Residue Method for Common Minor Elements

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By JOSEPH HAFFTY

SPECTROGRAPHIC ANALYSIS OF NATURAL WATER

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CONTENTS

ILLUSTRATIONS

TABLES

SPECTROGRAPHIC ANALYSIS OF NATURAL WATER

RESIDUE METHOD FOR COMMON MINOR ELEMENTS

By JOSEPH HAFFTY

ABSTRACT

A spectrographic method is described for the quantitative analysis of many minor elements in natural water. The excitation of the water residue using a direct-current arc provides a method for the detection of elements present in very low concentrations. The concentration of the elements is determined in percent of the dry residue. The results are readily expressed in parts per million by multiplying the determined percent concentration of an element by the dissolved solids content of the water sample. The method is flexible and can be applied to the analysis of water of variable composition and dissolved-solids content.

INTRODUCTION

Recently, the Geological Survey embarked on a program to utilize spectrographic techniques for determining minor elements in natural water. The use of these techniques is part of a joint program of the International Union of Geodesy and Geophysics and the U.S. Geological Survey to study world-wide runoff of dissolved solids and the geochemistry of minor elements in water. The present report describes the current spectrographic technique.

Many of the minor elements in natural waters exist in very low concentrations, therefore it is necessary that the analytical method be extremely sensitive. Preliminary experiments and a literature study of the various types of spectrochemical methods and excitation sources now in use, and which were utilized in similar problems, indicated that the excitation of the water residue using a direct-current arc would be a good choice.

Similar methods have been applied in the determination of minor elements in natural waters. In a survey of the water supplies of 24 cities, Braidech and Emery (1935) were able to determine about 30 elements spectrographically by volatilizing a few milligrams of residue. The results obtained were semiquantitative but indicated the good sensitivity attained by this procedure. The method of Gusiatskaia and Loginova (1955) converts the residue principally to sulfates by treatment with sulfuric acid but it was recognized that the concentra-

tions and relative proportions of calcium, magnesium, and sodium vary appreciably from sample to sample, causing variations in the relative intensities of the analytical lines, and, consequently, introducing analytical errors. Wolfe (1957) attempted to minimize this effect by incorporating gallium as an internal standard before the conversion of the residue to sulfates. However, as the procedure was designed for only a small number of elements, the problem was to develop a method adaptable to the determination of most of the common elements found in natural water. Since many elements are present, and since the direct-current source distills the elements into the arc in the order of their volatility, a single internal standard is precluded and advantage is taken of the "total energy" method as proposed by Slavin (1938 and 1939).

The method described here consists of the complete volatilization of 12 mg (milligrams) of water residue and synthetic standards mixed with 6 mg of spectroscopically pure graphite powder using a direct-current arc of 16 amperes. After processing the plates, the intensities of selected analytical lines are determined photometrically, emulsion calibration curves are prepared, and the concentrations of the elements are read from working curves established by the standards.

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PREPARATION OF STANDARDS

The chemical composition and physical characteristics of the matrix are important factors that affect the burning qualities of the arc and the intensities of the spectral lines. Therefore, it is important that the composition of the standard matrix material approximate the samples as closely as possible (Ahrens, 1954). The matrix of the standard was prepared to approximate the average composition of water of North America (Clarke, 1924, p. 5) and consists of 20 percent calcium as calcium carbonate, 5 percent magnesium as magnesium sulfate, 7.5 percent sodium as sodium chloride, and 2 percent potassium as potassium chloride. The matrix components were mixed together by first passing them through an 84-mesh stainless steel screen 6 or 7 times. The mixture was then transferred and mixed for 1 hour in a mortar.

Chemical compounds containing 0.1 gm of each of 22 elements of interest in the 2250–4750 A (Angstrom units) range of the spectrum were mixed in the same way as indicated above. The elements are listed in table 1 together with the wavelength of their analytical lines

TABLE 1.—*Analysis lines and concentration ranges of working curves based on synthetic water residue matrix standards*

[Asterisk indicates line-width method]

Compound used	Element	Wavelength, A		Concentration range (percent)
Ag_2O	Silver	Ag	3280. 68	0. 0001–0. 01
Al_2O_3	Aluminum	Al	3082. 16	. 0001– . 01
		Al	2660. 39	. 001–1. 0
		Al	2652. 49	. 001–1. 0
As_2O_3	Arsenic	As	2349. 84	. 1–1. 0
H_3BO_3	Boron	B	2496. 78	. 001– . 1
		B	2497. 77	. 001– . 1
$BaCO_3$	Barium	Ba	4554. 04*	. 001– . 5
BeO	Beryllium	Be	2348. 61	. 0001– . 003
		Be	3131. 07	. 001– . 03
Co_3O_4	Cobalt	Co	3453. 51	. 003– . 03
Cr_2O_3	Chromium	Cr	4254. 35*	. 0003–1. 0
		Cr	3021. 56	. 001– . 1
$CsClO_4$	Cesium	Cs	8521. 10*	. 003– . 1
CuO	Copper	Cu	3273. 96	. 0001– . 01
		Cu	3247. 54	. 0001– . 01
Fe_2O_3	Iron	Fe	2719. 03	. 001– . 1
		Fe	3025. 84	. 01–1. 0
Li_2CO_3	Lithium	Li	6707. 84*	. 0001– . 1
		Li	3232. 61	. 07–1. 0
Mn_3O_4	Manganese	Mn	2576. 10	. 001– . 1
		Mn	2949. 20	. 003– . 3
MoO_3	Molybdenum	Mo	3170. 35	. 001– . 1
NiO	Nickel	Ni	3414. 77	. 001– . 03
		Ni	3492. 96	. 001– . 03
$NaPO_3$	Phosphorus	P	2553. 28	. 1–1. 0
PbO	Lead	Pb	2833. 07	. 001–1. 0
RbCl	Rubidium	Rb	7800. 23*	. 001– . 03
		Rb	7947. 60*	. 001– . 03
SiO_2	Silicon	Si	2516. 12	. 001– . 1
		Si	2881. 58	. 001– . 1
SnO_2	Tin	Sn	2839. 99	. 001– . 1
		Sn	3175. 02	. 001– . 1
$SrCO_3$	Strontium	Sr	4607. 33*	. 001–1. 0
TiO_2	Titanium	Ti	3234. 52	. 001– . 1
		Ti	3241. 99	. 003– . 1
V_2O_5	Vanadium	V	3276. 12	. 003– . 3
ZnO	Zinc	Zn	3345. 02	. 1–1. 0

and concentration range. The final concentration of each element in this mixture was 2.29 percent.

The first standard was made to contain 1.00 percent of each element by mixing together the required weight of the minor element mixture with the matrix material. Mixing was accomplished by passing through a stainless steel screen and mixing with a mortar and pestle

as described above. The standards were made to contain the minor elements in concentrations of 1.0, 0.316, 0.1, 0.0316 . . . 0.0001 percent. As the relationship of line intensity to concentration is logarithmic, the concentrations chosen distribute the points equidistantly along the working curve. Separate standards having the same matrix and concentrations as the above standards were prepared for the rare alkali metals lithium, rubidium, and cesium as these elements have their sensitive analytical lines in the visible and near-infrared region of the spectrum. However, lithium was common to both standards.

ANALYTICAL PROCEDURE

A volume of water sample for which the content of dissolved solids had previously been determined is selected to yield 50–60 mg of residue. The water is evaporated on a steam bath in fused quartz or Vycor evaporating dishes to avoid boron or other element contamination associated with conventional laboratory equipment. The evaporating dish containing the residue is then placed under a heat lamp for about 20 minutes to remove last traces of water. The subsequent operations of scraping the residue from the sides of the dish, pulverizing and mixing with an agate pestle, and transferring the residue to a sample vial are also carried out under the heat lamp. All the items needed for the above operations are kept warm under the lamp until put to use to prevent the sample from coming in contact with cool surfaces. This is necessary to avoid moisture absorption by hygroscopic materials in the residue.

Twelve milligrams of sample and 6 mg of spectroscopically pure graphite powder are accurately weighed on a precision microbalance, mixed in a small pan, and transferred to a cupped electrode by means of a plastic funnel (which facilitates loading wihout loss of sample). Aluminum metal blocks about 4 inches long, 2 inches wide, and ½ inch thick into which several holes ¼ inch in diameter had been drilled are used to hold the sample-carrying electrodes. The aluminum electrode holders are then placed on a hot plate set at a temperature of 105° C, covered with a beaker, placed on the optical bench, and allowed to stand for about an hour before arcing. The aluminum blocks bearing the sample-carrying electrodes are kept on the hot plate until all samples are arced to prevent absorption of moisture by the residue. For quantitative work, all samples are analyzed in duplicate and arced on the same plate along with the nine standards. The average of the two determinations is reported.

All samples and standards are excited in the same manner in the direct-current arc. The series resistance is set up so that the arc is started at 5 amperes and after 10 seconds the arc is instantaneously

raised to 16 amperes by switching out a portion of the series resistance. The arc is continued for about 10 seconds beyond complete consumption of the sample (Slavin 1938 and 1939).

For emulsion calibration an iron bead arced at 5 amperes is exposed for 65 seconds through a 50 percent two-step quartz filter placed directly in front of the slit. The iron bead is formed prior to use by successively arcing portions of iron powder at 5 amperes in a large (about ¼-inch inner diameter) cupped electrode until the bead extends up above the sides of the cup. It is essential that a round-headed bead be used to obtain uniform results from plate to plate. The bead is arced until it becomes stable in its burning characteristics. A graphite rod ⅛-inch in diameter is used for the upper electrode. Preburn of the iron arc for 120 seconds is made before the iron spectrum is recorded to insure a stable reproducible burn. The wavelengths (in angstrom units) of iron lines chosen for calibration were as follows:

3157.04	3175.45	3217.34
3157.88	3178.01	3230.97
3165.01	3205.40	3233.97
3165.86	3207.09	3248.20
3168.86	3215.94	

The grating spectrograph used in this work permits a range of 2500 A of the spectrum to be covered in one exposure on two adjacent spectrographic plates. After processing the plates, transmittance measurements of selected analytical lines in the 2250–3500 A range are obtained by means of a projection comparator-microphotometer using a scanning slit at the plate. The plates are calibrated by means of a set of homologous iron lines (Hodge, 1951) using the two-step method as described by Harvey (1950). From the calibration curve constructed, intensity values are obtained from the standards which are used in constructing the working curves for the various elements, an example of which is shown in figure 1.

In the analysis of strontium, barium, and other elements whose analytical lines fall in the region of the spectrum 3500–4750 A and the rare alkalies in the region 6250–8750 A, a method of line-width measurement in use in the spectrographic laboratory of the Geochemsitry and Petrology Branch of the Geological Survey is incorporated. The microphotometer in use for this work is equipped with a constant speed scanning device. Line-widths are determined by measuring the scanning time at constant speed (0.5 mm per min) through the line by means of a stop watch. The time required to scan the line is then measured by clocking the time during which the percent transmittance remains below a selected figure. A working curve is constructed from the standards recorded on the same plate

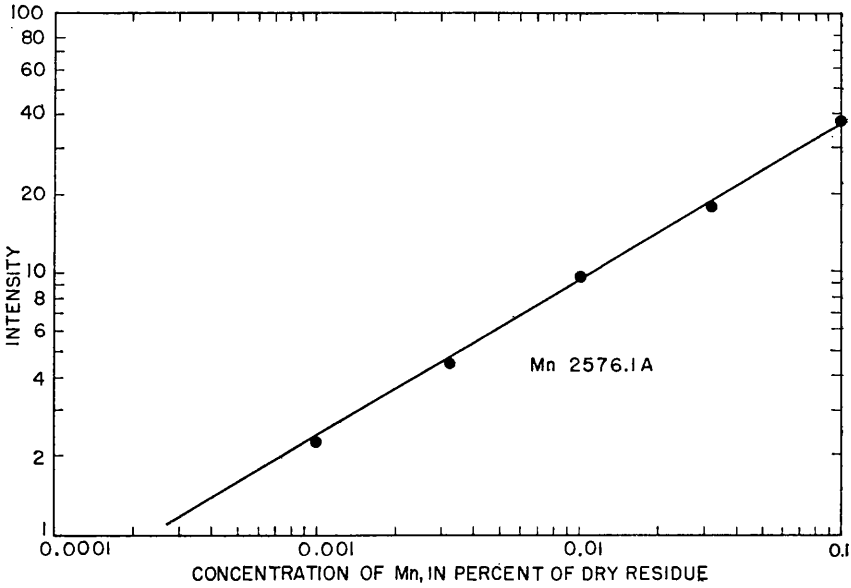

FIGURE 1.—Working curve for obtaining manganese values in natural waters.

as the unknown samples. The time in seconds is plotted linearly against the log of the percent concentration.

The concentrations of the various elements are determined in percent of the dry residue. The results are expressed in parts per million by multiplying the determined percent concentration of an element by the dissolved solids content of the water sample, for example—

100 ppm (dissolved solids) × 0.00001 (or 0.001 percent)=0.001 ppm

The following apparatus and working conditions are used:

Excitation source	A 250 volt direct-current generator is used to provide a current of 16 amperes. Series resistance is used to control the current in increments of 0.5 ampere.
Spectrograph	21-foot Wadsworth-mounted grating with 15,000 lines per inch giving a reciprocal linear dispersion of 5A per mm in the first order.
Wavelength region	2250–4750A and 6250–8750A.
Slit width	24 microns.
Illumination	Arc image focused on slit at 4× magnification by means of a quartz condensing lens. Light from the central 2-mm portion of the image at the slit is allowed to enter the spectrograph. For emulsion calibration purposes, 4 mm of the image is used.

Arc gap	Four millimeters maintained manually throughout arcing period.
Arcing exposure	10 seconds beyond complete consumption of sample.
Emulsion	Eastman type III–0 (thin) plate for wavelength range 2250–4750A, Eastman type 1–L for 6250–8750A.
Development	Type III–0 and 1–L developed for 4 minutes in Eastman D–19 developer at 20° C±½° C, with agitation using a rocking machine.
Fixing	Eastman Acid Fixer for 5 min at 20° C with agitation.
Washing	Running water for 10 min at 20° C.
Drying	Blower and heater.
Transmission	Controlled by means of neutral filters placed in the optical path.
Spectrum	First order.
Electrode, lower (anode)	Spectroscopic graphite rods ¼ in. in diameter and 1⅝ in. long. The cup (which is cut into one end) has a 0.144-in. inner diameter, a wall thickness of 0.15±0.001 in., and a 0.240±0.002 in. crater depth having a 60° truncated cone ending in a 0.031-in. diameter bottom.
Electrode, upper (cathode)	⅛-in. diameter ultra pure graphite rod, 1½ in. in length.
Exposure index	Fe 3157.0 in the calibration spectrum to give a transmittance reading of about 30 percent in the weaker step.

PRECISION AND ACCURACY

The precision of this method is illustrated by the data in table 2. The data were obtained from standards arced on various plates at different times. The elements listed were chosen to represent different orders of volatility (volatile, medium volatile, and involatile).

A measure of the accuracy is obtained by comparing the spectrographic results with those obtained by other techniques; namely, chemical and flame-photometric methods. In the absence of chemical data for the same natural water samples analyzed spectrographically, brine samples for which comparative data were available (table 3) were then selected. For the elements manganese, strontium, and iron, the spectrographic values have an average deviation of about 10 percent, 8 percent and 7 percent, respectively, from the values obtained by the other techniques. Comparative data for natural water are being obtained and evaluated to establish that the deviation for natural waters is of the same magnitude or less than that calculated for brines.

TABLE 2.—*Data on Precision of Method*

Element	*Average concentration percent*	*Coefficient of variation*	*Number of determinations*
Lead	0. 0032	5. 6	4
Chromium	. 0032	11. 9	3
Chromium	. 01	11. 6	4
Titanium	. 0032	1. 8	4
Titanium	. 01	16	4

Coefficient of variation, V, in this method, is calculated as follows:

$$V=\frac{100}{C}\sqrt{\frac{\sum d^2}{n-1}}$$

where:

C=average concentration, in percent,
d=difference of the determination from the mean,
n=number of determinations.

TABLE 3.—*Comparative results of analyses of Pennsylvania brine samples by chemical, flamephotometric, and spectrographic methods, in parts per million. The spectrographic results are the average of duplicate determinations.*

Sample	Manganese		Iron		Strontium	
	Chem.	Spec.	Chem.	Spec.	Flamephotometric	Spec.
53972	11. 6	11. 3				
53973	12. 4	12. 5	33	34		
53974	2. 5	2. 3	40	45		
53975	2. 4	2. 1	42	42		
54168	4. 1	5. 3	54	68		
54169	4. 3	5. 8	55	63		
54170	4. 5	5. 2	47	47		
54171	1. 4	1. 3	48	55		
54172	3. 7	3. 8	51	53		
54173			42	43		
54188					279	284
54189					79	59
54190					94	97
54191					64	54
54192					207	179
54193					196	192
54194					57	54
54195					62	63
54196					66	64
54197					110	101
54198					70	66
54199					79	74
54201					18	18

DISCUSSION

The method at present provides for analyzing 24 elements quantitatively. Experience in the analysis of various samples of natural water indicates that the elements listed in table 1 cover the range of minor elements that are generally found in natural water. However, 40 other elements in addition to the 24 elements for which the method provides are looked for in the spectrum of every unknown sample and when found are determined semiquantitatively. Noting the frequency with which certain additional elements occur indicates which elements are to be included in expanding the list of minor elements to be determined.

The advantage of the method is its extreme sensitivity and flexibility. Waters containing as low as 4 ppm and as high as 100,000 ppm dissolved solids have been analyzed. The matrix components and minor element content of the standards can be altered to suit the particular analytical problem at hand. For example, standards consisting of a matrix of sodium chloride and calcium carbonate in a ratio of 9:1, respectively, were used in the analysis of brines from Pennsylvania.

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