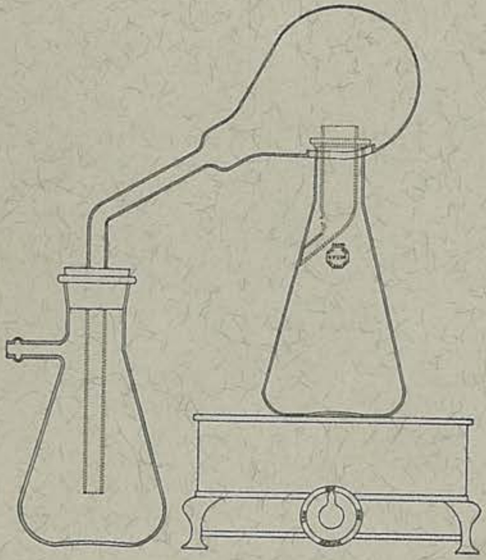
The Wet Ashing of Organic Matter Employing Hot Concentrated Perchloric Acid

THE LIQUID FIRE REACTION

by

G. FREDERICK SMITH



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The accompanying reprinted material was made necessary because of the active interest expressed by chemists both here and abroad. This exhausted the usual original number of reprints ordinarily distributed. This fact attests to the timeliness of the procedures described and to the active application of the same to the solution of problems associated with a widely employed analytical process of great potential value.

A valuable contribution to the same subject has been made by A. G. Hamlin,

"JOURNAL OF THE TEXTILE INDUSTRY"
Vol. 40, T343 (1949)

This valuable scientific contribution to the field of "LIQUID FIRE REACTIONS" was, through oversight, not referred to in the accompanying material. This paper was entitled:

Destruction of Organic Matter by Acid Ashing,
With Particular Reference to the Use of Perchloric Acid
in the Oxidation of Textile Materials.

G. FREDERICK SMITH, Ph.D.
Professor of Chemistry, University of Illinois
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THE WET ASHING OF ORGANIC MATTER EMPLOYING HOT CONCENTRATED PERCHLORIC ACID

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G. FREDERICK SMITH

The Noyes Chemical Laboratory of the University of Illinois, Urbana, Ill. (U.S.A.)

INTRODUCTION

The determination of traces of metal contaminants in the presence of large amounts of organic matter is habitually solved following a dry ashing procedure. An example is the determination of lead in such organisms as bone, liver, kidney or urine. The determination of the alkali metals, magnesium, phosphorus and other elements in hay, grain and feeds is another example. The estimation of copper in fish or oysters is a further illustration. The determination of small amounts of iron in leather formerly involved a dry ashing procedure. Many other illustrations could be cited.

All dry ashing procedures in the destruction of organic matter demand the use of rather large samples and a multiplicity of equipment. The electric muffles, platinum dishes, and other necessary apparatus, stamp these dry ashing procedures to be as troublesome as they are time-consuming.

The determination of chromium in chrom-tanned leather and medical catgut sutures serves to illustrate. A dry ashing procedure was formerly universally applied. In these cases chromium occurs in the 1-10 percentage range. A 1-3 g sample is sufficient for a macro-volumetric procedure. The dry ashing procedure retains the chromium in the residue from burning as acid insoluble chromic oxide. The dry ashing residue must be fused in a sodium carbonate-sodium peroxide flux in platinum. The chromic oxide of the ash is thus converted to sodium chromate. The ash fusion is dissolved in water and acid and the peroxide destroyed by boiling. The chromic acid thus formed may then be estimated by any of several common procedures.

Probably 50 per cent of the present production of leather involves the chrom-tanning process. The control laboratory for the tanning industry now employs a wet oxidation procedure exclusively of this determination of chromium in leather. The improved procedure involves the wet oxidation of the sample in hot concentrated perchloric acid. The chromium is simultaneously oxidized to chromic acid. The dissolution of the sample and the quantitative destruction of the organic matter requires 10-15 minutes. The excess oxidant (perchloric acid) need not be removed. Simple cooling and dilution only is required. The chromic acid is then estimated employing standard ferrous sulfate.

A tedious, complicated, formerly exclusively employed analyitcal procedure in the routine leather tanning control laboratory has thus been eliminated. It is replaced by a rapid, accurate, and universally accepted routine, perchloric acid wet ashing procedure[1].

The dissolution of samples of animal or vegetable origin by wet oxidation using perchloric acid in preparation for the determination of either metallic components or the non-metals sulfur and phorphorus, has been aptly designated *"The liquid fire reaction"*.

The dissolution of a sample of animal origin, such as liver, lung, kidney, hide, or bone, by oxidation using hot concentrated perchloric acid involves a complex series of reactions. Complicated organic structures are broken down into a series of fragments or degradation units. Each of these have characteristic reaction kinetics in contact with hot concentrated perchloric acid. The same type reaction mechanisms are involved in "the liquid fire reaction" as applied to samples of vegetable origin such as hay, grain, seeds, nuts, beans, wood, coal and many other products.

The study is here made of the oxidation of possible fragmentation degradation products of animal and vegetable origin using hot perchloric acid. Practical application of the procedure to a wide variety of natural products is subsequently described.

The oxidation of formic and oxalic acids by hot concentrated (70%) *perchloric acid employing vanadium as catalyst.* (*Generalities*)

Mixtures of glacial acetic acid and 70% perchloric acid have been subjected to boiling temperatures and no oxidation of acetic acid results. Instead the boiling of the mixed acids effects their separation. The lower boiling acetic acid is recovered unchanged in the distillate. This leaves, at 203° C, azeotropic compositioned perchloric acid of 72.5% strength. Thus the glacial acetic acid distillate may be condensed and recovered. There is no darkening of the hot mixed acids or other indication of a reaction of oxidation. There further is no indication that a perchloric acid-acetic acid azeotrope is formed. The separation of acetic acid from the boiling mixture is, however, slower than the individual boiling points of the two acids would indicate. This is because of the known compound formation between acetic acid and perchloric acid[2].

For propionic acid mixtures with perchloric acid essentially the same situation prevails. In this case, however, no known compound formation exists.

Acetic acid dissolved in 4 normal perchloric acid does not oxidize at a temperature of 55-70°C upon the addition of excess Ce(IV)[3], which condition provides an oxidation potential of 1.75 volts[4]. It is therefore clear that, since 70% perchloric acid at 180-200° C does not oxidize acetic acid, it requires a potential considerably greater than 1.75 volts to cause such oxidation reaction to occur (assuming that the oxidation reaction proceeds at a measurable rate).

The mechanism of the catalytic action of vanadium in the oxalic acid by hot concentrated (70%) *perchloric acid.*

The oxidation potential of vanadic acid according to the reaction, $VO_3^- + e^- + 4H^+ \rightarrow VO^{+2} + 2H_2O$, in strong acid solution has a value of approximately 1.45 volts. This value is exceeded in magnitude by 0.4 to 0.5 volts by hot concentrated (70%) perchloric acid. For this reason, if perchloric acid contains some organic material, such as oxalic acid, which may be easily oxidized by hot concentrated perchloric acid according to its reaction, $4HClO_4 + \triangle \rightarrow Cl_2 + 2H_2O + 2\text{-}O_2$, the reaction kinetics may be such that the oxidation of oxalic acid by vanadic acid is much more rapid. This will be conditioned upon the vanadate-vanadyl potential being high enough to oxidize the oxalic acid (or other oxidizable material which may be present). Provided, therefore, that the oxidation of V(IV) to V(V) is a more rapid reaction at a given temperature and concentration of perchloric acid than is the oxidation of the oxidizable material through perchloric acid, then a small quantity of vanadium will serve as catalyst for the given oxidation. Conditions thus described provide for the rapid reversal of the reaction, $VO_3^- + e^- + 4H^+ \longleftrightarrow VO^{+2} + 2H_2O$.

The same situation exists provided chromium is substituted for vanadium as catalyst. Here, however, there is an important limiting factor. The oxidation potential of the reaction $Cr_2O_7^{-2} + 6e^- + 14H^+ \rightarrow 2Cr^{+3} + 7H_2O$ attains a value in strong mineral acid solution of approximately 1.36 volts. Should this potential be too low to bring about the oxidation of a given material its use will be ineffective as catalyst and its addition fail to effect the reaction rate. In this case the reaction of oxidation will depend only on the oxidation potential of 70% perchloric acid at the temperature employed. The chromium oxidation from green chromic ion to orange dichromate is useful as an indicator proving the completion of the oxidation of any organic matter.

One valuable feature in the use of concentrated perchloric acid as oxidant at temperatures of 160-200° C is the tenacity with which it retains its available oxygen. In addition perchloric acid is hydrated and the loss of this water of hydration, when the 60-65% acid is heated gradually from 160° to 203°, does not go beyond nor exceed that of the azeotropic composition. Thus water is expelled slowly up to an acid composition of approximately 72.5% under ordinary atmospheric pressures. As the strong 60-65% perchloric acid is concentrated by boiling its oxidation potential increases slowly and stepwise. In other words the oxygen made available by its gradual decomposition to give chlorine and oxygen is controlled, and by regulation of the acid strength and by controlling its temperature, there may be adjusted a delicate balance between oxygen supply and demand. Such controlled oxidation reaction conditions are not provided by any other, widely applicable oxygen carrier, variable as desired by regulation of reaction temperature and reagent concentration.

The oxidation of oxalic acid by hot concentrated perchloric acid with vanadium catalysis

Hot 70% perchloric acid (20 ml) containing 4 mg of chromium (added as $K_2Cr_2O_7$) were heated to 195° in a 500 ml Vycor Erlenmeyer flask. The flask and contents were provided with a refluxing still head and fume eradicator as shown in Fig. 1 and maintained at 190-195° C by the electric hot plate shown in the reaction assembly. A sample of 5.00 grams of crystalline oxalic acid, $H_2C_2O_4 \cdot 2H_2O$, was added and the time required for complete oxidation noted. The point of complete oxidation is indicated by the chromium added as indicator. The hot perchloric acid solution of oxalic acid reduces the Cr(VI) to Cr(III) and the reaction solution is green. There is a brisk evaluation of CO_2 as the oxalic acid is oxidized and when this reaction is complete the Cr(III) rapidly oxidized to Cr(VI) with a color change from green to orange. The same reaction procedure is repeated with the addition of 0.15 to 0.75 mg of vanadium (added as saturated NH_4VO_3 dissolved in 70% perchloric acid) to serve as catalyst in reducing the time rate of oxidation. The results from a series of reactions are given in Table I.

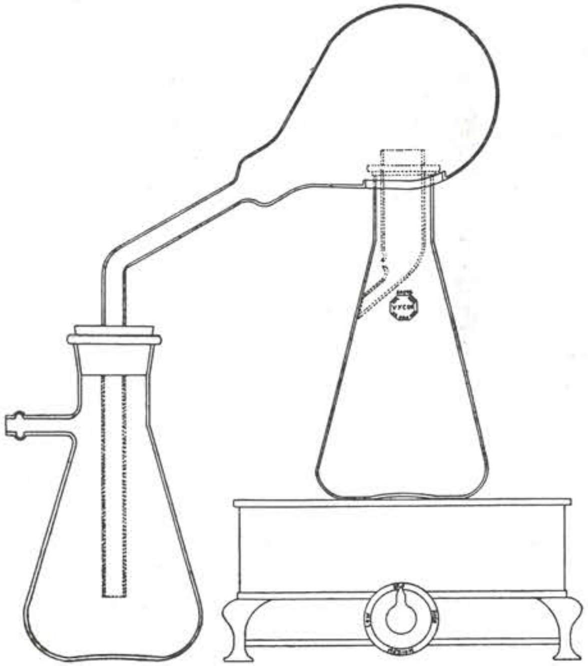

Fig. 1. Wet oxidation apparatus with refluxing still head and fume eradicator (aspirator bottle to serve as scrubber using dilute lye as absorbent).

TABLE I

THE OXIDATION OF OXALIC ACID BY 70% PERCHLORIC ACID AT 195-200° C WITH AND WITHOUT VANADIUM AS CATALYST

Oxalic acid taken 5.00 g, $H_2C_2O_4.2H_2O$· 20 ml 70% $HClO_4$. 10 mg $K_2Cr_2O_7$ employed as indicator. Vanadium added as NH_4VO_3 in 70% $HClO_4$, (0.1 ml = 0.15 mg V).

Vanadium added in mg	0.0	0.15	0.30	0.45	0.60	0.75
Reaction time in minutes	9.0	5.75	4.25	3.25	1.75	1.15

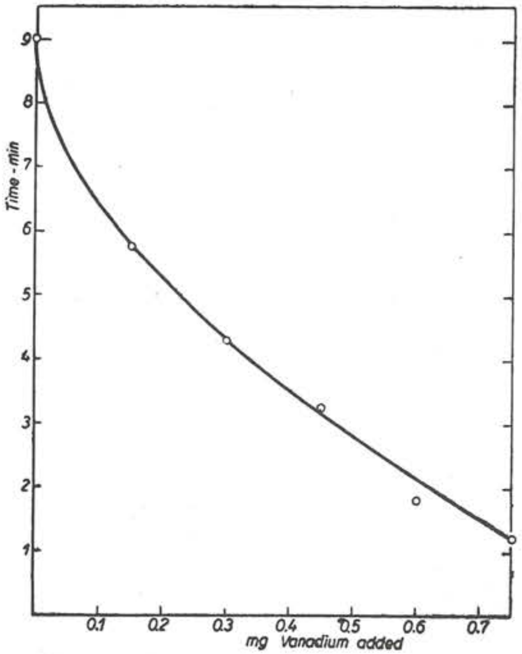

Fig. 2. Time rate of oxidation of $H_2C_2O_4 \cdot 2H_2O$ (5g) as catalyzed by vanadium.

The data of Table I are shown graphically in Fig. 2. The data of Table I indicate that the catalysis by vanadium is due to the instantaneous reaction of the vanadate-vanadyl couple, $VO_3^- + e^- + 4H^+ \longleftrightarrow VO^{+2} + 2H_2O$, in alternate directions. The reaction of the oxidation of oxalic acid by hot concentrated perchloric acid is not catalyzed by the Cr (VI)—Cr (III) couple as is shown by the fact that increased amounts of chromium do not alter the time interval of complete oxidation. Therefore, for the reactions of Table I chromium serves only as an indicator. The oxidation of oxalic acid from these facts requires a potential in excess of the Cr(VI)—Cr(III) couple but less than that of the V(V)-V(IV) couple. Since vanadium serves as catalyst the oxidation potential of hot 70-72% perchloric acid is sufficient to oxidize V(IV) to V(V) at an estimated potential of 1.8 to 1.95 volts, more rapidly, by far, than oxalic acid is oxidized by hot concentrated perchloric acid alone.

A hot perchloric acid solution of oxalic acid may be oxidized instantaneously by the addition of larger additions of vanadium than that indicated in the experiments of Table I.

The reactions of oxidation of oxalic acid by hot concentrated perchloric acid as catalyzed by vanadium are:

$$4\,\mathrm{HClO_4} + \triangle\ (195^\circ\ \mathrm{C}) \rightarrow 2\,\mathrm{Cl_2} + 7\,\mathrm{O_2} + 2\,\mathrm{H_2O}$$
$$14\,\mathrm{VO^{+2}} + 8\,\mathrm{HClO_4} \rightarrow 4\,\mathrm{Cl_2} + 14\,\mathrm{VO_3^-} + 4\,\mathrm{H_2O}$$
$$\mathrm{C_2O_4^{-2}} + 2\,\mathrm{VO_3^-} + 2\,\mathrm{H^+} \rightarrow 2\,\mathrm{CO_2} + 2\,\mathrm{VO^{+2}} + \mathrm{H_2O}$$

The oxidation of formic acid by hot concentrated perchloric acid

Since hot concentrated perchloric acid does not oxidize acetic acid, it might be assumed that formic acid would likewise be unattacked. Such is not the case. A sample of crystalline sodium formate when added to 70% perchloric acid at 195° C results in its very rapid oxidation to $\mathrm{CO_2}$ with a gush of gas evaluation.

For the purpose of estimating a time factor the reactants are best mixed at room temperature and then brought to 195°C on the hot plate. Chromium as indicator was again used. Its indicator effect differs from its reaction in the case of oxalic acid oxidation. The Cr(VI) is immediately reduced to Cr(III) which then forms a complex with formic acid which is colorless in low concentrations and faint blue in higher concentrations. After all uncomplexed formic acid has been destroyed a slow oxidation of the chromium-formate complex begins with the formation of the green chromic ion. This first formation of a green color indicates the practically complete oxidation of formic acid. Approximately 15 minutes is required for the formation of red chromic acid with the oxidation of the last trace of formic acid complexed with chromium.

Experimentally, 5 grams of anhydrous crystalline sodium formate was placed in a 500 ml Vycor Erlenmeyer flask and 20 mg of potassium dichromate added. After the addition of 20 ml of 70 percent perchloric acid, the flask and contents were placed on a 195° hot plate and allowed to react until the first green color appeared. The time required for the flask and contents to attain 195°C was found to be five minutes. At this point the reaction of oxidation becomes rapid

as indicated by the rapid evolution of carbon dioxide. The reaction mixture, at first colorless, turns green in thirteen minutes of heating which marks completion of the oxidation except for the small amount of formate held to retarded oxidation in its complex with chromium.

A repetition of the test oxidation with the addition of 0.75 mg of vanadium as catalyst gave duplicate experimental results. Allowing five minutes heating interval to attain a reaction temperature of 195°, which marked the point at which the oxidation reaction was initiated, the time required for the oxidation to be completed is eight minutes. Neither vanadium nor chromium serves as a catalyst for this oxidation. The reaction temperature at the completion of the oxidation was found to be approximately 210° as a result of the accumulation sodium perchlorate from the sodium formate originally added.

From the fact that both formic and oxalic acids may be so readily oxidized and removed from solution by the use of hot concentrated solutions of perchloric acid, it would be predicted possible to determine acetic acid in the presence of the other two. The operation would involve carrying out the reaction of oxidation in an apparatus provided with a reflux condenser to prevent loss of acetic acid by volatilization and the subsequent determination of acetic acid. This would be accomplished, presumably, by the titration of acetic acid in the presence of perchloric acid. This titration of acetic acid with standard base (in which reaction perchloric acid[5] does not interfere), has been described.

The reaction between hot concentrated perchloric acid and formaldehyde

The reaction between hot concentrated (70%) perchloric acid and formaldehyde is very slow. Experimentally it would appear that such a combination upon boiling results in the separation of the formaldehyde by volatilization. Then upon heating to the boiling point for 4-5 minutes there is a resultant mild explosion. The destruction of formaldehyde by digestion of a mixture of concentrated perchloric acid and nitric acid is very rapid even at moderately elevated temperatures. Thus if formaldehyde should be a degradation product in "the liquid fire reaction" its formation involves no complications. Simply add nitric acid to destroy promptly any formaldehyde present.

The oxidation of tartaric acid by hot concentrated perchloric acid

A sample of ammonium tartrate weighing 1 g was added to a 20 ml sample of 70% perchloric acid in a 500 ml Vycor Erlenmeyer flask. A 20 mg portion of $\mathrm{K_2Cr_2O_7}$ was added and the reactants heated from room temperature on a 195° hot plate. At 4 minutes the solution was green and at 8-10 minutes it was chocolate brown with evolution of $\mathrm{CO_2}$. There was some carbon char formation. At 27 minutes the solution was green following its apparent complete oxidation. In 15 additional minutes the solution was orange color from $\mathrm{CrO_3}$ formation.

Evidently the complex formation between the chromic ion and tartaric acid is very stable and slow to oxidize to CrO_3 as was the case with formic acid.

The reaction was repeated with the single modification that 1.5 mg of vanadium was added. At six minutes heating the solution turns straw colored and then chocolate brown in color. From 6-16 minutes CO_2 was evolved but no char resulted and the solution was green after all organic matter was destroyed. It required but 3 minutes continued heating until the solution was orange from CrO_3 formation.

Upon repeating the same conditions as just described with the addition of 2 ml of concentrated nitric acid it was found that at 4-6 minutes heating there was CO_2 evolution with little or no oxides of nitrogen being evolved and the solution was colorless. After 7 minutes the solution was green and all the organic matter was destroyed. At 15 minutes reaction time the solution was orange in color because of CrO_3 formation.

From these reactions it is seen that oxidation of tartaric acid by hot concentrated perchloric acid results in no violent reactions. Vanadium serves as an efficient catalyst in reducing the required oxidation time to half the period required in its absence also with the elimination of char formation. The best combination involves the use of vanadium as catalyst together with nitric acid to prevent the formation of dark brown degradation products and further reduce reaction time. The next experiment was made with the substitution of tartaric acid for ammonium tartrate.

A four gram sample of the crystalline tartaric acid was allowed to react with 20 ml of 70% perchloric acid to which was added 6 ml of concentrated nitric acid and 1.5 mg of vanadium as catalyst. At 195° C for 4 minutes no appreciable NO_2 was formed or CO_2 evolved and the solution was colorless. At 7 minutes NO_2 fumes were evolved and the solution was green. At 11.25 minutes an exothermic reaction set in with vigorous evolution of CO_2 and the solution was straw colored. At 11.5 minutes the exothermic reaction was at its maximum and there were copious white fumes from perchloric acid. At 11.75 minutes the solution turned orange from green due to CrO_3 formation and complete oxidation.

The oxidation of citric acid by hot concentrated perchloric acid

A sample of 1 g of citric acid was reacted as described above for tartaric acid. The reactants were 20 ml of 70% perchloric acid plus 20 mg of $K_2Cr_2O_7$ and 1.5 mg of vanadium. At 195° the solution was green in 4 minutes. CO_2 was being evolved at 6 minutes. At 10 minutes the solution was chocolate brown with one-half inch of foam from CO_2 evolution and there was some carbon deposited. At 15 minutes the solution was green and at 18 minutes the solution was orange owing to CrO_3 formation.

The oxidation reaction was twice repeated first with 1.5 mg of vanadium and again with 3.0 mg of vanadium. In each case 2 ml of concentrated nitric acid was also added. In both cases the reaction mixture was colorless with no NO_2 fumes. After 4 minutes the solution was still colorless, but NO_2 fumes and CO_2 evolution was brisk. After 5 minutes the solution was straw colored giving an exothermic activity with copious CO_2 evolution and it at once turned green. It required 20 additional minutes to bring about the CrO_3 oxidation.

From the last two experiments it is seen that nitric acid prevents the oxidation passing through the chocolate brown stage (partial carbonization or carmelization) and the presence of a small amount of vanadium speeds up the oxidation markedly.

A 4 g sample of citric acid was digested on a 195° hot plate in 20 ml of 70% perchloric acid with 10 ml of concentrated nitric acid. A 20 mg portion of $K_2Cr_2O_7$ was added together with 1.5 mg of vanadium. At 3.5 minutes there was no apparent oxidation and the solution was colorless. After 4 minutes reaction had just begun and the solution was straw colored from NO_2 and there was some CO_2 evolution. At 5 and at 6 minutes copious NO_2 fumes appeared and there was brisk evolution of CO_2 and the solution straw colored. At 7 minutes an accelerated exothermic reaction set in and at 10 minutes the solution was green and apparently all citric acid was destroyed. In an additional 11 minutes the CrO_3 formation resulted.

The influence of nitric acid as applied to the "liquid fire reaction"

In the case of the oxidation of oxalic, formic, citric and tartaric acids by digestion with hot concentrated perchloric acid as in the previous experiments, it has been shown that even though the organic materials have pronounced reduction potentials, no explosive reactions resulted. The oxidation potential provided by hot concentrated perchloric acid is known to be approximately 1.9 to 1.95 volts. Violent reactions would logically be predicted. The above-cited organic materials contain the carboxylic acid, methylene, and alcoholic OH groups.

Violent results may be encountered in oxidations involving hot concentrated perchloric acid.

This is for the reason that hot concentrated perchloric acid is a dehydrating agent. If ethyl alcohol is heated with concentrated perchloric acid, these dehydrating properties result in the esterification of the alcohol, ethyl perchlorate is formed and explosions result. Cellulose, sugars and polyhydric alcohols may be considered to be in the same category of reactants. None of these products are reactive with cold 72.5% perchloric acid. All, including cellulose, dissolve in 72.5% perchloric acid to give colorless solutions. Absolute ethyl alcohol may be mixed at ordinary temperatures with 72.5% perchloric acid without the least necessary apprehension. Pyrogallic acid dissolves in concentrated perchloric acid to give a colorless solution. This is not true in the case of nitric acid, both reactants at ordinary temperatures. In all these cases if the materials are in contact with hot concentrated perchloric acid explosions would certainly frequently result.

By what circumstance may "the liquid fire reaction" be applied with safety to the general destructive oxidation of organic materials?

An assurance involves the use of perchloric acid with the addition of nitric acid as a temporizing or damping reactant. By the use of nitric acid sugars, polyhydric alcohols, formaldehyde, and cellulose among other organic materials are readily oxidized and destroyed. Following the action of cold concentrated nitric acid, then the same reagent at rapidly rising temperatures, all readily oxidized organic matter is destroyed. The indicator for this oxidation is the evolution of copious fumes of brown oxide of nitrogen. When the reaction of nitric acid is complete, the high boiling, 60 to 72.5% perchloric acid, volatilizes and displaces the boiling nitric acid. With its elimination the 60% perchloric acid, upon further heating, concentrates slowly and progressively to the 72.5% water azeotrope. There is a steady stepwise increase in oxidation potential. All but the most difficultly oxidizable organic matter is thus more intensely reacted upon and destroyed. It is in this stepwise increase in oxidation potential that complex organic structures are broken up into fragmentation degradation products such as formic and oxalic acids. This fact accounts for their smooth rapid oxidation and elimination without carbonization and without violence of reaction.

The oxidation of cyclic ring nitrogen compounds

Such organic compounds as quinoline and other polycyclic ring nitrogen compounds are very resistant to destruction by oxidation in contact with hot concentrated perchloric acid. In case such materials are encountered several expedients apply effectively. Often the reaction of the destructive oxidation is catalyzed by the presence of a small amount of chromium or more effectively by the use of small additions of vanadium. In the determination of sulfur in coal following wet oxidation by hot mixed concentrated nitric and perchloric acids[6] use is made of the chromium or vanadium catalytic action. The oxidizing action may be made more intense by the use of mixed nitric, perchloric and sulfuric acids. In this application after the nitric acid has reacted at 140-150° and the excess is expelled, continued heating produces reaction potentials which continually increase first due to a steady increase in temperature and concentration of perchloric acid from 60 to 72.5%. Further heating then results in the formation of 80-100% perchloric acid in gradual stages. The accompanying gradual increase in oxidation potential provides for the destruction of the most stable aromatic nitrogen compounds. There is seldom need for such drastic treatment. The

process is somewhat objectionable because of the formation of insoluble calcium sulfate. In the absence of sulfuric acid any calcium present remains in solution as calcium perchlorate.

The oxidation of sulfur by hot concentrated (72.5%) perchloric acid

Concentrated perchloric acid (the boiling water perchloric acid azeotrope, B.P. 203° C) oxidizes elemental sulfur smoothly and without hazard. If a sample of 1-2 grams of flowers of sulfur are added to a sample of 12-20 ml of boiling concentrated perchloric acid the sulfur melts and floats on the surface of the boiling acid. It is rapidly oxidized to volatile and gaseous sulfur compounds with but 25 % or less of the sulfur being retained as sulfuric acid by the reaction mixture. The reaction is not in the least hazardous.

The oxidation of organic compounds by the persulfate ion in warm dilute sulfuric acid as catalyzed by the presence of silver has been described[7] by Feigl and Schäffer. In the decomposition of cupferrates, nickel dioximes, tannates, oxinates, methylene blue, and acid-base indicators among other organic materials, the organic matter is efficiently destroyed. By this process certain of the organometallic precipitates (such as Co(III)-α-nitroso-β-naphthalate) are not destroyed and in the case of the thio-compounds elemental sulfur is formed. By the perchloric acid decomposition of sulfur containing organic compounds no elemental sulfur can form and if the combination of hot concentrated perchloric acid with concentrated nitric acid is used as mixed oxidant, all the sulfur is retained after oxidation as sulfuric acid. This principle has been applied to the solution of copper sulfide ores as described by Diehl and Smith[8]. In the use of nitric acid as solvent for this purpose there results an isolation of elemental sulfur which complicates the sulfide ore dissolution.

Hot concentrated perchloric acid oxidized phosphorus in its lower valence states to phosphoric acid or phosphate in the absence of nitric acid. The oxidized phosphorus is retained quantitatively. It may be precipitated as the "yellow precipitate" in the presence of perchloric acid without attendant complications.

PRACTICAL APPLICATIONS IN THE WET OXIDATION OF NATURALLY OCCURRING ORGANIC MATERIALS

Important previous applications of routine control analytical processes

The analysis of chrom tanned leather[1] and medical catgut for chromium[9] has been previously cited. Hundreds of thousands of such determination are probably applied annually in the tanning industries. The determination of sulfur in rubber is a much used nitric-perchloric acid wet oxidation[10, 11]. The determination of very small amounts of iron in wine accounts for probably 100,000 annual control analyzes following the wet oxidation of the sample containing alcohol, sugar and

TABLE II

THE OXIDATION OF OLIVE OIL, SPICES, NUTS, TEA AND COFFEE BY HOT MIXED NITRIC AND PERCHLORIC ACIDS WITH AND WITHOUT VANADIUM AS CATALYST

(10.0 ml of concentrated nitric acid Sp. Gr. 1.42 plus 15 ml of 70 % perchloric acid for each oxidation. Hot plate temperature 235° C — $K_2Cr_2O_7$ added = 20 mg — Digestion apparatus assembly as previously described.)

Sample Taken	Sample Wt. g	HNO_3 Reaction Interval min.	$HClO_4$ Reaction Interval min.	$HClO_4$ Reaction Color	Conversion Time Green, Cr^{+3} to Orange, Cr^{+6} min.	Vanadium Added mg	Remarks
Nutmeg	1.0	1- 5.5	5.5-16.0	Chocolate Brown	1.0	None	Smooth reaction of $HClO_4$ oxidation
Olive Oil	0.5	1- 9.5	7.5-16.5	,, ,,	10.0	None	HNO_3 reaction mild
Caraway Seed	3.0	1- 4.5	5.5-14.0	,, ,,	6.5	None	HNO_3 reaction intense
Pecan Nuts	3.0	1- 4.0	4.5-33.5	,, ,,	24.5	None	HNO_3 reaction intense
Pecan Nuts	3.0	1- 3.5	3.5- 7.5	,, ,,	4.5	9	Both acids react vigorously
Ground Mustard	3.0	1- 4.5	4.5-15.0	,, ,,	5.5	None	NHO_3 reaction mild
Ground Pepper*	1.0	1- 5.0	5.0-12.5	,, ,,	3.0	None	HNO_3 reaction intense
Ginger*	1.0	1-10.5	10.5-12.0	Olive Green	Indeterminate	None	HNO_3 reaction intense
Tea	3.0	1- 4.5	4.5- 9.0	Chocolate Brown	3.0	9	HNO_3 reaction intense
Cloves	3.0	1- 3.0	3.0- 7.0	,, ,,	3.0	9	HNO_3 reaction intense
Coffee*	3.0	1-12.0	12.5-20.0	,, ,,	7.5	None	HNO_3 reaction intense
Coffee**	3.0	1- 6.0	6.0- 9.5	,, ,,	1.5	9	HNO_3 reaction intense
Cinnamon	3.0	1- 4.0	4.5- 6.5	Olive Green	2.0	None	HNO_3 reaction color blood red. Both HNO_3 and $HClO_4$ react intense

* The addition of vanadium as catalyst without effect in a duplicate experiment.

** Nitric acid added 15 ml instead of 10.

other more difficultly oxidizable organic matter[12]. The analysis of feeds, hay, grain and alfalfa [13] for the determination of phosphorus, the alkali metals and magnesia is a very popular routine procedure. Many other examples could be cited.

Using the same apparatus previously described, the following products have been chosen to illustrate the multiplicity of practical wet oxidation ("liquid fire" oxidation procedures).

The oxidation of olive oil, spices, nuts, tea and coffee

The results from this series of wet oxidations are given in Table II.

The oxidation of proteins

Proteins in general constitute a large group of a general type occurring in meat, casein, albumin, keratin, haemoglobin, elastin and collagens. The "liquid fire reaction" as applied to the destruction of organic matter such as oysters, fish, cheese, eggs, bones, blood and hair fall in this category. The proteins contain 50-55% of carbon, 15-17.5% of nitrogen, 19-24% of oxygen, hydrogen 6.5-7.5% and up to 5% of sulfur and in some cases phosphorus. They contain a major portion of carbon as the carbonyl group and should be predicted to have smooth oxidation reactions with both hot concentrated nitric and perchloric acids. By this mixed acid digestion, the total sulfur and phosphorus content is retained as sulfuric and phosphoric acid together with any alkali or heavy metal contaminants, if present.

As a typical example of protein oxidation and mineralization a case of the destructive oxidation of the popular food stuff, dried beef, was selected for study. The results are given in tabular form in Table III.

From an examination of the data of Table III it may be seen that the hot nitric acid is capable of oxidizing much of the material but its destructive action leaves the major portion of the organic matter to be oxidized after the nitric acid has been dispelled from the reaction mixture. The perchloric acid reaction may be tempered by using a lower reaction temperature, using vanadium as catalyst, or best by the use of larger proportions of perchloric acid. By the use of larger quantities of perchloric acid the rate of increase in acid strength (and accompanying gradual increase in oxidation potential) as the acid concentration passes gradually from 68-70% and on up to the $HClO_4$-H_2O water azeotrope at 72.5% acid concentration, more time is allowed for the perchloric acid oxidation. These facts permit the stepwise oxidation of the more easily destroyed organic degradation products at the lower perchloric acid concentration and at lower required oxidation potential. The same damping effect may be had by addition of water for dilution of the perchloric acid concentration after the nitric acid reaction is complete. A convenient modification in apparatus for addition of

TABLE III

THE OXIDATION AND MINERALIZATION OF DRIED BEEF BY REACTION WITH HOT MIXED CONCENTRATED NITRIC AND PERCHLORIC ACIDS

(All tests included 20 mg of $K_2Cr_2O_7$ as indicator to denote complete oxidation of organic matter.)

Sample Wt. g	HNO_3 Sp. gr. 1.42 ml	70% $HClO_4$ ml	Vanadium Added mg	Hot Plate Temp. 0° C	Time of HNO_3 Reaction min.	Time of $HClO_4$ Reaction min.	$HClO_4$ Color Reaction	Remarks
5.0	10	15	9	235	8	9	Green	Vigorous HNO_3 reaction with much foaming. Exothermic $HClO_4$ reaction
10.0	10	15	None	215	15	16	Dark Brown	Same as above
10.0	10	15	9	235	3	4	Dark Brown	HNO_3 reaction vigorous with 2 inches foam. $HClO_4$ reaction exothermic with charring. Final reaction of $HClO_4$ caught fire.
10.0	22	15	9	235	4.5	5.5	Dark Brown	Same as above.
10.0	15	25	9	235	3.5	9.5	Dark Brown	Final $HClO_4$ reaction exothermic from dark brown to green to light brown with slight carbonization.
8.5	15	25	9	215	13.0	13.0	Dark Brown	Same as above. No char.

water or acid is shown in Fig. 3. By either the addition of a few more ml of concentrated nitric acid at the time the exothermic perchloric acid starts, or the addition of a few ml of water, there is an extension of reaction time. This retardation may have a beneficial effect in preventing the formation of dark colored organic degradation products which may otherwise be time consuming in their oxidation.

The results from the study of a list of protein materials is given in Table IV.

From the examination of the data in Table IV it will be observed that the variation in reaction conditions has a marked effect on the results. The variable factors include temperatures, ratio of mixed acids employed, and the presence or absence of vanadium as catalyst.

The best reaction conditions are those which result in a complete oxidation without the formation of dark organic reaction products which give to the reacting

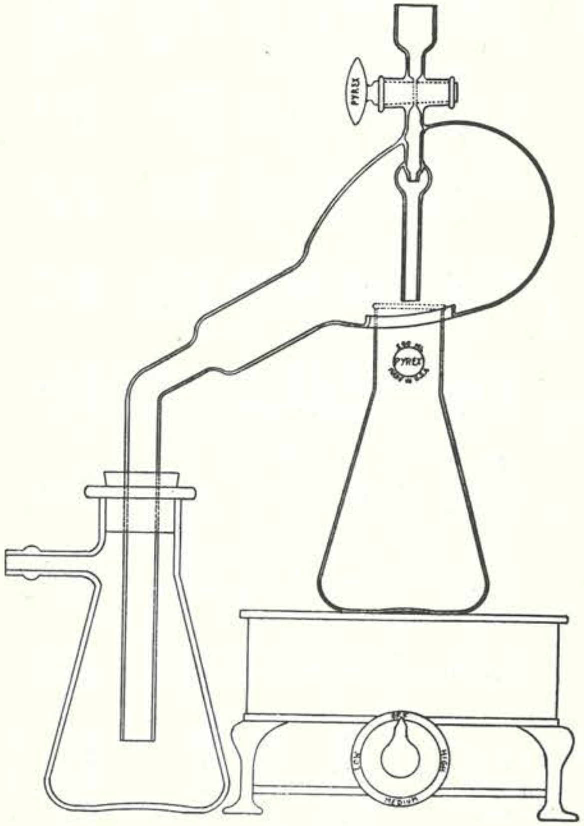

Fig. 3. Wet oxidation apparatus with modified fume eradicator tube.

TABLE IV

THE OXIDATION OF ANIMAL PROTEIN BY HOT CONCENTRATED PERCHLORIC ACID OR ITS MIXTURE WITH CONCENTRATED NITRIC ACID WITH AND WITHOUT VANADIUM CATALYST

(20 mg of $K_2Cr_2O_7$ added to serve as indicator for the completion of oxidation)

Sample Type	Wt. g	HNO_3 67% ml	$HClO_4$ 70% ml	Vanadium Added mg	Hot Plate Temp. °C	Time of Reaction HNO_3 min.	Time of Reaction $HClO_4$ min.	$HClO_4$ Reaction Color	Remarks
Egg White (Hard Boiled)	5.0	10	15	9	235	3.0	6.5	Green	Smooth reaction throughout. No pronounced exothermic surge.
	5.0	10	15	None	230	7.0	32.0	Green	
	1.0	None	20 (60%)	None	210	—	38.0	Chocolate	Omission of HNO_3 modifies reaction unfavorably.
	5.0	10	15	None	235	10.0	17.0	Green	
Hippuric Acid	1.0	10	15	9	235	10.0	12.5	Green	Hippuric acid ($C_6H_5CONHCH_2COOH$) gives C_6H_5COOH and NH_2CH_2COOH upon acidification.
Salmon Fillet (Fresh Frozen)	12.5	15	15	None	230	12.0	23.0	Chocolate	Smooth vigorous reaction throughout.
	12.5	15	15	9	215	7.5	24.0	Chocolate	Final oxidation stage carbonizes then caught fire and burned fast.
	12.5	15	15	None	215	15.0	17.5	Chocolate	Exothermic reaction at 32.5 min. Color from brown to green sudden.
	12.5	30	15	None	215	32.0	88.0	Chocolate	Reaction time consuming but very smooth and temperature throughout.
Halibut Fillet (Fresh Frozen)	12.5	15	15	None	230	15.0	17.0	Chocolate	Smooth vigorous reaction throughout.
Gelatin	3.0	15	15	None	235	12.0	4.0	Chocolate	
	3.0	10	15	9	235	5.0	6.5	Green	Addition of vanadium very beneficial. Alters reaction type.
Casein	2.0	10	15	None	215	13.0	17.0	Chocolate	
	2.0	10	15	0.75	215	13.0	9.0	Green	Vanadium very beneficial. Reaction of $HClO_4$ gave no darkened products.
Oyster (Fresh)	10.0	10	15	None	215	12.0	16.0	Green	$HClO_4$ reaction exothermic.
Egg Yolk (Hard Boiled)	3.0	10	15	None	230	10.0	19.0	Chocolate	
	3.0	20	15	None	230	22.0	9.0	Chocolate	
	3.0	15	30	None	230	15.0	4.0	Chocolate	
	3.0	10	15	9	235	3.0	3.0	Chocolate	Vanadium very effective in oxidation of dark reaction products.
Wool Yarn	3.0	10	15	None	230	4.0	20.5	Green	HNO_3 and $HClO_4$ reaction exothermic.
	3.0	10	15	0.75	215	4.5	10.0	Chocolate	Vanadium speeds reaction at lower temperature.
Pork Rib Bone	3.0	10	15	None	230	8.5	27.6	Green	$HClO_4$ reaction exothermic at end of oxidation.
Fresh Shrimp	5.5	10	15	None	235	10.0	15.5	Chocolate	
	6.5	10	15	9	235	10.0	15.5	Chocolate	No catalytic effect from vanadium.

solution a dark chocolate color. It is to be preferred that the reaction color be either that of NO_2 (a straw color) or green from chromic ion. The destructive oxidation of casein is thus favorably modified by the addition of a small amount of vanadium (0.75 mg). The reaction is not only free from the formation of dark colored reaction products but the oxidation is complete in one-third less time.

The addition of vanadium catalyst may not only fail to prevent the formation of dark organic degradation products, but it may enhance this type reaction. An example is that of the oxidation of fresh salmon meat. In this case the presence of less than 10 mg of vanadium causes an otherwise quiet reaction to catch fire at the end of the reaction period and burn with much vigor. Attempts in this case to prevent the formation of dark reaction products failed if the reaction temperature was lowered or the ratio of nitric to perchloric acid increased.

In the case of the oxidation of boiled egg yolk the presence of vanadium as catalyst was very effective.

It may be said that the studies in the case of the destruction of organic matter by the "liquid fire reaction" were regulated to require short intervals of time with modest additions of oxidizing acids. Without doubt, the time, temperature, and reagent addition variables may bring more acceptable reaction conditions if desired. Conditions are preferable which shorten the oxidation time without undue increase in reaction intensity.

The oxidation of cellulose and similar type products

This type material includes the oxidation of hay, alfalfa, grain, tobacco, wood, straw and cotton. In general such products are destroyed to a major extent by hot concentrated nitric acid. If perchloric acid alone is employed for their complete oxidation, unless quantities are limited and the temperature kept moderate by the use of 60-65% perchloric acid, the reaction will probably be intense resulting in uncontrollable oxidation rates. Fortunately by the use of mixed concentrated nitric and perchloric acids, the reactions of oxidation are smoothly and progressively applied in such manner that no hazard is ever encountered. The mineralization of hay, grain, and animal feed for the determination of phosphorus, calcium, magnesium and the alkali metals is most speedily carried out by digestion by the "liquid fire reaction". As compared with the older process of dry ignition to destroy organic matter, the process is much more rapid and the total recovery of the mineral components and phosphorus more free from troublesome complications.

Some illustrative wet oxidations of this class of materials are given in the data of Table V. This type destructive oxidation of hay, alfalfa, and animal feeds, has been employed previously for example in the work of GIESEKING, SNIDER AND GETZ[13], and others.

TABLE V

THE OXIDATION OF CELLULOSE AND CELLULOSE PRODUCTS, GLYCEROL, AND SUGAR, USING HOT MIXED NITRIC AND PERCHLORIC ACIDS

(20 mg of $K_2Cr_2O_7$ added to serve as indicator of complete oxidation.)

Sample Type	Wt. g	HNO_3 67% ml	$HClO_4$ 70% ml	Vanadium Added mg	Hot Plate Temp. °C	Time of Reaction HNO_3 min.	Time of Reaction $HClO_4$ min.	$HClO_4$ Reaction Color	Remarks
Rhubarb (Dried)	5.0	10	15	None	235	9.5	23.5	Chocolate	Nitric acid action energetic.
	5.0	10	15	9	235	4.5	9.0	Green	Vanadium catalysis of oxalic acid oxidation evident here.
Tobacco	3.0	10	15	None	235	8.5	11.5	Light Brown	Some char formation due to $HClO_4$ oxidation.
	3.0	15	15	None	235	14.0	8.5	Light Brown	Char formation diminished.
	3.0	15	15	9	235	6.5	12.5	Green	No char formation.
Cellulose	1.0	10	15	None	230	5.0	12.0	Green	HNO_3 reaction predominates.
Glycerol	1.0	10	15	None	230	3.0	17.0	Colorless	Practically exclusively a nitric acid reaction.
Cane Sugar	1.0	10	15	None	230	5.0	17.0	Colorless	HNO_3 reaction predominates.
Dried Grass	3.0	10	15	None	230	8.0	19.5	Dark Brown	Both HNO_3 and $HClO_4$ reaction vigorous.

TABLE VI

THE LIQUID FIRE REACTION AS APPLIED TO ION EXCHANGE RESINS AND NYLON

(20 mg of $K_2Cr_2O_7$ added to serve as indicator of complete oxidation.)

Material Oxidized	Sample Weight	67% HNO_3	70% $HClO_4$	Reaction Temp.	HNO_3 Effect	Time for Completion	$HClO_4$ Reaction Type	Remarks
	g	ml	ml	°C	min.	mm		
Dowex 50	1.0	10	15	230	—	20	Colorless	No evolution of NO_2
IR-120	2.0	5	10	215	—	14	Dark Brown	NO_2 absent. Foaming from CO_2 evolution pronounced
Nylon	2.0	None	15	215	—	37	Colorless	Rapid initial CO_2 evolution
Nylon	2.0	10	15	215	10	38	Dark Brown	Rapid CO_2 evolution from both acid reactions

The destructive oxidation of Nylon and artificial exchange resins.

The results from these oxidations are given in Table VI.

Oxidation of motor car lubricating oil

The liquid fire reaction is applied with difficulty to the wet oxidation of organic material which does not dissolve in hot concentrated perchloric acid. Motor car lubricating oil is an example of this type material. Any destructive oxidation reaction must take place at the interface formed by the two immiscible liquids. The two reaction components are deprived of homogeneous, inter-acting, oxidation-reduction, electron exchange. In such case the sample to be oxidized frequently carbonizes extensively during contact with hot concentrated perchloric acid. The reaction resulting from this accumulation of finely divided carbon (and carmelized, semi-soluble carbonaceous degradation compounds), may accelerate, uncontrollably. A deflagration accompanied by a flash of fire of varying degrees of intensity may follow.

The use of chromium or vanadium as catalyst often serves to alter the course of

the reaction materially. The carbonization reaction is modified in such manner as to form degradation products which are more easily oxidized. The reaction kinetics, thus altered, is frequently tempered, and violent interaction effectively retarded.

The addition of concentrated nitric acid to the reaction mixture is found to be most effective. The oxidation of the immiscible organic material is divided between the nitric acid oxidation (at 130-150° C) and the perchloric acid oxidation (at 150-203° C). The organic matter is thus progressively fractionated by acid attack from moderate nitric acid to intense perchloric acid oxidation. The gradual elevation of the temperature is an added reaction rate, controlling factor. The elimination of nitric acid from the boiling mixture results in a gradual elevation of temperature. The oxidation potential due to nitric acid increases accordingly. With the elimination of the nitric acid the perchloric acid reactivity sets in. Its oxidation potential increases as its concentration is augmented by rising temperature. The whole process is thus seen to be one of slowly increased reaction tempo with fractional destructive oxidation of the organic matter effectively controlled.

The determination of sulfur and of phosphorus in motor fuel oil is suggested following the destruction of organic matter by the liquid fire reaction. By the reaction of mixed nitric-perchloric acid, sulfur and phosphorus are oxidized to sulfuric and phosphoric acids. Perchloric acid does not interfere in the precipitation of either barium sulfate or the "yellow" phosphomolybdate precipitate if the determination of sulfur and phosphorus is desired.

The mineralization of motor car lubricating oil

The sample selected was number 20 grade motor car lubricating oil. The oxidant found best for its wet oxidation was a mixture of equal parts of 70% perchloric acid and 67% nitric acid. The temperature selected was a 200° C hot plate. The sample of fuel oil mineralized was approximately one gram for 40 ml of mixed oxidizing acids.

The reaction of oxidation is in two parts. From 140 to 152° C there is a steadily increased reaction tempo with a brisk evolution of NO_2 (from reduced nitric acid), accompanied by a rich lather-like foam surmounting the liquid reactants in the flask.

At a temperature of 152° C there was a recession of foam formation and fumes of perchloric acid suddenly appeared. The reaction at this point was exothermic and the boiling acid immediately turned from a straw color, due to NO_2, to colorless. A white, curdy, insoluble solid material separated at 15-17 minutes heating time and a faint deposition of black carbonaceous deposite sometimes formed which was immediately dispelled. The temperature increased rapidly from 152° to 198° at 15 to 18 minutes and the reaction was complete.

Repetition of the reaction a number of times gave practically identical results.

The use of 1 mg of vanadium as catalyst did not alter the results.

By carrying out the same reaction at a rate regulated by the hot plate temperature to require 2 hours for the complete reaction it is seen to follow three stages of oxidation. The first stage involves mainly reaction by nitric acid accompanied by the liberation of NO_2 with no fumes of perchloric acid. This reaction is complete when the NO_2 is no longer formed and foam production no longer results. The surface of the hot acid in the flask is coated with a colorless oil slick. The second stage of the reaction results in the oxidation of this oil slick to form first a curdy suspension which then oxidizes further forming an emulsion with the hot perchloric acid. As the temperature of the perchloric acid increases and its composition increases gradually to the azeotrope at 200-203°, the last trace of organic matter is oxidized and the boiling acid is colorless or slightly yellow due to formation of chlorine or chlorine oxides. From 15 to 16 ml of concentrated perchloric acid remained in the reaction flask after the reaction of oxidation was complete.

The general aspects of the oxidation are those of a distinctly fractional destruction of first the lower hydrocarbons, then a gradually increased destructive oxidation to leave paraffin type hydrocarbons. Finally, as the paraffin type hydrocarbons are destroyed, they form an emulsion with the boiling perchloric acid which converts a two phase system to essentially an emulsified homogeneous oxidation medium. The last stage of oxidation is smooth and devoid of carbonization although exothermic in kinetics.

An approximately 2 gram sample of No. 20 motor car lubricating oil was heated after addition of 20 ml of 70% perchloric acid only. The sample carbonized badly as the acid temperature reached the boiling point. Finally there was a flask of fire and the reaction mixture during 1 or 2 seconds had all the characteristics of a rocket fuel mixture. The reaction flask remained intact. The refluxing still head (Fig. 1) was ejected from the flask and the fume eradicator was broken. A black deposit of carbon remained to coat both the inside and outside of the reaction flask. An excess of perchloric acid was left in the reaction flask. Apparently most, if not all, the reactivity was in the gas phase rather than in the boiling acid. This phenomenon is obviously the result of reaction between hot vapors of perchloric acid as they passed through the supernatant layer of partially oxidized oil sample.

Tha analysis of fuel oil, and presumably crude oil, by oxidation with mixed nitric and sulfuric acid preparatory to the determination of metallic impurities is thus seen to be practical.

Perchloric acid explosion hysteria

Perchloric acid, beyond all reason, is one of the most feared reagents employed in widespread analytical applications. Perchloric acid on the other hand, in all justice to its scientific accomplishments, should be extolled for its remarkable virtue of exceptional stability. This is justified by examination of the above described experimental procedures.

The oxy-chlorine acids are four in number, hypochlorous, chlorous, chloric, and perchloric acids. Of these the first two are dealt with only in the form of their dilute aqueous solutions. The third (chloric acid) is never prepared in aqueous solutions stronger than 30% because beyond this strength the solutions explode. Only the last can be prepared and stored as the anhydrous, 100%, acid. A new method for its preparation, without apprehension of hazard, has just been described[14]. It is true that a bottle of anhydrous perchloric acid should be stored at very low temperatures to prevent slow, progressive, formation of accumulated decomposition products. Even at ordinary temperatures it may be stored for 20 to 30 days before spontaneous explosion results. The contact of anhydrous perchloric acid with wood, paper, rubber and other organic matter must of course be avoided.

The addition of one mol of water for each mol of anhydrous perchloric acid brings about a remarkable change. The melting point of the anhydrous acid (—112° C) is raised to +49.905°[15]. The crystalline monohydrate of perchloric acid (OH_2ClO_4) may be prepared in any quantity and stored for any extended period of time without the least decomposition or tendency towards explosive instability.

The addition of a second molecule of water to form the dihydrate ($OH_3ClO_4.H_2O$ or $O_2H_5ClO_4$ both the α and β forms being known) produces a material that has been shown to be a primary standard in acidimetry[16] and is a liquid at ordinary laboratory temperatures.

The concentration of dilute aqueous solutions of perchloric acid by heating, beyond 72.5% strength, cannot result at ordinary atmospheric pressures because of the formation of the perchloric acid-water azeotrope. Concentration by heating in vacuo (0-1 mm of mercury) does not permit increase in its strength beyond the dihydrate stage (73.605% $HClO_4$). These facts insure the limitation of acid concentration by heating, as in the above-described experiments, to concentrations which cannot, justifiably, be characterized as possible hazards.

Perchloric acid is now consumed to the amount of one hundred thousand pounds yearly of 70% concentration, as a conservative estimate, for application to "the liquid fire reaction". Its extended application to new analytical control procedures in industrial usage should be extended. The reactions studied as previously described were designed to proceed to completion at a rapid pace. By altering the reaction components and varying reaction temperatures the same ultimate results are possible at either an accelerated or retarded pace depending upon conditions.

SUMMARY

The wet ashing of a wide variety of organic compositions by the action of hot concentrated perchloric acid together with and without nitric acid and vanadium as catalyst has been described. These wet ashing procedures are known as "liquid fire reactions" because, although carried out at temperatures ranging from 100 to 235° C, organic matter is burned to carbon dioxide as completely as by dry ashing at high temperatures in electric heating muffles. The mineral components to be determined in the wet ashed samples are left in the excess of perchloric acid employed as oxygen donor and the often difficult dissolution of ash after the application of a dry ashing procedure is thus avoided. By the process as described the retention of sulfur and phosphorus is quantitative.

The study in detail has been made of the wet oxidation of a wide variety of natural products in 1 to 10 gram sample magnitudes. Apparatus design and reaction limitations have been described. Samples of carbohydrates, cellulose products, proteins and hydrocarbons in various natural organic products have been studied. The reaction mechanism has been postulated, the influence of vanadium as catalyst studied and temperature effects demonstrated. New analytical applications have been suggested.

RÉSUMÉ

L'auteur décrit une méthode de ,,minéralisation" pour un grand nombre de composés organiques, au moyen d'acide perchlorique, avec ou sans les catalyseurs, acide nitrique et vanadium. Ces procédés de minéralisation sont dits ,,liquid fire reactions", car ils s'effectuent à des températures comprises entre 100 et 235° C; la substance organique est transformée en anhydride carbonique, aussi quantitativement que par combustion sèche à hautes températures dans un four à mouffles électrique. Les composés minéraux à doser restent en solution dans l'excès d'acide perchlorique, (utilisé comme donneur d'oxygène); les difficultés de mise en solution sont ainsi évitées. Par ce procédé on retrouve quantitativement le soufre et le phosphore. Une étude systématique a été effectuée sur un grand nombre de composés variés (échantillon de 1 à 10 mg): hydrates de carbone, produits cellulosiques, protéines et hydrocarbures, dans différents produits naturels organiques. Le mécanisme de la réaction a été établi; l'influence du vanadium comme catalyseur a été étudié, ainsi que les effets de la température. De nouvelles applications analytiques sont proposées.

ZUSAMMENFASSUNG

Es wurde die Veraschung einer grossen Anzahl organischer Gemenge auf nassem Wege durch die Einwirkung von heisser konzentrierter Überchlorsäure zusammen mit oder ohne Salpetersäure und Vanadium als Katalysator beschrieben. Diese Verfahren der Veraschung auf nassem Wege sind als ,,flüssige Feuerreaktionen" bekannt, da, obwohl sie in einem Temperaturbereich zwischen 100 und 235° durchgeführt werden, organische Stoffe ebenso vollständig zu Kohlendioxyd verbrannt werden als bei Veraschungen auf trockenem Weg bei hohen Temperaturen in einem elektrisch geheiztem Muffelofen. Die in den auf nassem Wege veraschten Proben zu untersuchenden mineralischen Bestandteile bleiben in der als Sauerstofflieferanten benützten überschüssigen Überchlorsäure zurück und die oft schwierige Auflösung der bei der Anwendung der Veraschung auf trockenem Wege entstandenen Asche wird so vermieden. Schwefel und Phosphor werden bei dem so beschriebenen Prozess quantitativ zurückgehalten.

Im einzelnen wurde eine Untersuchung der Oxidation auf nassem Wege mit einer grossen Anzahl von Naturprodukten in Proben von 1-10 gr durchgeführt. Eine Zeichnung der Apparatur und die Begrenzungen der Reaktion wurden beschrieben. Es wurden Proben von Kohlehydraten, Zelluloseprodukten, Proteinen und Kohlenwasserstoffen in verschiedenen organischen Produkten untersucht. Der Reaktionsmechanismus wurde postuliert, der Einfluss von Vanadium als Katalysator untersucht und die Wirkung der Temperatur gezeigt. Es wurden neue analytische Anwendungen vorgeschlagen.

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