

fringent needles. The same treatment does not affect the cobalt crystals noticeably: Boiling a quinoline mount of the cobalt-nickel-quinoline mixed crystals left two species, the colorless birefringent needles and blue-violet crystals.

Quinoline has been used as a reagent in chemical microscopy by the authors for several years. A few examples of its applicability are: to identify cuprous chloride, cupric chloride, and ferrous chloride in deposits from metal systems; to estimate copper chloride in mixtures of copper sulfate and chloride; to test crystalline deposits from a Monel metal system for contamination by the system (indicated by growth of charac-

teristic copper, iron, and nickel chloride-quinoline crystals); to indicate absence of any appreciable amount of the metals listed in Table I; and to identify cuprous, cupric, and ferrous chloride, in chlorinated-silicon residues. The cuprous-quinoline crystals sprout from the opaque silicon mass very quickly. The cupric footballs and ferrous-quinoline crystals detach themselves from the mass readily.

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Quantitative Spectrochemical Determination of Barium and Strontium

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►A spectrochemical procedure is described for the quantitative determination of barium and strontium. It is applicable to any sample which can be dissolved in hydrochloric acid after fusion in a sodium carbonate flux. The prepared sample solution is analyzed spectrochemically using high voltage spark excitation. The coefficient of variation of the method is less than 5% for samples containing as little as 0.005% barium or strontium. Lower concentrations can be determined with attendant lowered precision and accuracy. Standards which approximate the sample chemical composition are used to yield results of maximum accuracy. Results obtained are compared with National Bureau of Standards certified values for six mineral type samples. The per cent strontium determined in granite and diabase compares favorably with results obtained by other instrumental techniques.

THE PRESENCE of barium and strontium in nature is widespread. Both elements occur to some extent in nearly all common minerals, especially in igneous rocks. Analytical data on the distribution and abundance of barium and strontium are unreliable in many instances, especially where the concentration of the elements approaches the detection limit of the method employed. Considering that the barium and strontium content of

some minerals may be greater than 1%, a determination of these elements should be included in any mineral analysis having a claim to completeness.

Chemical (3, 14, 18, 34), colorimetric (22), emission spectrographic (4, 5, 10, 16, 19, 27, 31, 35), flame photometric (6, 9, 15, 25, 28, 30), mass spectrometric (13), polarographic (7), and x-ray fluorescence (8, 17, 20, 21) analytical methods have been applied to the determination of barium and strontium in a variety of sample types with varying degrees of precision and accuracy. The absence of a reliable analytical technique for these elements is evident as only one standard sample is available which has a per cent composition for barium certified by the National Bureau of Standards to three significant figures. Only one sample has a strontium value with a reliable two significant figure certification. This value has appeared within the past two years and represents an increase of a factor of 2 over the previously certified value.

The need for a rapid and reliable analytical method for the determination of barium and strontium in mineral type samples of interest in geological studies led to the development of the spectrochemical technique described. This technique is applicable to any type sample which can be dissolved in hydrochloric acid subsequent to fusion in a sodium carbonate flux. Concentrations as low as 0.005% can be determined with a coefficient of variation of less than 5%. The concentration limit

can be extended lower with attendant lowered accuracy.

SPECTROCHEMICAL METHODS

Spectrochemical methods are readily adaptable to the determination of microgram quantities of elements, in almost any type sample, with reasonable accuracy and minimum sample manipulation. The methods are rapid and relatively free from interferences. Detection limits are lower than those obtainable by most other sensitive procedures.

Several methods for the analysis of solutions by spectrochemical techniques have been proposed; however, only two of the suggested methods have been widely used and several cannot justifiably be called solution excitation methods, as all liquid is evaporated prior to the application of energy to excite the residue.

The porous cup electrode which permits solution to seep through the thin bottom of a hollow electrode was introduced by Feldman (11). Although used extensively, it does not function well with solutions of high salt concentrations because of limitations imposed by the reduced capillary action of the electrode wall.

An electrode which introduces a fresh sample portion into an excitation zone by transportation of the sample solution on the periphery of a rotating disk is applicable to solutions of various concentrations and acidity. The rotating

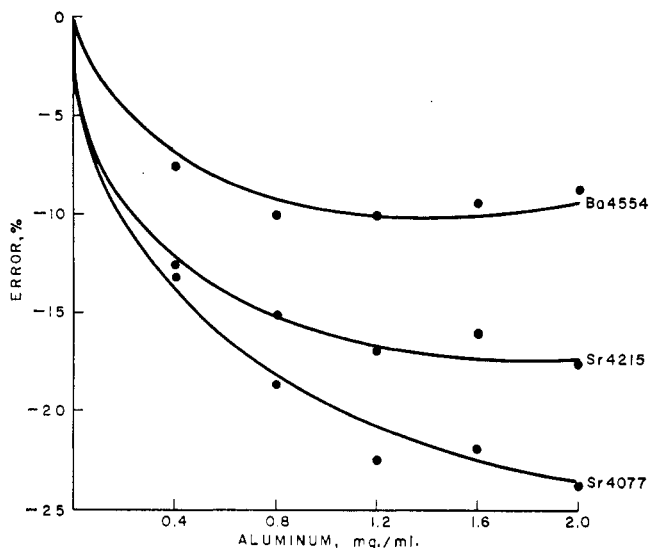


Figure 1. Relative error introduced by aluminum

electrode (26, 29) (Rotrode) is used in the procedure described, because it is easily adaptable to analysis of solutions of high salt concentration, and previous experience indicates easier control of the sample during excitation.

SAMPLE DECOMPOSITION

The great variety of naturally occurring mineralogical types and large differences in chemical composition introduce complications in the adaptation of a spectrochemical technique to the analysis of mineral type samples. Elements to be determined may be present in crystalline states which vary in behavior and cause major differences between samples of similar chemical composition. For maximum accuracy in the spectrochemical analysis of minerals and rocks, the samples and standards should have nearly the same general chemical composition and physical properties. However, there is an absence of a diversity of reliable chemically analyzed standard samples, and synthetic type minerals which are often substituted are known to produce erroneous results in most instances.

A solution analysis technique was chosen to eliminate the problems normally encountered in the spectrochemical analysis of powdered type mineral samples. A solution method permits easy removal of history and origin influences, as well as differences in crystalline composition, and allows simple addition of buffers and internal standards. This makes possible the use of synthetic standards which approximate the composition of the sample to be analyzed.

Fusion of a powdered sample with sodium carbonate according to standard rock and mineral analytical procedures, followed by dissolution of the fused melt in hydrochloric acid, was found

to be satisfactory. Besides serving as a fluxing agent, the large quantity of sodium chloride present in the solution was an effective spectrochemical buffer.

To determine the efficiency of the sodium carbonate fusion process, the silica residues of several samples were spectrochemically analyzed by a direct current arc procedure to establish quantitative recovery of barium and strontium in the prepared sample solution. The procedure used to examine the residues has a detection limit of 0.0001% for both barium and strontium. Examination of the spectrograms established that the recovery was quantitative, as the most persistent lines of the elements were either barely perceptible or not detected. It is believed that in the cases in which the elements were detected they were actually adsorbed on the silica surface rather than being present because of incomplete sample fusion.

MATRIX EFFECTS

The use of a spectroscopic buffer minimizes changes in excitation temperature, provides a common matrix material, and lowers detection limits by increasing the line-background ratio (2). In the described procedure the large quantity of sodium chloride serves as a buffer. However, because variations in the barium and strontium content were observed which had no apparent explanation, it was necessary to investigate the matrix effects caused by elements which normally occur in minerals and rocks as major constituents. The effects of various concentrations of aluminum, calcium, magnesium, and combinations of these elements were investigated. The amount of each element or mixture of elements used was selected on the basis of concentrations likely to be encountered in the

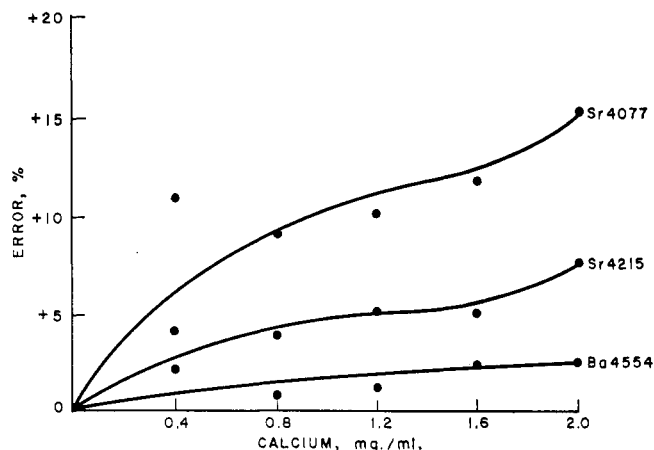


Figure 2. Relative error introduced by calcium

analysis of most common minerals and rocks.

Data from the analysis of a series of solutions containing sodium chloride as a buffer, indium as an internal standard, and varying concentrations of barium and strontium in the range of 2 to 10 γ per ml. were used to construct an accurate analytical curve. Similar solutions containing 5 γ of barium and 5 γ of strontium per ml. and various amounts of aluminum, calcium, magnesium, and mixtures of these elements were analyzed by the proposed spectrochemical procedure. The data obtained are presented in Figures 1 to 6. The ordinate represents the per cent relative deviation of the observed from the true barium and strontium concentration and the abscissa indicates the concentration of the interfering ions.

The graphs indicate a negative deviation for aluminum, and a similar deviation was reported by Mitchell and Robertson (23). Vallee and Margoshes (32), in a study of extraneous ions on flame photometric analyses, have also reported that the presence of appreciable quantities of aluminum depresses the emission intensity of strontium in a flame source. Fast and Nielsen (10) found an increase in the strontium radiation in the presence of calcium and magnesium, and data in Figures 2, 3, and 6 show a similar increase. Odum (25) proposed use of a family of calibration curves based on variations in calcium content to obtain maximum accuracy. The curves in Figures 4 and 5 indicate that the aluminum suppression of the radiation is stronger than the calcium or magnesium enhancement. In all cases, except the calcium and magnesium mixture, a maximum deviation is noted in the case of the strontium 4077 line.

The interference effects of iron and potassium were also investigated and, as the observed deviation was found to be consistently less than the calculated precision of the method, the interference effects were considered negligible.

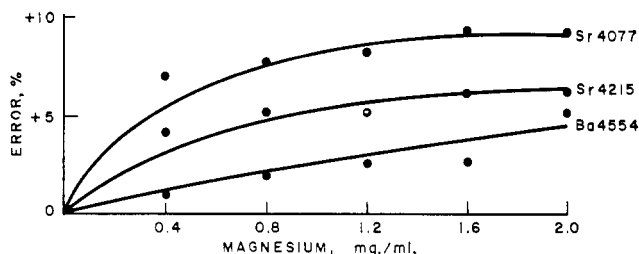


Figure 3. Relative error introduced by magnesium

The family of curves presented in Figures 1 to 6 indicates that some method of compensation is needed to obtain results with maximum accuracy, especially in cases where it is desirable to determine both barium and strontium. Unless the general chemical composition of the sample is known, it will be necessary to perform a preliminary survey analysis to determine the approximate composition of the sample so that the possible interferences may be compensated for by addition of the extraneous elements to the standards used in the preparation of the analytical curve. Any one of the several general spectrochemical procedures applicable to mineral type samples may be used; the common matrix procedure suggested by Weaver and Brattain (33) is satisfactory. In cases where errors up to 20% are tolerable, no correction for interferences is necessary.

The concentration of sodium chloride in the prepared sample solution influences the relative position of the analytical curves to some extent. The curves show a decrease in the intensity ratio as the concentration of sodium chloride increases. To eliminate variations caused from differences in buffer concentration, all sample and standard solutions are adjusted so that the concentration of sodium chloride is 22%.

INTERNAL STANDARD

The addition of an internal standard (2) to the sample for spectrochemical analysis provides compensation for factors which would otherwise present control difficulties. Indium, which is readily available in a spectrochemically pure state as the oxide, was found to be

Table I. Analytical Lines and Excitation Potentials

Element	Wave Length, A.	Excitation Potential, Volts
Indium (internal standard)	4511.3	3.01
Barium	4554.0	2.71
Indium (internal standard)	4101.8	3.01
Strontium	4077.7	3.03
	4215.5	2.93

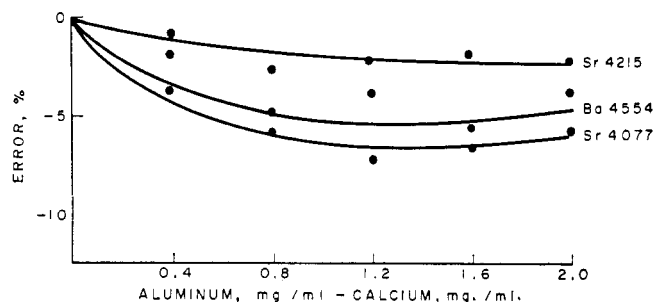


Figure 4. Relative error introduced by aluminum and calcium combined

Ratio 1 to 1

an ideal internal standard for barium and strontium. The wave lengths and excitation potentials (24) of the lines used in the procedure are presented in Table I.

STANDARDS

Variations caused by differences in general chemical composition and crystalline structure of the sample are eliminated by fusion and subsequent dissolution of the sample. This technique also allows use of reliable synthetic standards which have the same chemical composition as the sample under consideration.

Synthetic standards were prepared from commercially available spectrochemically pure barium carbonate and strontium carbonate, and reagent grade sodium carbonate. In addition, spectrochemically pure calcium carbonate and magnesium oxide and reagent grade aluminum chloride were added to prepare standards having the same general chemical composition as the samples. All salts used were dissolved in hydrochloric acid and predetermined aliquots were mixed with the internal standard solution and evaporated to dryness. The residue was dissolved in a measured volume of 0.5N hydrochloric acid.

Several standards varying in concentration from 0.5 to 10.0 γ of barium and strontium per ml. were used to construct calibration curves. These curves were prepared by plotting log relative intensity of a barium or strontium line to the indium internal standard line *vs.* log concentration. They show that linear calibration curves are easily obtainable in the 1- to 10-p.p.m. range, and the slope indicates that indium is a good internal standard for both barium and strontium.

Only six samples having a value for barium or strontium certified by the National Bureau of Standards are available. Only one of these, lead-barium glass No. 89, has a barium value certified to three significant figures. Argillaceous limestone No. 1a is certified to contain 0.23% strontium oxide. This value has appeared within the past

two years and is nearly twice the previously stated value of 0.12% strontium oxide. Results which agree with the current National Bureau of Standards certified value for the strontium content of this sample have been obtained by x-ray fluorescence analysis (21) and also by flame photometric analysis (9).

Two rock samples issued by the U. S. Geological Survey (12) have been analyzed by many different laboratories, and even though fair agreement exists between reported values for the major constituents, large variations are noted for the minor constituent percentages. Values ranging from 1100 to 3000 γ of barium per gram sample have been reported (1) for the granite sample (G-1). The reported strontium content of this sample varies from 120 to 900 γ per gram. The diabase sample (W-1) is reported to contain from 150 to 390 γ of barium per gram sample. The reported strontium content of this sample varies from 120 to 450 γ per gram. Recent determinations (13, 17, 31) of the strontium content of G-1 and W-1 suggest that the recommended values proposed by Ahrens (1) should be revised.

The absence of a variety of reliable chemically analyzed standard samples precludes dependence upon naturally occurring minerals for reference standards in spectrochemical analysis for barium and strontium.

APPARATUS AND MATERIALS

The Applied Research Laboratories (ARL) 2-meter grating spectrograph is used in the analysis described in this report. This instrument has a uniform dispersion of 5.2 A. per mm. in the first order when used with a 24,400-line-per-inch grating. An intensity control stand at the entrance slit is adjusted to allow 32% of the light intensity to enter the spectrograph. High voltage spark excitation is supplied by the ARL high precision source unit.

The spectrum is recorded on Eastman Kodak Co. spectrum analysis No. 2 film, which is processed according to standardized conditions in an ARL developing machine and film dryer. Spectrum analysis No. 1 film may also

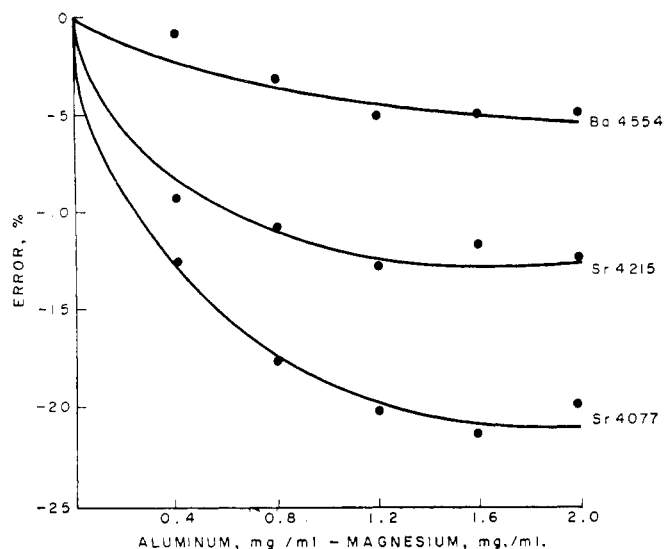


Figure 5. Relative error introduced by aluminum and magnesium combined

Ratio 1 to 1

be used if only a narrow concentration range is to be determined.

Transmission of the spectrum lines is measured on a Jarrell-Ash Co. microphotometer. Line relative intensities are computed on an ARL calculating board.

A United Carbon Products Co., Inc. (UCP), No. 106-U2 disk-type electrode is used to bring a portion of the prepared sample solution from a 2-ml. beaker into the analytical gap. This electrode is mounted on an ARL solution excitation stand and is rotated at 14 r.p.m. The counter electrode is UCP No. 104-U1.

Johnson, Matthey and Co., Ltd. (JM), spectrographically pure salts are used to prepare standards, and J. T. Baker Chemical Co. reagent grade anhydrous sodium carbonate is used as a flux to decompose the sample. JM spectrographically pure indium oxide dissolved in hydrochloric acid is used as an internal standard solution.

The hydrochloric acid solution is prepared by diluting 40 ml. of reagent grade concentrated hydrochloric acid to 1 liter with distilled water.

SPECTROCHEMICAL PROCEDURE

Sample Preparation. Weigh to the nearest 0.1 mg. a representative sample (not to exceed 200 mg.), which contains 10 to 100 γ of barium and/or strontium, into a platinum crucible. Add 2.0 grams of anhydrous sodium carbonate and stir the mixture with a platinum wire or smooth glass rod. Heat the mixture at red heat until the flux is fluid, and continue the heating until effervescence ceases. To ensure complete fusion, continue heating for 3 minutes while swirling the molten contents of the crucible.

After the fused melt cools to room temperature, place the crucible in a 250-ml. beaker and dissolve the fused contents in 25 ml. of 1 to 1 hydrochloric acid.

Remove the crucible from the beaker,

being careful to wash off completely the drops adhering to the crucible walls. Add 5.00 ml. of a solution containing 150 γ of indium oxide per ml. to provide indium as an internal standard. Place the beaker containing the prepared sample solution under an infrared lamp or on a hot plate and evaporate the solution to dryness.

Remove the beaker and dry salts from the heat source and cool to room temperature. Add 10.00 ml. of a 0.5N hydrochloric acid solution and stir the solution with a glass rod to ensure complete dissolution of all soluble salts. Transfer the solution to a small centrifuge tube and remove the silica precipitate by centrifugation. Transfer the supernatant liquid to a small vial.

Spectrochemical Analysis. Transfer a portion of the prepared sample solution to a small porcelain boat or other container suitable for use with a rotating disk sample electrode. (A beaker-type container approximately 8 mm. deep and 18 mm. in inside diameter, made by sawing off the bottom portion of a 10-ml. vial, has been found very satisfactory.) Place the container on the excitation stand and adjust the analytical gap between the sample and counter electrode to 4.0 mm. Rotate the sample electrode at 14 r.p.m. and adjust the container so that approximately one third of the rotating electrode is in the solution. Spark the solution using the excitation conditions in Table II.

Table II. Spectrograph and Excitation Source Settings

Capacitance	0.007 μ f.
Inductance	360 μ h.
Current	7 RF amperes
Intensity control	32% transmittance
Analytical gap	4.0 mm.
Entrance slit	30 μ
Grating aperture	70% open
Exposure	40 seconds

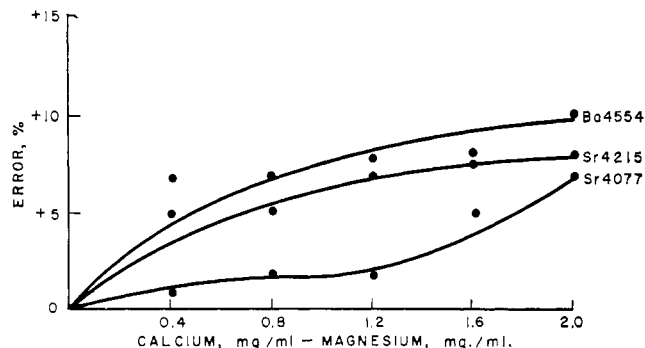


Figure 6. Relative error introduced by calcium and magnesium combined

Ratio 1 to 1

Film Processing. Develop the film in Eastman D-19 developer for 3 minutes at 68° F., rinse in an acetic acid short-stop bath for 30 seconds, fix in Eastman fixer for 10 minutes, wash for 10 minutes in running water, and dry on a film dryer.

Photometry and Calculations. Measure the transmittance of the internal standard and analytical lines (Table I) on the microphotometer adjusted to read 100% on an unexposed, developed segment of the film, and 0% with all transmitted light cut out. Convert the measured transmittances of the internal standard and analytical lines to log intensity ratios by means of a film calibration curve. Determine the barium and strontium concentration by reference to the appropriate calibration curve.

Standards Preparation. Prepare standards which approximate the composition of the samples to be analyzed by dissolving 2.0 grams of anhydrous sodium carbonate in 20 ml. of 1 to 1 hydrochloric acid. Add 5.00 ml. of a solution containing 150 γ of indium oxide per ml. Add varying amounts of barium and strontium from solutions prepared from spectrochemically pure salts so that a series of three or more standards brackets the concentration of barium and/or strontium expected to be found in the sample solutions. Adjust the solution so that the amount of major cations in the standards is approximately the same as in the sample solution. Evaporate the solution to dryness and dissolve in 10.00 ml. of 0.5N hydrochloric acid. Spark the solution using the excitation conditions shown in Table II.

Prepare calibration curves by plotting log relative intensity of the barium or strontium line to the indium internal standard line (Table I) vs. log concentration.

PRECISION AND ACCURACY

The barium and strontium determined in solutions of known concentration, and the amount of barium found in National Bureau of Standards sample No. 89 (lead-barium glass) were used to calculate the precision and accuracy of

Table III. Coefficient of Variation of Barium and Strontium Determination

Element	Barium	Barium	Strontium	Strontium
Added, γ /ml.	2.00	15.0	1.66	0.96
Determined, γ /ml.	1.88, 1.97 2.13, 2.07 2.00, 2.00 1.97, 1.97 2.07, 2.07 2.00, 2.07 1.94, 2.07 2.07, 2.20	14.5, 14.8 14.5, 14.0 15.0, 14.8 14.6, 15.2 14.9, 15.5 14.5, 16.0 16.2, 15.6	1.66, 1.73 1.65, 1.71 1.68, 1.75 1.57, 1.74 1.66, 1.67 1.60, 1.70 1.55, 1.66 1.59, 1.60	0.99, 1.00 0.96, 1.00 0.99, 0.97 0.90, 0.96 0.96, 0.93 0.94, 0.98 0.95, 0.96 0.91, 0.94
Coefficient of variation, %	4.4	4.2	3.3	3.1

Table IV. Coefficient of Variation of Barium Determined in National Bureau of Standards Sample No. 89

Barium, %	1.25
Certified by NBS	1.23
Determined	1.23 1.25 1.30 1.32 1.29 1.25 1.26 1.25 1.27 1.35 1.25 1.25 1.18 1.20 1.20 1.21 1.21 1.21 1.20
Coefficient of variation, %	3.6

Table V. Coefficient of Variation of Strontium Determination

Spectrum analysis No. 1		
Added, γ /ml.	18.06	14.68
Determined, γ /ml.	17.4 17.8 17.6 17.7 18.1 18.5 18.3 19.0 17.5 18.1 17.7 18.7 17.9	14.5 14.3 14.4 14.6 14.8 14.9 14.8 15.1 14.4 14.6 14.5 15.0 14.7
Coefficient of variation, %	18.6 2.7	14.9 1.7

the method. Data obtained are presented in Tables III and IV. Coefficients of variation of less than 5% are indicated. The percentage barium in standard sample 89 was determined from analysis of a prepared sample solution adjusted to contain 50 γ of barium per ml. The National Bureau of Standards certifies this sample to contain 1.40% barium oxide (1.25% barium). Data presented for each concentration range represent results from five separate analysts. The precision and accuracy of the method were found to be nearly equal.

The precision of the strontium determination can be improved by recording the spectrogram on spectrum analysis No. 1 film or plate which has a higher contrast and lower background density than spectrum analysis No. 2 emulsion. However, the sensitivity of No. 1 film is not as good as that of No. 2, and the slope of the film-emulsion-characteristics curve increases rapidly at approximately 3400 Å. Although No. 1 emulsion may be used satisfactorily for the determination of strontium in concentrations as low as 1 γ per ml., the detection limit of barium is considerably greater.

The precision obtainable by use of No. 1 film as a recording medium is illustrated in Table V. The data represent a series of replicate determinations by one analyst.

COMPARISON OF RESULTS

In Table VI, results obtained by the procedure described are compared with values reported by the National Bureau of Standards (NBS). Values listed for

NBS certified values were calculated from results which are certified as the per cent oxide, and these values, which include a subscript number, were calculated to one more significant figure than certified by the NBS.

A comparison of results obtained by this procedure with values obtained by other analysts using different techniques is presented in Table VII. These data indicate that the values recommended by Ahrens (1) should be revised. The three significant figure tabulation may not be entirely justified but was retained in the interest of consistency with the values reported by other authors.

DISCUSSION

A comparison of results indicates that the proposed emission spectrographic method competes favorably with other methods which are generally accepted as more accurate and precise. The proposed method is superior to chemical and other instrumental techniques at concentrations lower than 0.05% barium or strontium.

The action of sodium chloride as a spectrographic buffer is not ideal, because analytical curve displacement is not independent of the concentration variations of major constituents in the sample. It is possible that some other fluxing agent could be used which has buffering properties suitable enough so that matrix effects are entirely negligible. The addition of a large quantity of an aluminum, calcium, or magnesium salt to the prepared solution may also eliminate variations caused by sample differences. Analysts are usually concerned with one sample type, and for this reason an adjustment for the sample matrix is easy and is also considered desirable to obtain results of maximum accuracy.

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Table VI. Comparison of Values Certified by National Bureau of Standards with Barium and Strontium Determined Spectrochemically

Sample Designation	Barium, %		Strontium, %	
	NBS	Spectrochemical	NBS	Spectrochemical
Limestone, 1a	0.19 ₈	0.194
Dolomite, 88	<0.009	0.0055
Lead-barium glass, 89	1.25	1.25
Flint clay, 97	0.013 ₄	0.0141	...	0.0088
Plastic clay, 98	0.05 ₄	0.057	...	0.023
Portland cement, 177	...	0.0190	0.04 ₂	0.037

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Table VII. Comparison of Barium and Strontium Determinations

Method	Barium, %		Strontium, %	
	G-1	W-1	G-1	W-1
Spectrochemical (1)	0.130	0.0270	0.0280	0.0290
Spectrochemical (direct current arc) (31)	0.0287	0.0172
Isotope dilution (31)	0.0262	0.0178
(13)	0.0233	0.0177
X-ray fluorescence (17)	0.0263	0.0197
Spectrochemical (high voltage spark-solution)	0.108	0.0145	0.0256	0.0180

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Hydrolysis Reactions of Thioacetamide in Aqueous Solutions

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► Spectrophotometric measurements of the rate of disappearance of thioacetamide in acid solutions have confirmed previous chemical measurements; hydrolysis of the thio group is predominant and the rate of hydrolysis of the amide group is too slow to be measurable by the methods used. The second-order rate constant obtained spectrophotometrically for the sulfide hydrolysis is 0.21 liter mole⁻¹ min.⁻¹ at 90° C., the same as that calculated from measurements of the hydrogen sulfide evolved. In sodium hydroxide solutions amide group hydrolysis is predominant and the second-order velocity constant is 9 ± 1 liter mole⁻¹ min.⁻¹ at 100.3° C. The rate of thio group hydrolysis in sodium hydroxide solutions is approximately one fourth that of amide group hydrolysis. The thioacetate ion hydrolyzes to sulfide more slowly; the rate is first-order with respect to both thioacetate and hydroxyl ion, and the second-order rate is constant 0.019 ± 0.0015 liter mole⁻¹ min.⁻¹ at 90° C.

The energy of activation was calculated to be 19 kcal. per mole from 70° to 90° C.

A STUDY of the acid-catalyzed hydrolysis of thioacetamide (6) has shown that the rate of hydrolysis to acetamide and hydrogen sulfide is first-order with respect to the concentration of thioacetamide and of hydrogen ion and the second-order velocity constant has the value 0.21 ± 0.023 liter mole⁻¹ min.⁻¹ at 90° C. The hydrolysis of thioacetamide in acid solutions to give thioacetic acid and ammonium ion was negligibly slow, compared with the hydrolysis to acetamide and hydrogen sulfide. However, as the conclusions of that study were based entirely on measurements of the rate of production of hydrogen sulfide and the change in the hydrogen ion concentration, there appeared justification for an independent confirmatory method which would permit direct determination of the rate of disappearance of thioacetamide. Such measurements would afford more evidence as

to the relative rates of the sulfide and amide hydrolyses.

Rosenthal and Taylor (5) have followed the hydrolysis of thioacetamide spectrophotometrically by making use of the absorption peak of thioacetamide at about 260 mμ. This technique was used in the confirmatory study of the acid-catalyzed hydrolysis of thioacetamide reported below.

REAGENTS AND APPARATUS. Arapahoe thioacetamide, lot 1402, was used throughout this work for the preparation of stock solutions. This material had a melting point range 111.0-13.0° C. and dissolved to give clear, colorless solutions.

Reagent grade chemicals were used for all solutions.

A Beckman Model DU quartz spectrophotometer with hydrogen discharge lamp and 1-cm. quartz cells was used.

PROCEDURE. Reaction solutions containing thioacetamide and hydrochloric

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