

Chemistry of Strontium in Natural Water

GEOLOGICAL SURVEY WATER-SUPPLY PAPER 1496

*This water-supply paper was printed
as separate chapters A-D*



UNITED STATES DEPARTMENT OF THE INTERIOR

STEWART L. UDALL, *Secretary*

GEOLOGICAL SURVEY

Thomas B. Nolan, *Director*

The U.S. Geological Survey Library has cataloged this publication as follows:

U.S. Geological Survey.

Chemistry of strontium in natural water. Washington,
U.S. Govt. Print. Off., 1962.

iii, 97 p. illus., diagrs., tables. 24 cm. (*Its Water-supply paper
1496*)

Issued as separate chapters A-D.

Includes bibliographies.

1. Strontium. 2. Water-Analysis. I. Title. (Series)

CONTENTS

[The letters in parentheses preceding the titles are those used to designate the separate chapters]

	Page
(A) A survey of analytical methods for the determination of strontium in natural water, by C. Albert Horr-----	1
(B) Copper-spark method for spectrochemical determination of strontium in water, by Marvin W. Skoustad-----	19
(C) Flame photometric determination of strontium in natural water, by C. Albert Horr-----	33
(D) Occurrence and distribution of strontium in natural water, by Marvin W. Skoustad and C. Albert Horr-----	55

iii

A Survey of Analytical Methods for The Determination of Strontium in Natural Water

By C. ALBERT HORN

CHEMISTRY OF STRONTIUM IN NATURAL WATER

GEOLOGICAL SURVEY WATER-SUPPLY PAPER 1496-A

*This report concerns work done on behalf
of the U.S. Atomic Energy Commission
and is published with the permission of
the Commission*



UNITED STATES DEPARTMENT OF THE INTERIOR

FRED A. SEATON, *Secretary*

GEOLOGICAL SURVEY

Thomas B. Nolan, *Director*

CONTENTS

	Page
Abstract.....	1
Introduction.....	2
Chemical behavior of strontium.....	2
Analytical methods for strontium.....	3
Gravimetric methods.....	3
Volumetric methods.....	6
Spectrochemical methods.....	7
Emission spectroscopy.....	7
Flame spectrophotometry.....	9
Absorptiometry.....	11
X-ray spectroscopy.....	11
Polarographic methods.....	11
Chromatographic methods.....	12
Methods for radioisotopes.....	13
References cited.....	14

CHEMISTRY OF STRONTIUM IN NATURAL WATER

A SURVEY OF ANALYTICAL METHODS FOR THE DETERMINATION OF STRONTIUM IN NATURAL WATER

By C. ALBERT HORN

ABSTRACT

Strontium, an alkaline earth metal, is one of the more abundant trace elements in the lithosphere and is universally associated with calcium in igneous, sedimentary, and metamorphic rocks. During the weathering cycle, strontium is brought into solution and is transported principally as the bicarbonate.

The biological cycle of strontium parallels that of calcium. Natural strontium is not toxic to human life, but the artificially produced radioactive isotopes, especially strontium-89 and strontium-90, are highly toxic.

Chemical methods for determining strontium require separation of the element from other alkaline earth elements. The most reliable method for separating calcium from strontium is extraction with fuming nitric acid. Many methods have been reported in which organic solvents are used to extract anhydrous calcium nitrate from mixtures of calcium and strontium nitrate. Separations based on homogeneous precipitation or precipitate exchange and complex formation are also reported. In all these methods, reliable results can be attained only when corrections are applied to compensate for incomplete separations. Strontium is usually determined gravimetrically, or volumetrically by oximetric titration of equivalent oxalate. Other volumetric methods are rarely used.

Emission spectrochemical methods have been applied to water analysis. These methods have the advantage that preliminary separations or other treatment of the water sample are usually unnecessary. Instrumentation and operational techniques for spectrographic analysis are well standardized. Among methods of introducing the sample into the excitation source are direct atomization, use of rotating-disk or porous-cup electrodes, evaporation of the sample on the electrodes, and packing a cuffed electrode with the evaporation residue. The lower limit of detection is reported to be approximately 0.001 ppm.

Flame photometry is used extensively in analysis of solutions. Low-energy excitation produces simple spectra relatively free of interferences—an advantage in the analysis of complex solutions. Differences among methods are mainly in the choice of fuel and spectral line. The effects of some cations and anions on the emission of strontium have been studied. Strontium may be detected in amounts as small as about 0.2 ppm.

There are no satisfactory direct colorimetric methods for strontium. Indirect colorimetric methods are generally unsatisfactory and non-specific. X-ray spectroscopy may be applied to evaporated water residues.

Column and paper chromatographic methods are convenient for concentrating and separating small amounts of strontium in water samples. Adsorption and elution techniques for both column and paper chromatographic methods have been described by several authors.

Sensitive radiochemical methods of analysis for the radioactive isotopes of strontium, particularly strontium-90, have been developed.

INTRODUCTION

A comprehensive search of the chemical literature of the last 60 years was made for methods pertaining to the quantitative determination of strontium. From the several hundred references compiled, only the comparatively few that describe methods for the determination of strontium in natural waters and methods that are adaptable to natural waters are summarized in this report.

This report is part of a study of the occurrence of strontium in the ground waters and surface waters of the United States. Many helpful suggestions were received from John D. Hem, under whose direction this report was written.

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

CHEMICAL BEHAVIOR OF STRONTIUM

Strontium, an alkaline-earth metal, resembles calcium and barium in its chemical properties. Strontium is not abundant but is widely distributed in nature, and traces of it are contained in all calcium compounds (Meunier, 1926). The strontium content of igneous rocks varies from about 9 g per ton in ultrabasic rocks to 1,200 g per ton in nepheline syenites (Rankama and Sahama, 1950, p. 476). The crystal ionic radius of strontium (1.13A) is intermediate between that of calcium (0.99A) and that of potassium (1.33A) (Fauling, 1948, p. 346). Strontium thus may replace these metals in some minerals, especially in the feldspars, micas, pyroxenes, amphiboles, and apatites.

Strontium minerals are nearly everywhere present in limestones, dolomites, gypsum-bearing rocks, and salt deposits. The most common strontium mineral is celestite (SrSO_4).

Vinogradov and Borovik-Romanova (1945) have suggested the following deposition mechanism for celestite in conjunction with dolomite, limestone, and gypsum. The strontium content and the relative solubilities of strontium and calcium in sea water are such that celestite will not be deposited so long as limestone or dolomite

is being deposited. When the concentration of the solution rises to the point where deposition of gypsum begins, however, celestite will also be deposited. The result is a celestite enrichment of the upper zones of carbonate rocks in contact with gypsum. Celestite also is present in the shells of certain marine organisms.

Rankama and Sahama (1950, p. 295) give the average strontium content of sea water as 13 ppm. Odum (1951) in a statistical study of his own data and of data from several others found that 8.1 ppm is more nearly correct. Alexander and others (1954) in a study of the municipal water supplies of 50 cities in the United States found that the strontium content averaged 0.21 ppm in untreated surface water and 0.49 ppm in ground water.

During weathering, strontium is dissolved and transported principally as the bicarbonate, with lesser amounts as the sulfate and chloride (Rankama and Sahama, 1950, p. 480). Gallo (1935) reports that at 20° C in pure water, the solubility of strontium sulfate is equivalent to 63 ppm of strontium. The presence of other anions and cations increases the solubility of strontium sulfate.

Strontium is accumulated with calcium in the bones and milk of animals and in the leaves of plants. Naturally occurring strontium has no physiological importance and seems to be nontoxic to human beings. It is not listed as an industrial poison by Jacobs (1944), nor is a maximum permissible concentration for strontium in drinking water given by the U.S. Public Health Service (1946). The California State Water Pollution Control Board (1952, p. 376; 1954, p. 114) has found that strontium chloride and strontium nitrate are toxic to some aquatic animals and lists threshold concentrations for immobilization and lethal dosages for a few fresh-water fish.

The toxicity of radioactive isotopes of strontium, in particular those with long half-lives, is important because of the similar behavior of strontium and calcium in the life cycle. Strontium accumulates in bone tissue, to which radio-strontium causes radiation damage. The National Bureau of Standards (1953) lists 800 micromicrocuries per liter as the maximum permissible concentration of strontium-90 + yttrium-90 in water for continuous ingestion. The British Journal of Radiology (1955) also lists 800 micromicrocuries per liter as the maximum permissible concentration of SR⁹⁰ + Y⁹⁰.

ANALYTICAL METHODS FOR STRONTIUM

GRAVIMETRIC METHODS

The determination of strontium by gravimetric methods is generally complicated by the presence of much larger amounts of calcium and magnesium than the amount of strontium. These elements to-

gether with barium, if present, must be removed prior to the determination of strontium.

In the general scheme of analysis, the alkaline earth metals are precipitated as carbonates or oxalates prior to separating strontium from the other alkaline earths. Pochinok (1932) recommended that the precipitation be made by slowly adding ammonium oxalate or sodium carbonate to the boiling solution and then allow the solution to cool before filtering.

The separation of strontium from the other alkaline earth elements requires the utmost care and attention to detail to obtain satisfactory results. From solubility data, Davis (1942) concluded that selective precipitation of strontium as the chromate from aqueous ethanol should give a satisfactory separation. Fresenius and Ruppert (1891) had shown earlier that this procedure gave unreliable results. Rawson (1897) described a method in which the alkaline earth carbonates or oxalates were converted to nitrates and dried. Concentrated nitric acid was then used to extract soluble calcium nitrate from the mixture. Willard and Goodspeed (1936) found, in their studies of Rawson's method, that nitric acid of density 1.46 was the most satisfactory for the separation. Leliaert and Eeckhaut (1957), using isotope tracer techniques to study chemical methods of separation, found that for the most reliable results a double extraction with nitric acid should be made.

Fresenius (1893) described a method of separation in which a mixture of ethanol and ethyl ether is used to extract calcium nitrate from a mixture of anhydrous nitrates. This method was preferred by Noll (1931); however, he cautioned that to obtain good results, the separation must be made under completely anhydrous conditions, preferably in a dry box or in an atmosphere saturated with nitric acid (d. 1.46). Browning (1893) proposed the use of isoamyl alcohol, in which calcium nitrate is more soluble than in an ethanol-ether mixture, for separating strontium nitrate from calcium nitrate. Later study by Leliaert and Eeckhaut (1957) showed that 1 to 2 percent of the strontium is extracted with the calcium in a single extraction. After a second extraction, 0.2 to 1 percent of the calcium remained with the strontium in the residue. Szebelledy (1929a) described a method of separation by extraction of the soluble calcium nitrate with a mixture of absolute ethyl and isobutyl alcohols.

The methods by Browning (1893) and Szebelledy (1929a) have been shown (Noll, 1931) to be unsuited for the separation of large amounts of calcium from small amounts of strontium. The use of anhydrous acetone as an extraction reagent was reported by Shreve and others (1939), who recovered 99.7 percent of the strontium.

A method of separation by selective precipitation of strontium with a boiling 23 percent solution of ammonium sulfate has been described by Ukai (1931). However, he found that the method gave erratic results because of coprecipitation of calcium sulfate. Study of the homogeneous precipitation of strontium with dimethyl sulfate (Elving and van Atta, 1950) showed that calcium sulfate was coprecipitated at the concentration of reagent required to precipitate completely the strontium.

Leliaert and Eeckhaut (1957), using radioactive isotopes, made a critical study of most of the previously described methods for separating strontium and calcium. Their conclusions were that Rawson's method (1897) of separation with concentrated nitric acid and Fresenius' method (1893) of extraction of the nitrates with a mixture of ethanol and ethyl ether gave the most reliable results. They showed that results of highest accuracy can be obtained only when errors are evaluated and corrections are applied.

Szebelledy (1929b, 1932) reported a method for separating strontium and barium by conversion of the nitrate salts to bromides with hydrobromic acid followed by extraction of the more soluble strontium bromide with isobutyl alcohol. A correction factor must be applied to give accurate results. The separation may also be made by the precipitation of barium chromate in an alkaline solution (Macchia, 1928). Ballezo and Doppler (1956a) have recently reported a method of separating barium, calcium, and strontium by using precipitate exchange and complex formation. Barium is precipitated as the chromate in a solution containing sodium ethylenediaminetetraacetate in which strontium and calcium are soluble. The strontium is then separated from calcium by extraction of the anhydrous nitrate salts. The method was applied to mineral waters.

These same authors (1956b) described another method in which ammonium sulfate is added to a boiling solution of the mixed oxalates; the barium salt is thus converted to the insoluble barium sulfate. The precipitate is filtered after treatment with hydrochloric acid to dissolve the calcium and strontium oxalate. The calcium and strontium are reprecipitated as the oxalates, and the strontium oxalate is converted to the carbonate by treatment with potassium carbonate. The precipitate is filtered, washed, dried, and weighed, and then dissolved in dilute sulfuric acid. The calcium and strontium concentrations are then determined indirectly by titration of the equivalent oxalate.

Final determination of strontium may be made by several different methods. Pochinok (1932) and Haslam (1935) recommended that

the strontium be precipitated by the addition of a known excess of ammonium oxalate to the boiling solution and the excess titrated with standard permanganate. Ignition of strontium oxalate to strontium carbonate was found to give a positive error of about one part in a thousand. Strebinger and Mandl (1926) recommended precipitating strontium as the sulfate from an ethanolic solution and drying the precipitate at 170° to 180° C. A modification of the Dworzak and Reich-Rohrwig method (1931) for calcium was described by Penchev and Nonova (1955) for the macro-, semimicro-, and micro-determination of strontium. They precipitated strontium in a warm (50° to 55° C) solution with picrolonic acid. The precipitate was washed with carbon disulfide and dried in an air stream. Advantages were claimed over other methods. Determination of strontium as the secondary phosphate has been described by Denk and others (1956). The precipitation is carried out in a boiling, alkaline solution, and the final precipitate is dried at 120° to 130° C. Sodium and ammonium must be absent.

VOLUMETRIC METHODS

Titrimetric methods for the determination of strontium are few in number and generally are applied to the final determination of the element after separation from calcium, barium, and magnesium. The most widely used method has been described by Goodale (1936). The strontium is determined by titrating the equivalent oxalate from the acidified strontium oxalate precipitate with standard permanganate. Strontium is sometimes determined indirectly by precipitating it with a known amount of oxalate and then titrating the excess oxalate. Ballczo and Muthenthaler (1932) have reported a method for determining strontium in mineral water. The strontium from a large volume of water was concentrated on an alumina column pretreated with sodium hydroxide. The strontium was then eluted with dilute nitric acid. The eluate was filtered, evaporated to dryness, and fused with boric acid to convert the strontium to the borate salt. The residue was dissolved in a known volume of dilute hydrochloric acid, methyl alcohol was added, and the excess borate was evolved as methyl borate. The excess hydrochloric acid was determined by double titration with sodium borate in the presence of methyl-red and methylene-blue indicators. In the potentiometric method reported by Mayr and Burger (1930), strontium is precipitated by a measured excess of sodium oxalate. The excess oxalate used in the precipitation is then titrated potentiometrically with mercurous nitrate.

SPECTROCHEMICAL METHODS

Instrumental methods, including spectrochemical techniques in recent years, have been used extensively in analytical chemistry. Development of more precise methods of measurement of spectral intensity of excited samples has lead to a high degree of sensitivity and accuracy in analysis. Spectrochemical analysis has a distinct advantage in that a large number of samples may be analyzed in a short time and generally without preliminary chemical treatment or isolation of the particular element of interest. Emission spectrochemical methods permit the simultaneous determination of many elements in a single sample. Spectrochemical analysis has widespread application in studies of the geochemistry of trace or minor elements in a great variety of geologic material.

For facility of review, this field of analytical endeavor is divided into four parts: (1) Emission spectroscopy, in which the spectrum of an excited sample is recorded by means of photosensitive plates or films for subsequent measurement of the intensity of spectral lines; (2) flame spectrophotometry, in which a desired segment of the spectrum is isolated by means of filters or a monochromator and the spectral intensity measured by photoelectric methods; (3) absorptiometry; and (4) X-ray spectroscopy.

Instrumentation is beyond the scope of this review; but for excellent discussions of this subject, the reader is referred to Sawyer (1951), Brode (1943), Harrison and others (1948), and Willard and others (1948). A good introduction to spectrochemical analysis is given by Meegers (1946). Burriel-Martí and Ramírez-Muñoz (1957) have provided a comprehensive review of flame photometry in their recent outstanding work.

EMISSION SPECTROSCOPY

Spectrographic methods using direct solution excitation are well suited to the analysis of natural waters. Uzumasa and Okino (1933, 1934) sprayed the sample into a spark gap of 10,000 volts. They reported that the calcium and strontium lines were the most sensitive, and they were able to detect as little as 10^{-6} mole of these elements. Also, they showed that free hydrochloric acid interfered with the analysis. Bórovík-Romanova and others (1954), in their study of natural waters, made use of a "fulgerator" which introduced the solution to be tested into a 120-v, 2-amp, a-c arc by capillary action through a predrilled electrode. Using the sensitive strontium line at 4607A, they were able to detect as little as 10^{-5} percent (0.01 ppm) of strontium.

The porous-cup electrode technique, first described by Feldman (1949), was applied by Wilska (1951) to the analysis of natural waters. The sample is introduced into a hollow, upper electrode and fed into the spark by diffusion through the floor of the electrode. A minimum concentration of 0.07 ppm of strontium was determined with a precision of ± 4.95 percent standard deviation from the mean strontium content of the analysis line to the internal standard line. Hitchcock and Starr (1954), using the same technique, reported erratic results that were due to nonuniform porosity of the electrode material, selective diffusion, and dependency of feed rates on ion concentration. These authors claimed improved results with a rotating-disk electrode, which fed the sample continuously to a high voltage spark.

Rainwater (written communication, 1958) reports a procedure, using rotating carbon-disk electrodes, sensitive to ± 0.05 ppm of strontium in water samples. A detection limit of 0.001 percent, in dry residues, was also reported; the 0.001 percent corresponds to 0.001 ppm of strontium in water containing 100 ppm of dissolved solids.

Preferential volatilization of certain components of the sample occurs to a much lesser degree in the high voltage spark than in the d-c arc. For this reason, and because spattering effects are minimized, spark excitation is usually preferred. Continuous, uniform feed of the sample to the spark assures that the composition of the radiating vapor is identical with that of the sample solution.

High-temperature flames have also been used as a means of excitation in spectrographic procedures. An acetylene-air or acetylene-oxygen flame is generally used; but other fuels, including natural gas, propane, and hydrogen, have been used. Rusanov (1934), with the aid of a Lundegårdh burner and atomizer, determined the concentration of several alkali and alkaline earth metals by interposing a light-absorbing wedge between the flame and collimator slit. Relating the layer thickness of the wedge at the point of disappearance of a spectral line or band to the concentration of the element gave results accurate to within 10 to 15 percent of the true value. Hitchcock and Starr (1954) also used a flame for excitation of the solution. They found that internal standards were not necessary because the excitation is reproducible and is not subject to the random variations (Kolb and Streed, 1952) observed with the porous-cup and rotating-disk electrodes.

Excitation of evaporation residues is more widely applied than solution excitation. Nagaoka and Machida (1934) described a method in which the solution to be tested was evaporated on the surface of clean silver electrodes. They were able to detect as little

as 10^{-9} g of strontium. Impregnation of carbon electrodes with the sample solution was found by Hitchcock and Starr (1954) to give erratic results. They attributed the inconsistencies to nonhomogeneity of the residue caused by preferential absorption of the solution by the electrodes. These same authors also evaluated the cupped-electrode technique, wherein the evaporated residue is packed into a shallow cup cut into the end of a graphite electrode. Expulsion of sample from the electrode and difficulties in properly sampling the residues led to poor results. Briquetting the sample with pure graphite powder was claimed to improve the results.

FLAME SPECTROPHOTOMETRY

Flame excitation yields relatively simple line and band spectra of the more easily excited elements and compounds. Because the resulting spectrum contains only a few lines or bands, filters or small prism monochromators may be used to isolate the desired spectral area with a minimum of radiation interference.

Flame excitation of strontium gives two prominent spectral lines, 407.8 m μ and 460.7 m μ , and a spectral band, 681 m μ . The 460.7-m μ line is the most intense. The choice of using the 460.7-m μ line or the 681-m μ band for the determination is a matter of controversy. Chow and Thompson (1955) used the 460.7-m μ line with excellent results. A detection limit of 0.5 ppm of strontium at 460.7 m μ with a hydrogen flame and 5 ppm at 681 m μ with an acetylene flame was listed by Beckman Instruments, Inc. (1952). The intensity of the continuous or background radiation of the flame and solvents must be subtracted from total intensity at these wavelengths in order to obtain true element-emission intensity. Taylor and Paige (1955), in an evaluation study of flame-photometric methods, showed the 681-m μ wavelength and an acetylene flame to be the best. They pointed out that emission at this wavelength is less subject to interference by anions and cations present in the water. A standard deviation of 0.5 ppm or less was obtained for concentrations between 0 and 10 ppm of strontium.

In order to reduce radiation interferences, a minimum spectral width is used. Because this reduces the total amount of radiant energy admitted to the detector, the use of a photomultiplier tube, which amplifies the current generated by a factor of 100, is recommended.

The effects of cations and anions most common in natural water on the intensity of the emission of strontium have been studied by Huldt (1944), Ettre and Adam (1957), Taylor and Paige (1955), Chow and Thompson (1955), Sugawara and others (1956), Hinsvark and others (1953), and Berry and others (1946). Sodium, potassium,

and calcium enhance the emission of strontium in the flame. Aluminum, iron magnesium, sulfate, phosphate, and chloride ions cause a depression of the emission. Sugawara and others (1956) found that the addition of organic acids, particularly tartaric acid at 0.5 percent concentration, increases the intensity of emission. Ikeda (1956) reported that perchloric acid caused enhancement of the emission.

Flame-photometric methods for analysis of strontium in waters have been described by several authors. Chow and Thompson (1955) developed an "internal standard" technique in which a series of standards are prepared with a strontium-free synthetic sea water. An equal volume of sample is added to several of the standards, and the mixture is atomized. A plot is made of concentration versus net intensity of the emission at 460.7 m μ , and the strontium content is determined by the slope-intercept method. Any ions that cause interference would have equal effects on standards and unknowns. A method for determining strontium in rain, lake, and river waters was described by Sugawara and others (1956). They evaporated the samples to approximately one-sixteenth of the original volume and precipitated calcium and strontium with ammonium oxalate. Urea was added to prevent coprecipitation of magnesium. The precipitate was collected and dissolved in 1:1 hydrochloric acid, and tartaric acid was added. Strontium emission was read at 460.7 m μ . This method was found to have an average error of +1.5 percent.

Smales (1951) combined flame-photometric and radiochemical methods to determine strontium in sea water. A known amount of strontium containing the radioactive isotope, strontium-89, was added to a sample of sea water and coprecipitated with barium sulfate. The fraction of strontium coprecipitated is proportional to the decrease in activity of the filtrate. The amount of strontium required to restore the original flame intensity of the filtrate was then determined. The data obtained permitted the calculation of the strontium concentration in the original sample.

Skoustad (1957) has described a method in which a radiation buffer technique is used for determining strontium in water. Potassium chloride and ammonium citrate, 1.0 g and 0.5 g, respectively, are added to the samples and standards, which are made alkaline with potassium hydroxide. The final volume is 100 ml. The net intensity at 460.7 m μ plotted against strontium concentration yields a straight line.

Hubble (written communication, 1957) described a method similar to the method of Chow and Thompson (1955) in which a series of aliquots of a sample are diluted with equal volumes of several stand-

ard strontium solutions. The emission intensities at $460.7\text{ m}\mu$ are corrected for background intensity at $454\text{ m}\mu$ and plotted against concentrations of the standards. The strontium content is determined by the slope-intercept method. This method shows an error of 3 percent for the higher concentrations and 5 to 10 percent for the lower concentrations.

The procedures of Skougstad and Hubble have a detection limit of about 0.2 ppm of strontium.

ABSORPTIOMETRY

Colorimetric and absorptiometric methods for determining strontium are limited for practical application and are principally of academic interest. Most of the reagents, such as tannic acid, chloranilic acid, and ammonium purpurate (murexide), are useful only with pure solutions of strontium salts and give colors that are transient and fade rapidly.

Pollard and Marten (1956) have described a method for determining strontium with ethanolic murexide. The color was developed at a pH of 11.3, and the optical density of the solution was measured at $515\text{ m}\mu$. The authors also described a procedure in which o-cresolphthalein is used as a complexing agent. The determination was made at a pH of 10.6, and the optical density was measured at $575\text{ m}\mu$. In both procedures, the optical density must be determined rapidly to overcome fading caused by decomposition of the color complex. A sensitivity of 1.5γ is claimed for the method.

Welcher (1947, 1948) listed several methods for detecting strontium by reagents yielding colored solutions or precipitates. However, all are subject to interferences and are not useful analytically.

X-RAY SPECTROSCOPY

X-ray spectroscopic and fluorescence methods have been used for determining strontium in rocks and minerals. Noll (1932) and Lucchesi (1957) have described a procedure in which an analyzer crystal of lithium fluoride is used with yttrium as the internal standard. This analytical tool is widely used in the study and analysis of rocks and minerals and may be applicable to water analysis.

POLAROGRAPHIC METHODS

Polarographic methods have been used, though not extensively, for determining the alkali metals and alkaline earth metals in water. Only a few methods are reported for the polarographic determination of the alkaline earth metals. Zlotowski and Kolthoff (1944, 1945) have described the polarographic behavior of strontium and barium

and of strontium, barium, and calcium in water or water-alcohol solution with tetraethylammonium iodide as the supporting electrolyte. These investigators found that the strontium wave was well defined and that strontium could be determined in the presence of calcium and barium. They also showed that the best results were obtained using a 50 to 80 percent aqueous ethanol solution.

CHROMATOGRAPHIC METHODS

In recent years, paper and column chromatographic techniques have been successfully applied to the concentration, separation, and determination of strontium in various materials. Lerner and Rieaman (1954) collected a mixture of calcium, barium, and strontium on a column of Dowex-50 previously equilibrated with ammonium lactate. The column was eluted with ammonium lactate, and successive fractions were collected. The second fraction contained the strontium, which was then determined gravimetrically as the sulfate. Schumacher (1956) described a similar procedure in which 2.5 to 3 N hydrochloric acid is used as the eluent. Ballczo and Muthenthaler (1952) have described a method for strontium in mineral waters. Strontium was separated from calcium and magnesium by passing the sample through an alumina column pretreated with sodium hydroxide and eluting the strontium with nitric acid.

Paper chromatography of the group II-A elements was investigated by Ishibashi and Tsutsui (1956). Using an ethanol-water-hydrochloric acid system, they were able to separate strontium from 500 times as much calcium. They found no difference in R_f values when nitric acid (6N) was substituted for hydrochloric acid. Pollard, McOmie, and Marten (1956) determined gamma quantities of strontium and other group II-A metals in dolomites and limestones. The metals are separated as formates by downward elution of the chromatogram with a solvent consisting of methanol, formic acid, isopropyl alcohol, water, and ammonium formate. After isolation, strontium was determined colorimetrically as the orthocresolphthalein complex. Magee and Headridge (1955) described a methyl alcohol, n-butyl alcohol, γ -collidine, 6N acetic acid system for the separation of group II-A elements by downward elution. Strontium was detected by using sodium rhodizonate to develop the chromatogram. The method was applied to dolomites. A study of chromatographic separation of calcium and strontium, in which radioactive tracers were used, was reported by Burkser and Eliseera (1956). Separation by means of pyridine containing potassium thiocyanate or hydrochloric acid containing n-butyl alcohol and water was made on chromatographic paper that was impregnated successively with alco-

holic sodium hydroxide and hydrochloric acid. Good separations of the two elements were obtained by this method.

METHODS FOR RADIOISOTOPES

Increased use of radioisotopes in research, nuclear-power installations, and nuclear-weapons testing has resulted in an increase in the amount of radioactive materials being discharged into water courses. Gross assays of radioactivity of water samples will not adequately measure the hazard from nuclides such as strontium-90.

Radiochemical procedures for the assay of strontium-90 have been described in detail by Hahn and Straub (1955), Martell (1956), Goldin (1956), and Kahn and Goldin (1957). Because radioactive strontium occurs in extremely small concentrations, these investigators added natural strontium to the samples to serve as a carrier for the radioactive strontium. Strontium and other alkaline earth elements were then precipitated with sodium carbonate. The precipitate was collected and redissolved in acetic acid. The solution was buffered with ammonium acetate, a barium carrier added, and barium chromate precipitated by the addition of ammonium or potassium chromate. This precipitation removes radioactive barium and any lanthanum daughter that would interfere with the determination of radiostrontium. The strontium was again precipitated as the carbonate, and the collected precipitate was washed free of excess chromate ion. The precipitate was dissolved in hydrochloric acid; and ferric, zirconium, and either lanthanum or cerium chlorides were added as scavengers. The scavengers were precipitated as the hydroxides and removed by filtration. A final strontium carbonate precipitation was made. After the yttrium daughter had grown in, the mounted precipitate was subjected to β -assay (Reed, 1956). Alternatively, the yttrium daughter product was separated from the precipitate by extraction with 2-thionyltrifluoroacetone and the extract subjected to β -assay.

Isotope-dilution and neutron-activation techniques are the most precise and accurate methods for the determination of strontium in microgram quantities. In the isotope-dilution technique, an accurately measured amount of a radioactive strontium isotope of known activity is added to the sample solution. Strontium is then separated from the solution, usually by a gravimetric procedure, and the activity of the separated material is measured. The concentration of the original strontium in the sample is calculated from the ratio of the activities of the added and recovered isotope. This general technique is useful in determining the efficiency of wet chemical methods

of analysis. Alimarin and Bilimovich (1956) made a comprehensive review of chemical analysis by isotope dilution.

Leddicotte and Reynolds (1951) have described the use of a reactor at Oak Ridge for neutron-activation analysis. In principle the samples, together with standards, are placed in an intense flux of slow neutrons for a length of time sufficient to produce a measurable amount of a radioisotope of the element to be determined. Neutron bombardment of strontium produces strontium-87. The activity is measured, and the weight of element present, W, is found from the equation:

$$W = \frac{AM}{6.02 \times 10^{23} f\sigma_{ac} S}$$

where

- A = activity in disintegrations per second,
- M = chemical atomic weight of the element sought,
- f = slow neutron flux in neutrons/cm²/sec.,
- σ_{ac} = atomic cross section in cm², and
- S = saturation factor, $1 - e^{-\lambda t}$.

Although this method is expensive and time consuming, as little as 0.6 μ g of strontium may be determined with an error of ± 10 percent.

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. 643-654.
- Alimarin, I. P., and Bilimovich, G. N., 1956, Chemical analysis by isotope dilution: Khim. Nauka i Prom., v. 1, no. 1, p. 74-84.
- Balczko, H., and Doppler, G., 1956a, Alkaline-earth analysis. II. Separation and determination by the use of precipitate exchange and complex formation with ethylenedinitrilotetraacetic acid: Zeitschr. anal. Chemie., v. 152, p. 321-337.
- 1956b, Analysis of alkaline earths: Zeitschr. anal. Chernie., v. 151, p. 16-28.
- Balczko, H., and Muthenthaler, H., 1952, Enrichment and microtitrimetric determination of the strontium cation in mineral waters: M'krochemie ver. Mikrochim. Acta. v. 39, p. 152-165.
- Beckman Instruments, Inc., 1952, Operating instructions for the Beckman Model B Flame Spectrophotometer, Bull. 278: South Pasadena, Calif., 17 p.
- Berry, J. W., Chappell, D. G., and Barnes, R. B., 1946, Improved method of flame photometry: Indus. Eng. Chemistry, Anal. Ed., v. 18 p. 19-24.
- Borovik-Romanova, T. F., Korolev, V. V., and Kutsenko, Yu. I., 1954, Spectrographic determination of strontium and lithium in natural waters: Zhur. Anal. Khim., v. 9, p. 265-269.
- British Journal of Radiology, 1955, Recommendations of the international commission on radiological protection: British Jour. Radiology, v. 28, supp. 6, pt. C, p. 49.

- Brode, W. R., 1943, Chemical spectroscopy (2d ed.): New York, John Wiley and Sons, 677 p.
- Browning, P. E., 1893, Zur Trennung des Strontians vom Kalk: Zeitschr. anal. Chemie., v. 32, p. 468-470.
- Burkser, E. S., and Eliseera, G. D., 1956, Application of radioactive isotopes in partition paper chromatography for inorganic compounds: Trudy Komissii Anal. Khim., Akad. Nauk SSSR, Inst. Geokhim. i Anal. Khim., v. 7, p. 84-88.
- Burriel-Martí, F., and Ramírez-Muñoz, J., 1957, Flame photometry: Amsterdam, Elsevier Publishing Co., 531 p.
- California State Water Pollution Control Board, 1952, Water quality criteria: State Water Pollution Control Board, pub. 3, p. 376.
- 1954, Water quality criteria, Addendum no. 1: State Water Pollution Control Board, pub. 3, addendum no. 1, p. 114.
- Chow, T. J., and Thompson, T. G., 1955, Flame photometric determination of strontium in sea water: Anal. Chemistry, v. 27, p. 18-21.
- Davis, T. W., 1942, Solubility of strontium chromate and the detection of strontium: Indus. Eng. Chemistry, Anal. Ed., v. 14, p. 709-711.
- Denk, G., Dunkel, Renate, and Keller, C., 1956, Precipitation and determination of strontium as the secondary phosphate: Zeitschr. anal. Chemie., v. 152, p. 31-36.
- Dworzak, Rudolf, and Reich-Rohrwig, Wilhelm, 1931, Determination of calcium with picrolonic acid: Zeitschr. anal. Chemie., v. 86, p. 98-113.
- Elving, P. J., and van Atta, R. E., 1950, Separation and determination of barium, strontium, and calcium: Anal. Chemistry, v. 22, p. 1375-1378.
- Ettre, Kitty, and Adam, Janos., 1957, Flame photometric determination of alkaline-earth metals in the presence of foreign metals: Zeitschr. anal. Chemie., v. 155, p. 105-114.
- Feldman, Cyrus, 1949, Direct spectrochemical analysis of solutions: Anal. Chemistry, v. 21, p. 1041-1045.
- Fresenius, R., 1893, Über die Trennung des Strontians vom Kalk: Zeitschr. anal. Chemie., v. 32, p. 189-203.
- Fresenius, W., and Ruppert, F., 1891, Notizen über die verschiedene Löslichkeit der Chromate von Strontian und Kalk in verdünntem Weingeist und über die Möglichkeit der Trennung dieser beiden Alkalischen Erden als chromsaure Salze: Zeitschr. anal. Chemie., v. 30, p. 672-680.
- Gallo, G., 1935, Equilibrium of strontium sulfate and water at various temperatures: Am. Chim. Applicata, v. 25, p. 628-631.
- Goldin, A. S., 1956, Determination of strontium-90: U.S. Atomic Energy Comm. TID-7517, (pt. 1b), p. 323-334.
- Goodale, B., 1936, Volumetric determination of strontium: Chemistry and Industry, v. 1936, p. 896.
- Hahn, R. B., and Straub, C. P., 1955, Determination of radioactive strontium and barium in water: Am. Water Works Assoc. Jour., v. 47, p. 335-340.
- Harrison, G. R., Lord, R. C., and Loofbourow, J. R., 1948, Practical spectroscopy: New York, Prentice-Hall, 605 p.
- Haslam, J., 1935, The oxalates of calcium, strontium, and magnesium: Analyst, v. 60, p. 668-672.
- Hinsvark, O. N., Wittwer, S. H., and Sell, H. M., 1953, Flame photometric determination of calcium, strontium, and barium in a mixture: Anal. Chemistry, v. 25, p. 320-322.

- Hitchcock, R. D., and Starr, W. L., 1954, Spectrographic techniques as applied to the analysis of sea water: *Applied Spectroscopy*, v. 8, no. 1, p. 5-17.
- Huldt, L., 1944, Intensity anomalies in the flame spectrum of strontium on the addition of calcium: *Arkiv. Mat., Astron. Fysik*, v. B31, no. 1, 4 p.
- Ikeda, Shigiro, 1956, Flame spectrochemical analysis—VI, Determination of strontium: *Tohoku Univ. Research Inst. Sci. Repts., ser. A*, v. 8, no. 6, p. 457-462.
- Ishibashi, Masayoshi, and Tsutsui, Tensor, 1956, Paper chromatography of calcium, strontium, and barium: *Bunseki Kagaku*, v. 5, p. 437-439.
- Jacobs, M. R., 1944, Analytical chemistry of industrial poisons hazards and solvents: New York, Interscience Publishers, Inc., 806 p.
- Kahn, B., and Goldin, A. S., 1957, Radiochemical procedures for the identification of the more hazardous nuclides: *Am. Water Works Assoc. Jour.*, v. 49, p. 767-771.
- Kolb, A. C., and Streed, E. R., 1952, Intensity of spectral lines produced in nonhomogeneous flames: *Jour. Chem. Physics*, v. 20, p. 1872-1878.
- Leddicotte, G. W., and Reynolds, S. A., 1951, Activation analysis with the Oak Ridge reactor: *Nucleonics*, v. 8, p. 62-65, 78.
- Leliaert, G., and Eeckhaut, J., 1957, Investigation of chemical separation methods for calcium and strontium. Quantitative determination of both elements in calcium-strontium mixtures by the isotope dilution method: *Anal. Chim. Acta*, v. 16, p. 311-320.
- Lerner, Morris, and Rieman, William III, 1954, Quantitative separation of the alkaline-earths by ion-exchange chromatography: *Anal. Chemistry*, v. 26, p. 610-611.
- Lucchesi, Claude A., 1957, Determination of strontium by X-ray fluorescence: *Anal. Chemistry*, v. 29, p. 370-373.
- Macchia, O., 1928, Detection and determination of strontium, barium, and calcium: *Chem. Zeitung*, v. 52, p. 1281-1282.
- Magee, Robert J., and Headridge, James B., 1955, Separation of Group II-A elements of the periodic table by paper chromatography: *Analyst*, v. 80, p. 785-788.
- Martell, E. A., 1956, The Chicago sunshine method, absolute assay of strontium-90 in biological materials, soils, waters, and air filters: U.S. Atomic Energy Comm. AECU-3262, 59 p.
- Mayr, Carl, and Burger, Geo., 1930, Potentiometric titrations with mercurous nitrate and sodium oxalate as titrating solutions: *Monatsh.*, v. 56, p. 113-115.
- Meegers, W. F., 1946, Spectroscopy, past, present, and future: *Optical Soc. America Jour.*, v. 36, p. 431-448.
- Meunier, J., 1926, The detection and determination of strontium using spectrographic methods and the hydrogen flame: *Acad. Sci. (Paris) Comptes rendus*, v. 182, p. 1160-1162.
- Nagaoka, Hantaro, and Machida, Iwajiro, 1934, A microspectrometric method and its accuracy: *Imp. Acad. (Tokyo) Proc.*, v. 10, p. 629-631.
- National Bureau of Standards, 1953, Maximum permissible amounts of radioisotopes in the human body and maximum permissible concentrations in air and water: *Handb.* 52.
- Noll, W., 1931, Determination of strontium in minerals and rocks: *Zeitschr. anorg. Allg. Chemie*, v. 199, p. 193-208.
- 1932, Geochemistry of strontium: *Fortschr. Mineral. Krist. Petrog.*, v. 17, p. 440-442.

- Odum, Harold T., 1951, Notes on the strontium content of sea water, celestite radiolaria, and strontianite snail shells: *Science*, v. 114, p. 211-213.
- Pauling, Linus, 1948, The nature of the chemical bond: Ithaca, N.Y., Cornell Univ. Press, 450 p.
- Penchev, N. P., and Nonova, D. K., 1955, Macro-, semimicro-, and micro-determination of strontium as picrolonate: *Bulgar. Akad. Nauk., Izv. Khim. Inst. Sofia*, v. 3, p. 53-65.
- Pochinok, Kh. N., 1932, Determination of strontium as oxalate: *Appl'ed Chemistry (USSR) Jour.*, v. 5, p. 1078-1087.
- Pollard, F. H., and Marten, J. V., 1956, Spectrophotometric determination of the alkaline-earth metals with murexide, Eriochrome Black T, and with o-cresolphthalein complexation: *Analyst*, v. 81, p. 348-353.
- Pollard, F. H., McOmie, J. F. W., and Marten, J. V., 1956, Quantitative analysis of alkaline-earth metals by paper chromatography: *Analyst*, v. 81, p. 353-358.
- Rankama, Kalervo, and Sahama, T. G., 1950, *Geochemistry*: Univ. Chicago Press, 912 p.
- Rawson, S. G., 1897, The quantitative and qualitative separation of barium, strontium, and calcium: *Soc. Chem. Indus. (London) Jour.*, v. 16, p. 113-115.
- Reed, George W., Jr., 1956, Absolute β -assay with end-window Geiger-Muller Counters: U.S. Atomic Energy Comm. ANL-5608, 16 p.
- Rusanov, A. K., 1934, Rapid visual spectroscopic analysis of solutions: *Zavodskaya Lab.*, v. 3, p. 915-918.
- Sawyer, R. A., 1951, *Experimental spectroscopy*: New York, Prentice-Hall, 2d. ed., 358 p.
- Schumacher, Ernst, 1956, Isolation of potassium, rubidium, strontium, barium, and rare earths in stony meteorites: *Helv. Chem. Acta*, v. 39, p. 531-537.
- Shreve, R. N., Watkins, C. H., and Browning, J. C., 1939, Determination of strontium in the presence of calcium: *Indus. Eng. Chemistry, Anal. Ed.*, v. 11, p. 215.
- Skoustad, M. W., 1957, Flame photometric determination of strontium in water: U.S. Geol. Survey open-file report, 18 p.
- Smales, A. A., 1951, Determination of strontium in sea water by a combination of flame photometry and radio chemistry: *Analyst*, v. 76, p. 348-355.
- Strebinger, R., and Mandl, J., 1926, Microchemical determination of strontium: *Mickrochemie*, v. 4, p. 168-171.
- Sugawara, Ken; Koyama, Takashiro; and Kawasaki, Nobuko, 1956, Flame photometric determination of alkali and alkaline-earth elements in waters—II, Calcium and strontium: *Chem. Soc. Japan Bull.*, v. 29, p. 687-685.
- Szebelledy, Laszlo, 1929a, Separation and determination of calcium and strontium: *Magyar Chem. Folyoirat*, v. 35, p. 59-62.
- 1929b, Determination of strontium and barium: *Zeitschr. anal. Chemie*, v. 78, p. 198-206.
- 1932, Separation and determination of strontium and barium as bromides: *Magyar Chem. Folyoirat*, v. 38, p. 81-83.
- Taylor, A. E., and Paige, H. H., 1955, Determination of microgram quantities of strontium in solution. Evaluation of flame photometric methods: *Anal. Chemistry*, v. 27, p. 282-284.
- Ukai, Tatsiji, 1931, Separation of strontium and calcium by means of ammonium sulfate: *Chem. Soc. Japan Jour.*, v. 52, p. 622-626.
- U.S. Public Health Service, 1946, Drinking water standards: *Public Health Repts.*, v. 61, no. 11, p. 371-384.

- Uzumasa, Yasumitsu, and Okino, Histeru, 1933, Spectrographic chemical analysis I, A new method of spectral analysis of solutions: *Cher. Soc. Japan Jour.*, v. 54, p. 631-641.
- 1934, Spectrographic analysis II. A new method of spectrum analysis of solutions 2: *Chem. Soc. Japan Jour.*, v. 55, p. 622-626.
- Vinogradov, A. P., and Borovik-Romanova, T. F., 1945, Geochemistry of strontium: *Akad. Nauk SSSR Doklady*, v. 46, p. 211-214; *Acad. sci. U.R.S.S. Comptes rendus*, v. 46, p. 193-196 (1945) (in English).
- Welcher, F. J., 1947, 1948, *Organic Analytical Reagents*, v. 1, 2, 3, 4: New York, D. Van Nostrand Co., Inc.
- Willard, H. H., and Goodspeed, E. W., 1936, Separation of strontium, barium, and lead from calcium and other metals: *Indus. Eng. Chemistry, Anal. Ed.*, v. 8, p. 484.
- Willard, H. H., Merritt, L. L. Jr., and Dean, J. A., 1948, *Instrumental methods of analysis*: New York, D. Van Nostrand Co., Inc., 344 p.
- Wilska, Seppo, 1951, Quantitative spectral analysis of trace elements in water: *Acta Chem. Scand.*, v. 5, p. 1368-1374. Zlotowski, I., and Folthoff, I. M., 1944, Polarographic behavior of alkaline earth metals—I, Barium and strontium: *Am. Chem. Soc. Jour.*, v. 66, p. 1431-1435.
- 1945, Polarographic behavior of alkaline earth metals—II, The polarographic determination of calcium alone and in the presence of other alkaline earth metals: *Jour. Phys. Chem.*, v. 49, p. 386-405.

