2	2.2	7	105
Ytterbium, Yb (ppm)							
G-2	granite	8	0.80	0.07	0.78	8	103
GSP-1	granodiorite	9	1.9	0.1	1.7	6	110
QLO-1	quartz latite	34	2.5	0.1	2.32	4	107
Zinc, Zn (ppm)							
QLO-1	quartz latite	33	57	7	61	12	93
G-2	granite	8	81	2	**85**	2	95
GSP-1	granodiorite	9	99	6	**103**	6	96

No duplicate data available at this time

No method blank data available at this time

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Instrumental neutron activation by long count

By G.A. Wandless

Code: R030 Accepted: 2/16/95

Principle

Instrumental neutron activation analysis (INAA) selectively measures radioactive nuclide activity produced by nuclear reactions on naturally occurring isotopes The activity of the indicator radionuclide produced during irradiation is directly proportional to the amount of the element in the sample. The analytical determination is made by comparing the induced activity in the sample with well-characterized standards activated under identical conditions of neutron flux. The activities of the samples and standards are measured using gamma-ray spectroscopy. Gamma-ray radiation emitted by a radionuclide is converted to an electrical signal by a semiconductor detector. The electrical signal is analyzed by a multichannel analyzer. Semiconductor detectors, such as high-purity and lithium-drifted germanium detectors, are used to exploit their high resolution. Spectra produced are analyzed by software which locates peaks, identifies peaks, and calculates the area of each peak. Refer to Gordon and others (1968), Baedecker and McKown (1987), and Laul (1979) for more detailed descriptions of the principles of INAA.

Interference

Neutron activation analysis is matrix dependent. Samples with uranium concentrations higher than 100 ppm increases the detection limits for select rare earth elements, Mo and Zr from the generation of fission products. Detection limits are also effected by samples with high rare earth abundances, and ore-type samples. Ore-type samples require special counting and computer analysis for accurate determinations. Metamorphic marbles/limestones and quartzites, because of their very low abundances of most trace elements also require special handling and analysis. Samples that have low abundances of elements, such as Fe, Co, and Sc, will normally decrease the detection limits for other determined elements. A detailed discussion of other known interferences can be found in Baedecker and McKown (1987).

Scope

Not all elements will be detectable for all matrixes. Samples having unusual matrixes will require adjustments to the counting protocol. A minimum of 4 months is required for completion of the analysis. The technique is "non-destructive" and a sample may, with some restrictions, be analyzed by other methods if sample is limited. A lower limit on the concentration of an element is calculated by estimating the minimum detectable peak area above the observed background using the peak detection criteria used in the peak fitting algorithm. The minimum detectable peak is determined by 3 sigma. Reporting limits are matrix dependent and may be higher for routine analysis.

Element	*Lower limit (ppm)*	*Element*	*Lower limit (ppm)*
Ti	10,000	Br*, Ce, Co, Cr, Cs, Sb, Sm, Th, U, Yb	0.1
Ca, K	1,000	Eu, Hf, La, Lu, Sc, Ta, Tb	0.01
Ba, Cd*, Hg*, Zr,	100	Ir*	0.001
Ag*, Fe, Mo, Na, Ni, Sr,	10		
As, Gd*, Nd, Rb, Se, Tm, W*, Zn	1		

*Available by special request only and not validated

Apparatus

- Ge (Li), High-Purity Germanium, and Intrinsic Planar Germanium detectors
- Associated electronics for detector signal processing, i.e. amplifier, high-voltage power supply, analog-to-digital converter
- A multi-channel analyzer (ND6700), with a minimum of 4096 channels

Safety precautions

Samples returning from irradiation in the nuclear reactor are radioactive. Handling precautions are used to minimize exposure to gamma radiation. All personnel are monitored with radiation badges and dosimeters as regulated by the Nuclear Regulatory Commission.

Reagents

None

Procedure

1. For each irradiation at least one USGS reference sample is used as a QC monitor. Spiked Horse Mountain Obsidian (HMS) is used as a multielement standard and is run in triplicate.
2. Samples received for analysis are normally ground to 200 mesh and require no further treatment. Samples, standards, and QC monitor(s) are weighed (0.3 - 1.0 g) into appropriate containers and irradiated for 6.5 to 8 hours in a uniform neutron flux (2.4 x 10^{12} $ns^{-1}cm^{-2}$). An irradiation set is composed of a maximum of 40 containers, three aliquots of the HMS multi-element standard, a Ca/Ti standard and an Au standard, the remaining slots composed of samples and USGS reference materials.
3. The detector/data acquisition system is energy calibrated prior to sample counting by a source of known gamma-ray energies.
4. Data acquisition is performed by a multichannel analyzer adjusted for 0.1 keV/channel for low energy detectors and 0.5 keV/channel for high energy detectors.
5. Spectra are acquired for samples, standards, and QC monitor(s) on the same detector, at the same counting geometry. Data is collected at 6 to 7 days after completion of irradiation on a LEPD and a HPGe or Ge(Li) detector for short half-life nuclides. Data is collected for intermediate half-life nuclides after 11 to 14 days and for long half-life nuclides after 40 to 60 days; both on a HPGe or Ge(Li) detector. An additional count may be done on a LEPD after 90 days to analyze for Gd. This schedule may be altered as needed for ore-type samples or samples containing high concentrations of interference elements.
6. Spectra for the three HMS standards are collected near the beginning and at the end of each count sequence. The irradiation set is concentration calibrated by averaging the specific activity for each radionuclide. standard outlier tests are used to reject any anomalous results.

7. Data reduction is performed using the computer program, SPECTRA, Baedecker (1976), Baedecker and Grossman (1989) and Baedecker and Grossman (1994).
8. The precision, σ, is determined by counting statistics. Data for QC monitors are compared with expected result. Results that deviate from expected by more than 3 σ, determined by counting statistics, are checked for experimental error. Long term accuracy is determined by control charts.

Energy calibration of instrument

Detector	Low Energy	High Energy
Multichannel analyzer	2048 channels	4096 channels
	0.1 keV/channel	0.5 keV/channel
Gamma-ray source	^{57}Co, ^{241}Am, ^{182}Ta	^{60}Co, ^{237}Am, ^{88}Y, ^{137}Ba

Calculation

Elemental concentration are determined by calculating comparitor factors for standards (MCF) and for samples (SCF). The equations for those calculations are shown below. For more details of the calculations, refer to Baedecker (1977), Baedecker and Grossman (1989) and Baedecker and Grossman (1994).

$$MCF = \frac{(\textit{peak area}) \cdot \lambda \cdot t_c \cdot e^{\lambda t_d}}{(\textit{standard weight}) \cdot t_l \cdot (1- e^{-\lambda t_c})}$$

$$SCF = \frac{(\textit{peak area}) \cdot \lambda \cdot t_c \cdot e^{\lambda t_d}}{(\textit{sample weight}) \cdot t_l \cdot (1- e^{-\lambda t_c})}$$

$$CONCENTRATION = \frac{SCF}{\textit{Average } MCF}$$

where

l = the decay constant for the indicator radionuclide
t_d = the elapsed time between the start of the first count in the sample set and the start of the count being processed
t_l = live time duration of the count
t_c = clock time duration of the count

Assignment of Uncertainty

Table 62 is the analytical results for selected reference materials by the INAA long count protocol.

Table 62.—Analytical performance summary for elements by INAA long count

[A=Govindaraju, 1989; remaining *pv* from Potts and others, 1992]

Reston, VA laboratory data

Reference	*Description*	*n*	*Mean*	*s*	*pv*		*% RSD*	*% R*
Antimony, Sb (ppm)								
G-2	granite	18	0.10	0.02	0.078		17	127
SDC-1	mica schist	9	0.60	0.04	0.54		7	110
DNC-1	diabase	13	0.91	0.06	0.96		7	95
QLO-1	quartz latite	30	2.1	0.4	2.1		20	100
SCo-1	shale	11	2.46	0.07	2.50		3	98
GSP-1	granodiorite	27	3.4	0.1	3.2		3	106
AGV-1	andesite	12	4.5	0.2	**4.4**		5	102
Arsenic, As (ppm)								
G-2	granite	20	<0.8	--	0.27		--	--
AGV-1	andesite	8	1.2	0.2	0.84		19	145
QLO-1	quartz latite	30	2.9	0.5	3.5	?	18	84
SCo-1	shale	11	11.5	0.5	12.4		5	93
Barium, Ba (ppm)								
DNC-1	diabase	13	110	10	114		9	96
SCo-1	shale	11	546	31	570		6	96
SDC-1	mica schist	9	626	16	630		3	99
AGV-1	andesite	12	1,210	27	**1,221**		2	99
GSP-1	granodiorite	27	1,280	24	**1,310**		2	98
QLO-1	quartz latite	30	1,380	34	1,370		2	101
G-2	granite	22	1,820	40	**1,880**		2	97
Calcium, Ca (wt percent)								
SDC-1	mica schist	8	1.2	0.3	**1.00**		22	116
GSP-1	granodiorite	25	1.6	0.4	**1.46**		22	111
G-2	granite	18	1.5	0.2	**1.64**		16	94
SCo-1	shale	10	1.8	0.2	1.87		11	98
QLO-1	quartz latite	30	2.3	0.3	**2.27**		11	101
AGV-1	andesite	12	3.6	0.3	**3.53**		8	103
DNC-1	diabase	12	8.1	0.3	**8.05**		3	101
Cerium, Ce (ppm)								
DNC-1	diabase	13	8.0	0.3	10.6		4	76
QLO-1	quartz latite	30	50	1	54		2	92
SCo-1	shale	11	53	1	62		2	86
AGV-1	andesite	12	68	1	**66**		2	103
SDC-1	mica schist	9	88	2	93		2	95
G-2	granite	22	157	3	159		2	99
GSP-1	granodiorite	27	424	7	**406**		2	104

Table 62.—Analytical performance summary for elements by INAA long count—Continued

Reference	*Description*	*n*	*Mean*	*s*	*pv*		*% RSD*	*% R*
Cesium, Cs (ppm)								
DNC-1	diabase	10	0.26	0.05	*0.34*	A	19	77
GSP-1	granodiorite	27	1.02	0.04	0.95		4	107
AGV-1	andesite	12	1.28	0.04	**1.26**		3	101
G-2	granite	22	1.34	0.04	1.34		3	100
QLO-1	quartz latite	30	1.69	0.07	1.75		4	96
SDC-1	mica schist	9	4.0	0.1	**4.0**		3	99
SCo-1	shale	11	7.4	0.1	7.8		2	94
Chromium, Cr (ppm)								
QLO-1	quartz latite	21	2.15	0.06	3.2		3	67
G-2	granite	22	7.4	0.3	9		4	82
AGV-1	andesite	12	9.7	0.3	12		3	80
GSP-1	granodiorite	27	10.8	0.1	13		1	83
SDC-1	mica schist	9	62	1	64		2	96
SCo-1	shale	11	67	2	68		4	99
DNC-1	diabase	13	288	7	285		2	101
Cobalt, Co (ppm)								
G-2	granite	22	4.7	0.4	**4.6**		9	102
GSP-1	granodiorite	27	6.7	0.2	6.5		3	104
QLO-1	quartz latite	30	7.8	0.4	7.2		5	108
SCo-1	shale	11	10.7	0.3	10.5		2	102
AGV-1	andesite	12	15.5	0.3	**15.1**		2	103
SDC-1	mica schist	9	17.6	0.4	17.9		2	98
DNC-1	diabase	13	56	1	54.7		3	103
Europium, Eu (ppm)								
DNC-1	diabase	13	0.58	0.02	**0.59**		3	98
SCo-1	shale	11	1.03	0.02	1.19		2	86
G-2	granite	22	1.27	0.03	1.41		2	90
QLO-1	quartz latite	30	1.24	0.03	1.43		2	87
AGV-1	andesite	12	1.57	0.03	1.66		2	94
SDC-1	mica schist	9	1.56	0.02	1.71		1	91
GSP-1	granodiorite	27	2.13	0.04	**2.36**		2	90
Hafnium, Hf (ppm)								
DNC-1	diabase	13	1.01	0.03	1.01		3	100
QLO-1	quartz latite	30	4.5	0.1	4.6		2	98
SCo-1	shale	11	4.5	0.2	4.6		3	98
AGV-1	andesite	12	5.0	0.1	5.1		2	99
G-2	granite	22	7.8	0.2	**7.9**		2	98
SDC-1	mica schist	9	8.1	0.2	**8.3**		2	97
GSP-1	granodiorite	27	15.1	0.4	15.0		3	100

Table 62.—Analytical performance summary for elements by INAA long count—Continued

Reference	*Description*	*n*	*Mean*	*s*	*pv*	*% RSD*	*% R*
Iron, Fe (wt percent)							
G-2	granite	22	1.93	0.03	**1.87**	2	103
GSP-1	granodiorite	27	3.13	0.05	**3.01**	1	104
QLO-1	quartz latite	30	3.17	0.06	**3.04**	2	104
SCo-1	shale	11	3.59	0.05	**3.60**	1	100
AGV-1	andesite	12	4.98	0.07	**4.73**	1	105
SDC-1	mica schist	9	5.0	0.1	4.83	2	104
DNC-1	diabase	13	7.3	0.1	**6.95**	2	105
Lanthanum, La (ppm)							
DNC-1	diabase	13	3.84	0.08	3.8	2	101
QLO-1	quartz latite	30	27.6	0.6	27	2	102
SCo-1	shale	11	30	1	**29.5**	3	102
AGV-1	andesite	12	40.0	0.5	38	1	105
SDC-1	mica schist	9	43.3	0.6	**42**	1	103
G-2	granite	22	90	1	**86**	1	105
GSP-1	granodiorite	27	187	3	**183**	2	102
Lutetium, Lu (ppm)							
G-2	granite	22	0.098	0.007	0.113	7	86
GSP-1	granodiorite	27	0.22	0.01	0.22	4	102
AGV-1	andesite	12	0.241	0.005	0.28	2	86
DNC-1	diabase	13	0.30	0.02	0.32	6	92
SCo-1	shale	11	0.329	0.008	0.338	2	97
QLO-1	quartz latite	30	0.37	0.01	0.37	3	99
SDC-1	mica schist	9	0.61	0.02	0.53	3	116
Molybdenum, Mo (ppm)							
No reference material data available at this time.							
Neodymium, Nd (ppm)							
DNC-1	diabase	10	4.8	0.8	**4.9**	16	98
QLO-1	quartz latite	30	22	1	26	5	86
SCo-1	shale	11	24	1	26	4	91
AGV-1	andesite	12	28	8	34	28	83
SDC-1	mica schist	9	39	1	40	4	97
G-2	granite	22	49	2	53	4	92
GSP-1	granodiorite	27	191	3	**190**	2	101
Nickel, Ni (ppm)							
SCo-1	shale	11	2.2	0.1	2.30	6	96
GSP-1	granodiorite	22	<23	--	8.8	--	--
AGV-1	andesite	7	22	8	17	35	130
SCo-1	shale	11	27	2	27	9	101
SDC-1	mica schist	9	38	6	38	17	99
DNC-1	diabase	13	260	13	247	5	105

Table 62.—Analytical performance summary for elements by INAA long count—Continued

Reference	*Description*	*n*	*Mean*	*s*	*pv*	*% RSD*	*% R*
Potassium, K (wt percent)							
DNC-1	diabase	7	0.3	0.2	**0.19**	49	182
SCo-1	shale	11	2.2	0.1	**2.30**	6	96
AGV-1	andesite	12	2.9	0.9	**2.41**	30	122
SDC-1	mica schist	9	2.7	0.2	**2.72**	7	101
QLO-1	quartz latite	30	3.0	0.3	**2.99**	11	101
G-2	granite	20	3.8	0.5	**3.73**	12	103
GSP-1	granodiorite	26	4.8	0.5	**4.57**	11	106
Rubidium, Rb (ppm)							
DNC-1	diabase	9	7	1	4.5	? 17	154
AGV-1	andesite	12	70	2	**67**	2	104
QLO-1	quartz latite	30	75	2	**74**	3	101
SCo-1	shale	11	111	2	**112**	2	99
SDC-1	mica schist	9	127	3	127	2	100
G-2	granite	22	170	3	**170**	2	100
GSP-1	granodiorite	27	258	3	**254**	1	102
Samarium, Sm (ppm)							
DNC-1	diabase	13	1.51	0.05	1.38	3	109
QLO-1	quartz latite	30	4.88	0.09	**4.88**	2	100
SCo-1	shale	11	5.3	0.2	5.3	4	99
AGV-1	andesite	12	6.2	0.1	**5.9**	2	105
G-2	granite	22	7.4	0.3	**7.2**	4	102
SDC-1	mica schist	9	8.6	0.2	8.2	2	105
GSP-1	granodiorite	27	27.3	0.5	**26.8**	2	102
Scandium, Sc (ppm)							
G-2	granite	22	3.35	0.06	3.5	2	96
GSP-1	granodiorite	27	6.0	0.1	**6.1**	2	98
QLO-1	quartz latite	30	8.5	0.2	8.9	2	95
SCo-1	shale	11	11.3	0.2	10.8	2	104
AGV-1	andesite	12	12.0	0.1	**12.1**	1	99
SDC-1	mica schist	9	15.1	0.3	17	2	89
DNC-1	diabase	13	31.0	0.7	31.0	2	100
Selenium, Se (ppm)							
No reference material data available at this time							
Sodium, Na (wt percent)							
SCo-1	shale	11	0.67	0.03	**0.667**	4	101
DNC-1	diabase	13	1.43	0.04	**1.39**	3	103
SDC-1	mica schist	9	1.55	0.03	**1.52**	2	102
GSP-1	granodiorite	27	2.12	0.03	**2.08**	2	102
G-2	granite	22	3.04	0.05	**3.02**	2	101
QLO-1	quartz latite	30	3.14	0.09	**3.12**	3	101
AGV-1	andesite	12	3.23	0.06	**3.15**	2	102

Table 62.—Analytical performance summary for elements by INAA long count—Continued

Reference	*Description*	*n*	*Mean*	*s*	*pv*		*% RSD*	*% R*
Strontium, Sr (ppm)								
DNC-1	diabase	13	167	16	**145**		10	115
SCo-1	shale	11	177	11	**174**		6	102
SDC-1	mica schist	9	197	18	**183**		9	107
GSP-1	granodiorite	27	254	15	**234**		6	109
QLO-1	quartz latite	30	366	11	**336**		3	109
G-2	granite	22	522	24	**478**		5	109
AGV-1	andesite	12	719	20	**662**		3	109
Tantalum, Ta (ppm)								
DNC-1	diabase	12	0.12	0.02	0.098		21	119
QLO-1	quartz latite	30	0.94	0.02	0.82		2	114
G-2	granite	22	0.92	0.03	0.88		3	104
GSP-1	granodiorite	27	1.01	0.02	0.91		2	111
SCo-1	shale	11	0.93	0.01	0.92		1	101
AGV-1	andesite	12	0.98	0.02	0.92		2	107
SDC-1	mica schist	9	1.40	0.04	1.21		3	116
Terbium, Tb (ppm)								
DNC-1	diabase	13	0.38	0.02	0.41		6	92
G-2	granite	22	0.46	0.01	0.48		3	95
SCo-1	shale	11	0.66	0.02	0.70		2	94
QLO-1	quartz latite	30	0.65	0.02	0.71		4	92
AGV-1	andesite	12	0.66	0.02	0.71		3	93
SDC-1	mica schist	9	1.08	0.02	1.18		2	92
GSP-1	granodiorite	27	1.31	0.05	**1.36**		4	96
Thorium, Th (ppm)								
DNC-1	diabase	13	0.30	0.05	0.20	?	17	148
QLO-1	quartz latite	30	4.85	0.09	4.5		2	108
AGV-1	andesite	12	6.53	0.10	6.50		2	100
SCo-1	shale	11	9.2	0.1	9.7		1	95
SDC-1	mica schist	9	12.0	0.2	12.1		2	99
G-2	granite	22	24.8	0.4	**24.6**		2	101
GSP-1	granodiorite	27	109	2	**105**		2	104
Titanium, Ti (wt percent)								
DNC-1	diabase	7	0.8	0.2	**0.29**		22	272
G-2	granite	17	<1.5	--	**0.29**		--	--
QLO-1	quartz latite	28	<1.4	--	0.374		--	--
SCo-1	shale	6	0.6	0.1	0.376		21	167
GSP-1	granodiorite	26	<1.4	--	**0.393**		--	--
SDC-1	mica schist	8	1.0	0.2	**0.605**		17	167
AGV-1	andesite	6	1.3	0.7	**0.635**		52	202

Table 62.—Analytical performance summary for elements by INAA long count—Continued

Reference	*Description*	*n*	*Mean*	*s*	*pv*	*% RSD*	*% R*
Uranium, U (ppm)							
DNC-1	diabase	13	<0.3	--	0.10 ?	--	--
AGV-1	andesite	12	1.84	0.10	1.89	5	97
QLO-1	quartz latite	30	1.82	0.09	1.94	5	94
G-2	granite	22	2.0	0.3	**2.04**	14	96
GSP-1	granodiorite	27	2.3	0.2	2.2	7	105
SCo-1	shale	11	2.80	0.09	3.0	3	93
SDC-1	mica schist	9	2.74	0.07	3.14	3	87
Ytterbium, Yb (ppm)							
G-2	granite	22	0.81	0.06	0.78	8	104
AGV-1	andesite	12	1.79	0.09	**1.67**	5	107
GSP-1	granodiorite	27	1.9	0.2	1.7	8	114
DNC-1	diabase	13	2.04	0.08	**2.01**	4	101
SCo-1	shale	11	2.34	0.06	2.27	3	103
QLO-1	quartz latite	30	2.51	0.09	2.32	3	108
SDC-1	mica schist	9	4.5	0.1	4.0	2	112
Zinc, Zn (ppm)							
QLO-1	quartz latite	30	58	5	**61**	8	96
DNC-1	diabase	13	65	8	66	12	98
G-2	granite	22	81	3	**85**	4	95
AGV-1	andesite	12	84	6	**88**	7	95
SCo-1	shale	11	86	4	103	4	83
SDC-1	mica schist	9	94	6	103	7	92
GSP-1	granodiorite	27	98	4	**103**	4	95
Zirconium, Zr (ppm)							
DNC-1	diabase	11	<100	--	41	--	--
SCo-1	shale	11	160	20	160	13	100
QLO-1	quartz latite	30	184	29	185	16	99
AGV-1	andesite	12	218	24	**225**	11	97
SDC-1	mica schist	9	311	15	290	5	107
G-2	granite	22	321	24	**300**	7	107
GSP-1	granodiorite	27	571	26	530	5	108

No duplicate data available at this time

No method blank data available at this time.

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Twelve selected trace elements by energy-dispersive X-ray fluorescence spectrometry

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Principle

Energy-dispersive X-ray fluorescence spectrometry (EDXRF) is a method for the qualitative and quantitative analysis of elemental composition in solid or liquid samples. It is based on the instantaneous generation, detection, and measurement of characteristic X-rays emitted by the elements in a sample, when the sample is bombarded with high energy X-rays. This is a nondestructive analytical process that requires little or no sample preparation. With this method, 12 trace elements, Cr, Ni, Cu, Zn, Rb, Sr, Y, Zr, Nb, Ba, La, and Ce may be determined routinely. The analyst is referred to the literature (E. Bertin, 1975; Johnson and King, 1987; G. Andermann and J.W. Kemp, 1958) for more details on the use of EDXRF for geologic and geochemical applications.

Interferences

Spectral-line interferences include line overlap and absorption/enhancement (matrix effects). The problem of spectral-line overlap is shared by all emission and fluorescence methods. It is due to the incomplete resolution of two or more spectral lines or peaks. There are two types of spectral line overlaps in routine EDXRF analysis:

1. A Kb line from one element overlaps the Ka line from the adjacent heavier element in the periodic table (e.g., Ni Kb overlaps Cu Ka; Cu Kb with Zn Ka; Rb Kb with Y Ka; Sr Kb with Zr Ka; and Y Kb with Nb Ka).
2. L-series lines from one element interfere with K lines from another element (e.g., Ba Lr_1 with Cr Ka; La Lb_2, Cd Lb_1 and Lb_2 with Cr Ka; and Pb Lr with Y Ka).

All the above interferences can be removed by peak stripping or peak deconvolution techniques using computer algorithms.

Matrix effects (or absorption/enhancement) occur when radiation emitted by the analyte is reabsorbed by components in the sample before it reaches the detector. The effects are corrected by a scattered radiation method (Andermann and Kemp, 1958) which has been widely used for routine trace-element analysis of various geologic materials (K.K. Nielson, 1979; R.G. Johnson, 1984; P.G. Burkhalter, 1971; B.W. King, 1987). This correction method is based on the fact that the analyte-line intensity and Compton scatter radiation are affected in the same way by differences in mass absorption coefficients from one sample to another. Although the scatter line and the analyte line intensities vary with the matrix, their ratio is constant over a wide range of matrix compositions. Furthermore, if the energy of the scatter-target line is close to the energy of the analyte line, the absorption, particle size, packing density, and instrumental effects are more effectively corrected. The effect of secondary enhancement is not corrected by this method, but is usually negligible for elements with an atomic number greater than 26 (Fe).

Scope

This method is applicable to the analysis of the above-mentioned 12 trace elements in rocks, stream sediments, and soils samples in loose powder form (approximately minus 200-mesh). Because this method is nondestructive, the sample can be used for other chemical and instrumental analyses after EDXRF analysis. The formula used in the EDXRF laboratory for the calculation of lower limit of detection (LOD) is as follow:

$$\text{LOD} = \frac{3}{m}\sqrt{\frac{Rb}{T}}$$

where m is in counts/second/percent, Rb the background counting rate in counts/second and T the counting time.

The detection limits and calibration concentration ranges of the method are summarized in table 63.

Table 63.—Lower limit of detection and upper limit of calibration curve for the EDXRF method

Element	*Lower limit, ppm**	*Upper limit, ppm*
Cr	20	4,200
Ni	10	3,000
Cu	10	1,000
Zn	10	1,300
Rb	10	2,000
Sr	10	2,000
Y	10	200
Zr	10	2,000
Nb	10	500
Ba	30	4,700
La	30	1,300
Ce	30	500

*Represents the highest LOD observed, these limits may vary according to calibration.

Apparatus

- Kevex 0700/7000 Energy Dispersive X-ray Spectrometer
- Spectro-cups, 31-mm (Somar Laboratories, Inc., New York)

Reagents

None

Safety precaution

The Kevex X-ray spectrometers are adequately shielded to confine the X-rays. The systems are monitored routinely with a radiation-survey meter at intervals of 3 to 6 months. All laboratory personnel are required to wear film badges when operating the X-ray system.

Procedure

1. Sample preparation: A 1 to 2 g portion of the powdered sample or reference material is poured into a spectro-cup with a bottom made of stretched, ultra thin (<4µm) Mylar film held by two plastic rings. This rapid preparation requires no weighing. The powder can be tamped to assure a more uniform packing density.

The instrument (a Kevex model 0700/7000 X-ray spectrometer) is standardized according to the operating conditions in table 64.

Table 64.—Operating conditions for determination of elements by EDXRF

Spectral-line	K-alpha
Fe secondary target	Cr determination
Ge secondary target	Ni, Cu, and Zn determination
Ag secondary target	Rb, Sr, Y, Zr, and Nb determination
Gd secondary target	Ba, La, and Ce determination
Excitation target voltages	20 kV for Fe and Ge targets; 35 kV for Ag; and 58 kV for Gd target
Target currents*	2.0 mA for target Fe, Ge, and Gd; 1.5 mA for Ag target
Acquisition time*	100 s for targets Fe and Ge; 200 s for targets Ag and Gd

*These may vary from one X-ray tube to another.

2. Spectral acquisition—Up to 16 sample cups can be placed in the sample holder in the Kevex 0700 system. Fourteen cups are the job samples and two are reference materials. The analyst records sample ID numbers and corresponding positions in the sample carousel, selects the excitation condition for the elements of interest, and acquires the spectrum.
3. Spectrum processing—Escape peaks and background are subtracted from the spectra before peak-intensity extraction. Spectral line interferences (peak overlaps) are corrected by peak-stripping (subtraction). The net K-peak intensity for each element is then ratioed to the Compton scatter peak intensity from the secondary target used to produce that spectrum.
4. Calibration—A total of 36 international silicate rock standards (Abbey, 1983) are used for calibration (table 65). The ratios of peak intensity to Compton scatter intensity are used in a linear least-squares fit of the concentration data for each element. Reference materials (such as BCR-1 and GSP-1) are analyzed as check standards in every job.

Table 65.—Calibration standards used in the EDXRF method

AGV-1	BX-N	GSP-1	MAG-1	QLO-1	AN-G	DNC-1	GXR-1	MICA-Mg
RGM-1	BCR-1	DR-N	GXR-3	MICA-Fe	SCo-1	BE-N	DTS-1	GXR-5
MRG-1	SDC-1	BHVO-1	G-1	GXR-6	NIM-G	STM-1	BIR-1	G-2
JB-1	NIM-P	T-1	BR	GH	JG-1	PCC-1	W-1	W-2

Calculation

The concentration C_i of element i, in the unknown sample is calculated from the intercept B_o and slope B_1 of the best fit line of each calibration and the ratio of intensity I_i to Compton scatter radiation I_C as follows:

$$C_i = B_o + B_1(I_i/I_C)$$

Assignment of uncertainty

Table 66 is the analytical results of 12 trace elements for selected reference materials and duplicate samples.

Table 66.—Analytical performance summary for elements (ppm) by EDXRF

[Proposed values from Potts and others, 1992]

Reference	*Description*	*n*	*Mean*	*s*	*pv*	*% RSD*	*% R*
Barium, Ba							
GSD-2	stream sediment	10	190	7	*185*	4	103
GSD-5	stream sediment	10	440	17	*440*	4	100
GSD-4	stream sediment	10	460	15	*470*	3	98
GSD-3	stream sediment	10	610	12	*615*	2	99
BCR-1	basalt	91	679	17	**681**	2	98
GSD-1	stream sediment	10	940	16	*950*	2	99
GSP-1	granodiorite	91	1,280	37	**1,310**	3	98
Cerium, Ce							
BCR-1	basalt	91	53	16	**53.7**	31	99
GSD-3	stream sediment	10	65	5	*64*	8	102
GSD-4	stream sediment	10	78	8	*78*	10	100
GSD-1	stream sediment	10	80	9	*81*	11	99
GSD-5	stream sediment	10	88	4	*89*	5	99
GSD-2	stream sediment	10	190	11	*192*	6	99
GSP-1	granodiorite	95	381	20	**406**	5	94

Table 66.—Analytical performance summary for elements (ppm) by EDXRF—Continued

Reference	*Description*	*n*	*Mean*	*s*	*pv*	*% RSD*	*% R*
Chromium, Cr							
GSD-2	stream sediment	10	12	3	*12.2*	25	98
GSD-5	stream sediment	10	70	3	*70*	4	100
GSD-4	stream sediment	10	84	4	*81*	5	104
GSD-3	stream sediment	10	88	4	*87*	5	101
W-1	diabase	93	111	14	120	12	93
GSD-1	stream sediment	10	200	8	*194*	4	103
BR	basalt	96	318	19	380	6	84
BIR-1	basalt	10	347	9	382	3	91
JP-1	peridotite	10	3,190	57	2,970	2	107
Copper, Cu							
GSD-1	stream sediment	10	22	4	21.8	18	101
GSD-4	stream sediment	10	38	3	37.3	8	102
BR	basalt	92	67	5	72	7	93
W-1	diabase	91	104	7	**114**	6	91
BIR-1	basalt	10	117	4	**126**	3	93
GSD-5	stream sediment	10	138	6	137	4	101
GSD-3	stream sediment	10	185	2	177	1	105
GSD-6	stream sediment	10	400	7	383	2	104
Lanthanum, La							
GSD-3	stream sediment	10	37	3	*39*	8	95
GSD-4	stream sediment	10	40	4	*40*	10	100
GSD-1	stream sediment	10	40	4	*43*	10	93
GSD-5	stream sediment	10	47	7	*46*	15	102
GSD-2	stream sediment	10	90	3	*90*	3	100
GSP-1	granodiorite	95	180	25	**183**	14	98
Niobium, Nb							
BCR-1	stream sediment	60	12	2	14	17	86
GSD-3	stream sediment	10	16	2	16	16	100
GSD-4	stream sediment	10	18	1	18	6	100
GSD-5	stream sediment	10	19	2	19	11	100
GSP-1	stream sediment	60	25	2	26	8	96
GSD-1	stream sediment	10	35	2	35	6	100
GSD-2	stream sediment	10	95	2	95	2	100
Nickel, Ni							
GSD-5	stream sediment	10	35	3	*34*	9	103
GSD-4	stream sediment	10	40	3	*40*	8	100
W-1	diabase	91	66	8	75	12	88
GSD-1	stream sediment	10	78	4	*76*	5	103
BIR-1	basalt	10	176	4	166	2	106
BR	basalt	92	240	14	260	6	92
JP-1	peridotite	10	2,460	16	2,460	1	100

Table 66.—Analytical performance summary for elements (ppm) by EDXRF—Continued

Reference	*Description*	*n*	*Mean*	*s*	*pv*	*% RSD*	*% R*
Rubidium, Rb							
BCR-1	basalt	60	46	3	**47.2**	7	97
GSD-3	stream sediment	10	76	2	79	3	96
GSD-1	stream sediment	10	116	2	116	2	100
GSD-5	stream sediment	10	118	3	118	3	100
GSD-4	stream sediment	10	130	2	130	2	100
GSP-1	granodiorite	60	239	14	**254**	6	94
GSD-2	stream sediment	10	480	6	470	1	102
Strontium, Sr							
GSD-2	stream sediment	10	26	3	*28*	12	93
GSD-3	stream sediment	10	88	2	*90*	2	98
BIR-1	basalt	10	114	3	108	2	106
GSD-4	stream sediment	10	142	2	*142*	1	100
GSD-5	stream sediment	10	205	4	*204*	2	100
GSP-1	granodiorite	60	236	5	**234**	2	101
BCR-1	basalt	60	318	7	**330**	2	96
GSD-1	stream sediment	10	530	2	*525*	0.4	101
Yttrium, Y							
BIR-1	basalt	10	18	3	16	17	113
GSD-3	stream sediment	10	22	2	22	9	100
GSD-1	stream sediment	10	23	2	22.5	9	102
GSD-5	stream sediment	10	27	2	26	7	104
GSD-4	stream sediment	10	27	2	26	7	104
GSP-1	granodiorite	60	34	3	29	9	117
BCR-1	basalt	60	36	3	38	8	95
GSD-2	stream sediment	10	74	2	67	3	110
Zinc, Zn							
JP-1	peridotite	10	52	2	29.5	3	176
GSD-2	stream sediment	10	44	2	*44*	5	100
GSD-3	stream sediment	10	52	3	*52*	6	100
BIR-1	basalt	10	63	3	71	4	89
GSD-1	stream sediment	10	85	5	*79*	6	108
W-1	diabase	91	76	4	**84**	6	90
GSD-4	stream sediment	10	110	5	*101*	5	109
BR	basalt	92	123	9	160	8	77
GSD-5	stream sediment	10	260	7	*243*	3	107

Table 66.—Analytical performance summary for elements (ppm) by EDXRF —Continued

Reference	*Description*	*n*	*Mean*	*s*	*pv*	*% RSD*	*% R*
Zirconium, Zr							
BIR-1	basalt	10	21	3	22	14	95
GSD-4	stream sediment	10	181	2	188	1	96
BCR-1	basalt	60	193	10	190	5	102
GSD-3	stream sediment	10	210	3	220	1	95
GSD-5	stream sediment	10	214	3	220	1	97
GSD-1	stream sediment	10	305	4	310	1	98
GSD-2	stream sediment	10	440	5	460	1	96
GSP-1	granodiorite	60	537	12	530	2	101

Duplicate samples	*k*	*n*	*Mean*	*s*	*% RSD*	*Concentration range*
Ba	28	2	1,090	19	2	28 to 3,500
Ce	21	2	77	13	17	20 to 298
Cr	13	2	162	12	7	29 to 546
Cu	17	2	35	4	12	11 to 89
La	6	2	67	4	6	37 to 130
Nb	20	2	25	2	8	10 to 113
Ni	15	2	89	6	7	21 to 323
Rb	26	2	63	2	4	16 to 149
Sr	29	2	498	8	2	31 to 1,700
Y	27	2	27	4	14	12 to 53
Zn	29	2	86	6	7	25 to 168
Zr	28	2	197	6	3	63 to 738

No method blank information available at this time.

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Major element analysis by wavelength dispersive X-ray fluorescence spectrometry

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Principle

Ten major elements are determined in rocks and minerals by wavelength dispersive X-ray fluorescence spectrometry (WDXRF). The sample is fused with lithium tetraborate and the resultant glass disc is introduced into a wavelength dispersive X-ray spectrometer. The disc is irradiated with X-rays from an X-ray tube. X-ray photons emitted by the elements in the samples are counted and concentrations determined using previously prepared calibration standards. In addition to 10 major elements, the method provides a gravimetric loss-on-ignition.

Interferences

Interferences, with analysis by WDXRF, may result from mineralogical or other structural effects, line overlaps, and matrix effects. The structure of the sample, mineralogical or otherwise, is eliminated through fusion with a suitable flux. Fusion of the samples also diminishes matrix effects and produces a stable, flat, homogenous sample for presentation to the spectrometer. Selecting certain types of crystal monochromators eliminates many of the line overlap and multiorder line interferences. A mathematical correction procedure (deJongh, 1973) is used to correct for the absorption and enhancement matrix effects.

Scope

Concentrations of the elements in rocks and minerals are determined independent of the oxidation state and are reported in the oxidation state in which they most commonly occur in the earth's crust. The reporting limits (calibration range) for 10 elements by WDXRF are as follows.

Element	*Concentration range (percent)*	
SiO_2	0.10	99.0
Al_2O_3	0.10	58.0
Fe_2O_3	0.04	28.0
MgO	0.10	60.0
CaO	0.02	60.0
Na_2O	0.15	30.0
K_2O	0.02	30.0
TiO_2	0.02	10.0
P_2O_5	0.05	50.0
MnO	0.01	15.0
LOI (925°C)	0.01	100.0

Under normal circumstances of staffing and instrument maintenance, 700 samples per month can be analyzed with this method.

Apparatus

- Philips PW1606 simultaneous X-ray spectrometer
- Pt-Au alloy crucibles and molds (Taggart and Wahlberg, 1980a)
- Fluxer (Taggart and Wahlberg, 1980b)
- Two muffle furnaces with rocker attachments
- Hot plate and muffle furnace

Reagents

The samples are digested in Johnson Matthey Spectroflux 100 or equivalent brand (lithium tetraborate). The flux is ordered in homogenized 200 Kg batches (approximately 2½-year supply). The minus 60-mesh flux is dried for 2 days at 300°C and kept in vacuum sealed in Mason jars. After drying a loss-on-fusion is performed for each lot of flux from the manufacturer so that an appropriate amount of flux can be weighed out to yield 8.0000 g of lithium tetraborate after fusion. The platinum ware is cleaned in 50 percent reagent grade (not technical) HCl and rinsed in deionized water. The LiBr used as a nonwetting agent is prepared by neutralizing reagent grade concentrated HBr (48%) with $LiCO_3$. This solution is filtered, and diluted 1:1 with deionized water.

Safety precautions

Fusions and ignitions of samples in a muffle furnace must be performed under a high-velocity canopy hood. Boiling of the HCl cleaning solution is performed in a chemical fume hood with a safety sash. Safety glasses and special nonflammable, nonasbestos, heat-resistant gloves must be worn when removing the fluxer from the muffle furnace. Glass discs are sharp on the rear edge and should be handled with care. Dust from the flux must not be inhaled, so pouring of the powdered flux must be done in a chemical hood. Preparation of the LiBr solution must be done by slowly adding $LiCO_3$ to the HBr so the generation of CO_2 does not cause the acid to spill over the edge of the beaker. See the *CHP* and *MSDS* for further information concerning first-aid treatment and disposal procedures for chemical products used in this method.

Procedure

A 0.8000 g portion of minus 80-mesh sample is ignited in a tared 95 percent Pt/ 5 percent Au crucible at 925°C for 45 min. The weight loss is reported as percent loss on ignition (LOI). A charge of lithium tetraborate that will contribute 8.0000 g after fusion is added to the sample and the powders are thoroughly mixed. The combined weights of the sample and the flux are calculated to present are "infinitely thick" sample disc to the instrument. A 0.250 mL aliquot of the 1:1 LiBr solution is added as a nonwetting agent. Seven crucibles containing samples and seven empty molds are loaded onto the automatic fluxer and the loaded apparatus placed in the muffle furnace at 1,120°C. The samples are allowed to come to temperature, for 10 min, and are then homogenized in the furnace with an electric motor mechanism for 35 min. The fluxer is removed from the furnace, the molten mixtures are poured from the seven crucibles into their respective molds, and cooled to near room temperature. An essential feature of this method is the mold design (Taggart and Wahlberg, 1980a). Samples with high concentrations of Cu, Cr, Ni, Fe, Mn and high organic content require various special sample preparation techniques, and in some cases, cannot be prepared at all. Samples with arsenic or lead with concentrations in excess of 2,000 ppm, or with combined As/Pb concentration in excess of 3,000 ppm, cannot be prepared due to damage of the Pt/Au crucibles. Using the wavelength dispersive X-ray spectrometer, the major element concentrations are determined by comparing the intensities obtained from standards with those obtained from the sample. (Taggart and others, 1981; Taggart and others, 1987).

The following instrumental conditions are for the Phillips PW1606 spectrometer:

Tube	Rhodium, end window
Power	35Kv and 60ma
Time	100 s
Atmosphere	Vacuum

See table 67 for the parameters for each of the channels and detectors in the instrument. Sixty-two well characterized and available international standards are used for the calibration. The 15 standards used for the recalibration program are prepared and run in triplicate, while the remaining 47 standards are prepared and run in duplicate. Additionally, four spiked bromine standards, six spiked sulfur standards, 10 blanks with LiBr, and five blanks without LiBr are used in the calibration.

Table 67.—Operating conditions for determination of elements by WDXRF

[PX-1=Tungsten Carbide layered, TLAP=thallium hydrogen phtalate, PET=pentaerythritol tetrakis (hydroxymethyl) methane, InSb=Indium Antimonide, Ge=Germanium 111, LiF 200=lithium fluoride (200 lattice orientation), P-10 gas=90 percent argon + 10 percent methane]

Element	*Line*	*Crystal*	*Detector-gas*	*Window*
Na	Kα	PX-1	Flow, P-10	2 μm, polypropylene
Mg	Kα	TLAP	Flow, P-10	2 μm, polypropylene
Al	Kα	PET	sealed neon	25 μm, beryllium
Si	Kα	InSb	sealed neon	25 μm, beryllium
P	Kα	Ge	sealed neon	50 μm, beryllium
K	Kα	LiF 200	sealed krypton	100 μm, beryllium
Ca	Kα	LiF 200	sealed krypton	100 μm, beryllium
Ti	Kα	LiF 200	sealed krypton	100 μm, beryllium
Mn	Kα	LiF 200	sealed krypton	100 μm, beryllium
Fe	Kα	LiF 200	sealed krypton	100 μm, beryllium

The Philips PW1606 spectrometer is recalibrated every 2 weeks. The computerized recalibration is performed using discs from the original calibration and are used to set the slope of the calibration curve. The standards used include: AGV-1, DTS-1, BHVO-1, STM-1, NOD-P-1, MRG-1, BX-N, FK-N, GS-N, MICA-FE, NIM-D, NIM-P, GSR-4, GFS-401, and NBS-120C. Six blanks, prepared from the current batch of flux and LiBr are used for recalibration of the curve's intercept. This allows the original calibration to be maintained while compensating for minor changes in the reagents, P-10 gas, or instrument parameters due to equipment maintenance. Following a recalibration, a new disc of the quality control check standard TB-1 is prepared and counted to verify the calibration.

Long-term instrument drift is corrected using drift monitor analyses. Monitor intensity values obtained during the analyses are compared with monitor intensity values from the original calibration. Corrections are calculated by the spectrometer's software. Long-term drift monitoring cannot correct for short-term effects or significant changes in the operating parameters.

In order to keep track of instrumental short-term drift, at least every twelfth disc is an instrument check standard: AGV-1, TB-1, DTS-1, BCS 381, or BX-N. These standards represent the average, high and low for the 10 analyzed elements. If the analyzed disc exceeds three times the standard deviation of the counting statistics, analysis is halted and the instrument is checked using other discs. If the disc is corrupt, it is removed and another is made. If the instrument shows signs of drift, then a recalibration is performed, as previously described.

In addition to the instrument standards, a sample preparation check standard, TB-1 disc is prepared for every 20 samples produced and analyzed along with the samples. If this disc shows a deviation of 3 standard deviations or more, and the instrument standards show no deviation, then another sample of TB-1 is prepared. If it again shows deviation, then sample preparation is halted and the problem is located. If both the sample preparation standard and the instrument standard exceed control limits, then the instrument recalibration is performed.

Assignment of uncertainty

The WDXRF method for major element analysis is unique among analytical method packages in that it takes advantage of the summation of the determined elements. This summation acts as a measure of quality control. If an analysis includes the principal elements in a sample, then the total of their determinations should approach 100 percent. This check is the main reason that a LOI was initially incorporated in the package. If an analysis yields a total major element oxide determination of less than 97 percent or greater than 101 percent, then it is automatically repeated. Precision in the WDXRF method depends on the stability of the instrument, the orientation of this sample disc as it is presented to the instrument, and the homogeneity of the sample preparation.

Table 68 is the analytical results of 10 major elements for selected reference materials, duplicate samples, and method blanks. Some *pv* data are calculated from element-to-stoichiometric oxide conversion factors (see appendix A, table A1)

Table 68.—Analytical performance summary for elements (percent) by WDXRF

[A=Bureau of Analysed Samples Ltd., 1973; B=National Institute of Standards and Technology, 1992; remaining *pv* from Potts and others, 1992; LOI=loss on ignition; calc=value calculated as {H_2O^++H_2O^-+CO_2(+C)-(FeOx0.1113)}]

Reference	*Description*	*n*	*Mean*	*s*	*pv*			*% RSD*	*% R*
SiO_2									
BCS 381	slag	27	8.83	0.04	8.78	A		0.5	101
JA-2	andesite	30	56.5	0.2	56.18			0.3	101
GSD-6	stream sediment	30	60.67	0.07	**61.23**			0.1	99
SRM 2711	soil	30	63.67	0.06	**65.12**	B	*cv*	0.1	98
GSD-12	stream sediment	30	76.5	0.1	**77.29**			0.2	99
Al_2O_3									
BCS 381	slag	27	0.71	0.01	0.67	A		1	106
GSD-12	stream sediment	30	9.30	0.03	**9.30**			0.3	100
SRM 2711	soil	30	12.18	0.03	**12.34**	B	*cv*	0.2	99
GSD-6	stream sediment	30	14.14	0.04	**14.16**			0.3	100
JA-2	andesite	30	15.78	0.05	15.32			0.3	103

Table 68.—Analytical performance summary for elements (percent) by WDXRF—Continued

Reference	*Description*	*n*	*Mean*	*s*	*pv*			*% RSD*	*% R*
Fe_2O_3									
SRM 2711	soil	30	4.12	0.01	**4.13**	B	*cv*	0.2	100
GSD-12	stream sediment	30	4.86	0.01	**4.88**			0.3	100
GSD-6	stream sediment	30	5.88	0.02	**5.88**			0.3	100
JA-2	andesite	30	6.17	0.02	6.95			0.3	89
BCS 381	slag	24*	18.12	0.08	19.02	A		0.4	95
*Missing Fe_2O_3 values rejected due to Fe contamination									
MgO									
GSD-12	stream sediment	30	0.44	0.01	**0.47**			2	94
BCS 381	slag	27	0.82	0.01	1.03	A		1	80
SRM 2711	soil	30	1.72	0.01	**1.74**	B	*cv*	0.8	99
GSD-6	stream sediment	30	2.98	0.01	**3.00**			0.5	99
JA-2	andesite	30	7.28	0.03	7.68			0.4	95
CaO									
GSD-12	stream sediment	30	1.16	0.01	**1.16**			0.8	100
GSD-6	stream sediment	30	3.91	0.01	**3.87**			0.3	101
SRM 2711	soil	30	3.97	0.01	**4.03**	B	*cv*	0.3	98
JA-2	andesite	30	6.20	0.02	6.48			0.3	96
BCS 381	slag	27	48.1	0.1	49.0	A		0.2	98
Na_2O									
BCS 381	slag	27	0.21	0.02	---			10	---
GSD-12	stream sediment	30	0.33	0.01	**0.44**			3	75
SRM 2711	soil	30	1.47	0.01	**1.54**	B	*cv*	0.9	95
GSD-6	stream sediment	30	2.18	0.02	**2.31**			1	94
JA-2	andesite	30	3.08	0.02	3.08			0.6	100
K_2O									
BCS 381	slag	27	0.039	0.003	---			8	---
JA-2	andesite	30	1.83	0.01	1.80			0.5	101
GSD-6	stream sediment	30	2.43	0.01	**2.44**			0.4	99
GSD-12	stream sediment	30	2.92	0.01	**2.91**			0.3	100
SRM 2711	soil	30	2.93	0.01	**2.95**	B	*cv*	0.3	99
TiO_2									
GSD-12	stream sediment	30	0.260	0.003	**0.25**			1	104
BCS 381	slag	27	0.330	0.004	0.35	A		1	94
SRM 2711	soil	30	0.512	0.004	**0.51**	B	*cv*	0.8	100
JA-2	andesite	30	0.674	0.006	0.67			0.9	100
GSD-6	stream sediment	30	0.765	0.004	**0.78**			0.5	98

Table 68.—Analytical performance summary for elements (percent) by WDXRF—Continued

Reference	*Description*	*n*	*Mean*	*s*	*pv*			*% RSD*	*% R*
P_2O_5									
GSD-12	stream sediment	30	0.085	0.004	0.055			5	155
JA-2	andesite	30	0.187	0.004	0.15			2	127
SRM 2711	soil	30	0.214	0.003	**0.197**	B	*cv*	1	109
GSD-6	stream sediment	30	0.260	0.004	**0.23**			2	113
BCS 381	slag	27	15.4	0.04	15.7	A		0.3	98
MnO									
SRM 2711	soil	30	0.083	0.001	**0.0823**	B	*cv*	1	101
JA-2	andesite	30	0.107	0.001	0.11			0.9	100
GSD-6	stream sediment	30	0.126	0.001	**0.13**			0.8	100
GSD-12	stream sediment	30	0.184	0.001	**0.18**			0.5	100
BCS 381	slag	27	3.01	0.01	3.16	A		0.3	95
LOI (925°C)									
BCS 381	slag	27	0.24	0.07	---			29	---
JA-2	andesite	30	1.76	0.10	2.12 calc			5	83
GSD-12	stream sediment	30	2.72	0.02	2.50		?	0.8	109
GSD-6	stream sediment	30	5.70	0.06	5.83 calc			1	98
SRM 2711	soil	30	7.92	0.08	---			1	---

Duplicate samples	*k*	*n*	*Mean*	*s*	*% RSD*	*Concentration range*			*No of < (total)*	*No of < (pairs)*
SiO_2	56	2	60.25	0.07	0.1	30.89	to	96.13	0	0
Al_2O_3	56	2	14.81	0.02	0.1	0.79	to	27.29	0	0
Fe_2O_3	56	2	6.83	0.02	0.3	0.53	to	36.6	0	0
MgO	53	2	3.28	0.01	0.3	0.19	to	11.32	6	3
CaO	56	2	4.71	0.01	0.2	0.07	to	13.18	0	0
Na_2O	53	2	2.98	0.01	0.3	0.37	to	5.97	6	3
K_2O	56	2	2.43	0.01	0.4	0.08	to	9.37	0	0
TiO_2	56	2	0.809	0.002	0.2	0.073	to	2.85	0	0
P_2O_5	56	2	0.217	0.002	0.9	0.053	to	1.05	0	0
MnO	53	2	0.1007	0.0004	0.4	0.01	to	0.307	4	2
LOI	54	2	2.91	0.03	1	0.10	to	21.82	4	2
Total	56	2	99.4	0.1	0.1	96.48	to	100.34	0	0

Table 68.—Analytical performance summary for elements (percent) by WDXRF—Continued

Method blank	*n*	*Mean*	*s*	*3s*	*5s*
SiO_2	60	-0.01	0.01	0.04	0.07
Al_2O_3	60	0.03	0.01	0.04	0.07
Fe_2O_3	60	0.003	0.004	0.01	0.02
MgO	60	-0.01	0.009	0.03	0.05
CaO	60	0.008	0.001	0.003	0.005
Na_2O	60	-0.04	0.02	0.06	0.1
K_2O	60	-0.01	0.002	0.006	0.01
TiO_2	60	-0.02	0.001	0.003	0.005
P_2O_5	60	-0.02	0.002	0.006	0.01
MnO	60	-0.01	0.0004	0.001	0.002

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APPENDIX A

Table A1. Element to oxide conversion factors

Ag_2O	1.0741
Al_2O_3	1.8895
As_2O_3	1.3203
As_2O_5	1.5339
Au_2O	1.0406
B_2O_3	3.2202
BaO	1.1165
BeO	2.7758
Bi_2O_5	1.1914
CO_2	3.6644
CaO	1.3992
CdO	1.1423
Ce_2O_3	1.1713
CeO_2	1.2284
CoO	1.2715
Cr_2O_3	1.4615
Cs_2O	1.0602
CuO	1.2518
Dy_2O_3	1.1477
Er_2O_3	1.1435
Eu_2O_3	1.1579
FeO	1.2865
Fe_2O_3	1.4297
Ga_2O_3	1.3442
Gd_2O_3	1.1526
GeO_2	1.4408
HfO_2	1.1793
HgO	1.0798
Ho_2O_3	1.1455
In_2O_3	1.2091
IrO	1.0832
K_2O	1.2046
La_2O_3	1.1728
Li_2O	2.1527
Lu_2O_3	1.1371
MgO	1.6582
MnO	1.2912
MnO_2	1.5825
MoO_3	1.5003
N_2O_5	3.8551
Na_2O	1.3480
Nb_2O_5	1.4305
Nd_2O_3	1.1664
NiO	1.2725
OsO	1.0841
P_2O_5	2.2916
PbO	1.0772
PbO_2	1.1544
PdO	1.1504
Pr_2O_3	1.1703
Pr_6O_{11}	1.2082
PtO	1.0820
Rb_2O	1.0936
ReO	1.0859
RhO	1.5555
RuO	1.1583
SO_3	2.4972
Sb_2O_5	1.3284
Sc_2O_3	1.5338
SeO_3	1.6079
SiO_2	2.1392
Sm_2O_3	1.1596
SnO_2	1.2696
SrO	1.1826
Ta_2O_5	1.2211
Tb_2O_3	1.1510
Tb_4O_7	1.1762
TeO_3	1.3762
ThO_2	1.1379
TiO_2	1.6681
Tl_2O_3	1.1174
Tm_2O_3	1.1421
UO_2	1.1344
UO_3	1.2017
U_3O_8	1.1792
V_2O_5	1.7852
WO_3	1.2610
Y_2O_3	1.2699
Yb_2O_3	1.1387
ZnO	1.2448
ZrO_2	1.3508

Table A2. Weight-to-ppm-to-ppb equivalents

Weight percent	*ppm*	*ppb*	
1.0	10,000		
0.1	1,000		
0.01	100		
0.001	10		
0.0001	1	1,000	1 µg/g
0.00001	0.1	100	
0.000001	0.01	10	
0.0000001	0.001	1	1ng/g
0.00000001	0.0001	0.1	

Table A3. Grain size and sieve equivalents

Mesh opening *Microns*	*Inches*	*U.S. Standard Mesh No.*	*Tyler Mesh Equivalent*
850	0.0331	20	20
710	0.0278	25	24
600	0.0234	30	28
500	0.0197	35	32
425	0.0165	40	35
355	0.0139	45	42
300	0.0117	50	48
250	0.0098	60	60
212	0.0083	70	65
180	0.0070	80	80
150	0.0059	100	100
125	0.0049	120	115
106	0.0041	140	150
90	0.0035	170	170
75	0.0029	200	200
63	0.0025	230	250
53	0.0021	270	270
45	0.0017	325	325
38	0.0015	400	400

APPENDIX B

GLOSSARY OF SYMBOLS AND TERMS

Å—angstrom (unit of wavelength measure)

A—ampere (rate of flow of electric current)

A—absorbance

AAS, atomic absorption spectrometry—analytical technique based on the absorption of radiant energy by atoms. The majority of atoms introduced to a source of energy (flame or flameless) remain in a ground state. When a beam of light is passed through the energy source, ground-state atoms (elements) having the same wavelength absorb the radiation. The absorbed radiation is characteristic and proportional to the concentration of specific atoms.

ac—alternating current

Accuracy—degree of agreement between the measured value to the "true" or proposed value

AES, atomic emission spectrometry—analytical technique based on the emission of radiant energy by atoms. Free atoms (elements) are excited by a source of energy. As the excited atoms return to the ground state, they emit a characteristic radiation with an intensity proportional to the concentration of the atoms.

Aliquot—measured volume of a liquid which is a known fractional part of a larger volume

Anion—negatively charged ion, e.g. Cl^-, SO_4^{-2}, and PO_4^{-3}

Anode—electrode at which oxidation occurs and toward which anions move

Aqua regia—mixture of 3 parts 12 *M* HCl with 1 part 16 *M* HNO_3

Arc—high voltage used to excite a solid sample held in one of two arranged electrodes

Batch—quantity of test samples produced during an analytical process expected to be of uniform character

Bias—positive or negative deviation of the mean analytical result from the proposed or "true" value

Blank—the measured value of a sample that is free of the analyte of interest

c—cycle

°C—degree Celsius

Calibration—comparison of a measurement standard or instrument with another standard or instrument to report or eliminate by adjustment any variation in the accuracy of the measurement value

Cation—positively charged ion, e.g. Na^+ or Fe^+, Fe^{+3}, and NH_4^+.

Chemical hygiene plan—written document of a comprehensive laboratory safety program.

Chromatography—separation method in which the compounds of a solution are adsorbed at different locations on a fixed medium (stationary phase). The mobile phase (liquid or gas containing the sample) flows through the fixed medium. A detector signals the adsorbance time (related to characteristic species) and peak area (concentration).

cm—centimeter

Combustion—detection method using thermal conductivity. Usually the sample is oxidized and the volatile compounds are separated and measured for the element (e.g. carbon, sulfur, and hydrogen) of interest

conc—concentrate

Coulometry—analytical technique measuring the quantity of electricity used to carry out a chemical reaction in solution. The quantity of current is directly proportional to the amount of oxidation/reduction (ion concentration) at the electrode.

db—decibel

dc—direct current which flows in only one direction

DNA, delayed neutron activation analysis—technique based on neutron irradiation of samples inducing nuclear fission products. The subsequent decay by delayed neutron emission can be quantitatively counted for specific species (uranium and thorium).

Duplicate sample—a second aliquot of a randomly selected sample to assist in the evaluation of laboratory variance

Flame photometry—analytical technique based on the emission of radiation by atoms in a flame returning from an excited state (formed due to absorption). The measurement of wavelength and intensity of light emitted is proportional to a specific element and concentration. No light source is required as in AAS.

g—gram

Graphite furnace—a device used to electrically heat (about 2500°C) a sample for flameless AAS. A nitrogen or argon atmosphere is required around the device to prevent air oxidation.

Gravimetric analysis—process where the weight of the product of a reaction (precipitate, gas, or pure metal in electroplating) is measured and converted back to the weight of a specific species

Heavy metals—those metals which have ions that form an insoluble precipitate with sulfide ion

hp—horsepower

Hydride—compound of hydrogen, specifically containing H^- ions.

ICP, inductively coupled plasma—a device used as an excitation source for samples. The device creates a plasma (about 10,000 K) by interacting an induced magnetic field with argon gas.

id—interior diameter

in—inch

INAA, instrumental neutron activation analysis—technique based on the irradiation of samples by neutrons producing a radioactive isotope. The isotope emits characteristic gamma radiation in amounts indicative of specific elemental concentrations.

IR, infrared spectrometry—analytical technique based upon the radiation emitted in the wavelength from 0.75 to 400 micrometers (usually 2.5 to 16 µm is used). An instrument chops the IR radiation and passes it alternately through a sample and a standard reference. The interaction with IR radiation produces an absorption spectrum that is characteristic of a known compound.

ISE, Ion-selective electrode—half-cell consisting of a thin pH responsive membrane (glass, lanthanum fluoride, liquid, or gas permeable) housing an internal reference reservoir. The potential measured in an external solution is proportional to the logarithm of the ion concentration.

k—the number of subgroups or samples under consideration

λ—lambda; wavelength

μg—microgram (10^{-6} gram)

μm—micrometer (micron)

L—liter

LOD, limit of detection—the lowest qualitative concentration level of the analyte that can be determined with a stated level of confidence

LOQ, limit of quantification (determination)—the lowest quantitative concentration level of the analyte that can be determined with a stated level of confidence

Mass spectrometry—analytical technique based on the determination of the mass/charge ratio of an ion. Molecules are broken into charged particles and separated by a magnetic field. The fragments strike an electron-emitting surface generating a characteristic electrical signal. The relative numbers of each kind of ion is specific for a given compound (including isomers and organic mixtures).

Method blank—a sample containing deionized water and reagents which is carried through the entire analytical procedure

mg—milligram (10^{-3} gram)

min—minute

mL—milliliter

mm—millimeter

MSDS—Material Safety Data Sheets; required documents by OSHA regulations on all chemicals as to their possible health, fire, and other hazards

n—the number of observed values in a sample or subgroup, sample size

ng—nanogram (10^{-9} gram)

od—outside diameter

OSHA—U.S. Department of Labor's Occupational Safety and Health Administration

Oxidation—half-reaction involving a loss of electrons; a positive charge in valence

oz—ounce

pct—percent

pH—measure of hydrogen-ion concentration of a solution, defined as $-\log_{10}[H^+]$

Potentiometry—analytical technique based on 1) the measurement of the changes in electromotive forces through titration or 2) the direct measurement of an electrode potential

ppb—parts per billion

ppm—parts per million

psi—pounds per square inch

Precision—degree of agreement between measured values under repetitive testing of a sample; reproducibility of results

pv—proposed value

QA, quality assurance—a preventative program to assure that a product or service meets defined standards of quality

QC, quality control—the procedures used to ensure acceptable quality results are produced

***R*, sample range**—the absolute difference between the minimum and maximum values of a data set

***%R*, percent recovery**—the ratio of the observed value, X to the proposed value pv, expressed as a percentage,

$$\%R = \frac{X}{pv} \times 100$$

Reduction—half-reaction involving a gain of electrons; a negative charge in valence.

RF—radio frequency

RM, reference material—sample having one or more well established properties to be used for calibration, assessment of a measurement method, or assignment of values to materials.

rpm—revolutions per minute

***%RSD*, relative standard deviation**—the ratio of standard deviation, s to the arithmetic mean $\overline{X}$, expressed as a percentage,

$$\%RSD = \frac{s}{\overline{X}} \times 100$$

s—second

sensitivity—the ratio of change in signal to the change in analyte concentration

***s*, standard deviation**—the square root of the quantity (sum of squares of deviations of individual results from the mean, divided by one less than the number of results in the set),

$$s = \sqrt{\sum_{i=1}^{n} (X_i - \overline{X})^2 / n-1}$$

s_d, standard deviation for duplicate measurements—the square root of the quantity (sum of squares of the difference between the duplicate results, divided by two times the number of sets of duplicate samples),

$$s_d = \sqrt{\sum R^2 / 2k}$$

Sample—representative part of a larger whole, any quantity of the test (field) or reference substance

Specific gravity—ratio of the density of a substance to the density of a standard substance

Titrimetry—volumetric analysis by which the exact amount of reagent needed to combine with a specific species is measured. The total consumption of the species is signaled by a physical change (e.g. change of color, turbidity formation, conductivity) in the solution. The amount of the reagent needed is converted to the weight of the species.

***v*, degrees of freedom**—defined as n-1, refers to the number of independent deviations which are used in calculating standard deviation

X—observed value of a measurable characteristic

$\overline{X}$, arithmetic mean—the sum of n observed values divided by n,

$$\overline{X} = (X_1 + X_2 + \ldots X_n) / n$$

XRF, X-ray fluorescence spectrometry—technique based upon analyzing the emitted (fluorescence spectrum) radiation when a sample is irradiated with X-rays. The fluorescent intensity of a species is proportional to its concentration.