



Techniques of Water-Resources Investigations
of the United States Geological Survey

●
Chapter A2

**DETERMINATION OF
MINOR ELEMENTS IN WATER
BY EMISSION SPECTROSCOPY**

By Paul R. Barnett and E. C. Mallory, Jr.

●
Book 5

LABORATORY ANALYSIS

United States Department of the Interior

JAMES G. WATT, *Secretary*



Geological Survey

Doyle G. Frederick, *Acting Director*

First Printing 1971
Second Printing 1981

For sale by Distribution Branch, Text Products Section,
U.S. Geological Survey, 604 South Pickett Street, Alexandria, Va 22304

PREFACE

The series of manuals on techniques describes procedures for planning and executing specialized work in water-resources investigations. The material is grouped under major subject headings called books and further subdivided into sections and chapters. The unit of publication, the chapter, is limited to a narrow field of subject matter. This format permits flexibility in revision and publication as the need arises. Section A of Book 5 represents techniques used in water analysis. This chapter is the second of the series in water analysis.

Each chapter is published individually and is for sale by the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402.

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DETERMINATION OF MINOR ELEMENTS IN WATER BY EMISSION SPECTROSCOPY

Paul R. Barnett and E. C. Mallory, Jr.

Abstract

With the emission spectrograph, the analyst is able to determine many minor elements simultaneously in water samples. Spectrographic methods differ chiefly in techniques of preconcentrating the elements. For waters with dissolved solids of less than 1,000 milligrams per liter, the method of evaporating to dryness and determining the elements in the dried residue is sensitive, precise, and reasonably accurate. The lower limits of detection vary with the quantity of dissolved solids. Twenty-four elements are determined by this method.

For waters with more than 1,000 milligrams per liter of dissolved solids, it is necessary to separate the minor elements from the major constituents before spectrographically determining the former, in order to achieve adequate lower limits of detection. Such procedures generally require more time than the residue method. In the first of two such procedures given, 21 of the metallic elements are precipitated with thioacetamide prior to spectrographic determination. In an alternate procedure, 18 elements are precipitated quantitatively with complexing reagents 8-hydroxyquinoline, tannic acid, and thioanlide. This method is faster than the thioacetamide method, but at the sacrifice of some elements.

A Fortran IV computer program for processing densitometric data is given in the section "Computer Program."

Introduction

Applications

The emission spectrograph provides a means of reasonably rapid analysis of water samples for many elements, simultaneously. Elements for which methods are explicitly given in this chapter are enclosed with solid lines in the periodic table of figure 1. Some of these elements are ubiquitous in natural waters, and each of them has been found in various waters. One or more of the methods could be extended to include several more elements if the concentration of these elements should increase, through pollution or natural geochemical

processes, from its present low level to the lower limit of spectral detection.

Limitations

The spectrographic detection limits vary for different elements. The detection limits for arsenic, cadmium, and zinc, for example, are relatively poor, whereas the limits for silver and copper are very good. As a result of poor spectral sensitivity, a few of the elements frequently are not detected and must be reported as less than some computed value. However, the methods described here, all involving greater preconcentration, are considerably more sensitive than so-called direct methods such as rotating disk, porous cup, vacuum cup, and plasma jet.

Techniques

The three analytical methods described are (1) residue, (2) precipitation as sulfides, and (3) precipitation as organic complexes. The first simply consists of evaporating the water and analyzing the residue. In the second, certain elements are precipitated with thioacetamide, and the resultant sulfides converted to oxides and analyzed. In the third method, certain of the metallic elements are precipitated by complexing with tannic acid, thioanlide, and 8-hydroxyquinoline. The precipitates are ashed, and the resulting oxides analyzed.

Sampling

Collect the sample in a clean polyethylene bottle. Clean the bottle by filling with dilute nitric acid and allowing to stand overnight. Repeat with dilute hydrochloric acid. Rinse the bottle thoroughly in turn with tap water and de-ionized water. Invert on a rack until dry.

Filter the sample at time of collection through a 0.45-micron membrane filter, using

a plastic pressure-filter to minimize contamination and hasten the filtering. The U.S. Geological Survey field-filter kit (Skougstad and Scarbro, 1968) is suitable for this procedure. A 2-liter sample is sufficient if the dissolved solids exceed 100 mg/l (milligrams per liter). If the dissolved solids are less than this amount, proportionately more sample must be provided.

Immediately after filtration, add sufficient 1:1 double-distilled acid to the sample to lower the pH to 3 or less. Use nitric acid if the sample is to be analyzed by the residue method; use hydrochloric acid if the sample is to be analyzed by either of the precipitation methods.

Acknowledgments

The authors express their appreciation to M. W. Skougstad for his assistance in assembling this manuscript and to Darwin Golden for his help in performing the many requisite laboratory exercises.

Residue method

Ultraviolet region

This method is a modification of one originally described by Haffty (1960).

1. Summary

The water sample is evaporated to dryness, and the residue is mixed with graphite powder and with a matrix identical to that used in preparation of the standards.

The sample mixtures and the standards are packed into the cups of graphite electrodes and excited with a direct-current arc. Spectra of a complete series of standards and duplicates of each sample are recorded on Eastman type III-O plates. Analytical lines are measured on a microphotometer. The emulsion is calibrated by the two-step method, and transmittance readings of the analytical lines are converted to relative intensities (RI). The RI of the analytical line in the standards is plotted against the known concentration of the element for the construction of analytical curves on log-log paper. The transmittance of the corresponding line in the unknown is converted

to RI, and the concentration determined from the analytical curve.

In an alternative procedure to this manual processing of densitometric data, a digital computer is used to write the equation for the calibration curve, convert transmittance readings of analytical lines to relative intensities, compute the ratios of the RI of the line to the RI of a hypothetical internal-standard line of 20-percent transmittance, write the equation for each analytical curve, determine the percent concentration of each element in the unknowns, and from the dissolved-solids figure supplied compute the concentration of each element in the original water sample. (The hypothetical internal-standard line is necessary because the program was written to utilize internal standards if desired.)

2. Application

This method is applicable to the analysis of natural waters whose dissolved-solids concentrations do not exceed about 1,000 mg/l. For these waters, it is preferred over the two other methods described in this chapter because it can detect a greater number of elements.

The following elements may be determined in the ranges indicated:

Element	Concentration range, percentage of dried residue
Aluminum	0.0009-3.0
Barium	.0003- .3
Beryllium	.0006- .03
Bismuth	.003 - .03
Boron	.0015- .3
Cadmium	.006 - .03
Chromium	.0015- .03
Cobalt	.003 - .03
Copper	.0003- .3
Gallium	.0006- .03
Germanium	.015 - .03
Iron	.0015-3.0
Lead	.0015- .03
Manganese	.0015-3.0
Molybdenum	.0003- .03
Nickel	.0015- .03
Silver	.00015-.03
Strontium	.0003- .3
Tin	.003 - .03
Titanium	.0015- .03
Vanadium	.0015- .03
Zinc	.09 -3.0
Zirconium	.003 - .03

Lithium, rubidium, and cesium are also determined by analyzing the residue, but because

H																			He
Li	Be												B	C	N	O	F	Ne	
Na	Mg												Al	Si	P	S	Cl	A	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr		
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe		
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn		
Fr	Ra	Ac																	
													Yb	Lu					

Figure 1.—Minor elements commonly determined in water by emission spectroscopy.

the spectrographic procedure varies considerably from that for the elements listed above, the spectrographic method for these alkali metals is described separately in the section "Infrared region."

3. Interferences

As in all spectrochemical analysis, it is necessary to choose analytical lines that are not coincident with or too near a line of another element. For the relatively uncomplicated spectrum of a water residue, this is not a great task, and the lines given in table 1 are usually free of such interference. Matrix effect is a greater hazard, but is minimized as explained in the note on page 5.

4. Apparatus

4.1 Sample preparation equipment:

4.1.1 Aluminum blocks, $\frac{1}{2}$ by $5\frac{1}{2}$ by $6\frac{3}{4}$ inches, with seven rows of eight $\frac{1}{4}$ -inch holes countersunk to one-quarter inch and numbered consecutively from 1 to 56, for storing charged electrodes until arced.

4.1.2 Balance, analytical.

4.1.3 Balance, precision; 25-mg (milligram) capacity.

4.1.4 Cover glasses, 200-millimeter.

4.1.5 Evaporating dishes, borosilicate glass; approximately 850-ml (milliliter) capacity.

4.1.6 Film, plastic; Dow Saran, or equivalent.

4.1.7 Funnels, small, plastic; for filling electrode cup.

4.1.8 Glass Christmas-tree ornaments, 2- $2\frac{1}{2}$ -inch diameter. Remove the necks by scoring with a file, and remove the paint by immersion overnight in a beaker of hot cleaning solution. The temperature is maintained by placing the beaker on a hotplate in a fume hood. Remove and rinse each bulb with tap water and de-ionized water and store on a 50-ml beaker in a drying oven at 180°C until needed.

4.1.9 Shakers, high-speed impact, of small and intermediate sizes for mixing samples and standards.

4.1.10 Ultrasonic generators and tanks, for cleaning and homogenizing.

4.1.11 Vials, polystyrene, $\frac{1}{2}$ -inch diameter by 1-inch long.

4.1.12 Weighing pan, locally prepared from

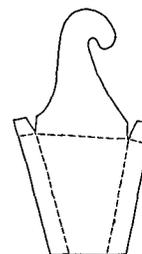


Figure 2.—Drawing of weighing pan; scale 1:1.

0.014-inch-thick magnesium sheet using the drawing in figure 2 on a 1:1 scale. The metal is bent at 90° dihedral angles along the dotted lines. The bending must be done on a hotplate because the metal will crack along the bends if done at room temperature.

4.2 Spectrographic equipment:

4.2.1 Arc stand; conventional arc stand with water-cooled electrode clamps.

4.2.2 Calculating equipment; all calculations are computerized except for the manual processing of line-width data.

4.2.3 Excitation source; a direct-current arc source at 220 volts and maximum current output of 13 amperes. Series resistance is used to control the current.

4.2.4 Microphotometer; capable of measuring the difference in transmittance of spectral lines with a standard deviation of not more than 0.2-percent transmittance. An attachment described by Barnett (1967) provides for the measurement of line widths to permit the use of lines too dark for ordinary microphotometry.

4.2.5 Spectrograph; the spectrograph has a reciprocal linear dispersion of 2.67 Å (angstroms) per mm, second order, and set in the wavelength region 2,200–3,500. Lines as close together as 0.07 Å can be resolved.

5. Reagents and materials

5.1 Purity of materials; all materials used for making standards or buffering samples must be of spectroscopic purity; that is, they should make no contribution to the analytical lines used. All equipment and apparatus with which the liquid or solid sample comes in direct contact must be kept as free as possible of the analytical elements.

5.2 Electrodes, high-purity graphite; commercially available preforms. Sample electrode cup has an inner diameter of 0.144 inch, a wall thickness of 0.015 inch, and a crater depth of 0.240 inch; the crater has a 60° truncated cone ending in a 0.31-inch-diameter bottom. Counter electrode high-purity 1/8-inch graphite rod (Ultra Carbon 1590, or equivalent).

5.3 Iron bead, or globule for plate calibration prepared from electrolytic iron powder in a graphite electrode formed locally on a lathe from 3/8-inch stock. Dimensions of this elec-

trode are length, 17/8 inch; cup diameter, nineteen sixty-fourths inch; cup depth, one-quarter inch; shank turned down to one-quarter inch at the lower one-half inch of electrode.

5.4 Photographic emulsion, Eastman III-O, or equivalent.

5.5 Photographic processing solutions; Kodak D-19 developer and Kodak Rapid Fixer with hardener, or equivalent.

5.6 Reagents (all powders):

Aluminum oxide	Magnesium oxide
Barium carbonate	Magnesium sulfate
Beryllium oxide	Manganous-manganic oxide
Bismuth oxide	Molybdenum trioxide
Boric acid	Nickel monoxide
Cadmium oxide	Potassium chloride
Calcium carbonate	Silicon dioxide
Chromium sesquioxide	Silver oxide
Cobaltous-cobaltic oxide	Sodium chloride
Cupric oxide	Strontium carbonate
Gallium oxide	Tin oxide (stannic)
Germanium dioxide	Titanium dioxide
Graphite powder	Vanadium pentoxide
Iron oxide (ferric)	Zinc oxide
Lead monoxide	Zirconium oxide

6. Procedure

6.1 Residue-On-Evaporation (R.O.E.); because the elements are determined in terms of percentage of the dissolved solids, a dissolved-solids determination must be made in order to report the elements in terms of micrograms per liter of sample.

6.1.1 Cool a tree-ornament bulb to room temperature in a desiccator and weigh to the nearest 0.1 mg.

6.1.2 Homogenize the sample by placing the polyethylene bottle containing the sample in an ultrasonic bath for 30 minutes. Immediately pipet a 50-ml aliquot into the glass bulb (resting on a 50-ml beaker). Place the bulb under a heat lamp and pass a gentle jet of clean compressed air across or into the opening of the bulb to aid evaporation. A glass tube drawn at the end serves as a suitable nozzle.

6.1.3 When the water has completely evaporated, place the bulb in a drying oven at 180°C for 1 hour, allow to cool to room temperature in a desiccator, and weigh. The increase in weight in milligrams multiplied by 20 is the R.O.E. in milligrams per liter. Re-

peat the determination until duplicate values obtained on *different* days differ by no more than 3 percent from their average. (Duplicates done together usually have good agreement because of identical conditions, but both are subject to the same possible errors.)

6.2 Preparation of residue:

6.2.1 Line an evaporating dish with plastic film. Pour about 500 ml of freshly homogenized sample into the lined dish. (If the R.O.E. of the sample is high, use less sample. More than 200 mg of residue is seldom needed and is more difficult to process than a smaller amount.) Cover the dish with a watch glass, place under a heat lamp, and pass a gentle stream of clean compressed air under the watch glass and across the sample. A 500-ml aliquot will go to moist dryness in about 14 hours. The evaporation can be allowed to proceed during the night if a timer is placed in the lamp circuit to turn off the lamp at the time of anticipated dryness. Prolonged heating after the water has evaporated may scorch the plastic film and thus spoil the residue. If insufficient residue is obtained with one filling, again homogenize the water sample and add more to the dish.

6.2.2 Transfer, as quantitatively as possible, the residue from the plastic film to a thoroughly cleaned agate mortar. Grind and mix thoroughly with an agate pestle, placing under a heat lamp occasionally whenever necessary to drive off moisture from hygroscopic materials. Transfer the homogenized residue to a glass vial and place in a drying oven at 180°C for 1 hour. Cool and store in a desiccator.

6.3 Preparation for arcing:

6.3.1 Weigh into a 1/2-inch-diameter by 1-inch-long polystyrene vial 75 mg high-purity graphite, 25 mg sample residue, and 50 mg buffer-matrix.

NOTE.—The matrix material has an element composition approximating the average major-element composition of North American waters (Clarke, 1924) and is made by thoroughly mixing the following high-purity compounds in the proportions indicated: CaCO₃, 46.6 percent; MgSO₄, 23.2 percent; NaCl, 18.3 percent; KCl, 3.6 percent; and SiO₂, 8.3 percent. The addition of 2 parts matrix to 1 part sample helps to smooth out major-element differences among samples and between the sample and the standards used for quantitative

comparison, and minimizes the variation in the intensity of minor-element lines due to differing matrices. Occasionally a particular element may be diluted below its detection limit, but is sacrificed in the interest of increased accuracy for the rest.

6.3.2 Mix for 3 minutes in a small, high-speed, impact shaker. Carefully weigh 24 mg into the magnesium weighing-pan on the precision balance and transfer to the electrode, using a plastic funnel. Tamp the charge firmly in the electrode cavity with a clean glass or graphite rod. Place the charged electrodes in sequence in numbered holes in an aluminum block. Preheat the sample end of the electrode to red heat in a flame to drive off any remaining water or gases that might cause expulsion of the sample during arcing. (Tests have indicated that the loss of elements listed on page 3 is negligible; however, such volatile elements as mercury and arsenic might be lost.) Store in the aluminum block on a hotplate or in a drying oven until arced, to prevent reabsorption of moisture.

7. Standards

Spectroscopic analysis is a direct-comparison method in which the spectral lines of the unknown are compared with the lines in a sample or standard whose element concentrations are known. The usual practice is to prepare a series of synthetic standards containing in decreasing concentrations the elements to be determined in the unknowns. (See section "Standard preparation for residue method—ultraviolet region.")

The elements to be determined are 23 in number, varying in percentage of the residue from as high as 1.0 for some elements to as low as 0.00005 for others. If all 23 elements were introduced at 1 percent in the first step of the series of standards, the mixture would consist of about 35 percent of the oxides of the elements and only 65 percent of the matrix material. Because of the matrix effect produced by such a situation, only those elements which sometimes occur in concentrations as high as 1 percent are put into the first steps, four more are introduced at 0.1 percent, and the other 15 at 0.01 percent.

The optimum number of steps for good analytical curves is three per order of magnitude.

The series 1.0, 0.1, 0.01, 0.001, etc., is a logarithmic series. If two intermediate steps are to be inserted between the numbers in this series, it is desirable that the new set also produce a logarithmic series. This can be accomplished by having a constant factor of 2.154435 (the cube root of 10) between the steps. Thus, the concentrations will be 1.0, 0.464, 0.215, 0.1, * * * 0.0000464 percent.

Internal standards are not used. The recommended procedure is to expose a series of external standards on each sample plate. Experience has shown that the precision of replicate analyses by this technique is better than that obtained when standards and samples are exposed on separate plates, even when internal standards are used. The addition of internal standards in the recommended procedure does not significantly increase the precision. The recommended procedure is also more economical of time both in preparation of samples and standards and in analyzing the spectra.

8. Excitation of samples and standards

8.1 Electrode system; the lower, sample-carrying electrode is the anode. Set and maintain the electrode gap at 4 mm.

8.2 Electrical parameters; open-circuit potential is 220 volts. Gradually increase the current to 8 amperes during the first 7 seconds and then quickly to 12 amperes for the remainder of the exposure.

8.3 Exposure conditions:

Spectral region ----- 2,200-3,500 A.
Slit width ----- 25 μ .
Slit length ----- 1.4 mm.
Neutral filter ----- 24-percent transmission.
Length of burn ----- To completion.

8.4 Emulsion calibration exposure; two-step filter (55 and 100 percent), 24-percent neutral filter, slit width 25 μ , slit height 4 mm, current of 4 amperes, 60-second exposure of Fe spectrum recorded near center of plate.

8.5 Replicate exposure; record each sample in duplicate and include a complete set of standards on every plate.

9. Photographic processing

Develop plates for 4 minutes at 20°C with mechanical agitation, rinse with water for 15 seconds, fix for twice the clearing time, wash with tap water for 20 minutes, rinse thorough-

ly with demineralized water, and dry in a plate drier.

10. Photometry

Measure with the microphotometer the percentage transmittances of the analytical lines by using the lines given in table 1. Make a background reading for each line by scanning a short distance on each side of the line and recording an average of the two maximum transmittances observed.

The analytical lines most frequently used are those given in table 1. The concentration ranges for ordinary densitometry are given for each line. The upper limit for most of these lines can be raised to the highest concentration occurring in the standards by using the line-width measuring device described by Barnett (1967). For some lines the range given is less than that which is possible to measure because of the limited range of the element in the standards.

Table 1.—Analytical lines—ultraviolet region

Element	Wavelength (A)	Concentration range (percentage of arcing mixture)
Aluminum (Al)	3,082.68	0.0003-0.01
	2,660.39	.005-.2
	2,652.49	.01-.5
Barium (Ba)	4,554.04	.0001-.001
Beryllium (Be)	3,130.42	.0002-.005
Bismuth (Bi)	3,067.72	.00001-.01
Boron (B)	2,497.73	.0005-.02
	2,496.78	.001-.05
Cadmium (Cd)	3,261.06	.002-.01
Chromium (Cr)	3,021.56	.0005-.01
Cobalt (Co)	3,453.50	.0005-.01
Copper (Cu)	3,247.54	.0001-.002
	3,273.96	.0002-.005
Gallium (Ga)	2,943.64	.0002-.005
Germanium (Ge)	3,039.06	.0005-.01
Iron (Fe)	2,719.02	.0005-.02
	2,723.53	.002-.2
Lead (Pb)	2,833.07	.0005-.01
Manganese (Mn)	2,576.10	.0005-.01
	2,949.20	.001-.05
	2,933.06	.002-.1
	2,572.76	.02-1.0
Molybdenum (Mo)	3,170.35	.0001-.01
	3,208.83	.001-.01
Nickel (Ni)	3,414.76	.0005-.01
	3,050.82	.001-.01
Silver (Ag)	3,280.68	.00005-.002
Strontium (Sr)	4,607.33	.0001-.002
Tin (Sn)	3,175.02	.001-.01
Titanium (Ti)	3,234.52	.0005-.01
	3,241.99	.002-.01
Vanadium (V)	3,183.41	.0005-.01
Zinc (Zn)	3,345.02	.02-.5
	3,345.57	.1-1.0
Zirconium (Zr)	3,279.26	.001-.01
	3,273.05	.002-.01

11. Emulsion calibration

Use the two-step method of emulsion calibration described in method E 116-67 (American Society for Testing and Materials, 1968). The details of this method are given in the section "Two-step method of emulsion calibration."

12. Preparation of analytical curves

12.1 Manual method; convert the percentage transmittance of the analytical line of the standards to relative intensity by reference to the emulsion-calibration curve. Plot this value against the known concentration of the element in the standard on log-log paper for all steps of the standard within the reliable microphotometer range. The curve fitted to these points is the analytical curve for the particular element line. Draw new analytical curves for each plate.

12.2 Computer method; percentage-transmittance values for internal-standard lines (assumed) and analytical lines of the standards are converted to Seidel-function values (Δ) and the inverse ratio computed. A second-order equation is determined for each analytical line with these ratios as a function of the concentration of the element in the standards. Details of the computer program for processing densitometric data are given in the section "Computer program."

13. Computations

13.1 Manual method; convert the percentage-transmittance values of the analytical lines to relative intensities by reference to the emulsion-calibration curve. (See section "Two-step method of emulsion calibration.") Use the analytical curves (item 12.1) to determine the percent concentrations corresponding to these relative intensities. Average the results from duplicate samples on the plate. Multiply the determined concentration of each element by 3 (to compensate for the 1:2 dilution with the buffer) and by the R.O.E. figure determined in item 6.1. Adjust the decimal point to report as micrograms per liter.

13.2 Computer method; the computations done manually in item 13.1 are executed by computer, and the following information is printed out: (1) Sample identification, (2)

replicate number, (3) RI of the line plus background, (4) net RI of the line, (5) RI of the internal-standard line plus background, (6) net RI of the internal-standard line, (7) ratio of the RI of the analytical line to the RI of the internal standard, (8) concentration of the element in the solids, (9) concentration factor (dilution factor times R.O.E. times 10 [to convert percentage times milligrams per liter to micrograms per liter]), (10) concentration of the element in the original water sample, and finally (11) average of replicate determinations.

14. Precision and accuracy

14.1 Two sets of data were accumulated for computing the precision of the method. The first set was acquired by repeating the analysis of a sample on a second plate and was done for about 12 samples on 24 plates in such a way that no plate recorded more than one of these samples. The formula for estimating precision by this method is

$$S.D. = \left(\frac{\sum d^2}{2n} \right)^{1/2}$$

where S.D. is the standard deviation, d is the difference between duplicate determinations of the element, and n is the number of duplicate pairs. Because there usually will be a wide variation in the magnitude of the values involved, it is better to take the logarithm of the values before using the formula. The standard deviation thus found is the logarithmic standard deviation (L.S.D.) and its antilogarithm is called the geometric deviation (G.D.), the factor by which the amount found may be multiplied and divided to find the range of one standard deviation. The G.D. for this computation is given in table 2, column 4.

Table 2.—Precision of analysis

Element	Set 1		Set 2	
	<i>n</i>	\bar{X} (percentage of residue) G.D.	<i>n</i>	\bar{X} (percentage of residue) G.D.
Al	11	0.0046 1.170	12	0.071 1.091
Ba	11	1.0080 1.108	13	1.0048 1.104
B	10	.0060 1.156	10	.046 1.152
Cr	10	.00055 1.436	11	.0018 1.094
Cu	10	.00055 1.436	12	.011 1.110
Co	10	.00055 1.436	10	.00091 1.140
Fe	10	.012 1.110	11	.050 1.057
Pb	10	.00055 1.436	11	.0019 1.111
Mn	9	.0030 1.140	9	.037 1.068
Mo	10	.00055 1.436	8	.012 1.063
Ni	10	.00055 1.436	12	.0020 1.164
Ag	10	.00055 1.436	12	.00074 1.075
Sr	10	1.029 1.120	13	1.031 1.104
V	10	.00055 1.436	12	.00061 1.209

¹ Measurements made by line-width method.

A second set of data for computing precision was accumulated by repeated analysis of a reference sample over a period of several months. The formula used for computing the standard deviation under these circumstances is

$$\text{S.D.} = \left(\frac{\sum X_i^2 - (\sum X_i)^2/n}{n-1} \right)^{1/2}$$

Again, the values were first transformed to logarithms in order to have precision expressed in the same way as for the first set. The G.D. for this computation is given in column 7 of table 2.

The generally better precision of the second set is due largely to the higher concentration of the elements, resulting in microphotometer readings in a more reliable range.

14.2 Accuracy is estimated by comparing the individual determinations of the elements in the same reference sample with the most probable values as determined by other methods, or as added to the sample when it was prepared. The formula used is that for computing the precision of set 1 in item 14.1. The results of this computation are given in the last column of table 3.

Table 3.—Accuracy

Element	Assumed true value ($\mu\text{g/l}$)	Average amount found ($\mu\text{g/l}$)	Number of determinations	G.D.
Al	540	555	12	1.092
Cr	15	13.7	11	1.094
Cu	119	82	12	1.32
Co	5	7.1	10	1.30
Fe	397	387	11	1.043
Pb	15	14.6	11	1.074
Mn	300	290	9	1.052
Ni	10	15.8	12	1.40
Ag	7	5.7	12	1.16
Sr	279	241	13	1.13
V	5	4.7	12	1.15
Average				1.16

In addition, the concentration of strontium found in 48 different samples were compared with the concentrations determined by atomic absorption. The values ranged from about $70\mu\text{g/l}$ to $3,500\mu\text{g/l}$. The G.D. was 1.13. The concentrations of manganese found in 22 samples, ranging from $50\mu\text{g/l}$ to $700\mu\text{g/l}$, were compared with atomic absorption determinations; the G.D. was determined to be 1.15.

Infrared region

1. Summary of method

A 1:1 mixture of sodium carbonate and the residue prepared in the previous discussion is ignited in a direct-current arc, and duplicate spectra are recorded on Eastman type I-N plates, along with a complete series of standards. The percent transmittances of appropriate analytical lines are measured on a microphotometer, and analytical curves are constructed by plotting known concentrations of the elements in the standards against percent transmission (or line width, as required). The concentrations of the elements in the samples are determined from these curves.

2. Application

This method is used to determine the following elements in the ranges indicated:

Element	Concentration range (percent)
Cesium	0.001-0.05
Lithium	.0001-.05
Rubidium	.0005-.05

3. Interferences

See this part in section "Ultraviolet region."

4. Apparatus

Same as in this part in section "Ultraviolet region," except that Eastman type I-N is used as the photographic emulsion.

5. Reagents (all powders)

Calcium carbonate	Rubidium chloride
Cesium carbonate	Silicon dioxide
Lithium carbonate	Sodium carbonate
Magnesium carbonate	Sodium chloride
Potassium chloride	

6. Procedure

Weigh 12 mg sodium carbonate and 12 mg of the residue prepared in the section "Ultraviolet region," item 6.2, in the weighing pan (item 4.1.12). Mix thoroughly in the pan with a toothpick or a small, clean artist's brush. Transfer to the electrode, preheat, and store as in the section "Ultraviolet region."

7. Standards

Prepare a series of standards with decreasing concentrations of the analytical elements in a matrix approximating the major-element composition of natural waters. Mix each standard with an equal weight of sodium car-

bonate. (Refer to section "Standards preparation for residue method—Infrared region" for details for preparation.)

8. Excitation of samples and standards

Use same electrode system and electrical parameters as in section "Ultraviolet region." Use the following exposure conditions:

- Spectral region ---- 6,560-9,300 A.
- Slit width ----- 25 μ .
- Slit length ----- 1.4 mm.
- Filter ----- Yellow, no neutral.
- Time ----- About 10 seconds beyond the disappearance of yellow color of sodium.

Do not record an Fe spectrum, because the emulsion is not calibrated. Record each sample in duplicate and include a complete set of standards on each plate.

9. Photographic processing

See this part in section "Ultraviolet region."

10. Photometry

Measure with a microphotometer the percent transmittances or the widths of the analytical lines given in table 4. Background correction

Table 4.—Analytical lines—Infrared region

Element	Wavelength (A)	Concentration range (percent)
Cesium (Cs) -----	8,521.10	0.001-0.05
Lithium (Li) -----	6,707.84	.001-.05
Rubidium (Rb) -----	7,800.23	.0005-.05
	7,947.60	.001-.05

is not feasible and is not necessary if exposure conditions are properly followed.

11. Emulsion calibration

The emulsion is not calibrated.

12. Preparation of analytical curves

Plot the untransformed transmittance value of the analytical line against the known concentration of the element in the standard on log-log paper for all steps of the standard within the reliable microphotometric range.

For the concentration ranges where line-width measurement is necessary (and this will be the rule rather than the exception) plot the line width on a linear scale against concentration on a logarithmic scale (semilog paper).

In either case, the curve fitted to the points is the analytical curve for the particular element line. Prepare a new curve for each plate.

13. Computations

From the percentage transmittance or the width of the line in the sample spectrum use the analytical curves to determine the percent concentration of the element in the sample. Average the results from duplicate samples on the plate. Multiply the determined concentration by the R.O.E. figure as determined in the section "Ultraviolet region," item 6.1. Adjust the decimal point to report as micrograms per liter.

14. Precision and accuracy

No statistical analysis has been made for either precision or accuracy. Random comparisons of lithium determinations with determinations by atomic absorption show good agreement.

Precipitation method—thioacetamide

When minor elements in water residues are determined spectrographically, high concentrations of the major constituents interfere by producing unpredictable matrix effects and by diluting the minor elements below limits of detection. Precipitation of minor elements can be used to remove major elements and to concentrate the minor ones before spectrographic analysis.

1. Summary

In the procedure described here, thioacetamide is used as the precipitant for both the acid and the ammoniacal sulfide groups of elements. Palladium is added to all samples as an internal standard. Tin is added to the acid sulfide group as a spectrographic buffer and coprecipitant; indium is used for the same purposes with the ammoniacal sulfide group.

2. Application

The thioacetamide procedure may be used to analyze a wide variety of waters, but is particularly suited to waters having dissolved solids in excess of 1,000 mg/1, in which cases the residue method has poor limits of detection. Quantitative precipitations are obtained for antimony, arsenic, beryllium, bismuth, cad-

mium, chromium, copper, iron, lead, titanium, ytterbium, yttrium, and zirconium. In addition, the following elements are nearly quantitatively precipitated and can be determined with satisfactory reliability: Aluminum, cobalt, lanthanum, manganese, molybdenum, nickel, silver, and zinc. If a more rapid procedure is desired, the method described in the section "Complexometric method" may be used, albeit at the expense of some reliability and the loss of beryllium, lanthanum, manganese, and ytterbium.

Samples may be preconcentrated by reduction of volume through evaporation up to saturation of the cooled sample or certain other practical limits explained in the following sections "Interferences" and "Procedure."

The elements quantitatively precipitated, their determinable concentration range, and the analytical lines used are given in the tables 5 and 6.

Table 5.—Elements precipitated by thioacetamide—acid group

Element	Analytical line (Å)	Concentration range (µg/l)
Antimony -----	2,598.06	5.0-500
Arsenic -----	2,780.20	10.8-500
Bismuth -----	3,067.72	.23-10.8
	2,989.03	10.8-232
Cadmium -----	3,261.06	5.0-232
Copper -----	2,824.37	5.0-500
Lead -----	2,873.32	5.0-232

Table 6.—Elements precipitated by thioacetamide—ammoniacal group

Element	Analytical line (Å)	Concentration range (µg/l)
Beryllium -----	3,131.07	0.23-10.8
Chromium -----	3,021.56	.5-23
Iron -----	2,723.58	.5-232
Titanium -----	3,241.99	1.1-50
Ytterbium -----	3,289.88	1.1-10
Yttrium -----	3,327.88	1.1-50
Zirconium -----	3,391.98	.23-23

Elements listed in table 7 are nearly completely precipitated under the conditions specified. Furthermore, the precipitations are sufficiently reproducible so that reliable comparisons can be made between samples and standards. This has been satisfactorily demonstrated by repeated comparisons of analytical data for all these elements (except lanthanum) with data obtained by independent methods, such as atomic absorption, colorimetric, and spectrographic residue determinations.

NOTE.—To gain an indication of the reliability of the lanthanum determinations, 30 µg/l of lanthanum was added to a water which had been analyzed and shown to contain no detectable amount of lanthanum. Comparison of the spiked sample with standards showed a value of 30 µg/l for the spiked sample.

Table 7.—Elements nearly completely precipitated by thioacetamide

Element	Analytical line (Å)	Concentration range (µg/l)
Aluminum -----	2,652.50	10.8-500
Cobalt -----	3,453.50	.23-23
Lanthanum -----	3,337.49	1.1-108
Manganese -----	2,949.20	2.3-50
Molybdenum -----	3,208.83	.5-108
Nickel -----	3,414.76	.5-108
Silver -----	3,382.89	.23-2.3
Zinc -----	3,345.02	2.3-500

3. Interferences

As in all spectrochemical analyses, analytical lines chosen must not be coincident with or too near a line of another element. Choosing such lines is not difficult because the major elements are removed, and so there are fewer lines in the spectrum. The lines given in tables 5, 6, and 7 are those which have no or only a minor amount of interference and are also of an intensity suitable for most water analyses.

The matrix effect described under the residue method is no problem since the sample and standard precipitates have identical matrices of either tin or indium oxides.

4. Apparatus

4.1 Sample preparation equipment; the chemical part of this procedure requires the usual equipment needed in an analytical laboratory.

4.1.2 Agate mortar and pestle; for grinding and mixing. Do not mix samples and carbon powder in plastic vials used in a mechanical mixer, because the precipitate tends to cling to the sides of the vials and thus uneven mixing results.

4.1.3 Aluminum blocks. (See section "Ultraviolet region," item 4.1.1.)

4.1.4 Balance, precision; 50-mg capacity.

4.1.5 Bottles, glass, 1-dram; with plastic caps.

4.1.6 Funnel, plastic; for filling electrode cup.

4.1.7 Furnace, muffle, electric; with automatic temperature control.

4.1.8 pH meter; maximum recoveries are obtained with the pH adjustments described under item 6.

4.2 See section "Ultraviolet region," items 4.2.1, 4.2.3, 4.2.4, and 4.2.5 for spectrographic equipment.

5. Reagents

5.1 Ammonium chloropalladite solution; internal standard (0.1 mg per ml Pd); dissolve 133.6 mg ammonium chloropalladite in 450 ml distilled-demineralized water acidified with 5 ml concentrated H_2SO_4 . Dilute to 500 ml. Dilute this solution 1:1 before use.

5.2 Ammonium hydroxide solution (1*N*); dissolve 68.5 g (grams) ammonia gas in 1 liter distilled-demineralized water to make 4*N* (normal) NH_4OH . Dilute 25 ml 4*N* NH_4OH to 100 ml.

5.3 Ammonium sulfite solution (0.2 percent, weight to volume); dissolve 0.5 g in 250 ml distilled-demineralized water. Prepare fresh before use.

5.4 Hydrochloric acid (12*N*); distill reagent-grade concentrated HCl, collecting only the middle one-third portion of distillate.

5.5 Hydrochloric acid (3*N*); dilute 25 ml of the redistilled 12*N* HCl to 100 ml with distilled-demineralized water.

5.6 Indium sulfate solution (1 mg In per ml); dissolve 1.209 g In_2O_3 in 40 ml concentrated H_2SO_4 , heating until solution is complete. Dilute to 1 liter with distilled-demineralized water.

5.7 Stannous chloride solution (1 mg Sn per ml); dissolve 0.3802 g $SnCl_2 \cdot 2H_2O$ in 4 ml concentrated HCl and dilute to 200 ml with distilled-demineralized water. Prepare fresh before use.

5.8 Stock solutions containing elements to be determined (standard solutions are made from these stock solutions):

Stock solution A, containing As, Bi, Cd, Cu, Pb, Mo.

Stock solution B, containing Sb.

Stock solution C, containing Al, Be, Cr, Co, Fe, Mn, Ni, Ag, Zn, Zr.

Stock solution D, containing Ti, La, Y, Yb.

Detailed instructions for preparing stock solutions and standards are given in the section

"Stock and standard solutions for thioacetamide method."

5.9 Thioacetamide solution (2 percent, weight to volume); dissolve 2 g CH_3CSNH_2 in distilled-demineralized water and dilute to 100 ml. Stir or expose the solution mixture to ultrasonic agitation until dissolved. Ignore any small amount of insoluble white residue which may appear.

5.10 Wash solution 1 (acid precipitation); dissolve 80 mg thioacetamide in distilled-demineralized water and dilute to 1 liter. Adjust the pH to 0.75 with 3*N* HCl.

5.11 Wash solution 2 (ammoniacal precipitation); dissolve 0.5 g ammonium sulfite and 2 g thioacetamide in distilled-demineralized water and dilute to 1 liter. Adjust the pH to 8.0 with 1*N* ammonium hydroxide.

6. Procedure

Collect a sufficient volume of representative sample according to the procedure in the section "Sampling."

6.1 Transfer measured volumes (table 8) of the samples into 400-ml beakers. Prepare

Table 8.—Volume of sample used according to specific conductance of sample

Volume (ml)	Specific conductance (μ mhos per cm)
1,000 -----	<2,000
500 -----	2,000-5,000
500 and 100 ¹ -----	5,000-10,000
100 and 10 ¹ -----	>10,000

¹ A water high in dissolved solids is usually high in some elements and low in others; then, two separate aliquots must be analyzed.

one aliquot each for the acid-sulfide and the ammoniacal-sulfide precipitations.

6.2 Add 2-5 ml HCl to keep salts from forming. Evaporate the acid-sulfide aliquots in 400-ml beakers to 100-ml volume. Waters containing more than 5,000 mg/1 dissolved solids may require more HCl. Dilute aliquots of less than 100 ml to 100 ml.

6.2.1 Pipet 100-ml aliquots of standards made from stock solutions A and B into 400-ml beakers. This gives standards of 500, 232, 108, 50, 23, 11, 5, 2.3, 1.1, 0.5, 0.23, and 0.1 μ g/l. Standards made from stock solutions A and B may be combined in the same beaker if they contain the same micrograms per liter. Evaporation is not necessary. Treat standards and samples alike from this point on.

6.2.2 Add 3 ml ammonium chloropalladite solution and 30 ml stannous chloride solution.

6.2.3 Adjust the pH to 0.75 with 3*N* HCl and add 20 ml thioacetamide solution.

6.2.4 Cover beaker with a watch glass and heat the sample to just below the boiling point. Cool and allow to stand overnight at room temperature.

6.2.5 Filter the solution through a fine filter paper (Whatman No. 42, or equivalent). Wash the precipitate several times, using the acid-thioacetamide wash solution 1. Discard the filtrate and washings.

6.2.6 Place the paper and precipitate in an uncovered porcelain crucible and ash in an oxidizing atmosphere at 450°C. Store ashed precipitates in a desiccator. Thoroughly grind and mix the cool, dry precipitate with an equal weight of spectrographic-grade powdered graphite in an agate mortar. Store in glass vials and keep in a desiccator.

6.2.7 Weigh a 24-mg portion of the sample-graphite mixture and tamp firmly with a glass rod into the cavity of a graphite electrode. (See section "Ultraviolet region," item 5.2.)

6.3 Evaporate the ammoniacal sulfide aliquots in 400-ml beakers to 100-ml volume. Add 2-5 ml HCl to keep salts from forming. Waters over 5,000 mg/l dissolved solids may require more HCl. Dilute aliquots of less than 100-ml to 100-ml volume.

6.3.1 Pipet 100-ml aliquots of standards made from stock solutions C and D into 400-ml beakers. This gives standards of 500, 232, 108, 50, 23, 11, 5, 2.3, 1.1, 0.5, 0.23, and 0.1 µg/l. Standards made from stock solutions C and D may be combined in the same beaker if they contain the same micrograms per liter. Evaporation is not necessary. Treat standards and samples alike from this point on.

6.3.2 Add 3 ml ammonium chloropalladite solution and 30 ml indium sulfate solution.

6.3.3 Adjust the pH to 7.0-7.2 with 1*N* NH₄OH and add 20 ml ammonium sulfite solution.

6.3.4 Add 20 ml thioacetamide solution, adjust the pH to 8.0 with 1*N* ammonium hydroxide and allow sample to stand overnight at room temperature.

6.3.5 Filter the solution through a fine filter

paper (Whatman No. 42, or equivalent). Wash the precipitate with several portions of wash solution 2, the ammoniacal-thioacetamide solution containing a small amount of ammonium sulfite.

6.3.6 Place the paper and precipitate in an uncovered porcelain crucible and ash in an oxidizing atmosphere at 450°C. Store ashed precipitates in a desiccator. Thoroughly grind and mix the cool, dry precipitate with an equal weight of spectrographic-grade powdered graphite in an agate mortar. Store in glass vials and keep in a desiccator.

6.3.7 Weigh a 24-mg portion of the sample-graphite mixture prepared in item 6.3.6 and tamp firmly with a glass rod into the cavity of a graphite electrode. (See section "Ultraviolet region," item 5.2.)

6.4. Use the same exposure conditions in the spectrographic procedure described in the section "Ultraviolet region," item 8 (Residue method), except for using a maximum of 8 amperes for excitation.

6.5 Use the same procedure for photographic processing described in the section "Ultraviolet region," item 9.

6.6 Measure with a microphotometer the percent transmittances of the analytical lines and their corresponding internal-standard lines.

6.7 Precautions:

6.7.1 Take extreme care to prevent contamination of standards or samples. Thoroughly clean all glassware with hydrochloric or nitric acid, then detergent, and finally demineralized water. Do not use chromic acid, because enough of this acid can remain on the glassware to cause contamination. Dry glass equipment on a pegboard with plastic pegs or on plastic film spread over a sheet of clear or white plastic. Avoid colored plastics, for they may contain trace metals. Plastic-coated spatulas are preferred to metal ones. Use wooden instead of metal filter racks. Store reagents and standards in plastic bottles.

6.7.2 A porcelain plate held above the samples by porcelain crucibles prevents particles of muffle lining from falling into samples being ashed.

6.7.3 If the dissolved-solids concentration of the sample exceeds 5,000 mg/l, omit the preconcentration by evaporation for the ammoniacal precipitations. Waters with dissolved solids of this magnitude require considerable hydrochloric acid to keep salts from forming during evaporation. More than the usual amount of ammonium hydroxide is required to adjust the pH to 8.0. Finally, the saturation point of the water is exceeded, and solid salts form. These salts are hard to dissolve during washing of the precipitate and will dilute the minor elements below limits of detection.

6.7.4 Use 2 or 3 filter funnels and papers to filter the precipitates obtained from water with dissolved solids above 5,000 mg/l. Washing the precipitates then removes most of the occluded filtrate which otherwise would dry to salts during the ashing process and thus dilute the minor elements below limits of detection.

6.7.5 Nitric acid is sometimes used to keep dissolved solids in solution or to oxidize excess organic material in a water sample. To remove nitric acid, evaporate the sample with no more than 10 ml sulfuric acid to sulfuric fumes, cool, add 10 ml distilled-demineralized water, and boil for a few minutes.

6.7.6 Hydrochloric acid is probably best for keeping dissolved solids in solution if the thioacetamide-precipitation method is to be used. Nitric acid in the samples would tend to decompose some of the sulfide precipitate.

7. Computations

Use same procedure as in the section "Ultra-violet region."

8. Report

Report elements below 10 $\mu\text{g}/\text{l}$ to one significant figure; for elements 10 $\mu\text{g}/\text{l}$ and higher, report results to two significant figures.

9. Precision

Precision data are not available.

Complexometric method

Precipitation of microgram amounts of minor elements with complexing reagents is faster than the thioacetamide method, because only one precipitation per sample is necessary.

The three complexing reagents used, however, often contain traces of the elements for which the waters are being analyzed. Purification of these reagents is, therefore, necessary if accurate determinations are desired below 10 $\mu\text{g}/\text{l}$. This method is a modification of the one described by Silvey and Brennan (1962).

1. Summary

In this procedure, the complexing reagents 8-hydroxyquinoline, tannic acid, and thionamide are used to concentrate traces of aluminum, arsenic, antimony, bismuth, cadmium, chromium, cobalt, copper, iron, lead, molybdenum, nickel, silver, titanium, vanadium, ytterbium, zinc, and zirconium. Indium is added as a co-precipitant and spectrographic buffer; palladium is added as an internal standard.

2. Application

The complexing reagents can be used to analyze the same types of waters described in the section "Precipitation method—thioacetamide," item 2.

When the complexing reagents were not purified the elements given in table 9 were quantitatively precipitated. The determinable

Table 9.—Elements completely precipitated—
complexometric method

Element	Analytical line (\AA)	Concentration range ($\mu\text{g}/\text{l}$)
Arsenic	2,780.20	50–500
Antimony	2,598.06	10.8–500
Bismuth	3,067.72	1.1–23
Cadmium	3,261.06	1.1–500
Cobalt	3,453.50	1.1–23
Molybdenum	3,170.35	.2–23
	3,208.83	2.3–108
Silver	3,382.89	.2–10.8
Titanium	3,241.99	1.1–108
Zinc	3,345.02	10.8–500
Zirconium	3,391.98	.2–108

concentration ranges and the analytical lines used are also shown.

Elements given in table 10 were nearly com-

Table 10.—Elements nearly completely precipitated—
complexometric method

Element	Analytical line (\AA)	Concentration range ($\mu\text{g}/\text{l}$)
Aluminum	2,660.39	10.8–500
Chromium	3,021.56	1.1–108
Copper	2,618.37	23–500
Iron	2,723.58	5–500
Lead	2,833.07	2.3–108
Nickel	3,414.77	10.8–50
Vanadium	3,102.30	1.1–50
Ytterbium	3,289.85	1.1–23

pletely precipitated under the conditions specified. Precipitations were sufficiently reproducible, and reliable comparisons could be made between samples and standards.

Precipitations for beryllium, lanthanum, manganese, and yttrium were found to be too erratic or incomplete for accurate determinations.

Silvey and Brennan (1962) used the complexometric procedure for gallium and germanium determinations.

3. Interferences

Interferences are the same as those described in the section "Precipitation method—thioacetamide," item 3.

4. Apparatus

The apparatus needed is the same for both the complexometric and thioacetamide methods.

5. Reagents

Purification of complexometric reagents is discussed in the section "Stock and standard solutions for complexometric method."

5.1 Acetic acid (17*N*); redistill reagent-grade acetic acid. 4*N* solution: dilute 100 ml 17*N* to 400 ml.

5.2 Ammonium acetate solution (2*N*); mix 1 liter 4*N* NH₄OH with 1 liter 4*N* acetic acid solution.

5.3 Ammonium chloropalladite solution, internal standard (0.1 mg Pd per ml); dissolve 133.6 mg ammonium chloropalladite in 450 ml distilled-demineralized water acidified with 5 ml concentrated H₂SO₄. Dilute to 500 ml. Dilute this solution 1:1 before use.

5.4 Ammonium hydroxide solution (4*N*); dissolve 137 g ammonia gas in 2 liters distilled-demineralized water.

5.5 8-hydroxyquinoline solution (5 percent, weight to volume); dissolve 25 g 8-hydroxyquinoline in 59 ml 17*N* acetic acid and dilute to 500 ml.

5.6 Hydrochloric acid (12*N*); distill reagent-grade concentrated HCl, collecting only the middle one-third portion of distillate.

5.7 Indium sulfate solution (1 mg In per ml); dissolve 1.209 g In₂O₃ in 40 ml concentrated H₂SO₄, heating until solution is complete. Dilute to 1 liter with distilled-demineralized water.

5.8 Stock solutions containing elements to be determined (standard solutions are made from these stock solutions):

Stock solution A, containing As, Bi, Cd, Cu, Pb, Mo, V.

Stock solution B, containing Sb.

Stock solution C, containing Al, Cr, Co, Fe, Ni, Ag, Zn, Zr.

Stock solution D, containing Ti and Yb.

Detailed instructions for preparing stock solutions and standards are given in the section "Stock and standard solutions for complexometric method."

5.9 Tannic acid solution (10 percent, weight to volume); dissolve and dilute to volume with 2*N* ammonium acetate. Make a fresh solution for each set of samples.

5.10 Thioanlide¹ solution (1 percent, weight to volume); dissolve and dilute to volume with 17*N* acetic acid. Make a fresh solution for each set of samples.

5.11 Wash solution (0.05 percent); dilute 100 ml 8-hydroxyquinoline solution to 1 liter with distilled-demineralized water. Adjust to pH 5.2 with 2*N* ammonium acetate.

6. Procedure

Collect a sufficient volume of representative sample according to the procedure in the section "Sampling."

6.1 Transfer measured volumes (table 8) of the samples into 400-ml beakers. Only 1 aliquot per sample is needed.

6.2 Add 2–5 ml HCl to keep salts from forming. Evaporate the aliquots in 400-ml beakers to 100-ml volume. Waters containing more than 5,000 mg/l dissolved solids may require more HCl. Dilute aliquots of less than 100 ml to 100 ml.

6.3 Pipet 100-ml aliquots of standards made from stock solutions into 400-ml beakers. This gives standards of 500, 232, 108, 50, 23, 5, 2.3, 1.1, 0.5, 0.23, and 0.11 μg/l. Evaporation is not necessary. Treat standards and samples alike from this point on. Standards of the same values (μg/l) made from stock solutions A and B may be combined. Standards of the same values made from stock solutions C and D may, likewise, be combined.

¹ Thio-glycollic-β-amino-naphthalide.

6.3.1 Add 3 ml ammonium chloropalladite solution and 30 ml indium sulfate solution.

6.3.2 Add 10 ml 8-hydroxyquinoline solution; adjust the pH to 1.8 with 4*N* NH₄OH (use a pH meter). If large amounts of iron are present, the solution will turn green at this point.

6.3.3 Add 45 ml 2*N* ammonium acetate solution, 2 ml tannic acid solution, and 2 ml thionalide solution.

6.3.4 Adjust the pH to 5.2 with 4*N* NH₄OH. An exact pH is important, so a pH meter should be used.

6.3.5 Let the sample sit overnight for complete precipitation.

6.3.6 Filter through a fine filter paper (Whatman No. 42, or equivalent). Wash thoroughly 10–12 times with the wash solution.

6.3.7 Place paper and precipitate in a porcelain crucible and ash off overnight at 450°C. A fluffy, golden-yellow precipitate is obtained. Store ashed precipitates in a desiccator.

6.3.8 Thoroughly grind and mix the cool, dry precipitate with an equal weight of spectrographic-grade powdered graphite in an agate mortar. Store in glass vials and keep in a desiccator.

6.3.9 Weigh a 24-mg portion of the sample-graphite mixture and tamp firmly with a glass rod into the cavity of a graphite electrode. (See section "Ultraviolet region," item 5.2).

6.4 Use the same exposure conditions in the spectrographic procedure described in the section "Ultraviolet region," item 8, except for using a maximum of 8 amperes for excitation.

6.5 Use the same procedure for photographic processing described in the section "Ultraviolet region," item 9.

6.6 Measure with a microphotometer the percent transmittances of the analytical lines and their corresponding internal-standard lines.

6.7 Precautions:

Precautions are the same as those described for the thioacetamide method. (See section "Precipitation method—thioacetamide," item 6.7.)

7. Computations

Computations are the same as those described in the section "Ultraviolet region," item 7.

8. Report

Report elements below 10 μg/l to one significant figure; for elements 10 μg/l and higher, report results to two significant figures.

9. Precision

Silvey and Brennan (1962), using synthetic samples, reported standard deviations for their method as shown in table 11. Precision data for this modification of their method are not yet available.

Table 11.—Standard deviations of synthetic samples [After Silvey and Brennan, (1962)]

Element	Analytical line (A)	Number of determinations	Standard deviation (percent)
Aluminum	2,652.49	22	±3.9
Bismuth	3,067.72	8	±2.6
Cadmium	2,980.63	18	±4.1
Chromium	2,780.70	18	±2.6
Cobalt	3,409.18	20	±2.0
Copper	2,824.37	22	±5.3
Gallium	2,450.07	18	±7.5
Germanium	2,651.58	22	±2.6
Iron	2,823.28	22	±1.0
Lead	2,833.07	20	±3.0
Molybdenum	3,208.83	16	±1.4
Nickel	3,414.76	20	±2.0
Titanium	3,239.04	22	±1.4
Vanadium	3,110.71	22	±2.8
Zinc	3,345.02	14	±5.8
Average			±3.3

Standards preparation for residue method—ultraviolet region

1. Prepare a standards matrix in the following proportions: Weigh 10 g graphite powder into a plastic mixing jar of 100-ml capacity. Shake to coat inside of jar. Pulverize, weigh, and add the following compounds:

CaCO ₃	4.662 g
MgSO ₄	2.325
NaCl	1.828
KCl	.356
SiO ₂	.829
Total	10.000 g
Graphite powder	10.000
Grand total	20.000 g

Put in four or five 3/8-inch-diameter plastic balls and mix thoroughly in mixer mill. (This

is the matrix used in making all steps of the standard series. More than this will be needed and may be made up in one batch if large mixing equipment is available.

2. For 1-percent Al, Fe, Mn, and Zn (5,000 mg),²

25 mg Al	→ (25×1.88946) mg Al ₂ O ₃	= 47.24 mg
25 mg Fe	→ (25×1.42973) mg Fe ₂ O ₃	= 35.74
25 mg Mn	→ (25×1.38831) mg Mn ₂ O ₃	= 34.71
25 mg Zn	→ (25×1.24476) mg ZnO	= 31.12

Total	-----	148.81 mg
Graphite powder	-----	148.81
Matrix prepared in step 1	-----	4,702.38

Grand total -----5,000.00 mg

NOTE.—Pulverize individual ingredients before weighing and weigh them in the following order: First, weight the graphite powder into a plastic mixing jar of 100-ml capacity. Shake to coat inside of jar. Weigh matrix next and add to jar. Weigh pulverized oxides last. Mix in mixer mill using four or five 3/8-inch-diameter plastic balls.

3. Dilution of 1-percent Al, Fe, Mn, and Zn to 0.464 and 0.215 percent. For 0.464-percent Al, Fe, Mn, and Zn, take 2.3208 g 1-percent standard and 2.6792 g of above matrix. For 0.215-percent, take 2.3208 g of 0.464-percent standard and 2.6792 g of above matrix.

The total amount made of each concentration is 5 g. The fraction of the elements in the new step is 0.464 (or 2.320/5, or 1/2.154) of that present in the previous step. It will be noted that the unused portion of each step is 5.00—2.32 or 2.68 g, enough to charge more than 100 electrodes.

4. Introduction of Ba, Sr, B, and Cu at the 0.1-percent step: First, prepare a mixture containing these elements at 1-percent concentration as

10 mg Ba	→ (10×1.43694) mg BaCO ₃	= 14.37 mg
10 mg Sr	→ (10×1.68489) mg SrCO ₃	= 16.85
10 mg B	→ (10×5.71946) mg H ₃ BO ₃	= 57.19
10 mg Cu	→ (10×1.25181) mg CuO	= 12.52

Total	-----	100.93 mg
Graphite powder	-----	100.93
Matrix prepared in step 1	-----	1,798.14

Grand total -----2,000.00 mg

Weigh graphite powder into mixing vial of appropriate size. Shake vial. Weigh matrix into vial. Pulverize in an agate mortar the in-

²The graphite powder is not taken into consideration when computing percentages, because the samples and standards contain identical (1:1) proportions of this material.

dividual element compounds above before weighing, weigh into vial, and mix thoroughly in mixer mill.

5. For 0.1-percent Al, Fe, Mn, Zn, Ba, Sr, B, and Cu, take 2.3208 g 0.215-percent Al, Fe, Mn, and Zn standard; 0.5000 g 1.0-percent Ba, Sr, B, and Cu mixture; and 2.1792 g matrix prepared in step 1 (5.0000 g total).

6. For 0.0464 and 0.0215 percent of these eight elements, take 2.3208 g 0.1 and 0.0464 percent, respectively, and 2.6792 g matrix prepared in step 1.

7. Introduction of 15 addition elements at the 0.01-percent step. First, prepare a mixture containing these elements at 1.0-percent concentration as

10 mg Be	→ (10×2.77530) mg BeO	= 27.75 mg
10 mg Bi	→ (10×1.11484) mg Bi ₂ O ₃	= 11.15
10 mg Cd	→ (10×1.14235) mg CdO	= 11.42
10 mg Cr	→ (10×1.46151) mg Cr ₂ O ₃	= 14.62
10 mg Co	→ (10×1.36197) mg Co ₃ O ₄	= 13.62
10 mg Ga	→ (10×1.34423) mg Ga ₂ O ₃	= 13.34
10 mg Ge	→ (10×1.44083) mg GeO ₂	= 14.41
10 mg Pb	→ (10×1.07723) mg PbO	= 10.77
10 mg Mo	→ (10×1.50031) mg MoO ₃	= 15.00
10 mg Ni	→ (10×1.27254) mg NiO	= 12.73
10 mg Ag	→ (10×1.07416) mg Ag ₂ O	= 10.74
10 mg Sn	→ (10×1.26961) mg SnO ₂	= 12.70
10 mg Ti	→ (10×1.66806) mg TiO ₂	= 16.68
10 mg V	→ (10×1.78518) mg V ₂ O ₅	= 17.85
10 mg Zr	→ (10×1.35080) mg ZrO ₂	= 13.51

Total	-----	216.29 mg
Graphite powder	-----	216.29
Matrix prepared in step 1	-----	1,567.42

Grand total -----2,000.00 mg

Pulverize before weighing and mix in mixer mill. Dilute the above mixture to 0.1 percent by taking 200 mg of the above mixture and 1,800 mg matrix prepared in step 1.

To make the standard containing 0.01 percent of each of the 23 elements, take 2.3208 g 0.0215-percent eight-element standard, 0.5000 g 0.1-percent 15-element standard (above), and 2.1792 g matrix prepared in step 1.

8. For concentrations 0.00464 through 0.0000464, proceed as in step 6.

9. Flow diagram to aid in preparing this series of standards (fig. 3).

Standards preparation for residue method—infrared region

Prepare a matrix as in the previous discus-

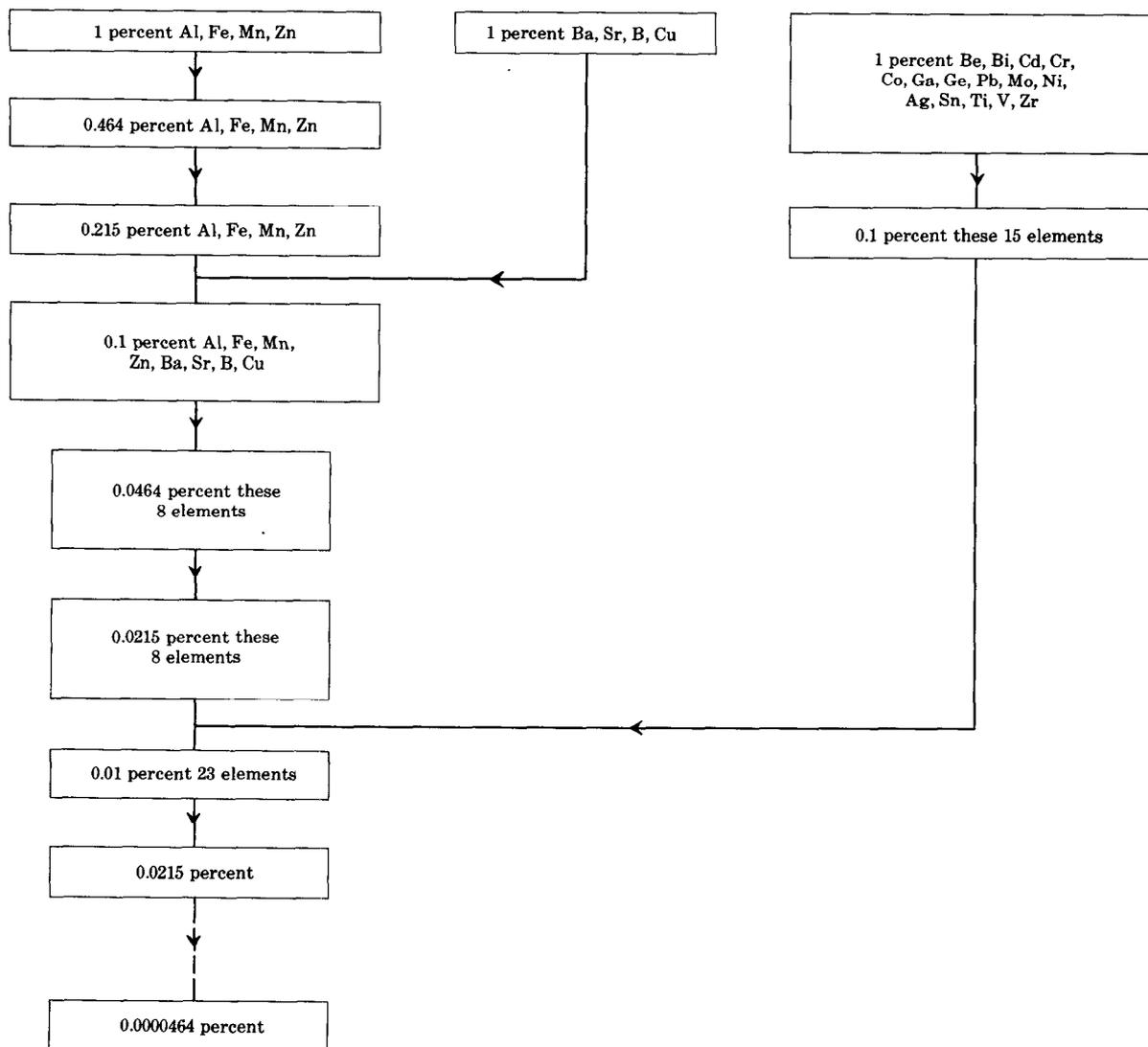


Figure 3.—Flow diagram for preparation of standards.

sion for the ultraviolet region. Then prepare a mixture containing 1 percent of cesium, lithium, and rubidium in this matrix by weighing the quantities of materials listed as follows:

Matrix	2,405.30 mg
Cs ₂ CO ₃ (25×1.22576=) ---	30.64
Li ₂ CO ₃ (25×1.14749=) ---	28.69
RbCl (25×1.41477=) -----	35.37
Total	2,500.00 mg

To this, add 2,500 mg sodium carbonate³ and mix thoroughly.

³ The sodium carbonate is not taken into consideration when computing percentages, because the samples and standard contain identical (1:1) portions of this material.

To prepare a 0.1-percent standard, mix together 0.5 g of the mixture just prepared, 2.25 g matrix, and 2.25 g sodium carbonate.

To prepare a 0.0464-percent standard, mix together 2.3208 g 0.1-percent standard, 1.3396 g matrix, and 1.3396 g sodium carbonate.

Repeat until 0.0001 percent is reached.

Stock and standard solutions for thioacetamide method

Four separate stock solutions are necessary to provide stable elemental mixtures used to make standard solutions. The components of

each of these stock solutions are given in table 12. Compounds used in stock solutions must be

Table 12.—Stock solutions for thioacetamide method
[Stock solutions require 50 mg/l of each element given]

Stock solution	Element	Compound used	Weight required (mg/l)	Solvent (Use 12N HCl; 36N H ₂ SO ₄)
A -----	As	As ₂ O ₃	66.02	10 ml HCl (warm only).
	Bi	Bi ₂ O ₃	55.74	10 ml HCl.
	Cd	CdO	57.12	10 ml HCl.
	Cu	CuO	62.59	10 ml HCl.
	Pb	PbO	53.86	15 ml HCl.
	Mo	MoO ₃	75.02	15 ml HCl.
B -----	Sb	KSbOC ₄ H ₄ O ₈ · ½ H ₂ O	137.14	H ₂ O.
C -----	Al	Al ₂ (SO ₄) ₃	(¹)	H ₂ O.
	Be	BeO	138.76	7 ml H ₂ SO ₄ .
	Cr	K ₂ Cr ₂ O ₇	141.45	H ₂ O.
	Co	Co ₂ O ₃	68.10	12 ml H ₂ SO ₄ .
	Fe	Fe ₂ O ₃	71.49	5 ml HCl for solvent, then fume in 5 ml H ₂ SO ₄ .
	Mn	Mn ₂ O ₃	69.42	5 ml HCl for solvent, then fume in 5 ml H ₂ SO ₄ .
	Ni	NiO	63.63	12 ml H ₂ SO ₄ .
	Ag	Ag ₂ O	53.71	5 ml H ₂ SO ₄ .
	Zn	ZnO	62.24	5 ml H ₂ SO ₄ .
	Zr	Zr(SO ₄) ₂ · 4H ₂ O	194.81	5 ml H ₂ SO ₄ .
D -----	Ti	(NH ₄) ₂ TiO(C ₂ O ₄) ₂ · H ₂ O	306.93	H ₂ O.
	La	La ₂ O ₃	58.64	3 ml H ₂ SO ₄ .
	Y	Y ₂ O ₃	63.50	10 ml H ₂ SO ₄ .
	Yb	Yb ₂ O ₃	56.94	10 ml H ₂ SO ₄ .

¹ Use a microburet to measure 3.175 ml of 10 percent spectrographic-pure solution.

of known high purity or the absence of harmful impurities otherwise confirmed. The compounds are dissolved separately, mixed together, and diluted to exactly 1 liter with distilled-demineralized water.

Stock solutions A and B contain those elements whose sulfides are precipitated from strongly acid solution. The oxides of all these elements except antimony are readily soluble in hydrochloric acid. Antimony must be prepared as a separate stock solution because of its tendency to hydrolyze and precipitate as a basic chloride in dilute hydrochloric acid solution. This stock solution is stable for at least 30 days.

Stock solutions C and D contain those elements whose sulfides or hydroxides are precipitated from neutral or slightly ammoniacal solution. Use either the high-purity oxide or sulfate of each element, except for chromium, where a dichromate salt is satisfactory, and titanium, where the most convenient compound is ammonium titanyl oxalate. This titanium stock solution is stable for at least 30 days.

Prepare a series of standard solutions decreasing in concentration by logarithmic steps.

1(a). Dilute 100 ml stock solution A to 1

liter with water. This gives a standard containing 5,000 μg/l of each element.

(b). Dilute 200 ml of the 5,000 μg/l standard with 229 ml water and 1 ml hydrochloric acid. This gives a standard of 2,325 μg/l.

(c). Dilute 200 ml of the 2,325 μg/l standard with 229 ml water and 1 ml hydrochloric acid to make a standard of 1,081 μg/l.

(d). Continue the dilutions as above so that standards of 503, 233, 108, 50, 23, 11, 5, 2.3, and 1.1 μg/l are obtained. Each standard solution contains 46.5 percent of the elements found in the next higher standard.

2. Dilute standards made from stock solution B the same as in step 1 except use 230 ml water. No acid is necessary.

3. Dilute standards made from stock solutions C and D the same as in step 1 except use 1 ml sulfuric acid instead of 1 ml hydrochloric acid.

Stock and standard solutions for complexometric method

The four separate stock solutions needed for the complexometric method are much like those used in the thioacetamide method except that vanadium is added to stock solution A, beryllium and manganese are omitted from stock solution C, and lanthanum and yttrium are omitted from stock solution D. The amounts of elements and the solvents used for A, B, C, and D are given in table 13.

Table 13.—Stock solutions for complexometric method
[Stock solutions require 50 mg/l of each element given]

Stock solution	Element	Compound used	Weight required (mg/l)	Solvent (Use 12N HCl; 36N H ₂ SO ₄)	
A -----	As	As ₂ O ₃	66.02	10 ml HCl (warm only).	
	Bi	Bi ₂ O ₃	55.74	10 ml HCl.	
	Cd	CdO	57.12	10 ml HCl.	
	Cu	CuO	62.59	10 ml HCl.	
	Pb	PbO	53.86	15 ml HCl.	
	Mo	MoO ₃	75.02	15 ml HCl.	
	V	NH ₄ VO ₃	114.82	5 ml HCl.	
	Sb	KSbOC ₄ H ₄ O ₈ · ½ H ₂ O	137.14	H ₂ O.	
	C -----	Al	Al ₂ (SO ₄) ₃	(¹)	H ₂ O.
		Cr	K ₂ Cr ₂ O ₇	141.45	H ₂ O.
Co		Co ₂ O ₃	68.10	12 ml H ₂ SO ₄ .	
Fe		Fe ₂ O ₃	71.49	5 ml HCl for solvent, then fume in 5 ml H ₂ SO ₄ .	
Ni		NiO	63.63	12 ml H ₂ SO ₄ .	
D -----	Ag	Ag ₂ O	53.71	5 ml H ₂ SO ₄ .	
	Zn	ZnO	62.24	5 ml H ₂ SO ₄ .	
	Zr	Zr(SO ₄) ₂ · 4H ₂ O	194.81	5 ml H ₂ SO ₄ .	
	Ti	(NH ₄) ₂ TiO(C ₂ O ₄) ₂ · H ₂ O	306.93	H ₂ O.	
	Yb	Yb ₂ O ₃	56.94	10 ml H ₂ SO ₄ .	

¹ Use a microburet to measure 3.175 ml of 10 percent spectrographic-pure solution.

Prepare a series of standard solutions decreasing in concentration by logarithmic steps as described in the previous discussion for the thioacetamide method.

Purification of chelating reagents.—Farquhar, Hill, and English (1966) passed a distilled-demineralized water solution of tannic acid through a cation-exchange resin column to remove trace elements. They purified 8-hydroxyquinoline with two dry distillations.

Dissolve thionalide in redistilled acetic acid and then recrystallize it by letting part of the acetic acid evaporate at room temperature.

Two-step method of emulsion calibration

Manual method

It is not necessary to convert transmittance values to densities or Seidel-function values if the following procedure is used. Take logarithmic paper with a two-cycle ordinate and a three-cycle abscissa. Plot the percentage transmittance of the weak step of each line, as ordinate, against the percentage transmittance of its corresponding strong step, as abscissa. Draw the best curve, called the preliminary

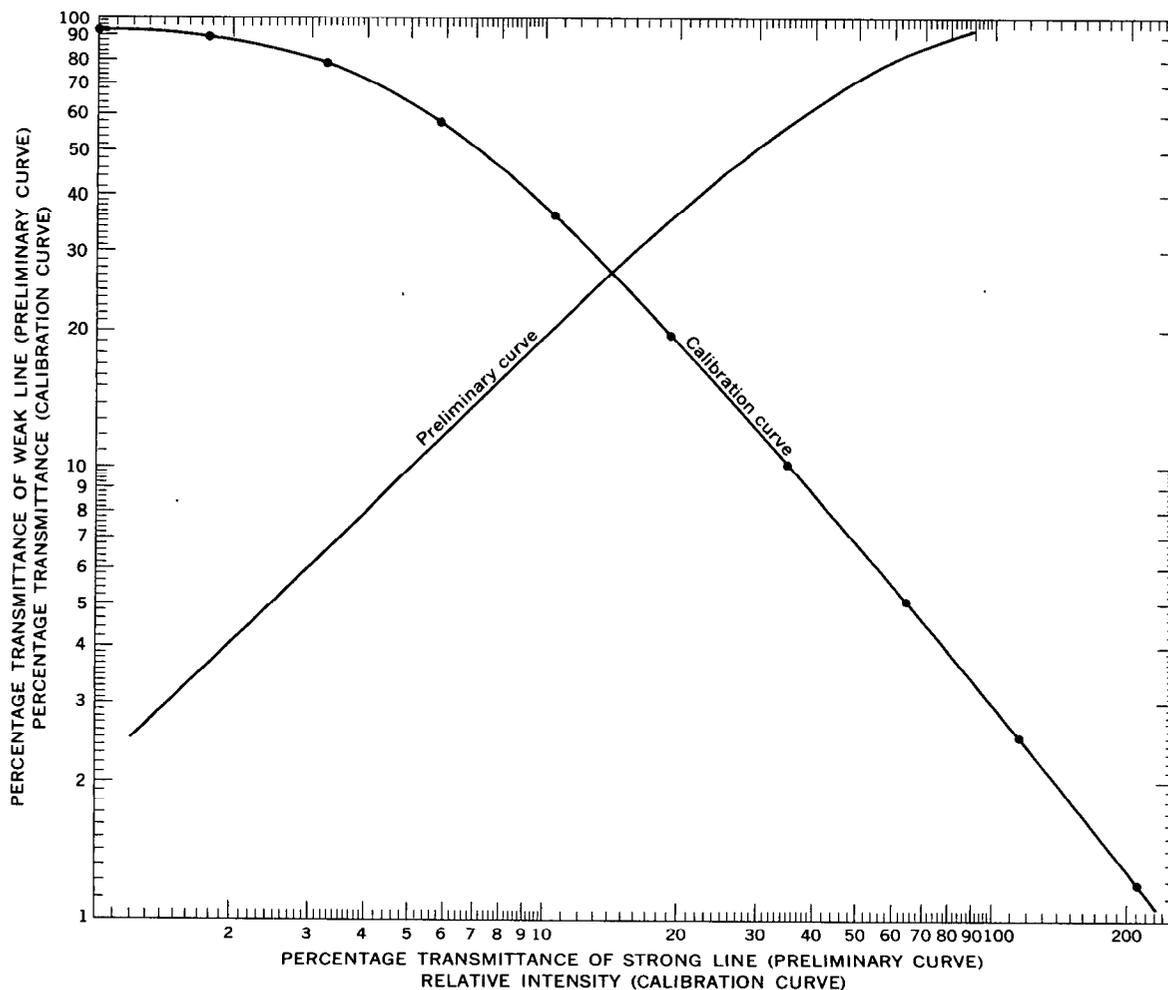


Figure 4.—Emulsion calibration curves.

nary calibration curve, through these points (fig. 4). Prepare a table similar to table 14.

Table 14.—Points for preparing calibration curve

Point	RI	Percentage transmittance
1	1	96
2	1.8	92
3	3.3	82
4	6.0	60
5	10.9	37
6	19.9	20
7	36	10.2
8	66	5.2
9	119	2.55
10	217	1.2

The first column assigns a number to the points to be plotted to construct the final calibration curve. To point 1 assign an arbitrary relative intensity (RI) of 1. To assign a RI to point 2 multiply the RI of point 1 by the transmittance ratio of the step filter (in this example, 100 percent/55 percent or 1.818). Multiply each RI thus obtained by this ratio to obtain the RI of the next point. To obtain the values in the column titled "percentage transmittance" assign a value in the best microphotometer range to one of the points of medium intensity, such as 20 percent, to point 6. Consider this the percentage transmittance of the weak line and from the preliminary calibration curve determine the percentage transmittance of the strong line (10.2 percent). Enter this as the percentage transmittance of point 7. Now consider this as the percentage transmittance of the weak line on the preliminary curve and determine the percentage transmittance of the strong line (5.2 percent). Continue this process to point 10. Go back to the assigned value of 20 percent for the transmittance for point 6 and now treat this value as the percentage transmittance of the strong line of the preliminary curve. The corresponding percentage transmittance of the weak line will be found to be 37. Enter this in the third column for point 5. Continue the procedure as before until the percentage transmittance for point 1 has been found.

Plot the pairs of values in the table on 2 by 3-cycle logarithmic paper. The ordinate (2-cycle) is the percentage transmittance and the abscissa (3-cycle) is the RI. Draw the best curve through the points. This calibration

curve is used to convert percent transmittance values to relative intensities.

Computer method

A computer program written in Fortran IV for use on the IBM 360 is ordinarily used instead of the manual method of plate calibration. The percentage transmittances of the weak and strong lines are converted into Seidel-function values (Δ) by means of the equation

$$\Delta = \log \left(\frac{100}{T} - 1 \right).$$

The equation of the regression line for these pairs of values is determined, and the coefficients are printed in the output. To establish the final calibration, the computer transforms coordinate pairs of weak-line-strong-line Seidel values from the preliminary curve to corresponding pairs of Seidel value-relative-intensity values in a manner similar to the previously discussed manual procedure. The quadratic equation of the curve through these points is determined, and the three coefficients are printed as output.

Computer program

The computer program used for processing densitometric data from spectrographic plates is given in table 15. The language is Fortran IV.

The variables used in the program are defined in the table; however, those defined by the program or by convention are not included. For convenience in reducing the number of variables some of them are used in portions of the program as variables not fitting the definitions.

The first phase of the program (program cards numbered A 310 through A 890) deals with plate calibration. The densitometer readings for the weak-step and strong-step halves of selected lines from the iron spectrum are transformed into Seidel-function values (cards A 390 and A 400) by the transformation

$$\Delta = \log \left(\frac{100}{T} - 1 \right), \quad (1)$$

Table 15.—Computer program for processing densitometric data

BL	Option for furnishing or computing coefficients of emulsion calibration curve.	DALINE	Percentage transmittance (analytical line in sample).
X	Densitometer readings for strong half of Fe lines.	CONCF	Concentration factor.
Y	Densitometer readings for weak half of Fe lines.	SRIR	Ratio of relative intensity of analytical line to relative intensity of internal-standard line (for standards).
RI	Relative intensity.	DRIR	Ratio of relative intensity of analytical line to relative intensity of internal-standard line (for samples).
GPT	The Seidel-function values used in writing equation of emulsion calibration curve.	RN	Replicate number.
SID	Sample identification.	SFAC	Factor to be applied to background before subtracting from line in standard.
CONSTD	Concentration of element in standard.	DFAC	Factor to be applied to background before subtracting from line in sample.
SBL	Background reading (percentage transmittance) (standard).		
STLINE	Percentage transmittance of line (sample).		
DBL	Background reading (sample).		

```

C          EMISSION SPECTROSCOPY      D0006                      A 10
C                                          A 20
C          TRANSLATED AND REVISED FROM B 5500                A 30
C          EXTENDED ALGOL EM SPEC D0006/USGS                 A 40
C          BY WAYNE C SCHOMBURG                               A 50
C          RE PAUL R BARNETT                                  A 60
C                                          A 70
C          DATE *26 SEPTEMBER 1968 (GEOMET SUBROUTINE ADDED) A 80
C          DATE ** 5 JUNE 1969 (MODIFIED BY BARNETT)         A 90
C          27 FEB 1970 CALL PUNCH WITH OPTION CDOPT (COL 75 = 1) A 100
C          CALL GEOMET WITH OPTION GEOPT (COL 80 = 1)         A 110
C          PCT DEV OF LAST ELEMENT FROM MEAN                 A 120
C                                          A 130
C          INTEGER BL,RN,CARD,CDOPT,GEOPT                    A 140
C          REAL NORM,MEAN                                     A 150
C          DIMENSION ID(10), X(50), Y(50), RI(50), GPT(50), COEF(4), NORM(3,4 A 160
C          1), EID(50,2), SID(50,2), CONSTD(50), SRL(50,50), STLINE(50,50), DB A 170
C          2L(50,50), DALINE(50,50), CONCF(50), EXA(50), SRIR(50,50), DRIR(50, A 180
C          350), EXB(50), RN(50), SFAC(50,50), DFAC(50,50), G(50,50)         A 190
C                                          A 200
C                                          A 210
C                                          A 220
C          EXD(X)=10.**X                                       A 230
C                                          A 240
C          CARD=5                                             A 250
C          LINE=6                                             A 260
C          IPCH=8                                             A 270
C                                          A 280
C          CALL JULDAT (IYR,IMO,IDY)                          A 290
C                                          A 300
C 110 READ (CARD,450,END=440) ID,BL,N,A,B,C,CDOPT,GEOPT     A 310
C      WRITE (LINE,520) ID,IMO,IDY,IYR                       A 320
C      IF (BL.EQ.1) GO TO 190                                 A 330
C      READ (CARD,460) (X(J),J=1,N)                          A 340
C      READ (CARD,460) (Y(J),J=1,N)                          A 350
C      SUMX=0.                                                A 360
C      SUMY=0.                                                A 370
C      DO 120 I=1,N                                           A 380
C      X(I)=ALOG10(100./X(I)-1.)                              A 390
C      Y(I)=ALOG10(100./Y(I)-1.)                              A 400
C      SUMX=SUMX+X(I)                                         A 410
C 120 SUMY=SUMY+Y(I)                                          A 420
C      XBAR=SUMX/N                                             A 430
C      YBAR=SUMY/N                                             A 440
C      SUMX=0.                                                A 450
C      SUMY=0.                                                A 460
C      SUMXY=0.                                               A 470
C      DO 130 I=1,N                                           A 480
C      XI=X(I)-XBAR                                           A 490
C      YI=Y(I)-YBAR                                           A 500
C      SUMX=SUMX+XI*XI                                         A 510
C      SUMXY=SUMXY+XI*YI                                       A 520
    
```

Table 15.—Computer program for processing densitometer data—Continued

130	SUMY=SUMY+YI*YI	A 530
	XVAR=SUMX/(N-1)	A 540
	BI=SUMXY/(N-1)/XVAR	A 550
	AI=YBAR-BI*XBAR	A 560
	SUMX=0.	A 570
	DO 140 I=1,N	A 580
140	SUMX=SUMX+(Y(I)-(AI+BI*X(I)))**2	A 590
	SE=SQRT(SUMX/(N-2))	A 600
	WRITE (LINE,530) AI,BI,SE	A 610
C		A 620
C	THIS COMPLETES REGRESSION FIT TO PRELIMINARY DATA	A 630
C		A 640
C	NOW ESTABLISH RELATIVE INTENSITY CURVE	A 650
C		A 660
	RI(5)=ALOG10(19.86949)	A 670
	DO 150 I=1,4	A 680
	J=5-I	A 690
150	RI(J)=RI(J+1)-ALOG10(1.818182)	A 710
	DO 160 I=6,8	A 720
160	RI(I)=RI(I-1)+ALOG10(1.818182)	A 730
	XI=ALOG10(4.0)	A 740
	GPT(5)=XI	A 750
	DO 170 I=1,4	A 760
	J=5-I	A 770
	GPT(J)=AI+BI*XI	A 780
170	XI=GPT(J)	A 790
	XI=ALOG10(4.0)	A 800
	DO 180 I=6,8	A 810
	GPT(I)=(XI-AI)/BI	A 820
180	XI=GPT(I)	A 830
	CALL FORMEQ (8,GPT,RI,NORM)	A 840
	CALL SIMEQ (3,NORM,COEF,&190)	A 850
	A=COEF(1)	A 860
	B=COEF(2)	A 870
	C=COEF(3)	A 880
190	WRITE (LINE,540) A,B,C	A 890
C		A 900
C	PHASE 2	A 910
	READ (CARD,470) NE,NC,NS	A 920
	READ (CARD,480) (EID(I,1),EID(I,2),I=1,NE)	A 930
	DO 200 I=1,NC	A 940
	READ (CARD,490) CONSTD(I),(SBL(I,J),SFAC(I,J),STLINE(I,J),J=1,8)	A 950
	IF (NE.LE.8) GO TO 200	A 960
	READ (CARD,510) (SBL(I,J),SFAC(I,J),STLINE(I,J),J=9,16)	A 970
	IF (NE.LE.16) GO TO 200	A 980
	READ (CARD,510) (SBL(I,J),SFAC(I,J),STLINE(I,J),J=17,24)	A 990
	IF (NE.LE.24) GO TO 200	A1000
	READ (CARD,510) (SBL(I,J),SFAC(I,J),STLINE(I,J),J=25,NE)	A1010
200	CONTINUE	A1020
	DO 210 I=1,NC	A1030
	IF (SBL(I,1).EQ.0) SBL(I,1)=99.9	A1040
	IF (STLINE(I,1).EQ.0) STLINE(I,1)=20.0	A1050
210	CONTINUE	A1060
	DO 220 I=1,NC	A1070
	DO 220 J=1,NE	A1080
	IF (SBL(I,J).EQ.0) GO TO 220	A1090
	SBL(I,J)=ALOG10(100./SBL(I,J)-1.)	A1100
	STLINE(I,J)=ALOG10(100./STLINE(I,J)-1.)	A1110
	SBL(I,J)=EXD(A+B*SBL(I,J)+C*SBL(I,J)**2)	A1120
	STLINE(I,J)=EXD(A+B*STLINE(I,J)+C*STLINE(I,J)**2)	A1130
220	CONTINUE	A1140
	DO 260 I=1,NC	A1150
	DO 260 J=1,NE	A1160
	IF (STLINE(I,J).EQ.0) GO TO 240	A1170

Table 15.—Computer program for processing densitometer data—Continued

	IF (SBL(I,J).EQ.0) GO TO 250	A1180
C		A1190
C	IF SBL = 0 AND A VALUE IS INPUT FOR STLINE, SRIR=STLINE/10	A1200
C		A1210
	FAC=1.	A1220
	CODE=SFAC(I,J)	A1230
	IF (CODE.NE.0) FAC=CODE/(CODE+1.)	A1240
	SRIR(I,J)=STLINE(I,J)-SBL(I,J)*FAC	A1250
	SBL(I,J)=SRIR(I,J)	A1260
	IF (J.EQ.1) GO TO 260	A1270
	IF (SRIR(I,J).LE.0) GO TO 230	A1280
	SRIR(I,J)=SRIR(I,J)/SRIR(I,1)	A1290
	GO TO 260	A1300
	230 WRITE (LINE,630) CONSTD(I),EID(J,1),EID(J,2)	A1310
	240 SRIR(I,J)=0.	A1320
	GO TO 260	A1330
	250 SRIR(I,J)=STLINE(I,J)/10.	A1340
	260 CONTINUE	A1350
C		A1360
	IF (NS.EQ.0) GO TO 320	A1370
C	THIS BRANCH WILL GIVE PRINTOUT OF SRIR (RATIOS) ONLY	A1380
C		A1390
	DO 270 I=1,NS	A1400
	READ (CARD,500) SID(I,1),SID(I,2),RN(I),CONCF(I),(DBL(I,J),DFAC(I,	A1410
	1J),DALINE(I,J),J=1,8)	A1420
	IF (NE.LE.8) GO TO 270	A1430
	READ (CARD,510) (DBL(I,J),DFAC(I,J),DALINE(I,J),J=9,16)	A1440
	IF (NE.LE.16) GO TO 270	A1450
	READ (CARD,510) (DBL(I,J),DFAC(I,J),DALINE(I,J),J=17,24)	A1460
	IF (NE.LE.24) GO TO 270	A1470
	READ (CARD,510) (DBL(I,J),DFAC(I,J),DALINE(I,J),J=25,NE)	A1480
	270 CONTINUE	A1490
	DO 280 J=1,NS	A1500
	IF (RN(J).NE.1) CONCF(J)=CONCF(J-1)	A1510
	280 CONTINUE	A1520
	DO 290 I=1,NS	A1530
	IF (DBL(I,1).EQ.0) DBL(I,1)=99.9	A1540
	IF (DALINE(I,1).EQ.0) DALINE(I,1)=20.0	A1550
	290 CONTINUE	A1560
	DO 310 I=1,NS	A1570
	DO 310 J=1,NE	A1580
	IF (DALINE(I,J).EQ.99.9.OR.DALINE(I,J).EQ.0) GO TO 310	A1590
	DBL(I,J)=ALOG10(100./DBL(I,J)-1.)	A1600
	DALINE(I,J)=ALOG10(100./DALINE(I,J)-1.)	A1610
	DBL(I,J)=EXD(A+B*DBL(I,J)+C*DBL(I,J)**2)	A1620
	DALINE(I,J)=EXD(A+B*DALINE(I,J)+C*DALINE(I,J)**2)	A1630
	FAC=1.	A1640
	CODE=DFAC(I,J)	A1650
	IF (CODE.NE.0) FAC=CODE/(CODE+1.)	A1660
	DRIR(I,J)=DALINE(I,J)-DBL(I,J)*FAC	A1670
	DBL(I,J)=DRIR(I,J)	A1680
	IF (J.EQ.1) GO TO 310	A1690
	IF (DRIR(I,J).LE.0) GO TO 300	A1700
	DRIR(I,J)=ALOG10(DRIR(I,J)/DRIR(I,1))	A1710
	GO TO 310	A1720
	300 WRITE (LINE,620) SID(I,1),SID(I,2),RN(I),EID(J,1),EID(J,2),DBL(I,J	A1730
	1),DALINE(I,J)	A1740
	DALINE(I,J)=0.	A1750
	310 CONTINUE	A1760
	320 WRITE (LINE,520) ID,IMO,IDY,IYR	A1770
	WRITE (LINE,550)	A1780
	K=2	A1790
	LIM=NE	A1800
	IF (NE.GT.10) LIM=10	A1810
	330 WRITE (LINE,560) (EID(I,1),EID(I,2),I=K,LIM)	A1820

Table 15.—Computer program for processing densitometer data—Continued

	DO 340 I=1,NC	A1830
	340 WRITE (LINE,570) CCNSTD(I),SRIR(I,1),(SRIR(I,J),J=K,LIM)	A1840
	IF (LIM.EQ.NE) GO TO 350	A1850
	K=K+9	A1860
	LIM=LIM+9	A1870
	IF (NE.LE.LIM) LIM=NE	A1880
	GO TO 330	A1890
C		A1900
	350 IF (CDOPT.EQ.0) GO TO 360	A1910
	WRITE (IPCH,640) IMO,IDY,IYR,ID	A1920
	CALL PUNCH (NE,NC)	A1930
C		A1940
	360 IF (NS.EQ.0) GO TO 110	A1950
	IF (GEOPT.EQ.0) GO TO 380	A1960
	DO 370 J=1,NS	A1970
	G(J,1)=0.0	A1980
	370 G(J,2)=0.0	A1990
	380 DO 430 K=2,NE	A2000
	N=0	A2010
	DO 390 I=1,NC	A2020
	IF (SRIR(I,K).EQ.0) GO TO 390	A2030
	N=N+1	A2040
	EXA(N)=ALOG10(SRIR(I,K))	A2050
	EXB(N)=ALOG10(CONSTD(I))	A2060
	390 CONTINUE	A2070
	CALL FORMEQ (N,EXA,EXB,NORM)	A2080
	CALL SIMEQ (3,NORM,COEF,&110)	A2090
	A=COEF(1)	A2100
	B=COEF(2)	A2110
	C=COEF(3)	A2120
	WRITE (LINE,520) ID,IMO,IDY,IYR	A2130
	WRITE (LINE,580) EID(K,1),EID(K,2)	A2140
	WRITE (LINE,590)	A2150
	MEAN=0.	A2160
	N=0	A2170
	DO 420 I=1,NS	A2180
	IF (DALINE(I,K).EQ.99.9.OR.DALINE(I,K).EQ.0) GO TO 420	A2190
	XI=EXD(A+B*DRIR(I,K)+C*DRIR(I,K)**2)	A2200
	JJ=RN(I)	A2210
	J=I+1-JJ	A2220
	G(J,JJ)=XI	A2230
	YI=XI*CONCF(I)	A2240
	DRIR(I,K)=EXD(DRIR(I,K))	A2250
C	COMPUTE MEAN	A2260
	MEAN=MEAN+YI	A2270
	N=N+1	A2280
	IF (I.EQ.NS) GO TO 400	A2290
	IF (SID(I,2).NE.SID(I+1,2)) GO TO 400	A2300
	IF (SID(I,1).NE.SID(I+1,1)) GO TO 400	A2310
	IF (DALINE(I+1,K).NE.0) GO TO 410	A2320
	400 MEAN=MEAN/N	A2330
	WRITE (LINE,600) SID(I,1),SID(I,2),RN(I),DALINE(I,K),DBL(I,K),DALI	A2340
	NE(I,1),DBL(I,1),DRIR(I,K),XI,CONCF(I),YI,MEAN	A2350
	PCT=ABS(YI-MEAN)/MEAN*100.	A2360
	WRITE (LINE,610) PCT	A2370
	MEAN=0.	A2380
	N=0	A2390
	GO TO 420	A2400
	410 WRITE (LINE,600) SID(I,1),SID(I,2),RN(I),DALINE(I,K),DBL(I,K),DALI	A2410
	NE(I,1),DBL(I,1),DRIR(I,K),XI,CONCF(I),YI	A2420
	420 CONTINUE	A2430
	IF (GEOPT.EQ.1) CALL GEOMET (NS,G)	A2440
	430 CONTINUE	A2450
	GO TO 110	A2460
	440 STOP	A2470

Table 15.—Computer program for processing densitometer data—Continued

```

C
450 FORMAT (10A4,I1,I2,3F9.5,4X,I1,4X,I1) A2480
460 FORMAT (16F5.1) A2490
470 FORMAT (5X,I2,3X,I2,3X,I2) A2500
480 FORMAT (15X,16A4,1X) A2510
490 FORMAT (5X,F10.0,8(1X,F3.1,F1.0,F3.1)) A2520
500 FORMAT (A4,A3,I1,F7.0,8(1X,F3.1,F1.0,F3.1)) A2530
510 FORMAT (15X,8(1X,F3.1,F1.0,F3.1)) A2540
520 FORMAT ('1','D0006 - EMISSION SPECTROSCOPY (2/27/70) ',15X,10 A2550
1A4,10X,'DATE ',I2,'-',I2,'-',I2) A2560
530 FORMAT ('0','PRELIMINARY CURVE COEFFICIENTS A = ',F9.4,8X,' B = ' A2580
1,F9.4,8X,' SE = ',F9.4//) A2590
540 FORMAT ('0','GAMMA CURVE COEFFICIENTS A = ',F9.4,8X,' B = ' A2600
1,F9.4,9X,' C = ',F9.4//) A2610
550 FORMAT ('0',50X,' RATIO RI ST LINE TO RI INT ST LINE') A2620
560 FORMAT ('0','CONC OF STD RI INT ST ',3X,9(3X,2A4)) A2630
570 FORMAT (' ',F10.6,F11.2,5X,9F11.2) A2640
580 FORMAT ('0','ELEMENT = ',2A4//) A2650
590 FORMAT (' ',SAMPLE ID RN B+L L INT STD B+L ', 'INT A2660
1STD L RATIO E(CONC) CONC FACTOR ELEMENT',8X,'MEAN A2670
2 PCT DEV') A2680
600 FORMAT (' ',1X,A4,A3,4X,I1,3X,F6.2,2X,F6.2,4X,F6.2,7X,F6.2,5X,F7.4 A2690
1,2X,F9.5,4X,F9.0,5X,F9.3,4X,F9.3) A2700
610 FORMAT ('+',120X,F6.2/) A2710
620 FORMAT ('0','ERRCR AT ',A4,A3,5X,I1,5X,2A4,5X,F5.2,5X,F5.2,5X,'V A2720
1ALUES SET TO ZERO') A2730
630 FORMAT ('0','SRIR SET TO ZERO AT ',F10.6,5X,2A4) A2740
640 FORMAT (' PAUL BARNETT',5X,I2,'-',I2,'-',I2,5X,20A4) A2750
END A2760-

```

```

C FORMEQ SUBROUTINE B 10
C SUBROUTINE FORMEQ (N,A,B,C) B 20
C DIMENSION A(50), B(50), C(3,4) B 30
C B 40
SUMX=0. B 50
SUMY=0. B 60
SUMX2=0. B 70
SUMX3=0. B 80
SUMX4=0. B 90
SUMXY=0. B 100
SUMX2Y=0. B 110
DO 10 I=1,N B 120
SUMX=SUMX+A(I) B 130
SUMY=SUMY+B(I) B 140
SUMX2=SUMX2+A(I)**2 B 150
SUMX3=SUMX3+A(I)**3 B 160
SUMX4=SUMX4+A(I)**4 B 170
SUMXY=SUMXY+A(I)*B(I) B 180
10 SUMX2Y=SUMX2Y+B(I)*A(I)**2 B 190
C(1,1)=N B 200
C(1,2)=SUMX B 210
C(2,1)=SUMX B 220
C(1,3)=SUMX2 B 230
C(2,2)=SUMX2 B 240
C(3,1)=SUMX2 B 250
C(2,3)=SUMX3 B 260
C(3,2)=SUMX3 B 270
C(3,3)=SUMX4 B 280
C(1,4)=SUMY B 290
B 300
B 310

```

Table 15.—Computer program for processing densitometer data—Continued

	C(2,4)=SUMXY	B 320
	C(3,4)=SUMX2Y	B 330
	RETURN	B 340
	END	B 350-
C	SIMEC SUBROUTINE	C 10
C		C 20
	SUBROUTINE SIMEC (N,A,X,*)	C 30
C		C 40
C	GAUSS-JORDAN REDUCTION WITH BEST PIVOTAL ROW	C 50
C	ARRAY A(N,N+1) WITH N+1 COLUMN = CONST TERMS	C 60
	DIMENSION A(3,4), X(3)	C 70
	LINE=6	C 80
	K=N+1	C 90
10	L=1	C 100
	D=0.	C 110
	DO 20 I=2,K	C 120
	IF (ABS(A(I-1,1)).LE.D) GO TO 20	C 130
	L=I-1	C 140
	D=ABS(A(L,1))	C 150
20	CONTINUE	C 160
	IF (L.EQ.1) GO TO 40	C 170
	DO 30 J=1,K	C 180
	D=A(L,J)	C 190
	A(L,J)=A(I,J)	C 200
30	A(I,J)=D	C 210
40	DO 50 I=1,N	C 220
50	X(I)=A(I,1)	C 230
	IF (K.EQ.1) RETURN	C 240
	IF (X(1).EQ.0) GO TO 80	C 250
	DO 70 J=2,K	C 260
	D=A(1,J)/X(1)	C 270
	DO 60 I=2,N	C 280
60	A(I-1,J-1)=A(I,J)-X(I)*D	C 290
70	A(N,J-1)=D	C 300
	K=K-1	C 310
	GO TO 10	C 320
80	WRITE (LINE,90)	C 330
	RETURN 1	C 340
90	FORMAT ('0','SOLUTION OF MATRIX VOID DETERMINATE ZERO')	C 350
	END	C 360-
C	GEOMET SUBROUTINE	D 10
C		D 20
	SUBROUTINE GEOMET (NS,X)	D 30
C		D 40
	DIMENSION X(50,50)	D 50
C		D 60
C		D 70
	LIST=6	D 80
C		D 90
	MAX=0	D 100
	SUM=0.0	D 110
	SUM1=0.0	D 120
	DO 10 I=1,NS	D 130
	IF (X(I,2).EQ.0.OR.X(I,1).EQ.0) GO TO 10	D 140
	MAX=MAX+1	D 150

Table 15.—Computer program for processing densitometer data—Continued

	SUM1=SUM1+X(I,1)+X(I,2)	D 160
	SUM=SUM+(ALOG(X(I,1))-ALOG(X(I,2)))*2	D 170
10	CONTINUE	D 180
	IF (MAX.EQ.0) GO TO 20	D 190
	SD=SQRT(SUM/(2.0*MAX))	D 200
	VALUE=EXP(SD)	D 210
	AVERAG=SUM1/(2.0*MAX)	D 220
	WRITE (LIST,40) AVERAG,VALUE	D 230
20	DO 30 J=1,NS	D 240
	X(J,1)=0.0	D 250
30	X(J,2)=0.0	D 260
	RETURN	D 270
C		D 280
	40 FORMAT ('0',45X,' AVERAGE = ',F9.5/'0',45X,'GEOMETRIC D	D 290
	EVATION = ',F9.5)	D 300
	END	D 310-
C	PUNCH SUBROUTINE	E 10
C		E 20
	SUBROUTINE PUNCH (NE,NC)	E 30
C		E 40
	DIMENSION CONSTD(50), SRIR(50,50), NRAT(50,50)	E 50
C		E 60
	IPCH=8	E 70
C		E 80
	DO 10 I=1,NC	E 90
	DO 10 J=1,NE	E 100
10	NRAT(I,J)=SRIR(I,J)*100.+0.5	E 110
	N=0	E 120
	K=2	E 130
	LIM=NE	E 140
	IF (NE.GT.8) LIM=8	E 150
20	N=N+1	E 160
	DO 30 I=1,NC	E 170
30	WRITE (IPCH,50) I,N,CONSTD(I),(NRAT(I,J),J=K,LIM)	E 180
	IF (LIM.EQ.NE) GO TO 40	E 190
	K=K+7	E 200
	LIM=LIM+7	E 210
	IF (NE.LE.LIM) LIM=NE	E 220
	GO TO 20	E 230
40	RETURN	E 240
C		E 250
	50 FORMAT (2I2,3X,F8.6,9X,7(13,5X))	E 260
	END	E 270-

where Δ is the Seidel-function value and T is percentage transmittance. These paired values are used as coordinants of points to which a regression line (preliminary calibration curve) is fitted. Cards A 550 and A 560 give the coefficients of the equation for this straight line. The equation of this curve is of the form

$$\Delta_w = A + B\Delta_s, \quad (2)$$

where Δ_w and Δ_s are the Seidel-function values of the weak step and strong step, respectively. Card A 600 gives the standard error of the points about the line.

Cards A 770 through A 890 determine the emulsion calibration curve from the preliminary curve by the same technique suggested in method E 116-67 (American Society for Testing and Materials, 1968), section 10g. Cards A 860, A 870, and A 880 produce the coefficients

of the equation of the new curve (a parabola). The equation is of the form

$$\log RI = A + B\Delta + C\Delta^2, \quad (3)$$

where RI and Δ are relative intensity and Seidel-function value, respectively.

The second phase processes the light transmittance of analytical lines in standards and samples and computes the concentration of each element in each water sample in the following steps:

1. Each transmittance value is converted to RI by successive applications of equations 1 and 3.

2. The net RI of each line is obtained by subtracting the RI of the background from the RI of the line.

3. The ratio of the RI of the line to the RI of the internal-standard line (RIR) is computed.

4. An equation of the form

$$\log \text{conc.} = \log [A + B(\text{RIR}) + C(\text{RIR})^2]$$

is determined for each analytical line, from the standards data.

5. The RIR for the line in the sample is substituted in this equation and the concentration of the element in the arcing mixture determined.

6. Replicate determinations are averaged.

7. The concentration in the water is computed by

$$\text{concentration in water } (\mu\text{g/l}) = \text{concentration in arcing mixture (percent)} / 100 \times \text{dilution factor} \times \text{R.O.E. (mg/l)} \times 1,000.$$

The forms used to record densitometric data and from which data cards are punched are illustrated in figures 5 and 6. On each form there are 80 numbered columns corresponding to the 80 columns of a data card. The rows (numbered on the left-hand margin to facilitate this explanation of the forms) correspond to the sequential arrangement of the cards in the data set.

Form 1

Row 1

The first 40 columns are used for plate identification and any other pertinent information.

These columns are "quoted" as the first line of computer printout. Column 41 provides an option in regard to plate calibration. A "0" (zero) or a blank indicates that data are supplied in rows 2 and 3 for the calibration computations. The number of pairs of these weak line-strong-line values must be given in columns 42-43. A "1" requires that coefficients from an emulsion calibration curve must be supplied (from another plate or average values from two or more plates) in columns 46-51, 55-60, and 64-69.

Rows 2 and 3

The calibration data as labeled are entered to the nearest 0.1 percent. All 16 fields need not be used.

Row 4

In columns 6-7 must be recorded the number of analytical lines read and recorded. The internal-standard line, real or hypothetical and always recorded as the first element line, is included in this number. In columns 11-12 must be recorded the number of steps of the standards read and recorded for all the element lines taken together. In columns 16-17 must be recorded the number of samples recorded on Form 2. Each replicate is counted as a sample.

Row 5

Entered here are the element symbol and the wavelength of the particular line, as, for example, Ba 4554. Columns 17-23 are reserved for an internal-standard line.

Row 6 to last step of standard

Columns 1-2 and 4 are used to keep the cards in proper sequence and are not used in the computer program. Columns 8-15 record the concentration of each step of the standard. If no decimal point is recorded, the computer puts a decimal point in column 15, and the placement of the digits in the other columns determines the size of the number.

Columns 25-27, 33-35, 41-43, etc., record the percent transmittance of the background adjacent to the analytical line to 0.1 percent, but without a decimal point (098 is equivalent to 9.8 percent, for example). Columns 29-31, 37-

PLATE IDENTIFICATION

1	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80
CLEAR DATA (% TRANSMISSION)																
2	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80
FILTERED DATA (% TRANSMISSION)																
3	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80

GAMMA CURVE COEFFICIENTS

A

B

C

L N

4	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80
---	---	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----

NE NC NS (NE=No. of element lines; NC=No. of concentrations of standard; NS=No. of samples)

5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80
---	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----

LINE IDENT.

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	
STD CARD CONCENT. OF SEQ SEQ STANDARD																									

L=0 or blank, must supply clear and filtered data. N=No. pairs of such data.
 L=1, leave N blank and supply gamma curve coefficients A, B, and C.

Figure 5.—Densitometer work sheet 1 for card punching.

LINE IDENT.		17	33	39	41	47	49	55	57	63	65	71	73	79
1	7 15 19	15	17	19	20	21	23	25	27	28	29	31	33	35
	R	CON	FAC	B	F	L	B	F	L	B	F	L	B	F
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
	15	16	17	18	19	20	21	22	23	24	25	26	27	28
	29	30	31	32	33	34	35	36	37	38	39	40	41	42
	43	44	45	46	47	48	49	50	51	52	53	54	55	56
	57	58	59	60	61	62	63	64	65	66	67	68	69	70
	71	72	73	74	75	76	77	78	79	80	81	82	83	84
	85	86	87	88	89	90	91	92	93	94	95	96	97	98
	99	100	101	102	103	104	105	106	107	108	109	110	111	112
	113	114	115	116	117	118	119	120	121	122	123	124	125	126
	127	128	129	130	131	132	133	134	135	136	137	138	139	140
	141	142	143	144	145	146	147	148	149	150	151	152	153	154
	155	156	157	158	159	160	161	162	163	164	165	166	167	168
	169	170	171	172	173	174	175	176	177	178	179	180	181	182
	183	184	185	186	187	188	189	190	191	192	193	194	195	196
	197	198	199	200	201	202	203	204	205	206	207	208	209	210
	211	212	213	214	215	216	217	218	219	220	221	222	223	224
	225	226	227	228	229	230	231	232	233	234	235	236	237	238
	239	240	241	242	243	244	245	246	247	248	249	250	251	252
	253	254	255	256	257	258	259	260	261	262	263	264	265	266
	267	268	269	270	271	272	273	274	275	276	277	278	279	280
	281	282	283	284	285	286	287	288	289	290	291	292	293	294
	295	296	297	298	299	300	301	302	303	304	305	306	307	308
	309	310	311	312	313	314	315	316	317	318	319	320	321	322
	323	324	325	326	327	328	329	330	331	332	333	334	335	336
	337	338	339	340	341	342	343	344	345	346	347	348	349	350
	351	352	353	354	355	356	357	358	359	360	361	362	363	364
	365	366	367	368	369	370	371	372	373	374	375	376	377	378
	379	380	381	382	383	384	385	386	387	388	389	390	391	392
	393	394	395	396	397	398	399	400	401	402	403	404	405	406
	407	408	409	410	411	412	413	414	415	416	417	418	419	420
	421	422	423	424	425	426	427	428	429	430	431	432	433	434
	435	436	437	438	439	440	441	442	443	444	445	446	447	448
	449	450	451	452	453	454	455	456	457	458	459	460	461	462
	463	464	465	466	467	468	469	470	471	472	473	474	475	476
	477	478	479	480	481	482	483	484	485	486	487	488	489	490
	491	492	493	494	495	496	497	498	499	500	501	502	503	504
	505	506	507	508	509	510	511	512	513	514	515	516	517	518
	519	520	521	522	523	524	525	526	527	528	529	530	531	532
	533	534	535	536	537	538	539	540	541	542	543	544	545	546
	547	548	549	550	551	552	553	554	555	556	557	558	559	560
	561	562	563	564	565	566	567	568	569	570	571	572	573	574
	575	576	577	578	579	580	581	582	583	584	585	586	587	588
	589	590	591	592	593	594	595	596	597	598	599	600	601	602
	603	604	605	606	607	608	609	610	611	612	613	614	615	616
	617	618	619	620	621	622	623	624	625	626	627	628	629	630
	631	632	633	634	635	636	637	638	639	640	641	642	643	644
	645	646	647	648	649	650	651	652	653	654	655	656	657	658
	659	660	661	662	663	664	665	666	667	668	669	670	671	672
	673	674	675	676	677	678	679	680	681	682	683	684	685	686
	687	688	689	690	691	692	693	694	695	696	697	698	699	700
	701	702	703	704	705	706	707	708	709	710	711	712	713	714
	715	716	717	718	719	720	721	722	723	724	725	726	727	728
	729	730	731	732	733	734	735	736	737	738	739	740	741	742
	743	744	745	746	747	748	749	750	751	752	753	754	755	756
	757	758	759	760	761	762	763	764	765	766	767	768	769	770
	771	772	773	774	775	776	777	778	779	780	781	782	783	784
	785	786	787	788	789	790	791	792	793	794	795	796	797	798
	799	800	801	802	803	804	805	806	807	808	809	810	811	812
	813	814	815	816	817	818	819	820	821	822	823	824	825	826
	827	828	829	830	831	832	833	834	835	836	837	838	839	840
	841	842	843	844	845	846	847	848	849	850	851	852	853	854
	855	856	857	858	859	860	861	862	863	864	865	866	867	868
	869	870	871	872	873	874	875	876	877	878	879	880	881	882
	883	884	885	886	887	888	889	890	891	892	893	894	895	896
	897	898	899	900	901	902	903	904	905	906	907	908	909	910
	911	912	913	914	915	916	917	918	919	920	921	922	923	924
	925	926	927	928	929	930	931	932	933	934	935	936	937	938
	939	940	941	942	943	944	945	946	947	948	949	950	951	952
	953	954	955	956	957	958	959	960	961	962	963	964	965	966
	967	968	969	970	971	972	973	974	975	976	977	978	979	980
	981	982	983	984	985	986	987	988	989	990	991	992	993	994
	995	996	997	998	999	1000								

B=Background; F=Fraction of background to be subtracted: 0=1.0, 1=0.5, 2=0.67, 3=0.75, 4=0.8; L=Line.

Figure 6.—Densitometer work sheet 2 for card punching.

39, 45-47, etc., record the transmittance of the analytical line. If no number is recorded for background but there is one for line transmittance, the computer multiplies this number by 10 and uses it as an RIR in later computations. This provides for using RIR's from other plates if perchance no standard is recorded on the present plate.

Columns 28, 36, 44, etc., record the code for the fraction of the background RI to be subtracted from the line RI. A "0" causes all the background to be subtracted; "1", 0.5; "2", 0.67; "3", 0.75; "4", 0.8; etc. This provides for the correction for any impurity in the matrix used for mixing with samples.

Columns 17-23 are reserved for the internal-standard line and have the same coding as the other fields of seven digits except that, if left blank, 999 is understood for the background and 200 for the line. This eliminates having to repeat the recording of these numbers for an imaginary internal standard.

Form 2

Line identification should not be repeated on punched card.

All rows

Columns 1-7, alphanumeric sample identification;

Column 8, replicate number;

Columns 9-15, the factor by which the concentration of the element (in percent) must be multiplied to compute the concentration of the element in the water (in $\mu\text{g}/\text{l}$) is

$$\text{R.O.E. (mg/l)} \times 1,000 \times \text{dilution factor} / 100$$

Columns 17-23, for internal-standard data for samples;

Columns 25-79, data from analytical lines in samples; each line must be in columns corresponding to those it occupies on Form 1.

Column 80, a card sequencing aid not used in computations.

If more than seven analytical lines are read, it is necessary to use a second sheet of both forms; if more than 15, a third sheet; and so forth. On Form 1 the first four rows are left blank for all sheets after the first. Row 5 is filled out with the proper data. Columns 17-23 on any sheet after the first are not used for

internal-standard lines, but for an analytical line. For the remaining rows the standards are numbered in sequence in columns 1-2 as before. In column 4 a "1" is entered for the first sheet, "2" for the second sheet, and so forth. The concentrations in columns 8-15 need not be entered on any sheet after the first. Columns 17-79 are used for data from analytical lines.

In setting up the data deck, all cards for each concentration are assembled together in sequence as indicated by the number in column 4.

On Form 2 the sample identification and replicate number are repeated on all sheets, but the concentration is not. Columns 17-79 contain analytical-line data corresponding to the lines listed in row 5 of Form 1. In column 80 is entered the card sequence number as in column 4 of the corresponding sheet of Form 1. Card assembly follows the same pattern as for the standards. All cards from the first spectrum of the first sample are assembled by the numbers in column 8. These are followed by all the cards from the second spectrum of the first sample, and so on for all the sample cards.

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