

# Water Analysis

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THIS present review of the literature of analytical chemistry applied to water analysis, the tenth in a series which began in 1949, covers a period extending from August 1960, the closing date for material included in the last review (17), through September 1962. A few papers published prior to August 1960 are included here, which were omitted from the last review because neither the publication nor an abstract was available to the authors at that time. Although published abstracts are the source of much of the material selected for review, the original literature has been consulted whenever feasible. An abstract reference is included with each reference to a publication which may not be readily available to most analysts in the United States.

An attempt has been made to include all available references to publications dealing with methods and techniques of water analysis. Because of the great increase in the number of publications appearing in this field each succeeding year, it is necessary to be very selective of papers to be included. Principally, papers are included in this review if the method or methods described can be judged to be of interest to analytical chemists whose work directly involves the analysis of natural waters or waste waters. A great many analytical methods and techniques published each year deal with the determination of substances in "aqueous solution." However, such papers have not been included unless the authors specifically indicated that the described method was developed for, or had been applied to, the analysis of natural waters or waste waters.

Within recent years there has been a significant increase in interest in the determination of organic materials and pollutants in water. The review sections on organics, including detergents, phenols, organic acids, and other compounds, represent a severalfold increase in the number of published papers over previous reviews. Recent emphasis on methods and instruments for continuous analysis and monitoring of surface waters for pollutants and contaminants, and for constituents important in connection with specific research problems, of water resources investigation has also resulted in a significant increase in the number of published papers dealing with automatic measuring equipment.

Other general and specific reviews

have been published. Notable among these, although limited almost exclusively to wastes and water pollution, are the annual literature reviews prepared by a Research Committee of the Water Pollution Control Federation (7, 12). Each of these annual reviews contains a section on analytical methods and includes methods for anions, biochemical and chemical oxygen demand, dissolved oxygen, oxidation-reduction potential, organics, cyanide, metals, and nitrogen compounds. Several review articles have appeared which deal specifically with instrumentation and automation of water analysis methods. A review of instrumentation available for continuous water analysis was prepared by Jones and Joyce (8, 9). This emphasizes principles and applications of several types of instruments based on colorimetric, coulometric, amperometric, conductometric, potentiometric, and polarographic measurements. Parker (13) reviewed a variety of analytical methods and equipment used in automatic monitoring of surface waters. A review of commercially available instruments for automatic or continuous measurement of dissolved oxygen, surface tension, residual chlorine, turbidity, and certain impurities such as silica, hardness, iron, and copper, that can be determined colorimetrically, was prepared by Serfass and Schneider (16).

Recent advances in instrumental techniques for water and effluent analysis were described by Malz (11) in a review which includes a discussion of gas-chromatographic methods for identifying phenols, and photometric, colorimetric, chelatometric, polarographic, and microanalytical methods for a number of other constituents. A description of methods useful for determining the major cations in marine and fresh waters was published by Carpenter (4). Rigby and Sinha (15) prepared an annotated bibliography on precipitation chemistry, including a list of 290 abstracts on the chemistry of atmospheric precipitation, covering a period from 1822 to 1960. Included in the bibliography are references to methods of collection and techniques of determining constituents in rain, dew, fog, hail, and snow.

Several handbooks and manuals of water analysis have been published. A manual of methods used by the U. S. Geological Survey for the collection and analysis of water samples was prepared

by Rainwater and Thatcher (14). This manual includes sections on the collection of water samples, the handling of samples before analysis, general laboratory equipment, instruments, and general techniques, as well as 79 detailed laboratory procedures for determining 50 water properties. The American Society for Testing Materials published a 1961 supplement to the 1960 printing of the second edition of its "Manual on Industrial Water and Industrial Waste Water" (3). The supplement contains several revisions of standard methods and tentative methods accepted by the society prior to June 1961. Methods accepted by the society through June 1960 were published as Part II of the manual (2).

A manual of methods useful for the analysis of sea water was prepared by Strickland and Parsons (18). It includes methods for determining common micronutrients and particulate organic matter. Methods developed at the U. S. Bureau of Mines for determining fluoride, bromide, iodide, total, organic, and borate-boron, alkalinity, acidity, potassium, calcium, magnesium, iron, and arsenic were described by Collins *et al.* (5). Kostrikin (10) prepared a report on methods of analysis of industrial water, including a bibliography of 41 references. Colorimetric and nephelometric methods for determining ferric iron, magnesium, calcium, chloride, and sulfate were described by Fiedler (6). Photometric methods for determining most of the common anions and cations, and special substances such as chlorine, phenol, and hydrazine, in drinking water and in waste water, were described in detail in a manual edited by Zimmerman (19). A compilation of methods for the complete chemical and physical (color and turbidity) analysis of fresh water was prepared by Alekin (1).

## ALKALI METALS

The flame photometer is widely used for determinations of the alkali metals. A number of investigators have described flame photometric methods for these elements and several have reported modifications of methods or instruments to improve sensitivity or reliability. A review of flame photometric methods for the determination of sodium and potassium in surface waters was prepared by Dojlido and Koziorowski (5A).

A proposed revision of standard methods for the flame photometric determination of sodium and potassium in water was prepared by Subcommittee 8930P of the American Water Works Association (11A). The proposed revision includes details of three recommended procedures: a direct-intensity measurement, an internal standard method, and a bracketing approach. A discussion of the principles of the methods as well as interferences, sensitivity, and accuracy is also included.

Grabarov (9A) used a direct flame photometric method to determine sodium and potassium in several hundred natural water samples. A recording flame photometer for the continuous determination of sodium in steam from high-pressure power plants was described by James and Fisher (10A). The recorder was provided with four scales: 0-10, 0-1, 0-0.1, and 0-0.01 p.p.m. Nijensohn and Avellaneda (12A) made certain modifications in a Crudo-Caamano flame photometer for the accurate determination of sodium in irrigation waters. The modifications provided more uniform air and gas pressures, more regular operation of the automatic siphon, and a sensitivity control. Calcium interference was removed by adding an excess of ammonium oxalate to the warm sample solution.

Olivari and Benassi (14A) reported that interference of other ions in the determination of potassium by flame photometry can be eliminated by acidifying the waters with 0.1% sulfuric acid. Sodium may also be determined in the acid solution. The sensitivity of the procedure is increased with a hydrogen-oxygen flame and a 0.7-mm. slit. A simple, rapid, and accurate method for the determination of lithium was described by Fishman (6A). Using a flame spectrophotometer equipped with a photomultiplier attachment and an oxygen-acetylene flame, water samples are atomized directly into the flame without pretreatment. As little as 0.02 mg. of lithium per liter can be detected. No interference was found from other ions which occur in natural waters.

Babina and Goshparenko (3A) described procedures for determining sodium, potassium, calcium, and strontium in natural waters using an acetylene-air flame and a photometer equipped with interference filters for isolation of the spectral lines. Godling and Speer (7A) used a flame-spectrophotometric method to analyze thermal waters for lithium, sodium, potassium, rubidium, and cesium. They investigated mutual interference effects of the alkalis and described procedures for determining these elements, making allowance for the interference effects observed. The analyses were made with

a Beckman DU spectrophotometer with an oxygen-acetylene flame and an apparatus attachment for spectral energy recording. Zaidel and Turkin (19A) determined sodium, potassium, calcium, and magnesium in snow and rain samples by both flame photometric and spectrographic methods. The spectrographic methods, using a porous-cup graphite electrode, provided greater sensitivity for magnesium. The use of a Thermite flame to excite the spectra of lithium and cesium was described by Aleskovskii, Setkina, Kochneva, and Lyadov (1A). An evaporated water sample was placed in a Thermite holder and ignited, and the spectra were recorded photographically.

Vinogradov (18A) described spectrographic methods for determining potassium, lithium, and rubidium in dry water residues with a sensitivity of 0.001%. Potassium sulfate was added to both samples and standards when determining rubidium in order to take advantage of the enhancement effects of potassium on rubidium emission and thus increase the sensitivity for this element. The reproducibility ranged from  $\pm 4$  to 14% for potassium,  $\pm 3$  to 14% for lithium, and  $\pm 7$  to 28% for rubidium. Arnautov (2A) described a spectrographic procedure for the determination of the alkali metals in solution. The sample solution was introduced by capillarity into a condensed spark discharge between a lower capillary electrode of graphite and an upper copper electrode. An accuracy to  $\pm 5$  to 6% was obtained using a medium quartz spectrograph.

Nozaki and Manabe (13A) reported an indirect colorimetric method for lithium, sodium, and potassium using ion-exchange resins. Water samples are treated first with an anion-exchange resin and then the alkali metals adsorbed on a cation-exchange resin, from which they are eluted separately as the chlorides. After evaporation of the excess hydrochloric acid, the residues are dissolved in water and the corresponding amount of chloride is determined by reaction with mercuric thiocyanate and ferric ammonium sulfate solutions. An error of less than 10% was observed for from 30 to 500  $\mu\text{g.}$  of sodium.

Prochazkova (15A) used tetraphenylborate for the separation and subsequent determination of potassium. The precipitated potassium tetraphenylborate was dissolved in acetone and titrated with 0.01N silver nitrate with potassium chromate as the indicator. The error for a water sample containing 0.7 to 2.0 mg. of potassium was  $\pm 6\%$ . Volumetric and gravimetric tetraphenylborate procedures for potassium in natural waters were described by Reznikov and Nechaeva (16A).

A direct method for determining

sodium in natural water, using a glass electrode, was investigated by Goremykin and Kryukov (8A). The electrode, sensitive to sodium ion activity in solution, gives an accuracy of  $\pm 2\%$  in neutral or alkaline solution, in samples where the equivalent ratio of calcium plus magnesium to sodium is not greater than 6, and in waters of mineralization not exceeding 6 grams per liter.

Caron and Sugihara (4A) reported a highly specific method for separating cesium from large quantities of sea water by ion exchange on thallos phosphotungstate. The solution is applied to a column prepared from a mixture of the heteropoly salt and filter paper pulp. All monovalent ions other than cesium are eluted with dilute thallos nitrate solution. Essentially quantitative recovery of cesium is achieved by eluting with 0.15M thallos nitrate solution. A method for the separation of cesium-137 from sea water was developed by Schmitt and Kautsky (17A). Cesium is first precipitated, along with other alkali metals, as the double hexanitratocobaltate salt. This precipitate is then dissolved in hydrochloric acid solution and the cesium separated by precipitation as  $\text{Cs}_2\text{BiI}_6$  using a reagent prepared from potassium iodide and bismuth oxynitrate dissolved in acetic acid solution. Cesium-137 is determined in the final precipitate by its  $\beta$ -radiation or by the  $\gamma$ -radiation of barium-137.

#### HARDNESS, ALKALINE EARTH METALS

Tatarinov (34B) described complexometric methods for determining total, permanent, and temporary water hardness. Total hardness is determined by titration with Trilon B solution. Permanent hardness is determined by the same titration performed on a second aliquot which has been boiled for one hour and filtered. The difference between the two values is taken as temporary hardness.

Total hardness can be determined by titration with potassium stearate solution according to Ceausescu (6B). An acidified sample is boiled to decompose bicarbonate, cooled, buffered with ammonium chloride-ammonium hydroxide solution, and titrated with potassium stearate solution, using Eriochrome Black T as the indicator, adding a slight excess of the titrant, and back-titrating with standard magnesium chloride solution. Interferences due to  $\text{Mn}^{+2}$ ,  $\text{Fe}^{+2}$ ,  $\text{Al}^{+3}$ , and  $\text{Cu}^{+2}$  are removed by precipitation with sodium sulfide or by masking with potassium cyanide. Babachev (1B) described rapid methods for determining calcium, magnesium, total hardness, carbon dioxide, and iron in water. Field methods for determining hardness, alkalinity, calcium, magnesium, and chloride were

described by Kononov (15B). A 20-drop sample aliquot is taken for each determination; titrant volumes are also measured by the number of drops used. Results are calculated by multiplying the number of drops by a corresponding conversion factor. Pasovskaya (22B) used an alcoholic solution of sodium oleate to determine total water hardness conductometrically. The method was tested on both synthetic and natural water samples and found to be suitable even for muddy and colored waters.

The use of glyoxal bis(2-hydroxyanil) to determine small amounts of calcium has been investigated by several authors. In alkaline solution, calcium forms a complex with this reagent, which is stable in an aqueous alcoholic solution and has maximum absorption at 520 m $\mu$ . Kerr (14B) determined optimum conditions of pH, temperature, and organic solvent, and the effects of several foreign ions. He found the method suitable for the determination of 0 to 4 p.p.m. of calcium, over which range the color obeys Beer's law. Umland and Meckenstock (36B) proposed using hexanol, in which case the calcium complex can be quantitatively extracted with chloroform. The calcium is then re-extracted with dilute acid and the red color developed by the addition of alkaline methanol-glyoxal bis(2-hydroxyanil) solution. Williams and Wilson (38B) described a similar procedure which, however, requires only 2 ml. of sample and can be carried out in a single test tube.

Improved precision in the determination of calcium was achieved by Carpenter (5B), who separated calcium by ion exchange prior to titration with EDTA. Dziedzianowicz and Oledzka (8B) compared flame photometric and complexometric titration methods for determining trace amounts of calcium, and found that titration with Complexon III solution gave the more accurate results. A conductometric method for determining calcium in bicarbonate waters was described by Bogusevich (3B).

Fabregas, Badrinas, and Prieto (9B) developed a new titrimetric procedure for magnesium in the presence of up to a 150-fold excess of calcium. The method is based on the differences in the stability constants of the EDTA and EGTA complexes of barium, calcium, and magnesium. A slight excess of 0.05M barium EGTA is added to an aliquot of sample, the sample buffered to pH 10, and barium sulfate precipitated by adding sodium sulfate. The magnesium is then titrated with 0.05M EDTA using methyl red-Eriochrome Black T indicator.

Colorimetric methods for determining magnesium were reported by Petrukhin (25B) using Titan Yellow, by Cheng

(7B), who described the preparation and use of a glycerol gel as a protective colloid, and by Ogata and Hiroi (21B), who investigated Xylidyl Blue II as a useful colorimetric reagent.

A flame photometric procedure for determining magnesium in atmospheric precipitations was reported by Turkin and Svistov (35B). The determination is carried out by measuring the intensity of the Mg 285.2-m $\mu$  line in an acetylene-air flame. The sensitivity is 0.5 mg. of magnesium per liter. Sodium and potassium at concentrations up to 20 mg. per liter do not interfere. Calcium salts cause a decrease in the intensity. Takagi (33B) constructed a copper electrode of unique design for the spectrographic analysis of ground water samples, especially for the determination of magnesium. An 0.8-mm.-wide vertical slit was cut to a depth of 10 mm. in the end of a 5-mm.-diameter rod, and the electrode then fitted with a polyethylene cup to contain the sample. Capillary action within the slit subjected a portion of the sample to excitation in a high voltage spark discharge.

The (ethylenedinitrilo) tetraacetate (EDTA) titration of calcium and magnesium has been investigated extensively. Skopintsev and Kabanov (27B) studied the method as applied to the analysis of sea water. They obtained accurate results on standard samples prepared to simulate sea water, titrating the sum of calcium and magnesium on one aliquot of sample using Eriochrome Black T indicator, and titrating calcium alone on a second aliquot using murexide. They recommended standardizing the titrant with standard zinc chloride solution prepared from pure zinc metal. Pate and Robinson (23B, 24B) made a detailed study of the EDTA titration method for determining calcium and magnesium in sea water. They recommended using Cal-red indicator for the calcium titration. They determined magnesium by difference, first titrating the sum of alkaline earths in a sample aliquot buffered with ethanolamine and with Eriochrome Blue Black B indicator, and then titrating calcium plus strontium in a separate aliquot.

Nogueira and Santos (19B) pointed out that results obtained by the EDTA method are comparable to results obtained by other methods, and that residual water samples containing large amounts of manganese must first be treated with sodium diethyldithiocarbamate and the manganese complex then extracted with carbon tetrachloride. A similar scheme was proposed by Solomin and Fesenko (29B) for the elimination of the interference of heavy metals, including up to 1100 p.p.m. of Fe<sup>+3</sup>, up to 20 p.p.m. of Al<sup>+3</sup>, Cr<sup>+3</sup>, Bi<sup>+3</sup>, Sn<sup>+4</sup>, Mn<sup>+2</sup>, Cu<sup>+2</sup>, Zn<sup>+2</sup>, Ni<sup>+2</sup>, Co<sup>+2</sup>, or Cd<sup>+2</sup>, and up to

50 p.p.m. of Pb<sup>+2</sup>, Hg<sup>+2</sup>, Ag<sup>+</sup>, or Sb<sup>+3</sup>. The complexometric titration was evaluated by Zinov'ev and Yurganov (39B), who recommended the addition of sodium sulfide to precipitate copper and zinc, and hydroxylamine to eliminate manganese interference.

The end point of the EDTA titration was determined potentiometrically by Strafelda and Rihova (30B) using a mercury indicating electrode. Magnesium is first precipitated with ammonium phosphate-ammonium hydroxide solution, an excess of standard EDTA solution is then added, and the excess is back-titrated with standard calcium solution. Salts of heavy metals and other alkaline earth metals interfere but most common anions do not interfere. Haslam, Squirrell, and Blackwell (12B) developed a method in which calcium and magnesium are directly titrated potentiometrically with standard EDTA solution. Calcium is determined by titration in alkaline solution containing an added known amount of mercuric ion. The solution is then acidified, the pH adjusted with ammonia solution, and the titration continued to give total calcium plus magnesium.

A complexometric method for determining calcium and magnesium in a single sample was described by Koros (16B). Calcium is first titrated with EDTA at a pH of less than 12, using murexide indicator. The sample is then acidified to destroy the murexide, the pH again adjusted with ammonium hydroxide, and the titration continued with Eriochrome Black T indicator. The advantages of using an inverse titration in the complexometric determination of calcium and magnesium were pointed out by Hahn (11B). Such titrations provide constant buffering and a sharper indicator color, and permit the use of a borax buffer. Complete directions are given for the preparation of buffer-EDTA and indicator solutions.

Complexometric titration methods for calcium and magnesium using sodium tripolyphosphate, Na<sub>5</sub>P<sub>3</sub>O<sub>10</sub>, were reported by Galkina and Zavgorodnii (10B). The procedures are similar to the usual EDTA titrations, titrating total alkaline earths in an aliquot buffered with an ammonia solution and Eriochrome Black T indicator, and titrating calcium alone in alkaline solution with murexide indicator. The indicators are prepared as dry solids, mixed with sodium chloride. The titrations may also be carried out potentiometrically using a smooth platinum electrode.

Several methods for determining strontium have been reported. Nozaki (20B) described two indirect colorimetric methods. In one method strontium is separated from other elements by precipitation as strontium chromate

and the chromium subsequently determined colorimetrically. In a second, less reliable method, strontium and other cations are first collected on Dowex 50 exchange resin. Elution with ammonium acetate solution collects strontium in a fraction which is subsequently converted into strontium chloride and the chloride measured colorimetrically. Simple and rapid flame photometric determinations of from 2 to 20 p.p.m. of strontium and from 100 to 1000 p.p.m. of calcium were reported by Uzumasa, Nasu, and Seo (37B). An oxalate precipitation separates calcium and strontium from other major cations in the sample. The precipitate is then converted to the oxide and dissolved in hydrochloric acid. The final solution for flame photometric measurement contains 10% of alcohol by volume. The error is  $\pm 5\%$  for strontium and  $\pm 2\%$  for calcium.

Lindstrom and Stephens (17B) proposed magnesium iodate tetrahydrate as a primary standard for the preparation of standard EDTA solutions. This compound is superior to the usual primary standards, calcium carbonate or zinc, having all the properties required of a primary standard, including stability, air-drying, ease of handling, and a high equivalent weight.

Routine phototurbidimetric methods for determining calcium, magnesium, chloride, and sulfate in mineral waters with an accuracy of 3 to 5% were described by Bernshtein (2B).

Using a high-resolution flame spectrophotometer, Rains, Zittel, and Ferguson (26B) determined strontium at concentrations of from 0.1 to 1  $\mu\text{g}$ . per ml. in the presence of up to a several-thousand-fold excess of calcium without prior separation of the calcium; calcium is, in fact, added as a radiation buffer. They investigated direct spectral, condensed-phase, and other types of interferences of many cations and anions, and recommended suitable methods for minimizing serious interferences. Strontium concentrations of from 0.005 to 1.0 p.p.m. were determined by a copper-spark spectrographic procedure described by Skougstad (28B). A spectroscopic buffer solution containing lanthanum as an internal standard is added to each sample aliquot taken for analysis. The line pairs Sr 4077.7/La 4077.3, Sr 4077.7/La 3949.1, and Sr 4215.5/La 3949.1 permit determination of strontium over the concentration range indicated.

A gravimetric method for determining barium in mineral waters was reported by Suchy (31B). The sample is evaporated to about 50 ml. and a saturated solution of sodium rhodizonate is added. The mixture is then heated to 50° C. and filtered, and the precipitate is washed with water and alcohol and dried at 130°. Strontium

interferes and must be removed; sodium, potassium, lithium, ammonium, magnesium, or calcium does not interfere.

Bril and Pruvot (4B) investigated the morin method for beryllium and found that in 60 volume % ethyl alcohol solution the sensitivity is increased to the extent that, under optimum conditions, a detection limit of  $5 \times 10^{-4}$   $\mu\text{g}$ . per ml. can be attained. Dispersed insoluble hydroxides of iron and manganese on exchange resin columns were used successfully by Merrill, Honda, and Arnold (18B) to collect less than 0.1  $\mu\text{g}$ . of beryllium from more than 100 liters of sea water. Elution is accomplished with 3 to 6M hydrochloric acid in the case of the iron resin, or with dilute nitric acid in the case of the manganese form resin. Final determination is made by emission spectroscopy. The general technique may be used to determine other trace elements such as thorium, rare earths, aluminum, and iron. A rapid method for the determination of traces of beryllium in mineral waters was described by Sulcek, Dolezal, and Michal (32B). Beryllium is concentrated by adsorption on a silica gel column, eluted with HCl, and determined fluorometrically with morin. Several possible interfering substances were investigated. Spectrophotometric procedures for determining beryllium from 0.05 to 0.3 p.p.m., iron from 0.5 to 3 p.p.m., and copper from 0.5 to 4 p.p.m., were described by Katsube, Uesugi, and Yoe (13B). The colorimetric reagent, Pontachrome Azure Blue B, is used, and the pH of the solution and the wavelength of measurement are adjusted for the specific ion to be determined. Interferences are removed by precipitation with 8-quinolinol and by ion exchange.

#### IRON, MANGANESE, CHROMIUM, ALUMINUM, AND RHENIUM

Levendusky and Megahan (11C) evaluated and developed analytical procedures for determining 0 to 20 p.p.b. amounts of iron, copper, chromium, nickel, and silica in power plant condensate. In general, established procedures are used with such modifications as were found necessary to provide a sensitivity of 1 p.p.b. or less. In some methods, concentration of the sample by evaporation or extraction is necessary. A detailed comparison of several colorimetric methods for determining iron in condensates was made by Herre (5C). The following reagents and methods were investigated: thioglycollic acid, potassium thiocyanate, sulfosalicylic acid, ferron(2-2'-bipyridine), and  $\alpha$ -phenanthroline. He recommended the thioglycollic acid and ferron methods as best suited for the

analysis of condensates, and gave complete details for their use.

Ferrous iron is commonly determined by omitting the reducing agent in the 1,10-phenanthroline procedure for the determination of total iron. The fact that reliable results are obtained only under very restricted conditions was pointed out by Lee and Stumm (10C), who recommended a procedure using bathophenanthroline. The procedure described gives reliable determinations of microgram quantities of ferrous iron in the presence of ferric iron. Nakashima and Sakai (13C) simplified the bathophenanthroline procedure by adding ethyl alcohol to the sample solution and eliminating the extraction step. The absorbance of the colored complex, insoluble in water but soluble in 10% alcohol solution, is then measured at 533 m $\mu$ ; Beer's law is obeyed between 5 and 100 p.p.b. of iron. Only copper, cobalt, cyanide, and citrate interfere. Collins and Diehl (1C) described the use of tripyridyl-triazine to determine iron in the parts per billion range in sea water. Ferrous iron forms an intense violet compound which may be extracted into phenyl nitrite from solutions containing sodium perchlorate. The absolute error is less than 0.1  $\mu\text{g}$ . per liter.

Takahashi and Sakurai (16C) described a procedure for the continuous coulometric titration of micro quantities of iron. The sample solution is passed through a Jones reductor and into a titration cell, where it is immediately titrated with electrogenerated bromide. The end point is determined potentiometrically. Ivanov (7C) pointed out that high concentrations of silicic acid in natural waters interfere with the exact determination of trace amounts of iron.

Ishibashi, Shigematsu, and Nishikawa (6C) concentrated manganese from sea water samples by coprecipitation with aluminum hydroxide prior to determination by the periodate method. Concentrations of 1 to 3  $\mu\text{g}$ . per liter were determined.

Goodman (4C) simplified the diphenylcarbazide method for hexavalent chromium by preparing the reagents as a single mixture of the dry powders rather than separate solutions. Kyuregyan (9C) determined chromium in water by oxidizing an acidified sample with a few drops of hydrogen peroxide and analyzing the resulting solution colorimetrically.

Giebler (3C) compared the aluminon, hematoxylin, Eriochrome Cyanine R, and Alizarin S methods for determining aluminum in natural waters. His findings indicate that the aluminon method is superior to the others. A relatively simple and reliable method, capable of detecting as little as 0.004 p.p.m. of aluminum, was described by

Knight (8C). The reagent, Solochrome Cyanine R, is added to a sample aliquot buffered with sodium acetate-acetic acid and the absorbance of the solution measured at 620 m $\mu$  after 10 minutes. Fluoride, large amounts of orthophosphate, pyrophosphate, and hexameta-phosphate interfere. Ascorbic acid eliminates interference by ferric iron. Tanaka, Nakagawa, and Handa (17C) reported that aluminum, in the concentration range of from 0 to 0.5 p.p.m., can be determined with pyrogallol red. The optimum pH range is from 4.8 to 5.2. Several ions interfere seriously. Palin (14C) pointed out the fact that the colors formed in the aluminon method for aluminum are a good match to the Lovibond color disks used for determining residual chlorine by the diethyl-*p*-phenylenediamine method.

Fluorometric techniques generally offer extreme sensitivity for determining trace amounts of aluminum. A rapid fluorometric procedure was described by Nagy and Polyik (12C). Water samples containing 5 to 50  $\mu$ g. of aluminum per liter are buffered with ammonium chloride-ammonium hydroxide solution, shaken with chloroform to extract organic substances, and shaken again with a chloroform solution of 8-quinolinol. The extract is then filtered through cotton and the fluorescence of the filtrate compared with that of standards similarly prepared. Will (18C) established optimum conditions for the fluorometric determination of aluminum in the part per billion range in high-purity boiler water condensate using morin reagent. The tolerance to a number of diverse ions was established. For aluminum concentrations of from 0.25 to 2.0 p.p.b., the standard deviation ranged from 0.09 to 0.06.

Less than microgram amounts of aluminum in reactor cooling water were determined by a neutron activation analysis procedure described by Emery and Leddicotte (2C).

Rodzaevskii and Lazarev (15C) described a method for determining very low concentrations of rhenium in mine waters. Rhenium is selectively adsorbed by activated carbon that has been treated with methylene blue solution and may thus be separated from interfering substances and determined colorimetrically as a thiocyanate complex.

#### COPPER, ZINC, CADMIUM, BISMUTH, LEAD, COBALT, AND NICKEL

Methods for polarographic scanning of trade wastes for copper, zinc, cadmium, lead, cobalt, and nickel were described by Porter, Ullmann, and Sanderson (19D) and by Ullmann *et al.* (31D). Using a quiet mercury pool cathode cell of special design they were

able to obtain voltammetric measurements of satisfactory accuracy down to concentrations of 0.1  $\mu$ g. per ml. By concentrating a 100-ml. sample to 10 ml., an original concentration of 0.01 p.p.m. may be determined. Polarographic methods were also proposed by Stanchev (25D), who described a method for determining copper, zinc, cadmium, and manganese, using hydroxylamine to eliminate copper interference, and by Shtukovskaya and Yazhenskaya (22D), who determined zinc and copper directly, and lead after preliminary concentration by coprecipitation with calcium carbonate. An application of the hanging-drop mercury electrode to the determination of trace quantities of copper, cadmium, and lead was reported by Kublik (13D). The determination of concentrations of the order of  $10^{-8}$ M is possible.

A method for determining copper and zinc in a single sample was proposed by Kolesnikova (12D). Sodium-potassium tartrate and acetate buffer are added (pH 5.5) and copper is extracted with a chloroform solution of lead diethyldithiocarbamate. The absorbance of the organic layer is measured at 440 m $\mu$ . For 2  $\mu$ g. of copper per ml. the accuracy is 0.1  $\mu$ g. Silver, mercury, bismuth, and lead are then removed from the aqueous layer by precipitation with sodium thiosulfate, and zinc is extracted with a solution of dithizone in carbon tetrachloride. The absorbance of the extract is measured at 520 m $\mu$ . Spectrophotometric methods for the determination of copper, lead, chromium, and manganese in sea water were described by Loveridge *et al.* (15D).

A cation-exchange method for concentrating traces of heavy metals, such as copper, nickel, cobalt, cadmium, and zinc, from natural alkaline waters was described by Golovaty and Khmel'nits'ka (9D). Brooks (4D) used an anion-exchange enrichment prior to the determination of trace elements in sea water. The strong chloro-complexes of certain trace elements, including bismuth, thallium, cadmium, zinc, and gold, are collected on a strongly basic anion-exchange resin, from which they may be eluted with nitric acid. Both the effluent and the resin are subsequently analyzed spectrographically, the effluent after evaporation to dryness with a sodium chloride matrix, and the resin after ashing with a similar matrix. Since the major constituents of sea water do not form strong complexes in dilute hydrochloric acid, the method provides a convenient means of separating and concentrating the trace elements noted.

Silvey (23D) and Silvey and Brennan (24D) reported spectrographic methods for determining up to 17 minor elements. By their technique, the insoluble heavy metal complexes formed

with 8-quinolinol, tannic acid, and thionalide, are separated by filtration, ashed, and subjected to direct current arcing conditions during spectrum analysis. Indium is added as a spectroscopic buffer and either indium or palladium as an internal standard. A rapid spectrographic method for determining copper, zinc, nickel, and chromium was described by Racine (20D). Using lithium as an added internal standard, these elements were determined at concentrations of from 1 to 100 p.p.m.

Five colorimetric methods for the determination of trace quantities of copper were evaluated by Tuck and Osborn (30D). The sodium diethyldithiocarbamate method lacks sensitivity and selectivity. Although the bicyclohexanone oxalyldihydrazide and oxalyldihydrazide methods are easy to carry out, they, too, lack sensitivity for the 2- to 10-p.p.b. range. The neocuproine and the 2,2'-diquinolyl methods are satisfactory, the latter method being generally preferable because of its superior color, simplicity, and reproducibility.

Abbott and Harris (2D) proposed the use of dibenzylthiocarbamic acid reagent for the determination of copper in potable water. The method requires only a single extraction of the acidified sample with a solution of zinc dibenzylthiocarbamate in chloroform, is suitable for routine use, and can be applied to the analysis of colored or turbid waters. Other metals likely to be present do not interfere; as little as 1  $\mu$ g. of copper can be detected in 50 ml. of sample. Trace amounts of copper can be determined with 1,5-diphenylcarbohydrazide, providing analysis conditions are carefully controlled, as was shown by Sato and Sakai (21D) and by Mrkva and Janackova (17D). A method for determining less than 2 p.p.m. of copper in water using oxalyldihydrazide-acetaldehyde reagent in an ammonium citrate solution was described by Capelle (5D). Tikhonov and Zhavoronkina (28D, 29D) compared a polarographic method and a colorimetric method (diethyldithiocarbamate) for determining copper in sea water. They described a procedure based on dithizone extraction and subsequent polarographic determination.

Several routine methods for determining copper in sea water solutions were investigated by Bowles and Nicks (3D). Seeking a method which can be used in the presence of magnesium, calcium, and chloride, which does not require an extraction, and which will determine from 0.02 to 1  $\mu$ g. of copper per liter with an accuracy of  $\pm 10\%$ , or better, they recommended either oxalyldihydrazide or disodium ethyl bis(5-tetrazolylazo) acetate complexing reagent. The former reagent was found to



offer greater sensitivity and to be less subject to interference from other metal ions. The latter reagent, however, can be made the basis of a relatively simple and rapid method of satisfactory accuracy. Certain modifications were proposed by Nemodruk and Stasyuchenko (18D) in methods for determining trace quantities of copper with nickel diethyldithiophosphate reagent. The modified procedure is claimed to be faster, simpler, and more accurate than previous methods. Copper and iron in the concentration range of from 0.4 to 100 p.p.b. and 2 to 200 p.p.b., respectively, in high-purity water were determined with an accuracy of  $\pm 20\%$  by a spot test method described by Kember (10D). A 50-ml. aliquot of sample is passed through a 1-cm. diameter disk of cellulose phosphate paper, a material having unusual ion-exchange properties. According to Fujimoto (7D), a simple semiquantitative determination of copper may be made by observing the color change of chelating resin beads caused by surface adsorption of copper when the resin is treated with a measured aliquot of sample.

Zakhar'ina (33D) described a complexometric method for determining zinc in drainage waters. Sodium sulfide is added to one of two identical samples. The samples are then adjusted to pH 4, ammonium buffer is added, and the samples are titrated with Trilon B, using Acid Chrome Dark Blue indicator. Zinc is determined from the difference in the titrations. A procedure for determining zinc by isotopic-dilution analysis and solvent extraction was proposed by Stary and Ruzicka (26D). A known amount of zinc-65 is added to a sample and the solution extracted with  $10^{-4}M$  dithizone in carbon tetrachloride at a pH of 7 to 9.5. The organic layer is separated and its activity measured by a scintillation counter. Zinc concentrations between 3 and 0.03  $\mu\text{g. per ml.}$  can be determined with a precision of  $\pm 1\%$ . Interfering ions are precipitated with diethanoldithiocarbamate.

A suggested dithizone method for determining cadmium was presented by Ganotes, Larson, and Navone (8D). The method is not affected by lead concentrations up to 6 mg., zinc up to 3 mg., and copper up to 1 mg. in the 25-ml. aliquot taken for analysis. The minimum detectable amount of cadmium is 0.5  $\mu\text{g.}$  The standard deviation is  $\pm 0.2 \mu\text{g.}$  at the 5- $\mu\text{g.}$  level.

Abbott and Harris (1D) proposed a dithizone method for determining lead in drinking water. Lead dithizonate is completely extracted into chloroform at pH 11.5. Precipitation of alkaline earth phosphates during the extraction is prevented or delayed by using sodium hexametaphosphate. Ferric iron up to 0.5 p.p.m. can be tolerated if a small

amount of hydroxylamine hydrochloride is added. Lead concentrations of from 0.02 to 0.50 p.p.m. can be determined with a precision of  $\pm 0.02$  p.p.m. Cosoveanu (6D) also described a colorimetric dithizone method for determining lead.

Several methods for cobalt using nitroso-R salt reagent have been published. Mikhalyuk (16D) compared the color developed in a sample with a series of standard cobalt solutions. The use of organic acids (malonic and tartaric) to prevent interference of other ions was described by Kyuregyan (14D). To determine cobalt in sea water, Thompson and Laevastu (27D) devised a somewhat more elaborate procedure. The cobalt in 6 to 10 liters of filtered sea water is collected by coprecipitation with magnesium carbonate on addition of sodium carbonate solution. The precipitate is recovered and dissolved in dilute hydrochloric acid, and the resulting solution is adjusted to a pH of 8.4 to 8.5 with sodium citrate-ammonia solution. The cobalt is then extracted with dithizone- $\text{CCl}_4$  solution, the extract evaporated, and the residue digested with concentrated sulfuric and perchloric acids. The resulting colorless solution is buffered to a pH of 8, nitroso-R salt solution added, and the absorbance measured at 415  $m\mu$ .

In connection with the development of a method for determining cobalt in sea water, Weiss and Reed (32D) made a study of the cocrystallization of cobalt with 1-nitroso-2-naphthol using cobalt-60 tracer. Under the conditions established, they showed that 99% of the cobalt was isolated from 50- and 100-liter samples. To determine cobalt, the precipitate is ashed, purified by anion exchange, and analyzed by a nitroso-R salt method. Kocheva (11D) concentrated cobalt from water samples by anion exchange and determined the cobalt spectrographically in the evaporated eluate.

#### SILVER, GOLD, AND MERCURY

Available methods for concentrating, separating, and determining trace quantities of silver were examined critically by Pierce (12E). As a result of his detailed evaluations, a method was developed for determining concentrations of from 0.2 to 20  $\mu\text{g.}$  of silver per liter. Silver is first extracted into a small volume of a concentrated solution of dithizone in carbon tetrachloride, from which it is removed selectively by re-extraction with aqueous ammonium thiocyanate. The thiocyanate is then destroyed, the silver dissolved in dilute nitric acid, and the determination made on a final dithizone-carbon tetrachloride extract, either by visual comparison with standards or by absorp-

tion measurement at 620  $m\mu$ . An accuracy of  $\pm 10\%$ , or better, is possible.

A procedure for determining silver in rain water samples was described by McNutt and Maier (10E). In this method, silver is collected by cation exchange, eluted with boiling sodium sulfite solution, and determined colorimetrically in the eluent, utilizing the permanganate color produced by catalytic, persulfate oxidation of manganese in the presence of a trace of silver ion. The method is very sensitive and special precautions must be observed to obtain reproducibility at the low concentrations of silver found in rain water.

Lai and Weiss (9E) used radiotracer techniques to study the cocrystallization of micro quantities of 27 different ions with thionalide and developed a method for the isolation of silver from sea water samples. The sample is acidified with acetic acid to a pH of 3.5 to 4.0, silver is coprecipitated from warm solution with thionalide, and the precipitate is cooled to 5° C., allowed to stand overnight, and filtered. The precipitate is then dissolved in nitric acid and the resulting solution wet-ashed and evaporated to dryness. This residue, dissolved in nitric acid, is extracted with small portions of tri-*n*-butyl thiophosphate in carbon tetrachloride, the organic solvent removed by evaporation, and the residue again wet-ashed. This final residue is then dissolved in a small volume of water to provide aliquots for the determination of silver by either the catalytic manganous-persulfate oxidation method or by the colorimetric *p*-dimethylaminobenzalrhodanine method. An average of five determinations gave a value for the silver concentration in a sea water sample as  $0.145 \pm 0.006 \mu\text{g. per liter.}$

Betteridge and West (3E) investigated several ion-association systems for selectively extracting microgram amounts of silver from aqueous solution. They developed a method based on an isobutyl methyl ketone extraction of the silver complex formed with di-*n*-butylamine and stearic or salicylic acid. In the presence of an auxiliary complexing agent, anthranilic acid diacetic acid, the system is highly selective and only mercuric ion interferes. The method may have application to the determination of trace amounts of silver in natural waters. A similar extraction procedure was discussed by Dagnall and West (4E), who proposed the use of pyrogallol red as a colorimetric reagent for the final determination of the extracted silver.

A detailed, critical review of colorimetric and spectrographic methods for gold was prepared by Beamish (2E). Although most of the methods discussed have been applied to the analysis of substances other than water, the material included in the review will

certainly be of value to anyone interested in determining this element in natural water samples. A stannous chloride precipitation method for separating gold, and final colorimetric determination by a confined spot technique, was described by Martinet and Cuper (11E).

A photometric dithizone method for determining mercury was described by Kato, Takei, and Okagami (8E). EDTA masks interference of zinc, lead, cadmium, and copper; chloride does not interfere. One to 25  $\mu\text{g}$ . of mercury is extracted with a dithizone-carbon tetrachloride reagent from a solution buffered to pH 5 with sodium acetate and acetic acid. The absorbance is measured at 490  $m\mu$ . Hamaguchi, Kuroda, and Hosohara (5E) also reported a dithizone method for determining mercury in sea water. Mercury is extracted repeatedly with dithizone in chloroform from a water solution containing hydroxylamine hydrochloride and EDTA, and then back-extracted into dilute sulfuric acid-potassium bromide solution. Finally, the mercury is extracted into a dithizone-chloroform solution at pH 6 and its absorbance measured at 510  $m\mu$ . The recovery of trace quantities of mercury was reported to be greater than 90%. Hosohara *et al.* (6E) stated that the amount of mercury found in sea water samples which had not been given an acid-oxidation treatment prior to analysis by the above method was only about one tenth as much as was found in samples which were heated with nitric-sulfuric acids or with acid-permanganate. A colorimetric method, involving coprecipitation of mercury with lead sulfide and separation by sublimation, was described by Aldin'yan (1E).

Didodecylthio-oxamide reacts with palladium in strong hydrochloric acid to form a yellow, water-insoluble complex which can be extracted into chloroform. This reaction has been used successfully by Jacobs, Wheeler, and Waggoner (7E) to determine palladium in the presence of high concentrations of diverse ions. The sensitivity is 0.005  $\mu\text{g}$ . per sq. cm.

#### VANADIUM, MOLYBDENUM, TITANIUM, ZIRCONIUM, TIN, AND URANIUM

Acid Chrome Blue K was used by Morachevskii and Tserkovnitskaya (9F) to determine 0.01 to 0.3 p.p.m. of vanadium photometrically. At pH 4.3 to 5.3 the reagent reacts with vanadium to form a stable, colored complex. Aluminum interference is removed by using tartaric acid; other ions do not interfere.

Molybdenum in natural waters was determined by Konovalov and Shokina (5F) by a method in which molybdenum is coprecipitated with  $\text{MnO}(\text{OH})_2$  and

subsequently determined in an isoamyl alcohol-carbon tetrachloride extract. Other elements which occur in natural waters do not interfere. As little as 0.5  $\mu\text{g}$ . of molybdenum per liter can be determined with an error of 0.25  $\mu\text{g}$ . per liter. Weiss and Lai (12F) described a method for determining molybdenum in sea water, in which 25 to 100  $\mu\text{g}$ . of molybdenum is first recovered by cocrystallization with  $\alpha$ -benzoin oxime at pH 2. The molybdenum- $\alpha$ -benzoin oxime crystals are dissolved in concentrated  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3\text{-HClO}_4$  and the resulting hexavalent molybdenum is purified by anion exchange. The molybdenum in the eluate then reacts with thiocyanate and is determined by measuring the absorbance of the complex.

A spectrophotometric method for determining titanium in natural water was described by Korkisch (6F). Titanium is first concentrated and separated from many other elements by passing it as a negatively charged ascorbate complex through an anion exchanger. The column is washed with 0.1N sulfuric acid containing sodium fluoride to remove other ions and titanium is eluted with sulfuric acid containing hydrogen peroxide. Ascorbic acid is added to the eluate and the resulting color measured spectrophotometrically.

A fluorometric method for determining zirconium by its reaction with quercetin was described by Hercules (3F). Zirconium is separated from interfering ions (Ti, V, Fe) by extraction into thenoyltrifluoroacetone in xylene. The fluorescence is measured at 505  $m\mu$  using an exciting wavelength of 440  $m\mu$ . Between 0.05 and 75  $\mu\text{g}$ . per 25 ml. can be measured with a reproducibility of about 4%. Kar and Sawhney (4F) reported a radiometric procedure for zirconium, estimating the phosphorus-32 removed during the precipitation of  $\text{ZrP}_2\text{O}_7$  from a  $\text{P}^{32}$ -labeled phosphate. Silver iodide is used as a carrier for the precipitate. Cerium and lanthanum interfere, in which case silver thiocyanate must be used as a carrier.

A spectrophotometric method for the determination of tin in water and certain biological materials was described by Oelschlager (10F). Tin is first separated by a basic ferric acetate precipitation, and the precipitate is dissolved in hydrochloric acid and extracted with ethyl acetate after addition of thiocyanate and ascorbic acid. The extract is evaporated to a dry residue, which is then dissolved in sulfuric acid and the tin oxidized with hydrogen peroxide. The tin is determined spectrophotometrically in this solution by the usual phenylfluorone-lauryl sulfate method.

The cocrystallization of trace quantities of various elements with 1-nitroso-

2-naphthol has been investigated by Weiss, Lai, and Gillespie (13F). Using radiotracers, they determined optimum conditions for the separation of cerium, zinc, iron, cobalt, zirconium, and uranium and developed a method for determining microgram amounts of uranium in sea water. After separation, the uranium is determined fluorometrically. The advantages of the organic cocrystallization separation over the usual inorganic carrier coprecipitation techniques are mainly speed, simplicity, and essentially complete separation of uranium from the bulk of inorganic substances in sea water and the elimination of elements which cause quenching of the uranium fluorescence. The coprecipitation of ultramicro quantities of uranium from water samples with methyl violet-thiocyanate and with sodium diethyldithiocarbamate-methyl violet-thiocyanate was investigated by Kuznetsov and Akimova (7F). Quantitative separation was attained at a pH of 3 to 3.5 with the first-named reagent, and at a pH of 7.8 to 8.6 with the latter reagent.

A comparison of three different methods for determining uranium in sea water was made by Wilson *et al.* (14F). The coefficient of variation of a fluorometric method was found to be 5% and was limited mainly by the inability to reproduce fusion conditions from sample to sample. A coefficient of variation of 1.4% was obtained using a polarographic method, whereas an isotope dilution method provided data having a coefficient of variation of only 0.52%. A detailed discussion of the polarographic method was given by Milner *et al.* (8F). Spivakovskii, Zimina, and Gavriluk (11F) described a luminescence method for determining traces of uranium in natural waters. Uranium is separated by coprecipitation with aluminum hydroxide and extracted with ether, and the extract carefully evaporated to dryness after adding sodium fluoride. The residue is then fused in a platinum wire loop and the luminescence of the bead compared with that of beads similarly prepared from solutions containing known amounts of uranium.

Hadobas (2F) described photometric and fluorometric methods for determining uranium in rocks and natural waters. Uranium is extracted from nitric acid solution with a butyl phosphate-gasoline mixture, from which it is re-extracted with ammonium carbonate solution. Morin is added to form, at pH 9, a reddish brown complex which is measured photometrically. Alternatively, the sample may be fused with a carbonate-fluoride flux and its fluorescence measured. Uranium above 5  $\mu\text{g}$ . could be determined with an accuracy of 20%. Iron, copper, cobalt, nickel, chromium, manganese, and zinc inter-

fere in the fluorometric method. Aoyama (1*F*) described a transmission type fluorometer for determining as little as 0.1 p.p.b. of uranium in natural water. Uranium is coprecipitated as uranyl phosphate by adding aluminum phosphate. The precipitate is dissolved in nitric acid containing aluminum nitrate and the resulting solution extracted with ethyl acetate. An aliquot of the extract is then placed in a dish containing a small amount of water and the organic solvent burned off. The sample is carefully dried and fused with a carbonate-fluoride flux to provide a cake whose fluorescence intensity can be measured.

#### BORON AND SELENIUM

A number of compounds may be used as colorimetric reagents for boron. Lishka (7*G*) evaluated four reagents, 1,1'-dianthrilmide, carmine, Victoria violet, and curcumin, for their suitability in determining boron in various types of surface waters. He pointed out the relative advantages and disadvantages of each and recommended a curcumin procedure as being most satisfactory from the standpoint of adequate sensitivity, simplicity, and speed of analysis. Navone (10*G*) made comparative analyses of sewage effluents using the carmine and curcumin procedures, and showed that adequate precision could be obtained with the curcumin method without prior concentration or ashing of the sample. On the other hand, reliable results by the carmine method were obtained only on samples which had been concentrated. Carmine and 1,1'-dianthrilmide procedures were investigated by Powell and Poindexter (15*G*, 16*G*). Although they found both reagents to be generally satisfactory, the latter reagent may be preferred because of its greater sensitivity. A procedure for determining small amounts of boron in water and other natural materials using carmine in sulfuric acid as the color reagent was described by Pitulescu (14*G*).

Several boron procedures using other organic colorimetric reagents have been reported. Scher (19*G*) described rapid methods using either quinalizarin or Alizarin Red S. After separation of boron by distillation, Hiirio determined from 0.00 to 0.50 p.p.m. of boron using quercetin as the complexing agent (5*G*), and 0.00 to 1.0 p.p.m. using neothorin (6*G*). Muraki *et al.* (9*G*) described a colorimetric method using methyl violet. A rapid, accurate colorimetric method for determining boron in waters underlying petroleum deposits was described by Bagbanly and Mirzoeva (2*G*).

Sensitive fluorometric methods for determining small amounts of boron have been reported by Gurkina and

Drobachenko (4*G*), using morin, and by Parker and Barnes (12*G*), using the fluorescence of the boron-benzoin complex which is formed in alcoholic sodium carbonate solution. These latter authors applied the method to the analysis of sea water samples, after removing interferences by an ion-exchange treatment.

An electrometric titration method for determining boron in natural waters was described by Barica (3*G*). Bicarbonates are destroyed by boiling with hydrochloric acid, the pH adjusted to 7.3, mannitol added, and the titration carried out with 0.01*N* NaOH solution. Samples containing large amounts of bicarbonates or silica must be given special treatment before analysis. Parker and Terry (11*G*) described a coulometric method for determining boron in heavy water. Hydroxyl ion is generated coulometrically and the titration, in the presence of mannitol, is followed potentiometrically. A spectrographic method for determining 0.4 to 8 p.p.m. of boron in saline waters was reported by Reynolds and Wilson (17*G*). Direct excitation of the sample by a high-voltage spark discharge, using the rotating disk technique and beryllium internal standard, permits rapid analysis with a standard error of about  $\pm 3\%$ .

Colorimetric methods for determining boron, bromide, iodide, and phosphate in highly mineralized waters were described by Viktorova and Kotova (21*G*). Accepted methods are used for the determinations after pretreatment of the sample with cation-exchange resin. Boron is determined with curcumin, bromide with fuchsin-chloroform extraction, iodide by nitrite oxidation, and phosphate by the molybdenum blue method.

Selenium(IV) reacts with 3,3'-diaminobenzidine to form an intensely colored piaszelenol. This reaction, or the formation of similar piaszelenols, may be made the basis of sensitive colorimetric or fluorometric methods for selenium in water. Magin *et al.* (8*G*) described a method which is suitable for determining 0 to 50  $\mu\text{g}$ . of selenium. The piaszelenol formed with 3,3'-diaminobenzidine may be extracted with benzene, toluene, or xylene, or with amyl or butyl alcohol. The addition of EDTA to the samples minimizes interferences due to multivalent ions. Rossum and Villarruz (18*G*) proposed two methods, both based on piaszelenol formation with 3,3'-diaminobenzidine but differing in the manner of sample treatment. In one method, all selenium is converted to selenium(VI) by acid permanganate, then quantitatively reduced to selenium(IV) by heating with dilute hydrochloric acid. The selenium is then determined by formation of the piaszelenol at a pH of 1.2 and extraction

with toluene, and the absorbance measured at 420  $m\mu$ . In the second method, they proposed the standard separation of selenium from possible interferences by distillation as the tetrabromide. Excess bromide carried over in the distillation is removed by precipitation as tribromophenol and selenium determined as above. Suzuki *et al.* (20*G*) described a method for determining selenium in water and other materials using 3,3'-diaminobenzidine. Aritoshi, Kiniwa, and Toei (1*G*) reported that *o*-phenylenediamine is superior to 3,3'-diaminobenzidine as a reagent for selenium. At pH 1.5 to 2.5, this reagent also forms a piaszelenol which may be extracted with toluene and its absorbance measured at 335  $m\mu$ . Of many ions tested only iron, tin, and iodide were found to interfere seriously. Iron interference may be masked with EDTA.

An extremely sensitive fluorometric method for selenium was described by Parker and Harvey (13*G*), who investigated the fluorescent properties of several piaszelenols. They recommended the use of 2,3-diaminonaphthalene, a reagent which forms a piaszelenol in strongly acid solution and which is 20 times more sensitive than the commonly used 3,3'-diaminobenzidine. The 4,5-benzopiazselenol formed with the proposed reagent is extracted with toluene and the fluorescent intensity excited by 366- $m\mu$  light is measured at 522  $m\mu$ . As little as 0.4 p.p.b. of selenium can be detected.

#### CHLORIDE, BROMIDE, AND IODIDE

Mercurimetric titration methods for chloride have been investigated by several authors. Acuna and Quitar (1*H*) compared mercurimetric and Mohr titrations and indicated a preference for the mercurimetric method. The use of a mixed indicator, diphenylcarbazone-bromocresol blue, for mercuric titration of chloride was proposed by Zinov'ev and Solov'eva (36*H*). According to Dumitru (5*H*) the mercurimetric titration may be carried out on turbid or colored samples if benzene is first added; the color change then takes place in the organic layer rather than in the turbid solution. The mercurimetric titration of chloride was followed conductometrically by Pasovskaya (24*H*).

The indirect colorimetric determination of micro amounts of chloride based on the fading of the color of the mercury-diphenylcarbazone complex was investigated by Kemula, Hulanicki, and Janowski (15*H*). They established optimum conditions for pH, temperature, and time for color development, as well as conditions for effective removal of interferences by a chloroform-diphenylcarbazone extraction. Provided experimental conditions are carefully con-



trolled, an accuracy of  $\pm 1.0 \mu\text{g}$ . may be attained; the error is somewhat greater if appreciable amounts of interfering ions, such as copper, nickel, cadmium, and lead, are present.

To estimate chloride concentrations in samples of high-purity water, Neuen-schwander (22H) treated up to 4 liters of sample with mixed-bed exchange resin, eluted the chloride with nitric acid, and estimated the chloride in the eluate by a turbidimetric method. Chloride concentrations as low as 0.003 p.p.m. can be detected. The use of an ion-exchange filter for the determination of 0.01 p.p.m. of chloride, and for 1 to 20 p.p.m. of iron and copper in steam condensate or in deionized water was described by Herre (12H). A spectrographic method for determining chloride in rain water samples was described by Zhavoronkina and Fal'kova (35H). The original samples are concentrated to one tenth their original volume, applied to a horizontal iron electrode, and excited with a low-voltage spark discharge or, alternatively, with a high-voltage spark discharge. A sensitivity of  $10^{-5}$  to  $10^{-4} \%$  is achieved with an accuracy of about 10 %. The Cl lines at 4819.5 and 4794.5 Å. are measured relative to background intensity. A quantitative spectrographic procedure for determining chlorine, bromine, iodine, and sulfur in water, using a graphite electrode with a capillary hole and 1-ml. glass receptacle for feeding water samples into an arc, was described by Kudymov, Malinina, and Varlamov (18H).

A system for estimating chloride concentrations of saline waters from conductivity measurements was devised by Stol (32H).

Iwasaki *et al.* (14H) developed a method for determining 0.1 to 50 p.p.m. of bromide by acid-permanganate oxidation of both bromide and iodide, the bromide being oxidized to free bromine and the iodide to iodate. The resulting bromine is extracted with carbon tetrachloride and determined indirectly by measuring the absorbance of the ferric thiocyanate complex formed in the aqueous layer when the extract is shaken with an alcoholic solution of ferric alum and mercuric thiocyanate. Shiota, Utsumi, and Iwasaki (29H) noted that the oxidation of iodine or iodide to iodate by acid permanganate is catalytically promoted by traces of bromide and described a procedure for determining bromide in the concentration range of from 0.005 to 0.13 p.p.m. Under controlled conditions of pH and temperature, and for a given reaction time, the amount of unreacted iodine is inversely proportional to bromide concentration. The oxidation is stopped by shaking the reaction mixture with carbon tetrachloride to remove unreacted iodine and the amount of iodine in the extract then determined as above.

The catalytic reaction has been investigated further by Fishman and Skougstad (9H), who proposed several modifications to facilitate the application of the method to the analysis of natural waters. Optimum conditions for the oxidation reaction were established and possible interferences by substances commonly found in natural waters were investigated.

Podgornyi and Bezler (25H) described a colorimetric method for determining bromide in natural waters. The method is based on the oxidation of bromide to bromine by potassium dichromate in sulfuric acid-hydrochloric acid solution and reaction of the free bromine formed with fuschin-sulfuric acid. The resulting rose-violet color is then extracted into chloroform and compared with standards. Ravikovich (27H) used a similar procedure for determining bromide in waters occurring below the petroleum layer in oil fields.

Kolomiitseva (17H) compared the methods of Belyaeva (2H) and Dragomirova (7H) for determining iodide in natural waters. Shlyakman and Yavorskaya (30H) described certain modifications which greatly simplify the Dragomirova method.

Schaefer and Hayn (28H) described a procedure for determining iodide in the presence of large amounts of chloride. Since chloride interferes in the nitrite method for iodide, the iodine formed as the first step of the reaction is extracted into carbon tetrachloride to prevent the formation of  $\text{I}^+$  in the presence of excess chloride. Iodine is then oxidized to iodate in the organic layer and subsequently determined iodometrically in the aqueous layer.

Iwasaki *et al.* (13H) found that a dilute solution of hydrogen peroxide in sulfuric acid will oxidize iodide to iodine, whereas chloride and bromide will not be oxidized. The iodine may then be extracted into carbon tetrachloride and reacted with an alcoholic solution of mercuric thiocyanate and ferric alum. Measurement of the absorbance of the resulting red ferric thiocyanate complex at 460  $\mu$  permits an estimation of the original iodide concentration.

The reaction between brilliant green and the anion complex  $\text{I}_2\text{Cl}^-$  was used by Lapin and Reis (19H) to determine iodide in potable waters. A water sample is evaporated to dryness with potassium carbonate and fused at 450° to 480° C. Sodium chloride solution, Brilliant Green, and toluene are added, and the solution is neutralized with phosphoric acid, stirred, and centrifuged. The blue complex formed in the toluene layer is then compared with standards. Novikov (23H) gave details of an iodide procedure based on the formation of the starch-iodide complex.

A precipitation - chromatographic technique for extracting iodide from

mineral water samples was described by Rastegina (26H). The sample is passed through a chromatographic column filled with mercuric nitrate-impregnated alumina. Mercuric bromide and chloride may be desorbed by washing with water. The mercuric iodide precipitate is then dissolved in dry ether and the iodide subsequently determined by a spot test.

A polarographic method for determining iodide was described by Yazhemskaya and Shtukovskaya (34H). The catalytic oxidation of arsenic(III) by cerium(IV) in the presence of a trace of iodide was followed amperometrically by Czarnecki (6H). By observing the magnitude of the limiting current at the start and during the oxidation, and by recording the time required for 50% cerium consumption, it is possible to determine 0.12 to 0.76  $\mu\text{g}$ . of iodide in the presence of a manyfold excess of chloride and bromide with an error of  $\pm 2.5\%$ . Costache and Junie (4H, 5H) proposed modifications of the catalytic method which included arresting the reaction after 20 minutes by adding silver ion and titrating the unreacted cerium(IV) with feroine (ferrous-*o*-phenanthroline complex). The sensitivity is 0.002  $\mu\text{g}$ .

The use of anion-exchange resins to collect iodide from relatively large volumes of water was discussed by Mariani and Maura (20H). A chromatographic method, using papers impregnated with silver chloride and silver chromate, was described by Ganchev and Koev (10H) for determining micro quantities of iodide, bromide, and chloride in natural waters.

Sousa (31H) proposed the use of a titration procedure in place of the lengthy drying and weighing of silver halide precipitates in the classical gravimetric method for determining mixed halides. Silver halide precipitates are collected from each of two sample aliquots and from one the chloride is removed by acid-dichromate oxidation to free chlorine. The two precipitates are then dissolved in an ammoniacal solution of potassium tetracyanonickelate, releasing an equivalent amount of nickel which is then titrated with EDTA solution, using murexide as an indicator. Titration of the first aliquot gives total chloride and iodide; titration of the second, iodide alone; chloride is determined by difference.

A rapid and accurate gas chromatographic procedure for determining chloride and bromide in aqueous solutions was developed by Bergmann and Martin (3H). The halides are first converted to the hydrogen halides in 80% sulfuric acid solution. The gases are swept out with helium into a liquid nitrogen trap, and analyzed at  $-78^\circ \text{C}$ . with a column of toluene and *n*-heptane on granular Teflon.

A critical survey of procedures for the

concurrent determination of halides by selective oxidation methods was prepared by Khramov (16H). Maura (21H) determined iodide and bromide in the presence of excess chloride after a preliminary ion-exchange separation. The addition of nitrous acid to a sample liberates iodine which is quantitatively retained on an exchange column as polyiodides; bromide is not retained. The iodide is eluted with sulfite solution and subsequently determined in the eluate.

Urone and Bonde (33H) used *o*-tolidine to determine chlorates in well waters. In strong hydrochloric acid solution *o*-tolidine reacts with chlorate to give a yellow color permitting visual comparison with standards or spectrophotometric measurements at 448 m $\mu$  for low concentrations and at 490 m $\mu$  for high concentrations. Beer's law is followed between 0.05 and 10 p.p.m.; the average deviation is 0.02 p.p.m. Chloride, ferric iron, and nitrite interfere, however.

Greenhalgh and Riley (11H) used Ph<sub>4</sub>AsCl to precipitate perchlorate from sea water. At low concentrations of perchlorate, Ph<sub>4</sub>AsClO<sub>4</sub> coprecipitates with Ph<sub>4</sub>AsReO<sub>4</sub> upon the addition of potassium perchlorate. The perchlorate is then determined in the mixed precipitate by infrared spectrophotometry. A sensitivity of 0.03  $\mu$ g. of chlorate per liter was obtained. Other ions found in sea water did not interfere.

#### FLUORIDE

The Scott-Sanchis method for fluoride was investigated by Lim (10J), who proposed certain modifications which result in more intense colors being developed in a shorter time. With the improved method it is possible to detect differences of 0.05 p.p.m. of fluoride over the concentration range of from 0.0 to 1.5 p.p.m. Jankovic (9J) found that a concentration ratio of Alizarin Red S to thorium nitrate of 3.5 to 5 provides increased sensitivity for fluoride for the concentration range of from 0.3 to 2.4 p.p.m. when the alizarin-thorium method is used. Maia (13J), in a comparison of several fluoride methods, indicated a preference for the zirconium-alizarin method. The thorium-alizarin, zirconium-alizarin, and aluminon procedures for fluoride were compared by Costache (4J).

Investigations of the steam distillation of fluoride have been made by Schmidt (15J) and D'Amore and Bellomo (5J). Ryabichkina (14J) described a double distillation procedure for determining fluoride in acid waters (pH less than 1.0). Fluoride is determined colorimetrically in the final distillate using alizarin reagent. An automatic distillation apparatus was described by Belack (2J). Heating of the distilling

flask is started when the sample is introduced and continued without further attention until the distillate temperature reaches 180° C., at which temperature the entire sample has been distilled.

Almeida and Pulido (1J) described a procedure for removing aluminum interference in the zirconium-alizarin method. Aluminum is extracted from alkaline solution with a chloroform solution of 8-quinolinol, after which the pH of the sample is adjusted to 5 to 7 and the fluoride determined in the usual manner. The necessity of separating fluoride by distillation was emphasized by Seelkopf and Romero (16J). A procedure using the lanthanum-alizarin complex was described by Greenhalgh and Riley (7J). The absorbance of the complex is measured at 622 m $\mu$ ; Beer's law is obeyed up to 1.7 p.p.m. of fluoride. Aluminum is removed by extraction of its oxinate in a continuous extractor. A relatively simple direct colorimetric method for determining trace amounts of fluoride was described by Yamamura, Wade, and Sikes (19J). The method is based on the formation of a stable cerium(III)-alizarin complexone-fluoride chelate which is soluble in acetonitrile or in acetone-water media. Of the common anions, only phosphate interferes.

A spectrophotometric method based on the reaction of fluoride with thorium chloranilate in aqueous methyl Cellosolve buffered at pH 4.5 was developed by Hensley and Barney (8J). The sensitivity may be varied by measuring the absorbance at 330 or 540 m $\mu$  and by varying the proportion of methyl Cellosolve in the solvent. A number of cations interfere but are removed by ion exchange. Most common anions do not interfere; phosphates, however, interfere seriously and require separation by distillation. Methods based on the bleaching effect of fluoride on the zirconium-Eriochrome Cyanine complex were described by Bengner (3J) and Valach (18J). The use of zirconium-Xylenol Orange as a reagent for the determination of fluoride in mineral waters was also described by Valach (17J).

Fresen, van Gogh, and van Pinxteren (6J) determined fluoride spectrophotometrically by usual methods after prior separation of fluoride by anion exchange. Both sulfate and fluoride are retained when a sample is passed through a column of the exchange resin. Elution with an ammonium chloride-ammonia solution buffered to pH 9.2 removes only the fluoride, leaving sulfate and other interfering anions absorbed on the column. Lubyanskaya (11J) and Lubyanskaya and Talipov (12J) determined fluoride in water by direct titration of the sample with zirconium nitrate after adding hydrochloric acid and alizarin-sulfonic acid. The end point occurs when the color of the solution changes

from yellow to violet. A correction must be made for the sulfate present. The sensitivity is not so good as that of most spectrophotometric methods but the procedure is simple and does not require complex apparatus.

#### SULFATE, SULFITE, AND SULFIDE

An indirect complexometric method for determining sulfate in mineral and mine waters was described by Sokolova (25K). Barium sulfate is precipitated by the addition of a known amount of barium chloride. An equivalent amount of magnesium chloride is then added and the solution titrated with Trilon solution, using Chromogen Black as indicator. Sesquioxides, manganese oxide, and copper interfere. A similar method involving precipitation of lead sulfate and titration of the excess lead with Trilon B with Eriochrome Black T indicator was proposed by Nechiporenko and Kriventsov (16K). Calcium does not interfere, but the presence of large amounts of chloride in the sample causes high values due to the formation of PbSO<sub>4</sub>.PbCl<sub>2</sub>. A direct titration of the lead in a separated precipitate of lead sulfate was proposed by Odler and Gebauer (17K), who dissolved the precipitate in sodium acetate solution and titrated with Complexone III using Xylenol Orange indicator. These authors also described an indirect titration procedure. A rapid, accurate method for determining sulfates in water and other natural materials was described by Badrinan (1K). The procedure involves precipitating lead sulfate, refluxing the solution containing the precipitate, adding alcoholic dithizone solution, and titrating with EDTA. After a similar precipitation and separation of lead sulfate, Vail, Kremer, and Mirnaya (26K) titrated the excess lead ions with either sodium sulfide or thioacetamide and determined the end point potentiometrically with a silver sulfide electrode. Ohlweiler (18K) determined the excess lead ions polarographically and Lipovskii (12K) described an amperometric titration technique using a dropping mercury electrode for following the precipitation of lead sulfate directly.

Scholz (24K) discussed several complexometric methods for determining sulfates in water. Rapid complexometric titration methods for determining sulfate, calcium, and magnesium in brackish waters were described by Price and Priddy (21K). The titrations with EDTA involve (1) calcium, magnesium, and excess barium (after precipitation of barium sulfate) in one aliquot, (2) calcium and magnesium in a second aliquot, and (3) titration of magnesium alone in a third aliquot.

The use of sodium rhodizonate as an indicator in the titration of excess

barium in an indirect sulfate method was discussed by Minami and Watanuki (14K). A similar procedure was described by Kerr (9K), who recommended evaporation of the acidified sample to a small volume and back-titration of the excess barium with 0.02N potassium sulfate solution.

A cation-exchange method for sulfate determination was developed by Pavlik and Mach (20K). After treatment with an exchange resin in the hydrogen form, noncarbonate hardness is determined in one portion of the eluate and barium sulfate is precipitated in another. The filtrate from the second portion, containing excess barium, is again treated with the exchange resin and the noncarbonate hardness determination repeated. The difference represents the sulfate concentration of the sample. A similar technique was developed by Ceausescu (3K) to provide rapid field methods for determining sulfates, chlorides, and nitrates in a single sample. In this procedure, however, the total acids are titrated with barium hydroxide solution, the soluble barium then titrated with potassium stearate solution to give the amount of chloride plus nitrate, and the chloride finally determined by a third titration with silver nitrate. The titration of barium ions with potassium stearate solution, using either phenolphthalein or Eriochrome Black T indicator, was discussed in detail in two other papers by the same author (2K, 4K).

Karas, Eliasek, and Palaty (8K) described a rapid titrimetric method using barium perchlorate as the titrant and thorin indicator; interferences are removed by a preliminary ion-exchange treatment. Ceausescu (5K) found that the addition of sodium fluoride, triethanolamine, hydroxylamine, and acetic acid minimizes the interference of most cations when titrating sulfate with barium using sodium alizarin sulfonate indicator.

The sulfate content of boiler waters was determined volumetrically by Gunther (6K). The sample is treated with barium oxalate and the excess oxalate, after filtering, titrated with permanganate. The method can be used only if the sample contains at least 250 mg. of sulfate per liter; samples containing less must be evaporated prior to analysis. Barium chloranilate reagent was used by Prochazkova (22K) for determining sulfate colorimetrically. Interfering cations are first removed by ion exchange, and the eluate is mixed with acetone and an acetone suspension of barium chloranilate. The color formed is measured at 530 m $\mu$ . Sulfate as low as 1 p.p.m. can be determined. Kunitskii and Lalabekova (10K) pointed out that, in the routine determination of sulfate by the benzidine method, a considerable saving of the reagent can be affected by

re-using the first portions of filtrate for subsequent determinations, merely replenishing it with small amounts of fresh reagent solution as necessary.

Ohlweiler and Meditsch (19K) proposed an absorptiometric method for sulfate based on the color formed when sulfuric acid and saccharose are heated. Chloride is first precipitated with silver acetate and the filtrate passed through Amberlite IR-120 cation exchanger. The acidified filtrate is then evaporated to dryness with saccharose and heated at 85° C. for 60 minutes. The residue is dissolved in 10 ml. of water and the brownish yellow color measured at 420 m $\mu$ . Beer's law is followed from 0 to 40 p.p.m. of sulfate.

A number of variables involved in the turbidimetric method for the determination of sulfate were critically examined by Rossum and Villarruz (23K), who developed an improved procedure which gives results having a precision comparable with that of gravimetric methods. Although the accuracy is not generally as good as the precision, its simplicity and convenience often recommend it in preference to other methods.

Methods used to determine several sulfur compounds in well waters, including sulfate, sulfide, thiosulfide, carbon oxy-sulfide, and sulfur, were described by Lorenz (13K).

The determination of traces of sulfide by an induced sodium azide-iodine reaction was described by Kurzawa (11K), and methods for determining free hydrogen sulfide were presented by Minami and Watanuki (15K) and Hou (7K).

#### SILICA, PHOSPHORUS, AND ARSENIC

Molybdenum blue methods for silica and phosphorus have been investigated by several analysts. Nemeryuk and Sineglazovai (6L) pointed out that the phosphorus - molybdenum complex formed at optimum acidity readily decomposes in the presence of 1.6 to 2N sulfuric acid, whereas the silicon-molybdenum complex does not. This permits a determination of silica in the presence of phosphate without interference. Molybdenum blue procedures for determining silica in water and in sea water were given by Ostrowski and Czerwinska (7L) and by Bahr *et al.* (1L). In the procedures described, phosphates are removed with the aid of sodium or ammonium oxalate. The use of mannitol to minimize phosphate interference was proposed by Visintin and Monteriolo (13L). Peskovoi (8L) described a completely automatic analyzer for determining from 0 to 10 p.p.m. of silicic acid in steam and potable waters. Three concentration ranges—0 to 0.1, 0 to 1.0, and 0 to 10 mg. of silicate per liter—may be provided.

Murphy and Riley (5L) described a single-solution reagent for use in the

molybdenum blue method for the determination of soluble phosphate. The reagent, an acidified solution of ammonium molybdate containing ascorbic acid and a small amount of antimony, reacts rapidly with phosphate to form a stable blue-purple compound whose absorbance is measured at 882 m $\mu$ . Most common substances, except arsenic, do not interfere with the determination. Sugawara and Kanamori (12L) recommended extracting phosphomolybdate into a 1-butanol-chloroform mixture, decomposing the complex, and determining the molybdenum thus released as the thiocyanate complex. The method is very sensitive and permits the determination of microgram amounts of phosphate ion. Sletten and Bach (10L) recommended the use of reagent-grade glycerol as the solvent for preparing stannous chloride, thus extending the shelf life of this reagent almost indefinitely.

Kabanova (3L) found that the organic phosphorus in sea water samples is completely mineralized when a small aliquot of sample is simply acidified with sulfuric acid and autoclaved for 8 hours at 1.75 to 2.0 atm. Arsenic may be eliminated during the autoclaving by adding a small amount of zinc. An apparatus for the automatic radiometric determination of phosphate ion in boiler water in the range of from 5 to 50 p.p.m. was described by Scott and Driscoll (9L). The excess of calcium-45 remaining after precipitation of calcium phosphate is counted in the supernatant liquid while the centrifuge is spinning. The authors point out the possibility of applying the same principle to the determination of chloride with silver-110.

Stratton and Whitehead (11L) described a colorimetric procedure for determining arsenic in water using silver diethyldithiocarbamate. Arsenic compounds are reduced to arsine with zinc in an acid medium and the gases passed first through a scrubber containing borosilicate glass wool impregnated with lead acetate and then into an absorbing tube containing silver diethyldithiocarbamate reagent dissolved in pyridine. A stable, colored substance is formed which shows maximum absorbance at 535 m $\mu$ . As little as 0.01 mg. of arsenic per liter can be determined. Most ions occurring in water do not interfere.

A colorimetric procedure for determining arsenic in mineral waters was proposed by Dzhokhadze (2L). Arsenic is collected by coprecipitation with ferric hydroxide; the precipitate is then dissolved in a small volume of hot hydrochloric acid and transferred to colorimeter tubes, and 1 to 2 ml. of copper sulfate in 1% hydrochloric acid and 5 ml. of 10% NaH<sub>2</sub>PO<sub>4</sub> in hydrochloric acid are added. The tubes are heated in a boiling water bath for 30 minutes

and the colors compared with standards prepared similarly. Ko (4*L*) reported an ion-exchange-spectrographic procedure for determining as little as 0.001 p.p.m. of arsenic and phosphorus in river water with a precision of  $\pm 0.001$  p.p.m. The arsenates and phosphates from a relatively large volume of sample are concentrated by anion exchange and eluted with nitric acid. Arsenic and phosphorus in the eluate are then determined by d.c. arc excitation with vanadium as the internal standard.

#### NITRATE, NITRITE, AND NITROGEN COMPOUNDS

A number of investigators have described procedures for determining nitrate ion based on the reduction of nitrate to nitrite and then taking advantage of the very sensitive diazotization-coupling reaction of the nitrite so formed. Different reducing conditions have been proposed and several different diazotizable amines and coupling compounds have been suggested. Lambert and Zitomer (29*M*) reduced nitrate with zinc in ammoniacal solution. Quantitative reduction, however, is critically dependent on temperature, time, and rate of stirring. The excess zinc is removed by filtration, the filtrate reacted with (4-aminophenyl)trimethylamine and *N,N*-dimethyl-1-naphthylamine, and the absorbance measured at 522  $m\mu$ . Provision is made for removal of nitrite or chlorine if either is present in the sample. A similar procedure was described by Hagino (20*M*), who used a modified Griess-Romijn reagent consisting of tartaric and sulfanilic acids and 1-naphthylamine. The diazotization is carried out in dilute acid (HCl) solution and the absorbance measured at 530  $m\mu$ .

The reduction with zinc was carried out in dilute acetic acid by Ritas (37*M*), who diazotized with 1-naphthylamine and sulfanilic acid and measured the absorbance at 435  $m\mu$ . After reduction with zinc, Bark (2*M*) determined 0 to 10 p.p.m. of nitrate by diazotization with *N*-(2-aminophenyl)morpholine and measurement of the absorbance at 435  $m\mu$ . Boiling the sample with ammonium chloride removes nitrite prior to the determination of nitrate. Price and Priddy (36*M*) prepared the reductant of powdered zinc, citric acid, and manganous sulfate as a dry mixture; diazotization and coupling were accomplished with sulfanilic acid and 1-naphthylamine. A rapid field method involving reduction with zinc and diazotization with *p*-nitrobenzene sulfonic acid and 1-naphthylamine was proposed by Hou (25*M*). Reduction of nitrate with metallic cadmium was used by Potzl and Reiter (35*M*) to determine nitrate in rain water samples by the diazotization-coupling method.

Nitrate concentrations between 0.05 and 3  $\mu\text{g.}$  per ml. were determined with an error of  $\pm 5\%$ .

Hora and Webber (24*M*) showed that, in the phenoldisulfonic acid method for nitrate, serious losses of nitrate occur in the presence of ammonium ions and that such losses are prevented by a preliminary evaporation of the sample with potassium hydroxide. Two phenoldisulfonic methods were investigated critically by Morette and Halot (34*M*).

The direct spectrophotometric determination of nitrate based on the formation of 4-nitro-2,6-xenol was investigated by Montgomery and Dymock (33*M*) and several modifications were proposed. This method was also investigated by Fadda and Alamanni (15*M*), who found the method superior to the brucine or phenoldisulfonic acid colorimetric methods. A method in which nitrate reduced by amalgamated zinc in hydrochloric acid and in the presence of strychnine gives a color proportional to nitrate concentration between 0.5 and 3.5 p.p.m. of  $\text{NHO}_3$  was discussed by Villeret and Lagadec (42*M*). Burakowski (6*M*) made a study and comparison of the phenoldisulfonic acid, the brucine, and the Nessler methods for their application to the determination of nitrate in precipitation waters. He recommended the brucine method as the simplest and least subject to interferences. Harrison (22*M*) found chromous chloride to be a very effective, reliable agent for reduction of nitrate to ammonia, giving blank tests of the order of only 0.04 p.p.m. of nitrogen. An improved titrimetric method, based on the addition of indigo carmine in excess and titration of the unoxidized reagent with potassium permanganate, was discussed by Ceausescu (7*M*) and by Ceausescu and Pirvu (9*M*). A titrimetric method based on a methylene blue titration of the nitrophenolate formed when the sample is evaporated with phenoldisulfonic acid was proposed by Ceausescu (8*M*).

A simple, rapid method for determining nitrate in drinking water was given by Hammond (21*M*). Two milliliters of sample are treated with 4 ml. of 0.025% 3,3'-dimethylnaphthidine, the mixture is diluted to 50 ml. with 1 to 1 sulfuric acid, and absorption is measured on a spectrophotometer or the color intensity compared visually with standards. Absorption follows Beer's law in the range of from 1 to 7 p.p.m. of nitrate. Chlorine, iron, and manganese interfere, as do amounts of nitrite in excess of 1 p.p.m. West and Lyles (43*M*) determined 0.2- to 5-p.p.m. nitrate concentrations by a spectrophotometric method based on the reaction between nitrate ion and chromotropic acid in acid solution. Absorption is

measured at 357  $m\mu$  and follows Beer's law up to 1 p.p.m. of nitrate; a separate calibration curve is necessary for the 1- to 5-p.p.m. range.

A technique for the simultaneous determination of nitrate, nitrite, and sulfate by infrared absorption spectrophotometry was described by Citron *et al.* (10*M*). The sample is first treated with anion-exchange resin in the bromide form to remove interferences from carbonate and phosphate. Potassium bromide is then added to the eluate and sample disks are prepared by freeze drying. The absorption spectra of the samples are compared with a disk of pure KBr over the range of 6 to 11 microns. Under optimum conditions the deviations observed were about 2% for each of the three ions and the results generally compared favorably with those obtained by other methods. Goldman and Jacobs (17*M*) proposed a direct ultraviolet absorption method. The sample is filtered and acidified, and its absorbance measured at 220 and 275  $m\mu$ . Nitrate absorbs at 220 but not at 275  $m\mu$  and absorbance at the longer wavelength is due to organic interference. The presence of chloride causes no interference but corrections must be calculated and applied for nitrite, chromate, and detergents.

A review of specialized methods and techniques for the determination of nitrite was prepared by Bark (3*M*). Bark and Catterall (4*M*) proposed two new reagents for the determination of micro amounts of nitrite, *N*-(2-aminophenyl)morpholine and *N*-(2-aminophenyl)piperidine. The reagents are sensitive to 0.05 p.p.m. of nitrite. Some variations in the Griess-Romijn reagent have been reported. Montgomery and Dymock (32*M*) recommended the use of sulfanilic acid and *N*-(1-naphthyl)ethylenediamine hydrochloride as a means of overcoming some of the limitations of the original method. Hagino (19*M*) found that if the final solution contains 40% by volume of ethyl alcohol, the solubility of the dye will be increased and the useful range of the method will be extended to 0.35 p.p.m. of nitrogen. Two variations of the Griess-Romijn procedure were also studied by Hagino (18*M*). In one method, extraction of the dye with a butyl alcohol-cyclohexanol mixture permitted determination of from 0.002 to 0.07 p.p.m. of nitrite. The second, direct method was suitable for the determination of from 0.05 to 1.0 p.p.m. of nitrite.

Details of a procedure for determining organic nitrogen in waters containing large amounts of mineral nitrogen were given by Dudova (14*M*). Ammonia is removed by distillation, nitrates and nitrites are reduced to nitric oxide which is removed by boiling, and the organic nitrogen is deter-

mined by a micro-Kjeldahl method. Kaplin and Datsko (27M) reported a rapid method for determining organic nitrogen by catalytic acid oxidation and formation of an indophenol dye which is extracted and estimated colorimetrically. Problems involved in the collection, preservation, and storage of samples for organic nitrogen determinations were discussed by Albertova (1M).

A procedure for the colorimetric determination of ammonia in precipitation water by the Nessler reagent was reported by Burakowski (5M). Lee, Harkness, and Jenkins (30M) determined ammonia in sewage and wastes by distillation into a saturated boric acid solution and titration with 0.007N sulfuric acid. They suggest that other forms of nitrogen can be determined similarly after either reduction or digestion. A relatively simple colorimetric method for determining ammonia in sea water was described by Gillbricht (16M). The method is based on the oxidation of ammonia by hypobromite, reaction of the excess hypobromite with Bordeaux Red solution, and comparing the absorbance of the resulting solution with that of a similar sample aliquot to which the two reagents have been added in like amounts but in reverse order. Several substances interfere with the determination.

The use of phenolate-hypobromite reaction in the determination of ammonia has been discussed by Datsko and Kaplin (11M), who investigated the several factors affecting accuracy and sensitivity of the method, and by Kaplin (26M) and Kaplin and Fesenko (28M), who recommended extraction of the indophenol dye with chloroform and re-extraction into water at pH 7, particularly for the analysis of turbid or colored samples. A method for the direct colorimetric determination of ammonia, based on the reaction with chloramine-T and pyrazolone and extraction of the resulting ammonia complex with carbon tetrachloride, was proposed by Strickland and Austin (41M).

Deshmukh and Tatwawadi (12M) described a colorimetric method for the determination of trace amounts of cyanide, based on the reaction with pyridine and chloramine-T. An indirect colorimetric method, based on the reaction of cyanide with the mercury complex of bis(2-hydroxyethyl) dithiocarbamic acid and subsequent measurement of the intensity of the yellow color resulting from the reaction of copper ions with the free reagent so formed, was developed by Hikime and Yoshida (23M). The method is useful for 0.2 to 4 p.p.m. of cyanide and is not subject to interference from many common anions and cations. A method for determining cyanides in waste

waters was described by Detlovitskaya (13M). Sulfides and thiocyanates are separated by precipitation with lead ions, the precipitate is dissolved in acid, and the HCN is separated by distillation, collected in NaOH solution, converted to  $\text{SCN}^{-1}$  with tetrathionate and ammonia, and finally determined colorimetrically with ferric ion. Russell and Wilkinson (38M) described a method for the separation and determination of cyanide in the presence of thiocyanate and ferri- or ferrocyanide complexes. The free cyanide is separated by distillation from hydrochloric acid solution containing zinc acetate and determined colorimetrically with a pyridine-benzidine reagent. Comments on the tartaric acid method for cyanide were reported by Schlichting (39M), and Lur'e and Panova (31M) commented on methods commonly used to determine both cyanide and residual chlorine in treated wastes.

A novel technique for determining small amounts of hydrocyanic acid in solution was developed by Schneider and Freund (40M). The method, based on gas-chromatographic analysis of air brought to equilibrium with a hydrocyanic acid solution, permits detection of as little as 0.025 p.p.m. of cyanide.

#### OXYGEN DEMAND

A new continuous recording electrical method for determining biochemical oxygen demand has been developed by Clark (2N, 3N). Sample digestion takes place in a closed system in which a pressure decrease occurs as oxygen is consumed and the released carbon dioxide is fixed chemically. The pressure drop is converted to an electrical current by means of a transducer; recording of this current during the reaction period permits a continuous record of the oxygen demand of the system. Although the equipment has been used to study synthetic sewage and pure substances with high B.O.D. values (1000 to 5000 mg. per liter), the author states that certain modifications will permit determinations within the range of 0 to 1000 mg. per liter of the 5-day oxygen demand.

Hennigan and Nemerow (5N) extracted water residues in a Soxhlet extractor using several different solvents, including methanol, ethyl alcohol, carbon tetrachloride, ether, chloroform, acetone, and benzene. The residues obtained, after solvent removal, were correlated with values obtained by the standard 5-day, 20° C. B.O.D. method. Satisfactory correlations were found for samples extracted with methanol or ethyl alcohol. Schuller (6N) found a correlation between the rate of oxygen utilization as determined by the Warburg apparatus and the decomposition of organic matter determined by the

permanganate titration. He also found that the B.O.D. values estimated by the Warburg method, after incubation for 24 hours at 25° C., were equivalent to 55% of the corresponding values obtained in the standard 5-day B.O.D. test.

A rapid test for pollution in waste waters was described by Thon (7N): On adding a standard catalase mixture to the sample, together with a small amount of silica gel, hydrogen peroxide solution, and a buffered solution of saponin, oxygen is released in proportion to the amount of organic contamination.

A statistical evaluation and comparison of several permanganate methods for determining chemical oxygen demand were made by Eliasek *et al.* (4N). The several methods compared were shown to be essentially equivalent. Four different methods, including permanganate, dichromate, and iodate methods, for determining chemical oxygen demand in various trade wastes were described by Zdybiewska (8N). A modification of the dichromate method for determining the oxidizability of sewage water was proposed by Bar (1N).

#### OXYGEN AND OTHER GASES

A summary and review of a number of different methods for determining dissolved oxygen in boiler water was prepared by Young (43P).

A modified Winkler method for measuring dissolved oxygen in water was proposed by Lo (23P). Oxygen is determined in one of two equal aliquots of water, and in the other the reducing chemicals are determined by reverse addition of manganese sulfate and sulfuric acid. The Winkler method was also studied by Burianek (14P), who pointed out that by maintaining accurately the interval between acidifying the sample and the final titration errors due to iron may be avoided. La Mont and Gordon (22P) suggested several improved sampling and analytical techniques for determining dissolved oxygen spectrophotometrically by the Winkler method. To avoid atmospheric contamination, hypodermic syringes are used to add the reagents to the sampling vessel. Chloroform is used to extract the liberated iodine and its color is measured. Dissolved oxygen in the part per billion range can be determined.

The use of an amperometric titrator and titration with phenylarsenoxide has been suggested by Goldman and Dietz (16P) for determining dissolved oxygen by the Winkler method. Using this technique, they found that the standard deviation of a number of samples averaged  $\pm 0.1$  in the range of 1.5 to 8.0 p.p.m. Ivanoff (18P) devised certain modifications and simplifications in the Winkler method to facilitate making dissolved oxygen meas-



urements on sea water samples aboard ship. A photometric determination of the equivalent iodine in solution was substituted for the usual titration. A brief description of a titration assembly for use with the Winkler method was given by Malone (24P). Needleman (29P) developed an apparatus for laboratory investigations of methods—for example, the Winkler method—for determining trace amounts of dissolved oxygen. The apparatus is so designed that all necessary reagents are made oxygen-free before the determinations are made and each reagent is added to the test sample through a separate entry. For standardization, a measured amount of air-saturated water is introduced by means of a syringe. The mean of the differences between the oxygen added and the oxygen measured is nil and the standard deviation of these differences is 0.0018 over the range of 0.00 to 0.50 p.p.m.

A colorimetric method using indigo carmine for determining 5 to 20  $\mu\text{g}$ . of dissolved oxygen per liter was reported by Buchoff and Ingber (13P). The yellow-green to blue color is compared visually against standards. The indigo carmine method or modifications of the method were also discussed by Santoro and Powell (35P) and by Babkin and Epeikina (5P). Rothstein and Shemyakin (34P) described a colorimetric method for measuring dissolved oxygen at concentrations of less than 0.1 mg. per liter. Leuco (colorless) methylene blue is oxidized to methylene blue in the presence of dissolved oxygen and the absorbance of the resulting solution measured at 660  $m\mu$  or compared visually with standards. Banks (6P) reported a simple, sensitive method using 3,3'-dimethylnaphthidine. At 0.007 p.p.m. the average error is  $\pm 0.0026$  p.p.m. Interference from ferrous iron is eliminated by ion exchange.

Several polarographic procedures have been reported. Barbi (7P) added an oxygen-free solution of *N* potassium chloride and hydrochloric acid to the water sample and measured the current at  $-0.20$  volt with respect to a silver-silver chloride-saturated potassium chloride electrode. Dissolved oxygen was then removed by bubbling nitrogen through the sample and the current was again measured; the difference between the two values is proportional to the oxygen present. A direct polarographic procedure which requires only a single reading without removing the oxygen was proposed by Kintzel and Brodziak (20P). Klima (21P) described a simple apparatus consisting of a sensitive galvanometer, a Kohlrausch drum, and a dropping mercury electrode. Morgan and Bewtra (23P) measured dissolved oxygen concentrations continuously using a dropping mercury electrode and photographic

recording of the galvanometer readings. The water sample is fed continuously into the cell. Schwabe and Vollrath (36P, 37P) discussed the advantages of using a rigid electrode in the polarographic method for determining dissolved oxygen and described equipment for the continuous measurement of oxygen dissolved in boiler feed water.

Stracke (38P) described an electrochemical method for measuring dissolved oxygen which he found to be more satisfactory for analysis of sludge-laden waters than polarographic, colorimetric, or paramagnetic methods. The system consists of a small, circular, gold or platinum cathode, and a large zinc anode dipping into the stream. The electrodes are kept clean by constant rotation against a polisher. A recording microammeter permits continuous measurement of the current which is proportional to the dissolved oxygen. Errors due to variations in the conductance of the sample and to temperature fluctuations are compensated by design of the equipment. The application of a plastic-covered, stationary platinum electrode system for measuring dissolved oxygen and B.O.D. was described by Eye, Reuter, and Keshavan (15P). The electrode provides data which compare with those obtained by the Winkler method.

An electrometric method, based on the reaction between oxygen and chromous ions, has been proposed by James and Stephen (19P). The chromous reagent is electrochemically generated in the sample; an excess of chromous ion is detected amperometrically with a platinum indicator electrode and a saturated calomel electrode. The method is sensitive and accurate to less than 2% at oxygen concentrations of the order of 3 parts per 100,000,000 parts of water. No standard solutions and only one deoxygenated solution are required.

Recent developments in the application of the wide-bore dropping mercury electrode for determining dissolved oxygen were discussed by Briggs and Knowles (11P). They described several types of cells and electrodes and the preparation of capillaries, reference electrodes, and reagents, and discussed briefly the effects of chemical interferences. Briggs and Mason (12P) described construction details of a rugged, portable instrument for routine determinations of dissolved oxygen. The equipment incorporates a wide-bore dropping mercury electrode maintained at 1.5 volts negative to a Ag/AgCl electrode and is temperature-compensated by transistors. Dissolved oxygen concentrations are read directly on a microammeter which provides two concentration ranges: 0 to 5 p.p.m. and 0 to 50 p.p.m.

A gold-mercury indicating electrode

system was devised by Albrecht (2P) for the continuous measurement of dissolved oxygen in boiler water. A portable, transistorized instrument, incorporating gold and zinc electrodes and providing direct readings of dissolved oxygen, temperature, and conductivity, was described by Ambuhl (3P).

Barbi and Sandroni (8P) developed an internal coulometric method for dissolved oxygen, based on the reaction of the copper(I)-ammonia complex with oxygen and the measurement of the total charge supplied by platinum and copper electrodes immersed in the ammonium hydroxide solution during subsequent reduction of the copper(II)-ammonia complex. Up to 50  $\mu\text{g}$ . of oxygen can be determined in 40 minutes, or less, with an error of  $\pm 5\%$ . Trace amounts of dissolved oxygen in boiler feed water were determined by a constant current coulometric method described by Hissel and Pire (17P). Potassium hydroxide plus potassium iodide, manganese sulfate, sulfuric acid, and an excess of thiosulfate are added successively to the sample. The remaining thiosulfate, after reduction of the liberated iodine, is oxidized electrolytically, and the amount of oxygen then determined indirectly from the time required for the electrolysis. The method is accurate to within 0.02  $\mu\text{g}$ . of oxygen per liter.

The technique and equipment for a continuous measurement of dissolved oxygen by gaseous phase exchange were described by Axt (4P). A radiometric method, based on the oxidation of thallium-240, was developed by Richter and Gillespie (32P, 33P).

Underwood (41P) and Underwood and Howe (42P) described visual and spectrophotometric techniques for determining carbon dioxide, carbonate, and bicarbonate in solutions. Carbon dioxide is rapidly converted to carbamic acid in the presence of the catalyst carbonic anhydrase and is titrated with sodium hydroxide with phenolphthalein as indicator or spectrophotometrically by measuring the absorbance of the carbonate ion at 235  $m\mu$ .

A rapid method for determining total carbon dioxide by absorption of distilled carbon dioxide in standard barium hydroxide solution and titration of the excess base was developed by Maros *et al.* (25P). Milburn and Beadle (27P) extracted the acid-liberated carbon dioxide in a modified van Slyke apparatus and measured the electrical resistance of a sodium hydroxide solution before and after absorption of the carbon dioxide. The method is sensitive to 0.3 p.p.m. in the 0- to 50-p.p.m. range, and to about 1 p.p.m. in the 0- to 200-p.p.m. range.

Berbenni (10P) precipitated carbon dioxide with a standard calcium solution and titrated the excess calcium

with EDTA using murexide as indicator. Details of an accurate, rapid method for determining the total carbon dioxide content of condensate samples were given by Aksel'rud and Litvinova (1P).

A system for the continuous coulometric determination of residual free chlorine was developed by Takahashi (40P). Electrolytically generated ferrous ion reacts with the chlorine and the reaction is followed potentiometrically by controlling the electrolysis current so as to maintain a given potential of the platinum-calomel electrode system used. Oxidizing substances, if present in the water, interfere, but most heavy metals do not.

Palin (30P, 31P) described volumetric methods for determining chlorine dioxide, chlorine, chloramines, free bromine, and iodine, using diethyl-*p*-phenylenediamine as an indicator in ferrous sulfate titrations.

Swinerton, Linnenbom, and Cheek (39P) developed a gas chromatographic method for the determination of small amounts of dissolved gases in aqueous solutions. The dissolved gases are stripped from solution by an inert carrier gas and separated and identified in a commercial gas partitioner. Gases such as oxygen, nitrogen, hydrogen, carbon dioxide, and methane, at concentrations above 0.3 p.p.m., may be determined in 2 ml. of sample solution. Gas chromatographic techniques for determining hydrogen and other gases in steam condensate were also discussed by Massart and Missa (26P). Classical gas analysis techniques were applied by Bastick and Guerin (9P) to the analysis of the mixture of gases collected by the vacuum degassing of water samples.

#### DETERGENTS

Many reviews, as well as new and modified methods for measuring detergents in water and waste water, have been reported in the past two years. Fischer (4Q), Nowacki (9Q), and Pohl (10Q) prepared extensive, critical reviews of the available methods for determining detergents in water and waste water. Justice (7Q) presented a report of the research program of the Association of American Soap and Glycerine Producers concerning the effects of detergents in water and waste water. A study was made to find a rapid, simple, and accurate method for determining alkylbenzene sulfonates (ABS). None of the methods investigated satisfied the desired criteria.

Abbott (1Q) proposed several modifications in the Longwell and Maniece method for determining traces of anionic surface-active materials. If the reagents used are pre-extracted, the blank is kept very low and traces of anionic materials can be detected. Furthermore, the sensitivity of the

method is increased 15% if the impurities in methylene blue are first removed. Hill, Shapiro, and Kobayashi (5Q) used a strong chromic-sulfuric acid mixture to oxidize all organic compounds, as well as chloride and nitrate, prior to determining ABS. The chrome sulfuric acid will not measurably attack ABS if the temperature is kept below 45° C. and the time of reaction is less than 30 minutes. The method of Longwell and Maniece was investigated by Boch *et al.* (2Q) for the determination of tetrapropylenebenzene sulfonate (TBS). In a cooperative study made by six different laboratories, considerable deviation occurred for concentrations of TBS below 0.5 mg. per liter. Wickbold (13Q) and Husmann, Schoch, and Thomasch (6Q) described methylene blue procedures for determining synthetic detergents.

A simple colorimetric field method for determining anionic detergents in well waters was described by McGuire *et al.* (8Q). The method gives results comparable to those obtained by the methylene blue procedure. Four milliliters of toluidine blue-O dye solution is added to 10 ml. of sample, the complex extracted into chloroform, and the color of the extract compared with standards. As little as 0.05 mg. of ABS per liter can be measured by interpolation of the color standards, and as much as 2 mg. per liter without dilution. The preparation of a chloroform extract of the methylene blue-ABS complex was used by Cohen (3Q) as a rapid screening procedure for determining ABS in the field. ABS between 0.2 and 1.5 mg. per liter can be measured by visual comparison with standards. Copper sulfate solutions are used to prepare permanent standards which are visually equivalent to known concentrations of ABS.

Ruzicka and Vilim (11Q) described a procedure for the continuous determination of ABS in waste water. ABS is continuously extracted with chloroform on a small column, methylene blue is added to the extract, and the complex is continuously analyzed by a recording photometer.

A simple test, described as the "Crits organic ring test" (12Q), was proposed as a means of detecting pollution by detergents or surfactants.

#### ORGANIC SUBSTANCES

Concentrations of phenol above 0.001 mg. per liter in water were determined by Kaplin and Fesenko (29R, 31R) using dimethylaminoantipyrine. The phenolic content can be determined either directly or after distilling the phenol from a sample containing sulfuric acid and copper sulfate. The reaction is carried out in the presence of potas-

sium ferricyanide; because substances which react with the cyanide compound interfere, distillation is generally preferable. The color substance formed is extracted into a chloroform-isoamyl alcohol mixture and its absorbance measured at 460 m $\mu$ .

Osaki (44R) made a comparison of the *p*-nitroaniline, 4-aminoantipyrine, and nitrosation methods for determining phenols in waste waters. The advantages and disadvantages of each method are discussed. An automatic analyzer which will mix the sample, add the reagents, and measure its absorbance was described by Ferrari (18R) for determining phenol with 4-aminoantipyrine and potassium ferric cyanide, and cyanide with alkaline picrate. Dyatlovskitskaya (13R), Ershov and Borisov (16R), Ozhiganov and Martynenko (45R), and Renzanigo and Siniramed (49R) described colorimetric procedures for determining phenol in water and waste water using antipyrine compounds.

Two photometric methods for determining phenol in waste water were evaluated by McRae, Griffiths, and Lane (39R). A mixture of nitrous acid and mercurous nitrite is used in one method and 2,6-dibromoquinonechlorimide in the other. The latter method is preferred.

Avdeenko *et al.* (2R) described an ultraviolet spectrum absorption method for determining phenols. The absorbance is measured directly in quartz cells at 265, 285, and 305 m $\mu$ . A formula is given to calculate the absorbance of the phenol present and a calibration curve is used to determine the concentration.

Various means have been attempted to prevent the loss of phenol in water samples from the time of collection to the time of analysis. Pfeil (47R) suggested adding 1 gram of copper sulfate per liter of sample for preserving phenol below 20 p.p.b. He found that at least 95% of the phenol remains in the water after 4 days when the phenol concentration is 10 p.p.b. or more, and between 50 and 80% at concentrations of 5 p.p.b. Kaplin and Fesenko (30R) added 5 grams of sodium hydroxide to each liter of water sample and prevented the phenol concentration from dropping appreciably.

An automatic monitoring system was described by Garnett and Cox (23R) for detecting phenols in process water. A complete description of the apparatus is shown and the calibration procedure is described.

Yanshina (61R) used the odor of chlorophenol or its luminescence under ultraviolet light to determine phenols in contaminated underground water. The phenols are converted to chlorophenol with CaCl(OCl). Dziegielewski (14R) determined phenols in waste waters by

a bromometric procedure. An outline of the procedure is given.

A new colorimetric method was developed by Faust and Aly (17*R*) for determining 2,4-dichlorophenol in natural waters. The phenol is extracted into petroleum ether from an acidified water sample. Ammonium phosphate solution is added to buffer the solution to pH 8.0 and 4-aminoantipyrine is added to develop the color. Concentrations of 2,4-dichlorophenol up to 1000  $\mu\text{g.}$  per liter can be measured with a sensitivity of 7  $\mu\text{g.}$  per liter.

Lur'e and Antipova (36*R*) determined hydroquinone in waste waters colorimetrically. Hydroquinone forms a yellow-brown color when reacted with ammonium hydroxide and an ammoniacal solution of cadmium sulfate.

Schwenk, Hachenberg, and Forderreuther (50*R*) described the detector, auxiliary equipment, and standardization procedures for determining trace quantities of alcohol, propionaldehyde, and acetaldehyde in water by gas chromatograph, using a flame ionization detector and packed columns of Perkin-Elmer BA.

Sokolov and Lobashov (55*R*) described a rapid method for determining 1,2-dichloroethane in waste water. The sample is partially evaporated and the 1,2-dichloroethane volatilized during evaporation of the first 8% of liquid. The vapor passes into an oven which oxidizes it to hydrochloric acid, water, and carbon dioxide. The hydrochloric acid is absorbed in sodium hydroxide, the solution neutralized with nitric acid, and the chloride determined with mercurous nitrate using diphenylcarbazide as indicator. Deyland Effenberger (11*R*) proposed a potentiometric method for determining trichloroethylene in industrial waters. Trichloroethylene is refluxed with ammonium persulfate and nitric acid. The hydrochloric acid liberated is absorbed in water and titrated with silver nitrate.

A simple method for determining chlorobenzene in water was proposed by Kisarov (33*R*). He distilled 2.75 liters of sample containing between 15 and 30 mg. of chlorobenzene per liter through a fractionating column and condenser, and collected 30 ml. of distillate in a measuring tube, the lower end of which is a microburet. A calibration curve is prepared by plotting the volume of known concentrations against concentration of chlorobenzene and determining the concentration in the sample from the volume of chlorobenzene found. Meleshchenko (41*R*) determined trichlorobenzene in water by the following procedure: Trichlorobenzene is extracted into acetone, the solvent evaporated, and the residue oxidized with potassium dichromate. The chlorine thus liberated is absorbed in cadmium iodide solution

and the liberated iodine determined either volumetrically or colorimetrically with starch.

A colorimetric method was described by Golubeva (24*R*) for determining between 0.2 and 0.3 mg. of nitrobenzene in samples of waste water. Details are given for procedure and reagent preparation. Volkov, Martynenko, and Kochyrova (58*R*) determined nitrocyclohexane in waste water by reaction with hydriodic acid and titration of the liberated iodine with sodium thiosulfate.

Trace amounts of lower fatty acids ( $\text{C}_2\text{--C}_6$ ) were determined by Emery and Koerner (15*R*) by gas chromatographic techniques. The equipment used was a Vapor Fractometer equipped with a flame ionization detector. The packing used in the column and the conditions of analysis are given.

Because humic acid concentrations in water are usually very small, Bohnsack (6*R*) used a column of ferric hydroxide to concentrate the humic acid. The humic acid is eluted from the column with 0.1*N* sodium hydroxide. Several methods, after elution, are described for the quantitative determination of humic acid. Bars and Fihkman (3*R*) extracted both naphthenic acid and humic acid with chloroform from an acidified water sample (50 to 200 ml.). The extract is filtered through a glass filter, the filtrate is evaporated to dryness, the residue is taken up in 5% sodium hydroxide solution, and the naphthenic acid concentration is determined turbidimetrically. The residue on the glass filter is dissolved in 5% sodium hydroxide and the humic acid determined colorimetrically.

Vinyl alcohol esters in water were determined by Filov (19*R*) and Fiber (20*R*) by saponification of the esters, isomerization of the vinyl alcohol to acetylaldehyde, and quantitative determination of the acetylaldehyde polarographically. A 0.1*M* lithium hydroxide solution is used both to saponify the ester and to carry out the polarographic analysis.

Lur'e and Panova (37*R*) described a colorimetric and a volumetric technique for determining aliphatic amines in industrial waste waters. The colorimetric method is based on the reaction of picric acid and amines to form a yellow salt solution which is measured in a photocolormeter. The volumetric method is based on the reaction of the pink eosin salt of the amines which gives a colorless solution when titrated with a sulfonated alcohol. A colorimetric method for determining amines in water was suggested by Pearce (46*R*). Aliphatic amines react with sulfonephthaleins in acid solution to give an unstable yellow color which is stabilized by extracting into chloroform. Colori-

metric methods are described by Kuper (34*R*) for determining dimethylaniline, sulfanilic acid, and chloroaniline in water. Dimethylaniline forms a colored compound when reacted with sodium nitrite. The other two compounds are determined by diazotization and coupling.

Free and total amino acids and amines in waste waters were determined colorimetrically by Jankovic (27*R*). In a method described by Semenov, Ivleva, and Datsko (53*R*) amino acids are collected from a natural water sample on an ion-exchange resin and eluted with 2*N* ammonium hydroxide. Ninhydrin and cadmium chloride are added to the amino acids, and the color is measured. Butyl or isobutyl alcohol in the solution gives a better color. Between 1 and 1.5  $\mu\text{g.}$  of amino nitrogen can be detected.

Fuchs (21*R*, 22*R*) compared the barium hypochlorite and xanthidrol methods for determining urea in swimming pool water. Lower results are obtained using xanthidrol; however, in the hypochlorite method, decomposition products of urea are determined along with urea.

Spectrophotometric methods were reported by Lur'e and Panova (38*R*) for determining furfural and its derivatives in industrial waste water.

Semenov, Ivleva, and Datsko (52*R*) described a trilonometric titration with murexide as indicator for microgram quantities of reducing sugars in natural water.

Methods for determining the chlorophyll content of sea water were studied by Kutyurin (35*R*) and Tyler (57*R*).

Hinden *et al.* (26*R*) determined DDT and other pesticides in concentrations as low as 0.5 and 2  $\mu\text{g.}$  per liter, respectively, by a combination of paper chromatographic, enzymic, and gas chromatographic methods. Malathion was determined by Stevanovic, Mlinar, and Kangrga (56*R*) by measuring ethyl succinate, sulfur, and phosphorus resulting from degradation of the compound.

The ultraviolet fluorescence of Rhodamine B was used by Marichal and Benoit (40*R*) for its determination in natural waters. The dye is extracted into isoamyl alcohol and measured in the part per billion range.

Jeffrey and Hood (28*R*) evaluated five methods for isolating organic materials from sea water. A review of several methods for detection and measurement of organic contaminants and for their removal from water and waste water was prepared by Middleton (42*R*). Camps, Selga, and Arias (10*R*), Wilson (60*R*), and Skopintsev and Timofeeva (54*R*) described procedures for determining organic carbon in sea water. Methods for determining organic carbon in natural water were reported by Semenov and Datsko (51*R*), Beisova

and Kryukov (5R), Beattie, Bricker, and Garvin (4R), and Brodovskaya (9R). A chromic acid method was used by Boroda and Gorbenko (7R) for measuring organic matter in mineral spring waters. A foaming action was used by Alfimov (1R) for determining organic material in sea water. Gentian violet is added to make the foam more visible.

Kempf (32R) isolated organic solvents and fuels from water by absorption on a column of calcium chloride, soda lime, and magnesium perchlorate. The column is weighed before and after the sample is passed through, and the difference in weight comprises the organic material. Extraction of organic material with chloroform from a column of activated carbon was used by Middleton, Greenberg, and Lee (43R) for isolating most of the organic contaminants from water.

A rapid method for determining petroleum products with boiling points above 140° C. was reported by Poplavskaya and Vorob'eva (48R). The organics are extracted from a waste water sample with benzene after addition of sodium chloride. The extract is dried with either sodium sulfate or calcium chloride, filtered into a copper flask, and diluted to 250 ml. with benzene. An aliquot is evaporated slowly from a bulb of known weight and the flask again weighed.

Methods for determining hydrocarbons in water were studied by Golubeva (25R), Dunton (12R), and Wehe and McKetta (59R).

Techniques for determining grease and other fatty materials in water were discussed by Bouquiaux and Mertens (8R).

#### RADIOACTIVITY

A considerable number of papers have been published dealing with methods for the determination of radioactivity of natural waters and for the determination of specific radioactive isotopes, including both naturally and artificially radioactive materials. Analytical procedures, in which  $\gamma$ -ray spectrometric techniques are used to simplify or eliminate chemical separations wherever possible, were described by Perkins (35S) for determining  $P^{32}$ ,  $Sc^{46}$ ,  $Cr^{51}$ ,  $Fe^{59}$ ,  $Co^{60}$ ,  $Cu^{64}$ ,  $As^{76}$ ,  $Zr^{95-97}$ ,  $Sb^{122}$ ,  $Ce^{141}$ ,  $La^{140}$ ,  $Eu^{152}$  (13 years),  $Th^{160}$ , and  $Np^{239}$  in reactor effluent waste water. Behounek and Zelenkova (1S) reported that the accuracy of the conventional method for determining the  $\beta$ -activity of waste waters is increased by the use of double filtration. This also permits the determination of the activity of mixtures of radioisotopes with very different  $\beta$ -spectra and also permits detection of  $Sr^{90}$  and  $Y^{90}$ .

Activities of the order of  $5 \times 10^{-6}$

to  $10^{-3} \mu\text{c. per ml.}$  can be determined in waste waters by techniques described by Krause (24S). Continuous measurements are made by placing a counter inside a cylinder through which the sample flows as a thin film by centrifugal action. Alternatively, the radionuclides are precipitated and removed by centrifugal filtering and the counter is placed within the confines of the filter paper. Self-absorption is kept to a minimum by limiting the deposition of solids on the filter paper to about 1.5 mg. per sq. cm. Hasenjäger (16S) described an automatic system for evaporating a 1-liter water sample for radioactivity measurement of the residue. A review and extensive bibliography of the origin, diffusion, and methods of tracing artificial radioactive material in the sea were prepared by Kautsky (21S). A method which gives satisfactory results with waters having an activity of from 0.4 to 40  $\mu\text{c. per liter}$  was described by Charruyer and Saumande (7S). Barium nitrate and sodium sulfate solution are added to a 500-ml. aliquot of sample, and the precipitate is collected on a bacteriological filter, dried, and counted directly.

Yamada, Yamamoto, and Takumi (46S) reported a method for the continuous monitoring of  $Sr^{90}$  in low-level radioactive waste water. A sensitivity of  $3 \times 10^{-7} \mu\text{c. per ml.}$  may be achieved by applying the Cerenkov effect, by cooling the photocathode to reduce thermal background of the photomultiplier, and by employing a coincidence method.

In a series of three articles, Grune (12S, 13S, 14S) described equipment used for field surveys of natural radioactivity in ground water. The special combined scaler-scintillation detector system is hand-portable and operable from either 110-volt a.c. or from batteries. Rapid yet accurate field methods are described for determining  $Rn^{222}$ ,  $Ra^{226}$ , and  $Pb^{210}$ . Ivanov (18S) described methods for the radiological testing of water basins including the analysis of waters, bottom sediments, and water organisms. Methods for the separation and measurement of the principal radioactive elements likely to be found in water were reported by Bizollon (4S). Very low total levels of radioactive contaminants, less than  $10^{-9}$  curie per liter, were determined by Shvedov *et al.* (42S) in fresh water samples concentrated by evaporation in an automatic evaporator or by carrier precipitation. The contaminants are separated into groups by chemical methods and radioactivities measured using an anticoincidence circuit with a STS-5  $\beta$ -counter and a VS-6  $\gamma$ -counter. Ralkova and Slunecko (38S) gave a detailed description of an improved cell counter and anticoincidence circuit which provides a background of only

0.8 curie per minute and a geometry efficiency of 94%, thus permitting the measurement of activities as low as  $5 \times 10^{-11}$  curie per liter, after a 10-fold concentration of the sample.

The use of formate buffer solutions as stable, easily prepared ion-exchange elutriants was recommended by Tsubota and Kitano (45S) for the determination of fission products and for the preparation of pure, carrier-free radioactive elements from mixed fission products. After treatment of the acidified sample with Dowex 50 X8, ruthenium is eluted with 0.2N HCl; zirconium, niobium, and uranium with 0.5% oxalic acid solution; cesium with ammonium formate buffer at a pH of 3.2; the rare earths with formate buffer at a pH of 3.8; and strontium with the formate buffer at a pH of 4.2. Further separation of the pH 3.8 fraction is achieved by evaporation, redissolving the residue in HCl, placing again on Dowex 50 X8, and eluting with formate buffer at a pH of 3.6, which then separates yttrium, cerium, praseodymium, and promethium. The separation of neodymium, praseodymium, cerium, and lanthanum is complete if the formate buffer is used at a pH of 3.4, as is the separation of strontium from barium at a pH of 4.2, and cesium from iron at a pH of 3.2.

A general discussion of equipment and methods for the measurement of radioactive materials in water was given by Haberer (15S) and the determination of the radioactivities of water residues was discussed by Bezzegh-Galantai and LeRoy (3S).

An evaluation of a large diameter NaI(Tl) well crystal was reported by Perkins (34S). This crystal permitted an increase in the sensitivity of measurement of the 15 radioisotopes studied by about one order of magnitude over that which could be obtained with a crystal 3 inches in diameter and 3 inches thick. Typical spectra of several types of samples are given, including a river water sample.

Methods commonly used by state and local health department and other laboratories for determining gross radioactivity and gross  $\beta$ -activity in natural water samples were evaluated by Mullins *et al.* (32S). Statistical analysis of data obtained by the distribution and analysis of two reference samples by 41 different laboratories provided the basis for several recommendations for obtaining maximum accuracy in these measurements.

McNaughton and Woodward (29S) described an analysis scheme for determining  $Cs^{137}$ ,  $Ce^{144}$ ,  $Sr^{90}$ , and  $Ba^{140}$  in rain water samples. Rain water is collected in a polyethylene tank containing carriers. The soluble cationic materials are then collected on an ion-exchange resin column and the isotopes separated

by successive elutions with 0.7M HCl, 1.5M ammonium lactate, and 4M HCl. The cesium and cerium fractions are radiochemically purified before counting with a  $\gamma$ -spectrometer and a low-background  $\beta$ -counter, respectively. After  $\text{Sr}^{90}$  and  $\text{Ba}^{140}$  are reabsorbed on an ion-exchange column, their  $\text{Y}^{90}$  and  $\text{La}^{140}$  daughters are eluted with ammonium citrate at a pH of 8 and precipitated with yttrium oxalate for counting in a low-background counter.

Cesium-137 may be concentrated from water samples with a recovery of 96.6% by coprecipitation with potassium lead hexanitratocobaltate according to a procedure described by Ponomareva, Zolotavin, and Meshalkin (36S). By this method,  $\text{Cs}^{137}$  can be determined in 1.5 hours with a sensitivity of  $10^{-10}$  curie per liter and without interference from  $\text{Sr}^{90}$ ,  $\text{Y}^{90}$ ,  $\text{Ce}^{144}$ ,  $\text{Pr}^{144}$ , and  $\text{Ru}^{106}$ – $\text{Rh}^{106}$ . Kyrs and Neumann (26S) reported that extraction with a solution of hexanitrodiphenylamine in nitrobenzene provides a rapid means of separating  $\text{Cs}^{137}$  from potable water. General methods for determining  $\text{Cs}^{137}$  and  $\text{Sr}^{90}$  and special methods for separating and determining these two isotopes in water and other environmental materials were described by Malvicini and Vido (31S). Bryant, Osmond, and Spicer (6S) reported methods for determining  $\text{Sr}^{90}$  and  $\text{Sr}^{89}$  in water and other materials, and for  $\text{Ce}^{141}$ ,  $\text{Ce}^{144}$ ,  $\text{Ba}^{140}$ , and  $\text{Cs}^{137}$  in water. One of the disadvantages of the use of an ion-exchange resin for removing trace quantities of radioisotopes from water samples—the requirement of sufficient resin to retain all exchangeable ions present in the sample—was overcome by Broadbank, Dhabanandana, and Harding (5S) who used a preformed precipitate of ammonium 12-molybdophosphate supported on filter paper to remove  $\gamma$ -quantities of  $\text{Cs}^{137}$  selectively from an acidified sample. Only relatively large amounts of thallous ions interfere. The precipitate is dried by suction and counted directly with a Geiger counter having a thin end window.

Ion-exchange techniques for the isolation and determination of radioactive strontium have been reported by several workers. Scheidhauer and Messaiguier (40S), using Dowex 50, concentrated both strontium and cesium; 4N  $\text{HNO}_3$  was used as the eluent. After removal of radium by coprecipitation with barium sulfate and complexing of zirconium with fluoride, the cesium is coprecipitated with cesium nitrate and ammonium phosphomolybdate and estimated by beta- and gamma-counting.  $\text{Sr}^{90}$  is precipitated as  $\text{SrCO}_3$  and  $\text{Y}^{90}$  extracted with thenoyltrifluoroacetone in order to discriminate between  $\text{Sr}^{89}$  and  $\text{Sr}^{90}$ . A similar method involving selective elution of the alkaline earth

ions by ammonium lactate solution was described by Knapstein (22S, 23S), who found that the presence of organic substances and silicates generally requires selective precipitation or even evaporation of the silicates with concentrated sulfuric and hydrofluoric acids. Gandino, Malvicini, and Vido (10S) suspended an exchange resin in a water sample for several hours and then eluted the recovered resin with HCl of various concentrations to separate the adsorbed ions and to determine radioactive strontium. Sinochkin *et al.* (43S) gave details for the preparation of zirconyl oxalate, an ion-exchange material which, when freshly prepared, permits a convenient separation of strontium from yttrium, and also described a method, based on the use of this material, for the determination of  $\text{Sr}^{90}$  in sea water.

A detailed procedure for the precipitation separation and determination of  $\text{Sr}^{90}$  in rain or snow was described by Shvedov *et al.* (41S). A 50- to 100-liter sample is evaporated to provide about 25 grams of dry residue, which is then redissolved, the silica is removed by dehydration and centrifuging, and then, generally following the usual methods of separating strontium by sulfate precipitation, barium is removed as the chromate, strontium nitrate is precipitated and finally precipitated as the oxalate, along with an yttrium carrier, and ignited to the oxide. Methods for determining  $\text{Sr}^{90}$  and  $\text{Cs}^{137}$  in sea water, involving oxalate and hydroxide precipitation and separation of the alkaline earth metals, were described by Malvicini and Vido (30S). The rhodizonate method of strontium separation was used by Zolotavin and Ponomareva (49S) to determine  $5 \times 10^{-11}$  curie, or more, of  $\text{Sr}^{90}$ , with a maximum relative error of  $\pm 10\%$ . The method is relatively rapid and is not subject to interference by  $\text{Cs}^{137}$ ,  $\text{Ru}^{106}$ ,  $\text{Ce}^{144}$ , or  $\text{Zr}^{95}$ . De Sa and Selling (8S) precipitated barium and strontium carbonates from 400 liters of rain water by a series of successive precipitations, and finally separated barium from strontium by precipitating barium chloride in a concentrated HCl and ether mixture. A 28.2% yield of strontium was obtained.

A complexometric method for determining  $\text{Sr}^{90}$  and  $\text{Y}^{90}$  using 1-(2-thenoyl)-3,3,3-trifluoroacetone was reported by Francois and Jesequel (9S). A 500-ml. sample is shaken for 5 minutes with the complexing agent, after which the aqueous phase is drawn off, evaporated in a stainless steel dish, and counted directly. Osmund *et al.* (33S) described improved routine methods for determining  $\text{Sr}^{89}$ ,  $\text{Sr}^{90}$ ,  $\text{Cs}^{137}$ ,  $\text{Ba}^{140}$ ,  $\text{Ce}^{141}$ , and  $\text{Ce}^{144}$  in rain and tap water using low-background counting equipment.

Rapid radiochemical methods for determining  $\text{Na}^{24}$  and  $\text{S}^{35}$  in sea water

samples were described by Love and Sam (28S). Separation of these isotopes from other radionuclides is accomplished by scavenging with lanthanum hydroxide, in the first instance, and by precipitating barium sulfate in the second instance. Jaworowski (19S) prepared a phosphate gel mat which successfully adsorbed  $\text{Sr}^{90}$ ,  $\text{Ce}^{144}$ ,  $\text{I}^{132}$ , and  $\text{La}^{140}$  from water samples adjusted to a pH of 9. Recoveries ranging from 77 to 99.5% were reported. A simple, rapid method suitable for field determinations of radioactive iodine was reported by Zabolotskiĭ and Yurasova (47S). Iodide is oxidized to iodate and all other radioactive contaminants are then precipitated with lanthanum hydroxide. Freshly precipitated silver iodide and sodium thiosulfate are then added to the clear filtrate, containing the radioactive iodate, stirred for about 5 minutes, and the activity of the silver iodide is then determined. Jaworski (20S) described the preparation of a silver iodide-asbestos fiber filter mat which successfully recovered 98% of the radioactive iodine present in rain water. The sample is acidified with sulfuric acid, sodium chloride added, and the sample then filtered at a rate of 100 ml. per minute. After washing and drying, the residue is removed and wrapped around a cylindrical glass Geiger-Müller counter for counting. Methods of analysis of potable waters for  $\text{I}^{131}$ ,  $\text{Ru}^{103}$ , and  $\text{Zr}$  plus  $\text{Nb}^{95}$  were described by Bentley *et al.* (2S).

Compact and portable equipment and a rapid reliable field method for determining  $\text{Rn}^{222}$  and  $\text{Ra}^{226}$  were described in detail by Higgins *et al.* (17S). The analytical procedure involves the deemanation of  $\text{Rn}^{222}$  from solution and the collection of the gases in a flask coated with powdered, silver-activated zinc sulfide, followed by  $\alpha$ -scintillation counting of the flask, using a specially designed detection unit. After removal of all radon, the sample is sealed for several days to allow a buildup of radon from radium in the sample and a repeat analysis made to permit calculation of the radium content. Another field method for determining radium and radon was described by Toth (44S). Radon, flushed from the sample, is led to an ionization chamber equipped with a torsion electrometer whose discharge rate is proportional to the ionizing current and hence to the amount of radon in the system. The sensitivity limit is  $3 \times 10^{-12}$  curie per liter with a relative error of  $\pm 10\%$  in the field or  $\pm 6\%$  in the laboratory. A simple, rapid field method for radium in which the analytical operations are kept to a minimum was described by Zharov (48S). Goldin (11S) developed a method for determining radium isotopes by  $\alpha$ -counting of a purified barium sulfate precipitate. The sensitiv-



ity of the method is about  $10^{-9}$  mg. of radium.

Lazarev, Nikolaev, and Grashchenko (27S) determined thorium isotopes in sea water by coprecipitating them with ferric hydroxide. Recoveries of from 77 to 98% were reported. Kuznetsov, Akimova, and Eliseeva (25S) found that  $\text{Th}^{234}$  is practically completely precipitated with methyl violet tannate at a pH of between 4 and 9. They developed methods for the colorimetric determination of thorium in sea or fresh waters based on its concentration and separation by this technique. Sackett (39S) described a direct method for determining the  $\text{Pa}^{231}$  content of sea water. The method, a modification of one developed by Potratz and Bonner (37S), involves the addition of a known activity of  $\text{Pa}^{233}$ , ferric solution, and acid to the filtered sample. The protactinium isotopes are then coprecipitated with ferric hydroxide, subsequently separated from the iron by double precipitation of  $\text{ZrO}(\text{IO}_3)_2$  from 4M  $\text{HNO}_3$  solutions, and finally purified by extraction from 6M  $\text{HCl}$  solution into diisobutylcarbinol. The protactinium is then back-extracted into dilute  $\text{HF}$  solution which is then evaporated on a platinum plate. Comparison of the  $\text{Pa}^{233}$   $\beta$ -activity of the residue with that of an aliquot of the original tracer solution given identical treatment permits an estimation of this isotope.  $\text{Pa}^{231}$  is determined from the  $\alpha$ -activity of the sample residue.

#### ISOTOPIC ANALYSIS

The second edition of an English language translation of "Isotopic Water Analysis," a 1957 publication of the Academy of Science of the USSR, Moscow (8T), is now available. The eight chapters of Part I consider such topics as isotopic composition of water, purification of water for isotopic analysis, density measurements, and flotation and refractometric methods. Detailed descriptions of apparatus, equipment, and methods are given in the ten chapters of Part II. Certain information, including data on the effectiveness of methods of water purification and the changes of concentration of deuterium in water during fractional distillation, have not been available prior to publication of this second edition.

A critical study of the falling drop method for determining small concentrations of deuterium oxide in water was made by Hytten *et al.* (2T). For optimum reproducibility, they recommended a drop size of 28 cu. mm. (equivalent diameter of 3.5 mm.), a timing tube 15 cm. long and 1 cm. in diameter, and control of temperature within  $\pm 0.001^\circ \text{C}$ . at  $27^\circ \text{C}$ . Under these conditions they reported an expected ac-

curacy of  $\pm 0.0015$  gram % for 0.1 to 0.2 gram % of  $\text{D}_2\text{O}$ . Krell (5T) also described an apparatus for determining 1 to 4% D or  $\text{O}^{18}$  with an accuracy of  $\pm 2 \mu\text{g}$ . ( $\pm 0.18$  to  $0.04\%$ ).

The temperature-float method, based on the measurement of the temperatures at which the densities of samples of different  $\text{D}_2\text{O}$  composition are the same, was described by Weingaertner *et al.* (11T). Optical devices to improve the observation of the float position and the temperature scale in the float method of determining 150 to 200 p.p.m. of  $\text{D}_2\text{O}$  in  $\text{H}_2\text{O}$  were developed by Otero de la Gandara, Benach, and Rejas (6T).

Other techniques for determining deuterium in water have been reported. Tamiya (10T) suggested using a platinum-zinc mixture as an improved catalyst for the reduction of water to hydrogen in the mass spectrometric determination of deuterium, thus minimizing errors due to isotope fractionation resulting from incomplete reduction. To eliminate the inconvenience of high temperature reduction of water to hydrogen, Jordan and Tgetgel-Scheilling (4T) proposed a method based on the catalytic exchange of D between  $\text{H}_2\text{O}$  and H. A 2-mg. sample is cooled in liquid hydrogen, treated with 1 ml. of catalyst, and warmed again to room temperature, and hydrogen is then introduced at a pressure of 100 mm. After 15 hours, the mixture is frozen in liquid nitrogen and the hydrogen withdrawn for isotopic analysis by mass spectrometry.

Infrared methods for determining deuterium and heavy water were described by Borgest (1T) and by Johnstone and Sawyer (3T). The first reference describes a method for determining deuterium in the range of concentrations from 0.003 to 0.020%, while the second describes a technique for determining 0 to 100% of water in heavy water.

Methods of tritium assay of natural waters were discussed by Schumacher (7T). A sensitive apparatus, consisting of an electrolysis circuit and a low-background counter, was described by Soifer (9T) for determining natural tritium in water for dating purposes. Water not older than 50 years can be distinguished and the error for waters less than 10 years old is  $\pm 1$  year.

#### MISCELLANEOUS

Total mineralization and ionic strength of naturally occurring waters can be estimated fairly accurately by measuring the electrical conductivity of a sample before and after diluting with an equal volume of distilled water, according to calculation procedures described by Vorob'ev, Myakushina, and Perfilova (32U). Group coeffi-

cients relating electrical conductivity with total mineralization were calculated by Beisova (2U) for three different types of water. For chloride, carbonate, and sulfate waters, the average errors ranged from 4 to 8%. Beisova, Kryukov, and Mavkovich (3U) also determined total mineralization with an accuracy of  $\pm 0.8\%$  by first passing the sample through the acid form of a cation-exchange resin and then measuring the electrical conductivity of the filtrate. This permits a calculation of the relative amounts of sulfate and chloride, and, together with separate determinations of chloride and bicarbonate, permits calculation of total mineralization as well as sulfate concentration. A similar procedure was described by Weisgerber (33U), whereby the sample, after passage through a strong acid exchanger, was titrated with 0.02N sodium hydroxide solution to determine the total strong acid concentration. Methods for determining total mineralization and certain specific ions were also described by Podgornyi and Fotiev (24U), Podgornyi (23U), and Suranova, O, and Naide (28U). In general, these methods have in common the use of a strong acid cation exchanger to determine total cation or anion equivalents, and specific determinations to provide a relatively simple and rapid procedure. An analytical scheme for the complete analysis for saline components was proposed by Ceausescu (8U); included in the determinations are bicarbonate, sulfate, chloride, nitrate, calcium, magnesium, and the alkali metals.

Brown and Hamon (5U) described the design and operating features of a portable inductive salinometer, suitable for measuring the salinity of sea water with an accuracy of approximately 0.003 p.p.m. Box and Wilson (4U) constructed a portable conductivity bridge capable of accurate salinity measurements in the range of from 3000 to 20,000 p.p.m.

Details of the design and operation of an automatic, continuous-flow colorimetric analyzer and an automatic titrimetric analyzer were discussed by Hack (13U). The equipment is suitable for many of the usual determinations, such as turbidity, pH, phosphate, silica, fluoride, hardness, and alkalinity.

The natural color of some waters interferes with certain determinations. Menke (20U) recommended the addition of solid copper acetate to coagulate colloidal color-causing substances in highly colored samples. In some cases, this proved to be more effective than treatment with activated carbon.

Problems involved in the measurement of the pH of totally demineralized water were reviewed by Süss (27U). Hirsch (15U) reported on a new design for a stationary, recording pH assembly

which can be used in strongly polluted waters with significantly less fouling of the electrode system by oil films and other contaminants.

Weisgerber and Kosfeld (34U) discussed the equilibria equations involved in the calculation of the concentration of hydroxide and carbonate species in water using  $m$  and  $p$  values. Experimentally they found satisfactory conformance of titration and theoretical values at the phenolphthalein end point and observed increased precision at the methyl orange end point when a mixed indicator of methyl red and tartrazine is used. A rapid, gas chromatographic method for determining low concentrations of carbonate, particularly at levels of less than 10 p.p.m., has been reported by Carpenter (7U). The method offers a sensitivity which is 100 times better than the usual gravimetric and volumetric methods; as little as 0.2 p.p.m. of carbonate can be detected. A titration method for determining low alkalinity using standard solutions containing bromocresol blue indicator was described by Babkin (1U) and an automatic, continuous coulometric determination of alkalinity was described by Takahashi (29U).

The use of diethyl phthalate as a standard for the measurement of turbidity was proposed by Petrovic, Jankovic, and Milojevic (22U). According to Molt and Tio (21U), color corrections are unnecessary if turbidity measurements are measured using a light filter having peak transmittance wavelength of 7200 Å. Veinberg *et al.* (31U) described a polar spectrohydronephelometer, an instrument for measuring the optical characteristics of sea and river water.

Emission spectrographic methods possess certain advantages for the determination of trace elements. These advantages are particularly important when many samples are to be analyzed for a considerable number of elements, many of which may be present at extremely low concentrations. Kleinkopf (16U), by arcing ashed water residues, determined twelve elements semiquantitatively, including Cu, Zn, Ag, Pb, Ni, Mo, Zr, V, Cr, Mn, Sn, and Ti.

Detailed procedures for determining several heavy metals, using chloroform extraction of solutions treated with sodium diethyldithiocarbamate and 8-quinolinol, were described by Eremenko (11U) and by Klimov and Eremenko (17U, 18U). Ni, Co, Ag, Cu, V, Sn, Mo, Ti, Al, Bi, Fe, Pb, and Mn were included in these determinations. Eremenko (12U) published a handbook describing methods for the spectrographic determination of trace heavy elements in natural waters. Certain trace elements, including Ni, Co, Cu, V, Mo, Sn, Bi, Fe, Ag, and Pb, were determined in sea water by

Zhavoronkina (36U) using a spectrographic method, and Racine (25U) described a spectrographic method used to determine metals in waste effluents. Haffty and Helz (14U) applied a direct-reading spectrographic technique to determine four major constituents in water. Samples and standards, after being mixed with a reference solution, were excited directly, using a rotating graphite disk. From 1 to 316 p.p.m. of sodium, 3 to 316 p.p.m. of calcium, 0.3 to 100 p.p.m. of magnesium, and 3 to 31.6 p.p.m. of silica were determined in a single sample in just a few minutes' time.

A comprehensive review of the emission spectroscopy of solutions has been prepared by Young (35U). This excellent review includes a bibliography of 280 references and covers such topics as solution flames, solution-impregnated electrodes, solution powder, porous cup, rotating disk, solution-direct spark, dropping electrode, atomizer, plasma jet, and concentration of impurities. Although the review includes applications to the analysis of a great variety of materials which can be brought into solution, it nevertheless is of considerable value to the chemist analyzing water samples because of the excellent summary of the many solution techniques which have been investigated.

A relatively simple coprecipitation method for concentrating several trace elements was developed by Degtyarenko, Libina, and Miller (9U). After coprecipitation with cadmium sulfide, the elements were determined colorimetrically. By the methods described, the following elements were determined at the limits of concentration indicated: Cu, 0.5 µg. per liter; Zn, 0.25 µg. per liter; V, 2 to 3 µg. per liter; Mo, 0.5 µg. per liter; W, 3 µg. per liter, and Ag, 0.5 µg. per liter. By extracting with dithizone and diethyldithiocarbamate solutions at pH of 3.0, 5.0, 7.0, and 9.0, and subsequent colorimetric analysis of the extracts, Marti and Herrero (19U) were able to determine between 0.1 and 10 p.p.m. of up to 40 trace elements in samples of medicinal mineral water. The field application of ion-exchange resins to collect copper, lead, zinc, cobalt, and nickel was described by Canney and Hawkins (6U). Detailed instructions for purifying the resin, preparation of the resin cartridge, and collection and elution of the elements are included. Using a 1-gallon sample, a 38-fold concentration is achieved and detection limits of from 0.2 to 1 µg. per liter can be achieved, even with field colorimetric methods. Tsubota (30U) used a dilute hydrochloric acid solution and various formic acid-ammonium formate buffer solutions first to elute the alkali metals and then to elute and separate

Fe, Al, Mn, Mg, Ca, and Sr. Following elution and separation, standard methods were used to determine the concentration of these elements.

The effectiveness of coprecipitation of trace elements with aluminum hydroxide in the presence of sodium sulfide, and with cadmium sulfide in the presence of ferric ion was studied by Sokolov, Polyakov, and Lushnikov (26U). Using radiotracers, they determined coprecipitation efficiencies for zinc, tin, niobium, gallium, and germanium. The efficiencies were in all cases better than those obtained by adsorption on activated charcoal. Eremenko (10U), using radiotracers, observed that the adsorption of microelements on the walls of flasks is negligible, that aluminum and iron may be dissolved from certain glass containers, and that small quantities of nickel, copper, lead, manganese, and iron may be adsorbed on filter paper during filtration. Rejection of the first portion of filtrate and double-rinsing of the glass bottle with the sample effectively eliminates loss of microelements.

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