Copper-Spark Method for Spectrochemical Determination of Strontium in Water

By MARVIN W. SKOUGSTAD

CHEMISTRY OF STRONTIUM IN NATURAL WATER

GEOLOGICAL SURVEY WATER-SUPPLY PAPER 1496-B

Prepared on behalf of the U.S. Atomic Energy Commission and published with the permission of the Commission

UNITED STATES GOVERNMENT PRINTING OFFICE, WASHINGTON : 1961

UNITED STATES DEPARTMENT OF THE INTERIOR

STEWART L. UDALL, *Secretary*

GEOLOGICAL SURVEY

Thomas B. Nolan, *Director*

For sale by the Superintendent of Documents, U.S. Government Printing Office
Washington 25, D.C.

CONTENTS

ILLUSTRATIONS

TABLES

COPPER-SPARK METHOD FOR SPECTROCHEMICAL DETERMINATION OF STRONTIUM IN WATER

By MARVIN W. SKOUGSTAD

ABSTRACT

This is a rapid, reliable procedure which utilizes the copper-spark technique and an internal standard-buffer solution added in constant amount to each sample. The choice of lanthanum as an internal standard and the three convenient analytical line pairs, Sr: 4077.7/La: 4077.3, Sr: 4077.7/La: 3949.1, and Sr: 4215.5/La: 3949.1, permit the determination of strontium from 0.005 to 1.0 ppm (parts per million) in water. Twenty-five milliliters of sample is sufficient and sample preparation is simplified so that a relatively large number of samples can be conveniently and economically handled.

The average deviation of successive repeat analyses was less than 5 percent of the amount present. Recovery of strontium added in known amount to water samples of widely different chemical composition (dissolved solids) ranged from 88 to 105 percent of the amount added. Most results obtained by the spectrographic method agreed reasonably with results obtained independently by a combination ion exchange-flame photometric method.

This procedure is particularly suited to the determination of strontium in natural waters at concentration levels of less than 1.0 ppm. Although the procedure was used only for the determination of strontium, it could be used for the determination of other elements.

INTRODUCTION

The need for a rapid and reliable method for the determination of strontium in natural water led to the development of the spectrographic procedure described here. It is based on the copper-spark technique described by Fred, Nachtrieb, and Tomkins (1947) and by Nachtrieb (1950) and is a modification of the procedure use by Alexander, Nusbaum, and MacDonald (1954) for the determination of calcium, magnesium, and strontium in water.

A previous report by Horr (1959) presented a survey of methods for the quantitative determination of strontium. Strontium generally occurs in fresh water in concentrations of 0.01 to 1.0 ppm. Chemical methods for determination of strontium are not satisfactory when ap-

plied to water analysis because of the difficulty of separating the small amount of strontium from the much larger amounts of calcium and magnesium normally found in natural water. Flame photometric and spectrographic techniques offer the greatest promise for the routine determination of strontium in water where a relatively large number of samples is to be analyzed. Flame photometric methods for determination of strontium in water have been described by Horr (written communication, 1961).

Emission spectrochemical methods are commonly used for the determination of trace and minor elements in a variety of materials including natural water. Sample-handling techniques vary with the type of material being analyzed; relatively simple techniques are used for analysis of metals and alloys, where solid, electrically conducting, self-electrodes are employed. Samples of rocks, minerals, ceramics, and other nonconducting materials are prepared somewhat less easily for spectrographic analysis; however, techniques for the analysis of these materials have become common and are extensively used. The handling of solutions for spectrographic analysis involves problems that are not encountered with the handling of solids, particularly in introducing the liquid sample continuously, uniformly, and in a reproducible manner into the spark or arc.

A great variety of techniques has been proposed for introducing solutions into an arc or spark source for emission spectroscopy. Three techniques in general use are the porous-graphite cup electrode, the rotating graphite or metallic-disk electrode, and the vacuum-cup electrode. These have all been successfully used in the analysis of solutions but, nevertheless, possess certain inherent limitations, as a lack of sensitivity for certain minor elements or a lack of reproducibility. If graphite electrodes are used, a significant part of the analytical spectrum is obscured by cyanogen bands and is thus rendered useless for accurate quantitative measurements. The region of serious cyanogen-band interference ranges from about 3600 to 4200 A (angstrom units), a region which includes the two most sensitive strontium spark lines, the doublet at 4077.7 and 4215.5 A. Cyanogen-band interference can be eliminated and sensitivity can be increased by use of a rotating metallic disk (Meloche and Shapiro, 1954).

There are several alternatives to direct solution excitation. Three commonly used alternatives are: complete evaporation of solution to yield a dry residue; precipitation of the desired ions from solution to yield a precipitate for excitation; and evaporation of a small quantity of the sample solution on the flat ends of a pair of graphite or metallic electrodes. All three alternatives are currently used by the U.S. Geological Survey in the analysis of water for minor constitu-

ents. The first two alternatives are particularly useful where several elements are to be determined; the additional laboratory steps required to prepare the sample for arcing are justified when a number of elements can be determined in a single sample. These methods also possess the advantage of concentrating extremely small amounts of the sought-for elements from a large volume of sample (Haffty, 1960; Silvey, 1961).

The inherent high sensitivity of some emission spectrographic methods permits the use of extremely small amounts of sample, even for the determination of trace elements in the sample. Hence, certain elements can be determined satisfactorily from a single drop of sample that has been evaporated on the flat end of a spectroscopic electrode.

Sensitivity for trace elements is poor if untreated graphite or carbon electrodes are used because of absorption of solution by the electrodes. The sensitivity is improved by treating the electrodes with kerosene or a similar material to render them nonabsorbent; and the sensitivity is significantly increased if metallic, rather than carbon or graphite, electrodes are used. Furthermore, the use of metallic electrodes eliminates the presence of cyanogen bands that obscure the most sensitive spark lines of strontium.

The use of copper electrodes is the basis of the copper-spark method. This method offers several advantages over others, particularly if only one or a few minor constituents are to be determined. Excitation by a high voltage, condensed-spark discharge results in a high degree of reproducibility and accuracy and in exceptionally good sensitivity for many elements. The absence of cyanogen-band interference permits use of the most sensitive strontium spark lines at 4077.7 and 4215.5 A. Only a small sample volume is required; an analysis can be made on 25 ml, or even less, of sample. The sample requires no preliminary treatment other than the addition of internal standard-buffer solution; thus, sample preparation and preliminary operations are greatly simplified. Finally, the method requires no additional spectrographic accessory equipment other than the copper electrodes, which are inexpensive, readily available, and generally free of strontium.

Spectrographic facilities of the Metallurgy Department of the Colorado School of Mines, Golden, Colo., were generously made available to personnel of the U.S. Geological Survey for the development of this procedure and for the analysis of a large number of water samples. Dr. N. C. Schieltz, of the School of Mines faculty, contributed many helpful suggestions during the course of this work. Flame photometric analyses were made by C. A. Horr and Darwin Golden of the Geological Survey.

This work was done on behalf of the U.S. Atomic Energy Commission.

PROCEDURE

Lanthanum was found to be preferable to molybdenum as an internal standard for the determination of strontium. Early experiments indicated that the duration of molybdenum emission in the spark was short in relation to the duration of strontium emission, possibly because the molybdenum tended to form the volatile trioxide. Lanthanum, conversely, possesses excitation characteristics similar to those of strontium (table 1) and volatilizes in the spark at about the same rate as strontium. Moreover, several spark lines of lanthanum are of suitable intensity and are close to the most sensitive strontium lines, 4077.7 and 4215.5 A. Two lanthanum lines, 3949.1 and 4077.3 A, were selected as internal standard lines for this procedure. The relative intensities of these two lines were such that, at the proper concentration of lanthanum in the sample and under the excitation conditions employed, strontium in concentrations of 0.005 to 1.0 ppm could be determined directly from but one sample exposure. The fact that all analytical curves obtained for the three line pairs selected were linear, or nearly linear, indicated the general suitability of lanthanum as an internal standard for the determination of strontium.

TABLE 1.—*Ionization potentials of strontium and lanthanum*

Element	Potential (volts)		
	First ionization	Spark resonance	Second ionization
Lanthanum	5.6	9.1	11.4
Strontium	5.67	8.7	10.98

INSTRUMENTATION

The spectrograph used for the procedure described in this report is a 3-meter concave grating instrument (modified Eagle mounting). The grating has a ruling of 6,000 lines per centimeter and a linear dispersion of 5.5 A per millimeter in the first order. Sample excitation is provided by a commercially available multiple-source unit that provides a high-voltage, condensed-spark discharge to the sample electrodes.

The spectral region from 3500 to 4800 A is photographed in the first order on Eastman Spectrum Analysis, Type 103–0, spectroscopic plates. Exposed plates are processed in mechanically agitated trays, and developer, stop bath, and fixing solutions are maintained at a

temperature of 20°±½°C. A densitometer-comparator is used for determining spectral-line densities.

REAGENTS

High purity strontium carbonate is used in the preparation of all standard strontium solutions. This reagent is stated by the manufacturer to be 99.99 percent pure and to contain no more than 3 ppm of sodium and 2 ppm of calcium as major impurities. All reagents used in the preparation of the internal standard-buffer solution are either of analytical grade or of c.p. quality. A test showed that, in the dilution used in the analytical procedure, the internal standard-buffer solution contributed no detectable strontium to the samples.

Internal standard-buffer solution.—Dissolve 0.15 g of $LaCl_3$, 0.60 g of ethylenediamine tetraacetate, disodium salt, 6.4 g of NaCl, and 3.1 g of $CaCO_3$ in 200 ml of dilute (1:50) HCl. Dilute to 500 ml.

Standard strontium solution, 100.0 ppm Sr.—Dry approximately 0.2 g of high purity $SrCO_3$ for 2 hours at 120°C. Cool in an efficient desiccator, and transfer 168.5 mg of the reagent to a 1-liter volumetric flask. Add 50 ml of distilled water to the $SrCO_3$ in the flask, and add dilute (1:10) reagent grade HCl in 0.5 ml portions until the salt is completely dissolved (about 2 ml of the dilute HCl will be required). Dilute to exactly 1 liter. Store in tightly capped polyethylene bottles.

The concentration of strontium in this solution is:

$$\text{ppm Sr} = \frac{\text{mg } SrCO_3 \times 0.5935}{\text{Liters of solution}}$$

Standard strontium solution, 10.00 ppm Sr.—Pipet exactly 50.0 ml of the 100.0 ppm standard Sr solution into a 500-ml volumetric flask. Dilute to the mark with distilled water. Store in tightly capped polyethylene bottles.

Standard strontium solutions, 0.010 to 1.28 ppm Sr.—Prepare a series of eight standard strontium solutions containing 0.010, 0.020, 0.040, 0.080, 0.16, 0.32, 0.64, and 1.28 ppm of Sr. Take appropriate aliquots of the 10.0 ppm of standard stock solution and dilute to volume with distilled water. Store in tightly capped polyethylene bottles.

COPPER ELECTRODES

Either 0.25-inch-diameter commercial semihard, electrolytic copper, or 7-mm diameter, high purity copper may be used for the electrodes. The slightly larger (7-mm) electrodes are preferred because of the greater ease of evaporation of a 0.1-ml drop of sample

603286 O - 61 - 2

solution on the electrode face without part of the liquid running down the side of the electrode. If commercial copper is used for the electrodes, a blank must be run to determine electrode composition. Strontium impurity in the copper is extremely unlikely but if other elements in the sample are to be determined, their possible presence in the copper electrodes must be determined.

Prepare a set of 40 or 50 electrodes by cutting copper rods into uniform lengths of about 3.5 cm. With the electrode mounted in a metal-turning lathe, machine one end flat with a tool designed to leave as smooth a surface as possible. While the electrode is still mounted in the lathe, use a small, fine mill file to cut a slight chamfer on the sharp edge of the electrode. Also, lightly file the side surface of the electrode back from the end about 1 cm to remove possible surface contamination. The electrode may be handled only with forceps from this point on and must be stored in a covered container that will protect the cleaned electrode from dust, dirt, and contamination from laboratory reagents. The electrodes will oxidize slowly in air on long standing and should preferably be cleaned just prior to use.

The electrodes must be cleaned again after each use in preparation for analysis of subsequent samples. They may be cleaned by washing with nitric acid; then by thoroughly washing successively with tap water, distilled water, and alcohol, and finally by air drying. As an alternate, they may be cleaned by remachining each electrode face. Either method gives satisfactory results; however, cleaning by remachining, which is preferred in this laboratory, assures the complete removal of the previous sample. It also eliminates the possibility of contamination of the electrode face by the cleaning agents or by impurities in the cleaning agents. Electrode contamination must be avoided when an extremely small amount of an element is to be detected.

SAMPLE PREPARATION

Pipet exactly 10.0 ml of water sample or standard strontium solution into a small weighing bottle or other suitable container. Then place the bottle on a magnetic stirrer; drop in a small stirring bar; and add, with a 100 microliter micropipet, exactly 100 microliters of internal standard-buffer solution. Stir the solution for 2 or 3 minutes to ensure complete mixing.

Transfer approximately 0.1 ml of the prepared sample or standard to each of four clean copper electrodes. Rinse the micropipet carefully between successive samples to avoid contamination of the subsequent sample. Possibility of contamination is reduced if, in a series

of standards, the most dilute standard is prepared first and is followed by the next more concentrated.

Exactly 0.1 ml of sample on each electrode is not essential although an effort should be made to provide a volume very close to this in order that all samples be as nearly comparable as possible. The preparation of four electrodes permits analysis of each sample or of each standard in duplicate.

Evaporation of the sample on the electrodes is facilitated and hastened by the small nichrome wire heaters shown in figure 1. The small

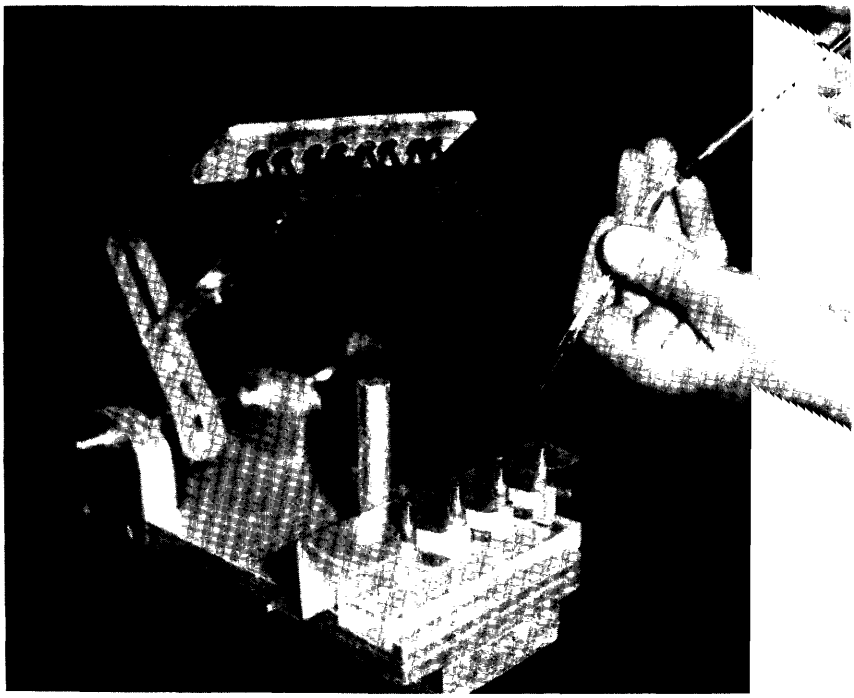

FIGURE 1.—Copper electrodes on which samples are evaporated.

clamp-jig holds four electrodes in a vertical position under the spiral nichrome wire heating elements. With the electrodes in position in the clamp, place a measured drop (0.1 ml) of sample on each electrode. Then lower the heating coils to within 1 cm of the top of each electrode, and apply voltage slowly to the heaters through a rheostat to warm the sample drop. After the sample is warmed for about 30 seconds, increase the voltage to evaporate the sample solution completely in as short a time as possible. Two to three minutes is sufficient.

If the sample drop is exposed directly to the high temperature of the heating coils operated at maximum voltage, the sudden expansion

of the drop will cause it to run down the side of the electrode; hence, it is necessary to gradually increase the temperature of the heating coils. With this precaution, pretreating the electrodes with a coating of grease or other material is unnecessary to prevent the sample solution from running down the side of the electrode.

When evaporation is complete, place the electrodes that contain the dry sample residue in a desiccator until ready for sparking.

EXCITATION CONDITIONS

The samples are sparked by using a high voltage, condensed spark discharge. Excitation conditions, specified in table 2, have given satisfactory reproducibility and sensitivity for strontium. Under these conditions and with the spectrographic equipment used, a sample that contains 0.005 ppm of strontium will just barely show a visible line at 4077.7 A.

PHOTOGRAPHIC PROCESSING

Develop the spectrographic plate for 4.0 minutes at 20°C in Kodak D–19 developer while continuously agitating. Rinse for 30 seconds in an acid stop bath and fix for 2 minutes (minimum) in Kodak Rapid Fixer. Wash the plate for 20 to 30 minutes in running water, rinse with distilled water, and dry.

TABLE 2.—*Excitation conditions*

Input voltage		108
Capacitance	μf	0.0025
Inductance		0
R.F. spark current		5.5
Prespark	sec	0
Exposure	sec	50
Slit width	μ	25

CALCULATIONS

The analytical and internal standard lines used for the determination of strontium and the approximate concentration range covered for each of three line pairs used are shown in table 3.

TABLE 3.—*Analytical and internal standard lines*

Range of strontium concentration (ppm)	Wavelength (A)	
	Strontium	Lanthanum
0.00–0.15	4077.7	4077.3
.10– .50	4077.7	3949.1
.40–1.0	4215.5	3949.1

Measure the transmittance of each analytical and internal standard line, and convert to relative intensities by means of an emulsion calibration curve. The emulsion calibration curve may be prepared by any one of the standard methods.[1]

Prepare a set of three working curves from the data obtained from the standard strontium solutions by plotting the intensity ratio of each line pair against the strontium concentration in parts per million on logarithmic coordinate paper. Typical working curves obtained are shown in figure 2.

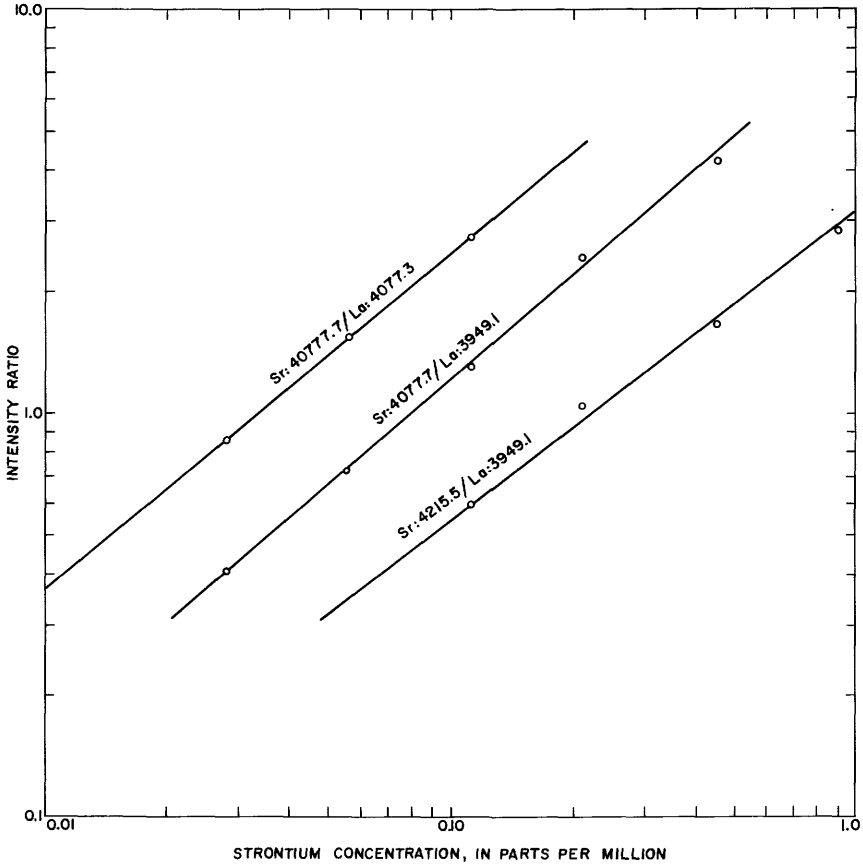

FIGURE 2.—Working curves for strontium.

Adjust the amount of lanthanum in the internal standard-buffer solution, after a trial run, so that when the strontium concentration in a standard sample or in a water sample is 0.030 ppm, the intensity

[1] Several specific procedures for constructing emulsion calibration curves are given in "Methods for Emission Spectrochemical Analysis," October 1957, A.S.T.M., Philadelphia, Pa.

ratio for line pair Sr:4077.7/La:4077.3 is close to 1.00. This concentration of lanthanum will provide optimum intensity ratios for this line pair for samples of less than 0.15 ppm of strontium and, at the same time, it will provide convenient intensity ratios for the other two line pairs for strontium concentrations up to 1.0 ppm.

When the strontium concentration exceeds about 0.15 ppm, the the strontium line at 4077.7 becomes so intense with respect to the adjacent lanthanum line at 4077.3 that the two lines are no longer resolved. Therefore, at concentrations in excess of 0.15 ppm, use of the line pair Sr: 4077.7/La : 3949.1 is necessary. Similarly, the strontium line at 4077.7 is, under the conditions of analysis, excessively intense at strontium concentrations more than 0.50 ppm. The line pair Sr: 4215.5/La : 3949.1 is, therefore, preferable when the strontium content exceeds 0.50 ppm and is suitable for concentrations as much as 1.0 ppm.

Analysis of samples.—Determine the intensity ratio of Sr/La for the appropriate line pair or pairs for each sample. From the corresponding analytical curve, determine the concentration of strontium. Two or three standard strontium solutions, preferably those that represent the high and low ends of the concentration range should be included with each series of samples analyzed; thus a constant check is provided on the validity of previously prepared analytical curves.

PRECISION AND ACCURACY

Each sample was sparked in duplicate on a single spectrographic plate, and the average of the two values for strontium concentrations obtained was taken as the value for the sample. Whenever the two values for strontium concentration differed by more than 10 percent, the sample was resparked on a subsequent plate. The reproducibility and the precision of the method were tested by analyzing several samples two or more times on different plates and at different times. The results of some of these repeated analyses, given in table 4, show that an average deviation of less than 5 percent of the amount present may be expected.

Recovery of strontium added to water samples was checked to obtain an indication of the accuracy of the method. A known amount of standard strontium solution was added to each of four natural-water samples of widely different composition with respect to major constituents. The strontium content of each of these samples was determined before and after the addition of the measured amount of strontium, and the difference in the two values thus obtained was compared with the amount added. Results are shown in table 5.

TABLE 4.—*Reproducibility in successive determinations of strontium*

Sample	Spectrographic plate	Concentration (ppm)	Average concentration (ppm)	Average deviation (ppm)	Average deviation (percent)
2596	38	0. 094			
	39	. 103	0. 102	0. 0053	5. 2
	40	. 109			
2791	78	. 19			
	83	. 18	. 185	. 005	2. 7
2885	29	. 045			
	36	. 045	. 045	. 000	. 0
2904	47	. 044			
	86	. 047	. 0455	. 0015	3. 2
2907	26	. 089			
	27	. 091	. 088	. 0023	2. 6
	37	. 085			
2910	27	. 075			
	37	. 076	. 0755	. 0005	. 7
2969	50	. 31			
	60	. 34	. 325	. 015	4. 6
3000	24	. 098			
	36	. 092	. 095	. 003	3. 2

TABLE 5.—*Recovery of strontium added to water samples*

Sample	Concentration of strontium (ppm)			
	Added	Calculated, total	Found	Difference
2972A	0. 00	----------	0. 08	----------
B	. 22	0. 30	. 29	−0. 01
C	. 11	. 19	. 20	+. 01
3342A	. 00	----------	. 27	----------
B	. 22	. 49	. 48	−. 01
C	. 11	. 38	. 37	−. 01
3435A	. 00	----------	. 23	----------
B	. 11	. 34	. 34	. 00
3535A	. 00	----------	. 11	----------
B	. 11	. 22	. 20	−. 02
C	. 22	. 33	. 29	−. 04

A large number of water samples was analyzed by flame photometer as well as by spectrograph. The flame photometric procedure involved a tenfold concentration of strontium from the sample by means of a strongly acidic cation exchange resin prior to analysis. The sensitivity of this procedure is 0.02 ppm of strontium. Agreement was reasonable between most of the results obtained with the two independent analytical methods (table 6.)

The flame photometric determinations were made with an independent set of standards. Thus the results are comparable to having the analyses performed by two different laboratories. The agreement between the results is considered to be satisfactory.

TABLE 6.—*Results of strontium determinations with the spectrographic method and with a flame photometric procedure*

Sample	Concentration of strontium (ppm)	
	Flame photometer	Spectrograph
3247	0. 03	0. 028
2714	. 04	. 040
3044	. 06	0. 040, . 046
3584	. 065	. 058
3078	. 14	. 14
3168	. 16	. 15
3077	. 23	. 16
2888	. 28	. 25
2599	. 22	. 26
2794	. 36	. 33
3348	. 48	. 34
2785	. 47	. 38
3456	. 73	. 64

SUMMARY

The copper-spark, spectrographic procedure described is suitable for the determination of stable, nonradioactive strontium in natural waters. A spectroscopic buffer solution, consisting of calcium and sodium chlorides in a 0.1-percent ethylenediamine tetraacetate solution and added in constant amount to each sample, minimizes the effects of differences in the composition and amounts of dissolved solids present in different waters.

Lanthanum is particularly suitable as the internal standard because its excitation characteristics are similar to those of strontium. Moreover, several lanthanum lines are close to the two most sensitive spark lines of strontium; therefore, by proper adjustment of lanthanum concentration and proper choice of analytical line pairs, strontium concentrations between 0.005 and 1.0 ppm may be determined from one sample and exposure.

High-voltage spark excitation and metallic (copper) electrodes provide satisfactory sensitivity, precision, and reproducibility. The method satisfies the requirements for convenience, speed, and accuracy. One chemist can analyze as many as 15 samples per day.

Although the method, as described, was devolped exclusively for determination of strontium in natural waters that contain less than 500 ppm of total dissolved solids, it undoubtedly can be used, with suitable modification, for the analysis of mineral waters and waters, that contain more than 500 ppm of dissolved solids.

REFERENCES CITED

Alexander, G. V., Nusbaum, R. E., and MacDonald, N. S., 1954, Strontium and calcium in municipal water supplies: Am. Water Works Assoc. Jour., v. 46, p. 643.

Fred, M., Nachtrieb, N. H., and Tomkins, F. S., 1947, Spectrochemical analysis by the copper spark method: Am. Optical Soc. Jour., v. 37, p. 279.

Haffty, Joseph, 1960, Spectrographic analysis of natural waters. Residue method for common minor elements: U.S. Geol. Survey Water-Supply Paper 1540–A.

Horr, C. A., 1959, A survey of analytical methods for the determination of strontium in natural water: U.S. Geol. Survey Water-Supply Paper 1496–A.

Meloche, V. W., and Shapiro, Rubin, 1954, Determination of calcium and magnesium in lake waters by means of a rotating silver disk electrode: Anal. Chemistry, v. 26, p. 347.

Nachtrieb, N. H., 1950, Principles and practice of spectrochemical analysis: New York, McGraw-Hill Book Co., 324 p.

Silvey, W. D., 1961, Concentration method for spectrochemical determination of strontium in water: U.S. Geol. Survey Water-Supply Paper 1540–F p. 11–22.

U.S. GOVERNMENT PRINTING OFFICE: 1961 O —603286