The Dualistic and Versatile Reaction Properties of Perchloric Acid

Illustrative Experimental Demonstration Procedures

and

The Colorimetric Determination of Iron in Raw and Treated Municipal Water Supplies

By

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The Colorimetric Determination of Iron in Raw and Treated Municipal Water Supplies by Use of 4:7-Diphenyl-1:10-Phenanthroline

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Introductory Commentary

The first section of this booklet deals with the general properties of perchloric acid. Descriptive experimental procedures in illustration of these "versatile and dualistic" properties are outlined. It is a companion work to the booklet, (1), entitled, "The Wet Ashing of Organic Matter Employing Hot Concentrated Perchloric Acid," by one of the present authors.

By the descriptive detailed procedures therein contained, trace element determinations of a wide variety of metals and non-metals may be motivated. Comparatively large samples (1 to 20 grams), of foods, feeds, grains, cellulose, wool, proteins, bone, animal tissues, leather, collagen, brain, lung, kidney, heart, and other animal organs, as well as many other type samples, may be rapidly, efficiently and safely wet ashed. Trace metal contaminations, or additives, such as Fe, Cu, Co, Cr, Mn, Pb, Zn, may be thus provided for. In addition non-metals such as sulfur and phosphorus may be determined following the "Liquid Fire Reaction" of this wet oxidation of sample organic matter.

The contents of this booklet have been published in foreign chemical journals. Their reprinting is provided as a convenience to American chemists to provide a wider coverage among readers.

The second section, "The Colorimetric Determination of Iron in Raw and Treated Municipal Water Supplies," provides a precision method which is applied through the use of the new organic reagent "Bathophenanthroline," (4,7-Diphenyl-1,10-Phenanthroline). The first section suggests extension of wet organic procedures in preparation for trace determinations of iron with the further use of "Bathophenanthroline" as chelation ligand as outlined in the second section.

"Bathophenanthroline" is both a ferroine and cuproine reacting ligand. Iron (II) may be determined in the presence of Cu (I). Conversely, copper may be determined in the absence of iron. In both applications the sensitivity attained is roughly twice as sensitive as in the use of 1,10-phenanthroline for the simultaneous determination of Fe (II) and Cu (I) as

(1) G. Frederick Smith, Anal. Chim. Acta, 8, 397-421 (1953)

previously described, (2). There is no loss of specificity but a gain of importance in sensitivity. In addition the use of "Bathophenanthroline" involves procedures of extraction using water immiscible organic solvents, which further enhance sensitivity.

It is the objective, through the reprinting of the work described in this booklet, that the material will span the breach between the inhibition caused by original publication abroad and duplication in the present form for more convenient accessibility in the U. S. A.

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(2) D. H. Wilkins and G. Frederick Smith, *ibid.* 9, 538-545 (1953)

The Dualistic and Versatile Reaction Properties of Perchloric Acid

Illustrative Experimental Demonstration Procedures

By G. FREDERICK SMITH

The manifold uses of perchloric acid and perchlorates are listed. The chemical properties of the various known hydrated forms of perchloric acid and the properties of salts of perchloric acid are described. A historical survey is given of the uses of perchloric acid and ammonium perchlorate, and of the manufacture of the acid.

Equipment and techniques are given in detail for experimental demonstrations of the properties of perchloric acid; the experiments are classified under non-oxidising properties, chemicals resistant to the action of hot concentrated perchloric acid, and the oxidising power of the hot concentrated acid. The last includes the solution of stainless steel for the determination of chromium and the "liquid fire" reaction as applied to the rapid wet-oxidative destruction of chromacised catgut for the chromium determination, of the organic matter in tobacco and of oxalic acid with vanadium as catalyst. Stoicheiometric oxidations with perchloric acid solutions of cerium^{IV} are demonstrated for use with aliphatic organic compounds. Titrations in non-aqueous solvents are described. Miscellaneous experiments include the non-destruction of wool, the thermal decomposition of ammonium perchlorate and the high density of a saturated silver perchlorate solution; finally a description is given of an explosive reaction.

Perchloric acid is now recognised as an irreplaceable, outstandingly unique, research and routine analytical reagent. The apprehension of hazard formerly and currently associated with its chemical properties, which discouraged the common use of this valuable chemical, is rapidly being dispelled.

Thirty-five years ago, the total annual consumption of perchloric acid in the United States was approximately 300 pounds. To-day, the yearly consumption has expanded to over a million pounds, chiefly in the form of 70 to 72·5 per cent. acid (approximately the composition of the perchloric acid - water azeotrope).

Perchloric acid is used in the control analytical laboratories of the following industries, in which hundreds of thousands of industrial determinations involving its use as a primary reactant are made weekly—

1. The iron, steel, special steel and non-ferrous alloy industries.
2. Processors of wine, beer and spirituous liquors.
3. Food, feeding-stuff and fertiliser manufacturers.
4. Fuel supply and consumer agencies[1] (coal, coke and wood products).
5. The leather-tanning industry.
6. Pharmaceutical, medicinal and biochemical processors (control).
7. The dairy product industry[2,3,4] (determination of butter-fat in ice-cream mixes, powdered and condensed milk, and similar products).
8. Soap and detergent manufacturers.
9. The manufacturers of explosives.
10. Manufacturers of organic chemicals, who use analytical control procedures involving titrations with perchloric acid in non-aqueous solvent media.

The industrial field involving large-scale operations in which perchloric acid and the metallic perchlorates are used includes the following types of application (probably 10 million pounds of alkali and alkaline-earth metal perchlorates is the average yearly consumption in the United States)—

1. Railway and highway signalling devices such as red and green fusees and percussion torpedoes.

2. Mine blasting by the Cardox system (frangible-disc bomb-type multiple-service carbon dioxide blasting mechanisms, triggered through the use of potassium perchlorate - carbon promoter cartridges).

3. "Jato"—jet assisted take-off airplane operations (potassium perchlorate - carbon reactors).

4. Anodic bright polishing of metals and alloys accompanied by metal surface pacification for corrosion resistance.

5. Metal de-burring operations (anodic electrolytic process: perchloric - acetic acid electrolyte).

6. The manufacture of fireworks.

7. The match industry.

8. Esterification processes in a wide variety of synthetic organic chemical industries (perchloric acid as reaction catalyst).

9. Electroplating and electro-winning with heavy-metal perchlorate solutions as electrolytes.

10. Silver perchlorate for processes used in electroplating on plastics. Saturated lead perchlorate solutions as radiation screens.

With this comprehensive list of metallurgical, agricultural, medicinal, food processing, dairy manufacturing, soap and explosives industries having adopted a wide variety of control operations involving the use of perchloric acid, it is difficult to rationalise widespread inhibitions based upon aspects of possible hazard. It would be much more logical to expect a growing tendency towards its adoption and exploitation on an even more extensive scale of applications, industry wide.

In the interests of promoting such an end, the most logical method of attack involves a more energetic system of college education of chemists taking training in general inorganic and analytical chemistry to include a study of the varied chemical properties of perchloric acid. This should be accompanied by a liberal training in laboratory exercises involving important procedures in which perchloric acid is used.

For chemists past their training careers, a series of illustrative experimental demonstrations covering a wide variety of perchloric acid applications would prove of material value. It is the purpose of the present paper to describe experimental techniques suitable for accomplishing such a task. First, it is appropriate to catalogue the basic properties of perchloric acid to serve as introductory material.

KNOWN FORMS OF PERCHLORIC ACID

The various hydrates of perchloric acid include the following—
(1) Anhydrous perchloric acid, $HClO_4$, m.p. approximately $-112°$ C.
(2) Oxonium perchlorate, OH_3ClO_4 (containing 84·79 per cent. of perchloric acid), m.p. $+49·905°$ C.
(3) Oxonium perchlorate monohydrate, $OH_3ClO_4.H_2O$ (73·60 per cent.), m.p. $-17·8°$ C.
    Dioxonium perchlorate, $O_2H_5ClO_4$. The m.p. of this beta form is approximately $-19·5°$ C.
(4) $HClO_4.2·5H_2O$ (69·05 per cent.), m.p. $-29·8°$ C.
(5) Dioxonium perchlorate monohydrate, $O_2H_5ClO_4.H_2O$ (65·02 per cent.); this is the alpha form, m.p. $-37°$ C.
    Trioxonium perchlorate, $O_3H_7ClO_4$, m.p. approximately $-43°$ C; this is the beta form. There are also some cryoscopic data indicating the existence of a gamma form.
(6) $HClO_4.3·5H_2O$ (61·44 per cent.), m.p. $-41·4°$ C, b.p. approximately $163°$ C.
(7) The perchloric acid - water azeotropic composition, 72·5 per cent. of $HClO_4$, b.p. approximately $203°$ C at 760 mm pressure.

The preparation of the anhydrous acid (1) is not complicated,[5,6] nor in reality hazardous. It may be stored after preparation, with safety, for only 10 to 30 days at ordinary temperatures. It explodes spontaneously if stored for longer periods, but the safe storage time can be much extended by use of liquid-air temperatures. The only hazard involved in its preparation is that of breakage of receiver containers, provided that the best synthetic process[5] for its preparation is followed. At ordinary temperatures, anhydrous perchloric acid causes explosions when in contact with wood, paper, carbon and organic solvents. Except for special requirements it should not be made or stored.

The preparation of oxonium perchlorate (2) follows the procedure for the preparation of the anhydrous acid (1) accompanied by dilution with acid in the form of one of the hydrates (3), (4) or (7). One mole of anhydrous perchloric acid is diluted by the addition of 1 mole of oxonium perchlorate monohydrate (3), for example, and the mixture upon cooling crystallises at ordinary temperatures, m.p. 49·905° C.[7] The crystalline oxonium perchlorate can be prepared in any quantity and may be stored for any extended period of time with no hazard.

The preparation of oxonium perchlorate monohydrate (3) involves the distillation of the perchloric acid - water azeotrope at a pressure of 2 to 7 mm of mercury. Its preparation in this form provides an acid of such precise composition that it is recommended as a primary standard of reference in acidimetry.[8] Alpha and beta forms with somewhat different melting points are known; these correspond to the formulae $O_2H_5ClO_4$ and $OH_3ClO_4.H_2O$.

Compositions (4) and (5) have been described by van Wyk[9] from cryoscopic phenomena. Three forms of (5) may be postulated having the formulae $O_3H_7ClO_4$, $O_2H_5ClO_4.H_2O$ and $OH_3ClO_4.3H_2O$.

Composition (7), the perchloric acid - water azeotrope, is prepared by the distillation of dilute aqueous solutions of the acid at 760 mm pressure. The dilute acid solution concentrates rapidly and a temperature of 203° C is reached at approximately 72·5 per cent. acid concentration. Distillation of (6) at 760 mm pressure is accompanied by appreciable decomposition to give chlorine and oxides of chlorine. By distillation under a reduced pressure of 2 to 7 mm, this decomposition is completely prevented, but a composition stronger than that of oxonium perchlorate monohydrate (3) is never attained, no matter how low the pressure is maintained during distillation. This fact is very fortunate. In any procedure involving the boiling of dilute solutions of perchloric acid, concentration of the acid is limited to the formation of the azeotropic composition, and the possibility that stronger acid may be formed, with the accumulation of either the anhydrous acid (1) or oxonium perchlorate (2), with their much increased oxidation potential, is completely non-existent. The same basic considerations govern the important use of perchloric acid as a dehydrating agent. The evolution of perchloric acid as the water azeotrope is accompanied by the dissipation of water through the dissociation of hydrated solutes having dissociation pressures that are appreciable at 203° C. An important example is the dehydration of silicic acid, as in the determination of silicon in steel and iron or silica in limestone and cement. The same considerations govern the displacement from solution of low-boiling acids such as hydrochloric and nitric, but not sulphuric or phosphoric.

CLASSIFICATION OF THE CHEMICAL PROPERTIES OF PERCHLORIC ACID

(a) Cold dilute or concentrated (0 to 73·60 per cent.) perchloric acid *is not an oxidising agent*.

(b) Hot dilute perchloric acid *is not an oxidising agent*.

(c) Perchloric acid of compositions less than 85 per cent. strength are completely stable under ordinary storage conditions for any extended period of time.

(d) Perchloric acid has the highest protonic activity of all acids.[10] Its protonic activity as the anhydrous acid is greater than that of 100 per cent. sulphuric acid, for example, by a factor of 10^6 (one million times greater).

(e) Hot concentrated perchloric acid (70 to 73·6 per cent.) *is a powerful oxidising agent*. The oxidation potential is approximately 2·0 volts, comparable to ozone in oxidation value.

(f) Hot concentrated perchloric acid is an efficient dehydrating agent.

(g) Hot concentrated perchloric acid is a remarkably efficient solvent for metals and alloys, ores and minerals.

(h) Mixtures of nitric, perchloric and sulphuric acids can be used to produce a stepwise gradual increase in oxidation potential from moderate to high and to extreme values, as governed by acid concentration and temperatures applied.

(i) Hot concentrated perchloric acid can be divested of its oxidising power by cooling and diluting it considerably by the instantaneous addition of water. Any excess of perchloric acid that has been used as an oxidant need not be removed to eliminate its effect as an oxidant. The excess of perchloric acid is effectively made non-oxidising in property by dilution with water.

(j) Hot concentrated perchloric acid serving as an oxidising agent decomposes to give chlorine, oxides of chlorine and oxygen as reduction products. At boiling temperatures the

acid of the azeotropic composition, or stronger, evolves traces of hydrogen peroxide as reduction products. This property proves perchloric acid to be, to a limited extent, a true per-acid.

(k) Glacial acetic acid can be mixed with concentrated perchloric acid in any proportions. The mixtures so prepared can be separated by distillation at atmospheric pressure.[11]

(l) Hot mixed fumes of perchloric acid and hydrogen are violently explosive.

CHEMICAL PROPERTIES OF SALTS OF PERCHLORIC ACID

(a) All salts of perchloric acid are soluble to a high degree in water and all organic solvents (with few exceptions). They have a large coefficient of increase in solubility with increase in temperature. Exceptions are the moderately soluble potassium, rubidium and caesium perchlorates, and phenols or hydrocarbons as organic solvents.

(b) The perchlorates of lead, barium, calcium and strontium, unlike the corresponding sulphates, are extremely soluble in water as well as in many organic solvents.

(c) Lead, silver[12] and mercury perchlorates, as their saturated solutions in water and organic solvents, are of high density. Saturated lead perchlorate solutions are employed as transparent screens to prevent transmission of radioactive emanations.

(d) The perchlorate ion is not reduced at the cathode in electrolytic processes such as electroplating or electro-oxidation. Hence, in electro-oxidations of the chlorate to the perchlorate ion, the partition type of cell design is not required.

(e) Metallic perchlorates serve often as electrolytes for superior electroplating operations. Examples are electroplating of tin,[13] lead,[14] bismuth[15] and cadmium. Silver, copper and indium[16] have also been deposited from perchlorate electrolytes.

(f) The perchlorates have the highest content of available oxygen of any known extensive series of compounds.

(g) The thermal decomposition of the alkali and alkaline-earth metal perchlorates results in the formation of the corresponding chlorides with the evolution of their total oxygen content. This behaviour differs from that of nitrates, which give oxides.

(h) Alkali-metal perchlorates and barium perchlorate retain all their oxygen at temperatures of 350° to 400° C, and some retain it to higher temperatures.

(i) Barium and strontium perchlorates, when used in the compounding of signalling devices, exhibit upon thermal decomposition the chloride spectrum, which is more intense than the corresponding oxide spectrum that results if the corresponding nitrates are used for colour production.

EARLY APPLICATIONS IN THE USE OF PERCHLORIC ACID AND AMMONIUM PERCHLORATE

Reasons should be given for the early industrial popularisation of perchloric acid and salts of perchloric acid, such as the sodium and ammonium salts.

The first large-scale use of perchloric acid involved the preparation of the ammonium salt, which did not involve the preparation of the acid in its manufacture. A mine blasting compound known as "Chidite" was used extensively in Canada because it was preferable to dynamite in cold climates as it was not, like nitroglycerin, adversely affected by freezing. "Chidite" was an ammonium perchlorate blasting composition. Its widespread use about 1910–20 resulted in large importations of ammonium perchlorate at prices ranging from 10 cents to as low as 5 cents per pound. This market was dissipated about 1920 through the competitive influences of other new non-freezing blasting explosives. But this commercial large-scale use of ammonium perchlorate served to lessen a common tendency to consider any perchlorate as ultra-sensitive in reactivity and not amenable to practical usage.

The most economical method for the manufacture of perchloric acid was described by Willard[17]; ammonium perchlorate was used as raw material. All of the perchloric acid manufactured in the United States between 1925 and 1935 was manufactured by the Willard process.

The earliest analytical application for perchloric acid was in the separation and determination of potassium in the presence of sodium, as a substitution for the familiar Fresenius chloroplatinic acid procedure. Few, if any, analytical applications were previously known.

The most important development in the use of perchloric acid in analysis, a method that may be said to have first created a large popular demand for the manufacture of the acid, was the origination, as described by Willard and Cake,[18] of the perchloric acid procedure for the dehydration of silica and determination of silicon in iron and steel and silica in ores and minerals. The widespread use of this important procedure soon stamped perchloric acid as an important commercial reagent chemical. Many new and important analytical applications rapidly followed.

With the advent of the second world war, it was no longer possible to manufacture perchloric acid in the United States (to meet the very great increase in demand) from ammonium perchlorate as raw material, as this could no longer be imported. This led to the application of the Kreider-Mathers[19] process, which uses sodium perchlorate as raw material. Government-operated defence plants were built at several strategic locations in the United States for the manufacture of sodium chlorate and perchlorate, as well as potassium perchlorate. By the Kreider-Mathers process, perchloric acid was manufactured in such quantities that carload lots were advertised for sale at as little as 41 cents per pound for 70 per cent. acid (in the 1940 era). Preparation of perchloric acid has also been carried out industrially by the electro-oxidation of sodium chlorate.[20]

THE KREIDER-MATHERS PROCESS IN THE MANUFACTURE OF PERCHLORIC ACID

The preparation of perchloric acid is indeed not complicated and is certainly not hazardous. Perchloric acid is a product of the salt of the earth.

A saturated solution of sodium chloride is oxidised electrolytically with a graphite anode and an iron cathode. Such cells account for an 85 per cent. conversion of sodium chloride to sodium chlorate. The sodium chloride is easily separated from this converted sodium chlorate by concentrating the sodium chlorate electrolyte by evaporation; the un-oxidised sodium chloride is removed as a relatively insoluble material after this concentration of electrolyte.

A saturated solution of sodium chlorate is then electrolysed with platinum anodes and iron cathodes. Such a procedure accounts for the conversion of sodium chlorate to perchlorate, and the oxidation can be carried to 99 to 99·5 per cent. completion. Cells used in this oxidation are shown in Fig. 1.

In the Kreider-Mathers process sodium perchlorate is treated by the addition of a large excess of concentrated hydrochloric acid. By metathesis, sodium chloride is almost quantitatively precipitated. By centrifugation, the precipitated sodium chloride is separated from the perchloric acid formed in its mixture with the excess of hydrochloric acid.

The perchloric acid-hydrochloric acid mixture is evaporated to a concentrate, the hydrochloric acid excess is recovered, and the aqueous solution of perchloric acid thus prepared is distilled *in vacuo* to provide the finished pure perchloric acid.

By this process the only chemicals employed are recovered and re-cycled. Only electrical energy and oxygen from the water of the electrolyte are consumed. The hydrogen evolved in the process even provides agitation, which eliminates any need for additional circulation of the cell electrolyte. The sodium chloride and hydrochloric acid raw materials are recovered for further processing of the acid in this continuous process. Other methods of preparation have been used for commercial manufacture.

Possibly the next most important commercialisation of perchlorate chemistry was the manufacture of magnesium perchlorate in the form of its anhydrous and partially dehydrated form to be used as a drying agent. This product in the anhydrous form was shown to have the drying efficiency of the best known desiccant, phosphorus pentoxide, and in addition had a very high drying capacity. Its commercial availability soon accounted for its adoption as preferred reagent in many types of analytical usage, including the determination of carbon in steel and iron and the determination of carbon and hydrogen in organic combustion analyses. Its use in these and many other analytical operations is now almost universal and it is recommended for such procedures in practically all textbooks and literature-cited references. For such determinations as those previously mentioned it is a companion reagent to the most important absorbents for carbon dioxide. It is also a quantitative absorbent for ammonia gas and has a high capacity in this role. The ammonia vapour pressure of the diammine of magnesium perchlorate is nil at room temperature and at temperatures even greater than 150° C. Anhydrous magnesium perchlorate has been used analytically in the quantitative absorption of alcohol vapours in the analysis of gas products such as natural gas, which frequently is adulterated with vapours such as ethanol to prevent freezing effects in the cold-weather transportation of natural gas in pipe-lines between the field of supply and the point, often many hundreds of miles distant, of the gas consumption. Anhydrous
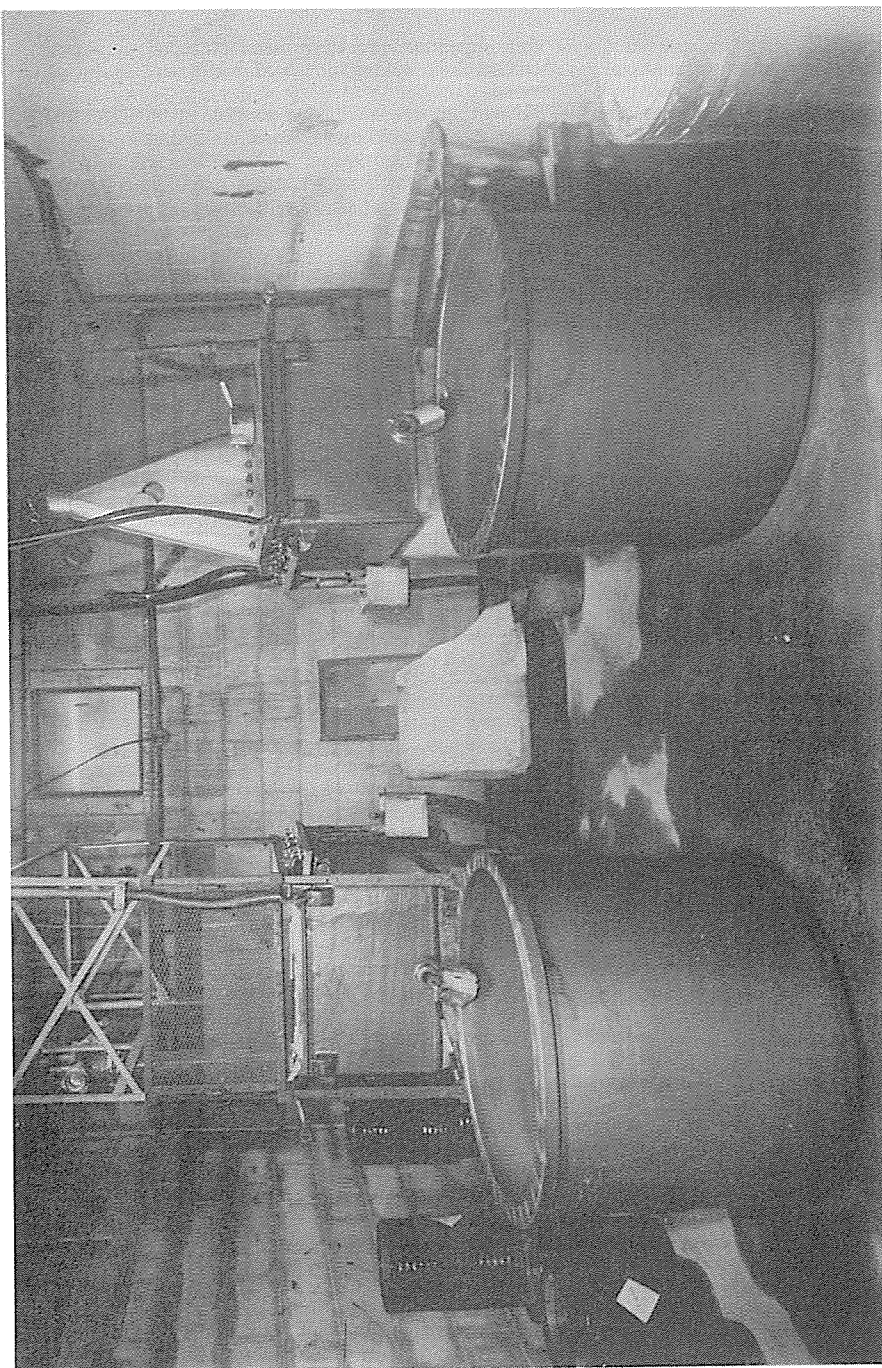
Fig. 1. Cells of 100 gallons capacity for use in the electrolytic oxidation of sodium chlorate to sodium perchlorate

magnesium perchlorate has also been used industrially in the liquefaction of air in the preparation of high-pressure tank oxygen and nitrogen.[21] Oddly, one incentive for such usage is the saving in power and decrease in hazard.

A very important application of perchloric acid to analysis, which served to popularise its use, was developed, namely, the quantitative oxidation of chromium from Cr^{III} to Cr^{VI}, as applied, among many other applications, to the determination of chromium in steel (particularly stainless steel). This usage has so many outstanding advantages that it is now practically universally employed.

Mention is made of these early uses for perchloric acid to establish a background of persuasion capable of overcoming the almost fanatical conviction of chemists that perchloric acid in all its aspects is an extremely unstable chemical and committed in all its possible applications to the ultimate end of disaster from explosions associated inevitably with all its proposed applications.

As a poignant illustration, there is the determination of sulphur in coal by the well-established procedure invented by Professor S. W. Parr at the University of Illinois. As first described and very widely employed, the procedure utilised potassium chlorate as the oxygen carrier to burn the coal in the Parr bomb, in addition to sodium peroxide, fulfilling the same purpose. So many explosions resulted from the utilisation of this procedure, because of the activity of the chlorate, that the method was often considered unduly hazardous. The proposal to use potassium perchlorate as a substitute for potassium chlorate was at first resisted on the grounds that, if chlorate was undesirable, perchlorate would be much worse. It proved upon test that the reverse was true. For the past 30 years the standard Parr bomb procedure for the determination of the heating value and sulphur content of coal has therefore made use of potassium perchlorate to replace chlorate as accelerator in this application.

To illustrate further, it can be shown that potassium perchlorate and sulphur may be ground together in a ball mill with no violent reaction resulting; this, as every chemist knows, would be disastrous if mixtures of potassium chlorate and sulphur were subjected to the same treatment.

One of the most outstanding properties of perchloric acid and the common perchlorate salts is indeed the extreme reluctance with which they release their oxygen content. By way of illustration one might cite the example of lithium perchlorate. The oxygen content is over 60 per cent. by weight, yet it may be heated above 400° C without the least loss of oxygen. The determination of the atomic weight of lithium and its ratio with oxygen now accepted in atomic-weight tables was established by the synthesis and analysis of anhydrous lithium perchlorate from fused lithium chloride.[22] This analysis was by thermal decomposition to yield the starting material and, by the conversion of fused lithium chloride to anhydrous fused lithium perchlorate, gave the ratio of lithium to oxygen directly.

With this partial summary of the fabulously versatile and dualistic properties of perchloric acid and its salts, together with its past record of world-wide scientific research and routine industrial and pedagogical utility, it is hard to conceive that acute apprehension of inevitable hazard can be associated with the problem of its extended popular utilisation. Such, however, is indeed the situation. Only by experimental demonstration of perchloric acid reactions is the hazard generally associated with such operations effectively dispelled.

EQUIPMENT PREREQUISITES FOR EXPERIMENTAL DEMONSTRATIONS

Experimental techniques involving hot concentrated perchloric acid of 72·5 per cent. strength with a boiling point of 203° C should be performed in Vycor-ware utensils. Pyrex glass, with care in usage, is adequate, but Vycor or quartz ware insures that heat strains can be applied to the ware without danger of fracture, while Pyrex-glass ware or its equivalent sometimes fails at critical times. Naturally, if a flask of boiling 72·5 per cent. perchloric acid breaks and spills its contents in contact with a wooden bench top, a fire is the result and, at least, although no explosion would result, damage is inevitable. It is often required that hot concentrated perchloric acid solutions be chilled as rapidly as possible from boiling point to ordinary temperatures. This is best done by immersing the flask and contents, with a swirling agitation of its contents, into an ice and water bath for a long enough time (5 to 6 seconds) so its contents can be diluted with water conveniently to destroy the oxidation reaction of the acid almost immediately. Such operations can be carried out in Pyrex ware

or its equivalent without breakage, but the work is so much better carried out in Vycor or quartz ware that their use is strongly recommended.

A well-ventilated fume hood, with forced draft and non-combustible construction and with electric hot-plates, is the proper place in which to conduct experiments with boiling concentrated perchloric acid. Experimentation of the same type can be performed equally well, and without the discomfort of evolved fumes of the acid, by the use of properly designed equipment, a full description of which has been previously made and of which line drawings are self-explanatory.

Use electrically heated variable-wattage electric hot-plates in preference to ring-stands, or use tripods together with wire gauze of nichrome for boiling flasks and beakers containing hot concentrated perchloric acid. If a round-bottomed flask is to be heated, never use an oil bath, as the organic chemist is so prone to do, because it is convenient. Instead, use a sand bath or a Wood's-metal bath. It is not out of place if you are apprehensive of possible violent reactions to use a protective screen and wall back-drop, preferably with a Transite board base or one of Alberene stone. These are just routine precautionary measures.

To dissipate fumes when perchloric acid fumes are to be taken off a boiling Erlenmeyer flask together with fumes of nitric or other acids, use a special design of fume eradicator, such as that shown in the line drawing, Fig. 2. In original experimental testing, use the
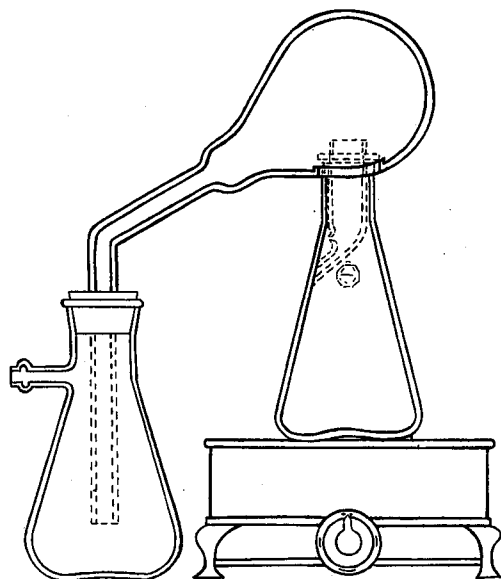

Fig. 2. Vycor reaction flask and hot-plate, with reflux still-head and fume eradicator in place

rule that you can learn all you need to know about the reaction with a small amount of material and reagents. Cut three fingers off an old pair of asbestos gloves for the thumb and two index fingers to enable you to remove hot Erlenmeyer flasks from a hot-plate. If Vycor ware or quartz vessels are used, they may be chilled rapidly by being covered with a small inverted beaker and placed directly under a running stream of tap water in a sink. Concentrated hot perchloric acid can be diluted with water without hazard when it has cooled to 140° to 150° C and in this respect is different, conveniently, from hot concentrated sulphuric acid.

Remember always that concentrated sulphuric acid to which concentrated perchloric acid has been added is the equivalent of anhydrous perchloric acid and should be used only as a reacting mixture when an extremely powerful oxidant is needed. If perchloric acid

alone is sufficient, avoid using this sulphuric-perchloric acid combination. Better yet, use only perchloric acid or perchloric-nitric acid mixtures.

EXPERIMENTS DEMONSTRATING NON-OXIDISING PROPERTIES OF PERCHLORIC ACID, EITHER DILUTE OR CONCENTRATED, AT ORDINARY TEMPERATURES

PREPARATION OF FERROUS PERCHLORATE—

Place 8 to 10 g of low-carbon steel (less than 0·1 per cent. of carbon, millet seed size of particle) in a 250-ml beaker. Cover the iron with 20 ml of 70 to 72 per cent. perchloric acid and add 4 to 5 ml of water. Solution of the iron will take place at a brisk pace with the evolution of hydrogen. After 10 to 15 minutes decant 4 to 5 ml of the solution into two 100-ml beakers. Add 75 ml of water to the first of these two beakers. Now add a gram or two of crystals of ammonium thiocyanate and stir. No colour production proves the absence of the ferric ion. To the second beaker add 10 to 15 ml of 70 to 72 per cent. perchloric acid. A white precipitate of $Fe(ClO_4)_2.6H_2O$ will form owing to its insolubility in 68 to 70 per cent. perchloric acid. The addition of water will redissolve the precipitate or, if preferred, before being diluted with water the contents of the beaker may be placed on a hot-plate, and when the acid is hot and fuming all the iron will be quietly oxidised to ferric perchlorate, dark brown when hot and almost colourless when cold (at best, slightly lavender in colour).

The low-carbon steel is selected because of its ready solubility under these conditions without giving too much discoloration due to precipitated carbon. The reaction gives ferrous perchlorate under conditions of the evolution of hydrogen and obviously one should not get a positive result in the test for ferric ion with thiocyanate. This experiment should not require a reaction time of more than 15 minutes and requires little attention, and accompanying experiments can be made simultaneously.

For large-scale preparation of ferrous perchlorate the same procedure is used with larger amounts. On this scale, keep the temperature below 70° C and let the reaction progress until the solution is green in colour and concentrated in iron. Filter it through glass cloth and add an excess of perchloric acid. Filter off the precipitate on glass cloth and use the filtrate for the solution of more iron and further preparation of $Fe(ClO_4)_2.6H_2O$.

THE REACTION OF NITRIC ACID AND PERCHLORIC ACID ON AQUEOUS PYROGALLOL—

Make a strong aqueous solution of pyrogallol. Add 25 to 30 ml of the solution to each of two 125-ml Erlenmeyer flasks. To the first add slowly 5 to 6 ml of concentrated nitric acid. The solution immediately darkens to chocolate brown owing to oxidation. Add to the second flask 25 to 30 ml of 70 to 72 per cent. perchloric acid. No darkening proves no oxidation. Finally, to the second Erlenmeyer flask of mixed solution of pyrogallol and perchloric acid add either a solution of potassium dichromate or a solution of cerium[IV] in perchloric acid. The same chocolate-brown oxidation products form as in the treatment given to the first Erlenmeyer flask of sample after the addition of nitric acid.

THE LACK OF REACTION BETWEEN PERCHLORIC ACID AND POTASSIUM IODIDE—

To a colourless solution of potassium iodide in a 125-ml Erlenmeyer flask add a portion of 70 to 72 per cent. perchloric acid and swirl the contents of the flask. Now dilute the flask contents with water and add starch indicator. The solution should give no starch-iodide blue. Now add a few drops of an aqueous solution of potassium iodate. The starch-iodide blue colour should at once appear. (Remember that an aqueous solution of potassium iodide that is strongly acid will liberate iodine owing to oxidation by air.) It is obvious that perchloric acid in the cold, even in material amounts, does not oxidise potassium iodide, which is so easily oxidised as to react with atmospheric oxygen in the low pH ranges.

THE NON-REACTIVITY OF POTASSIUM PERCHLORATE AND SULPHUR—

Crystals of potassium perchlorate, 4 to 5 g, are placed in a 4-inch porcelain mortar. Now add about 1 g of flowers of sulphur. Grind the mixture in the mortar with the pestle. The mixture does not explode; there would be a violent explosion were crystals of potassium chlorate substituted for the potassium perchlorate. A drop of concentrated sulphuric acid will not ignite the potassium perchlorate-sulphur mixture as it would the corresponding potassium chlorate-sulphur mixture.

EXPERIMENTAL DEMONSTRATION OF CHEMICALS RESISTANT TO THE ACTION OF HOT CONCENTRATED PERCHLORIC ACID

GLACIAL ACETIC ACID—

Place 5 ml of 70 to 72 per cent. perchloric acid in an 8-inch × 1-inch Vycor test tube. Add 5 ml of glacial acetic acid. Mix well and heat over a free flame to the boiling point of the mixture. There is no oxidation of the acetic acid and it may be stated that this mixture can be separated completely by fractional distillation at atmospheric pressures.

TEFLON—

Place a weighed (accurate to 0·1 mg) 1 sq. cm block of Teflon in a 8-inch × 1-inch Vycor test tube. Place also in the test tube 3 or 4 chips of carborundum to permit boiling without bumping or spirting. Now add 10 ml of 70 to 72 per cent. perchloric acid and mount the test tube in a clamp suspended at a slight angle over a gas micro-burner. Adjust the flame just to the point at which the acid boils but is not so hot as to cause perchloric acid fumes to escape from the open end of the test tube. Allow the boiling to continue for 15 to 30 minutes or longer. The Teflon cube, after removal from the hot acid, washing and drying, will be found to have lost no weight. A cube of Duriron answers the same purpose as Teflon and likewise is not attacked.

DIAMOND—

Boil a weighed (accurate to 0·1 mg) small diamond or two in an 8-inch × 1-inch test tube in the same manner as described for Teflon or Duriron in the previous experiment. The perchloric acid will be found not to have attacked the diamond to the least extent.

EXPERIMENTS ILLUSTRATING THE OXIDISING POWER OF HOT CONCENTRATED PERCHLORIC ACID

For these experiments the assembly of apparatus shown in the line drawing, Fig. 2, is a practical necessity if the use of a fume hood is to be avoided and the reactions are to be exhibited on a lecture-room bench. The aspirator pump used to drain off noxious volatile products must be mounted in the lecture-bench sink and the assembled apparatus is conveniently located on the bench near by. A protective screen of Lucite, 3 feet by 4 feet by ¼ inch thick, should be mounted on the audience side of the lecture table. This screen is entirely unnecessary for the experiments to be described, but provides protection for the audience in the event of the experimenter, through mental lapse, making additions of the wrong reagents or omitting to add requisite reaction components.

THE SOLUTION OF STAINLESS STEEL IN HOT CONCENTRATED PERCHLORIC ACID AND PREPARATION FOR THE DETERMINATION OF CHROMIUM—

Place 0·25 g of finely divided cuttings of stainless steel in a 250-ml Vycor flask. Add 15 ml of 70 to 72 per cent. perchloric acid and a few carborundum boiling chips. Insert a reflux still-head and place the flask on an electric hot-plate of sufficient wattage to maintain a temperature of boiling of the perchloric acid, as near 203° C as can be conveniently controlled. (A Powerstat or Variac transformer in the power line attached to the hot-plate is wonderfully convenient.) Place a fume eradicator over the reaction flask with a brisk intake of air to carry away fumes from the reaction flask. The steel begins to dissolve immediately, and until all is in solution the dissolved chromium, nickel and iron salts will continue to give the flask contents a green colour. When solution is complete, the hot concentrated perchloric acid in 1 or 2 minutes will oxidise the tervalent chromium to chromium trioxide and the contents of the flask turn orange in colour. After 1 or 2 minutes' boiling, or sooner, the oxidation is complete.

Remove, and place to one side, the fume-eradicator mechanism. Using three 1-inch lengths of 3 by 25-mm rubber tubing as finger-caps on the thumb and first two fingers of the hand (after a quick immersion of the capped fingers in water), remove the flask from the hot-plate and instantly immerse it in a slurry of chipped ice and water with a rapid swirling motion applied to the flask contents. After 5 or 6 seconds of this treatment rapidly add, from the rapid-flowing opening of a standard wash-bottle, 50 to 60 ml of cold water. It is very important that these operations be carried out as rapidly as possible. Wash and

remove the reflux still-head, which has been used to prevent loss of flask contents as spray particles, return the flask to the hot-plate and allow the liquid to boil for 3 or 4 minutes to purge it of dissolved chlorine. Now remove the flask from the hot-plate and cool its contents by immersing and swirling it in the ice-slurry - water bath, until it has cooled to about room temperature. Add a drop of ferroin indicator solution and titrate to the production of a grey, then orange solution, indicating the complete reduction of Cr^{VI} to Cr^{III}. Use ferrous sulphate as standard reductant.

The reason for the quick chilling of the solution after oxidation is to prevent reversal of oxidation owing to the presence of a trace of hydrogen peroxide formed as a reduction product of hot concentrated perchloric acid.

The reason for the use of boiling chips is to prevent "bumping" in the operation of expelling chlorine fumes. No "bumping" would occur in their absence during the solution and oxidation stage of the reaction.

The rubber finger-caps, if moistened with water, will not stick to the hot neck of the flask, as they are prone to do if the rubber is not moist.

The use of ferroin indicator for this titration is much better than the use of diphenylamine, which is so often recommended.

The use of 72·5 per cent. perchloric acid (the water - acid azeotrope) is much preferred to starting with 60 per cent. perchloric acid or 70 per cent. acid for the reason that, at less than 200° to 203° C, the chromium is not oxidised except by boiling the acid until it concentrates to the azeotropic composition.

If vanadium is present it will be oxidised to vanadic acid together with the chromium, and will be titrated simultaneously with the chromium present.

THE DESTRUCTIVE DECOMPOSITION OF CHROMACISED MEDICAL CATGUT FOR THE RAPID DETERMINATION OF CHROMIUM—

Place a 2-g sample of 1-inch lengths of the chromacised medical catgut in a 250-ml Vycor flask. Add 20 ml of 70 to 72·5 per cent. perchloric acid and 6 to 7 ml of 67 per cent. nitric acid. Arrange the reflux still-head and fume eradicator as in the previous experiment. Heat on the hot-plate at the same temperature as in the preceding experiment.

In 5 or 6 minutes a clear green solution of the sample results. After a further 7 or 8 minutes, a rapid exothermic reaction sets in with evolution of carbon dioxide and fumes of perchloric acid. In a total of 15 to 18 minutes the solution changes colour from green to orange with the complete oxidation of chromium^{III} to chromate. Complete the demonstration as described in the preceding experiment.

THE WET-OXIDATION OF ORGANIC MATTER IN TOBACCO—

A small cigar (3 to 3·5 g) is cut into two pieces, each approximately 2 inches long. These, including the cigar band and cellophane wrapping, are placed in a 250-ml Vycor flask, and 2 mg of ammonium vanadate and 10 to 15 mg of potassium dichromate are added (the first as catalyst and the second as an indicator of the completion of the reaction). Add 30 ml of a mixture of equal parts by volume of 67 per cent. nitric acid and 70 to 72·5 per cent. perchloric acid. Arrange the digestion on the hot-plate in the same way as in the previous two experiments.

After 7 or 8 minutes the nitric acid reaction is over (there is evolution of nitric oxide) and the nitric acid has boiled away. After 12 minutes white fumes of perchloric acid appear. After 20 minutes the reaction is over, as indicated by the orange colour due to chromate.

Tobacco is very resistant to wet oxidation because of its content of heterocyclic ring-nitrogen compounds. No carbonaceous degradation products are deposited in this digestion as finely divided carbon. The chromate will not be formed as long as any unoxidised carbon remains.

THE OXIDATION OF OXALIC ACID BY BOILING 70 TO 72·5 PER CENT. PERCHLORIC ACID: THE INFLUENCE OF VANADIUM AS CATALYST—

Hot 70 to 72·5 per cent. perchloric acid (20 ml) containing 4 mg of chromium (added as potassium dichromate) is placed in a 250-ml Vycor flask on the hot-plate of the apparatus assembly shown in Fig. 2. The hot-plate temperature should be sufficient to boil the perchloric acid, yet low enough to prevent the evolved fumes escaping from the reaction

flask. When the acid is boiling, add 5 g of crystalline oxalic acid from a small glass vial and place the still-head and fume eradicator in position with a brisk flow of water through the aspirator pump, which drains into the adjoining sink. Time the reaction to the point at which the chromium^{VI}, which is first reduced to give a violet colour and forms a complex with the oxalic acid ($H_2C_2O_4.2H_2O$), is converted to green and finally back again to orange after all the oxalic acid has been destroyed, so indicating that the reaction is over. The time of reaction should be 9 minutes from the point of addition of the oxalic acid.

Repeat the experiment with the addition of 0·3 mg of vanadium added as ammonium vanadate; the reaction time should now be 4½ minutes. Repeat with the addition of 0·75 mg of vanadium; the reaction time should be 1½ minutes.

Add the vanadium catalyst in the form of ammonium vanadate dissolved in 70 to 72·5 per cent. perchloric acid.

Sodium formate is another strong reducing agent that can be oxidised by a similar reaction. Vanadium is not a catalyst for the oxidation, however. As acetic acid is not oxidised under similar conditions, the procedure could serve as a differential oxidation of formic acid in the presence of acetic acid or oxalic acid in the presence of acetic acid.

Formaldehyde is not oxidised by hot concentrated perchloric acid. If mixtures of nitric and perchloric acid are heated in the presence of formaldehyde, the nitric acid rapidly destroys the formaldehyde. Mixed hot vapours of concentrated perchloric acid and formaldehyde are explosive.

EXPERIMENTAL DEMONSTRATION OF THE HIGH POTENTIAL ATTAINED IN OXIDATIONS WITH CERIUM^{IV} IN PERCHLORIC ACID SOLUTION

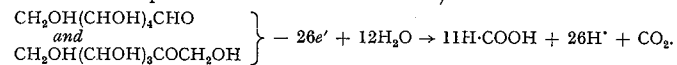The single-electrode potentials involved are the following—

$$Ce^{IV} + e' \; (1F \; HClO_4) \rightarrow Ce^{III} \; (1·71 \; volts)$$
$$(8F \; HClO_4) \rightarrow \quad\quad\quad (1·86 \; volts).$$
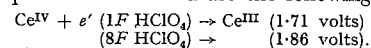
The high oxidation potential of the $Ce^{IV} \rightarrow Ce^{III}$ system can be brilliantly illustrated as directed in the following experiment.

Place 200 ml of a four-formal (4F) perchloric acid solution (68 ml of 70 to 72·5 per cent. perchloric acid diluted by addition of 132 ml of water) in a 400-ml beaker. Add 1 g of cane sugar and place the beaker and contents on a magnetic stirring device and, with a small rotor in the beaker, stir briskly. When the sugar has dissolved, add 0·2 ml of 0·025 M nitroferroin indicator (5-nitro-1:10-phenanthroline - ferrous complex solution).

The indicator is red and it imparts a red colour to the solution as long as sugar in excess remains unoxidised and a momentary excess of cerium^{IV} is not present. Add in 1 to 2-ml portions a solution of $H_2Ce(ClO_4)_6$ in concentrated perchloric acid (a solution of approximately N cerium^{IV} concentration). The reduced form of the nitroferroin indicator is at once oxidised to give a colourless solution, and then the excess of cerium^{IV} gives the solution a momentary red colour again, immediately supplanted by the yellow of the excess of cerium^{IV} present. The sugar is then rather quickly oxidised in part and the yellow colour is dispelled, which indicates that the cerium^{IV} has been reduced to cerium^{III} by the sugar excess present. The reduced form of the indicator, nitroferroin, is again produced and the solution turns red, as it was originally.

Another 1 to 2-ml portion of cerium^{IV} in perchloric acid is added and the phenomena described repeat. This can be repeated a number of times because there is a generous excess of sugar present and the nitroferroin indicator is reversible. The reaction of the oxidation of the sugar is that following (the cane sugar first hydrolysing to form one molecule of glucose and one molecule of fructose per molecule of sucrose added)—

$$\left.\begin{array}{l} CH_2OH(CHOH)_4CHO \\ \textit{and} \\ CH_2OH(CHOH)_3COCH_2OH \end{array}\right\} - 26e' + 12H_2O \rightarrow 11H \cdot COOH + 26H^{\cdot} + CO_2.$$

The momentarily produced red coloration of the solution when the cerium^{IV} is first added is caused by complex formation in which the $H_2Ce(ClO_4)_6$ is converted into such complex types as that represented by the formula $H_2Ce(OH)_2(ClO_4)_4$, which are red. These red intermediate complex materials are then dispelled as the cerium^{IV} is reduced to cerium^{III}. The reactions described have been used in the quantitative determination of glucose and of fructose. The oxidation of the former requires 12 equivalents and the latter 14 equivalents for a total of 26 equivalents per mole of cane sugar oxidised.

TITRATIONS IN NON-AQUEOUS SOLVENTS INVOLVING PERCHLORIC ACID

Many valuable volumetric analytical procedures, in which are used as solvent media such organic solvents as benzene, chloroform, carbon tetrachloride, nitrobenzene, nitromethane, acetic acid and similar solvents, are performed with perchloric acid in glacial acetic acid as standard solution. The preparation of the solutions required for the determination of amino-acids is as follows.

Perchloric acid, 0·1 N—Mix 8·5 ml of 72 per cent. perchloric acid with 200 to 300 ml of glacial acetic acid and add 20 ml of acetic anhydride. Dilute to 1 litre with glacial acetic acid and set aside overnight to permit complete reaction of acetic anhydride with the water present.

Sodium acetate, 0·1 N—Dissolve 8·2 g of anhydrous sodium acetate in glacial acetic acid and dilute to 1 litre with the same acid.

Methyl violet—Dissolve 0·2 g of methyl violet in 100 ml of chlorobenzene.

Potassium hydrogen phthalate—Primary-standard grade.

PROCEDURE—

Dissolve a sample containing 2 or 3 milli-equivalents of amino-acid in exactly 50 ml of 0·1 N perchloric acid. Add 2 drops of methyl violet indicator and titrate the excess of acid with 0·1 N sodium acetate; take the first permanent violet tinge as the equivalence point.

The perchloric acid is standardised against potassium hydrogen phthalate. About 0·5 g of potassium hydrogen phthalate is accurately weighed and added to 60 ml of glacial acetic acid. The mixture is heated and stirred to effect solution and is titrated, after cooling and addition of methyl violet indicator, by the perchloric acid solution of unknown strength in glacial acetic acid. The equivalence point is marked by the first discharge of the violet tinge of colour. The titrations are most conveniently made in a 125-ml Erlenmeyer flask with magnetic stirring.

Repeat the titration with the same weight of sample to prove duplication of results. A blank determination will give the needed ratio between the perchloric acid solution and the sodium acetate solution. From the results, the amount of amino-acid titrated can be readily calculated.

The many, many determinations now made in control laboratories by these types of titration in non-aqueous solvents have gone a very great way in dispelling the fear that perchloric acid in contact with organic compounds is a hazardous combination.

MISCELLANEOUS EXPERIMENTS ILLUSTRATING PROPERTIES OF PERCHLORIC ACID AND ITS SALTS

#### THE PERMANENCE OF WOOL FABRICS IN CONTACT WITH PERCHLORIC ACID—

The permanence of wool fabrics in contact with 70 to 72 per cent. perchloric acid may be illustrated by immersing a 4-inch square piece of wool suiting or a handful of wool knitting yarn in 40 to 50 ml of the acid. Allow contact for a reasonable time, say 5 minutes. Pour off the acid and rinse the wool with generous portions of distilled water, squeezing the fluid from the wool after each addition. Now rinse the wool in absolute ethanol two or three times and finally once with absolute ethyl ether. After a few flourishes of the wool in the air, it may be immediately passed out to an audience for inspection to prove no damage has resulted.

THERMAL DECOMPOSITION OF AMMONIUM PERCHLORATE—

The thermal decomposition of ammonium perchlorate is strikingly illustrated by placing 10 to 15 g of crystalline ammonium perchlorate in a 50-ml Vycor crucible. Cover the crucible with the lid made for it. Place the crucible and contents on a nichrome triangle on a tripod or ring and ring-stand assembly. Place a Meker burner at full flame close under the crucible and note the decomposition resulting.

The decomposing ammonium perchlorate will glow with such a hot localised incandescence as to make it ill-advised to observe it without dark glasses. There is little or no production of coloured nitrogen oxides and no violence is associated with the decomposition. Apparently the ammonium perchlorate first dissociates into perchloric acid and ammonia and the hot

perchloric acid oxidises the ammonia as fast as it is formed. The reaction of magnesium oxide with ammonium perchlorate at 255° to 260° C is as follows—

$$\text{MgO} + 2\text{NH}_4\text{ClO}_4 \xrightarrow{255° \text{ to } 260° \text{C}} \text{Mg(ClO}_4)_2 + 2\text{NH}_3 + \text{H}_2\text{O}.$$
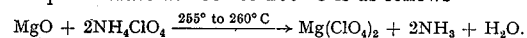
By the use of stoicheiometric mixtures this reaction *in vacuo* is complete, with 95 per cent. yields of magnesium perchlorate.

REACTION OF SULPHUR WITH PERCHLORIC ACID—

Place 25 to 30 ml of 72·5 per cent. perchloric acid in a 250-ml Vycor Erlenmeyer flask. Add a gram or two of flowers of sulphur. Heat the mixture to boiling after placing a fume eradicator over the flask to draw off the fumes. The sulphur melts on the surface of the boiling perchloric acid and oxidises very quietly. In this operation only about 25 per cent. of the sulphur is oxidised to sulphuric acid. The remainder passes off as gaseous sulphur - chlorine products.

A sulphur ore such as copper sulphide is much more rapidly dissolved by treatment with hot concentrated perchloric acid than it would be if concentrated nitric acid were used as solvent. Use has been made of this fact in the analysis of copper sulphide ores.

DENSITY OF A SILVER PERCHLORATE SOLUTION—

Make a saturated solution in water at 25° C with silver perchlorate as solute. Demonstrate that such a solution will cause a crystal of Iceland spar to float because of its high density.

DEMONSTRATION OF THE EXPLOSIVE REACTION BETWEEN SODIUM HYPOPHOSPHITE
AND HOT CONCENTRATED PERCHLORIC ACID

It would be worse than folly to maintain that mixtures of strong reducing agents with 70 to 72·5 per cent. perchloric acid are not in general hazardous. While some such strong reducing agents and hot concentrated 72·5 per cent. perchloric acid react through oxidation without hazard and under perfectly satisfactory control (as, for example, oxalic acid and formic acid), this is not always true or even the predominant rule. To illustrate such an explosive combination the following experiment is recommended.

Place 1 g of crystals of sodium hypophosphite in a 30-ml porcelain crucible. Add 8 to 10 drops of 72·5 per cent. perchloric acid. No reaction results because the perchloric acid is not hot. Place the crucible on a bare wire gauze placed upon an iron tripod. With a hot gas flame from a Terrill or bunsen burner (capable of producing a red-hot spot on the wire gauze 1 to 1½ inches in circumference), start heating the crucible contents. Quickly place a spacious corrugated Kraft-paper box over the reaction set-up. In about 30 seconds the reaction mixture will explode with a deafening roar. The crucible will be found, after removing the box, to have been not too badly shattered. The wire gauze will be found to have been forced into the shape of a wire-gauze funnel with an open bottom. This indicates that the blast has had all its force directed downward. This is an unfailing effect from all perchloric acid explosions, so far as is known.

The purpose of this experiment is to demonstrate that, with all the previously described experiments in which hot concentrated perchloric acid is used, a slip in error, which inadvertently results from not being sure of the reaction components one has compounded, can and does cause violent reactions to take place. But this is true of almost any type of reaction employed in chemical processes.

There can be little doubt that the development of practical industrial applications for perchloric acid ($\text{HClO}_4.2\text{H}_2\text{O}$) has gained favour all out of proportion to the knowledge of its chemical properties by the users of these processes. This fact has not been fully recognised. As a result, unfortunate hazardous situations have been encountered. Such situations would never have resulted had the properties of perchloric acid been familiar to the operating chemists. We demand of perchloric acid that it have properties that make it valuable for its many separate and distinct applications and then condemn it as hazardous when its basic chemical properties are forgotten and proper precautions in its use are ignored. The same can be said of many other chemicals that play similar roles, such as 90 per cent. hydrogen peroxide, gasoline, ethyl ether and many other everyday chemicals, the chemistry of which is familiar to most operating chemists.

Perchloric acid is safe—it is versatile and efficient to use. Perchloric acid may at the same time be hazardous if its properties are not recognised, its purpose in a given process fully understood and measures taken to avoid known possibilities of a hazardous complication.

Perchloric acid can be shipped in any quantities without hazard. It can be stored for any period of time without deterioration. To use it makes a convert and a persistent advocate. As its properties and stellar advantages become more and more familiar, its use pyramids from small-scale applications to large-scale industrial applications.

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Erratum—Page 17, Line 24, change "appearance" to "discharge."

The Colorimetric Determination of Iron in Raw and Treated Municipal Water Supplies by Use of 4:7-Diphenyl-1:10-Phenanthroline

By G. FREDERICK SMITH, W. H. McCURDY, JUN.,* AND HARVEY DIEHL

An organic analytical reagent, 4:7-diphenyl-1:10-phenanthroline (batho-phenanthroline), which is specific for iron, is described for the ultra-micro spectrophotometric determination of iron. The reagent has been applied to the determination of amounts of iron ranging from 1 to 10 μg in 100 ml of water. It forms a *tris* type molecular complex ferrous ion whose wavelength of maximum absorption is 533 mμ and molecular extinction coefficient is 22,400. An extraction procedure for the isolation of the coloured complex from its aqueous solution increases the sensitivity and extends the specificity to the point where no known interference by either metal cations or common anions such as chloride, nitrate, acetate, sulphate or chlorate occurs. The method has been applied to the determination of raw and purified well water provided by municipal water supply systems. Copper does not interfere.

THE ferroin reaction, which involves the formation of a red complex of ferrous iron with certain heterocyclic nitrogen compounds, has been extensively used for the colorimetric determination of small quantities of iron. The iron is first reduced to the ferrous state and then reacted with 1:10-phenanthroline, dipyridine, terpyridine or certain substituted derivatives of these compounds. References to the various procedures can be found in the work of Smith and Richter,[1] Brandt and Smith[2] and Welcher.[3] The method is in routine use for the determination of iron in wine, beer, foods, chemicals and many other products. It has been adopted as the official method for determining iron in water.[4]

In the determination of iron in treated water 1:10-phenanthroline, although a great improvement upon thiocyanate, is still not sufficiently sensitive as the lower limit is about 0·5 parts of iron per million, which is greater than the figure for iron in treated water. A new, substituted 1:10-phenanthroline, prepared by Case[5] and studied by Smith and McCurdy,[6] has now been found to be sufficiently sensitive to solve this problem. The new reagent is 4:7-diphenyl-1:10-phenanthroline and has been given the short name "bathophenanthroline." This name has been assigned because the absorption maximum of the ferrous derivative lies at a greater wavelength than that of 1:10-phenanthroline, viz., 533 mμ compared with 510 mμ (a bathochromic shift).

Not only is the molar extinction coefficient of the ferrous bathophenanthroline ion (22,400) greater than that of ferrous 1:10-phenanthroline (11,100) but the new reagent can also be extracted from aqueous solutions with certain immiscible solvents, such as *iso*amyl alcohol and *n*-hexyl alcohol. Two important advantages are gained from this:

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the iron in large samples can be easily concentrated into a small volume for measurement and it is easy to free the necessary reagents from iron, which eliminates the blank correction.

METHOD

REAGENTS—

Bathophenanthroline, 0·001 *M*—Prepare a 50 per cent. ethyl alcohol solution of batho-phenanthroline by dissolving 0·0334 g of the reagent ($C_{24}H_{16}N_2$, mol. wt. 334) in 50 ml of ethyl alcohol and by diluting with 50 ml of iron-free water. Store this solution in a glass-stoppered 125-ml Pyrex bottle. Alternatively, the reagent may be dissolved in the alcohol extracting solvent (without addition of water) and the complexing agent, together with a part of the extracting solvent, can be added to the test liquid. The first procedure is preferred. The reagent is also easily soluble in glacial acetic acid.

Hydroxylamine hydrochloride—A 10 per cent. solution. Reagent grade hydroxylamine hydrochloride contains appreciable amounts of iron. Prepare 100 ml of a 10 per cent. aqueous solution of hydroxylamine hydrochloride and add 3 to 4 ml of the 0·001 *M* batho-phenanthroline solution. Place the solution in a 125-ml conical separating funnel and add 10 to 20 ml of *iso*amyl alcohol. Shake the contents of the flask and allow 5 minutes for the supernatant alcohol solution of the extracted red iron impurity to collect. Draw off the colourless aqueous bottom layer into a second separating funnel and repeat the separation to insure complete removal of iron. Store the iron-free hydroxylamine solution in a 125-ml glass-stoppered Pyrex reagent bottle. The solution has a pH of 1·5 to 1·75. It has been shown that all excess of bathophenanthroline is extracted from the reagent purified in this manner. The small amount of extracting solvent left in the reagent is not detrimental.

Sodium acetate solution—Transfer to a 125-ml conical separating funnel 100 ml of a 10 per cent. solution of reagent grade sodium acetate solution and 3 to 4 ml of bathophenan-throline reagent. Add 2 ml of the 10 per cent. hydroxylamine solution to reduce the iron present. Extract the red iron complex by adding 10 to 20 ml of *iso*amyl alcohol and shaking the contents of the separating funnel thoroughly. When the two immiscible liquids have separated completely (after 5 minutes) draw off the lower aqueous layer into a second separating funnel and repeat the separation to ensure complete removal of iron. Store the acetate reagent in a 125-ml glass-stoppered Pyrex bottle.

*iso*Amyl *alcohol*—Reagent grade *iso*amyl alcohol can be used with no preliminary pre-paration. Technical grade *iso*amyl alcohol must be distilled before use. *n*-Amyl, *iso*amyl or *n*-hexyl alcohol may be used. The distribution coefficient of the 4:7-diphenyl ferroin complex between these alcohols and water could not be readily determined because of the great solubility of the complex in alcohol. However, the ferrous complex is more completely removed by one extraction with *n*-hexyl alcohol than by similar treatment with *iso*amyl or *n*-amyl alcohol. This is probably the result of *n*-hexyl alcohol being the least water-soluble alcohol of the group. Under ordinary conditions two extractions with *iso*amyl alcohol are sufficient to completely recover the iron. *n*-Hexyl alcohol may be preferable where the volume of sample is large and minute amounts of iron are present. In these circumstances one extraction is generally adequate. The distribution coefficient of the ferrous complex ion formed from 2:9-dimethyl-1:10-phenanthroline between various immiscible alcohols and water are as follows: *n*-amyl alcohol, 490 to 1; *iso*amyl alcohol, 1570 to 1; and *n*-hexyl alcohol, 3420 to 1. For bathophenanthroline the same order of magnitude of results should be attained.

Ferrous iron solutions—Samples of crystalline ferrous ammonium sulphate hexahydrate (Mohr's salt) or ferrous ethylenediamine sulphate tetrahydrate (Oesper's salt) can be used for preparing standard solutions. To prepare a standard solution containing 0·01 mg of iron per ml, accurately weigh 0·0702 g of Mohr's salt or 0·0684 g of Oesper's salt and dissolve it in conductivity water with 2·5 ml of concentrated sulphuric acid. Transfer this solution to a 1000-ml graduated flask, dilute to volume with conductivity water and mix thoroughly.

APPARATUS—

Separating funnels—For many applications 60 and 125-ml separating funnels are adequate. In some respects it is preferable to use a separating funnel with a cock of smaller bore than is usual and with the section above the cock longer and more tapered. This refinement is not, however, a prerequisite. Separating funnels with standard-taper ground stoppers and stopcocks are a material advantage.

Nessler tubes and rack—For 0·01 to 0·1 parts of iron per million, Nessler tubes are adequate and indeed preferable to ordinary spectrophotometric instruments such as the Cenco-Nelson spectrophotometer or similar instruments, because even a glass cell with a 5-cm light path is inadequate. For alcoholic solutions of the colour complex made from 0·01 to 0·06 parts of iron per million in increments of 0·01 p.p.m., Nessler tubes are required. An observation rack with 10 tube positions provides for 8 standard tubes, a blank and for a tube for the unknown.

Volumetric flasks and pipettes—A good stock of 10 and 50-ml calibrated volumetric flasks and pipettes of 1, 2, 5 and 10-ml capacity is required. The flasks should be of the standard-taper glass-stopper type.

PROCEDURE FOR THE DETERMINATION OF IRON IN TREATED WATERS—

Preparation of standard solutions—This type of determination involves 0·001 to 0·01 mg of iron in 100-ml water samples (1 to 10 parts of iron in 100 million parts of water).

Place 99 ml of iron-free water in a 125-ml separating funnel and add, by means of a pipette, 1 ml of standard iron solution containing 0·001 mg of iron. Add 2 ml of 10 per cent. hydroxylamine solution and 4 ml of 10 per cent. sodium acetate solution. This gives a solution whose pH is approximately 4. Add 4 ml of 0·002 M bathophenanthroline. The red ferrous complex appears at once and the excess of reactant forms a white turbidity because of its reduced solubility in the water solution. Add 10 ml of *iso*amyl alcohol, stopper the separating funnel and shake the contents thoroughly. Set the reactants aside for at least 5 minutes, transfer the lower aqueous layer to a second 125-ml separating funnel, repeat the addition of 10 ml of *iso*amyl alcohol, shake and set aside again for 5 minutes and finally draw off the aqueous lower layer and discard it. Transfer the coloured alcohol extracts to a 50-ml graduated flask, rinsing each separating funnel and stopper with generous portions of ethyl alcohol from a 5-ml pipette. Dilute the contents of the graduated flask to volume with ethyl alcohol, stopper the flask and mix its contents thoroughly. Transfer the coloured *iso*amyl alcohol solution of bathophenanthroline ferrous complex to a 50-ml Nessler tube.

Repeat this procedure in turn with 2·0, 3·0, 4·0, 5·0, 6·0, 8·0 and 10 ml of standard iron solution and prepare a blank containing all the reagents except the iron solution, giving a total of nine standards of reference. The composition of the solutions and their colour intensities remain unaltered for long periods if the tubes are protected against evaporation.

Preparation of test samples of purified water supplies—Municipal water plants generally supply city water mains with a product that is sufficiently free of iron to fall within the range covered by the standard Nessler tubes, whether the water samples are taken at the pumping station source or from the tap at the point of consumption. Treat 100-ml samples of water exactly as described above for the preparation of the standard Nessler tubes. The iron is readily estimated to the nearest hundredth part per million by comparing the unknown *iso*amyl extractions of the test samples with the standard Nessler tubes. By test, starting with additional known concentrations of iron added to 100 ml of iron-free water, duplicate colour intensities of the unknown solutions with standards was found.

Sampling of raw well water—This type of product may contain from one-tenth of a part to five parts per million of iron, although it is generally at or near the higher value. For this range a moderately efficient spectrophotometer is required for determining colour intensities. Hence, take 1 to 10-ml samples of raw water for analysis. It is important to sample the water at the source and to take samples immediately before analysis. If this is not possible, use a completely full sample bottle in order to help retard oxidation of iron in contact with atmospheric oxygen. If an appreciable length of time is likely to elapse between sampling and analysis, add 2 ml of iron-free hydrochloric acid solution to the sampling bottle before sampling to ensure no precipitation of iron and other impurities.

Preparation of standard reference data for the estimation of total iron in raw well water—By use of the standard iron solution containing 0·01 mg of iron per ml, the procedure just described can be applied to iron solutions at higher concentrations. At these concentrations a 60-ml separating funnel is used, as follows.

Add to five 60-ml separating funnels 5·0, 6·0, 7·0, 8·0 and 9·0-ml portions of iron-free water. With calibrated pipettes, add to these tubes 5·00, 4·00, 3·00, 2·00 and 1·00 ml, respectively, of standard iron solution containing 0·01 mg of iron per ml. Then add 2 ml of 10 per cent. iron-free hydroxylamine solution, 4 ml of 10 per cent. iron-free sodium acetate

solution and 4 ml of the bathophenanthroline. colour reagent. After mixing these components well, add 8 ml of *iso*amyl alcohol and shake the stoppered flask thoroughly. After 5 to 10 minutes (preferably 10 minutes) draw off the lower aqueous layer. Transfer the remaining coloured *iso*amyl alcohol to a 10-ml graduated flask. Using a 1-ml pipette, rinse the inner walls of the separating funnel, collect the rinsings in a graduated flask and dilute to the mark with ethyl alcohol. Determine the transmittance and optical density and plot the transmittance as ordinate and parts per million as abscissae to give a smooth graph. When the ordinates are optical density values, a straight line indicates conformity with Beer's law.

The analysis of raw well water—Treat samples of from 1·00 to 5·00 ml of raw water in a manner similar to that described for the preparation of the reference standard amyl alcohol extractants. Measure the optical density and determine the number of parts of iron per million present from the calibration graph. Typical experimental calibration data are shown in Table I.

TABLE I

THE TRANSMITTANCE AND OPTICAL DENSITY OF EXTRACTS OF STANDARD IRON SOLUTIONS IN THE *iso*AMYL ALCOHOL SOLUTION OF THE BATHOPHENANTHROLINE - FERROUS COMPLEX

Volume of extracted *iso*amyl alcohol - ethyl alcohol solution = 10 ml

Iron concentration, μg	Transmittance, %	Optical density
1·0	88·2	0·056
2·0	80·1	0·097
4·0	67·0	0·174
6·0	57·8	0·239
8·0	50·3	0·298
10·0	41·5	0·384

RESULTS

The data shown in Table I were obtained with a Beckman model B spectrophotometer and 1-cm quartz cells, at 533 mμ. Water was used to standardise the instrument. This accounts for the failure of the graphical representation of the data of Table I to give a straight line intercepting the horizontal and vertical axis at the origin. Less elaborate spectro-photometers such as the Cenco-Nelson photolometer give results almost as accurate. To enhance the absorption measurement, the following filters, in addition to the Corning "Alka" infra-red filter, have been found suitable: sextant green (No. 401); heat resistant yellow-green (No. 450); dark theatre blue (No. 503); colorimeter blue-green (No. 978); dark shade blue (No. 430); and signal green (No. 440). The first two are preferable, although the remainder are satisfactory and render the method only slightly less sensitive.

FACTORS CONTRIBUTING TO THE SUPERIORITY OF THE BATHOPHENANTHROLINE - FERROIN REACTION—

Specificity—The familiar acid anions of hydrochloric, sulphuric, nitric, acetic and perchloric acids do not interfere. If copper is present, certain anions such as iodide, thiocyanate, cyanide, thiosulphate, sulphide and phosphate may cause precipitation in the aqueous solution upon addition of bathophenanthroline, but such precipitates do not interfere with the quantitative extraction of the ferrous iron complex.

The following metal cations: Li, Na, K, Be, Mg, Ca, Sr, Ba, Ce····, Ce···, Pr··· and the rare earth metals in general, including Th····, Ti····, Zr····, V as vanadate and vanadyl ion, Cr···, W······, U······, Mn··, Fe···, Ru··, Os·······, Ni··, Pd···, Pt····, Ag·, Zn, Cd, Hg·, Hg·, B···, Al···, Ga···, Tl·, Sn····, Sn··, Pb··, P·····, As·····, As··· and Be·· do not interfere. Tellurates and selenates are reduced to the metal by hydroxylamine. Cobalt forms a light yellow colour but this is not extracted from acid solution.

Copper also forms a yellow complex bathophenanthroline complex ion that is a *bis*-rather than a *tris*-complex. This *bis*bathophenanthroline - cuprous complex is formed in neutral or alkaline solution and is transformed on acidification to the colourless *mono*-bathophenanthroline - cuprous complex. Therefore, with the conditions of acidity used (pH 4·0) the *mono*-cuprous complex extracted by *iso*amyl alcohol is colourless and without

interference in the iron determination. The molecular extinction coefficient of the *bis*bathophenanthroline - cuprous complex is 12,140 and represents the most delicate ferroin reaction complex at present described for use in the spectrophotometric determination of copper.

The present procedure for the determination of iron has been applied in the presence of copper with results as shown in Table II.

TABLE II
THE SPECTROPHOTOMETRIC DETERMINATION OF IRON IN PRESENCE OF COPPER
Measurements taken with a Carey recording spectrophotometer

Iron taken, mg	Copper present, mg	Optical density at 535 mμ	Molecular extinction coefficient found
0·09521	0·0000	0·777	22,700
0·02345	0·2578	0·212	22,200
0·04720	0·1281	0·385	22,750
0·09467	0·0623	0·801	22,850
0·19804	0·0289	1·575	22,200
		Mean =	22,540

The value found for the molecular extinction coefficient of the *tris*bathophenanthroline - ferrous complex in the presence of copper compares favourably with that found in the absence of copper (22,400). The reagent reacts with no known metal ion, other than Fe``, to give a coloured complex that can be extracted by *iso*amyl alcohol at pH 4·0.

Purification of reagents—A necessary accompaniment to the development of an extremely delicate reagent for isolating and determining a given element is that all reagents be entirely free from the element being determined. The more sensitive the reagent, the greater the necessity for purity of the accessory chemicals.

By the use of bathophenanthroline the accessory reagents, hydroxylamine, and sodium acetate in the form of their 10 per cent. aqueous solutions may be easily freed from iron, and the customary laboratory stocks of water and alcohols may be readily obtained iron-free from stock supplies or may be easily purified by simple distillation.

Recovery of reagents—*iso*Amyl alcohol as well as extracting the bathophenanthroline - ferrous complex also extracts the excess of organic reagent quantitatively from the aqueous solution, so all of the reagent can be recovered from the alcohol extract and, at the same time, the alcohol, if subjected to distillation, can be simultaneously recovered. The reagent can be recovered by a similar procedure to that of Smith and Cagle.[7]

Colour stability—A series of colour standards such as that described above is stable for long periods of time.

Colour sensitivity—The most important applications of bathophenanthroline are in the determination of iron at extremely low concentrations. The most effective range of concentrations for which it should be used is 0·001 to 0·01 p.p.m. For these concentrations, tall-form 375-mm Nessler tubes, which are recognised standard water analysis equipment, should be used.[4] The next best range is 0·01 to 0·1 p.p.m. and 300-mm Nessler tubes should be used, as described in this paper. The third range is 0·1 to 1·0 p.p.m. and 1-cm cells and a photolometer with suitable filters or a spectrophotometer operating at 533 mμ should be used. For higher concentrations it is proper to substitute 1:10·phenanthroline for bathophenanthroline. The limit of sensitivity of the more sensitive bathophenanthroline - ferroin reaction in the lowest range given above is the colour intensity of the blank determination, *i.e.*, it depends on the degree to which the reagents can be freed from iron.

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