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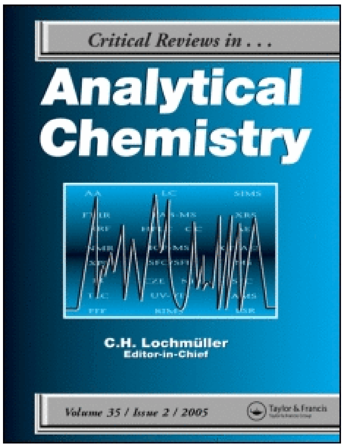

Critical Reviews in Analytical Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713400837

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To cite this Article Boltz, David F. and Lambert, Jack L.(1973) 'RECENT DEVELOPMENTS IN METHODS FOR THE DETERMINATION OF ANIONS', Critical Reviews in Analytical Chemistry, 3: 2, 147 — 199
To link to this Article: DOI: 10.1080/10408347308542660
URL: http://dx.doi.org/10.1080/10408347308542660

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RECENT DEVELOPMENTS IN METHODS FOR THE DETERMINATION OF ANIONS

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I. INTRODUCTION

In this review the main objective has been to document the significant new or modified methods for the determination of anions of nonmetals. Special attention has been given to indicating the chemical basis of each method and to providing information of interest to analytical chemists. Procedural and instrumental details have been minimized. Although it is often difficult to identify those topics which can be classified definitely as recent developments, emphasis has been given to the literature that has appeared within the past five years. However, selected earlier references relevant to particular methods have been included.

Relatively few new gravimetric and titrimetric methods have been proposed. The availability of direct-reading single-pan balances and a wide variety of electrometric and photometric end-point-detection methods have done much to improve classical gravimetric and titrimetric determinations of macro amounts of many anions. The necessity of rapidly determining trace amounts of anions has resulted in more attention being directed toward the use of physicochemical methods. Some of the most significant developments concern the fundamental chemical transformations necessary to utilize these methods of measurement: quantitative separations and the achievement of essentially 100% yields in the formation of dyes, complexes, and derivatives at the microgram level represent some of the essential aspects in the modern analytical technology for the determination of anions. In reviewing some recent advances in the determination of certain anions Belcher[56] emphasizes the importance of reaction chemistry.

Anion-selective Electrodes

The advent of ion-selective electrodes for the determination of anions has been an exceedingly important development. Many of these electrodes have selectivities, limits of detection (often 10^{-4} to 10^{-5} *M*), useful ranges (often 4 to 5 decades of ionic activity), and reproducibilities that are truly exceptional. However, there are also limitations that must be considered. For example, the effect of the ionic strength due to diverse ions may be appreciable in measuring very low activities of particular anions using liquid ion-exchange-membrane electrodes. One must consider the fact that the selectivity varies with the ratio of the activity of the desired ion to the activity of a potentially interfering ion that accompanies it.[429] The variation in liquid-junction potential with solutions of different electrolyte compositions and concentrations is another factor to be dealt with and is sometimes related to the selection of an appropriate reference electrode or salt bridge. The possible discrepancy between the total anion concentration and the activity measured must also be evaluated. In general, ion-selective electrodes may be classified as being of the liquid-membrane or solid-state heterogeneous type.

Anion-sensitive indicator electrodes for iodide, nitrate, bromide, and chloride have been prepared; the nitrate-selective liquid ion-exchange type, which gives a linear response over the range from 0.8 to 10^{-4} *M*, is the most useful.[227] A picrate-ion-selective membrane electrode consisting of a 1 *M* solution of tetra-(n-hexyl)ammonium picrate in methylene chloride has been investigated, and its selectivity ratios for several anions (nitrate, bromide, iodide, and perchlorate) have been evaluated.[40] The dependence of the selectivity factor of a liquid anion-exchange membrane electrode on the concentration of liquid exchanger has been investigated; the selectivity of the electrode increases as the concentration of organic salt decreases. The impedance also depends on the concentration of organic salt.[159]

A special type of solid-state ion-selective electrode is made by precipitating a silver sulfide or silver halide onto the surface of a carbon rod and then hydrophobizing this layer by impregnation with an organic solvent.[518] A nomograph for use in the standard addition technique in the direct potentiometric method using ion electrodes has been constructed by Karlberg.[324]

Indirect Methods

In the determination of anions it is often necessary to resort to indirect methodology in order to develop suitable procedures. The two methods most generally used in indirect analysis involve (1) the formation of stoichiometric compounds containing the desired constituent, and the subsequent determination of either an equivalent amount of another constituent or the excess reagent, or (2) the determination of the effect of the desired constituent on the formation of a compound or on a physicochemical measurement.

Sulfate has been determined by indirect atomic absorption spectrometric (AAS) methods in which the excess barium ion remaining after precipitation of barium sulfate was determined by measurement at 553.5 nm[175] or by dissolving the barium sulfate precipitate in disodium dihydrogen ethylenediaminetetraacetate and determining the barium equivalent to the sulfate.[89,492] The spectrophotometric determination of the chloranilate released upon the addition of mercury(II) chloranilate to a cyanide permits the determination of cyanide.[298] Two triphenylmethane dyes, Crystal Violet and Brilliant Green, are decolorized by the iodine liberated by the reaction of iodide in acidic solution with such anions as nitrite, chlorate, bromate, and periodate. This indirect spectrophotometric method is very sensitive.[493]

Cyanide has also been determined by an indirect spectrophotometric method based on its inhibition effect on the red silver(I)-1,10-phenanthroline-Bromopyrogallol Red ternary complex.[155] The atomic absorption inhibition titration (AAIT) technique developed by Looyenga and Huber[394] is another example of an indirect method. Silicate decreases the AAS absorbance due to magnesium. Thus, a standard solution of magnesium(II) is used to titrate a sample solution, and the titration mixture is aspirated into an AAS burner. The end point is detected by the increase in absorbance due to magnesium added in excess of that required to react with the silicate. Either the depression of the absorbance due to magnesium in the air-coal gas flame at 285.2 nm or the enhancement of the absorbance due to titanium has been used by Bond and O'Donnell[86] to determine fluoride.

Gas Chromatography

Another new approach to the determination of anions involves the formation of trimethylsilyl derivatives of anions and the gas chromatographic separation and detection of the TMS derivatives.[116] Orthophosphate, phosphite, arsenate, arsenite, carbonate, borate, oxalate, sulfate, and vanadate form TMS derivatives which have been separated by gas chromatography. Carbonate, sulfide, and sulfite have been determined by a gas chromatographic method in which the gases (CO_2, H_2S or SO_2) evolved on acidification were chromatographed on a silica gel column.[418]

Kinetic Methods

Kinetic methods for the determination of anions are being investigated and in general depend on the inhibiting or catalytic effect of the anion. Kinetic methods are often applicable to the microgram to nanogram level. The catalytic effects of phosphate on the reductions of molybdenum(VI) by ascorbic acid[510] and by tin(II)[357] have been used in a kinetic-photometric method for phosphate, the rate of reaction being linearly dependent on the phosphate concentration. A differential kinetic method for the simultaneous determination of phosphate and silicate is based on the fact that the heteropoly blue of phosphorus is formed more rapidly than that of silicate, and is performed using an automatic reaction rate apparatus.[302] A new spectrophotometric reaction-rate method for the determination of silicate involves the measurement of the initial rate of formation of α-12-molybdosilicic acid.[255] Bromide has been determined by its catalytic effect on the oxidation of iodide to iodate by permanganate.[579] Fluoride inhibits the zirconium-catalyzed reaction between iodide and perborate.[347]

Ion-association Complexes

Considerable attention has been given to the use of basic organic dyes to form colored complexes with anions.[417] Xanthene, triphenylmethane, oxazine, and thiazine dyes are the types of dyes usually employed. For example, Capri Blue, an oxazine derivative, forms an extractable complex with tetrafluoroborate.[553] In another interesting application Rhodamine B, a pyronine derivative, forms a fluorescent complex with molybdophosphoric acid which can be extracted into a 4:1 chloroform:butanol mixture. This spectrofluorometric method permits the determination of 0.05 to 5 μg of phosphorus as the orthophosphate.[335]

The formation and subsequent extraction of ion-association complexes using cationic metal chelates is a similar technique noted in anion analysis. Often the absorbance of the complex is measured directly. However, in several cases the metal-ion content of the complex has been determined by atomic absorption spectrometry. Thus, the absorbance of the perchlorato bis(2,9-dimethyl-1,10-phenanthroline)copper(1) complex can be measured spectrophotometrically, or the extract of this complex can be aspirated into an air-acetylene flame and the absorbance due to copper can be measured by atomic absorption spectrometry.[145] The reactions of onium cations (tetraphenylphosphonium, -arsonium and -stibonium etc.) with oxy anions and anionic halide and thiocyanate complexes have been discussed.[90]

Separation and Detection of Anions

A systematic procedure for classifying anions on a micro scale is based on performing the identification tests in the tip of capillary pipets.[399] Two capillary apparatuses suitable for the production of "nascent hydrogen" have been devised and have been used to detect nitrate, nitrite, sulfite, thiosulfate, and arsenate.[400] Cyanide, thiocyanate, and the hexacyanoferrates [(II) and (III)] can also be detected by capillary methods, the test reagent being PAR and mercury (II) nitrate.[398] The semiquantitative determination of chromate, chloride, bromide, iodide, bromate, chlorate, ferrocyanide, ferricyanide, thiocyanate, arsenate, and sulfite in a single drop of solution by circular thin-layer chromatography has been described.[270] An all-glass nichrome-wire-ring chamber has been used to separate and identify 20 anions (fluoride, bromide, iodide, chlorate, bromate, iodate, sulfide, sulfite, thiosulfate, sulfate, nitrite, nitrate, arsenite, ferricyanide, ferrocyanide, thiocyanate, oxalate, borate, phosphate, and chromate) within one hour.[271] Perrhenate, molybdate, and selenite anions have been separated on TLC sheets of silica gel, using methanolic solutions.[477] Silicate and phosphate have been partitioned by a TLC method using cellulose as the stationary phase and a 20:5:2 isopropanol:water:acetic acid solvent mixture.[478]

II. ANIONS OF ARSENIC

Arsenite and Arsenate

Prior Literature Reference

The most extensively used classical methods for the determination of arsenic have been presented by Abel.[1]

Titrimetric

Arsenite can be titrated with a standard solution of *N*-bromosuccinimide, using Bordeaux Red as indicator. The hypobromous acid produced from the *N*-bromosuccinimide oxidizes the arsenite. The method was found to be rapid and reliable in determining 0.6 to 6 mg of arsenic.[522] Arsenite has been titrated with permanganate by an electron spin resonance technique utilizing a circulating system in conjunction with a Varian flat fused quartz cell. Iodate is used to catalyze the reaction. A relative standard deviation of less than 1% was obtained using the ESR method of end-point detection.[5]

Opticometric

Atomic absorption spectrometry – Arsenic can be determined most satisfactorily by utilizing a nitrogen-separated flame. Separation of the flame is accomplished by a laminar flow of nitrogen which shields the hot interconal zone of the flame from atmospheric oxygen. A much lower flame background and less noise result. The limit of detection for arsenic at 193.7 nm was only one third of that obtained with a conventional air-acetylene flame. A linear calibration graph was found between 1 to 100 ppm of arsenic.[338] Kirkbright and Ransom[336] have also used nitrogen shielding with a nitrous oxide-acetylene flame and found a similar improvement in sensitivity, considering that a 5-cm slot burner was used instead of the 10-cm slot used in nitrogen shielded air-acetylene flame. One-hundred-fold excesses by weight of the following ions did not interfere: Al, Ba, Ca, Cd, Co(II), Cr(III), Fe(III), K, Mg, Mn(II), Na, Ni, Sr, V(IV), Zn, Zr, PO_4^{3-}, SO_4^{2-}, and NO_3^-.

More recent AAS determinations of microgram and sub-microgram levels of arsenic involve chemical conversion to arsine and the use of an argon-hydrogen flame.[160,193,289] A flameless AAS method utilizes arsine evolution and an electrically heated absorption tube in which arsine is thermally decomposed to yield arsenic. A linear calibration graph was obtained for up to 0.4 μg of arsenic.[136]

Madsen[407] has reacted the arsine with an 0.01 *M* solution of silver nitrate and measured the decrease in the concentration of silver ion. The following equation describes the chemical reaction involved.

$$2AsH_3 + 12\ AgNO_3 + 3H_2O \rightarrow 12Ag + 12HNO_3 + As_2O_3$$

Menis and Rains[426] investigated the use of an electrodeless discharge lamp and an argon (entrained air)-hydrogen flame for determining arsenic following a preliminary isolation of the arsenic by extraction with diethylammonium diethyldithiocarbamate and stripping process. A higher sensitivity was obtained when a nitrogen (entrained air)-hydrogen flame and a long (91-cm) absorption cell were used.[18] The effective concentration range was 0.1 to 1 μg of arsenic per ml. An argon-hydrogen-entrained air flame improves transparency and lowers the noise level and is also suitable under certain conditions for the atomization of arsenic.[320] Arsenate has also been determined indirectly by determining the molybdenum equivalent to arsenic in 12-molybdoarsenic acid which is isolated by extraction.[158,492]

Atomic emission spectrometry – Lichte and Skogerboe[380] have used an arsine generator and a microwave-induced plasma excitation to determine 5 to 50 ppb of arsenic by measuring the emission intensity at the 235-nm As line.

Spectrophotometry – The heteropoly blue method, in which molybdoarsenic acid is formed and then reduced, is a classical method suitable for determining 0.2 to 2 ppm of arsenic in the form of arsenate. The silver diethyldithiocarbamate method is gaining acceptance in many applications, especially in the absence of appreciable concentrations of metal ions.[607] Arsenate is reduced to arsine by zinc in a hydrochloric acid solution in a Gutzeit generator. The arsine is absorbed in a pyridine solution of silver diethyldithiocarbamate with the formation of a red color. This method is applicable to the determination of 1 to 10 μg of arsenic.[42,369] Arsenate in food samples has been converted to arsine and determined by the silver diethyldithiocarbamate method.[252] The extraction of arsenic(III) pyrrolidine-carbodithioate into chloroform and the measurement of its absorbance at 345 nm have also been suggested.[352] Trivalent arsenic may be extracted as the iodide with carbon tetrachloride, and then 8-mercaptoquinoline and acetone may be added to the extract to give arsenic(III) mercaptoquinolate. The absorbance is measured at 380 nm, where the molar absorptivity is 1.9×10^4 $1\text{-mol}^{-1}\text{-cm}^{-1}$.[562]

Voltammetry – Arsenic(III) has been reduced electrolytically to give a film of elemental arsenic on a platinum electrode. Then the heights of the anodic arsenic peaks are measured voltammetrically; they are found to be proportional to the concentration of arsenic(III) in solution.[597]

Radiometric

Traces of arsenate (15 μg of As(V)) have been concentrated by using ignited barium sulfate as carrier. The arsenate is eluted and determined by the heteropoly blue method. A correction factor, based on the radiometric measurement of the net recovery of arsenate in the concentration step, is applied.[323]

Hexafluoroarsenate

Hexafluoroarsenate anion forms an ion-association complex with tris(1, 10-phenanthroline)iron(II). This complex may be extracted into *n*-butyronitrile and the absorbance of the extract measured at 505 nm.[26]

III. ANIONS OF BORON

Prior Literature Reference

Much of the modern analytical methodology for the determination of borates has been summarized by Braman.[95]

Borate

Titrimetric

Borate has been precipitated as a barium borotartrate from a solution of pH 8. The precipitate is dissolved in perchloric acid and the tartrate determined either by titration with a cerium(IV) solution or by electrogenerated cerium(IV) in a coulometric titration.[414] Borate has been extracted with 3-methylbutane-1,3-diol prior to titration.[179]

Opticometric

Atomic absorption spectrometry – A highly reducing nitrous oxide-acetylene flame and the standard addition technique were employed in determining 0 to 200 μg of boron per milliliter.[257] Borate is extracted into a mixture of 2-ethyl-1,3-hexanediol and methyl isobutyl ketone, and the organic solution is aspirated into a nitrous oxide-acetylene burner. The absorbance is measured at 249.7 nm. The method is applicable to the determination of 3 to 45 ppm of boron in plants.[422]

Flame photometry – Borate in acidic solution, i.e., boric acid, reacts with 2-ethyl-1,3-hexanediol to give a complex extractable into chloroform. The organic phase was aspirated into an oxyhydrogen flame and the emission at 546 nm was measured.[4] Conversion of borate to the tetrafluoroborate permits the extraction of the tetrabutylammonium tetrafluoroborate ion-association complex into methyl isobutyl ketone, and the extract may then be aspirated into an oxyhydrogen flame.[408]

Spectrophotometry – The sensitivities, reagent concentrations, and wavelengths of measurement of 21 chromogenic reagents for the determination of borate have been compiled.[229]

The Methylene Blue-fluoborate method has been further investigated, especially in the application of the method to steel analysis, and it was found that iron catalyzes the reaction by which the BF_4^- species is formed and that the volume of the aqueous solution taken for extraction and the volume of 1,2-dichloroethane must be measured precisely.[70] Tetrafluoroborate reacts with antipyrine dyes, such as bis-(4-dimethylaminophenyl)-antipyrylcarbinol, to give a blue precipitate extractable into toluene. Conformity to Beer's law was reported in the range from 0.02 to 1 ppm of boron.[115] Tetrafluoroborate and *tris*(1,10-phenanthroline) iron (II) give an ion-association complex that is extractable into *n*-butyronitrile and that has an absorbance maximum at 520 nm.[27] Boric acid (at concentrations between 4 and 100 μg B/ml) forms a pyrocatechol complex which can be extracted as a tetraphenylphosphonium ion pair with methylene chloride at pH 4.6.[82]

The curcumin method is used extensively to determine less than 0.5 μg/ml of boron as borate.[110,390,560] The deleterious effect of an appreciable amount of water in the curcumin method for borate can be eliminated by the addition of propionic anhydride and oxalyl chloride, the latter catalyzing the water-anhydride reaction.[601] Isopropenyl acetate, with hydrochloric acid as a catalyst, has been found to give a less vigorous dehydration reaction when applying the curcumin spectrophotometric method for boron to aqueous solutions.[234] In applying the spectrophotometric curcumin method for borate to the direct determination of boron in steel, the absorbance obtained with the sample solution has been compared with the absorbance of another aliquot in which the borate was complexed with fluoride prior to the addition of the curcumin.[586] A 1:1 chelate is formed by curcumin and boric acid in aqueous media.[599]

Tetrabromochrysazin forms a colored 1:1 complex with borate in 96% sulfuric acid and has been used to determine the boron content of plants[646] and alloy steels.[325] Borate in saline water has been determined by extracting the Nile Blue A-borate complex with *o*-dichlorobenzene and measuring the absorbance of the extract at 647 nm.[448] The method is similar to that of Gagliardi and Wolf.[216] The distinctive absorption spectrum of the borate-quinalizarin complex in sulfuric-acetic acid medium is the basis of a modified, highly sensitive method for boron. The optimum concentration range is from 0.06 to 0.24 ppm of boron.[242] The optimum conditions for the formation of the blue 1:1 complex by the reaction of 1,1′-dianthrimide and borate in 95% (w/w) sulfuric acid, the effects of diverse ions, and a procedure suitable for the determination of 1 to 10 μg of boron have been published.[241] An indirect spectrophotometric method for borate using a tartrate buffer and barium chloranilate, and based on the determination of the liberated chloranilic acid has been proposed.[561] This method lacks specificity and is not as sensitive as most direct spectrophotometric methods for boron. Another indirect spectrophotometric method that has been proposed for the determination of borate is based on the removal of fluoride ion from a fluoride-molybdate reagent by the formation of tetrafluoborate, and the subsequent reduction of the molybdate to molybdenum blue.[121] The carminic acid method has been automated for the determination of boron in sewage, sewage effluents, and river waters,[389] and the curcumin method has also been automated.[295]

Fluorometry – Borate in water has been determined fluorometrically by using hydroxy-2-methoxy-4-chloro-4′-benzophenone in concentrated sulfuric acid. An excitation wavelength of 365 nm and an emission wavelength of 490 nm are used to determine borate over the range of concentrations from approximately 10 to 100 ppb of boron.[381]

Electrometric

Potentiometry – Carlson and Paul[122] describe a potentiometric method for the determination of traces of borate in which traces of borate are concentrated on an Amberlite X-243 boron-specific resin, the borate is converted to tetrafluoroborate by adding a concentrated solution of hydrofluoric acid to the resin column, and the tetrafluoroborate is eluted with sodium hydroxide and finally determined with a tetrafluoroborate-ion-selective ion membrane electrode. Tetrafluoroborate solutions corresponding to 0.2 to 20 ppm of boron were ultimately obtained for potentiometric measurement.

Mass Spectrometry

The surface ionization technique was employed to determine the $^{11}B/^{10}B$ ratio by mass spectrometry. The interfering ions in mineral water were removed by a mixed ion-exchange column prior to use of the isotope-dilution method.[228]

Chromatographic

Gas chromatography – Borate, when present as an ammonium salt, reacts with bis(trimethylsilyl)trifluoroacetamide in dimethylformamide to form a trimethylsilyl borate which can be chromatographed on a SE-30 or an OV-17 stationary phase.[117]

Tetrafluoroborate

Spectrophotometry – Tetrafluoroborate forms an ion-association complex with *tris*(1,10-phenanthroline)iron(II) which is extractable into *n*-butyronitrile.[27] The absorbance is measured at 520 nm.

Potentiometry – Tetrafluoroborate-selective electrodes of the liquid membrane type have been prepared and used to determine tetrafluoroborate concentrations above 10^{-5} molar. Nitrate and iodide ions are the main interfering anions.[122]

Tetraphenylborate

Spectrophotometry – The ion-association complex tetraphenylborate-bis(2,9-dimethyl-1,10-phenanthroline) copper(I) is extractable into chloroform or chlorobenzene. The absorbance is measured at 456 nm.[640]

Coulometry – Tetraphenylborate can be determined by a coulometric titration with electrogenerated silver ion.[468] This method was used to determine 1 to 10 mg of sodium tetraphenylborate.

IV. ANIONS OF THE HALOGENS

Prior Literature References

A comprehensive treatment of the analytical chemistry of the halogens (Cl, Br, and I), covering the available methodology prior to about 1960, has been written by Armstrong, Gill, and Rolf.[31] Methods for determining chloride, hypochlorite, chlorate, and perchlorate have been summarized by Oplinger.[459] The principal methods for the determination of bromide and bromate have been discussed by Stenger.[563] Stenger and Ettre[564] have outlined the main methods for the determination of iodides, iodates, and periodates. The determinations of fluoride have been reviewed by Horton[291] and, more recently, by Macdonald.[405]

Chloride

Titrimetric

It has been found that the premature flocculation of silver chloride in the argentimetric titration of chloride in butylammonium chloride destroys the validity of the dichlorofluorescein end point unless a high concentration of ethanol is present.[208] The argentimetric titration of chloride, using biamperometric end-point detection and a titration medium containing methanol, has been described for the determination of traces of chloride.[277]

Opticometric

Atomic absorption spectrometry – Chloride has been determined by two indirect atomic absorption spectrometric methods. In one the silver chloride is precipitated and filtered, the precipitate is dissolved in ammonia, and the equivalent silver is determined.[618] In the other method the excess silver remaining in the supernatant solution after precipitation of silver chloride is determined, the chloride being equivalent to the difference between the total amount of silver added and that found in the solution. The latter method has been applied to the determination of relatively high chloride concentrations in plant liquors.[190]

Spectrophotometry – Chloride has been determined by displacement of hydrogen cyanide upon addition of mercury(II) cyanide to a sulfuric acid solution and the distillation of the hydrogen cyanide. For concentrations of chloride between 0.014 and 0.43 μg/ml the pyridine-pyrazolone method was used to determine the equivalent cyanide. Bromide could be determined by a similar method, but iodide could not. A relative deviation of about ± 2% is obtainable.[74] A photometric method for chloride or bromide has been developed; it is based on the oxidation to chlorine or bromine with permanganate and the use of *o*-tolidine to develop a yellow color.[529,530]

Chloride reacts with mercury(II) thiocyanate to liberate thiocyanate ions, which react with iron(III) to give the $FeSCN^{2+}$ complex.[306] Further studies[200,207] have shown this method to be applicable over the range of concentrations from 0.05 to 2.5 ppm of chloride and to have a limit of detection of about 15 ppb. In a modification of this method, the liberated thiocyanate ions are extracted as *tris*(1,10-phenanthroline)iron(II) thiocyanate, an ion-association complex, into nitrobenzene.[639] Microdistillation of chlorine, formed in the oxidation of chloride by cerium(IV), into a basic solution may be used to separate micro amounts of chloride. The chloride then can be determined by measuring the extent to which it bleaches the color due to the $FeSCN^{2+}$ complex.[184] The procedure in which thiocyanate is displaced from mercury(II) thiocyanate by chloride and then reacts to form iron(III) thiocyanate has been automated for the determination of approximately 5 to 50 ppm of chloride in water.[170]

A new indirect ultraviolet spectrophotometric method for the determination of 0.1 to 8 ppm of chloride is based on (1) the formation of phenylmercury(II) chloride by reacting phenylmercury(II) nitrate with chloride, (2) the extraction of the phenylmercury(II) chloride into chloroform, (3) the formation of phenylmercury(II)diethyldithiocarbamate, and (4) the measurement of the absorbance at 297 nm.[62]

When excess solid mercury(II) iodate is added to solution of chloride in ethanol-water (1:1), mercury(II) chloride is formed. After the excess mercury(II) iodate has been removed by centrifugation, excess chloride is added to form the tetrachloromercurate(II) species and the ultraviolet absorbance of this is measured.[297] Chloride in blood serum and other biological fluids has been determined by measuring the absorbance of the hexachloroferrate(III) complex at 348 nm. Conformity to Beer's law was observed for test solutions containing 0.01 to 0.6 μmole of chloride per ml.[364]

Spectrofluorometry – Chloride has been determined by measuring the quenching effect of silver chloride on the fluorescence of sodium fluoresceinate when irradiated with radiant energy having a wavelength of 254 nm. The procedure has been applied to the determination of 10 to 50 ppb of chloride in water.[326]

X-ray spectrometry – Microgram amounts of chloride have been determined by precipitation as silver chloride and collected on a Millipore filter for measurement by x-ray fluorescence spectrometry, either by measuring the silver K-alpha spectrum[517] or the chloride-alpha spectrum.[218] Chloride (0.7 μg to 4 mg), thiocyanate (6 μg/ml), cyanide (10 to 100 μg), and phosphate (1 to 10 mg) have been determined by an indirect x-ray fluorescence method employing a reference element.[568]

Electrometric

Potentiometry – Although the silver indicator electrode has been used extensively for many years in argentimetric titrations of halides, the availability of selective-ion membrane electrodes has caused more attention to be given to the direct potentiometric determination of chloride. In general, three types of membrane electrodes have been employed. The first is a solid-state membrane electrode consisting of $AgCl/Ag_2S$ membrane in which fine particles of silver chloride are dispersed in a silver sulfide matrix. Sulfide, bromide, iodide, cyanide, and ammonia are the main interfering substances.[513] The second is a heterogeneous membrane electrode consisting of an inert silicone rubber impregnated with silver chloride.[488] This particular type of membrane electrode has been shown to give Nernstian response over a range of chloride concentrations from 5×10^{-4} M to 10^{-1} M with a relative error of about ± 2%.[498] The third is a liquid membrane electrode using a high-molecular-weight tetraalkylammonium salt, such as dimethyldistearylammonium chloride.[512] Chloride-selective electrodes of this third type are commercially available and have been incorporated into an apparatus for continuously monitoring the concentration of hydrogen chloride concentrations in a gaseous mixture.[376] Chloride in biological fluids has been determined directly, without centrifuging to remove the proteins, by using a chloride-sensitive membrane electrode.[465]

It has been reported that traces of chloride or bromide ions (10^{-3} to 10^{-6} M) have been titrated potentiometrically in 90% acetone – 10% water using silver nitrate as titrant and a platinum indicator electrode.[487] Chloride has been titrated using a chloride-ion selective electrode in 80% *p*-dioxane in the presence of a twofold excess of azide. The azide can also be titrated following the chloride end point.[542] It has been found feasible to circumvent interference due to bromide by oxidizing bromide to bromine prior to determining chloride by means of a chloride-selective electrode.[377]

Coulometry – Fletcher and Mannion[199] used silver sulfide as a permeable selective membrane for the coulometric titration of chloride. The technique included the generation of sufficient silver(I) to react with 95% of the chloride prior to the addition of the chloride sample in order to improve the response time of the indicator electrode and to permit the generation of silver ions in solutions containing oxidizing agents. This coulometric titration method is primarily applicable to the determination of about 0.1 to 3 mg of chloride. Chloride ion in amounts between 0.1 and 1000 μg can be titrated coulometrically with electrogenerated silver ion and an automatic coulometric system has been described.[151] Chloride has also been determined in biological materials by an automatic, coulometric-amperometric titration method.[150]

Radiometric

The chloride contents of biological fluids and tissues have been determined by a chlorine-36 isotope-dilution method in which a hot alkaline digestion is the isotopic exchange step.[149]

Chromatographic

A gas chromatographic method for the determination of low concentrations of chloride ion has been based on the formation of phenylmercury(II) chloride by adding phenylmercury(II) nitrate to an acidic chloride solution, extracting the phenylmercury(II) chloride by chloroform, and then injecting the chloroform solution into a gas chromatograph with a diethylene glycol adipate coating on a packed column.[60] The method is applicable to the determination of 0.4 to 7 μg of chloride per milliliter of the chloroform extract. Using a flame ionization detector, it was possible to determine chloride in aqueous solutions at concentrations as low as 0.008 ppm.

Microgram amounts of chloride and bromide ions in aqueous solutions have been determined by a gas chromatographic method. After adding sufficient sulfuric acid to give an 80% sulfuric acid solution, a helium sweep removes the hydrogen halides which are collected in a liquid nitrogen trap. A column containing toluene and *n*-heptane on granular Teflon, operated at a temperature of -78°C, is recommended.[67]

Chlorate

Titrimetric

Both nitrite and bisulfite have been found to be satisfactory reducing agents for chlorate. The resulting chloride can be titrated with silver nitrate using either dichlorofluorescein or chromate as indicator.[140]

Opticometric

The interference of chlorate in the formation of the color of the rhenium-α-furildioxime complex is the basis of a spectrophotometric method suitable for the determination of chlorate ion at concentrations up to 5 ppm.[591]

Chlorite

Titrimetric

In a critical study of methods for the determination of chlorite in the presence of hypochlorite, it was recommended that the hypochlorite be converted to hypobromite at pH 9 to 9.4 and the hypobromite destroyed by the addition of ammonium sulfate.[269] The chlorite was then determined iodometrically.

Hypochlorite

Electrometric

Hypochlorite has been titrated potentiometrically with copper(I) chloride.[327] Hypochlorite can be determined coulometrically with electrogenerated iron(II) in an acetate-buffered solution; the end point is detected amperometrically.[237] Chlorate can also be determined by a coulometric titration with electrogenerated titanium(III) in 2 *M* hydrochloric acid. Hence, mixtures of hypochlorite and chlorate can be analyzed by using one aliquot to determine hypochlorite and another to convert the hypochlorite to chlorate by hydrogen peroxide in basic solution prior to the determination of total chlorate.

Perchlorate

Gravimetric

Perchlorate can be determined gravimetrically by precipitation with tetraphenylphosphonium chloride. Chlorate does not interfere.[214] Diantipyrylpropyl methane reacts with perchlorate ions in acidic solution to give a fine crystalline precipitate that, after filtration and drying at 110°C, can be weighed or dissolved in acetone and titrated potentiometrically using sodium hydroxide and a glass-calomel electrode system.[8] Chloride, chlorate, and sulfate do not interfere, but periodate does.

Titrimetric

Solutions containing perchlorate ion in the range of concentrations from 3×10^{-3} *M* to 8×10^{-3} *M* have been titrated with tetraphenylarsonium chloride using the thermometric titration method. Most cations do not interfere with this titration, but permanganate and tetrafluoroborate do.[126] A precipitation-titrimetric method for perchlorate has been developed by Smith and Manahan[557] which involves the use of tetraphenylarsonium chloride as titrant and a perchlorate-sensitive liquid-membrane electrode as the indicator electrode. A similar procedure was developed for the determination of tetrafluoroborate using a tetrafluoroborate-sensitive electrode.

Opticometric

Atomic absorption spectrometry – An indirect AAS method for perchlorate is based on the formation of perchlorato-bis(2,9-dimethyl-1,10-phenanthroline)copper(I) which is extracted into ethyl acetate and aspirated into an air-acetylene flame. The absorbance at the 324.7 nm resonance wavelength of copper is proportional to perchlorate concentration in the range from 0.5 to 5 ppm.[145]

Spectrophotometry – Perchlorate forms a *tris*

(1,10-phenanthroline)iron(II) perchlorate ion-association complex extractable with *n*-butyronitrile,[211] a *tris*(2,2′-bipyridine)iron(II) perchlorate complex extractable with nitrobenzene,[636] and a bis(2,9-dimethyl-1,10, phenanthroline)iron(II) perchlorate complex extractable with ethyl acetate.[145,614] These methods are applicable to the determination of amounts of perchlorate between 5 and 125 μg.

The decrease of absorbance accompanying the precipitation of tetrapyridine copper(II) perchlorate has been utilized.[83] A redox reaction in which perchlorate was reduced to chloride by vanadium(III) to give an equivalent amount of vanadium(IV) was the basis of an indirect spectrophotometric method.[648] Absorbance measurements must be made at two wavelengths, 400 and 750 nm, so that a correction can be applied for the absorbance due to the excess vanadium(III). Trautwein and Guyon[590] have proposed a novel indirect spectrophotometric method based on the interference of the perchlorate ion on the development of the color due to the rhenium-furildioxime complex formed when perrhenate is reduced with tin(II) chloride in the presence of α-furildioxime.

Methylene Blue forms a complex with perchlorate that is very slightly soluble in aqueous solution. The Methylene Blue-perchlorate complex can be extracted with chloroform[85] or 1,2-dichloroethane,[572] or the excess Methylene Blue can be determined.[436] Other dyes and extractants have been used in modifications of this method.[226,598] In aqueous solutions buffered at pH-values near 6.5, Brilliant Green and perchlorate ions form a complex which is extractable into benzene and exhibits an absorbance maximum at 640 nm. The modified procedure recommended by Fogg, Burgess, and Burns[201] is applicable to the determination of 4 to 22 μg of ClO_4^- and has been used to determine perchlorate in potassium chlorate.

Perchlorate can be extracted into *o*-dichlorobenzene as tetrabutyl phosphonium perchlorate. On bringing this extract in contact with an aqueous solution containing iron(III) thiocyanate, an iron(III) thiocyanate-tetrabutylphosphonium complex forms in the organic layer. The absorbance is measured at 510 nm.[202] Perchlorate can be determined by infrared spectrometric measurement at 628 cm^{-1}. Chlorate is first reduced by chloride by boiling hydrochloric acid, the solution is evaporated to dryness, and the residue is incorporated into a potassium bromide pellet.[99]

Electrometric

Potentiometry – A liquid-membrane ion-selective electrode for measuring perchlorate ion is commercially available. The liquid is a *tris*(1,10-phenanthroline derivative) iron(III) complex.[512] Nernstian response has been reported over the range of concentrations from 10^{-1} *M* to 3 x 10^{-4} *M*.[294] A liquid-membrane electrode containing *tris*(1,10-phenanthroline) iron(II) as the ion exchanger has been reported to have much better selectivity for perchlorate ion over nitrate or iodide.[304] Solid-state perchlorate electrodes using salts obtained from the radical cations of several *p*-diamines gave almost Nernstian response over the range of concentrations of perchlorate from 10^{-1} *M* to 3 x 10^{-4} *M*.[546]

Coulometrically – Perchlorate can be converted to chloride by an oxygen-flask combustion and the resultant chloride can be titrated coulometrically.[535]

Radiometric

An isotopic dilution method employing chlorine-36 in labeled potassium perchlorate and the precipitation of potassium perchlorate has been described for the radiochemical determination of perchlorate.[314]

Bromide

Titrimetric

A recent collaborative study was made of the determinations of bromide and chloride by oxygen-flask combustion followed by the mercurimetric titration of the ionic halides. Excellent results were obtained by most of the collaborators.[566] Bromide in foods has been converted to bromate by oxygen-flask combustion and determined either titrimetrically or spectrophotometrically by measurement of the iodine liberated by the bromate on treatment with iodide in acidic solution.[172]

Opticometric

Spectrophotometry – Bromide reacts with the oxazine dye Nile Blue to form a salt extractable into chloroform. The absorbance of the extract is measured at 626 nm. The method is applicable to the determination of 1 to 6 ppm of bromide.[385] Bromide can be oxidized with hypochlorite, the excess of which is destroyed by formate. Bromate in acidic solution reacts with bromide to liberate bromine, which reacts with rosaniline. The absorbance of the tribromorosaniline is measured at 573 nm.[428] Oxidation of bromide with chloramine B and measurement of the resulting change in the absorbance of malachite green have also been reported.[107] A photometric determination of bromide by oxidation of bromide to bromate using hypochlorite, destruction of excess hypochlorite with formate, the liberation of bromine by the addition of bromide to the acidic solution of bromide, and the decolorization of the acid form of methyl orange by the bromine have been reported.[580] Beer's law was shown to apply over a wide range of bromide concentrations. Bromide reacts with sulfite and triphenylbenzylphosphonium ions to form a triphenylbenzylphosphonium bromosulfinate which is extractable into 1,2-dichloroethane. At 359 nm the molar absorptivity is 3.29×10^3. Iodide forms a similar complex having a molar absorptivity of 1.35×10^4 at 381 nm.[55]

The catalytic effect of bromide on the oxidation of iodide to iodate by permanganate in acidic solution is the basis of an indirect spectrophotometric method applicable to the determination of bromide over the range of concentrations from 1 to 100 ppb.[196] The inhibition by bromide of the chlorination of ammonia to form trichloramine has been used to determine 0.02 to 1.2 ppm of bromide. A trichloramine-nitrite oxidation product is ultimately assayed by the blue starch-triiodide complex, the absorbance of which decreases with increased bromide concentration.[651] A cadmium iodide-linear starch reagent is used. Traces of bromide (20 to 200 μg/l) in water have been determined automatically with a Technicon Autoanalyzer: bromine is generated by oxidation with chloramine T, and used to brominate phenolsulfonaphthalein at pH 4.6, yielding tetrabromosulfonaphthalein purple.[28]

X-ray spectrometry – Trace concentrations of bromide (0.1 to 10 ppm) in water have been determined by preconcentrating the bromide on an anion-exchange-resin disk and then measuring the intensity of the $\text{BrK}_{\alpha 1}$ emission line. All x-ray intensities, after correction for background, were compared with the value obtained from a standard disk containing 100 ppm of bromide. The analytical error by this x-ray spectrometric method was about 5%.[490]

Flame photometry – A flame photometric method for the determination of bromide, using the indium bromide band at 372.7 nm, has been described.[244,245]

Electrometric

Potentiometry – A solid-state-membrane ion-selective electrode consisting of silver bromide dispersed in a matrix of fused silver sulfide, or a membrane electrode having silver bromide dispersed in a silicone rubber matrix, gives a potential linearly dependent on the logarithm of the concentration of bromide over a wide range, approximately 7×10^{-5} *M* to 10^{-1} *M*.[274,498] Several minutes is usually required for attainment of the equilibrium potential. The direct potentiometric determination of bromide ion using a silver-silver bromide electrode has been found applicable over the range of bromide concentrations from 10^{-1} to 10^{-4} *M* bromide. Mercury(I), cyanide, dichromate, iodide, permanganate, and thiosulfate ions interfered by affecting the measured potentials.[476]

In the potentiometric titration of mixtures of bromide and chloride, the error in the bromide end point can be decreased by adjusting the electrolyte concentration to about 0.1 *M* in potassium nitrate. The flocculation of the silver bromide sol results in the rapid exchange of chloride, trapped in the silver bromide, with bromide ion remaining in solution.[92] Traces of bromide can be separated from relatively large amounts of chloride by the formation of cyanogen bromide, which is distilled and fixed in a sodium hydroxide solution. The bromide is then determined by differential ("null-point") potentiometry.[629]

Voltammetry – Halide ions in molten alkali nitrates have been determined by pulse polarography; a reversible one-electron reaction, producing a soluble product, is observed with a mercury electrode.[455] For example, bromide was determined in the range of concentrations from 5×10^{-4} *M* to 5×10^{-3} *M*.

Radiometric

Bromide can be determined radiometrically by adding mercury nitrate labeled with Hg-203, extracting the mercury(II) bromide complex into diethyl ether, and counting the gamma activity of the aqueous phase.[43] The bromide contents in the range from 10 to 200 ppm have been determined by neutron activation analysis in cigarettes and various other materials.[313]

Chromatographic

Bromide has been oxidized to bromine by permanganate and extracted into cyclohexane containing cyclohexene to give 1,2-dibromocyclohexane with an overall conversion of approximately 70%. The 1,2-dibromocyclohexane is determined by gas chromatography using 1,6-dibromohexane as an internal standard. The method is applicable to the determination of 0.1 to 1 ppm of bromide in blood.[24]

Bromate

Opticometric

Bromate oxidizes 4-nitrosoantipyrine to a yellow product, presumably 4-nitroantipyrine. Beer's law applies in the 25 to 140 ppm of bromate range. The absorbance maximum is at 525 nm.[489] Odler[456] has suggested 1,2,3-*tris*(2-diethylaminoethoxy)benzene hydrochloride as a reagent for the detection and quantitative colorimetric determination of bromate ions. Bromate and iodate can be determined by a spectrophotometric method in which the reagent is an equimolar mixture of isonicotinic acid hydrazide and 2,3,5-triphenyltetrazolium chloride. The iodate reacts with the reagent to give a color at room temperature, while bromate reacts with it only on heating.[268]

Bromite

Bromite in 0.5 M NaOH gives a polarographic reduction wave at about -0.88 V vs S.C.E. Measurement of the height of this wave has been used to determine amounts of bromite between 0.15 and 1.5 mg.[358]

Hypobromite

Titrimetric

Hypobromite can be titrated with ferrocyanide in the presence of bromite, bromate, and bromide, using a platinum indicator electrode for the potentiometric location of the equivalence point.[17] The sum of hypobromite and bromite can be determined by a back-titration procedure employing arsenite and iodine.

Perbromate

Opticometric

A sensitive spectrophotometric method for perbromate ion in the range of concentrations from 10^{-5} M to 10^{-6} M involves the extraction of a Crystal Violet-perbromate ion-association complex into chlorobenzene, and the measurement of its absorbance at 596 nm. Large concentrations (10^{-3} M) of bromide or bromate can be tolerated if an empirical calibration graph is prepared to permit compensating for shifts in extraction equilibria attributed to competition for the Crystal Violet cations. This method is less time-consuming than, and equal in accuracy to, the iodometric titrations reported previously.[22,23]

Electrometric

The fact that a perchlorate-selective electrode also responds to perbromate activity was used to detect the end point in the potentiometric titration of perbromate with an 0.05 M solution of tetraphenylarsonium chloride. This method is reported to be applicable in the range of concentrations from 10^{-1} to 10^{-4} M, indicating that the limit of detection is about 0.1 ppm of BrO_4^-.[96] It appears that perbromate ion would interfere in determinations of perchlorate made with such electrodes. Perbromate in a supporting electrolyte which is 0.05 M in $HClO_4$ and 0.05 M in $NaClO_4$ gives a single irreversible polarographic wave corresponding to the reduction to bromide.[310] Polarography can also be used to determine perbromate in the presence of bromate by employing a supporting electrolyte having a pH of about 6, at which value there is a wave that represents the reduction of perbromate only to bromate.

Iodide

Titrimetric

A method for iodide has been proposed using *N*-bromosuccinimide as titrant and methyl red as indicator, and has been applied to the assay of 20 to 50 mg of potassium iodide.[44] A chemical amplification method has been devised in which 10 to 200 μg of iodide is oxidized to iodate by periodate, the excess periodate being masked by molybdate. The iodate is then determined by an iodometric titration with a 2 x 10^{-3} M solution of thiosulfate.[57] A modified chemical amplification method for iodide is based on oxidizing iodide to iodate with bromine, destroying the excess bromine with formate, and adding silver iodide instead of potassium iodide to liberate 3 mol of iodine per initial mole of iodide. After removal of the excess silver iodide, this iodine is titrated with thiosulfate. By repeating this sequence of reactions with the iodide produced in the reaction with thiosulfate, an amplification factor of 36 was obtained.[210]

Opticometric

Atomic absorption spectrometry – Kirkbright, West, and Wilson[342] have taken advantage of the high transparency of the fuel-rich nitrogen-shielded nitrous oxide-acetylene flame for the determination of iodine using the 183.0-nm resonance line. In aqueous solution the limit of detection, approximately 12 ppm, is independent of whether the solute is nebulized as iodide, iodate, or periodate. Calibration graphs were linear over the range of concentrations from 25 to 1000 ppm of iodide in aqueous solution. An indirect AAS method, applicable to the determination of 0.6 to 5 ppm of iodide, has been based on the formation of the bis(1,10-phenanthroline)cadmium(II) iodide ion-association complex, extraction of the complex into nitrobenzene, and determination of the cadmium using the 228.8-nm line.[638] Fluoride, sulfate, and phosphate ions did not interfere.

Spectrophotometry – The Sandell-Kolthoff reaction, in which iodide ion acts as a catalyst for the reduction of cerium(IV) by arsenic(III), has been used in the development of a rapid automatic reaction-rate spectrophotometric method. This is based on measurement of the time required for a specified decrease in the absorbance of the cerium(IV), and applicable to amounts of iodide between 0.015 and 0.45 μg.[410] Iodide reacts stoichiometrically with iodine cyanide to give iodine and hydrogen cyanide, and the iodine can be determined by measuring the absorbance of either the aqueous solution of iodine or the carbon tetrachloride extract.[282] A displacement reaction has been described in which iodide displaces dithizone from mercury(II) dithizonate; the dithizone is extracted into toluene prior to measurement of the absorbance at 620 nm, a wavelength at which the mercury(II) dithizonate in toluene does not absorb.[7] Another procedure involves the addition of an excess of mercury(II) to form mercury(II) iodide, followed by determination of the excess mercury by the spectrophotometric-dithizone method, the absorbance being measured at 450 nm. Approximately 3 to 50 μg of iodide can be determined by either of these two procedures. Microamounts of iodide or bromide can be determined by using an oxidizing agent such as chloramine B, chloramine C, or hypochlorite to form I^+ or Br^+, which then react with a triphenylmethane dye, decreasing its absorbance. Brilliant Green is one of the dyes suitable for the determination of both iodide and bromide.[106] Iodide obtained by dehalogenation of organic bound iodine has been determined photometrically at 455 nm following oxidation to iodine by nitrite.[180]

The catalytic effect of iodide on the substitution of the ligand, 4-(2-pyridylazo)resorcinol (PAR) in Hg(II)-PAR by 1,2-cyclohordnodiomine-N,N,N′,N′-tetraacetic acid (CyDTA) is the basis of a kinetic method. Interfering cations can be removed by a cation exchanger. This kinetic-spectrophotometric method is especially applicable to the range of concentrations from 10^{-7} to 10^{-8} *M*.[215] A photometric-kinetic method for the determination of iodide (or bromide) on the basis of its catalytic effect on the decomposition of bromate in acidic solution has been suggested. In the determination of bromide the formation of bromine is monitored by following the decolorization of a methyl orange solution.[588]

Fluorometry – When iodide ions react with 2′,7′-bis(acetoxymercuri)-fluorescein, a 2:1 complex species is formed and the intensity of fluorescence decreases.[146] This fluorometric method has been applied to the determination of 1 to 10 μg of iodide. The quenching of the fluorescence of uranyl acetate by iodide has been used to determine 2 to 20 μg of iodide ion.[105]

Electrometric

Potentiometry – An iodide-sensitive electrode has been used for the direct determination of iodide, or for that of iodate after this is reduced to iodide with aluminum in sodium hydroxide solution.[463] Ruzicka and Rald[519] have described an iodide-selective electrode based on the use of a solution of iodine in carbon tetrachloride, benzene, and mesitylene. A very thin layer of this solution is adsorbed on porous graphite to give the ion-sensitive surface. No inner reference electrode is used. The electrode is not light-sensitive and can be used in solutions containing iodide at concentrations between 10^{-2} M and 10^{-6} M. Reducing agents and basic media are undesirable. The iodide content of refined selenium has been determined by a method employing the standard addition technique and an iodide-sensitive membrane electrode.[617] The selenium is fused with sodium hydroxide and the melt dissolved in water; upon acidification with sulfuric acid elemental selenium precipitates and sodium iodide remains in solution. This approach is also applicable to the determination of fluoride in selenium by substituting a fluoride-sensitive membrane electrode. Iodide at concentrations between about 10^{-2} and 10^{-4} M solutions have been determined chronopotentiometrically using a silver anode.[473] Mixtures of chloride, bromide, and iodide have been analyzed by this method. Very dilute iodide solutions ($\sim 10^{-7}$ M) have been analyzed by stripping analysis, in which a portion of the iodide is deposited onto a silver microelectrode by a controlled-potential oxidation. The number of coulombs consumed during the stripping step was found to be proportional to the product of the pre-electrolysis time and the bulk concentration of the iodide.[543]

Voltammetry – Microamounts of iodide have been determined by a polarographic-kinetic method in which the catalytic effect of iodide on the oxidation of arsenite by iodate is followed by recording the time dependence of the height of the polarographic wave of iodate. An addition method based on measurements of the times required to attain complete reaction for two sample solutions and a sample solution spiked with a known amount of iodide has also been suggested as a means of eliminating the adverse effect of diverse ions.[587]

Radiometric

An "iodinated" Dowex 2-X8 resin is used to isolate iodine-128 from an activated sample. This activation analysis method has been applied to the determination of iodide at the ppb level in biological fluids.[283] A radiometric method has been proposed in which a known amount of iodine-131 is added to the sample, the iodide is oxidized to iodine, the iodine is extracted into benzene, and this extract is equilibrated with a known amount of inactive iodide ion in an aqueous solution. The radioactivity is distributed between the two phases in direct properties to the quantity of iodine or iodide present in each phase.[502] A radiometric titration of 12 to 2000 μg of iodide using mercury-203 has been described.[319]

Chromatographic

Hasty[273] has demonstrated the feasibility of converting micro amounts of iodine to iodoacetone, which is then determined by gas chromatography, and also showed that it is possible to determine iodide in this way by oxidizing it with iodate prior to iodination.

Iodate

Titrimetric

Iodate can be titrated iodometrically in the presence of periodate if the latter is masked by complexing it with molybdate.[111] A procedure for the consecutive titration of iodate and periodate has been devised; it is based on the complexation of periodate with molybdate during the initial iodometric titration of the iodate and the subsequent demasking of the periodate by addition of oxalic acid to enable the periodate to be titrated similarly.[63]

Opticometric

Iodate in acidic solution reacts with a cadmium iodide-starch reagent to give a blue starch-iodine complex which serves as the basis of spectrophotometric method.[533] Nitrite interferes and must be removed by treatment with sulfamic acid.

Electrometric

Beran and Bruckenstein,[66] studying the voltammetry of iodate, observed that iodate is reduced irreversibly to iodide at a platinum electrode. The iodide thus formed reacts with more iodate to form iodine, which is then reversibly reduced to iodide. The rate of this catalytic reduction of iodate increases as its concentration increases, and becomes very fast, so that the limiting current becomes proportional to the concentration of iodate, when this concentration exceeds 2×10^{-4} M.

Periodate

Opticometric

Periodate can be determined in the presence of iodate by coprecipitating the periodate with aluminum hydroxide, dissolving the precipitate in sulfuric acid, and measuring the absorbance of periodate in this solution at 210 nm. Conformity to Beer's law was observed over the range of periodate concentrations from 2 to 35 ppm, and the molar absorptivity was 2.87 x 10^3 l-mol^{-1}-cm^{-1}.[71]

Fluoride

Titrimetric

The end point in the titration of fluoride with thorium nitrate has been improved by using Methylthymol Blue[129] as indicator and buffering the solution at pH 3.35 with glycine and perchlorate.[537] An ion-exchange column has been used to preconcentrate fluoride from water. After eluting the fluoride with an 0.1 *M* solution of potassium chloride, the fluoride is titrated to a preselected end-point voltage using thorium nitrate as titrant and a fluoride-sensitive indicator electrode.[383] A rapid method for determining fluoride in silicates utilizes pyrohydrolysis and automatic titration with thorium nitrate.[396] Samarium(III) has been used to precipitate samarium(III) fluoride and the excess samarium has been back-titrated with an EDTA solution using Methylthymol Blue as indicator.[147] Fluoroborate and fluorosilicates can also be determined by this method, but iron interferes. Fluoride has been determined titrimetrically by adding an excess of a standard cerium(III) solution to precipitate cerium(III) fluoride at pH 1.75, then determining the excess cerium(III) by back titrating with an EDTA solution, using Arsenazocresol Red as indicator.[642] Sulfate and fluoride ions in etching solutions have been separated on a strong anion-exchange resin at pH 5 to 6.5. The fluoride is eluted with an 0.1 *M* solution of ammonium chloride. An EDTA back-titration method using calcium chloride is used in the determination of fluoride.[449] A chemical amplification method for fluoride has been suggested; it is based on the reaction of calcium iodate and sodium fluoride to produce insoluble calcium fluoride in a solution containing 60 to 70% isopropyl alcohol and having a pH between 4 and 7. The iodate is titrated iodometrically after removal of the excess calcium iodate. A correction must be applied for the loss of iodate.[35] Either fluoride or perrhenate can be titrated with lead(II) to precipitate a slightly soluble compound containing lead, molybdate, perrhenate, and fluoride.[132] A turbidimetric titration method amenable to the determination of 1 to 10 mg of fluoride, in which neodymium(III) is the titrant, has been described.[505]

Silicon has been used to reduce the fluorides and oxyfluorides of the transition metals at about 900°C; silicon tetrafluoride is formed and is swept by nitrogen gas into an absorber. The fluoride is determined titrimetrically.[484]

Opticometric

Atomic absorption spectrometry – An indirect atomic absorption spectrometric method for the determination of fluoride has been based on the depression of the absorbance at the 285.2-nm resonance line of magnesium when an air-cooled gas flame is used. The method was applicable to the range of fluoride concentrations from 0.2 to 20 ppm.[86] Sulfate and phosphate ions interfere. Fluoride enhances the absorbance due to zirconium or titanium in a nitrous oxide-acetylene flame. With zirconium the concentration range should be about 5 to 200 ppm while with titanium the working concentration range is higher, 40 to 400 ppm.

Spectrophotometry – The SPADNS method is one of the most widely used colorimetric methods for the determination of fluoride. The reagent, containing zirconyl chloride and sodium 2-(parasulfophenylazo)-1,8-dihydroxy-3,6-naphthalenedisulfonate, is actually a zirconium-dye complex whose color is bleached by the fluoride as a zirconium fluoride is formed. The method is applicable up to 1.4 ppm of fluoride.[65] Chlorine interferes and must be removed by a careful pretreatment with sodium arsenate. A preliminary distillation is often necessary to eliminate interferences due to aluminum(III), iron(III), phosphate, and especially hexametaphosphate.

The determination of fluoride by measurement of the decrease in the absorbance of the zirconium-SPADNS complex after obtaining the fluoride from organic compounds by combustion in an oxyhydrogen flame has been investigated by Willis and Cave.[627] The rapid spectrophotometric method using the zirconium-Eriochrome Cyanine R complex is also popular and the effect of sulfate on its results can be corrected for by means of a nomograph.[421] The interference of plutonium in the Eriochrome Cyanine R spectrophotometric method for fluoride can be eliminated by reduction to plutonium(III) with mercaptoacetic acid.[500] The adsorption of fluoride on calcium phosphate was applied to the removal of fluoride from natural waters, salt solutions, urine, and plant extracts prior to the isolation of fluoride by a diffusion technique and its determination by a modified aluminum-Eriochrome Cyanine R procedure.[609] Solochrome Cyanine R and zirconium have been used in a spectrophotometric method for the determination of 0.25 to 2.5 μg of fluoride. The molar absorptivity is 2.4 x 10^4 $l \cdot mol^{-1} \cdot cm^{-1}$ at 540 nm.[167]

In aqueous methyl cellosolve solution at pH 4.5 thorium chloranilate reacts with fluoride ion to give thorium difluorochloranilate ($ThF_2C_6Cl_2O_4$) and liberate chloranilic acid, whose absorbance can be measured at 330 or 540 nm. This method is applicable to the determination of 0.5 to 50 ppm of fluoride; absorbance measurement at 330 nm is recommended for the low concentrations.[281]

Fluroide reacts with the red cerium(III)-alizarin chelate to form a blue complex.[58] Both the stability of the complex and its absorbance are increased by using a 15 to 20% acetonitrile or acetone solution.[59,232,344,643] This method is applicable to the determination of 1 to 25 μg of fluoride. The spectrophotometric determination of fluoride using the cerium(III)-alizarin chelate as reagent in 25% (v/v) dimethylsulfoxide has been recommended for the determination of 1 to 25 μg of fluoride.[253] Fluoride in potable waters has been determined by the "alizarin fluorine blue" method. The errors caused by high concentrations of sulfate and chloride can be corrected for.[330] A modified method is based on the reaction between fluoride and the cerium(III) chelate of "Alizarin Complexone," (3-[di(carboxymethyl) aminomethyl]-1,2-dihydroxyanthraquinone. The complex is extracted with a solvent mixture consisting of 5% triethylamine in *n*-pentanol prior to measurement of the absorbance at 570 nm. One recommended procedure is suitable for determining 0.1 to 1 μg of fluoride in 4 ml of an aqueous sample solution.[248] The catalytic effect of fluoride on the reaction between zirconyl chloride and Xylenol Orange is the basis of a spectrophotometric method for the determination of 0.005 to 0.05 ppm of fluoride.[118] The bleaching of a thorium-phenylfluorone lake has been used to determine up to 5 ppm of fluoride in water.[102] Interfering cations are removed by a cation-exchange resin. The lanthanum-alizarin spectrophotometric method for determining fluoride in urine has been automated.[256] A modified distillation apparatus and an improved procedure for the separation of fluoride from interfering cations and anions prior to spectrophotometric measurement have been developed by Wade and Yamamura.[612] The detection of 0.1 μg of fluoride by the ring-oven technique with thorium chloranilate as chromogenic agent has been reported by Barney.[46]

Spectrofluorometry – Traces of fluoride can be determined spectrofluorometrically by measuring the increase of the fluorescence intensity of the zirconium-Calcein Blue complex[254] resulting from the formation of a 1:1:1 ternary complex. An excitation wavelength of 350 nm and an emission wavelength of 410 nm are used. The recommended concentration range is about 0.01 to 0.06 ppm of fluoride. The fluorescence of the aluminum(III)-1-(2-pyridylazo)-2-naphthol chelate is quenched by fluoride ion, and the decrease of fluorescence intensity is proportional to the concentration of fluoride ion.[528] Phosphate ion interfered. The indirect fluorometric determination of 1- to 10-mg amounts of fluoride is based on the quenching of the fluorescence of the zirconium-flavonal chelate.[246]

Electrometric

Potentiometry – The development of the lanthanum-fluoride membrane electrode has been the most noteworthy advance in the determination of fluoride. This solid-state membrane electrode consists of a single crystal of LaF_3 doped with a divalent ion such as Eu^{2+}, and it gives a Nernstian response over the range of fluoride concentrations from 1 *M* to 10^{-6} *M*.[206,387] The main interferences are ions such as iron(III), aluminum(III), and silicon(IV), which complex fluoride ion; hydrogen ion, which protonates fluoride, especially at pH-values below 5; and hydroxide, which alters the electrode response when its concentration exceeds about 10% of that of fluoride. Thus, a pH range of 5 to 8 is usually satisfactory. Because the electrode responds to the activity of the fluoride ion the electrode response depends upon the ionic strength of the test solution. In order to minimize the ionic-strength effect Frant and Ross[205] have recommended the use of a "total-ionic-strength-adjustment buffer," which contains sodium chloride, sodium citrate, and acetic acid and is adjusted to pH 5.0 to 5.5. Both the standard and the test solution are diluted with an equal volume of this buffer prior to measurement. The citrate releases bound fluoride by forming more stable complexes with iron(III) and aluminum(III) ions. Lingane[388] has observed that the lanthanum fluoride membrane electrode exhibits a Nernstian response in 60 vol % ethanol and that stirring affects the potential when the pF exceeds 4.5, by minimizing the accumulation of fluoride ion at the surface of the membrane that would result from the solubility of lanthanum fluoride, but does not do so at higher concentrations of fluoride.

Bock and Strecker[80] have discussed the direct potentiometric determination of fluoride, and practical applications have been made to the determinations of fluoride in bone,[550] air,[181] toothpaste,[544] vegetation,[41] and silicate rocks.[303] In the standardization of the fluoride-selective electrode it has been found that potassium fluoride is superior to sodium fluoride as a reference standard for fluoride-ion activity.[507]

Peters and Ladd[474] have determined fluoride by direct potentiometry using the fluoride-selective electrode and have applied their method to a variety of ores in the range of concentrations from 100 ppm to 45% fluoride. In these applications the direct potentiometric method was found to be faster than, and as accurate as, the distillation or pyrohydrolysis method. The fluoride-ion electrode has been used to determine fluoride ion obtained by an oxygen combustion in a polyethylene or polypropylene flask.[547]

Lingane[387] has studied the use of the fluoride-selective membrane electrode for end-point detection in titrations of fluoride with thorium, lanthanum, and calcium ions. Lanthanum nitrate, as titrant, gave the largest rate of potential change at the equivalence point. It is advisable to titrate to the true equivalence point potential rather than to the point of maximum slope.

Eriksson and Johansson[185] recommend lanthanum(III) as the titrant for solutions more concentrated than 10^{-3} molar in fluoride. They use a fluoride-sensitive electrode and a computer evaluation of the equivalence point. The species formed in the potentiometric titration of fluoride with thorium(IV) and lanthanum(III) as titrant have been considered and a computer program has been employed to locate the equivalence points.[19] Anfalt and Jagner[20] reported a standard-addition titration method for the potentiometric determination of fluoride in sea water in which a standard fluoride solution was added and a fluoride-selective electrode was used to monitor the fluoride. A computer was used to locate the equivalence point. The fluorine contents of organic substances were determined by a potentiometric titration using lanthanum(III) nitrate as titrant and the fluoride-ion indicator electrode following combustion in a Kirsten hot flask.[204] Fluoride can be titrated potentiometrically in the presence of phosphate using a fluoride-ion-selective electrode by adsorbing the phosphate on zinc oxide prior to titration with lanthanum(III) nitrate at pH 5 to 7.[540]

An 8-quinolinol extraction of interfering polyvalent cations into a butyl cellosolve-chloroform mixture was employed by Ke and Regier[328] prior to the direct potentiometric determination of fluoride. The method was applied to the determination of fluoride in natural and waste waters. According to Harzdorf the automatic potentiometric titration of fluorides, using the nitrates of the rare earths or aluminum as titrants in the pH range 4 to 7, did not result in exact stoichiometry and he recommended the use of an empirical factor.[263] Tetraphenylantimony sulfate is the titrant in a potentiometric titration method for fluoride using a fluoride-ion-selective electrode. The tetraphenylantimony fluoride ion-association complex is extracted into chloroform after each addition of titrant before the residual fluoride in the aqueous phase is measured potentiometrically.[460] Although phosphate, arsenate, and sulfate do not interfere, nitrate, perchlorate, thiocyanate, and the halides must be removed.

Fluoride has been determined by an "analyte-addition potentiometric" technique in which aliquots of the "analyte" are delivered into a known volume of a standard solution of fluoride.[177] By measuring the emf change resulting from addition of the analyte and knowing the electrode response slope of the fluoride-ion-selective electrode it is possible to compute the concentration of the fluoride by the following expression:

$$C_a = C_o \left[\left(\frac{V_o + V_a}{V_a}\right) 10^{\Delta E/S} - \frac{V_o}{V_a}\right]$$

where C_a and C_o are the concentrations of the analyte and the standard solution, V_a and V_o are the corresponding volumes, S is the electrode response slope (in mV per pF unit), and ΔE is the change of emf resulting from the addition of the analyte.

Coulometry – Fluoride (0.5 to 2 mg) has been titrated with lanthanum(III) electrochemically generated by the oxidation of lanthanum hexaboride anode, using a lanthanum-fluoride-membrane electrode as an indicator electrode.[154]

Voltammetry – The shift of the uranium(V)-uranium(III) half-wave potential is proportional to fluoride concentration in the range from 0.05 to 20 ppm. Phosphate interferes at low acidity.[87] On adding thorium chloranilate to a solution of fluoride ion in 25% methyl cellosolve–75% water containing 0.1 *M* acetic acid and 0.1 *M* sodium acetate chloranilate ions are liberated and thorium fluoride is formed. Following removal of excess reagent and thorium fluoride, the chloranilate is determined by polarography. A linear response was obtained over the concentration range from 2 to 20 ppm of fluoride.[299]

Radiometric

A radiometric method for fluoride has been studied in which the fluoride solution is added to a column packed with radioactive zirconium selenite and the displaced radioactive selenium is eluted with hydrochloric acid. A linear calibration plot was obtained over the range from 20 to 100 μg.[123] A radiotracer method in which tantalum-182 is extracted as a fluoride complex from a sulfuric acid solution into diisobutylketone has been described; the counting rate is linear over the range from 400 to 840 μg of fluoride ion.[430] Fluoride has been determined in rocks by gamma activation, separation of fluorine-18 by distillation, and measurement of the radioactivity of either the distillate or the precipitated calcium fluoride.[287] Fluoride in amounts between 25 and 150 μg has been determined by an isotope-dilution method using fluorine-18 and tetraphenylstibonium sulfate as the reagent for extraction into chloroform.[124]

Thermometric

Fluoride ions, after separation from phosphate, sulfate, nitrate, and chloride by ion exchange, can be determined by either an injection enthalpimetric method or a flow microcalorimetric method; both are based on the enthalpy of precipitation of lead chlorofluoride.[315] The flow microcalorimetric method was employed in determining 40 to 400 μg of fluoride. Fluoride undergoes endothermic reactions with thorium(IV), cerium(IV), aluminum, and calcium ions as titrants. The particular titrant to be selected for the thermometric titration of fluoride depends upon the anions and cations present in the sample solution.[189]

NMR

Wide-line nuclear magnetic resonance spectrometry has been used to determine 100 to 1000 ppm of fluoride in aqueous solution.[194]

Kinetic

An indirect kinetic method suitable for the determination of concentrations of fluoride from 0.4 to 3.8 ppb utilizes the inhibiting effect of fluoride on the zirconium-catalyzed reaction between iodide and perborate. An automatic potentiostatic apparatus measuring the potential of the iodide/iodine redox system at a platinum electrode was employed to measure the different reaction rates.[347] Sulfate, phosphate, arsenate, EDTA, oxalate, citrate, and tartrate interfere because they also inhibit the reaction. A direct kinetochromic method for fluoride has been based on the catalytic action of fluoride on the relatively slow reaction between zirconium(IV) and Methylthymol Blue.[279] An effective molar absorptivity of 3.23×10^4 l-mol^{-1}-cm^{-1} at 586 nm was observed for a 60-minute elapsed time period. This kinetic method was used to determine 0.5 to 4.75 μg of fluoride. The catalytic effect of fluoride on the zirconium-Xylenol Orange reaction has been investigated by Knapp.[348]

Microdiffusion

Wharton[621] recommends a time of 16 to 24 hours and a temperature of 60°C for the isolation of small amounts of fluoride (4 μg) by the microdiffusion method. The microdiffusion separation of fluoride can be accelerated by adding hexamethyldisiloxane to the sample compartment. The formation and the volatilization of trimethylfluorosilane and the liberation of HF when this comes into contact with the basic collecting solution are the essential steps.[584] The use of the microdiffusion method for separating fluoride from dust and fumes in industrial atmospheres prior to spectrophotometric determination of the fluoride by the lanthanum-alizarin fluorine blue reagent has been investigated by Marchall and Wood.[412]

Pyrohydrolytic

The fluoride in minerals has been liberated as hydrogen fluoride by a pyrohydrolytic method: a flux of bismuth trioxide, sodium tungstate, and vanadium pentoxide is used, and the hydrogen fluoride is absorbed into a basic solution prior to determination of the fluoride by either the fluoride-selective electrode method or the lanthanum-alizarin fluorine blue spectrophotometric method.[139] Another pyrohydrolytic method using sodium or lithium ditungstate and a titrimetric determination has also been reported.[68]

Mixtures of Halogen Anions

Microgram amounts of iodide, chloride, bromide, and thiocyanate have been determined from chromatograms obtained on paper impregnated with silver nitrate or silver oxide.[9] Mixtures of the halide ions can be analyzed by this paper chromatographic method with errors less than 20%. Chloride can be determined in samples containing iodide and bromide with a solid-state silver-membrane electrode if the bromide and iodide are removed by treatment with chromic acid.[603] Trace amounts of chloride, bromide, and iodide in a 4:1 ethanol:water medium may be titrated amperometrically with mercury(II) nitrate, using a rotating palladium electrode.[262] A reagent solution containing thorium(IV) and silver(I) nitrates was used for the potentiometric titration of iodide, fluoride, bromide, and chloride in that order.[134] Bromide and chloride have been titrated amperometrically in anhydrous acetic acid, using a solution of cadmium acetate in acetic acid as the titrant, a rotating amalgamated copper indicator electrode, and a copper anode.[354] The end points represent the successive formations of cadmium bromide and cadmium iodide. Chloride, bromide, and iodide in algae have been determined polarographically following combustion of the sample.[120] Chloride and iodide were determined by measuring the heights of their anodic waves; bromide was oxidized with hypochlorite and the height of the cathodic wave of the resulting bromate measured. Iodide and bromide in biological samples have been determined by a neutron-activation method: iodine and bromine are extracted from the irradiated sample with a solution of trioctylamine in xylene, bromine is back-extracted with a sodium nitrate solution and precipitated as silver bromide, and iodine is back-extracted with an ammoniacal solution and precipitated as silver iodide. Gamma-ray spectrometry is used to measure the radioactivity of the iodine-128 and the bromine-82.[457]

Mixtures containing perchlorate and nitrate can be analyzed by first precipitating the perchlorate as tetraphenylphosphonium perchlorate and weighing this. The nitrate is then precipitated with N-(4-chlorobenzyl)-1-naphthylmethylamine. This latter precipitate may be weighed, or may be titrated with standard base.[301] Hypochlorite, hypobromite, chlorate, and bromate ions can be titrated potentiometrically with a standard solution of potassium hexacyanoferrate(II).[187] Mixtures of chloride and bromide ions can be analyzed by precipitating as a silver chloride-bromide solid solution. The heat of fusion of this mixed crystal precipitate is determined by differential scanning calorimetry and correlated with previously prepared reference DSC traces.[77]

Titrimetric and spectrophotometric methods for the determination of chloride, hypochlorite, chlorite, chlorate, perchlorate, and chlorine dioxide have been developed by Prince.[486] Hypochlorite, chloride, and chlorine dioxide are determined spectrophotometrically based on liberation of iodine through pH control. Perchlorate is calculated from the difference in the chloride obtained by reduction of all oxygenated species to chloride and the chloride obtained by reduction of all species except the perchlorate.

V. ANIONS OF NITROGEN

Prior Literature References

The analytical chemistry of nitrogen including nitrates, nitrites, and azides has been reviewed by Clear and Roth.[138] The spectrophotometric methods for the determination of nitrate and nitrite have been discussed critically by Taras.[582]

Nitrate

Titrimetric

Nitrate can be determined by a precipitation titration with diphenylthallium(III) sulfate; the end point may be located amperometrically in titrations of 0.005 to 0.02 M solutions, or potentiometrically, using a nitrate-selective electrode.[165,166] Mixtures of sulfuric and nitric acids may be analyzed for nitrate by passing them through a column of a strongly acidic cation-exchange resin in its lead form; sulfate is retained as $PbSO_4$, and the effluent contains an amount of lead equivalent (1 Pb(II) = $2NO_3^-$) to that of the nitrate present. The lead(II) is titrated by EDTA using Xylenol Orange as indicator.[520] A photometric titration method for nitrate has been proposed in which the nitrate is reduced to ammonium ion in acidic solution by chromium(II); in back-titrating the excess reagent with standard iodate, the absorbance is monitored at 850 nm.[235]

Opticometric

Atomic absorption spectrometry – Nitrate has been determined indirectly by extracting the ion-association complex Cu(2,9-dimethyl-1,10-phenanthroline)$_2$$NO_3$ into methyl isobutyl ketone and determining the copper by atomic absorption.[363]

Spectrophotometry – Most spectrophotometric methods for the determination of nitrate are based on (1) the nitration of an organic compound, (2) the oxidation of an organic compound, (3) the reduction of the nitrate to either nitrite or ammonia, or (4) the formation of an ion-association complex. Recently, the characteristic high ultraviolet absorptivity of the nitrate ion at 203 nm has been used in the spectrophotometric determination of nitrate.[30,224,288] The nitrate content in soil solutions was determined by measurement of the absorbance of nitrate ion at 210 nm.[130] The method was useful in determining 0.5 to 10 ppm of nitrate nitrogen. Sulfamic acid eliminates the interference of nitrite ion. Another ultraviolet spectrophotometric method involves the formation of nitrotoluene and extraction into toluene.[73] This method is suitable for determining 1 to 28 ppm of nitrate.

Nitrate has been determined spectrophotometrically by the brucine method; the range of applicability may be either 0 to 5 or 0.1 to 0.5 μg of nitrate nitrogen per gram of sulfuric acid, depending on the acidity employed. At low acid concentrations nitrite can be determined in the presence of nitrate by this brucine method.[191] The brucine method for nitrate has been studied by Jenkins and Medskar,[312] who found the addition of a high concentration of chloride to be helpful in obtaining reproducible results. The method was applied to the determination of nitrate in water. Hartley and Asai[259] have investigated the spectrophotometric method for the determination of nitrate using 2,6-xylenol and found conformity to Beer's law at 322 nm over the range of nitrate concentrations from 2 to 30 ppm. Silver sulfate was added to remove the interfering chloride ions by precipitation as silver chloride. Nitrate in soil has been determined photometrically using chromotropic acid in 70% sulfuric acid.[47] The working range was 1 to 10 ppm of nitrate. Traces (0.5 to 2 ppm) of nitrate and diphenylamine react to give a blue diphenylbenzidine product which is apparently stabilized by the presence of *p*-diaminodiphenylsulphone.[576]

Nitrate reacts with 1-aminopyrine to form a colored species exhibiting maximum absorbance at 456 nm and having a molar absorptivity reported to be 9.4 x 10^4 $l\text{-}mol^{-1}\text{-}cm^{-1}$.[526] The system does not conform to Beer's law, especially at lower concentrations. Nitrite can also be determined by this method.

The optimum conditions for reducing nitrate to nitrite with hydrazine sulfate have been investigated. 4-Aminoacetophenone and azulene, 8-anilino-1-naphthalene sulfuric acid, have been suggested as substitutes for N-(1-naphthyl)-ethylenediamine dihydrochloride in the diazotizing-coupling reagent.[525] A mixture of copper(II) sulfate, ammonium chloride, and dibasic sodium phosphate has been used to catalyze the reduction nitrate to nitrite by powdered cadmium in the presence of considerable chloride,[365] and the nitrite thus obtained has been determined by the Griess method. An automated method for the determination of nitrate in water is based on the reduction of nitrate to nitrite with hydrazine sulfate. The difference between the results obtained by classical diazotization-coupling method for a sample subjected to the reduction and for an untreated sample gives the nitrite equivalent to the nitrate in sample. This method serves to determine nitrate, in concentrations ranging from 0.05 to 10 μg nitrogen/ml, in 20 samples per hour.[322]

Nitrate has been determined indirectly by extracting the ion-association complex, bis(2,9-dimethyl-1,10-phenanthroline)copper(I) nitrate, into methyl isobutyl ketone and measuring the absorbance at 456 nm. This method is applicable to concentrations of nitrite between 0.5 and 4 ppm.[640,641] In the presence of silver acetate, tetraphenylphosphonium chloride forms an ion-association complex with nitrate which is extractable with chloroform. The ultraviolet absorbance of this extracted complex is measured.[113] The optimum concentration range is about 6 to 30 ppm of nitrate. The inhibiting effect of nitrate ion on the formation of the rhenium-α-furildioxime complex in the presence of tin(II) chloride has served as the basis of a spectrophotometric method for the determination of 3 to 35 ppm of nitrate.[78]

Spectrofluorometry – Sawicki[524] reduced nitrate to nitrite with hydrazine sulfate and then determined the nitrite using 2,3-diaminonaphthalene. This method is suitable for the determination of 0.1 to 1 ppm of nitrogen as nitrate. The fact that nitrate decreases the fluorescence of fluorescein by forming a nonfluorescent product is the basis of a fluorometric method for determining 0.01 to 0.1 ppm of nitrate.[37]

Electrometric

Potentiometry – The development of the nitrate-selective electrode has been the most significant development in methodology for the determination of nitrate. In this liquid-membrane electrode, a nickel(II)-1,10-phenanthroline derivative serves as the exchange site for the nitrate ion and the anion-exchange rate is the potential-determining factor. This electrode can be used over the range of pH-values from 2 to 12 but is subject to interferences from certain anions, including nitrite, perchlorate, iodide, bromide, sulfide, cyanide, acetate, and carbonate.[382] The range of utility of most nitrate-selective electrodes is from about 10^{-1} to 10^{-5} *M*. The performance of the liquid-membrane nitrate-selective electrode has been evaluated by Potterton and Shults.[485] The nitrate-selective electrode was found to give a potential varying linearly with the logarithm of the concentration of nitrate over the range from 10^{-1} to 10^{-4} *M*, but the value of $\Delta E/\Delta \log[NO_3^-]$ was 56.6 mV instead of the theoretical value of 59.16 mV at 25°C. The use of standards whose activities bracketed that of the unknown solution resulted in optimum accuracy and precision. Davies et al. described the construction and performance of two nitrate-selective electrodes based on poly(vinyl chloride) membranes containing the nitrate-ion exchangers employed in the Corning and Orion electrodes.[161] The poly(vinyl chloride) membrane electrodes are said to have lifetimes longer than, and selectivity constants very similar to, those of the commercially available nitrate electrodes. A nitrate membrane electrode prepared by polymerizing a mixture of phenol, formaldehyde, ammonia, and nickel nitrate to form a film for mounting has been described by Dobbelstein and Diehl.[169] The electrode gave a response of 60 mV per pNO_3 and 30 mV per pH unit. This electrode also responds to other univalent anions but not to sulfate and other multivalent anions or to cations other than hydrogen.

A nitrate-selective electrode has been used to determine nitrate in soils[97] and is said to be superior to the photometric brucine method.[461] The direct potentiometric titration of nitrate in soil extracts using the nitrate-selective electrode has been studied critically by Oien and Selmer-Oslen.[458] They used a 0.02 *N* copper(II) sulfate solution as extracting agent and compared the potentiometric method with the 2,4-xylenol and automated Griess methods. The three methods were in good agreement but some difficulties were encountered with the potentiometric method when the nitrate concentration was less than 2 ppm because of drift and poor precision. A comparison of the ion-selective electrode method and the Devarda reduction method for nitrate showed that saline waters and soils gave lower nitrate values by the potentiometric method because of salt interference and that nitrate values were higher in plant samples because of hydrolysis of some organonitrogen compounds.[427] The nitrate-selective electrode has been found satisfactory in the routine determination of nitrate in water.[329] The nitrate-nitrogen values in ground and surface waters were lower than those obtained by the phenoldisulfonic acid method and the steam-distillation method of Bremner and Keeney.[98] Nitrate in the aqueous extracts of dried plant tissues has been determined, at concentrations from 1 to 50 ppm, by Paul and Carlson.[470] Cation-exchange resins in the aluminum form and in the silver form eliminate interferences due to bicarbonate and chloride, respectively. The direct potentiometric method gave values comparing favorably with those obtained by the classical phenoldisulfonic acid-spectrophotometric method. The nitrate-selective membrane has been used to determine nitric acid in oleum.[503]

Voltammetry – Nitrate ion in an aqueous sulfuric acid-acetic acid solution reacts with 2,6-xylenol to produce 4-nitro-2,6-xylenol which is reducible at the dropping mercury electrode, giving a wave whose half-wave potential is −0.27 V vs the mercury-mercury(I) sulfate electrode.[260] A plot of the diffusion current against the concentration of nitrate is linear over the range of concentrations from 10^{-5} to 10^{-3} *M*. In anhydrous acetic acid solutions, nitrate has been titrated amperometrically with barium acetate using an amalgamated copper or silver indicator electrode and lithium chloride as the supporting electrolyte.[353]

Gasometric

Formic acid reduces nitrate: 2 mol of nitrate liberate 1 mol of nitrous oxide and 4 mol of carbon dioxide. The nitrous oxide can be determined by a gasometric method. Alternatively, the carbon dioxide can be isolated, absorbed, and weighed. Amide, azo, nitro, amine, oxime groups and ammonium ions give no gaseous products.[36] The reduction of nitrate with urea to generate nitrous oxide is the basis of a microgasometric method for nitrate.[272] In determining nitrogen in inorganic nitrates by the Dumas method, Ketchum found that mixing anthracene with the nitrate salt resulted in very high recoveries.[331]

Nitrite

Titrimetric

In order to circumvent the disadvantages of the permanganate oxidation of nitrite, which include the low rate of reaction and the decomposition and air-oxidation of the nitrous acid, Agterdenbos[6] has recommended oxidation with chloramine T (the sodium salt of *p*-toluenesulfochloramide). An excess of chloramine T is added to convert the nitrite to nitrate, and the excess is determined iodometrically. Copper(II) and ammonium ions interfere but can be removed by a cation-exchange resin column with only a slight error due to oxidation of the nitrite by air. Nitrite can be titrated photometrically with 3,3'-diaminobenzidine at pH 4.5 to 7. The absorbance is measured at 350 nm, where the yellow 1:1 reaction product has a molar absorptivity of 3.5×10^3. The colored product can also be extracted into *n*-butanol and nitrite determined by measuring the absorbance of the butanol solution at an appropriate wavelength.[386]

Opticometric

Atomic absorption spectrometry – Nitrite can be determined by oxidizing it to nitrate with cerium(IV) or permanganate, extracting the bis(2,9-dimethyl-1,10-phenanthroline) copper(I) nitrate ion pair into methyl isobutyl ketone, and determining the copper content of the extract by atomic absorption spectrometry.[292]

Spectrophotometry – A modified method based on a double extraction procedure of the azo dye produced by the diazotization of sulfanilamide followed by coupling with *N*-(1-naphthyl)ethylenediamine dihydrochloride has been developed. A neutral yellow-pink species is extractable into chloroform at pH-values between 8.5 and 10.5, and a retrograde extraction into aqueous hydrochloric acid gives a red species whose absorbance is measured at 543 nm. A 100-fold increase of sensitivity was obtained by using 1000 ml of sample, 100 ml of chloroform, and 10 ml of hydrochloric acid.[404] Nishimura, Matsumaga, and Matsuda[450] reported that the positively charged azo dye can react with the negatively charged *n*-dodecylbenzenesulfonate ion to give a complex extractable into carbon tetrachloride. In the application of this extraction-photometric method to the determination of nitrite in sea water, back extraction of the dye into an acetone-hydrochloric acid medium has been recommended to eliminate the difficulty encountered due to turbidity of the carbon tetrachloride layer caused by the high salt concentration.[416] In determining less than 0.3 ppm of nitrite Wada and Hattori[611] concentrated the azo dye on a Dowex 1 x 8 column and then eluted with a small volume of 60% acetic acid. 8-Aminoquinoline first reacts with nitrous acid to form a diazonium ion, which then couples with excess 8-aminoquinoline to give an azo dye which is extractable into *n*-heptanol. This spectrophotometric method is applicable to determine nitrite over the range of concentrations from 0.25 to 4 ppm. The molar absorptivity is 1.43×10^4 $l\text{-}mol^{-1}\text{-}cm^{-1}$.[203] The use of Cleve's acid, 1-naphthylamine-7-sulfonic acid, instead of 1-naphthylamine as the coupling agent following the diazotization of sulfanilic acid in the spectrophotometric determination of nitrite has been investigated and found to be satisfactory.[109]

Two moles of nitrite react with 1 mol of *p*-diaminodiphenylsulfone and 1 mol of diphenylamine to give an azo dye; this reaction is applicable to the spectrophotometric determination of nitrite at concentrations from 0.1 to 2.5 ppm at pH 1.8 or from 0.22 to 0.4 ppm at pH 0.1.[577]

An ultraviolet spectrophotometric method based on the measurement of the absorbance of 4-nitrosoantipyrine has been proposed.[471,615] 2,3-Diamino-naphthalene reacts with nitrite to form 2,3-naphthotriazole, which can be extracted with tetrachloroethylene and determined spectrophotometrically or fluorometrically.[623] 1,2,3-*Tris*(2-diethylaminoethoxy)benzene hydrochloride has been proposed as a colorimetric reagent for nitrite.[456] Nitrite can be determined spectrophotometrically in solutions of pH less than 5 by measuring the absorbance of nitrous acid at 357 nm. If nitrate is also present, a simultaneous method has been proposed based on the measurement of absorbance at 302 nm and 355 nm.[620] The molar absorptivity of nitrite is 23.3 at 355 nm and 9.12 at 302 nm. A method for the spectrophotometric determination of nitrate and nitrite in water and soil extracts has been automated;[280] it involves the reduction of nitrate to nitrite with copperized cadmium followed by the Griess method using sulfanilamide and N-1-naphthylethylenediamine.

Electrometric

Voltammetry – In a citric acid-citrate buffer of pH 2 nitrite can be determined polarographically, the diffusion current being measured at −1.2 V vs S.C.E.[21] Mixtures of nitrite and nitrate can be analyzed by using sodium azide to destroy the nitrite in another sample solution, adding uranyl ion as carrier and using the polarographic method for nitrate developed by Kolthoff.[350]

Coulometry – Nitrite has been determined by a coulometric titration method in which manganese(III) is pregenerated and the excess manganese(III) remaining after addition of the nitrite is back-titrated with electrogenerated iron(II).[103] The end point is detected potentiometrically.

Gasometric

Nitrite is reduced by anhydrous formic acid to give 2 mol of nitrous oxide and 6 mol of carbon dioxide from 7 mol of nitrite. The nitrous oxide can be isolated and measured volumetrically, or the carbon dioxide can be isolated, absorbed on anhydrone, and weighed.[36]

Hyponitrite

Hyponitrite, $N_2O_2^{2-}$, gives an ultraviolet absorbance maximum at 247 nm, where its molar absorptivity is 6.55 (± 0.2) x 10^3 l-mol^{-1}-cm^{-1} Beer's law was obeyed up to a hyponitrite concentration of 1.5 x 10^{-4} *M*.[482]

Mixtures of Nitrate and Nitrite

Nitrate and nitrite in mixtures have been determined by the nitrate-selective electrode by measuring the potential of the electrode first in the sample solution and then after oxidizing the nitrite to nitrate with permanganate. An equation was developed to calculate the initial concentrations of nitrate and nitrite when the recommended procedure is followed.[431] Mixtures of nitrate and nitrite have been analyzed by oxidizing nitrite to nitrate with permanganate and determining the volume of nitric oxide generated by the reaction of nitrate with sulfuric acid and mercury. The nitrite is then determined in a separate sample by reducing with sulfamic acid and measuring the resulting nitrogen.[605] Nitrite and nitrate have been determined by a spectrophotometric method in which nitrite is determined by a diazotization of the 4-aminophenyl(trimethyl)-ammonium ion and then coupling with N,N-dimethyl-1-naphthylamine. In another aliquot the diazonium cation formed from the nitrite is removed by a cation exchanger and the nitrate is reduced by zinc in an ammoniacal solution of pH 10.8 in the presence of manganese(II) hydroxide to give nitrite, which is determined as previously indicated.[369] The nitrite and nitrate contents of a mixture of alkali metal nitrites and nitrates have been determined by first titrating the nitrite with a standard acid solution of perchloric acid in methanol and then titrating both nitrite and nitrate in an acetic acid-acetic anhydride medium.[356]

VI. ANIONS OF PHOSPHORUS

Prior Literature References

The analytical methods for determining phosphorus have been reviewed in depth by Rieman and Beukeukamp.[504] Halmann's *Analytical Chemistry of Phosphorus Compounds* contains representative procedures for the gravimetric, titrimetric, and spectrophotometric determination of orthophosphate and suggestions for converting pyrophosphate, phosphite, hypophosphite, tripolyphosphate, and metaphosphate to orthophosphate.[84]

Phosphate

Gravimetric

The classical gravimetric methods based on the precipitation of magnesium ammonium phosphate, igniting, and weighing of the ignited magnesium pyrophosphate, and on the precipitation of ammonium molybdophosphate and the weighing of either this or the $P_2O_5 \cdot 24MoO_3$ obtained from it on ignition, are being replaced by the newer gravimetric method based on the precipitation of quinolinium molybdophosphate. Perrin[472] developed a gravimetric method in which the precipitate may either be dried at 250°C and weighed as $(C_9H_8N)_3PMo_{12}O_{40}$, or ignited at 550°C and weighed as $P_2O_5 \cdot 24MoO_3$. In general, the precipitation of quinolinium molybdophosphate is subject to fewer interferences than that of either ammonium molybdophosphate or magnesium ammonium phosphate. This gravimetric method has been studied rather extensively.[188, 622] Wendlandt and Hoffman[616] have made a thermoanalytical study of the quinolinium molybdophosphate precipitate and Lench[378] has used this method in determining phosphorus in iron and steel. The use of centrifugation to isolate the quinolinium molybdophosphate precipitate in the AOAC gravimetric method was found to decrease the amounts of reagents needed and effect a considerable saving in time.[423] Phosphate, after conversion to molybdophosphate, reacts with *N,N,N′,N′*-tetrakis(2-hydroxypropyl)ethylenediammonium diperchlorate to give a very insoluble precipitate $[C_{14}H_{32}O_4N_2H_2]_3\,(PMo_{12}O_{40})_2$, which can be dried at 110°C.[33] A gravimetric method for orthophosphate based on the precipitation and weighing of $Be_3(PO_4)_2$ has been reported.[567]

Titrimetric

A titrimetric method based on the total acidity of quinolinium molybdophosphate was developed by Wilson[628] who used the method to determine phosphate in fertilizers. The quinolinium ion is a stronger acid ($pK_a = 4.9$) than the ammonium ion ($pK_a = 9.2$) so that quinoline does not interfere in the titration. The following equation illustrates the stoichiometry:

$$(C_9H_8N)_3PMo_{12}O_{40} + 26\,OH^- \rightarrow HPO_4^{2-} + 12\,MoO_4^{2-} + 14H_2O + 3\,C_9H_7N$$

A mixture of phenolphthalein and thymol blue (2:3) is a suitable indicator. Ammonium salts interfere and must be destroyed by a preliminary treatment with sodium hypobromite. High concentrations of sulfate interfere so that Kjeldahl digestions are inapplicable. This method is considered to be superior to the total acidity method based on the ammonium molybdophosphate precipitate. Phosphate has been separated from silicate by precipitation as ammonium molybdophosphate and determined by the total acidity titration method.[406] The silicate was then determined gravimetrically by the quinolinium method. Dihydrogen phosphate can be titrated potentiometrically in either of two ways: in methanol with standard base, or in methanol-ethylene glycol with standard acid. By titrations in non-aqueous media it is also possible to differentiate monohydrogen phosphate and orthophosphate ions.[355] Phosphate can be titrated with a solution containing lanthanum nitrate, ammonia, and ammonium nitrate. At the end point the original fixed pH is reached.[556]

A titrimetric method employing chemical amplification for the determination of microgram quantities of phosphate is based on the formation of 12-molybdophosphoric acid, extraction of the heteropoly acid into isobutyl acetate to separate it from excess molybdate, a retrograde extraction into aqueous solution, reduction of the molybdenum to the quinquevalent state by a silver reductor, and titration of molybdenum(V) with cerium(IV).[340] A successive chemical amplification method for the determination of traces of phosphate has been suggested by Belcher and Uden.[64] In the first amplification step 12-molybdophosphoric acid is formed and extracted into isobutyl acetate. Equilibration of the organic extract with an ammoniacal solution results in the decomposition of the heteropoly complex and transfer of the molybdate to the aqueous phase. The molybdate is then precipitated as $MoO_2(C_9H_6ON)_2$ by 8-quinolinol. The precipitate is dissolved in hot phosphoric acid and the 8-quinolinol equivalent to the molybdenum is brominated with a standard bromate solution; the excess bromate is determined iodometrically. Another chemical amplification method for determining phosphate is based on (1) precipitating zinc ammonium phosphate and liberating hydrogen ion, (2) treatment with excess solid potassium iodide and potassium iodate, liberating iodine, and (3) titration of the iodine with a standard thiosulfate solution.[220] The method has been applied to the microdetermination of phosphorus in organic compounds.

Another titrimetric method for phosphate is based on the precipitation of zirconium phosphate by adding excess standard zirconium(IV) solution and back-titrating this excess with EDTA.[551] Since the stoichiometry is 1:1, the precipitate is believed to be $ZrO(HPO_4)$. Orthophosphate (10 to 50 μg of phosphorus) has been determined by a microtitrimetric method: excess standard thorium nitrate solution is added, and the excess is back-titrated with EDTA, using Xylenol Orange as indicator.[341] Similarly, phosphate has been determined by using lanthanum(III) as precipitant and determining the excess lanthanum by back-titrating with EDTA.[647] Orthophosphate can be titrated with cerium(III), at pH-values between 7.0 and 9.5 and at temperatures between 60° and 90°C, using Eriochrome Black T indicator. Cerium(III) phosphate precipitates during the titration, and the first excess of cerium(III) reacts with the blue indicator species to give a red species.[583] Polyphosphate, sulfate, aluminum(III), and iron(III) cause some interference. Traces of phosphate in solutions containing 40% acetone and having pH-values between 1.2 and 3 can be titrated photometrically with a standard molybdate.[11] Phosphate has been titrated potentiometrically with lead perchlorate, using a lead-ion-selective electrode.[541]

Opticometric

Atomic absorption spectrometry – Phosphate has been determined by an indirect method in which the molybdenum equivalent to the phosphorus in 12-molybdophosphoric acid is determined by atomic absorption spectrometry. One AAS procedure involves the extraction of molybdophosphoric acid into 2-octanol, aspiration of the organic extract into an air-acetylene flame, and measurement of the absorbance at the wavelength of the molybdenum line.[649] The 2-octanol may be replaced by *n*-butyl acetate and the air-acetylene flame by a nitrous oxide-acetylene flame.[362] Phosphate and silicate[300, 339] and phosphate, silicate, and arsenate[492] have been determined sequentially by the selective extraction of molybdoheteropoly acids and atomic absorption spectrometric measurement. The optimum concentration range is approximately 0.1 to 1.2 ppm of phosphorus.

Flame photometry – By using a cooled, shielded burner which prevents the entrainment of air and provides a fuel-rich air-hydrogen flame, an intense molecular emission of the HPO species is produced at 526.2 nm when phosphate solutions are aspirated into the flame. The detection limit is about 1 ppm of phosphorus. A linear calibration graph is obtained for up to 300 ppm of phosphorus when phosphoric acid solutions are aspirated, but departures from linearity were observed for potassium dihydrogen phosphate and sodium pyrophosphate solutions.[100] Phosphate in detergents has been determined by measuring the intensity of emission for the HPO band at 526.2 nm following an ion-exchange step to remove sodium and other interfering cations.[573] The phosphate content of detergents has also been determined by a similar flame photometric method, in which a cool hydrogen-nitrogen diffusion flame is used.[183] The flame photometric method is reported to give a linear calibration plot up to 1000 ppm of phosphorus using an oxyhydrogen flame.[162]

A flame emission photometric method for the determination of phosphate requires a constant total molar concentration of barium and calcium ions for a given phosphate concentration but allows different ratios of calcium to barium. The calcium emission at 630 nm is proportional to the concentration of calcium present, and the proportionality constant depends on the concentration of phosphate.[575]

Spectrophotometry – A number of spectrophotometric methods based on the formation of molybdophosphoric acid have been developed. One common approach is to form a dye-molybdophosphoric acid complex and extract it into an oxygenated solvent that is immiscible with water, such as butyl acetate.[39,589] Another is to use a retrograde extraction in which the molybdate equivalent to the phosphorus in the 12-molybdophosphoric acid is determined. Indirect methods based on the use of Acid Chrome Violet or Chrome Black Special,[32] phenylfluorone,[249] 2-amino-4-chlorobenzenethiol,[168] and carminic acid[375] have been reported. These indirect methods are applicable to the determination of 0.02 to 0.3 ppm of phosphorus.

Malachite Green reacts with molybdophosphoric acid to form a blue-green salt that is stabilized by poly(vinyl alcohol). The excess Malachite Green is decolorized by sulfuric acid. The optimum concentration of phosphate is about 1.1 to 1.2 ppm.[12] Phosphate, as molybdophosphoric acid, reacts with bis-(4-dimethyl-aminophenylantipyryl-carbinol) to give a blue complex containing three moles of reagent per mole of phosphate and having a molar absorptivity of 5.8×10^4 $l\text{-mol}^{-1}\text{-cm}^{-1}$ at 620 nm. Gelatin is used to stabilize the complex.[650] Traces of phosphate can be separated from large amounts of silicate and appreciable amounts of arsenate by extracting a molybdophosphoric acid with propyl acetate, isobutyl acetate, or butyl acetate at pH 0.2 to 0.5.[39,469] In investigating the formation of molybdophosphoric acid in solutions containing water together with 30 to 50% of a water-miscible solvent such as dimethyl-formamide, acetone, ethanol, or dioxane, it was found that the molar absorptivities in the ultraviolet region are larger in these solvent mixtures than in aqueous solution.[571] Molybdophosphoric acid can be extracted into propylene carbonate and the absorbance of the yellow extract measured at 308 nm. The optimum concentration range is 0.4 to 1.2 ppm of phosphorus.[309]

12-Molybdophosphoric acid has been reduced to heteropoly blue, then extracted with oxygenated solvents and determined by near-infrared absorbance measurements.[309,345,469] Reduced molybdophosphoric acid has been extracted with high molecular weight amines and non-oxygenated solvent systems[346] and with oxygenated solvents after complexation with safranine.[570]

Nitrate interferes seriously in the spectrophotometric heteropoly blue method for determining orthophosphate. Although several other procedures have been developed to avoid the interference of nitrate, the reduction of nitrate to ammonia by metallic aluminum in a sodium hydroxide solution is recommended.[174] If arsenic(V) is reduced to arsenic(III) with pyrosulfite ($Na_2S_2O_5$), the interference due to arsenic in the heteropoly blue method for phosphate is markedly reduced.[178] The ORNL GeMSAEC Photometric Analyzer has been used to determine phosphate by the heteropoly blue method; as many as 13 samples can be run simultaneously.[141]

The extraction of molybdovanadophosphoric acid into 1-pentanol is the basis of an ultraviolet spectrophotometric method. The optimum concentration range is 0.2 to 1.1 ppm of phosphorus when absorbance measurements are made at 308 nm.[308] The molybdovanadophosphoric acid method has been automated for the determination of phosphorus in plant tissue.[51] A kinetic-photometric method for the determination of micro amounts of phosphate based on the catalytic effect of phosphate on the reduction of molybdate with tin(II) chloride has been described.[357] The catalytic effect of phosphate on the reduction of molybdate to molybdenum blue by ascorbic acid has been studied and the reaction found to proceed in three steps. From measurements of the rate of the third step a kinetic-photometric method has been developed for the determination of phosphate corresponding to 0.02 to 0.8 μg of phosphorus/ml.[644] The catalytic effects of germanate and phosphate ions on the oxidation of iodide by isopolymolybdic acids depend on acidity. At pH 0.5 phosphate catalyzes the oxidation while the effect of germanate is negligible. Thus, a kinetic-photometric method was developed. By control of pH at 0.6 and at 0.9, a simultaneous kinetic photometric method for the determination of germanate and phosphate in their mixtures was also suggested.[10]

Spectrofluorometry – Small amounts (0.02 to 1.2 μg) of phosphorus as orthophosphate have been determined spectrofluorometrically by precipitating quinine molybdophosphate, removing the excess quinine by washing, dissolving the precipitate in a 9:1 mixture of acetone with 0.5 *M* aqueous sulfuric acid, and measuring the fluorescence of the resulting solution at 445 nm using an excitation of 352 nm.[334] Large amounts of silicate do not interfere and appreciable amounts of arsenic(III) and tungsten(VI) can be tolerated. Another somewhat similar approach is based on the formation of a fluorescent Rhodamine B-molybdophosphate complex and its extraction into a chloroform-butanol mixture.[335] An indirect method based on the quenching by orthophosphate of the fluorescence of an aluminum-morin complex has also been reported.[370]

X-ray spectrometry – X-ray emission spectrometry[379] has also been used to determine phosphorus.

Chromatographic

Gas chromatography – Trimethylsilyl phosphate has been formed and detected by gas chromatography.[116,222,264-267] Butts and Rainey[117] have studied the trimethylsilyl derivatives of phosphate and phosphite by gas chromatography and mass spectrometry. By using the ammonium salts and bis(trimethylsilyl)trifluoroacetamide, TMS derivatives of phosphite and phosphate were formed and were eluted on a SE-30 stationary phase. The TMS phosphite derivative is eluted before the phosphate derivative. The ammonium salts of dihydrogen phosphate and monohydrogen phosphate give the same derivative. The use of a strong-acid cation exchanger in its ammonium-ion form is recommended for conversion of sodium or potassium salts. Approximately 1 to 3 mg of phosphorus as an ammonium phosphate salt is derivatized.

A new approach to the determination of phosphate has been reported in which phosphate in aqueous solution is first extracted into an organic solvent mixture immiscible with water with the aid of a quaternary ammonium salt. The phosphate in the organic extract is then silylated with *N,O*-bis(trimethylsilyl)trifluoroacetamide containing 1% trimethylchlorosilane. Injection of an aliquot of this derivatized phosphate into a gas chromatograph equipped with a flame photometric detector gives peak areas proportional to concentrations of phosphate in the original aqueous sample solution between 0.2 and 1 ppm of PO_4.[415] The superior sensitivity of the flame photometric detector for phosphorus and sulfur indicates future developments of possible applicability in the ppb range. The inherent possibility of sequential determinations of anions by the derivatization-GLC method is especially attractive.

Radiometric

Phosphate has been determined radiochemically by forming tungstomolybdophosphoric acid using tungsten-185, extracting the heteropoly acid into 2-octanone, and then counting the residue obtained after evaporation of the organic solvent.[251] Neutron activation of phosphorus and the measurement of the P^{32} beta emitter is a well-known modern method.[76,94,238]

Hexafluorophosphate

Hexafluorophosphate (or hexafluoroarsenate) can be titrated with tetraphenylarsonium hydroxide by a partition-titration technique employing 1,2-dichloroethane as the water-immiscible organic solvent and permanganate as the indicator. The transfer of the permanganate to the organic phase occurs at the end point.[54] Hexafluorophosphate has also been determined by an amperometric titration using tetraphenylarsonium chloride as titrant.[3] Hexafluorophosphate reacts with *tris*(1,10-phenanthroline)iron(II) to give an ion-association complex which is extractable into *n*-butyronitrile. The absorbance of the extract is measured at 505 nm.[25]

Hypophosphite and Phosphite

Hypophosphite can be oxidized by dichromate in large excess to give orthophosphate at sulfuric acid concentrations above 7.5 *M*. A rapid titrimetric method is based on the back-titration of the excess dichromate with a standard iron(II) solution.[495] Hypophosphite ($PO_2{}^{3-}$) and phosphite ($PO_3{}^{3-}$) have been determined by a differential potentiometric titration method using a Pt-C electrode system. The sample is treated with excess copper(II) and the copper(I) resulting from reduction by hypophosphite is titrated with a standard oxidant, 0.1*N* cerium(IV) sulfate. After addition of iron(III) sulfate and heating, the iron(II) equivalent to the phosphite is titrated with the same oxidant.[453] Two-dimensional TLC, using first an acidic solvent and then a basic one, has been used to separate hypophosphorus, phosphorus, monophosphoric, and hexametaphosphoric acids.[604]

Pyrophosphate

Pyrophosphate is precipitated by *cis*-dichlorobis(ethylenediamine)cobalt(III) chloride in basic aqueous solution (pH 10 to 12). The formula of the precipitate is $NaCo(C_2H_4N_2)_2P_2O_7$. This gravimetric method is applicable to the determination of 20 to 80 mg of pyrophosphate.[545] Pyrophosphate (diphosphate) has been determined spectrophotometrically on the basis of the decrease in the absorbance of the iron(III) thiocyanate system resulting from formation of iron(III) pyrophosphate.[356]

VII. ANIONS OF SELENIUM AND TELLURIUM

Prior Literature References

The analytical chemistry of selenium and tellurium has been reviewed critically by Green and Turley.[231] Murashova and Sushkova[435] have reviewed photometric methods for the determination of selenium and tellurium, particularly those involving liquid-liquid extractions.

Selenite and Tellurite

Titrimetric

Mixtures of selenium(IV) and tellurium(IV) can be assayed by a differential titrimetric method. The sum of selenium and tellurium is first determined by adding an excess of permanganate and back-titrating the excess with a standard solution of iron(II), using ferroin as indicator. After further acidification with sulfuric acid and addition of osmium tetroxide as catalyst, excess standard arsenite is added, and the excess is determined by titration with permanganate. This second titration gives the amount of tellurium present.[439] Selenium(IV) in a sulfuric acid-condensed phosphoric acid solution has been titrated with permanganate using the photometric method of end-point detection.[437]

Opticometric

Atomic absorption spectrometry – A nitrogen-shielded air-acetylene flame[338] and a nitrogen-shielded nitrous oxide-acetylene flame[336] have been found to give a low flame background absorbance and low noise in measuring the absorbance due to selenium at 196.0 nm. Sensitivities of 1.3 ppm for a 10-cm air-acetylene flame and 6.5 ppm for a 5-cm nitrous oxide-acetylene flame have been reported. A slightly better sensitivity is achieved by the use of an argon-hydrogen flame.[336] Tellurium in antimony-gallium semiconductor alloys has been converted to the liquid chloride by treatment with chlorine gas and nebulized in a heated spray chamber to give a detection limit of 0.02 ppm.[600] Selenium in sulfur has been determined by using an air-acetylene flame and applying a background correction.[440] An indirect atomic absorption spectrometric method for the determination of selenium involves the reaction of selenite with 2,3-diaminonaphthalene to give naphtho[2,3-d]-2-selena-1,3-diazole, which then reacts with palladium(II) to give a complex extractable into chloroform. Extraction with chloroform prior to the reaction with palladium(II) removes the excess 2,3-diaminonaphthalene remaining in the aqueous phase and thereby prevents it from interfering by reacting with the palladium(II). The absorbance of palladium at 244.8 nm is proportional to the selenium concentration. A sensitivity of 0.017 ppm was reported.[372] Most AAS methods for tellurium involve an extraction in order to minimize the background absorbance at the 214.3 nm tellurium line.[411,516,633] Barnett and Kahn[45] have described the use of a deuterium background corrector to compensate for the background automatically, and have applied their procedure to the determination of tellurium in steel.

Flame photometry – A flame photometric method for tellurium, employing the doublet at 238 nm, has been suggested by Dean and Simms[164] but is not very sensitive.

Spectrophotometry – Cheng[131] has proposed a unique chemical amplification method for increasing the sensitivity of the spectrophotometric determination of selenium by the 3,3′-diaminobenzidine method. The multiplication involves the formation and separation of 5-(3,4-diaminophenyl)-2,1,3-benzoselenadiazole and its separation by extraction, a retrograde extraction in which the piazselenol is transferred to an acidic aqueous solution, the addition of selenious acid to the aqueous phase to form the dipiazselenol, which is then extracted into toluene, and finally the evaporation of the toluene and decomposition of the dipiazselenol by digestion with aqua regia and nitrate. The absorbance of the toluene extract of the dipiazselenol may be measured at 353 nm.[624] Selenite reacts with 2,3-diaminonaphthalene to give a piazselenol which can be extracted into toluene and the absorbance of the extract measured at 380 nm.[397] This spectrophotometric method can be used to determine up to 10 μg of selenium. Digestion of plant samples by a controlled wet-oxidation procedure using a silicone bath was used prior to the colorimetric determination of selenium by the 2,3-diaminonaphthalene method.[250]

Selenite and 1-pyrrolidinedithioate form a complex which is extractable into chloroform and has an absorbance maximum at 303 nm. The optimum concentration range is 2 to 8 ppm of selenium. A number of cations, tellurite, molybdate, and vanadate interfere.[392] An indirect spectrophotometric method for the determination of selenium has been developed in which the selenite is reduced in acidic solution by iodide and the liberated iodine is used to decolorize Brilliant Green or Malachite Green. The method is applicable to the determination of selenite over the range of concentrations from 0.002 to 0.8 μg/ml.[494] Selenious acid oxidizes phenylhydrazine *p*-sulfonic acid to a diazonium cation, which when coupled with 1-naphthylamine gives an azo dye having maximum absorbance at 520 nm. Conformity to Beer's law was observed over the range of concentrations from 0.1 to 1.6 ppm of selenium.[343] Ions that either reduce selenious acid to selenium (e.g., tin(II), arsenic(III), iodide, and sulfite) or oxidize the phenylhydrazine *p*-sulfonic acid (e.g., iron(III), molybdate, and chlorate) interfere. Appreciable amounts of tellurium(VI) and tellurium(IV) can be tolerated. Selenite or tellurite ions can be oxidized by permanganate, and the excess permanganate can be determined photometrically.[438] Chloroselenite or chloroselenate reacts with cyclohexanone in 7 *M* hydrochloric acid solution to form complexes that exhibit maximum absorbance at 345 nm.[153] Tellurite reacts with 1-pyrrolidinecarbodithioate to form a 1:4 complex extractable into chloroform. The absorbance is measured at 257 nm, with 0.1 to 1.4 μg/ml being the recommended concentration.[393] Tellurite reacts with thiourea to form a complex which is extracted into tributylphosphate in the presence of thiocyanate ion. Over the range of 1 to 75 ppm of tellurium a linear relationship between absorbance and concentration was observed when the absorbance was measured at 400 nm.[285] A higher sensitivity is obtainable by measuring the absorbance at 380 nm.

Fluorometry – Selenite and 2,3-diaminonaphthalene react to give a piazselenol that is extractable into toluene. The fluorescence is measured at 590 nm, using an excitation wavelength of 390 nm. This fluorometric method is suitable for the determination of less than 2 μg of selenium.[397] Selenium in cast iron has been determined fluorometrically using this fluorogen.[137] The interferences of many metal ions in the fluorometric determination of selenite by the 2,3-diaminonaphthalene method can be eliminated by the use of EDTA.[444]

Electrometric

Coulometry – Selenite has been determined by a coulometric titration method in which the selenium(IV) is reduced by iodide to give elemental selenium and free iodine. The resulting mixture is treated with a known excess of sodium thiosulfate, and the excess thiosulfate is determined by electrogenerated iodine.[467]

Chromatographic

Selenious acid reacts with 4-chloro-*o*-phenylenediamine to form 5-chloropiaselenol, which is extractable into toluene and can be determined chromatographically by injecting the toluene extract into a gas chromatograph with an electron-capture detector. The detection limit is about 0.4 μg of selenium.[441]

Radiometric

A chemical multiplication procedure was used in the radiometric determination of selenium, selenium-75-labeled selenious acid being used in forming the dipiazselenol.[624] The separation and determination of small amounts of tellurium have been reviewed by Bock and Tschopel[81] who indicate the most sensitive method to be neutron activation.

Mixtures of Selenite and Tellurite

Tellurite can be separated from selenite by forming a tellurium complex with Bismuthiol II and extracting it into chloroform from a solution of pH 4.5 to 4.7.[79] The separation of tellurite from selenite and several metal ions can be accomplished by means of an anion-exchange resin.[114] By control of pH and temperature, Poonia has used *m*-(mercaptoacetamido)phenol to selectively reduce selenite to selenium in the presence of selenate, and tellurite to tellurium in the presence of tellurate.[483]

VIII. ANIONS OF SILICON

Silicate

Prior Literature Reference

Shell[548] has discussed critically the gravimetric, titrimetric, and colorimetric methods for the determination of silicon.

Titrimetric – Wilson[628] developed a satisfactory titrimetric method for silicate based on (1) the formation of 12-molybdosilicic acid, (2) the precipitation of quinolinium molybdosilicate and (3) the measurement of the total acidity of this precipitate, using a strong base as titrant. Silicate (in amounts equivalent to 0.5 to 50 mg SiO_2) has been converted to molybdosilicic acid and titrated potentiometrically with tin(II) oxalate or 1-amino-2-naphthol-4-sulfonic acid.[171] Another method based on the formation of molybdosilicic acid involves extracting it into isoamyl alcohol, back-extracting into an acidic aqueous solution, reducing molybdate with hydrazine hydrochloride, adding excess standard EDTA, and back-titrating with a zinc(II) chloride solution using Eriochrome Black T as indicator.[608] Silicate has been titrated potentiometrically with 1 *M* potassium fluoride, using a titanium indicator electrode.[2] The analyte solution should be 3 *M* in hydrochloric acid and contain some iron(III) ions.

Opticometric

Atomic absorption spectrometry – Silicon can be determined directly using high-brightness hollow-cathode lamps, a nitrous oxide-acetylene flame, and the 251.6 nm line.[16,27] The limit of detection is about 1 ppm of silicon, and the working range extends from about 25 to 200 ppm of silicon. A much lower range of concentrations, 0.1 to 1.2 ppm, is obtained by an indirect AAS method. Molybdosilicic acid is extracted into a 5:1 mixture of diethyl ether and pentanol. The extract is subjected to acidic washings to remove excess molybdate, and then to treatment with a basic buffer solution to decompose the heteropoly acid and strip the molybdate from the organic phase. The resulting molybdate is finally determined by measuring the absorbance of the 313.3-nm resonance line of molybdenum.[300,339,492] Instead of determining the equivalent molybdate directly, one may precipitate it as lead molybdate and determine the excess lead ion remaining in the supernatant solution. This modification has been shown to give a linear graph for 0.5 to 7 μg of silicon.[595]

A novel atomic absorption inhibition titration for the determination of silicate in water is sensitive to about 0.5 ppm of silicon and suitable for the determination of silica at concentrations between 1 to 50 μg/ml.[394] The absorbance of the magnesium at 285.2 nm in a hydrogen-air flame is monitored while using a standard magnesium chloride solution as the titrant.

Atomic fluorescence spectrometry – An atomic fluorescence spectrometric method employing an electrodeless discharge tube source and a nitrogen-separated acetylene-nitrous oxide flame has been described.[337] The intensity of fluorescence of silicon atoms at 251.6 nm was measured and gave a linear calibration plot. The detection limit was 0.7 ppm of silicon.

Spectrophotometry – The conversion of polymeric silicic acid in water to a reactive form prior to spectrophotometric determination by the heteropoly blue method has been described.[432] Duce and Yamamura[173] have developed three pretreatments to extend the versatility of the heteropoly blue method for the spectrophotometric determination of traces of silicon. A treatment with hot sodium hydroxide converts nonreactive silicon species to the reactive monomer, a cation-exchanger removes cations and excess sodium hydroxide, and boric acid is added to complex fluoride. The interference of germanate in the spectrophotometric determination of silicate by the heteropoly blue method can be eliminated by precipitating the germanium with tannic acid and removing the excess tannic acid by extraction into isoamyl alcohol.[558] Silicate has been separated from phosphate, arsenate, and other interfering ions by passing the sample solution through a cation-exchange column and then through a weak base anion-exchange resin.[447] Silicate in water has been concentrated on a finely ground mixture of cation and anion exchange resins which is ignited and fused with sodium carbonate. The dissolved melt is then analyzed for silicate by the heteropoly blue method.[613] The heteropoly blue of silicon can be extracted into isoamyl alcohol if the aqueous layer is made 1.75 to 2.25 *M* in sulfuric acid just prior to extraction.[321] This modification is advantageous at low concentration of silicate. The heteropoly blue can also be extracted with 1,2-propanediol carbonate and the absorbance measured at 775 nm, the optimum concentration range being 0.25 to 1.2 ppm of silicon.[593]

In applying the β-molybdosilicic acid method to the determination of silica in natural silicates, Langer[371] applied corrections for phosphate, iron, and chromium, which interfere with the photometric measurements at 570 nm. Molybdosilicic acid, after being formed at low acidity, can be extracted from highly acidic solution into either ethyl acetate[531] or a 5:1 mixture of diethyl ether and pentanol.[592]

A differential kinetic method has been developed by Ingle and Crouch[302] for the simultaneous determination of silicate and phosphate. Under one set of conditions the initial rate of the relatively rapid formation of the heteropoly blue of phosphorus is measured to give a satisfactory determination of the phosphate. Under less acidic conditions the initial rate for the formation of β-12-molybdosilicic acid is measured, the 12-molybdophosphoric acid being formed much faster. This kinetic method was used with a spectrophotometric apparatus for the measurement of reaction rates to determine 1 to 10 ppm of silicon or phosphorus in the presence of 10 ppm of phosphorus or 50 ppm of silicon, respectively.

An indirect ultraviolet spectrophotometric method for the determination of silicon has been developed by extracting 12-molybdosilicic acid into a mixture of 5 vol of diethyl ether with 1 vol of pentanol mixture, stripping the molybdate into a basic buffer solution, and then converting it to peroxymolybdic acid.[594] Analogously, the equivalent molybdate can be determined either by ultraviolet absorbance measurement[300,592] or by a near infrared method in which the 2-amino-4-chlorobenzenethiol complex is formed and extracted into chloroform.[596] The limit of detection by the latter method is 0.034 μg of silicon per ml of aqueous solution. Fluosilicate can be extracted, as fluorosilicic acid, into a solution of trioctylamine in xylene.[464]

Electrometric

Voltammetry – Silicate, as molybdosilicic acid, has been determined at concentrations corresponding to 2 to 10 μg/ml of Si by a. c. polarography using a dropping mercury electrode.[403] An amperometric titration of silicate has been proposed in which silicate is converted to α-12-molybdosilicic acid and then titrated with iron(II).[112]

Chromatographic

Silicate anions form trimethylsilyl derivatives which have been separated by gas chromatography[634] and the derivatives of the anions SiO_4^{4-}, $Si_2O_7^{6-}$, $Si_3O_{10}^{8-}$, and $Si_4O_{12}^{8-}$ have been identified by mass spectrometry.[464]

IX. ANIONS OF SULFUR

Prior Literature Reference

The analytical chemistry of anions containing sulfur (SO_4^{2-}, SO_3^{2-}, S^{2-}, $S_2O_3^{2-}$, SCN^-, $S_2O_8^{2-}$, etc.) has been discussed by Heinrich, Grimes, and Puckett.[276]

Sulfate

Gravimetric

The determination of sulfate by the classical gravimetric method based on the precipitation of barium sulfate is still used quite extensively. The availability of rapid-weighing single-pan direct-reading balances has done much to reduce both the elapsed time and the operator time for performing the determination. In applying this gravimetric method to various materials, analysts have found that a preliminary removal of cations, particularly iron(III), by treatment with a cation-exchange resin in its hydrogen-ion form reduces errors due to contamination by coprecipitation.

Titrimetric

A precipitation-titrimetric method involving the precipitation of barium sulfate in 50% aqueous methanol and the use of an adsorption indicator, Alizarin Red S, has been developed.[212] Removal of certain cations (especially sodium, potassium, ammonium, iron(III), and aluminum) by the ion-exchange method is necessary in the application of this method. The sulfuric acid in the column effluent is partially neutralized by the addition of magnesium acetate; magnesium ion has a relatively low tendency to coprecipitate. Although appreciable amounts of chloride, bromide, and perchlorate can be tolerated, nitrate causes high results. A photometric titration of sulfate with barium chloride in 50% aqueous methanol using tetrahydroxyquinone as indicator has been suggested.[645] A microtitration of sulfate using thorin as an indicator has been applied to the determination of sulfate in water.[213] In the determination of 10 to 100 ppm of sulfate a 5 x 10^{-3} M solution of barium perchlorate in 80% ethanol was used. Sulfate in water has been determined titrimetrically, using barium chloride as titrant and a derivative of 2,7-bis(azo) chromotropic acid, "orthanil K," as indicator. A cation-exchange column was used to remove cations prior to titration. The operational range corresponded to about 0.1 to 1 mg of sulfate.[523]

The last of these methods may be modified by performing the titration at pH 4 in 50% aqueous acetone solution.[475] Sulfate can be determined titrimetrically in the presence of sulfonates with barium perchlorate as titrant and sulfanazo III, 2,7-bis(*o*-sulfophenylazo)chromotropic acid, as indicator. The sulfonates are first removed by precipitation and filtration as S-benzylthiuronium salts.[536] According to Hozumi and Umemoto[293] Arsenazo III is superior to thorin or sulfanazo III as an indicator in the titration of sulfate with barium in a non-aqueous medium. In the titrimetric determination of sulfate by titration with a barium nitrate solution in aqueous acetone medium, the use of Chlorphosphonazo III, [3,6-bis-(4-chloro-2-phosphonophenylazo] chromotropic acid, is recommended.[104,401] A semimicrotitrimetric method for the determination of sulfate in the presence of phosphate utilizes "nitchromazo," 2,7-bis(4-nitro-2-sulfobenzene-1-(azo)-1,8-dihydroxynaphthalene-3,6-disulfonic acid, as indicator and barium nitrate as titrant.[49] A microtitration method applicable to the determination of small amounts (2 to 6 mg) of sulfate uses an 0.01 *M* barium(II) nitrate solution as titrant, a 40 to 50% acetone or ethanol solution, and "nitchromazo" as indicator. Phosphate, arsenate, fluoride, chloride, nitrate, and perchlorate anions do not interfere.[50]

A titrimetric method based on the use of 4-amino-4′-chlorodiphenyl hydrochloride was developed in which the 4-amino-4′-chlorodiphenyl sulfate precipitate is washed free of chloride, and the total acidity of the precipitate measured by titration with standard sodium hydroxide. A mixture of phenol red and bromothymol blue is used as indicator. The method has been applied to the determination of sulfur in coal following conversion to sulfate by the bomb-combustion method.[625] Sulfate ion in dimethylsulfoxide is titrated with hydrochloric acid to give hydrogen sulfate ion, which has a much larger formation constant in DMSO than it has in water. Bromcresol green is the indicator and the end point is detected photometrically by monitoring the absorbance at 620 nm.[307] The method has been applied to the determination of sulfate in sea water. Sulfate can be isolated on an anion-exchange-resin column. After elution, a measured excess of lead(II) is added to the eluate and the excess titrated with EDTA using Xylenol Orange as indicator.[631] The alkaline earths can be complexed with EDTA and the iron and aluminum with CyDTA prior to the titration of sulfate with barium chloride. Excess barium ion displaces magnesium from the magnesium-EDTA complex to give a red color that signals the end point.[578] A titrimetric method for the determination of sulfate is based on the dissolution of barium sulfate in an EDTA solution at pH 12.5 with a complexometric titration of the large excess of EDTA with a standard zinc(II) solution using Zincon as indicator.[425]

Lambert and Manzo[368] developed a titrimetric method based on ion exchange of sulfate with iodate from granular barium iodate monohydrate and an iodometric titration using thiosulfate as the titrant. Although the method is applicable to the determination of 0 to 1000 ppm of sulfate, the best precision was secured at concentrations of 200 to 750 ppm. A titrimetric method for the determination of semimicro amounts of sulfate in the presence of phosphate has been developed by Jaselskis and Vas[311] who equilibrated sulfate with barium iodate in a solution containing 40% acetone and 0.1 *M* acetic acid solution and then determined the liberated iodate by an iodometric titration. A new microtitrimetric method for sulfate is based on an amplification reaction in which an acidic sulfate solution is treated with a known excess of a saturated barium bromate solution; an equivalent amount of bromic acid is generated as the barium sulfate is precipitated. The excess barium bromate is precipitated upon the addition of acetone, dissolved in hot water, and determined by an iodometric titration using thiosulfate as titrant. The procedure has been applied to the determination of sulfur in organic compounds following a Schöniger-flask combustion.[221] The removal of calcium ions in water samples by a cation-exchange resin is recommended prior to the titrimetric determination of sulfate using radio-frequency end-point detection.[574] Sulfate has been titrated with barium acetate using a high-frequency titrator to follow the change in conductivity.[409] Sulfate (1 to 25 mg) has been titrated with barium perchlorate in 70% ethanolic solution using thermometric end-point detection. The method is rapid and has few interferences, of which the severest arises from precipitation of inorganic compounds in the ethanolic solution.[626]

Opticometric

Atomic absorption spectrometry – Sulfate has been determined at low concentrations (20 to 100 ppm) by an indirect atomic absorption spectrometric method in which the excess barium remaining in the supernatant solution after the precipitation of barium sulfate is determined by measuring the absorbance due to barium using the 553.5-nm line.[175,606] The barium sulfate precipitate can be isolated and dissolved in disodium dihydrogen ethylene-diaminetetraacetate and the equivalent barium measured.[89,508,630] A method based on the precipitation of lead sulfate in an ethanolic solution and the determination of the lead remaining in the supernatant solution is accomplished by using the 283.3-nm resonance line.[509] An atomic absorption inhibition titration in which as little as 1 μg of sulfate/ml can be determined has been described by Looyenga and Huber.[395] The end point is based on an increase in absorbance due to the addition of an excess of magnesium(II) chloride, the titrant. The direct determination of sulfate utilizing a nitrogen-separated nitrous oxide-acetylene flame and a microwave-excited electrodeless-discharge lamp has been reported by Kirkbright and Marshall.[333] The 180.7-nm line was monitored. A linear calibration graph was obtained for aqueous potassium sulfate solutions over the range of concentrations corresponding to the 50 to 700 ppm of sulfur.

Flame photometry – Sulfate solutions aspirated into an air-hydrogen flame give rise to a band spectrum of many parts attributed to the formation of a bimolecular S_2 species.[100] Measurement at the molecular emission peak, 383.8 nm, results in a detection limit of about 10 ppm of sulfur. The emission intensity is proportional to the square of the sulfur concentration. The optimum concentration range is apparently less than 150 ppm of sulfur. Magnesium, calcium, copper, iron, sodium, potassium, and phosphate ions interfere. The cationic interferences can be eliminated by a preliminary separation using a cation-exchange resin in its hydrogen-ion form. A flame photometric method for the determination of sulfate in water has been based on the precipitation of barium sulfate and determination of the excess barium in the supernatant solution, using the 499.3-nm barium line.[479] Errors due to the incomplete precipitation of barium sulfate were compensated by the simultaneous analysis of standards and samples of about the same concentration. The method was used to determine concentrations of sulfate below 200 ppm.

Turbidimetry and nephelometry – The turbidimetric method, based on the formation of a barium sulfate suspension, is still used in determining sulfate in water.[13] The optimum concentration range is from about 4 to 40 ppm of sulfate when the absorbance is measured at 420 nm using 5-cm cells. A turbidimetric method based on the use of 4-amino-4'-chlorobiphenyl (CAD) hydrochloride has been suggested for the estimation of sulfate; the absorbance of the suspension is measured at 700 nm.[625] A nephelometric method applicable to the determination of 2.5 to 25 ppm of sulfate based on the formation of a suspension of CAD sulfate has been developed by Martin and Stephen.[413] In a recent comparison of the turbidimetric determinations of sulfate using barium chloride and CAD hydrochloride as reagents and the GeMSAEC photometric analysis system,[142] it was shown that better precision was achievable using the CAD procedure.[143] A precision and accuracy of about 1% was reported for the determination of 4 ppm of sulfate. No interference from orthophosphate was found as long as its concentration was less than 500 μg/ml. The absorbance was measured at 430 nm. Mendes-Bezerra and Uden have also proposed a nephelometric method for sulfate using CAD as reagent.[424] The working range of concentrations is from about 1 to 20 ppm of sulfate. 2-Aminopyrimidine hydrochloride reacts with sulfate in aqueous solution to produce the corresponding amine sulfate, which is colloidally dispersed. A nephelometric method based on the formation of this stable suspension is suitable for the determination of 0.1 to 5 ppm of sulfate.[565]

Spectrophotometry – An indirect spectrophotometric method in which solid barium chloranilate is added to precipitate barium sulfate and release an equivalent amount of the hydrogen chloranilate ion is used quite frequently. The excess barium chloranilate and the barium sulfate are removed by centrifugation or filtration. Interfering cations can be removed by a cation-exchange column. The hydrogen chloranilate has characteristic absorbance maxima in both the visible and ultraviolet regions, the latter being preferred because it provides much higher sensitivity.[69] The limit of detection is about 0.06 ppm of sulfate when the absorbance is measured at 322 nm and a 50% aqueous ethanol solution is used. The method is applicable to the determination of 0.05 to 0.5 mg of sulfate (0.5 to 5 ppm). An automatic method for the photometric determination of sulfate in natural waters over the range of concentrations from 5 to 400 ppm is based on the chloranilate method and the use of a Technicon AutoAnalyzer®.[217] Schafer[527] has applied the barium chloranilate method to the determination of sulfate obtained from coal ash, slags, and fly ashes. Another indirect spectrophotometric method depends on the precipitation of barium sulfate upon the addition of barium chloranilate and the extraction of the liberated chloranilate as the *tris* (1, 10-phenanthroline)-iron(II) chloranilate ion-association complex.[635] The absorbance of the extract is measured at 510 nm and conforms to Beer's law over the range of concentrations from 7 to 37 ppm.

A spectrophotometric method for determining 0.5 to 5 ppm of sulfate has been proposed using "nitchromazo," 2,7-bis-(4-nitro-2-sulfobenzene-1-azo)-1,8-dihydroxynaphthalene-3,6-disulfonic acid.[48] Barium(II) and "nitchromazo" react at pH 2 to form a pale blue 1:1 complex which reacts further with sulfate ion to give a violet product whose absorbance is measured at 640 nm. Chlorides, nitrates, perchlorates, and borates do not interfere and moderate amounts of phosphate, fluoride, and arsenate can be tolerated.

Another approach to the spectrophotometric determination of sulfate requires the reduction of sulfate to sulfide and the subsequent formation of methylene blue by the reaction of hydrogen sulfide with *p*-amino-*N*, *N*-dimethylaniline in the presence of iron(III) chloride.[243] This method is suitable for the determination of 20 to 300 ppm of sulfate; the interference of nitrate can be eliminated by adding zinc acetate, evaporating to dryness, and igniting at 320°C.[549] The zinc nitrate decomposes while the zinc sulfate is stable. Sulfate has been reduced to hydrogen sulfide by a mixture of hydriodic acid, acetic anhydride, and sodium hypophosphite, and the hydrogen sulfide may be absorbed in a solution containing the iron(III)-1,10-phenanthroline complex, which undergoes reduction to the *tris* (1,10-phenanthroline) iron(II) complex, whose absorbance is measured at 510 nm. The method is applicable to 100 ppm of sulfate.[163] Sulfate has been determined in propellants and nitrocellulose by reduction to hydrogen sulfide; addition of lead citrate and photometric measurement of the brownish yellow lead sulfide formed.[454]

A relatively recent development in the determination of sulfate has been the use of 4-amino-4'-chlorodiphenyl hydrochloride (CAD) to precipitate sulfate. Jones and Lethan[316] developed an ultraviolet spectrophotometric method suitable for the determination of 30 to 120 μg of sulfate. The sulfate is precipitated by adding a known amount of the CAD reagent and removing the resulting CAD sulfate precipitate by centrifugation. An 0.3-ml aliquot of the supernatant solution is diluted to 25 ml with 0.1 *M* hydrochloric acid and the absorbance of the solution is measured at 254 nm. The molar absorptivity of the reagent is 2.2×10^4 $\text{l-mol}^{-1}\text{-cm}^{-1}$. The amount of sulfate is calculated from the difference in the absorbances for the sample and blank determinations. Phosphate interferes but can be removed by precipitating it as magnesium ammonium phosphate since magnesium ions do not interfere.

A simple direct spectrophotometric method for determining sulfate in natural waters is based on the absorbance of the $FeSO_4^+$ complex at 325 nm, and is applicable over the range of sulfate concentrations from 10 to 500 ppm.[223] The amount of excess iron(III) must be strictly controlled and phosphate and fluoride must be absent.

The barium salt of dihydroxytoluquinone reacts with sulfate in an ethanolic solution to precipitate barium sulfate and liberate the anion of dihydroxytoluquinone, which has a purple color.[360] After filtration, the absorbance of the filtrate is measured at 515 nm. Conformity to Beer's law was reported for concentrations of sulfate up to 70 ppm.

The catalytic effect of sulfate on the zirconium-Methylthymol Blue reaction has been used to determine 0.1 to 2.4 ppm of sulfate by a kinetochromic spectrophotometric method.[278]

Spectrofluorometry – A direct spectrofluorometric method for the determination of 0.2 to 12 mg of sulfate is based on the enhancement of the fluorescence of the zirconium-Calcein Blue complex. An excitation wavelength of 350 nm and an emission wavelength of 410 nm are recommended.[581] Fluoride interferes seriously, giving high results, while phosphate and other anions forming precipitates or complexes with zirconium(IV) give low results. Iron(III) and cobalt(II) also interfere. An indirect spectrofluorometric method is based on the quenching by sulfate of the fluorescence of the thorium-flavonol complex.[442] The decrease in fluorescence of the yellow thorium-morin complex, which is proportional to the sulfate-ion concentration, has been made the basis of a fluorometric method for the determination of 10 to 40 μg of sulfate.[247]

X-ray spectrometry – The sulfate concentration of alkylbenzene sulfonate solution has been determined by a differential method in which the total sulfur content is determined by x-ray fluorescence spectrometry[361] and the sulfonate content by infrared spectrometry.

Electrometric

Potentiometry – Heterogeneous membrane electrodes consisting of an ion-exchange membrane[446,552] and barium sulfate in paraffin[195] were developed and used as indicator electrodes in the titration of sulfate. A Pungor-type membrane electrode of silicone rubber impregnated with barium sulfate was evaluated by Rechnitz, Lin, and Zamochnick.[499] Although this electrode gave a nearly Nernstian response over the range of concentrations from 10^{-1} to 10^{-4} M, it was concluded that halide concentratons above 10^{-3} M interfered, that a reliability better than ± 5% could not be obtained by direct potentiometry, and that the electrode was of very limited practical utility in its present state of development. A crystal membrane sulfate-ion-selective electrode consisting of 32 mol % Ag_2S, 31 mol % PbS, 32 mol % $PbSO_4$, and 5 mol % Cu_2S has recently been fabricated and shown to be subject to only very slight interference from iodide, bromide, and chloride at pH-values between 3 and 10.[496]

A lead-ion-selective electrode has been used as the indicator electrode in the potentiometric titration of sulfate with lead(II) perchlorate in 50% (v/v) aqueous dioxane.[515] The solubility product of lead sulfate is 1.6 x 10^{-8} in water but was estimated to be only about 10^{-14} in the 50% aqueous dioxane. Good precision is obtainable provided that the sulfate concentration exceeds 5 x 10^{-4} M. Chloride and nitrate ions interfere seriously if their concentrations exceed 100 times that of the sulfate. In another study of the potentiometric titration of sulfate with lead perchlorate in 60% dioxane at pH 4 to 6.5 using a lead-ion-selective electrode, the interference of fluoride was eliminated by complexing with boric acid. Phosphate ions interfere.[539] A pair of bismuth electrodes has been used to detect the end point in the constant-current potentiometric titration of sulfate with a mixture of lead and barium nitrate.[317] Another potentiometric method for sulfate is based on the change of pH that occurs at the end point when sulfate ion, in either an aqueous acetone or an aqueous ethanol solution of pH 7 to 7.5, is titrated with a titrant consisting of a mixture of 10 parts of 0.05 M barium nitrate with 1 part of 0.05 M lead nitrate. A change in pH of 1 to 3 units was measured with a glass-calomel electrode system.[52]

Voltammetry – An indirect polarographic method for sulfate is based on the displacement of chloranilate from barium chloranilate, which is added as a solid to a solution of sulfate in 50% aqueous methyl cellosolve containing 0.01 M acetic acid and 0.01 M sodium acetate. The diffusion coefficient of the chloranilate is measured at −0.5 V vs S.C.E. The method is applicable over the range of concentrations from 10^{-3} to 5 x 10^{-5} M.[299] The sulfate obtained from an oxygen-flask combustion has been determined polarographically by precipitating with a known excess of barium chloride and determining the concentration of excess barium ion polarographically.[75] An indirect polarographic method for sulfate is based on the precipitation of lead sulfate, dissolution of the precipitate in a saturated ammonium chloride solution, and measurement of the height of the lead wave.[391] Various applications of the amperometric titration of sulfate with lead(II) nitrate, which was critically studied much earlier by Kolthoff and Pan,[351] continue to be reported.[182,554]

Conductometry – A conductometric titration of sulfate in acetic acid medium is based on the addition of excess barium acetate to precipitate barium sulfate and titration of the excess with perchloric acid. This method was applied to the determination of 2 to 5 mg of sulfate.[225] A solution of sulfate may be passed through a cation-exchange column in the hydrogen-ion form and the liberated sulfuric acid may be titrated conductometrically with potassium hydroxide.[93] However, if fluoride is present, its amount must be determined spectrophotometrically and an appropriate correction applied to the titrimetric result.

Chromatographic

Gas chromatography – Butts[116] has reported the gas chromatographic separation of the trimethylsilyl derivatives of sulfate and other inorganic anions. Thus, ammonium sulfate reacts with bis(trimethylsilyl)trifluoroacetamide in dimethyl formamide to give $(TMS)_2SO_4$.

Mass spectrometry was used to confirm the identity of the chromatographic peaks with $(TMS)_2SO_4$ peak giving a parent m/e of 227 and a daughter m/e of 151.4.[117] A nonpolar SE-30 stationary phase was used in the GC separation. Both the flame photometric detector (FPD) and the flame-ionization detector (FID) were used; the FPD showed a much higher sensitivity. The minimum detectable amount of sulfur using the chemiluminescent emission principle of the FPD is 20 pg of sulfur.[233]

Sulfate has been reduced to hydrogen sulfide by using a 20% solution of tin(II) chloride in concentrated phosphoric acid at 250 to 317°C. A silica gel column, hydrogen as carrier gas, and carbon dioxide as internal standard were used. The peak area ratio for H_2S/CO_2 was linear for less than 4.4 mg of sulfur.[305]

Radiometric – On passing a solution of sulfate ion through a column of iodine-131-labeled barium iodate, iodate is displaced and the radioactivity of the effluent may be measured. This rapid radiometric method is applicable to the determination of 0.06 to 3.2 mg of sulfur as sulfate with a precision of ± 2.5%.[91] A hydrochloric acid solution of barium chromate labeled with chromium-51 may be used to precipitate barium sulfate. After neutralization, the barium sulfate and excess barium chromate are removed by filtration and the activity of the dissolved chromate, the amount of which is equivalent to that of the sulfate, is measured.[29]

Sulfide

Titrimetric

Hydrogen sulfide is formed by microbial action on organic matter under anaerobic conditions, especially in polluted waters. For determining high concentrations (100 to 250 ppm) of soluble sulfides, a titrimetic method based on the oxidation of sulfide with iodine is usually the method of choice. In practice it is necessary to remove the hydrogen sulfide from an acidified sample solution by entraining it in a stream of an inert gas such as nitrogen or carbon dioxide, and to remove it in turn from this stream by fixing it as zinc sulfide. After adding an excess of a standard iodine solution to the acidified zinc sulfide suspension, the excess iodine is titrated with a standard thiosulfate solution. Sulfite will interfere. A rapid, microtitrimetric method for sulfide uses *N*-bromosuccinimide as titrant to selectively oxidize iodide to iodine which oxidizes the sulfide to sulfur. Starch is the indicator.[521] Sulfide, particularly hydrogen sulfide, serves as an inductor for the iodine-azide reaction. By controlling the concentrations of iodide and azide, the induction factor can be kept constant so that the amount of iodine consumed is proportion to the amount of sulfide.[38] Sulfide has been titrated in the presence of chloride, iodide, bromide, thiocyanate, sulfite, and thiosulfate with a sodium plumbate(II) solution, using a sulfide-sensitive membrane electrode to detect the end point.[443] Hydrogen sulfide at the 100-μg level can be titrated with *o*-hydroxymercuribenzoic acid using either dithiofluorescein or dithizone as indicator. (At the 0.1- to 0.2-μg level a photometric determination using *o*-hydroxymercuribenzoic acid and dithiofluorescein is suggested.) A fluorometric titration with tetraacetoxymercurifluorescein can be used to determine amounts of hydrogen sulfide between 0.003 and 0.2 μg.[632] Sulfur in hydrocarbon liquids and gases can be determined as hydrogen sulfide after reduction, employing Raney nickel in 2-propanol to form nickel sulfide and then liberating hydrogen sulfide by treating this with acid.[230] The hydrogen sulfide can be absorbed in base and titrated with mercury(II) acetate, using dithizone as indicator.[192] An automated titration method for sulfide using a sulfide-selective electrode requires about 4 min and gives a standard deviation of 2% above the 90 μg level.[555]

Opticometric

Spectrophotometrically – Low concentrations of sulfide (0.2 to 2 ppm) can be determined by the Methylene Blue method, in which *p*-amino-*N*,*N*-dimethylaniline in the presence of iron(III) chloride reacts with hydrogen sulfide to form 3,7-bis(dimethylamine)phenazothianium chloride, a dye (C. I. Basic Blue 9 or Methylene Blue) exhibiting maximum absorbance in the vicinity of 610 nm and 670 nm. An anion-exchange resin was used to remove hydrogen sulfide from water or air. The column must be preconditioned with a sodium sulfide solution, for the resin initially absorbs some sulfide irreversibly. The sulfide is eluted with 4 *M* sodium hydroxide and determined spectrophotometrically by the Methylene Blue method.[462] Sulfide has been determined colorimetrically after reaction with *N*,*N*-diethyl-*p*-phenylenediamine in the presence of iron(III) to form Ethylene Blue, which exhibits an absorbance maximum of 670 nm.[501] This method is applicable to the determination of up to 100 μg of sulfur, depending on the thickness of the cell employed, and has been applied to the determination of trace amounts of sulfide in condensed steam.

Sulfide ion can be determined by an indirect spectrophotometric method involving the addition of mercury(II) chloranilate to a 50% aqueous ethanol solution containing the sulfide ion. The formation of mercury(II) sulfide releases chloranilate ion which exhibits maximum absorptivity at 330 nm. An apparent molar absorptivity of 3.2 x 10^4 1-mol^{-1}-cm^{-1} has been reported for the determination of sulfide.[298] Another indirect spectrophotometric method for the determination of sulfide is based on the displacement of Crystal Violet from a Crystal Violet-tetraiodomercurate(II) ion-association precipitate packed in a column through which the sulfide solution is allowed to percolate. The absorbance is measured at 590 nm and the calibration graph is linear up to 6 ppm of sulfide.[367] The reaction of I^+ and a triphenylmethane dye, such as Crystal Violet or Basic Turquoise Blue, is the chromogenic reaction in an indirect method. The sulfide is oxidized to sulfite by an oxidant such as chloramine B. The excess oxidant is determined by the addition of iodide to form an equivalent amount of I^+ which will decolorize the dye. The method is reported to be applicable over the range of sulfide concentrations from 0.025 to 0.640 μg/ml.[108] The ultraviolet absorption spectra for sulfide, thiosulfate, sulfite, and sulfate ions in aqueous solution have been studied, and the molar absorptivities of sulfide and thiosulfate have been reported to be 3 x 10^3 l-mol^{-1}-cm^{-1}.[186] Sulfide ions in ammoniacal solution react with iron(III) and an excess of nitrilotriacetic acid to produce a green color, which is stabilized by sulfite[491] and which is attributed to the formation of a colloidal basic form of iron(III) sulfide. The method is not very sensitive, but few anions interfere in it even when present in a 10- or 100-fold excess. Selenite inhibits development of the color. An automatic method for the determination of 1 to 10 ppm of sulfide in water has been based on the color produced by the reaction between nitroprusside and sulfide in basic solution.[128]

Fluorometry – An indirect spectrofluorometric method for sulfide has been based on the reaction of copper(II) and sulfide and the effect of copper(II) in quenching the fluorescence of 2-(*o*-hydroxyphenyl)benzoxazole.[610] A detection limit of 1 mg of sulfide was reported, and calibration plot was found to be linear up to a concentration of 100 mg/ml. A fluorometric method for the determination of sulfide, based on the quenching of the chemiluminescence of luminol and iodine, has been suggested by Lukovskaya and Markova.[402]

Electrometric

Potentiometry – The silver-sulfide solid-state ion-selective electrode gives rapid response to changes in sulfide concentration and is sensitive to sulfide concentrations as low as 10^{-19} *M*, although the optimum concentration is 1 to 10^{-7} *M* sulfide.[384,518] Mercury(II) interferes if its concentration exceeds 0.02 ppm. The sulfide-selective membrane has been studied by Schmidt and Pungor[532] who have evaluated its selectivity constants for a number of anions and cations.

Voltammetry – A polarographic method for sulfide depends on the stoichiometric reaction between methylmercury(II) iodide and sulfide. The diffusion current is due to the reductive fission of the mercury-iodine bond and decreases as the concentration of sulfide increases. The method is applicable to the determination of 1 to 7 ppm of sulfide.[236]

Coulometry – Microgram quantities of sulfide have been titrated coulometrically by electrogenerated silver(I) in a basic cyanide medium. The end point can be detected either potentiometrically or amperometrically.[119]

Sulfite

Opticometric

Atomic absorption spectrometry – An indirect AAS method for sulfite is founded on the reaction between sulfite ion and a suspension of mercury(II) oxide to form the $[Hg(SO_3)_2]^{2-}$ complex. The absorbance due to the mercury is measured using the 253.7-nm wavelength for mercury.[318]

Spectrophotometry – An indirect spectrophotometric method for sulfite is based on the reaction of mercury(II) chloranilate with sulfite ion in 50% aqueous ethanol: chloranilate ion is liberated, and its absorbance may be measured at 330 nm to permit the determination of sulfite at concentrations between 0.5 and 8 μg/ml. The apparent molar absorptivity for sulfite is 1.68 x 10^4 1-mol^{-1}-cm^{-1} [298] The liberated chloranilate can also be determined by polarography over the range of concentrations of sulfite from 8 to 160 ppm.[299] The ORNL GeMSAEC Photometric Analyzer and the parallel analysis technique were used to determine sulfite over the range of concentrations corresponding to 0.25 to 2.5 ppm of SO_2.[144]

Peroxydisulfate

Spectrophotometry – Peroxydisulfate reacts with iodide in solutions buffered at pH 6.85, liberating triiodide (I_3^-), which can be determined titrimetrically with thiosulfate or photometrically by measurement at 355 nm, where the molar absorptivity is reported to be 2.86×10^4 $l\text{-}mol^{-1}\text{-}cm^{-1}$.[209]

X. MISCELLANEOUS ANIONS

Cyanide

Opticometric

Atomic absorption spectrometry – An indirect AAS method based on the determination of the iron equivalent to it in the dicyano-*tris*(1,10-phenanthroline)-iron(II) complex has been described, and gives a linear response over the range of cyanide concentrations from 0.1 to 5 ppm.[157] An alternative method, based on the precipitation of silver cyanide and determination of the excess silver in the supernatant solution, is applicable over the range of cyanide concentrations from 0.3 to 2.1 ppm.

Spectrophotometry – The sensitive and highly selective pyridine-pyrazolone spectrophotometric method is extensively used to determine small amounts of cyanide.[15] An ultraviolet spectrophotometric method has been based on the reaction of cyanide and nickel ions in ammoniacal solution to form tetracyanonickelate (II), which exhibits an absorbance maximum at 267 nm.[534] The method is applicable to the determination of cyanide at concentrations from 0.5 to 20 ppm. A spectrophotometric method for traces of cyanide (~0.1 μg) is based on the formation of a stable complex of cyanide with hemoglobin.[53] Lambert and Manzo[366] added the very insoluble *tris*(1,10-phenanthroline)iron(II) triiodide to a cyanide solution, displacing an amount of the red *tris*(1,10-phenanthroline)iron(II) equivalent to the cyanide present, and measured the absorbance of this ferroin species. Cyanide has been determined on the basis of its reaction with mercury(II) Methylthymol Blue to form a colored complex.[452] Mercury(II) chloranilate, when added to an ethanol-water mixture containing cyanide ion, forms mercury(II) cyanide and liberates an equivalent amount of chloranilate ($C_6Cl_2O_4^{2-} \equiv 2CN^-$). The apparent molar absorptivity for cyanide when spectrophotometric measurements are made at 330 nm is 1.15×10^4 $l\text{-}mol^{-1}\text{-}cm^{-1}$.[298] The formation of the silver(I)-1,10-phenanthroline-Bromopyrogallol Red ternary complex is inhibited by cyanide. This inhibition reaction is the basis of an indirect spectrophotometric method for the determination of cyanide at concentrations from 0.26 to 2.6 ppm.[155]

Cyanide can be determined by employing a catalytic reaction in which *p*-nitrobenzaldehyde reacts with cyanide to give a cyanohydrin that then reacts with *o*-dinitrobenzene to give a purple color. The rate of change in absorbance depends on the concentration of cyanide and may be correlated with that concentration over the range from 45 to 450 ng/ml.[239] The rate of reaction of cyanide ion with 5,5′-dithiobis(2-nitrobenzoic acid) to give a thiolate anion can be increased by the presence of *N,N*-dimethylformamide. The absorbance of the thiol is proportional to the cyanide concentration.[296] In determining traces of cyanide in the presence of ferrocyanide, Roberts and Jackson[506] have found that the hydrogen cyanide can be distilled out under reduced pressure in the presence of zinc acetate without any decomposition of the ferrocyanide. The use of lead acetate instead of zinc acetate gave high results when the pyridine-pyrazoline spectrophotometric method was used to determine the cyanide in the distillate. It has been reported that free cyanide can be separated from complex cyanide by steam distillation.[286]

Fluorometry – A specific fluorometric method based on the fluorescence produced by the reaction of *p*-benzoquinone with cyanide has been developed by Guilbault and Kramer.[240] When cyanide ions react with 2′,7′-bis(acetoxymercuri)-fluorescein, the decrease of fluorescence intensity is proportional to the concentration of cyanide.[146] 2,3-Diaminonaphthalene (DAN) reacts with selenite to form an orange precipitate, DANSe, which is soluble in ethanol and reacts with palladium(II) chloride to precipitate $Pd_2(DANSe)_2Cl_4$. This precipitate is the reagent used in the indirect fluorometric determination of cyanide. Upon addition of the reagent to a cyanide solution the fluorescent DANSe species is released, as illustrated by the equation $Pd_2(DANSe)_2Cl_4 + 8\,CN^- \rightarrow 2\,DANSe + 2Pd(CN)_4^{2-} + 4\,Cl^-$ and may be extracted into hexane. The excitation wavelength is 377 nm and the emission wavelength is 520 nm. The method is applicable to the determination of amounts of cyanide from 10 to 100 μg.[419]

Polarimetry – Cyanide (and sulfide) ions, at concentrations between 10^{-5} and 10^{-7} M, can be determined by measuring their effects in decreasing the inhibitory effect of mercury(II) ions on the invertase-catalyzed hydrolysis of sucrose. The inhibition is measured in terms of optical rotation.[420]

Electrometric

Potentiometry – A silver-iodide membrane electrode is most suitable for determining cyanide in the range of concentrations from 10^{-3} to 10^{-5} M, although it can be used at both higher and slightly lower concentrations.[176] Two indirect potentiometric methods, both based on the determination of the silver ion in equilibrium with dicyanosilver(I) and using a silver-sulfide-membrane electrode, have been investigated for the determination of cyanide at low concentrations. The optimum range of concentrations using this approach was about 10^{-4} to 10^{-5} M.[199] An ion-selective electrode with a solid mixture of silver iodide and silver sulfide responds to the concentration of cyanide. The pH is optimally 12 to 13 but may be as low as 10 to 12 provided that it is kept constant at a predetermined value. Sulfide and iodide ions interfere. The response of the cyanide-selective electrode at different rates of flow of a solution streaming past it has been studied.[198] A silver-sulfide ion-selective electrode has been used as an indicator electrode in the potentiometric titration of cyanide and chloride.[148]

Voltammetry – Mercury(II) chloranilate, when added to an aqueous alcoholic solution containing cyanide ion, forms mercury (II) cyanide and releases an equivalent amount of chloranilate. The chloranilate ion has been determined polarographically by measuring the diffusion current at −1.5 V vs S.C.E. in a 50% aqueous ethanol solution 0.1 M in sodium acetate.[299]

Thiocyanate

Atomic absorption spectrometry – An indirect atomic absorption spectrometric method having an optimum concentration range of 0.5 to 2.0 ppm of thiocyanate has been developed.[156] The copper associated with the dithiocyanate-dipyridine copper(II) complex is determined.

Spectrophotometry – A method for the spectrophotometric determination of thiocyanate, based on the formation of a dithiocyanatodipyridine copper(II) complex and the extraction of this complex into chloroform, is applicable over the range of concentrations of thiocyanate from 2 to 40 ppm.[156,359] Thiocyanate reacts with a mixed-oxidation-state (III-V) rhenium species to give a colored complex exhibiting maximum absorbance at 390 nm. This method is applicable up to 5 ppm of thiocyanate.[445]

Potentiometry – A solid-state-membrane electrode consisting of a mixture of silver thiocyanate and silver sulfide can be used to determine thiocyanate over the range of concentrations from 10^{-1} to 10^{-5} M.[514] Bromide, iodide, cyanide, and sulfide ions interfere, and ammonia will also cause difficulty. Thus, substances that form complexes or insoluble precipitates with silver ion or that are reductants should be absent.

Organic Anions

Citrate, when treated with pyridine and acetic anhydride, gives a colored solution whose absorbance is measured at 435 nm.[258] *Formate* has been determined by measuring the color of a silver sol produced by the reduction of silver nitrate by formic acid.[284] The method has been applied to the determination of formate in corrosion products. An indirect spectrophotometric method for the determination of *oxalate* is based on the decrease of the absorbance of the red uranium(IV)-4(2-pyridylazo)resorcinol complex when this reacts with oxalate,[446] and is applicable up to 3 ppm of oxalate. *Oxalate* has been titrated potentiometrically with lead(II) perchlorate in 40% *p*-dioxane using a lead-ion-selective electrode as indicator electrode.[538]

Mercaptoacetate reacts with 2′,2′-bis(acetoxymercuri)fluorescein to give a species with a lower fluorescence intensity. The decrease of fluorescence intensity is proportional to the concentration of mercaptoacetate.[146]

The *pentachlorophenol*-ferroin ion association complex can be extracted into nitrobenzene and the iron in the complex determined by atomic absorption spectrometry.[637] *Phthalate* ions have been determined spectrophotometrically by forming anion-association complexes with neocuproin which are extractable into organic solvents.[640] A liquid membrane electrode containing tetraheptyl ammonium salicylate in 1-decanol gave Nernstian response over the range of concentrations of *salicylate* ion from 10^{-1} to 10^{-3} M at pH 8.5.[275] *Sorbate* is determined by an iodometric titration following a preliminary treatment with sodium chlorite and hydrochloric acid. The method is applicable to the determination of sorbic acid in foods.[559] *Tartrate* can be determined in the presence of citrate by oxidizing the tartrate with periodate under controlled conditions and then determining the iodate formed by a spectrophotometric iodometric method. Molybdate prevents the excess periodate from reacting to liberate iodine.[451] *Tartrate* reacts with β-naphthol in sulfuric acid medium to develop a color suitable for the determination of amounts of tartrate from 50 to 800 μg.[135] *Thioacetamide* (TAA) can be titrated with electrogenerated silver ion in a coulometric method employing potentiometric end-point detection.[332] *Xanthates* such as ethyl xanthate react with copper(II) to form copper(II) xanthates that are extractable into chloroform. The absorbance of the extract is measured at 305 nm.[481]

Anion Detergents

A spectrophotometric method has been devised for the determination of *alkyl aryl sulfonate* (LAS); it is based on the extraction of an ion-association complex with Methylene Blue into chloroform.[14] An atomic absorption spectrometric method involves the formation of the ion-association complex of bis(1,10-phenanthroline) copper(I) with the surfactant ion, extraction of the complex into isobutyl acetate or methyl isobutyl ketone, and the determination of the copper contained in it.[152,374] Anionic detergents such as lauryl sulfate have been determined by measuring the color of their ion-association complexes with ferroin, which are extractable into chloroform.[585]

Liquid membrane electrodes have been described that are suitable for potentiometric titrations of anionic detergents such as dodecyl sulfate, tetrapropylbenzenesulfonate, and dioctylsulfosuccinate.[219]

EDTA and NTA

An indirect titrimetric method for the determination of EDTA involves its complexation with bismuth(III) and back-titration of the excess bismuth with a standard EDTA solution using Pyrocatechol Violet to determine the end point photometrically.[602] EDTA can be determined spectrophotometrically after converting it to a strongly absorbing chromium(III) EDTA complex,[133,433] by its effect in inhibiting manganese(II)-catalyzed oxidation of Malachite Green by periodate,[434] and by a differential technique based on addition of excess iron(III) and measurement of the absorbances of the iron(III)-EDTA and excess iron(III) at their respective absorbance maxima, 258 and 305 nm in 0.05 *M* sulfuric acid.[72] The possible consecutive potentiometric titrations of NTA, EDTA, and DTPA with iron(III) have been described by Horacek and Pribil.[290] Nitrilotriacetate (NTA) has been titrated with copper(II) using a solid-membrane copper-ion-selective electrode.[497] Nitrilotriacetate, at concentrations from 1 to 10 ppm, can be determined polarographically by converting it to its 1:1 complex with cadmium and measuring the diffusion current of this complex. Sodium tripolyphosphate and sodium alkylbenzenesulfonate do not interfere.[34]

Carbonate

Gravimetric

A method for the determination of bicarbonate in water when anions of other weak acids are present includes a gravimetric determination of "total" carbon dioxide (carbon dioxide plus bicarbonate) and a titrimetric determination of free carbon dioxide. The bicarbonate is calculated from the difference between the results of these two determinations.[511] Mixtures containing carbonate, cyanide, and cyanate have been analyzed by determining carbonate and cyanate gravimetrically via the carbon dioxide evolved upon treatment with acid, the cyanide being complexed by addition of mercury(II); then hydrolyzing cyanate and using the Kjeldahl method to determine the ammonia obtained from it; and finally determining cyanide by an argentometric titration.[261]

Titrimetric

Carbon dioxide obtained from the combustion of carbon in steel has been absorbed in a mixture of *N,N*-dimethylformamide with water and monoethanolamine containing thymolphthalein and potassium iodide, and titrated coulometrically with electrolytically generated base to a photometric end point.[88]

Opticometric

The band at 7 μ, corresponding to the CO_3^{2-} asymmetric stretching mode, has been used for the infrared determination of carbonate.[373] Cyanate and sulfate were also determined, using the $SO_4{}^{2-}$ degenerate stretching band at 9 μ and the C = N stretching band at 4.6 μ. Carbonate can be determined by an infrared spectrometric method in which carbon dioxide is liberated and the absorbance measured at 4.32 and 2.72 μ.[480]

Chromatographic

Gas chromatography – Carbonate, if initially present as its ammonium salt, forms trimethylsilyl carbonate on reacting with bis(trimethylsilyl)trifluoroacetamide in dimethylformamide as solvent.[116] The carbon dioxide evolved from carbonate on treatment with acid in a closed system can also be swept by helium into silica gel column and determined by gas chromatography.[125]

Volumetric

A unique volumetric method for determining carbonate in dental enamel has been described in which the carbon dioxide liberated upon acid treatment is collected as a single bubble and flattened into a 100-μ layer between glass surfaces. The volume of carbon dioxide can be calculated from the area of the flattened bubble.[619]

XI. SUMMARY

The most significant recent developments in methods for the determination of anions have involved (1) the use of ion-selective electrodes in direct potentiometric measurements and potentiometric titrations, (2) the application of indirect and chemical amplification techniques in atomic absorption spectrometry, spectrophotometry, and spectrofluorometry, and (3) the utilization of extractable ion-association complexes, (4) the development of kinetic methods and associated instrumentation, and (5) the application of the combination of derivatization and gas chromatography.

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