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GEOLOGICAL SURVEY

Quality assurance manual for the Branch of Geochemistry, U.S. Geological Survey

by

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1. INTRODUCTION

1.1 Overview

This document constitutes the Quality Assurance Manual for the Branch of Geochemistry, U.S. Geological Survey. The manual describes the procedures for handling, sample preparation, analytical methods, use of instrumentation, written documentation, etc. to be followed in the laboratory.

1.2 Purpose

The purpose of the quality program is to provide an effective means of:

a. monitoring the reliability of analytical results generated by analysts within the Branch;
b. providing a measure of the accuracy and precision of the analytical methods;
c. providing a permanent record to assure integrity of sample results.

1.3 Scope

The range of activities under the program includes all operational methods currently in use by the Branch of Geochemistry and a specification of requirements to be met by the appropriate project chief and analyst.

Uniformity of methodology within each laboratory and between centers (Denver, Menlo Park, and Reston) is needed to remove methodology as a variable. The Branch consists of three centers at the following locations:

Western Region 415-329-4229
345 Middlefield Road
Menlo Park, CA 94025

Denver Federal Center 303-236-1800
Box 25046, MS 973
Denver, CO 80225

National Center 703-648-6201
12201 Sunrise Valley Drive
Reston, VA 22092

Field and mobile laboratories are subject to QA protocol.

Appendix B contains the accepted methods for operational geochemistry and was prepared with the assistance of many Branch chemists. Due to the necessity of revisions, addendums may be added for method modification. Reference to trade names or commercial products is for descriptive purposes only and does not imply endorsement by the U.S. Geological Survey.

No quality assurance program can eliminate all errors that may occur during analysis. The professional judgment of the staff must be coupled with the quality assurance procedures to ensure that quality data are consistently produced (Enseco, 1989, p. 5).

2. SAMPLE COLLECTION

The generation of quality data begins with collection of the sample. The Branch quality assurance program is concerned with the integrity of sample collection, but is not in effect until the sample is received by the sample control project.

2.1 Sampling

Sample collection is performed by personnel from, or in collaboration with, the U.S. Geological Survey, Geologic Division. The appropriate volume of sample should be collected to ensure detection limits can be met. Samples consist of natural materials found on the earth's crust; i.e. soil, rocks, plants, water, and stream sediments. Quality assurance of sampling operations is the responsibility of the project chief. Unique field numbers are assigned to each sample. Instructions for submitting samples to the Branch are contained in the "Sample Submittal Manual."

2.2 Containers

Samples are collected in containers appropriate for the material. Rocks, minerals, plants, and stream sediments are collected in clean cloth bags and/or kraft paper bags. Water samples are collected in prewashed polypropylene bottles. Checking for contamination in container lots is the responsibility of the geologist.

2.3 Preservatives

Water samples, to be analyzed for cations, are passed through a 0.45-µm membrane filter before acidifying with concentrated nitric acid to a pH below 2.0 (McHugh, 1983, p. 3). Water temperature and pH are measured at each sample site.

Solid samples are air dried, if collected wet, except under special circumstances, e.g., where moisture and pH are analyzed for in peat.

2.4 Duplicates

Duplicates of similar materials are collected at a sampling frequency determined by the field geologist to assess the sample site variability.

3. SAMPLE HANDLING

3.1 Sample Receipt and Log-in

Samples and the accompanying request for analysis (RFA) form (see appendix C) are received by the Sample Control Project of the Operational Geochemistry Section. Each RFA form is assigned a job number (a unique laboratory identification number that encodes the date received). A serial laboratory number is assigned to each sample field number.

The RFA form serves as the sample accountability record and the original form accompanies the job of samples to each assigned analyst. Exceptions may be made for split samples that are sent to different centers. A request can include up to 40 samples. Larger lots of samples are broken down into groups not to exceed 40. All samples should be logged into the sample control computer within 72 working hours of receipt.

Once a sample is checked out to an individual, the responsibility for the sample is shifted from sample control to that individual.

3.2 Potential Problems

The field geologist must notate on the RFA form any unusual or highly mineralized samples; the analyst is to notate analyses that occur in the field. Samples shall be notated on the RFA form, by sample control, under the following conditions:

--leaky bags
--plastic containers under high pressure
--discrepancies between information on sample label and RFA form
--radioactive or hazardous samples as mandated by the Branch Safety Officer

3.3 Blind Sample Insertion

Periodically, the sample control officer inserts blind quality assurance samples into a request. These samples are labeled as a QA sample of an unknown composition. The blind samples consist of in-house reference standards and international reference standards.

3.4 Sample Preparation

Solid samples require appropriate preparation prior to analysis. Rock, soils, plants, etc. are ground to approximately minus 100-mesh, mixed, and split so that several tests can be conducted on the sample simultaneously. One split of the sample is stored for future work. See specific analytical method (appendix B) for more detailed information. Sample containers are clearly marked with the appropriate laboratory ID numbers. The RFA is signed and dated when sample preparation is complete, by the responsible sample control person.

3.5 Sample Archiving

The prepared sample is archived indefinitely for future investigations. Prepped sample material, in excess of the filled sample container, is either returned to the submitter or discarded according to the sample preparation instructions on the RFA form.

4. REAGENTS, CONTAINERS, and LABORATORY SERVICES

4.1 Reagent Specification

The specification of reagent purity for each method of analysis is part of the bench-level protocol (see section 7.5). Analysts shall also be familiar with the Materials Safety Data Sheet (MSDS) posted in each laboratory. The MSDS lists precautions, affects of over-exposure, first-aid treatment, and disposal procedures, etc. for hazardous chemical products. In general, American Chemical Society (ACS) Reagent Grade or better is required for all tests. Reagents are labeled with date received, date opened, and if applicable, expiration date and special instructions. Reagents that are sensitive to light should be stored in dark bottles and in a dark, cool place while some reagents require refrigeration.

All reagent preparations are clearly labeled as to the contents, concentration, date of preparation, and initials of the preparer. Unstable reagents are prepared on a schedule as specified in the method of analysis and labeled with an expiration date.

Any reagent with hazardous or toxic fumes shall be used within a working exhaust hood. Protective clothing, gloves, and glasses are required.

All new reagent lots and preparations are tested by determining the reagent blank.

4.2 Container Specification

All volumetric glassware are Class A. Pulverized samples are stored in cardboard or polycon containers except reference samples that are usually stored in glass. Digestions are conducted in clean Teflon, borosilicate glass, porcelain, platinum, zirconium, or graphite containers, and solutions are stored in clean polyethylene or borosilicate containers prior to measurement. The selection of container is dependent upon the suitability for storage of strong acid or alkaline solutions. Detailed instructions for the use and care of laboratory ware are specified in the bench-level protocol.

"In general, laboratory ware is considered clean when it maintains a continuous film of distilled water over its entire inner surface. . . . Organic residues may require treatment with chromic acid. . . trace determinations may require rinsing with hot 50% nitric acid, (10% HCl,) or aqua regia, followed by distilled water. Apparatus should be dried and stored under conditions that will not allow it to become contaminated" (Garfield, 1984, p. 39).

4.3 Laboratory Services

The deionized or distilled water system must provide purified water so that it has at least a 7 megohm-cm resistivity.

Compressed air that is generated should be dry and oil-free.

Use of an efficient hood system is required for procedures generating hazardous or toxic fumes.

Voltage regulation is used on applicable instruments.

5. INSTRUMENT CALIBRATION AND MAINTENANCE

Instrument maintenance is a continuing process that is a part of the duties of each analyst in the laboratory (Jones, 1987, p. 6). Routine maintenance minimizes downtime and interruption of analytical work.

An instrument logbook with a unique label is maintained for each instrument in the laboratory. Each instrument is assigned a unique number and that number appears in the logbook. Analysts are required to record in the logbook all maintenance and calibration procedures at the time they are performed.

Preparation of calibration standards, procedures, and frequency are addressed in appendix B. Unless otherwise specified in the method, if deviations of the calibration verification value exceed the control (rejection) limits of ±3 standard deviations (s) from the established working value the analysis should be terminated, the problem corrected, the instrument recalibrated, and the run repeated. Warning limits are marked at ±2s (see section 8.2 for quality control [QC] checks and appendix D for the equation used to calculate s).

Periodic maintenance is performed on a schedule as specified in the analytical method or as indicated below:

5.1 Analytical Balances

Proper care of the balance is important due to the accuracy of the balance being a factor in the accuracy of weight-prepared standards and samples (U.S. Environmental Protection Agency [EPA], 1979, p. 3-1). Balances are calibrated biannually using Class S weights. The balance is checked daily for level and zero point adjustments and cleaned after each use. Balances should be mounted on a heavy, shockproof table away from drafts.

5.2 Atomic Absorption Spectrometers

Burner heads and nebulizer chambers are cleaned after each use. Optimization of nebulizers, wavelength alignment, and burner position are checked when used. Photomultipliers and lamps are replaced as required based upon regularly scheduled checks of energy sensitivity readings and lamp currents (Jones, 1987, p. 7).

5.3 Emission Spectrometers

Inductively coupled plasma (ICP) nebulizers and spray chambers are tested prior to beginning the day's calibration, and again if a QC sample indicates a problem, to ensure normal sensitivity and cleanliness. Photomultiplier tubes and integration circuits are tested during calibration to ensure normal linearity and baseline noise. A dc arc calibration can be expected to remain valid until the instrument is either moved or a new photographic emulsion is used, assuming an established temperature range is maintained.

5.4 Hot Plates, Furnaces, and Ovens

The temperature calibration of hot plates, furnaces, and ovens is checked quarterly using thermocouple-type thermometers, surface metal expansion type thermometers, optical pyrometers, or the melting points of pure metal standards to check the normal operating temperature. The heating element is to be checked for maintenance of the temperature within limits stipulated in the bench-level protocol.

5.5 Continuous-flow Automated Analyzers

Pump tubing is changed on a preset schedule which is part of the bench-level protocol for each different methodology. Optical alignment is performed on a regular schedule as specified in the individual methods (Jones, 1987, p. 7).

5.6 Pipettes

Oxford/Eppendorf repeating type pipettes are checked on a scheduled basis described in the bench-level protocol. Bottle top varieties are cleaned after each day's use and lubricated weekly.

5.7 pH/Selective-ion Meters

pH meters are calibrated, each time used, for accuracy and linearity using commercially prepared, National Bureau of Standards or equivalent, standard traceable buffer solutions (Jones, 1987, p. 7).

At least two buffers that bracket the expected pH of the samples are used for calibration (U.S. EPA, 1979, p. 3-3). Measurements of both buffers must be correct within the readability of the instrument after calibration. The temperature at the time of analysis should be noted. Electrodes shall be rinsed with distilled water after each reading and immersed in the appropriate solution for storage.

6. INSTRUMENT STANDARDIZATION PROCEDURES

Procedures, frequencies, and tolerances of standardization are specified for each analytical method in appendix B.

6.1 Preparation of Standards

Primary standards must be obtained from a reliable source and may require pretreatment (i.e. drying). Unless otherwise stated, all standard material used shall conform in high reliable purity to ACS Analytical Reagent Grade or Primary Standard Grade. Certain standards must be of spectroquality.

Standard solutions which are purchased and certified by the supplier are checked against the previously prepared standard before they are used to standardize the instrument. Supplier lot number and the date they are opened are recorded in the analyst logbook. Diluted standard solutions are labeled using the analysts initials, concentration of analyte, concentration of diluent, and the date of preparation. Standards should not be kept longer than recommended by the manufacturer or in the method.

For methods using solid standards, such as instrumental neutron activation and dc arc spectrography, standards are prepared either by spiking solution standards on solid substrates, mixing quantities of pure salts with solid materials, or using rock reference samples. Standard salts used in mixed standards must be 99.999 percent purity or better. New standards are compared to previous sets of standards for verification of accuracy.

6.2 Frequency of Standardization

Daily or more frequent standardization is the norm. In techniques using a large number of standards for the initial calibration (EDXRF or dc arc spectroscopy), the original calibration is reestablished with smaller subsets of the original standards.

6.3 Number of Standards

Calibrate, when possible, by a linear bracket of standards close to the sample concentration. For instruments in which absolute linearity cannot be established, use a calibration scheme of three or more standards per concentration decade.

6.4 Verification of Standardization

The standardization is verified initially by analyzing all of the standardizing samples. During a series of analyses, the standardization is rechecked periodically by analyzing one standard solution as a sample after, at most, every twentieth sample. Insofar as practical, the standard is chosen to be similar in concentration to the samples being analyzed. The result must meet the accuracy criteria specified in the standard method.

6.5 Reference Material Check

The accuracy of the method is verified by the analyst analyzing a standard or in-house reference material every 20th sample. The result must meet the method-specific accuracy criteria (see section 8.2 and appendix B).

7. ANALYTICAL PROCEDURES

7.1 Standard Methods of Analysis

Operational methods of analysis are contained in appendix B. Newer methods may be used which have been approved by the quality assurance program and are on file with the QA coordinator. Methods are identified by a unique three-digit number preceded by a letter. The letter prefix designates the instrumental method:

A	atomic absorption spectrometry
C	coulometric methods
E	emission spectroscopy
F	photoluminescent methods
G	gas chromatography
N	infrared spectroscopy
P	potentiometric methods
Q	other
R	radiochemical methods
T	thermal analysis
U	ultraviolet and visible absorption methods
X	x-ray methods

NOTE: The letter prefixs I, J, K, L, O, and Z are not to be used for operational methods.

The first two digits of the identifying number indicate the specific procedure and the last digit indicates a subsequent revision. Submitters may request a technique necessary for their study by checking the appropriate box under OPERATIONS GEOCHEMISTRY METHODS on the RFA form. Additional technique codes have been assigned for smaller suites of elements in order to assist with cost effectiveness if an entire package is not needed.

A historical file containing all methods, current and obsolete, is maintained for traceability purposes by the QA coordinator (Dux, 1986, p. 62).

7.2 Format for Writing Analytical Methods

The following format should be used to write an analytical method for validation.

Title -"should be brief and contain the name of both analyte, substrate" (Dux, 1986, p. 43), and designation of the measurement method.

1. General Discussion
   a. Principle - Briefly discuss the scientific basis of the method.
   b. Interference - List interferences and describe methods used to eliminate interferences.
   c. Scope - parameters measured; "range of analyte concentration for which the method is useful, type and nature of the matrix to which it can be applied, estimate of the time required for analysis" (Dux, 1986, p. 43), and minimum detectable concentration. It should enable the analyst to decide whether the method is suitable for any particular sample.

2. Apparatus
   Describe instruments and unusual apparatus required. Common laboratory equipment (glassware, balances) need not be listed.

3. Reagents
   Reagents should be described, including chemical name, purity, description of method of preparation for those which need preparation, shelf life if stability may be a problem.

4. Safety Precautions
   Describe any hazards peculiar to the method of analysis. These might include the need to work in a hood, need for special clothing, steps to avoid hazardous reactions.

5. Procedure
   Describe a strict time sequence and indicate critical steps in the analysis. Indicate in this section what reference samples are available and how frequently they should be analyzed, eg., calibration and standardization.

6. Calculation
   Give the equation(s) necessary to calculate the results of the analysis.

7. Assignment of Uncertainty
   Give all information on the accuracy and precision of the method in summarized form. Ultimately, the accuracy (and precision) goal of the method should be established on the end-use requirements (i.e. geochemical objective) rather than the

highest achievable. Generally, for major elements a relative standard duration (RSD) less than 1 to 2% is considered adequate, for minor elements a RSD less than 5%, and for traces less than 15%.

8. Bibliography
"Include references to the literature on which the method is based, or in-house documentation of validation studies" (Dux, 1986, p. 43).

7.3 Analytical Method Validation and Modification

Before any method is used to generate analytical data under the QA program, the method must be validated.

A copy of the analytical method, in proper format (see section 7.2), along with a research report containing the documentation for validation, must be submitted to the QA coordinator for acceptance. The report must include all analytical data used in evaluating the method.

Determine for each method the limit of detection (LOD), defined as the lowest concentration level that can be determined to be statistically different from a blank. The IUPAC definition is 3 standard deviations for a 99% confidence level.

Perform at least 10 replicate measurements of the reference materials, by the proposed method to be tested, on at least three non-consecutive days. Ideally, each analyte should be measured at the LOD, mid-point, and upper end of the calibration range, i.e. with a number of reference materials of varied concentration.

The arithmetic mean ($\bar{X}$) and standard deviation (s) are calculated in order to estimate accuracy and precision (see appendix D for equations used to calculate X and s). Depending upon the objective, the analytical method is generally considered sufficiently accurate if:

$$|\bar{X}-V| \leq 4s$$

V = "best defined reported value."

(The validation test is based upon one proposed by Sutarno and Steger, 1985, p. 445).

The individual performing the analysis and data calculations will be responsible for the examination of the finished data to determine that it is in statistical agreement with the analysis of previous samples. A secondary check by another analyst will confirm the validity of the data (Frankenberger, 1988, p. 10.2).

Improvement modifications should be validated and become an addendum to the written method. In general, modifications are changes in the technique that might be expected to affect results, e.g., different sample weight, dilution factor, pH. Such modifications of analytical procedures should be submitted in writing to the project chief and QA coordinator for approval.

7.4 Method Acceptance

Upon receipt by the QA coordinator, the method will be reviewed and designated an assigned number for traceability purposes. For operational use, "the proposed method should be at least equivalent to the current method with regard to precision, accuracy, limitation of interferences, productivity, the use of hazardous or toxic substances, and should be an improvement over the current method in at least one of these areas" (U.S. Geological Survey, 1989, p. 11). Upon QA approval, it will be dated as accepted. A dash, in place of the acceptance date refers to a method that is not expected to meet QA requirements but is considered useful for production work nonetheless. An example is the determination of water extractable boron by inductively coupled plasma-atomic emission spectroscopy (see appendix B).

7.5 Bench-level Protocol

For each standard method in the laboratory, there may be a specified procedure which details the application of the method using current equipment and facilities. This protocol is more specific than the written analytical method, and serves as an aid to the memory of the analyst, a training guide for new analysts, and as a record of the details of application of the method (Jones, 1987, p. 9). The protocol may be modified with the agreement of the analyst's supervisor and concurrence by the QA coordinator. The update must be filed with the QA coordinator.

7.6 Non-operation Methods of Analysis

"Special analyses" may be performed using small modifications of the approved methods. "Custom analyses" are those which require major modification of existing USGS methods, research, or other standard methods not previously validated in the laboratory.

These nonroutine methods of analyses must be notated under "NON-OPERATIONS" on the RFA form and deviations noted in the logbook. The logbook must document the exact modifications, or methodology, used to produce the results reported. Since the precision and accuracy statements contained in the operational methods are not available for special or custom methods, it may be necessary to include additional information on the estimated precision and accuracy of nonroutine analyses. This is done by reporting results for the analysis of spiked samples or reference materials, and/or duplicate analyses on the RFA form. The RFA form also contains a statement indicating that the methods used for non-operation analyses are not completely documented, therefore, the data must be used with caution (Jones, 1987, p. 9-10).

8. ANALYST QUALITY ASSURANCE/QUALITY CONTROL

8.1 Logbook

Each analyst maintains a logbook which contains notations concerning all instrument maintenance and repair procedures, preparation of new reagents and standards (check data verifying the accuracy of these solutions), standardization or calibration data, standard reference sample values, and other instrument parameters which document the validity of the data but are not printed on a hard copy (Jones, 1987, p. 10). All documentation in the logbook are made in ink and pages should not be removed. Corrections to logbooks or other data records are made by crossing a single line through the error and initialing the correction.

8.2 Quality Control Check (Reference Material, Duplicate, Method Blank) per Analytical Run

"Daily quality control is the responsibility of each analyst" (Gautier and others, 1986, p. 8). Each analyst analyzes standard reference materials (SRM) or in-house reference materials (RM). The frequency is immediately after calibrating each instrument and periodically throughout every set of determinations, approximately one every 20 samples, depending on the characteristics of the determination being performed. Unless otherwise stated in the standard method, analysts shall run a set of one duplicate, one analysis method blank, and two reference samples per 40 submitted samples.

The resulting indiscrete values are compared with previous in-control data by using X-R control charts (Ishikawa, 1982, p. 64) (see sections 8.3 and 8.4).

The quality control check values must meet certain specifications of precision and accuracy in order to proceed with the analysis. This specification is detailed in the standard method of analysis and was obtained during method validation (see section 7.3). If not specified, should the values of the control check samples indicate a value found outside the upper and lower control limits (UCL and LCL, respectively), of ±3s, the measurement process is considered out of control. The analyst may not report data until further measurements show the process is in control again. The reference material, duplicate, or blank sample shall be reanalyzed. Should the value obtained remain outside of the limit, the analysis shall be terminated, problem corrected, and the run repeated.

Data on points which indicate an abnormality and for which the cause has been found and corrected should not be included in recalculating the control lines. Another indicator of out-of-control is when the values are plotted on a control chart and "assume some sort of particular form even though they are all within the control limits" (Ishikawa, 1982, p. 75) (see sections 8.3 and 8.7).

8.3 X-Quality Control Charts

The quality control chart for accuracy consists of symmetrical "3-sigma control limits" placed above and below a central line (Committee E-11 on Statistical Methods, 1987, p. 77). Ninety nine and seven tenths percent of all the observed data should lie within the control limits, and the values should not assume a particular form in order for the analysis to be in a controlled state. For multi-element methods, the elements with the narrowest and widest variance are selected for control chart purposes.

Figure 1 indicates the features of a control chart with the acceptable range of occurrence (the region between the upper and lower control limits).

The control chart must indicate the analyst, the method of analysis, and results of the reference samples (see section 8.2). X-QC charts shall be constructed to be maintained by each analyst to show his/her laboratory is in a state of control.

A detailed discussion about control charts and how they are interpreted may be found in books by the ASTM, Kaoru Ishikawa, John Taylor, and James Dux; that are listed in the references cited.

8.4 R-Quality Control Chart

The quality control chart for precision consists of establishing the ranges of duplicate results. The ranges are plotted in a manner similar to the X-quality control chart (see fig. 2), however, the distribution will be somewhat different than that of the individual results about a mean. According to Taylor, the UCL will correspond to 3.267R and the UWL (upper warning limit) to 2.512R (1987, p. 193).

The estimation of standard deviation from duplicate measurements, s_d, is shown in appendix D. "However, if the analyte concentration varies widely and the standard deviation is proportional to analyte concentration, the calculated standard deviation will be larger than the imprecision associated with measurement at a given analyte level" (Dux, 1986, p. 16).

8.5 Analysis of Variance

Monthly, the analyst calculates the current standard deviation and mean and compares these values to the cumulative standard deviation and mean.

The difference in two estimates of standard deviation is determined by first assuming n_1 samples have been run to arrive at the cumulative mean $\bar{X}_1$ and standard deviation s_1. After a period of one month, n_2 more samples have been run, yielding a mean of $\bar{X}_2$ and s_2. A statistics book may be used by the analyst for the application of the F-test to determine if the new standard deviation s_2 appears to be significantly different from s_1. "If the precision has changed significantly, new limits will need to be calculated, based on the latest data. If not, control limits should be revised by combining data bases by pooling" (Taylor, 1987, p. 38).

A similar judgment is made for s_d from the corresponding R values using the F-test. In the case of small data sets, use of the T-test is recommended.

The difference in two estimates of the mean is calculated after determining the pooled standard deviation ($\bar{s}$ from the two estimates (see appendix D).

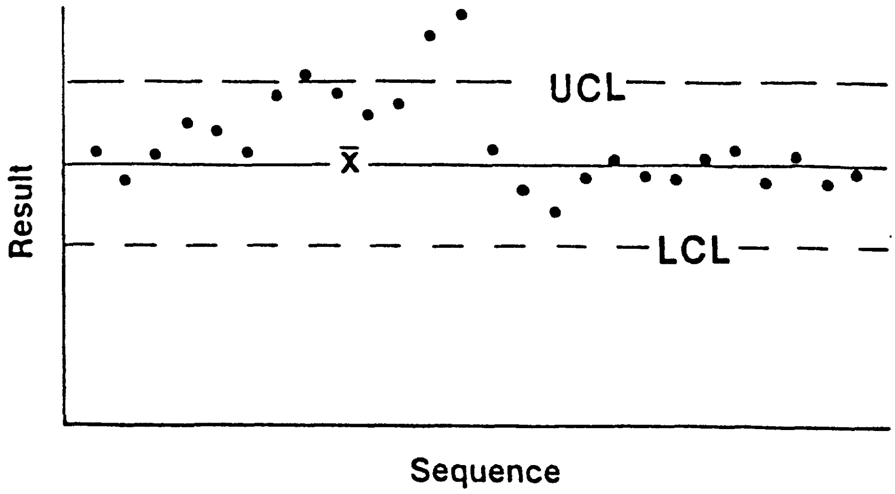

Figure 1. X-control chart.

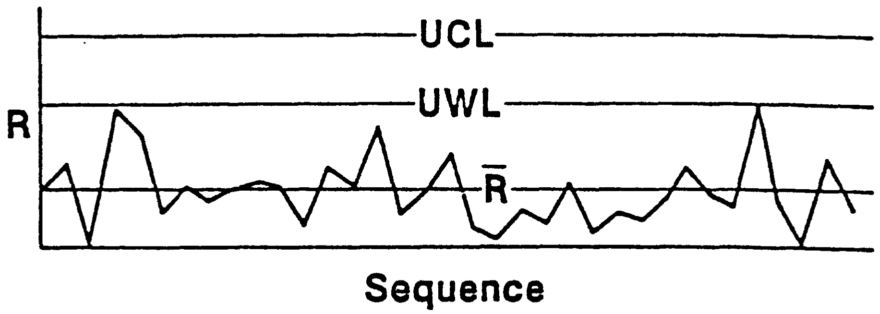

Figure 2. R-control chart. John Keenan Taylor. Quality Assurance of Chemical Measurements. (Chelsea, MI: Lewis Publishers, Inc., 1987), 140.

If $d \le U$, there is no reason to believe that the means disagree (Taylor, 1987, p. 29) and the data bases are combined by pooling. "Should the means be found to disagree significantly, the central line should be based on the latest data" (Taylor, 1987, p. 39).

8.6 Pooling Estimates of Standard Deviation and Mean

From Dux (1986, p. 21), if the means and standard deviations are not significantly different, a new cumulative mean ($\bar{\bar{X}}$) and standard deviation ($\bar{s}$) may be calculated from the entire population (see appendix D).

8.7 Non-randomness of Points on a Control Chart

The control chart is evaluated for abnormalities shown by: "(1) Some points are outside the control limits (including points on the limit lines), or (2) the points assume some sort of particular form even though they are all within the control limits" (Ishikawa, 1982, p. 74-75). A trend or run is an example of case (2).

A trend is a "continued rise or fall in a series of points" on a control chart (Ishikawa, 1982, p. 75). Seven consecutive points in a trend indicate an abnormality (see fig. 3).

A run is when "several points line up consecutively on one side only of the central line" (Ishikawa, 1982, p. 75). Seven points in a run indicate an abnormality (see fig. 4).

Both trend and runs indicate a process is not in control.

Some of the more common causes of a trend or run are as follows (Garfield, 1984, p. 188):

Symptom	Common Cause
Shift in mean	incorrect prep of standard incorrect prep of reagents contamination of sample incorrect instrument calibration analyst error
Trend of mean upward	deterioration of standard deterioration of reagents
Trend of mean downward	concentration of standard due to evaporation of solvent deterioration of reagents
Increase of variability	analyst performance, e.g., poor technique, deviation from procedure

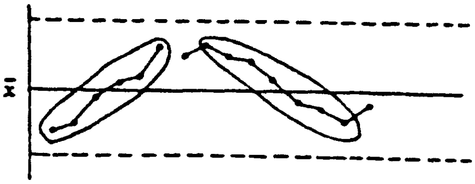

Figure 3. Trend. Kaoru Ishikawa. Guide to Quality Control. (White Plains, NY: Asian Productivity Organization, 1982), 75.

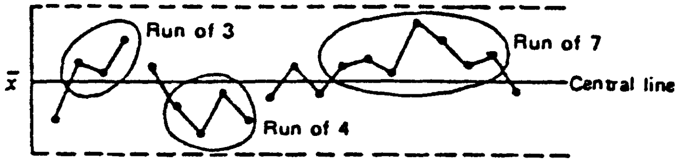

Figure 4. Runs. Ishikawa, 75.

8.8 Data Report

The "Branch geochemical database" refers to the RASS database resident on the Data General (DG) MV/600 Computer and the PLUTO database resident on the Hewlett Packard (HP) 1000 Computer. Data are reported to the sample control group on either handwritten reports for entry into the Branch geochemical database or automatically through instrument-sample control computer interfaces. The analyst is to sign his/her name, instrument identification number, and date the analyses are completed on the RFA form. A preliminary report is generated and checked by the analyst for correctness and completion of data. When all analyses have been reviewed and verified a final report is generated.

8.9 Training

All on-the-job training is the direct responsibility of the Project Chief. This responsibility may be delegated only to professional personnel. In the event that a new employee has to be trained by someone other than a professional, the training is always personally monitored by the Project Chief (Jones, 1987, p. 12).

Training is conducted by the supervisor from the Branch laboratory safety manual, QA manual, and bench-level protocols. The new employee is supplied with a copy of all pertinent procedural manuals. Before an employee is certified to be qualified on a given method or process, a set of quality control samples is analyzed by the trainee to verify that the process is being performed to USGS standards (Jones, 1987, p. 12).

Records are kept by the laboratory supervisor documenting the date and specific technical training an employee has completed.

9. LABORATORY-WIDE AND EXTERNAL QUALITY ASSURANCE

9.1 In-house Blind Samples

The Sample Control Officer at each Center inserts SRMs, in-house standards, and replicates as blind quality assurance samples, on a scheduled basis to verify the precision and accuracy of each laboratory method. The data from these analyses are plotted on quality control charts, which are reviewed bimonthly by the QA coordinator, the senior staff of the Laboratory, and the analysts. The data are reviewed for outliers (greater than methods stated accuracy) and trends within accuracy limits.

9.2 External Performance-audit Samples

The laboratory policy is to participate in all appropriate interlaboratory standard sample analysis programs. The laboratory regularly participates with other earth science laboratories to analyze proposed SRMs. The data from these analyses are evaluated by comparison with data from other participating laboratories.

9.3 Data Review

Completed analyses are subjected to a review, by the analyst or project chief, for internal consistency of data, such as total oxide balance and comparison of complementary determinations. Analyses which satisfy these checks are released to the submitter through the Branch geochemical database. Analyses which do not satisfy these relationships are referred to the analyst for inspection and resolution of the problems, requesting reanalysis of selected parameters as deemed necessary. Some nonroutine analyses (see section 7.6) can be explained as special cases not expected to meet ordinary criteria and these are released as is.

After analyses are released, 2 years are allowed for review of data by the submitter. During this time, additional reanalysis may be requested on the basis of the requestor's review of the analysis for geologic sense. After this time, the analyses will be archived and the data transferred to the Branch geochemical database unless other provisions are requested.

10. RECORDKEEPING AND MAINTENANCE

10.1 Data Entry

Considerable data are entered via a computer interface between the instrument and the Branch geochemical database. Some data, particularly visual semiquantitative dc arc emission spectrography and many single element methods, are entered manually. All manually entered data are checked for errors by the analyst.

10.2 Data Validation

Completed samples are reviewed as described in sections 8.2-8.8 and 9.3.

10.3 Data Reporting

Data reports for regular analyses involving operational methods are compiled in the Laboratory's control computer, and are sent to the requestor within 72 working hours of final verification by the analyst and Sample Control Officer.

10.4 Data Archiving

Laboratory records such as logbooks, printouts, tapes, and other raw data containing original results generated in the course of analysis are retained and easily located in files with reference to date, job number, and analyst. The laboratory database is retained on disk or tape.

10.5 Computer and Database Security

For the Data General (DG), incremental backup (catchups) of all active files is done once each day. Complete backups are performed weekly. The complete backup tapes are saved for 1 year. Incremental backup tapes are saved for 3 months. Tapes are stored in a room away from the computer. For the Hewlett Packard (HP), backups are performed once per week on each subsystem on alternating tapes. Once every 2 months the backup tape is copied to a complete backup disk. They are made on six alternating disks for 1-year storage.

Combination locks are used to restrict access to the computer room. Database security requires a user to be registered and data files to be password protected, with different levels of access available depending on the nature of the individual need. Any access other than a normal data transfer is detected by the computer and the line is automatically disabled. The line can only be re-enabled by the system manager.

The personal computer data base owner shall provide for in-house backup of materials. The level is dependent upon the hardware, amount of data generated, and from which recovery should be made in less than 1 day.

11. QUALITY ASSURANCE REPORTS

11.1 Corrective Action

Problems with errors and out-of-control situations are resolved at the bench level by the analyst. If the problem persists or cannot be identified, the matter is referred to the laboratory supervisor for further investigation.

11.2 Irregularity Report

A quality assurance irregularity report (see appendix C) and corrective action are required whenever a QA blind check sample result is rejected. The QA coordinator contacts the appropriate project chief with the report and follows up with the submission of an additional blind check sample for review.

11.3 Changes and Problems

Any changes in QA procedures, analytical procedures, etc. will be submitted in writing to the project chief and QA coordinator for approval (Frankenberger, 1988, p. 16.3). All significant QA problems are reported verbally to the project chief and QA coordinator as soon as possible along with recommendations for corrective action (Frankenberger, 1988, p. 16.2).

APPENDIX A REFERENCES CITED

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______1989, Dept. of Interior, Methods for Determinations of Inorganic Substances in Water and Fluvial Sediments: Techniques of Water-Resources Investigations of the United States Geological Survey, Book 5, Chapter A1.

APPENDIX B **ANALYTICAL METHODS**

Technique Code	OPERATIONS GEOCHEMISTRY METHODS	Page
A010	AA hydride generation--Se	38
A020	AA hydride generation--As	38
A030	AA flame--Au; HBr-Br$_2$	46
A040	AA graphite furnace--Au; HBr-Br$_2$	46
A050	AA flame--Au; HF, aqua regia, HBr-Br$_2$	52
A060	AA flame--Te; HF, aqua regia, HBr-Br$_2$	52
A070	AA flame--Tl; HF, aqua regia, HBr-Br$_2$	52
A080	AA graphite furnace--Au; HF, aqua regia, HBr-Br$_2$	52
A090	AA cold vapor--Hg	60
C010	Coulometric titration--CO$_2$	68
C020	Heat/weight loss, coulometry--moisture and total water	73
E010	ICP-AES--40 element	83
E020	ICP-AES--10 element; organometallic halide extraction	92
E030	ICP-AES--B; hot water extraction	97
E040	DC-Arc AES, semiquantitative--35 element; rock, stream sediment, soil	100
E050	DC-Arc AES, semiquantitative--37 element; concentrate	100
E060	Flame photometry--K$_2$O	107
E070	Flame photometry--Na$_2$O	107
F080	UV-Fluorescence--U	111
N010	Combustion IR--C total	114
N020	Combustion IR--S total	131
P010	Ion-selective electrode--Cl; Conway Cell	119
P020	Ion-selective electrode--F; LiBO$_2$	123
P030	Ion-selective electrode--F; Na$_2$CO$_3$-K$_2$CO$_3$-KNO$_3$	127
P040	Iodometric titration--S	136
P050	Potentiometric titration--FeO	139
P060	Ion-selective electrode--F; Na$_2$CO$_3$-ZnO	173
Q010	Sample type: rock	21
Q020	Sample type: stream-sediment	26
Q030	Sample type: soil	29
Q040	Sample type: concentrate	33
R010	DNAA--U and Th	146
R020	INAA--24 element; short count	151
U010	Visible absorption spectrometry--W	157
X010	EDXRF--Rb, Sr, Y, Nb, Zr	161
X020	EDXRF--Ba, Ce, La, minors	161
X030	EDXRF--Cu, Ni, Zn	161
X040	EDXRF--Cr	161
X050	WDXRF--major elements as oxides	166

Physical preparation of rock samples

By Cliff D. Taylor

Code: Q010 Accepted: 6/25/90

General discussion

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) reduction of the sample to a size that is more conveniently transported; (2) increasing the sample surface area to enhance the efficiency of subsequent chemical attack; (3) homogenizing the sample to ensure that a subsample is representative of the entire sample; and (4) separating the sample into components based on mineralogy, grain size, biologic versus lithologic origin, etc., for more specific chemical characterization. Sample preparation is, arguably, the most 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 ¼-inch 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 (150µ) and mixed to insure homogeneity for subsequent analysis.

Apparatus and materials

Sample cartons, 3-oz
Large sample funnel, plastic
Compressed-air source, dry air, 40 psi
Core splitter, if available
Rock hammer, 32-oz
Flexible hand pad, 6-in square
Steel plate, approximately 8 by 8-in by 1-in
"Chipmunk" jaw crusher
Knife, with long and thin steel blade
Brush, automotive parts cleaning, stiff bristle
Brush, wire
Braun vertical pulverizer with ceramic plates, catch pan, and cover plate
Silicon carbide, approximately 60- to 80-mesh
Jones splitter, with ½-in riffles
Tube-type revolving mixer, with tube diameter to accommodate sample cartons
Aluminum loaf 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. The use of gloves is not recommended. If they are worn, they should be close-fitting. 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. 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 excessive dust.

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 (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 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, (3) number of samples in the job, and (4) the lab number of the first and last sample in the tray.

Procedure

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 1½-inches, 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.

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-inch square 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.

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.

Turn the power to the crusher off and thoroughly clean the crusher mouth, jaws, and cheek plates by alternatingly 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 and 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. If such a cleaning gravel is not available, a small amount of the next sample to be prepared should be crushed and 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-inch crescent wrench and loosening the two lower adjustment nuts. The upper adjustment nut is then <u>slowly</u> 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 mesh 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 implacing 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% passes an 80-mesh screen and 80% passes a 100-mesh screen. Pour the prepared sample from the pan through the funnel into the carton. Fill the carton 2/3 to 3/4 full. Discard excess sample or save 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 tablespoon 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 minutes. 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.

Physical preparation of stream-sediment samples

By Thomas R. Peacock and Cliff D. Taylor

Code: Q020 Accepted: 6/25/90

General discussion

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) reduction of the sample to a size that is more conveniently transported; (2) increasing the sample surface area to enhance the efficiency of subsequent chemical attack; (3) homogenizing the sample to ensure that a subsample is representative of the entire sample; and (4) separating the sample into components based on mineralogy, grain size, biologic versus lithologic origin, etc., for more detailed chemical characterization. Sample preparation is, arguably, the most 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 thoroughly dry stream-sediment samples are disaggregated by hand, as necessary, and as much organic material as possible is removed. The samples are sieved to the specified particle size. The sieved fraction is generally ground in a mechanical pulverizer, placed in a 3-ounce container and mixed to insure homogeneity.

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 excessive dust.

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, (3) number of samples in the job, and (4) the lab number of the first and last sample in the tray.

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.

Arrange five sieves of the desired 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.

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. 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.

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 10 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 a sonic 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 (approximately minus-100 mesh), and then mixed in a tube-type mixing machine. Refer to the section of this manual entitled "the 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 ounce 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 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 pulverizer belt and grinding plates, for wear. Replace worn parts.

Physical preparation of soil samples

By Thomas R. Peacock

Code: Q030 Accepted: 6/25/90

General discussion

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) reduction of the sample to a size that is more conveniently transported; (2) increasing the sample surface area to enhance the efficiency of subsequent chemical attack; (3) homogenizing the sample to ensure that a subsample is representative of the entire sample; and (4) separating the sample into components based on mineralogy, grain size, biologic versus lithologic origin, etc., for more detailed chemical characterization. Sample preparation is, arguably, the most 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, generally minus-80 mesh (<180µ) using sieves with stainless-steel screens. The sieved fraction is pulverized if further reduction in grain size is required by the subsequent chemical analysis.

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
Acetone, C_3H_6O

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 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, 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 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, (3) number of samples in the job, and (4) the lab number of the first and last sample in the tray.

Procedure

Damp samples are dried overnight in a forced-air drying oven 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 wetter 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 before removing them. As an added precaution, the auger can be turned off. When the maximum downward travel of the auger has been reached, maintain this position approximately 30 seconds, 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 (1.70 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: Remember the flammable nature of the acetone. Used towels/Kimwipes should be disposed of in fire-proof containers.

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 minutes 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.

If pulverizing of the sieved sample is required, use the shatter-box to pulverize the sample to 100-mesh or less (<150μ) 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 minutes. 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 in the physical preparation of rocks method 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

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 pulverizer belt and grinding plates, for wear. Replace worn parts.

Physical preparation of heavy-mineral concentrates by heavy liquid and magnetic separation

By Cliff D. Taylor

Code: Q040 Accepted: 6/25/90

General discussion

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) reduction of the sample to a size that is more conveniently transported; (2) increasing the sample surface area to enhance the efficiency of subsequent chemical attack; (3) homogenizing the sample to ensure that a subsample is representative of the entire sample; and (4) separating the sample into components based on mineralogy, grain size, biologic versus lithologic origin, etc., for more specific chemical characterization. Sample preparation is, arguably, the most 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 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.

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-in square, mylar-covered plate
Static-eliminating sample brush
Cleaning brush
Microsplitter with 1/16-in 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

The heavy liquid separation step, use of bromoform, in this procedure presents a potentially severe health risk and must be conducted in a fume hood. Any personnel new to the procedure should familiarize themselves with the properties of bromoform, be able to recognize symptoms of exposure, and be aware of the possible effects of overexposure.

The heavy liquid bromoform, or tribromomethane, $CHBr_3$, 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, alcohols, 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 procedure.

Bromoform has a permissible exposure limit, set by OSHA, of 0.5 parts per million 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 ounces for a 150-pound man. See the MSDS for further information.

Protective equipment should be worn in a manner indicated by the manufacturer and should include a lab coat, 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 in working with acetone, insures the well being of the person conducting the procedure.

With the exception of the hazard inherent to the use of compressed air for cleaning purposes, the rest of the procedure does not require extra precautionary measures. 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-ounce 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

1. 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.

2. Sieve the dry concentrate through a 35-mesh screen (0.5 mm). Remove larger pebbles and fragments (>.5 inch) by hand to prevent possible damage to the screen.

3. 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.

4. 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

5. The separation is performed in a fume hood, see **Safety precautions** p. 61. 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.

6. 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.

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

8. Allow approximately 2 to 3 minutes 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.

9. After proper separation is ascertained, 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 sep funnel. Carefully avoid drawing off intermediate specific gravity mineral grains.

10. Allow as much of the bromoform as possible to drain into the Erlenmeyer, then remove the filter funnel to another Erlenmeyer marked "WASH". Thoroughly wash the separated "heavies" with acetone, in which bromoform is readily soluble, and allow to drain. Caution: acetone is a hazardous and extremely flammable substance. Treat accordingly.

11. 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.

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

13. When the large filter paper in step 12 is 2/3 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. This bromoform is reclaimed for reuse by repetitive washings with water to remove the acetone and separation of phases in a separatory funnel. 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 mL of bromoform is measured in a graduated cylinder, stoppered, and weighed. A specific gravity above 2.8 is considered acceptable.

14. 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

15. 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 (verticle 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 grams) into a rectangular, mylar-covered tray in a uniformly-spread layer and pass the tray ¼ inch to ½ inch below the horizontally configured, mylar-covered poles of the magnet, with the current set at .25 ampere. The highly magnetic minerals will adhere to the magnet. Switch off the current and catch the minerals on a clean paper sheet.

16. 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.

17. Lightly touch the remaining minerals on the tray to the poles of the magnet with the current set at 1.75 amperes. 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.

18. 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.

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

20. 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

21. 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 milligrams, proceed to hand grinding.

22. 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.

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

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 most importantly, the C_3 nonmagnetic fraction, present, in most cases, as two splits--one for spectrographic analysis and one for mineralogical identification.

Trace-level determination of arsenic and selenium using continuous-flow hydride generation atomic absorption spectrophotometry (HG-AAS)

By Eric P. Welsch, James G. Crock, and Richard Sanzolone

Code: A010, A020 Accepted: Provisional

Principle

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

$$3NaBH_4 + 4H_2SeO_3 \rightarrow 4H_2Se_{(g)} + 3H_3BO_3 + 3NaOH$$

$$3NaBH_4 + 4H_3AsO_3 \rightarrow 4AsH_{3(g)} + 3H_3BO_3 + 3NaOH.$$

The hydrides are stripped from the system and transported with inert gas to the atomizer of the atomic absorption spectrophotometer, in this case a heated quartz furnace. For Se, the furnace is heated by an air acetylene flame; the As furnace (Hatfield, 1987) is electrically heated to 850°C. Concentrations of the elements are determined using calibration standards in solutions of similar matrix.

Interference

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 (Cu, Fe, Ni, and Sn) of >500 ppm in the sample competing with As, and Se, for available $NaBH_4$ according to
$$M^{+2} + 2NaBH_4 \rightarrow M^{+1} + H_2 + B_2H_6$$
resulting in insufficient $NaBH_4$ for completion of the hydride-forming reaction.
2. High concentrations (>1,000 ppm in the sample) of one of the hydride-forming elements which similarly deplete the supply of $NaBH_4$ and prevent reaction completion for other hydride-forming elements.
3. The impedance of the hydride-forming process by incompletely digested organic material form organic-rich samples.

A further consequence at high metal concentrations in (1) is the reoxidation of the analyte to its higher oxidation state, preventing hydride formation, as, for example:

$$Cu^{+2} + As^{+3} \rightarrow Cu^{+} + As^{+5} .$$

Problems (1) and (2) are generally of minimal concern in environmental samples since the probability of high interference element concentrations are 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 digested (i.e., oxidized) to enable the reaction to reach completion.

Scope

The HG-AAS method described herein is useful for the determination of As and Se, in a wide variety of geochemical samples. The thoroughness of the digestion and the separation of the analyte elements from the bulk of the matrix (as hydrides) prior to their determination are key parameters. The optimum concentration ranges for the elements for this method are .2 to 2 ppm for Se and .2 to 40 ppm for As. Above these ranges, the options of sample dilutions versus alternative techniques, e.g. energy dispersive X-ray fluorescence (EDXRF) for Se, should be considered.

One day is required to complete digestion of the samples. The analyses of 40 samples for Se requires about 1½ hours of instrument time, while the As analyses takes about 4 hours.

Apparatus

Varian hydride generator
Atomic Absorption Spectrophotometer
Strip Chart Recorder
Gilson Medical Electronic (Middleton, Wisconsin) Model Minipulse, peristaltic pump equipped with standard Tygon pump tubing (figs. 5 and 6 show the flow rates used, in mL/min, which dictate the tubing required)
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
Arsenic manifold shown on figure 5
Selenium manifold shown on figure 6
Gilson 212B Autosampler or Technician Autosampler AA II
Data acquisition system consisting of a Spectrophysics (Sp) 4270 recording integrator and a Hewlett Packard 85b computer. A regular strip chart recorder may also be used for data acquisition.

Reagents

Arsenious oxide, As_2O_3
Nitric acid, HNO_3
Hydrochloric acid, HCl
Perchloric acid, $HClO_4$, double distilled
Hydrofluoric acid, HF
Hydroxylamine hydrochloride, $NH_2OH \cdot HCl$, suitable for mercury determination
Oxalic acid, $C_2H_2O_4$
Ascorbic acid, C_6HO_6
Potassium iodide, KI
Sodium borohydride, $NaBH_4$
Sodium hydroxide, NaOH

50% (v/v) Hydrochloric acid solution: Add "Baker Instra-Analyzed" concentrated HCl suitable for trace metals analysis, to an equal volume of demineralized water. The use of the "Baker Instra-Analyzed" or hydrochloric acid of similar purity is advised throughout the procedure for As. Reagent grade is adequate for Se.

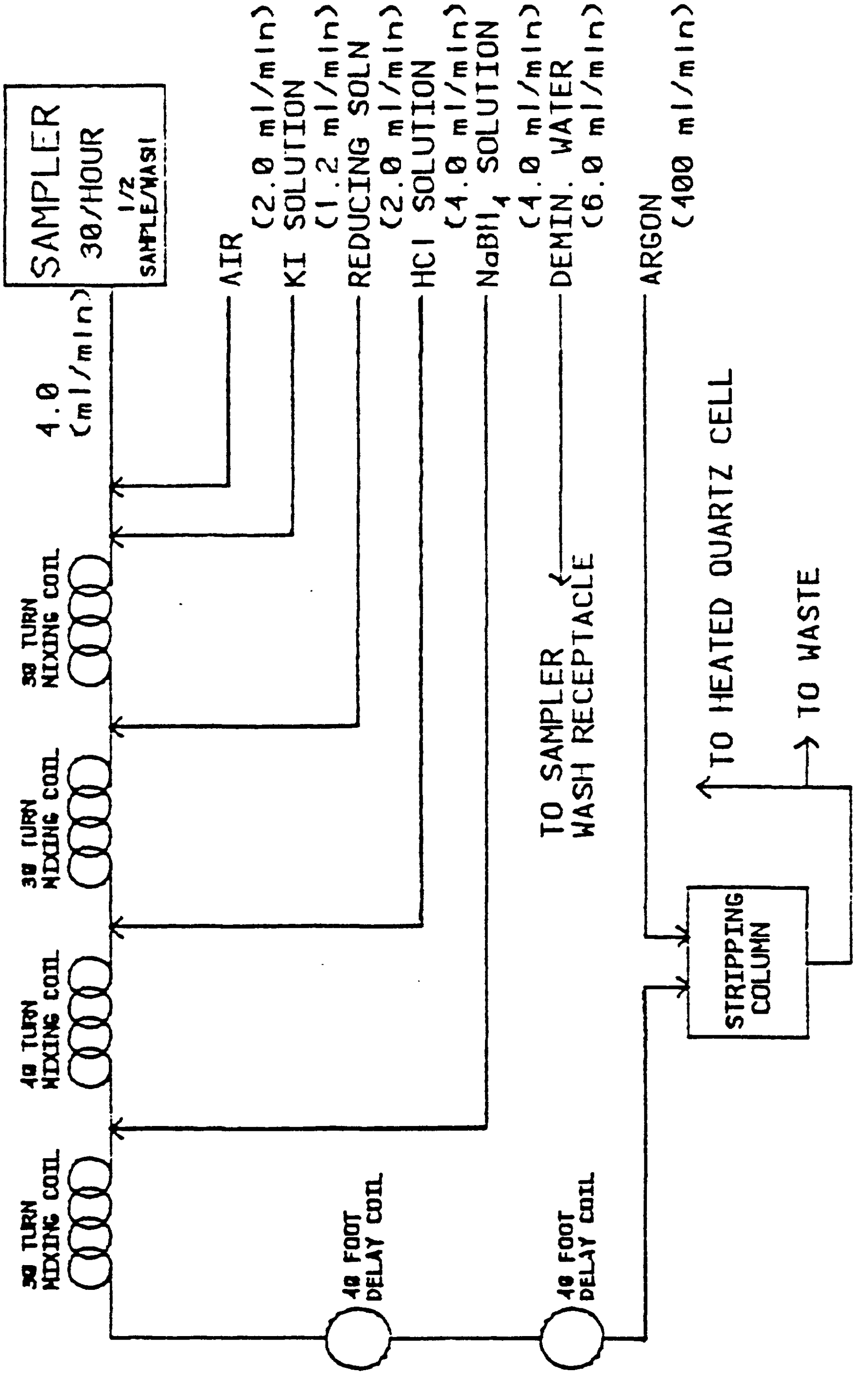

Figure 5. Arsenic manifold.

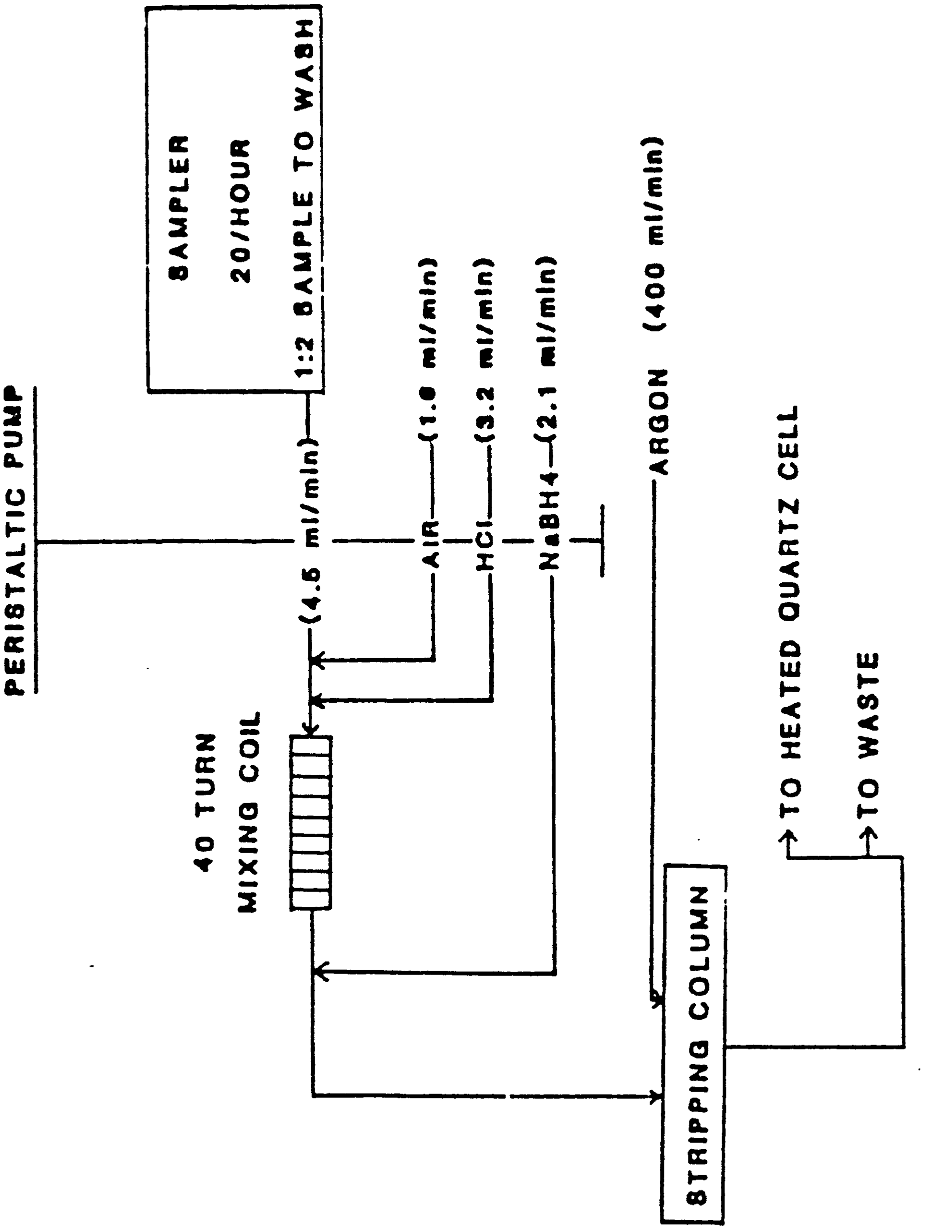

Figure 6. Selenium manifold.

Sodium borohydride solution: For As: dissolve 40 g sodium hydroxide and 5.0 g sodium borohydride in demineralized water and dilute to 1 L in a volumetric flask. Make fresh weekly. For Se: dissolve 3.5 g sodium borohydride and 5 g sodium hydroxide in water and dilute to 1 L. Make this solution fresh daily.

Potassium iodide solution: Dissolve 100 g potassium iodide in demineralized water. Add 1 g ascorbic acid. Dilute to 1 L with demineralized water. The solution is stable for at least a week.

Reducing solution: Pour 454 g of oxalic acid into a 2-L plastic bottle. Fill with demineralized water and shake well to mix. This will form a saturated solution of oxalic acid. There should be undissolved oxalic acid remaining. Dissolve 200 g of hydroxylamine hydrochloride in 800 g of the saturated oxalic acid solution.

Arsenic stock solution (1,000 µg/mL): Dissolve 1.320 g of arsenious oxide (As_2O_3) in a minimal volume of 20% potassium hydroxide. Slowly neutralize with 20% hydrochloric acid. Add 100 mL concentrated hdyrochloric acid in excess. Dilute to 1.000 L with demineralized water. The working standards of 10, 30, 50, 100 µg/mL are made from serial dilutions of this stock solution with 10% hydrochloric acid. The working standards are stable for at least 1 week.

Selenium stock solution (1,000 µg/mL) : A commercially prepared selenium atomic absorption standard is used to make serial dilutions of the working standards of 0.01 µg/mL in 10% hydrochloric acid (v/v).

Safety precautions

The principal hazards associated with the technique deal primarily with the decomposition of the samples and the use of concentrated acids. Of particular importance is hydrofluoric acid which has demonstrated the ability to adversely impact skin and bone. Treat HF exposure as an emergency. See the MSDS for precautions, effects of overexposure, first-aid treatment, and disposal procedures for reagents used in this method.

A working chemical exhaust hood should be used for the digestion procedure and over the atomic absorption instrument due to the evolution of H_2 gas and HCl vapors. There is the danger of H_2 ignition and flashback if the inert carrier gas is not turned on in advance.

Procedure

1. Weight .25 g sample (<80-mesh) into a 30-ml teflon bomb and moisten with 1 mL 1% HNO_3.
2. Add 6 mL $HClO_4$, 9 mL HNO_3, 10 mL HF and heat overnight at 105 to 110°C or until the solution is reduced to 2 mL.
3. Add 25 mL 50%(v/v) HCl and let stand for half hour.
4. Transfer the sample to a 60-mL polyethylene bottle and bring up to 54 g with distilled water.
5. Approximately 8 mL of the solution is decanted into 13 x 100-mm test tubes and placed in Gilson 212B autosampler.
6. As is analyzed on the system illustrated on figure 5 while Se is done on a Varian hydride system, figure 6, as per Varian's instructions.
7. Sample peaks are compared to standard peaks recorded on a strip chart reorder or a SP4270 integrator.

8. Five standards ranging from 10 to 200 ppb are used to calibrate for As and three standards ranging from 5 to 20 ppb are used for Se analyses.
9. Ten percent deviation from the norm of standards or reference samples is deemed unacceptable.

Standardization of Instrument

Estimate the As, or Se content of this digest solution using the standard operating conditions as shown in table 1. These are for a Perkin-Elmer model 2380 atomic absorption spectrophotometer.

Table 1. Operating conditions for determination of arsenic and selenium by hydride generation AAS

	As	Se
Grating....................	ultraviolet	ultraviolet
Wavelength (nm)............	193.7 or 197.2	196.0
Slit (nm)..................	0.7	0.7
Lamp setting...............	8 W	6 W
Source.....................	electrodeless discharge	electrodeless discharge
Cell (furnace) temperature.	850°C	850°C
Background correction......	not used	not used
Damping....................	4 (maximum)	4
Mode.......................	absorbance	absorbance
Strip chart recorder.................	10 mV full-scale response, 5 mm/min	chart speed
Absorbance check...........	5 µg As/L = 0.150 (193.7 nm)	10 µg Se/L = 0.300

A wide variety of reference standards are available for the hydride elements. For environmental work, a series of soil standards from the Canadian Geological Survey are often used because they have selenium concentrations between 1 and 4 ppm. Control standards developed by the Branch of Geochemistry are pond sediments containing selenium concentrations between 2 and 85 ppm. The arsenic in these samples ranges between 2 and 25 ppm. Selenium, arsenic, and antimony values for other standard samples are available from Abbey's work on reference materials (Abbey, 1983).

Recalibration of the hydride systems is done on a daily basis. Confirmation that the calibration has not shifted during the course of the day is accomplished using a reference standard at the end of the sample analysis. If the standard is different from the original value by more than 15%, a judgment evaluation is made regarding the need for re-analysis of the samples processed that day.

Assignment of uncertainty

Tables 2 and 3 present results for As and Se, respectively, obtained by this method for standard reference materials and values reported in the literature.

Table 2. Arsenic content of selected geologic reference materials

Reference sample (description)	$\bar{X}$ (ppm)*	s	% RSD	Literature value (ppm)	Reference
SJS (soil)	9.5	.069	1	9.1	in-house data
K-1 (soil)	1.3	.069	5	1.5	----Do-------
K-12 (soil)	16	4.03	25	19.5	----Do-------
GXR1 (jasperoid)	410	6.18	2	400 ± 50	Gladney and Burns, 1984
GXR2 (soil)	22	.20	1	21 ± 4	----Do-----------------
GXR3 (Fe-Mn mineral deposit	3900	47.1	1	4200 ± 400	----Do-----------------
GXR4 (Cu mill head)	76	6.93	9	97 ± 4	----Do-----------------
GXR5 (soil)	9.9	.42	4	10.9 ± 1.2	----Do-----------------
GXR6 (soil)	300	8.56	3	310 ± 30	----Do-----------------
GSD6 (stream sediment)	12	.29	2	13.6	Govindaraju, 1989
GSD12 (stream sediment)	98	2.59	3	115	----Do-----------------
GSS2 (soil)	12	.13	1	13.6	----Do-----------------
GSR4 (rock)	7.5	.15	2	9.1	----Do-----------------
MESS (marine sediment)	9.4	.36	4	10.6	----Do-----------------

*average of six replicates

Table 3. Selenium content of selected geologic reference materials

Reference sample (description)	$\bar{X}$ (ppm)*	s	% RSD	Literature value (ppm)	Reference
SJS (soil)	1.3	.055	4	1.0	in-house data
K-1 (soil)	54	.653	1	63	----Do-------
K-12 (soil)	3.0	.049	2	2.5	----Do-------
GXR2 (soil)	.65	.058	9	.57 + 0.17	Gladney and Burns, 1984
GXR4 (Cu mill head)	5.4	.155	3	5.6 + 0.6	----Do-----------------
GXR5 (soil)	1.0	.048	5	0.92 + 0.24	----Do-----------------
GXR6 (soil)	.81	.030	4	1.01 + 0.12	----Do-----------------
GSD6 (stream sediment)	.24	.016	7	0.3	Govindaraju, 1989
GSD12 (stream sediment)	.29	.041	14	0.25	----Do-----------------
GSS2 (soil)	.17	.022	13	0.16	----Do-----------------
GSR4 (soil)	.11	.030	27	0.1	----Do-----------------

*average of six replicates

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Determination of gold in samples of rock, soil, stream-sediment and heavy-mineral-concentrate by flame and graphite furnace atomic absorption spectrophotometry following dissolution by HBr-Br_2

By Richard M. O'Leary and Allen L. Meier

Code: A030, A040 Accepted: Provisional

Principle

Gold in rock, soil, stream-sediment, and heavy-mineral concentrates are determined by the flame atomic absorption method (Thompson, and others, 1968; Ward and others, 1969, O'Leary and Meier, 1986). The sample is treated with a hydrobromic acid-0.5% bromine solution. The gold-bromide complex that is formed is extracted from the acid solution with MIBK (methyl isobutyl ketone). The interference due to iron is removed by washing the organic solvent with dilute hydrobromic acid. The MIBK is atomized by flame or graphite furnace in an atomic absorption spectrophotometer (AAS) for estimation of gold content.

Interference

The only interference in the estimation is caused by the presence of an excessive amount of iron co-extracted into the MIBK. The iron is presumed to interfere by causing light scattering. The iron is removed by washing the MIBK extract with the 0.1M hydrobromic acid solution; the gold remains quantitatively in the ketone.

Scope

Gold can be determined in rocks, stream sediments, soils, and heavy-mineral concentrates with a lower limit of determination of .05 ppm by flame and .002 by graphite furnace atomic absorption. The flame AAS upper limit can be extended beyond 2 ppm by dilution of an aliquot from the MIBK layer. The graphite furnace upper limit is .050 ppm; higher concentrations are analyzed by flame. Approximately 50 samples can be analyzed per day.

Apparatus

Atomic-absorption spectrophotometer equipped with flame and graphite furnace atomizers
Centrifuge
Test tubes, 25x150-mm, disposable
Horizontal shaking machine
Hot plate
Muffle furnace
Porcelain evaporating dish, 60-mm diameter

Reagents

All chemicals should be of reagent grade and all water should be metal free.
Hydrobromic acid-0.5% (approximate) bromine solution: Add 5 mL bromine (Br_2) per 1L of concentrated hydrobromic acid (HBr).

Hydrobromic acid 0.1M, equilibrated: Dilute 12 mL concentrated hydrobromic acid to 1 L with water. Add 200 mL MIBK, shake thoroughly, allow phases to separate, and discard MIBK layer.

MIBK (methyl isobutyl ketone), 4-methyl-2-pentanone.

Stock gold solution, 1,000 μg/mL: Dissolve exactly 1.000 g gold in 100 mL hydrobromic acid-0.5% bromine solution. Heat gently to expel excess bromine. Cool and dilute to 1 L with concentrated hydrobromic acid.

Dilute gold solution, 100 μg/mL: Dilute 10 mL of 1,000 μg/mL stock gold solution to 100 mL with concentrated hydrobromic acid.

Dilute gold solution, 1μg/mL: Dilute 1 mL of 100 μg/mL gold solution to 100 mL with concentrated hydrobromic acid.

Standard gold solution in MIBK for flame AAS: 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 0.1N hydrobromic acid and shake.

Standard gold solution in MIBK for graphite furnace AAS: 0.025 and 0.050 μg/mL: Add 0.025 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 .1N HBr. Cap and shake vigorously for 2 minutes.

Safety precautions

All digestions and work with open or uncapped reagents must be done in a chemical hood. Protective clothing, eyeware and gloves must be worn. See the MSDS for precautions, effects of overexposure, first-aid treatment and disposal procedures for reagents used in this method.

Care must be taken when adding a sample containing carbonate materials to the hydrobromic acid-0.5% bromine solution. Rapid effervescence may cause loss of sample from the culture tube. Add sample slowly, mix, and add extra hydrobromic acid-0.5% bromine solution to insure a high acid concentration. The 65-mm funnels inserted in the tube will often serve to contain effervescing sample.

Procedure

1. Weigh 10 g sample into a porcelain evaporating dish.
2. Ignite sample at 700°C in a muffle furnace for 1 hour or until sulfides and organic matter are completely oxidized. The furnace must be adequately vented.
3. Transfer sample to a 25x150-mm test tube containing 10 mL hydrobromic acid-0.5% bromine solution.
4. Mix sample thoroughly and heat on a metal rack in a hot plate set on high until the tubes begin to tap.
5. Allow to cool, add 10 mL MIBK and 10 mL water, cap, and shake in a horizontal shaking machine for 3 minutes.
6. Centrifuge until layers separate and transfer the MIBK layer to a 25x150-mm test tube containing 40 mL equilibrated 0.1M hydrobromic acid. (The transfer of MIBK need not be quantitative but should consist of at least 4 mL for all subsequent analysis.) Cap, shake for 2 minutes, and allow phases to separate.

7. Estimate the gold content by atomizing the organic layer into the flame and/or graphite furnace of an atomic absorption spectrophotometer. When graphite furnace gold is requested, care must be taken to avoid contamination of the graphite furnace by samples containing high concentrations (>0.1 ppm) of gold. All samples must be first analyzed by flame. Only samples with concentrations less then 0.05 ppm gold should be analyzed by graphite furnace. Both flame values ≥ 0.05 ppm and graphite furnace values should be reported. Recalibrate flame or restope graphite furnace after every 10 samples.

Standardization of Instrument

Table 4 shows the operating conditions for a Perkin-Elmer Model 603 flame atomic absorption spectrophotometer.

Table 4. Operating conditions for determination of gold by flame AAS; dissolution by HBr-Br_2

Grating	ultraviolet
Wavelength	242.8 nm
Slit	0.7 nm
Lamp current	10 mA
Source	gold (hollow cathode lamp)
Integration time	1 second
Burner	boling (three slot)
Flame condition	oxidizing (lean blue)
Concentration mode	
1 µg/mL	0.084 absorbance units (instrument calibration setting = 1.00)
2 µg/mL	0.165 absorbance units (instrument calibration setting = 2.00)

The following operating conditions, table 5, are for a Perkin-Elmer 5000 equipped with a graphite furnace with Zeeman background correction.

Table 5. Operating conditions for determination of gold by graphite furnace AAS; dissolution by $HBr-Br_2$

Grating	ultraviolet
Wavelength	242.8 nm
Slit	0.7 nm, low
Lamp current	10 mA
Source	gold (hollow cathode lamp)
Purge gas	nitrogen
Dry cycle	
Ramp	10 sec
Hold	20 sec
Temp	120°C
Char cycle	
Ramp	1 sec
Hold	15 sec
Temp	500°C
Atomization Cycle	
Ramp	0 sec
Hold	3 sec
Temp	2000°C
REC	-1 sec
Read	-1 sec
Baseline	-6 sec
INT FLOW	0
0.025 µg/mL	0.300 ± 10% absorbance units calibration setting = .025
Concentration mode	0.02 µg/mL calibration setting = .050
Clean-up cycle	0.05 µg/mL
Ramp	1 sec
Hold	3 sec
Temp	2500°C

Calculation

The formula to calculate the gold concentration is:

$$\text{ppm} = \frac{\text{Volume of MIBK (mL)}}{\text{Sample weight (g)}} \times \text{AAS sample reading } (\mu g/mL)$$

Assignment of uncertainty

Tables 6 and 7 are tabulations of statistical data obtained by analyzing GXR (geochemical exploration reference) samples (Allcott and Lakin, 1975), in replicas of five, by the described procedure.

Table 6. Gold content of GXR samples by flame AAS; dissolution by HBr-Br_2

Reference sample (description)	Range (ppm)	$\bar{X}$ (ppm)	s	% RSD	Literature value[1] (ppm)
GXR1 (jasperoid)	2.6-3.5	3.0	9	0.28	3.3
GXR2 (soil)	Less than 0.05	--	--	--	0.036
GXR3 (Fe-Mn mineral deposit)	Less than 0.05	--	--	--	--
GXR4 (copper mill head)	0.28-0.40	0.35	11	0.04	0.470
GXR5 (soil)	Less than 0.05	--	--	--	--
GXR6 (soil)	0.04-0.07	0.06	17	0.01	0.095

[1] Govindaraju, 1989

Table 7. Gold content of GXR samples by graphite furnace AAS; dissolution by HBr-Br_2

Reference sample (description	$\bar{X}$ (ppm)	s	% RSD	Literature value[1] (ppm)
GXR1 (jasperoid)	2.98	0.13	4	3.3
GXR2 (soil)	0.022	0.002	9	0.036
GXR3 (Fe-Mn mineral deposit)	0.003	0.0006	20	--
GXR4 (copper mill head)	0.353	0.021	6	0.470
GXR5 (soil)	0.007	0.001	14	--
GXR6 (soil)	0.063	0.002	3	0.095

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Determination of gold, tellurium, and thallium, in rock, stream-sediment, and soil samples by flame, and gold by graphite furnace, atomic absorption spectrophotometry following dissolution by HF, aqua regia, and $HBr-Br_2$

By Richard M. O'Leary and T.T. Chao

Code: A050, A060, A070, A080 Accepted: Provisional

Principle

Gold, tellurium, and thallium in rock, stream-sediment, and soil samples are determined by the flame atomic absorption method (Hubert and Chao, 1985). The sample is decomposed with hydrofluoric acid, aqua regia, and hydrobromic acid-bromine solution. Gold, thallium, and tellurium are separated and concentrated from the sample digest by a two-step MIBK (methyl isobutyl ketone) extraction at two concentrations of hydrobromic acid. Gold and thallium are first extracted from 0.1M hydrobromic acid medium, then tellurium is extracted from 3M hydrobromic acid in the presence of ascorbic acid to eliminate iron interference. The elements are then determined by flame atomic absorption spectrophotometry (AAS). Gold can also be determined by graphite furnace AAS.

Interference

This method is not applicable for the determination of gold in a carbonaceous matrix (e.g. non-oxidized Carlin-type material) or soils and stream sediments rich in organics (>5%), due to a low recovery of gold in the presence of carbon. When determining gold in these types of materials, use the alternate atomic absorption gold method (10 g sample with dissolution by $HBr-Br_2$) in which the samples are roasted at 700°C to oxidize and remove the carbon. Iron is the major interfering element in the determination of the three analytes in geologic materials. Prior removal of iron by solvent extraction, reduction of iron by ascorbic acid, stripping the co-extracted iron, and selective extraction of the analyte may be used to eliminate the iron interference. Because iron is practically unextracted into MIBK at low concentrations of hydrobromic acid (Denaro, 1955), gold and thallium can be separated from iron by MIBK extraction from a sample solution adjusted to 0.1M hydrobromic acid concentration. It is for this reason that the procedure uses the two-step extraction to isolate gold and thallium first for determination. Tellurium can be extracted into MIBK from 3M hydrobromic acid, but an appreciable amount of iron is also extracted (Denaro, 1955), and interferes in tellurium determination (Chao and others, 1978; Zhou and others, 1984). Addition of ascorbic acid to reduce (Zhou and others, 1985) iron removes the interference completely. Therefore, the extraction of tellurium after addition of ascorbic acid constitutes the second phase of the two-step solvent-extraction procedure.

Scope

Gold, tellurium, and thallium can be determined in rocks, stream sediments, and soils with a lower limit of determination of .05 ppm for each element by flame atomic absorption spectrophotometry. The upper limit of determination can be extended beyond 20 ppm by dilution of an aliquot from the MIBK layer. The lower limit of determination for gold by graphite furnace is 0.002 ppm, concentrations greater than 0.05 ppm are determined by flame. Approximately 25 samples can be analyzed per person-day.

Apparatus

Atomic-absorption spectrophotometer equipped with a flame and graphite furnace atomizers
Beakers, Teflon, 100-mL
Centrifuge
Horizontal shaking machine
Hot plate, oscillating
Scoop, calibrated to deliver 2-g ascorbic acid
Vacuum system
Test tubes, 25x150-mm, disposable

Reagents

All chemicals should be reagent grade and all water should be metal free.

Ascorbic acid, $C_6H_8O_6$
Hydrobromic acid, HBr, concentrated (48%)
Hydrobromic acid-10% bromine solution: Dilute 10 mL of bromine (Br_2) to 100 mL with hydrobromic acid
Hydrochloric acid, HCl concentrated (37%)
Hydrofluoric acid, HF concentrated (49%)
Iron solution, 4% in 3M hydrobromic acid: Dissolve 4 g of pure iron (Fe) powder in concentrated hydrobromic acid, add 1 mL of bromine, and evaporate to dryness. Add 34 mL of concentrated hydrobromic acid, heat to dissolve the residue, and dilute to 100 mL with water.
MIBK (methyl isobutyl ketone), 4-methyl-2-pentanone
Nitric acid, HNO_3 concentrated (70%)
Gold (Au), tellurium (Te), and thallium (Tl) individual stock solutions, 1,000 µg/mL: Individually dissolve 1.000 g of pure gold, thallium, and 1.250 g of tellurium dioxide (TeO_2) in 20 mL of hydrobromic acid-10% bromine solution, heat gently to expel excess of bromine, and make up to volume in 1,000-mL volumetric flask with concentrated hydrobromic acid. The solution has a hydrobromic acid concentration of approximately 9M.
Combined Au and Tl standard solutions: Prepare five combined standards from the individual 1,000-ug/mL stock solutions and concentrated hydrobromic acid to contain the following volumes in six 250-mL volumetric flasks. Make up to volume with water.

Solution	Blank (mL)	S_1 (mL)	S_2 (mL)	S_3 (mL)	S_4 (mL)	S_5 (mL)
Au	0.0	1.0	2.0	5.0	10.0..20.0	
Tl	0.0	1.0	2.0	5.0	10.0..20.0	
HBr	55	53	51	45	35 15	

Te standard solutions: Prepare five combined standards from the individual 1,000-ug/mL stock solution, concentrated hydrobromic acid, and 4% Fe solution to contain the following volumes in six 250-mL volumetric flasks. Make up to volume with water.

Solution	Blank (mL)	S_1 (mL)	S_2 (mL)	S_3 (mL)	S_4 (mL)	S_5 (mL)
Te	0.0	1.0	2.0	5.0	10.0	20.0
HBr	75	74	73	70	65	55
4% Fe	25	25	25	25	25	25

Gold and thallium working standards in MIBK for flame AAS: Add 1.0 mL each of Blank, S_1, S_2, S_3, S_4, S_5 to six 25x150-mm test tubes. Add 19 mL of water and 4 mL of MIBK, stopper, shake for 5 minutes, and centrifuge. The concentration of Au and Tl in the MIBK working standard corresponds to 0.0, 1.0, 2.0, 5.0, 10.0, and 20.0 ppm of the metal based on a 4-g sample.

Tellurium and working standards in MIBK: Add 1.0 mL each of Blank, S_1, S_2, S_3, S_4, and S_5 to six 25x150-mm test tubes. Add 19 mL of 3M hydrobromic acid, 2 g of ascorbic acid, and mix to reduce iron and make the solution light yellow. Add 4 mL of MIBK, stopper, shake for 5 minutes, and centrifuge. The concentration of Te in the MIBK working standard corresponds to 0.0, 1.0, 2.0, 5.0, 10.0, and 20.0 ppm of the metal (based on a 4-g sample).

Dilute gold solution for graphite furnace AAS, 1 µg/mL: Prepare by serial dilution of the 1000 µg/mL stock solution.

Standard gold solution in MIBK for graphite furnace AAS, 0.025 and 0.050 µg/mL: Add 0.25 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 .1N HBr. Cap and shake vigorously for 2 minutes.

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 MSDS for further information concerning first-aid treatment and disposal procedures for chemical products used in this section.

Procedure

1. Weigh 4.0-g sample into a 100-mL Teflon beaker.
2. Wet sample with 2 mL of water.
3. Add 5 mL of concentrated nitric acid, 15 mL of concentrated hydrochloric acid, and 20 mL of concentrated hydrofluoric acid.
4. Place on an oscillating hot plate and evaporate to dryness at 100 to 110°C.
5. Add 5 mL of concentrated hydrobromic acid and evaporate to dryness at the same temperature as above. (Complete dryness is very necessary to insure good separation of the metals in the two-step solvent extraction.)
6. Add 0.22 mL of the hydrobromic acid-10% bromine solution and 5 mL of water.

7. Warm to dissolve residue, wash sample solution into a 25x150-mm disposable tube with water, and make up to 20 mL volume.
8. Add 4 mL of MIBK, cap, and shake for 5 minutes.
9. Centrifuge to separate the MIBK phase.
10. Determine the Au and Tl content of the MIBK layer. When graphite furnace gold is requested, care must be taken to avoid contamination of the graphite furnace by samples containing high concentrations (>0.1 ppm) of gold. All samples must be first analyzed by flame. Only samples with concentrations less than 0.05 ppm gold should be analyzed by graphite furnace. Both flame values ≥0.05 ppm and graphite furnace values should be reported. Recalibrate the flame AAS or reslope the graphite furnace AAS after every 10 samples.
    [Continue procedure for the determination of Te]
11. Remove and discard the remaining MIBK layer using the vacuum system.
12. Add 10 mL of concentrated hydrobromic acid and mix.
13. Add 2 g or more of ascorbic acid and mix to reduce the iron and decolorize the solution from brown to light yellow.
14. Extract with 4 mL of MIBK as above and use organic solution for the determination of Te.

Standardization of Instrument

Table 8 lists the operating conditions for a Perkin-Elmer 5000 atomic absorption spectrophotometer for determining Au, Tl, and Te by this method.

Table 8. Operating conditions for determination of gold, thallium, and tellurium by flame AAS

	Au	Tl	Te
Grating	UV	UV	UV
Source lamp	Hollow cathrode lamp	EDL	EDL
Integration time	1 second	1 second	1 second
Flame conditions	oxidizing (lean blue)		
Wavelength, nm	242.8	276.8	214.3
Slit, nm	0.7	0.7	0.2
Lamp current, mA	Use current as recommended on lamp		
Burner	Boling (3-slot)	Boling (3-slot)	Boling (3-slot)
Background correction	No	No	Yes
S_1 = X absorbance units	0.090	0.045	0.063
S_2 = X absorbance units	0.170	0.090	0.126
Lower determination limit, µg/g (ppm)	0.05	0.05	0.05

Calibration for gold, tellurium, and thallium, by flame AAS

Standard	µg	Instrument setting (ppm)
S_1	4	1.0
S_2	8	2.0
S_3	20	5.0
S_4	40	10
S_5	80	20

The following operating conditions, table 9, are for a Perkin-Elmer 5000 equipped with a graphite furnace with Zeeman background correction.

Table 9. Operating conditions for determination of gold by graphite furnace AAS; dissolution by HF, aqua regia, and $HBr-Br_2$

Grating	ultraviolet
Wavelength	242.8 nm
Slit	0.7 nm
Lamp current	10 mA
Source	gold (hollow cathode lamp)
Purge gas	nitrogen
Dry cycle	
Ramp	10 sec
Hold	20 sec
Temp	120°C
Char cycle	
Ramp	1 sec
Hold	15 sec
Temp	500°C
Atomization Cycle	
Ramp	0 sec
Hold	3 sec
Temp	2000°C
REC	-1 sec
Read	-1 sec
Baseline	-6 sec
INT FLOW	0
0.025 µg/mL	0.300 ± 10% absorbance units calibration setting = .025
Clean-up cycle	
Ramp	1 sec
Hold	3 sec
Temp	2500°C

Calibration for gold by graphite furnace AAS

Standard	µg	Instrument setting (ppm)
.025	.25	0.025
.050	.50	0.500

Calculation

When using the recommended sample weight, calibration standards, and instrument settings, the resulting sample reading is the actual element concentration in the sample reported as μg/g (ppm).

Assignment of uncertainty

Tables 10 and 11 are tabulations of statistical data obtained by analyzing the GXR (geochemical exploration reference) samples (Allcott and Lakin, 1975) in six replicas, by the described procedures.

Table 10. Gold, thallium, and tellurium content of GXR samples by flame AAS [N( ), not detected at limit of determination]

Reference samples (description)	Range (ppm)	$\bar{X}$ (ppm)	s	% RSD	Literature value[1] (ppm)
		Gold			
GXR1 (jasperoid)	3.5-.4.0	3.7	0.22	6	3.3
GXR2 (soil)	N(.05)	--	--	--	0.036
GXR3 (Fe-Mn mineral deposit)	N(.05)	--	--	--	--
GXR4 (copper mill head)	.47-.57	.51	0.04	8	0.470
GXR5 (soil)	N(.05)	--	--	--	--
GXR6 (soil)	.10-.13	.11	0.01	9	0.095
		Thallium			
GXR1	.38-.43	.41	0.02	5	--
GXR2	.77-1.1	.95	0.12	13	1.03
GXR3	2.5-3.0	2.8	0.20	7	3.6
GXR4	3.0-3.2	3.1	0.07	2	3.2
GXR5	.24-.27	.25	0.01	4	0.33
GXR6	1.8-2.1	1.9	0.12	6	2.2
		Tellurium			
GXR1	11-13	12.0	0.71	6	13
GXR2	.18-.28	.22	0.04	18	0.690
GXR3	N(.05)	--	--	--	0.009
GXR4	.59-.70	.64	0.05	8	0.970
GXR5	N(.05)	--	--	--	--
GXR6	N(.05)	--	--	--	0.018

[1] Govindaraju, 1989

Table 11. Gold content of GXR samples by graphite furnace AAS; dissolution by HF, aqua regia, and $HBr-Br_2$

Reference samples (description)		Range (ppm)	$\bar{X}$ (ppm)	s	% RSD	Literature value[1] (ppm)
GXR2	(soil)	.020-.021	.021	0.0006	3	0.036
GXR3	(Fe-Mn mineral deposit)	.001-.002	.002	0.0007	35	--
GXR5	(soil)	.004-.005	.005	.0005	10	--
GXR6	(soil)	.065-.077	.071	0.006	8	0.095

[1] Govindaraju, 1989.

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Determination of mercury in geologic materials by continuous flow-cold vapor-atomic absorption spectrophotometry

By Richard M. O'Leary, James G. Crock, and Kay R. Kennedy

Code: A090 Accepted: Provisional

Principle

To determine mercury in geologic materials, samples are digested with nitric acid and sodium dichromate in a closed Teflon vessel. After bringing to a constant weight, the digest is mixed with air and a sodium chloride-hydroxylamine hydrochloride-sulfuric acid solution and then Hg (II) is reduced to Hg° with stannous chloride in a continuous flow manifold. The mercury vapor is separated and measured using cold vapor-atomic absorption spectrophotometry (CV-AAS). This method is described in detail by Kennedy and Crock (1987).

Interference

Elements which may be present in the digest of a geologic material and found not to interfere with the determination of mercury using the presented CV-AAS method are: Zn (1000 ppm), Pb (1000 ppm), Cu (500 ppm), Cd (50 ppm), Bi (50 ppm), Co (100 ppm), Mn (1000 ppm), V (100 ppm), As (30 ppm), Sb (10 ppm), and Fe (500 ppm). Some elements do significantly reduce the observed atomic absorption signals from 10 ppb Hg solution. They are Ag, Au, Pt, Te, and Se. Interference from these elements has also been noted by previous investigators (Bartha and Ikrenyi, 1982 and Suddendorf, 1981). Of these, only Se poses a significant problem for nonmineralized geologic materials. There is no suppression of a 10 ppb Hg signal until the Se concentration in solution is greater than 200 ppb (25 ppm Se in sample). Samples with Se contents greater than 25 ppm should be diluted. Although a 1 ppm solution of the other elements causes greater than a 90% suppression of a 10 ppb 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 100 ppb in the digest (12 ppm in sample).

Scope

The method is applicable to many geologic sample matrices and offers a detection limit of 20 ppb Hg in the sample. Samples exceeding the working range of 0.02 to 3.4 ppm Hg in a 0.1-g sample require dilution. Approximately 40 samples can be analyzed per person-day.

Apparatus

Perkin Elmer 272 Spectrophotometer
Perkin-Elmer 056 Strip Chart Recorder
Technician 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 Heatlamp. Position around the flow-through cell and the phase separator

7.5-cm-thick x 25-cm-wide x 50-cm-long aluminum heating block, with 170-mm holes drilled through in a 10 by 10 matrix

See figures 7 and 8 for the flow-through cell and phase separator used in this method. These have been described by Fishman and Friedman (1989). Mixing coils are available from Technicon, Inc., Tarrytown, New York.

Reagents

Unless otherwise noted, chemicals are reagent grade and water is metal free.

25% (w/v) sodium dichromate solution: Dissolve 500 g reagent grade $Na_2Cr_2O_7 \cdot 2H_2O$ in sufficient demineralized water to bring the volume to 2.0 L.

Nitric acid wash: Dilute 40 mL "Baker Instra-Analyzed" grade HNO_3 (16M) to 4.0 L with water.

Stannous chloride solution: Dissolve 100.0 g $SnCl_2 \cdot 2H_2O$ (Baker, suitable for Hg determination grade) in 100 mL concentrated (12M) "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 water. This solution is stable for about 1 week with refrigeration.

Complex-reducing solution: Dissolve 30.0 g hydroxylamine hydrochloride and 30.0 g NaCl in about 500 mL demineralized water. Add very slowly 100.0 mL concentrated (18M) H_2SO_4, "Baker Instra-Analyzed" grade. When the solution is cool, dilute to 1.0 L with demineralized water.

Safety precautions

Normal laboratory safety procedures should be observed, including the use of protective eyeware, laboratory coat, and gloves. All chemical digestion activities should be performed in a chemical hood. See the 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

1. Weigh 0.100 g of sample into 16x100-mm disposable test tube.
2. Add 2.0 mL 16M HNO_3, and 0.50 ml of the sodium dichromate solution to the sample. Vortex wet the entire sample.
3. Place test tube in the aluminum heating block for 3 hours at 110°C. Remove from the heating block and allow to cool completely. (Overnight cooling is acceptable.)
4. Dilute sample to 12 mL with water, cap and shake for 5 minutes.
5. If the sample is mineralized or if it contains more than 10 ppm Se, 10 ppm Au, 10 ppm Ag, or 500 ppm As, transfer 1 mL to a second test tube, add 2 mL HNO_3, 0.5 mL of dichromate solution, and dilute to 10 mL with demineralized water.

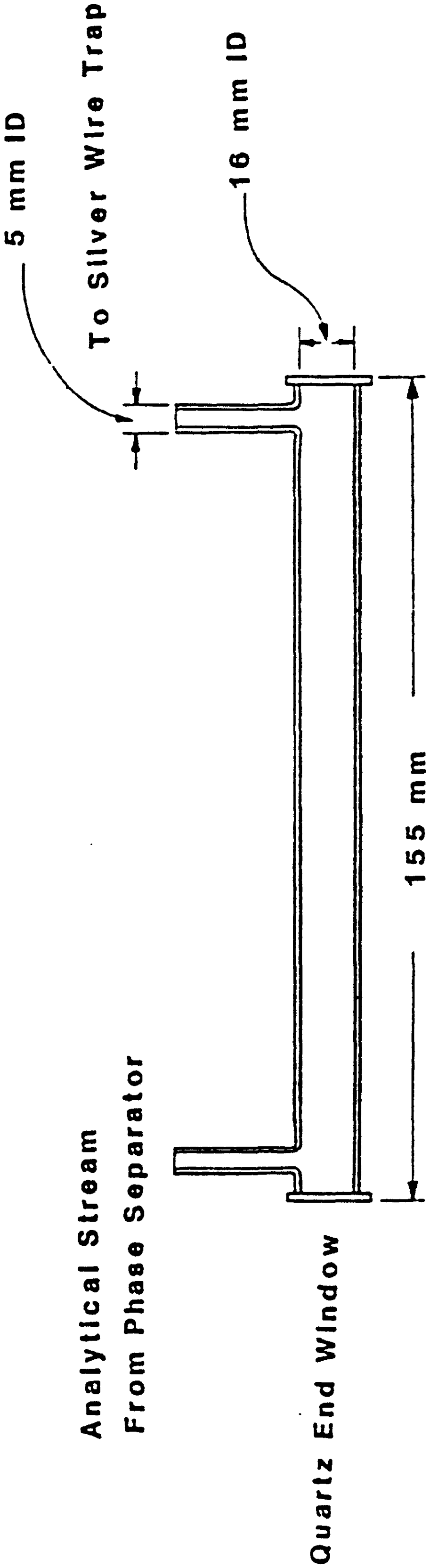

Figure 7. The flow-through cell used for the determination of mercury. The two 16-mm end windows of this cell are quartz and the remainder of the cell is Pyrex glass.

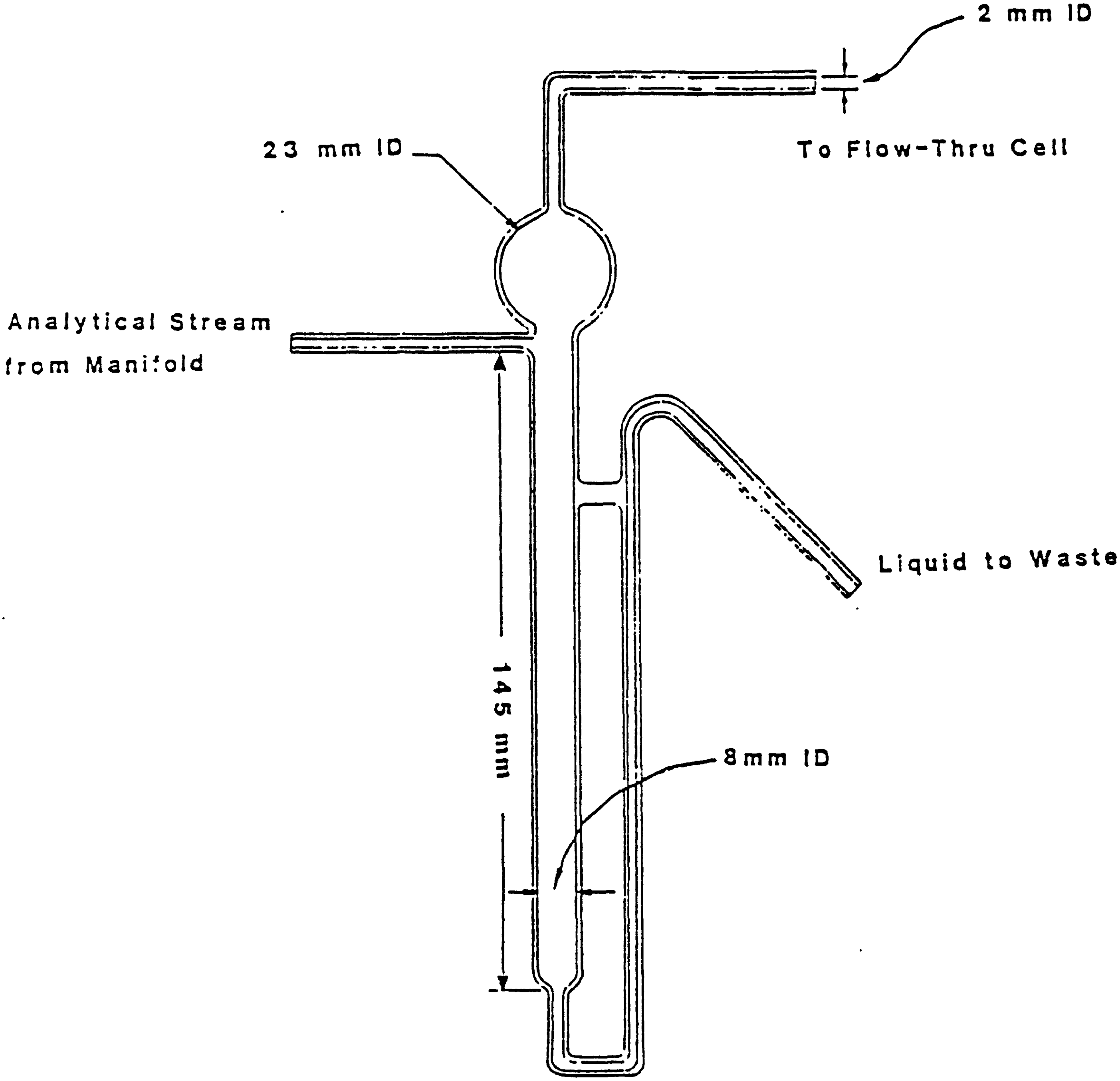

Figure 8. Phase separator used in the determination of mercury. The separator is made from Pyrex glass.

6. Prepare two reference samples, one duplicate sample and one blank for each job of 40 samples. Aqueous standards of 5 and 10 ppb Hg are used for the calibration curve with each day's analysis. This is prepared by dilution of a 100-µg Hg/mL standard with the final solution being 3M HNO_3 and 0.5% sodium dichromate (20 mL 16M HNO_3 and 2 mL of the sodium dichromate solution for a 100-mL volumetric flask).
7. Using the manifold illustrated in figure 9, modified from Koirtyohann and Khalil (1976), 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 10 ppb Hg solution, to reach baseline between 10 ppb Hg signals, and to allow the high dichromate concentration in the sample digest.
8. Solid geological reference materials taken through the entire procedure should be used as a quality control check. The calibration curve is checked at the beginning of every job (approximately 40 samples).

Standardization of Instrument

Instrument settings used for a Perkin Elmer 272 AAS Spectrometer and a Perkin-Elmer 56 Recorder are outlined in table 12.

Table 12. Operating conditions for determination of mercury by cold vapor-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
0.005 µg/mL	approx. 16 division on recorder paper

Calculation

The formula to calculate the mercury concentration is:

$$\mu g/g \text{ or ppm} = \left(\frac{\text{Concentration of standard } (\mu g/mL)}{\text{Recorder reading of standard (divisions)}}\right)$$

$$\left(\times \frac{\text{Total volume of sample solution (mL)}}{\text{Sample weight (g)}}\right)$$

$$\times \text{ Recorder reading of sample (divisions)}$$

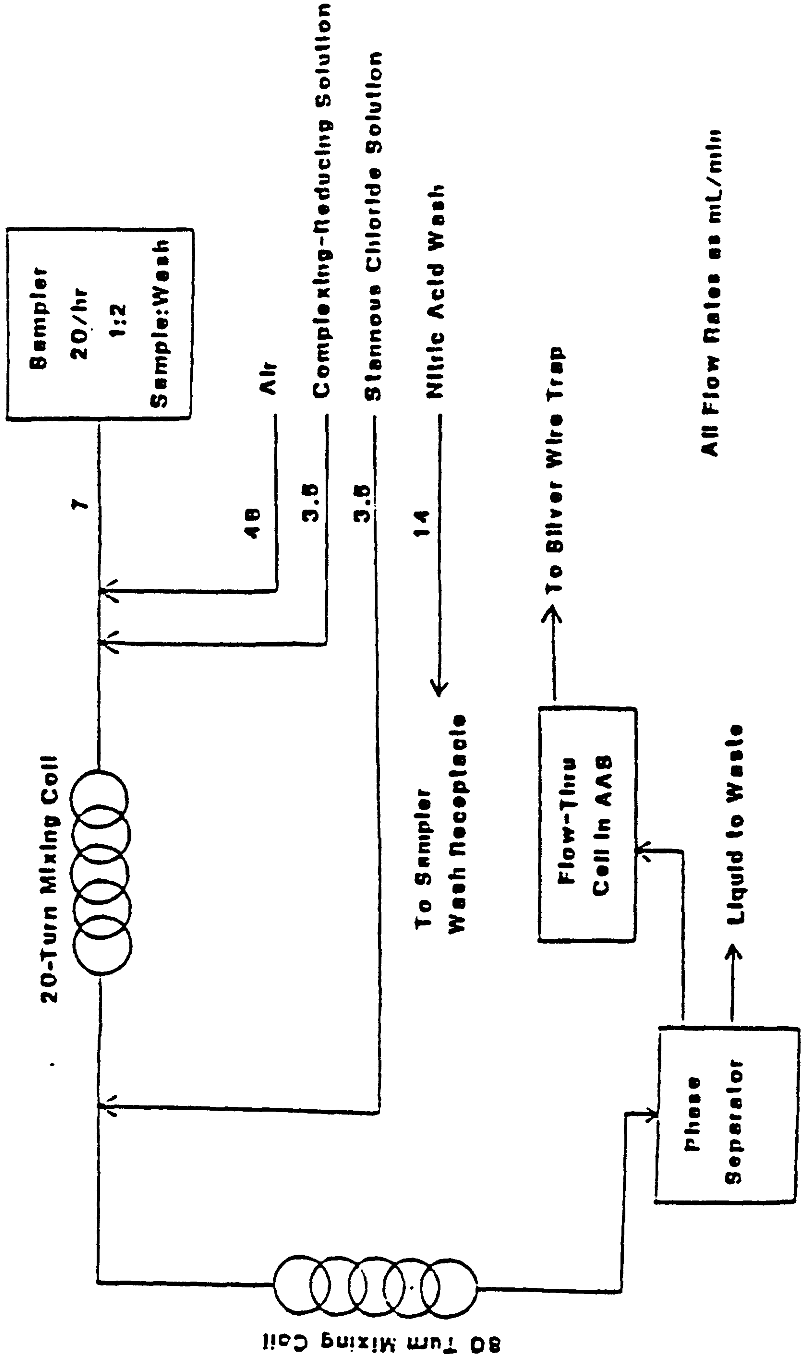

Figure 9. Manifold used for the automated generation of mercury vapor.

Assignment of Uncertainty

Short-term precision (mainly instrumental) of the method was determined by analyzing sixteen 0.010 ppm Hg solutions and was found to be 1.2% RSD. The overall precision of the method was determined by analyzing the USGS standard shale SGR-1 ten times. The mean was 0.170 ppm Hg with a RSD of 5.8%. A 0.21-µg Hg/L solution gives a signal of 0.0044 absorbance. The method has an in-sample detection limit of 0.02 ppm Hg using the described digestion procedure and operating conditions. The detection 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 13 shows that, in general, there is good agreement with this method and those in the literature.

Table 13. Mercury content of selected geologic reference materials

Reference sample (description)	$\bar{X}$ (ppm)	s	% RSD	Literature value (ppm)	Reference
GXR-1 (jasperoid)	3.3	0.1	3	3.9	Govindaraju, 1989.
GXR-2 (soil, residual)	3.3	0.0	0	2.9	--------Do-------
GXR-3 (Fe-Mn mineral deposit)	0.36	0.02	6	0.33	--------Do-------
GXR-4 (copper mill head)	0.13	0.01	8	0.11	--------Do-------
GXR-5 (soil, podzol)	0.17	0.00	0	0.158	--------Do-------
GXR-6 (soil, composite)	0.08	0.00	0	0.068	--------Do-------
NBS-1645 (river sediment)	1.2	0.2	17	1.1	--------Do-------
MESS-1 (marine sediment)	0.21	0.02	10	0.171	--------Do-------
BCSS-1 (marine sediment)	0.16	0.00	0	0.129	--------Do-------
SO-1 (soil)	0.04	0.00	0	0.02	--------Do-------
SO-2 (soil)	0.09	0.01	11	0.082	--------Do-------
SO-3 (soil)	<0.02		--	0.017	--------Do-------
SO-4 (soil)	0.04	0.00	0	0.032	--------Do-------
G-2 (granite)	0.06	0.00	0	0.051	--------Do-------
SGR-1 (shale)	0.17	0.01	6	0.27±0.01	Abbey, 1983.
SDO-1 (shale)	0.29	0.03	10	0.190	Govindaraju, 1989.
SCo-1 (shale)	0.08	0.00	0	0.052±0.001	Abbey, 1983.

Every daily run of samples is preceded by two 5 ppb Hg aqueous standards, a GXR-5 reference sample taken through the digestion procedure, and a digested reagent blank. The two aqueous standards establish the sensitivity; GXR-5 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 GXR-5 suggest the apparatus needs to be disassembled and cleaned with 4N HNO_3. This removes any residual Hg or organic carbon buildup. The sample digests are stable in the glass test tubes for up to 2 weeks.

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Determination of carbonate carbon in geologic materials by coulometric titration

By Elaine Brandt, Phillip Aruscavage, and Clara Papp

Code: C010 Accepted: Provisional

Principle

Carbonate carbon in geologic material is determined as carbon dioxide, CO_2, by coulometric titration. The sample is treated with hot 2N 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. Close attention must be given to the build-up of black sulfide precipitate in the prescrubber solution.

Scope

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. The detection limit is 0.01% CO_2 and samples containing up to 50% CO_2 may be analyzed. Sample size is adjusted from 0.5 g for the range 0.01 to 5% CO_2, 0.1 g for the range 5 to 10% CO_2, and 0.02 g for >10% CO_2.

Apparatus

Carbonate Carbon Apparatus Model 5030 with Carbon Dioxide Coulometer Model 5010, HP85 Computer with "COUL" program, or if available, programmable calculator.

Reagents

Perchloric acid, 2N: Dilute 170.3 mL $HClO_4$ (70%) to 1 L; store in a plastic bottle
Potassium hydroxide, KOH, 45% solution, Coulometrics
Hydrogen peroxide, H_2O_2, 30% solution, Baker reagent grade
Potassium iodide, KI, saturated solution: Add 2 g potassium iodide to 100 mL distilled water and stir for 2 hours on a magnetic stirrer
Coulometer solution: Proprietary solution of monoethanolamine and thymolphthalein indicator, Coulometrics
Silver sulfate solution: Add 1.5 g silver sulfate, Ag_2SO_4, to 100 mL distilled water and stir for 2 hours on a magnetic stirrer. Add 2 mL concentrated sulfuric acid, H_2SO_4, and mix. Store in a glass bottle.
Ammonium hydroxide, NH_4OH, concentrated.
Acetone

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 should be done under an operating chemical hood. Use perchloric hood for all analytical procedures involving $HClO_4$ and clean after use. Ammonia fumes from concentrated NH_4OH are extremely irritating to eyes and lungs. See the MSDS for precautions, effects of overexposure, first-aid treatment etc. for chemical products used in this method.

Procedure

Reference materials used for the analysis include USGS standards AGV-1 and SCo-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. Accurately weigh 0.5 g powdered sample 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% respectively.
2. Place a small, magnetic stirring bar in the clean coulometer cell beaker. Add 80 mL of the coulometer solution.
3. With a small spatula, add 0.1 g potassium iodide 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 (~¼ inch) the potassium iodide crystals covering the frit. As the anode wears away thorough 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 2N perchloric acid 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. Control samples should be at maximum, unless samples bump.

   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% T. Once the transmission control is set initially for the days run, it should not be changed. If it cannot be set to 100% 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 minutes as a blank determination. This time is in the program. After 5 minutes, 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 minutes 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 microgram difference in 2 minutes). Normal samples usually require 5 to 10 minutes. As an example, if the count is 20 µg at 6 minutes, 24 µg at 7 minutes, and 28 µg at 8 minutes, it can be assumed equilibrium has been reached. Often there will be duplicate counts on successive minute intervals at equilibrium and usually before 10 minutes.
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 <u>after</u> 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 of the 2N $HClO_4$ into it and continue shutdown by:
    d. turning off the air gauge;
    e. turning off the heater and pump switch.

    Follow this sequence to prevent any backflow 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 KI 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.

   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 concentrated hydrochloric acid and then thoroughly with water. Rinse with distilled water. Add silver sulfate solution (saturated) to the mark (4 mL) and add 9 drops 30% hydrogen peroxide. Reconnect the system. NOTE: Traces of hydrochloric acid, a result of insufficient rinsing with water, will react with silver sulfate to form a white precipitate of silver chloride.
2. Periodically check the platinum electrode wire for dirt or film. Wipe clean with tissue or clean with dilute nitric acid and rinse with distilled water.
3. If there is excessive frothing in the 45% 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 distilled water, remove the tube from the system. Clean the sintered glass plug by passing distilled water through it. Add 12 mL 45% KOH to the cleaned scrubber tube and re-assemble in the apparatus. Addition of a little water to the scrubber will usually correct the condition. After this has been done 10 times or so, it will be necessary to replace the KOH.
4. To clean the sintered glass frit in the silver sulfate sample scrubber, drain sample scrubber and rinse with H_2O. Fill the scrubber with

ammonium hydroxide and warm in a water bath to clean the frit. Rinse thoroughly with H_2O. When the disk is clean, the tube may be refilled with silver sulfate solution.

5. 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 distilled water.
6. If a run is interrupted for 1 hour or more, continue operating the system with the last determined sample in place.
7. Replace the cell solution if over 350,000 µg of 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 % CO_2

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

b. To determine % carbonate carbon

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

Assignment of uncertainty

The precision obtained in replicate analyses of USGS rock standards expressed as RSD is ~5.1 or less over a concentration range of 0.01-36% CO_2. Over a 1-month period, the mean and standard deviation for a granodiorite, GSP-1, were determined to be 0.10±0.003% CO_2 (n=12). The proposed value is a 0.11% CO_2 (Govindaraju, 1989).

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Determination of moisture and total water in silicate rocks

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

Code: C020 Accepted: Provisional

Principle

The total water in silicate rocks is determined by coulometry using the Karl Fischer titration method. 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 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 accuracy and precision of this method are comparable to those of the Penfield method used for the determination of total water in classical rock analysis. The moisture (H_2O^-) is determined by weight loss after heating the sample at 110°C.

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 both the H_2O^- and the H_2O^+ determinations, if it does not preclude their determination totally. The loss of volatile organic species at 110°C yields high results for H_2O^-. High results also are obtained for total or water due to combustion of the organic matter yielding H_2O and CO_2 (Jackson, and others, U.S. Geological Survey Bulletin 1770). Thus determination of water in samples of high organic content should be foresaken entirely. Sample preparation or grinding may also affect the water content of the sample. The 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. Finally, introduction of atmospheric water through an improperly sealed instrumental system yields erreoneous results.

Scope

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 H_2O. The limit of determination is 0.05% H_2O for all three types. Approximately 25 samples can be analyzed in a day.

Apparatus

Coulometric titrator, with microprocessor control unit, electrolytic cell, and printer, MCI Model CA-05
Vaporizer, 0 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 o.d. by 11-mm height

Reagents

Anode reagent solution, MCI, Aquamicron A
Calcium Carbonate, $CaCO_3$
Cathode reagent solution, MCI, Aquamicron C
Check solution, MCI, 3.8 to 4.1 mg H_2O per mL
Ethyl alcohol, C_2H_6O, reagent grade, anhydrous
Silica gel desiccant, indicating, 3 to 8 mesh, "Baker Analyzed" reagent
Molecular sieves
Nitrogen gas, Linde, prepurified grade
Lead oxide, PbO, C.P. (litharge)
Lead chromate, $PbCrO_4$, "Baker Analyzed" reagent, powder

The flux is prepared according to the instructions of Peck (Systematic Analysis of Silicates, Geological Survey Bulletin 1170, 1964). In this procedure 200 g of lead oxide and 100 g of lead chromate are heated 1 hour at 800°C in separate platinum crucibles. After cooling, the constituents are ground to just pass a 20-mesh sieve, mixed on a paper with 50 g of dry calcium carbonate and stored in a bottle having a tight seal cap.

Safety precautions

All work with open or uncapped reagents should be done in a chemical hood. In use, instrumentation should be vented into a chemical hood or a canopy 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** and in the MSDS. Effects of overexposure, first-aid treatment, and disposal procedures for reagents used in this method are, also, discussed in the MSDS.

Procedure

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 diaphram 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 per minute 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/sec 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 per minute. Allow the background to reach a low level, less than 0.07 µg/sec, 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 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 gm of 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 dessicator. 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. The composition of the volatile reagents contained in the solutions are given in table 14.

Table 14. Percent composition of volatile regent solutions used in the determination of combined water

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

To prevent inhalation of these harmful constituents the operation is carried out under a hood. A canopy hood is sufficient to remove volatile components associated with this operation. To enhance the removal of volatile components vented from the electrolytic cell in the stream of nitrogen gas, the vent tube is extended to a point near the exhaust duct of the canopy hood. If a regular chemical hood is used, the vent tube should be extended to the rear of the hood into the flow of the exhaust air stream.

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 dessicant 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 height 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/sec) 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 height 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 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 cathods 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 Staticmaster brush contains radioactive polonium which is a health hazard. The Nuclear Products instructions for handling and disposal are to be followed explicitly. Replace the Staticmaster cartridge after its expiration date. Return the used cartridge to the factory for disposal. Calibration weights should read to within ±0.2 mg of their reported values.

    The procedure is for routine analysis using a 50 ± 0.5 mg sample and 300 ± 20 mg of 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 weighings, 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, hornblendes, 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 o.d. 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 o.d. and 11-mm height. The cups are deformed by melting during the determination of combined water. The cup with the fluxed sample is discarded, according to safety regulations, after the determinations are completed.

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 o.d. 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-inch 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 seconds and is complete within 5 to 10 minutes 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% total water are usually complete within 6 minutes.
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 per minute, and follow the close-down procedure under steps a, c, d, and e. To commence operations increase the gas flow to 100 mL per minute, 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.

$$\text{Percentage } H_2O^- = \frac{\text{weight in grams of the water released from heating the sample}}{\text{weight in grams of the sample}} \times 100$$

The percent total water is calculated and printed out by the MCI-CA-05 titrator, taking into consideration the average 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

The accuracy of this method for H_2O^+ has been determined over a 1-month period using nepheline syenite STM-1. The mean and standard deviation are 1.46±0.03% H_2O^+ (n=12). The recommended value is 1.50% H_2O^+ (Govindaraju, 1989). The precision of the method was measured by running replicate determinations and determining the standard deviation of results. In the range 0 to 2 percent moisture and total water it is not uncommon to find an absolute standard deviation of ±0.02 percent.

References

Govindaraju, K., editor-in-chief, 1989, 1989 Compilation of working values and samples description for 272 Geostandards, Geostandards Newsletter: v. XIII, July, p. 12.

Jackson, L.L., Brown, F.W., and Neil, S.T., 1987, Major and minor elements requiring individual determination, classical whole rock analysis and rapid rock analysis, _in_ Baedecker, Philip A., editor, Methods for geochemical analysis: U.S. Geological Survey Bulletin 1770.

(The following manuals have been issued by Mitsubishi Chemical Industries, Ltd. and are used to solve problems in service and maintenance, replacement of parts, and repair of instrumentation and equipment.)

Instruction, maintenance, and troubleshooting manuals for Mitsubishi Titrator Model CA-05.

Drawing of parts and system curcuit connections for Mitsubishi Titrator Model CA-05.

Instruction manual for Mitsubishi Vaporizer Model VA-21.

Elemental analysis of geological material by inductively coupled plasma-atomic emission spectrometry

By Paul Briggs

Code: E010 Accepted: Provisional

Principle

Forty major and trace elements are determined in geologic materials by inductively coupled plasma-atomic emission spectrometry (ICP-AES) (Lichte and others, 1987; Crock and others, 1983). The sample is decomposed using a mixture of hydrochloric, nitric, perchloric, and hydrofluoric acid at low temperature. The digestion is taken to dryness, the residue treated with aqua regia, and the solution brought to 10 g with dilute nitric acid. The solution is nebulized into the ICP-AES plasma discharge for determination of the elements.

Aqueous rock standards and multi-element standard solutions are used to calculate the calibration curves for each determined element. Two standard samples, two reagent blanks, and two duplicate unknowns are processed with each lot of samples for quality control purposes.

Interferences

ICP-AES interferences may result from spectral line overlap, background shifts, and matrix effects. Spectral line interferences are resolved by applying mathematical correction factors determined by using single-element standards (Thompson and Walsh, 1983; Thermo, Jarrell, and Ash, 1979). Background shift corrections are made by measuring and subtracting emission in the vicinity of the analytical line. Matrix effects can generally be negated by proper matching of standard and sample matrices.

Scope

The ICP-AES analysis of major, minor, and trace elements has found wide application in geochemical studies. The method is routinely applied to the elemental analysis of rock, soil, and sediment samples for studies in petrogenesis, mineral deposits formation and exploration, and for investigations in environmental geochemistry. The lower limits of analyte concentration for which this method is useful are shown in table 18. Two hundred samples may be analyzed in a day; assuming the digestion is completed.

Apparatus

ICP-AES, 63-channel Jarrell-Ash ICP-AES polychromator, Model 1160 Plasma Atomcomp.
30-mL Teflon vessel (Savillex)
Hotplate with 50-position aluminum heating block
Acid dispensers (Labindustries)
Repeating pipet (Eppendorf)
60-mL square bottomed bottles with caps (Nalgene)

Reagents

Hydrochloric acid, concentrated reagent grade, 37% HCl
Nitric acid, concentrated reagent grade, 70% HNO_3
Hydrofluoric acid, concentrated reagent grade, 48% HF
Perchloric acid, concentrated double distilled, 70% $HClO_4$,
  G. Frederick Smith Co.
Aqua regia: 3 parts HCl per 1 part HNO_3
Demineralized (DM) water
Lutetium internal standard: 500 μg/mL, Lu as Lu_2O_3 in 5% (v/v) HCl

Safety precautions

All laboratory personnel must wear safety glasses, rubber gloves, and lab coats when working in the laboratory. All sample digestions must be performed in the perchloric acid hood; the latter is cleaned after use. See the MSDS for precautions, effects of overexposure, first-aid treatment, etc. for reagents used in this procedure. Adequately vent the RF generator and plasma chimney to exhaust the heat buildup. Use extreme caution handling the ICP-AES due to the potential lethal voltage associated with the instrument. Have the ICP serviced by trained personnel.

Procedure

A. Digestion of samples and rock standards

1. Select appropriate number of teflon vessels to contain samples, duplicate samples, standards, and blanks.
2. Weigh 0.200 g sample into Teflon vessel.
3. Add 100 μL of 500 μg/mL stock lutetium internal standard to each vessel with repeating Eppendorf pipet.
4. Rinse sample from side walls of Teflon vessel with 2 to 3 mL amount of DM water.
5. Slowly add 3 mL conc HCl.
6. Add 2 mL conc HNO_3, allow any reaction to subside.
7. Add 1 mL conc $HClO_4$ and 2 mL conc HF. Place sample on aluminum heat block at a controlled temperature of 110°C.
8. Evaporate sample to dryness on hot plate, usually overnight.
9. Remove from hotplate, add 1 mL conc $HClO_4$ and add water to the Teflon vessel until halffull.
10. Return to hot plate, evaporate to dryness. This step takes 4 to 8 hours. The temperature of hot plate should be increased to 150°C.
11. Remove vessel with dried sample from hot plate and cool.
12. Add 1 mL aqua regia to each sample with repeating Eppendorf pipet.
13. Transfer contents of each Teflon vessel to a 60-mL square-bottomed bottle, having first placed each bottle on top loading balance and tared to zero. Rinse the vessel with 1% HNO_3, pour into bottle and bring to final 10.0 g weight. Cap and label bottle.
14. Place capped bottles in drying oven set at 95°C for 1 hour.
15. Analyze sample solution by ICP-AES.

B. ICP-AES treatment of calibrating rock standards and multi-element solutions

Calibration curves are performed at the start of each day's run (see table 15 for operating conditions). The calibrating solutions include a reagent blank, U.S. Geological Survey reference rock BHVO-1, Canadian Certified Reference Materials Project rock sample SY-3, and four multi-element solutions to calibrate the elements not covered by the two rock standards. Determine the 40-element spectral array by direct intensity measurements at the wavelengths (see table 16). There is a direct correlation between the intensity of the emmitted light and the concentration. The actual calibration process involves nebulizing the standard solution, equilibrating the spray chamber with that solution for 20 seconds, start the calibration process by integrating that solution signal for 32 seconds, nebulize a rinse solution and repeat this process until all calibrating solutions are run. The dedicated computer that operates the instrument performs the iterations of taking the electronic signals and transforming that information to concentration readings to set the calibration curves.

C. ICP-AES treatment of interelement interferences.

The ICP-AES system makes 219 interelement corrections. The correction factors are based on a granitic type rock. The following is a list of the elements which produce the largest number of interferences: Al, Ce, Cu, Fe, Mn, Ti, U, and V. Interference factors for these elements, except Ce and Cu, are updated with each day's run. By applying a mathematical interelement correction, spectral interferences can be corrected. For instance, if 1,000 ppm of element A gives an interference signal on channel B equivalent to 10 ppm of element B, then a simple correction can be made when analysing for element B in the presence of element A (see Thompson and Walsh, 1983). These interelement interference factors are applied when calculating the element concentration (see Calculation.)

D. ICP-AES treatment of sample analysis

Once the instrument is calibrated, the interferring elements are updated, sample solutions are run. The actual analysis process is the same as the calibration, i.e., nebulization of sample solution, equilibration, integration, and rinse for each sample, blank, and rock standard.

E. Treatment of results

After sample analysis, the results are reviewed for precision and accuracy. The following is the sequence that is followed:

1. Check the low-voltage channel for bad sample burns, if one is found, that sample needs reanalysis.
2. Check the Lu channel for intensity counts (all readings should be within ±2000 counts), if not, those samples are redigested and reanalyzed.
3. Check duplicate sample analyses for precision, if elements are not within ±5% of each other, redigest and reanalyze samples.
4. Refere to the reagent blank analysis and determine which elements need to be subtracted from the sample analysis.

5. Determine which elements need to be normalized by comparing in-house reference values from your analysis to recommended in-house reference values.
6. Determine if further interelement corrections need to be made.

Once these determinations are made, use the ICP-AES computer and make the corrections. New sample analysis is ready to transfer to sample control for final reporting.

Table 15. Operating conditions for determination of forty elements by ICP-AES

Power	1250 W
Argon flow rate	18 L/min coolant 0.50 L/min, sample
Sample pump rate to nebulizer	0.70 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 16. Wavelengths used for analysis by ICP-AES

Element	Wavelength (nm)	Element	Wavelength (nm)
Ag	328.0	Na	588.9
Al	309.2	Nb	309.4
As	189.0	Nd	430.3
Au	242.7	Ni	231.6
Ba	455.4	P	213.6
Be	313.0	Pb	220.3
Bi	223.0	Sc	424.6
Ca	317.9	Sn	189.9
Cd	226.5	Sr	421.5
Ce	418.6	Ta	240.0
Co	228.6	Th	401.9
Cr	267.7	Ti	334.9
Cu	324.7	U	409.0
Eu	381.9	V	292.4
Fe	259.9	Y	321.6
Fe	271.4	Yb	328.9
Ga	294.3	Zn	213.8
Ho	345.6		
K	766.4		
La	398.8		
Li	670.7		
Lu	261.5		
Mg	285.2		
Mn	257.6		
Mo	202.0		

Calculation

$$\text{Element concentration} = \frac{\text{IR unknown}}{\text{IR standard}} \times \text{conc std} \times \frac{\text{wt of final solution}}{\text{wt of sample}}$$

$$+[\text{inter-element corrections}]$$

$$\text{IR unknown} = \frac{\text{Intensity reading of element}}{\text{Intensity reading of Lu}}$$

$$\text{IR standard} = \frac{\text{Intensity reading of element for calibration standard}}{\text{Intensity reading of Lu}}$$

Conc standard = Concentration of element in calibration standard

Interelement corrections

1. Determination of correction factor
   a. Analyze a known concentration of the single interfering element
   b. Determine the apparent interferred element
   c. Calculation of factor

$$\frac{\text{interfered element}}{\text{interfering element}} = \text{factor}$$

2. Application of factor to sample solutions
   (factor x sample solutions interfering element) -Sample solution interfered element = corrected sample interferred element

Assignment of Uncertainty

Table 17 is a tabulation of statistical data obtained by analyzing GSD-12 (Chinese sediment reference material) 11 times, by the described method. Also, included is a table of detection limits for the method (table 18).

Table 17. Comparison of method value to recommended value GSD-12 (sediment) by ICP-AES

[All values ppm except * in %]

		Method value (n=11)			Recommended value[1]		
Determination level	Element	$\bar{X}$	s	% RSD	$\bar{X}$	s	n
4	Ag	--	--	--	1.15	0.16	24
0.05	Al*	4.81	0.09	1.9	4.92	0.09	31
8	Au	X	--	--	(5.6 ppb)	2.3	5
1	Ba	200	5	2.5	206	23	45
1	Be	7.0	0	0	8.2	1.1	40
10	Bi	10	0	0	10.9	1.3	32
0.05	Ca*	0.85	0.02	2.4	0.83	0.05	39
2	Cd	4.0	0	0	4.0	0.4	28
4	Ce	57.6	2.8	4.9	61	5	24
1	Co	9.1	0.3	3.3	8.8	1.1	67
1	Cr	40.6	3.5	8.6	35	4	59
1	Cu	1280	87	6.8	1230	51	52
2	Eu	X	--	--	0.61	0.04	19
0.05	Fe*	3.47	0.08	2.0	3.41	0.13	43
4	Ga	13.9	0.7	5.0	14.1	0.7	20
4	Ho	X	--	--	0.94	0.09	15
0.05	K*	2.40	0.06	2.5	2.41	0.05	37
2	La	30.0	1.8	6.0	32.7	2.2	32
2	Li	40.3	1.4	3.5	39.0	1.5	28
0.005	Mg*	0.26	.01	3.8	0.28	0.07	38
4	Mn	1473	47	3.2	1400	73	60
2	Mo	7.0	0.4	5.7	8.4	0.9	34
0.005	Na*	0.31	0.01	3.2	0.33	0.03	41
4	Nb	8.3	1.5	18.0	15.4	1.6	39
4	Nd	24.4	1.4	5.7	25.6	3.6	18
2	Ni	12.3	.5	4.1	12.8	1.9	65
0.005	P*	0.023	0.005	21.7	0.024	0.003	43
4	Pb	293	17	5.8	285	16	41
2	Sc	5.0	0	0	5.1	0.6	24
10	Sn	19.1	3.0	15.7	54	7	25
2	Sr	24.5	0.5	2.0	24.4	4.1	41
40	Ta	X	--	--	3.2	0.3	11
4	Th	21.6	0.9	4.2	21.4	1.7	25
1005	Ti	0.136	0.005	3.7	0.151	0.007	45
2	V	44.3	1.1	2.5	46.6	5.3	56
2	Y	20.0	1.2	6.0	29.3	4.0	51
1	Yb	2.8	0.4	14.3	3.7	0.5	33
4	Zn	529	19	3.6	498	27	52

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[1] Xie, 1986

( ) Values do not meet criteria for recommended value

(P) Partial dissolution

(X) Insufficient unqualified data

Table 18. ICP-AES detection limits for forty elements

Element	Multi-acid 1 to 50 dilution lower limit
Al	% .005
Ca	% .005
Fe	% .005
K	% .05
Mg	% .005
Na	% .005
P	% .005
Ti	% .005
Ag	ppm 2
As	ppm 10
Au	ppm 8
Ba	ppm 1
Be	ppm 1
Bi	ppm 10
Cd	ppm 2
Ce	ppm 4
Co	ppm 1
Cr	ppm 1
Cu	ppm 1
Eu	ppm 2
Ga	ppm 4
Ho	ppm 4
La	ppm 2
Li	ppm 2
Mn	ppm 4
Mo	ppm 2
Nb	ppm 4
Nd	ppm 4
Ni	ppm 2
Pb	ppm 4
Sn	ppm 10
Sc	ppm 2
Sr	ppm 2
Ta	ppm 40
Th	ppm 4
U	ppm 100
V	ppm 2
Y	ppm 2
Yb	ppm 1
Zn	ppm 2

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Organometallic halide extraction applied to the analysis of geologic materials for 10 elements by inductively coupled plasma-atomic emission spectrometry

By Jerry Motooka

Code: E020 Accepted: Provisional

Principle

Inductively coupled plasma-atomic emission spectrometry (ICP-AES) has been applied to practically all types of materials. A widely used extraction technique (Aliquat/MIBK) (Viets, 1978) has been modified and adapted for use with 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% 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, B, Cd, Cu, Mo, Pb, Sb, Zn) are determined simultaneously.

Interferences

Organic solvent extraction provides preconcentration of the analyte species and when combined 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 high quality analytical data in a relatively short period of time, approximately 100 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. This method is applicable to practically all types of geologic materials, including ashed plants. The lower limits of determination are well below 1 ppm (see table 20) and the upper limits extend beyond four orders of magnitude.

Apparatus

Applied Research Laboratories Model 3580 ICP spectrometer.
Standard equipment for acid digestions done in water bath. See procedure for test tubes, etc.

Reagents

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

Aliquat 336-DIBK (diisobutylketone) 10% (v/v): Pour 200 mL Aliquat 336 (tricaprylmethylammonium chloride, obtainable from Henkel Chemicals, Minneapolis, Minn.) into a clean 1-L stoppered, graduated cylinder, dilute to 1 L with DIBK, 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% (w/v): Weigh 300 g ascorbic acid (U.S.P. Food grade or metal-free equivalent) and 150 g potassium iodide into a brown glass bottle, add 1 L water, stir, and warm over low heat until dissolved. Prepare fresh weekly. Note: Some potassium iodide has been found to contain cadmium and silver contaminants. However, if samples, standards, and blanks are prepared using the same bottle of reagents, small amounts of contaminants will not affect the accuracy of the results.

Hydrochloric acid, HCl

Hydrogen peroxide, H_2O_2, 30%

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 eyeware must be worn. A good ventilating system should be employed over samples when analysis is performed even though MSDS indicates health hazard for DIBK is only slight. See the MSDS for further information concerning first-aid treatment and disposal procedures for chemical products used in this method.

Procedure

1. Weigh 1.0 g of sample into a 25x150-mm disposable test tube (see below).
2. Add 5.0 mL of concentrated hydrochloric acid followed by 1.0 mL of 30% hydrogen peroxide dispensed in ½-mL portions, 15 minutes apart. Mix sample well after each addition of the hydrogen peroxide.
3. Allow samples to stand for 1 hour, mixing once after 30 minutes, and then place samples in boiling water bath for 20 minutes.
4. After sample is cool, add 4.0 mL of the ascorbic acid-potassium iodide solution, mix, and let stand for 20 minutes.
5. Accurately add 3.0 mL of 10% Aliquat 336 DIBK solution to each tube. Cap and shake for 5 minutes.
6. Centrifuge the samples 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.

Standardization of equipment

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

Table 19. Operating conditions for determination of the elements by ICP-AES

Nebulizer	Meinhard concentric glass, TR-30-C1
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, 5 sec each
Sample introduction rate	1.0 to 1.5 mL/min

Table 20. Suggested wavelength and lower limit of determination for 10 elements by ICP-AES

Element	ICP Wavelength (nm)	Lower limits of determination (μg/g)
Ag	328.0	0.045
As	193.7	0.600
Au	242.8	0.150
Bi	223.0	0.600
Cd	226.5	0.050
Cu	324.7	0.050
Mo	202.0	0.090
Pb	220.3	0.600
Sb	217.5	0.600
Zn	213.8	0.050

Assignment of uncertainty

Table 21 is a tabulation of data obtained in the original experimental phase with lower limits higher than indicated in previous wavelength table.

able 21. Tabulation of data for ten elements by ICP-AES and AA

lement	$\bar{X}$ ICP/DIBK	s	% RSD	$\bar{X}$ AA/MIBK	Element	$\bar{X}$ ICP/DIBK	s	% RSD	$\bar{X}$ AA/MIBK
GXR-1 (jasperoid)					GXR-2 (soil)				
Ag	31	0.50	1.6	32	Ag	17	0.19	1.1	18
As	440	5.3	1.2	468	As	15	0.47	3.1	16
Au	3.1	0.05	1.7	2.98	Au	N*(0.25)	--	---	0.022
Bi	1600	24	1.5	1640	Bi	N(1.0)	--	---	<1.0
Cd	2.6	0.05	2.1	2.89	Cd	3.6	0.05	1.3	3.85
Cu	1100	14	1.2	1250	Cu	74	0.74	1.0	71
Mo	19	0.23	1.2	20	Mo	0.95	0.02	2.5	1.1
Pb	720	10	1.4	780	Pb	650	8.5	1.3	712
Sb	96	1.3	1.4	105	Sb	38	0.46	1.2	39.6
Zn	770	20	2.6	714	Zn	500	5.5	1.1	518
GXR-5 (soil)					GXR-6 (soil)				
Ag	0.67	0.02	2.4	0.72	Ag	0.31	0.004	1.2	0.32
As	5.9	0.24	4.0	8.4	As	280	2.2	0.8	308
Au	N(0.25)	--	---	0.007	Au	N(0.25)	--	---	0.063
Bi	N(1.0)	--	---	<1.0	Bi	N(1.0)	--	---	<1.0
Cd	0.12	0.004	2.9	0.13	Cd	0.13	0.004	3.4	0.11
Cu	320	2.6	0.8	330	Cu	66	0.26	0.4	64
Mo	31	0.25	0.8	30	Mo	2.2	0.02	1.1	2.3
Pb	13	2.2	1.7	14	Pb	100	0.90	0.9	95
Sb	N(1.5)	--	---	<1.0	Sb	2.7	0.07	2.6	1.98
Zn	41	0.90	2.2	41.6	Zn	120	1.1	0.9	105

All results are in ppm, and ICP results are rounded to two significant figures.

*Not detected at values shown, ICP/DIBK results are a mean value of ten replicate digestions; AA/MIBK results are latest recommended values from O'Leary and Viets, 1986.

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Determination of water extractable boron in soil and stream-sediment samples by inductively coupled plasma-atomic emission spectroscopy

By K.C. Stewart

Code: E030 Accepted: -- --

Principle

Soil and stream-sediment samples are treated with boiling water using a modified procedure of Berger and Truog, 1939. The water-soluble boron is determined by emission at 2497Å after aspiration of the extract solution into an inductively coupled plasma-atomic emission spectrometer (ICP-AES).

Interferences

A potential spectral interference is caused by high iron in the extract solution due to the proximity of iron emission lines to the boron analyte line. The interference is corrected for by mathematical interference factors. See the ICP-AES--40 element analytical method for the treatment of interferences.

High content of organics or other colloid-forming material may cause variation in the aspiration rate of extract into the plasma, but most can be removed by filtering through a 0.45-micron filter.

Scope

A high concentration of boron in soil solution is toxic to plants (Eaton, 1935). This method should, therefore, be useful for evaluation of soils or stream sediments in environmental studies. Approximately 40 samples can be easily prepared in 1 day including labeling and weighing. Two hundred determinations can be made per day, so several preparations can be run at once. The determination limit is 400 ng/g in sample.

Apparatus

ICP-atomic emission spectrometer and ancillary equipment
50-mL polypropylene tubes with caps
Water bath

Reagents

Deionized water
Concentrated reagent grade nitric acid, 70% HNO_3
Nitric acid 5% (v/v) HNO_3: Add 50 mL concentrated nitric acid to 500 mL deionized water and dilute to 1 L.
Lutetium internal standard, 500 µg/ml, Lu as Lu_2O_3 in 5% (v/v) HCl
1,000 ppm boron standard (boric acid, Fisher Scientific reference solution)
Aqueous boron standards:

1 ppm	To a tared 100-mL plastic bottle, add 1 g of the 100 ppm boron standard. Add 1 g of the 500 ppm lutetium standard (see ICP-AES--40 element method). Bring to 100 g with 5% (v/v) nitric acid.

10 ppm	To a tared 100-mL plastic bottle add 10 g of the 100 ppm boron standard. Add 1 g of the 500 ppm lutetium standard. Bring to 100 g with 5% (v/v) nitric acid.
100 ppm	To a tared 100-mL plastic bottle, add 10 g of 1,000 ppm prepared ICP boron standard. Bring to 100 g with 5% (v/v) nitric acid.

USGS Standard Reference Water Sample standard: Add 1 g prepared, 500 ppm, lutetium standard to a tared 100-mL plastic bottle. Bring to 100 g with USGS Standard Reference Water Sample M86 (final concentration of Lu, 5 ppm).

Safety precautions

Caution must be exercised in working with boiling water baths to prevent burns, and in handling concentrated acids. Protective gloves, lab coat, and safety glasses should be worn and a fume hood used for the extraction procedure. See the MSDS for further information concerning first-aid treatment and disposal procedures for chemical products used in this method.

Procedure

A. Sample preparation

1. Select and label a sufficient number of large polypropylene tubes, with caps, for extraction of samples, duplicates, soil standards, and blanks.
2. Select and label an equivalent number of polypropylene ICP tubes. In addition, label tubes for aqueous boron standards and a USGS Standard Reference Water sample (two tubes per standard).
3. Weigh 5 g of air-dried sample into a large tared tube.
4. Add 10 g deionized water and cap. Shake to wet the entire sample.
5. Immerse tube in boiling water bath for 1 hour, remove and allow to cool just enough to handle.
6. Centrifuge for 15 minutes at 1,500 rpm.
7. Add two drops concentrated nitric acid and 30 μL prepared lutetium standard (500 ppm) to labeled ICP tubes.
8. With a pipet precalibrated to deliver 3 g of deionized water, transfer 3 mL of the supernatant from the centrifuged sample to the ICP tubes. Cap and mix. (The final concentration of lutetium is 5 ppm.)
9. To the standard tubes add either an aqueous boron standard (1 or 10 ppm) or USGS Standard Reference Water sample M86. These are reference samples only and are not used to calibrate the instrument.

B. Instrument calibration

Calibrating solutions are a reagent blank and multi-element standards including boron at 10 ppm. For calibration, see ICP-AES--40 element treatment of calibration solutions.

C. Treatment of interelement interferences

See ICP-AES--40 element, treatment of interelement interferences.

D. Procedure for analysis

See ICP-AES--40 element, treatment of sample analysis.

E. Treatment of results.

See ICP-AES--40 element, treatment of results. These results are multiplied by two to account for the additional dilution from extraction.

Assignment of uncertainty

It is difficult to assign an uncertainty for this method since there are no standard reference materials available for partial extractions. The closest is to report values determined for an in-house reference soil from the San Joaquin Valley, SJS-1 which has been extracted and analyzed with all samples for the past 3 years. Based on 100 separate preparations, the extractable boron from this soil is 5.2 ± 0.4 ppm, showing a relative standard deviation of 8%. USGS Standard Reference Water sample M86 gives a value of 218 ± 8 ppm; the concentration reported by Water Resources Division is 221 ± 62 ppm.

Calculation

The sample dilution factor of 2 will be automatically incorporated into the calculation by the ICP-AES, provided the sample preparer informs the ICP instrument operator.

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Direct-current arc emission spectrographic method for the semiquantitative analysis of rock, stream-sediment, soil, and heavy-mineral-concentrate samples

By B.M. Adrian, B.F. Arbogast, D.E. Detra, and R.E. Mays

Code: E040, E050 Accepted: Provisional

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 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 the analytical line by nearby spectral lines is normally checked by reference to wavelength tables (Massachusetts Institute of Technology, 1969) or an alternate analytical line. Most matrix effects due to large variations in chemical composition between samples and standards are offset by the addition of graphite to both. Silica, as quartz, is added to the samples only if the samples are silica poor, e.g., heavy-mineral concentrates.

Scope

Irrespective of sample matrix, the semiquantitative spectrographic method provides an excellent overview of the elements, and the concentration of the elements, in the sample (table 22). The method is readily adaptable for use in mobile field laboratories where it can quickly provide analytical data upon which field investigators can base decisions for further geochemical sampling. The method has an overall production of 40 samples per person-day.

Apparatus and materials

dc-arc emission spectrograph
Graphite electrodes (preformed capped 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 should be adequately 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. Equipment should be serviced only by trained, competent, electrical technicians.

Procedure

Weigh 10 mg of the prepared sample, add 20 mg of pure graphite, and mix in an aluminum weighing pan with a disposable wooden toothpick. For heavy-mineral-concentrate samples, weigh 5 mg of sample and add 25 mg of a 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 hole in the 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, initiate a current of 3 amperes with the arc gap set at 4 to 6 mm, after a few seconds increase power to 8 to 9 amperes, and burn the sample to completion at 12 to 15 amperes. Maintain the arc gap at 4 to 6 mm throughout the entire burn time of 2 minutes and 15 seconds. Process the emulsion with developer for 3 minutes, fix for 3 minutes, rinse in cold water and Photo-Flo, and dry. The same procedure is used to prepare standard emulsions 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 is between 2200 and 4800 Å in the second order.

The quality of semiquantitative spectrographic data is verified by arcing a reference standard and recording its spectrum on each emulsion prior to recording sample spectra. The concentration of all measured elements in this "control sample" must fall within defined tolerance limits before the analyses from other spectra on the same emulsion are accepted. Standard films are prepared once a year or whenever there is a change in standard operating conditions.

The principal standards used for the analysis of most geologic materials have been designated F-3 and F-4. The F-3 standards (table 23) contain concentrations of 23 trace elements in a stock matrix that approximates the matrix of average siliceous rocks. The F-4 standards (table 24) 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 25). For the semiquantitative procedure, these numbers are rounded to 50, 20, 10, and 5. 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 grams) 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 25).

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

Assignment of uncertainty

Disallowing results obtained near the detection levels, 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 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).

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Table 22.--Elements and limits of determination for the direct-current arc spectrographic analysis of rocks, stream sediments, and soils based on a 10-mg sample

[The spectrographic limits of determination 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 determination limit	Upper determination limit
	Percent	
Calcium (Ca)	.05	20
Iron (Fe)	0.05	20
Magnesium (Mg)	.02	10
Sodium (Na)	0.2	5
Phosphorus (P)	0.2	10
Titanium (Ti)	.002	1
	Parts per million	
Silver (Ag)	0.5	5,000
Arsenic (As)	200	10,000
Gold (Au)	10	500
Boron (B)	10	2,000
Barium (Ba)	20	5,000
Beryllium (Be)	1	1,000
Bismuth (Bi)	10	1,000
Cadmium (Cd)	20	500
Cobalt (Co)	10	2,000
Chromium (Cr)	10	5,000
Copper (Cu)	5	20,000
Gallium (Ga)	5	500
Germanium (Ge)	10	100
Lanthanum (La)	50	1,000
Manganese (Mn)	10	5,000
Molybdenum (Mo)	5	2,000
Niobium (Nb)	20	2,000
Nickel (Ni)	5	5,000
Lead (Pb)	10	20,000
Antimony (Sb)	100	10,000
Scandium (Sc)	5	100
Tin (Sn)	10	1,000
Strontium (Sr)	100	5,000
Thorium (Th)	100	2,000
Vanadium (V)	10	10,000
Tungsten (W)	20	10,000
Yttrium (Y)	10	2,000
Zinc (Zn)	200	10,000
Zirconium (Zr)	10	1,000
Palladium (Pd)*	5	1,000
Platinum (Pt)*	20	1,000

*Determined in heavy-mineral-concentrate samples only. Limits are for heavy-mineral-concentrate samples.

Table 23. Concentrations (in parts per million) of elements in F-3 standards

Ag	B	Ba	Be	Bi	Cd	Co	Cr	Cu	La	Mn	Mo	Ni	Rb	Sc	Sn	Sr	Ti	V	Y	Zn	Zr	P
																						Percent
										10							.002					
5		20								20							.005					
1		50						5		50		5					.01	10			10	
2		100				5	10	10	20	100	5	10	10			100	.02	20		200	20	
5	10	20	5		20	10	20	20	50	200	10	20	20	5		200	.05	50	10	500	50	
10	20	500	10	10	50	20	50	100	500	20	50	50	500	10	10	500	.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	.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	.5	500	100	5,000	500	
100	200	5,000	100	100	500	200	500	500	1,000	5,000	200	500	500	100	100	5,000	1	1,000	200	10,000	1,000	.2
200	500		200	200		500	1,000	1,000			500	1,000	1,000		200			2,000	500			.5
500	1,000		500	500		1,000	2,000	2,000			1,000	2,000	2,000		500			5,000	1,000			1
1,000	2,000		1,000	1,000		2,000	5,000	5,000			2,000	5,000	5,000		1,000			10,000	2,000			2
2,000								10,000					10,000									5
5,000								20,000					20,000									10

Table 24. Concentrations (in parts per million) of elements in F-4 standards

Ga	Ge	As	Au	Ca	Fe	Mg	Nb	Sb	W	Th	Nd	Pd	Pt
				20		10					5		
				10		5					2		
				5		2					1		
				2	.05	1							
				1	.1	.5			50		.5	2	
5	10			.5	.2	.2	20	100	100		.2	5	
10	20	200	10	.2	.5	.1	50	200	200			10	10
20	50	500	20	.1	1	.05	100	500	500	100		20	20
50	100	1,000	50	.05	2	.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 25. Dilution chart--three-step standards

Dilution no.	Mixture	Resulting standard (ppm)
1 (base mixture)...	_X_g of metal oxide +_Y_g of matrix =4 g	100
2...................	1.857 g of 100 ppm +2.143 g matrix =4 g	46.4
3...................	1.857 g of 46.4 ppm +2.143 g matrix =4 g	21.5
4...................	1.857 g of 21.5 ppm +2.143 g matrix =4 g	10
5...................	1.857 g of 10 ppm +2.143 g matrix =4 g	4.64

Flame photometric determination of K_2O and Na_2O in rocks and mineral separates

By Terry Fries, Joe Christie, and Sarah Pribble

Code: E060, E070 Accepted: Provisional

Principle

Sodium and potassium in rocks and mineral separates are determined by the method of flame photometry and are reported as their oxides (Cremer and others, 1984). The samples are fused with lithium metaborate in graphite crucibles and the fusion beads dissolved in 4% 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 presence of Rb in high concentration when 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 and Na_2O concentrations between .025% and 20% in two ranges. These ranges are from .025% to 2.9% and greater than 2.9%. 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: Dionized water with a resistivity of greater than 18 megohms/cm is used throughout this method. A Millipore Milli-Q with a Milli-R04 attachment water purification system is used to prepare all water used in this method.

Dehydrated human blood serum.

Nitric acid, HNO_3 4% (v/v): Prepare by adding 4 parts 70-71% (concentrated) nitric acid (Baker Instra-Analyzed Grade) to 96 parts water.

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.

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 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 -3.0% 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 accompanying the chosen K_2O standards. Two quality control samples are included in each run.
2. In a tared, size-00 black porcelain crucible weigh 100 ± 3 mg sample. Add 700 ± 5 mg of pure 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 1000°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 1000°C before being put into use.
4. Fuse the contents of the first six crucibles at 950°C for 15 minutes.
5. During the fusion, equip six dry 250-mL polypropylene beakers with dry 1 5/8-inch Kel-F magnetic stirring bars. Label six covers. Add 100 mL of 4% (v/v) HNO_3; begin stirring as the time approaches to remove the crucibles from the muffle furnace.
6. At the end of 15 minutes, 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 minutes 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% 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 distilled H_2O, 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 minutes for warm-up. The warm-up should take place during fusion and dilution steps.
12. Continually aspirate H_2O during warm-up. For 5 minutes during the warm-up, aspirate a dilute solution of reconstituted normal human blood serum (1 drop per 25 mL H_2O). 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 sec/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 seconds.

    All solutions must be read in the same manner.

    Typical aspiration order:

    a. duplicate standards
    b. 6 unknowns
    c. duplicate standards
    d. repeat the 6 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.

Concentration = ((slope x intensity) + intercept) x unknown wt./100

Assignment of uncertainty

Three whole rock samples and six mineral separates are used in the in-house program with two of the samples submitted as unknowns in each job. Results for in-house reference samples from 1980 to 1985, are presented in the following table.

Table 26. Summary of results from 1980 to 1985 for the QA determination of potassium and sodium

Sample	Scale	Nominal % K_2O	$\bar{X}$ (% K_2O)	n	s	% RSD	$\bar{X}$ (% Na_2O)	n	s	% RSD
A	Low	0.052	0.051	38	0.007	14	7.14	6	0.03	0.37
B		0.187	0.188	14	0.008	4.2	2.13	12	0.02	1.08
C		0.901	0.903	54	0.016	1.8	1.03	7	0.01	1.36
D		1.504	1.504	75	0.016	1.1	3.19	11	0.02	0.66
E		2.226	2.237	54	0.024	1.1	2.42	13	0.03	1.09
F	High	2.90	2.95	35	0.03	1.2	4.20	7	0.03	0.71
G		5.50	5.53	37	0.07	1.2	2.77	7	0.02	0.77
H		10.59	10.63	27	0.04	0.4	0.70	5	0.01	1.37
I		13.42	13.62	41	0.07	0.5	1.97	6	0.02	1.16

Bibliography

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Jackson, L.L., Brown, F.W., and Neil, S.T., 1987, Major and minor elements requiring individual determination, classical whole rock analysis, and rapid rock analysis, in Baedecker, P.A., ed., Methods for Geochemical Analysis: U.S. Geological Survey Bulletin 1770, p. G1-G23.

Determination of uranium in geologic materials by UV-fluorescence

By Delmont M. Hopkins

Code: F080 Accepted: Provisional

Principle

Uranium is determined in rock, soil, and stream-sediment samples by ultraviolet fluorescence (Centanni and others, 1956). The sample is subjected to a hot nitric acid digestion. Uranium is taken up in dilute nitric acid, and a salting agent (aluminum nitrate) is added that also complexes fluoride, phosphate, and sulfate ions that otherwise seriously hinder the extraction of uranium. The uranyl nitrate is extracted by ethyl acetate, which separates uranium from its quencher elements. A carbonate fluoride phosphor is obtained by fusing the extracted uranyl nitrate with sodium and potassium carbonate and sodium fluoride. The phosphor is placed in an ultraviolet fluorimeter and estimated for uranium content.

Interferences

The aluminum nitrate solution, a salting out agent, prevents the interference from anions. Uranium is separated from quenchers, elements that reduce the fluorescence, by extraction into ethyl acetate.

Scope

The hot nitric acid dissolution technique is suitable for non-silicate bound uranium in rocks, stream sediments, and soils. The method has a working range of 0.05 to 100 ppm in the sample before re-analysis is required using a smaller aliquot of ethyl acetate. Approximately 40 samples can be analyzed per day.

Apparatus

Aluminum heating block drilled to accommodate 25x150-mm disposable test tubes
Platinum crucibles, 10x35-mm inside diameter
Ultraviolet fluorimeter, Model Jarrell-Ash #7

Reagents

All chemicals should be of reagent grade and all water should be metal free.

Aluminum nitrate solution: Dissolve 1,000 g aluminum nitrate, 9-hydrate ($Al(NO_3)_3 \cdot 9H_2O$) in 500 mL of H_2O by heating.
Ethyl acetate, $C_4H_8O_2$
Nitric acid, HNO_3, concentrated
Nitic acid, 25% (v/v): Dilute 250 mL concentrated nitric acid to 1 L with H_2O.
Nitric acid, 15% (v/v): Dilute 150 mL concentrated nitric acid to 1 L with H_2O.

Sodium carbonate-potassium carbonate-sodium fluoride flux: Oven dry anhydrous sodium carbonate (Na_2CO_3), potassium carbonate (K_2CO_3), and sodium fluoride (NaF) at 105°C overnight. Separately grind sodium carbonate and potassium carbonate to pass an 80-mesh sieve and prepare a 5:5:1 mixture, by weight. Store in a dark container in a cool, dry area.

Stock uranium solution, 1,000 µg/mL: Dissolve exactly 0.211 g uranyl nitrate ($UO_2(NO_3)_2 \cdot 6H_2O$) in 100 mL of 25% nitric acid. Prepare 100, 10, and 1 µg/mL standard uranium solutions by successive 10-fold dilutions of 1,000 µg/mL stock uranium solution with 25% nitric acid.

Standard uranium phosphor: Pipette 0.2 mL of the 1-µg/mL standard uranium solution into a 25x150-mm disposable test tube containing 6 mL of 15% nitric acid and 10 mL aluminum nitrate and proceed from step 5 of procedure. The standard phosphor contains 0.1 µg uranium. A blank phosphor is prepared in the same manner, but with no uranium added.

Safety precautions

Normal laboratory safety procedures should be closely observed, including the use of protective eyeware, laboratory coat, and gloves. Also, all chemical digestion and fusion activities will be performed in a chemical hood. See the MSDS for precautions, effects of overexposure, first-aid treatment, and disposal procedures for reagents used in this method.

Procedure

1. Weigh 0.5 g sample into a 25x150-mm disposable test tube.
2. Add three boiling chips and 5 mL concentrated nitric acid.
3. Nestle each tube into a heating block and boil moderately to dryness.
4. Add 6 mL of 15% (v/v) nitric acid and boil for 5 minutes in heating block. Remove tube and add 10 mL of the aluminum nitrate solution.
5. After mixture has cooled, add 10 mL of ethyl acetate, cap, shake for 2 minutes, and then centrifuge to obtain a clean layer separation.
6. Pipette the 5-mL aliquot of organic layer and transfer to a clean, dry platinum crucible.
7. Ignite the ethyl acetate to remove the organic solvent.
8. Place the crucible over a Fisher burner to red heat for 10-20 seconds.
9. After the platinum crucible has cooled, add 2.0 g sodium carbonate-potassium carbonate-sodium fluoride flux and place the crucible on a quartz-covered triangle that is mounted over a Fisher burner. The height should be adjusted so that most of the flux melts within the first 45-60 seconds. Heat over burner for a total of 3 minutes. If an automatic fusion rotary burner is available, consult the operation manual for set-up procedure that best approximates these conditions.
10. Cool the crucible, remove the phosphor wafer, and measure the fluorescence with an ultraviolet fluorimeter. The estimation of uranium content is made with an ultraviolet fluorimeter using the manufacturer's operating procedure. The instrument is standardized by setting the 0.1-µg standard phosphor to read 50 divisions. Readings are taken for the blank phosphor and the sample.
11. Clean the platinum crucibles in hot 50% (v/v) hydrochloric acid.

Calculation

The amount of uranium present in the standard phosphor wafer used for fluorimeter calibration is 0.1 µg and the sample weight represented in the wafers routinely determined for uranium is 0.25 g (see steps 1, 6, and 10 in the procedure).

Uranium concentration in the sample is calculated using the following formula:

$$\frac{0.1\ \mu g}{50\text{-blank reading}} \times \frac{\text{sample reading-blank reading}}{0.25\ g} =$$

$$\text{Uranium concentration (ppm)} = \frac{0.4 \times (\text{sample reading-blank reading})}{50\text{-blank reading}}$$

Assignment of uncertainty

The following is a tabulation of statistical data obtained by analyzing the six GXR (geochemical exploration reference) samples (Allcott and Lakin, 1975), in replicas of five, by the described procedure.

Table 27. Uranium content of GXR samples by UV-fluorescence

Reference sample (description)	$\bar{X}$ (ppm)	s	% RSD	Literature value[1] (ppm)
GXR1 (jasperoid)	24.2	1.7	7	24±6
GXR2 (soil)	1.5	0.21	14	1.98±1.25
GXR3 (Fe-Mn mineral deposit)	2.0	0.28	14	2.26±0.87
GXR4 (coppermill head)	4.3	0.54	13	4.6±1.1
GXR5 (soil)	1.6	0.16	10	1.7±0.7
GXR6 (soil)	0.75	0.07	9	1.03±0.6

[1] Gladney, 1979

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Determination of total carbon in geologic materials by combustion

By Kenneth Joe Curry

Code: N010 Accepted: Provisional

Principle

Total carbon in geologic materials is determined using an automated carbon analyzer (Jackson and others, 1987). The sample (0.25-1 g) is heated to 1370°C in a resistance furnace in a regulated stream of oxygen. Total carbon is determined as the carbon dioxide evolved during the combustion with a detection limit of .05%. The CO_2 is measured by its absorption of infrared radiation.

Interferences

The determination of total carbon has potential interferences, mainly fluorine and molybdenum. Samples suspected to contain greater than 0.2 percent of these elements are analyzed using a reduced sample size. Also, a halogen trap must be installed in the flow system when higher concentrations of fluorine are present in the samples. A possible problem may be encountered due to abnormally rapid combustion of samples containing high concentrations of organic matter. This problem can usually be corrected by mixing a retardant (COM-AID) with the sample prior to combustion. The system must be "conditioned" prior to use on samples to avoid erroneous initial results. The conditioning can be accomplished by running exhausted (repeatedly heated) $CaCO_3$ samples. Samples with low boiling points may require covering with Al_2O_3 to assure complete carbon recovery.

Scope

The method is applicable to the analysis for total carbon in rocks, soils, and sediments, plants, mosses, and lichens. The range of concentration covered is from 0.05% to about 30% for normal sample sizes. Approximately 50 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, $Mg(ClO_4)_2$
Conditioners, exhausted $CaCO_3$ samples
Standards:
  Shale, SCo-1
  Soil, SO-4
  Dolomite, NBS88a
  Oil Shale, SGR-1

Safety precautions

The major potential danger in this procedure is thermal burns 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. Toxic gases may be produced during the combustion of samples, therefore, the instrument should be used under a working exhaust hood.

Procedure

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 to stop the oxygen flow.

B. 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 systems 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.

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 combusion boat (crucible) on the balance and then push the TARE key.
   5. The message center will display:
      PUT ONE GRAM IN CRUC A00000001 WT=0.000
   6. Place a 1-gram standard weight in the combustion boat.
   7. The message center will display:
      AUTO-CALIBRATION A00000001 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-gram standard weight from the balance.

D. Conditioning the instrument for analyses
   1. It is a standard operating procedure to change out the right side anhydrone tube daily. If this is not done, visible moisture or discolorization appears one-third of the way down the tube (usually after about 75 analysis).

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 give you an idea as to what range of concentration of carbon 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 one 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 gram
   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 gram 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 combution boat into the furance 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. <u>Calibration procedure</u>

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.

Calibration standards used for the CR-12 carbon analyzer

Calibration channel	Range % carbon	Sample size (g)	Calibration standard (description)	% Carbon
1	0.01-1	1.0	LECO (soil)	0.98
2	1-5	0.75	SO-4 (soil)	4.43
3	5-12	0.50	NBS88a (dolomite)	12.72
4	>12	0.25	SGR-1 (oil shale)	27.5

2. 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.
3. Select the standard for the range of percent carbon the samples fall in.
4. Place a combustion boat on the balance pan. The balance will automatically tare.
5. Weigh out the appropriate weight for the standard used (see table 28).
6. When the weight is stable, press the ENTER key.
7. To determine the percent carbon for the standards, follow the same sequence set-forth under **Conditioning the instrument for analysis,** step 11 through 19.

   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 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 set-forth under **Conditioning the instrument for analysis**, steps 8 through 19.

Calculation

Calculations are performed by the instrument's microprocessor, and the percent carbon is reported for each sample.

Assignment of uncertainty

The relative standard deviation is generally ±5% or better for samples with >0.1% C or an absolute standard deviation of ±0.05% C, whichever is greater. A triplicate analysis of 21 calcareous and siliceous marine shales gave relative standard deviations of less than 2% in the range 3% to 10% carbon. For samples with less than 0.1%, the absolute standard deviation is generally better than ±0.05% C. Table 28 lists reference values determined for total carbon by this method.

Table 28. Total carbon content in selected reference materials by combustion

Reference sample (description)	$\bar{X}$	n	s	% RSD	Literature value (%)
MAG-1 (marine mud)	2.28%	12	.009%	.39	2.15±.40[a]
GXR-2 (soil)	2.84%	12	.011%	.39	2.61±.24[b]

[a] Gladney and Roelandts, 1988.

[b] Gladney and Roelandts, 1990.

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Determination of chloride in geologic materials by ion-selective electrode following $KMNO_4$-H_2SO_4-HF dissolution

By Phillip Aruscavage

Code: P010 Accepted: Provisional

Principle

Chlorine in geologic materials is determined as chloride by the ion-selective electrode 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 detection limit for chloride in geologic materials is 0.01% concentration. Results above 0.01% are reported in no more than three significant figures to the nearest 0.01%. 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
An electronic toploading analytical balance is convenient for all weighings
Labware 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% Cl, which is not true of all analytical grades of KOH. The use of labware should be minimized and the few reusable pieces of plastic labware scrupulously cleaned after each use.

Oxidizing solution: Weigh 2.6 g of $KMnO_4$ into a 100-mL sterilized plastic or glass container (assuming the determination of 33 samples plus 7 standards or less). Add 50 mL of 15% sulfuric acid (H_2SO_4). (Previously mix and cool the sulfuric acid. If the concentrated sulfuric acid 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.) Swirl to dissolve the $KMnO_4$. To 40 mL of $KMnO_4$ solution, add 160 mL of concentrated HF from a plastic graduated cylinder and mix.

Reducing solution: Weigh 22.6 g of KOH into a 200-mL plastic or glass container. Add 140 mL of distilled water and swirl to dissolve. Let stand for 10 minutes and add 1.12 g of anhydrous Na_2SO_3. Transfer into a capped plastic bottle and shake well. Make up solutions fresh each day.

Safety precautions

The usual precautions, i.e., use of chemical hood, protective clothing, safety glasses, and gloves, should be observed when handling strong acids, plus added caution in handling the HF solution. See the MSDS for further information. When pipetting from the oxidizing solution is not in progress, the plastic container should be covered and care taken not to breathe the fumes.

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. Prepare the oxidizing and reducing solutions.
3. 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.
4. Pipette 2.5 mL of 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.
5. Pipette 3.0 mL of oxidizing solution into the outer compartment of each sample 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 excessie 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 osxillating shaker platform.

6. Repeat the process in #5 until all of the solid samples have been mixed with oxidizing solution. One or two cells should be used as reagent blanks.
7. Add the appropriate increments of standard (100 ppm or 1,000 ppm stock solution) to 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^-. 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 #5.
8. Allow the samples to mix on the oscillating platform overnight for a total of 16 to 17 hours. By implication this means that the above procedures are initiated in late afternoon. Abtou 2 to 3 hours are required for 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.
11. Remove the blank cell, unscrew its lid, and slightly immerse the previously rinsed (with Millipore water) and dried (gently wiped with a Kimwipe tissue) 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 ½ hour, but not much 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 to 10 minutes, before recording the value.
13. Repeat the process in #12 for each of the sample cells.

Calibration

For each day's set of determinations, a suite of seven synthetic standard solutions are prepared and carried through the same procedure as the samples. A calibration curve is derived from a semi-log plot of the mV readings versus the Cl-concentration values of the standards in ppm. The concentrations of the unknown samples are read from this concentration plot. 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.

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%. This value represents the percent of chloride in the rock, which is then rounded off to the nearest 0.01%. 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

An extensive examination of the precision of determination of chloride in 41 international geochemical reference standards demonstrated that for rocks with a chloride concentration greater than 200 ppm a mean precision of 2.5% could be obtained (Elsheimer, 1987). For rocks with a chloride content of 50 to 200 ppm a mean precision of 4% was obtained, and for those with a chloride content of from 20 to 50 ppm a mean precision of 13% was achieved.

The degree of accuracy obtainable is illustrated in the work of Elsheimer, 1987. Over a 1-month period in 1990, the mean and standard deviation for twelve relicate analyses of an andesite, AGV-1, were determined to be 0.014±0.003. The recommended value for AGV-1 is 0.019% Cl (Govindaraju, 1989).

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Determination of fluoride in silicates by ion-selective electrode following $LiBO_2$ fusion and HNO_3 dissolution

By Sarah Pribble

Code: P020 Accepted: Provisional

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; the potential is again checked; and the concentration of fluoride in the sample is computed using the potential difference and the Nernst equation.

Interferences

1,2-diaminocyclohexane-NNN'N'-tetracetic acid (DCTA) buffers the solution to pH 5.5. At a pH below 5, hydrogen complexes fluoride as the undissociated acid HF and the ion HF_2^-. At a pH greater than 7, hydroxide ion interferes when the level of hydroxide is greater than 1/10 the level of fluoride ion present. DCTA also controls Al and Fe interference.

Scope

Fluoride can be determined in silicate rocks and minerals with a lower limit of determination of 100 ppm and an upper limit of 2.7% without modification of this procedure. If a sample is suspected of having a fluoride concentration greater than 2.7%, 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 lithium metaborate.

Nitric acid, HNO_3, 4% (v/v): Prepare HNO_3 by adding 4 parts 70.71% nitric acid (Baker Instra-Analyzed Grade) to 96 parts distilled 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, dissolve in H_2O and dilute to 500 mL. Transfer to a polyethylene bottle for storage (1 mL = 1000 µg F).

Complexing buffer solution: Add 18.2 g of DCTA (1,2-diaminocyclohexane-NNN'N'-tetracetic acid) (available from Mallinckrodt), also known as DCYTA (1,2-cyclohexylenedinitrilo-tetracetic acid) (available from Eastman) to 1.5 L of H_2O and then 40% w/v NaOH solution (40 g NaOH pellets/100 mL solution) dropwise until the DCTA dissolves. Add 300 g sodium citrate ($C_6H_5Na_3O_7$) dihydrate and 60 g NaCl, adjust the pH to 6.85 with HCl and dilute to 2 L with H_2O. 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 MSDS for further information concerning first-aid treatment and disposal procedures used in this method.

Procedure

1. Mix 200 mg sample with 1200 mg $LiBO_2$. Transfer the mixture to a graphite crucible and fuse in a muffle furnace at 900°C for 10 minutes.
2. While the sample is fusing, add to an 8-oz (220 mL) polypropylene container a magnetic stirring bar and 100 mL of 4% (v/v) HNO_3 with the automatic pipet.
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 of buffer from the automatic pipet. Stir well, cover, and set aside.
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 of 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 minutes), 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 minutes.
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 minutes. This procedure should lead to a ΔE of -15 to 30 mV.

Calculation

Calculate the exact concentration of the initial solution using the following form of the Nernst equation:

$$C = \frac{C^*[(Vs/(Vx + Vs)]}{(\text{antilog } \Delta E/S)-[Vx/(Vx + Vs)]}$$

C = Sample concentration
C* = Concentration of addition before adding to sample
Vx = Sample volume
Vs = Volume of addition
ΔF = Potential difference between initial and final millivolt values with addition of standard
S = Millivolt span of electrode for decade of interest; i.e., the slope.
The units of C are µ/mL
therefore:

$$\%F = \frac{[\mu g/mL \text{ (i.e. C)}] \times (100 \text{ mL}) \times (100\%)}{(1000 \text{ } \mu g/g) \times (\text{wt. in mg})}$$

Report the values to two decimal places. A computer program is available for the above calculations on both the Tektronix 4051 and the HP-97.

Assignment of uncertainty

Table 29 shows the amount of fluoride (±10%) present in USGS rock standards, one of which is included with each group of samples for quality control purposes.

Table 29. Fluoride content of USGS rock standards by ion-selective electrode, $LiBO_2$ fusion

Reference sample (description)	$\bar{X}$ (ppm)	n	s	% RSD	Literature value[1] (ppm)
GSP-1 (granodiorite)	3,240	23	399	11.0	3,630
STM-1 (syenite)	779	27	72	7.9	910
AGV-1 (andesite)	362	17	57	13.4	425
RGM-1 (rhyolite)	305	27	33	9.7	342

[1] Govindaraju, 1989.

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Orion Instruction Manual fluoride electrodes model 960900.

Determination of fluoride in rock, soil, and stream-sediment samples by ion-selective electrode following Na_2CO_3-K_2CO_3-KNO_3 fusion and dissolution with citric acid

By Richard M. O'Leary and Delmont M. Hopkins

Code: P030 Accepted: Provisional

Principle

Fluorine in rock, stream-sediment, and soil samples is determined as fluoride by the ion-selective electrode potentiometric method (Hopkins, 1977; O'Leary and Meier, 1986). Samples are fused with a sodium carbonate-potassium carbonate-potassium nitrate flux and the fused sample is dissolved with citric acid. Sodium citrate buffer, which also serves as an ionic strength adjuster, is then added to this solution prior to determining the fluorine concentration by standard-addition technique.

Interferences

Fluoride ions form complexes with Al^{3+}, Fe^{3+}, Si^{4+}, and Be^{2+} ions. Citrate ions in a sodium citrate buffer solution are added to the analyte solution to prevent the formation of fluoride complexes with these metal ions. Addition of the buffer adjusts the pH between five and six to dissociate any HF formed if the pH is less than five and to prevent hydroxide ion interference at pH values above seven. Citric acid dissolution of the fused sample provides additional sodium, potassium, and citrate ions for ionic strength.

Scope

Fluorine can be analyzed in rock, stream-sediment, and soil samples with a lower limit of determination of 100 ppm. If the sample is estimated to contain 100,000 ppm or more fluorine, the solution containing citric acid and fused sample should be diluted to 100 mL with water. A suitable aliquot should be added to 25 mL of sodium citrate buffer, diluted to 100 mL, and fluoride then estimated. Approximately 50 samples can be analyzed per person-day.

Apparatus

Baker, 100-mL, graduated polypropylene
Magnetic stirrer (with stirring mechanism extended from motor to prevent heating of sample solution)
Orion reference electrode; model 90-01-00
Orion selective ion electrode; model 94-09A
Orion selective ion meter; model 407
Pyropot (Pyroco Products, Margat, Queensland, Australia 4019): Heating device accommodating 10 test tubes provides a controlled heat source for the fusion
Stirring bar, Teflon-coated magnetic
Test tube, disposable, 25x150 mm

Reagents

All reagents should be of reagent grade and all water should be metal free.

Citric acid, 1M: Dissolve 210.15 g citric acid monohydrate ($C_6H_8O_7 \cdot H_2O$) in 1 L H_2O.

Hydrochloric acid, 50% (v/v): Add 500 mL of concentrated hydrochloric acid (HCl) to 500 mL H_2O.

Sodium carbonate-potassium carbonate-potassium nitrate flux: Separately grind anhydrous sodium carbonate (Na_2CO_3), anhydrous potassium carbonate (K_2CO_3) (previously oven dried at 100°C overnight), and potassium nitrate (KNO_3) to pass an 80-mesh sieve, and prepare a 4:4:2 mixture, by weight.

Sodium citrate buffer, 1M: Dissolve 294 g sodium citrate dihydrate ($Na_3C_6H_5O_7 \cdot 2H_2O$) in 800 mL water and adjust the pH to 6.0 with 50% (v/v) HCl. Dilute this solution to 1 L.

Stock fluoride solution, 10,000 µg/mL: Dissolve 2.21 g sodium fluoride (previously dried at 110°C overnight) in 100 mL water.

Standard fluoride solution, 1,000 µg/mL: Dilute 10 mL of 10,000 µg/mL stock fluoride solution to 100 mL with water (prepare monthly).

Standard fluoride solution, 100 µg/mL: Dilute 10 mL of 1,000 µg/mL standard fluoride solution to 100 mL with water (prepare monthly).

Standard fluoride solution, 10 µg/mL: Dilute 10 mL of 100 µg/mL standard fluoride solution to 100 mL with water (prepare monthly). Store all fluoride standards in polyethylene bottles.

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 MSDS for further information concerning first-aid treatment and disposal procedures for chemical products used in this method.

Procedure

1. Weigh 0.05 g sample and mix with 2 g sodium carbonate-potassium carbonate-potassium nitrate flux in a disposable, 25x150-mm test tube.
2. Fuse at 700°C for 10 minutes in a Pyropot. Remove fused sample and roll it on heat-resistant surface.
3. Allow test tube to cool and add 15 mL of 1M citric acid.
4. Allow the mixture to digest until carbon dioxide evolution is no longer detected (15 minutes).
5. Transfer to a 100-mL polypropylene beaker containing 25 mL sodium citrate buffer.
6. Rinse the test tube with water, and add the rinse to the beaker.
7. Dilute the sample solution to 100 mL with water and add a Teflon-coated magnetic stirring bar.

Standardization of Instrument

1. Add 1 mL of 1,000- or 100-µg/mL sodium fluoride working standard to a 100-mL polypropylene beaker containing 15 mL of 1M citric acid and 2 g of the sodium carbonate-potassium carbonate-potassium nitrate flux.
2. Then add 25 mL of 1M sodium citrate buffer solution, dilute to 100 mL with water, and add a Teflon-coated magnetic stirring bar.

3. Place the electrodes of the ion meter in the solution while it is gently stirred on a magnetic stirrer.
4. Turn the calibration control for a center-scale reading, and then add 1 mL of the 1,000- or 100-µg/mL sodium fluoride working standard that was used initially.
5. Adjust the temperature control to give a reading of one on the known-addition scale.
6. Move the slope control until the sample temperature is read on the temperature scale. The percent of theoretical slope can be read on the slope scale.
7. The instrument is now calibrated and ready to determine fluoride content.

Estimation

1. Using a calibrated ion meter for estimation, rinse electrodes with water, blot them with absorbent tissue, and place them in the sample solution, which is gently being stirred.
2. Turn the meter calibration control knob until the needle points to midscale.
3. If the sample is expected to contain low concentration of fluorine, add 1 mL of 100 µg/mL F^- solution. If the sample is expected to contain greater than 10 µg/mL fluorine, then add 1 mL of 1,000 µg/mL F^- solution.
4. Allow approximately 5 minutes before taking a reading if the standard addition totals less than 100 µg fluorine. Allow 3 minutes for 100 to 500µg additions and 1 to 3 minutes for higher additions.
5. Reagent blanks are run with the samples to determine an average value of fluoride contamination. The average blank value is subtracted from the sample readings.
6. Recalibrate the instrument after every 20 samples.

Calculation

Calculate the fluoride concentration in the sample using the following formula:

$$\text{fluorine ppm} = \frac{(\mu\text{g/mL fluoride in standard})(\text{mL standard added})(\text{meter reading})}{\text{g of sample}}$$

Assignment of uncertainty

The following (table 30) is a tabulation of statistical data obtained by analyzing the six GXR (geochemical exploration reference) samples (Allcott and Lakin, 1975), in replicates of five, by the described procedure.

Table 30. Fluoride content of GXR samples by ion-selective electrode, Na_2CO_3-K_2CO_3-KNO_3 fusion

Reference sample (description)	$\bar{X}$ (ppm)	s	% RSD	Literature value[1] (ppm)
GXR1 (jasperoid)	1,053	19	2	1,260
GSR2 (soil)	257	14	5	450
GXR3 (Fe-Mn mineral deposit)	93,370	2,539	3	8.62%
GXR4 (copper mill head)	2,333	23	1	2,840
GXR5 (soil)	153	7	5	220
GXR6 (soil)	156	4	2	220

[1] Govindaraju, 1989

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Determination of total sulfur in geologic materials by combustion

By Kenneth Joe Curry

Code: N020 Accepted: Provisional

Principle

Total sulfur in geologic materials is determined using an automated sulfur analyzer (Jackson and others, 1985, 1987). Approximately 0.25 g of sample is mixed with 1 g of vanadium pentoxide flux and combusted in a resistance furnace at 1370°C in a regulated stream of oxygen. Total sulfur is determined as the sulfur dioxide evolved during the combustion with a detection limit of .05%. The sulfur dioxide is measured by its absorption of infrared radiation.

Interferences

Possible interfering elements are fluorine and molybdenum, both of which can coat the cell walls and the detector. Samples suspected to contain high concentrations of these elements should be analyzed 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 V_2O_5 to assure complete conversion of the sulfur to the dioxide.

Scope

The method is applicable to the analysis for total sulfur in rocks, soils, sediments, coals, plants, mosses, and lichens. The range of detection for sulfur is from 0.05% to about 30%. The method is of importance in geochemical, biogeochemical, and related environmental studies. 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
Conditioners, ground coal
Anhydrone, magnesium perchlorate, $Mg(ClO_4)_2$
<u>Standards</u>: LECO coal std. #1, #2, and #3
    SU-1 (nickle-copper-cobalt ore), Canadian Certified Reference Materials Project

Safety precautions

The major potential danger in this procedure is thermal burns 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. Toxic gases may be produced upon sample combustion, therefore, the instrument should be used under a working exhaust hood.

Procedure

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. If this is not done, visible moisture or discolorization appears one-third of the way down the tube (usually after about 75 analysis).
   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 conditioner (cover with 1 g of V_2O_5) 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 atomatically tare.
7. Add approximately 0.250 gram 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 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" noice 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. But, in low sulfur analysis, the amount of sulfur released is insufficient to start the analysis, so the ANALYZE key must be pressed again.
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 of sulfure (S, SO_3 or So_4) you wish to calibrate. The analysis of sulfide ore, SU-1 (Canadian Certified Reference Materials Project), using two calibration standards and different sample sizes, produce a mean value of 12.0% total sulfur content and a relative standard deviation of less than 3.0%. The total sulfur content in LECO coal standard #1 is approximately 0.45%, #2 is 1.03%, and #3 is 3.00%.
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. Then press the ENTER key.
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 V_2U_5 (about 1 gram) 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 stock 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 stock will be recalculated according to the new calibration value. The system will then revert to the Operation mode.

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 V_2O_5 (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 31 lists reference values determined by this method.

Table 31. Total sulfur content in selected reference materials by combustion

Reference sample (description)	$\bar{X}$	n	s	% RSD	Literature value (%)
MAG-1 (marine mud)	0.36%	10	.005%	1.39	0.39±.066[a]
SDO-1 (oil shale)	5.44%	10	.007%	0.2	5.35±.44[b]

[a] Gladney and Roelandts, 1988.

[b] Kane and others, 1990.

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Determination of sulfur in geologic materials by iodometric titration

By Richard M. O'Leary

Code: P040 Accepted: Provisional

Principle

Sulfur in rock, soil, and stream-sediment samples is determined by iodometric titration of sulfur dioxide gas released from the sample during combustion. The sample is ignited in a LECO induction furnace in a stream of oxygen. The SO_2 from the burning sample is titrated against iodine in titrators specifically designed for the procedure. Reference samples of known sulfur content are analyzed prior to analysis of unknowns to insure proper instrument working conditions.

Interferences

There are no documented interferences.

Scope

Sulfur can be analyzed in rocks, stream sediments, and soils with a lower limit of determination of 0.001% and an upper limit of 20%. Approximately 40 samples can be analyzed per day.

Apparatus

LECO Induction Furnace, Model 521 or 523
Clay combustion crucibles with lids
Combustion tube
LECO Sulfur Determinator
0.25-cc scoop for adding accelerators to crucibles, provided by LECO

Reagents

All chemicals are of reagent grade and the water is metal free
15% (v/v) hydrochloric acid: Dilute 30 mL concentrated HCl to 2 L with water
Potassium iodate, KIO_3
Potassium iodide, KI
Tin accelerator
Iron accelerator
Cylinder of oxygen with a two-stage regulator
Potassium iodate solution: For a 0.5-g sample, dissolve 0.222 g potassium iodate in water and dilute to 1 L in a volumetric flask. For a 0.10-g sample, dissolve 0.444 g potassium iodate in water and dilute to 1 L in a volumetric flask.
Starch solution: Dissolve 1.25 g Arrow starch in 33 mL cold water, then slowly add to 87 mL of boiling water while stirring. Allow to cool and add 3.75 g potassium iodide.

Safety precautions

Work with acid solutions must be conducted in a chemical hood and protective laboratory attire including apron or coat, gloves, and safety glasses must be worn. The analyst should be cognizant of and follow safety recommendations and procedures in the induction furnace manual. Combustible materials should not be discarded in the same metal container used for the discarded hot crucibles. See the MSDS for further information concerning first-aid treatment and disposal procedures for chemicals used in this method.

Procedure

Prior to the analysis of samples, a reference standard with known sulfur content is analyzed to insure proper instrument working conditions. USGS Geochemical Exploration Reference Sample number 1 (GXR1) containing 0.24% sulfur is suitable for this purpose.

1. Place 0.5 g of sample in a clay combustion crucible.
2. Add 1 scoop of tin accelerator and 1 scoop of iron accelerator and mix by stirring.
3. Place 1 scoop of iron accelerator on top of the mixture and cover with lid.
4. Place crucible on the pedestal of the furnace. Close the furnace and turn on filament voltage. Leave on for duration of day's analyses.
5. Fill the bell reservoir with 15% (v/v) HCl solution to just above the air tube. (Attempt to fill approximately the same volume each time.) Add 5 mL starch solution.
6. Set oxygen flow to 1 L per min.
7. Raise the pedestal to heating position.
8. Flip the titration switch to the "end point" position. When blue color appears, raise the titration switch to the neutral position and fill the titration tube. Flip the titration switch to "titrate."
9. Turn on high voltage switch.
10. Check for adequate heating of crucible by monitoring plate current, with a minimum current requirement of 350 mA and a desired current of 44 mA. (If plate current does not rise to suitable level after several minutes, rerun sample with an additional one-half scoop of iron).
11. When the colorless solution turns and remains blue, take the reading on the titration tube.
12. Lower crucible, drain titration vessel, and put titrator switch to neutral position. Discard the crucible in fire-resistant container.
13. Record reading on burette.
14. Repeat steps 1-13, until all samples are analyzed.

Calculation

When using a 0.5 g sample and a 0.222 g potassium iodate solution, the reading on the burette is the percentage of sulfur in the sample.

When using a 0.10 g sample and a 0.444 g potassium iodate solution, the reading on the burette is to be multiplied by 10 to obtain the percentage of sulfur in the sample.

Assignment of uncertainty

Table 32. Sulfur content in selected reference samples by iodometric titration

Reference sample (description)	$\bar{X}$ %	s	% RSD	n	Literature value[1] (ppm)
GXR2 (soil)	0.03	0.008	27	114	313
GSD6 (stream sediment)	0.07	0.01	14	20	800
GSD12 (sediment)	0.09	0.009	10	68	940

[1] Govindaraju, 1989.

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Determination of ferrous oxide in geologic materials by potentiometric titration

By Clara S.E. Papp, Phillip Aruscavage, and Elaine Brandt

Code: P050 Accepted: Provisional

Principle

A 0.5000-g portion of the sample is transferred to a platinum crucible; a mixture of sulfuric acid and hydrofluoric acid is added; the acids are boiled to dissolve the sample; and the crucible is immersed in a solution containing boric, sulfuric, and phosphoric acids. The analyte solution is titrated with potassium dichromate electrochemically by the automatic titrator (Peck, 1964; Cremer and others, 1984).

The oxidation of ferrous sulfate in air is strongly catalyzed by hydrofluoric acid (Hillebrand and others, 1953, p. 914). 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.

The analyte solution contains phosphoric acid, which complexes ferric iron, preventing the oxidation of the indicator before the end point of the titration is reached (Kolthoff and Sandell, 1952, p. 579-580). Boric acid prevents the catalytic oxidation effect of hydrofluoric acid by converting it to fluoboric acid (Hillebrand and others, 1953, p. 914). This conversion serves also to minimize the attack by hydrofluoric acid on the glassware.

Interference

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. Finely divided carbon obscures the end point of the titration. If the amount is small, the end point can be seen if a strong light is placed behind the solution; if it is large, the titration should be made electrometrically.

Tramp iron introduced during 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. Where careful hand grinding is used, the error can be tolerated, but enough iron is introduced from steel plates used in mechanical grinders to cause a serious error. If machine grinding is carelessly done, the error is so large that the ferrous oxide determination is unacceptable.

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, p. 907).

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, p. 911-912), in which the sample is decomposed by heating it with sulfuric acid in a sealed tube, is not entirely satisfactory. In another method, the sample is decomposed by fusion with sodium metafluoborate in an inert atmosphere (Groves, 1951, p. 183-186). 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. 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

Good results are obtained in the analysis of most silicates; but for a few silicates, the method must be modified, and for a few others it is unsatisfactory (see interferences). It takes approximately 15 minutes to process a sample. The minimum concentration reported is .01% FeO.

Apparatus

Brinkmann Metrohm 636 Titroprocessor
Metrohm Dosimat EJ65

Reagents

All reagents are analytical grade except the $K_2Cr_2O_7$ and electrolytic iron which is G. Frederick Smith Certified.

Saturated potassium chloride, KCl, solution: To 100 mL of distilled 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, conc.

Potassium Dichromate, $K_2Cr_2O_7$, 0.06262N: To prepare, assemble, and label a 2-L storage bottle, 2-L volumetric flask, standard iron solution and fill the distilled water bottle the night before preparing dichromate solution so all are at approximately the same temperature. This solution must be made and standardized in 1 day without interruption if possible. Start early!

Add about 1,000 mL of distilled water to a clean 2-L flask. Take the temperature of the water. Use table 33 to determine amount of potassium dichromate necessary for the temperature of the water. Weigh out in following manner: Replace the balance pans with 2-inch (6.4-cm) cover glasses. Weigh cover glasses and place the lighter glass on the right side. (With Sartorius balance, tare out the cover glass with the mechanical tare). Balance the glasses by adding weights, then add necessary weight for the amount of potassium dichromate needed for the temperature. Weigh out the potassium dichromate and remove the cover glass from balance. Using an eye drop bottle, wet the outer edges of the potassium dichromate on the cover glass to prevent any grains of dichromate from rolling off and spilling. Transfer the potassium dichromate to the volumetric flask through a small funnel using a water-wash bottle. Wash down the funnel, remove from flask and wash tip. Swirl the flask to dissolve dichromate, dilute to the mark with distilled water and mix. Take temperature of solution. There should be no change. Rinse clean storage bottle with a small amount of the solution. Transfer rest of the solution to bottle. (Rinse flask three times with distilled water and repeat from beginning until all storage bottles are filled). Label all bottles with date and initial.

Table 33. Amount of potassium dichromate necessary for temperature of water.

Temp of H_2O (°C)	$K_2Cr_2O_7$ required (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

Standardization of Potassium Dichromate: Take the temperature of the standard iron solution and pipette 50 mL into a clean 250-mL beaker for each bottle of dichromate solution. (Use calibrated pipette). Add 5 mL of conc. HCl and dilute to 100 mL with distilled water. Rinse and fill the clean burette with dichromate from the first bottle. Attach a thermometer to the burette with rubber bands, placing the bulb of thermometer near the 50-mL line on the burette.

Run a total iron titration on the solution in the beaker. Repeat for each bottle of dichromate solution. Check temperatures and amounts of titrant used for each beaker against figure on bottle of standard iron solution.

Standard Iron Solution: Weigh out 6.30 g of electrolytic iron on the analytical balance and transfer to a clean 250-mL Erlenmeyer flask. Place a funnel trap in the flask and add 25 mL of distilled water and 25 mL of conc. HCl. Cover the flask with a cover glass and place on a water bath until the iron dissolves--about 6 hours. Remove from the water bath and dilute to 100 mL with distilled water.

Filter through a 9-cm blue-ribbon paper into a clean 2-L volumetric flask. Wash the Erlenmeyer flask 3 times and the filter paper 10 times with 5% (v/v) HCl. Dilute to the mark and mix. Rinse a clean glass storage bottle with a small amount of the solution. Discard rinse. Carefully transfer the rest of the iron solution to the bottle.

Prepare three beakers of solution and titrate from the same bottle of dichromate as instructed in the directions for standardizing potassium dichromate.

Label the bottle with the amount of titer equal to 50 mL of iron solution, date, and your initials.

<u>"Dissolving" Solution (Boric Acid Solution)</u>: Weigh out 50 g of boric acid on electronic balance. Transfer to a clean 2-L beaker. Add 1,500 mL of distilled water, 175 mL of conc. sulfuric acid, and 200 mL of conc. phosphoric acid. 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.

<u>Standard Spike Solution</u>: Weigh 3.9-g ferrous ammonium sulfate, add to 500 mL of deionized water in a clean 1-L volumetric flask, add 11 mL conc. H_2SO_4, swirl to dissolve, then add deionized 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 MSDS for further information concerning first-aid treatment and disposal procedures for chemical products used in this method.

Procedure

USGS Standards are used to check the quality control for the analytical procedure. Each day, three to five "Spikes" are run to check the instrument.

Detailed Procedure Steps for Autotitrator

1. Turn dial on electric heater to 67 to 69. It needs at least 15 to 20 minutes to warm up.
2. Turn on Dosimat by pressing red lever on the left. (This <u>must</u> 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, (ex:110689) 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 <u>cannot</u> be reversed.
7. Press REPORT LIST button.
8. 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.
9. 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).
10. In a clean 250 ml beaker, place a magnetic stirring bar and add 50 ml of "dissolving" solution. Dilute to 150 ml with distilled water. This will be the first blank.
11. 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. Keep the electrode assembly to the left area of the beaker.

12. Turn on the stirrer (with the stirring rate at 3½) and start counting seconds. After shaking the bottle of Fe^{++} standard "Spike" solution, 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). When the seconds count reaches 30, press the GO button on the titroprocessor. (Use a new plastic tip on the pipettor each day or more frequently if necessary.)
13. While the titration is proceeding automatically the second blank may be prepared.
14. When the titration has been completed, the titroprocessor will print out the data for mV potential, volume of titrant used and the percent FeO. For the blank, only the volume of titrant will be used.
15. After the data has been printed out, stop the stirrer, lift the electrode assembly, wash off the electrodes with distilled water, and replace the beaker with the second blank solution. Repeat procedure as in the first blank run (#11-14).
16. Run a third blank. If the volume range for the three blanks is no more than 0.006 mL 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 volume (ex:0.129) then press ENTER button. Replace the solution beaker, after rinsing off electrodes with a small beaker of distilled water. Press REPORT LIST button (printer will list parameters) then note with a pen the job number, name of analyst, and name of submitter. Weigh accurately and record the weight of an approximate 0.5000-g sample in a tared platinum crucible. Four samples may be weighed initially, then an additional one can be weighed during the 10 minute heating time of the second sample. Determinations can be made in continuing order.

NOTE: To change the sample weight entry after the titration is completed and before another titration is started, punch "12", MOD, then the new weight, then the ENTER button. Then punch the DEL. BUF, 2nd button, then the PLOT, DIFF button. The result will now be recalculated with the new weight.

Calculation

$$\text{mL of .0626N } K_2Cr_2O_7 \text{ X } \frac{45}{(\text{wt. of sample})} \text{ x } 100 = \text{\% Fe 0}$$

Assignment of uncertainty

In the absence of complications, replicate determinations should agree within 0.1 percent (absolute). Failure to achieve such agreement is caused either by mineral segregation or by incomplete solution of the sample. The accuracy of this method was determined over a 1-month period using diabase W-2. The mean and standard deviation are 8.24±0.02% FeO (n=12). The recommended value is 8.34% FeO ±.093 (Flanagan, 1984).

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Determination of uranium and thorium in geologic materials by delayed neutron counting

By D.M. McKown and R.J. Knight

Code: R010 Accepted: Provisional

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 Th and U 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 U and Th employs two equivalent, sequential irradiation-counting cycles for each sample within an experiment set, consisting of individual uranium, thorium, and oxygen standards, and sample aliquots, using a custom-built, automated DN facility which 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 Th fission contribution relative to uranium and then a thermal neutron irradiation cycle is performed which yields predominately U 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; U/Th 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,n) 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 Be and F. Such samples are considered unsuitable for DN analysis.

Even under optimum conditions, Th and U 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 affect seriously 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, may yield erroneously high Th 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 3, and, similarly, for uranium if the ratio is greater than 50. Coal matrix samples are suitable for DN analysis if designated as such.

For suitable types of materials, the analysis of a 10 g sample aliquot exhibits detection limits of about 0.1 ppm for uranium and 1 ppm for thorium. Analytical precisions of ±5% for uranium and ±10% for thorium may be achieved for concentrations greater than 10 times the detection limit. The quantitative determination limits (defined as ±30% expected uncertainty) are about two times the detection limit.

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 Reactor Utilization Permit P-12, and reiterated in ORM (Operation Reference Manual), Section IV.

Procedure

Additional details of the procedure are in the on-site Operation Reference Manual (ORM). This manual is regularly updated and used for training. No analyst is allowed to operate the system without 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: 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 standard 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 standard reference rocks 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

The data reduction program DNCALC (ORM, Sect. VI) automatically generates and reports an analytical uncertainty estimate (coefficient of variation) for each U and Th value based on appropriate propagation of the counting statistics (measurement uncertainty) associated with each individiual sample and standard counting interval. The validity of these calculated coefficient of variation estimates has been experimentally verified by replicate analyses of reference materials exhibiting a range of U and Th concentrations.

The following values were reported by McKown and Millard (1987):

Element	Reference sample (description)	$\bar{X}$* (ppm)	%s sample	%s counting	Literature value[1] (ppm)
U	BCR-1 (basalt)	1.6	10	9	1.71±0.16
Th	BCR-1 (basalt)	6.0	3	2	6.0 ±0.6
U	G-2 (granite)	2.0	18	8	2.04±0.17
Th	G-2 (granite)	24.1	3	1	24.6±1.5

[1] Gladney and others, 1983.

*n=20.

For suitable types of samples (as described in a previous section), the analysis of a 10 g sample aliquot exhibits analytical precisions of ±5% for uranium and ±10% for thorium at concentrations greater than 10 times the detection limit.

At least one reference sample aliquot is analyzed with each experimental set of samples to serve as a data quality monitor. Limits of acceptability for the data set are established by the difference between individual quality control monitor results and the corresponding consensus reference value. The analyses are out of control if the mean difference exceeds three times the propogated standard deviation of the estimated measurement uncertainty for the quality control monitor and the uncertainty of the consensus value. The two "in-house" reference samples used for quality control are GPP (Granite-Pikes Peak, U = 5.4 ppm, Th = 29.2 ppm) and BTM (Basalt-Table Mountain, U = 4.1 ppm, Th = 14.4 ppm).

A quality control monitor is run with each sample set.

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Instrumental neutron activation of geologic materials by abbreviated count method

By G.A. Wandless and R.V. Knight

Code: R020 Accepted: Provisional

Principle

Neutron activation analysis is based on the measurement of the activity from radionuclides produced by neutron-induced nuclear reactions on naturally occurring isotopes of the element to be determined in the sample. The activity of the indicator radionuclide produced during the irradiation is directly proportional to the amount of the element of interest in the sample. The analytical determination is made by comparison of the induced activity in the sample and well-characterized standards activated under identical conditions of neutron flux. The activities of sample and standards are measured using gamma-ray spectroscopy, involving conversion of gamma-ray radiation emitted by the radionuclide by a semiconductor detector to an electrical signal which is analyzed by a multichannel analyzer. Semiconductor detectors, such as high-purity and lithium-drifted germanium detectors, are used because of their excellent resolution characteristics. Spectra produced are analyzed by computer software which locates peaks and calculates the area of each peak. The analyst is referred to Gordon, and others (1968), Baedecker and McKown (1987), and Laul (1979) for more detailed reports of the use of INAA.

Interferences

The method is matrix dependent. Decreased sensitivity and confidence for certain elements occur if the uranium concentration is greater than 100 ppm or the rare earth abundances are greater than 10,000 times chondrites or less than 5 times chondrites. Mineralized samples that are high in a few elements can cause problems with the analysis of other elements. High amounts of As, Zn, Sb, Au, W, and Mo require special counting and special computer analysis, as well as interfere with other elements. Metamorphic marbles/limestones and quartzites also require special handling and analysis. Samples that have low abundances of elements, such as Fe, Co, and Sc, can enable other elements to have an increased sensitivity.

Additional processes that interfere with activation analysis are physical and spectral. A detailed description of some of the known interferences are in Baedecker and McKown (1987).

Scope

The method is applicable to most igneous, metamorphic or sedimentary whole rock, soils, a few mineral phases, and a few very low-grade ores. It is not applicable to ultramafic or mineralized samples.

The method is designed to be a production method and not a research method. Compared to a research method, this method has decreased sensitivity and confidence. This is reported as an increase in error (%CV) for many elements.

Table 34 gives the elements determined and an estimation of their concentration at which a 10% error due to counting statistics could be expected. These were determined under idealized counting conditions and could improve or degrade with the matrix.

Table 34. Elements determined by instrumental neutron activation and an estimation of their concentration.

Element	Concentration a 10% error
Cs	0.26 ppm
Ba	73.00 ppm
Rb	12.00 ppm
Sr	98.00 ppm
Na	125.00 ppm
Th	0.11 ppm
U	0.58 ppm
La	0.43 ppm
Ce	3.90 ppm
Nd	10.00 ppm
Sm	0.07 ppm
Eu	0.10 ppm
Tb	0.15 ppm
Yb	0.65 ppm
Lu	0.06 ppm
Ta	0.30 ppm
Zr	126.00 ppm
Hf	0.18 ppm
Sb	0.21 ppm
Sc	0.07 ppm
Fe	402.00 ppm
Cr	2.70 ppm
Co	0.13 ppm
Ni	22.00 ppm
Zn	2.20 ppm

Procedure

1. For each irradiation at least one USGS standard rock is used for a QC monitor and at least one duplicate of the multielement standard HMS or CQS are included.
2. Samples, standards, and QC monitors are weighed into appropriate containers and irradiated in a uniform neutron flux for 8 hours.
3. Instrument energy calibration is performed prior to counting of samples by checking the gamma-ray spectrum from a source of known gamma-ray energies.
4. Data acquisition is performed by a multichannel analyzer adjusted for 0.1 keV/channel for the low energy detectors and 0.5 keV/channel for the high energy detectors.

5. Spectra are acquired for samples, standards, and QC monitor on the same detector, at the same geometry. Data is collected 9 and 23 days after completion of irradiation.
6. Data reduction is performed using the SPECTRA or SAMPO/INAA computer programs.
7. Accuracy and precision of the irradiation group is evaluated by agreement between standards and comparison of QC monitors with known values.

Calibration of instrument

Energy Calibration	Low Energy Detectors	High Energy Detectors
Multichannel analyzer	204B channels 0.1 keV/channel	4096 channels 0.5 keV/channel
Gamma-ray source	Co-57, Am-241 Ta-182	Co-60, Am-237, Y-88, Ba-137
or		
	pitchblende	pitchblende

Calculation

For details of appropriate calculations, the analyst is referred to Baedecker (1977).

Assignment of uncertainty

Tables 35 and 36 give the errors obtained with "in-house" reference samples of basalt (BTM) and granite (GPP). The errors are a summation of between run errors where one control sample of BTM or GPP was irradiated with each set. These summations are running averages and errors which are updated for each element after each run. The CV(n)% is the variance of the weighted mean. The procedure might not produce as high a precision on all samples due to other interferences (Baedecker and McKown, 1987).

Table 35. Concentration values obtained by analyzing a basalt (BTM) in replicates of 5, by instrumental neutron activation

Element	$\bar{X}$ (ppm)	CV(n)%	"In-house" accepted values[1] (ppm)
Cs	3.07	1.60	3.09
Rb	144	1.23	144
Ba	1,021	2.47	995
Sr	1,269	2.55	1,215
Na	23,300	0.17	2.28%
Th	15.0	2.04	14.4
U	4.1	1.97	4.1
La	45	1.46	44.6
Ce	89.2	1.60	89.3
Nd	40.4	1.33	39.6
Sm	7.8	1.54	7.85
Eu	1.91	1.20	1.89
Td	0.89	1.78	0.87
Yb	2.61	1.94	2.65
Lu	0.398	0.90	0.385
Ta	1.60	3.05	1.56
Zr	219	2.18	2.50
Hf	5.8	2.79	5.7
Sb	0.2	8.72	0.2
Sc	22.2	0.91	22.0
Fe	67,420	0.87	6.534%
Cr	36	1.23	36
Co	23.8	1.03	23.1
Zn	108	2.43	95

[1] Knight, 1990

Table 36. Concentration values obtained by analyzing a granite (GPP) in replicates of 9, by instrumental neutron activation

Element	$\bar{X}$ (ppm)	CV(n)%	"In-house" accepted values[1] (ppm)
Cs	1.72	0.27	1.73
Rb	199	1.10	196
Ba	691	0.73	661
Sr	211	2.07	215
Na	23,600	0.39	2.33%
Th	29.1	1.35	29.2
U	5.6	0.83	5.4
La	131	0.73	128
Ce	279	2.15	275
Nd	117	0.16	114
Sm	23.6	0.26	21.7
Eu	1.6	0.61	1.8
Tb	3.13	0.64	3.05
Yb	10.7	1.12	10.4
Lu	1.58	0.11	1.55
Ta	3.5	1.01	3.7
Zr	511	1.78	515
Hf	15.0	1.10	13.7
Sb	0.08	6.88	0.07
Sc	8.28	1.42	8.47
Fe	27,090	0.82	2.675%
Cr	11	1.05	9
Co	4.60	0.52	4.46
Ni	14.6	15.06	15
Zn	122	1.27	105

[1] Knight, 1990.

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Determination of tungsten in rock, soil, and stream-sediment samples by visible absorption spectrophotometry

By Richard M. O'Leary and Eric P. Welsch

Code: U010 Accepted: Provisional

Principle

Tungsten in rock, stream-sediment, and soil samples is determined by the visible absorption spectrophotometric method. The sample is decomposed by nitric and hydrofluoric acids and the residue is dissolved in 80% (v/v) hydrochloric acid. A clear aliquot of the solution is treated with stannous chloride to inhibit interferences, particularly from molybdenum. The blue tungsten dithiol complex is developed at 95°C within a ½-hour period. The complex is extracted into 4 mL heptane and the concentration of tungsten is determined by measuring the absorption at 630 nm with a visible wavelength-range absorption spectrophotometer.

Interferences

The addition of stannous chloride prevents formation of green molybdenum dithiol and eliminates a number of interfering elements that would otherwise compete with the tungsten for dithiol bonding sites.

No interference from lead, chromium, cobalt, nickel, manganese, molybdenum, and vanadium has been observed. However, copper and bismuth at 1,000 ppm concentrations cause a severe suppression of the absorbance reading of approximately 50%. The addition of potassium ferricyanide will reduce or eliminate this problem for samples with copper concentrations of 1,000 ppm and greater. Though not as often encountered in such high concentrations in geochemical samples, bismuth remains a problem. When it does cause a serious interference, complexing it with dithizone (Allen and Hamilton, 1952) is necessary before the tungsten color-development step.

Scope

Tungsten can be analyzed in rocks, stream sediments, and soils with a lower limit of determination of 0.5 ppm. The upper limit can be extended beyond 50 ppm by taking a smaller aliquot in step 3 of the procedure. Approximately 40 samples can be determined per person-day.

Apparatus

Boiling chips
Centrifuge
Heating block, drilled to accomodate 16-mm test tubes
Hot plate
Spatula, Teflon
Spectrophotometer, equipped with flow-through absorbance cell
Teflon beakers, 50 mL
Test tubes, 16x150 mm, disposable
Vacuum system

Reagents

All chemicals should be or reagent grade and all water should be metal free.

Dithiol, 1.5% solution: Acidify 1.5 g zinc dithiol (toluene-3, 4-dithiol, zinc derivative) with 2 mL concentrated hydrochloric acid and dissolve in 100 mL ethanol, preferably by immersion in a sonic bath, for 10 minutes or until a clear pink solution is obtained (prepare daily).

Heptane, $CH_3(CH_2)_5CH_3$

Ethanol, C_2H_5OH

Hydrochloric acid, HCl, 80% (v/v): Add 800 mL concentrated HCl to 200 mL water.

Hydrofluoric acid, HF, 49%

Nitric acid, HNO_3, concentrated

Potassium ferricyanide, 10% (w/v): Dissolve 10 g potassium ferricyanide ($K_3Fe(CN)_6$) in 100 mL water.

Stannous chloride, 30% solution: Dissolve 300 g stannous chloride ($SnCl_2 \cdot 2H_2O$) in 1,000 mL concentrated hydrochloric acid.

Stock tungsten solution, 1,000 µg/mL: Dissolve 0.897 g sodium tungstate, dihydrate ($Na_2WO_4 \cdot 2H_2O$) in 500 mL water.

Dilute tungsten solution, 100 µg/mL: Dilute 10 mL of 1,000 µg/mL stock tungsten solution to 100 mL with water.

Working solutions: Add 0.5 mL of the 100 µg/mL tungsten solution to three 16x150-mm test tubes, each containing a boiling chip. Then add 5 mL 80% HCl and 5 mL 30% stannous chloride solution. Prepare as per procedure starting at step 5 but extract into 8 mL heptane. Choose the standard yielding the median value for setting the concentration at 50 ppm (see **Standardization of Instrument**).

Safety precautions

All work with open or uncapped reagents must be done in a chemical hood. Protective clothing, eyeware, and gloves must be worn. See the MSDS for further information concerning first-aid treatment and disposal procedures for chemical products used in this procedure.

Procedure

1. Weigh 1-g sample into a 50-mL FEP Teflon beaker, add 5 mL concentrated nitric acid and 15 mL of concentrated hydrofluoric acid, place on a hot plate, and heat at 100°C overnight to dryness.
2. Transfer to a 16x150-mm test tube with two 5-mL portions of 80% (v/v) HCl and mix well. (After review of the dc arc emission spectrographic data or ICP data, if copper is in excess of 1,000 ppm in the sample, the sample should now be treated with 1 mL of 10% potassium ferricyanide. Mix, wait 10 minutes, and proceed to step 3).
3. Centrifuge and transfer a 5-mL aliquot to a second 16x150-mm test tube.
4. Add 5 mL of 30% stannous chloride solution and a boiling chip.
5. Place tube in a heating block set at 95°C for 10 minutes, then add 1 mL of 1.5% dithiol solution, and continue to heat for 30 minutes. (Dithiol solution should be injected down the center of the tube rather than the sides to avoid the formation of excessive amounts of tin dithiol).
6. Add 4 mL heptane to the cooled sample, cap, and shake for 1 minute.

7. Allow the layers to separate, and read absorbance of the organic layer on the spectrophotometer at 630 nm. Samples containing greater than 50 ppm tungsten should be reprocessed from step 3 using a smaller aliquot.
8. Recalibrate instrument after every 20 samples.

Standardization of Instrument

The operating conditions for a Bausch and Lomb Spectronic 710 spectrophotometer equipped with a flow-through system are listed in table 37.

Table 37. Operating conditions for determination of tungsten by visible absorption spectrophometry

Wavelength	630 nm
Mode	absorbance
Absorbance check	50 µg standard to give .700 absorbance units
Calibration	50 µg to read 50

Calculation

When using the recommended sample weight, calibration standard, and instrument calibration setting, the sample reading is the actual element concentration and is reported as µg/g (ppm). Dilution is required for readings greater than 50 ppm tungsten and concentrations are calculated as follows:

$$\text{ppm} = \frac{5}{\text{Volume of aliquot (mL)}} \times \text{Instrument reading}$$

Assignment of uncertainty

Table 38 is a tabulation of statistical data obtained by analyzing the six GXR (geochemical exploration reference) samples (Allcott and Lakin, 1975), in replicas of five, by the described procedure.

Table 38. Tungsten content of GXR samples by visible absorption spectrophotometry

Reference sample (description)	$\bar{X}$ (ppm)	s	% RSD	Literature value[1] (ppm)
GXR1 (jasperoid)	177	3.19	2	164
GXR2 (soil)	0.56	0.09	16	1.9
GXR3 (Fe-Mn mineral deposit)	12,100	2.78	2	1.07%
GXR4 (copper mill head)	16	0.90	6	30.8
GXR5 (soil)	1.6	0.10	10	1.11
GXR6 (soil)	2.0	0.09	5	1.9

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[1] Govindaraju, 1989.

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Determination of 12 selected trace elements in geologic materials by energy-dispersive X-ray fluorescence spectrometry

By Bi-Shia King and J. Lindsay

Code: X010, X020, X030, X040 Accepted: Provisional

Principle

Energy-dispersive X-ray fluorescence (EDXRF) spectrometry 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 selected 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, USGS Bulletin 1770, Chapter E and F, 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 the scatter-target line lies to the analyte line; the absorption, particle size, packing density, and instrumental effects are more effectively corrected. The matrix 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 (-200-mesh). Because this method is nondestructive, the sample can be used for other chemical and instrumental analyses after EDXRF analysis. The detection limits and calibration concentration ranges of the method are summarized in table 39.

Table 39. Lower limit of detection and upper limit of calibration curve for the EDXRF method

Element	Lower limit (ppm)*	Upper limit (ppm)
Cr	20	4200
Ni	10	3000
Cu	10	1000
Zn	10	1300
Rb	10	2000
Sr	10	2000
Y	10	200
Zr	10	2000
Nb	10	500
Ba	10	4700
La	10	1300
Ce	10	500

*Represents the highest LLD 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 concentric plastic rings. This rapid preparation requires no weighing. The powder can be tamped to assure a more uniform packing density.

Standardization of Instrument

Table 40. Operating conditions for a Kevex model 0700/7000 X-ray spectrometer

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 sec for targets Fe and Ge; 200 sec 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 41). 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 samples (such as BCR-1 and GSP-1) are analyzed as check standards in every job.

Table 41. Calibration standards used in the EDXRF method

AGV-1	BXN	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_0 and slope B_1 of the best fit line of each calibration and the ratio of intensity I_i to Compton scatter radiation C as follows:

$$C_i = B_0 + B_1(I_i/C)$$

Assignment of uncertainty

The precision of the intensity measurements is largely determined by counting statistics and is commonly better than ±5% relative at a concentration level of 50 ppm for most elements, except La and Ce. The exceptions are probably due to the inefficiency of the Si(Li) detector for high-energy X-rays (>33 keV) used in EDXRF analysis. The accuracy of the EDXRF determination is better than ±5% for most of the concentration ranges, assuming the error from the background subtraction is insignificant, although it may decrease to as much as ±50% near the lower limit of determination.

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High precision major element analysis of rocks and minerals by wavelength dispersive X-ray fluorescence spectroscopy

By Joseph E. Taggert, Jr., Ardith Bartel, and David F. Siems

Code: X050 Accepted: Provisional

Principle

Ten major elements are determined in rocks and minerals by wavelength dispersive X-ray fluorescence spectroscopy (WDXRF). The sample is fused with lithium tetraborate and the resultant glass disc is introduced into a wavelength dispersive X-ray spectrometer. The disk is irradiated with X-rays from an X-ray tube. X-ray photons emitted by the elements in the sample are counted and concentrations determined using previously prepared calibration standards. In addition to 10 major elements, the method provides a gravimetric loss on ignition at 925°C.

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 sample also diminishes matrix effects and produces a stable, flat, homogeneous sample for presentation to the spectrometer. Maximizing the efficiency of the optics of the X-ray spectrometer and 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 on 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 (table 42).

Under normal circumstances of staffing and instrument downtime, 500 samples per month can be analyzed with this method.

Apparatus

Phillips PW1600 simultaneous X-ray spectrometer
Pt-Au alloy crucibles and molds (Taggart and Wahlberg, 1980a)
Fluxer (Taggart and Wahlberg, 1980b)
Hot plate and at least two muffle furnaces
Special design fusion apparatus (fluxer)

Regeants

The samples are digested in Johnson Matthey Spectroflux 100 (lithium tetraborate). The flux is ordered in homogenized 250 k batches (approximately a 3-year supply). The minus-60-mesh flux is dried for 2 days at 300°C and kept in vacuum sealed mason jars. A loss-on-fusion is performed on each lot

Table 42. Elements that are determined and the concentration range over which the WDXRF instrument is calibrated

Element	Concentration range		
SiO_2	0.10%	to	99.0%
Al_2O_3	0.10%	to	28.0%
Fe_2O_3	0.04%	to	28.0%
MgO	0.10%	to	60.0%
CaO	0.02%	to	60.0%
Na_2O	0.15%	to	30.0%
K_2O	0.02%	to	30.0%
TiO_2	0.02%	to	10.0%
P_2O_5	0.05%	to	50.0%
MnO	0.01%	to	15.0%
LOI (925°C)	0.01%	to	100.0%

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 10% reagent grade (not technical) HCl and rinsed in deionized water. The LiBr used as nonwetting agent is prepared by neutralizing reagent grade concentrated HBr 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 in 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 flux must be done under a chemical hood. See the 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% Pt-5% Au crucible at 925°C for 45 minutes. The weight loss is reported as percent loss on ignition (LOI). An 8.0000-g charge of lithium tetraborate is added to the sample and thoroughly mixed. A 0.250-mL aliquot of a 50% solution of LiBr is added as a nonwetting agent. Seven crucibles 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 homogenized in the furnace with an electric motor mechanism and poured, while still molten, from crucibles into the molds at the end of 40 minutes. An essential feature of this method is the mold design (Taggart and Wahlberg, 1980b). Samples with high concentrations of copper, chrome, nickel, iron, manganese, and high organic content require special sample preparation techniques, and in some instances, cannot be prepared at all. The major element concentrations are determined by comparing the intensities obtained from standards to those obtained from the samples using the wavelength dispersive X-ray spectrometer.

Standardization of the Instrument

The following operating conditions are for the Phillips PW1600 spectrometer:

Tube........................Rhodium, end window
Power.......................35kV and 60mA
Time........................100 seconds
Atmosphere..................Vacuum

See table 43 for the parameters for each of the channels and detectors in the instrument. The instrument is calibrated using compiled "best values" (Abbey, 1978) for silicate standards. Only well characterized and available standards are used. These include 42 international reference materials.

Table 43. Instrument parameters for Phillips PW1600 X-ray spectrometer

[μm, micrometers; W multi, tungsten synthetic multilayer; TLAP, thallium hydrogen phthalate; PET, pentaerythritol tetrakis (hydroxymethyl) methane; InSb, Indium Antimonide; Ge, germanium (111); LiF, lithium fluoride (200); P10 gas, 90% argon + 10% methane]

Element	Line	Crystal	Detector-gas	Window
Na	Kα	Semifocused W multi	Flowcounter, P10	1 μm polypropylene.
Mg	Kα	Semifocused TLAP	----do----------	----do------------
Al	Kα	Semifocused PET	----do----------	----do------------
Si	Kα	Semifocused InSb	----do----------	----do------------
P	Kα	Semifocused GE	----do----------	----do------------
K	Kα	Semifocused PET	----do----------	----do------------
Ca	Kα	Semifocused LiF	Sealed argon	50 μm beryllium.
Ti	Kα	----do------------	----do----------	----do------------
Mn	Kα	----do------------	----do----------	----do------------
Fe	Kα	----do------------	----do----------	----do------------

Long-term instrument drift is corrected using drift monitor analyses. Monitor intensity values obtained during the original calibration are compared with monitor intensity values in subsequent analyses. Corrections are calculated by the spectrometer's computer program. Long-term drift monitoring cannot correct for short-term effects or significant changes in the operating parameters.

In order to follow instrument drift, every tenth sample is a standard check disc of basalt BB-1 or basalt TB-1. If the analysis of the check disc exceeds three times the counting statistics, counting is stopped, the data collected after the last successful analysis of the check disc is discarded and appropriate steps are taken to get back in control. Monitor updates are done every 20 to 40 samples followed by an analysis of the check disc. If the analysis of the check disc indicates the calibration is out of control, the calibration is re-established. If recalibration is necessary, nine of the original standard disks are used to set the slope of the curve, using a computer automated recalibration program. (1) The standards for the recalibration are the original 1980 discs of AGU-1, DTS-1, G-2, GSP-1, BR-N, DR-N, GS-N, BX-N, and NBS-120a. Nine blanks prepared from the current batch of flux and Libr are used for recalibration of the intercept, again using a computer automated program. In this manner, the original calibration can be maintained while compensation can be made for minor changes in the reagents. (2) The recalibration curve is verified by analyzing the well-characterized in-house standard BB-1. New BB-1 glass check discs are prepared in triplicate each month to check the sample preparation and to provide "fresh" check discs for counting after every tenth sample.

Assignment of uncertainty

Precision is the deviation of a set of determinations from their mean (random error), while accuracy is the degree of conformity with a standard (elimination of systematic plus random error) (Bates and Jackson, 1980).

Precision in the WDXRF method depends on the stability of the instrument and the precision of the sample preparation. Table 44 summarizes the results of tests performed on an in-house standard, BB-1 (Baker's Basalt). Column 1 lists the composition of the standard. Column 2 lists the theoretical precision limit of counting statistics by the PW1600 spectrometer measured on a disc of BB-1 when the tests were performed. These values are based on the square root of the total number of counts. Column 3 gives the standard deviation of a disc of BB-1 counted 50 times in 1.5 hours, and represents the actual short-term precision of the instrument. Column 4 lists the standard deviation of 49 separately prepared discs to check the precision of the sample preparation. A comparison of columns 5 and 6 shows that the precision of the instrument has remained the same or improved slightly on various channels over 3.5 years, illustrating the method's ability to correct the long-term drift. The data given above in columns 5 and 6 are actual examples of data collected on discs of BB-1 counted every tenth sample during operational analyses.

Table 45 shows an example of accuracy determined on the instrument with the analyses of seven standards in 1980 from Taggart and others, 1981; Abbey from Abbey, 1978; and again in 1985 from Taggart and others, 1987. In January of 1988, the crystal on the sodium channel was changed from a semi-focusing TLAP crystal to a semi-focusing synthetic multilayer crystal with a resulting three-fold increase in net counts resulting in a 1.7 improvement in precision.

The WDXRF method for major element analysis is unique among major element 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 principle elements in a sample, then the total of their determinations should approach 100%. 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 less that 98% or greater than 101% it is automatically repeated. Duplicate analyses are performed when totals are not within the 98% to 101% range. In this manner duplicates are directed at analyses most likely to be in error.

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Table 44. Tests of precision performed on in-house basalt standard BB-1 (Taggart, and others, 1987) by WDXRF

(1) Sample Composition		(2) Contribution of error by counting statistics	(3) Precision, one sample counted 50x in 1.5 hrs (std. deviation)	(4) 49 separately prepared discs counted once each, in 1.5 hrs (std. deviation)	(5) 1 disc counted 62x from 7/81 to 12/81 (std. deviation)	(6) 1 disc counted 62x from 1/85 to 5/85 (std. deviation)
SiO_2	52.8%	0.04	0.04	0.13	0.19	0.09
Al_2O_3	16.7%	0.03	0.02	0.07	0.05	0.05
Fe_2O_3[a]	9.35%	0.01	0.01	0.03	0.02	0.01
MgO	3.54%	0.02	0.02	0.02	0.06	0.04
CaO	6.60%	0.01	0.01	0.02	0.02	0.02
Na_2O	3.20%	0.03	0.03	0.09	0.07	0.04
K_2O	4.38%	0.01	0.01	0.01	0.03	0.01
TiO_2	0.88%	0.01	0.01	0.01	0.01	0.01
P_2O_5	0.60%	0.01	0.01	0.01	0.01	0.01
MnO	0.18%	0.01	0.01	0.01	0.01	<0.01

[a] Total Fe as Fe_2O_3

Table 45. Analyses in 1981 and 1985 of seven igneous rock standards (in weight percent) by WDXRF

[XRF (1981) from Taggart and others, 1981; Abbey from Abbey, 1978; XRF (1985) from Taggart and others, 1987]

	SiO_2	Al_2O_3	Fe_2O_3[a]	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	MnO
Andesite, AGV-1:										
XRF (1981)........	59.9	17.2	6.88	1.57	5.11	4.25	2.99	1.08	0.52	0.08
Abbey.............	59.72	17.22	6.84	1.55	5.00	4.31	2.93	1.05	0.50	0.10
XRF (1985)........	59.4	17.1	6.80	1.55	5.03	4.19	2.91	1.07	0.51	0.09
Dunite, DTS-1:										
XRF (1981)........	40.6	0.18	8.84	49.8	0.11	<0.2	<0.05	<0.02	<0.05	0.11
Abbey.............	40.68	0.29	8.60	49.83	0.13	0.01	0.00	0.01	0.00	0.11
XRF (1985)........	40.7	0.26	8.90	50.2	0.13	<0.15	<0.02	<0.02	<0.05	0.13
Granite, G-2:										
XRF (1981)........	69.9	15.6	2.73	0.81	1.98	3.94	4.54	0.49	0.13	0.02
Abbey.............	69.19	15.35	2.67	0.77	1.98	4.06	4.52	0.50	0.14	0.04
XRF (1985)........	69.0	15.2	2.64	0.85	1.95	3.91	4.45	0.49	0.13	0.02
Granodiorite, GSP-1:										
XRF (1981)........	67.2	15.2	4.32	1.01	2.04	2.61	5.51	0.66	0.29	0.02
Abbey.............	67.31	15.19	4.33	0.96	2.02	2.80	5.53	0.66	0.28	0.04
XRF (1985)........	67.0	14.9	4.32	0.96	2.02	2.67	5.47	0.68	0.29	0.03
Basalt, BRN:										
XRF (1981)........	38.4	10.2	13.0	13.3	14.0	2.91	1.38	2.70	1.10	0.18
Abbey.............	38.39	10.25	12.9	13.35	13.87	3.07	1.41	2.61	1.05	0.20
XRF (1985)........	38.6	9.89	13.1	13.3	14.0	3.01	1.36	2.71	1.09	0.20
Granite, GSN:										
XRF (1981)........	66.4	15.0	3.73	2.28	2.55	3.61	4.69	0.67	0.28	0.04
Abbey.............	65.98	14.71	3.75	2.31	2.51	3.78	4.64	0.68	0.28	0.06
XRF (1985)........	65.7	14.5	3.69	2.22	2.51	3.67	4.60	0.66	0.28	0.05
Lujavarite, NIM-SARM-3-L:										
XRF (1981)........	52.1	13.6	9.97	0.32	3.18	8.23	5.38	0.48	0.05	0.74
Abbey.............	52.45	13.59	9.96	0.28	3.24	8.30	5.46	0.49	0.06	0.76
XRF (1985)........	52.0	13.1	9.93	0.29	3.15	8.25	5.31	0.49	0.05	0.79

[a] Total Fe as Fe_2O_3.

Determination of fluoride in silicates and sediments by ion-selective electrode following a sodium carbonate-zinc oxide fusion

By Herbert Kirschenbaum and edited by Michael Doughten

Code: P060 Accepted: Provisional

Principle

Fluorine in silicates and sediments is determined as fluoride by the ion-selective potentiometric method (Ingram, 1970; Kirschenbaum, 1988). Samples are fused with a sodium carbonate-zinc oxide flux, leached with distilled water, and centrifuged. HCl is added to expel CO_2 and the sample is then further diluted with distilled water. An aliquot of the sample solution is then buffered with a sodium citrate-potassium nitrate solution. The fluoride concentration is determined by ion-selective electrode and the measured potential is compared to the measured potentials from a calibration curve of calibration solutions (F^- conc. vs. mV).

Interferences

The citrate buffer solution adjusts the pH of the solution to between 6.3 and 6.8. This helps eliminate the interferences due to OH^- and HCO_3^- at greater than pH 7. The buffer also eliminates the formation of HF at pH less than 5 which would bias the measurements low and helps eliminate interferences due to aluminum and iron.

Scope

Fluoride can be determined in silicates and sediments with a lower limit of determination of 50 ppm with a relative standard deviation of less than 10%. If the samples are greater than 5,000 ppm fluride the samples are diluted and reanalyzed. Approximately 70 samples can be analyzed in a week.

Apparatus

Orion Research Expandable Ion Analyzer model EA920
Orion Research combination fluoride electrode model 96-09
Graduated 4-oz polypropylene sample containers with polyethylene caps
Platinum crucibles (10-mL) with platinum covers
Hot plate
Electric furnace, Lindberg/Hevi-duty, 200-1,200°C
Centrifuge, 2,000 rpm, with rotor for 50-mL centrifuge tubes

Reagents

Hydrochloric acid, HCl, 50% (v/v): Prepare by adding 500 mL concentrated HCl to 500 mL distilled water.

0.2 M sodium citrate-0.2 M potassium nitrate solution: Dissolve 59 grams of sodium citrate dihydrate, $C_6H_5Na_3O_7$, and 20 grams of potassium nitrate, KNO_3, in distilled water and dilute to 1 liter.

Sodium fluoride standard: Purify the sodium fluoride, NaF, by first adding 10 to 15 mL of concentrated hydrofluoric acid, HF, to 3 grams of sodium fluoride in a platinum dish. Evaporate the resulting solution to dryness on a steam bath. Transfer the purified sodium flouride to a polyethylene vial.

Standard A: Prepare a stock solution of 1,000 µg/mL fluoride by dissolving 1.105 grams of the purified sodium fluoride in distilled water and diluting the solution to 500 mL.

Standard B: Prepare a 100 µg/mL fluoride standard by diluting 10.0 mL of standard A to 100 mL.

Standard C: Prepare a 10 µg/mL fluride standard by diluting 1.0 mL of standard A to 100 mL.

Calibration standards: Add 0.5 grams of anhydrous sodium carbonate, Na_2CO_3, and 50 mL of distilled water to each of 10 tared 4-oz polypropylene sample containers. Add 2 mL of 50% (v/v) HCl, swirl the containers to expel the CO_2, add the appropriate amount of standard B or C and dilute to 100.4 grams with distilled water, and cap the containers.

Zinc oxide, ZnO

Dilutions for preparation of calibration standards:

Pipet volume (mL)	Standard pipetted (B or C)	Final fluoride concentration (µg/mL)
0.2	C	0.02
0.5	C	0.05
1.0	C	0.10
1.5	C	0.15
2.0	C	0.20
3.0	C	0.30
4.0	C	0.40
8.0	C	0.80
1.0	B	1.0
2.0	B	2.0

Safety precautions

All work with uncapped reagents must be done in a chemical hood. Protective clothing, safety glasses, and gloves must be worn. See the MSDS for first-aid treatment and disposal procedures for the chemicals used in this procedure.

Procedure

1. Thoroughly clean each 10-mL platinum crucible by fusing with sodium carbonate, washing the crucible in 50% (v/v) hydrochloric acid, and rinsing with distilled water.
2. Weight 0.100 grams of sample (minus-100 mesh) and transfer to a 10-mL platinum crucible.
3. Add 0.5 grams of anhydrous sodium carbonate and 0.1 grams of zinc oxide to the crucible and mix thoroughly with a thin glass stirring rod. Zinc oxide aids in the decomposition of refractory fluorides.
4. Place samples in an electric furnace at 1,000°C and fuse for 30 minutes.

5. Allow crucibles to cool and place them on a low-temperature hot plate. Fill the crucibles with distilled water, cover, and warm overnight at 50° to 90°C to leach the fusion cake.
6. Transfer the contents of the crucible to a graduated polypropylene 50-mL centrifuge tube. Break up any lumps with a Teflon stirring rod and add distilled water to the 45-mL mark. Cap the centrifuge tube and shake.
7. Centrifuge at 2,000 rpm for 10 minutes.
8. Decant solution into a tared, graduated 4-oz polypropylene sample container. Add 2 mL of 50% (v/v) HCl and swirl container to expel all the CO_2. Place container on top loading balance and dilute to 100.4 grams with distilled water, and then cap the container.
9. Measure the potentials of the fluoride standard solutions and sample solutions by diluting one to one with the sodium citrate-potassium nitrate buffer and analyzing by selective-ion electrode. Samples having a fluoride ion concentration above 0.1 ppm in solution come to equilibrium in 5 minutes. Samples having a fluoride concentration below 0.1 ppm in solution may take 5 to 10 minutes to reach equilibrium.
10. Plot a calibration curve for the fluoride standards on one cycle semi-logarithmic graph paper. Plot the potential (mV) vs. the fluoride concentration (ppm). Determine the fluoride concentration of the samples by comparing their potentials against those of the standard solutions. The concentration of fluoride in the sample is 1,000 times that in solution.

Assignment of uncertainty

Table 46 shows the amount of fluoride determined by this method present in eight reference samples.

Table 46. Fluoride content in eight reference samples by ion-selective electrode following a sodium carbonate-zinc oxide fusion

Reference sample (description)	$\bar{X}$	n	s	% RSD	Literature values[1] (ppm)
USGS W-1 (diabase)	223	21	17.7	7.9	220
USGS BHVO-1 (basalt)	360	10	17.0	4.7	385
USGS G-2 (granite)	1,290	14	44.6	3.5	1,280
USGS AGV-1 (andesite)	453	4	9.6	2.1	425
USGS BCR-1 (basalt)	458	11	17.8	3.9	490
USGS GSP-1 (granodiorite)	3,500	4	(all replicates are 3,500)		3,360
USGS RGM-1 (rhyolite)	356	7	17.2	4.8	342
CRMP MRG-1 (gabbro)	234	1	--	--	240

CRMP: Canadian Certified Reference Materials Program

[1] Govindaraju, 1989.

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APPENDIX C FORMS

REQUEST FOR ANALYSIS (RFA)

Revised 8/90

SUBMITTER[1] ____________________
ADDRESS ____________________
____
PHONE NUMBER ____________________
PROJECT TITLE ____________________
PROJECT NUMBER ____________________
PROGRAM NUMBER ____________________
If previous work was done on these samples, list job numbers: ____________________

U.S. GEOLOGICAL SURVEY
BRANCH OF GEOCHEMISTRY, P.O. Box 25046
DENVER FEDERAL CENTER, MS 973
DENVER, CO 80225

Branch Chief Approval ____________________
(if required by Submitter's Branch)
QA Approval ____________________

SAMPLE TYPE[2]: rock, stream-sediment, soil, water, plant, coal, concentrate, other: ____________________

NUMBER OF SAMPLES ____________
PREP INSTRUCTIONS:
Special Requirements ____________
____
____
____

Disposition of Bulk:
☐ Discard
☐ Return to Submitter
Mineralogy by ____________

PAGE 1 OF ____________
FOR BGC USE ONLY:
JOB NUMBER ____________
LAB NUMBER ____________
Date received ____________
Counted and scanned by ______
Shelf ____________

PREP LAB

Prepared by ____________
Notes ____________
____
QC ____________

OPERATIONS GEOCHEMISTRY METHODS

Check technique(s) necessary for your study. Non-operation methods available through arrangement with the Chief, Analytical Geochemistry Section. Notate on reverse side.

Analyst sign and date   Instrument no.

☐ 40-element, ICP-AES ____________________
☐ 10-element, ICP-AES ____________________
☐ 35/37-element, dc-ARC AES ____________________
☐ Major elements as oxides, WDXRF ____________________
☐ INA short count (long count is analytical) ____________________
☐ As, AA hydride generation ____________________
☐ Au, AA flame (HBr-Br_2) ____________________
☐ Au, AA flame (HF) ____________________
☐ Au, AA graphite furnace (HBr-Br_2) ____________________
☐ Au, AA graphite furnace (HF) ____________________
☐ B, ICP-AES ____________________
☐ C, total combustion ____________________
☐ Cl, ion-selective electrode ____________________
☐ F, ion-selective electrode (Na_2CO_3-K_2CO_3-KNO_3) ____________________
☐ Hg, AA cold vapor ____________________

Analyst sign and date   Instrument no.

☐ S, total combustion ____________________
☐ S, iodometric titration ____________________
☐ Se, AA hydride generation ____________________
☐ Te, AA flame (HF) ____________________
☐ Tl, AA flame (HF) ____________________
☐ U, UV-fluorescence ____________________
☐ U, Th delayed neutron counting ____________________
☐ W, visible absorption spec. ____________________
☐ Rb, Sr, Y, Nb, Zr
☐ Ba, La, Ce, minors
☐ Cu, Ni, Zn
☐ Cr
} EDXRF ____________________
☐ CO_2, coulometric titration ____________________
☐ FeO, potentiometric titration ____________________
☐ $\pm H_2O$ ____________________
☐ K_2O, flame photometric ____________________
☐ Na_2O, flame photometric ____________________

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[1] Use asterisk (*) to denote contact person for multiple submitters.

[2] Please note known or suspected mineralized samples on coding sheet; note suspected high-concentrated elements.

ANALYTICAL GEOCHEMISTRY

NON-OPERATIONS

METHOD/ELEMENTS	ANALYST	COMP. DATE	INSTRUMENT USED	REFERENCE MATERIAL	SPIKE and/or DUPLICATE SAMPLE RESULTS

The methods used for nonroutine analyses may not be completely documented, therefore, the data should be used with caution.

REQUEST FOR ANALYSIS (RFA)

Revised 8/90

SUBMITTER[1] ____________
ADDRESS ____________
____
PHONE NUMBER ____________
PROJECT TITLE ____________
PROJECT NUMBER ____________
PROGRAM NUMBER ____________
If previous work was done on these samples, list job numbers: ____________

U.S. GEOLOGICAL SURVEY
BRANCH OF GEOCHEMISTRY
345 MIDDLEFIELD ROAD, MS 938
MENLO PARK, CA 94025

Branch Chief Approval ____________
(if required by Submitter's Branch)
QA Approval ____________

SAMPLE TYPE[2]: rock, stream-sediment, soil, water, plant, coal, concentrate, other: ____________

NUMBER OF SAMPLES ____________
PREP INSTRUCTIONS:
Special Requirements ____________
____
____
____

Disposition of Bulk:
☐ Discard
☐ Return to Submitter
Mineralogy by ____________

PAGE 1 OF ____________
FOR BGC USE ONLY:
JOB NUMBER ____________
LAB NUMBER ____________
Date received ____________
Counted and scanned by ____________
Shelf ____________

PREP LAB
Prepared by ____________
Notes ____________
____
QC ____________

OPERATIONS GEOCHEMISTRY METHODS

Check technique(s) necessary for your study. Non-operations methods available through arrangement with the Chief, Analytical Geochemistry Section. Notate on reverse side.

Analyst sign and date Instrument no.

☐ 40-element, ICP-AES ____________
☐ 10-element, ICP-AES ____________
☐ 35/37-element, dc-ARC AES ____________
☐ Major elements as oxides, WDXRF ____________
☐ INA short count (long count is analytical) ____________
☐ As, AA hydride generation ____________
☐ Au, AA flame ($HBr-Br_2$) ____________
☐ Au, AA flame (HF) ____________
☐ Au, AA graphite furnace ($HBr-Br_2$) ____________
☐ Au, AA graphite furnace (HF) ____________
☐ B, ICP-AES ____________
☐ C, total combustion ____________
☐ Cl, ion-selective electrode ____________
☐ F, ion-selective electrode ($LiBO_2$) ____________
☐ Hg, AA cold vapor ____________

Analyst sign and date Instrument no.

☐ S, total combustion ____________
☐ S, iodometric titration ____________
☐ Se, AA hydride generation ____________
☐ Te, AA flame (HF) ____________
☐ Tl, AA flame (HF) ____________
☐ U, UV-fluorescence ____________
☐ U, Th delayed neutron counting ____________
☐ W, visible absorption spec. ____________
☐ Rb, Sr, Y, Nb, Zr
☐ Ba, La, Ce, minors — EDXRF ____________
☐ Cu, Ni, Zn
☐ Cr
☐ CO_2, coulometric titration ____________
☐ FeO, potentiometric titration ____________
☐ $\pm H_2O$ ____________
☐ K_2O, flame photometric ____________
☐ Na_2O, flame photometric ____________

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Revised 8/90

SUBMITTER[1] ____________
ADDRESS ____________
____
PHONE NUMBER ____________
PROJECT TITLE ____________
PROJECT NUMBER ____________
PROGRAM NUMBER ____________
If previous work was done on these samples,
list job numbers: ____________

U.S. GEOLOGICAL SURVEY
BRANCH OF GEOCHEMISTRY
National Center, MS 972
12201 Sunrise Valley Dr.
Reston, VA 22092

Branch Chief Approval ____________
(if required by Submitter's Branch)
QA Approval ____________

SAMPLE TYPE[2]: rock, stream-sediment, soil, water, plant, coal, concentrate, other: ____________

NUMBER OF SAMPLES ____________
PREP INSTRUCTIONS:
Special Requirements ____________
____
____
____

Disposition of Bulk:
☐Discard
☐Return to Submitter
Mineralogy by ____________

PAGE 1 OF ____________
FOR BGC USE ONLY:
JOB NUMBER ____________
LAB NUMBER ____________
Date received ____________
Counted and scanned by ____________
Shelf ____________

PREP LAB

Prepared by ____________
Notes ____________
____
QC ____________

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Analyst sign and date   Instrument no.

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☐10-element, ICP-AES ____________
☐35/37-element, dc-ARC AES ____________
☐Major elements as oxides, WDXRF ____________
☐INA short count (long count is analytical) ____________
☐As, AA hydride generation ____________
☐Au, AA flame ($HBr-Br_2$) ____________
☐ Au, AA flame (HF) ____________
☐ Au, AA graphite furnace ($HBr-Br_2$) ____________
☐ Au, AA graphite furnace (HF) ____________
☐B, ICP-AES ____________
☐C, total combustion ____________
☐Cl, ion-selective electrode ____________
☐F, ion-selective electrode (Na_2CO_3-ZnO) ____________
☐Hg, AA cold vapor ____________

Analyst sign and date   Instrument no.

☐S, total combustion ____________
☐S, iodometric titration ____________
☐Se, AA hydride generation ____________
☐Te, AA flame (HF) ____________
☐Tl, AA flame (HF) ____________
☐U, UV-fluorescence ____________
☐U, Th delayed neutron counting ____________
☐W, visible absorption spec. ____________
☐Rb, Sr, Y, Nb, Zr
☐Ba, La, Ce, minors — EDXRF ____________
☐Cu, Ni, Zn
☐Cr
☐CO_2, coulometric titration ____________
☐FeO, potentiometric titration ____________
☐$\pm H_2O$ ____________
☐K_2O, flame photometric ____________
☐Na_2O, flame photometric ____________

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ANALYTICAL GEOCHEMISTRY

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QUALITY ASSURANCE IRREGULARITY REPORT

No.______

Part I

Date:____________________

Job number:____

Sample number(s) involved:______________________________________

Nature of QA irregularity:______________________________________

Name of analyst who performed work:______________________________

Signed: _________________
QA Coordinator

Part II

Steps taken to investigate irregularity:___________________________

Explanation of probable cause:__________________________________

Steps taken to prevent future occurrence:__________________________

Signed:___________________
Date:____________________

APPENDIX D GLOSSARY

A brief discussion of essential terms and symbols.

Accuracy--The difference between the mean value and the true value.

Bias--"A systematic error due to the experimental method that causes the measured value to deviate from the true value" (U.S. EPA, 1979, p. 7-3).

Blank--"The measured value obtained when a specified component of a sample is not present during the measurement" (Taylor, 1987, p. 245).

Blind sample--"A sample submitted for analysis whose composition is known to the submitter but is unknown to the analyst".

Calibration--"Comparison of a measurement standard or instrument with another standard or instrument to report or eliminate by adjustment any variation (deviation) in the accuracy of the item being compared".

Certified reference material (CRM)--A reference material, one or more of whose property values are certified by a technically valid procedure traceable to a documentation which is issued by a certifying body (see Taylor, 1987, p. 246).

Confidence Interval--"That range of values, calculated from an estimate of the mean and standard deviation, which is expected to include the population mean with a stated level of confidence".

Control limit--The limits on a control chart beyond which it is highly improbable that a point could lie while the system is in a state of statistical control.

Control chart--A graphical plot of test results against time within which limits around the average value define a state of control.

d--Difference of means,

$$d=|\bar{X}_1\bar{X}_2|$$

where $\bar{X}$ is the arithmetic mean.

Detection limit--"The smallest concentration. . . that can be measured by a single measurement with a stated level of confidence" (see Taylor, 1987, p. 247).

Double blind--A sample known by the submitter but neither its composition nor its identification is known to the analyst (Taylor, 1987, p. 247).

Duplicate sample--A second sample randomly selected to assist in the evaluation of sample variance (Taylor, 1987, p. 248).

k--The number of subgroups under consideration

n--The number of observed values.

Precision--The degree of agreement between values under repetitive testing of a sample.

Quality assurance--A program to continually monitor the reliablity of the results reported and to assure that a product or service meets defined standards of quality.

Quality control--The in-house system associated with a method test that ensures the results are satisfactory.

R--**Sample range**, the difference between the maximum and minimum values of a data set.

$\bar{R}$--Average range,

$$\bar{R}=(R_1+R_2+. . . +R_k)/k$$

where R is the sample range and k is the number of sets of duplicate samples.

Reference material (RM)--A substance, one or more properties of which are sufficiently well established to be used for the calibration of an appartus, the assessment of a measurement method, or for the assignment of values to materials (Taylor, 1987, p. 251).

Relative_standard deviation (RSD)--The ratio of standard deviation, s to the average X, expressed as a percentage.

$$RSD= \frac{s}{\bar{X}} \times 100$$

Significant figures--The method of expression of the precision of a determination to include all digits known with certainty and the first doubtful digit.

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) (Advisory Board, 1989, p. 93), that is,

$$s=\left[\sum_{i=1}^{n} (X_i-\bar{X})^2/n-1\right]^{\frac{1}{2}}$$

where X_i is the value of individual results, $\bar{X}$ is the arithmetic mean and n is the number of results in the set.

s_d--Standard deviation for duplicate measurements,

$$s_d= \sqrt{\Sigma R^2/2k}$$

where R is the difference between the duplicate results and k is the number of sets of duplicate samples (Taylor, 1987, p. 22).

$\bar{s}$--**Pooled standard deviation**, or new cumulative standard deviation

$$\bar{s}=\sqrt{v_1s^2{}_1+v_2s^2{}_2+.\ .\ .+v_ks^2{}_k/v_1+v_2+.\ .\ .+v_k}$$

where v is the degrees of freedom and **s** is the standard deviation.

Standard reference material (SRM)--A reference material distributed and certified by the National Bureau of Standards (Taylor, 1987, p. 252).

t--**Student t variate**, the value for t will depend on the number of degrees of freedom and the level of the confidence desired. It is obtained from statistic tables.

U--**Uncertainty of the difference**,

$$U=ts(n_1+n_2/n_1n_2)$$

where t is the student t variate, s is the pooled standard deviation, and **n** is the number of values.

v--**Degrees of freedom**, signifies the number of independent estimates that could be obtained from a specific set of data, n-1. (Taylor, 1987, p. 21).

Validation--"The process by which a sample measurement method or a piece of data is deemed useful for a specific purpose".

Warning limits--"The limits shown on a control chart within which most of the test results are expected to lie (within a 95% probability) while the system remains in a state of statistical control" (Taylor, 1987, p. 253).

X--"Observed values of a measurable characteristic; specific observed values are designated X_1, X_2, X_3, etc." (Committee E-11 on Statistical Methods, 1985, p. 2).

$\bar{X}$--**Arithmetic mean**, is the sum of the **n** observed values in a sample set divided by **n**.

$$\bar{X}=(X_1+X_2+.\ .\ .+X_n)/n$$

$\bar{\bar{X}}$--**Pooled mean**, or the weighted average of the means

$$\bar{\bar{X}}=(n_1\bar{X}_1+n_2\bar{X}_2+.\ .\ .+n_n\bar{X}_n)/n_1+n_2+.\ .\ .+n_n$$

based on different numbers of measurements (Taylor, 1987, p. 32).