



# Analytical methods for chemical analysis of geologic and other materials, U.S. Geological Survey

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**U.S. DEPARTMENT OF THE INTERIOR  
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## Analytical Methods

### Method codes

#### CHAPTER A Sample Preparation

##### A1 Rock sample preparation.

Cliff D. Taylor and Peter M. Theodorakos..... Q010

##### A2 Stream-sediment sample preparation.

Thomas R. Peacock, Cliff D. Taylor and Peter M. Theodorakos..... Q020

##### A3 Soil sample preparation.

Thomas R. Peacock..... Q030

#### CHAPTER B

##### Plant material preparation and determination of weight percent ash.

Thomas R. Peacock and James G. Crock ..... Q050,T17

#### CHAPTER C

##### Dry moist samples to constant weight under ambient conditions, calculate % moisture.

Steve A. Wilson and Matt Herron..... T18

#### CHAPTER D

##### Conductivity measured using a self contained Myron L Digital DS Meter model DC4.

Peter M. Theodorakos..... T28

#### CHAPTER E

##### Automated preset endpoint (4.5) total alkalinity titration using the Orion 960 Autochemistry system.

Peter M. Theodorakos ..... T04

#### CHAPTER F

##### The determination of twenty-seven elements in aqueous samples by inductively coupled plasma-atomic emission spectrometry.

Paul H. Briggs ..... E080,T02,T03

#### CHAPTER G

##### The determination of forty elements in geological and botanical samples by inductively coupled plasma-atomic emission spectrometry.

Paul H. Briggs ..... E011,T01

#### CHAPTER H

##### The determination of forty-four elements in aqueous samples by inductively coupled plasma - mass spectrometry.

Paul J. Lamothe, Allen L. Meier, and Stephen A. Wilson..... T21,T23





## INTRODUCTION

This manual presents validated analytical methods used by the Mineral Resources Team, Geologic Division. The manual updates the methods manual edited by Belinda Arbogast, Open-File Report 96-525 published in 1996. This edition contains a few methods that have not changed significantly from the 1996 edition, a number of methods that are essentially the same but involve changes in instrumentation or minor changes in the procedure, and a number of new methods that were recently developed and approved.

This manual is intended primarily for use by laboratory scientists; but can also assist laboratory users to evaluate the data they receive. The analytical methods are written in a step by step approach so that they may be used as a training tool and provide detailed documentation of the procedures for quality assurance. This manual is also available on the Internet at <http://geology.cr.usgs.gov/pub/open-file-reports/ofr-02-0223>.

## SAFETY POLICY<sup>1</sup>

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

<sup>1</sup> Sutley, 1994

## **ANALYTICAL METHOD FORMAT**

The written analytical methods contained in this volume reflect the procedures actually being used in the laboratory. Routine methods are written in the following standard format:

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

**PRINCIPLE**—brief discussion of the scientific basis

**INTERFERENCE**—physical or chemical conditions or processes which cause analytical error.

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

**APPARATUS**—instruments and special equipment required

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

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

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

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

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

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

## **METHOD VALIDATION**

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

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

## DEFINITION OF TERMS

### Limit of Detection

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

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

### Lower Reporting Limit

The terms "lower reporting limit", "lower limits of determination" and "lower limits of quantification" are confusing in the literature, and are described as either 5 sigma to 10 sigma. In this report the terms will be used for concentrations expected to be at or above five times the standard deviation determined from the method blank or low analyte concentration samples. Because of the different definitions given for these terms in the literature, the method descriptions will give the information in tables as 3s and 5s numbers. Given the varied matrices submitted to the laboratory and diverse data quality needs, these tables of method-blank and reference material results are included to assist in appropriate use of laboratory data.

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

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

### Limit of Quantitation

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

## ANALYTICAL PERFORMANCE SUMMARY

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

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

### Reference Materials

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

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

**REFERENCE** – sample name of the geochemical reference material

**DESCRIPTION** – identification of the reference material

*n* – number of observed measurements or samples in a subgroup

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

*s* – standard deviation

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

**bold typeface** indicates precision better than 10 percent relative (two sigma), normally based on five or more results from two or more independent techniques

certified value from the distributor of reference materials is designated “*cv*”

plain typeface indicates other compiled data; distinguished by a {?} question mark if there is additional uncertainty (for example, fewer than 3 reported results, large disparity in reported results, and/or data derived from only one non-definitive technique)

*italic typeface* indicates data abstracted from individual schemes of analysis fully described in the literature

**%RSD** – percent relative standard deviation

**%R** – percent recovery = (determined value/*pv*) x 100

## Duplicate Samples

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

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

$k$  – number of subgroups under consideration

$n-2$ , number of samples in the subgroup

*Mean* – arithmetic mean for duplicate measurements

$s$  – standard deviation for duplicate measurements

*%RSD* – relative standard deviation

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

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

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

## Method Blank

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

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

$n$  – number of observed measurements on completely independently prepared blanks

*Mean* – arithmetic mean

$s$  – standard deviation

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

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

If the chapter author thinks the reporting limits should not be the same as the  $3s$  and  $5s$  determinations on blanks, then a separate table of reporting limits will be included in that chapter.

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