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Techniques of Water-Resources Investigations
of the United States Geological Survey

Chapter A1

METHODS FOR DETERMINATION OF INORGANIC SUBSTANCES IN WATER AND FLUVIAL SEDIMENTS

By Marvin J. Fishman and Linda C. Friedman, Editors

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PREFACE

A series of chapters on techniques describes methods used by the U.S. Geological Survey for planning and conducting water-resources investigations. The material is arranged under major subject headings called books and is further subdivided into sections and chapters. Book 5 is on laboratory analyses; section A is on water. The unit of publication, the chapter, is limited to a narrow field of subject matter. "Methods for Determination of Inorganic Substances in Water and Fluvial Sediments" is the first chapter under section A of book 5. The chapter number includes the letter of the section.

This chapter was prepared with the assistance of many chemists and hydrologists of the U.S. Geological Survey as a means of documenting and making available the methods used by the U.S. Geological Survey to analyze water, water-sediment mixtures, and sediment samples.

Any use of trade names, commercial products, manufacturers, or distributors is for descriptive purposes only and does not imply endorsement by the U.S. Geological Survey.

This chapter supersedes "Methods for Determination of Inorganic Substances in Water and Fluvial Sediments" by M. W. Skougstad, M. J. Fishman, L. C. Friedman, D. E. Erdmann, and S. S. Duncan (U.S. Geological Survey Techniques of Water-Resources Investigation, book 5, chapter A1, 1979) and "A Supplement to Methods for the Determination of Inorganic Substances in Water and Fluvial Sediments" by M. J. Fishman and W. L. Bradford (U.S. Geological Survey Open-File Report 82-272, 1982).

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TECHNIQUES OF WATER-RESOURCES INVESTIGATIONS OF THE U.S. GEOLOGICAL SURVEY

The U.S. Geological Survey publishes a series of manuals describing procedures for planning and conducting specialized work in water-resources investigations. The manuals published to date are listed below and may be ordered by mail from the U.S. Geological Survey, Books and Open-File Reports Section, Federal Center, Box 25425, Denver, Colorado 80225 (an authorized agent of the Superintendent of Documents, Government Printing Office).

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METHODS FOR DETERMINATION OF INORGANIC SUBSTANCES IN WATER AND FLUVIAL SEDIMENTS

By Marvin J. Fishman and Linda C. Friedman, editors

Abstract

Chapter A1 of the laboratory manual contains methods used by the U.S. Geological Survey to analyze samples of water, suspended sediments, and bottom material for their content of inorganic constituents. Included are methods for determining the concentration of dissolved constituents in water, the total recoverable and total of constituents in water-suspended sediment samples, and the recoverable and total concentrations of constituents in samples of bottom material. The introduction to the manual includes essential definitions and a brief discussion of the use of significant figures in calculating and reporting analytical results. Quality control in the water-analysis laboratory is discussed, including the accuracy and precision of analyses, the use of standard-reference water samples, and the operation of an effective quality-assurance program. Methods for sample preparation and pretreatment are given also.

A brief discussion of the principles of the analytical techniques involved and their particular application to water and sediment analysis is presented. The analytical methods of these techniques are arranged alphabetically by constituent. For each method, the general topics covered are the application, the principle of the method, the interferences, the apparatus and reagents required, a detailed description of the analytical procedure, reporting results, units and significant figures, and analytical precision data, when available. More than 125 methods are given for the determination of 70 inorganic constituents and physical properties of water, suspended sediment, and bottom material.

Introduction

The Department of the Interior has a basic responsibility for the appraisal, conservation, and efficient utilization of the Nation's natural resources. As one of several Interior agencies, the U.S. Geological Survey's primary function in relation to water is to assess its availability and utility as a national resource for all uses. The U.S. Geological Survey's responsibility for water appraisal includes not only assessments of the location, quantity, and availability of water, but also determinations of water quality. Inherent in this responsibility is the need for extensive water-quality studies related to the physical, chemical, and biological adequacy of natural and developed surface- and groundwater supplies. Included, also, is a need for supporting research to increase the effectiveness of these studies.

As part of its mission the U.S. Geological Survey is responsible for generating a large part of the water-quality data for rivers, lakes, and ground water that is used by planners, developers, water-quality managers, and pollution-control agencies. A high degree of reliability and standardization of these data is paramount.

This chapter is one of a series that documents and makes available data-collection and analysis procedures used by the U.S. Geological Survey. The series describes procedures for planning and executing specialized work in water-resources investigations. The unit of publication, the chapter, is limited to a narrow field of subject matter. This format permits flexibility in revision and publication as necessary. For convenience the chapters on methods for water-quality analysis are grouped into the following categories:

- Inorganic substances
- Minor elements by emission spectroscopy
- Organic substances
- Aquatic biological and microbiological samples
- Radioactive substances
- Quality assurance

Provisional drafts of new or revised analytical methods are distributed to field offices of the U.S. Geological Survey for their use. These drafts are subject to revision based on use or because of advancement in knowledge, techniques, or equipment. After a method is sufficiently developed and confirmed, it is incorporated in a supplement to the chapter or in a new edition of the chapter and is then available from the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402.

Purpose

Rapid changes in technology are constantly providing new and improved methods for the study of water-quality characteristics. Therefore, methods manuals must be updated frequently in order to gain the advantages of improved technology. The purpose of this chapter is to record and disseminate methods used by the U.S. Geological Survey to analyze samples of water, suspended sediment, and bottom material collected in water-quality investigations. This chapter is an update of Techniques of Water-Resources Investigation (TWRI) of the U.S. Geological Survey, book 5, chapter A1, "Methods for determination of inorganic substances in water and fluvial sediments," by Skougstad and others, published in 1979 and of a supplement published by Fishman and Bradford in 1982.

Although excellent and authoritative manuals on water analysis are available (American Public Health Association and others, 1980; American Society for Testing and Materials, 1978, 1984), most of them emphasize primarily either municipal, industrial, or agricultural water utilization. No single reference or combination meets all requirements as a guide to the broader phases of water-quality investigations conducted by the U.S. Geological Survey. These investigations are intended to define the chemical, physical, and biological characteristics of the Nation's surface- and ground-water resources, as well as to indicate the suitability of these resources for various beneficial uses.

Scope

This manual includes techniques and procedures suitable for the analysis of representative samples of water and fluvial sediments. The methods and techniques include:

Gravimetry
Titrimetry
Atomic absorption spectrometry
Atomic emission spectrometry
Colorimetry
Electrometry
Ion-exchange chromatography
Sample preparation and pretreatment
Calculation methods

For each method, the general topics covered are application, principle of the method, interferences, apparatus and reagents required, a detailed description of the analytical procedure, reporting results, units and significant figures, and analytical precision data, when available. Each method, where applicable, applies to the determination of constituents in solution (dissolved), the determination of total or total recoverable constituents (substances both in solution and adsorbed on or a part of suspended sediment), and finally the determination of total or recoverable constituents from samples of bottom material.

This chapter includes methods for determining the following constituents and physical properties:

Dissolved constituents and physical properties

Acidity
Alkalinity
Aluminum
Antimony
Arsenic
Barium
Beryllium
Boron
Bromide
Cadmium
Calcium
Carbon-dioxide
Chloride
Chromium
Chromium(VI)
Cobalt
Copper
Cyanide
Fluoride
Hardness
Hardness, non-carbonate
Iodide

Dissolved constituents and physical properties—Continued

- Iron
- Lead
- Lithium
- Magnesium
- Manganese
- Mercury
- Molybdenum
- Nickel
- Nitrogen, ammonia
- Nitrogen, ammonia plus organic
- Nitrogen, nitrate
- Nitrogen, nitrite
- Nitrogen, nitrite plus nitrate
- pH
- Phosphorus
- Phosphorus, orthophosphate plus hydrolyzable
- Phosphorus, orthophosphate
- Phosphorus, hydrolyzable plus organic
- Potassium
- Selenium
- Silica
- Silver
- Sodium
- Sodium adsorption ratio
- Sodium, percent
- Solids, sum of constituents
- Solids, nonvolatile-on-ignition
- Solids, volatile-on-ignition
- Solids, residue on evaporation at 105 °C
- Solids, residue on evaporation, at 180 °C
- Specific conductance
- Strontium
- Sulfate
- Thallium
- Tin
- Vanadium
- Zinc

Suspended constituents

- Solids, nonvolatile-on-ignition
- Solids, volatile-on-ignition
- Solids, suspended, residue at 105 °C

Total recoverable constituents and physical property

- Aluminum
- Barium
- Beryllium
- Boron
- Cadmium
- Calcium
- Chromium
- Cobalt
- Color
- Copper
- Iron
- Lead
- Lithium
- Magnesium
- Manganese
- Mercury
- Molybdenum
- Nickel
- Potassium
- Silver
- Sodium
- Strontium
- Tin
- Zinc

Total constituents and physical properties

- Antimony
- Arsenic
- Cyanide
- Density
- Fluoride
- Nitrogen, ammonia
- Nitrogen, ammonia plus organic
- Nitrogen, nitrite
- Nitrogen, nitrite plus nitrate
- Oxygen demand, chemical
- Phosphorus
- Phosporus, orthophosphate plus hydrolyzable
- Phosphorus, orthophosphate
- Phosphorus, hydrolyzable plus organic
- Selenium
- Solids, nonvolatile-on-ignition
- Solids, residue on evaporation at 105 °C
- Solids, volatile-on-ignition
- Sulfide
- Turbidity

Constituents recoverable from bottom material

- Aluminum
- Barium
- Beryllium
- Boron
- Cadmium
- Calcium
- Chromium
- Cobalt
- Copper
- Iron
- Lead
- Lithium
- Magnesium
- Manganese
- Mercury
- Molybdenum
- Nickel
- Potassium
- Sodium
- Strontium
- Zinc

Total constituents in suspended or bottom material

- Aluminum
- Antimony
- Arsenic
- Boron
- Cadmium
- Calcium
- Chromium
- Cobalt
- Copper
- Cyanide
- Iron
- Lead
- Lithium
- Magnesium
- Manganese
- Nickel
- Nitrogen
- Nitrogen, ammonia
- Nitrogen, ammonia plus organic

Total constituents in Suspended or bottom material—continued

Nitrogen, nitrite plus nitrate	Silica
	Sodium
Oxygen demand, chemical	Solids, volatile on ignition
	Strontium
Phosphorus	Titanium
Potassium	Zinc
Selenium	

Each method is identified by one or more four-digit numbers preceded by a letter. The letter prefix designates whether the method applies to a physical characteristic (P), an inorganic substance (I), an organic substance (O), a radioactive substance (R), a biological characteristic or determination (B), an element determined by emission spectrographic method (E), or a sediment characteristic (S). The first digit of the identifying number indicates the type of determination (or procedure) for which the method is suitable, according to the following:

0--------Sample preparation.
1--------Manual method for dissolved constituents.
2--------Automated method for dissolved constituents.
3--------Manual method for analyzing water-suspended sediment mixtures.
4--------Automated method for analyzing water-suspended sediment mixtures.
5--------Manual method for analyzing samples of bottom material.
6--------Automated method for analyzing samples of bottom material.
7--------Method for suspended constituents.

The last three digits are unique to each method. Additionally, each method number has an appended two-digit number designating the year of last approval of that method. If revisions of a method are issued within the calendar year of last approval, suffixes A, B, and so forth are added to the year designation to identify such a subsequent revision. This numbering system simplifies the identification of each method and the updating of the chapter as new or revised methods are introduced.

Definitions

Reporting the results of analyses of water and fluvial sediment samples requires the use of several terms that are based on the combination of physical phases sampled (water or sediments) and the analytical methods used. These terms are defined below.

Dissolved.—Pertains to the constituents in a representative water sample that pass through a 0.45-μm membrane filter. The "dissolved" constituents are determined from subsamples of the filtrate. This convenient operational definition is used by Federal agencies that collect water data.

Suspended, recoverable.—Pertains to the constituents in a representative water sample that are retained on a 0.45-μm membrane filter and that are brought into solution by digestion (usually by using a dilute acid solution). Complete dissolution of all the particulate matter is often not achieved by the digestion treatment, and thus the determination may represent less than the "total" amount (that is, less than 95 percent) of the constituent in the sample. To achieve comparability of analytical data, equivalent digestion procedures would be required of all laboratories performing such analyses, because different digestion procedures are likely to produce different analytical results.

Determinations of "suspended, recoverable" constituents are made either by analyzing portions of the material collected on the filter or, more commonly, by calculating the difference between the dissolved and the total recoverable concentrations of the constituent.

Suspended, total.—Pertains to the constituents in a representative water sample that are retained on a 0.45-μm membrane filter. This term is used only when the analytical procedure assures measurement of at least 95 percent of the constituent determined. A knowledge of the expected form of the constituent in the sample, as well as of the analytical methodology used, is required to determine when the results should be reported as "suspended, total."

Determinations of "suspended, total" constituents are made either by analyzing portions of the material collected on the filter or, more commonly, by calculating the difference between the

dissolved and the total concentrations of the constituent.

Total, recoverable.—Pertains to the constituents in solution after a representative water-suspended sediment sample is digested (usually by using a dilute acid solution). Complete dissolution of all particulate matter is often not achieved by the digestion treatment, and thus the determination may represent less than the "total" amount (that is, less than 95 percent) of the constituent in the dissolved and suspended phases of the sample. To achieve comparability of analytical data, equivalent digestion procedures would be required of all laboratories performing such analyses, because different digestion procedures are likely to produce different analytical results.

Total.—Pertains to the constituents in a representative water-suspended sediment sample, regardless of the constituent's physical or chemical form. This term is used only when the analytical procedure assures measurement of at least 95 percent of the constituent in both the dissolved and the suspended phases of the sample. A knowledge of the expected form of the constituent in the sample, as well as of the analytical methodology used, is required to judge when the results should be reported as "total." (Note that the word "total" indicates both that the sample consists of a water-suspended sediment mixture and that the analytical method determines all of the constituent in the sample).

Recoverable from bottom material.—Pertains to the constituents in solution after a representative sample of bottom material is digested (usually using an acid or mixture of acids). Complete dissolution of all bottom material is often not achieved by the digestion treatment, and thus the determination may represent less than the total amount (that is, less than 95 percent) of the constituent in the sample. To achieve comparability of analytical data, equivalent digestion procedures would be required of all laboratories performing such analyses, because different digestion procedures are likely to produce different analytical results.

Total in bottom material.—Pertains to the constituents in a representative sample of bottom material. This term is used only when the analytical procedure assures measurement of at least 95 percent of the constituent determined. A knowledge of the expected form of the constituents in the sample, as well as of the analytical methodology used, is required to judge when the results should be reported as "total in bottom material."

A description of an analytical method must compare the result obtained by the method with the value that is sought, which is usually the true concentration of the chemical substance in the sample. Definitions of terms that are used for this purpose are given below.

Accuracy.—A measure of the degree of conformity of the values generated by a specific method or procedure with the true value. The concept of accuracy includes both bias (systematic error) and precision (random error).

Bias.—A persistent positive or negative deviation of the values generated by a specific method or procedure from the true value, expressed as the difference between the true value and the mean value obtained by repetitive testing of the homogeneous sample.

Limit of detection.—The minimum concentration of a substance that can be identified, measured, reported with 99-percent confidence that the analyte concentration is greater than zero, and determined from analysis of a sample in a given matrix containing analyte.

Precision.—The degree of agreement of repeated measurements by a specific method or procedure, expressed in terms of dispersion of the values generated about the mean value obtained by repetitive testing of a homogeneous sample.

Significant figures

The significant figures used by the U.S. Geological Survey in reporting the results of analysis in milligrams or micrograms per liter represent a compromise between the desire to achieve both precision of measurement and a degree of uniformity in tabulations of analytical data. A common method used to express the precision of a determination is to include all digits known with certainty and the first (and only the first) doubtful digit. This method has one obvious disadvantage: published data so reported may not be interpreted to mean the same thing by all users of the data.

Table 1.—Factors for converting milligrams per liter to milliequivalents per liter
[1975 atomic weights]

Ion	Sum of atomic weights	Conversion factor	Ion	Sum of atomic weights	Conversion factor
Ag^{+1}	107.868	0.00927	I^{-1}	126.9045	0.00788
Al^{+3}	26.9815	.11119	K^{+1}	39.0983	.02558
As^{+3}	74.9216	.04004	Li^{+1}	6.941	.14407
AsO_4^{-3}	138.9192	.02160	Mg^{+2}	24.305	.08229
Ba^{+2}	137.33	.01456	Mn^{+2}	54.9380	.03640
Be^{+2}	9.01218	.22192	Mn^{+4}	54.9380	.07281
BO_3^{-3}	58.8082	.05101	Mo^{+3}	95.94	.03127
Br^{-1}	79.904	.01252	Na^{+1}	22.9898	.04350
Ca^{+2}	40.08	.04990	NH_4^{+1}	18.0383	.05544
Cd^{+2}	112.41	.01779	Ni^{+2}	58.70	.03407
Cl^{-1}	35.453	.02821	NO_2^{-1}	46.0055	.02174
Co^{+2}	58.9332	.03394	NO_3^{-1}	62.0049	.01613
CO_3^{-2}	60.0092	.03333	OH^{-1}	17.0073	.05880
Cr^{+3}	51.996	.05770	Pb^{+2}	207.2	.00965
CrO_4^{-2}	115.9936	.01724	PO_4^{-3}	94.97136	.03159
CN^{-1}	26.0177	.03844	S^{-2}	32.06	.06238
Cu^{+2}	63.546	.03147	SeO_4^{-2}	142.9576	.01399
F^{-1}	18.9984	.05264	Sn^{+2}	118.69	.01685
Fe^{+2}	55.847	.03581	Sn^{+4}	118.69	.03370
Fe^{+3}	55.847	.05372	SO_4^{-2}	96.0576	.02082
H^{+1}	1.0079	.99216	Sr^{+2}	87.62	.02283
Hg^{+2}	200.59	.00997	V^{+2}	50.9415	.03926
HCO_3^{-1}	61.0171	.01639	VO^{+2}	66.9409	.02988
HPO_4^{-2}	95.97926	.02084	VO_3^{-1}	98.9397	.01011
$H_2PO_4^{-1}$	96.98716	.01031	Zn^{+2}	65.38	.03059

Chemical milliequivalents per liter are computed by multiplying the reported concentration of the individual constituents, in milligrams per liter, by the reciprocal of their equivalent weights.

The factors for the conversion of milligrams per liter to milliequivalents per liter for the more commonly determined constituents are given in table 1.

Milliequivalents per liter as reported by the Geological Survey are numerical expressions of milligrams per liter and for uniformity are carried to three decimal places regardless of the magnitude of the milligrams-per-liter value; the significant figures shown do not reflect the precision of the measurement; the milligrams-per-liter values do reflect that precision.

References

American Public Health Association, American Water Works Association, and Water Pollution Control Federation, 1985, Standard methods for the examination of water and wastewater (16th ed.): Washington, D.C., American Public Health Association, 1268 p.

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Quality control

Accuracy of analysis

Some errors are practically unavoidable in analytical work. Errors are inherent in the methods or instruments employed, or may arise from impurities in reagents and even in distilled or demineralized water. The analyst's skill and general judgment have a direct bearing on the accuracy of the analytical statement. After the chemical analysis of the water sample has been completed, the validity of the results can be evaluated by several methods. No one method of checking gives conclusive proof of the accuracy of the determinations, but the process of checking may reveal some dubious results or some additional constituents of the sample that were not considered in the analysis.

In addition, a quality assurance program is essential to ensure the validity of all analytical data (Office of Water Planning and Standards, 1976). A well-designed program must provide unbiased monitoring of the accuracy and precision of reported data and must also provide timely information to the analyst on errors and potential errors.

Within the laboratory, quality assurance should be practiced in all areas and on all levels with at least 10 percent of both dollar and manpower budgets devoted to quality-control and quality assurance activities. Operationally, a quality assurance program should consist of the standardization of all analytical methods, the preparation and use of reference materials, analysis of replicate samples, and a manual and (or) computer-assisted review of the analytical results.

Basic laboratory and field requirements

Any laboratory performing work for the U.S. Geological Survey, Water Resources Division, must be clean and free from atmospheric contaminants. Safety features and programs must meet State and Federal health and safety requirements. Personnel with education and experience in water chemistry must be involved both in performing the analyses and in supervising the laboratory.

The use of reference materials, spiked samples, and samples split between laboratories must constitute at least 15 percent of the workload for any parameter. The percentage for rarely used methods must be considerably higher. A data-review program must provide continual evaluation of the laboratory's performance.

The analysis of an improperly collected sample is meaningless. To minimize errors and variation in data due to sampling, field personnel must maintain records on sampling, including field measurements. Appropriate field measurements and information peculiar to the sample need to be supplied with the sample to the laboratory. Samples must be preserved, if required, and must be shipped without delay in bottles and containers appropriate to the determinations. Time-critical determinations need to be performed within the allowable time either in the laboratory or in the field.

Analyses performed in the field must be carefully monitored. Reference materials must be used, instruments must be calibrated regularly prior to going to the field, and personnel must be thoroughly trained for field analyses.

Chemical ionic balance

One of the most commonly used procedures for checking water analyses is the balancing of the chemical equivalents of the major ions. Because water is an electrically neutral system, the sum of the milliequivalents of the cations in solution must equal the sum of the milliequivalents of the anions. If all of the predominant ions have been determined, the milliequivalents per liter (me/L) of cations and anions should be in balance. All major ionic species must, of course, be determined and properly identified.

The hydrogen-ion content of acid water is included in the balance. The hydrogen-ion concentration is approximated from the hydrogen-ion activity as determined by the pH of the sample.

$$pH = \log_{10} \frac{1}{\alpha H^{+1}}$$

or

$$\alpha H^{+1} = 10^{-pH}$$

where αH^{+1} is the effective hydrogen-ion concentration (hydrogen-ion activity).

The calculated pH of standard solutions of sulfuric acid has been compared with determined pH, and the agreement is good up to 2.0 me/L H^{+1} (pH 2.70). Reproducibility and accuracy of ± 0.1 me/L H^{+1} is the best that can be anticipated under normal operating conditions and with most waters. Considerable error may be introduced in converting pH to hydrogen-ion concentration because of the effect of other ions on the activity of the hydrogen ion; however, this procedure is quite useful in determining acidity in low ionic strength water such as precipitation. See Kolthoff and Laitinen (1941) and Bates (1964) for a full discussion of the subject.

Table 2 gives hydrogen ion concentrations approximated from selected pH values.

Multivalent ions present difficulties in the ionic balance unless the ionic states are differentiated by the analysis. Orthophosphates may occur in water as PO_4^{-3}, HPO_4^{-2}, and $H_2PO_4^{-1}$; the proportion of each of these ions is related to the pH of the water. The PO_4^{-3} ion occurs only above about pH 10.5. Because natural waters almost never attain this pH, a general assumption can be made that the PO_4^{-3} ion is not present in natural waters. For the purpose of ionic balance, the proportion of HPO_4^{-2} and $H_2PO_4^{-1}$ present can be calculated from the pH relation as shown in table 3 for waters having pH values of 10.0 or less. If HPO_4^{-2} and $H_2PO_4^{-1}$ are included in the ionic balance, the milliequivalents per liter of alkalinity must be corrected because HPO_4^{-2} and $H_2PO_4^{-1}$ will partially titrate as alkalinity. Normally, this correction is not necessary because the concentration of phosphorus in water is seldom high enough to affect the ionic balance.

The values in table 3 were computed from the following chemical equilibrium relationships:

$$H_2PO_4^{-1} = H^{+1} + HPO_4^{-2}$$

$$K_i = \frac{[H^{+1}]\,[HPO_4^{-2}]}{[H_2PO_4^{-1}]}$$

$$\frac{[H^{+1}]}{K_i} = \frac{[H_2PO_4^{-1}]}{[HPO_4^{-2}]}$$

where

$$K_i = 6.2 \times 10^{-8}$$

Table 2.—Hydrogen-ion concentrations as approximated from observed pH values

pH	H^{+1} concentration (me/L)	pH	H^{+1} concentration (me/L)
4.25–3.85	0.1	3.05	.9
3.80–3.60	.2	3.00	1.0
3.55–3.50	.3	2.95	1.1
3.45–3.40	.4	2.90	1.3
3.35–3.30	.5	2.85	1.4
3.25–3.20	.6	2.80	1.6
3.15	.7	2.75	1.8
3.10	.8	2.70	2.0

Table 3.—Percent orthophosphate mixtures as related to pH

pH	HPO_4^{-2} (percent)	$H_2PO_4^{-1}$ (percent)	pH	HPO_4^{-2} (percent)	$H_2PO_4^{-1}$ (percent)
4.5	0.2	99.8	7.3	55.3	44.7
4.6	.2	99.8	7.4	60.9	39.1
4.7	.3	99.7	7.5	66.0	34.0
4.8	.4	99.6	7.6	71.2	28.8
4.9	.5	99.5	7.7	75.6	24.4
5.0	.6	99.4	7.8	79.7	20.3
5.1	.8	99.2	7.9	83.1	16.9
5.2	1.0	99.0	8.0	86.1	13.9
5.3	1.2	98.8	8.1	88.7	11.3
5.4	1.5	98.5	8.2	90.7	9.3
5.5	1.9	98.1	8.3	92.5	7.5
5.6	2.4	97.6	8.4	93.7	6.3
5.7	3.0	97.0	8.5	95.1	4.9
5.8	3.8	96.2	8.6	96.1	3.9
5.9	4.7	95.3	8.7	96.9	3.1
6.0	5.8	94.2	8.8	97.5	2.5
6.1	7.2	92.8	8.9	98.0	2.0
6.2	8.9	91.1	9.0	98.4	1.6
6.3	11.0	89.0	9.1	98.7	1.3
6.4	13.5	86.5	9.2	99.0	1.0
6.5	16.2	83.8	9.3	99.2	.8
6.6	19.8	80.2	9.4	99.4	.6
6.7	23.6	76.4	9.5	99.5	.5
6.8	28.2	71.8	9.6	99.6	.4
6.9	33.0	67.0	9.7	99.7	.3
7.0	38.3	61.7	9.8	99.7	.3
7.1	43.9	56.1	9.9	99.8	.2
7.2	49.5	50.5	10.0	99.8	.2

Other forms of phosphorus cannot be easily differentiated in this manner. More accurate procedures for the calculation of anionic species from pH and for the correction of activities to stoichiometric concentrations are given by Hem (1961, 1970), but such methods are not usually needed for routine water analysis.

Dissociation also must be considered in balancing analyses. Many of the determinations, particularly those for the heavy metals, do not differentiate between dissociated and undissociated constituents. Constituents that hydrolyze to give undissociated products that are determined with the ionized forms in the analysis cannot be included directly in the ionic balance. Published dissociation constants give some indication of the possible ionized concentration, but complete confidence cannot be placed in these values when considering complex solutions such as natural water.

The deviations from ionic balance can be expressed in terms of absolute quantities or as a percentage of the total ionic concentration. The analyst must use some type of sliding scale to evaluate the significance of the deviations for water of different concentrations. For example, normally, the deviation between milliequivalents per liter of cations and anions will approach 2 percent for a sample with a total (cations plus anions) milliequivalent-per-liter value of 20 and will approach 3 percent for a sample with a total milliequivalent-per-liter value of 7; however, the deviation may be as high as 12 percent for a sample with a total milliequivalent-per-liter value of 0.9.

Chemical balance is an indication of only the gross validity of the analysis. If only chemical-balance checks are used, very large errors in the determination of minor constituents can go unnoticed and compensating errors can go undetected. Large deviations indicate either a large error in one or more determinations or the presence of some undetermined constituent, but a good balance is not conclusive evidence that each of the determinations is accurate or that all constituents have been determined. Chemical balance is one tool for evaluating the validity and comprehensiveness of an analysis, but it must not be the only goal of the analyst.

Relation of residue on evaporation to calculated dissolved solids

Comparison of the residue on evaporation with the dissolved solids calculated from the analytical statement provides a rough check on the comprehensiveness of an analysis. However, the residue-on-evaporation value will be higher than the calculated dissolved solids if appreciable amounts of organic or undetermined inorganic materials are present, or if water of hydration is contained in the residue; the value will be lower if volatile solids are lost during evaporation. The calculated value may appear higher if weak acid radicals other than carbonate and bicarbonate (for example, phosphate, borate, and silicate) are included both individually and as part of the alkalinity value.

Relation of specific conductance to residue on evaporation

For most natural waters of mixed type the specific conductance, in microsiemens per centimeter at 25 °C multiplied by a factor of 0.65, approximates the residue on evaporation in milligrams per liter. This equation is not an exact relation because the conductance of a solution is dependent on the type and total quantity of ions in solution. More precise relations can be developed for specific water types.

The specific conductance in microsiemans per centimeter at 25 °C divided by 100 approximates the milliequivalents per liter of anions and cations. This relation is particularly helpful for detecting the location of error (in anions or cations), as well as for estimating the comprehensiveness of an analysis.

Precision of analysis

Each analytical procedure in this chapter includes a statement, if data are available, indicating the precision to be expected for that procedure. In general, these statements have been calculated from data obtained through

multi-laboratory analyses of test samples prepared by U.S. Geological Survey laboratories. For most procedures, precision data are within the concentration range specified; however, in some, the data do not cover the entire range, and in a few, the data are all below the lower range (for example, the determination of cobalt by direct atomic absorption spectrometry). Reference materials were not available for the latter element. At the other extreme, precision data for several procedures exceed the upper concentration limit and information is not available to determine if the samples were analyzed with or without dilution.

The precision is expressed in terms of the percent relative standard deviation, the ratio of the standard deviation to the mean times 100 percent. A convenient formula to calculate the standard deviation is

$$S_T = \sqrt{\frac{\sum_{i=1}^{n} (X_i - X)^2}{n - 1}}$$

where

i = an analysis,
n = number of analyses,
X_i = individual values of analyses,
X = average value of analyses,
and
S_T = standard deviation.

If enough data are available and if the precision appears to vary with the concentration of the constituent, the precision is also expressed in terms of a regression equation over a stated range. If the precision does not appear to vary with concentration, it has been calculated by pooling the individual standard deviations over the stated range, and the pooled standard deviation and its 95-percent confidence interval are stated.

The stated precision of the analytical method needs to be considered when interpreting analytical data. For example, a concentration of 15 mg/L for total-recoverable iron and a concentration of 17 mg/L for dissolved iron cannot be considered to be significantly different if the precision of the analysis is ±20 percent; however, these same two values are interpreted as significantly different if the analytical precision is ±5 percent.

Reference material

Reference materials must be used to monitor the analyses. Two forms of reference materials are used for water analyses: ampouled concentrates and prepared natural waters. Each type has certain advantages for quality control.

Ampouled concentrates are obtained from the U.S. Environmental Protection Agency, National Bureau of Standards, commercial sources, or are prepared by a Water Resources Division (U.S. Geological Survey) quality assurance support project, which is independent of the laboratories. Most constituents can be prepared as ampouled concentrates. These can later be diluted quantitatively with either distilled or natural water to provide a variety of matrices and final concentration levels. Such concentrates are particularly useful in method-development or method-comparison studies because data can be obtained both on precision and on percentage recovery.

Reference samples with working-level concentrations of stable constituents can be prepared in distilled or natural water. The quality assurance support project prepares a natural-water reference sample by collecting a sample of river water, running a preliminary analysis for the constituents of interest, spiking to higher levels of concentration if necessary, and stabilizing the solution. Stabilization is accomplished by filtering, stirring, and aerating quantities as large as 300 gallons of the solution for 3 days, then irradiating it with ultraviolet radiation. The prepared reference solution is then bottled and stored in sterile Teflon containers. Concentrations of the constituents in the solution are not quantitatively known, but the most probable values are determined from the mean results of determinations by several laboratories. Because these solutions are ready for immediate use without further dilution, they are suitable for introduction to the laboratory as "blind" samples for quality control purposes.

Spiked or unspiked natural water or sediment of unknown concentrations, split in a central

location and supplied simultaneously to several laboratories, is a further source of reference material. This type of reference material is of particular use in bottom-material analyses. Similarly, although probably of more limited usefulness, the duplicate samples submitted occasionally by field personnel can be evaluated for precision information.

The U.S. Geological Survey requires participation of its water laboratories in a designated quality control program. A part of this program requires frequent analysis of standard reference water samples and of blind samples of known composition. Complete records are maintained of each laboratory's performance on these reference samples, and deficiencies are promptly corrected.

The Central Laboratories

Use and documentation of standard laboratory procedures

The acceptance of a new method or the modification of an existing method for use in the U.S. Geological Survey Central Laboratories requires that several criteria be met:

1. A copy of the method in its final form and a research report must be presented. The report must include all raw analytical data used in evaluating the method, an evaluation of known and possible interferences, a single-operator-precision statement for distilled water and natural water solutions of the constituent being determined over the applicable concentration range of the method, and an estimate of the method's productivity and personnel requirements.
2. The method must be tested in one or more operating laboratories in parallel with the currently accepted method or methods for the same determination in order to develop a set of data that covers the concentration range of the method and the variety of natural water types that would be expected to occur nationwide. The evaluation of the results of this testing is the principal basis for accepting a new or modified method and for establishing its precision.
3. For general use, the proposed method should be at least equivalent to the current method with regard to precision, accuracy, limitation of interferences, productivity, and the use of hazardous or toxic substances, and should be an improvement over the current method in at least one of these areas.

Methods that do not meet all of the criteria may be conditionally accepted but are limited to the application for which they were specifically developed. Extension of the application requires additional verification.

Clear records must be maintained on the preparation of all standard solutions. All chemicals must conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, and dilution water must be distilled or demineralized (passed through mixed-bed exchange resins). The latter process must be used if ammonia- free water is necessary, and the water must be boiled immediately before use for carbon dioxide-free water.

The periodic calibration and recalibration of each instrument must be recorded by the analyst. Records must include the number of standards used, the type and date of preparation of stock solution, if applicable, and the sample identification (such as a sample number). Noticeable blank drift or changes in readings of standards must also be recorded and corrected.

The monitoring of analyses by use of reference materials must be part of the operational routine. Within the U.S. Geological Survey Central Laboratories each section chief ensures that a sufficient number both of standards and of reference materials are incorporated in each set of analyses to give confidence in the results of the set. Data are examined for indications of noticeable bias or inadequate precision; data are filed in the section and are available for regular inspection.

In addition, each section chief promptly receives and evaluates information on all reference samples submitted by the management. The largest proportion of reference materials is submitted daily by the laboratory management directly to the laboratory as unknowns. Field personnel submit to the laboratory, daily or week depending on the frequency of an analysis, samples that are totally "blind."

Analytical review procedures

Control charts for each method must be kept by the analyst and periodically reviewed by the section chief. The amount of scatter and the trends in values can then be easily spotted. Control charts on which reference samples near both the upper and lower range of the method are plotted may be particularly useful. See chapter A6 (Friedman and Erdmann, 1982) for more information on the preparation and use of control charts.

In addition to evaluating control-chart and reference-material data, the Central Laboratories quality-control staff reviews the completed analysis report for each sample prior to releasing the information. This review is aided by more than 100 computerized checks that are made prior to printing the analysis report. The computerized checks include computation of the ionic balance and comparison to an allowable-error curve; comparison of dissolved solids to specific conductance and of the dissolved solids-specific conductance ratio to predetermined expected ranges; a check on whether a total constituent concentration is equal to or greater than the corresponding dissolved concentration; and a check on the constituents known to interfere in current methodology above a certain concentration level.

The reviewer determines the validity of the individual error messages for each sample and examines the analysis report for anomalies. The reviewer must be aware of the problems in achieving a balance when multivalent ions or partially dissociated substances are present and must also be aware that the milliequivalents per liter cannot be expected to balance if the concentrations of all major ionic contributors are not determined. Likewise, the reviewer must realize that only predominant ions are checked by this equivalence and that a chemical ionic balance does not ensure accuracy, even of these major ions, because compensating errors can exist in both cations and anions.

Depending on reference-sample results or on other checks and after considering the precision of the method, the reviewer may decide to have a water-quality sample reanalyzed. The reviewer must take into account possible interferences in a method and should consider recommending to the analyst that a different method be used. The resulting concentration of the reanalysis must be examined carefully, possibly with further analyses made on the sample, before the value is accepted. If an error has been made, an updated value is entered into the data file, and a revised analytical report is generated. This report receives another check by the laboratory's quality control staff and is then released to the requestor.

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