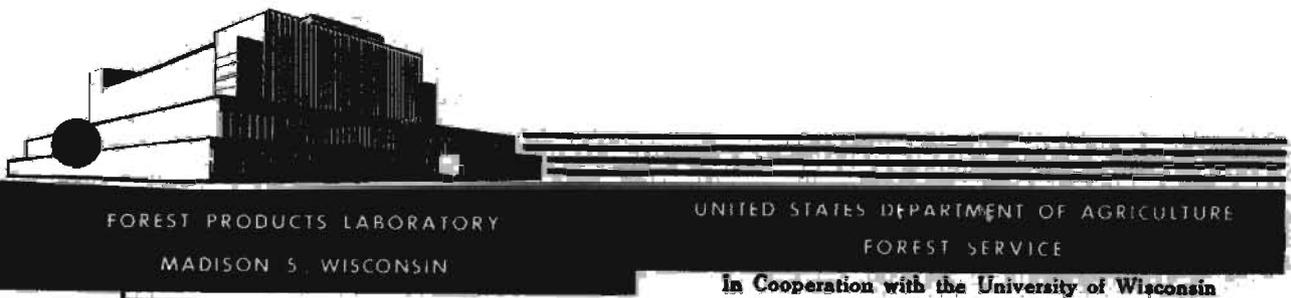
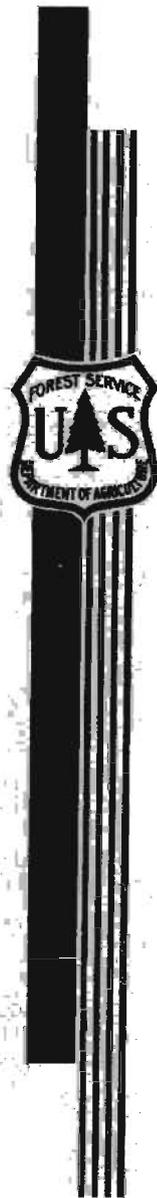


A REVIEW OF ARTICLES ON METHODS OF DETERMINING ARSENIC, BORON, CHLORINE, FLUORINE, AND ZINC IN VARIOUS MATERIALS

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A REVIEW OF ARTICLES ON METHODS OF DETERMINING ARSENIC,
BORON, CHLORINE, FLUORINE, AND ZINC IN VARIOUS MATERIALS

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Abstract

Reviews of articles describe different methods that have been used to analyze various materials containing arsenic, boron, chlorine, fluorine, and zinc. These methods may be useful in the analysis of preservatives treated wood. Many of the methods involve instrumental techniques.

Introduction

In the past, the analysis of preservatives treated wood for specific elements was made only in connection with research work. At treating plants, practical determinations of retentions in treated wood were based on the volume of solution absorbed by the charge as shown by gage readings, coordinated with an analysis of the treating solution. As a rule, the research worker was not unduly concerned, in analyzing treated wood, with the time required for each determination. The tendency was for him to adopt a method that would give results of reasonable accuracy, without searching for the shortest possible method.

¹Maintained at Madison, Wis., in cooperation with the University of Wisconsin.

With the advent of results-type specifications, whereby retention was checked by an analysis of a sample, the time required per analysis was more closely scrutinized. The assay of pentachlorophenol-treated poles constituted the first case of the confirmation of retention in commercial charges by the determination of a single element in a sample of the treated wood. The lime-fusion method was used exclusively at the start, but within recent years it has been supplanted at some treating plants by the copper pyridine method. When many analyses of penta are to be made, the X-ray emission spectrograph has been shown to save considerable time. The method is also applicable to determine several elements in treated wood. Unfortunately, because of the high cost of the instrument, it is not available in treating plant laboratories.

An increasing interest in analytical methods that require a minimum of time has arisen with the increasing interest in the possibility of assaying lumber treated with waterborne preservatives or fire retardants. Instrumental methods offer the best prospects. A variety of such methods are now being used for many purposes in other industries. The problem facing the wood preserving industry is to find which of those methods yield reliable results when applied to treated wood containing a mixture of the chemicals commonly used, and also which of the methods are most practical. Such a decision would take into consideration the initial cost and maintenance cost of the equipment, the training required on the part of the operator, and the time required per analysis.

From the standpoint of availability of equipment, three broad classes of laboratories are concerned with analysis of preservative treated wood:

- (1) The wood preservation section of a large research institution, which is equipped with costly, elaborate instruments that are needed for various lines of research, and may be used by the wood preservation group.
- (2) The laboratory of a treating plant that enjoys a steady business in some treatment that is controlled by chemical analyses. A modest investment in an instrument that reduces man hours per analysis might well be justified.
- (3) The laboratory of a treating plant that only occasionally takes orders calling for chemical analysis of a sample of treated wood. In such case, low cost of equipment is a prime requisite of a method.

In a similar manner the methods now used to determine chemical elements in wood may be divided into several classes, depending upon the degree to which they serve requirements of the industry. The classical wet methods for determining copper and chromium in treated wood yield results that are satisfactorily reproducible by different operators working in different laboratories. They require only low cost laboratory equipment. The time

required is not unduly burdensome when a small number of samples are to be analyzed. However, if results-type specifications for treated lumber are developed, more rapid methods for these elements would be highly desirable.

The classical wet methods for determining chlorine and arsenic require an intermediate precipitation step that adds somewhat to the total time. Experience has shown that, while the lime-ignition method for chlorine is moderately time-consuming, it is nevertheless a practical routine laboratory method for plants treating with pentachlorophenol under results-type specifications. The copper pyridine method is somewhat faster. When an X-ray emission spectrograph is available, the time per sample is very much reduced.

The determination of fluorides in treated wood by a modification of the Willard-Winkler distillation method yields fairly accurate results, but the method is too time-consuming to meet demands of commercial production.

The methods that have been proposed for determining boron in treated wood are tedious and subject to poor reproducibility.

Classical methods for determination of zinc are quite satisfactory for the analysis of treating solutions or for the analysis of treated wood that contains zinc and chromium. When wood contains arsenic as well as zinc and chromium, modifications in the method are needed. With the modified method, the determination of zinc is rather time-consuming and is not satisfactorily reproducible between different operators. The causes of the discrepancies in results no doubt will be found by further study of the method, but a faster method is still needed.

The following is a review of articles in the literature concerning methods for the determination of arsenic, boron, chlorine, fluorine, and zinc in organic materials. These elements are believed to be those for which there is the greatest need for improved methods in commercial wood preservation.

Arsenic

Determination of Arsenic in Treated Wood

Wilson, W. J. (Forest Research Inst., Ratura, New Zealand. Anal. Chim. Acta 22, 96-100 (1960)).

A modification of the method of Schulek and Villey (Chem. Abs. 23, 1588) of reduction to As^{+++} with hydrazine sulfate $(NH_2)_2H_2SO_4$ was found to give excellent results for As. A 1-gram wood sample is decomposed with

concentrated $\text{HNO}_3 + \text{H}_2\text{SO}_4$, reduced with $(\text{NH}_2)_2\text{H}_2\text{SO}_4$ solution, and the excess of reagent decomposed by fuming. The solution is diluted, then titrated with 0.01N $\text{Ce}(\text{HSO}_4)_4$ in the presence of 3 drops of 0.25 percent OsO_4 , to faint green with ferrous o-phenanthroline perchlorate indicator. Cu and Cr^{+3} do not interfere. (Chem. Abs. 54, 6401f.)

Reagents required. --Nitric acid, concentrated; sulfuric acid, concentrated; hydrazine sulfate--saturated aqueous solution; ceric sulphate 0.1N; ceric sulfate 0.01N; osmium tetroxide (0.25 percent in 0.1N H_2SO_4); and ferrous o-phenanthroline perchlorate--saturated aqueous solution.

Procedure. --Transfer a weighed 1.000-gram portion of treated wood, which has been ground to pass a 30-mesh sieve to a 200-milliliter Kjeldahl flask. Add 25 milliliters of concentrated HNO_3 and 3 milliliters of concentrated H_2SO_4 . Gently heat the contents of the flask until the initial vigorous reaction has subsided, and then apply more heat until strong fumes of H_2SO_4 appear. Should the digest show signs of charring, several drops of nitric acid will clear the solution. It may be necessary in the case of very resinous samples to add several additional small portions of HNO_3 . The final digest should be clear green.

Transfer the digested sample quantitatively to a 150-milliliter Erlenmeyer flask and heat to fumes of H_2SO_4 again.

Cool, add 1 milliliter of hydrazine sulphate solution, rinsing the neck of the flask with distilled water to wash all traces of hydrazine sulphate into the acid mixture. Heat to fumes once more and fume for 10 minutes. Cool and dilute with 40 milliliters of distilled H_2O . Add 0.5 milliliter of ferrous o-phenanthroline perchlorate indicator and titrate with standard ceric sulphate, approximately 0.01N (prepared by dilution of stock solution of 0.1N reagent), using a 2-milliliter microburette. The titrant should be added in 0.01 milliliter portions, and generally about 0.07 milliliter will be required (about 0.004 percent As_2O_5). At the end point the color changes from orange-red to faint green. The volume taken need not be recorded, but the end point should be stable in 15 seconds. Read the burette and add 3 drops of osmium tetroxide catalyst when the color of the reduced form of the indicator is restored; and titrate with the standard ceric sulfate, adding the titrant slowly as the end point is approached. Standardize the approximate 0.01N ceric sulfate by titrating aliquots of standard 0.01N arsenite solution carried through the above process, or alternatively 0.01N arsenite solution.

Boron

Quantitative Microdetermination of Boron in Organic Compounds by Combustion in Oxygen

Obtemperanekaya, S. I. and Likhosherstova, V. N. Vestnik Moskov Univ.,
Khim, Ser. II, 15, No. 1, 57-9 (1960).

The Schöniger method (Chem. Abs. 50, 9223d) for the determination of halogens and sulphur has been applied to the determination of boron in organic compounds.

The combustion took place in a 250-milliliter Erlenmeyer flask that contained 5 milliliters of 0.5N NaOH, 6 milliliters of distilled H₂O, and was filled with 0. The organic boron compound (5.111 to 11.946 milligrams) was wrapped in an ash-free filter paper and hung, in the flask, on a platinum wire attached to a ground glass stopper. The paper was ignited and inserted into the flask. After combustion, the solution was acidified with 0.5N H₂SO₄ to methyl red, boiled for a few minutes, and neutralized with 0.02N NaOH. Then 0.5 gram mannitol was added, and the solution was titrated with 0.02N NaOH with phenolphthalein indicator. The amount of boron was calculated. The method is rapid and can be applied for boron determination in presence of Fe, Cl, N, and K. The error does not exceed ± 0.2 percent.

Carminic Acid Determination of Boron

U. S. Department of Agriculture Handbook 60, 135 (1954).

The sample is mixed with CaO and ashed. The ash is dissolved in dilute HCl, and the solution is transferred to a volumetric flask, and made up to a standard volume. Varied amounts of the solution are transferred to Erlenmeyer flasks and a solution of carmine in concentrated H₂SO₄ is added. The transmittance is compared with that of standards that have been prepared with graduated amounts of H₃BO₃. A calibration curve is prepared.

Apparatus. -- A spectrophotometer or photoelectric colorimeter. Alkali-resistant (boron-free) glassware, porcelainware, platinum, or fused-quartz dishes. Avoid the use of borosilicate glassware.

Reagents required. -- Calcium oxide, powdered; hydrochloric acid, 1 to 1; hydrochloric acid, concentrated; sulfuric acid, concentrated; carmine (0.05 percent by weight in concentrated H₂SO₄, 0.920 gram per l. Shake until completely dissolved); and boric acid, 100 parts per million of boron. (Dissolve 0.5716 gram of boric acid in water to make 1 liter of solution.)

Procedure. -- Weigh a portion of the dry sample (usually 2.000 grams) containing not more than 1.00 milligram of boron and transfer to a porcelain casserole or platinum dish. Add 0.1 gram of powdered calcium oxide per gram of sample and mix well. Ignite as completely as possible in a muffle at 500° to 550° C., cool the residue, and moisten with water. Cover with a watchglass and introduce 3 milliliters of hydrochloric acid (1 to 1) per gram of sample. This should make the solution strongly acid. Heat on a steam bath for 20 minutes. Transfer quantitatively to a 100-milliliter-volume flask, fill to volume with H₂O, and filter through a dry filterpaper.

Prepare a series of standard solutions containing 0 to 10 parts per million of boron (0 to 1.00 milligram per 100 milliliters) by diluting 0, 2, 4, 6, 8, and 10 milliliters of dissolved boric acid to 100 milliliters. Pipet 2 milliliters of each of the standards and of the unknowns into Erlenmeyer flasks. Add 2 drops of concentrated hydrochloric acid to each standard and 2 drops of water to each unknown. Add 10 milliliters of concentrated sulphuric acid to each Erlenmeyer flask, mix, and cool. Add 10 milliliters of the carmine that has been dissolved previously in sulfuric acid, mix, and allow to stand at least 45 minutes for color development. Determine the transmittance at 5,850 angstroms or by means of a suitable yellow filter.

Calculations. -- Parts per million B in dry plant material equals (parts per million B from calibration curve times 100) per gram of sample.

Carminic Acid Procedure for Determination of Boron

Callicoat, Durward L. and Wolszon, John D. Anal. Chem. 31, 1434-7 (1959).

Lack of reproducibility in the carminic acid procedure for the determination of B prompted a reevaluation of the factors affecting the sensitivity and the precision of the method. Water content, the qualities of the carminic acid reagent and those of the H₂SO₄ were found to be significant variables in the method. A modified procedure for the determination of B by the method is proposed. The accuracy and precision of the proposed procedure is ±0.3 gamma of B over the range of 0 to 40 gamma of B. (Chem Abs. 53, 214003i).

Reagents required. -- Standard solution of boric acid. This solution is required for standardization.

Calcium hydroxide suspension, 8.00 grams of CaO per liter. This reagent is stored and transferred in polyethylene ware.

Sulfuric acid reagent. Two liters of reagent grade H₂SO₄ is carefully added to a chilled solution of 100 to 120 milliliters of H₂O and 5 milliliters of concentrated HCl. This range of H₂O addition gave complete development in 90 minutes with

the lots of acid and carminic acid used. For each batch of reagents prepared, the minimum amount of H_2O that will give complete color development in the desired period of development time is experimentally determined. This insures maximum sensitivity for that development time. The reagent is stored and dispensed by a self-filling burette system vented through drying tubes.

Carminic acid reagent. One gram of carminic acid per liter of concentrated H_2SO_4 .

Procedure. --Add 25 milliliters of the $CaOH$ suspension to 500-milliliter low-boron flasks containing nearly neutral boron samples that do not exceed 250 milliliters in volume. Evaporate the solution to dryness in a water bath at $90^\circ C$. Add exactly 40 milliliters of H_2SO_4 reagent, stopper, and swirl briefly to dissolve the residue. Add exactly 10 milliliters of the carminic acid reagent, mix thoroughly, and allow to stand at room temperature for 90 minutes (or the selected time interval).

The absorbency is measured at 610 millimicrons in relation to a reagent blank carried through the entire procedure. The boron content may be obtained from a calibration curve. The calibration curve should be checked frequently, and a new one is required whenever fresh batches of reagents are used. If desired, standard samples may be carried with the others, and the calculations carried out by method of Calkin and Stenger (Calkin, R and Stenger, V.A. Anal. Chem. 28, 399 (1956)).

Colorimetric Determination with Quinalizarin of Boron in Plants

Bardzicka, Boguinala and Krouse, Anna. Chem. Anal. (Warsaw) 5, 791-5 (1960). (see Boron, Chem. Abs. 49, 1472b.)

The following procedure is recommended for determining boron in plants: Ash a 0.5-to 2-gram sample that has been air dried and ground, roast briefly at $450^\circ C$., cool, and add 2 milliliters of saturated aqueous $Ca(OH)_2$ per gram sample. Dry, roast at $600^\circ C$. for 30 minutes, dissolve the ash in 10 milliliters 1N H_3PO_4 , filter, evaporate 5 milliliters of the filtrate, and dry the residue at $150^\circ C$. for 2 hours. After it is cool, dissolve the residue in 5 milliliters of concentrated H_2SO_4 , add a few crystals of Mohr's salt, and shake. To 1.5 milliliters of solution, add 1 milliliter 0.01 percent quinalizarin in concentrated H_2SO_4 , and determine the extinction within 24 hours on a Pulfrich photocolormeter with SG1 filter and 0.5-millimeter cell. The Beer-Lambert law was valid up to 10 milligrams boron per 25 milliliters solution. The error was not higher than ± 3.6 percent. (Chem. Abs. No. 4, 3292e.)

Semimicrodetermination of Boron in
Organic Compounds

Kuck J. A. and Grim, Elizabeth C. Microchem. J. 3, 35-41 (1959).

A semimicromethod for determining boron in organic compounds describes a high-pressure O bomb technique from which the H_3BO_3 present in the ignition residue is determined. Titration of H_3BO_3 in aliquots of the aqueous extract is made with dilute alkali by adding mannitol and then using a pH meter and a glass electrode. (Chem. Abs. 53, 12950g.)

Determination of Trace Quantities of Boron With
Two New Colorimetric Reagents

Grob, Robert L. and Yse, John H. Anal. Chim. Acta 14, 253-62 (1956).

A new method is described for decomposing fruit tree leaves and alfalfa with a mixture of 96 percent H_2SO_4 and 30 percent H_2O_2 , and distilling off the boron. Two boron complexes are formed with the reagents 5-benzamido-6'-chloro-1, 1'-bis (anthraquinonyl) amine (reagent I) and 5-p-toluidino-1, 1'-bis (anthraquinonyl) amine (reagent II). Solutions of the two complexes follow Beer's law over the boron range indicated: Reagent I, 0 to 0.5 gamma at wave length of 635 millimicrons and reagent II, 0 to 0.4 gamma at wave length 720 millimicrons. Standard deviation for determination of boron with reagent I was 0.001 gamma of boron; with reagent II, 0.002 gamma of boron. (Chem. Abs. 51, 4198e.)

Microdetermination of Boron by Flame Photometry of
the Barium Borotartrate Complex

Bovalini, Enrico, Pucini, Luigi, and LoMoro, Antonio. Ann. Chim. (Rome) 49, 1046-50, (1959). (See Chem. Abs. 52, 15335d.)

The precipitate of $Ba_5B_2C_{16}H_8O_2$, obtained as previously described, is determined by solution in HCl and barium estimation by flame photometry at 873 microns. This method works well for 4 to 20 gamma of boron. (Chem. Abs. 54, 1167g.)

Microdetermination of Boron in Organic
Boron Compounds

Yasuda, S. K. and Rogers, R. N. Microchem. J. 4, 155-61 (1960).

The procedures described utilize the Schöniger combustion technique (Chem. Abs. 49, 8734h) for the initial decomposition of a wide variety of compounds.

Any strong acids formed during the combustion are pretitrated coulometrically in a medium containing 25 to 30 percent MeOH and NaNO₃ as supporting electrolyte. Pelletized mannitol is added after pretitration, and the system is retitrated for H₃BO₃. Potentially interfering acids were studied in the presence of H₃BO₃ and found to show negligible effects. Usual sample sizes ranged from 2 to 7 milligrams. A single determination requires about 25 minutes.

Polarographic Determination of Boron

Lewis, D. T. Analyst 81, 531-6 (1956).

The addition of H₃BO₃ to a solution that contains 0.2M Na₂SO₃ and 0.33M mannitol yields mannitol-boric acid, which displaces HSO₃. The HSO₃ has E_{0.5} = -0.50 and -1.01 volt versus the Hg anode when a polarogram is taken. A plot of $h^2/(H^+)^2$ versus log C for the first wave is linear where h equals wave height in millimeters, (H⁺) is the measured value for the solution polarographed, and C equals moles per l of H₃BO₃. (Chem. Abs. 51, 1768b.)

Polarographic Determination of Boron. Mannitol-Sulfite System Applied in Rotating Cathode Polarography

Reynolds, G. F. and Terry, E. A. Ann. Chim. (Rome) 50, 177-89 (1960).

The method of Lewis (Chem. Abs. 51, 1768a) is sensitive to 2 to 4 gamma of B per milliliter. A linear relation exists between the height of the reduction wave and concentration. Boron can be determined to 0.2 gamma per milliliter by adding 30 milliliters of 0.005N Na₂SO₃ and 0.3M mannitol and 10 milliliters of 2.5 M KCl, degassing with hydrogen for 20 minutes, adding orthoboric acid to give 1.08 gamma per milliliter and a pH of 3.9, and running a polarogram.

Photometric Determination of Boron by Solvent Extraction Using Monemethylthionine

Pasztor, Laszlo C. and Bode, J. Daniel. Anal. Chem. 32, 1530-1 (1960).

The successful modification and application to steel analysis (Pasztor, L. C., Bode, J. D., Fernando, Q., Anal. Chem. 32, 277, 1960) of Ducret's methylene blue-boron method (Ducret, L., Anal. Chim. Acta 17, 213, 1957)

led to a study of other thionine derivatives. Azure C (monomethylthionine) is shown to be superior to methylene blue for the photometric determination of boron. Azure C with 1, 2-dichloroethane (reagent I) and mixtures of this reagent with 1, 2-dichloropropane or CCl_4 (reagent II) gives a lower reagent blank, and extends the concentrated range as compared to methylene blue. From 0.1 to 200 gamma of boron can be determined without diluting. The procedure involves solution in H_2SO_4 , ignition of any residue with Na_2CO_3 , and then the addition of 5 percent HF to form boron fluoride. The oxidation state is adjusted by titration with 0.1M KMnO_4 followed by the addition of 2 to 3 milliliters of 4 percent ferrous ammonium sulfate solution, and the volume is brought to 50 milliliters. Azure C is added and the complex is extracted into 1, 2-dichloroethane or reagent II (above). The absorbency is measured at 658 millimicrons with a calibration curve.

Wet Digestion of Plant Material Gives Low Boron Values

Hatcher, John T. Anal. Chem. 32, 726 (1960).

Results of plant material analyses for boron by dry ignition and by wet digestion procedures are compared. The results of wet digestion of 12 plant species, carried out in borosilicate glassware, were corrected by a small blank. Boron was determined colorimetrically with the carmine reagent (see Chem. Abs. 44, 6341b) and confirmed by the electrometric titration procedure (see Wilcos Chem. Abs. 26, 1214). Some H_3BO_3 is lost by volatilization from the acid solution. Time and temperature variations in digestion result in a lack of precision. Therefore, the wet digestion procedure is not satisfactory for the determination of boron in plant material. (Chem. Abs. 54, 1394h.) Procedure is listed in U. S. Department of Agriculture Handbook 60, 135 (1954).

Chlorine

Rapid Micromethods of Elemental Analysis

I. Determination of Chlorine in Organic Compounds

Olson, Edward G. and Krevis, Alan F. Microchem. J. 4, 181-6 (1960).

The sample is decomposed by a simplified Schöniger flask combustion in which no H_2O_2 is used so that time-consuming boiling off of the H_2O_2 is not

necessary. Also, it is not necessary to dispose of the CO_2 in solution. The liberated Cl^- is determined by coulometric titration with electrolytically generated Ag^+ . The method is rapid (20 to 25 samples can be determined in a day), and is suitable as a routine procedure that nontechnical personnel could handle.

Rapid Method for Microdetermination of Halogen in Organic Compounds

Cheng, F. W. *Microchem. J.* 3, 537-42 (1959).

This procedure consists of a Schöniger flask combustion technique with an improved method for mercurimetric titration of the halogen. The improvement involves the use of an alcohol-water mixture as the solvent in which the detection of the end point is greatly enhanced. This makes the mercurimetric titration suitable for microdetermination. (Chem. Abs. 54, 8439c.)

Spectrophotometric Method for the Determination of Chlorine in Organic Compounds: A Semimicro- and Micromethod

Lysyj, Ihor, *Microchem. J.* 3, 529-36 (1959).

Use is made of an O flask combustion technique. The Cl ions produced in the process of combustion are reacted with mercuric chloranilate to produce strongly colored chloranilic acid, which is measured spectrophotometrically. Materials that have been successfully determined include those containing from 0.1 to 50 percent Cl . S, N, and P do not interfere. Sample size is limited to 50 milligrams. (Chem. Abs. 54, 8439e.)

Titrimetric Methods for the Microdetermination of Halogens in Organic Compounds by the Rapid Combustion Procedure

I. The Determination of Individual Halogens

Fildes, J. E. and Macdonald, A. M. G. *Anal. Chim. Acta* 24, 121-7 (1961).

Critical studies were made of titrimetric microdetermination methods for Cl , Br , and I in organic compounds containing O, N, S, and halogens, after decomposition by rapid empty-tube combustion (Belcher and Ingram; *Chem. Abs.* 47, 4138g), and suitable methods are given. HNO_3 and H_2SO_4 do not interfere in the microdetermination of halogens by the $\text{Hg}(\text{CN})_2$ HgO method (Viebock, *Chem. Abs.* 26, 3206 as modified in *Chem. Abs.* 48, 4370f). The

sensitive amplification methods based on oxidation of I^- to IO_3^- (Leipert, Chem. Abs. 24, 2398) or of Br^- to BrO_3^- (Kolthoff, Chem. Abs. 31, 21235) followed by iodometric determination of the respective halate ion, give satisfactory results. To determine Cl or Br in the absence of N and S, burn the sample (B and I, Chem. Abs. 47, 4138g) by using an exactly measured absorption solution of 10 milliliters of 0.01N NaOH plus 0.5 to 1 milliliter of 30 percent H_2O_2 . After combustion, add a known excess of 0.01N H_2SO_4 , boil 2 to 3 minutes, cool and back-titrate with 0.01N NaOH to methyl red (methylene blue-screened) end point. To determine Cl in the presence of S or N, carry out the combustion, absorption, and titration with 0.01N NaOH as above, but match the end point against an equal volume of neutral distilled H_2O and screened methyl red indicator. Add 10 milliliters of saturated $Hg(CN)_2 \cdot HgO$, titrate the liberated OH^- with 0.01N H_2SO_4 to color matching the two solutions, add the same volume of 0.01N H_2SO_4 plus 10 milliliters $Hg(CN)_2 \cdot HgO$ solution to the second flask, and titrate with 0.01N NaCl until the color again matches that of the first solution. (Chem. Abs. 55, No. 9, 8155h.)

Determination of Cl^- Ion by Conductometric Titration with $Hg(NO_3)_2$.

Pasovskaya, G. B. Lab. Delo 1959, No. 4, 19-21.

The ion of bivalent Hg forms with the Cl ion a nondissociating compound easily soluble in water, which does not change its electrical conductivity with time. Experiments were made with solutions of pure NaCl, and the interfering ions were studied. The method was checked also on natural waters by comparing the Cl ion content with that obtained by the Mohr method. An aliquot, measured with a micropipet, was placed in the vessel for conductometric titration, diluted with distilled H_2O to 25 milliliters, one drop of methyl orange and N HNO_3 to an acid reaction were added, and then titrated with $Hg(NO_3)_2$. Ions of K, Na, NH_4^+ , Mg, Ca, Al, Fe, carbonates, bicarbonates, and silicates do not interfere even if present in large quantities. In the presence of sulfates, a larger quantity of N HNO_3 should be added.

Mercurimetric Determination of Chlorine and Bromine in Organic Compounds

Glukhovskaya, R. D. Trudy Tomsk. Gosudarst Univ. im V. V. Kuibysheva, Ser, Khim. 145-5-ya Nauch Kurf. 1954, 77-82 (Pub. 1957); (see Chem. Abs. 53, 3587c.)

A mercurimetric determination of halogens in organic compounds that uses a faster and simpler method of decomposition was developed. All present methods for the decomposition of organic compounds were discussed; fusion in a bomb is considered best. In a small tube or sealed ampule 80 to 100 milligrams of sample are placed together with 250 to 300 milligrams Na in a dry stainless steel bomb (Chem. Abs. 52, 1681h). The bomb is then closed and heated to redness for 15 to 20 minutes. The fusion is treated first with absolute alcohol, then with H_2O neutralized with 6N HNO_3 with phenolphthalein indicator, and filtered into a 100-milliliter-volumetric flask. After diluting to the mark, 10 milliliters of the dilute solution is acidified with 3 drops 0.5N HNO_3 , boiled, cooled and, after addition of 3 drops of alcohol diphenyl-carbazone solution (1 percent) titrated with 0.025N $Hg(NO_3)_2$ to a violet color. A second 10-milliliter portion is used for a Volhard determination. The results obtained by the mercurimetric method are better than those obtained by the Volhard method. In the case of $C_6H_4Cl_2$ and $C_6H_2Cl_3NH_2$ both methods give poor results because of incomplete decomposition of the organic substance. (Chem. Abs. 54, 9602g.)

Rapid Micromethod for Determination of Halogens in Organic Compounds

Sokalova, N. V., Orestova, V. A., and Nikolaeva, N. A. Zhur, Anal. Khim. 14, 472-7 (1959).

The outlined method is a modification of the Schöniger method (Chem. Abs. 49, 8734h). It uses a specially designed flask for combustion. The sample to be analyzed is wrapped in an ashless filter paper and clamped to the platinum mesh suspended on a platinum wire that is attached to the tip of the ground-glass stopper. The flask contains 10 milliliters of H_2O and the requisite reagents (KOH and H_2O_2 for Cl). The air in the flask is replaced by O and the sample is then oxidized. The halogens are then titrated in the same flask. (Chem. Abs. 54, 10647h.)

The Reaction of Pentachlorophenol With 4-Aminoantipyrine

Beneze, K. and Pleskova, A. Chem. Zvesti 11, 621-5 (1957) (German Summary).

A micromethod is described for the determination of pentachlorophenol. Colorless $(NH_4)_2S_2O_8$ was used for oxidation and Na_2CO_3 (see Gottlerb and March, Chem. Abs. 40, 12699) for pH. The antipyrine coloring of the pentachlorophenol is blue. (Chem. Abs. 52, 7948f).

Fluorine

Determination of Fluorine by Precipitation With Lead Chloronitrate

Comprehensive Analytical Chemistry, edited by C. L. Wilson and D. W. Wilson, P. 553-60. (287, W69, v. 113.)

The organic compound is fused in a bomb with alkali metal. Fluoride is precipitated as lead chlorofluoride and determined gravimetrically. The procedure is given in detail.

The sodium carbonate fusion is described as being of little present value.

Rapid Determination of Organically Bound Fluorine

Senkowski, B. Z., Wollich, E. G., and Shafer, E. G. E. Anal. Chem. 31, 1574 (1959).

The sample is burned in the presence of a small quantity of sodium peroxide in an atmosphere of oxygen, in a Schöniger borosilicate glass flask. In the resulting solution, fluorine is determined photometrically by Megregians procedure, which uses Eriochrome Cyanine R and Zirconyl chloride solutions. Small quantities of phosphate do not interfere, but larger proportions require a Willard-Winter distillation.

The Schöniger Combustion II. Microdetermination of Fluorine

Saep, H. Mededel. Vlaam. Chem. Ver 21, 49-73 (1959); (see Chem. Abs. 53, 16804e).

After an extensive survey of the literature on the determination of F, five different methods, tested in Saep's lab., are described in extensive detail. They comprise the determination of F: by (1) Titration with CeCl_3 and murexide; (2) titrimetrically with Fe^{+++} salts; (3) color imetrically with Fe^{+++} salicylate; (4) argentometric titration of the PbClF precipitate; (5) titration with $\text{Th}(\text{NO}_3)_4$ and Na alizarinsulfonate. The last method (Strenger and Kolthoff, Vol. Analysis, 1947, Vol II, p. 320) is most suitable for use after the Schöniger combustion (Mikrochimica Acta, 1956, 869-76) although some modifications were introduced. These are the use of mixed indicators (methylene blue - Na alizarinsulfonate), the addition of 40 percent iso-PrOH

before titrating, and the determination of the so-called $\text{Th}(\text{NO}_3)_4$ factor. This factor takes into account differences between determinations in a fluoride solution and after a Schöniger combustion. Only in the presence of CF_3 groups are too low values found, although the error is less than 1 percent. (Chem. Abs. 54, 4253c.)

Spectrophotometric Determination of Fluoride
by Using Lanthanum Chloranilate

Hoyashi, Kiyoko, Danzuka, Taeko, and Uene, Keihei. *Talanta* 4, 126-32 (1960).

It has been found possible to determine 2 to 200 parts per million fluoride with an accuracy of ± 2 percent if the proper reaction conditions are chosen. $\text{SO}_4^{=}$, Cl^- , and NO_3^- do not interfere up to 200 parts per million. Application of this procedure to F determination in organic fluorocompounds is described.

Coulometric-Acidmetric Titration of Fluoride
in Acetic Anhydride

Mather, William B., Jr., and Anson, F. C. *Anal. Chem.* 33, 132-4 (1961).

Fluoride can be titrated coulometrically by the generation of HClO_4 at an Hg anode. The solvent is Ac_2O containing a small amount of HOAc . NaClO_4 is the supporting electrolyte. The end point is determined potentiometrically with an accuracy of 2 to 3 points per thousand. Most anions act as bases in this solvent and are titrated with the fluoride to obtain total base, or are removed or exchanged for ClO_4^- . The method was applied to the determination of total base in mixtures of F^- with $\text{SO}_4^{=}$, Cl^- , NO_3^- , and $\text{CO}_3^{=}$. In the case of F^- and Cl^- and a few other binary mixtures, two end points are observed, making possible the simultaneous determination of both components. (Chem. Abs. 55, No. 11, 7144i.)

Determination of Sodium Fluoride in Wood

Kometani, T. Y. (Bell Telephone Laboratories).

Presented at 1961 meeting of AWPA.

When powdered lanthanum chloranilate is added to an acid-buffered fluoride solution, it reacts with the fluoride ion to produce insoluble La F_3 and a highly colored acid chloranilate ion. The absorbency is measured spectrophotometrically at 530 millimicrons. An absorption curve is made from standard sodium fluoride for comparison.

A Polarographic Method for Fluoride

Wallis, C. P. Talonia 5, 61-2 (1960).

A reagent containing o-nitrobenzenearsonic acid, $\text{TH}(\text{NO}_3)_4$, NaF, $\text{ClCH}_2\text{CO}_2\text{H}$, NaOH, and NH_4Cl is used as a blank for the determination. The addition of NaF to the reagent is necessary to avoid a flat portion of the calibration curve. Two milliliters of sample solution are neutralized with HClO_4 to a paramethyl red end point, and 1 milliliter of reagent is added. The method will detect gamma quantities of F^- . (Chem. Abs. 55, No. 4, 3279e.)

Submicro-Methods for the Analysis of Organic Compounds X. Determination of Fluorine

Belcher, R., Leonard, M. A., and West, T. S. J. Chem. Soc. 1959, 3577-9; (see Chem. Abs. 54, 4270e).

A sample of the compound, which has been previously dried over P_2O_5 and which is sufficient to give 10 to 40 gamma of F on combustion, is deposited on ashless filter paper that is folded so that it can be suspended from a platinum spiral. The paper is burned in a 250-milliliter flask containing approximately 30 milliliters of distilled water and an atmosphere of oxygen. After combustion, the solution is allowed to stand for 10 minutes with occasional shaking. The solution and washings are then transferred with 10 milliliters of 0.0004M alizarin complex on solution (1,2-dihydroxyanthraquinon-3-ylmethylamine-N, N-diacetic acid) and 2 milliliters of pH 4.3 acetate buffer to a 100-milliliter volumetric flask. After dilution to approximately 75 milliliters, 10 milliliters of 0.005M Ce^{+3} are added with swirling, then the solution is diluted to 100 milliliters and allowed to stand for 1 hour protected from light and drafts. The optical density of the solution is determined in 4-centimeter cells at 610 millimicrons against a blank containing only reagents. Within the range of 15 to 50 gamma the absolute accuracy is ± 0.5 percent. When the compound contains CF_3 groups, the sample should be covered with 1 milligram of KClO before it is folded into the paper. There is no interference from the other halides, sulfate or nitrate. (Chem. Abs. 54, 13952b.)

Photometric Determination of Fluorides

Itai, Takanobu and Nakashima, Toshiaki. Eisei Shikenjo Hokoku No. 77, 75-9 (1959).

The quantitative method of Bumsted and Wells (Anal. Chem. 24, 1595-7 (1952), Chem. Abs. 47, 659g) is improved to yield a more intense color by replacing H_2SO_4 with HCl . More reproducible results can be obtained by adding 50 gamma of F^- accurately and by making a wide range of F^- standard solutions, followed by the improved procedures. Recovery of about 3 milligrams of $\text{Zn SiF}_6 \cdot 6\text{H}_2\text{O}$ was 97 to 100 percent complete. (Chem. Abs. 55, No. 9, 8156g.)

Determination of Fluorine by Complexometric Titration

Okada, K. and Sugiyama, T. Am. Rept. Takomini Lab. 9, 185-92 (1957) (English summary).

F^- (1 to 20 percent) is precipitated as CaF_2 in aqueous, approximately 70 percent alcohol solution, by excess CaCl_2 solution (0.0025 or 0.005M). The dissolved excess Ca^{++} is titrated against EDTA with Eriochrome Black T as indicator and monoethanolamine as buffer. The limit of error is ± 1 percent. Cl^- , Bi^- , NO_3^- , and ClO_4^- do not interfere with the determination. (From C. Z. 1958, 12783.) (Chem. Abs. 55, No. 1, 215d.)

Zinc

Polarographic Determination of Cu, Zn, and Cr in a Catalyst

Sarancha, E. T. and Dzyubenko, M. C. Zavodskaya Lab. 26, 1077-8 (1960).

The half-wave potentials of Cu, Cr^6 , and Zn on a background of 1N NaOH solution are, respectively, -0.3, -0.8, and -1.35 gamma with respect to an Hg anode at the bottom of the electrolyzer. A solution containing all of these elements yields a polarogram with three distinct waves in which direct proportionality exists between the concentration of each component and the height of the corresponding wave. The method is tested on artificial mixtures, and used for determination of Cu, Zn, and Cr in a HNO_3 solution of the catalyst sample. (Chem. Abs. 55, No. 1, 234h.)

Evaluation of Methods for Trace Zinc Determination

Margerum, D. W., and Santacana, F. Anal. Chem. 32, 1157-61 (1960).

Eight methods for the determination of 6 to 60 gamma of Zn were evaluated in the presence of an excess of a variety of metallic impurities. All the methods included the separation of the Zn by either dithizone extraction in the presence of masking agents (method I) or anion exchange resin elution with HCl. The preferred method (I) uses bis (2-hydroxyethyl) dithiocarbamate as a masking agent in the dithizone extraction (Serfass, Chem. Abs. 43, 8904a; Butts, Chem. Abs. 45, 7280f). Trace studies with Zn⁶⁵ showed that 99 percent of the Zn was present in the final dithizone-CCl₄ phase. (Chem. Abs. 54, 24125 (1960).)

Procedure is given in Metal Finishing 49-4 50 (1950).

Determination of Zinc in Plants

Johnson, K. E. E., Linden, E. I., Brammell, W. S., and Benne, Erwin J. J. Assoc. Official Agr. Chem. 42, 363-7 (1959).

The one-color dithizone method (Chem. Abs. 50, 3162c) was revised to eliminate all steps not essential to accuracy, and reduce glassware to a minimum, to provide a method that can be completed in a few minutes' time, and to expedite handling of large numbers of samples. The method gives reproducible results, practically complete recovery, and agreement with A. O. A. C. method. (Chem. Abs. 53, 15868g.)

Note: This method does not give good separation according to Margerum and Santacana (Anal. Chem. 32, 1157, 1960).

Determination of Zinc in Plants and Soils

Verdier, E. T., Steyn, W. J. A., and Eve, D. J. J. Agr. Food Chem. 4, 354-60 (1957); (see Chem. Abs. 50, 8367d).

A critical investigation of the reliability of the dithizone and polarographic methods for the determination of Zn is presented. A satisfactory modification of the Cowling and Miller dithizone photometric method (Chem. Abs. 35, 2813²) was devised by the close study of the influence of pH on Zn extraction, transmittance curves, and accuracy of the technique. With this modified procedure, 24 determinations of Zn per day could be carried out. A modified polarographic method, aimed at the elimination of a preliminary separation step, was found to lend itself also to the simultaneous determination of Cu, Ni, Mn, and possibly Co. (Chem. Abs. 51, 16200a.)

Note: Margarum and Santacana (Anal. Chem. 32, 1157-61 (1960)) say that impurities can cause very high results, and they do not recommend using this method for dithizone extraction.

Dithizone as an Indicator for the Direct
EDTA Titration of Various Metals

Costa, A. Celse. Chemist Analyst 47, 39-40 (1958).

The direct EDTA titration of Zn, Cd, Pb, Bi, and Ni was effected with dithizone as indicator by using aqueous media containing a miscible organic solvent such as acetone, pyridine, EtOH, MeOH, or MeOH-BuOH mixtures. Best results were obtained with a 1:4 pyridine-water medium, adjusted to the appropriate pH. (Chem. Abs. 52, 16117h.)

Microdetermination of Zinc in Plant Material by Means of
EDTA and a Fluorescent Indicator. I. Method

Bodinas, A. Publs. Inst. Biol. Apl. (Barcelona) 28, 75-80 (1958).

The yellow to green fluorescing chelate of Zn with 8-hydroxyquinoline-5-sulfonic acid is used to determine the metal after the removal of interfering ions by EDTA in the presence of KCN. To 10 milliliters of solution containing 0.3-30 milligrams of Zn in a 50-milliliter thin-walled vessel, add 1 milliliter $\text{NH}_4\text{Cl-NH}_4\text{OH}$ buffer of pH 10, 1 milliliter of 0.2M KCN solution (stored in a dark flask) and 3 drops of indicator (0.2 percent aqueous 8-hydroxyquinoline-5-sulfonic acid dissolved with the aid of a few drops of triethanolamine). If traces of Ca plus Mg are present (as shown by a yellowish-green fluorescence with ultraviolet light), they are removed by adding 0.04 percent aqueous solution of Na_2EDTA until the fluorescence disappears. Add 1 milliliter of 0.2M (3.4 percent) aqueous chloral hydrate solution, and in the presence of Zn a brilliant yellowish-gold fluorescence will appear after 2 to 3 minutes. Add the Na_2EDTA solution from a 2-milliliter microburette until this fluorescence disappears. The titration value will correspond to the amount of Zn present (and Cl, should any be present). When using 32.7 gamma of Zn in solution, the recovery of 20 determinations was 31.3-34.0, average 32.62. (Chem. Abs. 53, 18754c.)

Zinc Determination with Zincon and the Protective Action of
Polyphosphates in the Estimation of Trace Elements

Binnerts, W. Tj. Chem. Weekblad 56, 66-7 (1960) (English summary).

After wet ashing, Zn determination with Zincon (0- (2-(a-(2-hydroxy-5-sulfophenylazo) benzylidene) hydrazino) benzoic acid) was performed in liver and in concentrated feed mixtures containing 0.003 percent Zn or more. This method is faster than Zn analysis with dithizone, after destruction at higher temperatures, described by Campen and Dumoulin (Chem. Abs. 54, 7434c). The interference in the estimation with Zincon of Cd, Co, Cu, Ni, and Pb was negligible. The strong binding capacity of $\text{Ca}(\text{H}_2\text{PO}_4)_2$ polymers for Zn at high temperatures, as reported by Campen and Dumoulin, is considered to be based on an adsorption process rather than on the formation of a real chemical bond. Milk ash and Ca salt plus phosphate mixtures, gave considerable protection during the combustion in the determination of Zn. It is supposed that addition of $\text{Ca}(\text{H}_2\text{PO}_4)_2$ before ashing will prove valuable in the estimation of trace elements. (Chem. Abs. 13984a.)

Polarographic Determination of Microquantities of Copper, Lead, and Zinc in Presence of Iron

Sakharov, A. A. Zavadshaya Lab. 25, 791-2 (1959).

With this method, one can determine gamma amounts of Cu, Pb, and Zn in solutions containing large amounts of Fe without previous removal of the Fe. The Cu and Pb are determined on a background of an ammoniacal solution of $\text{KNaC}_4\text{H}_4\text{O}_6$. For the determination of Pb and Zn, a background of a slightly acidic or neutral solution containing ascorbic acid to reduce Fe^{+++} to Fe^{++} is recommended. Since high galvanometer sensitivity is essential, dissolved O must be removed from the solution. Metol is preferable to NaS for this purpose because it acts faster, is stable in ammoniacal solutions in presence of sulfite, and is polarographically indifferent. Addition of ascorbic acid to the polarographic background obviates the necessity for using indifferent gases for removal of the dissolved O. In acidic and neutral solvents, Zn^{++} is reduced at the dropping mercury electrode at approximately -1 volt (saturated calomel electrode); Fe^{++} gives a reduction wave only at -1.5 volts, and does not prevent the measurement of the height of the Zn wave. (Chem. Abs. 53, 18745d.)

Polarographic Analysis with Complex-Forming Reagents. II. Determination of Zinc in the Supporting Electrolyte Containing Ethylenediaminetetraacetic Acid and NaOH

Nakogawa, Genkichi. Nippon Kagaku Zasshi 78, 1363-7 (1957); (see Chem. Abs. 52, 12673f).

Zinc is present as ZnO_2^- ion in 2M NaOH solution even in the presence of EDTA up to 4M. The half-wave potential of Zn in 2M NaOH is -1.51_4 volts versus saturated calomel electrode and -1.50_5 volts in NaOH-containing EDTA. Ni and Co dissolve in this 2M NaOH-containing EDTA as complexes, and do not disturb the polarographic wave of Zn. Therefore, Zn in Ni down to 1:1000 can be determined with this supporting electrolyte. Nitrates and Cd disturb the determination. (Chem. Abs. 52, 13520c.)

Complexometric Titration (Chelatometry) XLV Selective
Determination of Zinc in Slightly Acid Medium by
Means of Xylenol Orange and Methylthymal Blue

Janousek, I. and Studlar, K. Collection Czechoslov. Chem. Commun. 24, 3799-801 (1959). (In German) see Chem. Abs. 54, 3081h.

Investigation of masking reagents revealed that the cyanide complex of Zn at pH 6 is dissociated to such an extent that it reacts quantitatively with indicators and di-Na ethylenediaminetetraacetic acid (reagent I). Cyanide complexes of Cu, Ni, Hg, and Co are stable at this pH. In the determination of Zn in the presence of Cu, Ni, Co, Hg, Al, Ca, Mg, and Ag add 3 to 5 milliliters of 4 percent solution of NaF per 10 milligrams Al to the slightly acid solution, dilute to 150 to 200 milliliters, make slightly alkaline with NH_4OH , add solid KCN until solution is colorless or the precipitate has dissolved, add indicator (0.1 percent solution of xylenol orange in 10 percent EtOH), neutralize with 1:1 HCl to the yellow color, add 20 milliliters acetate buffer solution and titrate with 0.025M reagent I. The standard error is approximately ± 1 percent. Co interferes when present in amounts above 50 milligrams per 200 milliliters. (Chem. Abs. 54, 6406f.)

Use of Trilon B in the Determination of
Zinc in Biological Material

Gorbacheva, N. A. Aptechnoe Delo 7, No. 1, 25-8 (1958).

Reagents required. --0.01M trilon B (reagent I), 3.721 grams per liter. The titer was determined with 0.01M $ZnCl_2$. Indicator used was Chromogen Black, Special (ET-00) 1, and NaCl 200 parts NH_3 -buffer mixture: 350 cubic centimeters 25 percent NH_3 , 54 grams NH_4Cl , and 1 liter of water.

The neutral Zn solution is mixed with the NH_3 buffer (2 to 3 drops per cubic centimeter), 0.1 to 0.15 gram of the indicator is added, and the titration is carried out with reagent I until the color changes from violet-red to pure blue. Acid Zn solutions are neutralized with diluted NH_3 , by using a minimum amount

of methyl red as indicator. Error is ± 1.5 percent. When Zn is determined in the regular way, involving precipitation, filtration, and evaporation, the loss is 10 to 32 percent. (Chem. Abs. 53, 18754f.)

A New Back-Titrimetric Method for the Determination of Zinc with Methyl Red as an Adsorption Indicator

Nosu, Takanosuke, Technical Repts. Tohoku Univ. 24, 1-10 (1959).

A study was made of the factors involved in the determination on Zn with $K_4Fe(CN)_6$ by using methyl red as an absorption indicator. In this method, $K_4Fe(CN)_6$ is added in excess of the Zn present, methyl red indicator is added, and the excess ferrocyanide is back-titrated with $ZnCl_2$ solution. The color change at the end point is from pale yellow to blue. The color change occurs over a pH range from 1 to 6, with the optimum pH from 1.0 to 1.8. The titration is carried out between 60° to 70° . A maximum of 10 drops of 0.1 percent methyl red in alcohol is added per 100 milliliters of solution to be titrated. Zinc can be determined over the concentration range of 0.1 to 1.0 milligram per milliliter of solution. (Chem. Abs. 55, No. 8, 7165c.)

Determination of Zinc and Copper in Biological Material

Roker, K. O. Z. Anal. Chem. 173, 57-8 (1960).

To determine Zn and Cu in plant and other biological material, a sample containing 1 to 10 gamma of Cu and 10 gamma of Zn is ashed, dissolved, and Cu and Zn are extracted with dithizone. After purification, the extract is decomposed with $HClO_4$ and H_2SO_4 . The residue is taken up in a solution containing gelatin and KH phthalate at pH 5, and the Zn and Cu are measured polarographically. If only Zn is present, the procedure can be simplified. (Chem. Abs. 54, 13984e.)

The Use of EDTA to Eliminate Interferences in the Zinc-Ferrocyanide Titration

Davis, Donald G. and MacLendon, Henry T. Talanta 2, 124-7 (1959).

The use of EDTA as a masking agent in the titration of Zn with $K_4Fe(CN)_6$ permits an accurate determination of Zn in the presence of Fe, Ni, Pb, and Al when the pH is controlled at 2.0 to 2.1 and EDTA is added. (Chem. Abs. 53, 14820e.)

Spectrophotometric Determination of Zinc and Other Metals
with A, B, gamma, D-tetraphenylporphine

Bisque, Roman Edward and Banks, Charles V. U. S. Atomic Energy Comm. ISC-781, 28 pp. (1957).

Methods are given for the determination of trace amounts of Zn, K, NH_4^+ , Cd, Na, and Pb in metals or their oxides, which are soluble in AcOH or HCOOH. The method is based on the absorbency at 551 millimicrons of the A, B, gamma, D-tetraphenylporphine-Zn complex in AcOH. Corrections are given for the absorption because of traces of Ni^{+2} , and Fe^{+2} . An alternate procedure is given for use in the presence of traces of Cu^{+2} in Chem. Abs. 52, 3593a. (See also Chem. Abs. 51, 10308e.)

Polarographic Analysis by Complex-Forming Agents. I.
Determination of Zinc in the Presence of Ni or Co with
Nitriloacetic Acid as the Complexing Agent

Nakagawa, Genkichi. Nippon Kagaku Zasshi 78, 808-16 (1957).

Cobalt and Ni do not show polarographic waves in a solution of nitriloacetic acid (reagent I) at pH 9.0, while Zn shows the wave at -1.5 volts. The diffusion current is proportional to the concentrations of Zn and depends on the concentration of reagent I, Ni, or Co, and the pH of the solution. Zn (10^{-4}M) can be determined polarographically in a 0.4M solution of reagent I, which will mask 0.01M, Ni, or Co. (Chem. Abs. 52, 12673f.)

Photometric Determination of Zinc with Zincon-
Application to Water Containing Heavy Metals

Platte, J. A. and Marcy, V. M. Anal. Chem. 31, 1226 (1959).

The colorimetric test for Zn with Zincon is rapid and fairly sensitive, but lacks specificity. Many heavy metallic ions, particularly Cu, interfere. Zinc can be separated from some interfering substances with an anion exchange resin and HCl of various molarities, but the method is somewhat cumbersome and time consuming. In this method, heavy metals, including zinc, are complexed by adding cyanide to the sample. Chloral hydrate is added to free the Zn without destroying the other metallic complexes. The blue Zn-Zincon complex, formed on addition of Zincon to the sample buffered to pH 9, is measured with a spectrophotometer.

Complexometric Analysis of Cation Mixtures.

II. Complexometric Titration of Zinc and Copper
in the Presence of Murexide as Indicator

Z. Anal. Chem. 175, 1-4 (1960); (see Fortuin, Chem. Abs. 48, 8124c.)

Murexide changes from yellow to violet when it is used as an indicator in the titration of Zn with di-Na (ethylene-dinitrilo) tetra-acetate at pH 8 to 9. To determine Cu and Zn in the same sample, determine Cu and Zn by the procedure for Zn. To determine Zn in the presence of Cu, form the CN complexes at pH 8 to 9, destroy the Zn complex with HCHO and determine Zn only as before. The amount of HCHO must be controlled. (Chem. Abs. 55, No. 4, 2300h.)