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Concentration Method for the Spectrochemical Determination of Minor Elements in Water

GEOLOGICAL SURVEY WATER-SUPPLY PAPER 1540-B



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by WILLIAM D. SILVEY

SPECTROGRAPHIC ANALYSIS OF NATURAL WATER

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UNITED STATES DEPARTMENT OF THE INTERIOR

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CONTENTS

| | Page |
|------------------------------------|------|
| Abstract..... | 11 |
| Introduction..... | 11 |
| General discussion of methods..... | 11 |
| Experimental data..... | 13 |
| Apparatus..... | 17 |
| Spectrographic equipment..... | 17 |
| Chemical apparatus..... | 17 |
| Reagents..... | 17 |
| Procedure..... | 18 |
| Spectrographic analysis..... | 18 |
| Photometry..... | 19 |
| Applications of the method..... | 19 |
| Conclusion..... | 21 |
| Literature cited..... | 21 |

ILLUSTRATIONS

| | Page |
|--|------|
| FIGURE 2. Analytical curves and line pairs. Calibration curve..... | 15 |

TABLES

| | Page |
|--|------|
| Table 1. Accuracy using 10 percent indium..... | 14 |
| 2. Elemental ionization potentials..... | 14 |
| 3. Accuracy using 20 percent indium..... | 16 |
| 4. Precision obtained on five sets of determinations..... | 16 |
| 5. Accuracy of spectrographic determinations of aluminum in various water types as compared to chemical analysis..... | 16 |
| 6. Conversion of percent transmission to relative intensity..... | 20 |
| 7. Elemental lines and analytical range..... | 20 |

SPECTROGRAPHIC ANALYSIS OF NATURAL WATER

CONCENTRATION METHOD FOR THE SPECTROCHEMICAL DETERMINATION OF MINOR ELEMENTS IN WATER

By WILLIAM D. SILVEY

ABSTRACT

A combined chemical and spectrographic method is described, in which traces (1.0–0.005 mg) of copper, lead, manganese, aluminum, chromium, zinc, and iron are quantitatively determined in water samples.

The method of Heggan and Strock was modified to obtain more effective buffering in the arcing mixture. The lack of effective buffering in the arcing mixture of the original method resulted in poor analytical results. In the method presented the concentration of indium was increased from 10 to 20 percent in the arcing mixture. This changed the average percent deviation for a single determination from ± 64 percent to ± 19 percent in a wide range of synthetic samples analyzed.

The chemical procedure involves the concentration of the trace metals through the use of selected chelating reagents. The chemical procedure was found to be highly effective in recovering as little as 0.005 mg of copper, iron, manganese, aluminum, lead, chromium, and zinc.

INTRODUCTION

In July 1959, the Quality of Water Branch of the U.S. Geological Survey began a 3-year research project under a cooperative agreement with the California Department of Water Resources. The project was designed to study the occurrence and distribution of the minor elements found in the various types of water in California.

The first phase of the project involved a survey of the literature on spectrographic analysis of solutions and the development of methods suitable for the determination of the minor elements in water. This report describes a part of the method-development phase of the project.

GENERAL DISCUSSION OF METHODS

The application of spectrographic techniques to the analysis of minor elements in various types of water has many distinct advantages over conventional wet chemical methods. Some of these are: many elements, even unsuspected ones, are simultaneously determined, elemental interferences experienced in using wet methods are eliminated, and the spectrum on the plate or film becomes a semipermanent record of the analysis.

There are three general spectrochemical approaches to the quantitative analysis of minor elements dissolved in natural waters. These are: the direct sparking of the water and recording the resulting emissions as lines on photographic plates or films, the direct arcing of the residue obtained from the water by evaporation, and the chemical concentration of the minor elements by chemical precipitation, and subsequent arcing.

The last approach was selected as the most suitable for the analysis of California waters for the following reasons: First, the concentration procedure is selective rather than general. This is important in that it makes available for arcing in the electrode a larger amount of the desired elements without also increasing the quantity of extraneous metals and salts. This latter effect is quite important in the analysis of highly concentrated waters. In such cases the residue on evaporation usually contains so much extraneous material that the amount of residue that can be placed in the electrode contains too little of the desired elements to permit their detection.

Second, the minimum detection limit for a given element by the chemical separation method, therefore, does not depend on line sensitivity or any arbitrary concentration of the element desired. As much or as little solution is taken for analysis as may be required to produce the necessary quantity of the desired element in the electrode. Since it is not necessary to compute concentration values from the most sensitive lines, interferences are avoided and accuracy is improved.

Finally, the effect of matrix is completely eliminated by the concentration approach. By precipitation, the dissolved solids of alkali-alkaline metals are separated from the minor elements. A single element added for internal standardization and radiation buffering of the arcing mixture acts as a matrix constant, for it is added in an exact constant amount.

The chemical separation method is limited to the determination of those elements which are quantitatively precipitated by the chelating agents employed. Therefore, neither the minor constituents of the alkali-alkaline earth groups, nor the internal standard element are determined. Another disadvantage to the chemical separation procedure is the time factor. This method requires more time for sample analysis than either the residue or direct sparking procedures.

Many workers have devised methods for concentrating minor elements to within the analytical range of the spectrograph. Braidech and Emery (1937, p. 68-77) used concentration methods in spectrographically analyzing water supplies for 10 Ohio cities for major as well as minor elements. Cholak (1937, p. 26-7) concentrated bismuth for spectrographic analysis by precipitating Bi_2S_3 from solution.

He was able to detect as little as 0.04 ppm of bismuth. Schleicher and Kaiser (1937, p. 393-6) concentrated minor elements (copper, nickel, indium, gallium, and titanium) from mine waters by electrolysis prior to spectrographic analysis. Bertrand (1940, p. 406-8) concentrated molybdenum from sea water, and arced the resulting precipitate. Vinogradov (1940, p. 1002-6) concentrated copper from solutions made from various soils by using rubeanic acid. Borneman-Starynkevich, Borovich, and Borovskii (1941, p. 227-31) concentrated the rare earths by using oxalate precipitations. Mitchell and Scott (1943, p. 4-8) concentrated a group of trace metals (cobalt, nickel, molybdenum, copper, and zinc) by using 8-hydroxyquinoline. They were able to detect as little as 0.002 mg of metals in soil extracts. Later, Mitchell and Scott (1947, p. 330-6) modified their earlier method by using tannic acid, thionalide, and 8-hydroxyquinoline as precipitating reagents. They found (1948, p. 367-78) that cobalt, nickel, molybdenum, tin, lead, zinc, chromium, vanadium, titanium, beryllium, and germanium are quantitatively precipitated by using the three reagents. Burriel and Ramirez-Munoz (1951, p. 495-512) concentrated traces of bismuth from solution by using cupferron. Goback and Pohl (1951, p. 328-34) concentrated the trace metals by extracting their complexes with dithizone.

EXPERIMENTAL DATA

In the search for a method by which trace metals dissolved in various types of water could be spectrographically determined, the Heggan and Strock method was studied by the author.

Originally, Mitchell and Scott (1947) using 8-hydroxyquinoline, precipitated cobalt, nickel, molybdenum, copper, and zinc, using iron as an internal standard and silica as a spectroscopic buffer. The precipitate was ignited and the ashed oxides were then brought up to a predetermined weight by the addition of pure powdered quartz. They later (1948) modified this method by maintaining iron as the internal standard, but adding large amounts of alumina instead of silica for more effective buffering; and increasing the number of metals precipitated quantitatively by adding tannic acid and thionalide in addition to the 8-hydroxyquinoline. The metals precipitated included beryllium, cobalt, chromium, germanium, molybdenum, nickel, copper, lead, titanium, vanadium, and zinc. Heggan and Strock later (1953) modified the method by changing the internal standard to indium. They also determined additional elements that could be quantitatively precipitated using oxine, tannic acid, and thionalide; these include silver, aluminum, bismuth, cobalt, chromium, copper, gallium, germanium, iron, molybdenum, nickel, lead, tin, vanadium, zinc, cadmium, and indium.

TABLE 1.—*Accuracy using 10 percent indium*

| Element | Number of determinations | Analytical range (mg in electrode) | Average deviation (percent) | Coefficient of variation |
|-----------------------|--------------------------|------------------------------------|-----------------------------|--------------------------|
| Lead..... | | | | |
| Copper..... | 26 | 0.8-.005 | ±77 | 200 |
| Iron..... | 21 | .8-.005 | ±56 | 304 |
| Chromium..... | 21 | .8-.005 | ±18 | 21 |
| Zinc..... | 24 | .5-.025 | ±88 | 104 |
| Aluminum..... | 27 | .8-.005 | ±67 | 167 |
| Manganese..... | 19 | .8-.005 | ±81 | 116 |
| Total or average..... | 138 | | ±64 | 152 |

Initially, standard solutions were made, each containing seven heavy metals in equal amounts and at concentrations ranging from 0.001 to 2.0 mg per 100 ml. After a series of analytical curves was constructed, a series of synthetic samples was prepared. Each synthetic sample contained one of the seven metals as a major constituent and the other six metals in minor amounts. The spectrographic results of 126 determinations (table 1) indicated a rather high degree of inaccuracies, although the precision was excellent. Temperature fluctuations during the arcing period were the cause of the poor accuracy. Ahrens (1950, p. 115) makes the following statement concerning temperature fluctuations in the arc:

When a mixture of elements enters the arc column, the element of lowest ionization potential is the most important in controlling arc temperature. Therefore, in order to buffer successfully against temperature fluctuations in the arc source, a significant amount of an element of low ionization potential must be added to each specimen.

Because indium has the lowest ionization potential of the metals contained in the arcing mixture (table 2), its concentration should be the most significant in stabilizing the temperature of the arc. In an attempt to stabilize arc temperature and to improve accuracy, a new series of curves was constructed using 20 percent indium (twice the amount used previously). The resulting curves were similar to those obtained with 10 percent indium. (See fig. 2.) Subsequently, 221 determinations were made on synthetic samples with 20 percent indium added as an internal standard buffer. The results

TABLE 2.—*Elemental ionization potentials*

| Element | Ionization potential (volts) | Element | Ionization potential (volts) |
|---------------|------------------------------|----------------|------------------------------|
| Aluminum..... | 5.96 | Lead..... | 7.38 |
| Chromium..... | 6.74 | Manganese..... | 7.41 |
| Copper..... | 7.68 | Zinc..... | 9.36 |
| Iron..... | 7.83 | Indium..... | 5.76 |

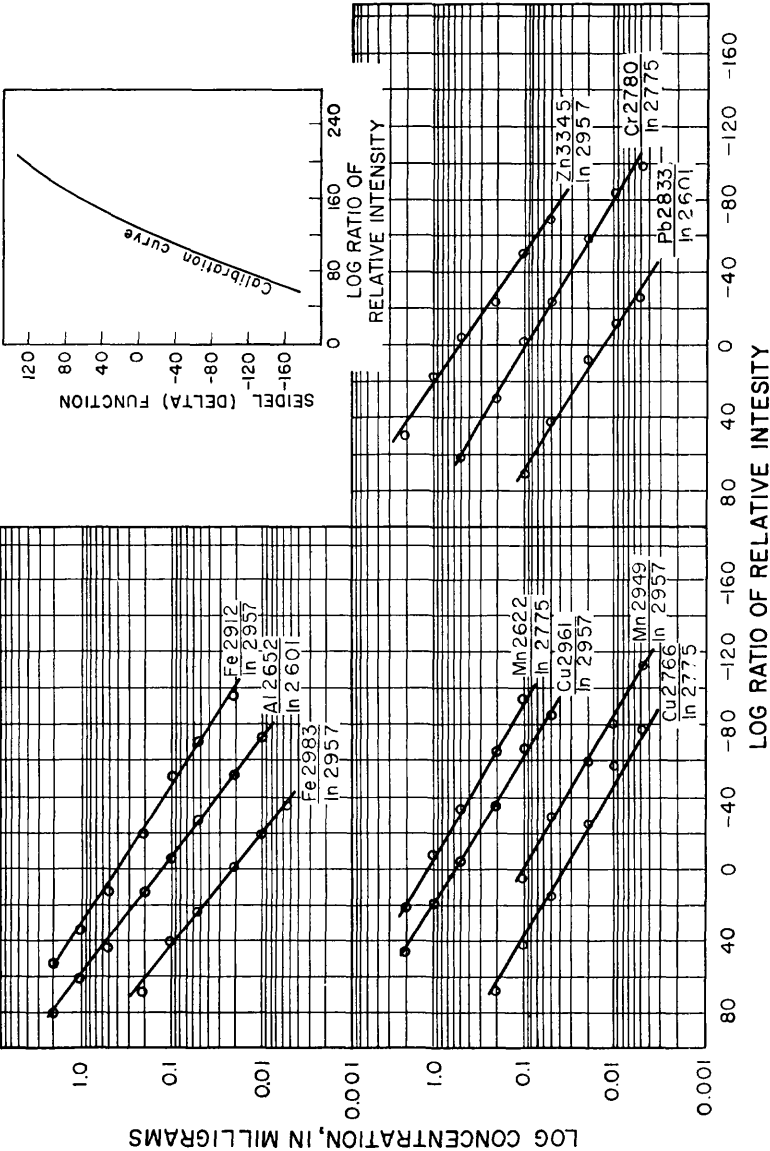


Figure 2.—Typical analytical curves and line pairs. Calibration curve.

TABLE 3.—Accuracy using 20 percent indium

| Element | Number of determinations | Analytical range (mg in electrode) | Average deviation (percent) | Coefficient of variations |
|-----------------------|--------------------------|------------------------------------|-----------------------------|---------------------------|
| Lead..... | 23 | 0.5-0.001 | ±25 | 12 |
| Copper..... | 38 | .5- .002 | ±16 | 19 |
| Iron..... | 44 | .5- .004 | ±17 | 23 |
| Chromium..... | 36 | .4- .004 | ±18 | 22 |
| Zinc..... | 34 | .5- .05 | ±24 | 29 |
| Aluminum..... | 30 | .5- .008 | ±17 | 22 |
| Manganese..... | 16 | .5- .002 | ±18 | 26 |
| Total or average..... | 221 | ----- | ±19 | 22 |

obtained were acceptable in both precision and accuracy. (Tables 3 and 4). The average difference between duplicate determinations was ± 0.09 mg within a concentration range of 1.5 mg to 0.1 mg.

TABLE 4.—Precision obtained on five sets of duplicate determinations, expressed as milligrams

| Element | No. 1 | | No. 2 | | No. 3 | | No. 4 | | No. 5 | | Average deviation |
|----------------|-------|-----|-------|-----|-------|-----|-------|-----|-------|-----|-------------------|
| Chromium..... | 1.2 | 1.3 | 0.2 | 0.2 | 1.1 | 0.8 | 0.2 | 0.3 | 0.2 | 0.2 | ±0.05 |
| Zinc..... | 1.1 | 1.1 | .6 | .9 | .8 | .7 | .8 | .8 | .4 | .3 | ±.05 |
| Lead..... | 1.1 | 1.1 | .1 | .2 | 1.0 | .8 | .2 | .1 | .2 | .2 | ±.04 |
| Copper..... | 1.3 | 1.7 | .3 | .3 | 1.5 | 1.2 | .6 | .4 | .09 | .09 | ±.25 |
| Manganese..... | 1.0 | 1.0 | .2 | .2 | .7 | .8 | .3 | .2 | .3 | .4 | ±.03 |
| Iron..... | 1.2 | 1.0 | .1 | .2 | .8 | .8 | 1.1 | .8 | .2 | .2 | ±.15 |
| Aluminum..... | 1.5 | 1.6 | .2 | .2 | 1.1 | 1.1 | .3 | .2 | .2 | .2 | ±.05 |
| Average..... | ----- | | | | | | | | | | ±0.09 |

The procedure for the determination of the seven elements was then applied to samples of natural water whose composition varied both in total amount of dissolved solids and in type of matrix. Values for aluminum are reported because it is consistently present in natural waters (table 5). These data also indicated an acceptable degree of accuracy when compared with chemical analysis.

TABLE 5.—Accuracy of spectrographic determination of aluminum, in milligrams, in various water types as compared to chemical analysis

[Aluminum: Al 2652/In 2601. Average deviation ± 0.002 mg]

| Chemical | Spectro-graphic | Conductivity (K $\times 10^6$) | Water type (bicarbonate, principal anion except where noted) |
|----------|-----------------|---------------------------------|--|
| 0.04 | 0.06 | 359 | Na>K>Ca |
| .16 | .10 | 418 | Na>K>Ca |
| .12 | .14 | 315 | Ca>Mg>Na |
| .11 | .08 | 369 | Ca>Mg>Na |
| .11 | .07 | 1,120 | Na>Ca>Mg |
| .05 | .05 | 714 | Na>Ca>Mg |
| .08 | .05 | 431 | Na>Ca>Mg |
| .07 | .04 | 244 | Ca>Mg |
| .16 | .16 | 1,060 | Ca>Mg>Na (bicarbonate-chloride) |
| .04 | .04 | 158 | Mg>Na>Ca |

APPARATUS

All apparatus is commercially available.

SPECTROGRAPHIC EQUIPMENT

Excitation source—Jaco 4100 De Luxe Varisource.

Spectrograph—A 2.5 meter grating spectrograph (Wadsworth mounting) equipped with a 15,000 lines per inch grating giving a reciprocal linear dispersion of 3.5 Å per mm in the second order where all the analytical work has been accomplished.

Camera—Spectrum Analysis No. 1, 35 mm film.

Microphotometer—Jaco model 200 Projection Comparator Microphotometer.

Developing equipment—Jaco Photoprocessor which contains developing, stop, fix, rinse baths, and air circulator, which blows heated air over wet film to dry it.

Calculating equipment—None required. Plot working curves on three-cycle semilog paper.

Balance—Chainomatic analytical balance.

Graphite electrodes—The anodes are high-purity graphite rods, 1.5 inches long and 0.18 inches in diameter. The part of the anode containing the sample is 0.125 inches in diameter and 0.19 inches deep. The anode is necked in 0.25 inches below the cup rim to a diameter 0.18 inches. The cathodes are high-purity graphite rods, 0.120 inches in diameter and 1.5 inches long. The tip of the cathode rods are truncated to an angle of 15°.

Miscellaneous equipment—Plastic electrode holders, which hold 40 loaded electrodes with plastic cover, film numbering device.

CHEMICAL APPARATUS

Burettes—Four 50 ml burettes and one 500 ml burette.

pH meter—One pH meter with automatic temperature compensator.

Igniting crucibles—Vitreosil igniting crucibles are preferred because the ignited precipitates do not adhere to the inner surfaces of the crucibles.

Sample mixing—Spex Industries, Inc. Wig-L-Bug.

Sample containers—Mixing vials constructed of polystyrene with slip-on cap. Ps clear plexiglass ball pestles.

Filter—One millipore filtering system.

Miscellaneous—Accessory materials, such as plastic covered stirring rods, rubber policeman, and beakers.

REAGENTS

All metal compounds used to make standard solutions and the internal standard-buffer mixture must be spectrographically pure and may be obtained from most spectrographic supply companies.

The precipitating reagents are as follows:

ammonium acetate from redistilled acetic acid and ammonium hydroxide.

nitric acid (distilled).

8-hydroxyquinolinol

tannic acid

thionalide

ammonium hydroxide (distilled)

indium solution as chloride

PROCEDURE

Before selecting the aliquot of sample to be taken for analysis, either a general knowledge of the concentrations of the sought elements in sample should be known, or a preliminary investigation should be made to determine the concentration range. When this range has been determined, the aliquot is taken in which the metal concentrations range between 2.0 and 0.005 mgs. In most water samples, a practical aliquot of 500 ml is taken for routine samples.

Filter water sample through a millipore filter. Acidify filtered sample with 5 ml of 6N HCl, evaporate to a volume of about 100 ml, and transfer quantitatively to a 400 ml beaker. Add reagents as follows:

10 ml of In solution (1 ml \cong 1 mg In).

10 ml of 5 percent 8-quinolinol in 2N acetic acid.

Adjust pH to 1.8 by adding concentrated ammonium hydroxide, then add:

45 ml of 2N ammonium acetate

2 ml of 10 percent tannic acid in 2N ammonium acetate

2 ml of 1 percent thionalide in acetic acid.

Adjust the final pH to 5.2 with concentrated ammonium hydroxide. Allow sample to stand over night before filtering to insure complete precipitation. Filter the sample solution and ash precipitate at 450° C over night.

Add sufficient high-purity graphite powder to the ignited sample to bring the total weight to 50 mgs. Transfer the precipitate-and-graphite mixture carefully to the polystyrene vials and mix on the Wig-L-Bug for 30 seconds. After mixing is complete, load half the sample into each of two electrodes to be arced as duplicates. No weighing is necessary. Store the electrodes in a suitable covered container until used for spectrographic analysis.

SPECTROGRAPHIC ANALYSIS

Excitation conditions:

| | |
|------------------|--|
| Amperage..... | 6.0 amp. |
| Voltage..... | 240 volts d.c. |
| Slit width..... | 40 microns |
| Slit height..... | 4 mm |
| Sector..... | 2 step log sector set at 30 percent transmission in second step |
| Pre-burn..... | none |
| Burn time..... | complete to sputter |
| Arc gap..... | 5 mm |

The only problem experienced during the arcing is the "popping-out" of the sample. While this does not affect the accuracy of the analytical results (the amount of sample "popping-out" has a constant ratio of indium-to-carbon-to-sample), it does affect the detectability range of some of the metals sought. For instance, if the detectability limit of copper is 0.01 mg and there is just that amount in the electrode, a "pop-out" of half the total sample leaves 0.005 mg of copper on the electrode during the burn. This amount would be below the limit of detectability and the copper would go unnoticed

in the sample spectrum. To prevent this effect Harvey (1950, p. 316) suggested that one drop of ethyl alcohol and one drop of 15 percent sugar solution be dropped on the loaded sample electrode and allowed to dry. This has been found to be generally effective.

Once the films have been exposed, the following development procedures are used:

Label film with light numbering device.

- | | | |
|-------------------------------------|-------------|-------|
| 1. Developer, D-11..... | 5 minutes | 20° C |
| 2. Water rinse..... | Few seconds | 20° C |
| 3. Stop, 5 percent acetic acid..... | 15 seconds | 20° C |
| 4. Water rinse..... | Few seconds | 20° C |
| 5. Fixing, X-ray fixer..... | 2 minutes | 20° C |
| 6. Water rinse..... | 5 minutes | 20° C |

After the film has been rinsed in running tap water, it is thoroughly rinsed with deionized water. It is then run through a wetting solution, which gives it a homogeneous wet surface. The film is then dried with warm air.

PHOTOMETRY

The calibration curve used to convert percent transmission values to relative intensities is based on the conversion of percent transmission to Seidel values (Δ) (Am. Soc. Testing Materials, 1957, p. 17), which are then plotted on linear graph paper against an arbitrary relative intensity scale numbering from 0-240 (fig. 1). Assuming that there is no appreciable change in gamma for the film batch used, a percent transmission conversion table may be made (see table 6) and used for the direct conversion of percent transmission to relative intensity. This table tends to eliminate many possibilities of mathematical error.

Element lines used were chosen because the element line is never seen in the blank, which is subjected to all reagents; there is no interference by other element lines; it has a reasonable detectability range (table 7).

Since many papers and textbooks cover the principles of the use of internal standards, little can be said about its use that has not been said already. The only point that can be made, based on this study, is that in internal standards, absolute control over the sample is not as necessary as in external standards.

APPLICATIONS OF THE METHOD

This method may be used most advantageously when the minor elements are associated with the alkaline-alkali metals in solution. It has been used for the determination of minor elements in many types of animal tissues, various types of vegetable matter, various types of water, fauna and flora in sea water, air samples, ores, metals,

TABLE 6.—*Conversion of percent transmission to relative intensity*

[Explanation: T, percent transmission; Δ, Seidel values; RI, relative intensity]

| T | Δ | RI | T | Δ | RI | T | Δ | RI | T | Δ | PI | T | Δ | RI |
|------|------|-----|------|-----|-----|------|------|-----|------|------|-----|------|-------|-----|
| 7.0 | 1.12 | 188 | 24.5 | .49 | 150 | 42.0 | .14 | 134 | 59.5 | -.17 | 119 | 77.0 | -.52 | 104 |
| 7.5 | 1.09 | 186 | 25.0 | .48 | 149 | 42.5 | .13 | 132 | 60.0 | -.18 | 118 | 77.5 | -.54 | 104 |
| 8.0 | 1.06 | 184 | 25.5 | .47 | 149 | 43.0 | .12 | 132 | 60.5 | -.18 | 118 | 78.0 | -.55 | 103 |
| 8.5 | 1.03 | 182 | 26.0 | .45 | 148 | 43.5 | .11 | 131 | 61.0 | -.19 | 118 | 78.5 | -.56 | 103 |
| 9.0 | 1.00 | 180 | 25.6 | .44 | 147 | 44.0 | .10 | 130 | 61.5 | -.20 | 117 | 79.0 | -.58 | 102 |
| 9.5 | .98 | 179 | 27.0 | .43 | 146 | 44.5 | .10 | 130 | 62.0 | -.21 | 117 | 79.5 | -.59 | 102 |
| 10.0 | .95 | 177 | 27.5 | .42 | 146 | 45.0 | .09 | 130 | 62.5 | -.22 | 116 | 80.0 | -.60 | 101 |
| 10.5 | .93 | 176 | 28.0 | .41 | 146 | 45.5 | .08 | 130 | 63.0 | -.23 | 116 | 80.5 | -.62 | 100 |
| 11.0 | .91 | 175 | 28.5 | .40 | 145 | 46.0 | .07 | 130 | 63.5 | -.24 | 116 | 81.0 | -.63 | 100 |
| 11.5 | .89 | 173 | 29.0 | .39 | 144 | 46.5 | .06 | 129 | 64.0 | -.25 | 115 | 81.5 | -.64 | 100 |
| 12.0 | .87 | 172 | 29.5 | .38 | 144 | 47.0 | .05 | 128 | 64.5 | -.26 | 115 | 82.0 | -.66 | 99 |
| 12.5 | .85 | 170 | 30.0 | .37 | 144 | 47.5 | .04 | 128 | 65.0 | -.27 | 114 | 82.5 | -.67 | 99 |
| 13.0 | .83 | 169 | 30.5 | .36 | 143 | 48.0 | .03 | 127 | 65.5 | -.28 | 114 | 83.0 | -.69 | 98 |
| 13.5 | .81 | 168 | 31.0 | .35 | 142 | 48.5 | .03 | 127 | 66.0 | -.29 | 114 | 83.5 | -.70 | 98 |
| 14.0 | .79 | 166 | 31.5 | .34 | 142 | 49.0 | .02 | 127 | 66.5 | -.30 | 114 | 84.0 | -.72 | 97 |
| 14.5 | .77 | 166 | 32.0 | .33 | 142 | 49.5 | .01 | 126 | 67.0 | -.31 | 113 | 84.5 | -.74 | 96 |
| 15.0 | .75 | 165 | 32.5 | .32 | 141 | 50.0 | .00 | 126 | 67.5 | -.32 | 113 | 85.0 | -.75 | 96 |
| 15.5 | .74 | 164 | 33.0 | .31 | 140 | 50.5 | -.01 | 125 | 68.0 | -.33 | 112 | 85.5 | -.77 | 95 |
| 16.0 | .72 | 162 | 33.5 | .30 | 140 | 51.0 | -.02 | 124 | 68.5 | -.34 | 112 | 86.0 | -.79 | 94 |
| 16.5 | .70 | 162 | 34.0 | .29 | 140 | 51.5 | -.03 | 124 | 69.0 | -.35 | 111 | 86.5 | -.81 | 93 |
| 17.0 | .69 | 161 | 34.5 | .28 | 139 | 52.0 | -.03 | 124 | 69.5 | -.36 | 111 | 87.0 | -.83 | 92 |
| 17.5 | .67 | 160 | 35.0 | .27 | 138 | 52.5 | -.04 | 124 | 70.0 | -.37 | 110 | 87.5 | -.85 | 92 |
| 18.0 | .66 | 159 | 35.5 | .26 | 138 | 53.0 | -.05 | 124 | 70.5 | -.38 | 110 | 88.0 | -.87 | 91 |
| 18.5 | .64 | 158 | 36.0 | .25 | 137 | 53.5 | -.06 | 124 | 71.0 | -.39 | 110 | 88.5 | -.89 | 91 |
| 19.0 | .63 | 157 | 36.5 | .24 | 137 | 54.0 | -.07 | 123 | 71.5 | -.40 | 109 | 89.0 | -.91 | 90 |
| 19.5 | .62 | 157 | 37.0 | .23 | 137 | 54.5 | -.08 | 122 | 72.0 | -.41 | 108 | 89.5 | -.93 | 89 |
| 20.0 | .60 | 156 | 37.5 | .22 | 136 | 55.0 | -.09 | 122 | 72.5 | -.42 | 108 | 90.0 | -.95 | 88 |
| 20.5 | .59 | 155 | 38.0 | .21 | 136 | 55.5 | -.10 | 122 | 73.0 | -.43 | 108 | 90.5 | -.98 | 87 |
| 21.0 | .58 | 154 | 38.5 | .20 | 135 | 56.0 | -.10 | 122 | 73.5 | -.44 | 108 | 91.0 | -1.00 | 86 |
| 21.5 | .56 | 153 | 39.0 | .19 | 134 | 56.5 | -.11 | 121 | 74.0 | -.45 | 107 | 91.5 | -1.03 | 85 |
| 22.0 | .55 | 153 | 39.5 | .18 | 134 | 57.0 | -.12 | 121 | 74.5 | -.47 | 106 | 92.0 | -1.06 | 84 |
| 22.5 | .54 | 152 | 40.0 | .18 | 134 | 57.5 | -.13 | 120 | 75.0 | -.48 | 106 | 92.5 | -1.09 | 83 |
| 23.0 | .52 | 151 | 40.5 | .17 | 134 | 58.0 | -.14 | 120 | 75.5 | -.49 | 106 | 93.0 | -1.12 | 82 |
| 23.5 | .51 | 151 | 41.0 | .16 | 134 | 58.5 | -.15 | 120 | 76.0 | -.50 | 105 | 93.5 | -1.16 | 80 |
| 24.0 | .50 | 150 | 41.5 | .15 | 134 | 59.0 | -.16 | 119 | 76.5 | -.51 | 105 | 94.0 | -1.20 | 78 |

and minerals. Its use in the field of water chemistry has been lacking primarily because the knowledge of minor elements in water has been more of academic than practical interest. Allied workers in the field of water studies believe that minor element data may be of great assistance in the solving of water problems. These include: the study of the distribution and abundance of traces of metals in salt water and areas where salt water encroachment is taking place, traces of metals in degraded and associated undegraded surface and ground waters. It is hoped that the knowledge of the distribution and abundance of minor elements in these various hydrospheric sources will lead to a solution of various pollution problems.

TABLE 7.—*Elemental lines and analytical range*

| Element | Wave length (Å) | Analytical range (mgs in electrode) | Element | Wave length (Å) | Analytical range (mgs in electrode) |
|-----------------|-----------------|-------------------------------------|----------------|-----------------|-------------------------------------|
| Zinc | 3345 | 1.0-0.025 | Copper | 2766 | .1-.0025 |
| Chromium | 2780 | .25-.0025 | Aluminum | 2652 | 1.0-.005 |
| Iron | 2912 | 1.0-.005 | Lead | 2833 | .05-.0025 |
| Do | 2983 | .25-.0025 | Indium | 2957 | Internal standard |
| Manganese | 2949 | .1-.0025 | Do | 2775 | Do. |
| Do | 2622 | 1.0-.05 | Do | 2601 | Do. |
| Copper | 2961 | 1.0-.025 | | | |

CONCLUSION

This study indicates that the analyst should give thorough study to his arcing mixture in the development of a spectrochemical method. In particular, he should consider the following aspects, (1) control matrix to the extent of making it a constant; (2) if matrix is introduced, it should not have a suppressive effect on elements sought; (3) control temperature of the arcing mixture through the use of a radiation buffer; (4) at all times subject the sample unknown to exactly the same excitation conditions used to excite standards.

Although the modification of the Heggan and Stroek method consisted of merely increasing the amount of indium added to the arcing mixture from 10 to 20 percent, many improvements were noted. Specifically, the arc column became very stable during the arcing period; most of the element lines were enhanced resulting in a lower limit of line detectability; the average percent deviation diminished from ± 64 to ± 19 percent for the seven metals.

The method presented can be readily utilized on a routine basis. It can be applied best to the analysis of samples that contain only trace amounts of metals. A wide variety of sample types may be analyzed for trace amounts of metals using the method. The chemist need only bring the sample into solution. From that point the spectrographic procedure is the same regardless of the starting material.

LITERATURE CITED

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