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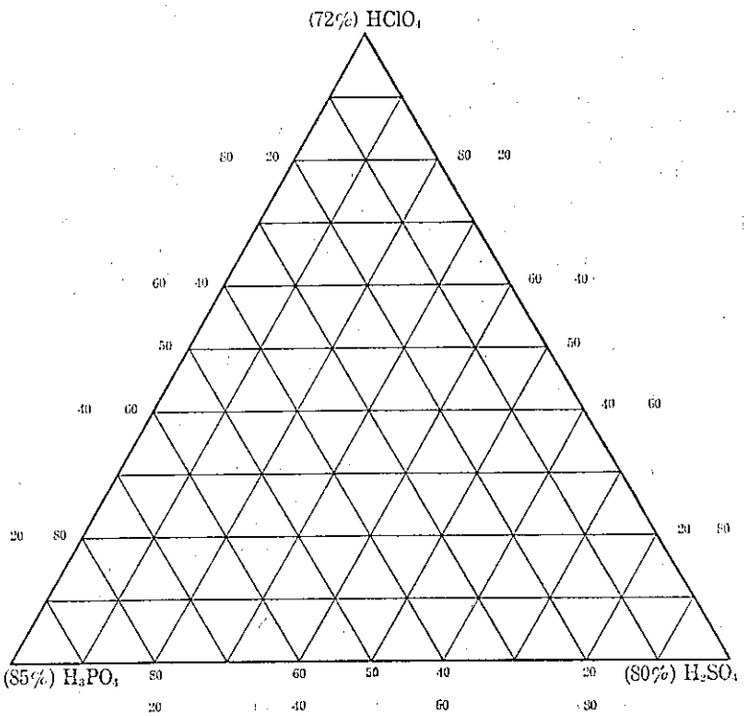
A Trip Into "The Promised Land"

With apologies to Eiderman

Mixed Perchloric, Sulphuric and Phosphoric Acids and Their Applications in Analysis



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MIXED PERCHLORIC, SULPHURIC AND PHOSPHORIC ACIDS AND THEIR APPLICATIONS IN ANALYSIS

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SECOND EDITION
1942

Published by

THE G. FREDERICK SMITH CHEMICAL CO.
867 McKinley Avenue P. O. Box 1611
COLUMBUS, OHIO

Printed in U. S. A. by

Twin City Printing Company
Champaign, Illinois

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PREFACE

This brochure is a companion work to that of "Perchloric Acid" the third edition of which appeared in November, 1934 *(1)*.* Analytical applications in the use of perchloric acid both in routine and research methods are rapidly increasing. Notable advances are being made in the determination of metals and non-metals in organic materials. The outstanding contributor in this field is Doctor Ernest Kahane, Paris, France *(2)*. Qualitative elementary analyses and quantitative procedures include detection and determination of nitrogen, sulfur, phosphorus, and arsenic in organic materials. The destruction of organic matter in these cases is provided by the use of perchloric acid or its mixtures with other mineral acids. Biological and toxicological methods for the determination of metals such as aluminum, iron, chromium, lead, etc., follow the same method of attack.

Methods are available for the quantitative destruction of organic matter in a wide variety of materials such as proteins, fats, oils, and waxes. Quantities up to a kilogram or even more can be employed. The destruction of organic matter prior to analysis of such products as rubber, coal, coke, leather, plants, soils, and organo-metallic medicinals, has been shown to be best carried out by using perchloric acid.

The conditions under which the perchloric acid oxidation of organic matter can be retarded in intensity from reactions of explosive violence to reactions devoid of hazard, are well known. These methods involve the addition of other mineral acids such as nitric, sulfuric, and phosphoric to serve as partial oxidizers or more often as diluents. Some perchloric acid oxidations of organic matter require the use of catalysts to promote a more rapid reaction. The oxidation of coal, coke, and leather are thus accelerated by the use of chromium, vanadium, or osmium as catalysts. Many additional applications in the use of perchloric acid to destroy organic matter will continue to be developed and described in the current literature. The advantages gained by such processes are outstanding. The use of such methods as have been thoroughly studied and are known to be without hazard, cannot be too strongly advised.

The use of mixtures of perchloric acid with sulfuric and phosphoric acids serves to advantage in the analysis of metallurgical materials while saving in cost of perchloric acid is thus accomplished by substituting for it suitable quantities of the latter two acids. Mixed

* Figures in parentheses refer to the bibliography in the appendix.

perchloric and phosphoric acids have remarkable solvent properties. Stainless steel, metallic tungsten, and certain ferro alloys, such as ferro-tungsten, are easily dissolved. The addition of sulfuric acid to such solutions forms no insoluble anhydrous ferric sulfate. Chromium can be oxidized quantitatively to the hexavalent form in a mixture of the three acids. The determination of chromium in chromite, stainless steel, or chrome-tanned leather, etc., may be accomplished by use of special methods employing these mixtures of perchloric acid with other mineral acids. Many additional applications may be predicted for future development.

It is hoped that the general and theoretical discussions in the following material, together with the detailed directions for analytical applications, will stimulate the reader to individual research effort in extending the rapidly increasing flow of scientific developments in the field.

The data in practically all the present work have been taken from studies which have appeared in recent issues of the various scientific journals. Much of this work has resulted from the writer's own research or that done together with his various collaborators.

PREFACE TO THE SECOND EDITION

The first edition of this booklet of 20,000 impressions has proven insufficient and a second edition has become necessary. The last nine pages of the previous edition have been omitted in the second edition to provide space for two important developments in the field of perchloric acid mixtures with other acids as industrial products and in the field of bright polishing of metals electrochemically. With the exception of the omission of the directions for the use of "Potassium Ferro- and Ferricyanides as Reference Standards in the Evaluation of Titanous Solutions" and "The Determination of Manganese in Ferro-Tungsten Using Perchloric and Phosphoric Acids," the second edition is a duplicate of the first. In place of the material thus omitted there has been substituted a reprint of the work reported in the *Journal of Research of the National Bureau of Standards*, Vol. 22, page 465 (1939), and the anodic bright polishing of stainless steel using an electrolytic bath of mixed perchloric and acetic anhydride. It is hoped that these changes will not detract from the popularity of the new edition as compared to the other. It is of course expected that the changes will add to the value of the new edition because the added topics are of tremendous practical importance.

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INTRODUCTION

Certain of the most important applications in the present use of perchloric acid for analysis have been known for nearly two decades. Practically the only early applications involved the separation and determination of potassium as alcohol insoluble perchlorate in the presence of alcohol soluble sodium perchlorate. This method was substituted to avoid the use of the more costly chloroplatinic acid of the familiar Fresenius method. Less than twenty years ago 60 per cent perchloric acid was sold at a figure approximating $4.50 per pound. New applications in its use were slow in development because of costs. The cost of perchloric acid remained high presumably because of shortage in demand.

This situation was ultimately altered through the fact that increasing amounts of anhydrous magnesium perchlorate to be used as drying agent began to be sold under various trade names such as "Dehydrite" and "Anhydrone." These products were manufactured for the first time about 1925, by the G. Frederick Smith Chemical Company. The increased demand for perchloric acid to be used in the manufacture of magnesium perchlorate, together with the planned intention of this company to popularize the use of perchloric acid as an indispensable analytical and industrial chemical, rapidly resulted in a drastic reduction in price.

As the price of 60 to 70 per cent perchloric acid of desired purity fell, the number of published procedures in which it was employed began to appear in great number. Total demand increased production and prices continued to fall. Methods in its use for research gradually became the methods of the control laboratory. To further lower its price, perchloric acid of 70 per cent concentration was made available in both purified and technical grades of purity at a further reduction in price. The latter grades of perchloric acid served equally well in place of the highly pure grades for such use as the determination of silica in ores and minerals, chromium and vanadium in alloy steels, chromium in leather, etc.

The change in price levels for the various grades of perchloric acid reduced the original cost from one fifth to one tenth its original sale price, and the possibility of further reductions was made more remote. For certain of the more important applications in the analyses of metallurgical products, limestone, lime, and cement, as well as for other comparatively large scale industrial applications such as electro-

plating operations, pickling bath chemicals, etc., numerous requests came to its manufacturers to further reduce the cost of perchloric acid. This has been done by the substitution of new methods for the old methods. The description of these new methods is the main aim of the present brochure. Sulfuric, nitric, and phosphoric acids have been shown to substitute for perchloric acid, formerly used alone in numerous applications. The added acids named in many cases greatly improve existing processes using perchloric acid alone. Savings of time, expense, and improvements in accuracy often result.

Certain other procedures reprinted in this brochure were developed as a result of requests on the part of industrial control laboratories to improve existing routine analytical processes not necessarily through economy in cost of chemicals. It has been impossible to keep pace with the demand for new and modified procedures but material progress is being made. The co-operation of those interested in particular cases encourages the belief that the series of booklets of which the present is a part (3, 4, 5, 6) are meeting a popular demand.

Perchloric acid has been said by Professor Ernest Kahane *(2)* Vol. 1, p. 6, "to be now taking its place in the most varied fields of technical chemistry and one is able, without exaggeration, to foresee the time when perchloric acid will be considered as indispensable as the three fundamental laboratory acids, sulfuric, nitric, and hydrochloric." Popular early belief that perchloric acid is hazardous, under all conditions, is now being dispelled. On the contrary the newer concept indicates that when properly applied, perchloric acid not only is without hazard but, without comparison, saves time and expense, improves accuracy, and simplifies many analytical and industrial procedures.

SECTION 1

PER-CHEMICAL PROPERTIES OF PERCHLORIC ACID

INTRODUCTION

Perchloric acid was formerly thought to have been erroneously named. Since perchloric acid had not until recently been formed as a product of the reactions of either ozone or hydrogen peroxide it was not thought to be a true per-acid. Furthermore, neither hydrogen peroxide nor ozone had been detected as reaction products in reactions involving the use of perchloric acid. As a result of recent developments both of these factors which prove that perchloric acid is a true per-acid have been established. First, the reaction products, following the use of hot concentrated perchloric acid as an oxidizing agent, have been shown *(7)* to give effects indicating clearly the presence of either hydrogen peroxide or ozone. Secondly, perchloric acid has been synthesized, using the reaction between moist chlorine and ozone, by Burns and Rollefson *(8)*.

Establishment of the fact that perchloric acid is in reality a per-acid, is of fundamental importance in the development of new methods for its use as an oxidizing agent in quantitative analysis and in other applications. The improvement of previously published methods known to be somewhat faulty as a result of undesirable effects caused by the reactions of traces of hydrogen peroxide or ozone, has resulted from the study of the newly developed facts. From a strictly theoretical viewpoint these new developments are also of great interest.

According to Byrns and Rollefson *(8)* moist chlorine and ozone under the influence of the silent electrical discharge react to form crystalline oxonium perchlorate, OH_3ClO_4. Dry chlorine and ozone react under the same conditions to form the oxides ClO and ClO_2. The latter oxide and ozone react to form ClO_3 and oxygen. The series of reactions between dry chlorine and ozone may be summarized as follows:

$$Cl_2 + O_3 \rightarrow ClO + ClO_2 \qquad 1.$$
$$ClO_2 + O_3 \rightarrow ClO_3 + O_2 \qquad 2.$$
$$ClO_3 + O_3 \rightarrow ClO_2 + 2O_2 \qquad 3.$$
$$ClO_3 + ClO_3 \rightarrow Cl_2 + 3O_2 \qquad 4.$$
$$ClO + ClO \rightarrow Cl_2 + O_2 \qquad 5.$$

The velocity constants for the reactions numbered 1, 3, and 5 have been determined. The time rate of ozone reaction has been expressed as follows:

$$-\frac{dO_3}{dt} = K \cdot Cl_2^{1/2} \cdot O_3^{3/2}$$

in which, at 50° C., the value of K has been found to be approximately 10 ml. per mol per second. At 100° C. the reaction is too rapid to measure.

In the presence of moisture chlorine reacts with ozone under the influence of the silent electrical discharge to form Cl_2O_7 which in turn reacts with water to form oxonium perchlorate. If the reduction of hot, concentrated perchloric acid by such mild reducing agents as trivalent chromium takes place at a minimum temperature of 200° C.; and since chlorine and oxides of chlorine are reduction products, it then becomes clear that ozone cannot exist as a reaction product. This leaves hydrogen peroxide as the only remaining actual per-chemical product of the destructive decomposition of hot, concentrated perchloric acid. Hydrogen peroxide is also known to react with chlorine. Its reaction rate must, therefore, be much slower than that between chlorine and ozone, at the temperature of oxidations involving perchloric acid. Experimental study of the hydrogen peroxide effect is best carried out using mixtures of perchloric with phosphoric or sulfuric acids.

A mixture of 72 per cent perchloric acid and 85 per cent phosphoric acids at a temperature of 205° C. is not capable of the quantitative oxidation of chromium to chromic acid. The chromic acid is reduced by the hydrogen peroxide formed during the decomposition of perchloric acid. Chromium, on the other hand, is quantitatively oxidized to chromic acid by 72 per cent perchloric acid alone at a somewhat lower temperature. The facts are in accord with theory if the reaction between chromic acid and hydrogen peroxide is less rapid than that between hydrogen peroxide and chlorine at the lower temperature. This is true as proven by the use of phosphoric acid mixed with perchloric acid, which can be heated above the boiling point of 72 per cent perchloric acid.

The formation of hydrogen peroxide as a decomposition product from perchloric acid is more extensive if the strength of acid is increased. This is easily accomplished by mixing 72 per cent perchloric acid with 95 per cent sulfuric acid. In a suitable mixture the oxidation of chromic salts to chromic acid can be made to take place at as low a temperature as 120° C. Under these conditions the production of hydrogen peroxide is greatly increased while the formation of chlorine

and oxides of chlorine is lessened. Chromic acid in the mixed perchloric and sulfuric acids is, therefore, more rapidly reduced. Using a mixture of perchloric, phosphoric, and sulfuric acids chromium may be quantitatively oxidized, whereas a mixture of the first two acids alone does not.

A proof of the formation of hydrogen peroxide which is very significant is found in the behavior of perchloric acid in the attack upon metals. Pure iron, such as Armco iron, is dissolved by hot, concentrated perchloric acid with an extremely energetic reaction. A mixture of one volume of 72 per cent perchloric acid with two volumes of 80 per cent sulfuric acid does not attack the same iron to any degree whatsoever at the same temperature. The iron is transformed to the passive state. Since either acid alone dissolves iron easily, the failure of the mixed acids to dissolve iron must be attributed to the formation of a third reactant. This product is thought to be hydrogen peroxide, and the assumption is in accord with previous knowledge, since hydrogen peroxide is known to transform iron to the passive state. The investigation is being extended along these lines.

The remainder of the material of the present section is a reprint of a paper by the author *(7)* entitled, "Mixed Perchloric and Sulfuric Acids. I. Simultaneous Oxidizing and Reducing Properties of Hot Concentrated Perchloric Acid." The experiments were performed at the University of Illinois at Urbana, Illinois.

The oxidation reactions of hot, concentrated perchloric acid are the basis of important reactions of quantitative analysis *(9, 10)*. The intensity of these oxidations is greatly influenced by the extent to which the acid has been dehydrated. With hot acid of strength greater than that corresponding to the formula $O_2H_5ClO_4$ *(11)*, simultaneous reducing properties are in evidence. These reducing properties are accounted for if either hydrogen peroxide or ozone is present in traces as a result of the decomposition. Reactions corresponding with this explanation can easily be demonstrated. The acid strength of 70 to 72 per cent perchloric acid is conveniently increased to 85 per cent or higher by the addition of sufficient 96 per cent sulfuric acid or fuming sulfuric acid. For many reactions of analytical importance, these principles require a close study of conditions. It is the purpose of this section to describe the general aspects of this subject.

DECOMPOSITION OF HOT PERCHLORIC ACID IN PRESENCE AND ABSENCE OF MILD REDUCING AGENTS

By concentrated perchloric acid, this section refers to that strength between 70 and 85 per cent $HClO_4$ by weight (roughly, that concen-

tration between dioxonium perchlorate and oxonium perchlorate, $O_2H_5ClO_4$ and OH_3ClO_4). Hot, concentrated perchloric acid decomposes mainly according to reaction 1. A secondary reaction, 2, is also possible to a slight extent.

$$4HClO_4 \rightarrow 2Cl_2 + 7O_2 + 2H_2O \qquad 1$$
$$2HClO_4 \rightarrow Cl_2 + 3O_2 + H_2O_2 \qquad 2$$

Both reactions are intensified in proportion as the concentration increases. Reaction 3 indicates the formation of oxonium perchlorate using concentrated or fuming sulfuric acid.

$$O_2H_5ClO_4 + H_2SO_4 \rightarrow OH_3ClO_4 + H_2SO_4 \text{ (hydrated)} \qquad 3$$

An important example of a reaction using hot, concentrated perchloric acid as an oxidizing agent is the oxidation of trivalent chromium to the hexavalent state in the process of Willard and Gibson *(10)* for the quantitative estimation of chromium in chromite, ferrochrome, and stainless steel. In a study of this method, Lundell, Hoffman, and Bright *(12)* state that the oxidation is never quite complete. The following reaction is shown to be quantitative only to the extent of 99.5 per cent completion:

$$Cr_2O_3 + 2HClO_4 \rightarrow 2CrO_3 + H_2O + Cl_2 + 2O_2 \qquad 4$$

If chlorine and oxygen are the only decomposition products, it is difficult to offer a reason for this. In the presence of a small amount of hydrogen peroxide the following reaction explains the fact:

$$2CrO_3 + 6HClO_4 + 3H_2O_2 \rightarrow 2Cr(ClO_4)_3 + 3O_2 + 6H_2O \qquad 5$$

Reactions 1 and 4 are much more intense than 2 and 5. The difference accounts for the 0.5 per cent reversal of reaction 4. Reactions 2 and 4 are intensified by increasing the strength of perchloric acid. By properly regulating conditions of time, temperature, and acidity, the Willard and Gibson method *(10)* can be made to give more accurate results, as will be shown in a subsequent section. The influence of hydrogen peroxide as described may easily be duplicated by the addition of a trace of it to a hot, dilute solution of chromic acid in perchloric acid. The chromium is instantly reduced to green chromic ion.

OXIDATION OF CHROMIC OXIDE TO CHROMIC ACID

Two hundred milligrams of chromic oxide were treated with 50 ml. of oxonium perchlorate (84.79 per cent $HClO_4$) and heated to 168° C. The reaction mixture was allowed to cool. Red crystals of chromic oxide, insoluble in concentrated perchloric acid, formed and the acid was colorless. Upon standing 12 hours at room temperature, the acid

became colored owing to the presence of green chromic perchlorate. Repeating the heating of the acid and oxidation of chromium, the results are duplicated (reactions 4 and 5).

The oxidation of chromic oxide was tested with increasing strengths of perchloric acid produced from various proportions of 15 per cent fuming sulfuric acid and 72 per cent perchloric acid (Table 1). Parallel experiments were made replacing chromic oxide by small amounts of manganese perchlorate, $Mn(ClO_4)_2 \cdot 6H_2O$. The manganese was momentarily oxidized to permanganate and the reaction rapidly reversed as shown by the immediate decolorization due to hydrogen peroxide formed simultaneously. The reaction is intensified in the presence of a little phosphoric acid.

TABLE I

OXIDATION OF CHROMIUM AND MANGANESE BY CONCENTRATED PERCHLORIC AND SULFURIC ACIDS

Sulfuric Acid 15 per cent fuming ml.	Perchloric Acid 72 per cent ml.	Temperature After Mixing From 25° C. to °C.	Cr_2O_3 Oxidation to CrO_3 °C.	Mn^{++} Oxidation to MnO_4^- °C.
10	10	82.4	136	150
12	8	84.4	128	137
13.3	6.6	86.5	120	128
15	5	88.4	119	125
10 (95%)	10	40.0	168	.....

The heat attained upon mixing the acids of Table I is an indication of the extent to which the perchloric acid has been dehydrated. Using 75 per cent sulfuric acid, mixing with 72 per cent perchloric acid results in no appreciable evolution of heat. The temperature after mixing was observed in a 30 ml. Dewar test tube, evacuated but not silvered, and the temperature maximum found using a small Anschütz thermometer.

It will be seen that the dehydration of perchloric acid by the sulfuric acid in all cases was equivalent, at least, to the formation of oxonium perchlorate, since the temperature at which the chromium was oxidized is equal to or less than that required by the 84.79 per cent perchloric acid as previously described. The greater the dehydration of perchloric acid, the lower is the temperature of oxidation. In all cases in Table I the oxidation of chromium was clearly reversed to an obvious extent, as shown by the color change resulting upon allowing the solutions to cool and stand. In the case of the higher concentrations of perchloric acid, the reduction was complete in a few hours. This indicates the magnitude of hydrogen peroxide formation as governed by perchloric acid concentration.

OXIDATION OF TRIVALENT CERIUM TO THE TETRAVALENT STATE

Solutions of cerous perchlorate in hot, concentrated perchloric acid are not oxidized to ceric perchlorate at 168° to 200° C. Mixtures of equal parts of 96 per cent sulfuric acid and 72 per cent perchloric acid oxidize cerous sulfate readily to sulfato-ceric acid at approximately 140° C. The reaction is:

$$7Ce_2(SO_4)_3 + 2HClO_4 + 21H_2SO_4 \rightarrow 14H_2Ce(SO_4)_3 + Cl_2 + 8H_2O \qquad (6)$$

Ceric sulfate is insoluble in 75 to 95 per cent sulfuric acid and in the reaction mixture of acids outlined above. The substitution of 75 for 96 per cent sulfuric acid is found to result in more complete oxidation of cerium at 185° C. In accordance with the principles previously described, this is accounted for through the practical elimination of hydrogen peroxide as a minor decomposition product of hot, concentrated perchloric acid.

The principle of reaction 6 has been applied to the preparation of ceric sulfate, both in the form of the anhydrous salt and in its addition compounds with ammonium sulfate. The data are included in a subsequent report. Ceric perchlorate has been prepared in solution by the electrolytic oxidation of cerous perchlorate in a perchloric acid solution by Fichter and Jenny *(13)*. It is possible that a mixture of perchloric and sulfuric acids may be found desirable in the quantitative determination of cerium. A preliminary study has been made with favorable results.

USES FOR MIXED ACIDS IN ANALYTICAL STUDIES

The many advantages found in the determination of chromium following perchloric acid oxidation *(10)* make the method popular in routine plant control analyses. With technical grades of 68 to 70 per cent perchloric acid (free from chromium) the method is less costly. By employing mixtures of perchloric and sulfuric acids, the method can be cheapened further and at the same time other advantages besides economy in the cost of perchloric acid can be shown.

Mixed perchloric and sulfuric acids have been used satisfactorily in the oxidation of potassium ferro- and ferricyanides to liberate the ferric ion as a standard procedure in the evaluation of titanous solutions. Perchloric acid alone can be used in this case, but the method is cheaper using the mixed acids.

The addition of perchloric acid to 96 per cent sulfuric acid for the destruction of organic matter in the familiar Kjeldahl nitrogen determination has been proposed. Attempts to diminish the time of digestion following this process in certain applications gives low results, presumably due to loss of nitrogen in the digestion period. If the concentration of sulfuric acid is lowered to 75 per cent and the 72 per cent perchloric acid is then added to the hot sulfuric acid, the oxidizing power is not materially diminished and there is little tendency toward the formation of hydrogen peroxide as a decomposition product. The change thus proposed may eliminate the disturbing reactions previously mentioned. The problem is being investigated in these laboratories.

The dehydration of silica by hot, concentrated perchloric acid in the method of Willard and Cake *(14)* has become an important analytical procedure. With a mixture of 96 per cent sulfuric acid and 72 per cent perchloric acid, the intensity of the dehydration may be sufficiently high without showing a tendency to convert the perchlorates present to sulfates. Such an application would result in the obvious advantage of economy in cost of perchloric acid where it is applicable. The subject is being investigated.

If the dehydration of perchloric acid by sulfuric acid is objectionable, other methods are available. Anhydrous magnesium perchlorate in various proportions can be dissolved in 72 per cent perchloric acid. Phosphoric anhydride or acetic anhydride may be substituted for the anhydrous magnesium perchlorate.

SIGNIFICANCE OF HYDROGEN PEROXIDE DECOMPOSITION OF PERCHLORIC ACID

It is difficult to demonstrate experimentally the formation of hydrogen peroxide by the decomposition of hot, concentrated perchloric acid according to reaction 2, except by interpretation of the resulting effects as shown. Attempts to distil out hydrogen peroxide at a low temperature by passing air through a mixture of 96 per cent sulfuric acid and 72 per cent perchloric acid were not successful. Such an experiment using anhydrous perchloric acid might be more successful. If the decomposition products of hot, concentrated perchloric acid do not include hydrogen peroxide, the reactions obtained are exactly analogous to those that would be obtained if hydrogen peroxide or ozone were formed. The odor of ozone was never apparent. The simultaneous formation of hydrogen peroxide and chlorine as decomposition products would be expected to result in side reactions destroying the hydrogen peroxide.

If hydrogen peroxide can be shown to be formed in the reactions of hot, concentrated perchloric acid, or is conceded to have been shown by the studies of the present data, then perchloric acid must be classi-

fied as a true per-acid. Present interpretations of the molecular structure of anhydrous perchloric acid and its lower hydrates do not include the assumption of oxygen to oxygen linkages, as would be the case if it had true per-acid properties. This question is of far less importance than is the knowledge of the practical influence of the formation of hydrogen peroxide upon the analytical applications.

TABLE II

THE SOLUBILITY OF CHROMIC ACID IN CONCENTRATED PERCHLORIC ACID

Solute — CrO_3, Solvent — 57 to 70% $HClO_4$, Temperature — 25° C. ± 0.05°

$HClO_4$ %	CrO_3 Solubility g/100 ml. Solution Duplicates	Av.	$HClO_4$ %	CrO_3 Solubility g/100 ml. Solution Duplicates	Av.
57.4	0.0710 0.0717	0.0714	66.5	0.0026 0.0019	0.0023
58.5	0.0500	0.0500	68.5	0.0007	0.0007
61.1	0.0139	0.0139	69.3	0.0000 0.0000	0.0000
62.3	0.0101	0.0101	72.5	0.0000	0.0000
63.3	0.0052 0.0059	0.0056			

The solubility of vanadium pentoxide (V_2O_5) in 72.5 per cent $HClO_4$ was found to be 0.136 g. per 100 ml. of solution. These data indicate that chromium can be separated quantitatively from vanadium when in the form of a mixture of chromic and vanadic acids. The separation was attempted by adding sufficient 72.5 per cent solution of perchloric acid to a water solution of chromic and vanadic acids to bring the acidity to 70 per cent. The precipitated chromic acid was filtered, using a fritted glass filtering crucible, and washed with 70 per cent perchloric acid. The chromic acid thus obtained was dissolved and titrated, using standard ferrous sulfate and the potentiometric end point. The chromic acid was found to be quantitatively separated from the vanadic acid. The data were compiled for the author by Mr. A. R. Hanke.

For the separation of the chromic acid the beaker and contents were transferred to the filtering crucible without particular care to remove chromic acid which may adhere to the reaction beaker. This portion of the precipitate is washed in the beaker using a stream of 70-72% perchloric acid from the wash bottle and the main bulk of the precipitate on the filtering crucible further washed in similar manner.

The filtrate is then placed to one side and the precipitation beaker then used to receive the filtrate from the filtering crucible during the next step that of solution of chromic acid in water. The filtrate thus obtained contains all the chromium free from vanadium. This solution acidified by use of dilute H_2SO_4 or HCl is diluted to 200 ml. and titrated with standard ferrous sulfate using a drop of 0.025 molar orthophenanthroline as indicator until the first faint pink color is produced.

The vanadium as vanadic acid dissolved in concentrated perchloric acid may then be determined in a variety of different methods. The solution may be diluted extensively and the vanadium reduced using a stream of sulfur dioxide gas, excess being expelled with a stream of air. The vanadyl solution thus obtained is then titrated using standard $KMnO_4$ solution.

The method as described should prove satisfactory in the presence of ferric iron, molybdenum, copper and nickel. It is possible that it might be extended to apply to steel analysis as well as to the purification of chromic acid to remove vanadium and other elements incidentally present. The study might be profitably extended in these directions.

Another procedure for the separation of chromium from elements commonly associated with it has been studied by H. H. Willard and students (private communication). This most interesting process involves the dropwise addition of concentrated hydrochloric acid to a boiling solution of chromic acid in strong perchloric acid using a special distillation apparatus. The chromium is thus volatilized as chromyl chloride and many interesting separations are thus possible, (see pages 59-64).

SECTION 2

THE DESTRUCTION OF ORGANIC MATTER USING PERCHLORIC ACID

The destruction of organic matter as a preliminary operation of quantitative analysis in the determination of mineral constituents as well as sulfur, phosphorus, and nitrogen in such materials as plant products, coal and coke, leather, protein fertilizers, animal tissues and organisms, blood, milk, etc., is frequently done by the process of ashing. In many cases the destruction of organic matter follows the familiar Kjeldahl digestion with concentrated sulfuric acid. Both these methods involve well-known difficulties. Both processes are time consuming. The Kjeldahl process has been shortened by the use of perchloric acid in small amount to speed up the reaction. In many cases the use of perchloric acid alone or mixtures of perchloric and nitric acids or perchloric acid with sulfuric acid, or all three together can be shown to provide the best conditions for the rapid wet oxidation of organic matter. It is the purpose of the present section to discuss in some detail the objects, principles, and practical applications of the wet oxidation of organic matter using mixed acids, including perchloric acid. Literature references will be cited, experimental conditions defined, and practical applications described.

PREVIOUS STUDIES

A two-volume brochure by Ernest Kahane *(2)*, theoretical principles in Vol. I, and practical applications in Vol. II is a very comprehensive work on the subject of wet oxidation of organic matter. A complete bibliography to the literature on the destruction of organic matter, using perchloric acid alone or mixtures of nitric and perchloric acid, and the three-component mixture nitric, perchloric, and sulfuric acid is contained in this work. Kahane has contributed more than any other single investigator to this field. Applications in the use of mixtures of perchloric and sulfuric acids in the oxidation of both organic and inorganic substances have been contributed by the present author and associates *(7, 9, 15, 16, 17)*. A mixture of perchloric acid and phosphoric acid as a solvent and as an oxidation medium has many applications, particularly in the analysis of steel and iron *(18)*.

Specific illustrations in the use of the above mixtures, with and without catalysts to speed up the often times slow decomposition of organic matter, are found in the following references:

Kjeldahl nitrogen determination *(19)*, chromium determination in leather *(16)*, sulfur determination in coal *(9)*, in rubber *(20, 21)*, aluminum determination in plants *(22)*, silica determination in vegetable substances *(23)*, the determination of sulfur in organic derivatives in general *(24)*, and the destruction of large amounts of organic matter using perchloric acid *(25)*.

GENERAL CONSIDERATIONS IN THE DESTRUCTION OF ORGANIC MATTER USING HOT CONCENTRATED PERCHLORIC ACID

Cold dilute or concentrated perchloric acid is not reduced by organic matter, nascent hydrogen, by electrolysis or catalytic hydrogenation, by hydrazine or hydroxylamine or Devarda's alloy, sodium amalgam, hypophosphorus acid, or sodium hydrosulfite. Perchloric acid is quantitatively reduced by a large excess of titanous ion only after long continued boiling. Organic matter from certain animal and vegetable sources can be oxidized at the boiling temperatures of 70-72 per cent perchloric acid only after an hour to several hours' boiling. For example, coal requires from 1-3 hours' boiling and leather an hour or more for complete destruction of the organic matter. In these cases *(9, 16, 17)* the reaction for quantitative determination of metallic or non-metallic elements must be hastened by the use of catalysts, such as chromium, vanadium, or osmic acid. Large amounts of elemental sulfur are safely oxidized by boiling with concentrated perchloric acid.

Hot concentrated perchloric acid (60-72 per cent) reacts with explosive violence with organic matter from many sources. Inorganic reducing agents, such as hypophosphorus acid, hydroxylamine, and hydrazine, explode with hot, concentrated perchloric acid. Oxidizable metals such as chromium, vanadium, and iron, are smoothly oxidized by hot, concentrated perchloric acid to chromic and vanadic acid and ferric iron only at temperatures in the range of 200° C. In these cases the excess oxidizing agent is made inactive by the simple process of cooling to ordinary temperatures. In this manner the oxidized elements are determinable, using the ordinary standard reducing agents without the slightest interference from the excess perchloric acid.

If organic matter reacts violently by boiling with hot, concentrated perchloric acid the reaction intensity is effectively slowed down by the following methods:

1. Dilute perchloric acid (40-60 per cent) is added to the organic matter and the mixture concentrated slowly by heating until the 70-72 per cent strength is attained. The rate of concentration governs the speed of oxidation of the organic matter.

2. Nitric acid (sp. gr. 1.42) is used to destroy the easily oxidized portion of the organic matter, after which concentrated (72 per cent) perchloric acid is added and the remaining difficulty oxdizable material quietly oxidized at the boiling temperature, approximately 200° C.

3. A mixture of concentrated nitric and perchloric acids is heated with the organic matter.

4. Concentrated perchloric acid is diluted by the addition of strong sulfuric acid. A suitable mixture consists of one volume of 72 per cent perchloric acid diluted with two volumes of 80 per cent sulfuric acid.

5. A mixture of concentrated nitric, perchloric and sulfuric acids is employed.

6. For the destruction of organic matter in large amounts a digestion with concentrated sulfuric acid at approximately 200° C. is treated dropwise by the addition of concentrated perchloric acid as fast as it is consumed. Animal organisms such as liver, brain, and kidney in amounts up to and including one kilogram have been effectively oxidized in this manner. This process is described by Kahane *(25)*.

Other properties of perchloric acid in addition to the above add to its advantages for the various quantitative applications in which it is employed. All metallic perchlorates are soluble in water and in a great variety of organic solvents. Hot, concentrated perchloric acid is a strong dehydrating agent, for example, silicic acid is quantitatively dehydrated *(14)*. By the processes for the destruction of organic matter as described the following elements are retained quantitatively, P, S, Si, Fe, Cr, Al, Ca, Mg, and K. Under special conditions arsenic is quantitatively retained *(26)*.

The following process for oxidation of organic matter in dried plant material, roots, grain, and straw, employs nitric and perchloric acid digestion as in method 3 of the above outline. This method substitutes for the ashing process such as that described by Howk and DeTurk *(27)*. The process results in the oxidation of sulfur and phosphorus completely to sulfuric and phosphoric acids. It has been employed for the determination of phosphorus, calcium, magnesium, and potassium. The original paper *(28)*, published from the Department of Agronomy at the University of Illinois, is reprinted complete with the exception of the summary and bibliography which is renumbered and the references cited included in the bibliography at the end of this booklet. This work was carried out by J. E. Gieseking, H. J. Snider, and C. A. Getz.

DESTRUCTION OF ORGANIC MATTER IN PLANT MATERIAL BY THE USE OF NITRIC AND PERCHLORIC ACIDS

The destruction of organic matter by some form of ashing generally precedes the determination of the mineral constituents in plant material. Two undesirable features of the ashing process suggest the need of a wet oxidation method similar to the Kjeldahl digestion: 1, The method of ashing commonly used for calcium and magnesium determinations is not applicable for potassium and phosphorus determinations on account of the loss of the more volatile compounds of potassium and phosphorus while ashing; and 2, the residues after ashing may be in a slowly soluble form.

Perchloric acid either alone or in mixtures with other acids has been widely used in the oxidation of organic materials of animal origin previous to the determination of the mineral constituents. Kahane and associates *(2)* have made the most comprehensive study of these methods and have developed a method of determining silica in plant materials *(23)*. Winter and Bird *(22)* have used perchloric acid similarly for determining aluminum in plants.

The properties of perchloric acid, as well as those of the perchlorate ion, make it a very desirable oxidizing agent for the analysis of organic substances. No water-insoluble perchlorates of the metals have been reported. Furthermore, cold perchloric acid, either dilute or concentrated, is not affected by ordinary reducing agents. The dehydrating action of perchloric acid on silica, shown by Willard and Cake *(14)*, aids in the quantitative separation of silica.

Since hot concentrated perchloric acid may react violently with organic substances, the reaction intensity must be controlled. It has been found advisable to pretreat samples of plant material with nitric acid before adding perchloric acid. With substances very high in fat it may be necessary to pretreat the sample several times with nitric acid before it can be oxidized with perchloric acid without a loss of a portion of the sample. The perchloric acid should be diluted with water and nitric acid.

Experimental Procedure

The following method of wet oxidation was applied to a wide variety of plant materials, including sweet clover (roots and tops), alfalfa hay, red clover hay, alsike clover hay, timothy hay, redtop hay, wheat straw, cornstalks, corncobs, corn (grain), and soy beans:

Place a 4-gram sample of the material to be oxidized in a 400-ml. beaker and add 10 ml. of nitric acid (sp. gr. 1.42). Cover the beaker with a watch glass and heat gently until any rapid initial reactions have subsided. Then heat to boiling and boil until the contents of the beaker are almost dry. Remove the beaker from the hot plate and add 10 ml. of dilute nitric acid (1 to 1) and 10 ml. of perchloric acid (70 to 72 per cent). Replace the cover glass and heat very gently to a low boiling temperature (avoid superheating). Maintain this temperature until all organic material has been removed from the sides of the beaker and from the solution, which will be indicated by a colorless or slightly colored solution. Remove the cover glass, allow the beaker to cool a few minutes, and wash any adhering salts into the beaker. (If the cover glass is washed with perchloric acid, the contents of the beaker need not be cooled.)

Evaporate to dryness at a temperature just below the boiling point in a clean hood. If potassium is to be determined on the residue, the ammonium salts should be removed at this point. After the removal of ammonium salts, add 5 ml. of hydrochloric acid (1 to 1) and 10 ml. of water. Heat until all salts are dissolved. Filter into a suitable volumetric flask. Wash the silica residue thoroughly with hot water and make the filtrate up to volume. Aliquot portions of the filtrate may be taken for subsequent analyses.

TABLE III

RECOVERY OF PHOSPHORUS, POTASSIUM, CALCIUM, AND MAGNESIUM ADDED TO PLANT MATERIAL AND OXIDIZED WITH PERCHLORIC ACID

	Added, Mg.	Total, Mg.	Recovered, Mg.	Added, Mg.	Total, Mg.	Recovered, Mg.
		Phosphorus			Potassium	
Wheat Straw	0	2.50	0	0	3.29	0
	2.00	4.50	2.00	0.60	3.91	0.62
	2.00	4.48	1.98	0.60	3.94	0.65
Sweet clover	0	2.00	0	0	1.92	0
	2.00	4.00	2.00	0.60	2.46	0.54
	2.00	3.95	1.95	0.60	2.49	0.57
		Calcium			Magnesium	
Wheat straw	0	8.2	0	0	3.01	0
	14.5	22.6	14.4	7.10	9.90	6.89
	14.5	22.6	14.4	7.10	9.99	6.98
Sweet clover	0	31.4	0	0	10.76	0
	14.5	45.9	14.5	7.10	17.91	7.15
	14.5	45.5	14.1	7.10	17.82	7.06

TABLE IV

TOTAL CALCIUM AND TOTAL MAGNESIUM FOUND IN PLANT MATERIAL
(When oxidized with nitric-perchloric acid and when ashed without treatment according to A.O.A.C. method)

	Sample Number	Calcium		Magnesium	
		By $HClO_4$ %	By ashing %	By $HClO_4$ %	By ashing %
Wheat straw	902	0.38	0.30	0.14	0.11
	907	0.22	0.18	0.10	0.08
Sweet clover tops	W407	1.58	1.53	0.55	0.50
Sweet clover roots	N309	0.36	0.29	0.38	0.23
Sweet clover tops	C	0.74	0.76	0.61	0.67
Sweet clover roots	C	0.18	0.17	0.31	0.25
Redtop hay	WS	0.26	0.18	0.27	0.16
Timothy hay	R408E	0.30	0.19	0.17	0.16
Alfalfa hay	R409E	2.24	2.29	0.51	0.51

TABLE V

TOTAL PHOSPHORUS AND TOTAL POTASSIUM FOUND IN PLANT MATERIAL
(When ashed with H_2SO_4 [method given by Wiley] and oxidized with nitric perchloric acid)

	Sample Number	Phosphorus		Potassium	
		By $HClO_4$ %	By ashing %	By $HClO_4$ %	By ashing %
Alfalfa hay	401	0.15	0.14	0.96	0.83
	403	0.20	0.22	0.73	0.69
	404	0.20	0.23	0.93	0.83
Red clover hay	408	0.20	0.20	0.80	0.67
	409	0.20	0.21	0.96	0.93
Alsike clover hay	401	0.15	0.15	1.16	0.99
	402	0.29	0.25	1.12	1.01
Wheat straw	902	0.25	0.22	1.69	1.50
	907	0.25	0.22	2.33	2.13

The above method was applied to the plant materials studied and calcium, magnesium, potassium, and phosphorus were determined. Known amounts of calcium from a standard solution of calcium acetate, magnesium from a standard solution of magnesium sulfate, and potassium and phosphorus from a standard solution of potassium dihydrogen phosphate were then added to a duplicate sample of the material and the determinations repeated, using the same procedure. The acids and salts used were taken from the usual laboratory stock of C. P. reagents. Calcium was precipitated as the oxalate and titrated with permanganate as directed by Wiley *(28)*. Magnesium was determined by the method of Handy *(29)* as modified by Truog and Chucka *(30)*. The method of Schueler and Thomas *(31)* was used for potassium. Phosphorus was precipitated as the phosphomolybdate and titrated with sodium hydroxide according to the method given by Treadwell and Hall *(32)*. Table III shows the amounts of calcium, magnesium, potassium, and phosphorus recovered.

In order to test the accuracy of the nitric-perchloric acid method of destroying organic matter a corresponding set of samples was ashed, and calcium, magnesium, potassium, and phosphorus were determined as before. The method of the Association of Official Agricultural Chemists *(33)* was used for ashing the samples previous to the determination of calcium and magnesium, and the sulfuric acid method of Wiley *(28)* was used for potassium and phosphorus. As a further comparison, the method of Howk and DeTurk *(27)* was used for phosphorus. Samples of wheat straw, redtop hay, sweet clover tops, and sweet clover roots were found to contain 0.26, 0.15, 0.18, and 0.32 per cent of phosphorus, respectively, by the Howk and DeTurk method, as compared to 0.27, 0.16, 0.19, and 0.32 per cent by the nitric-perchloric acid method. The results of the other comparisons are given in Tables IV and V.

Discussion of Results

The amounts of calcium, magnesium, potassium, and phosphorus added were very satisfactorily recovered with the use of the nitric-perchloric acid procedure (Table III).

Tables IV and V show that there is not always good agreement between the nitric-perchloric acid and the ashing methods. It will be noted from Table IV that in cases of disagreement calcium and magnesium are always lower when the samples are ashed. With the nitric-perchloric acid method one obtains a white residue of dehydrated silica, but when the sample is ashed for calcium and magnesium determinations, the residue is usually gray, indicating the incomplete oxidation of carbon. Furthermore, the calcium and magnesium in the ash are not readily soluble in the dilute acid used in extraction. Low results under such conditions suggest the incomplete removal of calcium and magnesium from the residue obtained upon ashing. Likewise, the ashing method for potassium tends to give lower results than the nitric-perchloric acid method. Since potassium compounds are volatile at high temperatures, a loss of potassium might be expected in using the ashing procedure.

The results of the three methods used for the phosphorus determinations agree very closely.

In view of these results and the plausible explanations thereof, it would seem that the proposed method of wet oxidation of this class of materials is from the standpoint of both accuracy and convenience superior to the ashing methods.

Essentially the same procedure as that described by Gieseking, Snider, and Getz *(34)* as the basis for the destruction of organic matter

in plant analysis has been described by H. W. Gerritz *(35)*. This method is also shown to be rapid and economical as well as accurate. The paper is entitled, "Digesting Biological Materials for Calcium and Phosphorus Analysis." The samples prepared for these determinations included feed concentrates, feces, and grasses. It is stated that "it should also be possible to determine mineral elements such as iron, magnesium and others not forming insoluble perchlorate salts on digestion." It is a coincidence that this statement was substantiated by the work of Gieseking, Snider, and Getz *(34)* working independently and publishing their data as companion papers in the same journal.

The procedure for the destruction of organic matter as described by Gerritz *(35)* and as used in the Agricultural Experiment Station at Pullman, Washington, is described as follows:

Weighed samples of suitable size are placed in 500 ml. Kjeldahl flasks. Twenty to 30 ml. of concentrated nitric acid are added and the flasks are placed on asbestos gauzes over medium flames. The contents are boiled gently with frequent mixing until the samples pass into a semi-colloidal solution. The particles of material become swollen and gel-like, then disintegrate, producing a finer suspension or a solution. Experience will indicate at what time this occurs, and the speed of the digestion may be accelerated materially by determining the length of time required for the material being analyzed to reach this stage. For the materials reported in this paper the flames were so adjusted that the treatment took 30 to 45 minutes. Heating to dryness must be avoided.

Ten milliliters of 70 per cent perchloric acid are now added to each and the flasks are placed over free flames. Very low flames are necessary during the perchloric acid oxidation and best results are obtained when just sufficient heat is applied to keep the solution boiling. Only a fine point of the flame should impinge on the flask. Higher temperatures tend to drive off the perchloric acid without materially accelerating oxidation.

When fuming begins, the flame is so adjusted that only a trace of the perchloric acid fumes reaches the upper region of the Kjeldahl neck. The heating is continued until the solution is practically colorless or only a faint yellow color remains. The solution is allowed to cool slightly and 50 ml. of distilled water are added. Vigorous boiling occurs which drives out the remaining nitrogen dioxide fumes, leaving a clear solution.

The solution is filtered into a volumetric flask, and the Kjeldahl flask is thoroughly washed with distilled water. When the solution has cooled it is made to volume and aliquots are taken for analysis. Calcium and phosphorus determinations may be completed by the usual procedures.

DISCUSSION OF RESULTS

Results by both an official method and the new method agree closely and the differences are essentially the same as differences between duplicates by the same digestion method.

The digestion is not difficult to conduct, but care must be taken that the sample is not boiled to dryness. Maximum speed of digestion will be obtained by noting

carefully the time required for the nitric acid to emulsify the material. Insufficient heat tends to make the digestion lengthy, while excess heat boils off the nitric acid before its maximum effect is obtained. It is not advisable, therefore, to boil the nitric acid over a free flame. Best results, together with a rapid digestion, were obtained by placing the flask on an asbestos gauze over a gas flame in a Kjeldahl digestion rack and turning on a full flame.

The digestion produces a clear solution in a short time, thus effecting a saving of time and apparatus when both calcium and phosphorus are to be determined on the same material. It is much more rapid than ashing and may therefore prove more efficient, even when calcium or other elements alone are to be determined. Iron, magnesium, and other elements not forming insoluble perchlorate salts might also be determined on the digest.

THE DETERMINATION OF CHROMIUM IN CHROME TANNED LEATHER. NITRIC, PERCHLORIC AND SULFURIC ACIDS AS OXIDANT FOR ORGANIC MATTER AND CHROMIUM

The destruction of organic matter in leather in preparation for the determination of chromium and of iron, according to the following reprinted directions *(16) (17)*, was developed by the author of this booklet in collaboration with V. R. Sullivan, working in the Chemical Laboratories of the University of Illinois. The data were originally published in *The Journal of the American Leather Chemists Association (16)*, and in *Industrial and Engineering Chemistry*, Analytical Edition (*17*).

Introduction

The rapid determination of chromium in chrome tanned leather involves the application of two major developments. First, the rapid destruction of the organic matter of the leather and filler material such as paraffin, with quautitative retention of chromium. Second, the quantitative oxidation of chromium to chromic acid and its subsequent determination using standard volumetric reducing agents. The most satisfactory reagents for the destruction of organic matter should provide for the quantitative oxidation of chromium in consecutive operations.

Perchloric acid and its combination with other mineral acids has become a favored method of attack following use in many existing methods of analysis. In the case of leather the present methods employ either perchloric acid alone or a combination of dry ashing and acid treatment. The more rapid decomposition of organic matter involves the use of perchloric, nitric and sulfuric acids together with promoter catalysts to hasten and temper the oxidation. The influence of such catalysts on the subsequent determination of chromium with test analyses completes the research.

The present section has for its object the description of methods which are at once rapid, accurate and precise. The saving in time is accompanied by a material reduction in the cost of reagents. Methods for increasing accuracy in the estimation of chrominm following oxidation with perchloric acid are described. The accurate determination of chromium in leather by the new method requires twenty to thirty minutes.

Earlier Studies

Based on the method of Liehtin *(36)* the trivalent chromium in the one-bath chrome tanning process can be determined using perchloric acid as oxidizing agent.

This process applies either to basic chromium sulfate or chloride baths such as "Tanolin." The application of the Lichtin method to the determination of chromium in partially spent tanning liquids was described by Cameron and Adams *(37)* and by Bergmann and Mecke *(38)*. The determination of chromium in tanned or partially tanned leather "in the blue" by these methods employs perchloric acid both for the destruction of organic matter and the oxidation of chromium. The chromium is determined iodometrically by Cameron and Adams and by use of ferrous sulfate with diphenylamine as indicator by Bergmann and Mecke. For analyses of finished chrome tanned leather which is heavily loaded in most cases by use of paraffin and similar agents the sample is either ashed before digestion with perchloric acid or the treatment is very cautiously applied over several hours time if the organic matter is also to be destroyed by the perchloric acid. In either case the time required is excessive.

General Considerations

The destruction of organic matter preparatory to mineral analysis in the wet way has been highly developed using perchloric acid as oxidant. In some cases the rate of oxidation is excessive and may become violent. The destruction of cellulose, sugars and starch are examples. In other cases such as the reaction with coal or coke and aromatic ring nitrogen compounds the decomposition requires several hours treatment.

The decomposition of organic matter using perchloric acid is retarded in rate by the addition of sulfuric acid. The effect is that of dilution. At the same time, the intensity of the oxidation is increased. Difficultly oxidizable organic matter is destroyed in much less time.

The addition of nitric acid to perchloric acid (by dilution and lower temperature of oxidation) is effective in the retarded destruction of easily decomposed organic matter. The use of nitric, perchloric and sulfuric acid combines the advantages in many cases. The destruction of protein material, collagen and keratin, as well as the "loading" agents such as wax and paraffin in leather analyses, can be best accomplished using the three acids. The addition of other catalysts, besides chromium already present, such as vanadium or osmic acid speeds and tempers the reaction. The oxidation is thus combined with a "cracking" of complex organic molecules to simpler products which in turn are easily oxidized by nitric acid. This is followed by their complete destruction by perchloric and sulfuric acids after elevating the temperature to remove excess nitric acid.

The determination of chromium in the wet ashed leather residue, after complete decomposition of organic matter by formation of chromic acid in mixed perchloric and sulfuric acids, has been studied by Smith, McVickers and Sullivan *(5, 53)*. The determination of chromium and vanadium in alloy steels has been developed into well known methods in general use which employ perchloric acid and the application in the case of chrome tanned leather follows similar lines.

Chrome tanned leather, besides the advantage of speed in its application as compared to the vegetable tanning process, is in demand because of its tensile strength, greater resistance to deterioration from heat and atmospheric influences, chemical fumes and moisture. The disadvantage of the chrome tanning process consists in the fact that it must be "loaded" with various products to gain the desired thickness and to eliminate slipping following wear. Chrome processed leather does not dye well. A suitable chrome tanned leather should contain at least 2.8 per cent of Cr_2O_3.

Choice of Acid Medium for the Wet Oxidation of Finished Chrome Tanned Leather

Factors involved in the wet ashing of leather using a mixture of nitric, perchloric and sulfuric acids may be classified as follows:

1. Leather type and sample weight.
2. Proportions of perchloric and sulfuric acid of definite strength required.
3. Amount of nitric acid employed and its effect.
4. Type and amount of catalyst required.
5. Temperature of digestion.

These topics will be discussed in the order given.

1. One gram samples of finished leather contain sufficient chromium to serve for individual determinations using 0.05 normal volumetric reagents. A two gram sample of leather "in the blue" is equivalent to the same amount of chromium. Finished leather samples should be ground to the consistency of corn meal or finer to insure a uniform sample. Certain types of finished leather are suitable for analysis in the form of chips of 1 to 2 mm. maximum dimension while others do not give uniformly precise chromium determinations in this form.

2. The proper proportion of 70 per cent $HClO_4$ and 80 per cent H_2SO_4 to be employed was determined by digesting one gram samples of finished leather with 10 ml. of the $HClO_4$ and graded addition of 1 to 20 ml. of the H_2SO_4. The most rapid and satisfactory destruction of organic matter results using 2 volumes of 70-72 per cent $HClO_4$ to 1 volume of 80 per cent H_2SO_4.

3. Some difficulty in the use of the two-component mixture of $HClO_4 + H_2SO_4$ was found by reason of the formation of crusts on the reaction flask and at the cool portions in the neck of the Erlenmeyer. These crusts result from the volatilization of products of "cracked" leather protein materials which do not volatilize chromium but which if not completely eliminated interfere with its subsequent oxidation. By addition of concentrated nitric acid to the perchloric and sulfuric acid mixture the "cracking" process results in the formation of more volatile organic materials which eliminates crust formation. As the destruction of organic matter progresses and the temperature of the reaction medium increases the nitric acid is completely volatilized. The oxidation of chromium to chromic acid following the destruction of organic matter is thus accomplished in the absence of nitric acid. Five milliliters of HNO_3 (Sp. Gr. 1.42) are suitable for each 15 ml. of mixed perchloric and sulfuric acids.

4. The chromium of the leather acts as a catalyst in the oxidation of the leather by perchloric acid. The trivalent chromium is oxidized to chromic acid by the $HClO_4$ and is in turn reduced by the organic matter present. The use of chromium for this purpose in the determination of sulfur in coal has been described by Smith and Deem *(9)*. Vanadium added in the form of ammonium vanadate reacts analogously in the latter case and was, therefore, applied to the oxidation of the leather in the present case. Approximately 30 mg. of ammonium vanadate was found to materially catalyze the reaction for each gram of leather destroyed. Osmic acid added in the form of OsO_4 dissolved in 0.1 N H_2SO_4 was found to be equally effective in minute concentrations. Using mixed $HClO_4 + H_2SO_4$ in the absence of HNO_3 the crust of "cracked" leather decomposition products on the digestion flask walls often flashed fire inside the flask due to the osmic acid effect. This effect was not obtained in case $HNO_3 + HClO_4 + H_2SO_4$ served as the oxidation medium. The use of vanadium as catalyst complicates the determination of

chromium somewhat which is not the case using osmic acid. Determinations of chromium in leather using no catalyst may be accomplished without much increase in digestion time but not at as low a reaction temperature. The reactions are smoother in the presence of added catalyst.

5. The temperature of digestion may vary from 175° to 205° C. Using a 500 ml. Erlenmeyer flask with a chestnut shaped loose fitting cap, such as that described by Smith and Getz *(15)*, or as in Figure 2, or a small glass funnel or thistle tube with shortened stem, the digestion can be carried out on the hat plate or with a wire gauze and free flame with close enough adjustment to suit the case. The excess HNO_3 is thus rapidly enough displaced to insure its rapid removal and yet provide its full oxidizing value. Subsequently this assembly of apparatus permits the final oxidation of organic matter without loss of perchloric acid except that used in destroying organic matter. The trivalent chromium is oxidized to chrome acid by the mixed $HClO_4 + H_2SO_4$ at 185° C.

Reagents Employed

Leather Oxidant. 2 volumes of 70-72 per cent C. P. perchloric acid are added to 1 volume of 80 per cent C. P. sulfuric acid (Sp. Gr. 1.73).

Nitric Acid. C. P. concentrated (Sp. Gr. 1.42).

Osmic Acid. One half gram of osmium tetroxide (OsO_4) was dissolved in 200 ml. of 0.1 N H_2SO_4.

Vanadic Acid. 2.0 g. of ammonium vanadate are dissolved in 1000 ml. of leather oxidant.

Potassium Permanganate. An approximately 0.05 N solution is made by dissolving 1.65 g. of $KMnO_4$ crystals per liter of water. The solution after standing 7-10 days is syphoned free of MnO_2.

Ferrous Sulfate. An approximately 0.05 N solution of $FeSO_4 \cdot 7H_2O$ was prepared by dissolving this salt in dilute H_2SO_4 (2.0 per cent by volume of 1-1 H_2SO_4).

Sulfato-Ceric Acid. An approximately 0.05 N solution of $(NH_4)_2Ce(SO_4)_3 \cdot 2H_2O$ (ammonium sulfato cerate) was prepared by dissolving 32 grams in each liter of molar H_2SO_4.

Indicators. A solution of diphenylamine sulfonic acid 0.005 M was prepared. To 0.16 g. of the barium salt in 100 ml. of water, there was added 0.25 g. of sodium sulfate. The indicator solution was then decanted free from the barium sulfate. A 0.025 M solution of ortho-phenanthroline ferrous complex in water was employed. It may be purchased in this form or be prepared by the solution of monohydrated ortho-phenanthroline (1.485 G.) in 100 ml. of water followed by the addition of 0.695 g. of $FeSO_4 \cdot 7H_2O$.

Standardization of Volumetric Solutions

0.05 Ferrous Sulfate. Samples of 25 to 50 ml. were transferred to 400 ml. beakers using calibrated pipettes and diluted to 150 ml. Three ml. of 85 per cent phosphoric acid were added and the titration made using 0.05 N permanganate in the usual manner. The ferrous sulfate solution was stored in a large volume Z and R automatic buret under H_2 from a small Kipp generator. After six weeks storage the normality had changed from 0.04798 to 0.04789 normal, a negligible change. Using pure $K_2Cr_2O_7$ and ortho-phenanthroline ferrous complex as indicator the value found was 0.04799 normal.

0.05 N Potassium Permanganate. Samples weighing 100 mg. of Bureau of Standards sodium oxalate after drying at 135° C. were dissolved in 100 ml. of water, acidified by addition of 10 per cent by volume of concentrated sulfuric acid, and titrated at 90° C.

0.05 N Sulfato-Ceric Acid. 25 to 50 ml. samples of solution were transferred to 400 ml. beakers using a calibrated pipette, and diluted to 150 ml. After the addition of 15-20 ml. of 1-1 sulfuric acid and 2 drops of ortho-phenanthroline ferrous complex as indicator these solutions were titrated with standard ferrous sulfate to the first pink color. The normality of this solution was 0.04914. Sulfato-ceric acid is to be preferred to potassium permanganate as oxidizing agent for chromium determinations in leather because of its permanent titer. The potassium permanganate must be re-standardized at frequent intervals.

Selection of Leather Samples and Preparation for Analysis

Five separate samples of chrome tanned leather were prepared for test analyses. Their classification is given in Table VI.

TABLE VI

TYPES AND DESCRIPTION OF LEATHER SAMPLES ANALYZED

Leather No.	Trade Name	Description
1	"Korry-Chrome"	Chips, coarse
1a	"Korry-Chrome"	Ground to fine division
2	not specified	Wood plane sample sifted
3	"Stadri"	Chips, coarse
4	not specified	Ground to fine division

Samples number one and three were sole leather sliced into one mm. sections approximately two mm. in length. Sample number one, by color test, was thought to be of non-uniform chromium content which was shown to be justified by subsequent analysis. It was in part ground to a meal and this sample after thorough mixing is numbered 1a. Sample number 3 appeared uniform and was analyzed in the form of chips as in the case of sample number 1. Samples number 2 and 4 were from light green sole leather which after slicing using a wood plane due to their fibrous and spongy nature gave a portion of slices which easily separated into a keratin rich portion and a portion of leather lintles which segregated readily. The fluffy portion was sifted out and thoroughly mixed to form sample number 2. Finally a portion of this same leather was ground to a meal and the total portion of the leather numbered sample 4.

The Rate of Destruction of Organic Matter With and Without Added Catalyst

Samples of one gram of leather in 500 ml. Erlenmeyer flasks with cover were treated with 10 ml. of 70-72 per cent $HClO_4$, 5 ml. of 80 per cent H_2SO_4 and 5 ml. of concentrated HNO_3 (Sp. Gr. 1.42). The samples quickly dissolved and were digested at approximately 200° C. Heavy brown fumes of oxides of nitrogen appear and after 10 minutes the action of the nitric acid is complete and the excess boiled out of the reaction mixture. An additional five minutes digestion decomposes

the remaining organic matter as shown by the oxidation of chromium to chromic acid. At this point the solution should be boiling smoothly with acid refluxing back from a position half way up the flask. After 2-3 min. the oxidation of chromium is complete and the solution ready for dilution and determination of chromium.

With vanadium as catalyst a solution of 2 volumes 70-72 per cent $HClO_4$ + 1 volume 80 per cent H_2SO_4 contained ammonium vanadate sufficient to give a concentration of 2 mg. per ml. 15 ml. of this solution plus 5 ml. of conc. NHO_3 were used in the digestion of the sample.

Similar acid treatment without vanadium but after addition of 0.2 ml. of 0.01 N osmic acid solution completed the comparison digestions. The results are shown in Table VII.

TABLE VII

THE TIME RATE OF DESTRUCTION OF ORGANIC MATTER AND OXIDATION OF CHROMIUM

Leather No.	Catalyst used and Time of Reaction in Minutes		
	No Catalysts	Osmic Acid	Vanadium
1a	41	17	16
3	22	17	12
4	18	17	11

The results in Table VII show that the oxidation without catalyst varies in rate with the sample, the more heavily weighted samples requiring the longer oxidation period. This effect cannot be attributed to the catalysis by the presence of varying chromium content since the samples are approximately the same in per cent chromium. Vanadium is more effective as catalyst than osmic acid. The digestion temperature was approximately 190° C.

The digestion data using various concentrations of acids and ammonium vanadate as catalyst are shown in Table VIII.

Recommended Procedures

1. **No Catalyst.** Weigh approximately one gram of leather (suitably prepared for maximum uniformity of sample) into a 500 ml. Erlenmeyer flask. Add 15 ml. of leather oxidant and 5 ml. of concentrated nitric acid. Stopper the flask with a thistle tube in which the stem is sealed off at a length of four inches and bent slightly to contact the side of the flask; in addition the bulb is vented by means of a small indentation to permit the escape of fumes during the digestion. The temperature of the digestion (175-200° C.) should be so adjusted that the solution boils quietly but not vigorously enough to result in sufficient condensation of vapors near the top of the flask as to force them over and down the outside. In a short time the solution will concentrate sufficiently for the oxidizing power of perchloric acid to become pronounced, evidenced by a slight charring, and followed a little later by the oxidation of chromium. In a few minutes the solution should be boiling quietly, with acid refluxing about half way up the flask and draining quietly back into the solution.

Chill the solution suddenly by immersing the lower part of the flask in a pan of cold water, preferably ice water, gently swirling the contents of the flask. The use of Vycor flasks is highly recommended to avoid risk of breakage.

4-5 seconds cooling is sufficient to prevent splattering on dilution. Dilute immediately with 30-40 ml. of water and boil 2-3 minutes to remove chlorine. Then dilute the solution to 200 ml. with water and cool to room temperature. Add 1 ml. of 85 per cent phosphoric acid and several drops of indicator (0.005 M solution of the sodium salt of diphenylamine-sulfonic acid) and titrate with standard $FeSO_4$ solution until the initial purplish color of the indicator changes to a light green. The color change is quite sharp, 1 or 2 drops of 0.04 N solution causing the change. The amount of Cr_2O_3 may be calculated from the volume of solution used.

2. **Catalyst Osmic Acid.** The procedure is exactly as outlined above, except that approximately 0.2 cc. (3-5 drops) of 0.01 M osmic acid are added along with the mixed acids at the start of the digestion.

3. **Catalyst Vanadium.** Several changes in the above procedure are necessary. The vanadium is added as ammonium vanadate, and is conveniently dissolved in

TABLE VIII

THE OXIDATION OF LEATHER WITH VARIABLE ACID AND CATALYST RATIOS
Leather Sample—1 Gram Sample No. 1, Temperature 185-200° C.

Volume 70-72% $HClO_4$ ml.	Volume 1-1 H_2SO_4 ml.	Catalyst $(NH_4)_3VO_4$ mg.	Time of Oxidation min.	Remarks
10	1	25	13	Crust formation
10	2	25	13	Crust formation
10	3	25	12	Crust formation
10	4	25	13	Least crust minimum fuming
10	5	25	15	Least crust minimum fuming
10	6	25	12	Least crust minimum fuming
10	8	25	10	Crust formation
10	10	25	9	Crust formation
4	10	25	16	Cr oxidation incomplete
6	10	25	16	Cr oxidation incomplete
8	10	25	16	Slight crust formation
10	10	25	14	Slight crust formation
12	10	25	13	Slight crust formation
8	10	10	17	Satisfactory performance
8	10	25	16	Satisfactory performance
8	10	50	17	Satisfactory performance
8	10	100	15	Satisfactory performance

the leather oxidant, about 2 mg. per ml. of leather oxidant. About 30 mg. are thus used. The digestion of the sample and preparation of the solution for titrating is as outlined above. The actual titration is as follows:

The total volume of the solution is about 200 ml. Add 2 drops of indicator (O-phenanthroline ferrous sulfate complex) and a slight excess of standard $FeSO_4$ solution as shown by the intense pink color of the indicator. Add 20-25 g. sodium acetate tri-hydrate and heat to 50° C. using a thermometer. Then run in standard $H_2Ce(SO_4)_3$ solution which will oxidize the excess $FeSO_4$ and also the vanadyl ion to the original vanadate. The pink color of the indicator gradually fades to a gray and then a single drop excess of cerate gives a light bluish-green color, modified slightly by the turbidity due to the precipitated barium sulfate, if barium

was present in the original leather. The $H_2Ce(SO_4)_3$ may be added fairly rapidly; if the end-point is over stepped, $FeSO_4$ may be added in slight excess, and the pink color of the indicator then discharged by the cautious addition of $Ce(SO_4)_2$. The reaction is somewhat slow, and a few seconds must be allowed for the appearance of the indicator color. The color change is sharp, however, and can be determined within one drop or two at the most. The net amount of $FeSO_4$ used after correcting for the $H_2Ce(SO_4)_3$ used in the back titration corresponds to the Cr_2O_3 present in the sample. Potassium permanganate may be substituted for ceric sulfate without change in method as here outlined.

Sample analyses using procedures 1, 2, and 3 were made and the results are shown in Tables IX, X and XI, respectively.

As a check on the accuracy in the determination of the leather chromium, samples were analyzed after the addition of known amounts of standardized solution of $Cr_2(SO_4)_3$ in 0.125 M sulfuric acid. This solution by analysis was found to contain 3.48 mg. Cr_2O_3 per ml. Five ml. portions of this solution were transferred using a calibrated pipette and the weighed samples of leather and oxidizing acids added.

After deduction of the known amount of Cr_2O_3 added, the per cent of Cr_2O_3 in the leather was calculated. The error in determination of total Cr_2O_3 was then calculated using the average determined value of Cr_2O_3 present in the sample. The experimental data was as follows:

TABLE IX

THE DETERMINATION OF Cr_2O_3 IN LEATHER ACCORDING TO PROCEDURE 1

Run No.	Leather No.	Leather Weight	Cr_2O_3 Added	$FeSO_4$ ml.	Cr_2O_3 found	Cr_2O_3 calc.	Error mg.	% Cr_2O_3 leather	% Cr_2O_3 av.	Average Error mg. Cr_2O_3
1	1	1.0483	——	29.76	.0361	——	——	3.44		
2	1	1.0210	——	29.20	.0354	——	——	3.47	3.46	
3	1	1.0483	.0174	44.66	.0542	.0537	+0.5	3.51		
4	1	1.0179	.0174	44.08	.0535	.0527	+0.8	3.55	3.53	+0.7
5	1a	1.0135	——	30.40	.0369	——	——	3.64		
6	1a	1.0060	——	29.20	.0354	——	——	3.52	3.58	
7	1a	1.0071	.0174	44.30	.0538	.0535	+0.3	3.61		
8	1a	1.0112	.0174	43.94	.0533	.0536	—0.3	3.55	3.58	±0.0
9	2	1.0079	——	31.04	.0377	——	——	3.74		
10	2	1.0116	——	31.06	.0377	——	——	3.73	3.73	
11	2	1.0682	.0174	46.60	.0566	.0573	—0.7	3.67		
12	2	1.0122	.0174	45.16	.0548	.0552	—0.4	3.70	3.68	—0.5
13	3	1.0280	——	30.06	.0365	——	——	3.55		
14	3	1.0117	——	29.66	.0360	——	——	3.56	3.56	
15	3	1.0209	.0174	44.50	.0540	.0538	+0.2	3.58		
16	3	1.0258	.0174	44.52	.0540	.0540	±0.0	3.57	3.58	+0.1
17	4	1.0064	——	31.20	.0379	——	——	3.76		
18	4	1.0118	——	30.88	.0375	——	——	3.70	3.73	
19	4	1.0439	.0174	46.90	.0569	.0564	+0.5	3.78		
20	4	1.0070	.0174	45.22	.0549	.0550	—0.1	3.71	3.75	+0.2

The results of Tables IX, X and XI are summarized in Table XII excluding values for leather number 1 which was of non-uniform composition.

From the examination of the data in Table XII summarizing that of Tables IX, X and XI, the leather samples gave results by all three methods which agree very satisfactorily. The determination of Cr_2O_3 is shown to be accurate to within 0.02 per cent and generally within 0.01 per cent. The average of all determinations

TABLE X

THE DETERMINATION OF Cr_2O_3 IN LEATHER USING PROCEDURE 2 WITH OSMIC ACID AS CATALYST

Run No.	Leather No.	Leather Weight	Cr_2O_3 added	$FeSO_4$ ml.	Cr_2O_3 found	Cr_2O_3 calc.	Error mg.	% Cr_2O_3 in leather	% Cr_2O_3 av.	Average Error mg. Cr_2O_3
21	1	1.0043	——	29.76	.0361	——	——	3.59		
22	1	1.0069	——	28.60	.0347	——	——	3.45		
23	1	1.0144	——	29.20	.0354	——	——	3.49	3.51	
24	1	1.0113	.0174	42.36	.0514	.0529	—1.5	3.36		
25	1	1.0095	.0174	41.54	.0504	.0527	—2.3	3.27	3.32	—1.9
26	1a	1.0090	——	30.16	.0366	——	——	3.63		
27	1a	1.0121	——	29.72	.0361	——	——	3.56		
28	1a	1.0091	——	29.16	.0354	——	——	3.51	3.57	
29	1a	1.0215	.0174	44.72	.0542	.0539	+0.3	3.60		
30	1a	1.0114	.0174	43.78	.0531	.0535	—0.4	3.53	3.57	±0.0
31	2	1.0460	——	31.95	.0388	——	——	3.70		
32	2	1.0126	——	30.70	.0373	——	——	3.68		
33	2	1.0261	——	31.00	.0376	——	——	3.67	3.68	
34	2	1.0138	.0174	45.72	.0554	.0547	+0.7	3.75		
35	2	1.0084	.0174	45.22	.0549	.0545	+0.4	3.72	3.73	+0.5
36	3	1.0068	——	29.20	.0354	——	——	3.52		
37	3	1.0082	——	29.34	.0356	——	——	3.53		
38	3	1.0142	——	29.30	.0356	——	——	3.51	3.52	
39	3	1.0044	.0174	43.22	.0524	.0528	—0.4	3.48		
40	3	1.0636	.0174	45.00	.0546	.0548	—0.2	3.50	3.49	—0.3
41	4	1.0129	——	31.06	.0377	——	——	3.72		
42	4	1.0030	——	30.88	.0375	——	——	3.74		
43	4	1.0136	——	30.86	.0375	——	——	3.60	3.72	
44	4	1.0200	.0174	45.96	.0558	.0554	+0.4	3.76		
45	4	1.0324	.0174	46.14	.0560	.0558	+0.2	3.74	3.75	+0.3

of Cr_2O_3 show this point. The addition of known amounts of Cr_2O_3 did not affect the accuracy in recovery of Cr_2O_3 in the leather indicating accurate recovery of leather chromium.

Digestion of Larger Samples of Leather Using Mixed $HNO_3 + HClO_4 + H_2SO_4$ and the Consumption of $HClO_4$ in the Process

According to data previously reported on the subject it is known to require approximately 5 ml. of 70 per cent $HClO_4$ for the destruction of one gram of organic matter. Using a mixture of $HNO_3 + HClO_4 + H_2SO_4$ less $HClO_4$ is required. The nitric acid oxidizes a large portion of organic matter in its place. By determination of the acid left after the removal of excess nitric acid and assuming

that the H_2SO_4 is without effect it was found that approximately 2 ml. of 70 per cent $HClO_4$ was consumed.

For the destruction of the organic matter in large samples of finished leather (5 grams) 25 ml. of leather oxidant are required and 25 ml. of concentrated HNO_3 preferably added in two portions. The second portion of nitric acid is added after the removal of most of the first portion during the digestion when the sample begins to char. The second addition completes the preliminary digestion.

TABLE XI

THE DETERMINATION OF Cr_2O_3 IN LEATHER USING PROCEDURE 3 WITH VANADIUM AS CATALYST

Run No.	Leather No.	Weight	Cr_2O_3 added	$FeSO_4$ excess ml.	$Ce(SO_4)_2$ ml.	$FeSO_4$ net	Cr_2O_3 found	Cr_2O_3 calc.	Error mg.	% Cr_2O_3 in leather	% Cr_2O_3 av.	Error mg. Cr_2O_3
46	1	1.0197	——	33.08	3.92	29.06	.0353	——	——	3.46		
47	1	1.0233	——	34.04	5.04	28.88	.0350	——	——	3.43	3.45	
48	1	1.0187	.0174	48.08	4.58	45.38	.0526	.0522	+0.4	3.46		
49	1	1.0395	.0174	48.08	4.62	43.34	.0526	.0533	—0.7	3.39	3.43	—0.2
50	1a	1.0112	——	32.06	2.32	29.68	.0360	——	——	3.56		
51	1a	1.0080	——	35.06	5.42	29.50	.0358	——	——	3.55	3.56	
52	1a	1.0105	.0174	48.08	3.88	44.10	.0535	.0534	+0.1	3.57		
53	1a	1.0060	.0174	48.06	4.10	43.86	.0532	.0533	—0.1	3.56	3.57	±0.0
54	2	1.0310	——	35.08	3.60	31.40	.0381	——	——	3.70		
55	2	1.0170	——	35.46	4.12	31.24	.0379	——	——	3.73	3.72	
56	2	1.0430	.0174	49.10	2.62	46.42	.0563	.0562	+0.1	3.73		
57	2	1.0508	.0174	49.56	2.94	46.54	.0565	.0565	±0.0	3.72	3.73	+0.1
58	3	1.0332	——	38.08	7.82	30.06	.0365	——	——	3.53		
59	3	1.0182	——	34.04	4.86	29.06	.0353	——	——	3.46	3.50	
60	3	1.0237	.0174	48.14	4.12	43.92	.0533	.0532	±0.1	3.51		
61	3	1.0090	.0174	49.56	6.14	43.26	.0525	.0527	—0.2	3.48	3.50	±0.0
62	4	1.0223	——	36.04	4.46	31.46	.0382	——	——	3.73		
63	4	1.0207	——	36.06	4.46	31.48	.0382	——	——	3.74	3.74	
64	4	1.0206	.0174	49.08	3.38	45.62	.0554	.0556	—0.2	3.72		
65	4	1.0444	.0174	49.60	3.22	46.30	.0562	.0565	—0.3	3.72	3.74	—0.2

TABLE XII

Leather Sample	% Cr_2O_3 Leather only	Procedure 1 Cr_2O_3 added	% Cr_2O_3 Leather only	Procedure 2 Cr_2O_3 added	% Cr_2O_3 Leather only	Procedure 3 Cr_2O_3 added
1a	3.58	3.58	3.57	3.57	3.56	3.57
2	3.73	3.68	3.68	3.73	3.72	3.73
3	3.56	3.58	3.52	3.49	3.50	3.50
4	3.73	3.75	3.72	3.75	3.74	3.72

VOLUMETRIC DETERMINATION OF IRON IN LEATHER

Wet Oxidation of Organic Matter Using Mixed Nitric, Perchloric, and Sulfuric Acids and Titration of Iron, Using Titanous Chloride

The wet oxidation of the organic matter in chrome-tanned leather by a mixture of nitric, perchloric, and sulfuric acids has been shown *(16)* to be rapid and quantitative. Following the destruction of organic matter, the chromium is oxidized to chromic acid by the excess of perchloric acid and is then determined, using an excess of ferrous sulfate, with back-titration using sulfato-ceric acid or potassium permanganate with ortho-phenanthroline ferrous complex as indicator. The presence of more than traces of iron in vegetable-tanned leathers is claimed to be detrimental. The wet oxidation of the organic matter in finished leathers following the previously cited method, if adaptable to the case of 5- to 10-gram samples, might make the volumetric determination of small amounts of iron possible by direct titration, using a standard solution of titanous chloride with ammonium thiocyanate as internal indicator. The determination of iron in finished chrome-tanned leather by the same process would also be possible. After reduction of the chromic acid by boiling with dilute hydrochloric to form chromic ion, if the green color thus produced does not mask the color of the thiocyanate end point, the process would be suitable.

The purpose of the following data is to describe conditions under which iron can be determined rapidly and quantitatively, in both vegetable- and chrome-tanned leather following wet oxidation, using standard titanous chloride. The influence of the chromic ion by color interference in this titration has been determined through a study of the potentiometric evaluation of the end point of the reaction. A series of finished leathers has been analyzed by the process, both in the presence and absence of chromium, and the accuracy of the process proved by the adulteration of prepared sample solutions of oxidized leather residues with known amounts of iron. Interest is added to this investigation by the attempt now being made to adapt iron salts as substitutes for chromium salts in the tanning of leather. (Iron salts for tanning have been used particularly in Russia and Germany, and are reported in their present state of development to give an inferior leather product. Iron, if present in amounts much in excess of a few hundredths of 1 per cent in vegetable-tanned leather, seems to have a detrimental effect due to ill-defined causes.) *(38, 39)*.

Reagents and Standard Solutions

Leather Oxidant. Two volumes of 70 to 72 per cent pure perchloric acid (sp. gr. 1.67) mixed with one volume of 80 per cent analytical reagent sulfuric acid (sp. gr. 1.73).

Nitric Acid. Analytical reagent grade (sp. gr. 1.42).

Ammonium Thiocyanate. A 10 per cent solution free from iron was prepared.

Potassium Ferricyanide. As ordinarily purchased from stock, this reagent is of high purity. It is prepared for use by being ground to a fine powder and dried at 135° to 140° C. for 1 hour or longer.

Titanous Chloride. Stock solutions in hydrochloric acid of approximately 20 per cent strength may be purchased. The technically pure grade supplied by the Vanadium Corporation of America was found to be very satisfactory. Iron, if present, had no undesirable influence following the operations subsequently to be described. Sufficient amounts of this solution to give an approximately 0.01 *N* solution were dissolved in a given volume of dilute (1 to 20) hydrochloric acid and stored under hydrogen using a Zintl and Rienäcker *(40)* automatic buret.

Standardization of Titanous Chloride. Accurately weigh individual 100-mg. samples of dry powdered potassium ferricyanide and transfer to the 500-ml. reaction flask shown in Figure 1. The side opening of the flask is closed during the digestion of the sample for the decomposition of the ferricyanide. Add 10 ml. of leather oxidant. Close the reaction flask with the refluxing digestion head shown in Figure 1 and digest just below the boiling point. The solution blackens from the formation of colloidal carbon. The carbon is soon oxidized leaving the solution almost colorless. When the reaction is complete a slight yellow color from free chlorine finally remains after a 15- to 30-minute digestion. A precipitate of anhydrous ferric sulfate is formed.

Cool somewhat, dilute with 20 to 30 ml. of water, and remove the refluxing digestion head, washing it inside and outside with a stream from the jet of the wash bottle. Boil the solution 2 to 3 minutes to remove chlorine and dissolve the

TABLE XIII

STABILITY OF APPROXIMATELY 0.01 *N* TITANOUS CHLORIDE STORED UNDER HYDROGEN

	[Reference Standard $K_3Fe(CN)_6$]			
Time, days	7	20	53	67
Normality	0.01424	0.01425	0.01421	0.01411

dehydrated ferric sulfate. Dilute the solution to 100 ml. with ice water and replace the side stopper of the flask with the gas bubbler tube (Figure 1). Add 10 ml. of ammonium thiocyanate solution and flush out the air using a brisk stream of carbon dioxide gas with the titration head shown in Figure 1 in place. Continue the passage of a brisk stream of carbon dioxide and titrate with the solution of titanous chloride to be standardized. The reaction between ferric sulfate and titanous chloride is slow and the last few drops are added at half-minute intervals.

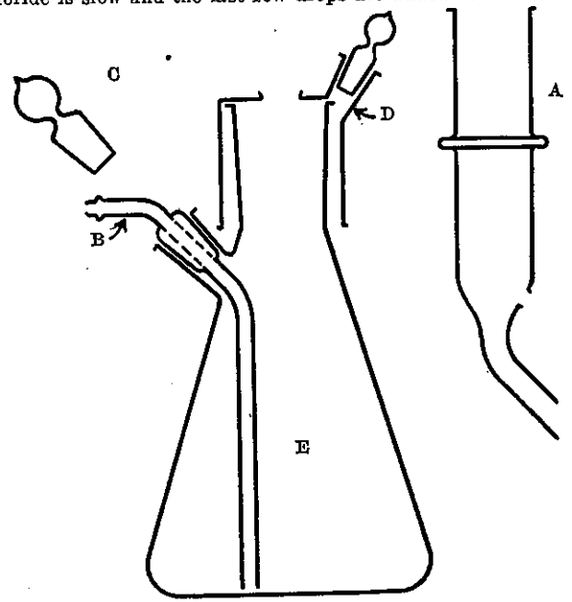


FIGURE 1. Digestion and Titration Apparatus

The color change from deep red to pink to colorless is sharp and can be determined within one drop of 0.01 *N* titanous chloride. Duplicate titrations are averaged, from which data the standard value of the solution is calculated using 329.19, the theoretical value for the equivalent weight of $K_3Fe(CN)_6$.

The stability of titanous chloride stored as described by Smith and Getz *(15)* was shown by repeated titration after long continued use. The data are given in Table XIII.

Preparation of Samples

Nine samples of leather were used for test analyses. Four were chrome-tanned, four were vegetable-tanned, and one sample was tanned by the combined vegetable-

and chrome-tanning process. The descriptions of these samples are given in Table XIV.

Attempts to prepare samples of vegetable-tanned leathers for analysis by use of a revolving-knife shredding mill always met with failure. Samples thus prepared were never uniform in iron content and errors of 100 per cent or more in the determined amount of iron, which is ordinarily present to the extent of 0.01 to 0.02 per cent in vegetable-tanned leathers, are not uncommon. This was proved beyond doubt by comparison analyses of vegetable-tanned leathers after shredding and in the form of chips: In the former case analyses were always high and in poor concordance; in the latter case duplicate analyses were always in agreement and much lower in value by comparison. In the case of chrome-tanned leathers the "loading agents," paraffins and waxes, prevent the abrasive effect on the knife blades of the shredding mill.

Titration of Ferric Iron

Effect of Green Chromic Ion. For the determination of iron in chrome-tanned leather, the influence of the green chromic ion upon the disappearance of the ferric

TABLE XIV

LEATHER SAMPLES ANALYZED

Leather No.	Trade Name	Type	Cr_2O_3 Content %	Sample Form
1	Korry-Krome	Chrome	3.57	Chips
2	Stadri No. 1	Chrome	3.73	Chips
3	Not specified	Chrome	3.50	Ground
4	Stadri No. 2	Chrome	3.73	Ground
5	Logger's Oak	Vegetable tanned	.....	Chips
6	Duxbak	Vegetable and chrome	.....	Chips
7	Tioga Oak	Vegetable tanned	.....	Chips
8	L and M	Vegetable tanned	.....	Chips
9	Armour's Joppa	Vegetable tanned	.....	Chips

thiocyanate color, after complete reduction by titanous ion, might be predicted to involve the development of a premature end point. Since the amounts of chromium in finished chrome leathers are within narrow limits the same, approximately 3.5 per cent Cr_2O_3, for a given weight of sample the amount of chromium present is fairly constant.

To learn the extent to which this premature end point affects the determination of iron, a series of analyses of a standard solution of ferric perchlorate by titration with approximately 0.01 *N* titanous chloride was made in the presence of increasing amounts of chromic ion. For this study a standard solution of ferric perchlorate (25.00 ml. equivalent to 18.15 ml. of 0.01424 *N* titanous chloride) was added to 10 ml. of leather oxidant and evaporated to fumes of perchloric acid. The solutions thus obtained were adulterated by addition of known amounts of potassium chromate diluted, hydrochloric acid was added, and the chromium reduced by boiling. The samples thus obtained were cooled by dilution and titrated with titanous chloride after the addition of ammonium thiocyanate using a stream of carbon dioxide in the titration apparatus shown in Figure 1.

The results of these analyses are shown graphically in Figure 2. The amounts of Cr_2O_3 in milligrams added are plotted on the horizontal axis and the corrections in terms of milliliters of 0.01424 *N* titanous chloride are plotted on the vertical axis. The end point, as in all subsequent determinations, was determined by transmitted light from a daylight lamp bulb against a white background. The color change at the end point is a change from an intense red color of the ferric

thiocyanate through an olive or yellowish green, finally to a clear light green with no tint of olive green. The last few drops of standard solution should be added with half-minute intervals between additions.

An examination of Figure 2 will show that the magnitude of the end-point error is directly proportional to the increase in amount of chromic ion present. The correction for the use of a 5-gram sample of chrome tanned leather is approximately 0.2 ml. of 0.01 *N* titanous chloride (185 mg. of Cr_2O_3). The correction in the case of vegetable-tanned leather is 0.05 ml. of 0.01 *N* titanous chloride, since in such case 10 to 15 mg. of chromic oxide were added during the destruction of the organic matter to indicate the completion of the reaction. The correction is to be added in each case, since the end point appears prematurely.

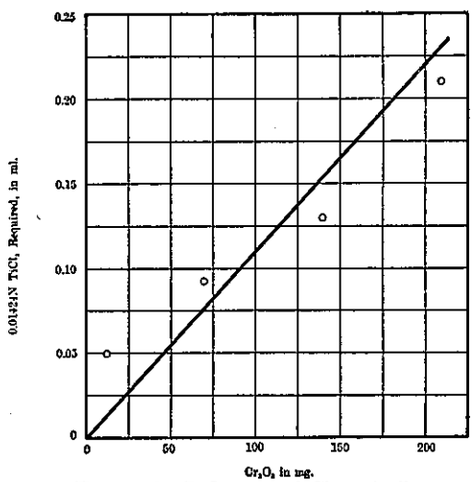


FIGURE 2. Influence of Chromic Ion on Thiocyanate End Point

The magnitude of the end-point error was further studied, using the potentiometric method. With a calomel half-cell and platinum wire reference electrode system and low hydrogen-ion concentration the magnitude of the end-point deflection was found to be approximately 200 mv. with 0.05 ml. of 0.01424 *N* titanous chloride. Conditions for these determinations duplicated essentially the experimental procedure given above for the visual end-point determination and the correction there found was substantiated. The visual end-point correction has been further tested by the separation of the iron in digested leather samples from the chromium, followed by volumetric determination.

Oxidation of Organic Matter and Preparation of Solutions

Procedure for Chrome-Tanned Leather. Weigh 5 grams of finished leather in the form of chips or shreds and place in a 500-ml. digestion flask (Figure 1) with the stopper adjusted in the side arm. Add 25 ml. of leather oxidant and 10 to 15 ml. of concentrated nitric acid. Digest at a moderate temperature (125° to 150° C.) on an electric hot plate or substitute device capable of satisfactory temperature control and with the refluxing digestion head in place, allow the reaction of oxidation to progress 15 to 30 minutes or until the mixture begins to blacken from deposited carbon. Add 10 ml. more of concentrated nitric acid and continue the digestion an additional 15 to 20 minutes, gradually raising the temperature to approximately 200° C. The excess nitric acid is completely volatilized at this point and fumes of perchloric acid appear in the flask. As soon as the last traces of organic matter are oxidized by the hot perchloric acid, the green solution turns orange because of oxidation of chromium to chromic acid. The decomposition of the last traces of organic matter and the oxidation of chromium are exothermal reactions and copious fumes of perchloric acid appear at this point.

Cool somewhat, wash and remove the refluxing digestion head, and add 50 ml. of 1 to 1 hydrochloric acid. Boil gently for 10 minutes to reduce chromic acid, evolve chlorine, and decompose possible traces of nitric acid which would react with

titanous chloride. Cool and dilute by the addition of 150 ml. of cold water. Replace the flask stopper with the gas bubbler tube, place the titration head (Figure 1) in position, and bubble a brisk stream of carbon dioxide through the reaction mixture. Titrate with 0.01 *N* titanous chloride (after the addition of 25 ml. of 10 per cent ammonium thiocyanate) until the red color begins to fade. Add the titrating liquid dropwise until the pink tinge fades to olive green. The final few drops of titanous chloride should be added at half-minute intervals until by transmitted light the solution turns clear green with no tinge of olive or yellowish green. Using an artificial light source against a white background, the end point is detected within one to two drops of titrating liquid. Add 0.2 ml. to the titer found, to correct for the premature end point due to the presence of the green chromic ion. The results of a series of analyses of chrome-tanned leather are given in Table XV.

TABLE XV

DETERMINATION OF IRON IN CHROME-TANNED LEATHER BY TITRATION WITH TITANOUS CHLORIDE

Leather No.	Leather Grams	0.0142 *N* $TiCl_3$ mg.	Fe_2O_3 Found Gram	Fe_2O_3 Found %
1	5.053	1.30	0.0015	0.029
	5.379	1.58	0.0018	0.033
	5.624	1.52	0.0017	0.031
				Av. 0.031
2	5.089	4.60	0.0052	0.103
	5.163	4.90	0.0056	0.108
	5.019	4.74	0.0054	0.107
				Av. 0.106
3	4.819	5.10	0.0058	0.120
	5.526	5.84	0.0066	0.120
	5.446	5.46	0.0061	0.114
				Av. 0.118
4	5.915	8.66	0.0098	0.166
	5.393	7.40	0.0086	0.160
	5.890	8.30	0.0097	0.164
				Av. 0.163

The analyses of the four samples of leather in Table XV were repeated and known quantities of iron (0.0041 mg. calculated as Fe_2O_3) added as ferric perchlorate solution, using a transfer pipet for the additions. The adulterated samples had been previously prepared just as for the analyses of Table XV and the ferric perchlorate solution added before the destruction of organic matter was completed. The data obtained are contained in Table XVI.

The values given for the calculated amounts of Fe_2O_3 shown in column 4 of Table XVI are based upon the analyses of each leather sample shown in Table XV, to which calculated Fe_2O_3 present in the leather, the amount of Fe_2O_3 added in the form of ferric perchlorate, has been added. The values in column 5 are obtained from the same figures. The values in column 6 were obtained on the assumption that the added iron had been correctly determined. The values in column 6, Table XVI, are therefore to be compared with the values of column 5, Table XVII. The agreement in the Fe_2O_3 content of the various samples is found to be satisfactory.

As a further check of the accuracy of the analyses, particularly the error, if any, involved in the end-point correction as applied in Tables XV and XVI, the same samples were digested as before to decompose organic matter and oxidize the chromium. The iron was then precipitated, together with any aluminum present, by ammonium hydroxide, filtered, washed, and dissolved in hot, dilute hydrochloric

acid. The solutions thus obtained were titrated with titanous chloride exactly as previously described but in the absence of chromium. The values thus obtained required no end-point correction and are given in Table XVII.

The values in the last two columns of Table XVII are taken from the results of Tables XV and XVI, respectively, and on the whole are satisfactorily comparable with them. The accuracy of the end-point correction found according to the data of Figure 2 as applied in Tables XV and XVI is thus proved.

TABLE XVI

DETERMINATION OF IRON IN CHROME-TANNED LEATHER AFTER ADULTERATION WITH ADDITIONAL IRON. TITRATION WITH TITANOUS CHLORIDE

Iron added as $Fe(ClO_4)_3$ solution equivalent in each case to 0.0041 gram of Fe_2O_3

Leather No.	Leather Grams	0.0142 *N* $TiCl_3$ Required ml.	Fe_2O_3 Found Gram	Fe_2O_3 Calcd. Gram	Error Fe_2O_3 mg.	Fe_2O_3 in Leather %
1	5.023	4.96	0.0056	0.0057	—0.1	0.032
	3.396	4.34	0.0049	0.0052	—0.3	0.024
	5.092	4.62	0.0053	0.0057	—0.4	0.024
					Av. —0.3	0.027
2	5.024	8.34	0.0095	0.0091	+0.4	0.108
	5.014	7.80	0.0089	0.0091	—0.2	0.096
					Av. +0.1	0.102
3	5.709	9.80	0.0111	0.0108	+0.3	0.123
	5.612	9.24	0.0105	0.0106	—0.1	0.114
	5.526	9.24	0.0105	0.0106	—0.1	0.116
					Av. ±0.0	0.118
4	5.251	11.30	0.0128	0.0126	+0.2	0.166
	5.786	11.24	0.0128	0.0135	—0.7	0.150
	5.171	11.00	0.0125	0.0125	±0.0	0.162
					Av. —0.2	0.159

Finally, additional samples of the same chrome-tanned leather were digested and prepared for titration with titanous chloride. The end-point of the titration was determined first visually using ammonium thiocyanate and with the same solutions potentiometrically, since the end point in the latter case always appears after the visual end-point. The values obtained are shown in Table XVIII.

TABLE XVII

DETERMINATION OF Fe_2O_3 IN CHROME-TANNED LEATHER BY TITRATION OF FERRIC IRON USING TITANOUS CHLORIDE AFTER SEPARATION OF IRON FROM CHROMIUM

Leather No.	Leather Grams	0.0142 *N* $TiCl_3$ Required ml.	Fe_2O_3 Found Gram	Fe_2O_3 Found %	Average Per Cent Fe_2O_3 in Leather: Cr absent	Cr present	Fe_2O_3 added
1	5.019	1.42	0.0016	0.032			
	5.067	1.40	0.0016	0.031	0.032	0.031	0.027
2	5.016	4.44	0.0051	0.101			
	5.054	4.36	0.0050	0.098	0.100	0.106	0.102
3	5.284	5.50	0.0063	0.118			
	5.665	5.70	0.0065	0.114	0.116	0.118	0.118
4	6.040	8.60	0.0098	0.162			
	6.072	8.60	0.0098	0.161	0.162	0.163	0.159

By examination of the data of Table XVIII it will be observed that the magnitude of the end-point error formerly determined—namely, 0.20 ml. of 0.0142 *N* titanous chlorides—is substantiated.

Preparation for Determining Iron in Vegetable-Tanned Leather

The preparation of finished vegetable-tanned leather for titration of iron using titanous chloride differs somewhat from the preparation of finished chrome-tanned leathers. The "loading agents," such as paraffin, waxes, and other fillers, used in the case of chrome-tanned leathers are absent. The absence of these fillers causes the leather to be more readily and vigorously oxidized if the same procedure is employed as that previously described. This fact makes it advisable to

TABLE XVIII

COMPARISON OF VISUAL AND POTENTIOMETRIC END POINTS

Leather No.	Leather Grams	0.0142 *N* $TiCl_3$: Visual ml.	Potentiometric ml.	Difference ml.	Fe_2O_3 Found: Visual %	Potentiometric %
1	5.009	1.30	1.50	+0.20	0.029	0.034
2	5.257	4.34	4.50	+0.16	0.094	0.097
3	4.578	4.92	5.04	+0.12	0.112	0.118
4	6.283	9.00	9.20	+0.20	0.161	0.165

pretreat the leather sample, using concentrated nitric acid alone to be followed by the addition of leather oxidant ($HClO_4 + H_2SO_4$). The iron present in finished vegetable-tanned leather varies from 0.01 to 0.03 per cent, which requires larger samples of leather for analysis. Even with suitable 6- to 8-gram samples of vegetable-tanned leathers (because of the absence of loading agents) as compared to 5-gram samples of chrome-tanned leather, the volume of leather oxidant required is less. The absence of chromium is beneficial, since the amount of iron present is low. The more vigorous nature of the attack by nitric acid requires that samples of vegetable-tanned leather be digested with greater care and hence somewhat greater time intervals are required for the destruction of organic matter. The complete destruction of organic matter is readily indicated if 20 to 25 mg. of potassium dichromate are added to the sample during the digestion. The chromium is reduced to chromic ion in the presence of organic matter and after its complete destruction is at once oxidized to chromic acid, from the orange color of which the digestion of the sample is known to be complete.

Procedure for Vegetable-Tanned Leather. The same apparatus and method of heating as that previously described for chrome-tanned leather are employed, using 8- to 10-gram samples.

Add 10 to 15 ml. of concentrated nitric acid plus 25 mg. of potassium dichromate and heat if necessary until the evolution of oxides of nitrogen diminishes materially. Add 15 ml. of leather oxidant and digest at gradually increasing temperatures until the nitric acid is completely evolved and the fumes of perchloric acid appear after a temperature of approximately 200° C. is attained and the last traces of organic matter destroyed and the orange color of chromic acid appears. If excessive charring occurs before the final oxidation stage is reached, add 5 to 10 ml. of concentrated nitric acid before heating to the last stage of the

reaction. The remainder of the analysis is conducted exactly as described in the case of chrome-tanned leather.

Test analyses of five leathers were carried out following the procedure as outlined. Check analyses of the same leathers were made either by the process of addition of known amounts of iron or by first separating the iron as ferric hydroxide. The results of these analyses are shown in Table XIX. A correction for premature thiocyanate end-point of 0.05 ml. of 0.0142 *N* titanous chloride was applied in each case.

TABLE XIX

DETERMINATION OF IRON IN VEGETABLE-TANNED LEATHERS BY TITRATION WITH TITANOUS CHLORIDE

Leather No.	Leather Gram	Fe_2O_3 Added Gram	0.0142 *N* $TiCl_3$ ml.	Fe_2O_3 Found Gram	Fe_2O_3 Found %	Fe_2O_3 Calcd. Gram	Error mg.	Method of Checking Analysis
5	8.267	.....	0.63	0.0007	0.009	.....	.....	.....
	7.903	.....	0.65	0.0007	0.009	.....	.....	.....
	7.992	0.0041	4.33	0.0049	0.010	0.0048	+0.1	Iron added
	8.256	0.0041	4.41	0.0050	0.011	0.0048	+0.2	Iron added
				Av.	0.010			
6	5.223	.....	1.20	0.0014	0.026	.....	.....	.....
	5.655	.....	1.10	0.0013	0.022	.....	.....	.....
	5.423	.....	1.10	0.0013	0.023	.....	.....	.....
				Av.	0.024			
7	6.575	.....	0.86	0.0010	0.015	.....	.....	Iron pptd.
	7.448	.....	1.15	0.0013	0.018	.....	.....	.....
				Av.	0.017			
8	8.096	.....	2.05	0.0023	0.029	.....	.....	.....
	7.205	.....	1.35	0.0015	0.021	.....	.....	.....
	7.513	.....	2.05	0.0023	0.031	.....	.....	.....
	7.445	.....	1.20	0.0014	0.018	.....	.....	Iron pptd.
				Av.	0.025			
9	8.782	.....	1.55	0.0018	0.020	.....	.....	.....
	8.962	.....	1.95	0.0022	0.025	.....	.....	.....
	4.652	0.0041	4.41	0.0050	0.019	0.0052	—0.2	Iron added
	9.072	.....	1.32	0.0015	0.017	.....	.....	Iron pptd.
				Av.	0.020			

Table XIX shows that in all cases, with the possible exception of sample 8, the analyses are satisfactorily consistent and closely duplicated by direct and modified procedures. Amounts of iron of the order of 1 to 2 mg. are determinable with an accuracy of ± 0.1 to 0.2 mg. or less.

The summarization of all results is given in Table XX. The second column gives the determination of Fe_2O_3, in presence of the chromium of the sample or the small amount added, by the recommended procedure. The third column gives the iron determination in cases in which iron was added to study the accuracy of recovery of the original iron present. The fourth column shows the determination of iron in case of its prior separation as ferric hydroxide. In Table XX the values are to be compared in the horizontal rows, and are found in comparatively excellent agreement.

Possible Hazardous Reactions

There are no hazardous reactions involved in the wet oxidation of the organic matter in leather following the process herein described. It should be noted, however, that the reactions of digestion, if pushed too vigorously through the use of too great application of heat, may result in the samples catching fire in the digestion flask. This need not result if some experience in carrying out the digestion is acquired. No explosions were obtained throughout the hundreds of digestions employed in connection with this work, and in no case was the use of a screen between operator and digestion equipment deemed necessary. After the

TABLE XX

SUMMARIZED RESULTS OF DETERMINATIONS OF Fe_2O_3 IN CHROME- AND VEGETABLE-TANNED LEATHERS

Leather No.	Fe_2O_3 Direct Titration: Or present or added %	Fe_2O_3 Direct Titration: Or present and Fe added %	Fe_2O_3 after Pptn. of $Fe(OH)_3$ %
1	0.031	0.027	0.032
2	0.106	0.102	0.100
3	0.118	0.118	0.116
4	0.163	0.159	0.162
5	0.009	0.011	.....
6	0.024	.....	.....
7	0.018	.....	0.015
8	0.027	.....	0.018
9	0.023	0.019	0.017

nitric acid oxidation is complete in the case of chrome-tanned leather the solutions boil gently and quietly until the perchloric acid concentrates to approximately 70 per cent strength, when a vigorous exothermal reaction takes place. For vegetable-tanned leathers the reaction temperature is lowered and the applied heat is checked if the reaction progresses too briskly. With the vegetable-tanned leathers using 25 ml. of nitric acid no charring results even with 8- to 10-gram samples.

THE DETERMINATION OF SULFUR IN ORGANIC COMPOUNDS FOLLOWING DESTRUCTIVE DECOMPOSITION OF ORGANIC MATTER USING MIXED NITRIC AND PERCHLORIC ACIDS

The destruction of organic matter by digestion with mixtures of nitric acid and perchloric acid and simultaneous oxidation of sulfur to sulfuric acid has been previously mentioned. The determination of sulfur in rubber by Kahane *(20)* follows the scheme. This method was further developed by Wolesensky *(21)*. The determination of sulfur in coal, following essentially the same method of attack and including the study of catalysts to speed up the rate of oxidation, has been described by Smith and Deem *(9)*. The latter two methods have been reprinted in previously cited material *(1)*, pp. 36 and 47. In general, this method for use in the destruction of organic matter has been applied to the determination of phosphorus and arsenic as well as of

sulfur and metallic components as described by Kahane *(2)*, Vol. II, pp. 55 ff.

The destruction of organic matter in the process of the determination of sulfur in organic sulfur compounds in which sulfur is present as a major, rather than as an incidental ingredient, has been studied in some detail by Kahane *(2)*, Vol. II, pp. 55 ff. The action of mixed nitric and perchloric acids is favorably modified by the addition of iodic acid following the Kahane procedure.

Even in view of the fact that sulfur has been shown to be quantitatively oxidized to sulfuric acid in the presence of organic matter, following destruction of this organic matter by using a hot mixture of concentrated nitric and perchloric acids as above cited; nevertheless, similar attack upon organic sulfur derivatives in general often results in the loss of sulfur by volatilization or mechanically. The subsequent determination of sulfur by precipitation of the sulfur as barium sulfate, after the removal of excess nitric and perchloric acids, therefore, gives rise to low results.

As stated by Kahane *(2)*, Vol. II, p. 59, numerous attempts have been made in the hope of preventing the loss of sulfur. The addition of bromine, hydrogen peroxide, and iodine have been shown to be ineffective in avoiding the liberation of hydrogen sulfide or sulfurous anhydride which appear to be the only forms in which sulfur escapes from the medium analyzed (the substance studied being not sufficiently volatil to be explained upon the basis of the liberation of organic sulfur).

It is true that satisfactory results have been obtained as a result of such additions, but only following treatment over a long period of time by the reagents, used either in the cold or at only slightly elevated temperatures, before pushing the attack by the acid proper, such as by the classical method of attack using bromine and nitric acid.

This type of procedure does not appear to be satisfactory because of the time required, approximately one hour, and because of the difficulty in correctly analyzing substances which are but slightly attacked by bromine and the other oxidizing agents studied.

Because of the impossibility of preventing loss of sulfide and sulfite sulfur it was decided to use a special apparatus designed to recover these and thus it was hoped to avoid such complications. . . . (This apparatus is shown in slightly modified form in Figure 3. The modification consists in the use of a glass-sealed condenser principle rather than an open-water bath in which the still head is immersed during use. The description of this apparatus by Kahane continues.)

This apparatus which is composed of a Kjeldahl flask (200-300 ml.) with a ground-in glass condenser which permits of condensing the vapors emitted by the reaction and at the same time oxidizing the sulfur by use of suitable reagents. The nitric acid reduction products liberated during the early stages of digestion (NO and NO_2) are poor oxidizers of sulfur, which appears to be also the case with bromine, hydrogen peroxide, and a few other current oxidizing agents. The type of condenser employed is governed by these considerations.

The only oxidizing agent which has been found to be suitable, at the same time rapid in action and conveniently employed, is iodic acid, thanks to which

the determination of sulfur in all the products studied has been correctly determined.

Apparatus. (Figure 3). The apparatus consists of a 200-300 ml. Kjeldahl flask with a ground joint condenser, termed a "W goose neck condenser" with four elbows. The goose neck is constructed in the form of a W with olive shaped enlargements blown in each arm of the W of approximately 10 ml. capacity. The first three branches of the W have single bulbs, the fourth branch is extended and has three bulbs. The emptying and washing of this condenser is accomplished in an extremely simple manner. As noted in Figure 3 the flask is inclined at an angle of 45° (position 1) and with the W goose neck attached the W assumes the position in which the solution in the goose neck fills the two bottom elbow blends. After the completion of the digestion the goose neck flask is rotated through an angle of 180° at the ground joint (position 2). The inclination of the elbows and the contour of the bulbs are now such that the contents empty readily into the flask. The goose neck need not be rinsed. Upon continued digestion of the contents of the flask (with condenser water cut off) the goose neck is rinsed automatically.

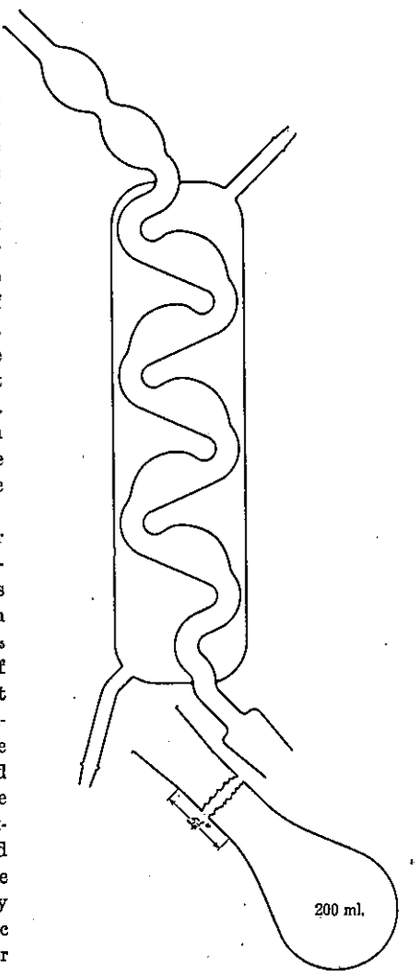


FIGURE 3. Kahane Apparatus for Destruction of Organic Matter in Sulfur Compounds Using HNO_3, HIO_3, and $HClO_4$ (Scale 1" = 4").

Method of Operation. A sample for analysis 100-200 mg. of the organic sulfur compound, accurately weighed, is transferred to the Kjeldahl flask. Then 0.5 ml. of a 10 per cent solution of I_2O_5 (iodic anhydride) are added and 2 ml. of a mixture of 2 parts of 66 per cent $HClO_4$, sp. gr. 1.61 to 1 part of concentrated HNO_3. (The mixture must be used in considerable excess of required amounts to facilitate the attack. For the larger size sample 3 ml. of the acid mixture should be employed.) A glass bead is added to facilitate ebullition. The goose neck condenser is previously charged with 0.5 ml. of 10 per cent iodic anhydride solution, diluted with water sufficiently to fill the two bottom elbows (to form a bubbler tube and with the condenser water running) and is connected with the flask immediately upon addition of the mixed acids. (Condenser water is not necessary unless the mixed acids employed to digest the sample are used in larger amounts than 3 ml.)

The reaction is launched spontaneously, but generally it is necessary to heat it. Iodine is evolved, then oxides of nitrogen of which the major part is condensed in the W goose neck. With the excess of HNO_3 expelled, the attack by the $HClO_4$ begins which is generally vigorous and marked by copious evolution of white fumes. The chlorine which is evolved in the course of this reaction reoxidizes the iodine in the condenser and it continues to oxidize reduced forms of sulfur which may be evolved at this point.

It is well to watch the digestion reaction with new types of materials. If the nitric acid attack has been pushed or if the perchloric acid is found to be present in insufficient excess, the digestion may be sufficiently vigorous to necessitate lessening the heat or discontinuing it entirely for a time.

The completion of the digestion is recognized when the ebullition becomes tranquil and the digestion liquid becomes colorless or but slightly yellow.

The contents of the digestion flask are cooled during a half minute before adding the liquid from the goose neck condenser to the digestion liquid in the flask. Thereupon is produced a vigorous evolution of vapors and spray which may disengage the ground joint. For this reason the bulbs of the goose neck have been made of sufficient capacity to return any spray formed to the reaction flask.

After this partial cooling of the flask and addition of the condenser contents to the reaction flask, the liquid is brought to boiling. Vapors ascend into the condenser where they liquefy and return to the flask, thus rinsing the condenser. The condenser then warms up and vapors escape. Water and nitric acid are eliminated, followed by the appearance of white fumes from $HClO_4$ which indicates the completion of the digestion. The last part of this concentration may be hastened by separating the flask and bubbler tube. Should oxidizable substances of volatil-nature be distilled into the bubbler tube during one digestion operation and then be returned to the digestion flask by inverting the bubbler tube, a second digestion is necessary with a recharged bubbler tube. An example in point is that of the analysis of chlorethylsulfonic acid.

As the volume of $HClO_4$ used in a single operation as described does not exceed 3 ml. it is unnecessary to remove any of it by evaporation. If larger amounts of $HClO_4$ have been used the excess may be dispelled by evaporation, care being taken to avoid over-heating.

After cooling, the digestion liquid is quantitatively transferred to a 200 ml. beaker and the flask rinsed with 25-30 ml. of water. This is then treated dropwise with a solution of 10 per cent hydrazine hydrate which reduces the iodic acid to iodine and then to iodide. The same result is obtained, perhaps less conveniently, by the use of formalin which acts as rapidly or by the use of sodium iodide which liberates a large quantity of iodine. Without this reduction the iodic acid would be precipitated as barium iodate together with barium sulfate, upon addition of barium chloride.

Add a little phenolphthalein and neutralize the solution with N/10 sodium hydroxide. Acidify slightly with hydrochloric acid and precipitate the hot solution by adding 5 per cent barium chloride dropwise in slight excess. Filter and wash the precipitated barium sulfide, dry, ignite and weigh.

The acid digestion requires 10-12 minutes, the concentration a few more minutes and neutralization a little additional time, so that all the operations down to the determination of $BaSO_4$ requires scarcely half an hour.

Applications. The method as described has been applied to the following chemicals: sulphur, zinc sulfide, sodium hyposulfite, ammonium thiosulfate, sul-

TABLE XXI

THE DETERMINATION OF SULFUR IN ORGANIC AND INORGANIC SULFUR DERIVATIONS

Substance	Formula	Sample g.	$BaSO_4$ g.	% S Found	% S Theory
Sulfur	S	0.0443	0.3215	99.6	100
		0.0406	0.2980	100.6	
Zinc sulfide	ZnS	0.1071	0.2568	32.89	32.86
		0.1140	0.2719	32.70	
Sodium thiosulfate	$Na_2S_2O_3 \cdot 5H_2O$	0.2900	0.5400	25.54	25.81
		0.2900	0.5420	25.65	
Ammonium thiocyanate	NH_4CNS	0.0380	0.1154	41.60	42.10
		0.0380	0.1159	41.80	
Sulphanilic acid	$C_6H_4 \langle {NH_2 \atop HSO_3} \cdot 2H_2O$	0.1507	0.1675	15.24	15.25
		0.1382	0.1540	15.27	
Benzolyl sulphimide	$C_6H_4 \langle {SO_2 \atop CO} \rangle NH$	0.4806	0.6023	17.20	17.48
		0.2232	0.2834	17.40	
Camphosulphonic acid	$C_{10}H_{15}O \cdot HSO_3$	0.3873	0.3870	13.71	13.80
		0.3090	0.3092	13.73	
Thio-urea	$CS(NH_2)_2$	0.1813	0.5495	41.54	42.10
		0.1230	0.3730	41.55	
Allyl thiourea	$NH_2CSNHC_3H_5$	0.3407	0.6792	27.33	27.60
		0.1940	0.3877	27.41	
Iodo-ethyl thiocyanamide	$NH_2CSNHC_2H_5 \cdot IC_2H_5$	0.4836	0.4115	11.67	11.76
		0.2892	0.2485	11.78	
Thiosulpho carbanyl acetylimide	$CH_3CONHCS_2CH_3$	0.0955	0.2968	42.60	42.94
		0.0406	0.1266	42.70	
Para-cresol sulphide	$S(C_6H_4CH_3)_2$	0.1226	0.1328	14.85	14.96
		0.3105	0.3341	14.77	
Triphenylphosphine sulphide	$S=P(C_6H_5)_3$	0.1233	0.0970	10.79	10.88
		0.0978	0.0779	10.92	
Cystine	$(SCH_2CHNH_2COOH)_2$	0.2038	0.3925	26.42	26.68
		0.2201	0.4227	26.33	
Cysteine hydrochloride	$HSCH_2CHNH_2COOH \cdot HCL$	0.3775	0.5650	20.52	20.32
		0.2321	0.3456	20.41	
Chlorethyl sulphoxide	$SO(C_2H_4Cl)_2$	0.2713	0.3612	18.26	18.29
		0.2600	0.3406	17.97	
		0.0947	0.1246	18.06	
Tritolyl thionyl chloride	$(CH_3C_6H_4)_3SCl \cdot H_2O$	0.6553	0.4230	8.86	8.92
		0.2296	0.1473	8.80	
Tri 3-4 dimethylphenyl thiouyl chloride	$(C_6H_3(CH_3)_2)_2SCl$	0.1559	0.0935	8.23	8.30
		0.1702	0.1020	8.22	
Tri 2-4 dimethylphenyl thionyl chloride	$(C_6H_3(CH_3)_2)_2SCl$	0.2688	0.1614	8.30	8.30
		0.1680	0.1001	8.17	

phanilic acid, camphosulphonic acid, benzoylsulfimide, thiourea, allyl-thiourea, cystine, cysteine, etc.

As may be seen the products examined have been most varied. They have in common the property of not being volatil. In fact the technique described does not apply in general to the study of products which volatilize before the oxidizing acids are able to act upon them.

The results obtained are in general accurate to one per cent. The error is almost always negative which is believed not to result from imperfect oxidation but to the determination of the sulfuric acid formed by precipitation as barium sulfate which in common with other classical methods gives rise to a number of small errors, especially in the presence of a great number of foreign materials.

A series of results described by Kahane *(24)* are given in Table XXI.

THE DETERMINATION OF ARSENIC IN ORGANIC ARSENICALS USING NITRIC, PERCHLORIC, AND SULFURIC ACIDS.

Introduction. The determination of arsenic in the presence of organic matter is often required in biological chemistry for the determination of arsenic in tissues, in toxicology for the investigation of accidental presence of arsenic, and in organic chemistry for the determination of arsenic in arsenicals.

The determination of arsenic in organic arsenicals is the most simple, since the amount of organic matter to be decomposed is smaller than in the other cases mentioned above. In the applications to physiological chemistry and toxicologic procedures, methods are essentially the same for the destruction of organic matter except that larger samples are employed *(2)*. Chapters II and III.

A study of the possible volatilization of arsenic when organic arsenicals are oxidized with a mixture of nitric, perchloric and sulfuric acids has been investigated. Unlike the determination of sulfur in the presence of organic matter using iodic, nitric, and perchloric acids, arsenic in the parallel case is not lost by volatilization if the proper acid mixture is used in sufficient volume for the quantity of organic matter to be decomposed.

The details as described by Kahane *(2)*, p. 69 ff. are as follows:

Procedure. 200-400 milligrams of the sample to be studied is accurately weighed and transferred to a Kjeldahl flask of 100 ml. volume and 5 ml. of the following mixture is added as well as a glass bead:

Conc. H_2SO_4 (95 per cent).....70 ml.
Conc. $HClO_4$ (66 per cent, sp. gr. 1.61).....20 ml.
Conc. HNO_3 (68 per cent).....10 ml.

A spontaneous attack is thus often produced with the evolution of heat and abundant liberation of oxides of nitrogen. In general there is little action in the cold and the heating is begun at once. As the nitric acid reacts upon most arsenicals upon heating, more or less pronounced evolution of oxides of nitrogen occurs which is followed by the distillation of excess nitric acid. Towards the end

of this first phase of the operation, the action by perchloric acid takes place in its turn which action is in general quite rapid but which almost without exception does not require discontinuing the heating. This second stage is completed very rapidly and the excess of perchloric acid is distilled out, with the characteristic evolution of sulfuric acid fumes following.

The time for this operation is a few minutes in case the heating has been pronounced and ebullition is maintained to drive off successively the nitric and perchloric acid excess. Since the use of a large excess of sulfuric acid has been provided there is no liability that the reaction will get out of control, the sulfuric acid acting as a diluent moderating the speed of reaction.

The heating is continued to remove completely excess oxides of nitrogen and chlorine. Ten minutes from the start of the reaction the heating is discontinued. The liquid ought then to be colorless.

If such is not the case, it is for the reason that an excess of nitric and perchloric acids have not been employed. In order to complete the attack it is necessary to add a few drops of a mixture of 2 vol. 66 per cent $HClO_4$ and 1 vol. of 68 per cent HNO_3 and reheating until fumes of sulfuric acid appear.

The determination of arsenic may then be carried out.

If the method of Schulak and Villecz is to be applied, add 0.25 g. of hydrazine sulfate to the partly cooled contents of the flask, using a funnel of sufficient length to reach through the neck of the Kjeldahl flask and into the flask's enlarged portion. The use of this glass funnel, stem somewhat longer than the neck of the flask, is to prevent deposition of hydrazine crystals on the neck, which would otherwise escape reaction because of their insolubility in sulfuric acid.

The heating is resumed without any particular precautions. An energetic effervescence is thus produced with the evolution of sulfurous acid and nitrogen. The boiling is continued during 10 minutes in order to insure complete decomposition of hydrazine sulfate.

After cooling, the contents of the flask are diluted with 20 ml. of water, once more cooled and 100-200 mg. of KBr added, followed by titration with N/10 $KBrO_3$ until the liquid is just colored a persistent yellowish.

1 ml. of N/10 $KBrO_3$ is equivalent to 3 mg. of arsenic.

Applications. The following arsenicals have been successfully analyzed for arsenic by Kahane following the method as described. Sodium cacodylate, sodium methyl arsenate (Products which are very resistant to the action of mixed nitric and sulfuric acids) dichlorphenylarsine, chlor-diphenylarsine, triphenylarsine, sodium-paraminophenylarsine, diphenylarsinic acid, and other products.

The results obtained attain an accuracy of 2 per cent of total arsenic. They are generally low which is believed to be due to incomplete reduction by hydrazine sulfate.

(Note by G. F. S. Instead of the use of a Kjeldahl flask as recommended by Kahane it is believed more appropriate to use the same apparatus previously described in the analysis of leather in the determination of chromium and of iron. The procedure as described by Kahane employing the Kjeldahl flask with its long neck guards against the loss of reactants through spray emission. The use of an Erlenmeyer flask with the still head previously described enables one to support the flask on a wire gauze over a free flame while the round bottom Kjeldahl flask must be supported in a clamp. The use of the still head substitutes for the Kjeldahl flask neck in accomplishing the same purpose and the titration of the flask contents is similarly more convenient after the still has been rinsed and removed because of the Erlenmeyer's flat bottom and much shorter neck.)

OTHER ILLUSTRATIONS AND EXAMPLES OF ADVANTAGES IN PERCHLORIC ACID DESTRUCTION OF ORGANIC MATTER

The Destruction of Organic Matter in Filtrates Following Precipitations Using Cupferron, 8-Hydroxyquinoline Tartaric Acid, Etc.

Quoting E. Kahane *(2)* Vol. I, pp. 36 ff. concerning the procedure previously described, the following generalizations are significant:

> These descriptions give a somewhat incomplete idea of the variety of procedures which are possible of utilization. In reality there are advantages to be derived from the use of perchloric acid in all wet oxidations at temperatures of 150-200° C. in which range its oxidizing power is effective. Perchloric acid then brings to bear an exceptionally rapid dissolving and oxidizing reaction in cases previously considered difficult to master. On the contrary the operator must follow strict rules in order to avoid unfortunate accidents. It is not necessary to know these rules when a series of known procedures are being followed such as those described in this work, but it is indispensable to assimilate them before attempting original research concerning the use of perchloric acid in unexplored fields or under conditions notably different from the usual case. . . .
>
> The advantage which it is important to bring out in the first place is the rapidity of the destruction of organic matter using perchloric acid. The duration of the reaction is naturally variable with the nature of the heating and it is necessary to carry out a given operation several times to attain maximum rapidity. It varies, likewise, with the nature of the substance and the technique of destruction adopted. . . . The attack is generally more rapid on vegetable substances such as cellulose or starch, it is slower with fat laden materials. It is very slow with oils and especially so for those rich in carbon.

A few additional facts should be kept in mind using concentrated perchloric acid as oxidizing agent. Hot, concentrated perchloric acid in addition to its oxidizing properties is an efficient dehydrating agent. Therefore, a mixture of, for example, glycerol and perchloric acid when hot is the equal of glycerol plus nitric acid plus sulfuric acid. The hot, dehydrating perchloric acid serves to esterify the glycerol and as a result the strongly oxidizing ClO_4 group is introduced into the molecule. Whether or not the perchloric acid ester of glycerol is equal in explosive power to nitroglycerine is not known. The corresponding ethyl ester of perchloric acid is violently explosive.

Organic molecules that contain hydroxy-groups might be predicted to reach with violence in the presence of hot, concentrated perchloric acid. Hydrocarbons such as paraffin, rubber, and rosin might be considered safe while sugar, starch, cellulose, etc., are easily broken down by the preliminary action of nitric acid with rapid and complete destruction by the subsequent perchloric acid effect. Succinic acid might be considered as similar to a hydrocarbon and tartaric acid as intermediate between an hydroxyl compound and a hydrocarbon. Organic ring nitrogen compounds are the most difficult to oxidize of all types. Coal for example requires the addition of catalysts to speed up its destruction by hot perchloric acid, if excessive time periods are not to be required.

The question of the use of filtrates from quantitative separations in which such reagents as cupferron and 8-hydroxy-quinoline, etc., have been used previously as precipitants, often requires destruction of the organic matter prior to subsequent operations. Filter paper cellulose or cotton are frequently desirable of decomposition to recover mineral constituents absorbed by them. Such problems as the removal of tartaric acid from a solution in which it has been used to prevent precipitation of iron for example are frequently met. These and many similar problems are readily and efficiently solved using an attack by sulfuric and perchloric acids or perchloric acid alone. A number of such materials have been studied and the data tabulated in the following material.

By GFS oxidant is meant a mixture of 2 vol. of 80 per cent H_2SO_4 with 1 vol. of 70-72 per cent $HClO_4$. This in many ways is a stronger oxidizing agent than 70 per cent $HClO_4$ and in other ways is less strong. When less strong, it is because the sulfuric acid is acting as a char-producing medium which breaks down the organic matter with the formation of tar-like decomposition products which are then oxidized by the perchloric acid more quietly than otherwise. Also the H_2SO_4 serves to dilute the perchloric acid and make its oxidizing strength more slow in playing its role in the destruction of organic matter. On the other hand, the sulfuric acid dehydrates the perchloric acid as the mixed acids lose water by concentration, and the oxidation strength of the perchloric acid is increased.

The hot plate temperature used was such that a 250 ml. beaker covered with a watch glass and containing 50 ml. of concentrated H_2SO_4 will attain the temperature of 200-215° C. The reaction mixtures described were all contained in 400 ml. beakers with cover glass and stirring rod in place. The stirring rod was used so that drops of dilute acid products collecting on the lower side of the cover glass and dropping into the hot acid below, do so by running down the stirring rod which they strike before reaching the hot acid. This avoids spattering to a great extent. In none of these tests was a screen employed or shield of any kind. A respectful distance was used by the operator during the study of unknown reactions. No violent reactions were encountered in any experiment. In two cases as noted with 8-hydroxyquinoline a fire and deflagration sufficient to lift the cover glass from the beaker was obtained using 60 per cent $HClO_4$ alone. These same reactions were quiet, using GFS oxidant. This oxidant can be purchased at a saving in cost for such reactions as compared to straight perchloric acid. The results of a series of tests are shown in the following table.

TABLE XXII

DESTRUCTION OF ORGANIC MATTER USING MIXTURES OF HNO_3, H_2SO_4, AND $HClO_4$

Organic Material Oxidized	Sample Wt. g.	70-72% $HClO_4$ ml.	68% HNO_3 ml.	G.F.S. Oxidant ml.	Reaction Time		Charring Reaction	Remarks
					HNO_3 Effect min.	Other Acids Effect min.		
Cellulose	1	5	5	....	6	8	None	Rapid End Reaction
Cellulose	2	5	12	....	6	12	None	Rapid End Reaction
Cellulose	1	3	5	....	5	7	None	Rapid End Reaction
Cellulose	2	3	10	....	7	10	Trace	Rapid End Reaction
Cellulose	1	....	5	3	5	6	None	2 ml. 70% $HClO_4$ added at end
Cellulose	2	....	10	3	7	24	Considerable	$HClO_4$ effect gone at end
Cellulose	2	....	10	5	8	10	None	Acid Proportions Correct
Cellulose	3	....	10	7.5	5	30	Considerable	Acid Proportions Poor
Cellulose	3	....	15	7.5	5	30	Considerable	Insufficient Oxidant
Cellulose	3	....	12	9	7	14	None	Acid Proportions Ideal
Tartaric Acid	1	3	4.5	....	15	17	None	HNO_3 not markedly effective
Tartaric Acid	1	....	5	5	10	11	None	Rapid End Reaction
Tartaric Acid	2	....	5	10	5	10	Trace	Acid Proportions Good
Tartaric Acid	2	....	10	10	9	13	Considerable	Carmel Sugar Odor
Tartaric Acid	3	....	13.5	9	13	17	Some	Acid Proportions Good
Tartaric Acid	1	5(60%)	....	....	....	30	Considerable	Rapid reaction at 13 min.

TABLE XXII (Continued)

DESTRUCTION OF ORGANIC MATTER USING MIXTURES OF HNO_3, H_2SO_4, AND $HClO_4$

Organic Material Oxidized	Sample Wt. g.	70-72% $HClO_4$ ml.	68% HNO_3 ml.	G.F.S. Oxidant ml.	Reaction Time		Charring Reaction	Remarks
					HNO_3 Effect min.	Other Acids Effect min.		
Cupferron	1	....	12	6	7	20	Some	Vigorous reaction in cold
Cupferron	2	....	12	6	7	17	Some	Acts same as with cellulose
Cupferron	3	....	32(35%)	8	....	25	Trace	Dilute HNO_3 Slows Reaction
Cupferron	4	....	40(35%)	10	....	90	None	Concentration rate slow
8-hydroxy-quinoline	2	....	....	10	....	30	Considerable	At End Dense $HClO_4$ Fumes
8-hydroxy-quinoline	1	10(60%)	....	....	....	20	Some	Rapid reaction at 7 min.
8-hydroxy-quinoline	2	10(60%)	....	....	....	11	Pronounced	Rapidly clearing at end of period beaker caught on fire with hissing noise
8-hydroxy-quinoline	4	15(60%)	....	....	....	10	Pronounced	Same as above
8-hydroxy-quinoline	3	....	....	15	....	30	Choc. Brown	2 ml. 70% added at end to replace that lost
Cotton	1	5	5	....	1	6	None	Reaction at end very brisk
Cotton	2	5	12	....	4	10	None	Reaction like that of Cellulose
Cotton	3	....	12	9	3.5	30	Pronounced	2 ml. 70% $HClO_4$ added at end
Cotton	4	....	15	10	3.5	20	Pronounced	Same as above

The reactions of Table XXII give results for a technique which involves no personal attention on the part of the operator. The organic materials to be destroyed are treated with the reagents listed and placed upon the hot plate to react without further attention. As can be readily seen in many cases, such as in the analysis of leather previously described, a more suitable procedure can be developed with modified apparatus and acid mixture. The data are useful, however, for the purpose of predicting reaction tendencies in practical laboratory adaptations.

THE DETERMINATION OF SILICA IN PLANT MATERIALS

In the method usually employed for the determination of silica in plant materials, the sample usually comparatively large and bulky is first ashed in an electrically heated muffle furnace, in a porcelain or preferably a platinum dish. The ash thus obtained is then fused, using as flux either sodium carbonate or a mixture of sodium carbonate and potassium carbonates. The fusion is then taken up with water, acidified with excess hydrochloric acid and the silica recovered after a double dehydration of the dissolved fusion melt.

The Willard and Cake method *(14)* for the dehydration of silica employs a single boiling period of 15-20 minutes with concentrated $HClO_4$. The mineralization of a sample of plant material, using a mixture of nitric and perchloric acids with final volatilization of excess nitric acid, leaves the perchloric acid residue also in form for the dehydration of silica. The method is not only much more rapid than the processes previously outlined, but gives an exceptionally pure dehydrated silica both after filtration, washing, and ignition and following evolution of SiO_2 as SiF_4, using HF and H_2SO_4. Insoluble salts or slowly soluble salts after dehydration, such as anhydrous sulfates, are not formed by the perchloric acid dehydration. Salts such as those of calcium, barium, lead, iron, aluminum, etc., are readily and excessively soluble and the incidental presence of sulfur in the plant material, which would be in part oxidized to sulfuric acid by the perchloric acid digestion of the organic matter, introduces no complications.

As shown by Fowler *(41)* the quantitative dehydration of silica by the use of hot, concentrated perchloric acid as applied to steel analysis is a more exact procedure than that following any other standard process. The procedure as described by La Matte, Kahane and Kahane *(42)*, for the determination of silica in plant products, following the use of perchloric acid to destroy organic matter and dehydrate the silica, as translated from the original *(2)* pp. 75-84 follows:

Five g. of the material are treated with a mixture of 20 ml. of fuming nitric

acid sp. gr. 1.49 plus 30 ml. of 66 per cent $HClO_4$ sp. gr. 1.61 in a 500 ml. beaker. The attack often begins in the cold but one should not hesitate to apply heat being careful to avoid the contents of the beaker frothing too much. There is no call to particularly slow down this first reaction during the course of which abundant vapors of nitric oxide are evolved. As soon as the nitric acid has exhausted its effectiveness a change in color of the evolved gases is easily noted. At this point the reaction is continued, to evolve the excess of nitric acid. At the completion of this evolution of nitric acid there is noted a change in the character of the ebullition, the bubbles formed becoming less pronounced. At this time only does the perchloric acid begin to play its part in destruction of organic matter left by the nitric acid. The perchloric acid attack begins during the elimination of the last fraction of nitric acid. It is indicated by an increasing evolution of bubbles of gas formed by its action. The action becomes spontaneous and accelerates often to such an extent that it is well to discontinue the heat for short intervals. The attack calms down after a fraction of a minute with the practical completion of the operation and the heating may be continued. White fumes of perchloric acid appear at once after which the beaker is covered to prevent further loss of perchloric acid and a brisk ebullition is maintained during 30 minutes.

The silica is thus dehydrated. The solution is cooled and 100-150 ml. of distilled water is added. Bring to the boiling point, filter on an ashless filter, wash with hot, dilute hydrochloric acid, dry, ignite, and weigh.

A perfectly white ignited silica is thus obtained, very compact and in the analysis of horse-tail plant (high in silica) straw, grains, and grasses, pine needles, and birch-wood sawdust, there remains no appreciable residue after treatment of the silica with hydrofluoric acid.

According to tests by Kahane and Kahane (loc. cit.) the sensitivity of this method is $\pm$ 0.1 milligram of silica. According to this estimate the solubility of silica in concentrated perchloric acid is less than 1 part in 500,000. In the presence of fluorine in the amounts ordinarily encountered in case of the plant products mentioned, the addition of 0.5 g. of boric acid prevents the interference of fluorine in the determination of silica. The advantage of the method aside from speed and accuracy consists in the fact that large as well as small amounts of silica are determined with equal facility. Atmospheric dust contamination, which would introduce appreciable quantities of silica in the case of the previously employed methods, is almost completely eliminated following the perchloric acid technique as described. The perchloric acid is easily obtained completely free from silica and the water and nitric acid are likewise easily freed from silica. The method is thus suited to the determination of micro-quantities of silica. This is the more certain since large samples of plant materials may readily be employed, followed by the evaporation of the excess oxidizing acids in preparation for the filtration of dehydrated silica.

Practically an analysis sufficiently exact to provide for the separation of a fraction of a milligram of silica can be carried out. Moreover, the study of the precipitate may lead to useful conclusions for

quantities approaching 0.1 mg. The technique does not differ essentially from that previously described, it simply being necessary to add boric acid, and to use a filter paper which is ashless beyond the sensibility of the balance to be employed to weigh the ash.

THE DESTRUCTION OF VICERA IN TOXICOLOGICAL INVESTIGATIONS. DETERMINATION OF CHROMIUM

The destruction of the organic matter in the case of 200-300 grams of such animal organisms as liver and heart or lung tissue, etc., for the determination of mineral constituents presents three special difficulties. The minimum of loss by volatilization or mechanical entrainment must be avoided. The weight of material necessary for analysis is large because of the small extent to which the elements sought are present. Vicera contains abnormal proportions of lipides which tenaciously resist oxidation.

Loss by volatilization in part, for example in the case of arsenic and mercury, results from permitting the arsenic to become reduced in the presence of hydrochloric acid, which condition also favors the loss of mercury. The destruction of large quantities of organic matter, particularly lipides, involves the necessity for precautions, using strong oxidizing agents such as perchloric acid to prevent violent reactions. These difficulties have been efficiently overcome as shown in the wet oxidation of vicera employing a mixture of nitric, sulfuric, and perchloric acids, described by Kahane *(2)* pp. 102 ff. The special assembly of apparatus for use in carrying out this process is shown in Figure 4. The practical application of the process to the toxicologic determination of chromium in animal tissue with a series of results attainable has been given by Daniel Barth *(43)*. The Barth description of the application of Kahane's procedure is as follows:

> 200 g. of tissue, either cut into pieces or not, are introduced into the round bottom 1500 ml. flask of the Kahane apparatus (Figure 4) and 80 ml. of concentrated nitric acid (sp. gr. 1.39) and 45-50 ml. of concentrated sulfuric acid (sp. gr. 1.81) as well as a few glass beads to facilitate boiling are added. Abundant frothing sets in at the beginning which subsides rapidly as soon as heat from the bunsen burner is generously applied at the back side of the flask, at the level of the liquid in the flask. The heating at the base of the flask may then be carried out intensively without danger, using a wire gauze and the free flame.
>
> The nitric acid reaction then follows accompanied by copious evolution of oxides of nitrogen. The sample is thus disintegrated and a super-natant layer of lipides accumulates.
>
> After a time the nitric acid digestion is complete, the fluid mass becomes brown colored and finally black. The heating is continued until a thick black liquid results which adheres slightly to the flask walls as observed, following a slight agitation of the flask. At this point the dropwise addition from the dropping

> funnel (Figure 4) of a mixture of 2 volumes of $HClO_4$ (66 per cent sp. gr. 1.61) and 1 volume of HNO_3 (sp. gr. 1.39) is begun.
>
> Under these conditions a liberation of white fumes resulting from the oxidizing action of the perchloric acid is observed. At the point of contact between the digesting liquid and the mixed acids added, copious evolution of gaseous products results. The mixed acids are added until the oxidation of the remaining organic matter is essentially complete, being careful not to employ an excess of perchloric

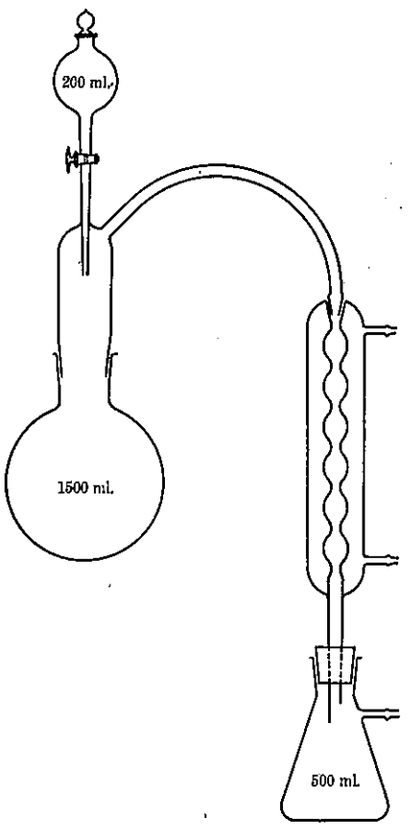


FIGURE 4. Digestion Assembly for Large Scale Destruction of Organic Matter in Toxicology

> acid which would result in the formation of insoluble ammonium perchlorate upon cooling the digestion liquid.
>
> The latter phase of the digestion necessitates only mild application of heat, since the action of the perchloric acid is exothermal.
>
> The destruction of organic matter is then completed by the addition of a few drops of nitric acid to the partially cooled sulfuric acid solution, obtaining a

colorless residue in the absence of chromium and a green solution in the presence of appreciable chromium.

The sulfuric acid residue is finally diluted with distilled water to reduce the acidity to approximately 10 per cent by volume. The solution is heated to boiling and 2-3 drops of 1 per cent silver nitrate solution added. The heating is discontinued and 1 g. of potassium persulfate dissolved in 20-30 ml. of water is added. The solution is then heated to boiling and thereupon retarded to repress the decomposition of the persulfate during the oxidation of the chromium. A second treatment with persulfate may be required in case chromium is present in sufficient amount.

Manganese if present gives rise to the characteristic color of permanganate. At this point all the chromium has been oxidized, as indicated by the subsequent oxidation of manganese, and the excess persulfate may be decomposed.

The flask is heated to boiling to destroy the excess of persulfate. After 5 minutes boiling the persulfate is destroyed, and the addition of 2-3 drops of hydrochloric acid brings about the reduction of the permanganate with the dis-

TABLE XXIII

SENSITIVITY OF THE TOXICOLOGIC DETERMINATION OF CHROMIUM

Cr added to the fat to be destroyed mg.	From destruction of organic matter Cr in residue mg.	Error %
52.95	53.02	+0.13
	52.53	—0.08
10.59	10.43	—1.5
	10.48	—1.0
1.05	1.02	—3.0
	1.03	—2.0
0.53	0.52	—2.0
	0.525	—1.0
0.105	0.100	—5.0
	0.104	—1.0
0.01	0.0093	—7.0
0.001	0.00081	—19.0
	0.00088	—12.0

appearance of the rose tint. (This discoloration is also an indication of the destruction of excess persulfate.)

If the liquid contains sufficient chromium, a yellow color develops and the heating can be continued for 5 minutes to assure the decomposition of excess persulfate without danger of reduction of chromium to a valence less than six (which has been tested by Barth). In this case a volumetric determination of chromium is suitable.

If after treatment with hydrochloric acid the solution remains colorless, it is preferable to discontinue the heat a short time after the decomposition of per-

manganate. There will then remain only possible traces of persulfate which will not interfere with the colorimetric determination of chromium.

It is in fact not practicable in this case to estimate the chromium content, since the liquid does not give evidence of its presence by the color resulting.

The flask is cooled, using a stream of running water over the flask and the colorimetric determination of chromium is made following the addition of a few drops of 2 per cent diphenylcarbazide dissolved in 95 per cent alcohol, and after the addition of phosphoric acid to complex the iron which may be present. (This is of particular importance in case the organic tissues being studied are rich in blood.)

The determination is carried out either with a colorimeter if the quantity of chromium is several gamma per ml., or by the use of nessler tubes if the amount of chromium is very small.

The results obtained using the technique described are shown in Table XXIII. In each case we have the destruction of the organic matter in 50 g. of beef fat to which has been added the amounts of chromium shown in the form of potassium dichromate. However, in the case of approximately 1 gamma of chromium the destruction of 20 g. of beef fat was carried out.

For summarization it is possible by the technique described to recover chromium with an error of 2-3 per cent when present in amounts from zero to 5 milligrams and in amounts from zero to 0.5 mg. with error of 5 per cent, that is to say within the range of accuracy of the reading of the colorimeter, and in amounts from zero to 0.001 mg. with an error somewhat greater than 10 per cent.

Barth, in the various studies in the toxicity of chromium *(43)* made complete analyses separately of all the organisms of dogs, which had been subjected to acute dichromate poisoning following the process above described. The dogs weighed in some cases as high as 14 kilograms, and the total sample organism weight varied between a few grams and several hundred grams.

There remains little doubt that following the method of Kahane, using digestions as described above, with mixed nitric, sulfuric, and perchloric acids, that animal organisms and tissues containing appreciable quantities of lipides are most effectively decomposed by the process as described by Barth, in actual practice. The process is more fully described by Kahane *(2)* pp. 102 ff. The possibility of losses by evolution (for example in the case of arsenic and mercury) are discussed, and precautions to avoid accidental destruction of samples which cannot be duplicated are considered. The method is precise, time saving, and superior to other wet methods for the destruction of organic matter containing fats and greases.

SECTION 3

MIXED PERCHLORIC, SULFURIC AND PHOSPHORIC ACIDS AND THEIR APPLICATIONS IN ANALYSIS INCLUDING CHROMIUM IN STAINLESS STEEL, MANGANESE IN FERRO-TUNGSTEN AND THE EVALUATION OF STANDARD TITANOUS SOLUTIONS

This section has for its objective the description of processes which are characteristic of those which it may be confidently predicted will be greatly augmented as time permits for carrying out the investigations in the field of the analysis of metallurgical materials. The analytical procedures about to be described were developed by the author in the laboratories of the University of Illinois, in Urbana, with the collaboration of students engaged in graduate work leading to advanced degrees. The plan of these investigations has had the three-fold aim, to save time, to save in cost of materials, and to increase accuracy. The methods are for these reasons particularly adapted to the use of the routine industrial control laboratory, and by reason of their comparison in practice with standard processes are equally adapted to special research programs. It is hoped that the advantages found in the use of mixtures containing the three acids $HClO_4$, H_2SO_4, and H_3PO_4 in the case of the methods about to be described, will stimulate interest upon the part of other investigators in such a manner as to enlist their service in extending the field of usefulness into other channels. It becomes increasingly apparent that applications in the use of perchloric acid as already collected together in the present and in previously printed *(3, 4, 5, 6)* brochures, but poorly represent the great number of possible uses. Perchloric acid as an aid in routine and research studies has been applied by an extended list of prominent analytical research experts. The list is obviously imposing and need not be specified at this time. The field may still, however, be favorably augmented and there is scarcely a branch of chemical specialization that cannot, without the shadow of a doubt, be favorably advanced in some way by the application of perchloric acid to the solution of its problem.

The following determination of chromium in stainless steel was developed by the author in collaboration with G. P. Smith and the report of the investigation published in the *Journal of the Society of Chemical Industry (18)*. A new process in standardization of titanous

solutions was developed by G. F. Smith and C. A. Getz and published in the *Analytical Edition of Industrial and Engineering Chemistry (15)*, which involves oxidation of organic matter using $HClO_4$.

THE DETERMINATION OF CHROMIUM IN STAINLESS STEEL, USING PERCHLORIC, PHOSPHORIC, AND SULPHURIC ACIDS

The determination of chromium in steel using perchloric acid in the oxidation of tervalent to sexavalent chromium has been established as a standard process for routine as well as umpire analyses. Several obvious obstacles to its use in this analysis were, of necessity, first eliminated. The cost of perchloric acid a few years past was almost prohibitive. The manufacturers of perchloric acid have reduced this factor by approximately 90% in the past 10 years. Misconceptions of probable hazard from violent reactions using perchloric acid for the analyses in question have been practically eliminated. Small but determinable tendencies towards low results in the determination of chromium following perchloric acid oxidation have been corrected through knowledge gained of side reactions which are easily controlled. Lastly, new oxidation-reduction indicators for use in these methods have been developed, particularly the high-potential indicator *o*-phenanthroline ferrous ion. Serious difficulties in the manufacture of this indicator have been but recently overcome *(5, 44)*.

Several improvements in the perchloric acid oxidation and determination of chromium in steel are still to be desired. An improved method for dissolving the sample to save materially the time required in preparing the sample for oxidation is most desirable. The time required for the oxidation of chromium after solution should be materially reduced. Lastly, the amount of perchloric acid should be cut down at least to half the present requirements. It is the object of the present section to describe methods for bringing about these improvements as applied to the determination of chromium in stainless steel. Extension in the application of the method to chrome-vanadium and chrome-tungsten steels is entirely feasible, and is at present being investigated in the determination of the various alloying elements. The new method, as described, is thought to be the most rapid of any precise method yet devised.

Previous Work

The perchloric acid oxidation of chromium and vanadium in steel was first described by H. H. Willard in 1919 *(12)*, p. 298. The determination of chromium in the absence of iron using perchloric acid, as in chrome alum, was described by Lichtin in 1930 *(36)*. The determination of chromium in steel was described by James in 1930 *(45)*, by Willard and Gibson in 1931 *(10)*, and by Willard and Young in 1934 *(46)*.

The perchloric acid oxidation of chromium in steel has been shown to be somewhat incomplete (99.5-99.9% complete) by H. B. Knowles *(12)*, p. 298. The peracid properties of hot concentrated perchloric acid have been shown by one of the present anthors to cause this effect *(7)*. The elimination of this error has been described also by Smith, McVickers and Sullivan *(5)*, p. 27 ff. An additional method is described in connection with the present work.

A saving in the amount of perchloric acid required for the oxidation of chromium is effected by using in its place a mixture of perchloric and sulphuric

acids. A suitable mixture consists of 1 volume of 70-72% perchloric acid with 2 volumes of 80% sulphuric acid. The influence of changes in the sulphuric acid concentration on the oxidation of chromium in the absence of iron has been investigated by Smith *(5)*, p. 27-31. An additional method is described in connection with the present work. Mixed perchloric and sulphuric acids alone are not suitable in the determination of chromium in steel because of the formation of insoluble anhydrous ferric sulphate.

The Solution of Stainless Steel in Mixed Perchloric and Phosphoric Acids

Stainless steel or plain carbon steels and iron are not soluble in a mixture of perchloric and sulphuric acids. The surface reaction is such as to transform the steel into the passive condition. Mixtures of concentrated perchloric and phosphoric acids, however, are remarkable solvents for iron and steel, including stainless steel and high-speed tungsten tool steels. Metallic tungsten is easily and completely soluble in such mixtures. The various solvent effects depend on the temperature to which the mixed acids are heated. Plain carbon steels, chrome-vanadium, nickel steels, including stainless steel, dissolve rapidly in a mixture of 1 vol. of 70-72% perchloric acid with 2 vols. of 85% phosphoric acid at 175°-190°. At this temperature the iron or chromium is not oxidised. The carbon of the steel is oxidised under these conditions. Unlike the solution of steel or iron containing the higher percentage of carbon in 70-72% perchloric acid at the given temperature, there is no possibility of violent reaction. The dilution of the hot concentrated perchloric acid by the larger volume of concentrated phosphoric acid causes the carbon to oxidise rapidly and quietly. Chromium steels and stainless chrome-nickel steels dissolve to form the corresponding phosphates of iron, chromium, and nickel as shown by the color of the solution, and the fact that the addition of sulphuric acid and further digestion at 190-205° does not form insoluble anhydrous nickel or ferric sulphates even after the iron is oxidised by raising the temperature to approximately 200°. The chromic salts are oxidised to the sexavalent form by the mixture of perchloric and phosphoric acids at 203-205°, best after the addition of sulphuric acid.

Tungsten tool steels containing up to 15-20% of tungsten dissolve in mixed perchloric and phosphoric acids at 175-190° with the precipitation of tungsten and tungsten carbide in a manner similar to their attack by hydrochloric or sulphuric acid. At 200-205° or above the iron is oxidised and the insoluble matter completely oxidised and dissolved. The tungsten forms phosphotungstic acid and the silicon forms silicotungstic acid while the carbon is oxidised. The addition of concentrated sulphuric acid to such solutions causes no precipitation of any type. Mixtures of perchloric and phosphoric acid are without doubt the most satisfactory solvents for tungsten steels yet discovered. Metallic tungsten dissolves in such mixtures at temperatures somewhat above 200° to form phosphotungstic acid and a clear solution. Ferro-tungsten is likewise soluble, but requires longer digestion. It may therefore be predicted that these observations and results open the way to a number of improved methods in the determination of the various alloying elements in special steels such as chromium, tungsten, vanadium, manganese, etc. The present section is a report of one such application; the others are in the progress of development.

Outline of Procedure for the Determination of Chromium

The procedure for chromium determination in stainless steel is as follows: 0.5 g. of the finely divided sample is weighed and transferred to a 500-ml. Erlenmeyer flask. 10 ml. of a mixture of 1 vol. of 70-72% perchloric acid plus 2 vols. of 85% phosphoric acid (GFS Phosfodant) are added and the flask top is closed using a special digestion head with the stem sealed off four inches long and bent slightly, to bring the end of the stem in contact with one side of the flask inside. The design of this special digestion head is shown as A in Figure 1 on page 28. The flask and contents are heated at 175-185°, using a hot plate or carefully controlled gas burner, during 2-5 minutes. The solution should have a clear green color and no oxidation of chromium should have occurred. 15 ml. of a mixture of 1 vol. of 70-72% perchloric acid plus 2 vols. of 80% sulphuric acid (GFS Oxydant) are added and the temperature is raised to 203-205°. After 4-5 minutes the chromic acid color appears and the oxidation is complete in an additional three minutes. The final solution is orange in color. At this point 10-20 mg. of potassium permanganate crystals are added. The beaker is at once removed from the source of heat, and with a swirling motion the flask is plunged into ice water with continued swirling for 6 to 7 seconds and the solution immediately diluted to 60-70 ml. with cold water.* 0.5 ml. of concentrated hydrochloric acid is added, while swirling the flask, and the mixture heated to boiling for 5 minutes to evolve chlorine, and cooled by addition of ice water to make a total of 250 ml. The cool solution is thus ready for determination of chromium in less than 20 minutes.

Two drops of 0.025 molar *o*-phenanthroline ferrous ion are added as indicator *(5)*, followed by a measured excess of 2-3 ml. of 0.1 *N*-ferrous sulphate. The reduced solution containing excess ferrous iron is colored pink from the reduced indicator, the depth of color being lessened by the green of chromium and nickel ions present. The excess of ferrous sulphate is back-titrated using 0.01*N*-sufatoceric acid. The trace of vanadium ordinarily present is reduced by the ferrous iron and reoxidised by the ceric sulphate. The end-point of the reaction is easily observed by the color transition from light pink to green. The chromium is determined from the volume of ferrous sulphate used corrected by subtracting the value of the cerate solution used in the back-titration.

The Per-Acid Properties of Hot Concentrated Perchloric and Its Influence on the Oxidation of Chromium

It has been previously shown *(7)* that a trace of hydrogen peroxide or ozone is produced as decomposition product from hot 70-72% perchloric acid. The presence of such products cannot be demonstrated qualitatively because of the simultaneous formation of chlorine. The reducing properties are easily shown in the case of the oxidation of chromium to chromic acid. Hot concentrated 70-72% perchloric acid rapidly oxidises tervalent to sexavalent chromium at 203°. The hydrogen peroxide or ozone is formed at this temperature in very small amount and slowly. The effect of this small amount of hydrogen peroxide in reducing chromic acid is excluded only if the perchloric acid is rapidly cooled and diluted. This elimination of the difficulty has been shown to be effective in the case of

* The rapid cooling of the hot flask and contents requires a special technique to prevent breakage. No breakage will result if the hot flask is plunged into the ice water for one-fourth second and withdrawn rapidly and then quickly immersed the second time and swirled for 6-7 seconds. At this time cold water can be added without causing spattering and the heat of dilution will then bring the flask contents almost to a boiling temperature. The use of "Vycor," the new Corning Glass Works development, eliminates all of this difficulty.

steel analyses by Willard and Young, especially in the case of stainless steel *(46)*. The same difficulty from the formation of traces of hydrogen peroxide has been shown by G. F. Smith *(5)*, p. 27-31, to affect results in the determination of chromium by oxidation using the mixture of perchloric and sulphuric acids. In the latter case the effect is more pronounced using mixed perchloric and sulphuric acids even at the lower temperatures of 180-185° because of the dehydration effect of the sulphuric acid. Mixtures of perchloric, phosphoric, and sulphuric acids oxidise chromium at 203-205° with the formation of somewhat more hydrogen peroxide. Rapid chilling and dilution of the solution is not sufficiently effective in arresting appreciable reduction of sexavalent chromium. The elimination of the error would be predicted if a suitable oxidising agent could be added which would reduce the hydrogen peroxide preferentially, leaving the chromium entirely in the sexavalent form. Potassium permanganate was found to act in this manner. Since the excess of permanganate is easily reduced without the reduction of chromium by the addition of hydrochloric acid to the diluted solution of chromic acid while boiling off the chlorine already present, the addition of the permanganate does not complicate the procedure or prolong the time required for the analysis.

Preparation of Standard Solutions and Control Experiments in the Determination of Chromium

Potassium permanganate and ammonium sulfato-cerate.—Potassium permanganate was standardized in the usual manner, using Bureau of Standards sodium oxalate. The solution of ceric sulphate was half molar in sulphuric acid and was prepared from C.P. ammonium sulfato-cerate, $(NH_4)_2Ce(SO_4)_3 \cdot 2H_2O$. The ceric sulphate was standardised also by means of Bureau of Standards sodium oxalate in sulphuric acid solution using excess of ceric sulphate and back-titration with ferrous sulphate, using *o*-phenanthroline ferrous ion as indicator. The ratio between the ceric sulphate and ferrous sulphate was determined using the same indicator. The permanganate was found to be 0.02347*N* and the ceric sulphate 0.00982*N*. These solutions were used for the back-titration of excess of ferrous sulphate.

Ferrous Sulphate.—An approximately 0.12*N* solution of ferrous sulphate in dilute sulphuric acid was standardised using both the permanganate and the ceric sulphate in the latter case using *o*-phenanthroline ferrous ion as indicator. The ferrous sulphate in both cases was found to be 0.1211*N* and was stored under hydrogen at all times. At the completion of the present work it was restandardised and found to have remained full strength throughout the investigation.

Determination of Chromium in Potassium Dichromate.—For the purpose of control it was important to learn the degree of precision with which chromium could be determined in the mixed perchlorie, phosphoric, and sulphuric acids following a procedure analogous to that proposed for the determination of chromium in stainless steel. Weighed samples of potassium dichromate were dissolved in 10 ml. of Phosfodant (see above) and the chromium was reduced to the chromic condition by the addition of sufficient hydrogen peroxide. After digestion for 5 minutes at 180° 15 ml. of Oxydant (as above) were added and the temperature was raised sufficiently (203-205°) to bring about the oxidation of chromium after 5 minutes boiling with heating continued 3 minutes longer. Approximately 15 mg. of potassium permanganate crystals were added and the flask contents were

swirled and chilled in ice water for 6-7 seconds and diluted to 60 ml. with water. The solutions thus prepared after the addition of 0.5 ml. of concentrated hydrochloric acid were boiled 5 minutes, cooled by dilution to 250 ml. with ice water, and 2 drops of 0.025 molar *o*-phenanthroline ferrous ion added. A slight excess of standard ceric sulphate was added to the disappearance of the pink color of the indicator.

Weighed samples of the same potassium dichromate were dissolved in a mixture of the same volumes of Phosfodant and Oxydant, diluted to 250 ml., and titrated in the same manner as in the previous case. A satisfactory agreement in the recovery of chromium was found, indicating precision in the oxidation of chromium in the mixed acid solution under the proposed conditions for determination in steel. The results are shown in Table XXIV.

TABLE XXIV

DETERMINATION OF CHROMIUM IN $K_2Cr_2O_7$ IN $HClO_4$–H_3PO_4–H_2SO_4 SOLUTION, WITH AND WITHOUT REDUCTION OF SEXAVALENT TO TERVALENT CHROMIUM

Sample wt., 0.1800 g. $K_2Cr_2O_7$. Chromium content calc. = 0.0636 g. 31.00 ml. 0.1211*N*-$FeSO_4$ added in each test.

0.0098*N*-$Ce(SO_4)_2$ required, ml.	Cr found red. and re-oxidation, g.	Cr found direct titration, g.	Diff. g.
3.10	0.0645	0.0643	+0.0002
3.00	0.0645	0.0643	+0.0002
5.30	0.0642	0.0642	±0.0000
4.50	0.0643	0.0643	±0.0000
4.60	0.0643		
	Av. 0.06438	0.06428	+0.0001
4.80*	0.0641	0.0641	0.0000
5.40*	0.0641	0.0642	—0.0001
	Av. 0.0641	0.06415	—0.00005

*A different sample of dichromate was used in these tests.

The results in Table XXIV prove that the recovery of chromium in potassium dichromate, following reduction and re-oxidation by the method as described, gives the same value as that obtained from the original potassium dichromate in the same acid medium without other treatment. The two separate samples of potassium dichromate show higher than theoretical values for chromium evidently present as chromic acid. The next logical step therefore consists in the analysis of the stainless steel to determine the influence of iron and the other common impurities which might affect the process adversely.

Determination of Chromium in Stainless Steel by the Procedure as Previously Outlined

Four samples of stainless steel were analysed by the procedure as outlined. Two of the samples were standards supplied by the U. S. Bureau of Standards. Two additional samples were analysed both by the new method and, as control, by the method of Willard and Gibson *(10)* modified to eliminate the hydrogen peroxide error as proved effective by Willard and Young *(46)*. In the latter method 70-72% perchloric acid is used for both solution of the sample and oxida-

tion of the chromium by boiling for 15-20 minutes and rapid chilling before dilution. It has been noted that certain stainless steels are not as easily soluble in 72% perchloric acid as in the Phosfodant mixture ($HClO_4 + H_3PO_4$). No samples of stainless steel have been encountered which are not readily soluble in the latter mixture practically as easily as a plain carbon steel. It can be definitely stated that no alloy steel yet encountered caused any violent reactions, high-carbon steels included. The solutions were all ready for titration of their chromium content in less than 20 minutes, which is the time required for the oxidation period alone, using the Willard and Gibson method. The results from 29 separate analyses are shown in Table XXV.

TABLE XXV

DETERMINATION OF CHROMIUM IN STAINLESS STEEL USING GFS PHOSPHODANT AND OXIDANT

Sample No.	Sample wt., g.	$FeSO_4$ 0.1211*N*, ml.	$Ce(SO_4)_2$ 0.00982*N*, ml.	Chromium found: Present method, %	Chromium found: Willard and Gibson, %	Cert. value, %
B. of S. 73	0.5065	35.00	12.70	14.07	14.01	13.93
	0.5004	34.00	7.50	14.00	13.98	13.93
	0.5048	35.50	17.50	*14.17	13.96	13.93
	0.5024	35.00	14.20	14.14	—	13.93
				Av. 14.07	13.99	13.93
B. of S. 101	0.5065	44.00	18.80	17.60	—	17.56
	0.5029	44.00	12.80	*17.93	—	—
	0.5022	44.00	25.40	17.53	—	—
	0.3571	30.50	5.30	17.67	—	—
				Av. 17.60	—	17.56
Stainless steel	0.5032	43.50	6.20	17.93	17.86	
	0.4991	43.50	10.00	17.95	17.78	
	0.5074	44.00	6.50	17.99	17.87	
	0.5074	44.50	16.60	17.93	—	
	0.5039	44.00	13.80	17.80	—	
				Av. 17.93	17.84	
Allegany metal	0.5050	30.00	6.30	12.25	12.15	
	0.5037	29.50	2.00	12.23	12.12	
	0.4988	29.50	3.20	12.30	12.13	
	0.4016	34.50	3.80	*12.86	12.17	
	0.4017	34.50	4.20	*12.87	12.16	
				Av. 12.26	12.15	

* Chlorine expelled in these cases by 3 minutes' boiling only. These values were excluded from the averages.

Table XXV indicates that the present method from an average of 25 separate determinations gave results corresponding closely to the Bureau of Standards certificate value and to the results obtained by the modified Willard and Gibson method. The agreement is slightly better by comparison of the new method with the straight perchloric acid method. The agreement is within 0.1% in either case. The tendency toward slightly high results might be attributed to a failure to boil off completely the chlorine formed in the oxidation period. Three minutes boiling is not sufficient but longer than 5 minutes does not alter the results. The results in

Table I indicate, until proven otherwise, that the values by the new process are more nearly exact than by other methods. At least low rather than high results would be expected. The total volume of 70-72% perchloric acid required per analysis is 8 ml. as compared with 15-20 ml. of 70% perchloric acid for the Willard and Gibson method. The preparation of the solutions for titration by the present method requires less than 20 minutes. By the Willard and Gibson method 30 minutes are required. The present method is therefore the most rapid of all methods for the determination of chromium in stainless steel since the Willard and Gibson method was formerly the most rapid known process. It is believed that the combined savings in time and cost of reagents render the present method the most attractive as a routine laboratory control method.

The following section is practically a complete reprinting from the *Journal of Research of the National Bureau of Standards*, Vol. 22, April, 1939. The publication was contributed by James I. Hoffman and G. E. F. Lundell:

VOLATILIZATION OF METALLIC COMPOUNDS FROM SOLUTIONS IN PERCHLORIC AND SULFURIC ACID

INTRODUCTION

Volatilization as chromyl chloride, CrO_2Cl_2, has been employed by Smith *(47)* as a means of eliminating chromium in determinations of manganese, nickel, and vanadium, in steels containing high percentages of chromium. Certain other chlorides, notably those of antimony, arsenic, germanium, mercury, selenium, and tin, are likewise known to be volatil at or below 200° C, the temperature at which chromyl chloride is distilled. The present work was undertaken to obtain further information on the elements mentioned, as well as on other elements that might be encountered in chemical analysis. In this, two distinct purposes were kept in mind. The first was to find possible separations of elements that can not be separated by distilling at temperatures below 200° C. The second was to obtain information on elements that might be lost unintentionally when solutions are evaporated with perchloric or sulfuric acid in such operations as dehydration of silicic acid or expulsion of fluorides. Distillations with hydrobromic acid were included because they are sometimes used, and because certain bromides are even more volatil than the corresponding chlorides.

Experimental Work

In Smith's procedure the steel is dissolved in an Erlenmeyer flask in a mixture of hydrochloric and perchloric acids, and the chromium is oxidised to the sexivalent state by heating the solution until copious fumes of perchloric acid are evolved. The chromium is then volatilized as chromyl chloride by adding successive small portions of sodium

chloride or hydrochloric acid to the hot solution. At least 99 per cent of the chromium is easily eliminated in this way.

In the present work, an Erlenmeyer flask was not suitable because it was desired to test the volatil portion as well as the residual solution in the flask. The distilling apparatus devised by J. A. Scherrer *(48)* is well suited for this purpose and has the added advantages that the hydrochloric or hydrobromic acid can be admitted at any desired rate, that the temperature of the solution can be observed at all times, and that rubber stoppers, which might cause serious explosions, are avoided.* The apparatus is illustrated in figure 5. The flask has a capacity of 200 ml., and the distance between the bottom of the flask and the outlet tube leading to the condenser is about 15 cm.

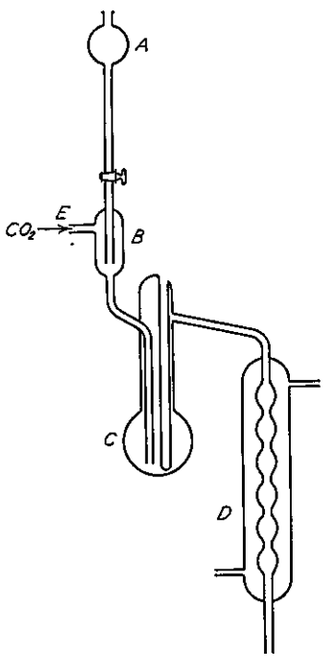


FIGURE 5. Distilling apparatus.

The following six types of distillations were investigated: (1) Distillation with perchloric and hydrochloric acids; (2) distillation with perchloric and hydrobromic acids; (3) distillation with perchloric, phosphoric, and hydrochloric acids; (4) distillation with perchloric, phosphoric, and hydrobromic acids; (5) distillation with sulfuric and hydrochloric acids; and (6) distillation with sulfuric and hydrobromic acids.

(1) *Procedure for distillation with perchloric and hydrochloric acids.*— To facilitate rapid heating of the contents of the flask, and at the same time to protect the upper portion of the flask from excessive heating, the bottom of the distilling flask was placed over a 4-cm. hole in a wire gauze with asbestos center. The distillate was collected in a beaker containing 100 ml. of cold distilled water, so placed that the tip of the condenser *D* was slightly immersed. From 25 to 100 mg. of the element under test, usually in the form of a

* It should be remembered that at the temperatures used in this work perchloric acid is a powerful oxidizing agent and may therefore react with explosive violence if it comes in contact with certain reducing substances, such as organic matter.

TABLE XXVI

RESULTS OBTAINED IN DISTILLATIONS AT 200 TO 220° C.

Element[1]	Approximate percentage volatilized from 20 to 100-mg. portions by distillation with—					
	HCl—$HClO_4$ (Procedure 1)	HBr—$HClO_4$ (Procedure 2)	HCl—H_3PO_4—$HClO_4$ (Procedure 3)	HBr—H_3PO_4—$HClO_4$ (Procedure 4)	HCl—H_2SO_4 (Procedure 4)	HBr—H_2SO_4 (Procedure 6)
Ag	0	0	0	0	0	0
Alkali metals[2]	0	0	0	0	0	0
Al	0	0	0	0	0	0
As^{III}	30	100	80	100	100	100
As^{V}	5	100	5	100	5	100
Au	1	0.5	0.5	0.5	0.5	0.5
B	20	20	10	10	50	10
Ba	0	0	0	0	0	0
Be	0	0	0	0	0	0
Bi	0.1	1	0	1	0	1
Cb	0	0	0	0	0	0
Cd	0	0	0	0	0	0
Co	0	0	0	0	0	0
Cr^{III}	99.7	40	99.8	40	0	0
Cu	0	0	0	0	0	0
Fe	0	0	0	0	0	0
Ga	0	0	0	0	0	0
Ge[3]	50	70	10	90	90	95
Hf[4]	0	0	0	0	0	0
Hg^{I}	75	75	75	75	75	90
Hg^{II}	75	75	75	75	75	90
In	0	0	0	0	0	0
Ir	0	0	0	0	0	0
Mg	0	0	0	0	0	0
Mn	0.1	0.02	0.02	0.02	0.02	0.02
Mo	3	12	0	0	5	4
Ni	0	0	0	0	0	0
Os[5]	100	100	100	100	0	0
P	1	1	1	1	1	1
Pb	0	0	0	0	0	0
Pd	0	0	0	0	0	0
Pt	0	0	0	0	0	0
Re	100	100	80	100	90	100
Rare earths[6]	0	0	0	0	0	0
Rh	0	0	0	0	0	0
Ru	99.5	100	100	100	0	0
Sb^{III}	2	99.8	2	99.8	33	99.8
Sb^{V}	2	99.8	0	99.8	2	98
Se^{IV}	4	2 to 5	2 to 5	2 to 5	30	100
Se^{VI}	4	5	5	5	20	100
Si	0	0	0	0	0	0
Sn^{II}	99.8	100	0	99.8	1	100
Sn^{IV}	100	100	0	100	30	100
Sr	0	0	0	0	0	0
Ta	0	0	0	0	0	0
Te^{IV}	0.5	0.5	0.1	0.5	0.1	10
Te^{VI}	0.1	0.5	0.1	1	0.1	10
Th	0	0	0	0	0	0
Ti	0	0	0	0	0	0
Tl^{I}	1	1	1	1	0.1	1
U	0	0	0	0	0	0
V	0.5	2	0	0	0	0
W	0	0	0	0	0	0
Zn	0	0	0	0	0	0
Zr	0	0	0	0	0	0

[1] Valences given in this column are those of the elements in the distilling flask at the beginning of the distillation.

[2] This includes lithium, sodium, potassium, rubidium, and cesium.

[3] The results given here are those obtained by heating the sulfuric or perchloric acid solutions in the distilling flask to 200° C. before admitting the hydrochloric or hydrobromic acid. During the heating, GeO_2 separated. By adding hydrochloric or hydrobromic acid to the solution before heating, separation of GeO_2 did not occur, and the germanium readily passed into the distillate.

[4] Since pure hafnium was not available, this test was made by decomposing 2 g. of cyrtolite and distilling as indicated. Spectrochemical tests showed that hafnium was one of the constituents of the mineral. It is supposed to contain 3 to 5 per cent of HfO_2.

[5] At 200 to 220° C. no osmium was volatilized from the solutions containing sulfuric acid; however, at 270 to 300° C. the osmium was completely volatilized.

[6] This includes scandium, yttrium, and lanthanum in addition to the rare earths, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutecium. A mixture in which all these elements were known to be present was used in this distillation.

[7] In distilling from sulfuric acid, a few tests were made in which hydrochloric acid containing sulfurous acid was added to the hot sulfuric acid solution in the distilling flask. This was done to keep the thallium in the univalent state. No thallium was found in the distillates, whereas a little (about 1 mg.) was always found if the thallium was first oxidized.

solution of its chloride or perchlorate, was introduced into the distilling flask through *A*; then 15 ml. of 60 per cent perchloric acid was added, and the stopcock was closed. A moderate stream of dry carbon dioxide was admitted through tube *E* and bubbled through the solution in the distilling flask. This swept the vapors from the flask into the condenser and prevented bumping by keeping the solution agitated. After the stream of gas was started, the contents of the flask were rapidly heated to 200° C. with a Tirrill burner. The temperature was observed with a thermometer placed in the thermometer well of the flask. Hydrochloric acid, sp. gr. 1.18, from bulb *A* was now introduced through the inlet tube beneath the surface of the hot solution in the flask at such a rate that the temperature remained between 200° and 220° C. After 15 ml. of hydrochloric acid had been admitted, during the course of 20 to 30 minutes, the distillation was stopped, and the distillate and residual solution in the flask were examined.

(2) *Distillation with perchloric and hydrobromic acids.*—The same procedure was used as in (1), except hydrobromic acid (the 40 per cent reagent) was substituted for hydrochloric acid.

(3) *Distillation with perchloric, phosphoric, and hydrochloric acids.*—The same procedure was used as in (1), except 5 ml. of sirupy phosphoric acid was added to the contents of the flask before the solution was heated and the hydrochloric acid admitted.

(4) *Distillation with perchloric, phosphoric, and hydrobromic acids.*—The same procedure was used as in (3), except hydrobromic acid was substituted for hydrochloric acid.

(5) *Distillation with sulfuric and hydrochloric acids.*—This corresponded exactly with (1), except sulfuric acid (sp. gr. 1.84) was substituted for perchloric acid.

(6) *Distillation with sulfuric and hydrobromic acids.*—This corresponds with (2), except sulfuric acid was substituted for perchloric acid.

The results of the tests are given in table XXVI.

Discussion of Results

1. *Separation of Chromium.* This work confirms the statement of Smith *(47)* that by distilling with perchloric and hydrochloric acids chromium can be satisfactorily separated from manganese in analyses of steels containing high percentages of chromium. The amount of manganese volatilized is entirely negligible in any ordinary analysis.*

* For example, in determinations of manganese in 1-g samples of 18 chromium-8 nickel steel (NBS Standard Sample 101) after volatilizing the chromium as chromyl chloride, 0.559 and 0.558 per cent, respectively, were obtained as compared with the certificate value, 0.555 per cent.

2. *Separations of Other Elements.* Complete distillation can probably be obtained in a reasonable time with those elements in table 1 that have passed into the distillate to the extent of 50 per cent or more, but such a procedure would most likely be impractical in the case of boron.

The table shows that arsenic, antimony, and tin can be volatilized, and additional work indicates that a practical method can probably be developed for separating small percentages of these from as much as 5 g. of lead, by distilling with hydrobromic and perchloric acids at 200° to 220° C.

If the reactions of the neighboring elements in the periodic system can be used as a criterion, it should be possible to volatilize the element masurium by distilling with perchloric and hydrochloric acids.

Selenium can be separated from many other elements by distillation with hydrobromic and sulfuric acids *(49)* (procedure 6).

Rhenium can be separated from molybdenum by distilling from a mixture of perchloric and phosphoric acids to which hydrobromic acid is slowly added (procedure 4). In a distillation involving 0.25 g. of molybdenum, the presence of molybdenum was detected in the distillate, but the amount was less than 0.05 mg. *(50)*.

Since preliminary experiments indicated that molybdenum can be volatilized in part by distilling at 200° to 220° C. with sulfuric and hydrochloric acids or with sulfuric and hydrobromic acids, additional distillations were made at temperatures as high as 300° C. in an attempt to get complete separation of molybdenum. These distillations were continued for at least one hour, and as much as 50 ml. of the halogen acids were used. Even with these more drastic treatments, volatilization was far from complete. The use of dry gaseous hydrogen chloride with either perchloric or sulfuric acid likewise failed to effect sufficient volatilization to offer promise of a separation of molybdenum from such elements as tungsten or iron.

3. *Losses That May Cause Errors in Analytical Procedures.* An inspection of table 1 is sufficient to show that many elements may be lost entirely or in part in evaporations with sulfuric or perchloric acid in many of the usual analytical operations. The losses indicated for gold, bismuth, molybdenum, phosphorus, tellurium, vanadium, and thallium are small, but may cause serious error if the material being analyzed contains high percentages, as for example, gold in dental gold alloys. On the other hand, with the usual small amounts of vanadium in steels, the loss in distillations with perchloric and hydrochloric acids is seldom of any consequence.

Loss of chromium during its oxidation with perchloric acid likewise is of importance. If hydrochloric acid is present during the oxidation, chromyl chloride may be formed and volatilized. A slight loss of chromium may occur even if no hydrochloric acid is added before or during the oxidation with perchloric acid, because hydrochloric acid is probably one of the products of the reaction when trivalent chromium is oxidized by perchloric acid. In five experiments in which 0.1 g. of chromium as the sulfate was oxidized with perchloric acid and heated for 5 minutes at 200° to 220° C. in the apparatus illustrated in figure 1, from 0.2 to 0.4 mg. of chromium was found in the distillates. This probably is the chief cause for the slightly low results obtained in the determination of chromium by oxidation with perchloric acid *(51)*. Of interest is the action of phosphoric acid in preventing volatilization of vanadium, molybdenum, tin, and bismuth in the hydrochloric-phosphoric-perchloric acid series (procedure 3), or of vanadium and molybdenum in the hydrobromic-phosphoric-perchloric acid series (procedure 4).

ELECTROLYTIC BRIGHT POLISHING OF STAINLESS STEEL, USING MIXED SOLUTIONS OF PERCHLORIC ACID, ACETIC ANHYDRIDE, AND WATER

Considerable commercial application is now being made of the principle of the electrolytic oxidation of dull metal surfaces. The process is one of constituting the sample to be bright polished as the anode in a suitable electrolyte. An iron, or better, an aluminum cathode is used. The chemical composition of the electrolyte may vary in type, depending upon the metal or alloy to be polished, or upon the particular preference of the operator, or upon limitations of the requirements of the particular task at hand.

The electrolytic bath employed may be mainly composed of nitric, orthophosphoric, hydrofluoric, sulfuric or perchloric acids. Besides one or more of these mineral acids, there is often added such organic acids as acetic acid or its anhydride, acetic anhydride. For bright polishing of certain alloys, use is made of an electrolyte of nitric acid and methyl alcohol.

The literature on the subject of bright polishing of metals and alloys is extensive. It is beyond the scope of this booklet to speak of any procedures other than those which involve the use of perchloric acid as an electrolyte component.

One of the earliest publications on this subject was made by Jacquet and Rocquet *(52)*. Their procedure has been further described and accepted as an approved procedure in the "Electrolytic Preparation of Iron and Steel Micro-Specimens of a Wide Variety of Materials" *(53)* as described by Pellisier, Marcus, and Mehl.

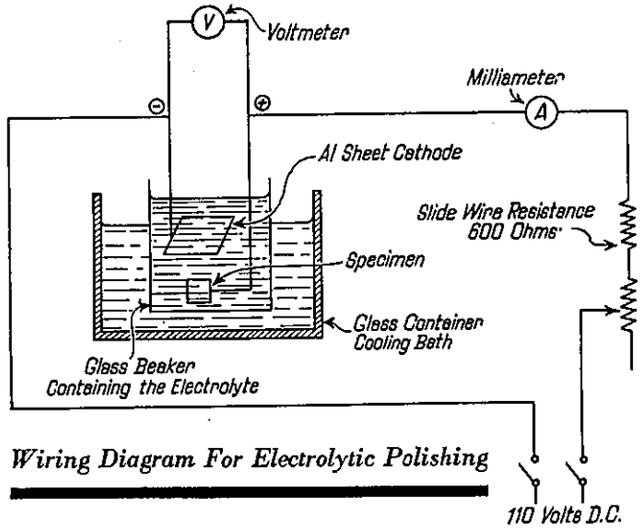
It was natural to extend the operation to commercial procedures of bright polishing of metal stampings, ornamental metal items, or even to extend the application to the bright polishing of plain metal surfaces, such as sheets and tubes. This has been done, and particularly for the bright polishing of stainless steel (18 chromium-8 nickel) sheet, tube, and stampings.

The following data art taken from the paper by Pellissier, Markus, and Mehl *(53)* somewhat abbreviated:

The recommended electrolyte is made by pouring slowly, a little at a time, 765 ml. of pure acetic anhydride into a cooled vessel containing 185 ml. of 65 per cent perchloric acid (sp. gr. 1.61) and then adding 50 ml. of distilled water. The mixture should be prepared at least 24 hours before use.

The object to be bright polished is freed from all foreign matter and made the anode in a bath of the electrolyte, using an aluminum cathode. A schematic wiring diagram is shown in Figure 6.

Adjustment of current density appears to be the most important item in technique; at too low a current density, deep and objectionable etching of the surface to be polished occurs, and at too high a current density, gas is evolved at



Wiring Diagram For Electrolytic Polishing

FIGURE 6

the specimen and causes uneven polishing. Current density is satisfactory when, upon changing the cell voltage, no appreciable change in current density occurs.

Sample surfaces produced by this procedure are shown in the photomicrographs

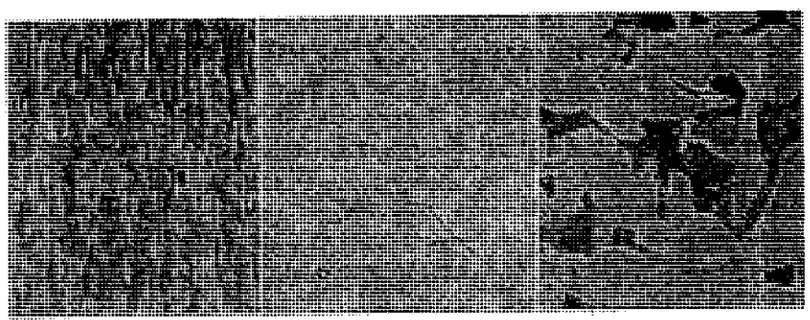


FIGURE 7

Scratches From 000 Paper on Steel Specimen (100×) | Inclusions and Quenching Crack (200×) Unetched | Hot Rolled 0.30% C Steel (100×) Electro-Polished, Nital Etched

shown in Figure 7 as applied to steel. The same type of results are obtained in the case of stainless steel.

The current density should be between four and six amperes per square decimeter of anode surface. During the electrolysis the temperature must not exceed 30 degrees centigrade (86 degrees F.); hence the electrolyte must be sometimes

cooled. The solution should be agitated, and since its resistance is high, direct current at a voltage of at least 50 volts is required.

It is to be cautioned that mixtures of perchloric acid and acetic anhydride, while not hazardous to make or to store for use in bright polishing, must be kept from spilling where they can contact organic matter, such as wood or paper, which may be later heated or come into contact with hot objects. A fire may thus result. The mixture of these two acids described for bright polishing is not hazardous to use as an electrolyte as long as it is stored under desirable conditions.

The Table XXVII data for use in electrolytic polishing of metals was taken from the paper by Pellissier, Markus and Mehl.

TABLE XXVII

Electrolytic Polishing of Metals

Metal	Solution	C.D.*	Voltage	Temp. °C.	Time Min.	Remarks
All carbon steels, martensitic, pearlitic, and sorbitic; Armco and white cast iron; 3% silicon steel	Acetic anhydride, 765 cc. Perchloric acid, 185 cc. sp.gr. 1.61 (65%) Distilled water, 50 cc. 0.5% Al	4 to 6	50†	<30	4 to 5	Prepare solution 24 hr. before using. Use moderate agitation. Al increases viscosity which permits more vigorous agitation and current density of 3. Can use at current density of 10 for austenitic steels. Prepare samples to 000 paper. Fe or Al cathode.
Austenitic steels‡	Acetic anhydride, Perchloric acid (65%) 2 parts to 1 part	6	50†	<30	4 to 5	Same as above.
Iron and silicon-iron	Orthophosphoric acid sp.gr. 1.316	0.6	0.75 to 2.0			Iron cathode.
Tin	Perchloric acid (sp.gr. 1.61), 194 cc. Acetic anhydride, 800 cc.	9 to 15	25 to 40†	15 to 22	8 to 10	Stir solution if length of electrolysis is over 10 min. Polish to 000 paper. Tin cathode. Electrodes 2 cm. apart.
Copper‡	Orthophosphoric acid sp.gr. 1.3 to 1.4	0.05 to 0.75	2	Room	>5	Polish to 0000. Copper cathode. Electrodes 2.2 cm. apart.
Copper‡	Pyrophosphoric acid 530 g. per l.	8 to 10	1.6 to 2.0	15 to 22	10 to 15	Polish to 00000 paper. Copper cathode.
Cobalt	Orthophosphoric acid sp.gr. 1.35		1.2			Rough metallographic polish. Cobalt cathode.
Aluminum‡	Perchloric acid (sp.gr. 1.48) Acetic anhydride, 2 parts to 7 parts	3.0 to 5.0	50 to 100†	<50	15	Allow 4 to 5 g. per l. to enter solution. Polish to 000 paper. Aluminum cathode.
Zinc‡	Potassium hydroxide 25% solution	16	6	Room	15	0000 paper. Solution agitated by air or nitrogen. Copper cathode. Electrodes 2.5 to 15 mm. apart.
Lead	Acetic acid, 650 to 750 cc. Perchloric acid, 350 to 250 cc.	1 to 2			3 to 5	0000 paper, horizontal anode. Use current density of 20 to 25 for 1 to 2 min. to remove flowed layer. Copper cathode.
Pb-Sn alloy	Same as above	2				
Tin + 3% Sb	Same as for tin, above	9 to 15	25 to 40†	15 to 22	8 to 10	Same as for tin, above.
Copper + 3.2% Co Copper + 2.4% Fe	Orthophosphoric acid sp.gr. 1.35	0.07	2		5 to 10	Polish to 000 paper. Copper cathode. Electrodes horizontal and ½ in. apart.
Brass, 70-30,‡ (1 constituent)	Orthophosphoric acid 430 g. per l.	13 to 15	1.9			
66.7-33.3 Brass‡	Orthophosphoric acid 990 g. per l.	2.5 to 3				
Two-constituent 60-40 brass ‡	Pyrophosphoric acid 530 g. per l.	9 to 11	1.9			
Aluminum bronze; Leaded bronze (85 Cu, 10 Sn, 3 Zn, 2 Pb)	Orthophosphoric acid 990 g. per l.	1 to 2				
Phosphor bronze, silicon bronze, monel, nichrome, nickel, and ‡ metals	Methyl alcohol (abs.), Nitric acid (conc.), 2 parts to 1 part		40 to 50†	20 to 30	Seconds	Cathode of stainless steel cloth in bottom of dish. Distance between electrodes ½ to 1 in.

*Current density in amperes per square decimeter. †External applied voltage. ‡See last item in table.

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