

Procedures for Analyzing Metal-Finishing Wastes

Methods designed to screen out interfering substances
and selected for accuracy and reproducibility of results.

Reference Data Publication developed from

American Electroplaters' Society Research Project
at Lehigh University, and expanded by the

Metal-Finishing Industry Action Committee

**OHIO RIVER VALLEY
WATER SANITATION COMMISSION**



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Procedures for Analyzing Metal-Finishing Wastes

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Foreword

At the suggestion of its Metal-Finishing Industry Action Committee the Ohio River Valley Water Sanitation Commission sponsored a project at Lehigh University to aid in developing methods of analysis applicable to wastes from electro-plating processes and metal-conditioning operations. In particular, the objective was to secure methods that would screen out substances whose presence interferes with or otherwise distorts results from standard analytical procedures. The project was placed at Lehigh to utilize the data and background previously developed by the American Electroplaters' Society in the conduct of research on impurities in plating solutions. Dr. Earl J. Serfass, head of the department of chemistry, and director of the AES project, acted as director of the Commission's project. The analytical work and writing of the methods was done by Dr. Ralph Muraca, associate professor of chemistry.

This manual has three sections. The first contains methods of analysis for cyanides and metals that have been field-tested, revised and recommended by member companies of the Metal-Finishing Industry Action Committee. They have been evaluated by the eight state pollution-control agencies represented on the Engineering Committee of the Commission and have met with approval.

Correlation of these methods of waste analysis with analytical procedures employed for stream surveys was accomplished with the assistance of Mr. William Lamar, district chemist of the U. S. Geological Survey. Additional correlation of these methods with those used in toxicity studies was developed with the cooperation of Mr. Jacob Cholak of The Kettering Laboratory. Accuracy and reproducibility of results were the criteria used in selecting these procedures for the analysis of metal-finishing wastes. The methods, or parts of them, may assist in the analysis of other industrial wastes but their limitations for such use have not been established.

The second section contains methods adapted from "Standard Methods for the Examination of Water, Sewage and Industrial Wastes" and revised for specific applicability to the concentrations of interfering ions found in metal-finishing wastes.

The third section provides the additional methods necessary to make a complete analysis of plating wastes. These methods are from the forthcoming 10th edition of Standard Methods and are reproduced here with permission of the American Public Health Association.

Field testing of the methods was coordinated by William J. Neill. As members of the Metal-Finishing Industry Action Committee of the Commission, Mr. Neill and Walter J. Pinner, both of whom are past presidents of the American Electroplaters' Society, provided the liaison with that organization. John E. Kinney, staff sanitary engineer, served as committee coordinator and represented the Commission's interest in development of the methods; he was aided in mechanical production of the manual by Elmer C. Rohmiller, staff assistant. Acknowledgment is made of the availability of a federal grant under Public Law 845, a portion of which was used to defray most of the cost of the Lehigh University project.

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Contents

Sampling Metal-Finishing Wastes.....	1
General Considerations.....	3
Section I	
Cyanide.....	7
Cyanate.....	15
Cadmium.....	21
Chromium.....	28
Copper.....	36
Iron.....	42
Lead.....	48
Manganese.....	56
Nickel.....	60
Zinc.....	65
Section II	
Ammonia.....	73
Dichromate Oxygen Consumed.....	77
Chloride.....	80
Chlorine.....	83
Nitrate-Nitrite Nitrogen.....	86
Ortho-phosphate.....	89
Sulfate.....	93
Section III	
pH.....	97
Residue.....	100
Total Solids.....	100
Suspended Matter.....	101
Dissolved Matter.....	101
Settleable Solids.....	101

SAMPLING METAL-FINISHING WASTES

This is a review of the precautions that should be observed in collecting samples of metal-finishing wastes for analysis.

A satisfactory sample of wastes must meet the following basic requirements:

- a. It must be thoroughly representative of the material being examined.
- b. It must be uncontaminated through the sampling technique or by contact with the sample vessel.
- c. It must be properly and thoroughly identified.
- d. It must be of adequate size for subsequent laboratory examination. While recognizing that a lesser volume of sample might satisfy requirements for a given analytical measurement a minimum volume of sample of one gallon is recommended for analysis. Such volume represents the final composite amount to be available for laboratory analysis. Individual samples collected to make up this composite need not be one gallon each.

Procedures to follow in sampling will always require the exercise of judgment. This is developed with experience. Depending upon the purpose and physical characteristics of the sampling points, the sampling procedures and techniques should be determined by the technical staff responsible for the program.

Fundamental principles which apply generally to sampling techniques are as follows:

- a. The sampling point should be where the wastes are homogeneous. Natural or induced turbulence can be used to provide a homogeneous mixture.
- b. Location of sampling stations so as to permit proper evaluation of the individual types of waste is important. This may mean sampling each sewer or tank drain before the wastes mix with others in a common or collecting sewer. There is also the need to choose a sampling point that will give samples representative of the waste discharged from the plant. This determines the need for treatment of the wastes and indicates any neutralization that takes place within the plant from mixture of the wastes.
- c. Where it is impossible to get a homogeneous mixture then the sample should be a composite of the cross section of the flow. Collection of samples for settleable solids, floating solids or oily matter requires added attention; such samples may indicate surface or bottom conditions only. If possible, the samples should be collected at a point where the velocity is sufficient to prevent deposition of solids.

- d. Sufficient samples and/or composites should be taken to obtain a true picture of variations of waste discharge through changes in plant operation. (See "Planning and Making Industrial Waste Surveys" for additional discussion on this point.)
- e. The following data should be recorded at the time of taking a sample:

Location
Date and time of collection
Flow rate or volume
Temperature of water
Appearance
Remarks
Name of collector
Analyze for -

- f. Clean sampling containers are necessary in the collection of a sample. The container should be made of material that will not be affected by the sample and should be flushed with waste water before the sample is taken. Collection of samples of waste in polyethylene plastic bottles has several drawbacks which somewhat counteract their advantages. After standing for reasonably long periods of time in contact with colored or turbid wastes it is almost impossible to clean the bottles by the usual methods. It is also difficult to see whether the bottle is clean. These bottles also make it difficult to do physical observations on the samples and make it impossible to determine whether a representative portion of the sample is being removed after shaking.
- g. Optimum analysis will be provided if the sample is analyzed at the time of collection.
- h. Personnel should be instructed in safety precautions that should be observed when taking samples.
 - 1. Toxic and flammable gases collect in sewers.
 - 2. Sampling in deep sewers should be made by two men.
 - 3. A safety rope should be provided for men entering deep sewers.
 - 4. Sewers flowing with high velocity are dangerous.

Specific considerations for collecting and analyzing metal-finishing wastes include:

- 1. Sampling equipment -- materials used in sampling equipment and containers should be such as not to contaminate the sample.
- 2. Preservation of samples -- Some contaminants will change in concentration over a period of time. To eliminate such possibilities there are several methods employed: Minimize contact with air; adjust pH; refrigerate; stop oxidation or reduction processes by addition of chemicals; store sample out of direct sunlight.
- 3. Separation within samples -- On standing samples tend to separate. Solids precipitate and oily matter goes to the surface. Samples should be well shaken before portion is taken for analysis. For some wastes it is found that metals collect in the sludge and there may be but a small concentration in the supernatant. Testing of both filtered and unfiltered samples provides a better picture of the waste and eliminates the possibility of underestimating the strength of the waste.
- 4. Oily matter -- Analysis for oily matter should be made directly on the sample as collected. Glass bottles tend to adsorb oily matter so transfer of waste from one bottle to another results in error.

GENERAL CONSIDERATIONS

- (1) Numerous methods for the colorimetric determination of a given substance are presented in the literature. These methods of analysis are generally designed to work in the presence of a limited number of substances since very few analytical reactions are specific. When a reaction is specific, the desired constituent can be determined in the presence of all other materials without exception, but when the reaction is not specific the interfering substances must be removed. The removal of these interfering materials generally involves a complex procedure, the length of which is governed by their number and character.

The procedures proposed here are adaptations of methods that have been reported in the literature. Since the proposed procedures have been developed for the express purpose of analyzing for 5 to 50 ppm. of a substance in the presence of 100-5000 ppm. of each of about 23 elements, they are of necessity very long, for many steps are required to remove interfering materials.

- (2) These procedures may be used for the analysis of the required substance in the presence of other elements within the limits prescribed below. However, when the amounts of the individual impurities are known or when a reasonable estimate of their quantity can be made, the procedures can be materially shortened; this is noted in each procedure.
- (3) The range of 5 to 50 ppm. for the substance being analyzed was selected after a consideration of the tentative allowable impurities in an effluent. This range can be varied almost at will by changing the sample size and the dilution volumes in the procedures.

For many of the procedures, a table shows the modifications that must be made in the recommended procedure to allow for the analysis down to 0.01 ppm. Of course this low range is not achieved in the presence of 5000 ppm. of other ions.

- (4) The concentration of 5000 ppm. for each of the other substances in the effluent was selected as an upper limit. Although at first sight this concentration is high, in many cases industrial waste solutions contain this amount of a number of elements. The recommended procedures will, therefore, be capable of almost universal application since they have been tried in the presence of high concentrations of many elements. In certain instances, these high concentrations would be exceptionally troublesome and so the amount of certain elements was restricted.
- (5) The sensitivity of each procedure has been arbitrarily established as that value which can be determined with a relative error of $\pm 50\%$, and each procedure has been designed to furnish this accuracy at a concentration of 5 ppm.

It is to be understood that these procedures are intrinsically capable of an accuracy of $\pm 5\%$ throughout the entire range of 5 to 50 ppm. However, when tests are carried out, variable conditions in the different laboratories will introduce uncertainties in the analysis for a material, particularly when its concentration is small. These uncertainties make it desirable to claim that the limit of accuracy of these methods is $\pm 50\%$ in the vicinity of 5 ppm. while in the higher concentration range of 50 ppm. an accuracy of $\pm 5\%$ can be expected. The indicated accuracy of $\pm 50\%$ in the vicinity of 5 ppm. should easily be achieved by all analysts.

- (6) The recommended procedures presented here may be used directly upon a sample of unknown origin without fear of interference from other substances. This extremely desirable advantage is, in a measure, offset by the length of each procedure. Many of the recommended procedures can be made simple and short when there is certainty that interfering elements are absent or below a certain concentration. A knowledge of the origin of the sample, of course, precludes this certainty.

Table I shows the concentration of the substances which interfere with simplified analytical procedures; the table indicates that the recommended procedures listed herein will be capable of successfully avoiding the interferences. At first sight, it might seem that there is no need to ever use the recommended procedures so long as, say, the mercury concentration of a sample that is to be analyzed for copper is below 10 ppm. This is far from the truth for it is to be understood that this table holds only when copper is in the range of 5 to 50 ppm. and, furthermore, a maximum error of $\pm 50\%$ may be expected when the copper concentration is 5 ppm. In other words, when copper is present at 5 ppm., the presence of 10 ppm. of mercury may contribute a color to the final solution which will be interpreted as equivalent to 2.5 ppm. of copper. The column marked "concentration ratio" indicates that in the analysis for copper, whenever the concentration of mercury is twice the concentration of copper (2:1) a 50% relative error may result. The data in Table I may also be taken to indicate that shortened forms of the recommended procedures are available whenever the interferences are present in an amount less than indicated.

In certain cases, the interference of an element may not take the form of adding to the measured color; the interference occurs at some other point in the scheme. Table I does not indicate this. In each method, a section entitled "variations in the recommended Procedure" adequately shows the necessary changes that will circumvent this type of interference.

- (7) Inspection of Table I shows that the elements that cause interference in most of the procedures are: bismuth, silver, tin, copper, lead, and cadmium, in descending order. Although bismuth is the major offender, fortunately it is rarely found in effluents. Also tin and silver, because of their many insoluble or easily hydrolyzable salts, are rarely found in effluents.

A consideration of the interferences and the peculiarities of the respective methods leads to the suggestion that the analytical procedures offered here should be applied in the following order when analyzing a sample of effluent.

- * (a) preliminary examination
- * (b) free chlorine
- * (c) nitrites-nitrates
- * (d) chlorides
- * (e) cyanates
- * (f) ammonia
- * (g) free cyanide
- * (h) total cyanide
- * (i) chemical oxygen demand
- (j) lead
- (k) copper
- (l) cadmium
- (m) iron
- (n) nickel
- (o) zinc
- (p) chromium (VI)
- (q) total chromium
- (r) manganese
- (s) phosphate
- (t) sulfate

This list allows the selection of a simplified procedure if possible, on the strength of the previous analysis. Also, this list shows that certain analyses must be carried out first, since the composition of the sample may change on standing. The analyses marked with an asterisk should be carried out as soon as possible and their order in the list indicates the relative importance of their being carried out first.

TABLE I

Concentration of interfering substances that will provide $\pm 50\%$ relative error at 5 ppm. and $\pm 5\%$ at 50 ppm.

Analytical Procedure	Interference	Must use recommended procedure if over:	Conc. Ratio	Max. Conc. of each non-interfering element
Copper	mercury	10 ppm.	2:1	5000 ppm.
	bismuth	10	2:1	
	lead	10	2:1	
	silver	10	2:1	
Lead	tin	3 ppm.	3:5	100 ppm.
	bismuth	3 ppm.	3:5	
Iron	bismuth	0.5 ppm.	1:10	5000 ppm.
	copper	150	150:1	
	antimony	150	150:1	
	tin	150	150:1	
	silver	2	2:5	
Chromium	iron	100 ppm.	20:1	5000 ppm.
Manganese	chloride	15 ppm.	3:1	5000 ppm.
	all colored elements	100	20:1	
Zinc	mercury	1 ppm.	1:5	5000 ppm.
	bismuth	1	1:5	
	copper	1	1:5	
	cadmium	1	1:5	
	tin	1	1:5	
	iron	100 ppm.	20:1	
Cadmium	silver	1 ppm.	1:5	5000 ppm.
	mercury	1	1:5	
	copper	1	1:5	
Free Cyanide	Thiocyanate	100 ppm.	2:5	5000 ppm.
Total Cyanide	Thiocyanate	100 ppm.	2:5	
Cyanates	Ammonium	2 ppm.	2:5	5000 ppm.
	Ag, Pb, Bi, Cu,	10 ppm.	2:1	
	Cd, Sb, Sn, Cr,			
	Mn, Co, Ni,			
	Zn, Al, Ca, Ba, Sr	100 ppm.	20:1	

TABLE I (continued)

Analytical Procedure	Interference	Must use recommended procedure if over:	Conc. Ratio	Max. Conc. of each non-interfering element
Free Chlorine	-----	-----	-----	Zn, As, Sb, Bi, Ni, Cu, PO_4 , Cd, Cr(III), Co, Pb, Ba, Ag, Hg, at 50 ppm.; Ferric iron at 10 ppm.; 0.5 ppm. Mn (IV); 5 ppm. nitrites All others 1000 ppm.
Chloride	bromide thiocyanate iodide	} Procedure does not compensate for interferences.		5000 ppm.
Chemical Oxygen Demand	-----	-----	-----	-----
Phosphate	arsenic silica fluoride	2 ppm. 2 ppm. 2 ppm.	2:5 2:5 2:5	5000 ppm.
Sulfate	fluoride phosphate oxalate Chromate	2 ppm. 60 ppm. 2 ppm. 2 ppm.	2:5 12:1 2:5 2:5	5000 ppm.
Oil, Solids	-----	-----	-----	-----
Nitrite-Nitrates	(See Cyanates)	SEE	CYANATES	

Preparation of Sample for Chemical Analysis:

Generally, the samples as collected may be used directly in any of the subsequent analytical procedures. However, oleaginous materials are troublesome in certain of these methods. Therefore, it is preferable to remove oil from the effluent by extraction with carbon tetrachloride.

Recommended Procedure:

Extract about 250 ml. of the well-mixed effluent in a separatory funnel with three separate 10 ml. portions of carbon tetrachloride. Reject the solvent layers.

COLORIMETRIC DETERMINATION OF TOTAL AND FREE CYANIDES

Abstract

A colorimetric procedure for the determination of the total cyanide content of effluents in the concentration range of 0.2 to 50 ppm. is presented. The method was found to yield satisfactory results under a wide range of conditions and sample concentrations. The procedure was developed, tested and studied under conditions involving the simultaneous presence of twenty four common metallic impurities with concentrations 1000 times as great as that of the cyanide.

The method makes use of a distillation procedure for concentrating and removing the cyanides by refluxing the sample with dilute sulphuric acid and cuprous chloride. The liberated HCN is collected in caustic and converted into cyanogen chloride by chloramine-T. The cyanogen chloride is allowed to react with pyridine in the presence of 1-phenyl-3-methyl-5-pyrazolone resulting in a deep blue color, the intensity of which is proportional to the cyanide concentration.

Colorimetric Determination Total and Free Cyanides in Effluents

The classical method for the determination of free cyanide, such as sodium cyanide or other cyanides which are easily dissociated into CN^- , (Liebig's modified method ⁽¹⁾) is widely used when relatively large quantities of cyanide are present. This method is not easily applicable to the analysis of cyanides in effluents for only small quantities are present in a properly treated effluent.

In order to extend the sensitivity of methods for the analysis of cyanides into the microquantity region, colorimetric procedures are generally employed. One of the first of these methods was due to Waller (2) and was based on the formation of an ephemeral coloration with sodium picrate in alkaline cyanide solutions. A method that was proposed by Viehovever

and Johns (3) utilized the formation of prussian blue. Another version of this procedure has recently been proposed by Gettler and Goldbaum (4) and was modified by Hubach (5) for use in determining cyanides in wines. Hubach's modification is based on the use of cuprous chloride as a catalyst for the decomposition of complex cyanides into HCN. A method involving the oxidation of o-cresolphthalein by cyanide in the presence of a copper catalyst was proposed by Nicholson (6).

In the procedure proposed by Aldridge (7) for the determination of small amounts of cyanide, an orange color is developed from pyridine-hydrochloride with the cyanogen halide that is formed by the treatment of cyanide (or thiocyanate) with an N-halosulfonamide. Epstein (8) modified this procedure by forming glutaconic aldehyde from the reaction of cyanogen halide with pyridine and subsequently producing a blue pyrazolone dye by condensing the aldehyde with 1-phenyl-3-methyl-5-pyrazolone.

All simple cyanides and complex cyanides can be decomposed into HCN by treatment with dilute acid. With more concentrated acid, ammonia, carbon monoxide, and formaldehyde are also formed. Some complex cyanides, especially ferrocyanides, ferricyanides, and cobalticyanides are only slowly decomposed by boiling with dilute acid. It was shown by Hubach (5) that the addition of cuprous chloride to a dilute solution of sulphuric acid catalyzes the decomposition of ferrocyanides. During the investigation of this procedure, no difficulty was encountered in decomposing complex cyanides, in fact, Bassett and Corbet (9) showed that the decomposition of cobalticyanides by boiling, dilute sulphuric acid was stoichiometrically complete, although slow.

The distillation of HCN from both simple and complex cyanides by means of boiling, dilute sulphuric acid affords both a concentration and an isolation of the total cyanide content. A joint effort of the research committees of projects number 2 and 10 of the American Electroplater's Society (10) had already shown that the distillation of HCN was suitable for analyzing plating solutions.

Description of the Method:

A sample of the effluent is introduced into the distilling flask (Figure 1) by means of the funnel tube. A slow stream of air is allowed to bubble into the sample by the gentle application of suction to the safety trap; the stream of air is controlled so as to prevent the loss of the liquid in the absorption trap. Then, the contents of the distilling flask are heated to cause a slow refluxing. At this point dilute sulphuric acid is added in small increments via the funnel tube. This is followed by the addition of cuprous chloride. The refluxing, together with the slow passage of air is continued for at least 2 hours. It has been found that this amount of time is necessary for the complete removal of the cyanide from the sample. The stream of air serves to flush out the HCN vapors as they are formed and to carry them into the absorption medium. Refluxing is necessary to prevent a concentration of the acid in the distilling flask. The absorption trap contains a solution of sodium hydroxide in which HCN is very soluble through a reaction yielding sodium cyanide.

The sodium hydroxide-sodium cyanide solution in the absorption is then neutralized to about pH 9 to remove excess base and diluted to a fixed volume. Aliquot portions of this solution are then treated with Chloramine-T to form cyanogen chloride. The cyanogen chloride is then allowed to react with pyridine to form glutaconic aldehyde which in turn is treated with 1-phenyl-3-methyl-5-pyrazolone to form a blue dye. The chemistry of the reactions leading to the color formation are described by Epstein (8), q.v. It was found that the color formation could take place only in the presence of bis(1-phenyl-3-methyl-5-pyrazolone) and that the color intensity was linearly related to the concentration of cyanide in the range 0.2 to 1.2 micrograms of CN^- .

The presence of large amounts of thiocyanic in the sample will cause a small error owing to the volatility of thiocyanic acid. The thiocyanic acid reacts like cyanide in that it will be converted to cyanogen chloride which, in turn, will form the identical blue dye with the pyridine-pyrazolone reagent.

Many workers have experienced difficulty in using the cuprous chloride distillation because of the presence of large quantities of cupric chloride in the cuprous salt. When cupric chloride is present, a loss of cyanide will result:



Since the absence of cupric chloride cannot be absolutely assured, it is necessary to standardize the analytical procedure by using known amounts of cyanide and obtaining a calibration curve. Differences between the amounts introduced and the amounts recovered may be attributed largely to the presence of cupric chloride. A large number of investigators have erroneously attributed these differences to incomplete decomposition of the complex cyanides.

At first sight, it would seem that procedures using MgCl_2 (10) yield better results than procedures using $\text{Cu}_2 \text{ Cl}_2$. When pure solutions of cyanide are used, distillation with Mg Cl_2 release HCN more rapidly for the complex cuprocyanides formed with $\text{Cu}_2 \text{ Cl}_2$ release HCN slowly when boiled with acid. However, metal finishing wastes usually contain complex cyanides which release HCN slowly, and so little advantage is to be gained by the use of Mg Cl_2 . Furthermore, there is always the possibility that an alkaline sample of metal finishing waste contains substances which can oxidize cyanide, especially in acid solutions. When such oxidants are present, the use of cuprous chloride presents interference to a certain extent, for the initial addition of cuprous chloride to the alkaline cyanide solution binds cyanide as a complex cyprocyanide. On acidification, the oxidizing substances which escaped reduction in alkaline solution are destroyed and the cuprocyanide ions remain virtually untouched.

Sensitivity of the Method:

The sensitivity of the method is defined as the number of micrograms of cyanide which must be present in 1 ml. of the 100 ml. sample of effluent taken for analysis in order that this quantity can be determined with a relative error of $\pm 50\%$. This corresponds to a cyanide concentration of 0.1 ppm. or 10 micrograms of CN^{-} in the distilling flask. With suitable modification, involving sample size and other dilutions, the sensitivity can be greatly increased. The sensitivity of the method is not governed by the amount of impurities present in the sample.

Limit of Detection of the Method:

The limit of detection of the method is defined as the number of micrograms of cyanide which must be present in 1 ml. of the 100 ml. sample of effluent taken for analysis so that an extinction of 0.005 for a 1-cm. cell thickness at 620 millimicrons will be obtained in step 15. This corresponds to 0.02 ppm. or a concentration of 0.2 microgram of cyanide in the distilling flask.

The limit of detection can be greatly increased by suitable modifications of the method. There seems to be no impediment to lowering the limit of detection to any desired value save the limitations imposed by the size of the distillation equipment. The limit of detection is independent of the quantities of the impurities present.

Discussion of Blanks:

The presence of colored substances in the sample will not interfere for the cyanide is removed by distillation. The color of the blank is governed wholly by the Chloramine-T and the pyridine-pyrazolone reagents. It has been found that when freshly prepared reagents are used, the blank has an extinction essentially equal to that of distilled water, but a slight extinction may occur because of refractive index differences and the inevitable colorations which are associated with organic reagents.

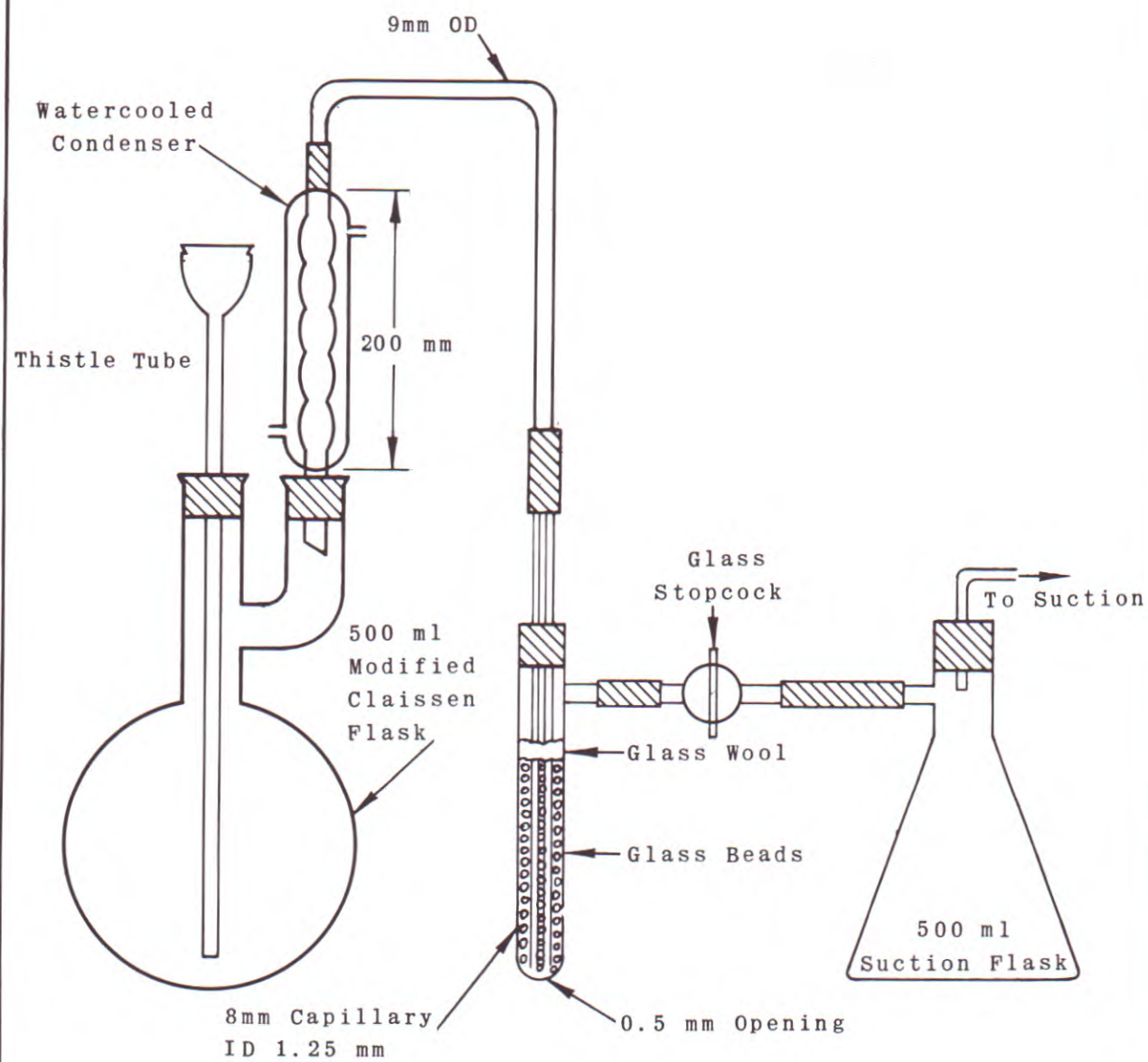
Recommended Procedure:

This procedure is designed to be used for the accurate determination of total (free and complex) cyanide in effluents in the range of 0.2 microgram to 1.2 micrograms per ml. in a 100-ml. sample of effluent. If analyses are to be made on effluents containing more than 1 ppm. but less than 5 ppm. of cyanide, use 25-ml. samples. For concentrations in the range of 5 to 50 ppm. use 2-ml. samples.

Reagents Required:

- (1) Sodium Hydroxide: 4% (w/v). Dissolve 40 gm. of sodium hydroxide pellets and make up to 1 liter.
- (2) Sulphuric Acid: 1:1. Pour 500 ml. of concentrated sulphuric acid into 500 ml. of water. Cool before using.
- (3) Cuprous Chloride: Use finely powdered reagent grade material.
- (4) Hydrochloric Acid: (N). Dilute 83.5 ml. of concentrated acid to one liter.
- (5) Chloramine-T: (1%) Dissolve 1.0 gm. of the powder in 100 ml. of water.
- (6) 1-Phenyl-3-methyl-5-pyrazolone: A satisfactory product can be obtained from Eastman Kodak Co. (No. 1397).
- (7) Pyridine: Use only reagent quality material.
- (8) Bis (1-phenyl-3-methyl-5-pyrazolone): This dimer must be prepared as follows: Dissolve 17.4 gm. of the pure 1-phenyl-3-methyl-5-pyrazolone in 100 ml. of 95% ethanol. Twenty five grams of freshly distilled phenylhydrazine are added and the mixture refluxed for at least 4 hours. The insoluble portion which is filtered off and washed with hot alcohol is bis-(1-phenyl-3-methyl-5-pyrazolone.).
- (9) Pyridine-Pyrazolone reagent: Note: Prepare as needed a few minutes before each analysis. Solution A: Add 0.25 gm. of 1-phenyl-3-methyl-5-pyrazolone to 50 ml. of distilled water. Heat the solution to about 60°C. with stirring. Replace the water lost by evaporation if necessary. Cool to room temperature. Solution B: Dissolve 0.01 gm. of the bis-pyrazolone in 10 ml. of pyridine.

Immediately before use, pour solution A into a filter and catch the filtrate. Then pour solution B through the same filter and catch the filtrate in the same container with solution A. Stir well and immediately pipette the solution into the 10 ml. volumetric flask containing the cyanide-chloramine-T mixture. (See step 14).
- (10) Sodium Cyanide Solution: Stock solution; 1 gm. of CN^- per liter as sodium cyanide;



CYANIDE DISTILLATION APPARATUS

Weigh 1.884 gm. of pure sodium cyanide and dilute to 1 liter.

Take 10 ml. of the stock solution and dilute to 1 liter. This is equivalent to 10 micrograms of cyanide per ml. Make up this solution fresh as needed. For purposes of establishing a calibration curve, take 2,4,6,8,10 and 12 ml. samples of this solution and dilute to 100 ml. in each case. These solutions, containing 0.2, 0.4, 0.6, 0.8, 1.0, and 1.2 micrograms per ml., are used as samples in step 12.

Procedure:

- (1) Set up the equipment shown in Figure 1, adhering to dimensions as much as possible.
- (2) Introduce 100 ml. of the alkaline effluent into the distilling flask by means of the funnel tube.
- (3) Fill the absorption trap a little over half full with 3 mm. glass beads and arrange a wad of glass wool over them to aid in holding them down as well as preventing spray carry-over. Then add enough 4% NaOH solution so that a gentle stream of air bubbling through the trap will not cause a loss of the absorption medium by over flow.
- (4) Start a gentle stream of air bubbling into the sample solution by gently applying suction to the system and using the stopcock or clamp to control the flow of air so that no carry-over of the absorption medium in the trap will occur.
- (5) Gently heat the contents of the distilling flask, gradually boiling it at such a rate that a slow refluxing action occurs.
- (6) Now add 50 ml. of 1:1 H_2SO_4 in small increments via the funnel tube.
- (7) Pour 0.5 gm. of finely powdered cuprous chloride into the funnel tube and wash into the distilling flask by means of a stream of water from a wash bottle.
- (8) Continue the refluxing and the passage of air for two and one half hours.
- (9) Disconnect the delivery tube leading into the absorption trap and wash the solution in the absorption trap into a 150 ml. beaker. In washing the absorption trap, take care that no beads fall into the beaker. The beads in the trap must be washed well.
- (10) Neutralize the solution in the beaker with 1N HCl to a pH of about 7.5, at no time having an excess of acid present (avoiding loss of cyanide by evolution of HCN).
- (11) Quantitatively transfer the contents of the beaker to a 100 ml. volumetric flask and bring to the mark with water.
- (12) Transfer 1 ml. of this solution to a 10 ml. volumetric flask by means of a pipette.
- (13) Add 0.2 ml. of 1% Chloramine-T solution, stopper and shake well. Let the solution stand at least 1 minute in a cool place.
- (14) Add 8 ml. of the freshly prepared pyridine-pyrazolone reagent and bring the volumetric flask to the mark with water. Stopper and shake well.
- (15) Wait at least 8 minutes and then read the extinction of the solution in a photometer at 620 millimicrons. If the pyridine-pyrazolone reagent is made fresh, sufficient accuracy will be had by using distilled water as a reference liquid. If desired, the

reference liquid may be made by mixing 1 ml. of water, 0.2 ml. of Chloramine-T, 8 ml. of the pyridine-pyrazolone reagent and diluting up to 10 ml. in a volumetric flask.

- (16) If necessary, convert the scale readings of the photometer to extinction. Subtract the blank reading from the sample reading. If a calibration curve is being established, plot these corrected readings versus micrograms of cyanide added. If a sample is being run, read the amount of cyanide present from the calibration curve. Recall that the calibration curve is established on a basis of a 100 ml. sample of effluent. If a 25-ml. sample is taken for analysis, multiply the micrograms of cyanide read from the calibration curve by 4. For a 2 ml. sample, multiply by 50.
- (17) A colorimeter employing a Klett-Summerson No. 66 red filter or an Evelyn No. 580 filter may be used in place of a spectrophotometer with no significant loss in sensitivity.

Recommended Procedure for Free Cyanide:

This procedure is to be used for the determination of "free" cyanide in effluents in the range of 0.2 micrograms to 1.2 micrograms of cyanide per ml. in an original sample effluent of 100 ml. For cyanide contents greater than 1 ppm. but less than 5 ppm. use 25-ml. samples, and for contents of 5 to 50 ppm. use 2-ml. samples.

The "free" cyanide content of the sample as determined by this procedure represents the HCN which can be liberated from the sample by boiling with dilute acetic acid. The alkali metal and alkaline earth cyanides as well as the simple complex cyanides such as those of zinc and cadmium liberate HCN upon treatment with acetic acid. Since these cyanides, if present in an effluent, would liberate HCN upon dilution, the importance of determining their presence is obvious.

Reagents Required:

Same as for the procedure for Total Cyanide; also: Glacial Acetic Acid: Reagent Grade.

Special Equipment:

Same as for the procedure for Total Cyanide.

Procedure:

Omit steps 3 to 7 of the Procedure for Total Cyanide. In place of these steps, substitute the following:

Add 50 ml. of Glacial Acetic Acid in small increments via the funnel tube.

Variations of the Recommended Procedures:

When the composition of the effluent is known, the recommended procedures can generally be shortened.

The following table summarizes the changes that can be made in the procedures when the

composition of the effluent is known. Unless otherwise stated, the concentration of each of the other elements in the total sample taken for analysis must not exceed 20,000 micrograms.

Composition of the Effluent	Changes in the recommended procedure
No complex cyanides (iron, cobalt, etc. absent).	Use the procedure for free cyanide.
All metals below 5 ppm. Thiocyanate absent.	To a 10 ml. sample in a test tube, add 2 ml. of Chloramine-T solution. Immediately stopper and shake. After one minute, add 3 ml. of the pyridine pyrazolone reagent, stopper and shake. After 20 minutes, measure the % T using a red filter. Use calibration curves.

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COLORIMETRIC DETERMINATION OF CYANATES

Abstract

A colorimetric procedure for the determination of the cyanate content of effluents in the range of 5 to 50 ppm. is presented. The method was found to give satisfactory results in the presence of 100 ppm. of each of 23 elements and ammonium, cyanide, and thiocyanate ions in simultaneous admixture.

In this method, the ammonia formed by the acid hydrolysis of cyanate is distilled off and collected. Nessler's solution is then added to the distillate and the intensity of the yellow-orange color which is formed is measured with a colorimeter.

The procedure can be shortened if the content of each substance other than cyanate is below 1 ppm. A table summarizes the ways in which the procedure can be shortened when the amounts of the materials other than cyanate are known or can be estimated.

Colorimetric Determination of Cyanates in Effluents

This method for the determination of microquantities of cyanate involves the hydrolysis of the cyanate ion to ammonia and the subsequent determination of the ammonia by Nessler's reagent. A survey of the literature revealed no specific organic reagent suitable for the direct colorimetric determination of cyanate.

The hydrolysis of cyanate to ammonia was proposed as a procedure for cyanate analysis by Herting (1). Leboucq (2) showed that the acid hydrolysis of cyanate was quantitative and that the determination of the resulting ammonia could be used to indicate the amount of cyanate.

Kleppinger (3), Serfass, et al. (4) have shown that micro-quantities of cyanate can be estimated by hydrolyzing the cyanate and determining the ammonia by means of Nessler's reagent. The proposed method is an adaptation of Kleppinger's and Serfass's determination of cyanates in cyanide baths.

Description of the Method:

The ammonium salts already present in the sample are removed by boiling with excess alkali hydroxide in the presence of alkali sulfide. It has been found that prolonged boiling of cyanates in the presence of excess alkali does not cause appreciable hydrolysis or loss when carried out under the conditions prescribed in this procedure. The solution is then acidulated and boiled again to cause hydrolysis of the cyanate to ammonium salts to remove cyanides, nitrites, sulfites, sulfides, etc.

The ammonium salts resulting from this hydrolysis are transferred to a Kjeldahl distillation apparatus together with a large excess of sodium hydroxide containing sodium sulfide. The liberated ammonia is collected in dilute acid and the amount of ammonia present in the distillate is determined by Nessler's reagent either with a colorimeter (turbidimeter) or by optical comparison in Nessler tubes in accordance with well-established procedures.

The acidity of the solution in which the hydrolysis of the cyanate is being carried out must be carefully controlled since a high concentration of acid, which may result from concentration by prolonged boiling, will promote the hydrolysis of small quantities of residual cyanide to ammonium formate. The volume of solution prior to the addition of the Nessler's reagent has an effect on the final color; therefore, the volumes indicated in the procedure must be observed. Sodium sulfide is added during the boiling with alkali in order to insure the complete release of ammonia from metallic-ammonia complexes such as the cobalt amines.

Sensitivity of the Method:

The sensitivity of the method is defined as the number of micrograms of cyanate ion which must be determined with a relative error of $\pm 50\%$. For the following recommended procedure, this corresponds to 5 ppm. or 500 micrograms of cyanate in the 100 ml. sample taken for analysis.

Limit of Detection of the Method:

The limit of detection of the method is defined as the number of micrograms of cyanate ion which must be present in the 100 ml. sample taken for analysis so that an extinction of 0.005 will be obtained in Step 8 for a 1 cm. cell thickness at 400 millimicrons. For the recommended procedure, the limit of detection is 100 micrograms of cyanate ion (1 ppm.).

Discussion of the Blank:

A blank is used to compensate for the presence of traces of cyanate or ammonia in the reagents.

Discussion of the Sample:

If the sample is alkaline, it may be stored for short periods of time without deterioration, that is, without loss of cyanate due to hydrolysis. If the sample is acid or neutral, the hydrolysis of the cyanate is in progress and consequently the sample immediately must be made alkaline for storage.

Since the recommended procedure does not involve a step for the removal of organic matter which may react with or liberate cyanates in alkaline or acid medium, the presence of such organic substances will invalidate the analysis. The determination will not be applicable to those samples containing organic materials which liberate ammonia on acid hydrolysis or hydrolyze to form compounds in basic medium which will subsequently yield ammonia on acid hydrolysis.

The presence of oxidizers in the effluent must be taken into consideration since it is conceivable that cyanides may be oxidized to cyanates in basic medium; oxidation in acid medium is not likely to occur because HCN is evolved. Powerful reducing agents also should be absent since cyanate can well be reduced to cyanide. An example of this is afforded by stannous ion which will reduce cyanate in basic but not in acidic solution.

During the investigation of this method, it was found that commercial "c.p." alkali cyanides contain cyanates, and this must be taken into consideration when the method is used.

Recommended Procedure:

This procedure is designed to be used for the determination of 5 to 50 ppm. of cyanate ion in a 100 ml. sample of effluent.

Reagents Required:

- (1) Sodium Hydroxide-Sodium Sulfide Solution: Saturate 250 ml. of 25% w/v NaOH solution with H₂S gas. Mix this solution with 750 ml. of 25% w/v NaOH solution.
- (2) Sulfuric Acid Solution: 1:4.
- (3) Hydrochloric Acid Solution: Approximately N/10.
- (4) Gum Arabic Solution: 2% w/v.
- (5) Nessler's Solution: Dissolve 50 g. of potassium iodide in approximately 35 ml. of cold ammonia-free water. Slowly add a saturated solution of mercuric chloride until the first slight precipitate of red mercuric iodide persists, and then add 400 ml. of a clarified 9 N solution of sodium hydroxide. Dilute the solution to one liter with ammonia-free water and allow it to settle. Siphon off the clear supernatant liquid.
- (6) Standard Ammonia Solution: Dissolve 0.787 g. of pure, dry, ammonium sulfate in water and dilute to one liter.

$$\begin{aligned} 1 \text{ ml.} &= 215 \text{ micrograms of } \text{NH}_4^+ \\ &= 500 \text{ micrograms of cyanate} \end{aligned}$$



In establishing a calibration curve, 1 ml. of this solution used in Step 3 corresponds to 5 ppm. of cyanate in a 100 ml. sample of effluent taken for analysis in Step 1 of the recommended procedure.

Special Equipment:

- (1) Kjeldahl distillation equipment with 300 ml. flasks.

Recommended Procedure for the Determination of Cyanates:

- (1) Pipette a 100 ml. sample of the oil-free effluent into a 250 ml. beaker.

In running a blank or establishing a calibration curve, use 100 ml. of water.

If the effluent is strongly acid, cautiously neutralize it with dilute sodium hydroxide solution.

- (2) Add 5 ml. of sodium hydroxide-sodium sulfide solution. Bring to a vigorous boil, and continue the boiling for one half hour. Do not allow the volume of the solution to drop below 75 ml.; add water when necessary.
- (3) Cool the solution in the beaker, and neutralize with 1:4 sulfuric acid, using phenolphthalein or another indicator to approach the neutral point.

Add 5 ml. of 1:4 sulfuric acid in excess of the neutral point. (Note: Too large an excess of sulfuric acid will cause the hydrolysis of cyanides to ammonia).

In establishing a calibration curve, 1 ml. of the standard ammonia solution added at this point corresponds to 5 ppm. of cyanate ion in the 100 ml. sample used in Step 1.

Bring to a brisk boil and continue boiling for one half hour.

Do not allow the volume of the solution to fall below 75 ml.; add water when necessary.

- (4) Cool and transfer to the Kjeldahl distilling flask. Set a 125 ml. Erlenmeyer flask containing 20 ml. of 0.1 N HCl so as to receive the distillate. Be sure that the end of the condenser dips well under the acid in the flask.

Add 20 ml. of the sodium hydroxide-sodium sulfide solution and immediately connect the flask to the distilling apparatus. Then, shake the flask so as to mix the contents very well.

Collect between 50 and 60 ml. of distillate in the acid solution.

- (5) Transfer the distillate to a 100 ml. volumetric flask and dilute to the mark.
- (6) Pipette 10 ml. of this solution into a 100 ml. volumetric flask.

Add 3 drops of a 2% gum arabic solution; swirl the contents of the flask.

Add 1 ml. of Nessler's reagent and mix well.

Dilute up to the mark with water, shake well and wait 5 minutes.

- (7) Set the colorimeter to zero with water using a blue (No. 42) filter. With a spectrophotometer, set the instrument to full scale with water at about 400 millimicrons.

The intensity of the developed color (turbidity) can be estimated by comparing the sample against Nessler's standards.

- (8) Transfer the solution from step (6) to the sample cuvette and read the colorimeter.
- (9) If necessary, convert the scale readings of the photometer to optical density. Subtract the blank reading from the sample readings. If a calibration curve is being established, plot these corrected readings versus ppm. of cyanate ion. If a sample is being run, read the amount of cyanate ion from the calibration curve.

Variations of the Recommended Procedure:

If the composition of the effluent is known, the recommended procedure for cyanate ion can be materially shortened.

The following table summarizes the changes that can be made in the recommended procedure for cyanate ion when the composition of the sample is known. Unless otherwise stated, the concentration of other elements must not exceed 100 ppm.. For effluents containing greater quantities of these elements, dilution will be necessary. The effluent should be between pH 2 and 9. The use of Rochelle Salts to prevent precipitation of hydroxides was recently proposed by Dodge and Zabban (5).

Composition of Effluent	Changes in the Recommended Procedure for the Determination of Cyanates:
Ammonium salts below 2 ppm.; this includes ammonia bound in complexes.	Omit step 2.
Colorless sample and all elements below 5 ppm. each.	Pipette a 100 ml. sample of effluent into a 250 ml. beaker. Add 20 ml. of 0.1 N HCl. Boil for 15 minutes, but do not let the volume fall below about 70 ml. Add water when necessary. Cool to room temperature, add 1 g. of Rochelle Salts, and transfer to a 100 ml. volumetric flask. Dilute to the mark, shake, and start with step 6 of the recommended procedure.
Silver, lead, bismuth, copper, cadmium, antimony tin, iron, chromium, manganese, cobalt, nickel, and ammonia below 10 ppm. each.	Pipette a 100 ml. sample of effluent into a 250 ml. beaker. Add 20 ml. of 0.1 N HCl. Boil for 15 minutes, but do not let the volume fall below about 70 ml. Add water when necessary. Cool to room temperature, add 1 g. of Rochelle Salts, and transfer to a 100 ml. volumetric flask. Dilute to the mark, shake, and start with step 6 of the recommended procedure.
Cyanides over 100 ppm.; alkali metals, alkaline earths, zinc, and aluminum below 100 ppm. each; all other elements below 10 ppm. each.	Pipette a 100 ml. sample of effluent into a 250 ml. beaker. Add 20 ml. of 0.1 N HCl. Boil for 15 minutes, but do not let the volume fall below about 70 ml. Add water when necessary. Cool to room temperature, add 1 g. Rochelle Salts, and transfer to a 100 ml. volumetric flask. Dilute up to the mark, shake, and start with step 6 of the recommended procedure.
Ammonia over 100 ppm.; all other elements below 100 ppm. each.	Follow the recommended procedure.
Ammonia over 100 ppm.; cyanide over 100 ppm.; all other elements below 100 ppm. each.	Follow the recommended procedure.
Alkali metals and alkaline earths below 100 ppm. each; all other elements below 10 ppm. each; cyanide and ammonia below 1 ppm. each; pH 5-9.	Pipette a 100 ml. sample of effluent into a 250 ml. beaker. Add 20 ml. of 0.1 N HCl. Boil for 15 minutes, but do not let the volume fall below 70 ml.. Add water when necessary. Cool to room temperature and transfer to a 100 ml. volumetric flask. Add 1 g. Rochelle Salts; dilute to the mark, shake, and start with step 6 of the recommended procedure.

A Shortened Procedure for 0.1 to 5 ppm. Cyanate:

The shortened scheme of analysis presented below is designed for the determination of cyanates in water samples where the concentration of all substances and especially ammonia, is about the same as the cyanate content.

The sample should be adjusted to a pH of 2 to 9. Do not omit blanks.

Composition of the Effluent	Shortened Procedure
Cyanate 0.1 to 1 ppm.	Take a 500 ml. sample of the effluent and put into a 1000 ml. beaker. Add 20 ml. of conc. HCl. Boil for 30 minutes but do not allow volume to fall below 250 ml. Transfer to a Kjeldahl flask and start at step 4. Omit step 5. Nearly neutralize the distillate using litmus paper. Add 3 drops of 2% gum arabic solution and 1 ml. of Nessler's reagent. Dilute to 100 ml.; wait 5 minutes. Continue with step 7.
Cyanate 1 to 5 ppm.	Pipette a 100 ml. sample of the effluent into a 250 ml. beaker. Add 20 ml. of 0.1 N HCl. Boil for 15 minutes, but do not let the volume fall below about 70 ml. Add water when necessary. Cool to room temperature, add 1 g. of Rochelle Salts, and transfer to a 100 ml. volumetric flask. Dilute to the mark. Start with step 6 of the procedure, but use a 50 ml. aliquot and add 3-5 ml. of Nessler's reagent.

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COLORIMETRIC DETERMINATION OF CADMIUM

Abstract

A colorimetric procedure for the determination of the cadmium content of effluents in the range of 5 to 50 ppm. is presented. The method was found to yield satisfactory results in the presence of 500 to 5000 ppm. of each of 27 ions in simultaneous admixture.

The method is a mono-color procedure employing dithizone as the color forming reagent. Silver, mercury, and copper, which interfere, are extracted with dithizone at a low pH at which cadmium does not complex with dithizone. The solution is made slightly alkaline, and interference from nickel and cobalt is eliminated by complexing with dimethylglyoxime. The solution is then made more alkaline and the cadmium is removed as the red dithizone complex, which is measured with a colorimeter.

The procedure can be materially shortened if the concentrations of silver, mercury, copper, nickel and cobalt are below 0.5 ppm. A table summarizes the changes that can be made when the amounts of the materials other than cadmium are known or can be estimated.

A modified procedure for the analysis of water samples where the concentration of cadmium is as low as 0.01 ppm. is also included.

Colorimetric Determination of Cadmium in Effluents

The colorimetric determination of trace quantities of cadmium is conveniently carried out by the use of diphenylthiocarbazone (dithizone) in strongly basic solutions. Numerous investigators have modified the original Fischer-Liopoldi (1) scheme employing dithizone to permit determination of cadmium in the presence of a wide range of impurities such as may be found in plating baths (2), biological matter (3) and minerals (4).

The method described is based on the fact that very few elements interfere in the extraction of cadmium from strongly basic media, and those that do (silver, mercury, copper, nickel, and cobalt) can easily be removed by a preliminary extraction with dithizone and dimethylglyoxime.

The procedure presented is a modification of the monocolor method of Shirley, Benne, and Miller (5).

Description of the Method:

A preliminary fuming with nitric and sulfuric acids is carried out to decompose organic material that may retain cadmium in a form which will not react with dithizone. Hydrochloric acid is added to the diluted digestion mixture after the fuming operation to precipitate the major portion of the silver that is present. Insoluble substances are then removed by filtration or centrifugation.

The solution is adjusted to a pH of 2 and extracted with a strong solution of dithizone in chloroform. Copper, mercury, and the remainder of the silver are removed by this extraction. Cadmium is not extracted at this pH.

The solution is next adjusted to a pH of 8.5-9 and dimethylglyoxime is added. On extraction of the solution with chloroform, nickel is removed. The cobalt dimethylglyoxime complex, which is not extracted by chloroform, will not react with dithizone.

The solution is made strongly basic with sodium hydroxide and the cadmium is extracted with dithizone in carbon tetrachloride. Zinc is also extracted with cadmium at this pH, and if the zinc is present in large excess (greater than 500:1), it is difficult to extract the last traces of cadmium and low results will be obtained. The small amount of zinc which is extracted together with cadmium is removed by washing the solvent layer with a 2% solution of sodium hydroxide.

The intensity of the red cadmium-dithizone complex is measured at 515 millimicrons wave length in a spectrophotometer or in a colorimeter equipped with a suitable filter.

The recommended procedure was found to yield excellent results for concentrations of 5 to 50 ppm. of cadmium in solutions containing in simultaneous admixture 500 ppm. each of Cu^{+2} , Co^{+2} , Zn^{+2} , and 5000 ppm. each of the following ions: Ag^{+} , Hg^{+2} , Pb^{+2} , Bi^{+3} , As^{+3} , Sb^{+3} , Sn^{+2} , Cr^{+3} , Al^{+3} , Fe^{+3} , Mn^{+2} , Ni^{+2} , Ca^{+2} , Sr^{+2} , Ba^{+2} , Mg^{+2} , Na^{+} , K^{+} , NH_4^{+} , CN^{-} , CNS^{-} , PO_4^{-} , SO_3^{-} , S_2O_3^{-} , and organic materials such as tartrates and acetates.

Sensitivity of the Method:

The sensitivity of the method is defined as the smallest number of micrograms of cadmium which can be determined with a relative error of $\pm 50\%$. For the following recommended procedure this corresponds to 5 ppm. or 25 micrograms of cadmium in the 5 ml. portion taken for analysis.

Limit of Detection of the Method:

The limit of detection of the method is defined as the number of micrograms of cadmium which must be present in the 5 ml. sample taken for analysis so that an extinction of 0.005 will be obtained in step 13 for a 1 cm. cell thickness at 515 millimicrons wave length. For the recommended procedure, the limit of detection is 2 micrograms of cadmium ion (0.4 ppm.).

Discussion of the Blank:

A blank must be run together with the sample to compensate for impurities in the reagents.

Recommended Procedure:

This procedure is designed to be used for the determination of 5 to 50 ppm. of cadmium in a 5 ml. sample of effluent.

Reagents Required:

- (1) Nitric Acid: Concentrated, 16 N; reagent grade.
- (2) Sulfuric Acid: Concentrated, 36 N; reagent grade.
- (3) Hydrochloric Acid: Concentrated, 12 N; reagent grade.
- (4) Chloroform: Reagent grade; preferably distilled over calcium oxide before use.
- (5) Carbon Tetrachloride: Reagent grade, redistilled over calcium oxide prior to use.
- (6) Ammonium Hydroxide, Concentrated: Pass ammonia gas from a cylinder into distilled water kept cold by immersion in an ice bath. Store in a plastic container.*
- (7) Sodium Potassium Tartrate Solution: 20% w/v. This solution is purified by extraction with 0.01% dithizone in carbon tetrachloride. The dithizone and yellow oxidation product of dithizone are removed by extraction with successive portions of chloroform until the extracts remain colorless. The solution is then extracted with carbon tetrachloride to remove any chloroform. Store in a plastic container.
- (8) Dimethylglyoxime Solution: 1% w/v. in alcohol.
- (9) Dithizone, 0.01% in Carbon Tetrachloride: Since reagent grade dithizone may be contaminated to some degree by the oxidation product of dithizone (diphenylthiocarbodiazene), the following procedure is strongly recommended for preparing the dithizone solution.

Dissolve 100 mg. of pure dithizone in 50 ml. of chloroform. Filter the solution through paper into a separatory funnel. Extract with three 50 ml. portions of 1% ammonium hydroxide. Discard the chloroform and extract the ammoniacal solution with three 10 ml. portions of carbon tetrachloride. Reject the carbon tetrachloride extracts. Precipitate the dithizone in the ammoniacal solution with 2 ml. of concentrated HCl. Extract the solution with carbon tetrachloride until the aqueous layer becomes colorless, or almost so. Combine the extracts and dilute to one liter with carbon tetrachloride.

- (10) Dithizone, 0.1% in Chloroform.
- (11) Sodium Hydroxide Solution: 10% w/v. Store in a plastic container.
- (12) Sodium Hydroxide Solution: 2% w/v. Store in a plastic container.
- (13) Standard Cadmium Solution: Dissolve 100 mg. of pure cadmium metal in 20 ml. of distilled water containing 5 ml. of concentrated HCl. Dilute this solution to one liter with distilled water. Store in a plastic container. Pipette 25 ml. of this solution into a 100 ml. volumetric flask, add 1 ml. of concentrated HCl, and dilute to the mark with distilled water. The latter solution, which is the Standard Cadmium Solution, should be stored in a plastic container.

1 ml. = 25 micrograms of cadmium

* The plastic containers recommended are polyethylene bottles readily available from chemical supply sources.

For establishing a calibration curve, 1 ml. of this solution taken as a sample corresponds to 5 ppm. of cadmium for a 5 ml. sample of effluent taken for analysis.

Recommended Procedure for the Determination of Cadmium:

- (1) Pipette a 5 ml. sample of the effluent into a 125 ml. erlenmeyer flask.

In running a blank, use 5 ml. of distilled water.

In establishing a calibration curve, use 5 ml. of distilled water and add 1 ml. of the standard cadmium solution for each of 5 ppm. of cadmium.

- (2) Add 5 ml. of concentrated nitric acid and 1 ml. of concentrated sulfuric acid and evaporate to strong fumes of sulfur trioxide. Hold at this temperature for 5 minutes.

Note: If the residue after fuming is discolored by organic carbon, cautiously add 2 ml. of concentrated nitric acid and fume again. Repeat as many times as is necessary. More concentrated sulfuric acid may be needed to prevent the mixture from going to dryness.

- (3) Cool the solution and dilute with about 25 ml. of water.

Add 0.5 ml. of concentrated hydrochloric acid.

- (4) Filter the solution, if necessary, through a medium porosity sintered glass funnel, saving the filtrate.

Wash the filter at least three times with 5 ml. portions of water. Combine the filtrate and washings.

- (5) Transfer the filtrate and washings to a 100 ml. volumetric flask and dilute to the mark with water.

- (6) Pipette a 10 ml. aliquot from the above solution into a 150 ml. beaker.

Add 5 ml. of 20% sodium potassium tartrate solution.

Adjust to a pH of 2.0 with concentrated hydrochloric acid or ammonium hydroxide.

- (7) Transfer the solution to a separatory funnel.

Extract with 5 ml. portions of 0.1% dithizone in chloroform until the dithizone layer remains green. Reject the extracts.

Wash with 10 ml. portions of chloroform until the solvent layer remains colorless. Reject the washings.

Wash with one 5 ml. portion of carbon tetrachloride and reject the washing.

- (8) Transfer the water solution from the separatory funnel to a 150 ml. beaker.

Add 5 ml. of 20% sodium potassium tartrate solution.

Adjust to a pH of 8.5-9 with concentrated ammonium hydroxide or HCl.

Transfer the solution to a separatory funnel.

Add 5 ml. of 1% dimethylglyoxime solution and shake vigorously for 30 seconds.

Extract with three 10 ml. portions of chloroform or until any white precipitate resulting from excess dimethylglyoxime has been removed. Reject the extract.

Wash the solution once with a 5 ml. portion of carbon tetrachloride and reject the washing.

- (9) Add 10 ml. of 10% NaOH solution. Extract the water solution in the separatory funnel with 5 ml. of 0.01% solution of dithizone in carbon tetrachloride.

Transfer the carbon tetrachloride layer to a clean separatory funnel.

Extract the water solution in the first separatory funnel with another 5 ml. portion of 0.01% dithizone in carbon tetrachloride. Combine the extracts.

Continue to extract the aqueous layer with 3 ml. portions of dithizone until the extracts remain colorless or slightly yellow showing that all the cadmium has been removed.

- (10) Wash the combined dithizone extracts with two 20 ml. portions of 2% NaOH solution. Reject the washings.

Wash the combined dithizone extracts with one 20 ml. portion of distilled water. Reject this washing.

- (11) Filter the red solution of cadmium-dithizonate complex in the separatory funnel through a small filter paper into a 25 ml. volumetric flask. Wash the filter paper with a little carbon tetrachloride and add this washing to the contents of the flask.

Dilute to the mark with carbon tetrachloride and shake.

- (12) Set the Klett-Summerson colorimeter to zero with carbon tetrachloride. Use a green (No. 54) filter. With a spectrophotometer, set the instrument to read 100% transmission at 515 millimicrons.

- (13) Transfer the solution from step 11 to the sample cuvette and read the colorimeter within 15 minutes.

- (14) If necessary, convert the scale readings of the photometer to optical density. Subtract the blank reading from the sample reading. If a calibration curve is being established, plot these corrected readings versus ppm. of cadmium. If a sample is being run, read the amount of cadmium from the calibration curve.

Variations of the Recommended Procedure:

If the composition of the effluent is known, the recommended procedure for cadmium can be shortened.

The following table summarizes the changes that can be made in the recommended procedure for cadmium when the composition of the sample is known. Unless otherwise stated, the concentrations of Cu^{+2} , Co^{+2} and Zn^{+2} should not exceed 500 ppm., and the concentrations of other elements should not exceed 5000 ppm. For effluents containing greater quantities of these elements, dilution will be necessary. The effluents should be adjusted to a pH between 2 and 9.

Composition of Effluent:	Changes in the Recommended Procedure for the Determination of Cadmium
Organic matter absent	Omit steps 1 to 5 inclusive. Pipette 5 ml. of the sample into a 150 ml. beaker, add 0.5 ml. of concentrated HCl, filter if necessary, transfer to a 100 ml. volumetric flask, and dilute to the mark. Proceed with step 6 of recommended procedure.
Organic matter absent, silver, mercury and copper each below 0.5 ppm.	Omit steps 1-7 inclusive. Pipette a 5 ml. sample of the effluent into a 100 ml. volumetric flask and dilute to the mark with water. Pipette a 10 ml. aliquot from this solution and start with step 8 of the recommended procedure, but add 10 ml. of 20% sodium potassium tartrate solution instead of the 5 ml. required in this step.
Organic matter absent, nickel and cobalt each below 0.5 ppm.	Omit steps 1 to 5 inclusive. Pipette a 5 ml. sample of the effluent into a 150 ml. beaker, add 0.5 ml. of concentrated HCl, filter if necessary, transfer to a 100 ml. volumetric flask and dilute to the mark. Start with step 6 of the recommended procedure and omit step 8 in following through the scheme. In step 9 add 5 ml. of 20% sodium potassium tartrate solution before adding the 10 ml. of 10% NaOH solution.
Organic matter absent, silver, mercury, copper, nickel and cobalt each below 0.5 ppm.	Omit steps 1 to 8 inclusive. Pipette a 5 ml. sample of the effluent into a 100 ml. volumetric flask and dilute to the mark. Pipette a 10 ml. aliquot of this solution into a separation funnel, add 10 ml. of 10% sodium potassium tartrate, and proceed with step 9 in the recommended procedure.
Organic matter present, copper, cobalt, and zinc each below 500 ppm. and all other elements below 5000 ppm. each.	Follow the recommended procedure.

A Shortened Procedure for Cadmium in the Range 0.01 to 5 ppm.:

The following procedure is designed for the analysis of water samples when the concentration of each of the heavy metals including cadmium are very low and the only elements of appreciable concentration are the alkali metals and alkaline earths. The effluent should be nearly neutral (between pH 2 and 9).

Composition of the Effluent:	Shortened Procedure
<u>Cadmium</u> 0.01 to 0.1 ppm.; alkali and alkaline earth metals below 10 ppm.; all other elements below 2 ppm.; silver, mercury, copper, nickel, cobalt and organic matter absent.	Pipette a 100 ml. sample of effluent into a separatory funnel, add 1 ml. of 20% sodium potassium tartrate solution, and 15 ml. of 10% NaOH solution. Extract with 5 ml. of 0.01% solution of dithizone in carbon tetrachloride. Transfer the extract to another separatory funnel. Continue to extract with small portions of dithizone until the extracts are colorless or slightly yellow. Wash the combined extracts with two 20 ml. portions of 2% NaOH followed by one 20 ml. portion of distilled water. Reject the washings. Transfer the cadmium dithizonate to a 25 ml. flask, dilute to the mark with carbon tetrachloride and read on a colorimeter with a green filter.
Cadmium 0.1 to 1 ppm. All other materials at the concentrations listed above.	Use a 10 ml. aliquot of the 100 ml. sample and proceed by the above procedure.
Cadmium 1 to 5 ppm. All other materials at the concentrations listed above.	Take a 10 ml. sample and use a 1 ml. aliquot and proceed by the above procedure.

NOTE: For effluents containing cobalt, nickel, copper, mercury and silver and where it is desired to analyze for cadmium between 0.01-5 ppm., use the sample sizes indicated above and use the recommended procedure.

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COLORIMETRIC DETERMINATION OF CHROMIUM

Abstract

Colorimetric procedures for the determination of the hexavalent and total chromium content of effluents in the range of 5 to 50 ppm. are presented. The methods were found to give satisfactory results in the presence of as much as 5000 ppm. of each of 23 cations in simultaneous admixture.

The method for total chromium makes use of a treatment with hot, concentrated acids to remove organic materials and an extraction of iron with cupferron and chloroform. The chromium is oxidized to the hexavalent state by silver and persulfate in the presence of permanganate. The addition of a solution of s-diphenylcarbazide produces a red-violet coloration the intensity of which is measured at 540 millimicrons.

The method for the determination of hexavalent chromium is based upon the formation of a red-violet color with s-diphenylcarbazide.

These procedures can be materially shortened if the iron content is below 100 ppm. and organic materials are absent. A table summarizes the changes which can be made when iron is below 100 ppm. and organic matter is absent.

Colorimetric Determination of Chromium in Effluents

The analytical methods for the determination of microquantities of chromium make use of colors which can be developed from hexavalent chromium. The color of hexavalent chromium is intense enough for general use; however, increased sensitivity may be obtained by reacting the chromate with certain organic reagents. An example of a method based on the intensification of the yellow color of hexavalent chromium, cited by Koenig (1), depends upon the reaction of disodium-1, 8-dihydroxynaphthalene-3, 6-disulfonate (Chromotropic salt) in acid medium with chromate to give a soluble, red colored compound. Garrat (2) made use of this reaction to increase the limit of detection of chromium in steel.

The formation of a red-violet coloration in acid medium by the interaction of hexavalent chromium and s-diphenylcarbazide was first noted by Cazeneuve (3) and the analytical use of this reaction was introduced by Moulin (4). The colored product formed is of unknown compo-

sition. The reaction is extraordinarily sensitive and nearly specific for chromium. Only hexavalent molybdenum gives a similar color, but the color formation proceeds slowly, and its intensity is much less than that of the corresponding chromium compound. At very low acidities, mercury salts will produce a blue or blue-violet coloration; this interference can be eliminated by the selection of correct conditions. Of the remaining common elements, the yellow or yellow-brown compound formed from ferric ion may interfere; but this interference may be avoided by measuring the intensity of the color of the chromium complex at an appropriate wave-length. Since the reaction of the ferric iron with s-diphenylcarbazide is slow in sulfuric acid solution, precise results for chromium can be obtained if the intensity of the red-violet chromium complex is measured immediately after the addition of the reagent; furthermore, the color due to ferric ion itself is not strong if chlorides are absent. The use of phosphoric acid to decolorize ferric iron leads to a decrease in the red violet color on standing (5).

In order to determine the hexavalent chromium content in an effluent, no elaborate preliminary treatments are necessary. The effluent is acidulated with sulfuric acid (0.2N) and then treated with a solution of s-diphenylcarbazide. The intensity of the red-violet color is measured with a photometer within 2 minutes. The effect of iron is eliminated in the blank by reducing the chromate with ferrous sulfate.

The determination of the total chromium concentration of an effluent, requires oxidation to bring all chromium salts to the hexavalent state so that a reaction with s-diphenylcarbazide can be brought about. Chromium can be oxidized by fuming perchloric acid, permanganate, persulfate catalyzed by silver ion, periodate, chlorine, lead peroxide, bismuthate, fusion with carbonate and nitrate, or fusion with sodium peroxide. Since chromate itself is a strong oxidizing agent, any oxidation procedure that will cause the formation of hexavalent chromium will also cause the formation of permanganate. Generally, the oxidation of chromium is carried out in an alkaline medium and most elements are precipitated and removed by this treatment leaving the soluble chromate. By this procedure only colored, alkalisoluble substances will interfere with the determination of the intensity of the color of the chromate-diphenylcarbazide complex. On the other hand, the precipitation of hydrous oxides causes losses of chromium by adsorption and mechanical entrainment, particularly if the quantity of these hydrous oxides is large.

Of the elements which are likely to be present in industrial effluents, only copper, nickel, cobalt, iron, and manganese are colored or form colored products in their oxidized states in acid medium. With the exception of manganese, these elements could interfere with the chromate determination if it weren't for the fact that a blank can be made to correct for their presence. The case for manganese is simple; the color of permanganate that would result from the simultaneous oxidation of manganese and chromium can be removed by reaction with HCl. In view of the above discussion, an acid oxidation is preferable.

Description of the Methods:

(a) Total Chromium: A preliminary fuming with nitric and sulfuric acids is carried out to decompose organic material which may retain chromium in a form which will not react with s-diphenylcarbazide. Insoluble substances remaining after dilution of the digested mixture are removed by filtration or centrifugation. Iron, vanadium, and molybdenum, which form colored compounds with s-diphenylcarbazide, are extracted as the cupferrides from a portion of the diluted digestion mixture. The faint coloration produced by mercury in a weakly acid solution does not perceptibly influence the chromium determination. The solution is then oxidized with ammonium persulfate in the presence of silver as a catalyst and permanganate is added to insure the complete oxidation of chromium to the hexavalent state.

The permanganate color is destroyed by boiling with hydrochloric acid. The addition of s-diphenylcarbazide causes the formation of a characteristic red-violet color, the intensity of which is determined photometrically at 540 millimicrons wave-length or with a suitable green filter. The red-violet color is stable for at least 2 hours.

(b) Hexavalent Chromium: For the determination of hexavalent chromium in effluents, the acidity of the sample is adjusted to 0.2 N in sulfuric acid, s-diphenylcarbazide is added and the intensity of the red-violet coloration that is developed is measured photometrically.

If the sample contains materials which can be oxidized by hexavalent chromium in acid solutions (cyanides!), the method will obviously fail. Also, if the hexavalent chromium is not present in a form that is suitable for reaction with the s-diphenylcarbazide, the results will be invalid. Highly colored materials, such as organic dyes may be present provided that they do not absorb strongly at 540 millimicrons wave-length when diluted.

In view of the varied composition of industrial wastes, it is strongly advised that results obtained for hexavalent chromium by this method be examined for possible errors from the above sources.

The recommended procedures were found to yield excellent results for 5 to 50 ppm. of chromium in solutions containing 5000 ppm. of each of the following ions in simultaneous admixture: Ag^+ , Hg^{+2} , Pb^{+2} , Bi^{+3} , Cu^{+2} , Cd^{+2} , As^{+5} , Sb^{+5} , Sn^{+4} , Al^{+3} , Fe^{+3} , Mn^{+2} , Ni^{+2} , Co^{+2} , Zn^{+2} , Ca^{+2} , Sr^{+2} , Ba^{+2} , Mg^{+2} , Na^+ , K^+ , NH_4^+ , P as PO_4^{-3} , and organic materials such as tartrates.

Sensitivity of the Method:

The sensitivity of the method is defined as the number of micrograms of chromium which can be determined in the 10 ml. with a relative error of $\pm 50\%$. For the following recommended procedure, this corresponds to 5 ppm. or 50 micrograms of chromium in the 10 ml. sample taken for analysis.

Limit of Detection of the Method:

The limit of detection of the method is defined as the number of micrograms of chromium which must be present in the 10 ml. sample taken for analysis so that an extinction of 0.005 will be obtained in Step 14 for a 1 cm. cell thickness at 540 millimicrons for the total chromium procedure and Step 6 for a 1 cm. cell thickness at 540 millimicrons for the hexavalent chromium procedure. For the recommended procedures, the limit of detection is 10 micrograms of chromium (1 ppm.).

The limit of detection can be increased by taking larger samples, provided that the concentration of each of the other elements remains below 5000 ppm.

Discussion of the Blanks:

(a) Total Chromium: A blank is used to compensate for the presence of traces of chromium in the reagents. On long standing, solutions of s-diphenylcarbazide may develop a color which might contribute an error to the results; however, this may be circumvented by the use of freshly prepared reagent solutions.

(b) Hexavalent Chromium: A blank is necessary to compensate for the colored materials which may be present in the effluent and for any color which may be developed by substances other than chromium which react with s-diphenylcarbazide. Iron particularly interferes in this procedure. The effect of iron and other color-forming materials is minimized by using a blank which is made by reducing the hexavalent chromium with a crystal of ferrous sulfate. The slight incremental of iron content introduced by the ferrous sulfate is negligible. The difference in color intensities between the treated and untreated samples is attributed solely to the color of the hexavalent chromium complex with s-diphenylcarbazide. This procedure for correcting for interferences from iron and other colored substances fails when

these substances are reduced by ferrous sulfate to a colorless state or when the shade of the color is changed by the reduction; e.g. permanganate.

Recommended Procedures

These recommended procedures are designed to be used for the determination of 5 to 50 ppm. of chromium in a 10 ml. sample of effluent.

Reagents Required:

- (1) Nitric Acid: Concentrated, 16 N; reagent grade.
- (2) Sulfuric Acid: 36 N; reagent grade.
- (3) Hydrochloric Acid: Concentrated, 12 N; reagent grade.
- (4) Phosphoric Acid: 85% syrup; reagent grade.
- (5) Cupferron Solution: 5% w/v. in water. Freshly prepared.
- (6) Chloroform: Reagent grade.
- (7) Silver Nitrate Solution: Approximately N/10.
- (8) Ammonium Persulfate: Reagent grade.
- (9) Potassium Permanganate Solution: Approximately N/10.
- (10) Ferrous Sulfate: Reagent grade.
- (11) s-Diphenylcarbazide Solution: 0.5% w/v in 1:1 acetone and water. Prepare fresh as needed.
- (12) Sulfuric Acid Solution: 1:3.
- (13) Standard Chromium Solution: Dissolve 0.141 g. of reagent grade potassium dichromate in distilled water and dilute to one liter.

1 ml. = 50 micrograms of chromium

For establishing a calibration curve, 1 ml. of this solution taken as a sample corresponds to 5 ppm. of chromium for a 10 ml. sample of effluent taken for analysis in step one of both recommended procedures.

Recommended Procedure for the Determination of Total Chromium:

- (1) Pipette a 10 ml. sample of the effluent into a 150 ml. beaker.

In running a blank, use 10 ml. of water.

In establishing a calibration curve, use 10 ml. of water and add 1 ml. of the standard chromium solution for each 5 ppm. of chromium.

- (2) Add 5 ml. of concentrated nitric acid and evaporate the solution to dryness, but do not bake.

Cool and add 5 ml. of concentrated nitric acid followed by 2 ml. of concentrated sulfuric acid. Evaporate to strong fumes of sulfur trioxide. Gently fume for 5 minutes.

If the residue after fuming is discolored by organic carbon, cautiously add 2 ml. of concentrated nitric acid and fume again. Repeat as many times as is necessary. It may be necessary to add more concentrated sulfuric acid to prevent the mixture from going to dryness.

- (3) Cool the solution to room temperature. Add about 50 ml. of water and add 8 ml. of concentrated sulfuric acid. A total of about 10 ml. of about 10 ml. of concentrated sulfuric acid should be present in the solution at this point of the procedure. If necessary, heat to aid solution.

- (4) Filter the solution, if necessary, through a Whatman #42 paper, saving the filtrate. If possible, use a centrifuge.

Wash the filter at least three times with 5 ml. portions of water. Combine the washings and filtrate.

- (5) Transfer the filtrate and washings to a 100 ml. volumetric flask and dilute to the mark with water. Shake well.
- (6) Pipette 5 ml. of this solution into a separatory funnel. Chill the solution by immersing the funnel in an ice bath.

Add 5 ml. of 5% cupferron solution and shake very well. Let stand in the ice bath for one minute with an occasional swirling.

- (7) Extract the solution in the separatory funnel with three separate 5 ml. portions of chloroform.

Wash the combined chloroform extracts in another separatory funnel with one 5 ml. portion of water. Combine this wash water with the extracted solution in the first separatory funnel. Reject the chloroform layer.

Transfer the solution from the separatory funnel to a 250 ml. beaker and wash the funnel with a small amount of water. Add this washing to the main solution.

- (8) Adjust the volume of the solution in the beaker to about 100 ml. Add 5 ml. of silver nitrate solution and 0.5 g. of ammonium persulfate and cautiously bring the solution to a boil. If, on boiling, the solution turns dark in color due to small amounts of cupferron which have been carried over, cool the solution and add 0.5 g. of ammonium persulfate and slowly bring to a boil. Repeat the cooling and addition of persulfate until no dark color develops on heating for one or two minutes.

- (9) To the warm solution, add N/10 potassium permanganate dropwise until the solution is pink in color.

Boil the solution for at least 5 minutes. If the solution is not pink at this point, add permanganate as before and repeat until the pink color persists on boiling for 5 minutes.

- (10) Add 5 drops of hydrochloric acid to the gently boiling pink solution and continue heating for 3 minutes. If the pink color has not been destroyed, add 2 more drops of HCl and boil for two minutes. Repeat the HCl treatment until the hot solution is not pink. Do not allow the volume of the boiling solution to drop below about 75 ml.

- (11) Cool the solution to room temperature. The volume at this point should be about 75 ml.

Filter the solution through sintered glass, or centrifuge. Asbestos mats may be used in the filtration, but paper or organic matter should not be permitted to come into contact with the solution.

Wash the filter with two 5 ml. portions of water and combine the washings and filtrate.

- (12) Transfer the filtrate and washings to a 100 ml. volumetric flask.
Add 1 ml. of s-diphenylcarbazide solution. Bring to the mark with distilled water and shake well.
- (13) Set the colorimeter to zero with water. Use a green (No. 54) filter. With a spectrophotometer, set the instrument to read full scale at 540 millimicrons.
- (14) Transfer the solution from step 12 to the sample cuvette and read the colorimeter.
- (15) If necessary, convert the scale readings of the photometer to optical density. Subtract the blank reading from the sample readings. If a calibration curve is being established, plot these corrected readings versus ppm. of chromium. If a sample is being run, read the amount of chromium from the calibration curve.

Recommended Procedure for the Determination of Hexavalent Chromium:

- (1) Pipette two separate 10 ml. samples of the effluent into 100 ml. volumetric flasks. One of these samples will serve as a blank.

In establishing a calibration curve, use 10 ml. of water and 1 ml. of the standard chromium solution for each 5 ppm. of chromium.

- (2) Dilute with about 25 ml. of water and cautiously add 40 ml. of 1:3 sulfuric acid. Do not allow the solution to become very hot. Cool to room temperature.
- (3) Dilute to the mark with water. Shake well.

- (4) Transfer a 5 ml. portion of this solution to a 100 ml. volumetric flask.
Add 1 ml. of s-diphenylcarbazide solution and bring to the mark with water. Shake well.

Treat the blank as follows: Transfer a 5 ml. portion of the solution from Step 3 to a 100 ml. volumetric flask. Add 2 or 3 small crystals of ferrous sulfate and shake until dissolved. Add 1 ml. of s-diphenylcarbazide solution; no red color should develop. If a red color develops, add small crystals of ferrous sulfate until the color is discharged. Dilute to the mark with water. Shake well.

- (5) Set the colorimeter to zero with water. Use a green (No. 54) filter. With a spectrophotometer, set the instrument to read full scale at 540 millimicrons.
- (6) Transfer the solution from Step 4 to the sample cuvette and read the colorimeter within 2 minutes.
- (7) If necessary, convert the scale readings of the photometer to optical density. Subtract the blank reading from the sample readings. If a calibration curve is being established, plot these corrected readings versus ppm. chromium. If a sample is being run, read the amount of chromium from the calibration curve.

Variations of the Recommended Procedures:

If the composition of the effluent is known, the recommended procedure for total chromium can be materially shortened. The procedure for hexavalent chromium cannot be shortened.

The following table summarizes the changes which can be made in the recommended procedure for total chromium when the composition of the sample is known. Unless otherwise stated, the concentrations of other elements must not exceed 5000 ppm. For effluents containing greater quantities of these elements, dilution will be necessary. The effluent should be between pH 2 and 9.

Composition of Effluent	Changes in the Recommended Procedure for the Determination of Total Chromium
Organic matter absent	Omit steps 2 and 3. Add 50 ml. of water to the samples and then carefully add 10 ml. of sulfuric acid. Start with step 4 of the recommended procedure.
Organic matter absent and iron below 100 ppm.	Omit steps 2 and 3. Add 50 ml. of water to the samples and then carefully add 10 ml. of concentrated sulfuric acid. Start with step 4 of the recommended procedure. Omit steps 6 and 7. Pipette 5 ml. of the solution from step 5 into a 250 ml. beaker and start with step 8. In step 11 before cooling to room temperature, add 0.5 ml. of 85% H_3PO_4 .
Iron below 100 ppm.	Omit steps 6 and 7. Pipette 5 ml. of the solution obtained in step 5 into a 250 ml. beaker and start with step 8. In step 11 before cooling to room temperature, add 0.5 ml. of 85% H_3PO_4 .
Organic matter present and all other elements except chromium at 5000 ppm.	Follow the recommended procedure.

A Shortened Procedure for Chromium (0.01 to 5 ppm.):

The following procedure is designed for the analysis of water samples where the concentration of each of the interfering elements, especially iron, is low and the only elements present in relatively large quantities are the alkali metals and calcium.

Composition of the Effluent	Shortened Procedure
Chromium 0.01 to 0.1 ppm. Barium and lead below 0.1 ppm. All other elements below 5 ppm.	<u>Total Chromium</u> In Step 1, of the recommended procedure for total cr., use 250 ml. of the effluent. Omit steps 3, 4, 5, and 6. Chill the solution in a separatory funnel. Add 5 ml. of 5% cupferron solution and shake very well. Let stand in ice for one minute with an occasional swirl. Continue with the procedure starting with Step 7.

	<p><u>Hexavalent Chromium</u> Pipette a 200 ml. sample of the effluent into a 250 ml. volumetric flask. Add 0.5 ml. conc. sulfuric acid. Add 2 ml. of s-diphenylcarbazide solution. Dilute to the mark. For a blank, treat a sample similarly, except add crystals of ferrous sulfate before adding the s-diphenylcarbazide. Start with step 5 in the recommended procedure for hexavalent chromium; use a 5 cm. cuvette in step 6.</p>
Chromium 0.1 ppm. to 1 ppm.	<p><u>Total Chromium</u> Use 25 ml. of the effluent in step 1, in the recommended procedure for total cr. Follow the above shortened procedure for total cr.</p> <p><u>Hexavalent Chromium</u> Pipette 25 ml. of the effluent into a 100 ml. volumetric flask. Add 3 ml. of 1:3 sulfuric acid, and add 50 ml. of water. Add 1 ml. of s-diphenylcarbazide solution and dilute to the mark. Start with step 5 for the recommended procedure for hexavalent cr. For a blank treat a sample similarly, except add crystals of ferrous sulfate before adding s-diphenylcarbazide.</p>
Chromium 1 ppm. to 5 ppm.	<p><u>Total Chromium</u> Use a 50 ml. sample in step 1, in the recommended procedure for total chromium.</p> <p><u>Hexavalent Chromium</u> Use a 50 ml. sample in step 1, in the recommended procedure for hexavalent cr.</p>

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COLORIMETRIC DETERMINATION OF COPPER

Abstract

The colorimetric procedure for the determination of the copper content of effluents in the range of 5 to 50 ppm. which is described herein was found to yield satisfactory results in the presence of as much as 5000 ppm. of each of twenty cations in simultaneous admixture as well as in the presence of organic materials and phosphates.

The sample is treated with hot, concentrated acids to remove organic matter; the copper is extracted by a chloroform solution of mercaptobenzothiazole changed to the strongly colored orange yellow complex diethyldithiocarbamate and measured with a colorimeter.

The procedure can be shortened when less than 10 ppm. of each metal is present, and a table summarizes the changes which can be made when the amounts of the elements other than copper are known or can be estimated.

Colorimetric Determination of Copper in Effluents

The two generally used methods for the colorimetric determination of copper depend upon the formation of highly colored complexes with dithizone or sodium diethyldithiocarbamate. Although dithizone is the more sensitive reagent, mercury, silver, iron, and bismuth interfere with the color formation unless special measures are taken. Many heavy metals give colorations with sodium diethyldithiocarbamate; but the most troublesome are nickel, cobalt, and bismuth. The dithizone method is particularly less desirable since many elements in high concentrations will interfere, notably zinc, lead, cadmium, nickel, etc.

It was found that an extraction with mercaptobenzothiazole will separate the copper from the other elements which might interfere with the subsequent color development with sodium diethyldithiocarbamate. The use of mercaptobenzothiazole was first recommended by Spacu and Kuras (1) as a precipitant for copper. Serfass and Levine reported that copper mercaptobenzothiazole could be quantitatively extracted from aqueous solution by amyl acetate (2), and that the weakly colored extract could serve for the estimation of copper. The color could be intensified by the addition of sodium diethyldithiocarbamate.

Description of the Method:

A preliminary fuming with nitric and sulfuric acids is carried out to decompose organic matter that may retain copper in a form which will not react with mercaptobenzothiazole. Any insoluble substances which remain after dilution of the digestion mixture are removed by filtration or centrifugation. The addition of hydrochloric acid to the residue that remains after digestion removes silver as the chloride, while fuming with sulfuric acid precipitates the greater part of the lead.

The diluted digestion mixture is then adjusted to a pH of 3.5 to insure the complete extraction of copper by mercaptobenzothiazole. Serfass and Levine (2) found that this pH was favorable for the extraction by amyl acetate. When amyl acetate is used, troublesome emulsions are often encountered; the use of chloroform as suggested in this procedure, eliminates this difficulty.

An alcoholic solution of sodium diethyldithiocarbamate is added to the chloroform extract and the developed color is measured at 435 millimicrons on a spectrophotometer or with a blue filter on a colorimeter.

The recommended procedure was found to yield excellent results for concentrations of 5 to 50 ppm. of copper in solutions containing 5000 ppm. of each of the following ions in simultaneous admixture: Ag^+ , Pb^{+2} , Sn^{+2} , Cd^{+2} , As^{+3} , Sb^{+3} , Al^{+3} , Cr^{+3} , Fe^{+2} , Mn^{+2} , Ni^{+2} , Co^{+2} , Zn^{+2} , Ca^{+2} , Sr^{+2} , Ba^{+2} , Mg^{+2} , Na^+ , K^+ , NH_4^+ , P as PO_4^{-3} , and organic materials such as tartrates. The valence state of the ions in the sample is of no concern because of the action of nitric acid during the fuming step.

It was ascertained that bismuth, mercury, silver and lead were the only metals that formed complexes with mercaptobenzothiazole along with copper under the conditions of the chloroform extraction. Of these metals, silver and lead could be easily removed during the preliminary digestion, but the concentration of mercury and bismuth could not be reduced to the point where they would not interfere. The removal of large quantities of mercury and bismuth would add too many steps to the analysis and since large amounts of mercury and bismuth are seldom encountered in effluents, no steps for their removal are included in the procedure. However, it was found that the recommended procedure gave satisfactory results in the presence of 25 ppm. each of mercury and bismuth in simultaneous admixture with the 5000 ppm. of each of the elements previously mentioned.

Sensitivity of the Method:

The sensitivity of the method is defined as the smallest number of micrograms of copper which can be determined with a relative error of 50%. For the following recommended procedure, this corresponds to 5 ppm. or 50 micrograms of copper in the 10 ml. sample taken for analysis.

Limit of Detection of the Method:

The limit of detection of the method is defined as the number of micrograms of copper which must be present in the 10 ml. sample taken for analysis so that an extinction of 0.005 will be obtained in Step 15 for a 1 cm. cell thickness at 435 millimicrons. This corresponds to 5 micrograms of copper (0.5 ppm.).

The limit of detection can be increased by taking a larger sample, provided that the concentrations of mercury and bismuth remain below 25 ppm. and the concentration of each of the other elements remains below 5000 ppm.

Discussion of the Blank:

A blank is used to compensate for the color due to mercaptobenzothiazole and the traces of copper that are present in the other reagents. Freshly prepared solutions of mercaptobenzothiazole and sodium diethyldithiocarbamate give very low blanks.

Recommended Procedure:

This procedure is designed to be used for the determination of 5 to 50 ppm. of copper in a 10 ml. sample of effluent.

Reagents Required:

- (1) Nitric Acid: Concentrated, 16 N; reagent grade.
- (2) Sulfuric Acid: 36 N; reagent grade.
- (3) Hydrochloric Acid: Concentrated, 12 N; reagent grade.
- (4) Sodium Tartrate Solution: 25% w/v.
- (5) Sodium Hydroxide Solution: 20% w/v.
- (6) Tartaric Acid Solution: 50% w/v.
- (7) Sodium Acetate - Acetic Acid Buffer Solution: Mix 30 ml. of glacial acetic acid with 72 ml. of distilled water and add 6 g. of sodium acetate trihydrate.
- (8) Mercaptobenzothiazole Solution: 1% w/v in alcohol. Prepare fresh daily.
- (9) Chloroform: Reagent grade.
- (10) Sodium Diethyldithiocarbamate Solution: 1% w/v in alcohol. Prepare fresh daily.
- (11) Alcohol: methyl or ethyl; reagent grade.
- (12) Standard Copper Solution: Dissolve 0.050 g. of electrolytic copper in 12 ml. of 1:1 nitric acid and dilute to one liter.
1 ml. = 50 micrograms of copper.
For establishing a calibration curve, 1 ml. of this solution taken as a sample corresponds to 5 ppm. of copper for a 10 ml. sample of effluent taken for analysis in step 1 of the procedure.

Procedure:

- (1) Pipette a 10 ml. sample of the effluent into a 150 ml. beaker.

In running a blank, use 10 ml. of water.

In establishing a calibration curve, use 10 ml. of water and add 1 ml. of the standard copper solution for each 5 ppm. of copper.

- (2) Add 10 ml. of concentrated nitric acid and 10 ml. of concentrated sulfuric acid. Evaporate to heavy fumes of sulfur trioxide.

Add 5 ml. of concentrated nitric acid and again bring to fumes of sulfur trioxide. Gently fume for five minutes. Do not allow the solution to go to dryness. Add sulfuric acid if necessary.

If the residue after fuming is discolored by organic carbon, cautiously add 5 ml. portions of nitric acid and fume again. Repeat as many times as is necessary.

- (3) Cool to room temperature. Add 50 ml. of water and 1 ml. of concentrated hydrochloric acid. Stir and let stand for one or two minutes. (Important)
- (4) Filter the solution, if necessary, through a medium porosity sintered glass funnel, saving the filtrate. If possible, use a centrifuge.

Wash the filter at least three times with 5 ml. portions of water. Combine the washings and filtrate.
- (5) Transfer the filtrate and washings to a 100 ml. volumetric flask and dilute to the mark with water.
- (6) Transfer 20 ml. of the solution to a 150 ml. beaker.

Add 15 ml. of 25% sodium tartrate solution. Stir well.
- (7) Adjust the pH of the solution to 3.5 by means of the addition of 20% sodium hydroxide solution or 50% tartaric acid solution.
- (8) Quantitatively transfer this solution to a separatory funnel using a minimum of water.

Add 10 ml. of sodium acetate-acetic acid buffer. Mix well.
- (9) Add 5 ml. of 1% mercaptobenzothiazole solution. Shake well for two minutes and let stand for 5 minutes with an occasional swirling.
- (10) Extract the solution with two separate portions of 5 ml. of chloroform, each time shaking well for at least one minute. Save the chloroform layer.
- (11) Wash the chloroform with two separate 5 ml. portions of water. Shake very well. Discard the washings.
- (12) Transfer the washed chloroform layer to a clean separatory funnel that has been thoroughly rinsed with alcohol (no water). Add 1 ml. of 1% sodium diethyldithiocarbamate solution. Shake well.
- (13) Transfer the solution to a 25 ml. volumetric flask; rinse the separatory funnel with a 5 ml. portion of alcohol and add this to the volumetric flask. Dilute to the mark with alcohol. Mix very well.
- (14) Set the Klett-Summerson colorimeter to zero with a solution of 3 volumes of alcohol and 2 volumes of chloroform. Use a blue filter (No. 42). With a spectrophotometer, set the instrument to read full scale at 435 millimicrons.
- (15) Transfer the solution from step 13 to the sample cuvette and read the colorimeter.
- (16) If necessary, convert the scale readings of the photometer to optical density. Subtract the blank reading from the sample reading. If a calibration curve is being established, plot these corrected readings vs. ppm. of copper. If a sample is being run, read the amount of copper present from the calibration curve.

Note: The use of burettes for accurately dispensing volumes of reagents starting at step 9 will aid considerably in eliminating error in color densities.

Variations of the Recommended Procedure:

If the composition of the effluent is known, the recommended procedure can be altered to suit particular samples. In general, the procedure will be materially shortened if the concentration of each element, other than copper, is less than 10 ppm.

The following table summarizes the changes that can be made in the recommended procedure when the composition of the sample is known. Unless otherwise stated, the concentrations of other elements must not exceed 5000 ppm. each except for mercury and bismuth which are not to exceed 25 ppm. each. For effluents containing mercury and bismuth in greater quantities, the sample should be diluted.

Composition of Effluent:	Changes in the Recommended Procedure:
Organic matter absent:	Omit steps 1 to 5 inclusive. Use a 10 ml. sample of effluent, add 1 ml. of concentrated sulphuric acid and 1 ml. of concentrated HCl. Dilute to about 50 ml. and transfer to a 100 ml. volumetric flask. Start with Step 6 of the recommended procedure.
Organic matter, lead, and silver absent:	Omit steps 1 to 5 inclusive. Take a 10 ml. sample, dilute to 100 ml. in a volumetric flask, and start with step 6 in the recommended procedure.
Organic matter absent; all other elements, below 10 ppm.; pH 2 - 8.	Omit steps 1 to 8 inclusive. Take a 20 ml. sample of effluent and transfer to a separatory funnel. Add 10 ml. of sodium acetate-acetic acid buffer and start with Step 9 of the recommended procedure.
Organic matter present, mercury and bismuth less than 25 ppm.	Follow the recommended procedure.

A Shortened Procedure for Copper in the range 0.01 to 5 ppm.

These procedures have been designed for the analysis of effluents which contain small amounts of copper and also small amounts of other interfering elements.

For the procedures indicated below, the lead and silver content should be under 0.1 ppm. each. Also, mercury and bismuth should be under 0.05 ppm.

Composition of Effluent	Shortened Procedures
Copper 0.01 to 0.1 ppm.	Use 200 ml. in step 1. Omit step 5, adding 15 ml. of 25% sodium tartrate solution and then proceed with step 7. In step 15, use a 5 cm. cuvette.
Copper 0.1 ppm. to 1 ppm.	Use 25 ml. in step 1. Follow the above directions.
Copper 1 ppm. to 5 ppm.	Use 50 ml. in step 1. Follow the recommended procedure.

References

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COLORIMETRIC DETERMINATION OF IRON

Abstract

A colorimetric procedure for the determination of 5 to 50 ppm. of iron in effluents is presented. The method was found to yield satisfactory results in the presence of as much as 5000 ppm. of each of 23 ions in simultaneous admixture as well as in the presence of organic materials.

The procedure involves a preliminary treatment with hot, concentrated acids to remove organic materials and an extraction of the iron content of the sample by isopropyl ether from a 6 N. hydrochloric acid solution. After reduction of the iron, the addition of orthophenanthroline causes the formation of a strongly colored orange-red complex, the intensity of which is measured with a colorimeter.

The procedure can be materially shortened in certain instances and a table summarizes the changes which can be made when the amounts of the elements other than iron are known or can be estimated.

Colorimetric Determination of Iron in Effluents

The two commonly used methods for the colorimetric determination of iron depend on the formation of highly colored red complexes with thiocyanate or orthophenanthroline. Although the thiocyanate method has been widely accepted because of its sensitivity and simplicity, the instability of the red color limits its use. Orthophenanthroline was selected as the reagent in this method since the orange-red color that is developed with ferrous iron is stable for long periods of time. In addition, it does not require close pH control and is very sensitive.

A critical study of the ferrous ortho-phenanthroline color development and interferences was carried out by Fortune and Mellon (1). Almost all of the interferences noted by these authors are eliminated in the method described here by the extraction of iron with isopropyl ether as suggested by Mellon, Butts, and Gahler (2).

Description of the Method:

Since organic matter may retain iron in a form which can not be extracted by isopropyl ether, a preliminary fuming with nitric and sulfuric acids is necessary. Any insoluble substances which remain after dilution of the digestion mixture are removed by filtration or centrifugation.

After selection of an appropriate aliquot, hydrochloric acid is added to make the total acidity about 6 N and the iron in solution is extracted by isopropyl ether. It has been found that the extraction of iron by isopropyl ether is at a maximum when the HCl content of the solution is 6-8 N. Swift (3) has reported that Bismuth (III) is not extracted by isopropyl ether from a 6 N HCl solution, while Mylius and Huttner showed that only 17% of tin (IV) is extracted by ethyl ether.

The iron is then extracted from the isopropyl ether by water. After reduction of the Fe (III), ortho-phenanthroline is added and the intensity of the developed color is measured with a colorimeter or a spectrophotometer.

Although considerable amounts of arsenic, thallium, antimony, and tin may be extracted by the isopropyl ether, no difficulty was encountered when the recommended procedure was tried on concentrations of iron in the range of 5 to 50 ppm. in solutions containing 5000 ppm. of each of the following ions in simultaneous admixture: Ag^+ , Hg^{+2} , Pb^{+2} , Bi^{+3} , Cd^{+2} , Cu^{+2} , As^{+3} , Sb^{+3} , Sn^{+2} , Al^{+3} , Mn^{+2} , Ni^{+2} , Co^{+2} , Zn^{+2} , Ca^{+2} , Sr^{+2} , Ba^{+2} , Mg^{+2} , Na^+ , NH_4^+ , P as PO_4^{-3} , Cl^- , and organic materials such as tartrates. The valence state of the ions in the sample is of no concern because of the reduction step in the procedure.

Almost the entire amount of the tin content of the sample is removed as stannic acid in the preliminary fuming with nitric acid. The remaining amount, even if extracted by the isopropyl ether, is below the interference limit. Bismuth and antimony are largely precipitated as the basic salts by the dilution subsequent to the preliminary sulfuric acid fuming.

Sensitivity of the Method:

The sensitivity of the method is defined as the number of micrograms of iron which can be determined with a relative error of $\pm 50\%$. For the following recommended procedure this corresponds to 5 ppm. or 125 micrograms of iron in the 25 ml. sample taken for analysis.

Limit of Detection of the Method:

The limit of detection of the method is defined as the number of micrograms of iron that must be present in the 25 ml. portion of sample taken for analysis so that an extinction of 0.005 for a 1 cm. cell thickness at 508 millimicrons will be obtained in Step 16. This corresponds to about 15 micrograms of iron (0.5 ppm.) for the method described.

The limit of detection can be increased by taking a larger sample, provided that the concentration of each of the other metal ions do not greatly exceed 5000 ppm.

Discussion of Blank:

A blank is used to compensate for the amount of iron in the reagents used in the procedure. Generally, the high quality reagents that are available to laboratories contain so little iron that the blank will show little color. However, since iron is such a common element, reagents are likely to pick up considerable quantities. Therefore, it is strongly recommended that a blank be run along with every sample.

Recommended Procedure:

This procedure is designed to be used for the determination of 5 to 50 ppm. of iron in a 25 ml. sample of effluent.

Reagents Required:

- (1) Nitric Acid: Concentrated, 16 N; reagent grade.
- (2) Sulfuric Acid: 36 N; reagent grade.
- (3) Isopropyl Ether: Reagent grade.
- (4) Hydrochloric Acid: Conc. reagent grade.
- (5) Hydroxylamine Hydrochloride Solution: 10% w/v.
- (6) Ortho-Phenanthroline Solution: 0.20% w/v. Dissolve 0.20 g. of the monohydrate in 100 ml. of lukewarm water.
- (7) Sodium Acetate Solution: 20% w/v.
- (8) Standard Iron Solution: Dissolve 0.125 g. of electrolytic iron in 50 ml. of 1:3 nitric acid. Boil to expel oxides and dilute to 1 liter with water.
1 ml. = 125 micrograms of iron.
For establishing a calibration curve, 1 ml. of this solution taken as a sample corresponds to 5 ppm. of iron for a 25 ml. sample of effluent taken for analysis in Step 1 of the procedure.

Procedure:

- (1) Pipette a 25 ml. sample of the effluent into a 125 ml. Erlenmeyer flask.

In running a blank, use 25 ml. of water.

In establishing a calibration curve, use 25 ml. of water and add 1 ml. of the standard iron solution for each 5 ppm. of iron.
- (2) Add 25 ml. of concentrated nitric acid and 15 ml. of concentrated sulfuric acid.

Heat until fumes of sulfur trioxide are given off. Continue fuming for 10 minutes. If charring develops, add 10 ml. of concentrated nitric acid and bring to fumes of sulfur trioxide again. Repeat until the carbon is destroyed. Do not allow the solution to go to dryness. Add 10 ml. of concentrated sulfuric acid if necessary.
- (3) Cool the solution to room temperature and cautiously add 50 ml. of distilled water.
- (4) Immediately filter the solution through a medium porosity sintered glass funnel saving the filtrate. If possible, use a centrifuge.

Wash the filter a number of times with small amounts of distilled water. Combine the washings and the filtrate.
- (5) Transfer the filtrate and washing to a 100 ml. volumetric flask and dilute up to the mark with distilled water.

- (6) Transfer 25 ml. of the solution into a separatory funnel.
- (7) Add 25 ml. of concentrated HCl. Shake to mix the contents.
- (8) Extract the iron from the other metals by shaking about 1 minute with 25 ml. of isopropyl ether. Save both layers.
- (9) Extract the aqueous layer two more times with 25 ml. portions of isopropyl ether; combine all the ether extracts. Reject the water layer.
- (10) Wash the combined isopropyl ether extracts with 25 ml. of water. Save both layers.
- (11) Again extract the ether layer with 25 ml. of water. Reject the ether and combine the aqueous extracts.
- (12) Place the combined extracts in a 150 ml. beaker and add 10 ml. of hydroxylamine hydrochloride solution.
- (13) Add 10 ml. of ortho-phenanthroline solution.
- (14) Adjust the pH of the solution to 3.5 by adding sodium acetate solution. Allow to stand at least 2 minutes.
- (15) Transfer the solution to a 100 ml. volumetric flask and dilute to the mark with distilled water.
- (16) Determine the optical density with a colorimeter using a No. 54 green filter or on a spectrophotometer at 508 millimicrons after first setting the instrument with water.
- (17) If necessary convert the scale readings of the photometer to optical density. Subtract the blank readings from the sample readings. If a calibration curve is being established, plot these corrected readings vs. ppm. of iron. If a sample is being run, read the amount of iron present from the calibration curve.

For higher concentrations of iron, the calibration curve shows a significant deviation from a straight line; thus, it will be necessary for each laboratory to establish its own working curve.

Variations of the Recommended Procedure:

The recommended procedure has been designed to yield a value for the iron content of effluents which is not influenced by the presence of other elements. If the composition of the effluent is known, the recommended procedure can be altered to suit the particular sample. In general, the procedure will be materially shortened if the concentration of each element, other than iron, is less than 150 ppm. Exceptions to this generalization are bismuth and silver, which should be essentially absent, and mercury (II) and nickel which should be no greater than 15 ppm. The following table summarizes the changes that can be made in the recommended procedure when the composition of the sample is known.

Composition of Effluent	Changes in the Recommended Procedure
Organic matter absent.	Omit steps 1 to 5 inclusive. Use a 25 ml. sample of effluent, and dilute to 100 ml. in a volumetric flask. Start with Step 6 of the recommended procedure.
All elements except iron below 15 ppm. each; bismuth below 0.5 ppm.; organic matter absent.	Omit steps 1 to 13 inclusive. Dilute a 25 ml. sample of the effluent to 100 ml. with water. Transfer a 25 ml. aliquot of this solution to a 150 ml. beaker and start with step 12.
Copper, antimony and tin less than 150 ppm.; bismuth less than 0.5 ppm.; organic matter absent.	Omit steps 1 to 5 inclusive. Take a 25 ml. sample and dilute to 100 ml. in a volumetric flask. Start with step 7.
Copper, bismuth, antimony, and tin greater than 150 ppm. but less than 5000 ppm.	Follow the recommended procedure in its entirety.

Stop-Go Method for Iron:

Although many routine iron analyses are carried out using thiocyanate as the color developer, it is felt that ortho-phenanthroline presents the advantage of producing a highly stable color. If color comparison is made using Nessler tubes, the standards will be stable for many months.

The stop-go method presented employs ortho-phenanthroline and will be applicable when the concentration of each of the impurity elements is less than 15 ppm. with the exception of bismuth which must be less than 0.5 ppm.; organic material should be absent or negligible.

The stop-go procedure is outlined for determining iron at 5 ppm. But the procedure can be used for iron concentrations of 5-50 ppm. be used for iron concentrations of 5-50 ppm. by making comparison standards of these concentrations.

Procedure:

Preparation of the color comparison standard for Iron at 5 ppm.

- (1) Pipette 4 ml. of the standard iron solution (see recommended procedure) into a 100 ml. volumetric flask. Add 1 ml. of concentrated nitric acid and dilute to the mark. This solution contains 5 micrograms of iron per milliliter.
- (2) Pipette 5 ml. of the above solution into a 100 ml. Nessler tube; add 5 ml. of 10% hydroxylamine hydrochloride solution, 10 ml. of 0.2% ortho-phenanthroline solution, and 15 ml. of 20% sodium acetate solution.
- (3) Dilute to the mark and shake.

Color Development and Comparison of an Effluent Sample

Pipette 5 ml. of the effluent into a 100 ml. Nessler tube; add 5 ml. of 10% hydroxylamine hydrochloride solution, 10 ml. of 0.2% phenanthroline solution, and 15 ml. of 20% sodium

acetate solution. Dilute to the mark, shake, and compare with the color comparison standard from 3 above. If the effluent contains silver, add hydroxylamine hydrochloride and filter into the Nessler tube.

A Shortened Procedures for 0.01 to 5 ppm. of Iron.

These procedures are designed for the analysis of effluent samples where the concentration of each of the heavy metals is below 5 ppm. and tin and bismuth are below 0.1 ppm. each.

Composition of the Effluent	Shortened Procedure
Iron 0.01 to 0.1 ppm.	Use a 1000 ml. sample in step 1. Omit steps 5 and 6. Dilute the filtrate and washings of step 4 (less than 50 ml.) with an equal volume of conc. HCl. Start with step 8. In step 15 use a 50 ml. volumetric flask.
Iron 0.1 ppm. to 1 ppm.	Use a 300 ml. sample in step 1. Follow the above procedure.
Iron 1 ppm. to 5 ppm.	Use a 25 ml. sample in step 1. Follow the above procedure.

References

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2. Mellon, M. G., Butts, P. G., and Gahler, A. R., Sewage and Industrial Wastes, 22, 1543 (1950).
3. Swift, E. H., "Introductory Quantitative Analysis" pp 431, Prentice-Hall, Inc., New York, 1950.

COLORIMETRIC DETERMINATION OF LEAD

Abstract

This monocolor method for the determination of 5-50 ppm. of lead consists of an extraction of the reduced effluent with a solution of dithizone at a pH of 2-3 to remove interfering elements, particularly bismuth and tin. A subsequent extraction at a pH of 8-9 in the presence of cyanide serves to remove the lead as the dithizonate from the sample. After removing the excess dithizone by extraction at a pH of 11.5, the intensity of the color of the lead dithizonate is estimated by means of a colorimeter or a spectrophotometer.

The procedure can be shortened when less than 2-3 ppm. of each metal is present and a table summarizes the changes which can be made for these samples.

Colorimetric Determination of Lead in Effluents

The colorimetric determination of trace quantities of lead is conveniently carried out by the use of diphenylthiocarbazone (dithizone) in cyanide medium at a pH of 8-9. Although numerous investigators have developed schemes of analysis for lead in the presence of large quantities of a small number of other substances such as in plating baths (1), steel (2), or tin (3); there has been no indication that these procedures can be used to analyze for lead in the presence of moderate quantities of a large number of elements.

The following recommended procedure is based on the fact that the elements which interfere with the extraction of lead at a pH of 8-9 in cyanide medium can be removed by a preliminary extraction. The relationship of the metals extracted to the pH of the aqueous phase has been admirably presented by Wichman (4) in a descriptive paper concerning the dithizone system and its application to the analysis of trace metals, and his provisional equilibrium curves for metal dithizonates in chloroform have served as a guide in the development of the method described below.

Since an effluent may contain a great number of impurities, the analytical procedure for lead must be shown capable of yielding the accurate value in the presence of the commonly occurring elements. The recommended procedure was developed by using a solution that contained 100 ppm. of each of the following ions: Ag^+ , Hg^{+2} , Bi^{+3} , Cu^{+2} , Cd^{+2} , As^{+3} , Sb^{+3} , Sn^{+4} , Fe^{+3} , Al^{+3} , Cr^{+3} , Ni^{+2} , Co^{+2} , Mn^{+2} , Zn^{+2} , Ca^{+2} , Sr^{+2} , Ba^{+2} , Mg^{+2} , Na^+ , K^+ , and NH_4^+ . Since the oxidized forms of some elements destroy dithizone, the pre-

liminary step of the analysis involves the reduction of the sample. The absence of cyanide ion in the test solution is of no consequence for the preliminary fuming procedure removes it. Complex cyanides are also decomposed by this treatment and so do not interfere with the analysis for lead. The concentration of 100 ppm. for each ion was selected arbitrarily. It is obvious that certain of these ions namely sodium potassium, calcium, barium, strontium, magnesium, aluminum, arsenic, antimony, and nitrogen as (NH_4^+) could be present in very high concentrations since these do not react with dithizone. Furthermore, with the exception of the alkali metals, calcium, and magnesium, the elements present in the sample are usually below 100 ppm. in effluents that are suitable for discharging into rivers and streams. The method has not been investigated on test samples in which the concentration of each of the interfering ions is greater than 100 ppm.

Description of Method:

The elements which interfere with the extraction of lead in cyanide medium at pH 8-9 are tin (II), thallium, and bismuth. Thallium is so rarely encountered that its interference is hardly worth consideration. On the other hand, bismuth and in particular tin occur quite frequently.

The sample is first fumed with sulphuric and nitric acids to remove organic compounds and then reduced with hydrazine to lower the oxidation state of those elements or compounds which are capable of oxidizing dithizone. The reduction assures that tin and iron will be in their lower valence states. At a pH of 2-3, dithizone forms complexes with copper, bismuth, tin, mercury, and silver. Thus, bismuth and the tin which remains after the fuming procedure are removed so that they can not interfere with the lead extraction at pH 8-9. A strong solution of dithizone (0.1%) in chloroform is used to extract the relatively large quantities of bismuth, tin, copper, etc.

After the removal of the interfering elements, tartrate is added to prevent the formation of hydroxides, and the solution is brought to a pH of 8-9 with ammonium hydroxide and sodium cyanide. By means of a dilute solution of dithizone, lead is then extracted. Since an excess of dithizone is used, the pink color of the lead dithizonate is masked by the intense green color of the excess dithizone, so the excess dithizone is removed from the carbon tetrachloride layer by the use of an alkaline cyanide solution, leaving the orange red lead dithizonate in the organic solvent. The solution of lead dithizonate is finally diluted to a given volume and the color intensity is determined by means of colorimeter, a spectrophotometer, or by comparison with standards.

The maximum absorption of lead dithizonate in carbon tetrachloride occurs at about 520 millimicrons (1) and this absorption maximum nearly coincides with the transmission maximum of a Wratten filter number 53 or 54 (green). It is, therefore, possible to use a colorimeter to determine the concentration of lead (loc. cit.).

The use of hydrazine as the reducing agent may lead to some difficulties, since the reduction of ferric and stannic ions proceeds quite slowly. The preliminary reduction step must be carried out carefully in accordance with the procedure.

Sensitivity of the Method:

The sensitivity of the method is defined as the smallest number of micrograms of lead which can be determined with a relative error of $\pm 50\%$. For the following recommended procedure this corresponds to 5 ppm. or 50 micrograms of lead in the one ml. portion taken for analysis taken in step 7.

Limit of Detection of the Method:

The limit of detection of the method is defined as the number of micrograms of lead which must be present in the 1 ml. portion taken for analysis in step 7 so that an extinction of 0.005 for a 1 cm thickness at 520 millimicrons will be obtained in step 19. This corresponds to about 0.5 microgram of lead (0.5 ppm.) for the method described below.

The limit of detection is influenced by the purity of the reagents used in the determination, and the value of 0.5 ppm. was obtained experimentally with reagents that were essentially free of lead. Since dithizone separations are not perfect, that is, some lead escapes extraction, the lower limit will be influenced by the total amount of lead present. For example, if 1 microgram of lead escapes, under the conditions of extraction, and the reagents contain 1 microgram of lead, then any lead introduced by the sample will be collected by the dithizone and a color indication corresponding to the amount present in the sample will be obtained. On the other hand, if the amount of lead in the sample and the reagents does not exceed 1 microgram, no color indication for lead will be obtained. In view of this consideration it may seem advisable to omit the steps recommended for the purification of the reagents. If the reagents are found to contain very little lead, then the purification steps are not necessary. When the reagents contain large quantities of lead, the blank will be high and it will be nearly impossible, with the usual colorimeters, to ascertain the presence of small increments of lead from the sample. Another reason for the purification of the reagents is to effect removal of substances which oxidize dithizone. The oxidation of dithizone results in high blanks since the oxidation product of dithizone (diphenylthiocarbodiazone) also exhibits some absorption at 520 millimicrons.

Recommended Procedure

This procedure is designed to be used for the accurate determination of lead in effluents in the range of 5 to 50 ppm.

Reagents Required:

- (1) Hydrazine Acetate: Hydrazine hydrate in a concentration of 60-65% hydrazine can be obtained almost lead free from Matheson Coleman and Bell Incorporated, E. Rutherford, New Jersey. Mix 15 ml. of this product with 50 ml. of glacial acetic acid and then dilute to 100 ml with water.
- (2) Hydrochloric Acid: Distill concentrated commercial acid in a Pyrex apparatus. The distillate will be approximately 22% HCl.
- (3) Ammonium Hydroxide: Pass ammonia gas from a cylinder into redistilled water in a Pyrex container kept cold by an ice bath. Store in plastic bottles.
- (4) Sodium Tartrate Solution: 10% w/v to purify, shake with 0.025% dithizone in carbon tetrachloride until the organic solvent layer appears pure green in color. Wash away the traces of dithizone in the solution by extraction with pure chloroform until the solution is water white. Then extract twice with carbon tetrachloride.
- (5) Dithizone, 0.1% w/v in Chloroform: To remove the chief impurity, diphenylthiocarbodiazone, proceed as follows: The purification depends upon the insolubility of diphenylthiocarbodiazone in basic aqueous solutions. Dissolve 250 mg. of dithizone crystals in 50 ml of CHCl_3 ; filter through a small paper and wash the filter with several small portions of chloroform. Transfer the filtrate to a separatory funnel and extract with portions of a 1:100 solution of ammonium hydroxide until the chloroform layer is nearly devoid of green color. Discard the chloroform layer and wash the

combined extracts of ammonium hydroxide with four 15 ml. portions of chloroform. Discard the chloroform extracts. Precipitate the dithizone by the addition of 2 ml. of concentrated HCl; shake to completely neutralize the ammonia. Extract the precipitated dithizone with 25 ml. portions of chloroform and finally dilute the combined chloroform extracts with pure chloroform to a volume of nearly 250 ml. The solution keeps well in the cold; it is preferably kept in the refrigerator or in cold running water. In lieu of keeping the solution cold, make up fresh as needed. The decomposition of this solution is evidenced by a gradual decrease in green color.

- (6) Dithizone, 0.025% w/v in Carbon Tetrachloride: Dissolve 125 milligrams of dithizone in 50 ml. of chloroform and filter through a small filter paper. Wash the filter paper with small portions of pure chloroform and combine all filtrates. Extract the filtrates with 1:100 NH_4OH until the CHCl_3 layer is nearly devoid of green color. Wash the aqueous layer with pure CCl_4 to remove traces of chloroform and diphenylthiocarbodiazene. Reject the carbon tetrachloride extracts. Neutralize the ammonium hydroxide by shaking well with 2 ml. of conc. HCl. Extract the precipitated dithizone with pure carbon tetrachloride. Dilute the carbon tetrachloride extracts to 500 ml. with pure solvent. This solution must be kept cool at all times in a refrigerator or, less desirably, in running water.
- (7) Potassium Cyanide: 10% w/v. Dissolve 10 grams of the purest salt in 100 ml. of distilled water.
- (8) Tartaric Acid Solution: 50% w/v. Dissolve 50 grams of the pure crystallized acid in 100 ml. of water.
- (9) Acetic Acid: N/10. Dilute 6 ml. of pure glacial acetic acid to one liter with distilled water.
- (10) Thymol Blue Indicator: 0.04% w/v. Solution in water.
- (11) Alkaline Potassium Cyanide: To 175 ml. of pure concentrated ammonium hydroxide add 15 ml. of 10% KCN solution (see above) and 7.5 ml. of a solution of lead free 10% sodium sulfite. Dilute to 500 ml. with water. To remove the lead from sodium sulfite, add 10 gm. of sodium sulfite, exsicc., to 100 ml. of water and extract with 0.1% dithizone solution until the color of the organic layer is pure green. Remove traces of chloroform by four or five extractions with pure carbon tetrachloride.
- (12) Standard Lead Solution: 1 ml. = 100 micrograms of lead. Dissolve 100 milligrams of the purest lead metal in a mixture of 2 ml. of conc. HNO_3 and 2 ml. of water. Heat gently if necessary. Quantitatively dilute to 1 liter with pure water. Store in plastic bottles.
- (13) Carbon Tetrachloride: Use only reagent quality. The commercial material often contains carbon disulfide and the recovered material may even contain phosgene or sulfur compounds. Since all of these substances react with alkali, shake 100 ml. of the solvent with 50 ml. of a 50% solution of KOH in ethanol. Repeat this extraction several times. Now wash the CCl_4 with 25-50 ml. portions of concentrated H_2SO_4 several times. The final washing with the acid should show no discoloration. Wash the CCl_4 with a dilute solution of sodium bicarbonate; wash repeatedly with water until the washings are perfectly neutral to litmus paper. Dry over night with CaCl_2 and distill. Instead of drying, distill about 10% of the solvent and then collect the clear distillate. Do not distill the last 50-100 ml. after collecting the main fraction.
- (14) Chloroform: All chloroform, especially the reclaimed solvent must be treated as follows: Drain off all water. Wash with conc. H_2SO_4 until the solvent and the acid layers are clear and colorless. Use 50-100 ml. of acid per 1000 ml. of solvent. Shake the solvent with a dilute solution of sodium bicarbonate and then wash thoroughly. Add calcium oxide to dry the solvent. Separate from the CaO and add 2% of its volume of

pure, absolute methanol. Distill the solvent slowly while keeping a pellet of CaO in the still. Reject the first 50-100 ml. and do not allow the still to go to dryness.

- (15) Water: Distilled water sometimes is not as pure as it should be. If blanks run on the water show a considerable amount of heavy metals, redistill it using Pyrex glass stills and receivers. To test the water, add about 1 ml. of KCN (10%) to 1 ml. of the water and shake with 1 ml. of 0.025% dithizone. The dithizone layer should show no pink coloration.
- (16) Sulphuric Acid: Conc., 36 N, reagent grade.
- (17) Nitric Acid: Conc., 16 N, reagent grade.

Recommended Procedure:

- (1) Pipette a 20 ml. sample of the effluent into a 125 ml. erlenmeyer flask. In running a blank, use 20 ml. of water. If a calibration curve is to be established, add 1 ml. of the standard lead solution for each 5 ppm. of lead.
- (2) Add 3 ml. of concentrated sulfuric acid and 5 ml. of concentrated nitric acid to the contents of the flask. Slowly bring the solution to boiling and continue heating until strong fumes of SO₃ are evolved. Fume for at least 5 minutes. If the liquid in the flask is discolored from organic decomposition products after fuming, cool the contents, add 5 ml. more of concentrated nitric acid and again bring to fumes. Repeat, if necessary, until all organic matter has been decomposed. Do not allow the solution to go to dryness; add 2 ml. of concentrated sulfuric acid, if necessary.
- (3) Cool the residue in the flask. Dilute with 10 ml. of water. Add 10-15 drops of phenolphthalein indicator, and nearly neutralize the solution with 1:1 ammonium hydroxide.
- (4) Add 20 ml. of hydrazine acetate and heat to 90-95°C. in a water bath for at least 10 minutes. Cool.
- (5) Add 20 ml. of 10% sodium tartrate solution. Adjust the pH of the solution in the beaker to about 2.5 (using a pH meter) by adding either ammonium hydroxide or 50% tartaric acid solution.
- (6) Quantitatively transfer the contents of the beaker to a 100 ml. volumetric flask and bring to the mark with N/10 acetic acid.
- (7) Pipette exactly 5 ml. of the solution in the volumetric flask into a separatory funnel. This corresponds to 1 ml. of the effluent in a total volume of 5 ml.
- (8) Extract the solution in the funnel with separate 3 ml. portions of 0.1% dithizone in chloroform until the organic layer has a pure green color. Shake well each time and carefully drain off and discard the chloroform layer.
- (9) Extract the solution with two 5 ml. portions of pure chloroform. This serves to remove the entrained dithizone. Reject the chloroform layers.
- (10) Remove the chloroform that remains behind by extracting once with a 5 ml. portion of carbon tetrachloride. Reject the carbon tetrachloride layer.
- (11) Add 10 ml. of 10% sodium tartrate; also add 5 drops of thymol blue indicator. If necessary, add concentrated ammonium hydroxide to make the indicator turn blue.
- (12) Add 10 ml. of 10% KCN. Adjust the pH to 8.5 by adding 50% tartaric acid or ammonium

hydroxide until the indicator turns to a green color.

- (13) Extract with a 5 ml. portion of 0.025% dithizone in carbon tetrachloride. Shake well and carefully transfer the solvent layer to another separatory funnel. Do not allow any of the aqueous phase to run into the carbon tetrachloride extract.
- (14) Successively extract the aqueous phase with 2 ml. portions of 0.025% dithizone solution until the green color of dithizone persists for at least two extractions. Combine all these extractions with the one from the previous step. When multiple samples are run, as with a calibration curve, be sure to use the same amount of dithizone solution for all extractions. The color of the blank increases as the number of extractions increases, owing to the diphenylthiocarbodiazone content of the dithizone.
- (15) Extract the aqueous phase with one 5 ml. portion of pure carbon tetrachloride and add it to the other extracts.
- (16) To the combined extracts of carbon tetrachloride, add 20 ml. of alkaline KCN and shake well. The green coloration of dithizone will be replaced by the pink coloration of lead dithizonate; the alkaline aqueous solution will be colored yellowish due to the formation of a salt of dithizone.
- (17) Drain off the carbon tetrachloride layer into a 25 or 50 ml. volumetric flask. Extract the aqueous phase with two 2 ml. portions of pure carbon tetrachloride. Combine all the extracts and reject the aqueous layer.
- (18) Dilute the extracts in the volumetric flask to the mark by adding pure carbon tetrachloride and shake well.
- (19) Filter the carbon tetrachloride solution through small, dry papers to remove suspended droplets of water. Read the color intensity of this solution using pure carbon tetrachloride as a reference liquid on a colorimeter equipped with a green Wratten filter No. 53 or 54 or with a spectrophotometer at 520 millimicrons.
- (20) If necessary, convert the scale reading of the photometer to optical density. Subtract the blank reading from the sample readings. If a calibration curve is being established, plot these corrected readings versus micrograms of lead added. If a sample is being run, read the amount of lead present from the calibration curve.

Variations of the Recommended Procedure:

When the composition of the effluent is known, the recommended procedure can usually be shortened to suit particular samples.

The following table summarizes the changes that may be made in the recommended procedure when the composition of the sample is known. Unless otherwise stated, the concentration of each element must not exceed 100 ppm.

Composition of Effluent	Changes in the Recommended Procedure
Organic matter absent:	Pipette a 20 ml. sample into a 125 ml. flask, add 10-15 drops of phenolphthalein indicator and nearly neutralize the solution with 1:1 ammonium hydroxide. Start with step 4 of the recommended procedure.

COLORIMETRIC DETERMINATION OF MANGANESE

Abstract

The colorimetric procedure for the determination of the manganese content of effluents in the range of 5 to 50 ppm. that is presented, yielded satisfactory results in the presence of as much as 5000 ppm. of each of twenty four cations in simultaneous admixture, as well as, in the presence of large amounts of organic materials.

The method makes use of a treatment with hot, concentrated acids to remove organic materials and chlorides and a subsequent oxidation of the manganese to permanganate with potassium periodate. The intensity of the permanganate color together with interfering colorations is measured; a blank, made by bleaching the permanganate color of a similarly treated sample corrects for the interfering colorations.

Colorimetric Determination of Manganese in Effluents

A commonly used method for the colorimetric determination of manganese involves its oxidation to permanganate by means of persulfate or periodate. From the time of its introduction by Willard and Greathouse (1), periodate has been widely accepted as the most suitable oxidizer. A study of the effect of a large series of cations and anions on the development of the permanganate color by periodate was carried out by Mehlig (2). He noted no interference with development of the color although certain of these ions produced troublesome turbidities while others, such as copper, nickel and chromate, decreased the sensitivity of the method because of their color.

Description of the Method:

Since reducing substances such as organic matter, chlorides, etc., will interfere with the formation of permanganate, their removal is effected by a preliminary fuming with nitric and sulfuric acids (3). Insoluble substances which remain after dilution of the digestion mixture are removed by filtration or centrifugation.

Phosphoric acid is added to eliminate the color of ferric ion prior to the oxidation of manganese with periodate. After dilution to a suitable volume, the optical

density of the solution is measured at 525 millimicrons. For a blank the permanganate color of a sample treated similarly is destroyed by means of HCl. In this way, the blank is made to correct for the presence of other colored ions.

Sensitivity of the Method:

The sensitivity of the method is defined as the smallest number of micrograms of manganese which can be determined with a relative error of $\pm 50\%$. For the following recommended procedure this corresponds to 5 ppm. or 100 micrograms of manganese in the 20 ml. sample taken for analysis.

Limit of Detection of the Method:

The limit of detection of the method is defined as the minimum number of micrograms of manganese which must be present in the 20 ml. portion of the sample taken for analysis so that an extinction of 0.005 for a 1 cm. thickness at 525 millimicrons will be obtained in step 11. For the recommended procedure, the limit of detection is 40 micrograms of manganese (2 ppm.).

The limit of detection is greatly influenced by the concentration of colored ions which may be present in the sample since they increase the value of the extinction, and the precision of the usual photometric devices are considerably less at high values of extinction. The indicated limit of detection, 2 ppm., has been experimentally verified in solutions containing 5000 ppm. of each of 23 of the common cations.

Most photometers have a scale which is not sufficiently extended to permit the reading of as small a value as 0.005 in the vicinity of 0.6 extinction. Consequently, the limit of detection of manganese rises above 2 ppm. whenever the inherent color of the sample yields extinction values greater than 0.600. The limit of detection can be increased by taking a larger sample provided that the amount of each ion present does not exceed a total of 100,000 micrograms.

Discussion of Blank:

The blank is used to compensate for the color of ions like copper, nickel, cobalt, and chromium (VI), which may contribute to the absorption of light by the permanganate developed in the sample. Since both sample and blank are treated alike, it is necessary to remove the permanganate color of the blank by means of HCl additions.

Recommended Procedure:

This procedure is designed to be used for the determination of 5 to 50 ppm. of manganese in a 20 ml. sample of effluent.

Reagents Required:

- (1) Nitric Acid: Concentrated, 16 N; reagent grade.
- (2) Sulfuric Acid: 36 N; reagent grade.
- (3) Hydrochloric Acid: Concentrated, 12 N; reagent grade.
- (4) Phosphoric Acid: 85% syrup; reagent grade.

COLORIMETRIC DETERMINATION OF NICKEL

Abstract

A colorimetric procedure for the determination of 5 to 50 ppm. of nickel in effluents is presented. The method was found to yield satisfactory results in the presence of as much as 5000 ppm. of each of 23 cations in simultaneous admixture as well as in the presence of organic materials.

The method makes use of a treatment with hot, concentrated acids to remove organic matter and an extraction of the nickel content of the sample as the dimethylglyoxime complex with chloroform. The intensity of the color of the nickel dimethylglyoxime complex is measured with a colorimeter after its extraction from the chloroform solution.

The procedure can be materially shortened if the content of the individual metals which are present is below 15 ppm. A table summarizes the changes which can be made when the amounts of the elements other than nickel are known or can be estimated.

Colorimetric Determination of Nickel in Effluents

The commonly used method for the colorimetric determination of nickel depends upon the formation of the red colored complex of nickel (II) dimethylglyoxime. Nickel (II) dimethylglyoxime is soluble in chloroform and this serves as the method of separating minute amounts of nickel from large quantities of other elements. Although copper is also extracted to some extent, it can be removed from the chloroform solution by washing with a dilute solution of ammonia. Of the usual elements which are likely to be present, only cobalt forms a complex with dimethylglyoxime. Fortunately, the cobalt complex is not soluble in chloroform to a significant extent, although large amounts of cobalt interfere by consuming reagent.

Since manganese may interfere with the extraction of nickel (II) dimethylglyoxime by oxidizing it to nickelic (IV) dimethylglyoxime, which is insoluble in chloroform, a reducing agent such as hydroxylamine hydrochloride is added to keep manganese in the divalent state.

Description of the Method:

A preliminary fuming with nitric and sulfuric acids is carried out to decompose organic matter which may retain nickel in a form which will not react with dimethylglyoxime. Insoluble substances which remain after dilution of the digestion mixture are removed by filtration or centrifugation.

The diluted digestion mixture is treated with hydroxylamine hydrochloride and then made ammoniacal in the presence of citrate. After the addition of a solution of dimethylglyoxime, the nickel complex is extracted with chloroform. The chloroform layer is then washed with a dilute solution of ammonia to remove copper. The nickel (II) dimethylglyoxime complex which is in the chloroform layer is removed by washing with a dilute solution of hydrochloric acid. The acid solution of nickel dimethylglyoxime complex is treated with bromine water to oxidize the nickel and then made ammoniacal; the nickel (IV) dimethylglyoxime complex which forms has a very intense brown to red color (1). The full intensity of the color is developed almost immediately and is stable for about 15 minutes. However, it increases slowly on long standing and eventually fades (2). The intensity of the color of the nickel (IV) dimethylglyoxime complex follows Beer's law up to about 100 ppm. The developed color is measured at 525 millimicrons on a spectrophotometer or with a green filter on a colorimeter.

The recommended procedure was found to yield excellent results for 5 to 50 ppm. of nickel in solutions containing 5000 ppm. of each of the following ions in simultaneous admixture: Ag^+ , Hg^{+2} , Pb^{+2} , Bi^{+3} , Cu^{+2} , Cd^{+2} , As^{+3} , Sb^{+3} , Sn^{+2} , Al^{+3} , Cr^{+3} , Fe^{+3} , Mn^{+2} , Co^{+2} , Zn^{+2} , Ca^{+2} , Sr^{+2} , Ba^{+2} , Mg^{+2} , Na^+ , K^+ , NH_4^+ , P as PO_4^{-3} , and organic materials such as tartrates. The valence state of the ions in the sample is of no concern because of the action of nitric acid during the fuming step.

Sensitivity of the Method:

The sensitivity of the method is defined as the number of micrograms of nickel which can be determined with a relative error of $\pm 50\%$. For the following recommended procedure this corresponds to 5 ppm. or 100 micrograms of nickel in the 20 ml. sample taken for analysis.

Limit of Detection of the Method:

The limit of detection of the method is defined as the number of micrograms of nickel which must be present in the 20 ml. sample taken for analysis so that an extinction of 0.005 will be obtained in Step 16 for a 1 cm. cell thickness at 525 millimicrons. This corresponds to 20 micrograms of nickel (1 ppm.) for the recommended procedure.

The limit of detection can be increased by taking a larger sample, provided that the concentration of each of the other elements remains below 5000 ppm.

Discussion of the Blank:

A blank is used to compensate for the presence of traces of nickel in the reagents.

Recommended Procedure:

This procedure is designed to be used for the determination of 5 to 50 ppm. of nickel in a 20 ml. sample of effluent.

Reagents Required:

- (1) Nitric Acid: Concentrated, 16N; reagent grade.
- (2) Sulfuric Acid: 36N; reagent grade.
- (3) Ammonium Hydroxide: concentrated 15N; reagent grade.
- (4) Hydroxylamine Hydrochloride Solution: 10% w/v.
- (5) Sodium Citrate Solution: 10% w/v.
- (6) Dimethylglyoxime Solution: 1% w/v in alcohol.
- (7) Ammonium Hydroxide Solution: 1:50.
- (8) Hydrochloric Acid Solution: 0.5N.
- (9) Bromine Water: Saturated (5 ml. C.P. bromine plus 100 ml. of water).
- (10) Chloroform: Reagent grade.
- (11) Standard Nickel Solution: Dissolve 0.448 g. of reagent grade Nickel Sulfate - 6 water of crystallization, in distilled water and dilute to one liter.

1 ml. = 100 micrograms of nickel

For establishing a calibration curve, 1 ml. of this solution taken as a sample corresponds to 5 ppm. of nickel for a 20 ml. sample of effluent taken for analysis in Step 1 of the recommended procedure.

Procedure:

- (1) Pipette a 20 ml. sample of the effluent into a 150 ml. beaker.

In running a blank, use 20 ml. of water.

In establishing a calibration curve, use 20 ml. of water and add 1 ml. of the standard nickel solution for each 5 ppm. of nickel.

- (2) Evaporate the solution to a small volume, but not to dryness.

Add 5 ml. of concentrated nitric acid and evaporate to dryness, but do not bake.

Cool and add 5 ml. of concentrated nitric acid followed by 2 ml. of concentrated sulfuric acid. Evaporate to strong fumes of sulfur trioxide. Gently fume for 5 minutes.

If the residue after fuming is discolored by carbon, cautiously add 2 ml. of concentrated nitric acid and fume again. Repeat as many times as is necessary. It may be necessary to add more concentrated sulfuric acid to prevent the mixture from going to dryness.

- (3) Cool to room temperature. Add 50 ml. of water, stir, and let stand for a few minutes.
- (4) Filter the solution, if necessary, through a medium porosity sintered glass funnel, saving the filtrate. If possible, use a centrifuge.

Wash the filter at least three times with 5 ml. portions of water. Combine the washings and filtrate.

- (5) Transfer the filtrate and washings to a 100 ml. volumetric flask and dilute to the mark with water.
- (6) Pipette 20 ml. of the solution into a separatory funnel.
Add 5 ml. of hydroxylamine hydrochloride solution; shake well. A precipitate may form.
- (7) Add 10 ml. of sodium citrate solution; shake well. Now add concentrated ammonium hydroxide until the solution is definitely ammoniacal; shake well.
Add 5 ml. of dimethylglyoxime solution; shake well.
- (8) Extract the solution with three separate portions of 5 ml. of chloroform, each time shaking for at least one minute. Save the chloroform layers.
- (9) Wash the chloroform extract with one 10 ml. portion of 1:50 ammonium hydroxide. Shake for at least one minute; save both liquid layers.
- (10) Extract the ammoniacal layer with one 5 ml. portion of chloroform. Combine the chloroform extracts and reject the aqueous layer.
- (11) Shake the chloroform with 5 ml. of 0.5 N HCl. Pour off the chloroform into a separatory funnel; save the HCl by draining it into a 100 ml. volumetric flask. Wash the separatory funnel, which contained the acid layer, with a little water; these washings are united with the HCl in the volumetric flask.
- (12) Repeat Step 11. This time discard the chloroform.
- (13) Add 15 drops of saturated bromine water to the contents of the volumetric flask. Add concentrated ammonium hydroxide until the bromine color is destroyed and then 4 or 5 drops in excess.
- (14) Add 1 ml. of 1% dimethylglyoxime solution.
Bring to the mark with water. Shake well.
- (15) Set the colorimeter to zero with water. Use a green (No. 54) filter. With a spectrophotometer, set the instrument to read full scale at 525 millimicrons.
- (16) Transfer the solution from Step 14 to the sample cuvette and read the colorimeter within 15 minutes.
- (17) If necessary, convert the scale readings of the photometer to optical density. Subtract the blank reading from the sample reading. If a calibration curve is being established, plot these corrected readings versus ppm. of nickel. If a sample is being run, read the amount of nickel from the calibration curve.

Variations of the Recommended Procedure:

If the composition of the effluent is known, the recommended procedure can be altered to suit particular samples. In general, the procedure will be materially shortened if the concentration of cobalt, copper, chromium, iron, and manganese are below 15 ppm. each.

The following table summarizes the changes which can be made in the recommended procedure

when the composition of the sample is known. Unless otherwise stated, the concentrations of other elements must not exceed 5000 ppm. For effluents containing greater quantities of these elements, dilution will be necessary. The effluent should be acidic or neutral.

Composition of Effluent	Changes in the Recommended Procedure
Organic matter absent.	Omit steps 1 to 5 inclusive. Take a 4 ml. sample of the effluent, and start with step 6 of the recommended procedure.
Organic matter absent; all elements except Nickel below 15 ppm.	Pipette 4 ml. of the effluent into a 100 ml. volumetric flask, add 5 ml. of 0.5 N HCl, and then add bromine water, dropwise, until the solution is straw-yellow in color. Add 5 ml. of 10% sodium citrate solution and then add ammonium hydroxide until the solution is ammoniacal and any precipitate which may have formed is redissolved. Follow the recommended procedure starting with step 14.
Organic matter absent; cobalt, iron, copper, manganese, and chromium below 100 ppm., all other elements below 5000 ppm.	Follow the above procedure adding 5 ml. of hydroxylamine hydrochloride solution and 10 ml. of sodium citrate solution. For a blank, use 4 ml. of the effluent but do not add dimethylglyoxime in step 14. The blank obtained in this way will be somewhat in error due to the lack of coloration which dimethylglyoxime develops with certain other elements. However, this error will be within the limits of $\pm 50\%$ in the range of 5 ppm. of nickel and $\pm 10\%$ in the 50 ppm. range.
Manganese less than 15 ppm.	Omit the addition of hydroxylamine hydrochloride solution from the recommended or shortened procedures.
Organic matter present; iron, cobalt, copper, chromium, and manganese greater than 100 ppm. but less than 5000 ppm.	Follow the recommended procedure.

References

- (1) Rollet, A., Compt. Rend., 183, 212 (1926).
- (2) Sandell, E. B., "Colorimetric Determination of Traces of Metals", 1st ed., pp. 339-345, Interscience Publishers Inc., New York, 1944.

COLORIMETRIC DETERMINATION OF ZINC

Abstract

A colorimetric procedure for the determination of the zinc content of effluents in the range of 5 to 50 ppm. is presented. The method was found to yield satisfactory results in the presence of 100 to 5000 ppm. of each of 25 ions in simultaneous admixture.

The method is a mono-color procedure employing dithizone. Interfering elements are eliminated by a cupferron extraction and by complexing with cyanide and thiosulfate. After removal of the excess dithizone, the intensity of the red zinc-dithizone complex is measured with a colorimeter.

The procedure can be materially shortened if the concentration of each substance other than zinc is below 1 ppm. A table summarizes the changes which can be made when the amounts of the materials other than zinc are known or can be estimated: modified procedures are included for the analysis of water samples in which the concentration of zinc is as low as 0.01 ppm.

Colorimetric Determination of Zinc in Effluents

The colorimetric determination of trace quantities of zinc is conveniently carried out by the use of diphenylthiocarbazone (dithizone) in cyanide-thiosulfate medium at a pH of 5 to 5.5. Numerous investigators have developed schemes of analysis for zinc in the presence of a wide range of impurities such as in plating baths (1), biological matter (2), and minerals (3).

The method is based upon the fact that the interference of many elements in the extraction of zinc at a pH of 5 to 5.5 is effectively limited by the use of cyanide and thiosulfate as complexing agents (4).

Complexing agents, such as the alkyldithiocarbamates, have been used to render the action of dithizone more nearly specific for zinc (5,6). However, the advantages of these reagents over thiosulfate and cyanide as a complexing medium are limited, and the manipulations involved are as numerous as those in the method recommended here.

The proposed method is a modification of the mono-color method reported by Sandell (7).

Description of the Method:

A preliminary fuming with nitric and sulfuric acids is carried out to decompose organic material which may retain zinc in a form which will not react with dithizone. Hydrochloric acid is added to the digestion mixture after the fuming in order to precipitate any silver that is present. Insoluble substances remaining after dilution of the digestion mixture are removed by centrifugation or filtration.

Cupferron is added to complex iron and copper and the cupferrides are extracted with chloroform.

The solution is made basic and cyanide is added to complex nickel and cobalt. The pH of the solution is adjusted to about 5.5 and thiosulfate is added to eliminate interference from mercury, lead, bismuth, copper, cadmium, tin, and manganese.

The solution is extracted with dithizone in carbon tetrachloride, the excess dithizone is removed by washing with a weak solution of sodium sulfide, and the intensity of the resulting red color is measured at 535 millimicrons wave length in a spectrophotometer or in a colorimeter equipped with a suitable filter.

The recommended procedure yields excellent results for concentrations of zinc in the range of 5 to 50 ppm. in solutions containing in simultaneous admixture 100 ppm. each of Hg^{+2} , Bi^{+3} , Cu^{+2} , Cd^{+2} , Sn^{+2} , 5000 ppm. each of the following ions: Ag^{+} , Pb^{+2} , As^{+3} , Sb^{+3} , Cr^{+3} , Al^{+3} , Fe^{+2} , Mn^{+2} , Ni^{+2} , Co^{+2} , Ca^{+2} , Sr^{+2} , Ba^{+2} , Mg^{+2} , Na^{+} , K^{+} , NH_4^{+} , CNS^{-} , $\text{PO}_4^{=}$, SO_3^{-} , and organic materials such as tartrates and acetates.

Sensitivity of the Method:

The sensitivity of the method is defined as the smallest number of micrograms of zinc which can be determined.

For the following recommended procedure this corresponds to 5 ppm. or 25 micrograms of lead in the 5 ml. sample taken for analysis in step 1.

The method is actually capable of an accuracy of $\pm 5\%$ at 5 ppm.; however, there are numerous factors, such as coprecipitation, solid solutions, etc., which control the accuracy of the determination. For the high concentrations of substances that are likely to be present in effluents, these factors may operate to decrease the accuracy with which the zinc may be determined. It is these reasons that a $\pm 50\%$ relative error has been indicated instead of the $\pm 5.0\%$ which usually can be realized.

Limit of Detection of the Method:

The limit of detection of the method is defined as the number of micrograms of zinc which must be present in the 5 ml. sample taken for analysis in step 1, so that an extinction of 0.005 will be obtained in step 17 for a 1 cm. cell thickness at 535 millimicrons. For the recommended procedure, the limit of detection is 2.5 micrograms of zinc ion (0.5 ppm.).

Discussion of the Blank:

A blank must be run along with the sample since the reagents and the glassware used in the determination contain a surprisingly large amount of zinc. In addition to the error which may be introduced by the accumulation of zinc from various sources, an additional error will develop from the oxidation products of the dithizone used in the extraction. It will be found in using this procedure that the extinction of the blank will be quite high.

Satisfactory results can be obtained only if the blank is faithfully carried through the same steps along with the sample.

Special Precautions:

Dithizone is the only reagent that has been found satisfactory for the direct colorimetric determination of zinc in low concentration in the presence of many other elements. However, it has not been widely used since in general practice contamination from glassware and reagents yield erratic results. This inability to obtain reproducible results has caused operators to refute the value of dithizone as a reagent for zinc or has caused them to doubt the value of the analytical procedure.

It has been found that ordinary glass containers are by far the largest source of zinc contamination to chemicals and solutions stored in them. For this reason, all reagents must be rendered zinc-free in order that as low a blank reading as possible be obtained. Furthermore, it is strongly recommended that these purified reagents be stored in plastic bottles.

All glassware, especially the separatory funnels used in the extractions, should be thoroughly washed, rinsed with concentrated nitric acid, dried with acetone, and then rinsed well with zinc-free distilled water. Separatory funnels should be kept stoppered as much as possible, and the plugs should be greased with silicone grease.

The solubility of glass is at a minimum in hot concentrated acids and consequently very little contamination of the sample will result during the fuming steps of the procedure. It is possible to eliminate zinc contamination from this source by the use of silica vessels when fuming the sample, in fact, the use of silica-ware in place of glassware will eliminate almost all possibilities of contamination from vessels and equipment. Plastic is a satisfactory substitute for beakers, bottles, etc.

Water may be made nearly free of zinc by distilling in Pyrex equipment. Ideally, a silica still and receiver should be employed. The purified water should be stored in silica, plastic containers, or glass containers which have been coated with silicones. For routine laboratory work, water taken directly from a laboratory still with a block tin condenser will be found satisfactory.

Recommended Procedure:

This procedure is designed to be used for the determination of 5 to 50 ppm. of zinc in a 5 ml. sample of effluent.

Reagents Required:

- (1) Nitric Acid: Concentrated, 16 N; reagent grade.
- (2) Sulfuric Acid: 36 N; reagent grade.
- (3) Hydrochloric Acid: Concentrated, 12 N; reagent grade.
- (4) Cupferron Solution: 5% w/v in zinc-free distilled water. Prepare fresh as needed.
- (5) Chloroform: Reagent grade; preferably redistilled over calcium oxide prior to use.
- (6) Carbon Tetrachloride: Reagent grade; redistilled over calcium oxide prior to use.
- (7) Ammonium Hydroxide, Concentrated: Pass ammonia gas from a cylinder into zinc-free dis-

tilled water in a plastic container kept cold by immersion in an ice bath. Store in a plastic container.

- (8) Sodium Cyanide Solution: 5% w/v in zinc-free distilled water. Store in a plastic container.
- (9) Sodium Acetate Solution: 0.5 M. This solution is made zinc-free by extraction with 0.01% dithizone in carbon tetrachloride. The dithizone and yellow oxidation product of dithizone are removed by extraction with successive portions of chloroform until the extracts remain colorless. The solution is then extracted with carbon tetrachloride to remove any chloroform. Store in a plastic container.
- (10) Sodium Thiosulfate Solution: 50% w/v in zinc-free distilled water. Store in a plastic container.
- (11) Dithizone, 0.01% in Carbon Tetrachloride: Since even reagent grade dithizone may be contaminated to some degree by the oxidation product of dithizone (diphenylthiocarbodiazone), the following procedure is strongly recommended for preparing the dithizone solution.

Dissolve 100 mg. of pure dithizone in 50 ml. of chloroform. Filter the solution through paper into a separatory funnel. Extract with three 50 ml. portions of 1% ammonium hydroxide. Discard the chloroform and extract the ammoniacal solution with three 10 ml. portions of carbon tetrachloride. Reject the carbon tetrachloride extracts. Precipitate the dithizone from the ammoniacal solution with 2 ml. of concentrated HCl. Now extract the solution with carbon tetrachloride until the aqueous layer becomes colorless, or almost so. Combine the extracts and dilute to one liter with carbon tetrachloride.

- (12) Sodium Thiosulfate-Acetate Wash Solution: Mix 225 ml. of 0.5M sodium acetate solution, 10 ml. of 50% sodium thiosulfate solution, and 40 ml. of 10% nitric acid, and add water to make 500 ml. of solution. Remove traces of zinc by shaking with dithizone as prescribed with the 0.5 M sodium acetate solution. Store in a plastic container.
- (13) Sodium Sulfide Solution: 1% w/v in zinc-free distilled water. Store in a plastic container.
- (14) Sodium Sulfide Wash Solution: Dilute 40 ml. of 1% sodium sulfide solution to one liter with zinc-free distilled water. Store in a plastic container.
- (15) Standard Zinc Solution: Dissolve 100 mg. of reagent grade zinc in 10 ml. of 1:1 HCl and dilute to one liter with zinc-free distilled water. Store this solution in a plastic container. Pipette 25 ml. of this solution into a 100 ml. flask and dilute up to the mark with zinc-free distilled water. This latter solution, which is the Standard Zinc Solution, should be stored in a plastic container.

1 ml. = 25 micrograms of zinc

For establishing a calibration curve, 1 ml. of this solution taken as a sample corresponds to 5 ppm. of zinc for a 5 ml. sample of effluent taken for analysis in step one of the recommended procedure.

Recommended Procedure for the Determination of Zinc:

- (1) Pipette a 5 ml. sample of the effluent into a 125 ml. erlenmeyer flask (preferably silica).

In running a blank, use 5 ml. of zinc-free distilled water.

In establishing a calibration curve, use 5 ml. of zinc-free distilled water and add 1 ml. of the standard zinc solution for each of 5 ppm. of zinc.

- (2) Add 5 ml. of concentrated nitric acid and 1 ml. of concentrated sulfuric acid and evaporate to strong fumes of sulfur trioxide. Gently fume for 5 minutes.

If the residue after fuming is discolored by organic carbon, cautiously add 2 ml. of concentrated nitric acid and fume again. Repeat as many times as is necessary. More concentrated sulfuric acid may be needed to prevent the mixture from going to dryness.

- (3) Cool the solution and dilute with about 25 ml. of water.

Add 0.5 ml. of concentrated hydrochloric acid.

- (4) Filter the solution, if necessary, through Whatman No. 42 paper, saving the filtrate. Centrifugation is preferable.

Wash the filter at least three times with 5 ml. portions of water. Combine the filtrate and washings.

- (5) Transfer the filtrate and washings to a 100 ml. volumetric flask and dilute to the mark with water.

- (6) Pipette a 10 ml. aliquot from the above solution into a 150 ml. beaker.

Add 0.2 ml. of concentrated sulfuric acid.

- (7) Transfer the solution to a separatory funnel. Chill by immersing the funnel in an ice bath.

Add 5 ml. of the 5% cupferron solution and shake very well. Let stand in the ice bath for at least one minute with an occasional swirling.

- (8) Extract the solution in the separatory funnel with separate 10 ml. portions of chloroform until the chloroform layer remains clear. Reject the chloroform extracts.

Extract with one 5 ml. portion of carbon tetrachloride and reject this extract.

- (9) Transfer the water solution from the separatory funnel to a 150 ml. beaker. Wash out the separatory funnel with a little water and add this washing to the contents of the beaker.

- (10) Add concentrated ammonium hydroxide to the solution in the beaker until it is distinctly alkaline.

Add 15 ml. of 5% sodium cyanide solution.

Add concentrated hydrochloric acid and adjust the pH of the solution with a pH meter to 3-4. (Caution, perform this operation under a hood).

Add 25 ml. of 0.5 M sodium acetate and adjust the pH of the solution to between 5 and 5.5 with concentrated HCl or NH_4OH .

- (11) Transfer the contents of the beaker to a 125 ml. separatory funnel.

Add 20 ml. of 50% solution of sodium thiosulfate, and shake the contents of the flask well.

Composition of the Effluent	Shortened Procedure
<p>Zinc in the range 0.01 to 0.1 ppm. Alkali and alkaline earth metals below 10 ppm. and all other elements below 1 ppm. Organic matter absent.</p>	<p>Take a 100 ml. sample of effluent. Add 10 ml. of a 10% sodium citrate solution and 1 ml. of concentrated ammonium hydroxide (the pH should be between 8-9). Extract with three 5 ml. portions of 0.01% dithizone in CCl₄. Shake the combined dithizone extracts with 20 ml. of 0.01 N HCl. Separate the acid layer, adjust its pH to 5 to 5.5 with 0.5 M sodium acetate, add 5 ml. of 50% sodium thiosulfate, and extract with 3 ml. portions of 0.01% dithizone in carbon tetrachloride until the extracts remain green in color. Wash with 5 ml. portions of 0.04% sodium sulfide until the wash solution remains clear, and dilute to 50 ml. with carbon tetrachloride in a volumetric flask. Read on a colorimeter with a green filter.</p>
<p>Zinc in the range 0.1 to 1 ppm. All other materials at the concentrations listed above.</p>	<p>Use a 10 ml. aliquot of the 100 ml. sample and proceed by the above procedure.</p>
<p>Zinc in the range 1 to 5 ppm. All other materials at the concentrations listed above.</p>	<p>Take a 10 ml. sample and use a 1 ml. aliquot and proceed by the above procedure.</p>

References

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COLORIMETRIC DETERMINATION OF AMMONIA

Abstract

A colorimetric procedure is presented for the determination of 5 to 50 ppm. of ammonia in effluents. The method was found to yield satisfactory results in the presence of 100 ppm. of each of 23 cations in simultaneous admixture.

In this method, the ammonia content of the effluent is distilled off in the usual Kjeldahl equipment and the ammonia in the distillate is determined by Nessler's reagent.

A simplification of this method is possible when the concentration of each substance in the sample, other than ammonia, is below 10 ppm.

Colorimetric Determination of Ammonia in Effluents

Since the determination of ammonia in small quantities is almost generally carried out by means of Nessler's reagent, no literature survey was undertaken to determine the various methods available for the analysis of ammonia. The only point of question was whether ammonia could be evolved from an alkaline solution in the presence of large amounts of salts. Serfass, Levine, and Davis (1) have shown that the presence of a large amount of nickel salts does not interfere with the liberation of ammonia from an alkaline solution. On the other hand, the work of Serfass, Muraca, and Gardner (2) has already indicated that ammonia can be evolved quantitatively from boiling alkaline solutions containing large amounts of a large number of elements. Therefore, the usual Nesslerization procedure can be used.

Description of the Method:

The sample of the effluent is placed in a Kjeldahl flask, made alkaline with sodium hydroxide, treated with sodium sulfide, and boiled. The distillate is collected in dilute acid and the ammonia present in the distillate is determined by Nessler's reagent either with a colorimeter (turbidimeter) or by comparison in Nessler tubes. The sodium sulfide is added during the boiling with alkali in order to insure the rapid and complete release of ammonia from metallic-ammonia complexes such as the cobalt ammines. When mercury (I) is present in the effluent, it will react with ammonia:



The addition of a sulfide will release the ammonia:



Since the recommended procedure does not involve a step for the removal of organic matter which may liberate ammonia in alkaline medium, the determination will be in error when such substances are present in the sample.

The procedure yielded excellent results in the presence of 100 ppm. of each of 23 common cations, together with nitrates, sulphates, tartrates, cyanides, and thiocyanates.

Sensitivity of the Method:

The sensitivity of the method is defined as the number of micrograms of ammonium ion which can be determined with a relative error of $\pm 50\%$. For the following procedure, this corresponds to 2 ppm. or 200 micrograms of ammonium ion in the 100 ml. sample taken for analysis.

Limit of Detection of the Method:

The limit of detection of the method is defined as the number of micrograms of ammonium ion which must be present in the 100 ml. sample taken for analysis so that an extinction of 0.005 will be obtained in Step 8 for a 1 cm. cell thickness at 400 millimicrons. For the recommended procedure, the limit of detection is 50 micrograms of ammonium ion (0.5 ppm.).

Discussion of the Blank:

A blank is used to compensate for the presence of traces of ammonia in the reagents.

Discussion of the Sample:

If the sample is alkaline, it must be analyzed immediately or loss of ammonia by vaporization will occur. If the sample is acid or neutral, the hydrolysis of any cyanates present is in progress and consequently the sample must be analyzed immediately. The acidified sample may be stored for long periods of time if cyanates are absent.

Recommended Procedure

This procedure is designed to be used for the determination of 5 to 50 ppm. of ammonium ion in a 100 ml. sample of effluent.

Reagents Required:

- (1) Sodium Hydroxide-Sodium Sulfide Solution: Saturate 250 ml. of 25% w/v NaOH solution with H_2S gas. Mix this solution with 750 ml. of 25% w/v NaOH solution.
- (2) Hydrochloric Acid Solution: Approximately N/10.
- (3) Gum Arabic Solution: 2% w/v.
- (4) Nessler's Solution: Dissolve 50 g. of potassium iodide in approximately 35 ml. of cold, ammonia-free water. Add slowly a saturated solution of mercuric chloride until the first slight precipitate of red mercuric iodide persists, and then add 400 ml. of a clarified 9 N solution of sodium hydroxide. Dilute the solution to one liter with ammonia-free water and allow it to settle. Siphon off the clear supernatant liquid for use.

- (5) Standard Ammonia Solution: Dissolve 0.732 g. of pure, dry ammonium sulfate in water and dilute to one liter.

$$1 \text{ ml.} = 200 \text{ micrograms of } \text{NH}_4^+$$

For establishing a calibration curve, 1 ml. of this solution used in Step 3 corresponds to 5 ppm. of ammonia in a 100 ml. sample of effluent taken for analysis in Step 1 of the recommended procedure.

Special Equipment:

- (1) Kjeldahl distillation equipment with 300 ml. flasks.

Procedure:

- (1) Pipette a 100 ml. sample of the oil-free effluent into the Kjeldahl flask.

In running a blank or establishing a calibration curve, use 100 ml. of water. Each ml. of the standard ammonia solution corresponds to 2 ppm. of ammonium ion in the sample.

- (2) Set a 125 ml. Erlenmeyer flask containing 20 ml. of 0.1 N HCl so as to receive the distillate. Be sure that the end of the condenser dips well under the acid in the flask.

- (3) Add 40 ml. of the sodium hydroxide-sodium sulfide solution to the Kjeldahl flask and immediately connect the flask to the distilling apparatus. Then shake the flask so as to mix the contents very well.

Collect between 50 and 60 ml. of distillate in the acid solution.

- (4) Transfer the distillate to a 100 ml. volumetric flask and dilute to the mark.

- (5) Pipette 10 ml. of this solution into a 100 ml. volumetric flask.

- (6) Add 3 drops of a 2% gum arabic solution; swirl the contents of the flask.

Add 1 ml. of Nessler's reagent and mix well.

Dilute up to the mark with water, shake well and wait 5 minutes.

- (7) Set the colorimeter to zero with water using a blue (No. 42) filter. With a spectrophotometer set the instrument to read full scale with water at about 400 millimicrons.

The intensity of the developed color (turbidity) can be estimated by comparing the sample against Nessler standards.

- (8) Transfer the solution from Step 6 to the sample cuvette and read the colorimeter.

- (9) If necessary, convert the scale readings of the photometer to optical density. Subtract the blank reading from the sample readings. If a calibration curve is being established, plot these corrected readings versus ppm. of ammonium ion. If a sample is being run, read the amount of ammonium ion from the calibration curve.

Variation of the Recommended Procedure:

If the composition of the effluent is known, the recommended procedure for ammonium ion can be materially shortened.

The following table summarizes the changes which can be made in the recommended procedure for ammonium ion when the composition of the sample is known. Unless otherwise stated, the concentration of other elements must not exceed 100 ppm.. For effluents containing greater quantities of these elements, dilution will be necessary. The effluent should be between pH 2 and 9. The use of Rochelle Salts to prevent precipitation of hydroxides was proposed by Dodge and Zabban (3).

Composition of Effluent:	Changes in the Recommended Procedure for the Determination of Cyanates:
Alkali metals, alkaline earths, zinc, and aluminum below 100 ppm. each; all other elements below 10 ppm. each. Cyanides, thiocyanates, and sulfides below 1 ppm.	Pipette a 10 ml. sample of effluent into a 100 ml. volumetric flask and add about 50 ml. of water. Add 1 g. of Rochelle Salts. Shake, and start with step 6 of the recommended procedure.

Procedure 0.01 to 5 ppm. of Ammonia:

The following procedures indicate the steps to be taken in the analysis for ammonia 0.01 to 5 ppm. when the effluent contains less than 5 ppm. each of other elements.

The effluent should have a pH of 2 to 9 and should contain less than 0.05 ppm. each of cyanides, thiocyanates, and sulfides for 0.1 to 5 ppm. of ammonia.

Range of Ammonia	Procedure
0.01 to 0.1 ppm.	Use the recommended procedure. In step 1 use a 50 ml. sample. Omit step 4. Neutralize the distillate obtained from step 3 using NaOH solution and litmus paper. Using the entire distillate, proceed with step 6. Make the comparison nephelometrically using prepared Nessler standards in 100 ml. tubes.
0.1 to 1 ppm.	Pipette a 50 ml. sample of the effluent into a 100 ml. volumetric flask and add about 0.2 g. of Rochelle Salts. Shake, and start with step 6. In step 8, use a 5 cm. cuvette.
1 to 5 ppm.	Pipette a 25 ml. sample of the effluent into a 100 ml. volumetric flask and add about 0.2 g. of Rochelle Salts. Shake, and start with step 6. In step 8, use a 2 or 5 cm. cuvette.

References

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DICHROMATE OXYGEN CONSUMED

Abstract

A procedure for the determination of the chemical oxygen demand of effluents is presented. This procedure is essentially the same as that recommended by the A.P.H.A. for industrial wastes. The most recent A.P.H.A. recommendations involving the use of dichromate as the oxidizing agent and silver sulfate as catalyst have been followed.

Determination of Chemical Oxygen Demand

The chemical oxygen consumed value is an important parameter for stream and industrial waste studies. Since the carbon and not the nitrogen, in organic matter is oxidized by chemical oxidants, oxygen consumed is sometimes erroneously considered as indicating the amount of carbonaceous organic matter present. Chemical oxygen consumed determinations, however, indicate only a part of the organic matter, the proportion varying depending upon the chemical oxidant used, the structure of the organic compounds and the manipulative procedure.

The oxygen consumed test does not differentiate unstable from stable organic matter. Therefore, the chemical oxygen consumed is not directly correlated with biological oxygen demand values on industrial wastes, sewage plant effluents or stream samples. The oxygen consumed is of value in estimating the "strength" of certain trade wastes and sewages. It is particularly useful when the biochemical oxygen demand cannot be determined. The Dichromate Reflux Method has been selected for the oxygen consumed determination because it has been found that this procedure has advantages in reproducibility, applicability to a wide variety of samples and manipulative advantages over other oxidants.

Description of the Method:

The acidified sample is refluxed for two hours in the presence of 0.05N $K_2Cr_2O_7$ to oxidize organic matter. Following dilution, the dichromate consumed is determined by titration with standard ferrous sulfate solution using 1, 10-phenanthroline as indicator.

Although the Dichromate Reflux Method gives much more complete oxidation than the permanganate method, certain straight chain aliphatic compounds, aromatic hydrocarbons and pyridine are not oxidized to any appreciable extent.

Unstable samples should be tested without delay and samples containing settleable solids should be homogenized by means of a blender for ease of representative sampling. Initial dilutions in volumetric flasks should be made on those wastes containing a high oxygen consumed value in order to reduce the error which is inherent in measuring small sample volumes.

Precision of Method:

The method is quite accurate and may be used on a wide variety of wastes even though the back titration is less than 1 ml. With four different industrial wastes and four organic compounds the method gave a mean coefficient of variation of .0084 and a maximum of .0175 and a minimum of .0046. When silver sulfate was used as a catalyst in five different cases the mean coefficient of variation was .0093 with a maximum of .0129 and a minimum of .0058.

(note, coefficient of variation is the standard deviation expressed as per cent/)

1. Apparatus:

- (1) The reflux apparatus used in this method consists of a 300 ml. round bottom flask (Corning No. 4320) with ground glass neck 24/40 and a Friedrichs condenser (Corning No. 2600).

2. Reagents:

- (1) Standard dichromate, 0.2500 normal dissolve 12.2591 grams of C.P. $K_2Cr_2O_7$, previously dried at 103°C. for two hours, in distilled water and dilute to one liter.
- (2) Standard ferrous ammonium sulfate, approximately .2500 normal. Dissolve 98 grams of C.P. $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$ in distilled water. Add 20 ml. of H_2SO_4 , cool and dilute to one liter. This solution must be standardized against the $K_2Cr_2O_7$ daily.
- (3) Concentrated sulfuric acid, A.C.S. grade.
- (4) Ferroin indicator. The 1,10-phenanthroline ferrous sulfate indicator (0.025 molar) may be purchased already prepared from the G. Frederick Smith Company, Columbus, Ohio. If it is desired to prepare the indicator solution, 14.85 grams of 1,10-phenanthroline (monohydrate), together with 6.95 grams of $FeSO_4 \cdot 7H_2O$ is dissolved in H_2O and diluted to one liter.
- (5) Silver sulfate crystals, A.C.S. grade.

Recommended Procedure:

Standardization of ferrous ammonium sulfate:

- (1) Dilute 25.00 ml. of the standard dichromate solution to about 250 ml.
- (2) Add 20 ml. of H_2SO_4 and allow to cool.
- (3) Titrate against the ferrous ammonium sulfate using the ferroin indicator.

- (4) To 50 ml. of sample or an aliquot diluted to 50 ml. with distilled water in the round-bottom flask, add 25 ml. of the standard dichromate solution. Carefully add 75 ml. of concentrated H_2SO_4 (2:3) mixing after each addition. Attach the flask to the Friedrichs condenser and reflux the mixture for two hours. Pumice granules or glass beads should be added to the reflux mixture to prevent bumping.
- (5) Cool and then wash down the condenser with about 25 ml. of distilled water. Transfer the contents to a 500 ml. Erlenmeyer flask, washing out the reflux flask four to five times with distilled water.
- (6) Dilute the mixture to about 350 ml. and titrate the excess dichromate with the standard ferrous ammonium sulfate, using the ferroin indicator. Generally two to three drops of the indicator are used. This, however, depends upon the individual analyst. The color change is sharp, changing from a blue-green to a reddish-blue.
- (7) A blank consisting of 50 ml. of distilled water instead of the sample, together with the reagents, is refluxed along with the sample.

NOTE: More complete oxidation of many organic compounds such as straight chain alcohols and acids may be obtained by the use of silver sulfate as a catalyst. One gram of silver sulfate is added directly to the mixture before refluxing, or the silver sulfate may be dissolved in the concentrated H_2SO_4 at the rate of 1 gram for every 75 ml. of acid.

Calculations:

$$\text{D.O.C., p.p.m.} = \frac{(a-b) \times \text{Normality of Reagent} \times 8000}{\text{Volume of Sample}}$$

D.O.C.,	Oxygen Consumed
a	ml. of $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4$ used for blank
b	ml. of $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4$ used for sample

VOLUMETRIC DETERMINATION OF CHLORIDE

Abstract

A volumetric procedure for the determination of the chloride content of effluents is presented. A modification of the Volhard procedure is adapted for this type of sample.

Volumetric Determination of Chloride in Effluents

The usual Volhard titration procedure can be used for the determination of the chloride content of effluents, provided certain substances are absent. This titration can not be carried out in the presence of materials which can reduce the titrant to metallic silver or which can complex silver ions. Examples of these materials are:- ferrous salts, stannous salts, cyanides, fluorides, and ethylenediaminetetra acetic acid.

When anions such as ferrocyanide thiocyanate, iodide, and bromide are present, the titration will be in error because the silver salts of these anions will be formed in preference to silver chloride.

The procedure described below will not differentiate hypochlorites and chlorites from chlorides.

Description of the Method:

The solution is acidified with nitric acid and boiled to removed SO_2 , CO_2 , HCN , I_2 , etc. An excess of standard silver nitrate is added to the cool mixture and back titrated with the standard thiocyanate solution using ferric alum as indicator. Nitro-benzene is used to prevent the decomposition of the silver chloride by the excess thiocyanate.

Limit of Detection of the Method:

The limit of detection of the method is defined as the minimum number of micrograms of chloride which must be present in the 100 ml. sample taken for analysis so that a difference of 0.2 ml. (calculated as ml. of AgNO_3) will be obtained between the volumes of silver nitrate solution used in Step 4 and that indicated in Step 7. For the recommended procedure, the limit of detection is 200 micrograms of chloride (2 ppm.).

Recommended Procedure:

This procedure is designed to be used for the determination of 5 to 500 ppm. of chloride in a 100 ml. sample of effluent.

Reagents Required:

- (1) Silver Nitrate Solution: Dissolve 4.8027 g. of dried AgNO_3 in 1 liter of distilled water. 1 ml. = 0.0010 g. Cl.
- (2) Potassium Thiocyanate Solution: Dissolve 2.8 g. of reagent KCNS in 1 liter of distilled water.
- (3) Ferric Alum Solution: Saturated.
- (4) Phenolphthalein Indicator: 1% w/v. Dissolve 1 g. of phenolphthalein in 100 ml. of alcohol.
- (5) Nitric Acid, 1:1: Dilute nitric acid with an equal volume of distilled water.
- (6) Nitrobenzene: Reagent grade.

Procedure:

- (1) Pipette 100 ml. of the sample into a 250 ml. erlenmeyer flask.
- (2) Add 2-3 drops of phenolphthalein indicator solution and then add drops of 1-1 nitric acid until the solution is distinctly acid.
- (3) Add 5 ml. of 1:1 nitric acid and boil for 2-3 minutes. Cool.
- (4) Add from a burette the standard solution of silver nitrate until an excess of approximately 2 ml. is present, accurately measuring the amount added.
- (5) Add 3 ml. of nitrobenzene; shake vigorously to coagulate the precipitate and to coat it with a film of nitrobenzene.
- (6) Add 1 ml. of ferric alum indicator solution.
- (7) Add potassium thiocyanate solution from a burette until a permanent reddish brown color appears that does not fade after 5 minutes. Accurately measure the amount of KCNS used.
- (8) Calculate the ppm. of Cl in the sample by the following formula:

$$\text{ppm. of Cl} = 10 (\text{mlAgNO}_3 - \text{mlKCNS} \times f)$$

f is determined as follows:

Titrate with the potassium thiocyanate solution 25.00 ml. of the standard AgNO_3 contained in a 250 ml. erlenmeyer flask together with 75 ml. of water, 1 ml. of ferric alum, and 5 ml. of 1:1 HNO_3 . Accurately record the volume of KCNS that is necessary to give a permanent reddish brown color which does not fade after 5 minutes.

$$f = \frac{25.00}{\text{ml KCNS}}$$

CHLORINE

Abstract

A colorimetric method is presented for the determination of 5 to 50 ppm. of chlorine in effluents.

The method makes use of the standard A.P.H.A. orthotolidine reagent to develop a coloration with free chlorine in a highly diluted sample of the effluent.

Colorimetric Determination of Chlorine

The usual colorimetric procedure for determining chlorine in water, which involves the formation of a color with orthotolidine has not been thoroughly investigated with respect to cationic interferences. The presence of ferric and manganic compounds, oxidizing agents, and nitrites has been shown to effect the results obtained by this method. On the other hand, the extreme sensitivity of the test and the ease with which it can be carried out offer many advantages.

Description of the Method:

A sample of effluent is diluted with chlorine free water, a suitable aliquot is treated with ortho-tolidine, and the intensity of the developed color is determined by comparison against permanent standards.

It was easily ascertained that the presence of many elements in concentrations as high as 1 ppm. each did not affect the formation of the ortho-tolidine color with chlorine. These elements are: zinc, arsenic, antimony, bismuth, nickel, copper, phosphorous as phosphate, cadmium, chromium (III) cobalt, lead, barium, silver, and mercury.

Certain elements can be tolerated in much higher concentrations, (as much as 20 ppm. of sodium, potassium, calcium, magnesium, aluminum, chloride, nitrate and sulfate), while certain elements must be essentially absent.

Since the concentration range of free chlorine is 5 to 50 ppm. for this procedure, and

the maximum amount of the usual elements will seldom exceed 50 ppm. in a chlorinated effluent of the type that will originate from the waste disposal plant of a metal finishing industry, it was decided that by proper dilution, interferences from these elements could be minimized.

Color comparators are available which can be used conveniently for determining the free chlorine content of a water sample in the range of 0.1 to 1 ppm. A 50-fold dilution of the effluent will reduce the chlorine content from 5 ppm. to 0.1 ppm. which places it in the range of these instruments. By this dilution the concentration of many substances is reduced to the point where they do not interfere.

Sensitivity of the Method:

The sensitivity of the method is defined as the number of micrograms of free chlorine which can be determined with a relative error of $\pm 50\%$. For the following procedure this corresponds to 5 ppm. or 50 micrograms of chlorine in a 10 ml. sample.

Limit of Detection of the Method:

The limit of detection of the method is defined as the number of micrograms of chlorine which must be present in the 10 ml. sample in order that a difference of 0.05 ppm. of chlorine can be detected in a clear sample in the comparator. This corresponds to 25 micrograms for the procedure described below.

Recommended Procedure:

This procedure is designed to analyze for free chlorine (HOCl , Cl_2 , Chloramines, etc.) in the range of 5 to 50 ppm. in the presence of a maximum of 1000 ppm. each of sodium, potassium, calcium, aluminum, magnesium, sulfates, chlorides, and nitrates: 50 ppm. each of zinc, arsenic, antimony, bismuth, nickel, copper, phosphate, cadmium, chromium (III), cobalt, lead, barium, silver, and mercury, 10 ppm. of ferric iron; 5 ppm. of nitrites and 0.5 ppm. of manganic manganese.

The procedure is essentially that presented in "Standard Methods for the Examination of Water and Sewage" 9th edition (1946).

Reagents Required:

- (1) Ortho-Tolidine: Dissolve 1.35 g. of ortho-tolidine dihydrochloride in 500 ml. of distilled water. Add this solution, with constant stirring, to 500 ml. of dilute HCl which has been made by mixing 350 ml. of water with 150 ml. of conc. HCl . Store this reagent in amber bottles in the dark; keep cool and away from rubber, and do not use after six months.
- (2) Test Water: Add sufficient chlorine to ammonia-free distilled water to maintain about 1 ppm. excess chlorine; allow to stand 30 minutes, then boil at least 30 minutes. Prepare and use this water within 96 hours.

Special Equipment:

Hellige pocket-size water testing comparator or its equivalent. Permanent standards, 0.1-1.0 ppm. chlorine.

Procedure:

- (1) Pipette a 10 ml. sample of the effluent into a 500 ml. volumetric flask and dilute to the mark with test water. If a precipitate separates, centrifuge or allow to settle.
- (2) Pipette 10 ml. of the diluted effluent into the sample tube of the comparator and add 0.5 ml. of the ortho-tolidine solution. Mix well. Preferably, keep the sample in a dark room or cabinet.
- (3) Fill the other tube of the comparator with test water and add 0.5 ml. of the ortho-tolidine solution. Mix well.
- (4) Let both tubes stand for at least 10 minutes to obtain full color development.
- (5) Match the intensity of the developed color with the permanent standards. Use the tube obtained in step (3) as a color compensator.
- (6) Multiply the ppm. of chlorine obtained in this way by 50 to obtain the actual chlorine content of the sample.

Procedures for The Analysis of 0.1 to 5 ppm. of Chlorine:

The procedures indicated below are merely modifications of the recommended procedure. Only the sample sizes differ.

Range	Procedure
0.1 to 1 ppm.	Follow manufacturer's directions supplied with the color comparator, or, just omit step 1 of the recommended procedure and use a 10 ml. sample of the effluent in step 2. Omit step 6.
1 ppm. to 5 ppm.	Dilute 10 ml. of the effluent to 50 ml. in step 1. Multiply by 5 in step 6.

DETERMINATION OF NITRATE-NITRITE NITROGEN

Abstract

This procedure for the determination of nitrate and nitrite nitrogen is essentially that currently recommended by the A. P. H. A. except that a distillation of ammonia is used to remove interfering substances.

The procedure involves a removal of ammonia from the sample, a reduction of the nitrate and nitrite content to ammonia by aluminum, the distillation of the ammonia, and the determination of the ammonia content of the distillate in the usual manner with Nessler's reagent.

Determination of Nitrate-Nitrite Nitrogen in Effluents

The determination of nitrite and nitrate nitrogen in effluents may be of importance in policing a potable water supply where it becomes necessary to trace the source of abnormally large quantities of nitrogen. The method presented here does not differentiate between nitrite and nitrate nitrogen.

Description of the Method:

The sample is made alkaline and boiled to remove ammonia. Then, the nitrate and nitrite content of the sample is reduced by aluminum metal in an alkaline medium. The resulting ammonia is distilled off after the addition of sodium sulfide and the distillate is treated with Nessler's solution in the usual fashion. Organic compounds which may react with ammonia in basic solution or which may generate ammonia on reduction or hydrolysis in basic medium obviously will invalidate the results that are obtained by this method.

Sensitivity of the Method:

The sensitivity of the method is defined as the number of micrograms of nitrogen which can be determined with a relative error of $\pm 50\%$. For the following recommended procedure, this corresponds to 2 ppm. or 200 micrograms of nitrogen in the 100 ml. sample taken for analysis.

Limit of Detection of the Method:

The limit of detection of the method is defined as the minimum number of micrograms of nitrogen which must be present in the 100 ml. sample taken for analysis so that an extinction of 0.005 will be obtained in Step 8 for a 1-cm. cell thickness at 400 millimicrons. For the recommended procedure, the limit of detection is 50 micrograms of nitrogen (0.5 ppm.).

Recommended Procedure

This procedure is essentially the method appearing in "Standard Methods for the Examination of Water and Sewage" 9th edition (1946), except that a distillation is carried out to remove ammonia from interfering substances.

Reagents Required:

- (1) Sodium Hydroxide Solution: Dissolve 250 g. of NaOH (special low in N) in about 1250 ml. of water. Add several strips of aluminum foil and allow the evolution of hydrogen to continue overnight. Concentrate the solution by boiling and dilute to 1 liter.
- (2) Aluminum Foil: Use strips of 30-gauge pure aluminum sheet about 10 cm. long, and 6 mm. wide.
- (3) Sodium Hydroxide-Sodium Sulfide Solution: Saturate 250 ml. of 25% w/v NaOH solution with H_2S gas. Mix this solution with 750 ml. of 25% w/v NaOH solution.
- (4) Hydrochloric Acid Solution: Approximately N/10.
- (5) Gum Arabic Solution: 2% w/v.
- (6) Nessler's Solution: Dissolve 50 g. of potassium iodide in approximately 35 ml. of cold, ammonia-free water. Add slowly a saturated solution of mercuric chloride until the first slight precipitate of red mercuric iodide persists, and then add 400 ml. of a 9 N solution of sodium hydroxide. Dilute the solution to one liter with ammonia-free water and allow it to clarify by settling. Siphon off the clear supernatant liquid.
- (7) Standard Nitrogen Solution: Dissolve 1.445 g. of dry reagent grade potassium nitrate and dilute to exactly one liter.

1 ml. = 0.20 mg. nitrogen

Special Equipment:

Kjeldahl distillation equipment with 300 ml. flasks.

Procedure:

- (1) Pipette a 100 ml. sample of the effluent into a casserole and add about 10 ml. of NaOH solution.

For a blank use 100 ml. of distilled water.

When establishing calibration curves, use 100 ml. of water and add 1 ml. of the potassium nitrate solution for each 2 ppm. of nitrogen.

- (2) Concentrate the sample to about 20 ml. by boiling.
- (3) Rinse the concentrated sample into a 300 ml. Kjeldahl flask and add 3 strips of the aluminum foil. The volume of liquid should be about 60-75 ml. Connect the flask to

the condenser via the spray trap. Allow the reduction to take place for at least 8 hours at a minimum temperature of 20°C.

- (4) Place the Kjeldahl flask in its place in the distillation apparatus.
- (5) Set a 125 ml. Erlenmeyer flask containing 20 ml. of 0.1 N HCl so as to receive the distillate. Be sure that the end of the condenser dips well under the acid in the flask.
- (6) Add 40 ml. of the sodium hydroxide-sodium sulfide solution to the Kjeldahl flask and immediately connect the flask to the distilling apparatus. Then shake the flask so as to mix the contents very well.

Collect between 50 and 60 ml. of distillate in the acid solution.

- (7) Transfer the distillate to a 100 ml. volumetric flask and dilute to the mark.
- (8) Pipette 10 ml. of this solution into a 100 ml. volumetric flask.
- (9) Add 3 drops of a 2% gum arabic solution; swirl the contents of the flask. Add 1 ml. of Nessler's reagent and mix well.

Dilute up to the mark with water, shake well, and wait 5 minutes.

- (10) Set the colorimeter to zero with water using a blue (No. 42) filter. With a spectrophotometer set the instrument to read 100% T with water at about 400 millimicrons.

The intensity of the developed color (turbidity) can be estimated by comparing the sample against Nessler standards.

- (11) Transfer the solution from step (6) to the sample cuvette and read the colorimeter.
- (12) If necessary, convert the scale readings of the photometer to extinction. Subtract the blank reading from the sample readings. If a calibration curve is being established, plot these corrected readings versus ppm. of nitrogen. If a sample is being run, read the amount of nitrogen from the calibration curve.

Variation of the Recommended Procedure:

When the composition of the effluent is known, the recommended procedure for nitrites and nitrates can be materially shortened.

The following table summarizes the changes which can be made in the recommended procedure when the composition of the sample is known. Unless otherwise stated, the concentration of other elements must not exceed 100 ppm. For effluents containing greater quantities of these elements dilution may be necessary. The effluent should be between pH 2 and 9.

Composition of Effluent:	Changes in the Recommended Procedure:
Alkali metals, alkaline earths, zinc, and aluminum below 100 ppm. each; all other elements below 10 ppm. each. Cyanides, thiocyanates, and sulfides below 1 ppm.	Pipette a 10 ml. sample of effluent into an evaporating dish. Add 25 ml. of water and 5 ml. of NaOH solution. Evaporate to about 15 ml. Transfer to a 125 ml. flask and dilute to about 50 ml.; Add 1 piece of aluminum foil and stopper loosely. Transfer to a 100 ml. volumetric flask and start with step 8 of the recommended procedure.

COLORIMETRIC DETERMINATION OF ORTHO-PHOSPHATE

Abstract

This colorimetric procedure for the determination of orthophosphates in effluents is a modification of the standard method recommended by the A. P. H. A.

The modifications are necessary so as to eliminate the interference of fluorides, arsenic, silica, and highly colored substances.

Briefly, the method makes use of a fuming with nitric and sulfuric acid to destroy organic materials and remove fluorides. Arsenic is then removed by repeated evaporations with hydrochloric acid and the phosphate content of the sample is precipitated as ammonium phosphomolybdate and removed from highly colored material by filtration. After dissolving away the ammonium phosphomolybdate from silica, it is reduced to molybdenum blue and the intensity of the color is measured.

Colorimetric Determination of Ortho-phosphate in Effluents

The procedures for the determination of ortho-phosphate which have been presented in the literature generally use the formation of the highly insoluble, yellow precipitate of ammonium phosphomolybdate for the separation of the ortho-phosphate from other substances. When large quantities of the phosphate are present, a gravimetric separation is possible, but when only small quantities are present, a colorimetric procedure obviously must be employed. Since turbidimetric measurements of the precipitated compound are not as elegant as when measurements can be carried out on colored solutions, most procedures for the analysis of small amounts of phosphorus involve the reduction of the insoluble ammonium phosphomolybdate to a soluble, blue compound of unknown structure. There exists great disagreement among chemists as to which reducing agent is the most effective and yields the most reproducible results. Although the authors have found that certain photographic developers of the amidol or metol class are superb reducing agents, it was decided that the 1-amino 2-naphthol 4-sulfonic acid recommended by the A.P.H.A. would be more acceptable to other chemists than the reagents which reflect the whims of the writers.

Description of the Method:

The precipitation of ammonium phosphomolybdate in solutions which are strongly acid with nitric acid is nearly specific for ortho phosphates. Only fluoride, arsenic, silica, and some organic materials interfere with the precipitation.

The sample of the effluent is fumed with nitric and sulfuric acids thereby causing the decomposition of organic matter and the simultaneous expulsion of fluorides. The arsenic content of the sample (which has been oxidized to arsenate by the nitric acid in the fuming steps) is reduced by the addition of potassium iodide and then volatilized by repeated fumings with HCl. The repeated fumings have incidentally caused the dehydration of the silica; this and all other insoluble substances are removed by filtration. Ammonium phosphomolybdate is then precipitated and filtered to separate it from substances which might interfere with the formation of molybdenum blue. The precipitate is dissolved, reprecipitated and then reduced. The intensity of the blue color is measured in a colorimeter or a spectrophotometer.

If the effluent contains organic matter which will decompose and form orthophosphoric acid, the results of the analysis will also include this phosphorus.

Recommended Procedure:

This procedure is designed to be used for the determination of orthophosphates in effluents in the range of 5 to 50 ppm. in the presence of a maximum of 500 ppm. of each of the common cations, and organic material. With the exception of the preliminary treatment steps, the procedure is identical with that presented in "Standard Methods for the Examination of Water and Sewage", Ninth Edition, 1946.

Reagents Required:

- (1) Sulfuric Acid: Conc., 36 N, reagent grade.
- (2) Nitric Acid: Conc., 16 N, reagent grade.
- (3) Hydrochloric Acid: Conc., 12 N, reagent grade.
- (4) Potassium Iodide Solution: 10% w/v; dissolve 10 g. of the salt in 100 ml. water.
- (5) Ammonium Molybdate Solution: Dissolve 75 g. of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ and 75 g. of Ammonium nitrate in 900 ml. of distilled water. Cool, add 60 ml. of concd. Ammonium hydroxide and dilute to 1 liter. Filter the solution before using.
- (6) Ammonium Nitrate: Use reagent grade crystals.
- (7) Nitric Acid, 1:100: Dilute 1 ml. of conc. nitric acid with 100 ml. of water.
- (8) Ammonium Hydroxide, 1:1: Dilute one volume of conc. ammonium hydroxide with an equal volume of water.
- (9) Sulphuric Acid, 1:4: Dilute one volume of conc. sulfuric acid with four volumes of water.
- (10) Amino-Naphthol Solution: Grind 0.5 g. 1-amino 2-naphthol 2-sulfonic acid, take up with 5 ml. of sodium sulfite solution (20 g. sodium sulfite per 100 ml.) and dissolve in 195 ml. of sodium metabisulfite solution (160 g. $\text{Na}_2\text{S}_2\text{O}_5$ per liter). Do not use an amount of sodium sulfite greater than necessary to get the amino-acid in solution since it makes the solution less stable. Heat the solution, if necessary, to 50°-60° C. to hasten dissolving. Keep the solution in a dark stoppered bottle and prepare fresh every

two weeks. Use the purified grade of the amino-acid since the technical quality will not give satisfactory results.

- (11) Standard Phosphate Solution: Dissolve .7164 g. of dry potassium dihydrogen phosphate and dilute to 1 liter with water.

1 ml. = 0.50 mg. phosphate

Procedure:

- (1) Pipette 100 ml. of the effluent into a 250 ml. flask.

In running a blank, use 100 ml. of distilled water.

In establishing a calibration curve, use 1 ml. of the standard phosphate solution for each 5 ppm. of phosphate and then add enough distilled water to make a total of 100 ml.

- (2) Add 10 ml. of concentrated sulfuric acid and 5 ml. of concentrated nitric acid to the contents of the flask. Slowly bring the solution to boiling and continue heating until fumes of sulfur trioxide are copiously evolved. Fume for at least 5 minutes. If the liquid in the flask is discolored from organic decomposition products after fuming, cool the contents, add 5 ml. more of concentrated nitric acid and again bring to fumes. Repeat, if necessary until all organic matter has been decomposed. Do not allow the solution to go to dryness; add sulfuric acid if necessary.
- (3) Cool the residue in the flask. Add about 25 ml. of water and cool again.
- (4) Add 5 ml. of potassium iodide solution and bring to a boil. Boil about 5 minutes or until iodine vapor ceases to come off.
- (5) Add 10 ml. of concentrated hydrochloric acid and boil down until fumes of sulfur trioxide are about to come off.
- (6) Cool; then add 10 ml. of concentrated HCl and again boil down to fumes of sulfur trioxide.
- (7) Cool; then add about 25 ml. of water and filter the solution through asbestos, fine sintered glass, or sintered stainless steel. Wash the filter with small portions of water. Combine the washings and the filtrate.
- (8) Dilute the filtrate and washings to about 75 ml. Add 20 ml. of concentrated nitric acid, 1 g. ammonium nitrate, and heat to 80°C.
- (9) Add 15 ml. of ammonium molybdate solution and stir until precipitation begins. Digest the precipitate for 1 hour at a temperature of 40°C.
- (10) Filter the precipitate and wash twice with 5 ml. portions of 1:100 nitric acid. Reject the filtrate and washings.
- (11) Dissolve the precipitate in the filter with 10-25 ml. of 1:1 ammonium hydroxide. Catch the filtrate in a 100 ml. volumetric flask.
- (12) Add about 25 ml. of water and 5 ml. of ammonium molybdate solution.
- (13) Add 1:4 sulfuric acid until the yellow color of the phosphomolybdate appears; then add 1 ml. more of 1:4 sulfuric acid.
- (14) Add 5 ml. of the amino-naphthol solution and dilute to 100 ml. with distilled water.

- (15) Allow to stand 5 minutes.
- (16) Read the color intensity of this solution using water as a reference liquid on a colorimeter equipped with a red Wratten filter No. 66 or with a spectrophotometer at 820 millimicrons.
- (17) If necessary, convert the scale reading of the photometer to extinction. Subtract the blank reading from the sample readings. If a calibration curve is being established, plot these corrected readings : versus ppm. of ortho-phosphate added. If a sample is being run, read the amount of ortho-phosphate present from the calibration curve.

Variations of the Recommended Procedure:

When the composition of the effluent is known the recommended procedure can be altered to suit particular samples.

The following table summarizes the changes which can be made in the recommended procedure when the composition of the sample is known. When organic material that is liable to complex phosphorous compounds or molybdenum is absent and when the arsenic and silica content is negligible (say below 1 ppm. each), the lengthy procedure which has been presented reduces to the simple procedure recommended by the A.P.H.A. (loc. cit.). Unless otherwise stated, the concentration of each element must not exceed 500 ppm.

Composition of the Effluent	Changes in the Recommended Procedure
Organic matter absent.	Omit steps 2 and 3. Reduce the 100 ml. sample to about 15 ml. and add 10 ml. of conc. H_2SO_4 before starting with step 4.
Arsenic "Absent".	Omit steps 3, 4, 5, and 6.
Organic matter, arsenic, and silica "Absent".	Omit steps 2 to 7 inclusive. Between steps 1 and 8, make the sample acid with H_2SO_4 and reduce the volume to about 75 ml.
Organic matter, arsenic and silica "absent" and all elements except Ca, Al, Na, K, NH_4 , Mg, Zn, and Cd are below 2 ppm. (i.e. solution is colorless):	Pipette a 50 ml. sample of the clear effluent into a 100 ml. volumetric flask. Add one drop of phenolphthalein indicator and make the solution just acid by the use of ammonium hydroxide or sulfuric acid. Now add 1 ml. more of 1:4 sulfuric acid. Start with step 14 of the recommended procedure.

VOLUMETRIC DETERMINATION OF SULFATE

Abstract

A volumetric procedure for the determination of sulfate in effluents in the range of 5 to 50 ppm. is presented.

The method makes use of a combination of hydroxide and silver ion precipitations to remove ions which might interfere with the indicator for the titration. Fluorides are removed by repeated evaporation with hydrochloric acid and organic matter, if present, is rendered innocuous by oxidation with peroxide. The titration of the sulfate content is carried out using tetrahydroxyquinone as the indicator.

When thiocyanates, phosphates, etc. are absent, the procedure can be materially shortened. A table concisely indicates the changes that can be made in the procedure when the composition of the effluent is known.

Volumetric Determination of Sulfate in Effluents

The usual methods for the determination of sulfate in solutions make use of the formation of barium sulfate which is weighed directly or, for volumetric procedures, the amount of a standard solution of barium ions that is necessary to cause a completion of the precipitation is measured. Since for this analysis the range of 5-50 ppm. of sulfate has been selected, it is obvious that a gravimetric procedure is impractical since even if a 100 ml. sample would be chosen the weight of barium sulfate which would be obtained would be only 1.2 milligrams for 5 ppm.. Although this amount of precipitate could be weighed with sufficient accuracy, the mechanical difficulties would be considerable and the coprecipitation effects would severely affect the precision and accuracy of the method.

The volumetric method described in "Standard Methods for the Examination of Water and Sewage" seemed to be sufficiently rapid to warrant investigation. A survey of the literature revealed that the use of tetrahydroxyquinone as an indicator had not been thoroughly investigated and so it could not be ascertained whether the presence of antimony, bismuth, tin, etc. interfered with the indicator end-point. However, it was certain that anions such as fluorides, phosphates (over 60 ppm.), chromate, oxalate, etc., would also react with the standard barium solution and so render the results questionable. In particular, the presence of organic materials that might complex barium had to be borne in mind.

Description of the Method:

The sample is made acid and boiled to remove HCN, SO₂, CO₂, etc. Then, the neutralized solution is treated with silver nitrate in excess mainly to precipitate thiocyanate, phosphate, etc. Since the solution is nearly neutral, the hydrated oxides of most of the cations that are liable to interfere are also precipitated at this point. Fluorides are removed by a repeated fuming with hydrochloric acid, which also serves to cause a preliminary decomposition of organic material. The residue is then oxidized with alkaline peroxide to complete the oxidation of complexing organic substances. Then, the sulfate content is determined by titration with standard barium chloride solution using tetrahydroxyquinone as the indicator.

The method was tested on solutions containing 100 ppm. of the common cations, chlorides, acetates, tartrates, oxalates, cyanides, thiocyanates, and sulfites.

Limit of Detection of the Method:

The limit of detection of the method is defined as the minimum number of micrograms of sulfate ion which must be present in the 100 ml. sample taken for analysis so that a difference of 0.2 ml. barium chloride will be obtained between the volume used for the sample and for the blank. For the recommended procedure, the limit of detection is 100 micrograms of sulfate ion (1 ppm.).

The limit of detection can be increased by taking a larger sample.

Recommended Procedure:

This procedure is designed to be used for the determination of 5 to 50 ppm. of sulfate in a 100 ml. sample of the effluent.

Reagents Required:

- (1) Hydrochloric Acid: Concentrated, 12 N, reagent grade.
- (2) Sodium Hydroxide: 20% w/v; dissolve 20 g. of reagent NaOH in 100 ml. water.
- (3) Phenolphthalein Solution: 1% w/v; dissolve 1 g. of the indicator in 100 ml. of methanol.
- (4) Sodium Hydroxide: 1% w/v; dissolve 1 g. of reagent NaOH in 100 ml. water.
- (5) Nitric Acid: 1:1; dilute conc. HNO₃ with an equal volume of water.
- (6) Tetrahydroxyquinone Indicator: ordinary commercial salt.
- (7) Isopropyl Alcohol: reagent quality, 98%.
- (8) Barium Chloride Solution: 1 ml. = 0.5 mg sulfate.
Dissolve 1.085 grams of anhydrous barium chloride and dilute to exactly one liter. The anhydrous salt is made by drying the pure dihydrate for 8 hours at 150°C.
- (9) Silver Nitrate Solution: 2% w/v; dissolve 2 g. of the salt in 100 ml. of water.
- (10) Perhydrol: Use reagent grade, 30% hydrogen peroxide.

Procedure:

- (1) Pipette a 100 ml. sample of the effluent into a 250 ml. Erlenmyer flask.
In running a blank, use 100 ml. of water. It will be necessary to use a blank to correct for the indicator error.
- (2) Add 10 drops of phenolphthalein solution.
- (3) Make the sample definitely acid by the addition of 1:1 HNO_3 .
- (4) Boil for at least 5 minutes.
- (5) Add 1% NaOH solution until the indicator is pink.
- (6) Add 2% silver nitrate until the precipitation is complete and add 5 ml. in excess.
- (7) Filter the solution through Whatman's No. 40 paper, catching the solution in an evaporating dish. Do not wash the filter or the flask.
- (8) If a voluminous precipitate remains in the paper, return the filter paper and its contents to the flask and add 25 ml. of water and 5 ml. of 1:1 nitric acid. Break up the paper and its contents with a stirring rod. Slurry the contents so as to cause as complete a dissolution as possible.
- (9) Add a few drops of phenolphthalein indicator and then add 20% NaOH solution until a faint pink color develops.
- (10) Filter through a No. 40 Whatman's paper, catching the filtrate in the evaporating dish.
- (11) Wash the filter and flask with small portions of water. Combine the filtrates and washings in the evaporating dish.
- (12) Add 10 ml. of conc. HCl to the contents in the evaporating dish.
- (13) Evaporate to dryness on a water bath.
- (14) Add 25 ml. of conc. HCl and again evaporate to dryness.
- (15) Dissolve as much of the residue as possible in about 25 ml. of water, and filter it into a 150 ml. beaker through a Whatman's No. 40 paper. Wash the filter paper with several portions of water. Combine the filtrate and washings.
- (16) Add 5 ml. of 20% NaOH solution and cautiously add 2-3 ml. of 30% hydrogen peroxide.
- (17) Heat to boiling and boil for at least 5 minutes, or until the peroxide is decomposed.
- (18) Add several drops of phenolphthalein indicator and by using dilute NaOH or HCl adjust the solution until it is just colorless to the indicator.
- (19) Add 25 ml. of isopropyl alcohol.
- (20) Add 0.20 g. of tetrahydroxyquinone indicator.
- (21) Titrate with the standard solution of barium chloride until the yellow color of the solution changes to red.

(22) Subtract the number of milliliters of barium chloride solution used for the blank from the number of milliliters used for the sample.

(23) Calculate the ppm. of sulfate from the following:

$$\text{ppm. of sulfate} = \text{net ml. of barium chloride} \times 5$$

Variations of the Recommended Procedure:

If the composition of the effluent is known, the recommended procedure for sulfate ion can be materially shortened.

The following table summarizes the changes which can be made in the recommended procedure for sulfate ion when the composition of the sample is known. Unless otherwise stated, the concentration of other elements must not exceed 100 ppm.

Composition of Effluent:	Changes in the Recommended Procedure:
All metals below 5 ppm. Fluorides, thiocyanates, and phosphates absent (i.e. below 0.2 ppm.) and organic matter negligible	Pipette a 100 ml. sample into an evaporating dish and evaporate to about 25 ml. after acidifying with HCl using phenolphthalein indicator. Start at step 18.
All metals below 5 ppm. Fluorides absent (below 0.2 ppm.) organic matter negligible; phosphates present.	Use recommended procedure up to step 11; omit steps 12, 14, 16 and 17. Time may be saved by using a 25 ml. sample and cutting down all volumes prior to step 15.
Organic matter absent or negligible	Omit steps 16 and 17
Thiocyanates, phosphates, and borates, absent or below 0.2 ppm.	Omit step 6
Fluorides absent	Omit steps 12, 13 and 14. Between steps 11 and 15, evaporate to about 25 ml.

pH

The pH is the logarithm of the reciprocal of the hydrogen-ion concentration -- more precisely, of the hydrogen-ion activity -- in moles per liter. The pH enters into the calculation of carbonate, bicarbonate, and carbon dioxide; into the calculation of the corrosion or stability index; and into the control of water treatment. The practical pH scale extends from 0, very acid, to 14, very alkaline, with the middle value of pH 7 corresponding to exact neutrality at 25°C. Whereas "alkalinity" and "acidity" express the total reserve or buffering capacity of a sample, the pH value represents the instantaneous concentration of hydrogen-ion.

Selection of method: The pH can be measured either colorimetrically or electrometrically. The colorimetric method requires a less expensive investment in equipment but suffers from severe interference contributed by color, turbidity, high saline content, colloidal matter, free chlorine, and various oxidants and reductants. The indicators are subject to deterioration, as are the color standards with which they are compared. Moreover, no single indicator encompasses the pH range of interest in water. In poorly buffered liquids, a term applicable to some waters, the indicators themselves may alter the pH of the sample which they are expected to measure, unless the indicators are preadjusted to nearly the same pH as the sample. For these reasons, the colorimetric method is suitable only for rough estimation and will not be described in this manual.

A. General Discussion

1. Principle: Several types of electrodes have been suggested for the electrometric determination of pH. Although the hydrogen gas electrode is recognized as the primary standard, the glass electrode in combination with the reference potential provided by a saturated calomel electrode is most generally used. The glass electrode system is based on the fact that a change of 1 pH unit produces an electrical change of 59.1 millivolts at 25°C.

2. Interference: The glass electrode is relatively immune to interference from color, turbidity, colloidal matter, free chlorine, oxidants or reductants, as well as high saline content, except for a sodium error at high pH. The error caused by high sodium ion concentrations at a pH above 10 may be reduced by using special "low sodium error" electrodes. When employing ordinary glass electrodes, approximate corrections for the sodium error may be made by consulting a chart which the manufacturer can furnish for the particular make and catalogue number of electrode. Temperature exerts two significant effects on pH measurements: (1) the electrodes themselves vary in potential with temperature; and (2) ionization in the sample varies with temperature. The first effect can be compensated by an adjustment which is provided on the better commercial instruments. The second effect is inherent in the sample and is taken into consideration by recording both the temperature and the pH of each sample.

This procedure is taken from "Standard Methods for the Examination of Water, Sewage and Industrial Wastes" (10th Edition) by permission of A.P.H.A.

Table A -- Effect of Temperature on pH
Values of Buffer Solutions

Temperature	pH 4 Buffer	pH 7 Buffer	pH 9 Buffer
0°C	4.01	7.08	9.46
5	4.01	7.05	9.38
10	4.00	7.02	9.33
15	4.00	7.00	9.27
20	4.00	6.98	9.22
25	4.01	6.96	9.18
30	4.01	6.95	9.14
35	4.02	6.94	9.10
40	4.03	6.94	9.07
45	4.04	6.93	9.04
50	4.06	6.93	9.01
55	4.08	6.94	8.98
60	4.10	6.94	8.96

D. Procedure

Because of the differences between the many makes and models of pH meters which are available commercially, it is impossible to provide detailed instructions for the correct operation of every instrument. In each case, the manufacturer's instructions must be followed. The glass electrode and the calomel electrode should be thoroughly wetted and prepared for use in accordance with the given instructions. The instrument can be standardized against a buffer solution with a pH approaching that of the sample and then the linearity of electrode response can be checked against at least one additional buffer of a different pH. The readings with the additional buffers will afford a rough idea of the limits of accuracy to be expected of the instrument and the technique of operation.

E. Care of Electrodes

Electrodes must be kept clean and checked regularly at two pH values (for example: 4.0 and 9.0). The procedure for cleaning electrodes will vary with the contaminating material as follows:

- (1) Wipe any film from the electrode with the proper solvent, or mild detergent, using soft tissue, being sure to remove all film.
- (2) Remove all solvent or detergent with distilled water and soft tissue.
- (3) If necessary, immerse the glass electrode in 2% HCl for 2 hours or longer, then rinse thoroughly and store immersed in distilled water.
- (4) When not in use, always keep electrodes immersed in distilled water.

F. Precision and Accuracy

The precision and accuracy attainable with a given pH meter will depend upon the type and condition of the instrument employed and the technic of standardization and operation. With the proper care, a precision of 0.02 pH unit and an accuracy of 0.05 pH unit can be achieved with the better battery models. Line-operated instruments, on the other hand, are less accurate, 0.1 pH unit representing the limits of accuracy under normal conditions.

B. Apparatus

Where flow type electrodes are unavailable, or where stirring may be inadequate as in the case of ordinary immersion, dipping, type electrodes, the best procedure is to wash the glass electrode 6 or 8 times with portions of the sample, particularly when an unbuffered measurement follows one on a buffered solution. Flow type electrodes are recommended for the accurate measurement of relatively unbuffered waters such as condensates. Measurements on buffered waters can be obtained on open samples. Equilibrium should be established between the sample and the electrode system as shown by the absence of drift, before readings are accepted as final. If the water is hot or if the pH is over 10, special glass electrodes should be used and the assembly should be standardized under conditions of temperature and concentration as close as possible to those of the sample, taking into account the manufacturer's recommendations. The analyst should constantly be on the alert for possible erratic results arising from mechanical or electrical failures such as weak batteries, cracked glass electrodes, plugged liquid junction, and fouling of the electrodes with oily or precipitated materials.

C. Buffer Solutions

Electrode systems are calibrated against buffer solutions of known pH value. Since buffer solutions may deteriorate because of mold growth or through contamination, it may be advisable to prepare them freshly as needed by dissolving dry buffer salts in distilled water. Commercially available buffer tablets or powders of tested quality may also be used. It is good practice to calibrate the electrodes with a buffer whose pH is close to that of the samples, so as to minimize any error resulting from nonlinear response of the electrode. In making up buffers from solid salts, it is imperative that all of the material be dissolved, otherwise the pH may be incorrect. Polyethylene bottles are preferable for the storage of buffers and samples, although pyrex glassware may be employed. Limitations of space permit information on the preparation of only three buffer solutions at practically spaced intervals, pH 4, 7, and 9, for standardization purposes and for checking the linearity of electrode response.

In general, analytical reagent grade chemicals are satisfactory for the preparation of the following buffer solutions. Where a high degree of accuracy is required, however, it is advisable to use salts of buffer quality supplied by the National Bureau of Standards. The pH values of 3 buffer solutions at the indicated temperatures are listed in Table A. The tabulated pH values were obtained with salts of the highest purity.

1. pH 4 buffer solution: Dissolve 10.2 g anhydrous potassium biphthalate, $\text{KHC}_8\text{H}_4\text{O}_4$, using boiled and cooled distilled water. Dilute to 1.0 liter.

2. pH 7 buffer solution: Dissolve 1.361 g anhydrous potassium dihydrogen phosphate, KH_2PO_4 , and 1.420 g anhydrous disodium hydrogen phosphate Na_2HPO_4 , both of which have been dried overnight at 110-130°C. Use distilled water which has been boiled and cooled. Dilute to 1.0 liter

3. pH 9 buffer solution: Dissolve 3.81 g sodium tetraborate decahydrate, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, also called borax, using boiled and cooled distilled water. Dilute to 1.0 liter.

RESIDUE

A. Residue on Evaporation

The results on total, volatile and fixed residues are subject to considerable error because of losses of volatile compounds during evaporation, of carbon dioxide and volatile minerals during ignition, and to the presence of calcium oxide in the ash. In the interpretation of results these possible errors must be recognized.

1. Procedure for Residue on Evaporation

Evaporate 100 ml. of sample in an ignited and tared dish, dry to a constant weight at 103°C., cool in desiccator and weigh. Drying for one hour at 103°C. is usually sufficient. On samples with a pH below 4.3, NaOH is added and a pH of 4.3 maintained during evaporation. The amount of Na added is subtracted from the weight of residue. Warning: The determination of residue by evaporation may be of limited value for estimating the effect of an effluent on receiving water, but it may be useful as a control in plant operation. A large number of solids crystallize as hydrates, which lose water at various temperatures and form decomposition products before all their water of hydration is given off. This is true also of various colloidal suspensions. In addition, volatile compounds are lost during evaporation and ignition. It is essential for the analyst to understand that the procedure given for residue on evaporation is quite arbitrary and the results generally will not represent the weight of actual dissolved and suspended solids.

Results for residues high in oil or grease content may be of questionable value due to the difficulty of drying to constant weight in a reasonable time.

The mg. per liter shall be reported as parts per million total solids.

$\text{ppm total residue} = \text{mg. of residue} \times 1000 \div \text{ml. of sample.}$

2. Accuracy and Precision

The accuracy of all the solids determinations in sewage and industrial waste is not determinable because there is no universal standard against which the accuracy can be determined.

3. Procedure for Total Volatile and Fixed Residue

Total volatile and fixed solids are determined by igniting the above total solids at 600°C. in an electric muffle to constant weight (usually requiring 10 to 15 minutes). The mg. loss on ignition per liter shall be reported as parts per million volatile solids and the mg. residue per liter as parts per million fixed solids. Calculate as above.

This procedure is taken from "Standard Methods for the Examination of Water, Sewage and Industrial Wastes" (10th Edition) by permission of A.P.H.A.

B. Suspended Matter

In special cases where it is desired to exclude material such as oil, variations in the procedure to extract the oil from the suspended matter on the mat are allowable.

The amount of suspended matter removed during filtration depends on the thickness of the asbestos mat used in the Gooch crucible. Accordingly a mat thickness of 3 mm. is arbitrarily established in this procedure and the importance of uniform mat thickness should be recognized.

1. Reagents and Apparatus

1.1 Asbestos cream. Prepare a cream with distilled water by adding 15 g. acid washed, medium fiber asbestos which is prepared particularly for Gooch crucible determinations, to 1000 ml. of distilled water. Some asbestos sold for this purpose contains too much fine asbestos powder. This fine material should be removed by repeated decantations.

1.2 Gooch crucible and mat. An asbestos fiber mat is prepared in a 30-ml. Gooch crucible by adding sufficient homogeneous suspension of the asbestos cream (approximately 0.3 g. dry weight asbestos) to produce a mat 3 mm. thick with gentle suction. Wash with 100 ml. distilled water, dry at 103°C. for 1 hour, cool in desiccator and weigh. If volatile matter is to be determined by ignition, the crucible and mat must be ignited, cooled and weighed.

2. Procedure for Total Suspended Matter

Measure out 50 to 100 ml. of well-mixed sample with a wide mouth pipette or measuring flask and filter through the weighed Gooch crucible using suction. Wash with distilled water, dry at 103°C. for one hour, cool in a desiccator and weigh.

Report the mg. solids per liter as parts per million suspended matter. For samples of high suspended matter the original sample may be diluted and an aliquot portion analyzed.

C. Dissolved Matter

Dissolved matter may be obtained by difference between the total residue and suspended matter, or may also be determined by evaporating a filtered sample in accordance with A,1.

D. Settleable Solids

1. By Volume

Fill an Imhoff cone to the liter mark with a thoroughly mixed sample. Settle for 0.75 hour, gently stir the sides of the cone with a rod or by spinning, settle 0.25 hour longer and record the ml. of settleable solids in the cone.

2. By Weight

This technique defines settleable solids as that matter in waste effluents which will not stay in suspension during the settling period either by virtue of settling to the bottom or floating to the top.

3. Procedure

3.1 Determine the suspended matter, B,2 in a sample of the waste under investigation.

3.2 Pour a well-mixed sample of the waste into a glass vessel not less than 9 cm. in diameter, using a quantity of sample not less than 1 liter and sufficient to insure a depth of 20 cm. A glass vessel of greater diameter and larger volume of sample may be used.

3.3 Allow to stand quiescent for 1 hour and without disturbing the settled material or that which may be floating, siphon 250 ml. of the sample from the center of the container at a point half way between the surface of the settled material and the liquid surface.

3.4 Determine the suspended matter in ppm. in all or in an aliquot portion of this supernatant liquor in accordance with standard procedures. This value in ppm is equivalent to the non-settling matter.

ppm. by weight of settleable matter = ppm. suspended matter - ppm non-settling matter.

Bibliography

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Symons, George E., and Morey, B. The effect of drying time on the determination of solids in sewage and sewage sludges. Sew. Works J., 13, 936 (1941)

Fischer, A. J., and Symons, G. E. The determination of settleable sewage solids by weight. Water Works & Sew., 91, 37 (1944).

ADDITIONAL MANUALS

devoted to waste control in metal-finishing plants, which are available from the Ohio River Valley Water Sanitation Commission, are:

PLATING-ROOM CONTROLS FOR POLLUTION ABATEMENT

A manual of principles and practice for curbing losses of solutions and metals that otherwise might find their way into water courses. Compiled by the Metal-Finishing Industry Action Committee, this manual describes methods for reducing wastes by reducing dragout, rinsing effectively, preventing losses, and purifying contaminated solutions. (20 pp., illus.) Price 50¢

PLANNING AND MAKING INDUSTRIAL WASTE SURVEYS

Detailed instructions for measuring volume of flow, obtaining representative samples and calculating waste loads. The manual is designed to aid those people who have had little or no experience in measuring industrial waste. Diagrams show how to construct and install measuring and sampling devices. Tables are included to assist in computing the rates of flow. The manual was compiled by the Metal-Finishing Industry Action Committee. (44 pp., 27 illus.) Price \$1.00

METHODS FOR TREATING METAL-FINISHING WASTES

An evaluation of various disposal methods and their applicability to specific waste control conditions. Ten procedures for handling cyanide are included as well as methods for treating chromium, oil and paint. The manual was compiled by the Metal-Finishing Industry Action Committee. (72 pp., 16 illus.) Price \$2.00

DISPOSAL OF SPENT SULFATE PICKLING SOLUTION

An evaluation of methods for treating spent solutions resulting from sulfuric acid pickling to reduce stream pollution. Compiled by the Steel Industry Action Committee of the Commission, this manual describes methods for neutralization of acid solutions and for recovery of acid and iron salts. Flow diagrams and a nomograph for determining weight of alkaline agent required to neutralize acid solutions are included (76 pp., 17 illus.) Price \$2.00

Questions on individual plant waste problems should be directed to the state pollution control agency concerned.

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