Analytical Applications of

Periodic Acid (H_5IO_6) and Iodic Acid (HIO_3)

and Their Salts

5th Edition

Revised

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By

G. FREDERICK SMITH, Ph.D.

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PREFACE

Volumetric analytical reagents for use in the quantitative determination of *inorganic cations* and anions are well represented by the group of oxygen acids of chlorine, bromine and iodine. Of these procedures the volumetric bromate, iodate, and periodate procedures predominate. Chlorites have been employed to a limited extent. The older procedures employing iodic acid have been made more practical by the use of internal redox indicators in place of the previous well known Andrews-Jamieson carbon tetrachloride or chloroform technique. The use of improved redox indicators has measurably improved and simplified volumetric bromate procedures for the same reason.

The use of periodic acid in the analysis of *organic compounds* and in studies of their structure, has become of increasing importance. Some of the reactions have been employed as routine control laboratory methods. Other reactions have been applied to the study of the structural relationships associated with intricate questions of organic interpretation. The clarification of controversial multiple choice formulations in the study of molecular configurations in the field of sugar research have resulted from periodic acid reaction studies. Important biological chemical structural studies have materialized from the use of periodic acid. Amino acid reactions with periodic acid have recently proven of value in the field. The first important application of the use of periodic acid in the field of organic reactions was made by Professor L. Malaprade of the University of Nancy in France. The present edition of this booklet has been provided with an introductory commentary contributed by Professor Malaprade. Former editions of this booklet have featured the important contributions of Professor H. H. Willard of the University of Michigan.

As a result of the stimulative impetus applied to the subject by the earlier editions of this booklet, standard procedures in the use of periodic acid have been made the official methods of such organizations as, *The American Public Health Association, The American Water Works Association* in their official organ, ''Standard Methods of Water Analysis,'' and the *Association of Official Agricultural Chemists* through their ''Methods of Analysis'' (6th Edition 1945, XII 932 pp).

The 5th Edition of this booklet features material otherwise widely scattered throughout chemical literature. The bulk of the material added as extensions to the 4th Edition of this booklet deal with the study of organic compounds. It is, therefore, appropriate as well as educational to be able to include an introductory commentary from the pen of Professor L. Malaprade (see frontispiece), of the University of Nancy in France. The Malaprade reaction has in full measure served as a background for a greatly extended series of applications in the use of periodic acid in theoretical and practical procedures in analyses both routine and in structural interpretation.

G. FREDERICK SMITH

Urbana, Illinois
January, 1950

INTRODUCTORY COMMENTARY

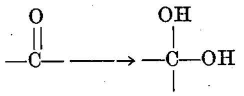
THE APPLICATION OF PERIODIC ACID AND PERIODATES TO THE DETERMINATION OF ORGANIC COMPOUNDS

Periodic Acid or its alkali salts are reduced in dilute aqueous media (tenth molar for example) to iodic acid or iodates by certain organic compounds in accordance with quantitative reactions which make possible the determination of the reducing agents. One of the products of the reaction may be determined or more generally, an excess of periodic acid or periodate is employed and the excess determined by different methods the most common involving reaction between arsenious acid and the periodates in the presence of bicarbonate.

The use of periodic acid itself is not a prerequisite, a periodate in the presence of non-interfering acid (dilute sulfuric acid) will have the same effect. The metaperiodates of sodium or potassium, ($NaIO_4$ and KIO_4), the dimesoperiodate of potassium, ($K_4I_2O_9 \cdot 9H_2O$) introduce no complications being obtainable in sufficiently pure form and, moreover, are commercially available.

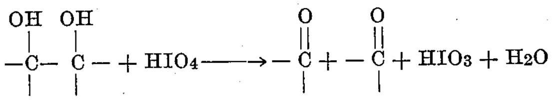
The compounds not only duplicate such oxidants as permanganate, chromic acid, and cerate salts: Periodic acid is of such nature in numerous cases that it alone permits convenient precise and selective determinations.

With consideration of compounds containing carbon hydrogen and oxygen, periodic acid oxidations are limited to those which provide two hydroxyl radicals attached to two adjacent carbons (in the alpha position), aldehydes and ketones being assumed to be hydrated:



$$-\overset{\overset{\displaystyle O}{\|}}{C}- \longrightarrow -\underset{|}{\overset{\overset{\displaystyle OH}{|}}{C}}-OH$$

The quantitative reaction is then represented by:



$$-\underset{|}{\overset{\overset{\displaystyle OH}{|}}{C}}-\underset{|}{\overset{\overset{\displaystyle OH}{|}}{C}}- + HIO_4 \longrightarrow -\underset{|}{\overset{\overset{\displaystyle O}{\|}}{C}} + -\underset{|}{\overset{\overset{\displaystyle O}{\|}}{C}} + HIO_3 + H_2O$$

If the products of such primary reaction possess further reducing properties they react further with periodic acid. It is thus possible stepwise to follow the reactions of periodic acid on ethylene glycol, glycerol, mannitol, glucose (linear formulation), levulose, glyoxal, etc.

L. Malaprade

Thus, for example, the reaction with glycerol is:

first:

$$CH_2OH - CHOH - CH_2OH + HIO_4 \longrightarrow CH_2OH \cdot CHO + HCHO + HIO_3 + H_2O$$

then:

$$CH_2OH - CHO + HIO_4 \longrightarrow HCOOH + HCHO + HIO_3$$

combined:

$$CH_2OH - CHOH - CH_2OH + 2HIO_4 \longrightarrow HCOOH + 2HCHO + 2HIO_3 + H_2O$$

The nature of the other radicals attached to the carbon atoms bearing hydroxyls is not without influence on the speed of reaction: the α-glycols, α-aldehyde-alcohols, α-ketone alcohols are oxidized rapidly in the cold; when one of the two carbons represents an acid group the reaction is much slower and does not become appreciable up to 100° hence may be neglected at ordinary temperatures, (oxalic and lactic acids).

Although very general, these preceding remarks are not absolute: molecular transposition of an intermediate product may modify the course of the reaction (inositol). According to recent investigations, α-amino alcohols also react upon periodic acid.

The general reaction scheme, the selectivity which it implies, result in the use of periodic acid in studies of molecular structure (starch, cellulose, sugars and derivatives, etc.) and for analyses in which selectivity is of no lesser interest; mentioning among others the determination of α-glycerophosphate in presence of β-glycerophosphates, and the analysis of anti-gels: glycerol, ethylene glycol, propylene glycol.

Another notable characteristic of periodic acid oxidations is that varying the pH of the solutions modifies only the speed of the reaction.

The use of the metaperiodates $NaIO_4$ or KIO_4 or dimesoperiodate, $K_4I_2O_9$ may simplify the analyses. The first is not acid to methyl orange, the second to methyl red and the third to phenolphthalein.

The introduction of periodates into the solutions of oxidizable organic materials, previously neutralized, will permit determinations by titration of hydrogen or hydroxyl ions freed by the reaction. An excess of KIO_4 stirred into an aqueous solution of glycerol liberates for each molecule of the latter, one molecule of formic acid ($HCOOH$) which may be titrated; better, if besides glycerol, ethylene glycol is present, the analyses is still valid since the latter gives only formaldehyde as oxidation product.

The reduction by $K_4I_2O_9$ is represented as:

$$K_4I_2O_9 + 2R + H_2O \longrightarrow 2KIO_3 + 2R \cdot O + 2\,KOH$$

If $R \cdot O$ is not neutralized by the liberated potash, this is titrated giving a determination of R—. Tartrates may thus be determined, 2,3-butane-diol and moreover inorganic compounds such as H_2O_2 or Na_2SO_3. The same reaction will provide a determination of dimeso-periodate by reaction with neutral tartrate.

L. Malaprade

University of Nancy
France
July, 1949

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CHAPTER I

GENERAL CONSIDERATIONS IN THE USE OF PERIODIC ACID (HIO_4) AND ITS SALTS

INTRODUCTION

Periodic acid and its salts are not true "per"-acid derivatives.

"True per-acids may be defined as those which are either formed by the action of hydrogen peroxide on ordinary acids, or else give rise to hydrogen peroxide on treatment with dilute sulfuric acid; with concentrated sulfuric acid many of them evolve ozonized oxygen, thus behaving similarly to the metallic peroxides and to hydrogen peroxide itself." (T. Slater Price, "Per-Acids and Their Salts," Longmans, Green and Co., 1912, page 2.)

Thus using a typical example, the reaction is given of the hydrolysis of perdisulfuric acid to permonosulfuric acid (Caro's acid) with the liberation of hydrogen peroxide.

$$\begin{array}{ccc} H_2S_2O_8 + H_2O & = & H_2SO_4 + H_2SO_5 \\ \text{(Perdisulfuric Acid)} & & \text{(Permonosulfuric Acid)} \\ H_2SO_5 + H_2O & = & H_2SO_4 + H_2O_2 \end{array}$$

Acidified solutions of periodic acid or its salts do not similarly react with the formation of hydrogen peroxide. Likewise, periodates are not formed in solution by oxidation using hydrogen peroxide. Periodates are not therefore per-acid derivatives.

Persulfates (sodium, potassium, and ammonium) are more familiar analytical reagents than are the alkaline periodates (sodium and potassium). This fact is not justified if comparison is made between the versatilities of their analytical application.

It is the purpose of the following discussion to draw attention to an increasing number of available analytical procedures involving the use of periodic acid and its salts.

The Nomenclature of Periodic Acid and the Periodates

Unlike chlorine, the heptoxide of which (Cl_2O_7) has been prepared the analogous iodine heptoxide (I_2O_7) is not known. In Table I the various periodic acids and salts, some of which are themselves hypothetical, are classified as "hydrates" of the hypothetical iodine heptoxide.

TABLE I

The Periodic Acids

Hypothetical Hydrated Heptoxide	Empirical Acid Formula	Name of Acid[1]	Formula of Known Salt
$I_2O_7 \cdot 7H_2O$	H_7IO_7	Ortho-Periodic acid	None known
$I_2O_7 \cdot 6H_2O$	$H_{12}I_2O_{13}$	Diortho-Periodic acid	$Y_4I_2O_{13} \cdot 11H_2O$
$I_2O_7 \cdot 5H_2O$	H_5IO_6	Para-Periodic acid	$Na_2H_3IO_4$
$I_2O_7 \cdot 4H_2O$	$H_8I_2O_{11}$	Dipara-Periodic acid	$Cu_4I_2O_{11} \cdot H_2O$
$I_2O_7 \cdot 3H_2O$	H_3IO_5	Meso-Periodic acid	$Pb_3(IO_5)_2$
$I_2O_7 \cdot 2H_2O$	$H_4I_2O_9$	Dimeso-Periodic acid	$K_4I_2O_9$
$I_2O_7 \cdot 1H_2O$	HIO_4	Meta-Periodic acid	KIO_4

[1] Greek derivatives: Ortho—regular, Para—beside, Meso—intermediate, Meta—beyond.

The Basicity of Paraperiodic Acid. Paraperiodic acid is undoubtedly a tribasic acid as indicated by the formation of mono-, di-, and trisodium salts of the formulas NaH_4IO_6, $Na_2H_3IO_6$ and $Na_3H_2IO_6$, when a solution of paraperiodic acid is neutralized stepwise by the addition of sodium hydroxide. The dissociation of paraperiodic acid may be indicated as follows:

$$H_5IO_6 \overset{K_1}{\rightleftarrows} H^+ + H_4IO_6^- \overset{K_2}{\rightleftarrows} H^+ + H_3IO_6^- \overset{K_3}{\rightleftarrows} H^+ + H_2IO_6^-$$

The dissociation constants have been evaluated by Rae (*1*) and by others. The values given were:

$$K_1 = 2.3 \times 10^{-2} \text{ and } K_2 = 10^{-6}$$

Price and Kroll in a later investigation (*2*) assign the values

$$K_1 = 0.11 \text{ and } K_2 = 2.5 \times 10^{-8}$$

The value for K_3 is too small to be indicated in a potentiometric titration of paraperiodic acid by sodium hydroxide there being but two potential "breaks" in the data thus obtained as indicated in the graphical representation of a set of typical titrational data as shown in Figure 1. René-Dubrisay (*3*) has described a titrimetric procedure by means of which periodic acid gives undoubted indication of the third hydrogen ion.

The most complete study of the physical constants of paraperiodic acid in aqueous solutions has been made by Crouthamel, Meek, Martin and Banks (*4*). They show that this acid is the only solid periodic acid which is capable of existence in equilibrium with aqueous solutions of the acid.

---

1. Rae, *J. Chem. Soc.*, 876 (1931).
2. Price and Kroll, *J. Am. Chem. Soc.*, 60, 2726 (1938).
3. René-Dubrisay, *Compt. rend.* 157, 1150 (1913).
4. Crouthamel, Meek, Martin, and Banks, *J. Am. Chem. Soc.*, 71, 3031 (1949).

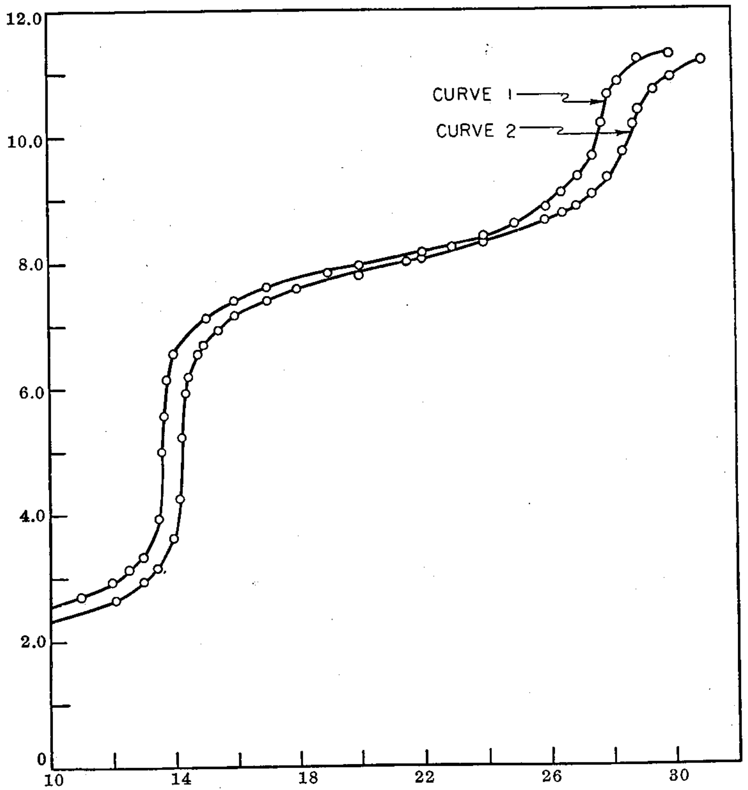

FIG. 1. Potentiometric titration curves of H_5IO_6
(pH on vertical axis. Ml. of alkali on horizontal axis)

Previously determined values for the three stage dissociation of H_5IO_6 to give $H_4IO_6^-$, $H_3IO_6^=$, and $H_2IO_6^{-3}$ ions have been re-investigated by Banks and associates and the following values determined:

$$K_1 = 2.30 \times 10^{-2} \ (H_4IO_6^-) \text{ or } pK = 1.63$$
$$Ka = K_2 = 4.35 \times 10^{-9} \ (H_3IO_6^=) \text{ or } pK = 8.36$$
$$K_3 = 1.05 \times 10^{-15} \ (H_2IO_6^{-3}) \text{ or } pK = 14.98$$

The corresponding pK values for orthophosphoric acid have been given as 1.96, 7.13, and 12.30. The agreement is seen to be very close, and for titrations of either periodic or phosphoric acids the same indicators may be employed.

Banks and associates have made a spectrophotometric study of potassium metaperiodate in the ultra-violet region (210-270 mμ) employing the Cary recording instrument and 1 cm. silica cells. The optical density is a definite function of pH. Measurements at pH 5 are satisfactory at ordinary ionic strengths, (± 1.5 pH for solutions of low ionic strength). Nitrates, sulfates, carbonates and carboxylates interfere but potassium, sodium or perchlorate ions as well as small amounts of ammonium ions are without effect.

The change in optical density when plotted against wave length shows for different pH values, two isobestic points one at 213 mμ and the other at 244 mμ when solutions of potassium metaperiodate are examined.

The formulation $K_4I_2O_9 \cdot 9H_2O$ frequently postulated is probably better represented as $K_2H_3IO_6 \cdot 3H_2O$. The probability of any equilibria involving the formation of the dimesoperiodate ion $I_2O_9^{-4}$ is of no importance in dilute solutions.

Formulae of known salts of periodic acid are given in Table II.

The Metallic Periodates

The formulation of the metallic periodates, the preparation of which has been described in recent published descriptions of periodates, are tabulated in Table 2. In many cases the formula is given with literature reference, and reference to the original description of the compound's preparation leaves much doubt as to authenticity of the compound as formulated.

The Oxidation Potential of Periodic Acid. A study of the single electrode potential of periodic acid has been made by Abel and Smetano (*5*) based upon the use of peraperiodic acid as material studied. The value given for the periodate-iodate system was 1.51 volts. Their result was predicated upon the assumption that the periodic acid was completely dissociated and to have the formula HIO_4. As pointed out by Latimer (*6*) since periodic acid will quantitatively oxidize the manganous ion to permanganate (E° = 1.52 volts) the value 1.51 volts appears too low. From purely chemical evidence the following single electrode potential is given by Latimer (*7*):

$$H_5IO_6 + H^+ + 2e^- = IO_3^- + 3H_2O \qquad E^\circ = \text{ca } 1.7 \text{ volts}$$

Assuming the same type of oxidation of water by periodic acid as that postulated by Smith and Duke (*7*) ozone may be postulated to form according to the following type reactions taking place in acid solution:

$$2H:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:H \longrightarrow \left[\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:H\right]^+ + \left[:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:H\right]^- + 2H^+ + 2e^-$$

$$H_5IO_6 + 2H^+ + 2e^- \longrightarrow HIO_3 + 3H_2O$$

$$\left[:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:H\right]^- + H^+ \longrightarrow H_2O$$

$$6\left[\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:H\right]^+ \longrightarrow O_3 + 3H_2O$$

---

5. Abel and Smetano, *Monatsch.*, 60, 181 (1932).
6. Latimer, "Oxidation Potentials," pp. 60-61 Prentiss Hall. (1938).
7. Smith and Duke, *Ind. Eng. Chem., Anal. Ed.*, 15, 120 (1943).

TABLE II

Formulation of Known Periodates and Literature Reference to Their Description

Monovalent Metals	Divalent Metals	Trivalent Metals	Tetravalent Metals
NaH_4IO_6 (*1*) $Na_2H_3IO_6$ (*1*) $Na_3H_2IO_6$ (*1*) $(NH_4)_2H_3IO_6$ (*5*) $(CN_3H_6)_2H_3IO_6$ (*5*) (Quanadine) $(CN_3H_6)_3H_2IO_6$ (*5*) (Quanadine) Ag_5IO_6 (*3*)	$Pb_3H_4(IO_6)$ (*6*) $Cu_5(IO_6)_2 \cdot 7H_2O$ (*11*) $Cu_5(IO_6)_2 \cdot 5H_2O$ (*11*) $Hg_5(IO_6)_2$ (*12*) (Salts of Paraperiodic Acid, H_5IO_6)	FeH_2IO_6 (*10*)	$CeHIO_6 \cdot 6H_2O$ (*11*) $ThHIO_6 \cdot 5H_2O$ (*11*) ....
$NaIO_4$ (*2*) KIO_4 (*2*) $CsIO_4$ $CsIO_4 \cdot HIO_3 \cdot 2H_2O$ (*4*) NH_4IO_4 (*5*)	....	$Al(IO_4)_3 \cdot 3H_2O$ (*9*) $Fe(IO_4)_3$ (*7*) (Salts of Metaperiodic Acid, HIO_4)	....
Ag_3IO_5 (*1*)	$Zn_2(IO_6)_5$ (*13*) $Pb_3(IO_5)_2$ (*6*) $Mn_3(IO_5)_2$ (*10*) (Salts of Mesoperiodic Acid, H_3IO_5)	$CeIO_5 \cdot 4H_2O$ (*4*) $YIO_5 \cdot 4H_2O$ (*4*)	....
$Ag_4I_2O_9$ (*1*) $K_4I_2O_9$ (*4*)	$FeH_2I_2O_9$ (*7*) (Salts of Dimesoperiodic Acid, $H_4I_2O_9$)		....
(Salts of Diorthoperiodic Acid, $H_{12}I_2O_{13}$)		$Y_4I_2O_{13} \cdot 11H_2O$ (*8*)	....
....	$Cu_4I_2O_{11} \cdot H_2O$ (*11*) Salts of Diparaperiodic Acid	$Al_2H_2I_2O_{11}$ (*10*) $La_2H_2I_2O_{11} \cdot 3H_2O$ (*1*)	....
....	$4ZnO \cdot I_2O_7 \cdot 5H_2O$ (*2*) $5ZnO \cdot I_2O_7 \cdot 14H_2O$ (*2*) $2CaO \cdot I_2O_7 \cdot 3H_2O$ (*2*) $2.3BaO \cdot I_2O_7 \cdot 3H_2O$ (*2*) Undesignated Periodate	$Bi_2O_3 \cdot 2I_2O_7 \cdot 7H_2O$ (*10*) $Tl_2O_3 \cdot I_2O_7 \cdot 3H_2O$ (*10*)	$7 \cdot TiO_2 \cdot I_2O_7$ (*11*) $4SnO_2 \cdot I_2O_7$ (*11*) $3ZnO_2 \cdot I_2O_7 \cdot 17H_2O$ (*11*) $2PbO_2 \cdot I_2O_7 \cdot 5H_2O$ (*10*)

1. Partington and Bahl, *J. Chem. Soc.*, 1086-91, 1771 (1934).
2. A. E. Hill, *J. Am. Chem. Soc.*, **51**, 2678 (1928).
3. Malaprade, *Ann. chim.* [10], 104-222 (1929).
4. H. L. Wells, *Am. Chem. J.*, **26**, 278 (1911).
5. Rosenhein und Lowenthal, *Kolloid Z.*, **25**, 53-60 (1919).
6. Willard and Thompson, *J. Am. Chem. Soc.*, **56**, 1828 (1934).
7. Kimmins, *J. Chem. Soc.*, **55**, 148 (1899).
8. Sobinery, Aggarwal, and Singh, *J. Indian Chem. Soc.*, **23**, 177 (1946).
9. Eakle, *Z. Kryst*, **16**, 576 (1896).
10. Raychoudbury, *J. Indian Chem. Soc.*, **16**, 269 (1939).
11. Bahl, Singh and Bali, *J. Indian Chem. Soc.*, **18**, 587 (1941).
12. Rammelsberg, *Ann. Physik*, **134**, 524 (1868).
13. Kahane, *Bull. Soc. chim.* (1947).

By similar type reactions periodic acid in alkaline solution may be postulated to give rise to hydrogen peroxide from the union of a positive and negative hydroxyl.

Similar considerations may be said to come into play to explain the instability of permanganate solutions and perchloratoceric acid solutions. All of these reactions are exceedingly slow under conditions excluding the presence of reductants but may be catalyzed to fairly rapid reactions but certain catalysts such as finely divided platinum.

CHAPTER II

THE PREPARATION OF PERIODIC ACID, AND IODIC AND THEIR SALTS

Sodium para-periodate is readily prepared following the method of the discoverers, Ammermuller and Magnus (*Pogg. Ann.*, 28, 514 [1833]), as further described by Kimmins (*J. Chem. Soc.*, 51, 356 [1887]) and A. B. Lamb (*Am. Chem. J.*, 51, 134 [1902]) and most recently by A. E. Hill (*J. Am. Chem. Soc.*, 51, 2678 [1928]). Quoting the latter reference:

"The sodium periodate was prepared from pure sodium iodate, passing through the stage of the tri-sodium-para-periodate, $Na_3H_2IO_6$, which was eventually converted into the meta-periodate, $NaIO_4$. To a solution of pure sodium iodate five equivalents of sodium hydroxide were added and the solution stirred mechanically while a rapid stream of chlorine gas was passed through. The very insoluble sodium salt begins to precipitate within a few minutes. The stream of chlorine was continued until the solution gave an odor of hypochlorites and was nearly neutral; after the treatment with chlorine was interrupted, an additional equivalent of sodium hydroxide was added and the mixture well stirred for several hours. In the presence of an excess of base, which is essential to the formation of the tri-sodium salt, the reaction occurring is represented by the equation $NaIO_3 + Cl_2 + 4NaOH = Na_3H_2IO_6 + 2\,NaCl + H_2O$; yields averaged above 80%. The solid salt was filtered in a Büchner funnel and washed repeatedly; because of its very low solubility, the loss on washing is negligible. In order to convert this salt to the meta-periodate, $NaIO_4$, it was treated with water and nitric acid in the ratio of 150 cc. of water and 45 cc. of concentrated nitric acid to 100 g. of salt; the solution was heated until the salt dissolved completely, and then allowed to stand for twenty-four hours at room temperature. The crystals thus formed are of large size and even contour; because of their low rate of dissolving, they could be washed rapidly on a Büchner funnel without considerable loss, and they analyze within 0.1% of the theoretical composition; the yields varied from 60 to 85%, dependent largely upon the time allowed for crystallization.

"The potassium meta-periodate was likewise prepared from the iodate with four to five equivalents of base by oxidation with chlorine. Unlike the case of the sodium salt, the potassium salt is freely soluble in excess base, and does not appear in solid form until the solution has become nearly neutral. It was then, after cooling, rendered acid with a slight excess of sulfuric acid and allowed to stand until the insoluble meta-periodate, KIO_4, had precipitated. The yields obtained, after washing and drying, ran as high as 95%. As in the case of the sodium salt, the well-washed product analyzed always within 0.1% of the theoretical composition without the necessity for recrystallization.

"The periodic acid used was prepared by the method used by Wells, Lamb, and others: the sodium salt was converted into (supposedly) Ag_3IO_5 by long stirring with three equivalents of silver nitrate solution, and the precipitate decomposed, after thorough washing, by a slow stream of washed chlorine gas passed into a cold aqueous suspension. After filtration from the silver chloride, the solution was evaporated to a small volume over a free flame and finally in a desiccator over sulfuric acid; the periodic acid crystallized in the form of its hydrate $HIO_4 \cdot 2H_2O$, which may be dried over sulfuric acid without loss of water. Since no data have been recorded as to the solubility of this acid, it may be of use to state that analysis of the mother liquor shows the solubility to be about 53% at room temperature, and the density about 2.3.

"The periodates were analyzed by measuring their oxidizing action upon potassium iodide in acid solution. The free alkali present was determined by titration with standard sodium hydroxide solution, using methyl orange as indicator; the meta-periodates are neutral to that indicator, as previously shown by others (*1*); Loewenthal, "Inaugural Dissertation," Berlin (1918), so that any excess alkali can be accurately determined.

Meta-periodic acid can be obtained from para-periodic acid by vacuum drying at 100° C. and 12 mm. pressure (Lamb, *loc. cit.*).

Meta-periodic acid is midway in acid strength between hydrochloric acid and acetic acid and hence is neither a weakly nor a strongly ionized acid.

Preparation of Trisodium Periodate from Sodium Iodide. This method was described by Lange and Paris (*2*). To a 660 ml. of sodium hydroxide solution (Sp. gr. 1.332) after dilution to 2000 ml. in a 5 liter pyrex round bottom flask, 50 g. of sodium iodide is added. Heat the solution to boiling and add gradually, with vigorous stirring, 80 g. of pure bromine. The oxidation of the alkaline iodide solution results in the formation and precipitation of $Na_3H_2IO_6$ and the solution must be thoroughly agitated to keep this heavy precipitate in suspension. The boiling should be continued for 15 minutes after the addition of the bromine. The reaction is $NaI + 10NaOH + 4BR_2 = Na_3H_2IO_6 + 8NaBr + 4H_2O$.

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1. Rosenheim and Loewenthal, *Kolloid Z.*, 5, 53 (1919).
2. Lange and Paris, *J. Pharm. Chim.*, 21, 403 (1935).

Filter the precipitate using 4 inch Büchner funnel with a filter of glass cloth. Wash the trisodium peraperiodate on the filter with 200 ml. of cold water added in small portions. The salt is finally air dried and upon analysis will be found to be 97-99 per cent pure. Drying may be at 110° C.

This product may be converted to paraperiodic acid by the process previously described by Hill according to the directions given by Wells (*3*), as follows:

Suspend the $Na_3H_2IO_6$ in 3000 ml. of water in a 4000 ml. pyrex beaker provided with an efficient turbin stirrer. Neutralize the suspension by the addition of just sufficient nitric acid and with vigorous agitation add an equivalent amount of silver nitrate in aqueous solution to form $Ag_2H_3IO_5$. When all the sodium salt is thus precipitated the product is filtered and washed until free from acid. The silver salt is suspended in water in the same manner as above described and sufficient bromine added to precipitate silver bromide while heating the suspension to 70 degrees. Filter off the silver bromide and remove the excess of bromine by passing a rapid stream of air through the solution. Finally concentrate the solution of periodic acid on a steam bath as far as possible. Lastly evaporate the solution thus obtained in vacuo over sulfuric acid to crystallize. The yield of paraperiodic acid H_5IO_6 is 93 per cent.

Preparation of Mono- and Disodium Paraperiodates. From an examination of the data shown graphically in Figure 1, page 3, conditions (*4*) may be easily described for the preparation of mono- and disodium paraperiodates, NaH_4IO_6 and $Na_2H_3IO_6$. The process requires paraperiodic acid made easily available by the electro oxidation of iodine as described on pages 13, 14, 15. A strong solution of H_5IO_6 in water is prepared and this solution is treated by the addition of a solution of 3 to 5 *N* sodium hydroxide. The progress of the neutralization is followed using a glass electrode and is arrested when the pH, originally at approximately 2, has been increased to the value 5. The addition of base is then discontinued and the solution evaporated to crystallize the product which is filtered and centrifuged. The same treatment to produce a pH of 10 governs the preparation of the salt $Na_2H_3IO_6$.

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3. Wells, *Am. Chem. Jour.*, 26, 278 (1901).
4. Procedure of the author unpublished.

Preparation of Periodates of Sodium, Potassium and Barium by Oxidation of Iodate by Chlorine or Persulfate. The following description is reproduced from the "Inorganic Syntheses" (*5*) by permission of the publishers. (Likewise the procedure for the preparation of periodic acid subsequently described.)

"The Periodates of the alkali metals (*6*) are best prepared by oxidation of iodate by chlorine (*7*). The oxidation can also be effected by persulfate (*8*) but this is inferior as a preparative method and is to be recommended only when no ready supply of chlorine is available.*

Procedure. Sodium Iodate. This compound, from which all of the following are prepared, may be readily obtained by oxidation with an excess (at least 20 per cent) of sodium chlorate.

In a 5-l flask, 125 g. of pure sodium chlorate is dissolved in 500 ml. of water at 45° C. After acidification with 2 ml. of concentrated nitric acid, 100 g. of iodine is added. The mixture is warmed until reaction just begins (at 50° C., if the acidity is correct). To prevent loss of iodine, the mouth of the flask is lightly closed with an inverted beaker. Provision should be made for immersing the flask in cold water in case the reaction becomes too vigorous. Complete disappearance of the iodine ordinarily requires 10-15 minutes. The iodate solution is then ready to be oxidized to periodate.

A. Sodium Paraperiodate, Chlorine Method. The best yields are obtained

1. $NaIO_3 + 3NaOH + Cl_2 \longrightarrow Na_2H_3IO_6 + 2NaCl$
2. $NaIO_3 + 4NaOH + Cl_2 \longrightarrow Na_3H_2IO_6 + 2NaCl + H_2O$

when the alkali concentration is near that expressed by (2). Under these conditions, nearly pure $Na_3H_2IO_6$ is formed although a small amount of the other salt may be present.

To a solution of sodium iodate from 100 g. of iodine are added 140 g. of solid sodium hydroxide and, if necessary, 100 to 200 ml. of water to allow ready mixing. The mixture is heated to boiling, and chlorine is passed in as rapidly as possible without spattering. This is best accomplished by passing the chlorine in through a glass tube not less than 1 cm. in inside diameter, which is used as a hand stirrer. (A smaller tube is apt to clog.) Best yields are obtained when the solution is boiled rapidly and stirred vigorously. The reaction is finished when the alkali has been neutralized and chlorine is no longer absorbed (10 to 15 minutes).

The solution is made slightly alkaline with sodium hydroxide (to change any $Na_2H_3IO_6$ to the less soluble $Na_3H_2IO_6$, cooled, and filtered. The precipitate is washed several times with cold water (below 20° C.) and dried at 110° C. The yield is about 225 g. (97 to 98 per cent). The I_2O_7 content is 62.2 to 62.8 per cent; $Na_3H_2IO_6$ demands 62.23 per cent.

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5. Inorganic Syntheses, Vol. I, pp. 168-75. McGraw Hill (1939). Courtesy of McGraw-Hill Book Co.
6. Hill, *J. Am. Chem. Soc.*, **50**, 2678 (1928).
7. Langois, *Ann. Chim Phys.* [3], **34**, 257 (1852); Ann. **83**, 153 (1852).
8. Müller and Jacob, *Z. anorg. Chem.*, **82**, 308 (1913).

* The description of the analysis for I_2O_7 is described on p. 170, Ref. (5).

B. Sodium Paraperiodate, Persulfate Method.† To the sodium iodate

$$K_2S_2O_8 + NaIO_3 + 4NaOH \longrightarrow Na_3H_2IO_6 + K_2SO_4 + Na_2SO_4 + H_2O$$

from 100 g. of iodine 40 g. of sodium hydroxide is added in portions.‡ After dilution to 1200 ml., the solution is heated to boiling and vigorously stirred mechanically while 213 g. of potassium persulfate is added and then 170 g. of sodium hydroxide in small portions. The boiling is continued for 15 minutes. The solution is cooled to 40° C., filtered on a fritted-glass filter (or decanted), and the precipitate is washed with cold water. If cooled below 40° C., large amounts of sulfate crystallize. Even when prepared as described, the precipitate usually gives a test for sulfate after numerous washings. After drying at 110°, the yield is 223 to 227 g. of 94 to 97 per cent purity, based on the I_2O_7 content.

Sodium Metaperiodate. For each 100 g. of sodium paraperiodate,

$$Na_3H_2IO_6 + 2HNO_3 \longrightarrow NaIO_4 + 2NaNO_3 + 2H_2O$$

200 ml. of water and 55 ml. of concentrated nitric acid (a 50 per cent excess) are added. If not clear, the solution is filtered through asbestos and evaporated on a steam bath until crystals appear. The solution is cooled to 20° C., filtered, and the precipitate is washed with cold water, centrifuged and dried at 110° C. It forms brilliant clear crystals.

If the solution is cooled to too low a temperature, white crystals of $NaIO_4 \cdot 3H_2O$ are formed. The transition point is 34.4° C. but the solution can be cooled much below this point if more of the trihydrate phase is present.

Yields of 61 to 62.1 g. (84 to 86 per cent) are obtained, of purity 99.5 to 99.8 per cent. The remaining periodate may be separated from the sodium nitrate by adding potassium nitrate, which precipitates potassium periodate. This gives an additional 10 to 12 g. (13 to 15 per cent).

Potassium Metaperiodate. This compound can be obtained in good yield by oxidation of the iodate with chlorine in alkaline solution. Since the soluble salt $K_4I_2O_9$ exists in alkaline solution instead of the insoluble KIO_4 no precipitation occurs until all the alkali is neutralized.

The directions for the preparation differ from those for the preparation of sodium paraperiodate only in that 135 g. of potassium chlorate is used and 195 g. of pure potassium hydroxide. Since the latter always contains water, its percentage purity must be known. The yield is nearly 180 g. (98 to 99 per cent), and the purity is 99.5 per cent.

Impure periodate residues are conveniently recovered by adding potassium nitrate to the acid solution, as described under sodium metaperiodate.

Barium Paraperiodate. The sodium periodate from 100 g. of

$$2Na_3H_2IO_6 + 3Ba(NO_3)_2 \longrightarrow Ba_3H_4(IO_6)_2 + 6NaNO_3$$

iodine (about 225 g.) is suspended in a liter of boiling water containing 10 ml. of concentrated nitric acid (to increase the solubility of the periodate). A moderate excess of barium nitrate (325 g.) dissolved in hot water is added, and the solution is boiled for 1½ to 2 hours with vigorous stirring. The solution then is neutralized with barium hydroxide and allowed to cool. The barium periodate

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† The presence of ammonium salts is very detrimental to this reaction.

‡ Some precipitation occurs as a result of oxidation by the chlorine formed in the preparation of the iodate.

which crystallizes is washed with hot water several times by decantation (stirring up the crystals each time) and then on a Büchner funnel. If the salt gives more than a faint test for sodium, it is again boiled with barium nitrate solution containing nitric acid and treated as before.

The yield is nearly quantitative. Although the salt cannot be analyzed directly for I_2O_7 because of its insolubility in the buffered solution, (borax + boric acid) a nearly pure product is indicated by the results obtained when it is used to prepare periodic acid.

The same salt may be prepared from potassium metaperiodate by adding two equivalents of potassium hydroxide and proceeding as with the sodium salt.

If the salt is to be used for preparing periodic acid it need not be dried.

Periodic Acid. Of the older methods for the preparation of periodic acid,

$$Ba_3H_4(IO_6)_2 + 6HNO_3 \longrightarrow 2H_5IO_6 + 3Ba(NO_3)_2$$

the most satisfactory for obtaining large quantities is the electrolytic oxidation of iodic acid at an anode of platinum plated with lead dioxide, the cathode solution being dilute nitric acid (*8a*). The iodic acid for this preparation is conveniently made by the electrolytic oxidation of iodine (*11*). However, periodic acid prepared in this way often contains considerable iodic acid after a year, even when carefully protected from light and dust, doubtless due to traces of platinum derived from the electrode.

The following method of making periodic acid is adapted to large scale preparation, and the acid so prepared is stable at least over a period of several years. It depends upon the fact that barium nitrate is insoluble in nitric acid of Sp. Gr. 1.42 whereas periodic acid is readily soluble.

Temp., C.	H_5IO_6, g. per 100 ml.	H_5IO_6, g. per 100 g. solution
−12° ± 1°	5.68	3.95
26° + 0.05°	7.82	5.41

The solubility rises rapidly above 25° C. and is about ten times as great in water as in concentrated nitric acid. If dry barium periodate (*26*) is treated with concentrated nitric acid, the barium nitrate is so finely divided that it is difficult to filter and wash. This is avoided by using more dilute acid or by treating the moist salt with concentrated acid.

Procedure. One hundred grams of barium periodate is moistened with 75 ml. of water and treated with 200 ml. of colorless* nitric acid (Sp. Gr. 1.42). The mixture is kept at 60 to 70° C. for an hour with frequent stirring, cooled to 30 to 40° C., and the barium nitrate filtered off on a fritted-glass Büchner funnel. It is washed with colorless, concentrated nitric acid until free from periodate, which is best done by thoroughly stirring it with the washing acid.

The filtrate and washings are concentrated at 60 to 70° C. *in vacuo* (water pump). If the solution becomes cloudy because of the separation of a little barium nitrate or iodic acid, it is filtered, the precipitate is washed with nitric acid, and the filtrate and washings are evaporated until periodic acid begins to separate. Sometimes a little more barium nitrate separates first and must be removed. Upon cooling, clear, brilliant crystals of periodic acid are formed. The solution shows a great tendency to supersaturation, and ample time should be allowed after cooling before the crystals are removed. These are centrifuged and dried in the air or *in vacuo* at 50° C. The mother liquor is evaporated for a second recovery. The yield is 46 to 51 g. (90 to 96 per cent, and the purity 99.5 to 99.9 per cent. The addition of potassium nitrate to the second mother liquor recovers the remaining periodic acid as potassium metaperiodate.

8a. Willard and Ralston, *Trans. Electrochem. Soc.*, 62, 239 (1932).

* It is essential that the acid used in this preparation be free from nitrous fumes and nitrous acid, which reduce periodic acid to iodic acid, which may also be formed if the temperature gets too high at any time. If, in spite of precautions, some iodic acid is formed, it may be removed from the periodic acid by recrystallization from colorless, concentrated nitric acid in which it is but slightly soluble.

The Preparation of Dimeso- and Metaperiodic Acids from Paraperiodic Acid (*9, 10*). These two acids, $H_4I_2O_9$ and HIO_4, are prepared by the thermal dissociation of peraperiodic acid, H_5IO_6 according to the following reactions:

$$H_5IO_6 + 80^\circ\ C. \longrightarrow H_4I_2O_9 + 3H_2O$$
$$H_5IO_6 + 100^\circ\ C. \longrightarrow HIO_4 + 2H_2O$$
$$H_4I_2O_9 + 100^\circ\ C. \longrightarrow 2HIO_4 + H_2O$$

The thermal decomposition of paraperiodic acid does not give mesoperiodic acid nor result in the formation of I_2O_7 by further dehydration of metaperiodic acid. It is incorrect to formulate paraperiodic acid as metaperiodic acid dihydrate $HIO_4 \cdot 2H_2O$. This follows from the study of its basicity (page 2). The formation of insoluble periodates such as potassium metaperiodate, (KIO_4), upon the addition of potassium salts has probably led to this mis-interpretation.

Solutions of paraperiodic acid in water are not permanently stable although the decomposition accounting for instability according to the reaction:

$$3H_5IO_6 \longrightarrow 3HIO_3 + O_3 + 6H_2O$$

is but minutely determinable. This reaction accounts for the odor of ozone in contact with solutions of paraperiodic acid. Following the explanation of the above reaction, contrary to the statement of page 1, periodic acid may be said to be correctly characterized by the term per-acid. Solutions of various alkali periodates likewise give off the unmistakable odor of ozone without accompanying material reduction in oxidizing value.

THE ELECTROLYTIC OXIDATION OF IODINE AND IODIC ACID

By far the most satisfactory method so far devised for the preparation of iodic and periodic acids has been described by Willard and Ralston (*11*). The apparatus assembly for these two electrolytic oxi-

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9. Lamb, *Am. Chem. J.*, 51, 134 (1902).
10. Partington and Bahl, *J. Chem. Soc.*, 1088 (1934).
11. Willard and Ralston, *J. Electrochemical Soc.*, 42, 239 (1932).

dations is shown in the accompanying drawing. The details are clear from examination of the drawing, Figure 2.

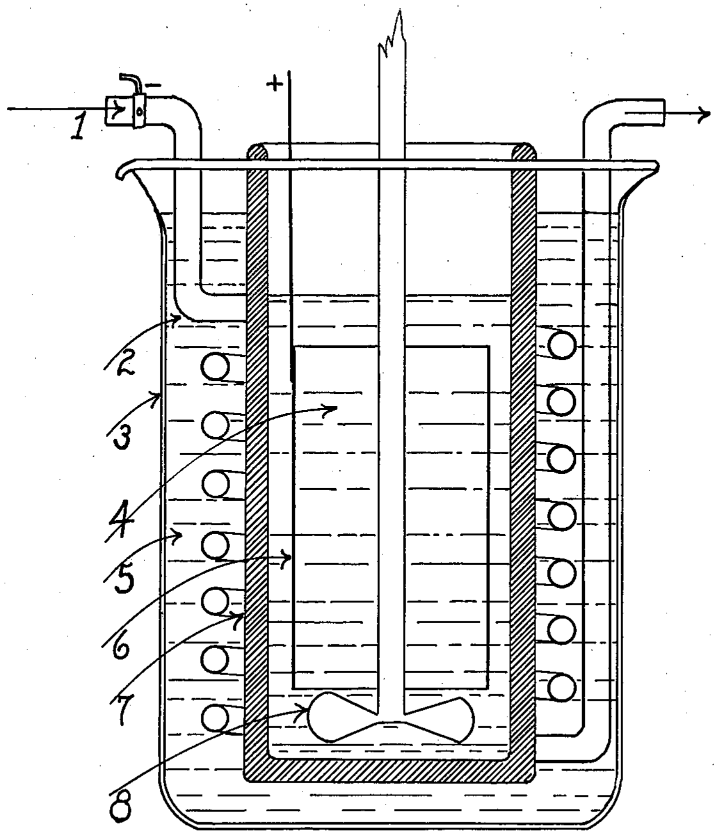

FIG. 2

1. Tap water inlet. 2. Gold plated copper tube cathode. 3. Pyrex beaker 2000 ml. 4. Anolyte. 5. Catholyte. 6. Platinum anode. 7. Porous ceramic cup. 8. Mechanical stirrer.

For the oxidation of iodine to iodic acid a bright platinum gauze anode is used and a current density of 0.11 amperes per square cm. is employed. The anolyte was 0.4 *N* in hydrochloric acid and the iodine introduced into the bottom of the porous anolyte vessel was kept in solution in the anolyte by stirring well throughout the entire electrolysis. The cathode was a gold plated cooling coil surrounding the porous cup and the catholyte used was 2 *N* nitric acid. The catholyte was maintained at a higher level around the porous cup 4-5 cms. and the nitric acid was fortified from time to time to compensate for its electrolytic reduction to ammonium nitrate. When the oxidation of iodine was complete the electrolysis of the HCl was continued with the evolution of chlorine. The anode is now changed to a lead dioxide on platinum gauze anode and the electrolysis was completed to form periodic acid.

The preparation of crystalline iodic acid HIO_3 of crystalline H_5IO_6 is carried out, after appropriate oxidation to either of the two stages described above, by crystallization from strong nitric acid and filtration centrifugally. The moist crystals thus obtained are dried over KOH in vacuo with moderately elevated temperature.

The current efficiency and yield of HIO_3 and H_5IO_6 by the process of Willard and Ralston are excellent and the process is to be preferred as compared to those previously described for many reasons. The preparation of potassium bi-iodate from HIO_3 prepared electrolytically is much more satisfactory than by other methods. The details of the electrolytic oxidation of iodine and iodic acids should be obtained by consulting the original paper.

Preparation of Potassium Bi-iodate from Iodic Acid

Potassium iodate is prepared by neutralization of iodic acid prepared by the Willard and Ralston method. Forty-two grams of crystalline HIO_3 is dissolved in 170 ml. of water and half neutralized by the addition of potassium hydroxide. Heat the mixture to boiling and add 6 drops of concentrated hydrochloric acid and cool after all has dissolved. Cool and separate the $KH(IO_3)_2$ from the mother liquors by centrifugal drainage. Purify by thrice recrystallizing and dry at 100° C. A product is thus obtained which is 99.97 to 100 per cent pure and is a most excellent material to employ as a standard of reference in the preparation of a stable acid for use in standardizing unknown solutions of bases.

The Use of Potassium Bi-iodate as a Standard Substance in Alkalimetric Titrations

The use of potassium bi-iodate in the standardization of alkali solutions is described by Kolthoff and Berk (*12*). The study was made of the purification of $KH(IO_3)_2$ by repeated crystallization from water and drying at 100° C. For the standardization of alkali it has distinct advantages, as its equivalent weight is very high and iodic acid is a strong acid which may be used with all indicators which show a color change between dimethyl yellow and phenolphthalein. The solutions of the bi-iodate can be stored for years without change. Measured portions of a standard stock reagent of suitable normality are taken

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12. Kolthoff and Berk, *J. Am. Chem. Soc.*, 48, 2799 (1926).

using a transfer pipet diluted to suitable volume and titrated with unknown solution of alkali. The molecular weight of $KH(IO_3)_2$ is 389.948. The rational equivalent weight (weight to be taken when weighed in air with brass weights and no vacuum correction) is 389.85. A tenth normal solution of $KH(IO_3)_2$ is, therefore, prepared by weighing 38.9850 gms., using brass weights, and dissolving in enough water to make 1000 ml. of solution.

Results using $KHIO_3$ in the standardization of a known strength of base solution (borax) have been made by Kolthoff and Berk (*loc. cit.*) starting with a certain preparation and repeating following purification. By this process of recrystallization the following series of determinations of the purity found were: 99.0 per cent, 99.72 per cent, 99.97 per cent, 99.97 per cent, 99.99 per cent. The product is thus seen to be satisfactorily pure after 3 recrystallizations. This method of standardizing unknown alkaline solutions cannot be too strongly recommended.

CHAPTER III

COLORIMETRIC AND VOLUMETRIC DETERMINATION OF MANGANESE AFTER OXIDATION WITH PERIODATE. THE ANALYSIS OF STEEL

This method (*1*) depends upon the oxidation in acid solution of manganous salts to permanganate by means of periodate, the reaction being represented by the following equation:

$$2\,Mn(NO_3)_2 + 5KIO_4 + 3H_2O = 2HMnO_4 + 5KIO_3 + 4HNO_3$$

Only a small excess of periodate is required, but the reaction must be carried out in an acid solution sufficiently concentrated to prevent precipitation of the manganese.

This method is especially adapted for the determination of manganese in water, soil, ores, iron, and steels. It is free from all the faults of other methods and yields results of a high degree of accuracy.

Reagents. 1. Sulfuric acid, sp. gr. 1.84; nitric acid, sp. gr. 1.42; or phosphoric acid, sp. gr. 1.70.

2. Potassium or sodium periodate. Solid.

3. Standard manganous sulfate solution. This solution is prepared by reducing an accurately measured volume of standard permanganate solution with sulfur dioxide, boiling off the excess of sulfur dioxide, cooling and diluting to the proper volume to give a manganese concentration of 0.1 mg. per cubic centimeter. The permanganate solution is prepared by dissolving the best grade of "analyzed" potassium permanganate in water that has been distilled from alkaline permanganate and redistilled. This gives a very stable solution which is then carefully standardized against sodium oxalate of known purity.

If the highest degree of accuracy is not required, the standard permanganate solution may be diluted to give a manganese content of 0.02 mg. per cubic centimeter and this solution employed directly for the comparison.

Procedure. The following is the "General Procedure" given by Willard and Greathouse, who were the first to propose the use of periodate for the oxidation of manganous salts to permanganate in the colorimetric estimation of manganese:

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1. H. H. Willard and L. Greathouse, *J. Am. Chem. Soc.*, 39, 2366 (1917).

The material to be analyzed is brought into a solution containing in 100 cc. at least 10 to 15 cc. concentrated sulfuric, 20 cc. of nitric or 5 to 10 cc. of syrupy phosphoric acid, or mixtures of two or more acids. The solution should previously have been freed from reducing agents by boiling with nitric acid, a little persulfate being added if carbon compounds are present, as with steel; if chloride is present it should be evaporated with nitric and sulfuric acids to fumes of the latter. Two-tenths to 0.4 g. of KIO_4 or $NaIO_4$ is added, or an equivalent amount of $Na_3H_2IO_6$, the solution boiled for a minute, kept hot 5 to 10 minutes, cooled, diluted to the proper volume, and compared with a standard of known manganese content similarly prepared. When ready for comparison the solution should not contain much more than 1 mg. of manganese per 50 cc., otherwise the color will be too dark.

In the presence of considerable iron, either sulfuric or phosphoric acid must be present, since ferric periodate is insoluble in fairly concentrated nitric acid but readily soluble in the other acids. A very large concentration of acid does no harm in any case, neither does a longer time of heating.

Color comparisons may be made by any of the usual methods.

1. The periodate method is free from all the faults of other methods and yields results of a high degree of accuracy.

2. Solutions of manganous salts oxidized by periodate have exactly the same color as pure permanganate solution.

3. Occasionally difficulty is caused by variation in tint with sulfuric and phosphoric acid solutions, arising from the brownish color of the carbon compounds after solution in nitric acid. This effect is especially noticeable when the carbon content is 0.8 per cent or more. To overcome this, the sample is dissolved in a mixture of 15 cc. nitric acid, 15 cc. water, and 15 cc. phosphoric or sulfuric acid, 1 g. of ammonium persulfate added and the solution decolorized by boiling 3 to 5 minutes. Analyses made by Willard and Greathouse, using steels with carbon content between 0.8 and 1.0 per cent, were accurate to within about ±0.003 per cent of the manganese present. The manganese content varied in the different steels between 0.3 and 0.8 per cent.

Richards (*2*) proves that for very small amounts of Mn in biological work there can be too much acid and he gives the maximum concentration. Biological chemists have investigated the periodate method for Mn and reported favorably in several cases. Richards' paper is subsequently included in this booklet.

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2. Richards, *Analyst*, 55, 554 (1930).

4. Determinations in which HNO_3, H_2SO_4, and H_3PO_4 were used separately and in various concentrations were made by Willard and Greathouse. In all cases the only effect of increasing the concentration of acid above the minimum required to prevent precipitation is to increase the rate of oxidation of the manganese. This minimum concentration of acid increases with the concentration of manganese, and varies with different acids, being lowest for phosphoric acid. The well-known stability of manganic phosphates probably accounts for the non-appearance of precipitates of iodates or periodates of manganese even in solutions of very low acid concentration.

5. The only effect of varying the concentration of periodate is a slight increase in the speed of the reaction as the concentration of periodate is increased. Willard and Greathouse found complete oxidation was obtained in a manganese solution containing only 0.1 g. KIO_4. The theoretical requirement was 0.052 g. KIO_4. They also obtained complete oxidation of 0.06 g. of manganese in 100 cc. of solution containing 2 g. KIO_4. This cannot be accomplished by any of the other methods. Even larger amounts of manganese can be oxidized, but such solutions are so deeply colored as to be of no practical value.

6. Periodic acid readily oxidized hydrochloric acid to chlorine according to the equation:

$$2HCl + HIO_4 = Cl_2 + HIO_3 + H_2O$$

The complete removal of chloride is obtained by heating the solution of sample with excess of periodate until the odor of chlorine has disappeared.

7. The presence of ammonium salts does not affect the intensity of the color, the tint of the solution, or the speed of oxidation of manganese solutions oxidized to permanganate by periodate.

8. "A remarkable feature of the solutions oxidized by periodate is their great stability when a slight excess of the reagent is present. Such a solution, kept for 3 months in a stoppered flask, when compared with a similar solution freshly oxidized showed no change whatever. This makes it possible to leave the standard solution in the colorimeter, renewing it only occasionally instead of preparing a fresh solution each time, as is necessary when persulfate is used." (Willard and Greathouse, *loc. cit.*)

9. The common metals do not interfere in this method except in so far as they themselves impart a color to the solution. The color due to ferric salts may be removed by the addition of phosphoric acid, but to correct for the color due to other metals the same amount must

be added to the standard. A number of metals, such as silver, lead, bismuth, and mercury, form iodates or periodates which are insoluble in dilute acids, but by using a high concentration of acid these remain in solution, since the amount of periodate added is small.

10. If a strong reducing agent, such as a ferrous salt, is present, the periodate will be reduced to free iodine which will color the solution and render it useless. All substances of this kind are removed by boiling or evaporation with nitric acid.

11. In many cases, Willard and Greathouse did not remove the color due to ferric salt, but made the proper correction by adding to the standard the same amount of iron in the form of ferric nitrate. Their results are given in the following table:

TABLE III

The Determination of Manganese in Steel
No Phosphate Acid Added. Standards of Comparison With Iron Added.

Metal No.	Description of Material	Weight of Sample	KIO_4 Added	C Pres.	Mn Pres.	Mn Found.	Diff.
		Gram	*Gram*	%	%	%	%
1	Basic Open Hearth, 1% C Sample 16	1.000	0.5	1.05	0.405	0.403	—0.002
2	Acid Open Hearth, 0.1% C Sample 18	1.000	0.3	0.10	0.412	0.409	—0.003
3	Bessemer 0.8% C Sample 23	0.500	0.5	0.81	0.775	0.771	—0.004
4	Acid Open Hearth, O.2% C Sample 19	0.500	0.3	0.21	0.760	0.752	—0.008
5	Bessemer, 0.2% C Sample 9a	0.500	0.3	0.25	0.918	0.913	—0.005
6	Bessemer, 0.4% C Sample 10a	0.500	0.3	0.45	0.916	0.902	—0.014
7	Iron D, Sample 6	0.500	0.3	2.89	1.410	1.407	—0.003
8	Am. Foundry Assn. Iron B	1.000	0.5	3.11	0.415	0.404	—0.011

12. In Table IV are recorded the results of Willard and Greathouse when the same steels were used as in the preceding table but with phosphoric acid added to the sample and no iron. The phosphoric acid reacts with ferric salts to form a colorless complex ferric ion. The metals are referred to by number only.

"These solutions differed only slightly in tint from the pure permanganate standard used, and such comparisons are readily made after a little practice. When more than 1 gram of iron is present its color becomes appreciable, but if the *standard* contains *no* phosphoric acid, the addition to it of 5 per cent of the weight of the iron in the sample gives sufficient color to correct for this.

TABLE IV

The Determination of Manganese in Steel
Phosphoric Acid Added. No Iron in Standard.

Metal No.	Weight of Sample	KIO_4 Added	Mn Pres.	Mn Found.	Diff.
	Gram	*Gram*	%	%	%
1	1.0000	0.5	0.405	0.402	—0.003
2	1.0000	0.3	0.412	0.412	±0.000
3	0.5000	0.5	0.775	0.770	—0.005
4	0.5000	0.3	0.760	0.755	—0.005
5	0.5000	0.3	0.918	0.905	—0.013
6	0.5000	0.3	0.916	0.905	—0.011

13. "Two determinations were made using iron ores of known manganese content. One gram samples were dissolved in platinum dishes with 15 cc. phosphoric acid, 5 cc. hydrofluoric acid, and a little nitric acid, and heated until all fluoride had been volatized. The resultant mass was dissolved in water, oxidized with 0.3 g. KIO_4 and diluted to 250 cc. The usual method of dissolving the ore in hydrochloric acid could have been used equally well. To expel all chloride and to oxidize ferrous salts it is necessary to add 10 cc. of nitric acid and 15 cc. of sulfuric acid and evaporate the solution to fumes of the latter." The results are given in the following Table V.

TABLE V

The Determination of Manganese in Iron Ore

Description of Ore	Weight of Sample	Mn Pres.	Mn Found.	Diff.
	Gram	%	%	%
U.S.B.S. No. 28, Norrie Ore	1.000	0.465	0.460	—0.005
U.S.B.S. No. 29, Magnetite	1.000	0.07	0.068	—0.002

"The presence of chloride is not permissible, but if only a little is present it can be oxidized to chlorine by adding large excess of periodate. It has been stated in various references to this method that the presence of chloride would not interfere. This is true only to a limited extent and only where the operator has taken care to add sufficient periodate to oxidize all the chloride. It is preferable to remove chloride by evaporation with nitric or sulfuric acid.

"In steel analyses the use of ammonium persulfate to remove the color due to carbon is probably the most satisfactory and quickest method to accomplish this, although two other methods are given.

"If the salt $Na_3H_2IO_6$ is used instead of KIO_4 or $NaIO_4$, somewhat more will be required. For example, instead of 0.2 to 0.4 g. it would be necessary to use 0.3 to 0.6 g.

"Chromium is oxidized to some extent by this reagent, the less the higher the acidity of the solution. If not much is present this can be made practically negligible and compensated for by adding the same amount of chromium to the standard. The green color of small amounts of chromium in the trivalent form does not interfere seriously with the determination of manganese, but if oxidized to the form of chromic acid an accurate comparison becomes impossible because of the great intensity of the color." (Willard and Greathouse, *Loc. cit.*)

VOLUMETRIC AND GRAVIMETRIC DETERMINATION OF MERCURY AS PERIODATE

Mercuric periodic was first prepared in 1834 by Bengieser (*3, 4*) by the action of sodium periodate on mercuric nitrate. Later it was prepared by Lautsch (*5*) and by Rammelsberg (*6*) who treated mercuric oxide with a nitric acid solution of periodic acid. It was described as an orange-red salt having the composition of $Hg_5(IO_6)_2$, not decomposed at 100° C., but completely volatile on ignition. It was insoluble in water.

In the course of an investigation on periodates this salt was studied, particularly with reference to its suitability for the quantitative determination of mercury (*3*).

Experimental Data

Mercuric nitrate, dissolved in nitric acid of varying concentrations, was precipitated by the addition of excess of sodium periodate. Precipitation was complete at concentrations not greater than 0.15 *N*. At 100° C. the salt was appreciably soluble in water, but below 50° C. the solubility was practically negligible.

A sample of the salt was thoroughly washed with hot water, dried at 100° C. for 4 hours, and analyzed gravimetrically for iodine and mercury. It was dissolved in dilute nitric acid, tartaric acid was added, and the solution made ammoniacal. A slight excess of sulfite was added to reduce the periodate and the mercury was precipitated from the hot ammoniacal solution by hydrogen sulfite. After standing one hour, the mercuric sulfide was filtered through a filtering crucible with porous porcelain bottom, washed with hot water containing a little hydrogen sulfide, then with pure water, dried 2 hours at 100° C., and weighed. The filtrate was oxidized to sulfate by pure hydrogen peroxide, the excess removed by boiling, a little arsenite added to reduce any iodate, and after acidifying with nitric acid, the iodide was precipitated and weighed as silver iodide. The results were: found, 74.75, 74.73, 74.76 per cent of HgO, average 74.75 per cent, which is the theoretical value; 25.30, 25.26 per cent of I_2O_7, average 25.28 per cent, theory 25.25 per cent. The salt is thus shown to be the pentamercuric para-periodate, $Hg_5(IO_6)_2$.

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3. Willard and Thompson, *Ind. Eng. Chem., Anal. Ed.*, **3**, 398 (1931).
4. Bengieser, *Ann.*, **17**, 259 (1934).
5. Lautsch, *J. prakt. Chem.*, **100**, 86 (1867).
6. Rammelsberg, *Ann. Physik*, **134**, 524 (1868).

Some of this salt was recrystallized by dissolving it in concentrated nitric acid and diluting with water, the bright red crystals washed and dried. They proved to be less pure than the precipitated salt. Analysis showed 73.83, 73.50, 73.76, 73.90 per cent of HgO, average 73.75 per cent, compared with the theoretical 74.75 per cent; and 25.26, 25.38, 25.30, 25.28 per cent of I_2O_7, average 25.30 per cent, compared with 25.25 per cent.

The iodine in mercuric periodate was determined volumetrically in two ways:

Method A. The salt was dissolved in excess of potassium iodide, acidified with hydrochloric acid, and the liberated iodine titrated with thiosulfate:

$$Hg_5(IO_6)_2 + 34KI + 24HCl = 5K_2HgI_4 + 8\ I_2 + 24KCl + 12H_2O$$

Method B. The salt was dissolved in an excess of standard arsenite by adding considerable concentrated hydrochloric acid, and the excess was titrated back with iodate using a little chloroform as indicator (*7, 10*):

$$Hg_5(IO_6)_2 + 6H_3AsO_3 + 12HCl = 5HgCl_2 + 2ICl + 6H_3AsO_4 + 6H_2O$$

In six titrations of the precipitated salt by these methods the maximum variation from the theoretical value was only 0.02 per cent.

Quantitative Determination of Mercury

Mercury is usually weighed as metal or as mercuric sulfide. Precipitation of the latter in hydrochloric acid solution is not entirely satisfactory (*8*), especially in the presence of zinc, cadmium, and copper, because of contamination with other sulfides. Volumetrically, mercury may be determined in a number of ways, most of which are not particularly accurate, the thiocyanate titration (*9*) being a common and accurate one.

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7. Andrews, *J. Am. Chem. Soc.*, 25, 756 (1903).
8. Hillebrand and Lundell, "Applied Inorganic Analysis," p. 170, Wiley, '29.
9. Hillebrand and Lundell, *Ibid.*, p. 173.
10. Jamieson, "Volumetric Iodate Methods," p. 18, Chemical Catalog, 1926.

It has been found that mercury can be determined gravimetrically or volumetrically by precipitation as mercuric periodate, $Hg_5(IO_6)_2$, in the presence of aluminum, zinc, cadmium, nickel, copper, calcium, and magnesium. The method is rapid, convenient, and accurate, and the end point in the volumetric method is very sharp. Iron interferes because it is precipitated as ferric periodate. Attempts were made to keep it in solution as the complex fluoride, but under these conditions the mercury was not completely precipitated. Chloride and other halides must be absent, because they prevent complete precipitation of mercury, doubtless owing to the slight ionization of mercuric halides. The maximum permissible acidity for complete precipitation is 0.15 *N* nitric or 0.1 *N* sulfuric acid, and under these conditions a large excess of periodate is required.

TABLE VI

Gravimetric Determination of Mercury as $Hg_5(IO_6)_2$

Mercury Taken	Mercury Found	Error	Acid Present
Gram	*Gram*	*Mg.*	
0.0497	0.0497	0	Nitric
0.1243	0.1240	− 0.3	Nitric
0.1563	0.1563	0	Nitric
0.2904	0.2903	− 0.1	Nitric
0.3882	0.3885	+ 0.3	Nitric
0.5493	0.5492	− 0.1	Nitric
0.5721	0.5721	0	Nitric
0.4799	0.4798	− 0.1	Sulfuric
0.6313	0.6311	− 0.2	Sulfuric
0.4852	0.2563	−228.9	Hydrochloric *

* Effect of hydrochloric acid in preventing precipitation is shown.

Procedure. A sample of pure mercury was dissolved in nitric acid, sp. gr. 1.2, and the solution evaporated to dryness. It was taken up with 150 cc. of 0.15 *N* nitric acid or 0.1 *N* sulfuric acid, heated to boiling, and the mercury precipitated by adding slowly, with constant stirring, 2 grams of sodium or potassium periodate dissolved in 50 cc. of water. It was cooled, filtered through a filtering crucible with a sintered-glass or porous porcelain bottom, washed with warm water, dried at 100° C. for 2 to 3 hours, and weighed as $Hg_5(IO_6)_2$. The results are shown in Table VI.

Volumetric Determination

Method A. The filtered and washed precipitate of mercuric periodate in the crucible was treated with 2 or 3 grams of solid potassium iodide and 10 to 15 cc. of water, stirring until all the periodate had dissolved. The solution was washed into a 150-cc. conical flask (most conveniently a suction flask), acidified with 10 cc. of 2 *N* hydrochloric acid, and the liberated iodine titrated with 0.1 *N* sodium thiosulfate, using starch as indicator.

Method B. The precipitate in the crucible was treated with an excess of standard arsenite and then concentrated hydrochloric acid added until it dissolved, about 35 cc. being required if the volume at the end of the titration is about 100 cc. The solution was washed into a 150-cc. glass-stoppered conical flask, and titrated with 0.1 *N* potassium iodate until it had a light brown color. Four or five cubic centimeters of chloroform were then added and the titration continued, shaking after each addition until the purple color of the iodine just completely disappeared. The solution at the end point should contain between 28 and 45 cc. of hydrochloric acid, sp. gr. 1.18, per 100 cc.

The results, both with pure mercury and in mixtures with other metals, are shown in Table VII. In the first three experiments method *B* was used; in all others, method *A*. The mercuric salt was precipitated from a nitric acid solution.

TABLE VII

Volumetric Determination of Mercury as $Hg_5(IO_6)_2$

Mercury Taken	Mercury Found	Other Metals Present	Error
Gram	*Gram*	*Gram*	*Mg.*
0.3645	0.3646		+0.1
0.2071	0.2070		−0.1
0.0513	0.0513	0.20 Ni	0
0.2556	0.2558	0.15 Al	+0.2
0.1327	0.1327	0.18 Cd	0
0.1903	0.1902	0.17 Zn	−0.1
0.1064	0.1065	0.13 Cu	+0.1

If a chloride solution is to be analyzed, the mercury may first be precipitated as metal or sulfide and then converted into nitrate or sulfate.

VOLUMETRIC DETERMINATION OF MANGANESE AFTER OXIDATION BY PERIODATE

Willard and Greathouse (*11*) have shown that manganese can be determined colorimetrically by oxidation to permanganate with a small excess of periodate. The solution thus obtained is stable for weeks, a fact confirmed by others. It seemed desirable, therefore, to make this the basis of a volumetric method by removing the excess

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11. Willard and Greathouse, *J. Am. Chem. Soc.*, 39, 2366 (1917).

of periodate. This was accomplished by precipitation as mercuric periodate, after which the permanganate was titrated by adding excess of standard ferrous sulfate and back titrating with permanganate. Although bismuth periodate is the least soluble of all, its presence caused certain errors which made its use for this purpose impossible.

Precipitation of Periodate as Mercuric Salt

It was found that periodate could be completely precipitated as the mercuric salt, $Hg_5(IO_6)_2$ (*12*). Although more soluble than the bismuth salt, it is still sufficiently insoluble even in the concentration of acid used for the oxidation of manganese, provided a large excess of mercuric ion is present. The mercuric salt has a very decided advantage in that it is much more easily filtered. There is also no possibility of further oxidation of the mercury by permanganate. Experiments showed that amounts of manganese up to 30 mg. could be accurately determined by oxidation to permanganate in a solution containing either phosphoric, sulfuric, or phosphoric and sulfuric acids. There was no blank correction to be applied. In this respect there is a slight advantage over the bismuthate method. Iron ores can be quickly dissolved in phosphoric acid and this method applied directly to the solution, but this is not possible with bismuthate.

Experiments using standard permanganate were carried out to determine the accuracy of the method. Samples of 25 to 40 cc. of 0.05 *N* permanganate were reduced with ferrous sulfate in a solution containing, in a volume of 100 cc., about 10 to 15 cc. of 85 per cent phosphoric acid, or mixtures of 3 or 4 cc. of phosphoric acid with 3 or 4 cc. of concentrated sulfuric acid, and oxidized by adding 0.3 to 0.5 gram of sodium or potassium periodate and heating just to boiling for 15 minutes. The solution was cooled to room temperature, diluted to 150 cc., and 2 to 5 grams, of mercuric nitrate, $Hg(NO_3)_2 \cdot 2H_2O$, dissolved in a little water, were added to precipitate the excess periodate and nearly all of the iodate. The solution was filtered into an excess of 0.05 *N* ferrous sulfate through an asbestos mat 3 to 4 mm. thick on a 9-cm. No. 17G sintered-glass filtering funnel. A Büchner funnel would doubtless be almost as satisfactory. The precipitate of mercuric periodate was washed four times with water, and the excess of ferrous sulfate was titrated back with standard permanganate. The results obtained were the same within 0.01 cc. as in the direct titration of the ferrous sulfate with permanganate. When chromium was present, it was found that in the presence of sulfuric acid about 60 per cent of it was oxidized when the content

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12. Willard and Thompson, *Ind. Eng. Chem. Anal. Ed.*, 3, 398 (1931).

was about 1.5 mg., thereby giving high results for manganese. However, this tendency is very much minimized in phosphoric acid solutions, so that an accurate determination of manganese can be made in the presence of 1 mg. of chromium. Because of the difficulty in washing out all the permanganic acid from very large precipitates of mercuric periodate, only 0.3 gram of sodium or potassium periodate should be used for 15 mg. or less of manganese. Accurate results can be obtained however, with as much as 30 mg. of manganese, using, in this case, 0.5 gram of periodate. With larger amounts such voluminous precipitates are formed that all the permanganic acid cannot be removed by washing. Instead of the meta-periodate, the para-periodate, $Na_3H_2IO_6$, may be used. Manganese is more readily oxidized and the permanganic acid formed is more stable in a phosphoric acid solution, so that this acid is desirable when considerable amounts of manganese are present.

The concentration of acid may vary within wide limits as far as oxidation of manganese is concerned, although with large amounts of the latter, manganese dioxide may form unless phosphoric acid is present. A fairly high concentration of acid increases the rate of oxidation. The solubility of mercuric periodate, however, is increased under these conditions, so that it is advisable to dilute the solution before removing the excess of periodate. Concentrations not greater than 5 cc. of sulfuric acid, sp. gr. 1.83, or 15 cc. of 85 per cent phosphoric acid per 100 cc. are recommended. Mixtures of the two acids are desirable, because the mercuric periodate is more crystalline in the presence of sulfuric acid, and without some phosphoric acid, manganese dioxide may form.

The weight of mercuric nitrate required for complete precipitation of periodate varies from 5 grams with 5 cc. of sulfuric acid to 2 grams with 15 cc. of phosphoric acid per 100 cc.

Titration of the permanganic acid with arsenite instead of ferrous sulfate is impossible because of an indefinite end point.

Chloride must be absent. Cobalt interferes as in the bismuthate method. When periodate is added to a solution of cobaltous sulfate, the solution becomes dark brown, owing to oxidation of the cobaltous salt. In steel containing 1.13 per cent of manganese and 0.5 per cent of cobalt, 1.32 per cent of manganese was obtained. Cerium also interferes because it is oxidized to a ceric salt.

Procedure for Steel or Iron Free from Chromium

Dissolve 1 gram of steel containing not more than 0.15 mg. of chromium in 4 cc. of concentrated sulfuric acid and 25 cc. of water. To the hot solution, add, cautiously, 1 cc. or more of concentrated nitric acid to oxidize the ferrous iron and carbonaceous matter, and boil to remove nitrous fumes. Any graphite present will do no harm and will be filtered out later. Dilute to 50 or 75 cc., add 3 cc. of 85 per cent phosphoric acid (or an equivalent amount of more dilute acid) and 0.3 gram of sodium or potassium periodate. Boil gently for 15 minutes to oxidize the manganese, dilute to 150 cc., cool to room temperature, and add slowly, with constant stirring, 4 to 5 grams of mercuric nitrate ($Hg[NO_3]_2 \cdot 2H_2O$) dissolved in a little water. Filter immediately through a fairly large asbestos filter into an excess of standard ferrous sulfate, wash with cold water four or five times, and titrate back with standard permanganate.

The influence of the presence of moderate amounts of chromium in steel is shown by the data of Table VIII.

TABLE VIII

Effect of Chromium on the Determination of Manganese in Steel

Material Used	Acid Present	Approx. Wt. of Sample	Chromium Present	Manganese Present	Manganese Found
		Grams	*Mg.*	%	%
B. S. Steel, No. 10c	Phosphoric	1.1	4.0	1.13	1.160
B. S. Steel, No. 10c	Phosphoric	1.0	3.0	1.13	1.153
B. S. Steel, No. 10c	Phosphoric	1.0	2.0	1.13	1.148
B. S. Steel, No. 10c	Sulfuric	1.3	2.0	1.13	1.232
B. S. Steel, No. 10c	Phosphoric	1.0	1.5	1.13	1.143
B. S. Steel, No. 10c	Phosphoric	1.0	1.0	1.13	1.138
B. S. Steel, No. 10c	Phosphoric	1.0	0.5	1.13	1.139
B. S. CrNi Steel, No. 32b	Phosphoric	1.14	7.3	0.624	0.661
B. S. CrNi Steel, No. 32b	Phosphoric	1.04	6.6	0.624	0.664
B. S. CrNi Steel, No. 32b	Phosphoric	1.18	7.6	0.624	0.749
B. S. CrNi Steel, No. 32b	Phosphoric	1.20	7.7	0.624	0.686

Procedure for Steel or Iron Containing Not Over 0.1 Per Cent of Chromium

Dissolve 1 gram in a mixture of 15 cc. of water and 15 cc. of 85 per cent phosphoric acid. Oxidize the ferrous iron and carbonaceous matter by adding carefully to the hot solution 1 or 2 cc. of concentrated nitric acid, and boil to remove nitrous fumes. Dilute to 100 cc., add 0.3 gram of sodium or potassium periodate, boil gently 15 minutes to oxidize the manganese, dilute to 150 cc., and cool to room temperature. Precipitate the periodate by adding slowly, with constant stirring, 2 to 3 grams of mercuric nitrate dissolved in a little water, and filter immediately through a fairly large asbestos filter into excess of standard ferrous sulfate containing 10 cc. of 50 per cent sulfuric acid to prevent precipitation of mercuric phosphate. Wash with cold water four or five times and titrate back the filtrate and washings with standard permanganate. The filtration will be slower than when sulfuric acid is present during precipitation, but the time required, including washing, should not be more than 3 minutes. The effect of chromium with and without phosphoric acid is shown in Table IX.

TABLE IX

Determination of Manganese in Various Materials

Material Analyzed	Acid Used	Approx. Wt. of Sample	Chromium Present	Manganese Present	Manganese Found
		Grams	%	%	%
B. S. Steel, No. 10c	Phosphoric	1.06	0.01	1.13	1.136
B. S. Steel, No. 10c	Phosphoric	1.03	0.01	1.13	1.132
B. S. Steel, No. 10c	Sulfuric	1.29	0.01	1.13	1.138
B. S. Steel, No. 10c	Sulfuric	1.01	0.01	1.13	1.139
B. S. Cast Iron, No. 4c	Phosphoric	1.04	0.016	0.897	0.890
B. S. Cast Iron, No. 4c	Phosphoric	1.18	0.016	0.897	0.894
B. S. Cast Iron, No. 4c	Sulfuric	1.14	0.016	0.897	0.898
B. S. Cast Iron, No. 4c	Sulfuric	1.13	0.016	0.897	0.912
B. S. Steel, No. 21b	Phosphoric	1.26	0.021	0.564	0.570
B. S. Steel, No. 21b	Phosphoric	1.12	0.021	0.564	0.562
B. S. Steel, No. 16b	Phosphoric	1.10	0.007	0.381	0.389
B. S. Steel, No. 16b	Phosphoric	1.24	0.007	0.381	0.388
B. S. Steel, No. 16b	Sulfuric	1.02	0.007	0.381	0.390
B. S. Steel, No. 26b	Sulfuric	1.22	0.007	0.381	0.392
Steel A	Phosphoric	1.47*	0.065	1.99	1.99
Steel A	Phosphoric	1.46*	0.065	1.99	1.98
Steel A	Sulfuric	0.49	0.065	1.99	2.02
Steel A	Sulfuric	0.43	0.065	1.99	2.00
B. S. Mn Bronze, No. 62	Phosphoric	0.69	....	1.59	1.61
B. S. Mn Bronze, No. 62	Phosphoric	0.62	....	1.59	1.64
B. S. Norrie Iron Ore, No. 28	Phosphoric	1.00	....	0.465	0.446
B. S. Norrie Iron Ore, No. 28	Phosphoric	1.09	....	0.465	0.447
B. S. Bauxite, No. 69	Phosphoric	1.27	....	0.426	0.421
B. S. Bauxite, No. 69	Phosphoric	1.26	....	0.426	0.420

* These samples contain nearly 30 mg. of manganese.

Procedure for Iron Ore and Other Oxide Ores

Place 1 gram in a 250-cc. Pyrex beaker, and add 15 cc. of 85 per cent phosphoric acid and a few drops of concentrated sulfuric acid. Stir until all the ore is free from the bottom of the beaker, cover and heat until fumes of sulfuric acid are given off, taking care that it does not froth over or cake on the bottom. If the ore is not dissolved by this time, keep it hot for a longer time, stirring occasionally, but not allowing the temperature to rise, because the beaker would be attacked. Cool until the mass begins to be viscous, then add quickly 100 cc. of water, and heat. Everything should dissolve except some gelatinous silica. From here on the procedure is the same as for steel containing 0.1 per cent of chromium.

Procedure for Bronze

Dissolve 1 gram in a mixture of 3 cc. of concentrated nitric acid, 10 cc. of 85 per cent phosphoric acid, and about 7 or 8 cc. of water. Then dilute to 50 or 75 cc. and proceed as above. Owing to the deep blue color of the copper salt, the back titration with permanganate is conveniently carried out electrometrically or by use of alphazurine indicator (*13*).

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13. Willard and Thompson, *Ind. Eng. Chem., Anal. Ed.*, 3, 399 (1931).

If the amount of manganese is between 15 and 30 mg., the amount of periodate in the above procedures should be increased to 0.5 gram.

Results obtained by this method with different materials are shown in Table IX. In all cases phosphoric acid was used with the sulfuric to prevent formation of manganese dioxide.

This procedure was described by Willard and Thompson (*3*). It has since been adopted in a great many standard routine procedures.

DETERMINATION OF MANGANESE IN TUNGSTEN AND FERROTUNGSTEN *

Mixed Perchloric and Phosphoric Acids as Solvent and Sodium Bismuthate or Potassium Periodate as Oxidizing Agents

Metallic tungsten, ferrotungsten, and tungsten steels are soluble completely with no precipitation of tungstic acid by treatment with mixed perchloric and phosphoric acids. The most rapid solubility occurs at a temperature of 200° to 215° C. The tungsten is held in solution probably as phosphotungstic acid. Most, if not all, of the silicon is dissolved but dehydrated silica if formed does no harm.

The determination of manganese in metallic tungsten and ferrotungsten is generally carried out following a fusion with sodium peroxide. An alternative procedure consists in dissolving the sample using hydrofluoric acid in a platinum dish followed by nitric acid to oxidize the iron and perchloric acid to volatilize excess hydrofluoric acid. These two procedures are more rapid than the method to be described. The first requires constant attention and the other involves the use of platinum dishes and hydrofluoric acid. Both may be preferred as routine methods because of their speed. By the method to be described a longer period of time is required to dissolve the sample, but no attention is required during this treatment and the use of platinum and the troublesome hydrofluoric acid is avoided.

Provided perchloric acid and phosphoric acid can be shown to have no interfering action during oxidation of manganese using either sodium bismuthate or potassium periodate, the present method for solution of ferrotungsten and tungsten metal in preparation for determining manganese has many advantages over either the fusion method or hydrofluoric acid treatment. In addition, the troublesome formation of insoluble tungstic acid is entirely avoided.

The determination of manganese in nitric acid solution following oxidation using bismuthate is well known and the same determination in the presence of phosphoric acid and sulfuric acid, as will be shown, requires but slight modification. The determination of manganese following oxidation to permanganic acid using potassium periodate was developed by Willard and Thompson (*13a*). The general subject of mixed perchloric, sulfuric, and phosphoric acids and their applications in analysis was developed by Smith (*13b*).

Samples for Analysis

Bureau of Standards ferrotungsten, No. 75: W, 75.2 per cent; Mn, 1.16 per cent.

British Chemical Standards, No. 202-2: W, 80.7 per cent; Mn, 0.55 per cent.

Union Carbide and Carbon sample (courtesy of H. E. Cunningham), works analysis: W, 79.79 per cent; Mn, 0.24 per cent.

Bureau of Standards sample No. 75 was the only one of this list in which a series of analysts coöperated in determining the value for manganese. The mean value, 1.16 per cent manganese, represented the average value by nine separate analysts. The minimum value given was 1.14 per cent and the maximum found was 1.19 per cent. The British Chemical Standard No. 202-2 is seen to show the highest tungsten content, but the manganese value was given as the findings of but one analyst.

Solution of Tungsten and Ferrotungsten in Mixed Perchloric and Phosphoric Acids

Weigh into 500-ml. Erlenmeyer flasks 1-gram samples of ferrotungsten or tungsten metal in a finely divided condition. Provide each flask with refluxing heads. Add 30 ml. of a mixture of 1 part of 72 per cent perchloric acid and 2 parts of 85 per cent sirupy phosphoric acid, and place flask and contents over a readily regulated burner and wire gauze. Heat gradually to 190° C. At 155° C. the acid mixture loses water and at 190° C. the solvent action begins in the case of ferrotungsten and the solution turns green with the precipitated tungsten scarcely attacked. Continue to heat to 200° to 215° C. and maintain at this temperature until all is in solution, which should be complete in 45 to 60 minutes with ferrotungsten and in a slightly longer time interval with tungsten metal. The reactions involved are omitted in the interests of brevity.

From this point the determination of manganese depends upon the choice of oxidizing agents employed. The silicon present is all or in part in solution as silicotungstic acid. Any not in solution does not interfere with subsequent operations.

Oxidation of Manganese Using Potassium Periodate

The solution of ferrotungsten or tungsten metal prepared as above described is cooled somewhat and diluted to 200 ml. with water. Add 0.3 gram of potassium periodate and heat to a gentle boil for 15 minutes to oxidize the manganese. Cool

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* Smith, McHard and Olsen, *Ind. Eng. Chem., Anal. Ed.*, 8, 350 (1936).

13a. Willard and Thompson, *ibid*, 3, 398 (1931).

13b. Smith, "Mixed Perchloric, Sulfuric, and Phosphoric Acids and Their Applications in Analysis," G. Frederick Smith Chemical Co., Columbus, Ohio, 1935.

and add 4 to 5 grams of mercuric nitrate dissolved in water which precipitates the excess periodate (and iodate):

$$2Mn_3(PO_4)_2 + 15KIO_4 + 9H_2O \longrightarrow 6HMnO_4 + 15KIO_3 + 4H_3PO_4$$
$$2KIO_4 + 5Hg(NO_3)_2 + 4H_2O \longrightarrow Hg_5(IO_6)_2 + 2KNO_3 + 8HNO_3$$

Filter the precipitated iodate and periodate through a Büchner funnel with asbestos filtering mat into a 500-ml. filtering flask containing an excess of standard ferrous sulfate. Wash the precipitate four times with water and titrate the excess ferrous sulfate with standard permanganate.

The amount of periodate used is sufficient to oxidize 15 mg. of manganese. Phosphoric acid being present aids in the oxidation of manganese and prevents interference from 1 to 1.5 mg. of chromium which is seldom present in tungsten or ferrotungsten. It is possible to oxidize twice as much manganese if 0.5 gram of periodate is used, but it is less convenient because of the bulk of mercuric salt to be filtered. By periodate oxidation of manganese the chlorine and possible traces of hydrochloric acid formed during the solution of the sample are either boiled off or oxidized to chlorine and evolved as such. Results of a series of analyses by this process are shown in Table X.

TABLE X

Determination of Manganese in Ferrotungsten

(B. of S. No. 75, 1.16% Mn. $HMnO_4$ filtered into 50.00 ml. of 0.0434 *N* $FeSO_4$ and excess of latter back-titrated using 0.0588 *N* $KMnO_4$)

Sample	0.0588 *N* $KMnO_4$ Required	Manganese Found		Error	
	Ml.	*Mg.*	%	*Mg.*	%
0.8941	21.00	10.32	1.154	—0.05	—0.006
1.2299	14.26	14.70	1.195	+0.44	+0.035
0.9895	19.65	11.22	1.134	—0.25	—0.026
0.8268	20.03	9.49	1.148	—0.10	—0.012
		Av.	1.158	+0.01	

A series of six additional determinations not tabulated for the sake of brevity showed the following percentages of manganese found: 1.158, 1.144, 1.170, 1.157, 1.172, and 1.164, or an average of 1.161 per cent to compare with the certificate value of 1.16 per cent manganese.

Oxidation of Manganese Using Sodium Bismuthate

Dissolve the sample as above described, cool somewhat, and add 20 ml. of concentrated nitric acid. Boil gently until the chlorine and hydrochloric acid formed in the solution of the sample are decomposed or boiled off and the nitric acid has been evolved. Cool the contents of the flask by immersion in cold water and transfer the contents to a 400-ml. beaker. Reduce any violet color present, due to partially oxidized manganese, with a little ferrous sulfate solution. Add 15 ml. of concentrated sulfuric acid, bring to a boil, and add sodium bismuthate in small amount until the first definite pink color. Boil gently 5 minutes and reduce any pink or brown color with ferrous sulfate solution. Bring again to a gentle boiling temperature and add 1 gram of sodium bismuthate with stirring. Stir for a few minutes without additional heat and cool in a bath of cold water with continuous stirring.

Allow the oxidized solution and excess bismuthate to stand 10 minutes. Filter through an asbestos Gooch crucible into an excess of standard ferrous sulfate contained in a 500-ml. filter flask or its equivalent. Wash the precipitate left in the crucible with cold water and titrate the excess ferrous sulfate, using standard ceric sulfate and diphenylamine sulfonic acid as indicator to the first pink color which persists.

o-Phenanthroline indicator does not serve in this case because of the presence of tungsten. The use of permanganate in place of ceric sulfate does not give a definite end point, as is the case after periodate oxidation of manganese as previously described. Results of 14 consecutive analyses of B. of S. ferrotungsten No. 75 showed an average value of 1.155 per cent of manganese compared to the certificate value 1.16 per cent, and the values varied from 1.14 per cent to 1.18 per cent. Four consecutive determinations are recorded in Table Xa.

TABLE Xa

Determination of Manganese in Ferrotungsten

(B. of S. No. 75, 1.16% Mn. $HMnO_4$ filtered into 25.00 ml. of 0.05356 *N* $FeSO_4$)

Weight of Sample	0.02888 *N* Ceric Sulfate Required	Mn Found	Error
Gram	*Ml.*	%	%
0.9227	12.88	1.152	—0.008
0.9634	11.12	1.161	+0.001
0.9541	11.05	1.174	+0.014
0.8952	13.10	1.179	+0.019
		Av. 1.166	

The ceric sulfate used in Table Xa was standardized using pure iron and B. of S. sodium oxalate, in the former case using *o*-phenanthroline as indicator, and in the latter case the potentiometric end point. The two values were found to be the same. The ferrous sulfate solution was then standardized against the ceric sulfate, using both a potentiometric and *o*-phenanthroline indicator system.

Seven consecutive determinations of manganese in sample No. 202-2 British Chemical Standards ferrotungsten were made using the bismuthate method. The average of these determinations was found to be 0.70 per cent. The variation in these results was from 0.68 to 0.73 per cent of manganese with one result of 0.77 per cent obviously in error.

Five consecutive determinations of manganese in the Union Carbide ferrotungsten, the works analysis for which showed 0.24 per cent of manganese, gave an average result of 0.183 per cent with a maximum range 0.175 to 0.191 per cent.

Colorimetric Determination of Copper Using Dimethylglyoxime and Potassium Periodate

The following procedure for the colorimetric determination of traces of copper in distilled water and in tap water was described by Kolthoff (*14*).

Reagents. Saturated solution of potassium periodate in water (0.35 g. of the salt in 100 cc. of water); 0.1% dimethylglyoxime in alcohol (the saturated solution which Clarke and Jones (*14*) used contains about 1.6 g. of glyoxime in 100 g. of alcohol and is much too concentrated for our purpose). It may be mentioned that an old solution of dimethylglyoxime which had been kept for some years in an ordinary bottle gave a much less sensitive reaction. The reason was that the solution had become strongly alkaline to phenolphthalein.

Procedure. To 10 cc. of water add 0.2 to 0.3 cc. of 0.1% dimethylglyoxime and 1 cc. of saturated potassium periodate solution. Observe the color after three to five minutes' standing. A violet-red color shows the presence of copper; sensitivity: 0.1 mg. of copper in a liter ($1:10^7$).

Notes. (1) It makes no difference whether the dimethylglyoxime or the periodate is added first. In order to avoid confusion with nickel, it is advisable to add the dimethylglyoxime first. (2) The red-violet color develops gradually and attains a maximum sensitivity after about five minutes' standing. After long standing, the color fades. Still the procedure described can be applied for the colorimetric determination of traces of copper in distilled water if comparisons are made within fifteen minutes after addition of the reagents. In this way it was found that distilled water in this Laboratory contained 0.2 to 0.4 mg. of copper in a liter. (3) In working with a larger volume than 10 cc. even smaller amounts than 0.1 mg. of copper in a liter can be detected. (4) Small amounts of the alkali chlorides and other neutral alkali salts have no influence upon the reaction. Small amounts of sodium bicarbonate (less than 1 g. in a liter) have no influence; with larger amounts the sensitivity decreases somewhat, but even in the presence of 10 g. of sodium bicarbonate per liter, 1 mg. of copper in a liter could be detected easily. (5) Calcium and magnesium, especially in the presence of bicarbonate (tap water) interfere, as they precipitate with the periodate. This difficulty can be overcome by adding to 10 cc. of water 1 cc. of 4 *N* sulfuric acid and 50 mg. of sodium bicarbonate. In this way it could be shown that the Minneapolis tap water contains less than 0.1 mg. of copper in a liter. It is still more convenient to add a buffer solution to the water instead of the combination of sulfuric acid and bicarbonate. The more acid the solution the less sensitive is the reaction. Finally, it was found that with an acetate buffer of pH 5.8 ± 0.2, good results are obtained.

Acetate Buffer. One hundred cc. of *N* sodium acetate and 7 cc. of *N* acetic acid.

Procedure. To 10 cc. of water, 1 cc. of buffer solution is added and then dioxime and the periodate as described above; the sensitivity after standing for five minutes is 0.15 mg. of copper in a liter.

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14. Kolthoff, *J. Am. Chem. Soc.*, **52**, 2222 (1930).

The latter procedure can be applied for the detection of copper in tap water if not more than traces of zinc or lead are present; 10 mg. of zinc in a liter has very little influence (color somewhat weaker than in blank without zinc); in the presence of larger amounts of zinc, the latter is precipitated as zinc periodate and the sensitivity decreases very much. The same holds for lead. A solution with 1 mg. of copper in a liter in the presence of 10 mg. of lead per liter gives a distinct reaction though a somewhat weaker color than without the lead. Ferric iron also interferes. Still 1 mg. of copper per liter in the presence of 10 mg. of iron per liter gives a distinct reaction. Addition of 1 to 2 drops of *N* disodium phosphate (Na_2HPO_4) before the addition of the buffer gives a great improvement. Under these conditions 1 mg. of copper in the presence of 20 mg. of iron per liter can easily be detected. Other cations such as cadmium, zinc or manganese all interfere, as they precipitate with the periodate. Therefore, the rhodanine reaction is of much more general application than the glyoxime reaction. The latter can only be applied in those cases in which the solution does not contain more than traces of other metal salts.

THE COLORIMETRIC DETERMINATION OF MANGANESE IN BIOLOGICAL MATERIAL*

The possible importance of manganese as a factor in animal metabolism has been indicated by various authors (*15*). With a view to studying more closely the function of this element in nutrition, it has been necessary to work out a technique for the accurate and rapid determination of small amounts of manganese in biological material, particularly in that of animal origin.

While various methods of determining manganese, as described in the literature, are fairly satisfactory under the conditions given, investigation has shown that in dealing with such minute amounts as are liable to occur in animal tissues, certain precautions are necessary which seem to have been overlooked by most workers.

The persulfate method of oxidation of the manganese to permanganate, in readiness for the colorimeter comparison, has been widely used since its introduction by Marshall (*16*) in 1901, and Wester (*17*) has worked out very carefully the conditions under which it can be used for the determination of very small amounts of manganese in such materials as the ash of plants. The periodate method of Willard and Greathouse (*18*) seems preferable to that of Marshall in that it requires no catalyst, and is claimed by its authors to be free from various faults of previous methods. It was originally applied to the determination of manganese in steels and iron ores, and the present paper seeks to show, as Wester has done for the per-

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* Richards, *Analyst*, **55**, 554 (1930).

15. See references in Skinner and Peterson, *J. Biol. Chem.*, **79**, 679 (1928).
16. Marshall, *Chem. News.*, **83**, 76 (1901).
17. Wester, *Rec. Trav. Chim. Pays-Bas.*, **39**, 414 (1920).
18. Willard and Greathouse, *J. Amer. Chem. Soc.*, **39**, 2366 (1917).

sulfate method, the conditions under which it may be used for the determination of minute amounts in organic material. It will be seen that, due regard being paid to one or two details in the procedure, the periodate method is preferable in the estimation of larger amounts.

Proposed Modifications

It has been found that in the application of the periodate method to the determination of traces of manganese, two points in particular require attention: (1) The acidity of the solution to be oxidized, and (2) the removal of chlorides.

I. Acidity of the Solution During Oxidation. (*a*) *Danger of Excess Acidity.* Willard and Greathouse, in describing their method, emphasize the danger of having insufficient acid present, and state that a very large concentration of acid does no harm. This is no doubt true for the amounts of manganese dealt with in their tests, but the lowest amount they used was 2.5 mg. of manganese, a quantity much beyond the amount present in a workable sample of most organic materials.

If the amount of manganese present is very small, *e. g.*, 0.005 mg. or less, as quite frequently occurs in the analysis of animal organs, the danger lies in excess of acidity, rather than in its insufficiency. In such cases an acidity of 15 per cent sulfuric acid (*i.e.*, 15 cc. of concentrated acid per 100 cc. of solution) is the maximum permissible. An acidity of 20 per cent is sufficient to prevent the full color from developing, or to cause it to fade rather rapidly, the solution generally assuming a yellow tint. Moreover, it has been found that if the color has been destroyed by excess of acidity, it cannot be fully restored by subsequent dilution of the solution.

In a recently published paper Skinner and Peterson (*19*) report that in a few instances during the oxidation with periodate, the permanganate color faded as the volume was reduced—a difficulty which they overcame by the addition of a few drops of syrupy phosphoric acid to the boiling solution. As their paper was published after the present tests of the method were satisfactorily concluded, I have not tested whether a coloration that has faded from excess of acidity can be restored by means of phosphoric acid, but it may be stated that with the acidity carefully restricted, no such fading has been experienced.

(*b*) *Rate of Color Development at Different Acidities.* Willard and Greathouse state that increase of acidity increases the rate of color development, and while this is true for the concentrations of 15 per cent sulfuric acid and over, with which they chiefly deal, it is not quite accurate where lower acidities are concerned. For all the amounts of manganese tested (0.0025-0.5 m.g.) the rate of oxidation appears to be a minimum when the concentration of sulfuric acid is about 9-10 per cent, the color appearing only very slowly at this concentration. Above this point the rate does increase with increasing acidity, but below it the rate increases as the acidity diminishes. Below 1 per cent the color develops very rapidly, but the solutions show the same yellowish tint and tendency to rapid fading as are found when the acidity is too great.

In view of these observations—the possibility of fading if the acidity is greater than 15 per cent or less than 1 per cent, and the slowness of the reaction at 9-10 per cent, it is recommended that in dealing with animal tissues conditions should be regulated so that the final acidity is about 5-6 per cent.

In the analysis of plant material, which has in general a higher manganese content, it is very seldom *essential* that this low acidity should be maintained, but it is simpler to adopt the same procedure for all classes of material, and to increase the acidity to 15 to 20 per cent after addition of the periodate, if it is evident that considerable amounts of manganese are present.

It seems probable, in view of our results, that the ''unexplained failures'' sometimes experienced by Reiman and Minot (*20*) in using solutions of greater acidity than 2 per cent nitric acid, have occurred in cases where the manganese present was very small in amount, and the variable acidity in the final solution arising from their acid-sulfate-fusion method of ashing, happened to overstep the limit permissible for traces of manganese.

II. The Removal of Chlorides. According to Willard and Greathouse the presence of chloride does not interfere with the oxidation, as the chlorine may be driven off by adding excess of periodate. This may, however, involve boiling the solution for a considerable time before the color comes up at all, and if the chlorine is incompletely removed, there is danger of the color fading to some extent before the estimation is finished. If little manganese is present, this continued boiling is inadvisable, in view of the careful regulation of the acidity which has been found necessary. Hence it is recommended that all chlorides should be destroyed before the oxidation stage, by repeated evaporation with concentrated sulfuric acid—a point on which Wester also lays stress (*21*).

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19. Skinner and Peterson, *J. Biol. Chem.*, **79**, 679 (1928).

20. Reiman and Minot, *J. Biol. Chem.*, **42**, 329 (1920).

21. Wester, *Biochem. Z.*, **118**, 158 (1921).

Details of Method as Adopted

I. Preparation of the Material for Oxidation. The process of wet ashing and the acid-sulfate-fusion method described by Reiman and Minot, are both cumbersome in view of the large number of routine analyses to be carried through, and the necessity for ease in manipulation at all stages of the determination. The method adopted therefore is that of ordinary ashing, with subsequent treatment of the ash with various acids.

Ash the material as completely as possible (in a silica basin) at a lowered heat, and evaporate to dryness with a little concentrated hydrochloric acid. Add a few cc. of sulfuric acid (33 per cent by volume), and 3-4 drops of concentrated nitric acid, and evaporate carefully to dryness on a water bath and sand bath, finishing off by gentle ignition over a Bunsen flame. Add 2-2.5 cc. of sulfuric acid (33 per cent) and a little water, and evaporate to white fuming stage, thus removing all traces of chlorides.

After cooling, dilute and filter into a small flask (50 cc.) for oxidation. Add to the solution one or two small pieces of pumice stone, previously purified by boiling with 5 per cent sulfuric acid and a little periodate. Evaporate down to about 10 cc. when the concentration of sulfuric acid will be 5-6 per cent (allowing for the loss of acid at the fuming stage), and the solution is ready for oxidation.

II. Oxidation. Add 0.3 g. of sodium periodate (or potassium periodate) and insert a loosely-fitting pear-shaped glass stopper in the neck of the flask. Heat to boiling, and immerse in boiling water for 30 minutes. (Wooden test-tube holders serve to hold the flasks in position in the bath.)

If the whole solution is required for the color comparison, cool, and transfer for the determination to the colorimetric tube described below.

If the solution has sufficient color to require dilution, either (*a*) dilute to the appropriate volume with 5 per cent sulfuric acid that has been boiled with a little periodate, or (*b*) add water till it has nearly the required dilution, and heat for 15 minutes longer in the bath. Transfer to a calibrated flask, make up to volume, and estimate the manganese by comparing with the standard solution.

III. Colorimetric Tubes. The tubes used are 10-cc. calibrated cylinders of uniform bore (with a total capacity of 12-13 cc. and length of 12-13 cm.) graduated in tenths of a cc. and made without the usual flange at the bottom, so that the tubes can be held closely together for the color-comparison. These tubes are most suitable for very dilute solutions. With a standard which contains 0.001 mg. of manganese per cc., 7-10 cc. give a very convenient depth of tint for matching, but a detectable pink color can be obtained with as little as 1 cc., and differences of 0.2 cc. give distinctly recognizable differences in tint.

If preferred, a colorimeter may be used when the solution is sufficiently strong, but in many cases the amount of manganese in organic materials is so small that it would require an excessive amount of material to give sufficient depth of color for the colorimeter. Hence we prefer to work always with the above tubes, and usually, with the above standard, bring the unknown solution approximately to this strength by choosing suitable amounts of material for oxidation, and by suitable dilutions.

It may be noted that Wester, in his critical study of the persulfate method, found it necessary to have special colorimetric tubes made with ground-glass caps, to protect the solutions from the action of reducing fumes. With the periodate method, we have found no necessity for such covers, under ordinary laboratory conditions.

IV. Standard Solutions. (*a*) *Stock Solution of Manganese Sulfate.* Pure potassium permanganate (0.144 g.) is dissolved in about 100 cc. of water, and reduced by sulfur dioxide. Instead of passing in sulfur dioxide, it is much simpler to generate the gas in the solution itself, by means of sulfuric acid and sodium sulfite or bisulfite. The solution is heated till the reaction takes place, and the excess of sulfur dioxide is then boiled off. This method of reduction does not seem to interfere in any way with the stability of the standard solution. Dilute to 1 liter (1 cc. of this solution = 0.05 mg. of manganese).

(*b*) *Standard Solution for Comparison.* Oxidize 20 cc. of stock solution with periodate in the usual way, and make up to 1 liter with 5 per cent sulfuric acid (previously boiled with periodate). (One cc. of this solution = 0.001 mg. of manganese.) This is the most useful concentration for the colorimeter tubes above described, but stronger solutions may be used if desired.

(*c*) *Stability of Standard Solutions.* Willard and Greathouse state that a remarkable feature of the solutions oxidized by periodate is their great stability when a slight excess of the reagent is present. Such a solution, kept for 3 months in a stoppered flask, when compared with a similar solution freshly oxidized, showed no change whatever.

We have found that even the very dilute standard described above (0.001 mg. of manganese per cc.) shows the same stability observed by Willard and Greathouse.

V. Purity of Reagents. A great advantage of the procedure outlined is the fact that the only chemicals introduced during the ashing process are the strong acids—hydrochloric, nitric, and sulfuric—and tests have shown that there is no difficulty in obtaining these entirely free from manganese. Nor have we ever found in our tests that any manganese is introduced as impurity from the silica basins, when subjected to the action of the acids as directed in the estimation. Reiman and Minot, on the other hand, find that the quartz beakers used in their acid-sulfate-fusion process frequently contain manganese, which is dissolved during the fusion process, resulting in contamination, which may amount occasionally to as much as 0.020 mg.

The only other chemical introduced in the present method is the periodate, which is almost invariably quite free from manganese. In only one lot have we found a slight manganese impurity, amounting to only 0.0005 mg. for 0.3 g. periodate, the amount used in the determination.

Modifications of Usual Procedure

The procedure described above is applicable to the great majority of vegetable and animal tissues, but in a few cases a slight modification of procedure is necessary: (*a*) for substances containing much calcium, *e. g.,* milk; (*b*) for substances containing much iron and very little manganese, *e. g.,* blood.

(*a*) *Substances Containing Much Calcium.* Unless most of the calcium is removed, it is difficult to avoid loss by spurting in evaporation to dryness with sulfuric acid. There is also danger of the minute amount of manganese present (*e. g.,* in milk) being carried down with the calcium sulfate if the ash is treated with sulfuric acid in the usual way. The procedure adopted is as follows:

Determination of Manganese in Milk. One hundred cc. of milk in a silica basin are evaporated down on the water-bath, protecting from possible contamination by particles of rust, which may contain considerable manganese. After ashing completely, and taking down to dryness with hydrochloric acid, the ash is moistened with a little water, and broken up as finely as possible. Twenty-five cc. of boiling sulfuric acid (33 per cent by volume) are added with careful stirring. After thorough cooling (overnight, if convenient), filter off into another silica basin, washing 5-6 times with 5 cc. of 33 per cent sulfuric acid. (NOTE: The filter paper must have been previously tested for its resistance to this strength of acid. If the paper available is not strong enough for 33 per cent acid, 20-25 per cent may be used, as this will remove sufficient of the calcium sulfate to permit subsequent evaporation to dryness. Ten per cent acid does not remove the calcium sufficiently.) Evaporate the filtrate to dryness and proceed as usual, except that it may be necessary, when filtering at the final stage before oxidation, to re-filter several times before washing, in order to get an absolutely clear solution.

(*b*) *Substances Containing Much Iron and Very Little Manganese.* If the amount of manganese present is minute, and the ratio of iron to manganese is high, *e. g.,* in blood and spleen, proceed thus: After evaporation to dryness with sulfuric acid, and ignition over a Bunsen burner, instead of adding 2-2.5 cc. of sulfuric acid (33 per cent), use a mixture of 1-2 cc. of syrupy phosphoric acid and 0.5 cc. sulfuric acid. The phosphoric acid is used to reduce the yellow tinge of the iron salt at the final matching stage. Further procedure is as usual. With no other animal tissue do we find this medification necessary. In the case of liver, the high amount does not interfere, on account of the dilution necessitated by the high manganese content of liver.

Tests of Method

The method has been applied in a large number of analyses of plant and animal tissues, with very satisfactory results, judged by (1) concordance of parallel determinations of the same sample, and (2) recovery of added manganese from the sample analyzed.

Some results for different classes of material are shown in Tables XI and XII.

TABLE XI

Concordance of Parallel Determinations

Substance		Manganese Content of Various Samples (Mg. of Mn per 100 G. of Dry Matter)				Average (Mg. of Mn per 100 G. of Dry Matter)
Grass..........................		61.3	61.2	61.7	61.2	61.4
Tapioca..........................		0.676	0.673	0.698	0.681	0.682
Potatoes (peeled).......	I	0.707	0.705	0.711	0.704	0.707
	II	1.19	1.15	1.18	1.18	1.18
	III	0.467	0.475	0.473	0.475	0.472
	IV	0.677	0.638	0.655	0.650	0.655
		(Mg. of Mn per 100 G. of Moist Tissue)				(Mg. of Mn per 100 G. of Moist Tissue)
Liver (vari. species)....	I	0.371	0.368			0.370
	II	0.229	0.227			0.228
	III	0.412	0.420			0.416
	IV	0.231	0.237			0.234
	V	0.248	0.250			0.249
	VI	0.137	0.144	0.137		0.139
Kidney..........................	VII	0.152	0.162			0.157
	II	0.174	0.174			0.174
Spleen *		0.018	0.018			0.018
Milk †	I	0.0039	0.0048	0.0042	0.0038	0.0041
		0.0043	0.0039	0.0040	0.0045	
		0.0044	0.0039	0.0040	0.0045	
	II	0.0037	0.0039	0.0040	0.0037	0.0041
		0.0051	0.0043			

* By modification of method for substance containing much Fe and little Mn.
† By modification of method for substance containing much Ca.

TABLE XII

Recovery of Added Manganese

Substance	Amount Analyzed	Mn Added	Total Mn Found	Mn in Substance Taken	Added Mn Found	Recovery
	Gram	*Mg.*	*Mg.*	*Mg.*	*Mg.*	%
Grass	2.011	0.25	1.48	1.23	0.25	100
	2.010	0.25	1.46	1.23	0.23	92
	2.011	0.50	1.76	1.23	0.53	106
	2.011	0.50	1.74	1.23	0.51	102
	2.010	1.00	2.16	1.23	0.93	93
	2.013	1.00	2.20	1.23	0.97	97
Tapioca	10.003	0.025	0.095	0.068	0.027	108
	10.007	0.050	0.122	0.068	0.054	108
Milk	100 cc.	0.0025	0.0067	0.0041	0.0026	104
	100	0.0025	0.0067	0.0041	0.0026	104
	100	0.0050	0.0097	0.0041	0.0056	112
	100	0.0050	0.0095	0.0041	0.0054	108
	100	0.010	0.0133	0.0041	0.0092	92
	100	0.010	0.0136	0.0041	0.0095	95
	100	0.020	0.0241	0.0041	0.0200	100
	100	0.020	0.0237	0.0041	0.0196	98
	100	0.040	0.0440	0.0041	0.0399	100
	100	0.040	0.0435	0.0041	0.0394	99
	34	0.080	0.080	0.0014	0.0786	98
Blood	25	0.0025	0.0039	0.0012	0.0027	108
	25	0.0050	0.0063	0.0012	0.0051	102
	25	0.020	0.0194	0.0012	0.0182	91
	25	0.040	0.397	0.0012	0.0385	96
	25	0.080	0.0756	0.0012	0.0744	93

THE DETERMINATION OF MANGANESE IN PLANT MATERIALS BY THE PERIODATE METHOD

In connection with investigations on the manganese content of plants carried on in this laboratory, the periodate method (*22*) was used extensively. It was found that this method, which is outlined in the official methods (*23*) for plant materials, can be modified advantageously.

The fundamental principle of this method is oxidation by a periodate in an acid solution that must be free from reducing agents. In the determination of manganese in ashed plant materials, the principal reducing agent to be removed is the hydrochloric acid used in dissolving the ash. The procedure given in the official methods calls for boiling with sulfuric and nitric acids in order to expel the hydrochloric acid. To ascertain whether it would not be practicable to omit this troublesome reducing agent, manganese determinations were made by dissolving the ashed plant material in nitric, sulfuric, and phosphoric acids, respectively, instead of in hydrochloric acid, the periodate being added directly to these solutions. The addition of sulfuric acid to the nitric and phosphoric acid solutions was omitted because it proved to be of no advantage. This simple modification made the procedure less troublesome, and resulted in a saving of time. The quantity of chlorine in the ash of plants is generally very small and is well taken care of by the periodate, which is added in excess.

The procedure as outlined in the official methods calls for the addition of ferric nitrate to the standard permanganate solution. This precaution had been suggested by Willard and Greathouse, who worked with materials rich in iron, such as steels and ores, because the color imparted by the iron salts interferes with the matching of the permanganate solutions. Plant materials, however, contain very little iron, and the small quantities present are generally prevented from imparting color to the solutions by the excess of phosphoric acid in plant ash. It was found quite safe, therefore, to omit the ferric nitrate. On the other hand, the addition of periodate to the standard permanganate solution was found to be very useful, since it serves as an excellent preservative.

A new precaution that was found to be necessary was the guarding of the solutions against alcohol vapors and other volatile reducing substances. The alcohol vapors in the laboratory air were found to pale or even to destroy completely the permanganate color in some cases. The color is restored on heating, but the determinations must be completed while the solutions are still hot, or the color disappears again.

Results obtained by the procedure as outlined in the official methods, and by dissolving the plant ash directly in nitric, sulfuric, and phosphoric acids, are offered for comparison in Table XIII. The materials selected for comparison were two cereal grains high in manganese, two cereal grains low in manganese, and wheat straw and corn stalks, which are much higher in manganese than the respective grains.

The modified procedure is as follows:

> Ash the plant materials in platinum dishes in an electric muffle. Add 5 cc. of nitric, sulfuric, and phosphoric acids, respectively, and 20 cc. of distilled water to each dish. Heat the dishes on a steam bath for a few minutes and wash the contents into beakers. Heat the solutions to boiling and keep at this temperature after the addition of 0.3 gram of potassium periodate until the full development of the permanganate color occurs.

21a. Davidson and Capen, *J. O. A. C.*, 12, 310 (1933).
22. Willard and Greathouse, *J. Am. Chem. Soc.*, 39, 2366 (1917).
23. Methods of Analysis, *A. O. A. C.*, 42, (1925).

A Schreiner colorimeter was used for comparing the solutions. The differences in the results obtained are within the limits of experimental error, but, if anything, better results are obtained by the modified procedure. Of the three acids used, phosphoric acid proved to be most suitable, as it developed the permanganate color in the shortest period of time; sulfuric acid was next in order, and nitric acid was last. In the determinations recorded in the table, the maximum time required for the full development of the permanganate color in the phosphoric acid solutions was only 2-3 minutes from the time the solutions were brought to boiling.

TABLE XIII

*Comparison of Results of Manganese * Determinations Made by the Periodate Method According to Official and Modified Procedures*

Plant Materials	Official Procedure	Nitric Acid	Sulfuric Acid	Phosphoric Acid
	%	%	%	%
Wheat	0.0085	0.0085	0.0073	0.0085
Rye	.0091	.0110	.0110	.0110
Rice	.0049	.0045	.0055	.0061
Corn	.0013	.0012	.0012	.0015
Wheatstraw	.0229	.0259	.0224	.0274
Cornstalks	.0076	.0076	.0076	.0076

* Mn_3O_4.

COLORIMETRIC METHODS FOR THE DETERMINATION OF MANGANESE IN PLANT MATERIALS *

The development of convenient analytical apparatus and easy and accurate methods of analysis is always followed by an increased volume of useful research.

Thus the potassium periodate method adopted by the Association of Official Agricultural Chemists for plant analysis has stimulated research relating to the rôle of manganese in plant and animal life and to the manganese content of food stuffs. However, other methods are available for the colorimetric method of determination of small quantities of manganese. The lead peroxide method suggested by Crum (*24*) in 1845 was the first attempt to determine manganese colorimetrically. Because this method has been universally considered to be unsatisfactory, it has not been used in this investigation. The sodium bismuthate method, however, suggested by Reddrop and Ramage (*25*) in 1895, and the ammonium persulfate method, suggested by Marshall (*26*) in 1901, were widely used for the estimation of small quantities of manganese until the discovery of the potassium periodate method by Willard and Greathouse (*27*).

The adoption of the periodate method by the A.O.A.C. was not preceded by extensive collaborative work, and there is no record of any collaborative work to test the comparative merits of the principal colorimetric methods used by different investigators. The object of this investigation, therefore, was to compare the periodate method with the sodium bismuthate and the ammonium persulfate methods and also with the gravimetric method for determining manganese in plants outlined in the official methods (*28*).

Materials and Procedures

Five cereals, wheat straw, and four leafy vegetables with a sufficiently wide range of variation in their manganese content were selected for analysis. Two inorganic manganese compounds, potassium permanganate and manganic oxide (Kahlbaum's) were also analyzed.

The periodate method used was a modification reported previously by the writers (*29*). Phosphoric acid was used in preparation of the solutions. This modified procedure overcomes without special precautions the difficulties encountered by Richards (*30*). Skinner and Peterson (*31*) also found that this modified procedure is helpful in overcoming the interference of calcium salts in analyzing animal materials for manganese. The sodium bismuthate method used was the modification outlined by Gortner and Rost (*32*), who used a high concentration of sulfuric acid to hasten the oxidation of the manganese and to prevent the precipitation of basic bismuth salts. The ammonium persulfate method as outlined by Newcomb and Sankaran (*33*) was used.

To prevent the retention of manganese by silica the acid-insoluble residue was digested with hydrofluoric and sulfuric acids. The difficulties experienced by Gortner and Rost (*32*) while using this procedure on soils were not encountered as practically all the residue went into solution after the digestion.

Manganese in Plant Materials

Wheat, rye, corn, rice, oats, wheat straw, lettuce, kale, beet tops, and broccoli were ground in air-dried condition and analyzed for manganese by the periodate and persulfate methods. Some of these materials were also analyzed by the bismuthate method.

The results are given in Table XIV. The determinations by the periodate and the persulfate methods are in close agreement, and in four out of five cases the determinations by the bismuthate method

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* Davidson and Capen, *J.A.O.C.*, **14**, 457 (1935).

24. Crum, *Ann. Chem. Phar.*, **55**, 219 (1845).

25. Reddrop and Ramage, *J. Chem. Soc.*, **67**, 775 (1895).

26. Marshall, *Chem. News*, **83**, 76 (1901).

27. Willard and Greathouse, *J. Am. Chem.*, **39**, 2366 (1917). Complete bibliography on development of colorimetric methods for the estimation of manganese till 1916.

28. Methods of Analysis, *A.O.A.C.*, **40**, (1925).

29. Davidson and Capen, *Assoc. of Off. Agr. Chem.*, **12**, 310 (1929).

30. Richards, *Analyst*, **55**, 554 (1930).

31. Skinner and Peterson, *J. Biol. Chem.*, **88**, 347 (1930).

32. Gortner and Rost., *J. Ind. Eng. Chem.*, **6**, 522 (1912).

33. Newcomb and Sankaran, *Ind. J. Med. Research*, **16**, 788, (1929).

TABLE XIV

Manganese in Plant Materials

(Percentage of Mn_3O_4 on air-dried basis)

Plant Materials	Methods		
	Potassium Periodate	Ammonium Persulfate	Sodium Bismuthate
Wheat	0.0073	0.0073	0.0070
Rye	0.0099	0.0099	....
Corn	0.0010	0.0010	0.00058
Rice	0.0014	0.0015	....
Oats	0.0067	0.0070	....
Wheatstraw	0.0218	0.0209	0.0161
Lettuce	0.0209	0.0218	0.0161
Kale	0.0157	0.0160	....
Beet tops	0.0182	0.0167	0.0152
Broccoli	0.0051	0.0061	....

are much lower than those obtained by the other two methods. It also took considerably longer time to develop the permanganate color with sodium bismuthate than with potassium periodate or ammonium persulfate. When allowed to stand for about 24 hours the permanganate color developed with potassium periodate and ammonium persulfate suffered no change, while the color developed with sodium bismuthate faded quite appreciably. The claim of Gortner and Rost (*Loc. cit.*) and others that oxidation with ammonium persulfate does not develop the true permanganate color was not substantiated by these results. Gortner and Rost obtained better results with sodium bismuthate than with ammonium persulfate.

However, a close examination of their results shows that they were not comparing the relative merits of these two methods, but were comparing the methods for preventing retention of manganese by silica, and what they actually found was that the fusion with sodium carbonate used by them for this purpose is more suitable for soils than digestion with hydrofluoric and sulfuric acids used by Hillebrand (*34*) for the same purpose in rock analysis. When they repeated the digestion with hydrofluoric acid three times, their results obtained with the persulfate method were practically identical with those obtained with the bismuthate method.

The results in Table XIV show that the potassium periodate and ammonium persulfate methods are equally suitable for the determination of manganese in plant materials. Ammonium persulfate is much cheaper than potassium periodate. On the other hand, when the plant materials contain an appreciable quantity of chlorides the ash must be ignited with sulfuric acid to expel the chlorine if the persulfate method is used, while in the use of the periodate method chlorides (in contradistinction from hydrochloric acid) do not interfere.

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34. Hillebrand, *U. S. Geol. Survey Bull.* 422, (1910).

Manganese in Inorganic Manganese Compounds

Aliquots of 1 cc. of 0.1 *N* potassium permanganate solution, to which enough sodium oxalate was added to destroy the pink color, and of 2 mg. of manganic oxide dissolved in nitric acid were evaporated, respectively, nearly to dryness and analyzed for manganese by the three methods. The results, given in Table XV, show again that identical and practically theoretical values for manganese were obtained by the periodate and persulfate methods, while those obtained with the bismuthate methods were considerably lower.

TABLE XV

Manganese in Potassium Permanganate and in Manganic Oxide

Manganese Compounds	Aliquot	Theoretical quant. of Mn_3O_4	Mn_3O_4 determined by the		
			Potassium Periodate Method	Ammonium Persulfate Method	Sodium Bismuthate Method
	1 cc. of		*Mg.*	*Mg.*	*Mg.*
Potassium Permanganate	0.1 N sol'n	1.52	1.52	1.52	1.37
Manganic Oxide	2 mg.	1.93	1.98	1.98	1.67

Gravimetric Determination of Manganese in Plant Materials

Wheat, rye, wheat straw, lettuce, and kale were analyzed gravimetrically for manganese. The results are given in Table XVI. Column 1 of this table gives the manganese values by the periodate method (taken from Table XIV; column 2 gives the gravimetric values and column 3 gives the values obtained by dissolving the gravimetric precipitates and oxidizing them with potassium periodate.

TABLE XVI

Determination of Manganese in Plant Materials by the Gravimetric and Potassium Periodate Methods

(Percentage of Mn_3O_4 on air-dried basis)

Plant Materials	Potassium Periodate Method	Gravimetric Method	Manganese in Grav. Precip. Det'n by Potass. Periodate
Wheat	0.0073	0.022	0.0058
Rye	0.0099	0.031	0.0079
Wheatstraw	0.0218	0.042	0.0130
Lettuce	0.0209	0.108	0.0184
Kale	0.0157	0.080	0.0151

A comparison of the three columns of this table shows that the gravimetric values are much higher and their periodate values much lower than the values obtained by the potassium periodate method directly. Evidently foreign material was precipitated with the manganese, while the precipitation of the manganese itself was not complete.

The results demonstrate that the gravimetric method is not accurate for estimating small quantities of manganese in plant materials, thus corroborating the generally accepted view.

The Colorimetric Determination of Manganese in Water Using the Periodate Method of the "Standard Methods for the Examination of Water and Sewage" *

The following directions apply to the determination of manganese below 10 ppm and in the absence of excessive amounts of manganese. Under these conditions the periodate procedure is indicated as a preferable method.

1. **Reagents.** (*a*) *Manganese sulfate standard solution.* Dissolve 0.1438 g. of $KMnO_4$ in distilled water to which has been added 2 to 3 ml. of 2N H_2SO_4. Reduce by adding 0.4 g. of $NaHSO_3$. Boil off the excess SO_2 and dilute to 1 liter with distilled water.

(*b*) *Sodium paraperiodate-sulfuric acid solution.* Prepare a H_2SO_4 solution by adding 120 ml. of concentrated H_2SO_4 to 1500 ml. of distilled water and diluting to 2 liters. Add 2.4 g. of $Na_3H_2IO_6$, heat to boiling and place, for 30 minutes, in a boiling water bath.

(*c*) *Manganese color standards.* Add 1.2 ml. of concentrated H_2SO_4 and 30 ml. of sodium paraperiodate-sulfuric acid reagent to exactly 20 ml. of standard $MnSO_4$ solution. After thoroughly mixing, add 0.3 g. of solid $Na_3H_2IO_6$, heat to boiling and place, for 30 minutes, in a boiling water bath. Cool and dilute to 1 liter with H_2SO_4 reagent. This standard contains 0.001 g. of permanganate manganese per liter. Prepare a series of color standards in accordance with Table XVII and store in glass stoppered bottles which have been cleaned with hot dichromate cleaning solution, washed and dried.

2. **Procedure.** Add 3 or 4 drops of concentrated sulfuric acid to 100 ml. of the water sample and evaporate to dryness in an evaporating dish. Measure out 100 ml. of sodium paraperiodate-sulfuric acid reagent. With this, moisten the residue and transfer to a 250 ml. Erlenmeyer flask. Then wash the dish thoroughly by repeated use of all the remaining acid reagent, pouring the washings into the flask. Add 0.3 g. of solid sodium paraperiodate, heat to boiling and place the flask in a boiling water bath for 30 minutes. Cool to room temperature and transfer the solution to a 100 ml. Nessler tube. Compare with standards and read directly in parts per million provided a 100 ml. portion of the sample was used for the test.

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* Reprinted from "Standard Methods for the Examination of Water and Sewage," American Public Health Association, 1790 Broadway, New York 19, N. Y., 1946. pp. 56-57 by permission of the publishers.

TABLE XVII

Color Standards for Determination of Manganese

Use 100 ML Comparison Tubes

Permanganate Manganese	Reagent (a, b)	ppm of Mn when 100 ml. sample is used
Ml.	*Ml.*	
0.0	100.0	0.0
2.5	97.5	0.025
5.0	95.0	0.05
7.5	92.5	0.075
10.0	90.0	0.1
20.0	80.0	0.2
30.0	70.0	0.3
40.0	60.0	0.4
50.0	50.0	0.5
60.0	40.0	0.6
70.0	30.0	0.7
80.0	20.0	0.8
90.0	10.0	0.9
100.0	0.0	1.0

In all cases prepare a comparison tube containing no permanganate manganese, but 100 ml. of sodium paraperiodate-sulfuric acid solution as a blank, as this reagent has a color greater than that which might be interpreted as zero manganese.

CHAPTER IV

QUANTITATIVE DETERMINATION OF ORGANIC COMPOUNDS

POLYALCOHOLS IN THE PRESENCE OF EACH OTHER *

The work of Malaprade (*1*) on the action of periodic acid and periodates on polyalcohols has opened up a new field in the analysis of a number of organic compounds. Hudson (*2, 3*) and co-workers have made valuable use of the Malaprade reaction in their studies of sugars, Fleury (*4, 5*) and associates have applied the reaction to several organic compounds, and Nicolet and Shinn (*6*) have shown the reaction to be applicable to alpha-amino alcohols. Price and Kroll (*7*) have given a thorough discussion of the kinetics of the periodate oxidation of 1, 2-glycols.

The Malaprade reaction has been applied by the authors to the quantitative determination of certain polyalcohols in the presence of each other, particularly glycerol and ethylene glycol. The reaction has also been used to distinguish qualitatively between solutions of ethylene glycol and glycerol. By using an acid dichromate oxidation in conjunction with the Malaprade reaction, a solution containing three glycols may be analyzed for each of the three components. This procedure is useful in the investigation of unknown solutions suspected of containing mixed glycols.

Glycerol and ethylene glycol may be determined in the presence of each other by either an acidimetric-iodometric procedure or a single acidimetric titration using a glass electrode in a potentiometric method.

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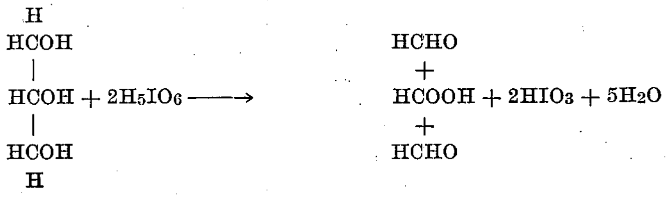
* Reprint of paper by Charbonnier and Coleman, *Ind. Eng. Chem., Anal. Ed.*, 12, 384 (1940).

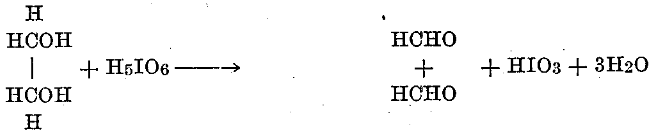
1. Malaprade, *Bull. Soc. Chim.* (4) 43, 683 (1928): (5) 1, 833 (1934).
2. Hann, Maclay, and Hudson, *J. Am. Chem. Soc.*, 61, 2432 (1939).
3. Maclay, Hann, and Hudson, *Ibid.*, 61, 1660 (1939).
4. Fleury, *Mikrochemie*, 25, 263 (1938).
5. Fleury and Boisson, *Compt. rend.*, 204, 1264 (1937): 208, 109 (1938).
6. Nicolet and Shinn, *J. Am. Chem. Soc.*, 61, 1615 (1939).
7. Price and Kroll, *Ibid.*, 60, 2726 (1938).

The reactions of glycerol and ethylene glycol with periodic acid are given in the equations:



$$\begin{array}{l}\mathrm{H}\\\mathrm{HCOH}\\\;|\\\mathrm{HCOH} + 2\mathrm{H_5IO_6} \longrightarrow\\\;|\\\mathrm{HCOH}\\\mathrm{H}\end{array}\qquad\begin{array}{l}\mathrm{HCHO}\\\;+\\\mathrm{HCOOH} + 2\mathrm{HIO_3} + 5\mathrm{H_2O}\\\;+\\\mathrm{HCHO}\end{array}$$

Glycerol



$$\begin{array}{l}\mathrm{H}\\\mathrm{HCOH}\\\;|\quad + \mathrm{H_5IO_6} \longrightarrow\\\mathrm{HCOH}\\\mathrm{H}\end{array}\qquad\begin{array}{l}\mathrm{HCHO}\\\;+\quad + \mathrm{HIO_3} + 3\mathrm{H_2O}\\\mathrm{HCHO}\end{array}$$

Ethylene Glycol

Periodic acid may be considered as a monobasic acid or a dibasic acid according to the pH to which it is titrated. This is shown in Figure 1 (page 3), which gives the potentiometric titration of a solution of periodic acid. It is seen that the first hydrogen is neutralized at a pH of about 5.5, and the second hydrogen at a pH of about 10.0. The inflection in pH at the second equivalence point is not very sharp.

The first equivalence point comes at about the mid-point of methyl red indicator and it is possible to use this indicator for the titration. The change in pH at the second equivalence point is not sharp enough to permit the use of an indicator and a potentiometric method must be used. If we consider the reactions given above and regard periodic acid as a monobasic acid, with glycerol two equivalents of acid goes to form three equivalents and with ethylene glycol one equivalent goes to form one equivalent. If periodic acid is considered as a dibasic acid, in the case of glycerol four equivalents go to form three equivalents, and in the case of ethylene glycol two equivalents go to form one equivalent.

It is possible, therefore, in an aqueous solution containing glycerol and ethylene glycol, to determine glycerol acidimetrically using methyl red as an indicator and to determine ethylene glycol by titrating potentiometrically to a pH of about 10.0. Alternatively, and more accurately, the ethylene glycol may be determined by an iodometric method.

Reagents and Apparatus

Standard sodium thiosulfate solution, 0.2 *N*. Potassium dichromate solution, 24 grams per liter. Potassium iodide solution, 20 per cent by weight.

Periodic acid solution, approximately 0.05 *N*, as a monobasic acid. Dissolve 11 grams of periodic acid (The G. Frederick Smith Chemical Company, Columbus, Ohio) in distilled water, dilute with distilled water to 1000 ml., and filter through a sintered glass filter. Store the solution in a dark-glass bottle and keep closed with a glass stopper. This solution decreases slowly in oxidizing power with time. A blank on the solution must be run each day that analyses are made.

Standard sodium hydroxide solution, 0.1 *N*.

Erlenmeyer flasks, capacity 1000 ml. Glass-stoppered flasks are preferred, but rubber stoppers may be used if care is taken that no solution comes in contact with the rubber. Erlenmeyer flasks, with ground-glass joints, capacity 500 ml.

Glass electrode pH meter. Any suitable apparatus is satisfactory.

Procedure

Acidimetric-Iodometric. In order to ensure the necessary excess periodic acid, the sodium thiosulfate required for a sample should not be less than four-fifths of the sodium thiosulfate required by the blank. For 50 ml. of 0.05 *N* periodic acid, this corresponds to about 0.09 gram of glycerol and 0.125 gram of ethylene glycol. Take a sample of a size that will not contain oxidizable matter in excess of that equivalent to 0.09 gram of glycerol. Dilute the sample to 50 ml. in a 1000-ml. Erlenmeyer flask. Pipet in exactly 50 ml. of the periodic acid solution and mix. Stopper with a glass or rubber stopper and allow to stand for 40 to 80 minutes at room temperature.

At the end of the oxidation period, add about 100 ml. of distilled water and mix. Titrate in the flask with 0.1 *N* sodium hydroxide. Run in about 20 ml. of the sodium hydroxide and then add exactly 2 drops of methyl red indicator solution. Do not add more than this quantity of indicator. Continue the titration to the disappearance of the pink color. As the end point is approached, the sodium hydroxide solution must be added drop by drop and the color of the solution observed carefully. Make all buret readings to 0.01 ml.

Take the solution that has been titrated, and add 150 ml. of distilled water, 30 ml. of 20 per cent potassium iodide solution, and 25 ml. of 6 *N* sulfuric acid. Titrate the solution with 0.2 *N* sodium thiosulfate to a light orange color. Add 2 ml. of fresh starch indicator solution and titrate to the disappearance of the starch-iodine color. When the titration is completed, the solution is colored pink owing to the methyl red indicator present. The end point is very sharp, and care must be taken that it is not overrun. Make all buret readings to 0.01 ml.

Run a blank using 50 ml. of distilled water instead of the sample and do both the acidimetric and iodometric titrations.

Calculation

1 ml. of *N* sodium hydroxide = 0.09206 gram of glycerol (acidimetric)

Let B = ml. of sodium hydroxide for blank on the periodic acid solution

A = ml. of sodium hydroxide for sample

Then

$$\frac{(A - B) \times \text{acidimetric glycerol factor} \times \text{normality} \times 100}{\text{Weight of sample}} = \%\text{ of glycerol} = G$$

1 ml. of *N* sodium thiosulfate = 0.023015 gram of glycerol (iodometric by periodic acid). Let B′ = ml. of sodium thiosulfate for blank, A′ = ml. of sodium thiosulfate for sample

Then

$$\frac{(B' - A') \times \text{iodometric glycerol factor} \times \text{normality} \times 100}{\text{Weight of sample}} = T$$

Where T = glycerol and ethylene glycol calculated as % of glycerol

If E = % of ethylene glycol, then E = 1.348 (T − G).

Dichromate Oxidation. In case the solution contains a third glycol, which is not oxidized by periodic acid, it may be determined by a separate dichromate oxidation. Diethylene glycol is an example of such a compound.

Take a sample one half the size of that taken previously and dilute to 25 ml. with distilled water in a 500 ml. Erlenmeyer flask with an interchangeable ground-glass connection. Pipet in 25 ml. of potassium dichromate solution containing 24 grams of potassium dichromate per liter and measure in 40 ml. of concentrated sulfuric acid. Add a few glass beads, connect the flask with a water-cooled condenser, and boil vigorously on a hot plate for 20 minutes. Rinse down the condenser and walls of the flask, cool to room temperature, and dilute to about 300 ml. with distilled water. Add 10 ml. of 20 per cent potassium iodide solution, mix, and titrate with 0.2 *N* sodium thiosulfate until the color of the solution becomes lighter. Add 1 ml. of starch indicator solution and continue the titration to the end point, which is the change from a dark opaque to a clear green color.

Run a blank using 25 ml. of distilled water instead of the sample.

Calculation

1 ml. of *N* sodium thiosulfate = 0.006576 gram of glycerol (dichromate oxidation)

Let B = ml. of sodium thiosulfate for blank, A = ml. of sodium thiosulfate for sample

Then

$$\frac{(B - A) \times \text{dichromate glycerol factor} \times \text{normality} \times 100}{\text{Weight of sample}} = X$$

(X = glycerol, ethylene glycol, and diethylene glycol calculated as % of glycerol)

(X − T) × 0.807 = % of diethylene glycol.

Potentiometric. Titrate a solution of 50 ml. of the periodic acid solution in 150 ml. of distilled water with 0.1 *N* sodium hydroxide, using a glass electrode pH meter to follow the change in pH. Determine the first equivalence point by noting the maximum change in pH with addition of sodium hydroxide. This equivalence point will be found to occur at a pH of about 5.5. Add more 0.1 *N* sodium hydroxide, equal to the volume required to reach the first equivalence point, and measure the pH of the solution. This will be about 10.0.

Oxidize a solution of the sample with periodic acid as described above. Dilute with 100 ml. of distilled water and titrate with 0.1 *N* sodium hydroxide to the first equivalence point, using the glass electrode pH meter to locate the point as in the blank. Record the volume of 0.1 *N* sodium hydroxide used, A. Continue the titration with 0.1 *N* sodium hydroxide to the pH found for the second equivalence point of the blank. Record the volume of sodium hydroxide as X.

Calculation

1 ml. of *N* sodium hydroxide = 0.09206 gram of glycerol = 0.06205 gram of ethylene glycol

Let B = ml. of sodium hydroxide for blank at first equivalence point
A = ml. of sodium hydroxide for sample at first point
X = ml. of sodium hydroxide for sample at second point

Then

$$\frac{(\mathrm{A}-\mathrm{B}) \times \text{glycerol factor} \times \text{normality} \times 100}{\text{Weight of sample}} = \%\text{ of glycerol}$$

$$\frac{(3\mathrm{B}-\mathrm{X}-\mathrm{A}) \times \text{ethylene glycol factor} \times \text{normality} \times 100}{\text{Weight of sample}} = \%\text{ of ethylene glycol}$$

Analytical Results

The results obtained by analyzing aliquots of synthetic solutions containing known amounts of glycerol and ethylene glycol, using the acidimetric-iodometric procedure and the potentiometric acidimetric procedure, are given in Table XVIII. The synthetic solutions were prepared from separate solutions which were standardized by oxidation with acid dichromate.

TABLE XVIII

Analysis of Glycerol-Ethylene Glycol Solutions

Glycerol Present	Glycerol Found, A.-I.[a]	Error	Glycerol Found, Pot.[b]	Error	Glycol Present	Glycol Found, A.-I.[a]	Error	Glycol Found, Pot.[b]	Error
Mg.	*Mg.*	%	*Mg.*	%	*Mg.*	*Mg.*	%	*Mg.*	%
48.8	47.7	−2.25	53.2	+9.02	153.0	160.8	+ 5.10	155.9	+1.90
......	48.3	−1.02	49.6	+1.64	......	154.9	+ 1.24	......	......
49.1	49.7	+1.22	49.6	+1.02	149.4	149.0	− 0.27	153.9	+3.01
97.5	96.7	−0.82	101.0	+3.59	102.0	105.3	+ 3.24	103.7	+1.67
......	......	......	97.3	−0.21	......	......	......	103.9	+1.86
98.2	98.0	−0.20	98.4	+0.20	99.6	102.3	+ 2.71	106.1	+6.53
146.3	143.7	−1.78	150.5	+2.87	51.0	57.6	+12.94	50.5	−0.98
......	145.4	−0.62	145.0	−0.89	......	54.7	+ 7.25	53.9	+5.69
147.2	146.7	−0.34	149.1	+1.29	49.8	50.7	+ 1.81	52.7	+5.82

[a] A.-I. = acidimetric-iodometric procedure.
[b] Pot. = potentiometric acidimetric procedure.

The potentiometric titrations of a blank and of three samples containing varying percentages of glycerol and ethylene glycol are shown by the curves given in Figure 3. It is to be noted that there is a slight increase in the pH at the first equivalence point due to the fact that periodic, iodic, and formic acids are being titrated. With increasing amounts of formic acid, the pH at the first equivalence point is increased slightly.

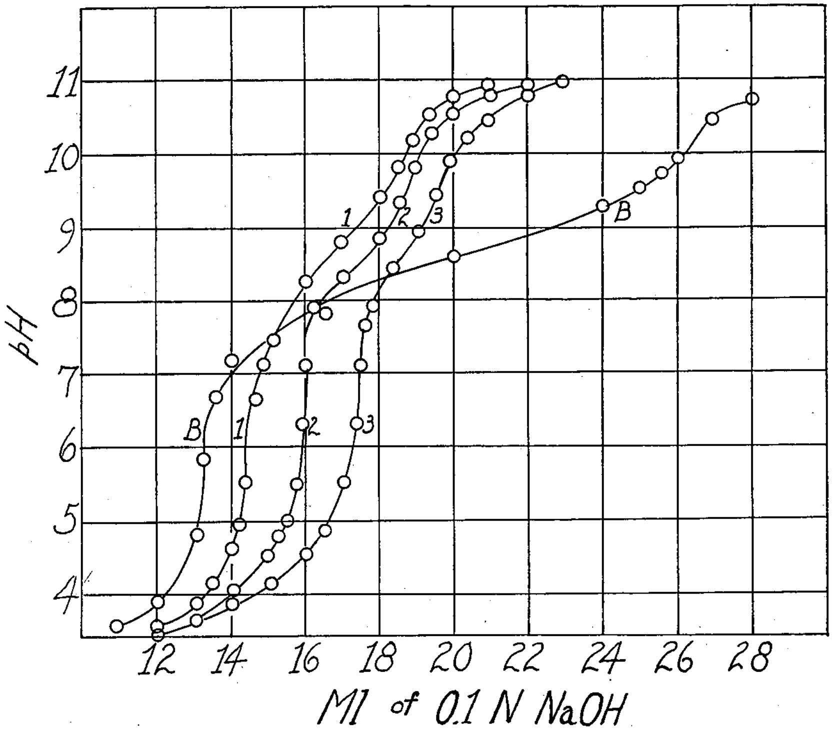


FIG. 3. Potentiometric titration of solution of H_5IO_6 and glycerol-ethylene glycol samples.

The results obtained by analyzing aliquots of solutions containing glycerol, ethylene glycol, and diethylene glycol, using the acidimetric-iodometric procedure on one aliquot and the acid dichromate oxidation on a second aliquot, are given in Table XIX.

Table XX gives the results reported by six different laboratories using the acidimetric-iodometric procedure in analyzing a given sample of material for glycerol and ethylene glycol. The material was extracted with water and aliquots of the extract were analyzed. The individual results are given for each laboratory to show the variations

TABLE XIX

Analysis of Solutions Containing Glycerol, Ethylene Glycol, and Diethylene Glycol

Glycerol		Error	Ethylene Glycol		Error	Diethylene Glycol		Error
Present	Found		Present	Found		Present	Found	
Mg.	*Mg.*	%	*Mg.*	*Mg.*	%	*Mg.*	*Mg.*	%
98.2	93.6	−4.68	52.4	56.3	+7.44	42.4	41.2	−2.83
49.1	47.7	−2.85	101.2	103.1	+1.88	42.4	40.7	−4.01
49.1	48.7	−0.81	53.1	53.5	+0.75	84.9	81.2	−4.36

TABLE XX

Analyses for Glycerol and Ethylene Glycol

(On a given sample by six different laboratories using the acidimetric-iodometric procedure)

	Laboratory						Grand Av.	Maximum Variation
	1	2	3	4	5	6		
Glycerol, %	8.74	8.78	8.82	9.13	8.75	8.61	8.88	0.67
	8.92	8.93	8.95	9.28	8.75	8.85		
	8.82	9.06	8.81	9.16	8.76	8.64		
	8.92	9.01	8.85	9.16	8.74	8.63		
Av.	8.85	8.95	8.86	9.18	8.75	8.68		
Ethylene glycol, %	4.90	5.51	5.08	4.95	5.41	5.57	5.29	1.25
	4.72	5.59	5.46	4.88	5.77	5.27		
	4.87	5.26	5.20	5.02	5.82	5.97		
	4.72	5.33	5.24	5.09	5.94	5.27		
Av.	4.80	5.42	5.25	4.99	5.74	5.52		

encountered by a given analyst. The error in the determination of ethylene glycol is always higher than the error for glycerol, since the ethylene glycol is not determined directly.

Qualitative Test to Distinguish Between Glycerol and Ethylene Glycol Solutions

Since glycerol reacts with periodic acid to produce formic acid, whereas ethylene glycol does not, a simple test may be devised to distinguish between the two when present alone.

Take about 2 ml. of the solution to be tested, add a drop of methyl red indicator solution, and cautiously neutralize with dilute sodium hydroxide or dilute acid, leaving the solution just on the alkaline side of methyl red. Take about 2 ml. of a solution of periodic acid, add a drop of methyl red, and adjust to the neutral point of the indicator, leaving the solution just on the alkaline side. An adjusted solution of sodium paraperiodate or potassium metaperiodate may be used. Mix the sample with the periodate solution and observe. If glycerol is present, the solution will turn pink immediately.

Determination of Glycerol in Presence of Other Organic Compounds

The acidimetric method for glycerol has been found very valuable in the determination of glycerol in the presence of a variety of organic compounds. It is only necessary that the other compounds do not react with periodic acid or if they do react, then no acid is formed.

Examination of Unknown Solutions

Solutions known to contain polyalcohols may be examined by oxidizing with periodic acid as described and calculating the results of the acidimetric and iodometric titrations to per cent of glycerol. An acid dichromate oxidation may also be made on the solution and the result calculated to per cent of glycerol. If all three values check, then glycerol is the only material present. If the values are different, a mixture of polyalcohols is indicated and a comparison of the figures obtained will permit some conclusions to be drawn as to the nature of the alcohols.

The determination of diglycols ($C_2HOH\cdot CO\cdot CH_2OH$) in the presence of monoglycols such as ethylene glycol ($C_2H_5OH\cdot C_2H_5OH$) as in the analysis of refined grade monoglycols wherein the diglycols are present in amounts of 1-3 per cent has been described by Francis (*8*). The method may also be applied to determinations having larger diglycol contents. The precision is ±0.1 to 0.2 per cent for small amounts of contaminating diglycol.

The method depends upon the oxidation of the monoglycols by use of excess periodic acid in neutral solution followed by distillation of the aldehydes thus formed to give a resulting solution containing excess periodic acid, iodic acid as a reduction product from periodic acid, and the diglycol to be determined which has remained unchanged throughout.

The solution thus obtained from an aliquot portion of the original sample is then made alkaline with sodium carbonate and the periodic acid reduced by the addition of hydrogen peroxide followed by distillation to reduce the volume to 20 ml. This sample is made acid with sulfuric acid an excess of 0.1 *N* potassium dichromate added and the diglycols oxidized by 45 minutes refluxing. The resulting sample is diluted to 1000 ml. and a 10 ml. aliquot portion diluted to 100 ml. employing 0.1 *N* sodium hydroxide.

The excess dichromate is then determined polaragraphically with standardization and blank determinations appropriately provided. The oxidation by dichromate gives an empirical factor for the oxidation reaction but one which is reproducible. Typical analyses are given to justify the claims of accuracy following this procedure.

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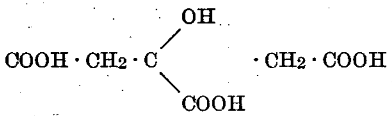
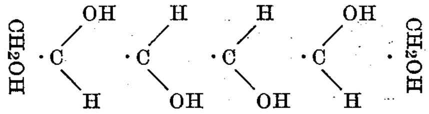
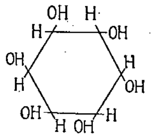
8. Francis, *Anal. Chem.*, 21, 1238 (1949).

TABLE XXI

The Oxidation of Organic Compounds Containing Alcoholic Groups By Periodic Acid at Ordinary Temperatures *
"The Malaprade Reaction"

Reagent Oxidized	Moles HIO_4 Req'd	Re-action Time Hours	Temp. De-grees O	Reaction Products	Equivalent For $H_2Ce(ClO_4)_6$ Oxi-dation in 4 N $HClO_4$	Time of Re-action Min	Temp C	Liter-ature Refer-ence **
C_2H_5OH (Ethyl Alcohol)	0	24	RT	None	Color Reaction		RT	*(1)*
$CH_2OH \cdot COOH$ (Glycolic Acid)	0	48	19	None				*(1)*
 $COOH \cdot CH_2 \cdot C(OH)(COOH) \cdot CH_2 \cdot COOH$ (Citric Acid)	0	24	14	None	14	30	10	*(1, 2)*
$COOH \cdot CH_2 \cdot CHOH \cdot COOH$ (Malic Acid)	0	24	14	None	8	15	25	*(1, 2)*
$CH_2OH \cdot CH_2OH$ (Ethylene Glycol)	2	6 (44)	RT	$2HCHO + H_2O + HIO_3$				*(1)*
 $CH_2OH \cdot C(OH)(H) \cdot C(H)(OH) \cdot C(H)(OH) \cdot C(OH)(H) \cdot CH_2OH$ (Dulcitol)	10	1 (24)	21	$2HCHO + 4HCOOH + H_2O + 5HIO_3$				*(1)*
$CH_2OH \cdot (CHOH)_5 \cdot CH_2OH$ (Volemitol)	12	1 (24)	19	$2HCHO + 5HCOOH + H_2O + 6HIO_3$				*(1)*
 (Anositol)	12	20	RT	Principle reaction $HCOOH + 6HIO_3$ Side reaction with HIO_3 to form CO_2				*(1)*
$CH_2OH \cdot (CHOH)_4 \cdot CH_2OH$ (Mannitol)	10	1	RT	$2HCHO + 4HCOOH + H_2O + 5HIO_3$				*(1)*
$COOH \cdot (CHOH)_2 \cdot COOH$ (Tartaric Acid)	2	1	15	$2CHO \cdot COOH + H_2O + HIO_3$	6	10	26	*(1, 2)*
$CH_2OH \cdot (CHOH)_4 \cdot COOH$ (Gluconic Acid)	8	2	RT	$HCHO + 3HCOOH + CHO \cdot COOH + H_2O + 4HIO_3$	6	10	26	*(1, 2)*
$COOH \cdot (CHOH)_4 \cdot COOH$ (Saccharic Acid)	6	1	RT	$2HCOOH + 2CHO \cdot COOH + H_2O + 3HIO_3$				*(1)*
$CH_2OH \cdot CO \cdot CH_2OH$ (Dihydroxyacetone)	2	1	22	$HCHO + CH_2OH \cdot COOH + HIO_3$				*(1)*
$CH_2OH \cdot (CHOH)_4 \cdot CHO$ (Glucose)	10	1 (24)	23	$HCHO + 5HCOOH + 5HIO_3$	12	15	45	*(1, 2)*
$CH_2OH \cdot (CHOH)_3 \cdot CO \cdot CH_2OH$ (Fructose)	8	1 (24)	20	$HCHO + 3HCOOH + CH_2OH \cdot COOH + 4HIO_3$	14	45	15	*(1, 2)*
$CH_2OH \cdot CHOH \cdot CH_2OH$ (Glycerol)	4	1	RT	$2HCHO + HCOOH + H_2O + 2HIO_3$	8	15	55	*(1, 2)*
$CH_2OH \cdot (CHOH)_2 \cdot CH_2OH$ (Erythritol)	6	1	RT	$2HCHO + 2HCOOH + H_2O + 3HIO_3$				*(1)*
HCHO (Formaldehyde)	0	0	RT	None	2	10	26	*(2)*

* Each ml. of M/10 periodate will oxidize one ml. of M/10 polyhydric alcohol containing 2 alcoholic groups or one ml. of M/20 polyhydric alcohol containing 2 alcoholic groups, etc. A typical reaction condition is that given for the oxidation of ethylene glycol 20 ml. of M/40 sodium periodate + 1 ml. of 20 per cent sulfuric acid + 15 ml. of M/40 glycol + 4 ml. of water, total 40 ml. Reaction time 1 hour or longer. The periodate solution is made by reacting 7.35 g. of $Na_3H_2IO_6$ with 75 ml. of N H_2SO_4 with dilution to 1000 ml. and is M/40 or 0.05 N. The excess periodate is most frequently determined by adding excess standard sodium arsenite in the presence of $NaHCO_3$ with KI as catalyst (2 ml. of 10 per cent aqueous solution) allowing 5 minutes for reaction between periodate and arsenite and the determination of excess arsenite by titration with standard iodine.

** The use of $H_2Ce(ClO_4)_6$ as oxidant in 4 F $HClO_4$ solution involves the use of excess oxidant, a short time interval for reaction followed by back titration of excess Ce(IV) in 2 F $HClO_4$ solution with standard oxalate in 2 F $HClO_4$ at room temperature employing nitro-ferroin as indicator. The main differentiation between this Smith and Duke determination and that of the Malaprade reaction consists in the mechanism of the reaction including the oxidation of HCHO to HCOOH by the former process. Sucrose, cellulose, cellulose acetate, biacetyl and 2, 3 butylene glycol have also been determined as described in reference (2). RT denotes room temperature. Time in parentheses indicated permissible extension of time.

1. Lange, "The Action of Periodic Acid on Polyalcohols," Les Editions Vega, 43, Rue Madame, Paris, France (1933), 214 pp.
2 Smith, "Cerate Oxidimetry," The G. Frederick Smith Chemical Company, Columbus, Ohio, 1942, IX + 123 pp.

The Determination of Glycerol in the Presence of Sugar

The following procedure was described by Fleury and Fatome (*9*) and is based upon the removal of the sugar by precipitation with barium hydroxide in alcoholic solution and subsequent determination of glycerol following reaction by periodic acid as follows:

$$CH_2OH \cdot CHOH \cdot CH_2OH + 2HIO_4 = 2HCHO + HCOOH + 2HIO_3$$

The sugar must first be removed because periodic acid would bring about its oxidation simultaneously.

Procedure. Since the determination of glycerol is only practical when working with relatively small samples an aliquot portion of the original sample is employed. Such aliquot part should contain not more than 20 mg. of glycerol nor 0.35 g. of glucose or 0.17 g. of invert sugar. A blank determination may be made by estimation or roughly by determination of the residue following evaporation. By this process one part of glycerol in 20 parts of sucrose or 12 parts of glucose is suitable.

Elimination of Sugar. The reagents to be employed are $Ba(OH)_2 \cdot 10H_2O$, 96% ethyl alcohol, sulfuric acid (1 vol. + 4 vol. H_2O) and a solution of approximately 0.1 *N* NaOH.

The sample for analysis is placed in a 50 ml. graduated flask and 1.25 g. of pulverized $Ba(OH)_2 \cdot 10H_2O$ is added. Mix the contents of the flask and place the sample in the refrigerator for 2 hours. At the end of this time fill the flask to the mark with 96 per cent alcohol. A precipitate will form and the sample is returned to the refrigerator.

After 15 to 24 hours the contents of the flask is centrifuged 2-3 minutes to obtain a clear super-natant liquid. Withdraw 25.00 ml. of this containing half the glycerol free from sugar. Precipitate the excess of barium by use of the dilute sulfuric acid using phenolphthalein as indicator and a slight excess of sulfuric acid. If preferred the barium may be removed as carbonate employing a stream of CO_2 gas as a precipitant for a period of 2-3 minutes.

If following this process a precipitate or at least a turbidity is not obtained indicating the complete elimination of sugar the sample should be discarded.

Elimination of Alcohol. After placing a mark on the evaporation beaker indicating the sample volume, add 25 ml. of distilled water and evaporate at 95° to the original volume. This evaporation may be carried out on the water bath avoiding overheating by placing the sample beaker on top not down in the water bath preferably with a circle of filter paper beneath it.

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9. Fleury and Fatome, *Journ. de Pharm. et de Chim.*, 21, 297 (1935).

After evaporation transfer the sample from its containing beaker to an Erlenmeyer flask rinsing the beaker contents into the flask. Neutralize with 0.1 *N* NaOH leaving the solution only faintly acid. The precipitated $BaSO_4$ may be filtered out but its presence does not interfere. Trial determinations have shown that by this process the alcohol is sufficiently well removed to cause no complications.

Determination of Glycerol. The solution of glycerol thus prepared which is slightly acid with H_2SO_4 is treated by the addition of a standard solution of periodic acid the excess of which is later determined. The method of Lange (*10*) is employed for the determination of excess HIO_4. This consists in adding to the periodic acid solution in the presence of bicarbonate, an excess of standard sodium arsenite with the use of KI as catalyst. By this process the HIO_4 may be determined in the presence of HIO_3 following the reaction:

$$H_3AsO_3 + HIO_4 = HIO_3 + H_3AsO_4$$

and the excess arsenite titrated using standard iodine solution. From the quantity of iodine consumed the excess of periodic acid employed may be calculated and in turn the amount of HIO_4 required to oxidize the glycerol.

Reagents. The term "solution M" refers to a solution containing one gram molecule per liter.

a. 0.1 *M* HIO_4 using sulfuric acid to free the HIO_4 from its sodium salt. Using $Na_3H_2IO_6$ (Mol. wt. 294) place 2.94 g. of the periodate in a 200 ml. graduated flask and add 30 ml. of normal sulfuric acid. Agitate to effect solution which is rapid and complete on 100 ml. dilution.

If $K_2H_3IO_6$ (Mol. wt. 304) 3.04 g. is employed it is treated as described in the case of the sodium salt. These solutions are stable upon storage at least for several months.*

b. Solution of 0.1 *N* arsenious acid. To a 150 ml. beaker add the required amount of standard of reference purity As_2O_3 (As_2O_3 g./40) and after the addition of a few pellets of sodium hydroxide add 10-15 ml. of water swirl the beaker contents to dissolve the As_2O_3. Finally add sufficient dilute sulfuric acid to neutralize the excess alkali and transfer the beaker contents to a 200 ml. graduated flask, dilute to the mark and thoroughly mix the flask contents. The resulting solution will be exactly 0.1 *N* in Na_3AsO_3.

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10. J. Lange, "The Action of Periodic Acid on Polyalcohols." Les Éditions Vega, 43 Rue Madame, Paris 1933, p. 21.

* AUTHOR'S NOTE. H_5IO_6 may be substituted for $Na_3H_2IO_6$. In this case the Mol. Wt. is 227.96 and 2.28 g. are, therefore, substituted for the crystalline periodate.

c. A solution of 0.1 N iodine.
d. A solution of approximately 0.1 N H_2SO_4.
e. A saturated solution of sodium bicarbonate.
f. A 10 per cent solution of KI to be used as catalyst.

Standardization of Periodic Acid. Using a 100 ml. conical flask add from a calibrated pipet 5.00 ml. of the periodic acid to be standardized. Add 5 ml. of the saturated sodium bicarbonate and 2 ml. of iodide solution. A pipet sample of 15.00 ml. of standard sodium arsenite solution is then added and the solution thus obtained allowed to stand 15 minutes at room temperature. Titrate the excess arsenite using the 0.1 N iodine solution standardized by titration using the standard arsenite solution. Indicate the volume of iodine required by the value C. Starch is employed as indicator.

Determination of Glycerol. Add to the glycerol containing sample a pipet of 5.00 ml. of periodate solution. Allow 15 minutes for reaction at 15-22° C. Find the volume C′ of 0.1 N iodine required as in the paragraph next above.

Necessarily C′ is less than C after the oxidation of glycerol and the difference represents the amount of periodate required for this oxidation. The periodic acid before oxidation is 15 — C ml. of 0.1 N solution. After oxidation the titre is found to be 15 — C′. Accordingly, ml. 0.1 N reagent required for the oxidation is (15—C) — (15 — C′) = C′ — C. Since 1 ml. of 0.1 N periodic acid is equivalent to one-half milli-molecule of glycerol the calculation is as follows:

$$\text{Mg glycerol} = (C' - C)/2 \times 4.6 = (C' - C)\ 2.3$$

This determination limits the amount of glycerol per sample for the amounts of reagent described to 23 milligrams.

The Determination of Glycerol in Wine. The principal components of wine which react with periodic acid are glycerol, the sugars, certain acids such as tartaric acid, and butylene glycol $CH_3 \cdot CHOH \cdot CHOH \cdot CH_3$ present in traces. Defecation employing lead acetate eliminates organic acids in part and together with defecation by barium hydroxide to eliminate sugars, gums, pectins, tartrates all interferences are eliminated. Acetic and lactic acids are not eliminated but these do not interfere. Moreover, any ethyl aldehyde present (B.P. 21 degrees) will be eliminated together with the alcohol by evaporation after defecation. One interference not eliminated is butylene glycol ordinarily present in minute amount.

Space does not permit a detailed description of the procedure employed as described by Fleury and Fatome (*11*).

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11. Fleury and Fatome, Ann. de Fermentation, 1, 285 (1935).

CHAPTER V

DETERMINATION AND SEPARATION OF POTASSIUM AS PERIODATE *

The Gravimetric Determination of Potassium

The determination of potassium as periodate, KIO_4, offers a number of advantages. It has a high molecular weight, and can be determined volumetrically by a very exact titration. It is only sparingly soluble, a saturated solution at 25° C. being 0.022 molar (*1*). It contains about the same percentage of potassium as the chloroplatinate and cobaltinitrite and much less than the perchlorate.

The first experiments along this line were made by Greathouse (*2*), who added periodic acid to the solution, 2 or 3 ml. in volume, and completed the precipitation by adding alcohol, free from aldehyde. He carried out a few gravimetric and volumetric determinations, the results being usually slightly low, but did very little on the separation of potassium from other metals. At that time the price of iodine was high, and the preparation of periodic acid was an expensive process. Since that time two satisfactory methods for preparing the acid have been published and the reagent has become less expensive. As the reagent is now available, it seemed desirable to make an extensive investigation of this method of determining and separating potassium, and in particular, to find a better solvent than ethyl alcohol which is so easily oxidized that it is almost impossible to avoid some reduction of periodic acid to iodic acid.

The reaction used in titrating periodate to iodate was first suggested by Müller and Friedberger (*3*):

$$IO_4^- + 2I^- = IO_3^- + I_2$$

and is quantitative only in a neutral solution buffered by carbonic acid-bicarbonate or boric acid-borate, preferably the latter. The free iodine is then titrated by standard arsenite. This method has the advantage that iodate does not interfere, as it would if the periodate

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* Reprinted from the work of Willard and Boyle, originally published in Ind. Eng. Chem., Anal. Ed. 13, 137 (1941).

1. Hill, A. E., *J. Am. Chem. Soc.*, 50, 2678 (1928).
2. Greathouse, L. H., dissertation, University of Michigan, 1917.
3. Müller, E., and Friedberger, O., *Ber.*, 35, 2652 (1902).

were reduced to iodide. In the latter process, however, the equivalent would be much smaller—one eighth of the molecular weight.

The periodate method for potassium is both rapid and accurate, and can be applied to amounts of potassium as low as 0.4 mg.

Experimental

Selection of a Solvent. As indicated above, the selection of the proper solvent is a matter of prime importance. It must possess the following properties: (1) It must not be appreciably oxidized by periodic acid during the time required for the analysis, 0.5 to 2 hours. (2) It should be miscible with water at least to the extent of about 10 per cent of the latter by volume. (3) Potassium periodate must be insoluble in the solvent and yet it must dissolve sodium periodate and such other salts as might be present.

As explained above, Greathouse (*1*) used ethyl alcohol, free from aldehyde, since the aldehyde is more easily oxidized than the alcohol. This, however, was not an ideal solvent because some oxidation of the alcohol invariably occurred. Among the solvents which are less affected by oxidizing agents is tertiary butyl alcohol; this was therefore first investigated. It was found, however, to dissolve so little sodium periodate as to be useless for the purpose. Admixture of ethyl acetate did not improve matters. Other solvents tried in which sodium periodate was insoluble were dioxane, the carbitols, Cellosolve, and diethylene glycol.

It was found that if ethyl acetate was added to ethyl alcohol, the resistance of the latter to oxidation was considerably increased, whereas its solvent power was not diminished.

A quantity of 95 per cent ethyl alcohol, free from aldehyde, was prepared by refluxing the alcohol for 2 or 3 hours after the addition of 0.5 gram of sodium hydroxide and 2.5 grams of silver nitrate per liter. The alcohol was then distilled and mixed with an equal volume of anhydrous ethyl acetate. The mixture was miscible with the quantities of water which were required and showed considerable resistance to oxidation by periodic acid. One gram of periodic acid dissolved in 100 ml. of the solvent showed the first traces of free iodine after standing at room temperature for 24 hours. Since in most cases the time required for the separation of potassium was from 15 minutes to 1 hour, it is apparent that only very slight oxidation of the organic solvent could occur. The magnitude of this effect is shown by the fact that the average of a long series of gravimetric determinations (only part of which are recorded in this paper) showed an error of +0.02 mg., and the volumetric determinations, 0.05 mg. This would indicate that the precipitates contained a trace of iodate owing to very slight reduction by the solvent, because the percentage of potassium in the iodate is only slightly less than in the periodate, whereas the iodate is not determined at all in the volumetric process. These results are much better than those obtained by Greathouse (*1*). It was also found possible to reduce considerably the concentration of periodic acid.

Preparation of Reagents. The periodic acid used was recrystallized from concentrated nitric acid until free from iodic acid. Some of it was prepared by the eletectrolytic process (*4*) (see page 13) and although originally free from iodic acid, some batches were found to contain a good deal of the latter after standing for a month or two. This is probably due to the catalytic effect of traces of colloidal platinum derived from the electrodes. A solution of periodic acid to which considerable colloidal platinum is added evolves oxygen rapidly. The acid prepared by the chemical process (*5*) is always entirely stable. Small amounts of iodate are easily detected as follows:

One-half gram of the periodic acid is dissolved in 25 ml. of water, a few drops of 0.25 *M* silver nitrate are added, and the solution is warmed until the yellowish-brown silver periodate dissolves, which should occur readily at about 80° C. If iodic acid is present, a white flocculent precipitate of silver iodate will form. If the brown silver periodate is not completely dissolved by heating, a drop or two of nitric acid, free from nitrous acid, should be added.

The potassium and sodium periodates used were purified by recrystallization and tested for iodate by the method of Willard and Thompson (*6*). This is similar to the method suggested above, except that most of the periodate in the sample to be tested is first removed by the addition of an excess of potassium nitrate, after which the solution is acidified with nitric acid and tested for iodate by the addition of silver nitrate. In this way it is possible to detect 0.03 per cent of iodate in periodate.

The potassium nitrate used in this work had been carefully purified and dried at 105° to 110° C. for several hours. An attempt was made to fuse the salt at about 300° C., but the resulting material contained considerable nitrite.

General Procedure

A sample weighing 0.1 to 0.2 gram is dissolved in water in a 150-ml. beaker. If potassium chloride is used it must be evaporated to dryness with 10 ml. of concentrated nitric acid; otherwise the chloride will cause reduction of periodic acid. To the nitrate dissolved in 4 to 5 ml. of water 3 ml. of water containing 1 gram of periodic acid are added, the mixture is stirred, and 3 or 4 minutes are allowed for the potassium periodate to precipitate. Ninety milliliters of the alcohol-ethyl acetate mixture are added and the solution is allowed to stand in an ice bath for 0.5 hour with continuous mechanical stirring. It

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4. Willard, H. H., and Ralston, R. R., *Trans. Electrochem. Soc.*, 62, 239 (1932).
5. Willard, H. H., "Inorganic Syntheses," Vol. I., p. 172, New York. McGraw-Hill Book Co., 1939.
6. Willard, H. H., and Thompson, J. J., *J. Am. Chem. Soc.*, 56, 1827 (1934).

is essential that the precipitation be carried out as indicated. If periodic acid is added to the alcohol-ethyl acetate solution, the precipitate will be gelatinous and difficult to filter, whereas if it is first formed in aqueous solution it is crystalline. The solution is filtered through a Gooch crucible and the precipitate washed with anhydrous ethyl acetate which has been cooled to 0°. It is dried in the oven for 10 minutes at 105° C., cooled, and weighed.

If volumetric results are desired, the crucible with the precipitate is placed in a 250-ml. beaker, to which are added 125 ml. of a solution containing 5 grams of boric acid and 5 grams of sodium tetraborate. The potassium periodate dissolves readily in this solution, which has a pH of about 7.5. It is unnecessary to take the crucible out of the solution.

When the potassium periodate has dissolved, 3 grams of potassium iodide are added and the iodine is titrated with 0.1 *N* arsenite solution, prepared by dissolving 4.945 grams of arsenious oxide in a solution of 10 grams of sodium bicarbonate, warmed to about 80° C. The solution is then saturated with carbon dioxide and diluted to 1 liter. Although the solution was made up from arsenious oxide of known purity, it was standardized by titration against pure potassium and sodium periodates and the values obtained in this way were taken as correct. In some cases the normality found in this way deviated from the theoretical value by as much as 0.0012.

Periodic acid was always weighed out in the solid form and dissolved just before use to avoid any danger of decomposition on standing. Gravimetric results were satisfactory only when a nitrate was used, but were high with sulfates, though volumetrically the sulfates did not interfere. The latter procedure is usually preferable because it is not affected by the presence of iodate or of inert materials which may be insoluble in the organic solvent.

When the amount of potassium present is very small, it is desirable to increase the amount of periodic acid to 1.5 or 2 grams. If not much sodium or other metal is present, the initial volume of water should be decreased to 5 ml., although this is not absolutely necessary. The time for precipitation should be increased to 1 or 1.5 hours. If less than 0.4 mg. of potassium is present the results are unreliable, even though the volume of water is reduced and the amount of periodic acid increased.

Results of Analyses

In all the analyses described below, unless otherwise stated, the same conditions were used—namely, 90 ml. of solvent, 1 gram of periodic acid, 7 to 8 ml. of water, and 30 minutes stirring at 0° C. The

precipitate obtained was, in all cases, crystalline, and showed no tendency to adhere to the beaker. The results of a series of determinations are shown in Table XXII.

It is obvious that potassium can be completely separated from 70 mg. of sodium, but that there is a slight error when 140 mg. are present. It was subsequently found that the limit could be raised to 100 mg. By doubling the volume of alcohol-acetate mixture potassium was readily separated from 190 mg. of sodium.

TABLE XXII

Determination of Potassium as Periodate in Presence and Absence of Sodium

Wt. of K as Nitrate	Na Added as Nitrate	Wt. of KIO_4	Error in K	
			Gravimetric	Volumetric
Gram	*Mg.*	*Gram*	*Mg.*	*Mg.*
0.0794	....	0.4676	+0.1	....
0.0490	....	0.2887	+0.1	0.0
0.0405	....	0.2391	+0.1	+0.1
0.0382 [a]	....	0.2241	—0.1	—0.1
0.0307	....	0.1809	0.0	—0.1
0.0224	....	0.1313	—0.1	....
0.0030	....	0.0171	—0.1	—0.1
0.0600	68	0.3524	—0.1	0.0
0.0428	73	0.2518	0.0	0.0
0.0464	135	0.2746	+0.3	+0.3
0.0420	135	0.2517	+0.8	+0.6
0.0481 [a]	140	0.2842	+0.2	+0.2
0.0407 [a]	143	0.2406	+0.2	+0.1
0.0440 [a]	190	0.2598	+0.2	—0.1
0.0335 [a]	190	0.1980	+0.1	0.0
0.0017	54	0.0098	0.0	....
0.0013	54	0.0077	0.0	—0.2
0.0007	54	0.0041	0.0	0.0
5 ml. of water used				
0.0008	....	0.0045	0.0	+0.2
0.0008	....	0.0043	—0.1	0.0
0.0008	27	0.0045	0.0	0.0
0.0008	27	0.0052	+0.1	+0.1
0.0004	27	0.0025	0.0	—0.1
0.0004	27	0.0020	—0.1	—0.1

[a] 180 ml. of alcohol-acetate mixture used.

Effect of Temperature, Sulfate and Free Acid

In previous experiments the temperature was 0° C. A series of experiments was run in which the solutions were maintained at room temperature for 15 and 60 minutes, respectively. In both cases the results were 0.2 to 0.6 mg. too low.

Weights of potassium nitrate varying from 0.05 to 0.15 gram were taken and 40 mg. of sodium added as sulfate. In a series of 12 volumetric determinations the error varied from —0.2 to +0.2 mg., with an average of practically zero. In this case the gravimetric results were always too high because of contamination with sodium sulfate.

In Table XXIII are shown the results obtained when free nitric, phosphoric sulfuric, perchloric, and boric acids are added. In the case of perchloric acid, some of the potassium is precipitated as perchlorate and apparently is not quite converted into periodate within 45 minutes. The other acids do not interfere.

TABLE XXIII

Determination of Potassium as Periodate in Presence of Free Acid

Wt. of K as Nitrate	Acid Added	Wt. of KIO_4	Error in K	
			Gravimetric	Volumetric
Gram		*Gram*	*Mg.*	*Mg.*
0.0524	0.5 ml. concd. HNO_3	0.3092	+0.2	0.0
0.0289	0.5 ml. concd. HNO_3	0.1695	—0.1	+0.1
0.0608	5 drops H_3PO_4, 85%	0.3575	0.0	—0.2
0.0561	5 drops H_3PO_4, 85%	0.3302	0.0	—0.1
0.0572	1 ml. concd. H_3PO_4	0.3377	+0.2	0.0
0.0603	1 ml. concd. H_3PO_4	0.3570	+0.4	+0.1
0.0461	5 drops concd. H_2SO_4	0.2806	+0.5	0.0
0.0580	5 drops concd. H_2SO_4	0.3408	—0.1	+0.1
0.0451	200 mg. H_3BO_3	0.2658	+0.1	0.0
0.0444	200 mg. H_3BO_3	0.2630	+0.3	+0.3
0.0447	5 drops $HClO_4$, 70% [a]	0.2623	—0.1	—0.4
0.0541	5 drops $HClO_4$, 70% [a]	0.3179	—0.1	—0.5

[a] Stirred 45 minutes.

Separation from Other Metals

The results in Table XXIV show that volumetric determination of potassium is satisfactory in the presence of moderate amounts of magnesium, calcium, lithium, aluminum, zinc, nickel, and cobalt, but not ammonium, iron, manganese, and chromium. In the latter cases oxidation to permanganate and chromate occurs and the titration is not possible. The separations are better when 180 ml. of alcohol-acetate mixture are used. The results are somewhat better when 8 ml. of water rather than 7 ml. are present.

The gravimetric results are satisfactory with calcium (in the absence of sulfate), magnesium, and lithium.

TABLE XXIV

Separation of Potassium from Metals as Periodate

Wt. of K as Nitrate	Metal Added	Wt. of KIO_4	Error in K	
			Gravimetric	Volumetric
Gram	*Mg.*	*Gram*	*Mg.*	*Mg.*
0.0403	16 Ca (as nitrate)	0.2731	0.0	—0.1
0.0530	32 Ca (as nitrate)	0.3119	0.0	—0.1
0.0486	20 Mg (as sulfate)	....	....	0.0
0.0464	21 Mg (as nitrate)	0.2732	+0.1	0.0
0.0608	50 Al (as nitrate)	0.3579	0.0	—0.1
0.0615	100 Al (as nitrate)	0.3654	+1.1	—0.1
0.0452	102 Al (as nitrate)	0.2718	+1.0	0.0
0.0405 [a]	98 Al (as nitrate)	0.2468	+0.5	+0.1
0.0424	100 Al (as sulfate)	0.2530	+0.6	0.0
0.0400	100 Al (as sulfate)	0.2383	+0.3	+0.2
0.0484	62 Zn (as nitrate)	0.2876	+0.5	—0.1
0.0406	62 Zn (as nitrate)	....	....	—0.1
0.0498	92 Co (as nitrate)	0.2959	+0.5	—0.2
0.0406	88 Co (as nitrate)	0.2400	+0.2	+0.2
0.0423	77 Ni (as nitrate)	0.2513	+0.4	+0.2
0.0395 [a]	79 Ni (as nitrate)	0.2336	+0.2	+0.2
0.0413	5 Fe^{+++} (as nitrate)	0.2773	+5.8	—0.9
0.0358	5 Fe^{+++} + 5 drops H_3PO_4	0.2355	+4.2	—1.3
0.0579	50 Mn (as sulfate)	0.3757	+6.0	....
0.0341	3 NH_4 (as sulfate)	0.2243	+4.0	+4.6
0.0516	60 Li (as carbonate)	0.3037	0.0	....
0.0401	69 Li (as carbonate)	0.2371	+0.2	—0.1

[a] 180 ml. alcohol-acetate mixture used.

Although calcium does not interfere when present as nitrate, there is serious interference when it is present as sulfate. Not only was the reaction at the end point slow, indicating that something was dissolving during the process, but the results were always too low. Apparently this is due to the formation of the insoluble double salt, $CaSO_4 \cdot K_2SO_4$, so that it was impossible to convert all the potassium to periodate. This should be kept in mind if silicates have been decomposed by evaporation with hydrofluoric and sulfuric acids. Attempts to decompose feldspar by evaporation with hydrofluoric and phosphoric acids were unsuccessful.

The cobalt solution became green upon the addition of periodic acid. Ferric iron is readily precipitated as periodate and therefore interferes even when present in small amounts. It was thought that the addition of phosphoric acid, forming a complex with the iron, would prevent its precipitation. Although some effect was noticeable in the gravimetric result, there was no improvement in the volumetric. In the absence of phosphoric acid the precipitate was brick-red, whereas in its presence it was white.

Rubidium and cesium behave like potassium, although no quantitative experiments were made.

In the presence of chromium and manganese, which are oxidized by periodic acid, the color was so intense that no titration was possible, although if not over 1 mg. of manganese is present the end point can be seen.

The periodate method is applicable to the determination of potassium in the mixed chlorides obtained by the J. Lawrence Smith method, providing they are converted into nitrates by evaporation with nitric acid.

Quantitative Determination of Lead as Periodate

As shown by Willard and Thompson (*7*) proper conditions were described for the precipitation of pure triplumbic paraperiodate, $Pb_3H_4(IO_6)_2$. This salt was found to be sufficiently insoluble in very dilute acids to make possible its use in the volumetric and gravimetric determination of lead.

Lead may be separated from Ni, Cu, Zn, Cd, Al, Ca, and Mg by its precipitation from 0.025 *N* nitric acid solution by the addition of sodium metaperiodate, $NaIO_4$. The precipitated lead may be weighed or determined volumetrically. For the latter purpose it is dissolved in concentrated hydrochloric acid containing an excess of standard arsenite. The excess of arsenite is then determined by iodate titration using chloroform as indicator (*8*).

The validity of the procedure was experimentally proven as follows:

Weighed samples of Mallinckodt's reagent quality lead or Kahlbaum's sheet lead were dissolved in nitric acid and evaporated to dryness. The dry salt was then dissolved in 200 ml. of 0.025 *N* nitric acid and the lead precipitated at 100° C. by the slow addition of 2 grams of $NaIO_4$ dissolved in 50 ml. of water. When the amount of lead was very small no precipitate formed until 1 ml. of the periodate solution had been added. When this occurred it was necessary to decrease the acidity to 0.006 *N*; otherwise the precipitate did not have the theoretical composition. After the periodate was added, the solution was cooled in ice water and the cold solution stirred for 30 minutes, because supersaturation was pronounced. The lead periodate was filtered on a porcelain filtering crucible, washed with ice water, and dried for 2 hours at 110° C. It was then weighed as $Pb_3H_4(IO_6)_2$. Results of analyses are shown in Table XXV.

To determine lead volumetrically the method of Andrews (loc. cit.) was used, because the best solvent for the salt is concentrated hydrochloric acid. The equation for the reaction can be expressed as follows:

$$Pb_3H_4(IO_6)_2 + 8HCl + 6H_3AsO_3 = 3PbCl_2 + 2ICl + 6H_3AsO_4 + 6H_2O$$

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7. Willard and Thompson, *J. Am. Chem. Soc.*, **56**, 1828 (1934).
8. Andrews, *J. Am. Chem. Soc.*, **25**, 756 (1903) cf. Jamieson, "Volumetric Iodate Methods" Chemical Catalogue Co., Inc., New York, 1926.

TABLE XXV

Gravimetric Determination of Lead as Triplumbic Paraperiodate $Pb_3H_4(IO_6)_2$

Lead Taken	Lead Found	Error
Gram	*Gram*	*Mg.*
0.7001	0.7001	±0.0
0.6953	0.6954	±0.1
0.6028	0.6025	−0.3
0.5596	0.5596	±0.0
0.5591	0.5588	−0.3
0.5553	0.5552	−0.1
0.3853	0.3852	−0.1
0.1145	0.1147	+0.2
0.1121	0.1122	+0.1
0.0735	0.0734	−0.1

If arsenious acid is present in excess, all the chlorine will react with it to form arsenic acid. The excess arsenious acid can then be titrated with iodate, using chloroform as indicator. After precipitation as previously described the procedure for the volumetric determination was made as follows:

The precipitate was filtered into a Gooch crucible, the bottom of which was covered by a filter-paper disk, washed thoroughly and transferred to a 150 ml. conical flask. An excess of arsenious oxide previously dissolved in a concentrated solution of sodium hydroxide, or a suitable volume of a standard arsenite solution was added to the flask. Concentrated hydrochloric acid was slowly added to the cold solution, the flask being agitated until all the lead periodate dissolved, which required 35 to 40 ml., and the solution was titrated with 0.1 *N* potassium iodate until it was a light brown in color. A little chloroform was then added and the titration completed. The volumetric determination gave excellent results, the error being less than 0.2 per cent and the presence of copper, aluminum, zinc and cadmium did not interfere.

CHAPTER VI

VOLUMETRIC IODATE PROCEDURES

NEW INDICATORS FOR IODATE-IODINE MONOCHLORIDE ANDREWS ANALYTICAL PROCEDURES *

The use of iodate as oxidant in volumetric analysis at high concentrations of hydrochloric acid was originally developed by Andrews (*1*) and further popularized by Jamieson (*2*). The Andrews iodate-iodine monochloride reactions, while precise and versatile, require a high hydrochloric acid concentration (2.5 to 6 *M*), and the use of carbon tetrachloride or chloroform as immiscible solvent to indicate the completion of the reaction, by the presence or absence of a violet coloration.

The present paper describes conditions under which the Andrews reactions can be applied using dyestuff internal indicators, the color destruction of which corresponds with the completion of the oxidations involved. The iodate-iodine monochloride reactions are simplified and made more rapid and convenient, without appreciable loss of accuracy or versatility.

The Andrews (*1*) procedures as extended by Jamieson (*2*) have been reviewed by Lang (*2*). In order to apply the Andrews reactions to solutions at much lower concentrations of hydrochloric acid, Lang used (*3*) potassium cyanide to cause the formation of iodine cyanide in place of iodine monochloride. By this change starch may be employed as indicator, but this development is burdened by the presence of hydrogen cyanide. The same advantages are attained by the Berg modification, which employs acetone to form iodo-acetone in place of iodine monochloride or iodine cyanide (*3*). The applications in this case are limited in number. The determination of iron by the Andrews procedure in the presence of organic matter was described by Heisig (*4*). The dyestuff indicators, some of which are used in the present work, were studied by Smith and Bliss (*5*).

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* Smith and Wilcox, *Ind. Eng. Chem.*, 14, 49 (1942).

1. Andrews, L. W., *J. Am. Chem. Soc.*, 25, 756 (1903).
2. Jamieson, G. S., "Volumetric Iodate Methods," New York, Chemical Catalog Co., 1926.
3. Boettger, W., "Newer Methods of Volumetric Analysis," tr. by Oesper, Part 4, New York, D. Van Nostrand Co., 1938.
4. Heisig, G. B., *J. Am. Chem. Soc.*, 50, 1687 (1928).
5. Smith, G. F., and Bliss, H. H., *J. Am. Chem. Soc.*, 53, 2091 (1931).

Requirements of Internal Indicators

In the iodate-iodine monochloride reactions using carbon tetrachloride or chloroform as an extraction solvent indicator, the equivalence point is determined by the disappearance of the iodine color on the addition of the first slight excess of iodate. A dye suitable for use as an internal indicator for such reactions should be stable in the presence of iodine, iodine monochloride, and strong hydrochloric acid. It should be destroyed under the same conditions by the first slight excess of iodate, should have no appreciable blank correction at sufficient concentrations to produce a vivid color change, and should be applicable at room temperature and at slightly increased temperatures.

Accordingly, the dyes studied for use as indicator reagents by Smith and Bliss were examined for use in the present application (Table XXVI).

TABLE XXVI

Application of Smith and Bliss Internal Oxidation Indicators

Indicator	British Colour Index No.	Color Change	Remarks
Naphthol Blue Black	246	Green to faint pink	Fairly satisfactory
Brilliant Ponceaux 5R	185	Orange to colorless	Satisfactory
Amaranth	184	Red to colorless	Satisfactory

Reagents. Iodate solution, 0.025 *M*. Indicators, 0.2 per cent aqueous solutions. Iodine monochloride made by dissolving 0.279 gram of potassium iodide plus 0.172 gram of potassium iodate in 250 ml. of water and adding to 250 ml. of hydrochloric acid (sp. gr. 1.19).

Procedure. Ten milliliters of iodine monochloride solution plus 35 ml. of concentrated hydrochloric acid were diluted to 100 ml. Indicator (0.5 ml.) and 0.05 ml. of 0.1 *N* potassium iodate were added. Temperature, 35° C.

Of the sixteen dyes found by Smith and Bliss (*5*) to be applicable to bromate oxidations, only those listed in Table XXVI were found suitable for use in the Andrews reaction. Failure in most cases was due to the lesser oxidation potential provided by iodate as compared to bromate, the higher acidities employed, or the oxidizing properties of iodine or iodine monochloride under the conditions selected. It is possible that similar dyes not found suitable for bromate reactions by Smith and Bliss (*5*) may also be applicable here. The indicators of Table XXVI are sufficiently versatile to cover all practical uses.

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5. Smith and Bliss, *J. Am. Chem. Soc.*, 53, 2091 (1931).

Effect of Temperature and Acid Concentration

For this purpose 10 ml. of iodine monochloride and 0.5 ml. of indicator were added to sufficient hydrochloric acid to give a concentration of 1 to 7 molar hydrochloric acid upon dilution to 100 ml. One drop (0.05 ml.) of 0.1 *N* iodate solution was added to these solutions at temperatures of 25° to 70° C. and the effect was noted.

At a hydrochloric acid concentration of 1 to 5.0 molar, the indicators listed in Table XXVI were not destroyed at temperatures from 25° to 90° C.

Upon addition of iodate, Amaranth is satisfactorily destroyed at acidities of 3.0 to 5.0 *M* at 30° or above. Brilliant Ponceaux 5R is satisfactory at acidities greater than 3.0 *M* at 25° to 30° and at higher temperatures in 4.0 to 5.0 acidity. Naphthol Blue Black is slower in its respopnse to iodate oxidation, but is satisfactory at 3.0 to 5.0 molar acid strength.

Indicator Blank Correction

One milliliter of indicator under the conditions of titration is destroyed by the addition of 0.05 ml. of 0.1 *N* iodate solution. The indicator blank is therefore negligible, since less than 0.5 ml. of indicator is required for each titration. Since the dyes used as indicators are destroyed at the completion of the reaction, the reactions are not reversible. A tendency of the indicators to fade as the equivalence point is reached is counteracted by delaying their addition until the color of the solution being titrated indicates that completion is near. Just before the equivalence point is reached an additional small portion of indicator may be added.

Determination of Arsenic

An approximately 0.1 *N* solution of sodium arsenite was titrated by the Andrews procedure. A pipet sample of 25 ml. of arsenite was transferred to a 500-ml. glass-stoppered Erlenmeyer flask, and hydrochloric acid and water were added to make a 100-ml. volume, 4.4 *M* in hydrochloric acid. After addition of 10 ml. of chloroform the solution was titrated with approximately 0.1 *N* potassium iodate, the stoppered flask being well shaken after each dropwise addition of iodate in approaching the equivalence point. The end of the reaction is indicated by the change in the chloroform from violet to colorless.

The same procedure was followed for the indicator method, except that the titration was carried out in a 400-ml. beaker and a few drops of the indicator employed were added in place of chloroform after almost all of the iodine color had disappeared from the solution upon the addition of standard iodate.

The titrations were carried out at room temperature and the color changes indicated in Table XXVI were found to be sharp and distinct. The results by the two methods were identical, using the three indicators described above.

Determination of Arsenic in Pure Arsenic Trioxide. Weighed portions of Bureau of Standards arsenic trioxide were transferred to 400-ml. beakers, 5 ml. of water and 0.5 gram of sodium hydroxide were added, and the sample was dissolved. Then 35 ml. of concentrated hydrochloric acid (sp. gr. 1.19) were added, and enough water to make 100 ml. These solutions were titrated, using a solution containing 5.3505 grams of potassium iodate per liter (1 ml. = 0.0049465 gram of arsenic trioxide). After most of the iodine color had disappeared 0.5 ml. of indicator 184 (Amaranth) was added and the titration was completed. The color changed from red to light yellow. Reactions were at room temperature. The results are shown in Table XXVII.

TABLE XXVII

Determination of Arsenic Using Amaranth as Indicator

As_2O_3 Taken	KIO_3 Required	As_2O_3 Found	Error in As_2O_3 Found
Gram	*Ml.*	*Gram*	*Gram*
0.1995	40.25	0.1993	−0.0002
0.1996	40.29	0.1995	−0.0001
0.1995	40.30	0.1995	0.0000
0.1998	40.32	0.1996	−0.0002
0.1121	22.65	0.1120	−0.0001
0.2019	40.76	0.2018	−0.0001

Essentially the same results were obtained with Naphthol Blue Black and Brilliant Ponceaux 5R. The reactions, when Naphthol Blue Black is used as indicator, are slow at the end.

Determination of Antimony

Antimony was determined by the present method and by a bromate procedure described by Smith and May (*6*).

The iodate solution used for the determination of arsenic, reported in Table XXVII, is equivalent to 8.0882 mg. of antimony per ml. An approximately 0.1 solution of potassium bromate was prepared by dissolving 1.3916 grams of pure potassium bromate in enough water to make 1 liter of solution. An approximately 0.1 *N* solution of potassium antimonyl tartrate was prepared by dissolving 16.7 grams of the salt in 1 liter of water.

Samples of 25.00 ml. of the potassium antimonyl tartrate solution were measured into 400-ml. beakers, 50 ml. of concentrated (sp. gr. 1.19) hydrochloric acid were added, and dilution was made to 100 ml. with water (6.2 *N* in hydrochloric acid). The resulting solutions were titrated with potassium iodate, using a potentiometric end-point determination. The same procedure was employed using the indicators described above. Finally the bromate solution was used to standardize the potassium antimonyl tartrate solution and portions equivalent to a known amount of antimony were evaluated, using standard iodate (Table XXVIII).

Table XXVIII shows that using iodate, the potentiometric and indicator methods for the determination of the equivalence point give the same results. The iodate method using indicators 184, 185, and

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6. Smith, G. F., and May, R. L., *Ind. Eng. Chem., Anal. Ed.*, **13**, 460 (1941).

TABLE XXVIII

Determination of Antimony

(Comparison of iodate and bromate procedures using indicator and potentiometric end-point determination)

Iodate Required in Iodate Procedures			
Potentiometric procedure	Indicator 184	Indicator 185	Indicator 246
Ml.	*Ml.*	*Ml.*	*Ml.*
25.10	25.10	25.10	25.13
25.10	25.10	25.07	25.12
25.15	25.10	25.03	25.05
Av. 25.11	25.10	25.06	25.10

(Iodate procedure compared with bromate procedure, $KBrO_3$ as standard, Bordeaux, as indicator)

KIO_3 Required, Indicator 184	Sb Taken	Sb Found	Error	No. of Determinations
Ml.	*Gram*	*Gram*	*Gram*	
25.55 to 25.60	0.1559	0.1555 to 0.1550	—0.0001 to —0.0003	10

246 gives the same results as the bromate method (*7*) using Bordeaux as indicator.

For the antimony determination indicator 184 is most satisfactory, the color change using indicator 185 is not so satisfactory, and indicator 246 is slower in reaction. The Andrews-Jamieson method was found unsuited to the determination of antimony in a tartrate solution because of the failure of the carbon tetrachloride or chloroform to develop a violet color during the progress of the reaction.

Determination of Iron

The Andrews method as developed by Heisig (*8*) was compared with the present method.

The Heisig method was applied by taking a 25.00-ml. portion of a standard ferrous sulfate solution, to which were added 50 ml. of concentrated hydrochloric acid, and diluting the whole to 100 ml. with water. Then 10 ml. of iodine monochloride, prepared as described above, were added and the solution was titrated, using 0.1 *N* potassium iodate after addition of carbon tetrachloride as indicator.

The indicator method was applied in exactly the same manner, except that carbon tetrachloride was replaced by Amaranth, Brilliant Ponceaux 5R, and Naphthol Blue Black, which were added after the iodine liberated in the reaction was almost all oxidized by the iodate added. The Heisig procedure and the present method with all three indicators were found to agree within 0.1 per cent.

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7. Smith and Bliss, *J. Am. Chem. Soc.*, **53**, 4291 (1931).
8. Heisig, *J. Am. Chem. Soc.*, **25**, 756 (1903).

Iron was determined in Bureau of Standards ingot iron (Sample 55) containing 99.85 per cent of iron, following the present internal indicator method, and results were compared with the Heisig method using a solution of ferrous sulfate. The latter solution was also evaluated by comparison with standard permanganate and ceric ions with perfectly satisfactory agreement. The solution of iodate was thus found to be 0.1009 *N*. The same iodate solution when standardized using pure arsenic trioxide and the Andrews method or the present method gave a value 0.1000 *N*. It was therefore concluded that the iodate solution for use in the determination of iron must be standardized using iron as reference and that low results are obtained if arsenic trioxide is used as standard of reference.

Samples of the ingot iron were weighed into 250-ml. beakers, 10 ml. of concentrated hydrochloric acid (sp. gr. 1.19) were added, and the beakers were placed on the hot plate until dissolved. The resulting solution was cooled and passed through a Walden silver reductor to reduce the iron, treated with 40 ml. of concentrated hydrochloric acid, and diluted to 100 ml. with water. To this solution 10 ml. of iodine monochloride solution were added and the liberated iodine was titrated with potassium iodate until the iodine color disappeared. A 0.5-ml. portion of indicator 184 was added and the titration was completed. The results are shown in Table XXIX.

TABLE XXIX

Determination of Iron Using Amaranth as Indicator

Sample Bur. Standards 55	Fe Taken	0.1009 *N* KIO_3	Fe Found	Fe Error
Gram	*Gram*	*Ml.*	*Gram*	*Gram*
0.1458	0.1456	26.10	0.1457	+0.0001
0.1420	0.1418	25.40	0.1417	—0.0001
0.1509	0.1507	26.98	0.1506	—0.0001
0.1469	0.1467	26.26	0.1466	—0.0001
0.1427	0.1425	25.55	0.1426	+0.0001
0.1429	0.1427	25.60	0.1429	+0.0002

In Presence of Organic Matter. An advantage in the determination of iron by the Heisig method (*8*) or the bromate method of Smith and Bliss (*9*) consists in the fact that most organic material does not interfere. The same can be shown to be true of the present method.

A sample of 5.5761 grams of Bureau of Standards ingot iron 55 was dissolved in 100 ml. of hot concentrated hydrochloric acid, cooled, and passed through a Walden silver reductor. The resulting solution was diluted to 1000 ml. in a volumetric flask. Samples of 25.00 ml. of this standard solution were titrated as described in Table XXX in the presence of organic reagents.

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9. Smith and Bliss, *ibid*, **53**, 2091 (1931).

TABLE XXX

Determination of Iron in Presence of Organic Matter Using Iodate and Amaranth

(Iron taken for each titration, 0.1382 gram)

Organic Matter Present		0.1009 N KIO_3	Fe Found	Fe Error
	Grams	*Ml.*	*Gram*	*Gram*
Tartaric acid	2	24.51	0.1381	−0.0001
		24.52	0.1382	±0.0000
		24.50	0.1380	−0.0002
Citric acid	2	24.54	0.1383	+0.0001
		24.55	0.1383	+0.0001
		24.52	0.1382	±0.0000
		24.54	0.1383	+0.0001
95 per cent ethanol	10 ml.	24.53	0.1382	±0.0000
		24.57	0.1384	+0.0002
		24.56	0.1383	+0.0001
Sodium oxalate	1	24.53	0.1382	±0.0000
		24.54	0.1383	+0.0001
		24.53	0.1382	±0.0000
Glycerol	10 ml.	24.54	0.1383	+0.0001
		24.56	0.1384	+0.0002
		24.55	0.1383	+0.0001

Table XXX shows that the internal indicator procedure is admirably adapted to use in the presence of organic matter.

Determination of Thallium

An approximately 0.2 N thallous nitrate solution was prepared by dissolving 13.3 grams thallous nitrate in 500 ml. of molar perchloric acid. The solution was standardized potentiometrically by titration using standard ceric sulfate. The titration was made at 7.0 N strength of hydrochloric acid using the platinum-calomel electrode system, 10.00 ml. of the thallous solution were found to contain 0.19895 gram of thallium as the average of a number of consecutive determinations.

Six 10-ml. portions of the standard thallous nitrate solution were transferred by pipet to 250-ml. beakers, 40 ml. of concentrated hydrochloric acid were added, and the solution was diluted to 100 ml. with water. The resulting solutions were titrated, using standard iodate which had been standardized using pure arsenic trioxide and the Andrews reaction and found to be 0.09996 N. As soon as the iodine color had almost disappeared 0.5 ml. of Amaranth was added as indicator coloring and the titration completed to the destruction of the indicator color. The six samples required from 19.46 to 19.48 ml. of iodate which corresponds to 0.1988 and 0.1990 gram of thallium.

The results by the indicator method are thus seen to duplicate the results by the Andrews-Jamieson procedure and the ceric sulfate potentiometric procedure of Willard and Young (*10*).

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10. Willard and Young, *J. Am. Chem. Soc.*, **52**, 36 (1930).

Determination of Thiosulfate

Comparison was made between the titer obtained following the Andrews-Jamieson method and the internal indicator procedure.

A solution of approximately 0.1 N sodium thiosulfate was made by dissolving 12.4 grams of sodium thiosulfate pentahydrate in 1000 ml. of water.

The Andrews-Jamieson method consisted in diluting a 25.00-ml. sample of thiosulfate with 50 ml. of concentrated hydrochloric acid and 25 ml. of water in a 500-ml. glass-stoppered Erlenmeyer flask, to which 5 ml. of chloroform were added as indicator. This solution, which is approximately 5 molar in hydrochloric acid, was titrated using 0.1 N potassium iodate until the last faint trace of violet color in the indicator was dispelled.

The same procedure was applied in the use of internal indicators 184, 185, and 246 except that 0.5 ml. of the indicator was used in place of chloroform. The internal indicators were not added until the liberated iodine was practically all oxidized to iodine monochloride.

Amaranth served best of the three indicators. The results by the new procedure were found to be precisely the same as by the Andrews method.

Determination of Thiocyanate

Three solutions of approximately 0.1 N potassium thiocyanate were prepared by dissolving approximately 1.6 grams of the salt in 1000 ml. of water, and were titrated using approximately 0.1 N potassium iodate solution by the Andrews-Jamieson method and with Amaranth as indicator.

The Andrews-Jamieson method was carried out by transferring 25.00 ml. of potassium thiocyanate solution to a 500-ml. Erlenmeyer flask and adding 50 ml. of concentrated hydrochloric acid, 25 ml. of water, and 5 ml. of chloroform. The titration was begun immediately to prevent air oxidation at this high acidity, adding the solutions of iodate until the last trace of violet color was dispelled from the chloroform.

Using the indicator method, the chloroform was omitted and 0.5 ml. of indicator 184 was added after most of the iodine formed had been oxidized to iodine monochloride. The results using the Andrews procedure and the present method with any of the three indicators described were practically identical in 18 comparison determinations. The thiocyanates must be titrated without delay after the solution is made 5.0 M with hydrochloric acid to prevent oxidation in part by contact with air.

Determination of Sulfurous Acid

The determination of sulfurous acid was found to give exactly the same results by the Andrews-Jamieson method and the internal indicator procedure. The variation in no case was greater than one part per thousand. Indicator 184 was preferred because of the sharpness of the color change.

Using a saturated solution of sulfur dioxide in water at room temperature as sample for analysis, 25.00-ml. portions were transferred to 500-ml. glass-stoppered Erlenmeyer flasks, 40 ml. of concentrated hydrochloric acid were added, and the samples were diluted to 100 ml. with water. After addition of 5 ml. of chloroform the solutions were titrated with 0.1 *N* potassium iodate solution until the disappearance of the violet color from the chloroform. The same procedure was followed with internal indicators 184, 185, and 246, except that the chloroform was omitted and 0.5 ml. of indicator solution was added after disappearance of the iodine color with the oxidation to iodine monochloride.

Determination of Hydrogen Peroxide

By the Andrews-Jamieson procedure hydrogen peroxide is determined by addition of the peroxide to a sodium hydroxide solution of sodium arsenite. The solution of excess standard arsenite after reaction with hydrogen peroxide is acidified using a large excess of hydrochloric acid, and the unoxidized arsenite is oxidized to arsenate using standard iodate with chloroform as indicator.

A solution of hydrogen peroxide was prepared by diluting 50 ml. of ordinary commercial peroxide to 500 ml. A solution of sodium arsenite was prepared by dissolving 4.9 grams of arsenic trioxide in a slight excess of sodium hydroxide and diluting to 1000 ml. with water. The arsenite solution was standardized using the methods described above and found to be 0.0940 *N*. A solution of 10 grams of sodium hydroxide pellets in 100 ml. of water was used for the preparation of the arsenite solution for reaction with the peroxide to be determined.

The Andrews-Jamieson method was applied by taking 30.00-ml. portions of the 0.0940 *N* arsenite, to which were added 10 ml. of 10 per cent sodium hydroxide solution using a 500-ml. glass-stoppered Erlenmeyer flask as container. Samples of 11.00-ml. volume of the unknown hydrogen peroxide solution were slowly added from a buret to the alkaline arsenite solution with constant agitation. After allowing 2 minutes to complete the reaction, 40 ml. of concentrated hydrochloric acid were added and the flask and contents were shaken vigorously. Five milliliters of chloroform were then added and the solution of the excess arsenite was titrated, using 0.1 *N* potassium iodate until the violet color of the chloroform indicator was dispelled.

The same procedure was applied in the case of internal indicators 184, 185, and 246, except that the chloroform was omitted and 0.5 ml. of the indicator solutions was added after the oxidation of iodine to iodine monochloride was almost complete.

From an examination of Table XXXI it is observed that hydrogen peroxide can be determined using either the Andrews-Jamieson method or the internal indicator method with concordant results. Indicator 184 is preferred because of the sharpness of the color change involved.

Determination of Hydrazine and Phenylhydrazine

The determination of hydrazine has been described by Jamieson (*11*) and there should be no complications in applying the scheme to the determination of phenylhydrazine. However, the phenylhydrazine ordinarily contains some impurity which is extracted by the chloroform used as indicator, which prevents the detection of the presence or absence of a violet coloration at the equivalence point of the reaction.

TABLE XXXI

Determination of Hydrogen Peroxide

(30.00 ml. of 0.0940 *N* sodium arsenite plus 10 ml. of 2.5 *N* NaOH 11.00 ml. of unknown H_2O_2 solution approximately 0.1822 *N*. Titration of excess arsenite by 0.1000 *N* KIO_3)

Potassium Iodate Required			
Andrews-Jamieson method	Indicator 184	Indicator 185	Indicator 246
Ml.	*Ml.*	*Ml.*	*Ml.*
8.23	8.18	8.20	8.17
8.20	8.23	8.22	8.25
8.19	8.23	8.19	8.13
Av. 8.21	8.22	8.20	8.17

For determination of hydrazine, a solution of approximately 0.1 *N* $N_2H_4 \cdot H_2SO_4$ in water was used. For the Andrews-Jamieson procedure 25.00-ml. portions of the hydrazine sulfate solution were transferred to 500-ml. glass-stoppered Erlenmeyer flasks and 40 ml. of concentrated hydrochloric acid were added, followed by dilution to 100 ml. with water.

The resulting solutions were titrated using 0.1 *N* potassium iodate, after the addition of 5 ml. of chloroform, until the color changed from violet to colorless upon the addition of the last drop of iodate solution.

The same procedure was applied in the internal indicator procedure, except that no chloroform was added and 0.5 ml. of indicators 184, 185, and 246 was added after the iodine liberated by the first addition of iodate was oxidized almost completely to iodine monochloride (Table XXXI).

For the determination of phenylhydrazine an approximately 0.1 *N* solution was prepared by dissolving 1.2 ml. of the product in 1000 ml. of hydrochloric acid made by diluting 100 ml. of concentrated acid with water.

The procedure employed in the titration of hydrazine sulfate was employed in the titration of 25.00-ml. portions of phenylhydrazine solution, except that beakers were employed and the iodate oxidation was followed potentiometrically (*12*).

The internal indicator procedure then was applied in the same manner, except that 0.5 ml. of indicators 184, 185, and 246 was added after the reaction of the oxidation of iodine was almost complete. The results of a series of titrations are given in Table XXXII.

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11. Jamieson, G. S., "Volumetric Iodate Methods," New York, Chemical Catalog Co., 1926.

12. Smith, G. F., and Sullivan, V. R., *J. Soc. Chem. Ind.*, **41**, 104 T (1937).

TABLE XXXII

Determination of Hydrazine and Phenylhydrazine

(Approximately 0.1 *N* $N_2H_4 \cdot H_2SO_4$ in water, 25.00 ml. taken for analysis. Approximately 0.1 *N* $C_6H_5 \cdot NH \cdot NH_2$ in dilute HCl solution, 25.00 ml. taken for analysis. Oxidant, 0.1000 *N* potassium iodate solution.)

Sample	Potassium Iodate Required			
	Andrews method	Indicator 184	Indicator 185	Indicator 246
	Ml.	*Ml.*	*Ml.*	*Ml.*
$N_2H_4 \cdot H_2SO_4$	22.95	22.90	22.95	22.95
	22.87	22.89	22.95	22.95
	22.85	22.90	22.93	22.97
	Av. 22.92	22.90	22.94	22.95
$C_6H_5 \cdot NH \cdot NH_2$	17.50	17.45	17.40	17.50
	17.45	17.50	17.35	17.40
	17.40	17.45	17.35	17.55
	Av. 17.45	17.47	17.36	17.48

Table XXXII shows that for the determination of both hydrazine and phenylhydrazine the Andrews-Jamieson procedure and the use of internal oxidation indicators give essentially the same results. Indicators 184 and 185 are preferred in the determination of hydrazine and indicator 185 is preferred in the determination of phenylhydrazine.

CHAPTER VII

REACTION CHARACTERISTICS IN THE OXIDATION OF ORGANIC COMPOUNDS

The chief advantage found in the volumetric oxidation-reduction reactions of *inorganic* analysis is their property of being *specific.* The reactions are in a great many cases simple electron exchanges such as in the reactions of cerate oxidimetry in the determination of iron, titanium, vanadium, iodine and mercury. Such reactions are strictly reversible and have definite electrode potentials under specified conditions. The preparation of solutions for analysis by the use of standardized procedures which are direct and stoichiometric are subject to many variations in technique. The oxidation potentials are of wide variation in magnitude and highly specific. Reaction velocities are in general ample and in many cases specific catalysts are known and may be employed to alter the reaction kinetics. A multiplicity of redox indicators are available and serve for a wide variety of reaction conditions. Conditions may be altered, under which influence, the single electrode reaction of both the oxidant and the reductant in a given redox volumetric procedure may be increased or decreased. Iron in the ferrous state may be converted to complex ion types which have single electrode potentials of oxidation ranging from 0.5 to 1.25 volts. Ce (IV)-Ce (III) single electrode potentials may be varied from 1.28 to 1.86 volts depending upon the acid environment and the type of the cerate ion employed. The vanadium (V)-vanadium (IV) single electrode potential may be varied from 1.0 to 1.4 volts depending upon the acid concentration under which it is employed. The Cr (VI)-Cr. (III) may be altered from 1.1 to 1.3 volts depending upon acidity.

For these reasons volumetric redox reactions in inorganic analysis may be devised which are highly specific and free from inhibitions.

Conditions for the quantitative oxidation of organic compounds are in most cases directly the opposite. Such reactions are frequently too slow for use in direct oxidation and require excess oxidant with back titration of the excess. Often the reactions are not strictly stoichiometric and precise. The reactions are not specific. Side reactions involving similar organic compounds present interferences. In practically all cases the reaction kinetics are unknown and information concerning oxidation potentials is not available. Intermediate, stepwise reactions always play a role from the initiation of a particular oxidation to its final completion the rate controlling properties of which often demand reaction times of from five minutes to 30 hours. Most quantitative organic oxidation reactions involve the use of excess standard oxidant with subsequent determination of the required excess. Most reactions being empirical require blank determinations. The analyses of mixtures selectively are almost always burdened with the necessity for duplicate analyses by separate and distinct companion procedures to identify and determine degradation products.

The routine determination of the composition of industrial products, in organic chemistry and the study of the various manufacturing operations involved in their preparation, are, however, in some cases well established. As an illustration, one might cite the determination of glycerol in the soap industry. Procedures are available for the isolation of interfering organic reactants and the final quantitative estimation of glycerol by volumetric procedure employing dichromate oxidation in hot sulfuric acid solution. The reaction time is 60 to 90 minutes and the process involves the quantitative determination of the excess dichromate added. This process is a standard procedure. An improved procedure has been described by Smith and Duke (*1*) together with comparison with the performance of the older process as a control.

A survey of the procedures in the volumetric determinations of organic compounds has been given by the present author in the book *Cerate Oxidimetry* (*2*).

The general procedures of greatest importance are the following:

1. Dichromate oxidations in sulfuric acid solution. Typical example, the oxidation of glycerol.
2. Bromate — Bromide oxidations in acid solution. The bromination of 8-hydroxy quinoline is an illustration (*3*).
3. Potassium permanganate in alkaline solution (the Stamm reaction). A general procedure for the oxidation of organic matter to carbon dioxide (*4*).
4. Ce(IV) in nitric or perchloric acid solution. The oxidation of organic aliphatic compounds to form HCOOH and Ce(III) as end products.
5. Periodic acid oxidation in acid solution. The oxidation of aliphatic organic compounds with CO_2, HCOOH, CH_3COOH, HCHO and HIO_3 as end products.
6. Iodic acid in hot sulfuric acid with CO_2 and I_2 as end products (*5*). Methods 4 and 5 and particularly method 5 are used in the characterization of organic type compounds as well as for analytical determination.

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1. Smith and Duke, *Ind. Eng. Chem. Anal. Ed.*, 12, 201 (1940).
2. Smith, "Cerate Oxidimetry." The G. Frederick Smith Chemical Company, Columbus, Ohio, 1942, pp. 88-123.
3. Smith and May, *J. Am. Cer. Soc.*, 22, 31 (1939).
4. Oesper, "Newer Methods of Volumetric Analysis." D. Van Nostrand 1938, pp. 55-64.
5. Williams and Woods, *J. Am. Chem. Soc.*, 59, 1408 (1937).

7. Selenium oxide as an oxidizing agent in organic compounds. An extensive review paper by Vène (*6*) with discussion of experimental conditions, precautions and recovery of SeO_2 includes bibliography with 91 references.
8. Lead tetraacetate is frequently employed but requires non-aqueous solvents (*7, 8, 9, 10, 11, 12*).

The Qualitative Identification of Organic Compounds Employing Oxidation-Reduction

For use in the identification of organic compounds a series of general tests following the use of oxidation-reduction reactions would include the following:

1. Bromine in carbon tetrachloride. A positive test for unsaturation. The reagent (Br_2 in CCl_4) is decolorized upon its addition to solutions of organic compounds having double or triple bands (olefinic and acetylenic linkages) without the evolution of hydrogen bromide which is insoluble in carbon tetrachloride. A characteristic reaction is:

$$C_6H_5CH = CH_2 + Br_2 \longrightarrow C_6H_5CH\,Br\,CH_2\,Br$$

2. Potassium permanganate (Baeyer's test). A positive test if the permanganate is decolorized, indicating the presence of ethylenic or acetylenic linkages. The reaction is made in water or acetone media at ordinary temperatures. If the reaction is heated further oxidation occurs with final cleavage of the carbon chain. A characteristic reaction is:

$$RCH = CHR \longrightarrow RCHOHCHOHR$$

The solution tested should remain neutral as the oxidations are more extreme in alkaline media. The use of zinc permanganate serves the purpose both of oxidant and buffer to maintain neutrality due to the formation of insoluble zinc hydroxide.

3. The Perchlorato-cerate and Nitrato-cerate test for alcoholic and phenolic hydroxyl groups. A characteristic reaction is:

$$C_2H_5OH + Ce(NO_3)_6^{=} + [HNO_3] \longrightarrow CeC_2H_5O(NO_3)_5 + HNO_3$$

The nitrato-cerate ion formed from the alcohol is intensely red. By using the perchlorato-cerate ion in the presence of perchloric acid the test is more delicate. Alcohols and phenols up to ten carbons respond to the test. Water or dioxane is used as solvent. Dioxane is employed in testing for phenols. The test by the permanence of the red color produced distinguishes in part between primary, secondary and tertiary alcohols. Hydroxy acids and aldehydes as will many other organic hydroxy compounds respond to the test. Aldehydes, ketones, acids, alkyl halides, esters and other common organic compounds containing only C, H, O, or halogen atoms do not interfere.

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6. Vène, *Bull. soc. chim.* 12, 506 (1945).
7. Criegee, *S. taber. Ges. Beförder, Ges. Natur w. Marburg*, 69, 25 (1934), [C. A., 29, 6820 (1935)].
8. Baer, *J. Am. Chem. Soc.*, 62, 1597 (1940).
9. Criegee, *Angew. Chem.*, 50, 153 (1937) and 53, 321 (1940).
10. Criegee, *Ann.*, 495, 211 (1932).
11. Criegee, *Ber.*, 64, 260 (1931) and 65, 1770 (1932).
12. Karrer and Hirohata, *Helv. Chim. Acta*, 16, 959 (1933).

4. Periodic acid test (the Malaprade reaction). A positive test when applied to the identification of 1,2 glycols, α-hydroxy aldehydes, α-hydroxy-ketones, 1,2-diketones and α-hydroxy acids. Olefins, secondary alcohols, 1,3-glycols, ketones and aldehydes are not affected when the test is properly applied.

The periodic acid solution (0.5 g. H_5IO_6 per 100 ml. H_2O), a two-ml. portion, is acidified by the addition of 0.05 ml. (1 drop only) of concentrated nitric acid. Add a small portion of the material to be identified, shake the solution and add 1 or 2 drops of a 3 per cent aqueous solution of silver nitrate. A white precipitate of silver iodate insoluble in dilute nitric acid indicates a positive test. (Silver periodate is soluble in dilute nitric acid.)

A typical illustrative reaction is:

$$CH_2OH \cdot CH_2OH + H_5IO_6 + [HNO_3] \longrightarrow 2HCHO + HIO_3 + 2H_2O$$

5. Alkaline silver nitrate (Tollens' reagent). A typical reaction for aldehydes. An illustrative reaction is as follows:

$$HCHO + Ag_2O \longrightarrow 2Ag\ (\text{Mirror}) + HCOOH$$

The silver reagent is prepared by reacting in a thoroughly clean test tube (to facilitate mirror formation) containing 2 ml. of a 5 per cent silver nitrate solution. Add a drop of 10 per cent sodium hydroxide solution to precipitate Ag_2O. Add dropwise a 2 per cent solution of ammonia until the precipitated silver oxide is just dissolved upon shaking the test tube contents. Avoid an excess of ammonia. The solution of the organic compound upon addition to the test reagent gives a positive test when a silver mirror is formed on the inner walls of the test tube.

6. Fehling's solution. A test for reducing sugars. A typical reaction is the following:

$$RCHO + 2CuO \longrightarrow RCOOH + Cu_2O$$

Fehling's solution is prepared by mixing equal volumes of the two following solutions: $CuSO_4 \cdot 5H_2O$, 34.6 g. of the blue crystals in 500 ml. of water. Sodium potassium tartrate (173 g.) and sodium hydroxide (70 g.) in 500 ml. of water. A positive test results in the formation of a precipitate of Cu_2O.

7. Iodic acid. A strong sulfuric acid solution of iodic acid as a general oxidant (somewhat selective only). A positive test is indicated by the formation of iodine identified by its color. A typical reaction is as follows:

$$5\ COOH \cdot COOH + HIO_3 + [H_2SO_4] + \text{heat} \longrightarrow 10CO_2 + I_2 + 6H_2O$$

The main distinctions in reactivity involve reactions positive with primary alcohols (up to octyl alcohol) as distinct from polyhydric alcohols and fatty acids. Phenolic compounds and aniline derivatives are oxidized. For generalization consult Williams and Woods (*13*).

Periodic Acid Oxidations of Organic Compounds. The Malaprade Reactions

The Malaprade reaction (*14, 15, 16*) is based upon the oxidation intensity of periodic acid used in excess on aliphatic polyhydroxyalcohols of 2 to 6 carbons when in dilute (0.2*M*) aqueous solution at ordinary temperatures. The reaction is that of the cleavage of the carbon bond in compounds in which two adjacent carbon atoms each bear an oxygen atom either as a hydroxyl or carbonyl group. Such reactions are carried out in basic, neutral or mineral acid solution, ordinarily sulfuric acid, and with a small excess of periodic acid. Because the reactions are not instantaneous and because degradation products such as formaldehyde and formic acid are reducing in character they are studied at room temperature or lower in some cases. The reduction product is always iodic acid.

The study of the periodic acid organic oxidations requires analytical procedures for the determination of the excess periodic acid employed in the presence of its end reduction product iodic acid. Such oxidations require that molecular cleavage products such as formaldehyde and formic acid may require quantitative isolation or determination to verify stoichiometric valuations. Such analytical procedures have been described and are readily achieved.

Since periodic acid oxidations of organic compounds are time consuming, and since most of the reactions are to some extent empirical, the procedures are of limited use but are now being more actively studied for quantitative analytical determinations. For example, the determination of glycerol in the soap industry employs the dichromate procedure quite generally even though such reaction is carried out under practically the same reaction conditions (except that the reaction is carried out at higher temperature) as the periodic acid oxidation of glycerol. This is in part true because the equivalent weight of glycerol when oxidized by excess chromic acid is the molecular weight divided by 14 whereas its equivalent weight by periodic acid oxidation is the molecular weight divided by 4. If the reaction time must be shortened, the oxidation of glycerol can be carried out by the perchlorato-cerate method (*17*) by the use of which the determination of glycerol requires one-fourth as much time and the equivalent weight is the molecular weight divided by eight.

The very great value of the study of periodic acid oxidations of organic matter consists in its use in promoting a specific type of molecular cleavage. Complex organic molecules of controversial or unknown structural composition have been found to react with periodic acid to cleave the molecule into two or more simpler molecular species whose composition is readily recognized. Studies of the complex sugars or of complex biological preparations including alpha hydroxy amino-acids (*18*) have been greatly clarified through their

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13. Williams and Woods, *J. Am. Chem. Soc.*, 59, 1408 (1937).
14. Malaprade, *Bull. Soc. Chim de France*, 43, 683 (1928).
15. J. Lange, "Action de L'Acide Periodic sur les Polyalcools," Les Editions Vega 43, Rue Madame, Paris, France, 1933.
16. Marcel Grandchamp, Thesis, "Contribution á l'Etude de l'Oxydation Periodique Des Dérivés α Hydroxyamines et α Diamines, 1948, Presses Du Temps Present, 12, Rue LaGrange, Paris, France.
17. Smith and Duke, *Ind. Eng. Chem., Anal. Ed.*, 12, 201 (1940).
18. Nicolet and Shinn, *J. Am. Chem. Soc.*, 61, 1615 (1939)

examination following periodic acid oxidation. When it is recognized that the chemical synthesis of biologically important organic compounds or other organic complex molecules must, by nature, follow only after an accurate analysis of structural configurations, the importance of studies involving periodic acid oxidations becomes apparent.

The cleavage of organic molecules by periodic acid oxidation involves the breaking of carbon to carbon linkages which carbons carry hydroxyl or carbonyl substituent groups. Thus in the case of the oxidation of a simple compound such as ethylene glycol the periodic acid supplies one atom of oxygen in being reduced to iodic acid and the carbon to carbon bond is broken with degradation of the ethylene glycol to two molecules of formaldehyde. On the other hand, periodic acid under the same conditions is without action on such an equally simple organic molecule as ethyl alcohol. The simple amino acid serine of the formula $CH_2OH \cdot CHNH_2 \cdot COOH$ (*18*) upon oxidation using periodic is broken down to form one molecule of formaldehyde and one molecule of glyoxalic acid with the liberation of one molecule of ammonia. The same type reaction results when monoethanol amine ($CH_2OH \cdot CH_2 \cdot NH_2$) is similarly oxidized by periodic acid. The oxidation of serine is comparable to the oxidation of glycerol and the oxidation of monoethanol amine is analogous to the oxidation of ethylene glycol as clearly indicated by the following reactions:

$$\underset{\text{(ethylene glycol)}}{CH_2OH \cdot CH_2OH} + H_5IO_6\,[H_2SO_4] \longrightarrow \underset{\text{(formaldehyde)}}{2HCHO} + HIO_3 + 3H_2O$$

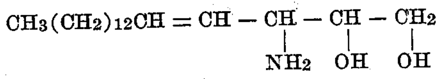
$$\underset{\text{(ethanol amine)}}{CH_2OH \cdot CH_2 \cdot NH_2} + H_5IO_6 + [H_2SO_4] \longrightarrow 2HCHO + HIO_3 + 2H_2O + NH_3$$

$$\underset{\text{(glycerol)}}{CH_2OH \cdot CHOH \cdot CH_2OH} + H_5IO_6 + [H_2SO_4] \longrightarrow HCHO + \underset{\text{(glyoxalic acid)}}{CHO \cdot COOH} + HIO_3 + 3H_2O$$

$$\underset{\text{(serine)}}{CH_2OH \cdot CHNH_2 \cdot COOH} + H_5IO_6 + [H_2SO_4] \longrightarrow HCHO + CHO \cdot COOH + HIO_3 + 2H_2O + NH_3$$

(The ammonia liberated forms ammonium sulfate in the above acid reactions.) Primary and secondary amines are readily oxidized while tertiary amines remain unattacked.

As an illustration, we have the role of periodic acid oxidations when applied to the establishment of the correct structural formula of sphingosine. In 1931, Klenk and Diebold (*19*) after a thorough study of this product assigned to it the structural formula



$$CH_3(CH_2)_{12}CH = CH - \underset{NH_2}{\underset{|}{CH}} - \underset{OH}{\underset{|}{CH}} - \underset{OH}{\underset{|}{CH_2}}$$

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19. Klenk and Diebold, *Z. physiol. Chem.*, **198**, 25 (1931).

based upon a splitting of the double bond and division of the compound into palmitaldehyde and a product which was erroneously identified as dl-α-amino-*N*-butyric acid. This study was repeated by Carter and associates (*20*) utilizing periodic acid as reactant and the position of the amino group was proven to be between the two hydroxyl substituents rather than as indicated in the formula given.

The kinetics of the reactions of periodic acid as studied in the case of the oxidation of pinacol has been reported by Price and Kroll (*21*). As an example of the use of periodic acid in the quantitative determination of certain polyhydroxy alcohols in the presence of each other, the work of Allen, Charbonnier and Coleman (*22*) has been given previously.

The Quantitative Determination of Periodic Acid in the Presence of Iodic Acid

Three general methods are available for use in the determination of periodic acid in the presence of iodic acid and are as follows:

1. The reduction of periodic acid in neutral solution buffered by excess sodium bicarbonate. Excess of sodium arsenite (as catalyzed by the presence of the iodide ion), is added and after 5 minutes the excess arsenite is titrated employing standard iodine solution.

2. The oxidation of a solution of manganous sulfate in the presence of sodium carbonate by periodic acid to form MnO_2 and iodic acid. The amount of HIO_4 reduced to HIO_3 is determined by the liberation of iodine in acid solution by the MnO_2 following the addition of excess KI and the titration of the liberated iodine by standard sodium thiosulfate. The MnO_2 is most conveniently determined after isolation following centrifugation.

In most cases the products of oxidation of an organic compound, such as formaldehyde or formic acid or both, do not interfere in the determination of the periodic acid employed. Therefore, use is made of the first and most convenient of the two methods outlined. In case the products of the oxidation are to be examined further, and for the purpose of eliminating periodic acid from a reaction medium leaving only sodium iodate, excess sodium carbonate, sodium sulfate and the organic degradation products; the second method is employed.

3. The iodimetric determination of periodic acid and the simultaneous determination of its iodic acid reduction product may be applied. By determining the iodine liberated from a sulfuric acid

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20. Carter, *J. Biol. Chem.*, **170**, 285 (1947).
21. Price and Kroll, *J. Am. Chem. Soc.*, **60**, 2726 (1938).
22. Allen, Charbonnier, and Coleman, *Ind. Eng. Chem.*, *Anal. Ed.*, **12**, 384 (1940).

solution of the periodic acid upon the addition of excess iodide employing thiosulfate to evaluate the iodine formed, a blank determination is obtained. Following the use of the same procedure to the mixture of HIO_4 and HIO_3 resulting from a given organic oxidation procedure the amount of HIO_4 reacted may be determined. In this case it must be shown that the reaction products from the oxidation do not interfere.

4. The I_2O_7 content of periodates in the presence of iodates may be determined as follows: The weighed sample is covered with 20 ml. of water, and 5 to 10 drops of 6 *N* HCl is added to hasten solution. No chlorine is liberated from the acid of this concentration. The solution is diluted to 100 ml., made just alkaline to phenolphthalein paper with borax, buffered with borax and boric acid (*23*), and an excess of potassium iodide is added. Under these conditions, the periodate is reduced to iodate. The liberated iodine is titrated with 0.1 *N* arsenite. The reaction involved is as follows:

$$NaIO_4 + 2NaI + 4H_3BO_3 = NaIO_3 + I_2 + Na_2B_4O_7 + 6H_2O$$

The Determination of Periodate Alone or in the Presence of Iodic Acid by Titration Using Arsenite. A volume 5.00 to 25.00 ml. of neutral sodium paraperiodate, $Na_2H_3IO_6$, or metaperiodic acid, H_5IO_6 (equal to 5-6 ml. of 0.1 *M* reagent), is placed in a 500 ml. Erlenmeyer flask. This amount of periodate solution will require 10-12 ml. of 0.1 *N* arsenite for reaction as indicated in the following reactions:

$$\text{(a)}\quad H_5IO_6 + Na_3AsO_3 \longrightarrow Na_3AsO_4 + HIO_3 + 2H_2O$$

$$\text{(b)}\quad HIO_3 + NaHCO_3 \longrightarrow NaIO_3 + H_2CO_3$$

$$\text{(a + b)}\quad H_5IO_6 + Na_3AsO_3 + NaHCO_3 \longrightarrow Na_3AsO_4 + NaIO_3 + H_2CO_3 + 2H_2O$$

The solution of meta periodic acid is buffered by the addition of 5 ml. of a saturated solution of sodium bicarbonate in excess of that required to neutralize the periodic acid employed. An excess of standard 0.1 *N* sodium arsenite solution is then added followed by one ml. of 20 per cent sodium iodide solution to serve as catalyst. After 5 minutes at ordinary temperature the excess of arsenite is titrated using a standard solution of 0.05 *N* iodine.

Results obtained using this procedure are not comparable in accuracy to values obtained if the periodic acid or periodate solution were treated with excess potassium iodide in acid solution and the liberated iodine determined by titration using sodium thiosulfate. The reactions are suitable and make available a procedure for the determination of periodic acid in the presence of iodic acid. The ability to perform this determination provides for the determination of the required amount of periodic acid to accomplish the oxidation of an unknown amount of an organic compound under which conditions iodic acid is formed simultaneously. It must be noted that by this procedure the equivalent weight of periodic acid is the molecular weight divided by 2 whereas by the method employing iodine liberation carries an equivalent weight the molecular weight divided by eight. The accuracy with which periodates may be determined by the arsenite procedure is proportionally diminished. The results obtained by the latter procedure, however, duplicate the procedure being described to within 1 or 2 per cent accuracy. This procedure is not interfered with by the presence of the usual degradation products of a given oxidation of an organic compound such as formic acid or formaldehyde. The reaction involved in case neutral sodium para-periodate is employed in place of meta-periodic acid is as follows:

$$Na_2H_3IO_6 + Na_3AsO_3 + NaHCO_3 \longrightarrow NaIO_3 + Na_3AsO_4 + Na_2CO_3 + 2H_2O$$

The reactions of oxidation employing periodic acid as oxidant are often carried out in sulfuric acid solution. They require reaction times of from one-half to 24 hours at room temperature or somewhat less. The reactions of the determination of excess periodic acid employed as given above follow neutralization of the sulfuric acid and the addition of a definite excess of sodium bicarbonate.

The function of the addition of a small amount of iodide to catalyze the reduction of periodate by arsenite is explained by the following reactions:

$$H_5IO_6 + 2KI \longrightarrow HIO_3 + I_2 + 2KOH + H_2O$$

$$I_2 + Na_3AsO_3 + 2NaHCO_3 + H_2O \longrightarrow Na_3AsO_4 + 2NaI + 2H_2CO_3$$

If the reaction for the periodic acid-arsenious acid analysis is not carried out in the presence of sufficient sodium bicarbonate the loss of iodine may occur from the iodide added as catalyst. The use of potassium iodide as catalyst allows the last two reactions given to be complete in 5 minutes.

The Preparation of Periodate and of Arsenite for Use in the Malaprade Reaction. Sodium pera-periodate is prepared by the solution of 7.35 grams of $Na_2H_3IO_6$ by the addition of 75 ml. of normal sulfuric acid employing a 1000 ml. graduated flask with final dilution by distilled water to the mark. This solution is approximately 0.05 normal and is stable upon long storage.

The preparation of the arsenite solution involves the solution of 4.948 grams of C.P. As_2O_3 using a 1000 ml. flask. Solution of the

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23. Müller and Wegelin, *Z. anal. Chem.*, 52, 755 (1913).

arsenious acid is effected by warming it with 50 ml. of 2 N sodium hydroxide until all has dissolved. Neutralize by the addition of a small amount of sulfuric acid using phenolphthalein as indicator. Dissolve 20 grams of sodium bicarbonate in 500 ml. of cold water and add this solution to the volumetric flask and dilute to the mark giving a 0.1 N solution of sodium arsenite.

Advantages Attained by the Arsenite Determination of Periodic Acid. These may be listed as follows:

1. The process is simple and requires the use of none but familiar analytical reactants.
2. C.P. periodic acid or periodates are not a prerequisite since the process involves a blank determination of the oxidant.
3. Iodic acid, following the procedure as described, does not react with arsenite.
4. It permits of the determination of small amounts of polyhydric alcohols following reduction of periodic acid to iodic acid.
5. The method is specific for periodic acid.

The Determination of Periodic Acid in the Presence of Iodic Acid Employing Manganese Carbonate. The oxidation of manganous sulfate to manganese dioxide in sodium carbonate solution results in the reduction of periodates to iodates. The precipitated manganese dioxide is then separated by centrifugation. The precipitated is washed by suspension in wash liquid and re-centrifugation to remove the iodate formed and other products of the oxidation. The manganese dioxide thus formed, corresponding to the amount of periodate reduced, is then determined by the reaction of potassium iodide in acid solution upon the manganese dioxide to liberate a corresponding amount of iodine. The iodine is then titrated by sodium thiosulfate. The basic reactions are as follows:

$$MnSO_4 + Na_2H_3IO_6 + Na_2CO_3 \longrightarrow MnO_2 + NaIO_3 + Na_2SO_4 + NaOH + H_2CO_3$$

$$MnO_2 + 2KI + 2H_2SO_4 \longrightarrow MnSO_4 + I_2 + K_2SO_4 + 2H_2O$$

The reactions are applicable following reduction of excess periodate in the presence of iodate and the reaction products from the oxidation of organic matter such as formate and formaldehyde. This process, besides being suited to the determination of periodate in the presence of iodate, is distinct from the periodate, arsenite reactions previously described. It has the advantage that the solution of reactants, following centrifugal removal of $MnO_2 + MnCO_3$ has the same reactants as the original solution of organic material for oxidation with only the addition of sodium sulfate as added component. The process is more involved than the periodate-arsenite reaction. The procedure requires a blank determination to account for the minute quantity of manganese carbonate oxidized to MnO_2 by the influence of atmospheric oxygen.

Procedure Applying the Manganese Carbonate Reduction of Periodates in the Presence of Iodates. The reagents employed in this determination are as follows:

Sodium Carbonate Solution. 143 g. of $Na_2CO_3 \cdot 10H_2O$ per 1000 ml.
Manganese Sulfate. 10 g. of $MnSO_4 \cdot 4H_2O$ per 1000 ml.
Periodate Solution. 10 g. of H_5IO_6 or $Na_3H_2IO_6$ per 1000 ml.
Sodium Sulfate. 50 g. of $Na_2SO_4 \cdot 7H_2O$ per 1000 ml.
Potassium Iodide. 20 g. KI per 100 ml.
Sulfuric Acid. 200 g. of conc. H_2SO_4 (sp. gr. 1.84) per 1000 ml.

The method of operation involves, reduction of periodate by oxidation and precipitation of manganese dioxide, centrifugation and washing of MnO_2 and the determination of its available oxygen.

Oxidation and Precipitation. Centrifuge tubes of 40 ml. capacity are cleaned by treatment with chromic acid-sulfuric acid and rinsed with distilled water. To these are added the blank determination and reaction determination reagents in the following order, for the blank:

First. Sodium carbonate 3.0 ml.
Second. Manganese sulfate 10.0 ml.
For the determination of $MnSO_4$—$Na_2H_3IO_6$ reaction:
First. Neutral solution of $Na_2H_3IO_6$ representing not more than 3 ml. of molar reagent periodate.
Second. Sodium carbonate 3 ml.
Third. Manganese sulfate 10 ml.

Mix by swirling the contents of the centrifuge tubes. In the blank there is observed a white precipitate of manganese carbonate which turns slightly darker in contact with atmospheric oxygen. In the second reaction tube the original formation of manganese carbonate is seen to rapidly transform to a dark brown dense granular precipitate. Sometimes there is also observed a momentary slight violet coloration analogous to a dilute solution of manganate. The reaction of the formation of manganese dioxide is practically instantaneous and may be centrifuged after five minutes. Separation of manganese dioxide by centrifugation may, however, be delayed 2 to 3 hours without alteration.

Centrifugation and Washing. After centrifugation, decant the supernatant liquid allowing 2 to 3 minutes draining time to eliminate as much as possible the soluble reaction products. The washing operation must be efficient. Add a volume of sodium sulfate solution equal to the starting volume to the centrifuge tubes and agitate the precipitate efficiently into suspension employing a glass rod for this purpose, washing the surface of stirring rod after use, using a stream of sodium sulfate solution from the wash bottle. A thorough agitation of precipitate and wash liquid together is essential. The success of the washing operation is dependent upon this manipulation. Repeat this centrifugal washing operation 3 times.

Determination of Available Oxygen in MnO_2. Add 2 ml. of potassium iodide solution to the manganese dioxide in the centrifuge tube followed by 0.4 ml. of the sulfuric acid solution from a transfer pipet. Promote rapid reaction between MnO_2 and KI by agitation of the reactants employing a stirring rod, finally rinsing the stirring rod into the centrifuge tube with distilled water. Add 20 ml. of water, swirl the contents of the centrifuge tube and titrate the liberated iodine using standard 0.1 *N* sodium thiosulfate without addition of starch indicator until the color of iodine is just completely eliminated.

The difference between the amounts of sodium thiosulfate required for the blank and for the periodate solution represents the quantity of periodate reacted. Each milliliter of 0.1 *N* sodium thiosulfate is equal to 9.59 mg. of HIO_4, or 14.04 mg. of $Na_3H_2IO_6$.

The Determination of Mixed Formaldehyde and Formate in Presence of Iodic Acid After Removal of Periodic Acid. The oxidation of an organic compound employing an excess of periodic acid in dilute sulfuric acid solution in accordance with a typical reaction such as the oxidation of glycerol is in accordance with the reaction:

$$CH_2OH \cdot CHOH \cdot CH_2OH + 2H_5IO_6 + [H_2SO_4] \longrightarrow$$
$$2HCHO + HCOOH + 2HIO_3 + 5H_2O$$

The resulting solution contains periodic and iodic acids as well as sulfuric acid, formic acid and formaldehyde. Assuming the reaction products to be as given the determination of glycerol following this procedure involves only the determination of the excess of periodic acid employed. Two procedures are available for this determination, the periodic acid reduction in bicarbonate solution employing standard arsenite and the manganous carbonate procedure in sodium carbonate solution with iodimetric determination of the manganese dioxide formed, have been previously described. Both the latter two methods suffer no interference from iodic acid, formic acid or formaldehyde.

The reaction given for glycerol is general for polyhydroxy alcohols such as ethylene glycol, glycerol, erythritol, arabinol, and mannitol

following the consumption of 2, 4, 6, 8, and 10 equivalents as represented in the following type reaction:

$$CH_2OH \cdot (CHOH)_n \cdot CH_2OH + (n+1)H_5IO_6 \longrightarrow$$
$$(n+1)HIO_3 + 2HCHO + mHCOOH + (2m+1)H_2O$$

The formic acid or formaldehyde are not oxidized further at ordinary temperatures. As will be seen in subsequent material other type carbon compounds are oxidized by periodic acid such as glucose, an aldehyde sugar and fructose a carbonyl sugar. By consideration of these latter cases and in consideration of the oxidation of alpha-hydroxamines and related compounds, it may be advisable to have available a method for the determination of formaldehyde and formic acid in the presence of periodic acid and iodic acid.

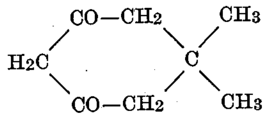
The removal of periodic acid from mixtures of periodic, iodic and formic acids and formaldehyde is carried out by the manganese carbonate method previously described. The oxidation of formic acid and formaldehyde in the presence of iodic acid is provided for if a sodium carbonate solution of potassium permanganate is employed. The reactions are as follows: (Reaction at water bath temperature under a reflux condenser requires 20 minutes).

$$3HCHO + 4KMnO_4 \longrightarrow 4MnO_2 + K_2CO_3 + 2KHCO_3 + 2H_2O$$
$$3HCOOK + 2KMnO_4 \longrightarrow 2MnO_2 + 2K_2CO_3 + KHCO_3 + H_2O$$

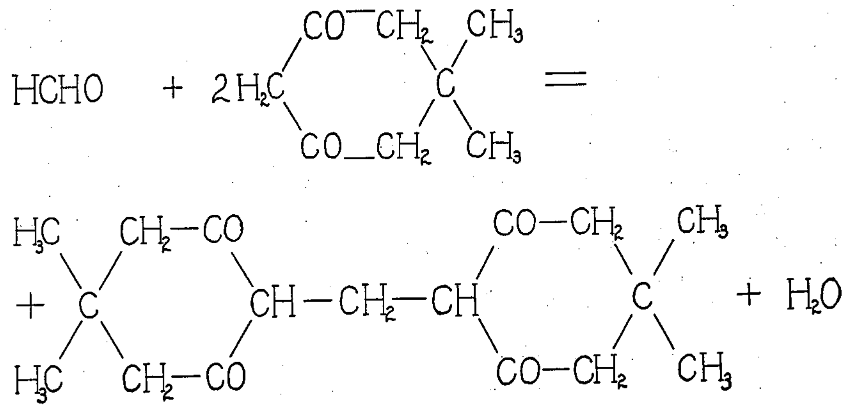
The measure of the total formic acid and formaldehyde is thus obtained by determining the MnO_2 formed iodimetrically. It then remains to devise a scheme for the determination of formaldehyde in the presence of formic acid. By this means together with the determination of the total formaldehyde plus formic acid, the formic acid present is defined by difference. Two methods to accomplish this purpose are available. The first of these procedures involving iodimetry employs Nessler's reagent. The second involves precipitation of formaldehyde employing the organic precipitant dimédon (5,5-dimethyldihydroresorcinol), sometimes called méthone.

The Nesslerization process for the determination of formaldehyde involves the removal of the mercurous iodide from the solution (which also contains iodate) by filtration and washing prior to its iodimetric determination. The presence of iodate does not interfere with the oxidation of formaldehyde to formic acid. The precipitated mercurous iodide after filtration employing a sintered glass crucible is dissolved in potassium iodide and oxidized employing standard iodine solution in the customary manner. The Nesslerization procedure for the determination of formaldehyde in the presence of iodic and formic acids has been demonstrated to give excellent results also in the determination of furfurol benzaldehyde and piperonal.

Dimédon or 5,5-dimethyldihydroresorcine has the formula:



It is a saturated six-membered ring compound containing an active methylene group and the reaction may be formulated as follows:



The product formed is crystalline, of definite melting point (188-189°) and has the molecular weight 292 or almost 10 times that of formaldehyde. The mechanism of reaction is the same for other aldehydes such as benzaldehyde. Dimédon does not react to precipitate with glucose, lactose or arabinose. It does not react with ketones in alcoholic solution up to 100 degrees. It may be employed in weakly acid, neutral or alkaline solution. Boiling alkalies are without effect but strong mineral acids decompose it with formation of the original materials.

The dimédon method for the determination of formaldehyde is applicable to solutions containing the products of a periodic acid oxidation of organic matter after reaction by arsenite to remove excess periodic acid.

The procedure to be applied is as follows:

The neutral aqueous solution containing formaldehyde is precipitated by a 2 fold excess of a 1 per cent aqueous solution of diméthon (20 times the weight of formaldehyde to be precipitated in terms of dimédon). Allow the precipitated solution to stand at room temperature for 6 hours. It is practical to heat the reaction ingredients 6 minutes at the boiling point followed by standing 1 hour before filtration but the sensitivity of the reaction is diminished. The precipitate is collected employing a sintered glass crucible washed with distilled water, dried at 110-115 degrees and weighed. The weight of precipitate multiplied by 0.10274 gives the weight of formaldehyde present.

Determination of Aldehydes

First. **By use of Nessler's Reagent.** Bongalt and Gros, J. Pharm. et Chim., **26,** 5 (1922). Nessler's Reagent: 13.55 g. $H_gCl_2 + 36$ g. KI diluted to 500 ml. with distilled water to be used in sodium hydroxide solution.

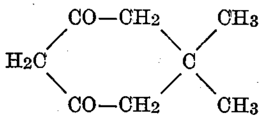
Second. **Cyanimetric procedure.** In $NaHCO_3$ medium HCN reacts with aldehydes to form nitriles $RCHO + HCN = R \cdot CHOH \cdot CN$.

The reaction mixture, after oxidation by use of HIO_4 in $NaHCO_3$ medium, is quantitative. An excess of HCN is added and the excess back titrated employing iodine. As a result of the ready dissociation of cyanhidrins (the reverse of the above reaction), the color change for the iodine titration should be taken as the first faint yellow which persists unmistakably. The dissociation of the cyanhidrins is retarded by keeping the temperature down.

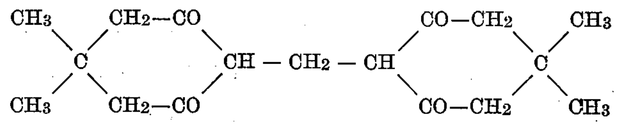
Procedure. Use an approximately 0.05 *N* solution of KCN which is equivalent closely to a 0.1 *N* solution of iodine. After the determination of the HIO_4 reduced during the oxidation of the sample by the arsenite procedure the sample is treated by the addition of 15 ml. of the KCN solution and 10 ml. of a saturated $NaHCO_3$ solution. After 12 hours in a well-stoppered flask, after cooling to 5-10° C. the excess KCN is titrated with standard 0.1 *N* iodine solution.

Remarks. One molecule of HCHO corresponds to 2 atoms of iodine and: If the sample is of considerable volume the end point phenomena is obscured. In this case the sodium bicarbonate solution is replaced by the use of solid sodium bicarbonate and use 0.1 *N* or 0.2 *N* solution of KCN.

Third. **Identification of aldehydes.** The test employs 1,1-dimethyl-3,5-diketocyclohexané (methone)



melting point 148-149°. The reaction with HCHO gives a precipitate of



Conditions favorable for the test are a pH of 4.6 with the precipitant (0.5% or saturated aqueous solution) added in 20 fold excess to the aldehyde to be precipitated. The precipitate is filtered, dried to constant weight at 60° and for methylenedimédone the melting point is 188-189°. The method is applicable following the HIO_4 oxidation in bicarbonate medium in the presence of HIO_3. The results should be very nearly quantitative.

Survey of Periodic Acid Reactions Reported in the Literature

The reactions of periodic acid as applied to practical procedures of analysis in the field of inorganic chemistry have been extensively covered in the previous material of this book. The reactions of iodic acid (*24*) have been referred to (pages 73-82) in a less comprehensive description including literature references. The studies which have been made in the field of organic periodic acid oxidations were reviewed exhaustively and critically by C. S. Hudson (*25*) and cover the literature up to and including March, 1942. The references cited by Hudson are a list of 171. The book by Lange (*26*) "Action de L'Acide Periodique Sur Les Polyalcools" is an important contribution to the study of practical considerations involving the Malaprade reaction and has a bibliography of 47 references. For the study of the oxidation of amino-acids and alcohols particularly in the field of biological chemistry the Ph.D. dissertation of Marcel Grandchamp (*27*) is a valuable reference.

Nicolet and Shinn (*28*) have extended the original Malaprade reaction to apply to the oxidation of compounds containing contiguous carbon to carbon linkages in which one carbon carries oxygen in the form of hydroxyl or carbonyl and the other a primary amine substituent, thus Fleury and Guitard (*29*) found the oxidation for monethanolamine $CH_2OH \cdot CH_2NH_2 + HIO_4 \longrightarrow 2HCHO + NH_3 + HIO_3$

Nicolet and Shinn applied the procedure to the oxidation of serine following the reaction:

$$CH_2OH \cdot CHNH_2 \cdot COOH + HIO_4 \longrightarrow HCHO + CHO \cdot COOH + NH_3 + HIO_3$$

This oxidation is similar to the determination of glycerol by periodic acid treatment. The reaction unlike the Malaprade procedure is best applied to solutions containing sodium bicarbonate rather than

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24. Oesper, "Newer Methods of Volumetric Analysis," Van Nostrand, New York, 1938. Chapter IV pp. 69-98 contains a rather up-to-date review of volumetric iodate methods with 91 literature references.
25. C. S. Hudson, Chapter 8, Vol. II, "Organic Reactions" by Roger Adams. John Wiley, 1947.
26. Lange, J., "Action de L'Acide Periodique Sur Les Polyalcools." Les Editions Vega, 43 Rue Madame, Paris, 1933.
27. Grandchamp, Marcel, Ph.D. Thesis, "Contribution à l'Etude de l'Oxidation Periodique des Dérivés α-Hydroxylamines et α Diaminés." University of Paris, Presses Du Tempo Present, 12 Rue La Grange, Paris, France.
28. Nicolet and Shinn, *J. Am. Chem. Soc.*, 61, 1615 (1939).
29. Fleury and Guitard, *Bull. Soc. Chim. biol.* 28, 651 (1946).

sulfuric acid in moderate concentrations and in general require more time than corresponding oxidations of similar compounds containing only hydroxyl or carbonyl linkages. Tertiary amines are not attached under the same conditions such as for that of diethylaminoethanol (*28*). Secondary amines such as diethanolamine which have alcohol radicals are rapidly oxidized, for example: $NH(CH_2CH_2OH)_2$ as shown by Nicolet and Shinn (*28*).

Van Slyke and associates have studied the oxidation of hydroxylysine (*30*), a hydrolytic product from gelatin, $NH_2 \cdot CH_2 \cdot CHOH \cdot CH_2 \cdot CH_2 - CHNH_2 \cdot COOH$. It reacts with HIO_4 to evolve ammonia. β-hydroxyglutamic acid obtained from the hydrolysis of casein is oxidized (*28, 31*) by periodic acid according to the following reaction:

$$COOH \cdot CHNH_2 \cdot CHOH \cdot CH_2 \cdot COOH + HIO_4 = CHO \cdot CH_2 \cdot COOH + NH_3 + CHO \cdot COOH + HIO_3$$

The reaction of H_5IO_6 used by Carter and collaborators (*32*) in correcting the previously recorded structure of sphingosine has already been referred to (page 88). The action of periodic acid on hydroxyproline was studied by Carter and Neville (*33*). Although the reaction mechanism is not known, the oxidation has been shown to take place in 24 hours with the formation of HCHO. Amino acids having no alcohol functional group behave differently towards periodic acid. The natural amino acids are practically not attacked by HIO_4 at room temperature. The cleavage of the $-CH\,NH_2 \cdot CHOH$ group by periodic acid is dependent to a marked degree on the pH of the solution oxidized. The reaction rates may be suitable to provide for the determination of one amino acid in the presence of another. Such an example has been described by Carter and Loo (*34*).

Reactions of Grandchamp, some of whose studies are confirmatory of previously published work, are characterized in the following outline: (*35*)

The Oxidation of Amino-Acids and Alcohols. Stoichiometric Reactions

$$\underset{\text{Ethanolamine (Colamine)}}{NH_2 \cdot CH_2 \cdot CH_2OH} + HIO_4 \xrightarrow{NaHCO_3} HIO_3 + NH_3 + 2HCHO \quad (15\text{ min.} - 22° - \text{pH } 8.0)$$

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30. Van Slyke, Hiller, McFadden, Hastings and Klemper, *J. Biol. Chem.*, 138, 287 (1940). Van Slyke, Hiller and McFadden, *J. Biol. Chem.*, 141, 681 (1941).
31. Martin, Singe and Bell, *Biochem. J.*, 35, 294 (1941).
32. Carter, Glick and Norris, *J. Biol. Chem.*, 170, 301 (1947).
33. Carter and Neville, *J. Biol. Chem.*, 170, 301 (1947).
34. Carter and Loo, *J. Biol. Chem.*, 174, 723 (1948).
35. Grandchamp, Marcel, Ph.D. Thesis, University of Paris. Presses Du Temps present, 12 Rue La Grange, Paris, France, (1948) 106 pp.

$$\underset{\text{Aminomethylpropanol}}{NH_2 \cdot C \cdot (CH_3)_2 \cdot CH_2OH} + HIO_4 \xrightarrow{NaHCO_3}$$

$$HIO_3 + NH_3 + CH_3COOH_3 + HCHO \text{ (5 min. — 20° — pH 9.3)}$$

$$\underset{\text{Serine}}{CH_2OH \cdot CH \cdot NH_2 \cdot COOH} + HIO_4 \xrightarrow{NaHCO_3}$$

$$HIO_3 + NH_3 + HCHO + CHO \cdot COOH \text{ (1 min. — 20° — pH 7.5)}$$

$$\underset{\text{Serine}}{CH_2OH \cdot CH \cdot NH_2 \cdot COOH} + 2HIO_4 \xrightarrow{H_2SO_4}$$

$$2HIO_3 + NH_3 + HCHO + HCOOH + CO_2 \text{ (48 hrs. — 15° — pH 2.5)}$$

$$\underset{\text{Diethanolamine}}{NH \cdot (CH_2 \cdot CH_2OH)_2} + 2HIO_4 \xrightarrow{NaHCO_3}$$

$$2HIO_3 + NH_3 + 4HCHO \text{ (1 min. — 15° — pH 8.0)}$$

Non-Stoichiometric (Empirical) Reactions

Tertiary Amines + HIO_4 at pH 7-8 are slowly attacked and incompletely oxidized to give ammonia and formaldehyde at 25° C. Only at elevated temperatures are side reactions ever material. Examples are $CH_3 \cdot N \cdot (CH_2CH_2OH)_2$, $N \cdot (CH_2CH_2OH)_3$, $(C_2H_5)_2N \cdot CH_2CH_2OH$ and $CH_2 \cdot NH_2 \cdot COOH$ (glycocol).

Diamines

Diamines such as ethylene diamine ($CH_2NH_2 \cdot CH_2NH_2$) are not oxidized by periodic acid to give stoichiometric reactions. The optimum condition is a pH of 7-8 at ordinary temperatures.

Analytical Applications

The hydrolysis of phospholipides results in the formation of a mixture of colamine (ethanolamine) and serine ($CH_2OH \cdot CH \cdot NH_2 \cdot COOH$). By reaction for 48 hours at 16° C. and at a pH of 3 their simultaneous oxidation is carried out with a determination of the periodic acid required and a determination of the amount of NH_3 evolved from both amines. By this scheme a differential determination is provided. The results are accurate to within 2 per cent approximately.

A method has been described for the determination of mono-, di-, and triethanolamines in their mixtures. The method depends upon a determination of the periodic acid oxygen demand, the total alkalinity and the determination of the ammonia evolved. By difference the concentration of triethanolamine which does not react with periodic acid may be determined. The reactions are carried out in acid solution for the oxidation. Results are accurate to within 2-5 per cent.

APPENDIX

Types of Organic Compounds Oxidizable by Periodic Acid

1. Carbocyclic Polyhydroxy compounds. Example, inositol. A small group of reactions.
2. Carbohydrates. Example, glucose. A large group approximately 100 illustrations in published data.
3. Alpha-diketones and alpha-ketols. Example, dihydroxyacetone. A small group of tested reactions.
4. Hydroxyamino acids. Example, serine and diethanolamine. Approximately 20 studied applications.
5. Polyhydroxy and Hydroxyketo Acids. Examples, saccharic or tartaric acids. Number of applications.
6. Polyhydroxy Alcohols. Example, glycerol. Numerous recorded illustrations.
7. Steroids. A long list of structure studies on biochemical applications.
8. Miscellaneous compounds. Example, glyoxylic acid.

Commercially Available Periodic Acid and Periodates as Oxidants in the Study of Organic Oxidation Reactions and for Spectrophotometric Processes

1. H_5IO_6—Paraperiodic Acid. Hygroscopic and readily water soluble.
2. $NaIO_4$—Sodium metaperiodate. A preferred reagent. Water soluble 12.6% at 25°.
3. KIO_4—Potassium metaperiodate. But slightly water soluble. Favored for colorimetric analyses.
4. $Ba_2I_2O_9$—Barium dimesoperiodate. Used to prepare (in situ) H_5IO_6 by reaction with H_2SO_4.
5. $Na_3H_2IO_6$—Trisodium paraperiodate. Used in H_2SO_4 solution as proved reagent in polyalcohol oxidations.

Types of Applications

1. H_5IO_6 or $Na_3H_2IO_6$ plus H_2SO_4 is favored for oxidations of ethylene glycol type compounds or in cases in which the presence of metal ions is objectionable.
2. $NaIO_4$ in aqueous solution (pH 4.0) is substituted for type 1 for the most readily oxidized type of organic compound such as ethylene glycol or in case formic acid is a reaction by-product to be evaluated acidimetrically.
3. $Na_3H_2IO_6$ in buffered solution (pH 4.2 — $HC_2H_3O_2 + NaC_2H_3O_2$) as a substitute for 2 where quantitative determination of HCOOH is not in demand.
4. $Na_3H_2IO_6$ in the presence of sodium bicarbonate. Used in the determination of amino acids at a pH of 7-9.
5. $Na_3H_2IO_6$ in sodium hydroxide solution for the oxidation of amino alcohols to be followed by the determination of NH_3 as a product of the reaction.
6. KIO_4 in sulfuric acid solution as a substitute for paraperiodic acid.

Solution Conditions for Periodic Acid Oxidation of Organic Compounds

1. In dilute solutions of sulfuric acid for example in the oxidation of polyalcohols, sugars and polyhydroxy-mono and di-carboxylic acids. $NaIO_4$ is often used here since its solution has a pH near 4.
2. In sodium bicarbonate solution applied particularly to amino acids (pH 7-9).
3. In buffered or unbuffered solutions pH 4-4.5 for reactions in which HCOOH is to be evaluated.
4. In sodium hydroxide solution for oxidation of amino alcohols or acids to be followed by determination of ammonia.
5. In solutions free from metallic cations employing H_5IO_6 as oxidant.
6. Reaction temperatures are generally restricted to room temperature or below. Some reactions are carried out at the boiling point such as the oxidation of malonic acid but in these cases the reaction products give empirical results.
7. Aqueous solutions are universally employed with few exceptions. Organic solvents such as dioxane, methanol, tertiary butyl alcohol, etc., have been employed.
8. Procedures for the oxidation of, and structural studies of sugars and related products have been given by Hudson (*1*).

Bibliography of Recent Published Researches Based Upon the Use of Periodic Acid

The literature references to the use of periodic acid in the study of organic compounds both in analysis and in studies of structure has been given by Hudson (*1*). Additional literature references since 1942 are now to be summarized, bringing the subject matter up to 1949.

Miscellaneous Studies Employing Periodic Acid

The Progressive Oxidation of Cotton Cellulose by Periodic Acid. Davidson, J., *Textile Inst.*, **32**, T 109 (1941).

Mandelic Acid, Action of Periodic Acid Upon. Courtois, *Ann. pharm. franc.* **2**, 148 (1944).

The Oxidation of Cellulose With Buffered Periodic Acid. Joyne and Maris, *Ber.* **77B**, 383 (1944).

On Oxidative Decarboxylation With Periodic Acid. Sprinson and Chargaff. *J. Biol. Chem.*, **164**, 417, 433 (1946). (39 References.)

The Magnetic Structure of Periodates.
 I. Periodic Acid. Aggarwal and Singh, *J. Indian Chem. Soc.*, 22, 158 (1945).
 II. Periodates of Na, Ag, Hg, and La. *J. Indian Chem. Soc.*, 23, 177 (1946).

Action of Periodic Acid on Malonic Acid. Fleury and Courtois, *Compt. rend.* **223**, 633 (1946).

Streptomyces Antibiotics. XI. The Structure of Tetra-acetylbisdesoxystreptobiosamine. Brink, Kuehl, Flynn, and Folkers. *J. Am. Chem. Soc.*, **68**, 2405 (1946).

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1. Hudson, "Organic Reactions," Roger Adams et. al., John Wiley, New York, 1947. Vol. II, Chapter 2.

Periodic Oxidation of Certain Active Methylene Groups. Heubner, Ames, and Bubl, *J. Am. Chem. Soc.* **68**, 1621 (1946).

Oxidation of Lignin Sulfonic Acids by Periodic Acid. Pennington and Ritter, *J. Am. Chem. Soc.*, **68**, 1391 (1946).

Electrical Conductance. Aqueous Solutions. III. KIO_4 and $KReO_4$ at 25 Degrees. Jones, *J. Am. Chem. Soc.*, **68**, 240 (1946).

Action of H_5IO_6 on Mono and α-α′ Disubstituted Alkyl Glycols. Delaby and Chabrier, *Bull. Soc. chim.* (1946) 113.

H_5IO_6 in Preparation and Assay of Medicinals. (89 References.) Courtois, *Products pharm.*, **2**, 65 (1947).

Detoxification of Shigella Paradysenteriae Using H_5IO_6. Goebel, *J. Exptl. Med.*, **85**, 499 (1947).

Periodic Acid Oxidation of Phenols. Pennington and Ritter. *J. Am. Chem. Soc.*, **69**, 187 (1947).

Dihydroxymaleic Acid and Its Relation to Iodine, Iodate, and Periodate. Lindblad, *Arkiv. Kemi. Mineral. Geol.*, **25A**, 1947 (in English 42 pp.).

The Dissociation of Periodic Acid. Ianova and Nieman, *Doklady Akad. Nauk*, **60**, 1005 (1948); C.A. **42**, 8583 (1948).

Action of Periodic Acid on Malic Acid. Fleury and Courtois, *Bull. soc. chim. France* (1948) 190.

The Positions Occupied by Substituents in Water Soluble Cellulose Ethers. Sonnenberg, Svensk, *Papperstidn*, **51**, 50 (1948); C.A. **42**, 6531 (1948).

Inactivation of Biologically Active Proteins and the Virus of Western Equine Encephalomyelitis by Periodic Acid. *J. Expt. Med.*, **87**, 445 (1948).

The Periodic Acid Routine Applied to the Kidney. McManus, *Ann. J. Path.*, **24**, 643 (1948).

Histological and Histochemical Uses of Periodic Acid. McManus, *Stain Technol.*, **23**, 99 (1948).

Studies on Sugars Employing Periodic Acid

Determination of Degree of Organic Acidity in Presence of HIO_3 and H_5IO_6. Arragon, *Compt. rendu.*, **211**, 558 (1940).

Oxidation of Ketoses by Periodic Acid. Khouvine and Arragon, *Compte. rend.*, **212**, 167 (1941); *Bull. soc. chim.*, **8**, 676 (1941).

Periodic Acid Test for Constitution of Polysaccharides. Burry, Dillon, and McGettrick, *J. Chem. Soc.*, (1942), 183.

Oxidation of Amygdaloside, (Amygdalin) by Periodic Acid. Courtois and Valentino, *Bull. soc. chim. biol.*, **26**, 469 (1944).

Oxidation of Inositol by Periodic Acid. Fleury, Poirot, and Fieret. *Compt. rend.*, **220**, 664 (1945).

Polysaccharide End Group Determination. Brown, Dunsten, Halsall, Hirst, and Jones. *Nature*, **156**, 785 (1945).

Oxygen Consumption by Carbohydrate by Periodic and Sulfuric Acids. Hultin. *Svensk. Kem. Tids.* **57**, 300 (1945). (German) C.A. **40**, 3728 (1946).

Difructose Anhydrides, Reaction of Periodic Acid Upon. McDonald and Jackson. *J. Res. Nat'l Bur. Standards*, **35**, 497 (1945).

Action of Periodic Acid on Sucrose. II. Hydrolysis at 100 Degrees by H_5IO_6 Followed by Bromine. Fleury and Courtois, *Bull. soc. chim.*, 12, 548 (1945).

Periodate Oxidation of Sugars in Neutral Phosphate Buffer. Lindstedt, *Nature*, 156, 448 (1945).

Melezitose Monohydrate and Its Oxidation by Periodate. Richtmeyer and Hudson, *J. Org. Chem.*, 11, 610 (1946).

Analytical Study of the Oxidation of Lactose and Maltose by Periodic Acid. Courtois and Ramet, *Bull. soc. chim. Biol.*, 29, 240 (947).

Intermediate Products of Oxidation of Lactose by Periodic Acid. Courtois, *Bull. soc. chim. Biol.*, 29, 248 (1947).

Action of Periodic Acid on Glucose Phenylosozone. Chargaff and Magasanik, *J. Am. Chem. Soc.*, 69, 1959 (1947).

Behavior of α and β Chloraloses With H_5IO_6 and Structure. Fleury and Jolly, *Compt. rend*, 225, 688 (1947).

Oxidation of Inositol by Periodic Acid. Fleury, Poirot, and Fievet, *Ann. pharm. franc.*, 5, 209 (1947).

Behavior of Glucose Towards Periodic Acid. Fleury and Fievet-Guinard, *Ann. pharm. franc.*, 5, 404 (1947).

Action of H_5IO_6 on a Cyclohexose Osazone. Magasanik and Chargaff. *J. Am. Chem. Soc.*, 70, 1928 (1948).

Periodic Acid Oxidation of Chloraloses. Analytical and Theoretical Consequences. Giffon, *Compt. rend.*, 226, 93 (1948).

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