# THE ANALYST

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# THE ANALYST

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the Journal of the Society
for Analytical Chemistry

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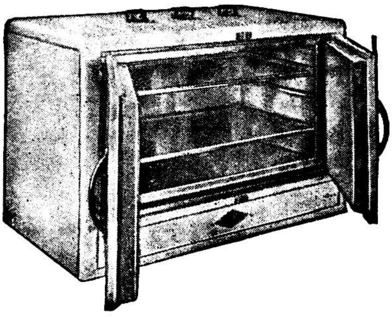

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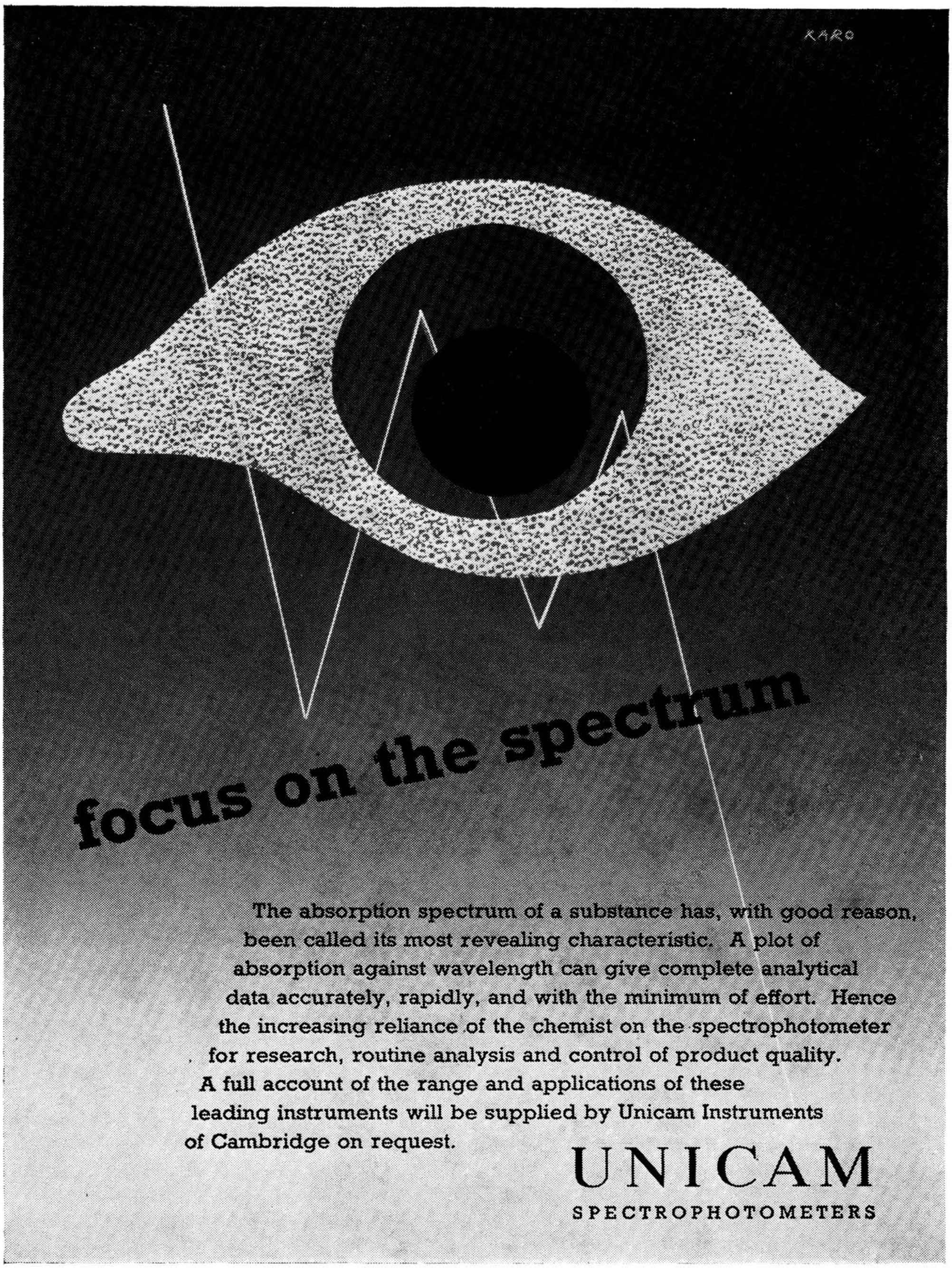
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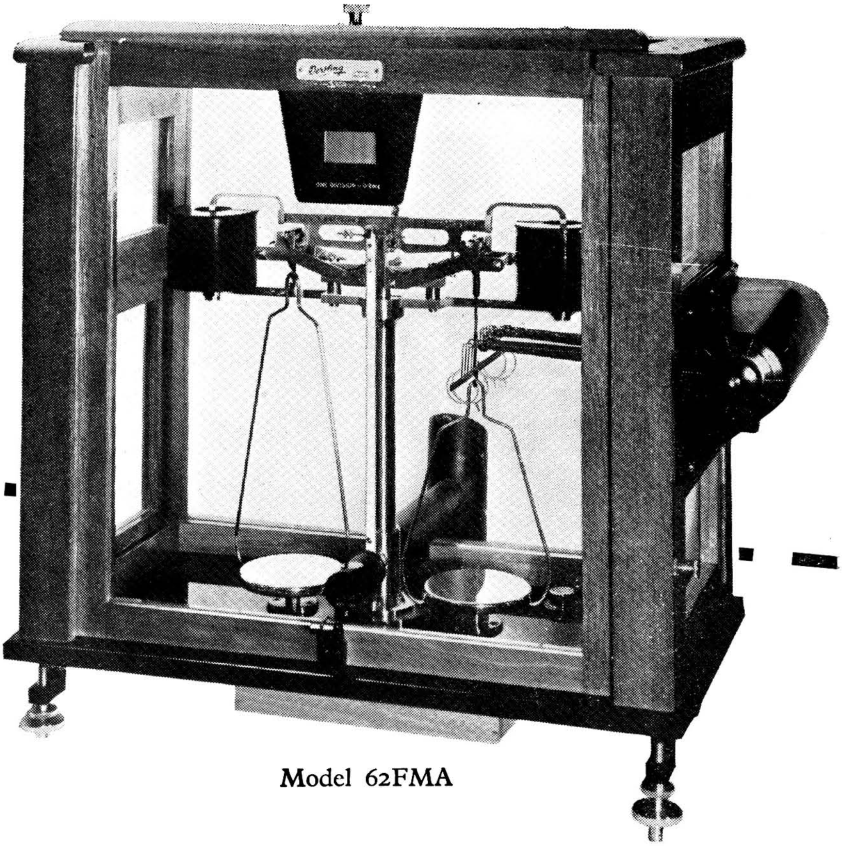

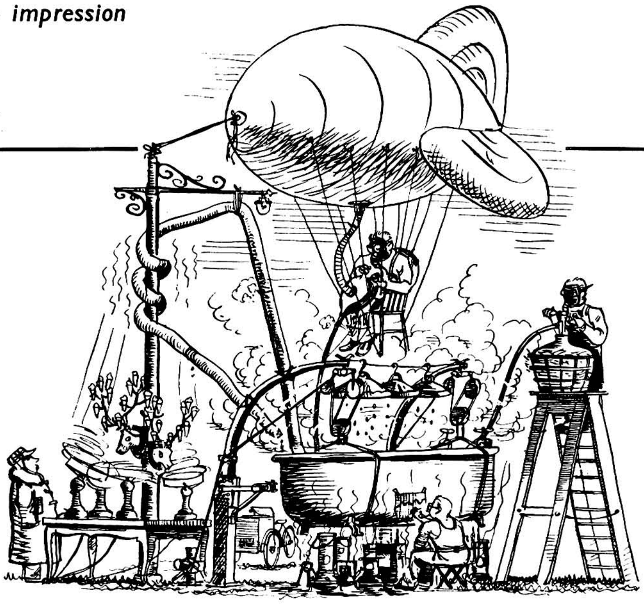

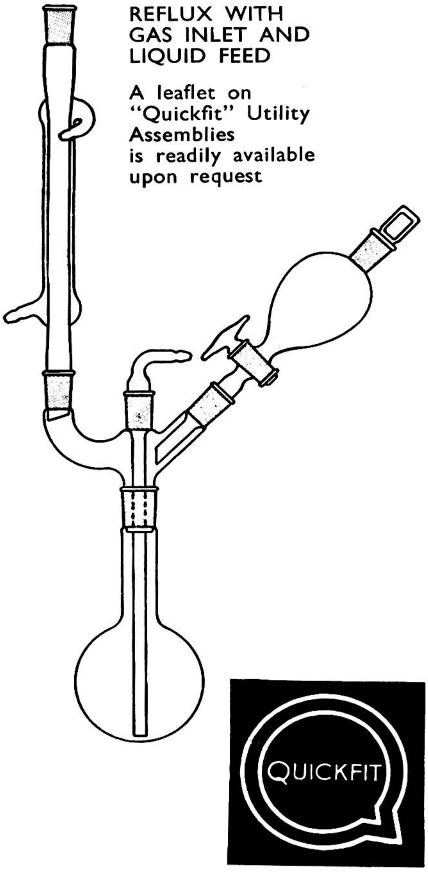

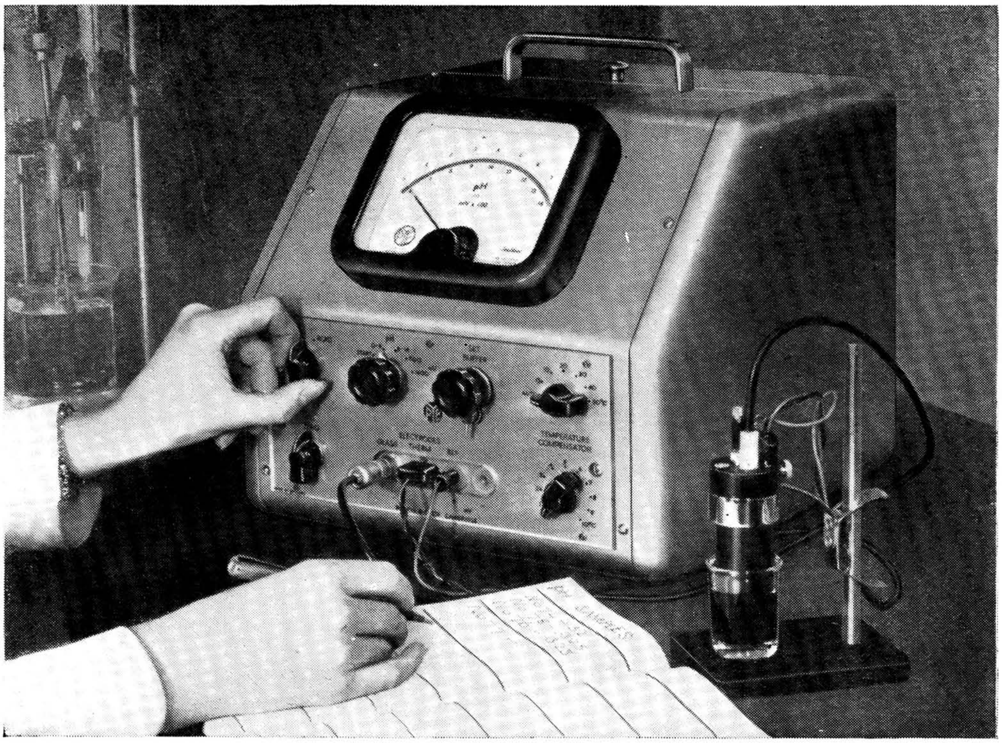

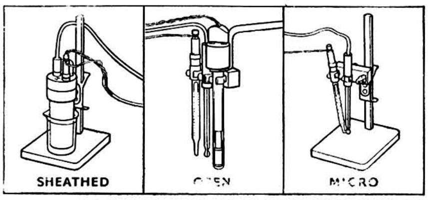
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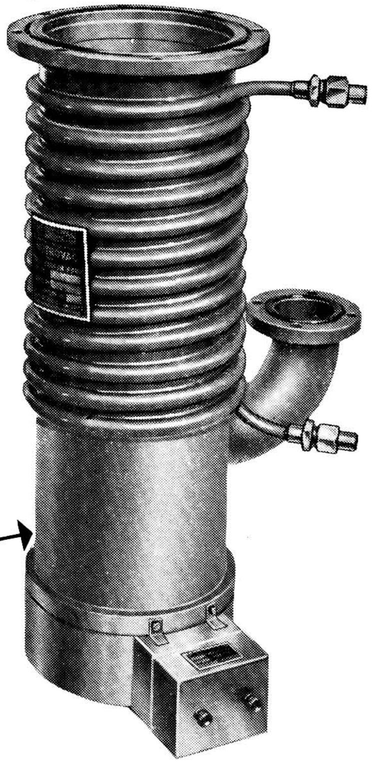
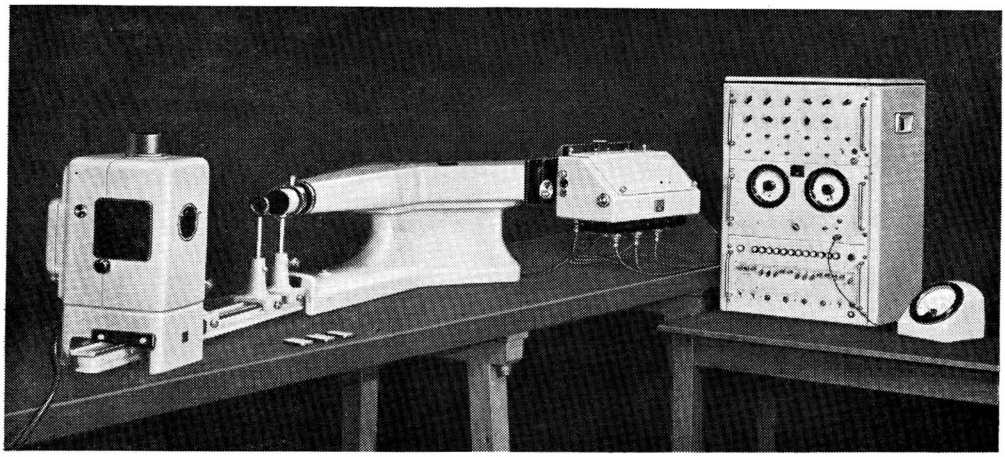
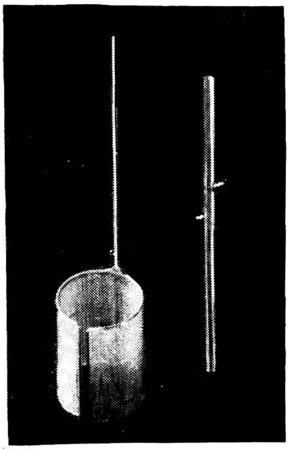
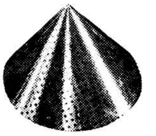
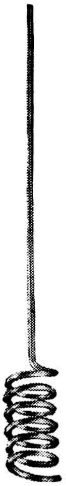
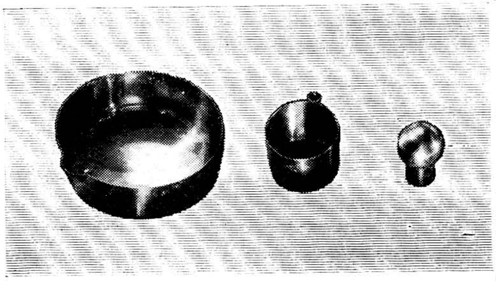


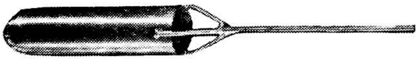


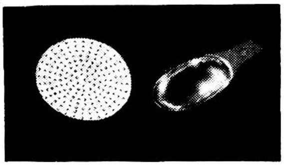






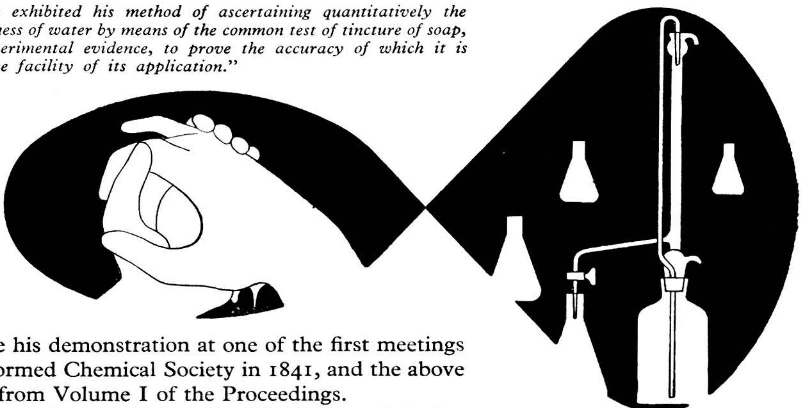






**The common test of tincture of soap**

*" Dr. Clark then exhibited his method of ascertaining quantitatively the comparative hardness of water by means of the common test of tincture of soap, illustrated by experimental evidence, to prove the accuracy of which it is susceptible and the facility of its application."*



Dr. Clark gave his demonstration at one of the first meetings of the newly formed Chemical Society in 1841, and the above is an abstract from Volume I of the Proceedings.

The B.D.H. catalogue still includes Clark's Soap Solution and testifies to the remarkable permanence of his technique. Greater accuracy and convenience in total hardness determination, however, are now obtained from the B.D.H. Hardness Solutions and Indicator based on the use of ethylenediamine-tetracetic acid as advocated by Schwarzenbach and others.

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JANUARY, 1955 Vol. 80, No. 946

THE ANALYST

# Leading Articles

It has now been agreed by the Publication Committee of the Society to issue from time to time editorial or leading articles, and it has fallen to me as President to write the first of these. It seemed appropriate to deal with the question of the recent developments, especially as they affect our publications.

Twelve months have elapsed since the Society took on its new name. For the previous 79 years the scope of the Society had steadily increased until even the full version of the old name, Society of Public Analysts and Other Analytical Chemists, no longer embraced all its activities: it had, in fact, become The Society for Analytical Chemistry many years before the name was changed. The Society has already much to offer. There are integrated in it the Microchemistry, Physical Methods and Biological Methods Groups; regional activities are encouraged by the Sections—North of England, Scottish and Western, the last having been inaugurated in May, 1954. *Analytical Abstracts* began publication at the beginning of 1954, and last year also saw the introduction of the Junior Membership grade for the age-group 18–27 years. The Council has spent much time and thought in devising ways in which the younger as well as the more senior members can be better served.

Through its Policy Committee, recently strengthened, the Council has suggested some further services. Reports of Council's activities will be published from time to time in *The Analyst*, and reports of the Society's activities will continue along the expanded lines started last year. Whilst the journal's main activity will continue to be the dissemination of new and original work, space is already being found for the publication of more general articles. The recent policy of publishing summaries of lectures dealing with the general analytical aspects of some particular subject, but not containing sufficient original work to warrant publication as papers, has permitted *The Analyst* to record many valuable observations that would otherwise have been lost to all save those who were fortunate enough to have been present at the meetings at which the lectures were delivered. During the year a symposium was held at which six such papers were presented and discussed; the account published in the August *Analyst* shows the extent to which such general meetings can be reported.

The Society has also recently begun to hold some exceptionally interesting and important meetings at which lectures are given by internationally famous authorities. The publication of their lectures in full will add to the value of the sets of *Analysts* owned by members—Full and Junior alike. Lectures by Professor Harold Burton and Professor G. Frederick Smith on Perchloric Acid are printed in this issue. Soon we shall have heard Professor Schwarzenbach on "Complexones," and his lecture, too, will appear in the pages of the journal.

There is a further class of paper that, although not original, has begun to be included in *The Analyst*'s pages, namely, the Critical Review. This class of paper gives a personal appraisal of the existing methods for some form of analysis, and must be written by an authority on the subject. In the near future we shall be publishing one on "The Analysis of Sea-water" (by H. Barnes)—others in hand include "Zone Electrophoresis on Filter-paper" (by L. F. J. Parker), "Recent Advances in Non-ferrous Analysis" (by G. W. C. Milner), "Ferrous Metallurgical Analysis" (by B. Bagshawe), "The Determination of Niobium and Tantalum" (by W. H. Bennett) and "Analytical Applications of Ethylenediaminetetra-acetic Acid" (by R. E. Stuckey).

The "leading articles," of which this is the first, will be short; they will draw attention to recent developments in analysis and techniques, and will point to new publications and new applications of established techniques, and it is hoped that they will be instructive. Although the very nature and need for topicality will prevent these "leading articles" from appearing regularly, it is hoped that they will appear frequently.

D. W. KENT-JONES
*President*

# Helping Medicine

ANALYTICAL chemistry has a way of insinuating itself into what may sometimes, at first blush anyway, appear rather unlikely places. The more by so doing it establishes its ubiquity, the greater become its claims to be considered a discipline in its own right. These thoughts pass—and not for the first time—through our mind when we study particulars of the latest publication on chromatography, surely an analytical technique if there ever was one. The names of experts such as A. J. P. Martin, R. Consden, A. C. Chibnall, Tudor Jones, S. M. Partridge and C. E. Dent, to mention only half a dozen of the nineteen contributors, guarantee its excellence as a guide to recent practice: its catholicity and amplitude of cover are made clear by the range of contents, from general principles to amino-acid metabolism, from inorganic chromatography to antibiotics and vitamins, as well as such techniques as gas - liquid chromatography and paper chromatography. These are, again, only more or less random selections from the sixteen chapters, which have an introduction by Dr. A. J. P. Martin, the Nobel prizeman, who won his prize with Dr. R. L. M. Synge for work on this very subject.

The publication is one of a series; among other subjects covered in it have been viruses, blood coagulation, mental health, malaria research, skin disorders, and in fact almost every part of medical research on which work is in active progress. For the publication on chromatography is, in fact, No. 3 of Vol. 10 of the *British Medical Bulletin*, a periodical that has been running for eleven years under the auspices of the British Council. It has the object, *inter alia*, of maintaining British prestige among oversea scientists by the issue of regular authoritative monographs on current research in medicine and the cognate sciences. We do not know which medical colleague first thought it desirable to emphasise the connection between recent medical advances and analytical methods used in the research laboratory—to say nothing of those applied in diagnosis and as a check on treatment—but in doing so he certainly paid a tribute, a willing one, we are sure, to that ubiquity of analytical chemistry mentioned near the beginning of these comments.

A. L. B.

# PROCEEDINGS OF THE SOCIETY FOR ANALYTICAL CHEMISTRY

## DEATHS

WE record with regret the deaths of

William Bacon
Percy Edgerton.

## SCOTTISH SECTION

A JOINT Meeting of the Section with the Glasgow and West of Scotland Section of the Royal Institute of Chemistry was held at 7.15 p.m. on Friday, November 26th, 1954, in Room 24, Royal Technical College, Glasgow. The Chair was taken by Professor Hugh Nicol, M.Sc., Ph.D., F.R.S.E., F.R.I.C.

A lecture on "Sea Water" was given by H. Barnes, B.A., Ph.D., D.Sc., F.R.I.C. (see summary below).

### SEA WATER

DR. H. BARNES said that the seas covered some 70 per cent. of the surface of the earth, and oceanography was the study of all the many and varied aspects of the oceans. This great volume of water contained over $5 \times 10^{16}$ tons of salts—enough to cover the land of the globe to a depth of 153 metres.

Because of its complex composition the total solids were difficult to determine by direct analysis or by evaporation, and for the purposes of physical oceanography (where the total salt content, with its influence on density and its importance as an indicator of physical processes, was of more interest than the ionic composition), an arbitrary quantity—the salinity—had been used. This was determined from the chlorinity, also arbitrarily defined, the original standard being sea-water maintained at Copenhagen, against which all subsequent samples had been standardised. More recently this had been "permanently" standardised against atomic-weight silver.

The major elements bore a constant ratio to one another—a factor first established by Professor Dittmar from his analyses of the samples brought back by the Challenger Expedition, the analyses being made in the Royal Technical College, Glasgow.

There were other important elements—the nutrient elements—the primary ones being phosphorus, nitrogen and silicon, the first two being required for the metabolic activities of the organisms and the third for the siliceous skeletons of the diatoms. All these underwent a cyclical process—absorption by anabolic processes, return by excretion and bacterial or chemical decompositions. In the case of silica it would seem to be largely a chemical process of re-solution, but the available evidence led to contradictory hypotheses. There was much here in common with the silicosis problem.

The economic aspects of the seas were in their infancy; common salt, salts of magnesium, potassium and calcium, together with bromine and metallic magnesium, were already being extracted, but the untapped resources were enormous. A great deal remained to be done: the chemistry might be simple but the chemical engineering problems associated with further advances would be difficult.

THE Section, as a member of the Federation of Technical Societies in Glasgow, made its first official attendance at the Ramsay Chemical Dinner on December 2nd, 1954, held at the Central Hotel, Glasgow, under the Chairmanship of Sir William G. Ogg, M.A., Ph.D., LL.D., F.R.S.E. Dr. Eric Linklater, C.V.E., M.A., proposed the toast of the Profession of Chemistry.

The Society was represented by the President, Dr. D. W. Kent-Jones, B.Sc., F.R.I.C.

## PHYSICAL METHODS GROUP

THE Tenth Annual General Meeting of the Group was held at 6.30 p.m. on Tuesday, November 30th, 1954, in the Meeting Room of the Chemical Society, Burlington House, London, W.1. Mr. A. A. Smales, B.Sc., F.R.I.C., was in the Chair. The Group Officers and Elected Members of the Committee for the forthcoming year are as follows:—*Chairman*—Mr. A. A. Smales. *Vice-Chairman*—Dr. J. E. Page. *Hon. Secretary and Treasurer*—Mr. R. A. C. Isbell, Hilger & Watts Ltd., 98, St. Pancras Way, London, N.W.1. *Members of Committee*—Messrs. W. Furness, H. M. N. H. Irving, C. A. Parker, R. A. Wells, T. S. West and A. F. Williams. Messrs. C. A. Bassett and D. C. Garratt were re-appointed as Hon. Auditors.

The Annual General Meeting was followed by an Ordinary Meeting of the Group, which took the form of a discussion on "Possibilities in the Establishment of Standard Samples for the Determination of Some Trace Elements."

## BIOLOGICAL METHODS GROUP

THE Tenth Annual General Meeting of the Group was held at 6.15 p.m. on Friday, December 10th, 1954, in the Meeting Room of the Chemical Society, Burlington House, London, W.1. The Chairman of the Group, Dr. L. J. Harris, F.R.I.C., presided. The following Officers and Committee Members were elected for the forthcoming year:—*Chairman*—Dr. L. J. Harris. *Vice-Chairman*—Mr. K. L. Smith. *Hon. Secretary and Treasurer*—Mr. K. A. Lees, Glaxo Laboratories Ltd., Sefton Park, Stoke Poges, Bucks. *Members of Committee*—Messrs. H. O. J. Collier, J. I. M. Jones, S. K. Kon, S. A. Price, G. F. Somers and E. C. Wood. Mr. J. W. Lightbown was re-appointed Hon. Recorder, and Messrs. D. M. Freeland and J. H. Hamence were re-appointed as Hon. Auditors.

The Annual General Meeting was followed at 6.30 p.m. by an Ordinary Meeting of the Group, at which Dr. L. J. Harris was in the Chair. The following papers were presented and discussed: "The Evaluation of Vegetable Purgatives," by J. W. Fairbairn, B.Sc., Ph.D., F.R.I.C., F.P.S., F.L.S.; "The Disc - Plate Method of Assay with *Neurospora* Mutants for Thiamine, Pyridoxin, Choline, Inositol and *p*-Aminobenzoic Acid," by E. C. Barton-Wright, D.Sc., F.R.I.C., and N. J. Butler; "Observations on the Biological Estimation of Vitamin E," by T. Moore, D.Sc., Ph.D.

# Perchloric Acid and Some Organic Perchlorates*

BY H. BURTON AND P. F. G. PRAILL

(*Presented at the meeting of the Society on Wednesday, July 21st, 1954*)

The history of perchlorates is summarised and various methods of preparation of the acid are noted. The action of perchloric acid and some organic perchlorates on various types of organic compounds, *e.g.*, anhydrides and ethers, is discussed with particular reference to the formation of, especially, the alkyl perchlorates and related compounds. The simple alkyl esters of perchloric acid have long been known to be highly explosive; in the free state they possess many of the properties of covalent compounds. Consequently, when experiments that can lead to their formation are carried out, the risk of serious explosion is always present.

GROWING interest in the applications of perchloric acid to analytical chemistry makes the recognition of its properties imperative. Perchloric acid and the perchlorates have a notorious reputation; this is due to numerous explosions that have been recorded (Hackl[1]; Meyer and Spormann[2]; Kahane[3]; Zahn[4]; Balks and Wehrmann[5]; Young and Campbell[6]; and others to be mentioned later) and also to the lack of extensive investigations of their properties. Whilst it is not intended that the hazardous properties of perchloric acid should be belittled, it is thought that a better understanding of its character may dispel some of the fears that have

---

* Much of the chemistry of perchloric acid and perchlorates is summarised in "The Chemical Elements and Their Compounds," by N. V. Sidgwick, Oxford University Press, 1950, pp. 1230 to 1236; see also—

Gmelin's "Handbuch der Anorganischen Chemie," Eighth Edition, System No. 6, "Chlor," Verlag Chemie, Berlin, 1927, pp. 362 to 409.

"Perchloric Acid," Volume I, Second Edition, G. Frederick Smith Chemical Co., Columbus, Ohio, 1933.

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

E. Kahane, "L'Action de l'Acide Perchlorique sur les Matières Organique et ses Applications à la Chemie Analytique," Hermann et Cie, Paris, 1934.

A. Vialard-Goudu, "Contribution à l'Étude de l'Acide Perchlorique, Action sur les Composés, Organiques," Danel, Lille, 1937.

prevented its general use. We wish to emphasise the distinction between anhydrous perchloric acid and the 70 to 72 per cent. solution of the acid that is obtainable commercially. In this account, perchloric acid will refer to the solution, unless otherwise stated.

The history of the perchlorates begins with the discovery of potassium perchlorate by Stadion[7] in 1816. Stadion observed the formation of the salt in cooled mixtures of potassium chlorate and concentrated sulphuric acid. He prepared an aqueous solution of perchloric acid from the new salt. A simple ester, ethyl perchlorate, was prepared by Hare and Boye[8] as early as 1841, by the distillation of a concentrated solution of barium ethyl sulphate and barium perchlorate. The hazardous nature of the preparation and the instability of the product were soon recognised. Subsequent observations that anhydrous perchloric acid reacted explosively with organic materials, such as alcohol, ether, wood or paper (Roscoe[9]), seem to have acted as a deterrent to further investigations. It is as well to remember that, often, concentrated aqueous solutions of the acid can behave in the same way if they become absorbed in suitably porous media, *e.g.*, wood, linoleum or grain; such mixtures are very sensitive to impact and heat (Elliott and Brown[10]; Kabic[11]).

Various methods of preparing the acid have been recorded. Most of these are based on the reaction of sulphuric acid (Roscoe[9]; Vorlander and Von Schilling[12]; van Emster[13]; Mathers[14]) or hydrogen chloride (Kreider[15]; Smith and Friedman[16]) with metal perchlorates, or on the thermal decomposition (Serullas[17]; Hampel[18]) or electrolysis (Goodwin and Walker[19]; Schumacher[20]) of chloric acid—

$$3HClO_3 = HClO_4 + Cl_2 + 2O_2 + H_2O.$$

Hydrofluosilicic acid has been used in place of sulphuric acid (Roscoe[9]; Caspari[21]). Nitrogen-free perchloric acid can also be prepared from mixtures of ammonium perchlorate and nitric acid (Willard[22]).

Aqueous solutions of the acid can be concentrated at atmospheric pressure to an azeotropic solution containing 72·4 per cent. of perchloric acid, which boils at 203° C. Distillation of this solution at ordinary pressure is accompanied by some decomposition to chlorine, chlorine oxides and oxygen. At pressures of 2 to 7 mm of mercury, the solution can be concentrated to 73·6 per cent. of acid; this corresponds to the dihydrate (Smith and Goehler[23]). Aqueous perchloric acid is a colourless, hygroscopic, oily liquid ($d_{25^\circ} \simeq 1{\cdot}7$), which is much less dangerous than the anhydrous acid.

The latter can be prepared as a colourless mobile liquid ($d_{20^\circ} \simeq 1{\cdot}767$) from the aqueous solution by distillation under very carefully controlled conditions (Goehler and Smith[24]). The following series of interesting reactions result in the formation of about 10 per cent. yields of the anhydrous acid—

$$\begin{aligned} 4HClO_4.2H_2O &\rightarrow 2HClO_4.3H_2O + 2HClO_4.H_2O, \\ 2HClO_4.H_2O &\rightarrow HClO_4.2H_2O + HClO_4 \text{ (anhydrous).} \end{aligned}$$

A more recent method for producing the acid in high yields (greater than 70 per cent.) involves reaction of the hydrated acid with fuming sulphuric acid (Smith[25]).

Anhydrous perchloric acid boils undecomposed at 16° C at 18 mm (van Wyk[26]), but cannot be distilled without decomposition at ordinary pressure. Its extrapolated b.p. at 760 mm is 130° C and its m.p. is −112° C (Smith[25]; van Wyk[26]). On keeping, the anhydrous acid gradually becomes coloured owing to the formation of decomposition products. When this occurs, it may explode spontaneously. Pure samples do not explode when stored for about 30 days at ordinary temperatures, and they may be stored for as long as 60 days at liquid-air temperatures without the formation of colour (Smith[25]). Perchloric acid dissolves in water with the evolution of much heat (Berthelot[27]; Goodeve and Marsh[28]). It is this large heat of solution that undoubtedly initiates the explosive reaction of the anhydrous acid with organic solvents. The acid forms a number of hydrates (van Wyk[26]), the most interesting of which is the monohydrate. The X-ray diagram of this compound is analogous to that of ammonium perchlorate (Volmer[29]), and the Raman spectrum has the characteristic absorption of the $ClO_4^-$ ion (Fonteyne[30]; Redlich, Holt and Bigeleisen[31]; Millon[32]). Hence, the monohydrate is to be considered as the salt, hydroxonium perchlorate, $H_3O^+\}ClO_4^-$ (Smith and Goehler[33]).

In its chemical properties, perchloric acid differs considerably from periodic acid and from chloric acid, in that it is a poor oxidising agent at ordinary temperatures. At elevated temperatures, however, its oxidising properties are considerable. As might be expected from the preceding discussion, both the anhydrous acid and concentrated aqueous solutions of the acid are strong dehydrating agents.

Perchloric acid was formerly regarded as the strongest acid known; recently, however, it has been shown (Gillespie[34]) that in concentrated sulphuric acid it is weak compared with substances such as disulphuric acid ($H_2S_2O_7$). It cannot be over-emphasised that the strength of an acid is dependent on the basicity of the solvent in which it is dissolved. Perchloric acid is a relatively strong acid in many organic solvents, but it must not be assumed that the strength of the acid in such solutions is necessarily comparable to its strength in water. The anhydrous acid is strongly ionised in nitromethane (Wright, Murray-Rust and Hartley[35]) and considerably so in nitrobenzene (Murray-Rust, Hadow and Hartley[36]).

When anhydrous perchloric acid is mixed with an organic solvent, its molecules become modified, and it is these modifications that must form the basis of our subsequent discussion. Solvation of the perchloric acid molecule will almost certainly induce a change in the polarity of the bond uniting the hydrogen atom and the perchlorate group, that is, it may become more polar than in the original molecule. The formation of a conjugate acid, as in the formation of acetic acidium perchlorate, $[AcOH_2]^+ClO_4^-$, from acetic acid, can be considered to represent the extremity of this process. These conjugate acid perchlorates may exist almost entirely as ion pairs or they may dissociate into free, or solvated, ions. The extent of this dissociation will govern the strength of perchloric acid in the solvent and hence its usefulness as a strong acid for analytical procedures in anhydrous media. If the conjugate acid is unstable, it may react other than as a solvated proton, *e.g.*, the ion $[Ac_2OH]^+$ may act as an acylating agent.

Subsequently the perchloric acid may undergo a more pronounced change, as in the formation of an ester from an alcohol. Alternatively, the perchloric acid may form an organic perchlorate without the intervention of a conjugate acid, *e.g.*, when it adds across a double bond in an unsaturated molecule.

Usually, under conditions in the neighbourhood of room temperature, the properties of these solutions are largely dependent on the weak nucleophilic properties of the perchlorate ion. As the conditions become more drastic, the oxidative character of the ion becomes more pronounced, and here another application of perchloric acid is exemplified. The point at which these two properties begin to overlap differs with the system involved and must be determined each time by careful consideration of the system and by experiment.

In the discussion that follows it will be seen that the usefulness of perchloric acid stems from three properties: (*a*) its ability to form sparingly soluble salts with many organic bases, (*b*) its properties as a strong acid in non-aqueous solution and (*c*) its oxidative properties at relatively high temperatures.

## ORGANIC SALTS OF PERCHLORIC ACID

The substances to be considered in this section are those in which the central atom has a complete outer electron shell of eight electrons, as in the oxonium, sulphonium and ammonium salts. Carbonium perchlorates, in which the central atom has an outer shell of six electrons, are more profitably discussed in the later sections.

The fact that perchloric acid forms well-defined crystalline salts with basic materials, such as alkaloids, has been known for a long time (Fraude[37]). In 1910 it was suggested that concentrated perchloric acid might be used with advantage for the isolation and identification of many ketones and feebly basic nitrogen derivatives, especially those that do not form picrates (Hofmann *et al.*[38,39]). An additional advantage is that perchloric acid is more readily eliminated from its salts than picric acid is from picrates.

It has been pointed out by Hofmann *et al.*[40] that the solubility of the ammonium salt usually decreases in the order—

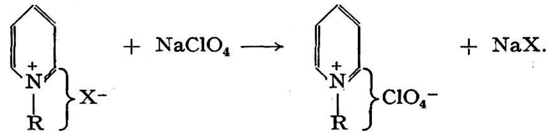
$$R{\cdot}NH_3^+\}ClO_4^-,\ R_2NH_2^+\}ClO_4^-,\ R_3NH^+\}ClO_4^-,\ R_4N^+\}ClO_4^-.$$

Compounds with more than one active centre, *e.g.*, benzidine, may form mono- and di-perchlorates. Many of these salts decompose explosively on heating, *e.g.*, aniline perchlorate explodes at 250° C (Spallino[41]). The temperature of ignition (not the *explosion temperature*) of many perchlorates of this type is in the region of 250° to 300° C (Datta and Chatterjee[42]).

A method for the purification of pyridine via the perchlorate (Arndt and Nachtway[43]) has sometimes led to explosions (Zacherl[44]; Kahn and Olting[45]). It would seem that the explosion could be caused by traces of ethyl perchlorate, or more likely ammonium perchlorate, which lower the kindling temperature of the mixture. However, Moureu and Munsch[46] consider that the explosions were probably due to traces of chlorates. A method that precludes danger by avoiding the use of alcohol and ammonia has recently been developed (Arndt and Severge[47]). Pyridine perchlorate exists in the form of colourless needles, m.p. 288° C, decomp. at 335° to 340° C. It can be detonated by a blow from a hammer.

Diazonium perchlorates generally have low solubilities in water. The dry salts explode violently and some, *e.g.*, *o*-tolyldiazonium perchlorate, even in the damp state (Hofmann and Arnoldi[48]).

Quaternary ammonium perchlorates can be prepared by double decomposition reactions, *e.g.*, pyridinium perchlorates can be made by pouring the quaternary alkyl sulphate or toluene-*p*-sulphonate into aqueous sodium perchlorate (Allen and Wilson[49])—



Oxonium and sulphonium salts are characterised by the structure—


$$R'\!:\!\ddot{M}\!:\!R''$$
$$\ddot{R}$$

in which the groups R, R′ and R″ may be alkyl, aryl or hydrogen. In general, the sulphonium salts are more stable than the corresponding oxonium derivatives.

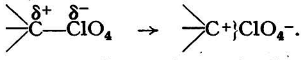
Compounds of the type $R_2OH^+\}ClO_4^-$ (**I**) are readily hydrolysed; those of the type $R_3O^+\}ClO_4^-$ (**II**), where $R_3$ represents a cyclic structure, are not (Hofmann *et al.*[40]). Salts of the type $R_3O^+\}X^-$ (**III**), where $R_3$ represents three alkyl groups, are very unstable (Meerwein *et al.*[50]). Examples of compounds of type **I** are found in the loose-addition compounds of perchloric acid with ketones or with ethers, *e.g.*, dioxan (Smeets[51]). Aromatic ketones form highly coloured perchlorates (Pfeiffer *et al.*[52]), which have characteristic decomposition points. These compounds often decompose spontaneously on keeping, to give perchloric acid and the ketone, *e.g.*, *p*-methoxybenzophenone perchlorate consists of yellowish-brown unstable crystals, whilst benzalacetophenone perchlorate can be isolated as fine yellow needles, which remain stable for 5 to 6 days.

Substances of type **II** are familiar in the form of compounds that contain a pyran nucleus, *e.g.*, the benzopyrylium, flavylium, xanthylium and the corresponding pyronium salts. Whether many of these compounds should be considered as oxonium salts or as carbonium salts has been the object of much discussion (Hill[53]; Shriner and Moffett[54]), but need not be considered here.

This section has been based on one of the most important classical applications of perchloric acid, and many hundreds of perchlorate salts of the above types have been prepared. No attempt has been made to catalogue these; rather it has been the purpose to give a general idea of the principles involved in their formation. Most of these compounds have characteristic crystalline properties and decomposition points. Little hazard is involved in handling them (except the diazonium salts), unless they are overheated or detonated.

## PERCHLORIC ESTERS AND RELATED COMPOUNDS

In addition to forming salts such as the above, perchloric acid is able to interact with suitably constituted organic materials to form alkyl, aralkyl, acyl or aroyl perchlorates. These substances are distinguished by having a perchlorate group directly attached to carbon. As yet, there is no evidence for perchlorates in which the perchlorate group is directly attached to an aromatic ring. We shall see that many of these compounds are mainly covalent in their properties and that others behave as typical salts. This obviously depends on the degree of polarisation of the bond between carbon and the perchlorate group—



Relatively few of these substances have been isolated, and in many instances their physical properties have not been determined owing to their instability. However, it is possible to produce many of the perchlorates in solution by metathetical reactions of alkyl, or acyl, halides with silver perchlorate—

$$R{\cdot}X + AgClO_4 \rightarrow R{\cdot}ClO_4 + AgX,$$

or by the action of perchloric acid on acid anhydrides—

$$(RCO)_2O + HClO_4 \rightleftharpoons RCO{\cdot}ClO_4 + R{\cdot}COOH.$$

These solutions resemble those containing the corresponding compounds from other strong acids, *e.g.*, the hydrogen sulphates or sulphates, the chloroaluminates, the trifluoroacetates, and so on. For example, the perchlorates can act as alkylating or acylating agents in modified Friedel - Crafts reactions. Some consideration will be given to reactions of this type, partly because they have been of special interest to us and partly because they may play a significant role in the initial stages of certain analytical processes, such as titrations or destructions.

## THE SYSTEM: ACETIC ACID - ACETIC ANHYDRIDE - PERCHLORIC ACID

One of the most extensively investigated organic perchlorates is acetyl, or acetylium, perchlorate, $CH_3CO{\cdot}ClO_4$. This is mainly because mixtures of acetic anhydride and perchloric acid have been widely used for acetylation and for polishing metal surfaces in metal finishing processes.

When aqueous perchloric acid is added to acetic anhydride, rapid combination of water with the anhydride occurs, with the evolution of a considerable amount of heat (Kahane[55]), *e.g.*—

$$2{\cdot}5Ac_2O + HClO_4.2{\cdot}5H_2O = 5AcOH + HClO_4 + 18{\cdot}4 \text{ Kcal}.$$

The resulting solution may be considered as a solution of anhydrous perchloric acid in acetic acid, together with acetic anhydride if this was used in excess. Some disastrous explosions have been caused by these mixtures (Kuney[56]), so their explosive properties have been examined rather more than have those of other organic perchlorates (Medard, Jacquet and Satorius[57]; Jacquet[58]; Medard and Satorius[59]).

The most explosive mixture is the one in which complete combustion occurs—

$$CH_3{\cdot}COOH + HClO_4 = 2CO_2 + 2H_2O + HCl.$$

The above authors state that in comparison with practical explosives the effect is mediocre. However, such mediocrity is of little consolation when the effects of explosion under laboratory conditions could lead to serious injury, or worse!

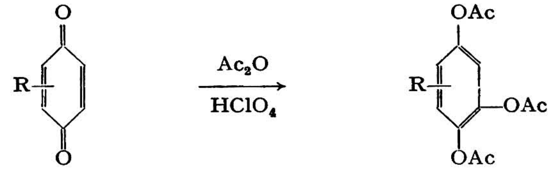
A rough calculation will illustrate the potentialities of an explosion from a mixture such as the above. Assuming the equation represents an approximation to the truth, molar quantities of acetic and perchloric acids under explosion conditions give rise, almost instantaneously, to five molecules of gas, *i.e.*, $5 \times 22{\cdot}4$ litres at S.T.P. A second and very rough approximation, that the ideal gas laws hold under these conditions, gives the volume of gases at the explosion temperature, which is about 2500° C, as 1137 litres. That is, 1 g of mixture gives about 7 litres of gas.

Mixtures containing less than 55 per cent. by volume of perchloric acid are incapable of detonation, and it has been shown that mixtures prepared by using perchloric acid with a density of less than 1·5 are not explosive. Further, the mixtures are less apt to explode if the ratio of acetic anhydride to acid is high. Finally, it should be mentioned that all the explosions that have been investigated have been due to the use of potentially dangerous mixtures together with faulty equipment or technique.

It is possible that in the solutions under discussion the following entities could occur: acetic acidium perchlorate, $AcOH_2^+\}ClO_4^-$; acetic anhydridium perchlorate, $Ac_2OH^+\}ClO_4^-$; acetylium perchlorate, $Ac^+\}ClO_4^-$ (Burton and Praill[60]): the formation of $Ac_3O^+\}ClO_4^-$ (Usanovitsch and Jatzimirski[61]) has also been postulated.

The acid-catalysed acetylation of alcoholic and phenolic hydroxyl groups is well known. For example, acetylation of glucose (Kruger and Roman[62]) and cellulose[63] is rapidly and efficiently performed in the cold, with acetic anhydride plus a trace of perchloric acid. The method has been extended to the acetylation of other sugars and polyhydric alcohols (Nicholas and Smith[64]). It has been found, however, that anomerisation of sugar acetates occurs very readily in the presence of perchloric acid (Painter[65]). For example, β-glucose pentacetate is rapidly converted to an equilibrium mixture containing about 90 per cent. of the α-anomer. Certain acid-sensitive alcohols of the type $R{\cdot}CH(OH){\cdot}CH_2{\cdot}NO_2$, where R is an aromatic nucleus, may be acetylated by similar treatment (Burton, Duffield and Praill[66]). The method is also useful for acetylating steroid compounds (Whitman and Schwenk[67]; Barton *et al.*[68]) and certain alkaloids, *e.g.*, cevadin (Stoll and Seebeck[69]).

This reagent has been found to be one of the most efficient for carrying out the Thiele acetylation of quinones (Mackenzie and Winter[70]; Burton and Praill[71,72]), *i.e.*—



The corresponding triacetates are produced in good yields, even from relatively unreactive materials such as 2-methyl-1:4-naphthaquinone.

The formation of a C–C bond by solutions of acetyl perchlorate, especially in nitromethane, has been shown to occur in the acylation of suitably constituted aromatic compounds such as anisole (Burton and Praill[60,73]), *m*-xylene and, to a less extent, toluene (Burton and Praill[74]). Ketones such as acetophenone or *p*-methylacetophenone also react; these give benzoylacetone and *p*-toluoylacetone, respectively. These compounds are possible intermediates in the formation of certain pyrylium salts prepared by the action of hot acetic anhydride and perchloric acid on acetophenone or toluene (Diels and Alder[75]). In this connection it is interesting to recall the self-acetylation of acetic anhydride (Burton and Praill[60]).

All these reactions are readily explained by considering acetyl perchlorate to give rise to the electrophilic acetyl carbonium ion, acetylium, $CH_3{\cdot}CO^+$. In the presence of acetic anhydride, the formation of acetic anhydridium ions, $Ac_2OH^+$, and acetylium ions leads to acetylation. Experiments with acetyl chloride and silver perchlorate mixtures (Burton and Praill[73]) indicate that the acetic anhydrium ions are less effective than the acetylium ions. The catalytic action of perchloric acid in these experiments is important because it means that often only relatively small amounts of perchloric acid need be used. The hazards from explosive oxidation are consequently reduced. This catalytic action in the presence of acetic anhydride is illustrated by the following sequence of reactions—

$$Ac_2O + HClO_4 \rightleftharpoons Ac_2OH^+\}ClO_4^- \rightleftharpoons Ac^+\}ClO_4^- + AcOH,$$
$$R{\cdot}H + Ac^+ \text{ (or } Ac_2OH^+) \rightarrow R{\cdot}Ac + H^+ \text{ (or } AcOH_2^+),$$
$$Ac_2O + H^+ \rightleftharpoons Ac_2OH^+ \rightleftharpoons Ac^+ + AcOH \text{ . . . and so on.}$$

The possibility of the formation of these ions is strengthened by other evidence, such as the acidity of acetyl perchlorate (Mackenzie and Winter[70]), and some kinetic evidence (Painter[65]; Mackenzie and Winter[70]). The low conductivity of acetyl perchlorate in liquid sulphur dioxide (Seel and Bauer[76]) would indicate a small dissociation into ions in this solvent.

At room temperature the acetic acidium ion, $CH_3{\cdot}COOH_2^+$, has no acetylating properties, even towards such reactive compounds as quinol (Burton and Praill[60]). Experiments by Hall, Conant and Werner[77,78,79,80] on the system acetic acid - perchloric acid have led to a useful method for estimating weak bases. This method is dependent on the fact that weak bases appear stronger when water is replaced by a more acidic solvent. Titration can be conducted potentiometrically or by use of an indicator, *e.g.*, crystal violet. The perchloric acid in glacial acetic acid can be prepared as described above, that is, by adding the 72 per cent. aqueous solution to the calculated amount of acetic anhydride. It is advisable to keep the mixture below 20° C to prevent discolouration of the solution.

Potassium hydrogen phthalate has been recommended as a primary standard (Seaman and Allen[81]; Markunas and Riddick[82]). The standardised solution can then be used for titrating such substances as amino-acids or various salts of carboxylic acids. Many inorganic salts can be titrated by this means, especially if mercuric acetate is added to the substance being titrated (Pifer and Wollish[83]). Crystal violet undergoes a number of colour changes, *i.e.*, violet → blue → green → yellow, and the colour change at the end-point depends on the system involved. It is therefore advisable to determine the colour at the potentiometric end-point. Many other indicators and solvents, including mixed solvents, have been used for a wide variety of estimations of this acid - base type, and the subject has recently been reviewed (Irving[84]; Stagg[85]; Riddick[86]). High-frequency oscillometer techniques (Wagner and Kauffman[87]) and spectrophotometry (Reilly and Schweizer[88]) have increased the range of these titrations in non-aqueous media. Perchloric acid is much better for this type of determination than sulphuric acid, which undergoes secondary reactions more readily with the other reagents, or than hydrogen chloride, which suffers disadvantages from its volatility.

The intense colours that perchloric acid gives with various substances can often be made the basis of methods for their determination. For example, the intense red colour given by tryptophan in the presence of carbohydrate and perchloric acid has been used for determining deoxyribosenucleic acid (Cohen[89]) and for measuring tissue destruction in cases of burning (Keyser[90]). Recently, a new colour reaction for steroids, which utilises perchloric acid, has been reported (Tauber[91]).

It is very unlikely that there is any danger in the use of these techniques provided that local overheating effects are avoided.

### ALKYL AND ARALKYL PERCHLORATES—

Reference has already been made to the early preparation of ethyl perchlorate by Hare and Boye[8] (p. 5). Esters of the type $HO(CH_2)_2{\cdot}O{\cdot}(CH_2)_2{\cdot}ClO_4$ and $Cl{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}ClO_4$ were prepared by Hofmann and his collaborators[92] by the action of 60 per cent. perchloric acid on ethylene oxide and epichlorohydrin, respectively. These compounds are colourless oils that explode on heating or on percussion.

In 1936, Meyer and Spormann[93] re-investigated the preparation and properties of some alkyl perchlorates. Methyl, ethyl and propyl perchlorates can all be prepared by distillation of the barium alkyl sulphate with barium perchlorate—

$$Ba(RSO_4)_2 + Ba(ClO_4)_2 = 2RClO_4 + 2BaSO_4,$$

or by the reaction of the alkyl halides with a solution of silver perchlorate in ether; cautious evaporation of the ethereal solution then gives the ester.

Methyl perchlorate can also be prepared by the reaction between anhydrous perchloric acid and diazomethane in dry ether (Meyer and Spormann[93])—

$$CH_2N_2 + HClO_4 = CH_3{\cdot}ClO_4 + N_2.$$

The esters are colourless oils; the methyl ester boils at about 52° C, the ethyl ester at 89° C. They are very powerful explosives and are considerably more sensitive than the corresponding nitrate esters. Meyer and Spormann took considerable precautions when studying these compounds. They stated that, in spite of the greatest foresight, it was not possible to avoid explosions of the ester (one author, W. S., lost the tips of three fingers). We hold it impossible to over-emphasise that the simple alkyl esters are extremely dangerous in the free state. In this connection, mention should be made of a number of accidents (Hillebrand and Lundell[94]; Knuth[95]; Deiss and Meyer[96]) resulting from the standard method for determining perchlorates or potassium, *i.e.*, as the sparingly soluble potassium perchlorate. Explosions have occurred when attempts have been made to concentrate the aqueous-alcoholic filtrate after the separation of most of the potassium salt. This may be due to traces of residual perchloric acid or to the formation of the highly explosive ethyl ester. Attempts to recover alcohol from such solutions should be strongly discouraged.

The alkyl perchlorates are not miscible with water and are only slowly hydrolysed by it. This behaviour parallels that shown by chlorine heptoxide, $Cl_2O_7$, which reacts only slowly with water (Michael and Conn[97]). This is explained (Goodeve and Marsh[28]) by the fact that perchloric acid has a limited solubility in the heptoxide and forms a protective sheath round the drop. The water diffuses slowly through this protective sheath and so hydrolysis proceeds only slowly. If a solution of ethyl perchlorate in alcohol is added to alcoholic potassium hydroxide, immediate precipitation of potassium perchlorate occurs.

Little is known about the chemical properties of these compounds. We have found[98] that methyl perchlorate, formed *in situ* from methyl iodide and silver perchlorate, alkylates anisole in the *para* position. The metathetical reaction between the primary alkyl halides and silver perchlorate is relatively slow (Burton and Praill[98]; Redies and Iredale[99]). As would be expected, the reaction with tertiary halides, *e.g.*, *tert.*-butyl chloride, is much more rapid. If the reaction is carried out in benzene, *tert.*-butylbenzene and *p*-di-*tert.*-butylbenzene can soon be isolated (Burton and Praill[100]). Further evidence for the alkylating properties of *tert.*-butyl perchlorate is given by the formation of 4-*tert.*-butylphenol and 2:4-di-*tert.*-butylphenol in mixtures of phenol, *tert.*-butanol and perchloric acid (Sears[101]). The alkylation of toluene by *cyclo*hexyl perchlorate has also been reported (Cauquil and Barrera[102]; Cauquil, Barrera and Barrera[103]).

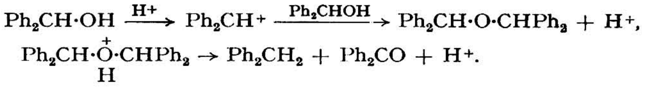
The interesting trichloromethyl perchlorate, $CCl_3 \cdot ClO_4$, is formed by metathesis of carbon tetrachloride with silver perchlorate in the presence of traces of hydrogen chloride (Birckenbach and Goubeau[104]). It is a colourless explosive mobile liquid, which begins to decompose at 40° C. The ester is miscible with carbon tetrachloride; it reacts with ethylene dibromide and phosphorus oxychloride.

THE ARALKYL PERCHLORATES—

The arylmethyl perchlorates form a closely related series of compounds, which show a progressive increase in stability as each hydrogen of the methyl group is replaced by phenyl.

Triarylmethyl perchlorates are typical carbonium salts, as illustrated by their relatively high conductivity in non-aqueous media (Hofmann, Kirmreuther and Thal[105]; Lifschitz and Girbes[106]; Ziegler and Wollschitt[107]) and by their absorption spectra (Hantzsch[108]; Anderson[109]). These perchlorates were among the first carbonium salts to be prepared (Gomberg[110]; Gomberg and Cone[111]). They are readily formed by the action of perchloric acid on the corresponding carbinols, or by metathesis of the chloride with silver perchlorate in a suitable solvent, *e.g.*, nitrobenzene. The triarylmethyl perchlorates are beautifully crystalline materials of relatively high melting point and are usually highly coloured. In fact, Brand, Gabel and Rosenkranz[112] made use of the disappearance of the colour of the perchlorate by titration with alcohol in order to determine the relative stability of the salts.

Although much of the information about the triarylmethyl perchlorates must be applicable to the diarylmethyl salts, the latter have not been investigated very extensively. However, diphenylmethyl perchlorate, prepared *in situ* from diphenylmethyl chloride and silver perchlorate, converts benzene to triphenylmethane in good yield at room temperature (Burton and Cheeseman[113]). With diphenylmethanol and perchloric acid in benzene, the main products are bisdiphenylmethyl ether, benzophenone and diphenylmethane; smaller amounts of triphenylmethane are also produced. These results have been interpreted (Burton and Cheeseman[114]) in terms of the following reactions—



$$Ph_2CH \cdot OH \xrightarrow{H^+} Ph_2CH^+ \xrightarrow{Ph_2CHOH} Ph_2CH \cdot O \cdot CHPh_2 + H^+,$$

$$Ph_2CH \cdot \underset{H}{\overset{+}{O}} \cdot CHPh_2 \rightarrow Ph_2CH_2 + Ph_2CO + H^+.$$

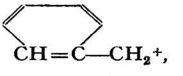
The properties of benzyl perchlorate show that it is an exceedingly reactive substance. So much so, in fact, that it rapidly polymerises in solution unless it reacts with the solvent (Burton and Praill[115]). The substance was probably first prepared by the reaction, in sunlight, of iodine and silver perchlorate with toluene, but only polymeric materials were isolated (Birckenbach and Goubeau[116])—

$$PhMe + IClO_4 \rightarrow PhCH_2I,$$
$$PhCH_2I + AgClO_4 \rightarrow PhCH_2ClO_4 + AgI.$$

It has been shown that benzyl perchlorate reacts rapidly with benzene or toluene to give high yields of diphenylmethane and *p*-methyldiphenylmethane, respectively (Burton and Praill[98,115]). The ready formation of these products has been ascribed to the high reactivity of the benzyl cation, $PhCH_2^+$. In a solvent in which no such alkylation occurs, *e.g.*, nitromethane, there is evidence of polymerisation of the benzyl cation (Burton and Praill[115]; Monicelli and Hennion[117]), thus—

$$nPhCH_2^+ \rightarrow (PhCH)_n + nH^+.$$

The benzyl cation may be regarded as a special case of the substituted allyl cation—



and it is interesting to note that other substituted allyl cations polymerise readily under similar conditions (Burton and Munday[118]).

Evidence for the intermediate formation of the benzyl cation in the debenzylation of certain aromatic ethers by acetylium perchlorate has been obtained (Burton and Praill[119]), and there is some indication that relatively unreactive ethers, *e.g.*, methyl ethers, may be split by this reagent. The possible formation of alkyl perchlorates by reactions of this type must always be borne in mind.

Some evidence for the possible explosive character of benzyl perchlorate is given by the explosion that occurred when an attempt was made to destroy benzylcelluloses by boiling with perchloric acid (Sutcliffe[120]).

Most of the above data refer to reactions in which an alkyl perchlorate is definitely formed; this may undergo subsequent fission to carbonium and perchlorate ions. A second type of reaction to be considered is one in which a proton from perchloric acid reacts with a molecule to give a carbonium ion, which may, momentarily at any rate, exist as the alkyl perchlorate. As an example of this kind of reaction we may consider the telomerisation of butadiene and of isoprene (Jenner and Schreiber[121]; Jenner[122]) to give a number of esters, *e.g.*—

$$n\mathrm{CH_2{=}CH{\cdot}CH{=}CH_2} + \mathrm{R{\cdot}COOH} \xrightarrow{\mathrm{HClO_4}} \mathrm{H(CH_2CH{=}CHCH_2)}_n\mathrm{{\cdot}O{\cdot}COR}.$$

Sufficient has now been said to illustrate the potentialities of perchloric acid in reactions of this type. Clearly, it is not merely the presence of anhydrous perchloric acid in organic solution that causes the explosive reactions observed by Roscoe.[9] However, the mixtures that have been mentioned may contain up to 10 per cent. w/v of the anhydrous acid and must therefore be considered as potentially explosive. Among the main characteristics of an explosive are its sensitivity, its power and the velocity of propagation of the explosion.

For the perchlorates the sensitivity varies over a wide range, from the very sensitive simple alkyl esters to the much less sensitive triarylmethyl perchlorates. It is apparent that the sensitivity of these compounds is reduced in solution. This is partly due to a dilution effect and partly to a modification of the molecular structure from a purely covalent form to a more polar entity. The covalent perchlorate group is much less stable than the perchlorate ion, doubtlessly owing to the lack of symmetry in the former.

Once sufficient energy has been supplied to the perchlorate to initiate its decomposition, the rate of reaction is of the same order as that for other common explosives. Apart from the thermochemical aspects of explosions, it is the velocity of the decomposition that determines whether or not the reaction is explosive.

The power of the explosive is governed largely by the pressure of the gases produced in the decomposition. The position is especially favourable for the simpler alkyl perchlorates because the stoicheiometry of the compounds means that almost complete oxidation of the organic residue can occur, *e.g.*—

$$2\mathrm{CH_3{\cdot}ClO_4} \rightarrow 2\mathrm{CO_2} + 3\mathrm{H_2O} + \mathrm{Cl_2} + \tfrac{1}{2}\mathrm{O_2}.$$

The products are completely gaseous, so a large increase in volume (or pressure at constant volume) occurs. The power is increased further by the expansion of the gases owing to the high temperature of the explosion, frequently several thousand degrees centigrade.

These facts are important because they give an indication of the methods that should be employed for the destruction of organic matter with perchloric acid. It is clear that these must depend on the prevention of appreciable concentrations of organic perchlorates, or of anhydrous perchloric acid, being formed during the destructions. This can be achieved by performing a preliminary destruction with nitric acid or nitric acid - sulphuric acid, followed by cautious dropwise addition of perchloric acid to the mixture. The latter should contain a fair excess of nitric or sulphuric acid, or both, although it should be noted that the use of sulphuric acid can lead to the formation of anhydrous perchloric acid. The temperature should be high enough for the perchloric acid to react as fast as it is added. It is not recommended that destructions of organic material be carried out in perchloric acid alone. Materials, such as machine oils and greases, that do not dissolve readily in the oxidising medium are liable to cause most trouble with perchloric acid (*cf.* Zahn[4]; Sutcliffe[120]). Under these conditions it is difficult to avoid localised heat effects.

This represents a reasonably safe general method for carrying out destructions, and is essentially due to Kahane, who has worked out methods for estimating B, I, S, N, P, As, Si, and the metals (Kahane *et al.*[123,124,125,126]). There are many examples in the literature, where various techniques for using perchloric acid have been described for the determination of trace elements in materials of plant and animal origin.[127–140] Others have been mentioned in a recent critical review of the subject (Middleton and Stuckey[141]). The relative advantages, or otherwise, of these modifications might well be considered in the light of the present discussion, taking into account the various mishaps that have been recorded. Treatment of tervalent antimony (Hillebrand and Lundell[94]) or bismuth compounds (Nicholson and Reedy[142]) with perchloric acid can be very hazardous.

The use of perchloric acid for Kjeldahl estimations of nitrogen has the advantage of speed, but there is some uncertainty about the accuracy of the results (Bradstreet[143]).

Recently, the whole question of the wet-ashing of organic matter has been considered in an admirable paper by Smith.[144] The procedures used have been called "liquid-fire reactions" because they result in the complete oxidation of organic matter to carbon dioxide and water at relatively low temperatures (100° to 235° C). The method has many advantages over dry-ashing procedures at high temperatures. A wide range of materials has been considered and it has been found that often the decomposition proceeds smoothly if catalysed by vanadium. The mechanism of the decompositions is described in terms of the oxidation potentials of the various oxidising systems used.

It will be apparent that many interesting aspects of the perchlorates have had to be omitted from this review, *e.g.*, nitrosonium and nitronium perchlorates, the perchlorates of the halogens and of the metals. However, mention must be made of magnesium perchlorate ("anhydrone") (Willard and Smith[145]) and its trihydrate ("dehydrite") (Smith, Brown and Ross[146]), which are frequently used as drying agents. If these are used for drying organic liquids, the origin of the drying agent should be determined, because, in the process for its preparation, traces of perchloric acid may have been retained in the salt. Explosions have been known to occur when these compounds are used, possibly owing to the formation of free perchloric acid, or perchloric esters, in the system (Stross and Zimmerman[147]). These substances are not recommended for drying such easily polymerisable materials as styrene (Lilley and Foster[148]). It should also be pointed out that many metallic perchlorate - solvent complexes are explosive in the dry state, *e.g.*, the silver perchlorate - benzene complex (Brinkley[149]).

An attempt has been made to give an outline of some of the fundamental aspects of the chemistry of perchloric acid, rather than to lay down rules as to when the acid can be used without hazard. At present we feel that this cannot justifiably be done, but that each case must be considered in the light of the above discussion and in the light of experiment. We do not underrate the hazards involved, but there is no doubt that danger can often be avoided if careful consideration is given to experimental conditions and to subsequent operations.

Undoubtedly, perchloric acid will become another useful reagent in the chemist's armoury, provided that familiarity never breeds contempt.

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# The Dualistic and Versatile Reaction Properties of Perchloric Acid

## Illustrative Experimental Demonstration Procedures

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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 ra material. Government-operated defence plants were built at several strategic locations the United States for the manufacture of sodium chlorate and perchlorate, as well potassium perchlorate. By the Kreider - Mathers process, perchloric acid was manufactu in such quantities that carload lots were advertised for sale at as little as 41 cents per po for 70 per cent. acid (in the 1940 era). Preparation of perchloric acid has also been carr 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 no 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 lar excess of concentrated hydrochloric acid. By metathesis, sodium chloride is almost quanti tively precipitated. By centrifugation, the precipitated sodium chloride is separated fro the perchloric acid formed in its mixture with the excess of hydrochloric acid.

The perchloric acid - hydrochloric acid mixture is evaporated to a concentrate, th hydrochloric acid excess is recovered, and the aqueous solution of perchloric acid thus prepare 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 manufacture of magnesium perchlorate in the form of its anhydrous and partially dehydr form to be used as a drying agent. This product in the anhydrous form was shown to h the drying efficiency of the best known desiccant, phosphorus pentoxide, and in additi had a very high drying capacity. Its commercial availability soon accounted for its adopti as preferred reagent in many types of analytical usage, including the determination of carb in steel and iron and the determination of carbon and hydrogen in organic combus analyses. Its use in these and many other analytical operations is now almost univer and it is recommended for such procedures in practically all textbooks and literature-ci references. For such determinations as those previously mentioned it is a companion reag to the most important absorbents for carbon dioxide. It is also a quantitative absor for ammonia gas and has a high capacity in this role. The ammonia vapour pressu the diammine of magnesium perchlorate is nil at room temperature and at temperatures greater than 150° C. Anhydrous magnesium perchlorate has been used analytically in quantitative absorption of alcohol vapours in the analysis of gas products such as nat gas, which frequently is adulterated with vapours such as ethanol to prevent freezing eff in the cold-weather transportation of natural gas in pipe-lines between the field and the point, often many hundreds of miles distant, of the gas consumption.

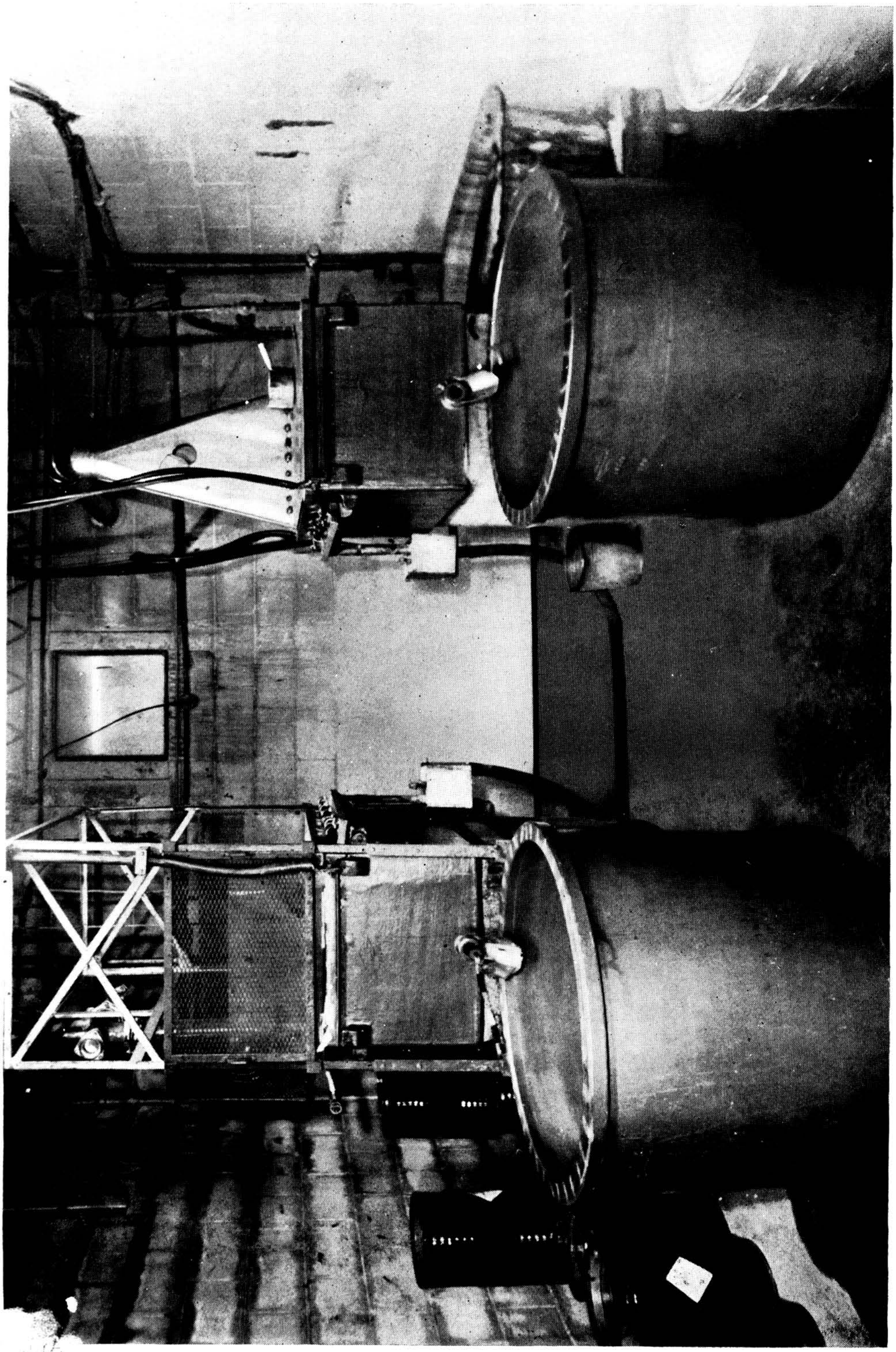

Fig. 1. Cells of 100 gallons capacity for use in the electrolytic oxidation of sodium chlorate to sodium perchlorate

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 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.

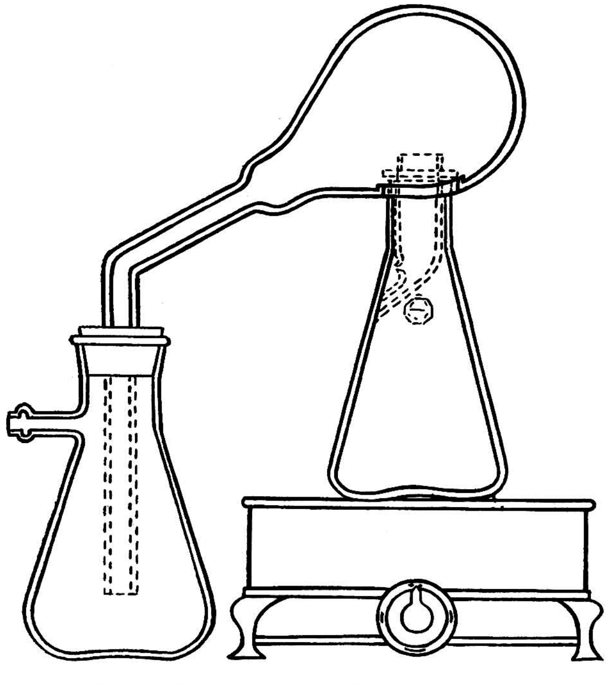

Fig. 2. Vycor reaction flask and hot-plate, with reflux still-head and fume eradicator in place

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 to 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—

$$\begin{aligned}\mathrm{Ce^{IV}} + e'\ (1F\ \mathrm{HClO_4}) &\rightarrow \mathrm{Ce^{III}}\ (1{\cdot}71\ \text{volts})\\ (8F\ \mathrm{HClO_4}) &\rightarrow \qquad (1{\cdot}86\ \text{volts}).\end{aligned}$$

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 (4*F*) 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)—

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

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 appearance 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—

$$MgO + 2NH_4ClO_4 \xrightarrow{255^\circ \text{ to } 260^\circ\text{C}} Mg(ClO_4)_2 + 2NH_3 + H_2O.$$

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 ($HClO_4.2H_2O$) 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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# The Determination of Pentaerythritol as the Dibenzylidene-acetal and its Chromatographic Separation from Commercial Material[*]

BY K. SPOREK AND A. F. WILLIAMS

The reaction of benzaldehyde with pentaerythritol to form the dibenzylidene-acetal is used as the basis of a method for the determination of pentaerythritol. A study has been made of the effects of formaldehyde, dipentaerythritol and liquid polyhydroxy compounds on the accuracy of the procedure and hence its applicability to liquors from the manufacturing process and to the commercial material. A chromatographic procedure has been developed for the separation of fairly pure pentaerythritol from impure samples; it is sufficiently pure to permit the use of the benzaldehyde procedure for its determination. This separation is based on the use of Celite adsorbent with acetone and acetone containing added water as solvents for extraction.

PENTAERYTHRITOL is a white solid, m.p.[†] 262° to 263° C, with four —$CH_2OH$ groups spaced around a central carbon atom. It is widely used in the paint industry in the formation of alkyd resins. It is manufactured by the interaction of formaldehyde and acetaldehyde with lime or caustic soda, and because solid di- and poly-pentaerythritols and liquid polyhydroxy compounds can also be formed, the exact analysis of plant liquors and commercial

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[†] Determined by one of the authors (K. S.) on pentaerythritol made by hydrolysis of the dibenzylidene-acetal derivative that had been purified by repeated crystallisation from acetone.

products has always presented some difficulties. The most reliable procedure for the determination of pentaerythritol is based on the formation of the dibenzylidene-acetal complex with benzaldehyde,[1] but unfortunately, it is only applicable to fairly pure materials. A number of factors that affect this determination have been investigated in considerable detail. It has been shown that the presence of formaldehyde causes low results, whereas the presence of liquid hydroxy compounds and dipentaerythritol may cause high results. In these circumstances it was necessary to develop a separation procedure so that reasonably pure pentaerythritol could be isolated before the application of the benzaldehyde procedure.

Experiments showed that whereas the liquid hydroxy compounds were soluble in a number of organic solvents, pentaerythritol and dipentaerythritol were sparingly soluble. Pentaerythritol has a solubility in water of about 5 g per 100 ml at 20° C, whereas that of dipentaerythritol is about 0·2 g. With acetone and acetone containing 10 per cent. of water used, in turn, as solvents, a chromatographic method for the determination of pentaerythritol in reaction liquors and commercial products has been developed, Celite being used as the adsorbent. First, the liquid hydroxy compounds are extracted with acetone and then the pentaerythritol is extracted with the aqueous acetone. The pentaerythritol is determined in this second extract, after removal of the acetone, by the benzaldehyde procedure. The direct determination can, however, be made on commercial samples of pentaerythritol containing not more than about 2 per cent. of dipentaerythritol as impurity, but above this concentration the errors are significant.

## Direct Benzaldehyde Condensation Procedure

### DETERMINATION OF PENTAERYTHRITOL IN COMMERCIAL SAMPLES OF PENTAERYTHRITOL CONTAINING ONLY DIPENTAERYTHRITOL AS IMPURITY

Experience in this laboratory indicates that probably the only reliable procedure for the determination of pentaerythritol is that based on the formation of its dibenzylidene-acetal derivative, which is a well-defined crystalline compound that melts at 159·5° C and is fairly insoluble in a dilute aqueous methanolic solution of hydrochloric acid containing benzaldehyde. The origin of the method is obscure, but the reaction was used by Kraft, who published[1] the results of a detailed investigation of the procedure. We have made extensive use of the method with only minor modifications involving closely controlled experimental conditions. When applied to the determination of the amount of pentaerythritol in commercial samples containing not more than about 2 per cent. of dipentaerythritol, which is the principal impurity in such samples, the procedure described below gave good results. Results for pure pentaerythritol and various samples containing a range of dipentaerythritol contents are shown in Table I. The effect of larger concentrations of dipentaerythritol is described on p. 32.

TABLE I

DETERMINATION OF PENTAERYTHRITOL BY THE BENZALDEHYDE PROCEDURE

| Weight of pentaerythritol taken, g | Weight of dipenterythritol taken, g | Dipentaerythritol in mixture, % | Pentaerythritol found (corrected), % |
|---|---|---|---|
| 0·506 | nil | nil | 100·0 |
| 0·505 | nil | nil | 99·9 |
| 0·499 | 0·005 | 1 | 100·0 |
| 0·499 | 0·010 | 2 | 100·1 |
| 0·501 | 0·021 | 4 | 101·3 |

### METHOD

REAGENTS—

*Benzaldehyde reagent*—One part of freshly distilled benzaldehyde or fresh AnalaR material mixed with 5 parts of anhydrous methanol.

*Hydrochloric acid, concentrated.*

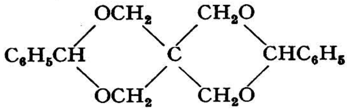
*Wash solution*—One part of methanol mixed with 1 part of water, the mixture being maintained at 0° C.

PROCEDURE—

A known weight (0·4 to 0·7 g) of the sample was dissolved in 15 ml of water in a 100-ml conical flask by warming. The solution was heated to boiling, 15 ml of the benzaldehyde reagent were then added and the contents of the flask were mixed by swirling. Next, 12 ml of concentrated hydrochloric acid were added immediately and the flask was again swirled for 5 minutes. The flask was stoppered with a ground-glass stopper and shaken occasionally until cool; it was then set aside at room temperature overnight. After cooling in a bath of ice for 1 hour, the reaction mixture was diluted with 25 ml of ice-cold wash solution, mixed thoroughly and then filtered through a tared sintered-glass crucible (porosity grade No. 1, 2 or 3; previously dried at 110° C) in which was placed a short glass rod to aid filtration. Any residual precipitate was easily washed from the flask by swirling with the ice-cold wash solution, a total of about 100 ml being used. The crucible was dried to constant weight at 100° to 110° C.

As the dibenzylidene-acetal derivative of pentaerythritol was slightly soluble in the wash solution, it was necessary to apply a correction to the weight of precipitate found. This solubility was 0·0135 g under the conditions used, and it was determined by performing the procedure on a sample of pure pentaerythritol. From a knowledge of the weight of pentaerythritol taken and the amount of dibenzylidene-acetal derivative found, the amount of pentaerythritol lost in the reaction was determined.

The formula for dibenzylidenepentaerythritol is—



$$\text{and pentaerythritol, \% w/w} = \frac{(\text{weight of precipitate, g} + 0{\cdot}0135\text{ g}) \times 0{\cdot}436 \times 100}{\text{weight of sample, g}}.$$

### FACTORS THAT AFFECT THE BENZALDEHYDE PROCEDURE

A number of factors that were considered to have some effect on the dibenzylidene-acetal method were studied in relation to the possible use of the procedure for the determination of pentaerythritol in impure materials and those derived from plant processes. These factors included the effect of formaldehyde, dipentaerythritol and liquid hydroxy impurities, all of which may be present in plant reaction liquors. A more detailed examination of the effect of high concentrations of dipentaerythritol was required, because of its possible presence in large amounts in commercial samples of pentaerythritol.

Of the reagents used in the benzaldehyde procedure, it was found that the only reagent requiring careful attention was the benzaldehyde. It was essential to ensure that only redistilled material was used, or preferably AnalaR material. The results were poorer with impure benzaldehyde, probably owing to the presence of benzoic acid.

EFFECT OF FORMALDEHYDE—

Determinations of pentaerythritol were made on mixtures of pure pentaerythritol and formaldehyde by the method described above. The results for different pentaerythritol - formaldehyde mixtures are shown in Table II.

TABLE II

DETERMINATION OF PENTAERYTHRITOL BY THE BENZALDEHYDE CONDENSATION REACTION: EFFECT OF FORMALDEHYDE

| Pentaerythritol taken, g | Formaldehyde added, g | Pentaerythritol found, % of original | Remarks |
|---|---|---|---|
| 0·510 | None | 98·0 | Slow precipitation of the complex in the presence of formaldehyde |
| 0·496 | 0·4 | 80·5 | |
| 0·517 | 1·2 | 43·1 | |
| 0·553 | 2·0 | 19·2 | |

The results indicate the marked effect of the presence of formaldehyde in causing low results for the determination of pentaerythritol. In reaction liquors the effect of formaldehyde alone is such that the value found for pentaerythritol might be less than 80 per cent. of the amount present.

EFFECT OF DIPENTAERYTHRITOL—

Table I shows that quantities of dipentaerythritol up to about 2 per cent. of the pentaerythritol present do not appreciably affect the result for pentaerythritol. It was not known whether plant liquors would contain more than 2 per cent. of dipentaerythritol, and it was considered possible that such samples of pentaerythritol might be encountered in practice. Further experiments were made in order to discover the influence of larger amounts of dipentaerythritol (more than 4 per cent.) on the benzaldehyde method and the results of these experiments are shown in Table III. These results show that the errors in the determination of pentaerythritol increase as the amount of dipentaerythritol in the sample is progressively increased.

TABLE III

DETERMINATION OF PENTAERYTHRITOL BY THE BENZALDEHYDE CONDENSATION REACTION: EFFECT OF DIPENTAERYTHRITOL

| Mixture | | | | |
|---|---|---|---|---|
| Pentaerythritol, g | Dipentaerythritol, g | Dipentaerythritol in mixture, % | Pentaerythritol found, % | Remarks |
| 0·537 | 0·022 | 4 | 101·6 | |
| 0·482 | 0·046 | 9 | 101·8 | |
| 0·506 | 0·074 | 13 | 102·5 | |
| 0·492 | 0·088 | 15 | 104·5 | |
| 0·500 | 0·147 | 22 | 109·0 | |
| 0·655 | 0·193 | 23 | 111·0 | Precipitate visibly contaminated with oily dipentaerythritol derivative |
| 0·629 | 0·371 | 37 | 128·0 | |
| 0·547 | 0·697 | 56 | 137·0 | |
| 0·545 | 0·698 | 56 | 160·0 | |

Dipentaerythritol reacts with benzaldehyde to form an oily product that may be incompletely removed by the wash liquor and so cause high results for pentaerythritol.

EFFECT OF LIQUID HYDROXY COMPOUNDS—

The liquors derived from the plant process in the manufacture of pentaerythritol may contain impurities that exist as a syrup when separated from the aqueous solution. The exact nature of these compounds is not known, but preliminary experiments have shown that they contain hydroxyl groups and loosely bound formaldehyde groups. These compounds seriously interfere with the benzaldehyde procedure for the determination of pentaerythritol, as they cause high results. Like dipentaerythritol, they form an oily product that cannot be completely removed from the crystalline pentaerythritol derivative by washing. As will be seen later, they can be separated from pentaerythritol and dipentaerythritol by making use of their solubility in acetone. Whereas there does not appear to be any direct chemical method for the determination of small amounts of dipentaerythritol in fairly pure pentaerythritol, small amounts of these syrupy impurities can be determined colorimetrically with chromotropic acid, with which their formaldehyde linkage apparently reacts.[2]

The results for the determination of pentaerythritol in mixtures containing syrupy hydroxy compounds by the benzaldehyde condensation procedure are shown in Table IV. A supply of these compounds was produced by extracting them with dry acetone from samples of "purge" liquor (a waste plant material containing large amounts of these compounds) that had been submitted to a chromatographic separation.

The acetone was removed from the extracts of the hydroxy compounds, and the syrup was dried in a desiccator under reduced pressure; there was no appreciable loss due to volatility. The results show the error in the determination of pentaerythritol by the benzaldehyde method with increasing amounts of the impurities.

TABLE IV

DETERMINATION OF PENTAERYTHRITOL BY THE BENZALDEHYDE CONDENSATION REACTION: EFFECT OF LIQUID HYDROXY COMPOUNDS

| Mixture | | | | |
|---|---|---|---|---|
| Pentaerythritol, g | Liquid hydroxy compounds, g | Liquid hydroxy compounds, % | Pentaerythritol found, g | Recovery,* % |
| 0·506 | 0·132 | 21 | 0·528 | 104 |
| 0·584 | 0·173 | 23 | 0·617 | 106 |
| 0·632 | 0·323 | 34 | 0·695 | 110 |
| 0·596 | 0·430 | 42 | 0·633 | 106 |
| 0·584 | 1·096 | 65 | 0·714 | 122 |
| 0·654 | 1·497 | 70 | 0·933 | 143 |
| 0·452 | 2·008 | 82 | 0·802 | 177 |
| 0·626 | 3·020 | 83 | 1·060 | 170 |

No higher values of recovery were found owing to complete exhaustion of the benzaldehyde reagent.
* All precipitates were very crude.

### DISCUSSION OF THE DIBENZYLIDENE-ACETAL PROCEDURE—

It has been shown that the benzaldehyde condensation procedure cannot be used for the direct determination of pentaerythritol in plant liquors or unknown commercial products that might contain more than 2 per cent. of dipentaerythritol. The presence of formaldehyde in liquors causes low results and the presence of liquid hydroxy impurities cause high values for pentaerythritol. Although the effect of formaldehyde could be removed by steam-distillation of the liquor, the difficulty due to the other impurities is not readily overcome.

Preliminary experiments on synthetic mixtures of pentaerythritol, dipentaerythritol and liquid impurities showed that it might be possible to find solvents that could be used in conjunction with a chromatographic method for the separation of pentaerythritol in a sufficient degree of purity to be suitable for determination by the benzaldehyde condensation procedure. Further work was done with this aim in view.

## Chromatographic Procedure

### PRELIMINARY STUDY OF THE SOLUBILITY OF PENTAERYTHRITOL, DIPENTAERYTHRITOL AND LIQUID IMPURITIES IN VARIOUS SOLVENTS—

In order to develop a chromatographic procedure for the separation of the pentaerythritol, it was necessary to choose a suitable solvent. Approximate determinations of the solubilities of pentaerythritol and dipentaerythritol in a number of common solvents were therefore made. The solubilities were determined by stirring an excess of the solid with the appropriate solvent. After sufficient time had been allowed for saturation, the solvent was separated from the solid, the solution was evaporated to dryness and the residue was weighed. The results for a number of solvents at various temperatures are shown in Table V.

TABLE V

SOLUBILITY OF PENTAERYTHRITOL AND DIPENTAERYTHRITOL IN VARIOUS SOLVENTS

| | Solubility | |
|---|---|---|
| Solvent | Pentaerythritol, g per 100 ml | Dipentaerythritol, g per 100 ml |
| Water .. .. .. .. | 5·983 (21·5° C) | 0·197 (24° C) |
| Pyridine .. .. .. .. | 1·229 (20° C) | 0·052 (24·5° C) |
| Methanol .. .. .. .. | 0·485 (20° C) | 0·024 (27·5° C) |
| Butanol .. .. .. .. | 0·105 (28·5° C) | 0·014 (28·5° C) |
| *iso*Propanol .. .. .. .. | 0·050 (25° C) | 0·012 (27·5° C) |
| Acetone .. .. .. .. | 0·021 (22° C) | nil |
| Ethyl methyl ketone .. .. | 0·011 (24·5° C) | nil |
| Ether .. .. .. .. | nil | nil |
| Chloroform .. .. .. .. | nil | nil |
| Benzene .. .. .. .. | nil | nil |

These results show that of the solvents examined the best for pentaerythritol is water. The solubility of dipentaerythritol in water is small. The liquid impurities were found to be soluble in water and in acetone. The results show that the solubility of pentaerythritol in a number of organic solvents including acetone is very small; similarly for dipentaerythritol. It was considered that if a suitable adsorbent could be found and used in conjunction with acetone and acetone - water mixtures, it might be possible to separate the pentaerythritol from the liquid impurities chromatographically in a sufficiently pure state to permit the determination of pentaerythritol to be completed by the benzaldehyde procedure.

### CHOICE OF ADSORBENT FOR USE IN THE CHROMATOGRAPHIC SEPARATION OF PENTAERYTHRITOL WITH ACETONE AND ACETONE - WATER MIXTURES—

In view of the results of the solubility determinations, it was considered that attempts should be first made to separate liquid impurities from a suitable adsorbent by means of acetone and to follow this with a further extraction with acetone containing water in order to extract pentaerythritol. From the results shown in Table V it did not seem to be practicable to separate pentaerythritol directly by one extraction without also extracting the liquid impurities.

Experiments showed that under fairly dry conditions a large proportion of liquid impurities could be extracted chromatographically from a sample without appreciable extraction of pentaerythritol. If the solvent was then changed to acetone containing 10 per cent. v/v of water, pentaerythritol could be quantitatively extracted with only slight extraction of the remaining impurities, the impurities extracted being insufficient to interfere with the benzaldehyde procedure used for the final determination of pentaerythritol. Preliminary experiments involved a search for suitable adsorbent for use in conjunction with the solvents. Both alumina and cellulose proved too retentive for both the liquid impurities and pentaerythritol, but Celite was found to be a suitable adsorbent.

## METHOD

### REAGENTS—

*Celite No. 535 for chromatography.*

*Acetone, pure grade (less than 0·3 per cent. of water)*—Specific gravity should not exceed 0·787 at 15·5° C/15·5° C.

*Solvent mixture*—900 ml of acetone mixed with 100 ml of water.

*Benzaldehyde reagent*—One part of freshly distilled benzaldehyde or fresh AnalaR material mixed with 5 parts of anhydrous methanol.

*Hydrochloric acid, concentrated.*

*Wash solution*—One part of methanol mixed with 1 part of water, the mixture being maintained at 0° C.

### PREPARATION OF COLUMN—

The tube used for the chromatographic extraction was 1·8 to 2·0 cm in diameter and 28 cm long with a funnel at its top to facilitate introduction of the sample into the column. It terminated in a short length of glass tubing (6 mm in diameter) and was made water-repellent by applying silicone treatment before use.

About 5 g of Celite No. 535 were weighed into a 250-ml beaker and slurried with about 50 ml of acetone. The mixture was poured into the chromatograph tube at the base of which a small piece of cotton-wool had been placed. A further 50 ml of acetone were used for washing the beaker. These washings were poured into the column and the solvent was allowed to drain to the level of the Celite. The outlet of the column was closed with a small rubber stopper.

### PREPARATION OF THE SAMPLE—

Sufficient sample was weighed into a 150-ml beaker to provide preferably about 0·4 to 0·7 g of pentaerythritol, although smaller amounts were used. For plant liquors the sample was evaporated to 5 ml and then heated just to boiling and 5 g of Celite No. 535 were added. The mixture was thoroughly stirred with a stout glass rod and then heated in the beaker at 100° C for 1 hour. The sample was placed in a desiccator and kept under reduced pressure for 30 minutes.

When analyses were required on solid samples, 5 ml of water were added to an appropriate weight of sample and after addition of Celite the above procedure was followed. Complete solution of the sample in water was not always possible, as it depended on the amount of dipentaerythritol present.

### EXTRACTION AND DETERMINATION OF PENTAERYTHRITOL—

The contents of the 150-ml beaker were well mixed with 10 ml of acetone with the aid of a stout glass rod. The mixture was transferred to the top of the prepared column, the beaker was washed three times with 10-ml quantities of acetone and the eluate was collected in the original beaker. The column was washed twice with 20-ml portions of acetone, each time the solvent being allowed to drain to the level of the Celite. The beaker containing the liquid hydroxy compounds was replaced by a 500-ml conical flask and the column was then extracted with 350 ml of acetone containing 10 per cent. of water. This acetone - water extract containing the pentaerythritol was evaporated to 50 ml on a steam-bath and the residual solution was then transferred to a 100-ml conical flask fitted with a ground-glass neck. The evaporation on the steam-bath was continued until the volume of the solution was reduced to about 15 ml. Pentaerythritol was then determined by precipitation of the dibenzylidene-acetal derivative as described on p. 30. In the calculation of the result of the determination it was necessary to add 10 mg to the amount of pentaerythritol found. This represented the solubility of pentaerythritol in the dry acetone used as solvent in the first extraction for the removal of liquid impurities. It would be necessary to perform this blank determination on any particular batch of acetone that might not be completely free from water.

## RESULTS

### DETERMINATION OF PENTAERYTHRITOL WITH IMPURITIES ABSENT—

The results shown in Table VI were found for aqueous solutions containing known amounts of pentaerythritol by the full chromatographic procedure described on p. 34. They show excellent recoveries for pentaerythritol after adding 10 mg (representing the solubility of pentaerythritol in dry acetone) to the amount determined in the acetone - water solvent.

TABLE VI

CHROMATOGRAPHIC SEPARATION OF PENTAERYTHRITOL ON CELITE ADSORBENT

| Pentaerythritol taken, g | Weight of pentaerythritol found in acetone extract, g | Weight of pentaerythritol found in acetone - water extract by benzaldehyde condensation method, g | Total pentaerythritol found with 10-mg correction, g |
|---|---|---|---|
| 0·340 | 0·011 | 0·329 | 0·339 |
| 0·396 | 0·014 | 0·383 | 0·393 |
| 0·399 | 0·010 | 0·387 | 0·397 |
| 0·463 | 0·010 | 0·454 | 0·464 |
| 0·502 | 0·010 | 0·493 | 0·503 |
| 0·702 | 0·011 | 0·689 | 0·699 |

### EFFECT OF LIQUID IMPURITIES—

Table VII shows the amounts of liquid impurities extracted by the two solvents in the chromatographic procedure. The liquid impurities used in these experiments were obtained

TABLE VII

CHROMATOGRAPHIC SEPARATION OF LIQUID IMPURITIES ON CELITE ADSORBENT

| Liquid impurities taken, g | Weight of liquid impurities found in acetone extract, g | Weight of liquid impurities found in acetone - water extract, g | Liquid impurities recovered (total), g |
|---|---|---|---|
| 0·503 | 0·438 | 0·044 | 0·482 |
| 1·024 | 0·940 | 0·054 | 0·994 |

from plant purge liquor by means of the chromatographic procedure described on p. 34. The results show that the liquid impurities are not extracted quantitatively by the dry acetone and that a further portion is extracted by the acetone - water. However, it will be seen from Table VIII that there is no appreciable interference by these residual liquid impurities with the determination of pentaerythritol.

TABLE VIII

CHROMATOGRAPHIC SEPARATION OF PENTAERYTHRITOL AND LIQUID IMPURITIES FROM MIXTURES CONTAINING BOTH SUBSTANCES

| Mixture | | Weight of liquid impurities found in acetone extract, | Weight of pentaerythritol found in acetone - water extract (by benzaldehyde condensation method), | Pentaerythritol found (with + 10 mg correction), |
|---|---|---|---|---|
| Pentaerythritol, g | Liquid impurities, g | g | g | g |
| 0·595 | 0·089 | 0·069 | 0·582 | 0·592 |
| 0·593 | 0·100 | 0·063 | 0·589 | 0·599 |
| 0·561 | 0·174 | 0·131 | 0·559 | 0·569 |
| 0·754 | 0·540 | 0·403 | 0·756 | 0·766 |
| 0·641 | 0·546 | 0·385 | 0·650 | 0·660 |
| 0·606 | 0·659 | 0·490 | 0·618 | 0·628 |

### EFFECT OF DIPENTAERYTHRITOL—

Because commercial pentaerythritol might contain high concentrations of dipentaerythritol, a number of analyses of pentaerythritol - dipentaerythritol mixtures were made by the chromatographic separation - benzaldehyde condensation procedure. As the solubility of dipentaerythritol in water is small compared with that of pentaerythritol (see Table V), the sample did not always dissolve in water before absorption on Celite. Results for mixtures of pentaerythritol and dipentaerythritol are shown in Table IX. They show that even with mixtures containing more dipentaerythritol than pentaerythritol, the results are good.

TABLE IX

CHROMATOGRAPHIC SEPARATION AND DETERMINATION OF PENTAERYTHRITOL IN MIXTURES CONTAINING DIPENTAERYTHRITOL

| Mixture taken | | Amount of pentaerythritol (+ 10 mg correction) found, |
|---|---|---|
| Pentaerythritol, g | Dipentaerythritol, g | g |
| 0·421 | 0·281 | 0·431 |
| 0·406 | 0·607 | 0·398 |
| 0·467 | 0·901 | 0·469 |
| 0·460 | nil | 0·459 |

## CONCLUSIONS

Factors affecting the benzaldehyde procedure for the determination of pentaerythritol have been examined and it has been shown that the procedure cannot be applied directly to commercial samples of unknown purity or to liquors from the manufacturing process. A chromatographic method is described for the separation of pentaerythritol before the application of the benzaldehyde procedure. It is applicable to commercial samples and liquors.

## REFERENCES

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# Determination by Radioactivation of Small Amounts of Rubidium and Caesium in Sea-water and Related Materials of Geochemical Interest*

By A. A. SMALES and L. SALMON

Neutron radioactivation analysis has been applied to the determination of rubidium and caesium in the range $10^{-5}$ to $10^{-8}$ g. The radiochemical separations with carrier were based mainly on cobaltinitrite and caesium bismuth iodide precipitation, respectively, rubidium-89 and both isomers of caesium-134 being counted finally as chloroplatinates.

The method has been used for the determination of the two elements in sea-water (after a preliminary concentration on a cation-exchange resin) and directly in seaweeds, marine sediments and coals.

The rubidium and caesium contents of North Atlantic sea-water were found to be 120 and 0·5 µg per litre (parts per thousand million), respectively.

A brief mention is made of the determination of milligram amounts of sodium by neutron irradiation, chemical separations being avoided by the use of γ-ray spectrometry.

In the estimation of a tolerable discharge rate into the sea for radioactive effluent containing fission-product caesium, it is necessary to know the natural caesium content of sea-water and the extent of the concentration of this element by seaweeds. The work described in this paper was undertaken to supply this information and was extended to include rubidium because of its related geochemical interest.

Several authors have given values for the rubidium content of sea-water, the method usually used being concentration of the rubidium from the water by evaporation or chemical precipitation and optical or X-ray spectrographic analysis of the concentrate. Goldschmidt, Berman, Hauptmann and Peters[1] reported that the salts from the North Sea waters contained 0·0006 per cent. of rubidium, *i.e.*, the sea-water contained 210 µg per litre. This value was again quoted by Goldschmidt[2] in 1937 and apparently misquoted by Wattenburg[3] as 20 µg per litre. Since then, Kovaleva and Bukser[4] have give 240 µg per litre for English Channel water, 340 µg per litre for Mediterranean water and 450 µg per litre for Black Sea water; Ishibashi and Harada[5] give 35 µg per litre for coastal water from the Wakayama Prefecture.

Borovik-Romanova[6] has given values between 100 and 200 µg per litre for sea-water from the Black, Barents, Okhotsk, Japan and Karkii Seas and from the Greek Archipelago, less than 30 µg per litre for the Caspian Sea and 5700 µg per litre for Lake Inder.

The only determination of caesium in sea-water reported so far is that by Harada,[7] who concentrated caesium by perchlorate and cobaltinitrite precipitation followed by fractional crystallisation and completed the analysis spectrographically; he reported values from 2 to 10 µg per litre and gave the sensitivity of his spectroscopic method as 26 µg of caesium. The figure generally quoted, *e.g.*, by Sverdrup, Johnson and Fleming,[8] is 2 µg per litre and this value seems to have appeared from the paper of Goldschmidt[9] onwards and to be derived from the rubidium to caesium ratio of about 100 to 1 found in carnallite crystals from salt deposits by Jander and Busch.[10]

Spectrographic determinations of the rubidium content of dried seaweed from the Pacific Ocean and the Barents and Caspian Seas were made by Borovik-Romanova,[11,12] who gave values of 1·2 to 6·6 p.p.m.; freshwater plants examined by the same author contained 1·4 to 5·2 p.p.m. and land plants 1 to 10 p.p.m. Black and Mitchell[13] quote values from 25 to 250 p.p.m. for oven-dried seaweeds, while values for land plants examined by Bertrand and Bertrand[14] ranged from 2·1 to 81 (average, 20·3) p.p.m. for flowering plants and from 2·8 to 354 p.p.m. of rubidium for non-flowering plants (material dried at 105° C).

No determinations of the caesium in seaweeds appear to have been made, although Bertrand and Bertrand[15] report values, which seem surprisingly high, for land plants of

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between 3 and 88·5 (average, 22) p.p.m. on the dried material (they give 0·2 $\mu$g as the sensitivity of their caesium method). Tobacco-leaf ash analysed by Yamagata[16] contained 0·17 p.p.m.

All the work described so far has involved emission or X-ray spectroscopy. Neutron radioactivation was chosen for our work because of the much greater sensitivity attainable; a brief mention of this work has already been made.[17]

After the work described in the paper had been completed, Brooksbank and Leddicotte,[18] in a description of the separation of rubidium and caesium by ion exchange, briefly mentioned the determination of "in the order of 0·02 per cent." of caesium in rubidium carbonate by radioactivation and by emission spectroscopy.

## FEASIBILITY OF THE RADIOACTIVATION METHOD—

The nuclear characteristics involved in the determination of rubidium and caesium are shown in Table I.

TABLE I

NUCLEAR DATA FOR RUBIDIUM AND CAESIUM

| Target nuclide | Abundance, % | Product on neutron irradiation | Radiation and energy | Half-life | Isotopic activation cross-section, barns |
|---|---|---|---|---|---|
| $^{85}$Rb | 72·8 | $^{86}$Rb | $\beta^-$, 1·8 MeV<br>$\gamma$ | 19·5 day | 0·85 |
| $^{87}$Rb | 27·2 | $^{88}$Rb | $\beta^-$, 5 MeV | 18 minutes | 0·14 |
| $^{133}$Cs | 100·0 | $^{134m}$Cs | $e^-$, 0·13 MeV | 3·1 hour | 3·0 |
| | | $^{134}$Cs | $\beta^-$, 0·66 MeV<br>$\gamma$ | 2·3 year | 26·0 |

Because of its short half-life, rubidium-88 was not used in this work; however, rubidium-86 is satisfactory, as it has a high maximum $\beta$-energy and a satisfactory half-life. It can be calculated that for an irradiation in a flux of $10^{12}$ neutrons per sq. cm per second for one half-life, 1 $\mu$g of rubidium will give $1·3 \times 10^5$ disintegrations per minute. If a counting efficiency of 10 per cent. and a lower limit of detection of 8 counts per minute are assumed, the ultimate sensitivity for rubidium is $6 \times 10^{-10}$ g.

Calculation, similar to that for rubidium, shows that 1 $\mu$g of caesium will give $4 \times 10^5$ disintegrations per minute of the 3·1-hour isomer on irradiation for a one half-life period. However, because of the time required for chemical separation and the low energy of the conversion electrons emitted, the ultimate sensitivity is likely to be only about $10^{-9}$ g. For the 2·3-year isomer, irradiations for a period of a half-life are impracticable, but some of the work to be described has involved irradiations of 3 months, under which conditions 1 $\mu$g of caesium gives $5 \times 10^5$ disintegrations per minute. Decay and absorption losses are small and hence an ultimate sensitivity of $10^{-10}$ g of caesium is possible if the 2·3-year caesium-134 isomer with a 3-month irradiation period is used.

Both caesium isomers were used in the present work.

## EXPERIMENTAL

### IRRADIATION—

Solid samples examined for caesium by means of the 3-hour isomer, or for rubidium, were usually irradiated for periods of between a few hours and 2 days. The samples were sealed in short lengths of polythene tubing, which were packed together in a standard 3-inch × 1-inch aluminium can for irradiation in the "self-serve" positions in the Harwell Pile. Solid samples requiring longer irradiation (*e.g.*, 3 months) were packed in silica tubes plugged with aluminium foil, and batches were irradiated together in the thermal column of the pile. This method of packing rather than the use of sealed silica ampoules is preferred for long irradiations of material that produces gaseous products by radiation decomposition.

Small quantities of liquids were sealed in small silica ampoules, while for irradiations of 10-ml quantities of liquids, the apparatus described by Pate[19] was used.

STANDARDS—

Dilute standard aqueous solutions of rubidium and caesium salts in sealed silica ampoules were used, when possible, for simultaneous irradiation with samples. Sometimes quantities of the pure salts or suitable solid dilutions made by grinding them with sucrose were used in sealed silica ampoules.

CHEMICAL SEPARATION—

Radiochemical methods are available for the separation of both rubidium and caesium from irradiated bismuth, uranium and thorium (*e.g.*, Meinke[20]) and similar techniques were used in this work, although precipitation of caesium bismuth iodide was found to give much better decontamination of caesium from potassium than the more usual silicotungstic acid reagent. Ion exchange has been used as a radiochemical separation method for the alkali metals,[17] but is much slower than the precipitation methods. The separation of rubidium from potassium is not readily achieved by precipitation methods, but such a separation was not needed in the present work as potassium-42 with a 12·8-hour half-life was allowed to decay to an insignificant level before measurement of the 19·5-day rubidium-86. However, if potassium is present in the sample, it will accompany rubidium, and if the amount is significant, a correction will be required for the chemical yield of rubidium. As an example, if a 100-mg sample containing 1 per cent. of potassium was used, then the correction for 50 mg of rubidium would be about 2 per cent. Similarly, rubidium and caesium are not easily separated by precipitation methods, and although such a separation is described below for the caesium determination, it is inconvenient and unnecessary in the rubidium determinations on samples such as those discussed in this paper, *i.e.*, where the rubidium content is greater than the caesium content by a factor 10 to 100 and where irradiation and decay periods of a few days are used.

Generally the heavier alkali metals were separated from the gross activity due to other elements by preliminary precipitation as perchlorate, before proceeding to "scavenging" precipitations and subsequent precipitations of cobaltinitrite (for rubidium) or bismuth iodide (for caesium) in the presence of hold-back carriers. The rubidium and caesium were finally precipitated as chloroplatinates for chemical-yield determinations and counting. To test the "decontamination" attainable with the chemical separation finally used, tracer experiments with a number of neutron-irradiated elements and inactive caesium were performed. In all the results in Table II, the final caesium precipitate did not contain detectable amounts of the original tracer used.

TABLE II

ELEMENTS COMPLETELY SEPARATED FROM CAESIUM BY THE METHOD DESCRIBED IN THE PROCEDURE

| Radionuclide | Original activity, counts per minutes | Half-life |
|---|---|---|
| $^{24}$Na | $10^8$ | 15 hours |
| $^{38}$Cl | $6 \times 10^7$ | 38 minutes |
| $^{64}$Cu | $5 \times 10^7$ | 12·9 hours |
| $^{65}$Ni | $5 \times 10^6$ | 2·5 hours |
| $^{69}$Zn | $3 \times 10^7$ | 52 minutes |
| $^{71}$Ga | $10^7$ | 14·3 hours |
| $^{72}$Ge | $10^7$ | 82 minutes |
| $^{76}$As | $3 \times 10^7$ | 26·8 hours |
| $^{82}$Br | $10^7$ | 35 hours |
| $^{90}$Y | $5 \times 10^6$ | 65 hours |
| $^{116}$In | $10^8$ | 54 minutes |
| $^{128}$I | $10^8$ | 25 minutes |
| $^{139}$Ba | $10^6$ | 85 minutes |
| $^{140}$La | $3 \times 10^7$ | 40 hours |

The chemical yield in the procedure was usually about 70 per cent.

MEASUREMENT OF RADIOACTIVITY—

For the radiochemical separation 50-mg quantities of the two elements were used as carriers, the final chemical yield being determined gravimetrically on the dried chloroplatinate precipitate prepared finally. This precipitate was suitable for counting under an end-window Geiger counter of the GM4 type, although because of the low energy of the conversion electrons from the 3-hour caesium-134 isomer, an EHM2 thin-window Geiger tube was used. Correction for self-absorption was also necessary and values for a correction curve, which is shown in Fig. 1, were produced by precipitating different weights of caesium chloroplatinate with a fixed amount of radioactive caesium. Decay or absorption curves or both were determined for all samples to test for radiochemical purity, and typical examples are shown in Figs. 2, 3, 4 and 5.

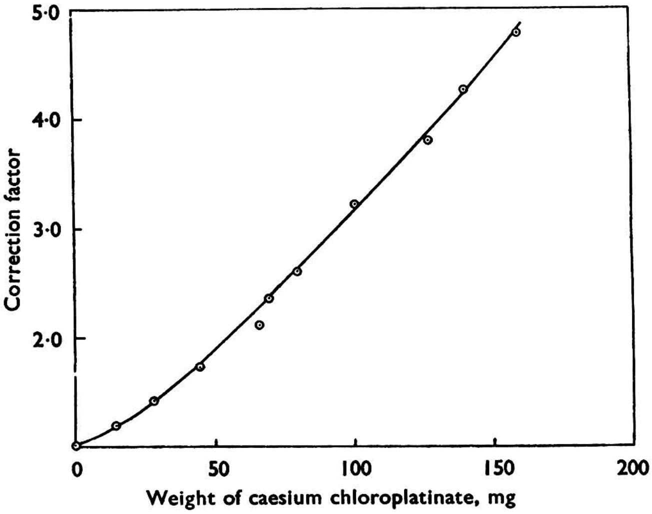

Fig. 1. Self-absorption correction for caesium-134 conversion electrons in caesium chloroplatinate

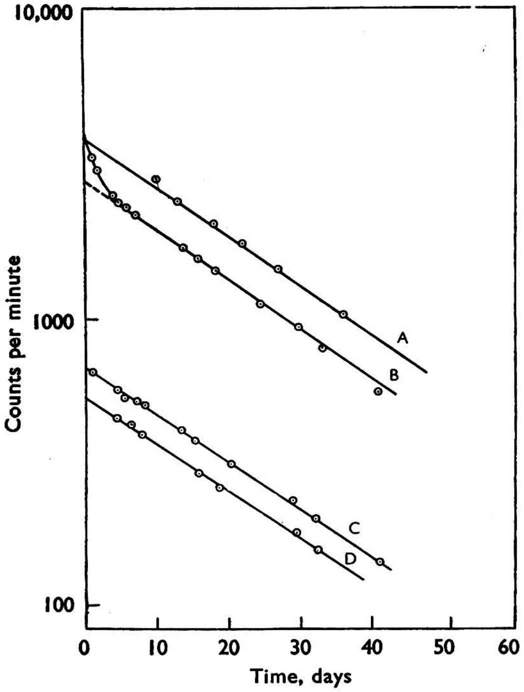

Fig. 2. Decay curve for rubidium-86 (half-life, 19 days). Curve A, standard; curve B, seaweed; curve C, coal; and curve D, sea-water

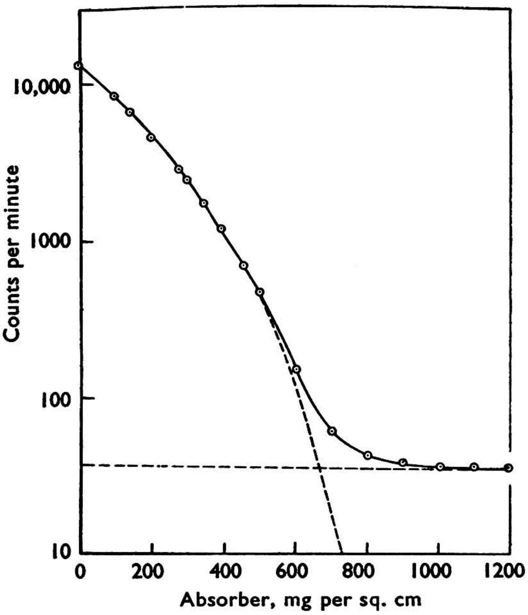

Fig. 3. Absorption curve for rubidium-86

PRELIMINARY CONCENTRATION OF CAESIUM AND RUBIDIUM FROM SEA-WATER BEFORE IRRADIATION—

Although several determinations of caesium using the 3-hour isomer were made by direct irradiation of 10-ml quantities of sea-water for 3-hour periods, the precision of the results was not good. Such determinations are difficult, not only because of the low caesium level, but also because of the high associated activity, which is 10 to 100 millicuries per sample. Some method of concentrating the caesium was therefore desirable and preferably at the same time it should involve some separation from sodium and chlorine, the two major contributory elements to the high activity.

The need for concentrating rubidium is not so great and direct results are quoted later. However, as the concentration method used for caesium also applied to rubidium, determinations of rubidium have also been made after concentration.

Ion exchange was chosen for the method of concentration, as it was already well known from the work of Beukenkamp and Rieman[21] and Kayas[22] that separations of the alkali metals were feasible by this technique, and although the conditions used by these authors were somewhat different from those required for sea-water, in which the sodium to caesium ratio is approximately $10^7$, nevertheless the possibility of concentration of caesium was explored.

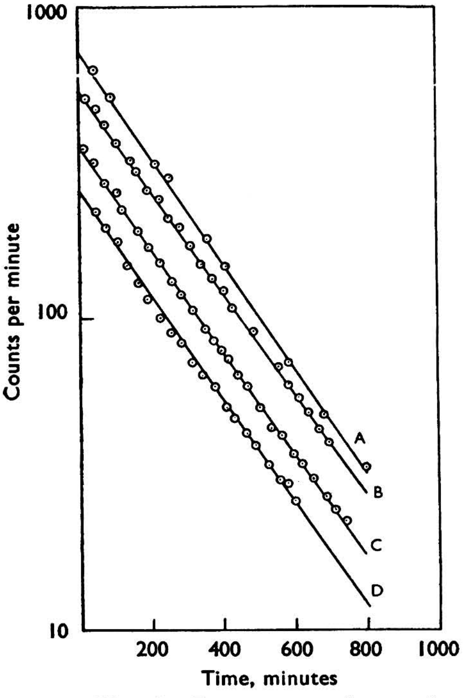

Fig. 4. Decay curve for caesium-134 (half-life, 3 hours). Curve A, seaweed; curve B, coal; curve C, standard; and curve D, sea-water

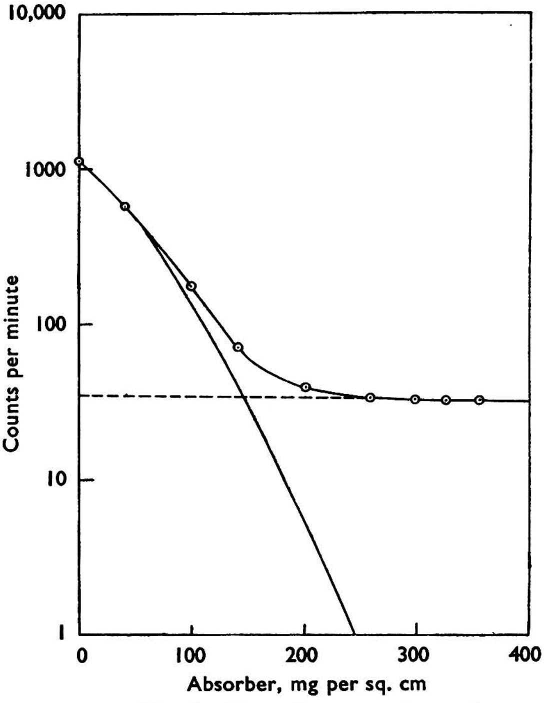

Fig. 5. Absorption curve for caesium-134 (half-life, 2·3 years)

The choice of resin was made by first determining the equilibrium distribution coefficients, $K_d$, for caesium between sea-water containing added carrier-free caesium-137 and the several types of resin, in the usual manner by shaking weighed portions of the dry resin with known volumes of sea-water, and then conducting column experiments to measure the amount of sea-water that could be passed through a 1-g $\frac{1}{4}$-inch diameter column of the 100-mesh resins showing the highest $K_d$ values before caesium began to appear in the effluent, caesium-137 again being used to indicate caesium breakthrough. The column technique is shown in Fig. 6 and the results are in Table III.

From these results Amberlite IR-100 was chosen for the determinations discussed below. However, neither this resin nor Amberlite IR-105 appears to be commercially

TABLE III

CHOICE OF ION-EXCHANGE RESIN FOR CONCENTRATION OF CAESIUM FROM SEA-WATER

| Resin ($NH_4$ form) | Type | $K_d$ | Caesium breakthrough volume, ml (flow-rate, 0·5 ml per minute) |
|---|---|---|---|
| Amberlite IR-100 | Phenol - sulphonic acid | 69 | >100 |
| Amberlite IR-105 | Phenol - sulphonic acid | 61 | |
| Zeo-Karb 315 | Phenol - sulphonic acid | 55 | 100 |
| Zeo-Karb 215 | Phenol - sulphonic acid | 39 | 70 |
| Zeo-Karb 225 | Sulphonic acid | 23 | |
| Amberlite IR-120 | Sulphonic acid | 19 | |
| Amberlite IRC-50 | Carboxylic acid | ~2 | |

$$K_d = \frac{\text{Caesium concentration in resin}}{\text{Caesium concentration in solution}}$$

available now. Zeo-Karb 315 can be recommended, as the results with it have been consistent. So that there was an ample safety factor, 50-ml samples were used in the caesium determinations, while 10-ml samples were used for the rubidium determination, separate tracer experiments with this element showing its complete retention from the sample volume of sea-water.

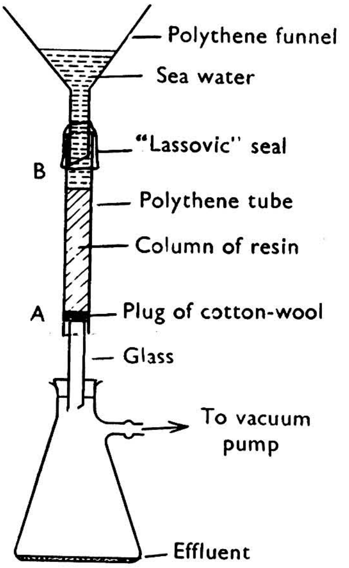

Fig. 6. Apparatus for uptake of caesium on ion-exchange resin

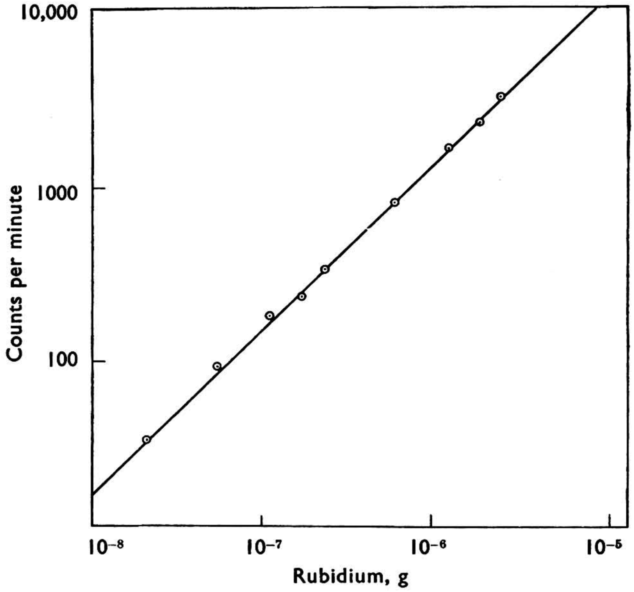

Fig. 7. Determination of rubidium in aqueous solution

The resin was treated before use by washing it with redistilled 5 *N* hydrochloric acid, then with ammonium chloride solution prepared from redistilled ammonia and hydrochloric acid, and finally with distilled water. After passing the required volume of sea-water sample through it, the resin was washed with 1 to 2 ml of distilled water and sucked as dry as possible, the polythene tube was cut at points A and B in Fig. 6, the plug of cotton-wool was removed and then the ends of the tube were sealed by heating them. The tube was then ready for a 3-hour irradiation for rubidium or caesium.

## METHOD

### PROCEDURE FOR RUBIDIUM—

After the irradiated samples have "cooled" for a suitable length of time, say 1 week, open the containers and transfer the contents to 150-ml beakers containing 50·0 mg of rubidium as sulphate in a few millilitres of water. Add 10 ml of nitric acid, sp.gr. 1·42, and

1 ml of sulphuric acid, sp.gr. 1·84, and heat the mixture carefully to oxidise organic matter. Complete the oxidation by adding small quantities of nitric acid and finally by heating to fumes after the addition of 5 ml of perchloric acid, sp.gr. 1·70. Cool the solution and transfer it to a 50-ml centrifuge tube, absolute ethanol being used for rinsing. Spin the precipitated rubidium perchlorate in a centrifuge, wash the precipitate three times with ethanol and each time transfer the supernatant liquid to the active-waste storage container. Dissolve the precipitate in 10 ml of water containing a few drops of 10 *N* hydrochloric acid. At this stage take a suitable aliquot of the irradiated standard and to it add 50·0 mg of rubidium carrier and then continue the radiochemical separation for both samples and standard.

Add 10 mg of ferric iron as chloride, stir the solution, add sodium hydroxide solution until it is permanently alkaline and then heat to boiling. Spin the precipitate in a centrifuge and filter the supernatant liquid into another 50-ml centrifuge tube. Wash the ferric hydroxide with 2 to 3 ml of water, spin it and pour the supernatant liquid through the same filter-paper. Discard the precipitate and filter-paper.

Just acidify the filtrate with glacial acetic acid and add an excess of a freshly prepared 10 per cent. aqueous solution of sodium cobaltinitrite. Allow the precipitate to settle for a few minutes, spin it and discard the supernatant liquid. Wash the precipitate three times with water, spinning it in a centrifuge each time and discarding the supernatant liquids. To the precipitate add 2 ml of diluted nitric acid (1 + 1) and boil the mixture gently until it has dissolved; cool the solution and add to it a further 2 ml of the diluted nitric acid and 15 ml of absolute ethanol. Precipitate the rubidium chloroplatinate by the addition of 1 ml of 10 per cent. w/v platinum chloride solution, spin the precipitate and wash it three times with ethanol. Make a slurry of the precipitate with a small quantity of ethanol and transfer it to a weighed aluminium counting tray, dry it under an infra-red lamp and finally cool it and weigh it to determine the chemical yield, making allowance for the potassium, if this is significant.

Finally determine the rubidium activity with a Geiger counter or other suitable type of counter, correct the measured activity for background and counter dead-time (if necessary) and then check for radiochemical purity by plotting a decay and absorption curve.

Then—

$$\text{Weight of rubidium in sample} = \text{Weight of rubidium in standard} \times \frac{\text{Corrected count rate of sample}}{\text{Corrected count rate of standard}}.$$

PROCEDURE FOR CAESIUM—

After the irradiated samples have "cooled" for a suitable time, say 30 minutes for the 3-hour isomer or 10 days for the 2·3-year isomer, open the containers and treat the contents as for rubidium, 50·0 mg of caesium carrier being used instead of rubidium, to the point at which the filtrate and washing from the ferric hydroxide precipitation step have been just acidified with glacial acetic acid, and include the treatment of standards at the corresponding stage.

Add a further 0·5 to 0·8 ml of glacial acetic acid, cool the solution to 0° C and add 1 ml of bismuth tri-iodide reagent (prepared by dissolving 20 g of bismuth tri-iodide and 20 g of sodium iodide in 50 ml of water containing 2 ml of glacial acetic acid and filtering). Allow the mixture to remain in the ice-bath for 5 minutes, then spin it in a centrifuge, discard the supernatant liquid, and wash the precipitate three times with ethanol, centrifuging each time. Dissolve the precipitate by boiling it with 10 ml of 0·2 *N* hydriodic acid to which has been added 1 ml of a solution containing 10 mg per ml of sodium, potassium and rubidium (as chlorides). Cool the mixture to 0° C, add to it 1 ml of bismuth tri-iodide reagent and again spin the precipitate in a centrifuge and wash it three times with ethanol; next dissolve it in 2 ml of hot diluted nitric acid (1 + 1) and remove the free iodine by boiling. Cool the solution, add a further 2 ml of diluted nitric acid (1 + 1), and then 15 ml of absolute ethanol and 1 ml of 10 per cent. platinum chloride solution. Spin the precipitated chloroplatinate and wash, dry and weigh it as for rubidium; determine the activity using a thin window Geiger counter (type EHM2) or other suitable type of counter and correct the measured activity for self-absorption, decay, background, counter dead-time (if necessary) and chemical yield. Check the radiochemical purity either by decay or absorption measurements and calculate the caesium content.

## RESULTS

### SEA-WATER—

Direct determination of caesium in 10-ml quantities of sea-water, as mentioned previously, gave poor precision, but an indication of approximately 0·5 μg per litre.

Direct determination on 10-ml quantities for rubidium are reported in Table IV.

TABLE IV

DETERMINATION OF RUBIDIUM IN SEA-WATER BY DIRECT IRRADIATION

| Location | Depth, metres | Rubidium content, μg per litre |
|---|---|---|
| 44°N 15°W (approximately) .. .. | 800 | 124 |
| | 1600 | 121 |
| 46°28′N 8°01′W .. .. .. .. | 20 | 130 |
| | 500 | 131 |

Determinations of caesium by means of the 3-hour isomer (50-ml sample) and of rubidium (10-ml sample), both after ion-exchange concentration, are reported in Table V.

TABLE V

DETERMINATION OF RUBIDIUM AND CAESIUM IN SEA-WATER AFTER CONCENTRATION BY ION EXCHANGE

| Location | Depth, metres | Rubidium found, μg | Rubidium content, μg per litre | Caesium found, μg | Caesium content, μg per litre |
|---|---|---|---|---|---|
| 49°02′N 15°19′W .. .. | 20 | 1·13 | 113 | 0·0285 | 0·57 |
| | | 1·02 | 102 | 0·028 | 0·56 |
| | 1200 | 1·12 | 112 | 0·0245 | 0·49 |
| | | 1·08 | 108 | 0·0265 | 0·53 |
| | 2000 | 1·32 | 132 | 0·0255 | 0·51 |
| | | 1·12 | 112 | | |
| | 3000 | 1·18 | 118 | 0·025 | 0·50 |
| | | 1·07 | 107 | | |
| | 4000 | 1·20 | 120 | 0·0255 | 0·51 |
| | | 1·20 | 120 | 0·0265 | 0·53 |
| | Bottom | 1·36 | 136 | 0·023 | 0·46 |
| | | | | 0·023 | 0·46 |
| Coastal .. .. .. | | | | 0·021 | 0·42 |
| | | | | 0·023 | 0·46 |
| 48°19′N 7°26′W .. .. | 40 | | | 0·0225 | 0·45 |
| 48°38′N 6°26′W .. .. | 40 | | | 0·021 | 0·42 |
| | 40 | | | 0·0225 | 0·45 |
| | 40 | | | 0·021 | 0·42 |
| Treated resin blank .. .. | | <0·01 | <1 | <0·0005 | <0·01 |

TABLE VI

DETERMINATIONS ON SEA-WATER CONTAINING ADDED RUBIDIUM AND CAESIUM

| Rubidium added, μg | Total rubidium, μg | Rubidium found, μg | Caesium added, μg | Total caesium, μg | Caesium found, μg |
|---|---|---|---|---|---|
| — | | 1·11* | — | | 0·022* |
| 0·50 | 1·61 | 1·51 | 0·002 | 0·024 | 0·024 |
| 1·00 | 2·11 | 2·12 | 0·004 | 0·026 | 0·028 |
| 1·50 | 2·61 | 2·61 | 0·008 | 0·030 | 0·031 |
| 2·00 | 3·11 | 3·07 | 0·010 | 0·032 | 0·033 |
| 2·00 | 3·11 | 3·22 | 0·012 | 0·034 | 0·034 |
| 3·00 | 4·11 | 4·40 | 0·020 | 0·042 | 0·047 |
| | | | 0·06 | 0·082 | 0·081 |
| | | | 0·10 | 0·122 | 0·122 |

* Result on sea-water used as starting material.

To test the general applicability of the method to sea-water, determinations were made on a sample of sea-water to which known additions of rubidium and caesium had been made. Unfortunately, it was not possible at these concentrations to prepare artificial sea-water of sufficient purity and therefore recourse was made to the addition technique. Results of such experiments are shown in Table VI. Results of rubidium determinations on distilled-water solutions of a rubidium salt are shown in Fig. 7.

### SEAWEED—

Determinations of rubidium and caesium were made on several samples of oven-dried seaweed, both the 3-hour and the 2·3-year isomers being used for caesium. The results are shown in Table VII.

TABLE VII

RUBIDIUM AND CAESIUM IN SEAWEED

| Seaweed | Wet weight / Dry weight | Ash as percentage of dry weight | Element and caesium isomer used* | | Sample weight, g | Found, µg | Dry weed, p.p.m. | Wet weed, p.p.m. |
|---|---|---|---|---|---|---|---|---|
| *Ascophyllum nodosum* | 4·78 | 25·1 | Rb | | 0·7882 | 5·36 | 6·80 | 1·42 |
| | | | Rb | | 0·8257 | 5·78 | 7·00 | 1·46 |
| | | | Cs | S | 0·9950 | 0·094 | 0·098 | 0·021 |
| | | | Cs | S | 0·9112 | 0·087 | 0·095 | 0·020 |
| | | | Cs | L | 1·2337 | 0·115 | 0·093 | 0·019 |
| | | | Cs | L | 1·4105 | 0·137 | 0·097 | 0·020 |
| *Fucus serratus* .. | 4·13 | 19·7 | Rb | | 0·9715 | 6·85 | 7·05 | 1·70 |
| | | | Rb | | 0·6236 | 5·02 | 8·05 | 1·95 |
| | | | Cs | S | 0·8643 | 0·066 | 0·076 | 0·018 |
| | | | Cs | S | 0·7788 | 0·054 | 0·069 | 0·017 |
| | | | Cs | L | 0·9921 | 0·072 | 0·073 | 0·018 |
| | | | Cs | L | 0·7420 | 0·062 | 0·083 | 0·020 |
| *Fucus vesiculosus* | 4·48 | 20·3 | Rb | | 0·8982 | 9·79 | 10·9 | 2·43 |
| | | | Cs | S | 0·8214 | 0·091 | 0·111 | 0·025 |
| | | | Cs | L | 0·8461 | 0·088 | 0·104 | 0·023 |
| | | | Cs | L | 0·7420 | 0·072 | 0·097 | 0·022 |
| | | | Cs | S | 0·9089 | 0·099 | 0·109 | 0·024 |
| *Laminaria digitata* | 8·64 | 34·6 | Rb | | 0·9620 | 19·0 | 19·7 | 2·28 |
| | | | Rb | | 0·7675 | 14·4 | 18·8 | 2·18 |
| | | | Cs | S | 0·6324 | 0·069 | 0·109 | 0·013 |
| | | | Cs | S | 0·9212 | 0·081 | 0·088 | 0·010 |
| | | | Cs | S | 0·8964 | 0·100 | 0·111 | 0·013 |
| *Laminaria saccharina* | 11·31 | 36·4 | Rb | | 0·7809 | 12·6 | 16·1 | 1·42 |
| | | | Cs | S | 1·0032 | 0·157 | 0·157 | 0·014 |
| | | | Cs | S | 0·6056 | 0·056 | 0·092 | 0·0083 |
| | | | Cs | L | 0·8434 | 0·083 | 0·098 | 0·0087 |
| *Porphyra umbilicalis* | 6·42 | 20·8 | Rb | | 0·5686 | 2·27 | 4·00 | 0·63 |
| | | | Rb | | 0·7649 | 2·90 | 3·80 | 0·59 |
| | | | Cs | S | 0·9328 | 0·043 | 0·052 | 0·0081 |
| | | | Cs | S | 0·9421 | 0·049 | 0·052 | 0·0081 |
| | | | Cs | S | 0·6754 | 0·036 | 0·054 | 0·0084 |
| *Rhodymenia palmata* | 10·62 | 38·7 | Rb | | 0·8289 | 9·53 | 11·5 | 1·08 |
| | | | Cs | S | 0·8663 | 0·111 | 0·128 | 0·012 |
| | | | Cs | S | 0·7428 | 0·091 | 0·122 | 0·011 |
| | | | Cs | L | 0·9777 | 0·147 | 0·150 | 0·014 |

* S, isomer with short half-life used. L, isomer with long half-life used.

TABLE VIII

RUBIDIUM AND CAESIUM CONTENTS OF MARINE SEDIMENT PILOT CORE SAMPLES

| Sample depth, cm | Element determined | Sample weight, g | Found | |
|---|---|---|---|---|
| | | | µg | p.p.m. |
| 5 | Rb | 0·0722 | 0·070 | 9·7 |
| | Cs | 0·4792 | 0·162 | 0·34 |
| 10 to 15 | Rb | 0·0638 | 0·061 | 9·6 |
| | Cs | 0·1579 | 0·080 | 0·51 |
| 25 to 35 | Rb | 0·1176 | 0·285 | 24·2 |
| | Cs | 0·2150 | 0·318 | 1·48 |

TABLE IX

RUBIDIUM AND CAESIUM CONTENT OF COALS FROM COUNTY DURHAM

| Sample | Ash, % | Element and caesium isomer used* | | Sample weight, g | Found | |
|---|---|---|---|---|---|---|
| | | | | | µg | p.p.m. |
| Fencehouses boiler .. | 16·9 | Rb | | 0·0738 | 1·28 | 17·4 |
| | | Rb | | 0·0852 | 1·08 | 12·7 |
| | | Cs | S | 0·1125 | 0·17 | 1·5 |
| | | Cs | S | 0·0954 | 0·13 | 1·4 |
| | | Cs | S | 0·0593 | 0·083 | 1·4 |
| | | Cs | L | 0·1025 | 0·13 | 1·3 |
| Hetton D.C. boiler .. | 21·0 | Rb | | 0·0579 | 1·84 | 31·7 |
| | | Rb | | 0·0634 | 1·75 | 27·6 |
| | | Cs | S | 0·0657 | 0·21 | 3·2 |
| | | Cs | S | 0·0589 | 0·22 | 3·8 |
| | | Cs | L | 0·0607 | 0·24 | 4·0 |
| Morden boiler .. .. | 11·0 | Rb | | 0·0748 | 1·52 | 20·3 |
| | | Rb | | 0·0860 | 1·58 | 18·4 |
| | | Cs | S | 0·0638 | 0·13 | 2·1 |
| | | Cs | L | 0·0770 | 0·17 | 2·2 |
| Pelton boiler .. .. | 15·1 | Rb | | 0·0827 | 2·10 | 25·4 |
| | | Rb | | 0·0867 | 2·84 | 32·8 |
| | | Cs | S | 0·0700 | 0·23 | 3·3 |
| | | Cs | S | 0·0915 | 0·28 | 3·1 |
| South Hetton boiler .. | 21·1 | Rb | | 0·0864 | 1·94 | 22·5 |
| | | Rb | | 0·0764 | 1·91 | 25·0 |
| | | Cs | S | 0·0669 | 0·18 | 2·7 |
| | | Cs | S | 0·0667 | 0·18 | 2·8 |
| | | Cs | L | 0·0690 | 0·21 | 2·9 |
| Usworth boiler.. .. | 16·7 | Rb | | 1·7501 | 30·6 | 17·5 |
| | | Rb | | 1·9318 | 31·7 | 16·4 |
| | | Rb | | 2·0038 | 34·5 | 17·2 |
| | | Rb | | 1·7996 | 31·5 | 17·5 |
| | | Rb | | 2·1460 | 37·6 | 17·5 |
| | | Cs | S | 0·0507 | 0·11 | 2·2 |
| | | Cs | L | 0·1458 | 0·33 | 2·3 |
| Beamish Mary small coking | 9·66 | Rb | | 0·0950 | 1·00 | 10·5 |
| | | Rb | | 0·1009 | 1·06 | 10·5 |
| | | Cs | S | 0·0922 | 0·14 | 1·5 |
| | | Cs | S | 0·0818 | 0·13 | 1·6 |
| Craghead coking .. | 8·60 | Rb | | 0·1009 | 0·859 | 8·5 |
| | | Rb | | 0·1075 | 0·965 | 9·0 |
| | | Cs | S | 0·0968 | 0·072 | 0·75 |
| | | Cs | S | 0·1017 | 0·079 | 0·78 |
| Esh coking .. .. | 7·37 | Rb | | 0·0735 | 0·534 | 7·26 |
| | | Rb | | 0·0775 | 0·570 | 7·35 |
| | | Cs | S | 0·0590 | 0·046 | 0·78 |
| | | Cs | S | 0·0727 | 0·057 | 0·79 |
| Malton coking .. .. | 15·0 | Rb | | 0·0975 | 1·13 | 11·6 |
| | | Rb | | 0·0898 | 1·09 | 12·1 |
| | | Cs | S | 0·0741 | 0·099 | 1·33 |
| | | Cs | S | 0·0848 | 0·11 | 1·34 |
| South Pelaw coking .. | 6·66 | Rb | | 0·1069 | 0·594 | 5·6 |
| | | Rb | | 0·1063 | 0·672 | 6·3 |
| Waterhouses coking .. | 8·48 | Rb | | 0·1273 | 1·43 | 11·3 |
| | | Rb | | 0·0801 | 0·993 | 12·4 |

* S, isomer with short half-life used. L, isomer with long half-life used.

MARINE SEDIMENTS—

Determinations of caesium and rubidium were made on scrapings (dried at 105° C) from a marine sediment pilot core from the equatorial Atlantic Ocean; three samples of this material were available in another connection. Although it is recognised that the significance of results on such samples is not great, they may be of some value and are shown in Table VIII.

COAL—

Although much information on the concentrations of trace elements in coal is available,[23] there seems to be a lack of results for the heavier alkali metals, presumably because of lack of sensitivity of the spectrographic methods generally used. Therefore, the amounts of rubidium and caesium in a number of County Durham coals were determined and the results are shown in Table IX. It should be noted that the sample of coal was used for the determination, in order to avoid any loss on ashing. The ash figure is given for each determination so that comparison may be made with other results. Reproducibility of results is indicated by the values from five determinations on Usworth boiler coal.

## DISCUSSION OF RESULTS

From Tables IV and V it can be seen that the average rubidium content of sea-water is 120 $\mu$g per litre with a standard deviation of $\pm 10$ $\mu$g per litre, while that for caesium (from Table V) is $0{\cdot}5 \pm 0{\cdot}05$ $\mu$g per litre. Hence the presently quoted value according to these figures is too high for rubidium by a factor of almost 2 and for caesium by a factor of 4. As the "doubtful" derivation of the quoted caesium figure, as mentioned earlier, is from

TABLE X

ALKALI METAL CONTENTS AND RATIOS IN SEA-WATER AND THE EARTH'S CRUST

| | Sodium | Potassium | Rubidium | Caesium |
|---|---|---|---|---|
| Sea-water, g per litre .. | 10·77† | 0·39† | $1{\cdot}2 \times 10^{-4}$ | $5 \times 10^{-7}$ |
| Ratio to sodium .. .. | | $3{\cdot}6 \times 10^{-2}$ | $1{\cdot}1 \times 10^{-5}$ | $4{\cdot}6 \times 10^{-8}$ |
| Ratio to potassium .. | | | $3{\cdot}1 \times 10^{-4}$ | $1{\cdot}3 \times 10^{-6}$ |
| Ratio to rubidium .. | | | | $4{\cdot}2 \times 10^{-3}$ |
| Earth's crust, p.p.m.* .. | $2{\cdot}8 \times 10^{4}$ | $2{\cdot}6 \times 10^{4}$ | $3{\cdot}1 \times 10^{2}$ | 7 |
| Ratio to sodium .. .. | | 0·92 | $1{\cdot}1 \times 10^{-2}$ | $2{\cdot}5 \times 10^{-4}$ |
| Ratio to potassium .. | | | $1{\cdot}2 \times 10^{-2}$ | $2{\cdot}7 \times 10^{-4}$ |
| Ratio to rubidium .. | | | | $2{\cdot}3 \times 10^{-2}$ |

* Values from Goldschmidt.[2] † Values from Sverdrup, Johnson and Fleming.[8]

TABLE XI

SODIUM, RUBIDIUM AND CAESIUM CONTENTS OF SEAWEEDS AND THE ENRICHMENT FACTORS FROM SEA-WATER

| Sample | Sodium, p.p.m. (on wet seaweed) | Rubidium, p.p.m. | Caesium, p.p.m. | Rubidium to sodium ratio | Caesium to sodium ratio | Caesium to rubidium ratio |
|---|---|---|---|---|---|---|
| *Ascophyllum nodosum* .. | $1{\cdot}01 \times 10^{4}$ | 1·4 | 0·020 | $1{\cdot}4 \times 10^{-4}$ | $2{\cdot}0 \times 10^{-6}$ | $1{\cdot}4 \times 10^{-2}$ |
| *Fucus serratus* .. | $0{\cdot}97 \times 10^{4}$ | 1·8 | 0·018 | $1{\cdot}9 \times 10^{-4}$ | $2{\cdot}0 \times 10^{-6}$ | $1{\cdot}0 \times 10^{-2}$ |
| *Fucus vesiculosus*.. | $0{\cdot}98 \times 10^{4}$ | 2·4 | 0·024 | $2{\cdot}5 \times 10^{-4}$ | $2{\cdot}5 \times 10^{-6}$ | $1{\cdot}0 \times 10^{-2}$ |
| *Laminaria digitata* | $0{\cdot}61 \times 10^{4}$ | 2·2 | 0·012 | $3{\cdot}6 \times 10^{-4}$ | $2{\cdot}0 \times 10^{-6}$ | $0{\cdot}55 \times 10^{-2}$ |
| *Laminaraia saccharina* .. | $0{\cdot}46 \times 10^{4}$ | 1·4 | 0·010 | $3{\cdot}1 \times 10^{-4}$ | $2{\cdot}2 \times 10^{-6}$ | $0{\cdot}7 \times 10^{-2}$ |
| *Porphyra umbilicalis* .. | $0{\cdot}47 \times 10^{4}$ | 0·61 | 0·008 | $1{\cdot}3 \times 10^{-4}$ | $1{\cdot}8 \times 10^{-6}$ | $1{\cdot}3 \times 10^{-2}$ |
| *Rhodymenia palmata* .. .. | $0{\cdot}32 \times 10^{4}$ | 1·08 | 0·013 | $3{\cdot}4 \times 10^{-4}$ | $4{\cdot}1 \times 10^{-6}$ | $1{\cdot}2 \times 10^{-2}$ |
| Average .. .. | $0{\cdot}69 \times 10^{4}$ | 1·58 | 0·015 | $2{\cdot}3 \times 10^{-4}$ | $2{\cdot}4 \times 10^{-6}$ | $1{\cdot}0 \times 10^{-2}$ |
| Sea-water .. .. | | | | $1{\cdot}1 \times 10^{-5}$ | $4{\cdot}6 \times 10^{-8}$ | $4{\cdot}2 \times 10^{-3}$ |
| Average "enrichment factor" relative to sodium | | | | 21 | 52 | |

calculated ratios of rubidium to caesium found in carnallite, the revision needed is surprisingly small.

From these newly determined values it is of interest to calculate some of the ratios of the alkali metals for the different types of material examined and hence determine any relative enrichment. For this purpose the sodium contents of some samples were separately determined by radioactivation without chemical concentration, the intensity of the 2·76 MeV $\gamma$-radiation from sodium-24 being measured on a $\gamma$-ray spectrometer, and compared with standards irradiated simultaneously.

First, the revised values of the ratios in sea-water are compared with those for the earth's crust in Table X; the determined values for sodium in seaweeds and from these the relative enrichment of rubidium and caesium in seaweeds are given in Table XI; and similar results for coal in Table XII.

## Table XII

### Sodium, rubidium and caesium contents of coal ash and enrichment factors from the earth's crust

| Sample | Sodium, p.p.m. | Rubidium, p.p.m. | Caesium, p.p.m. | Rubidium to sodium ratio | Caesium to sodium ratio | Caesium to rubidium ratio |
|---|---|---|---|---|---|---|
| Fencehouses boiler coal* .. .. | $4\cdot9 \times 10^{3}$ | 92 | 8·3 | $1\cdot9 \times 10^{-2}$ | $1\cdot7 \times 10^{-3}$ | $0\cdot9 \times 10^{-1}$ |
| Hetton D.C. boiler coal .. .. | $3\cdot8 \times 10^{3}$ | 141 | 17·0 | $3\cdot7 \times 10^{-2}$ | $4\cdot5 \times 10^{-3}$ | $1\cdot2 \times 10^{-1}$ |
| Morden boiler coal | $7\cdot9 \times 10^{3}$ | 175 | 19·5 | $2\cdot2 \times 10^{-2}$ | $2\cdot5 \times 10^{-3}$ | $1\cdot1 \times 10^{-1}$ |
| Malton coking coal | $2\cdot7 \times 10^{3}$ | 79 | 8·9 | $2\cdot9 \times 10^{-2}$ | $3\cdot3 \times 10^{-3}$ | $1\cdot1 \times 10^{-1}$ |
| Average .. .. | $4\cdot8 \times 10^{3}$ | 122 | 13·4 | $2\cdot6 \times 10^{-2}$ | $3\cdot0 \times 10^{-3}$ | $1\cdot1 \times 10^{-1}$ |
| Earth's crust .. | $2\cdot8 \times 10^{4}$ | 310 | 7·0 | $1\cdot1 \times 10^{-2}$ | $2\cdot5 \times 10^{-4}$ | $2\cdot3 \times 10^{-2}$ |
| Average "enrichment factor" relative to sodium | | | | 2·4 | 12 | |

* Sodium, rubidium and caesium were determined in the coal, but calculated to the value in the ash.

## INTERFERING ELEMENTS

### CHEMICAL—

The method described is generally applicable, although in some determinations there might arise the need for extra decontamination steps in the chemical procedure. The need for such extra steps will be apparent from the decay and absorption curves and it is usually a simple matter to design additional chemical steps for the removal of the contaminant, either by "scavenging" or by extra precipitations of the rubidium or caesium in the presence of added "hold-back" carriers.

But in the determination of rubidium in samples containing caesium at levels greater than about one-tenth that of the rubidium (see p. 39), a special step to separate the two elements will be necessary and the ion-exchange method is of value in this connection. An alternative radiometric approach might be to make use of the differing maximum $\beta$-particle energies of rubidium-86 (1·8 MeV) and caesium-134 (0·66 MeV) by counting through about 250 mg per sq. cm of aluminium.

### NUCLEAR—

At the levels and in the samples dealt with in this paper, manufacture during irradiation, of rubidium-86 or caesium-134 from elements other than rubidium and caesium is negligible. However, if large amounts of either strontium or yttrium are irradiated, rubidium-86 might be formed by the following reactions—

$$ {}^{86}_{38}\mathrm{Sr} + {}^{1}_{0}n \rightarrow {}^{86}_{37}\mathrm{Rb} + {}^{1}_{1}\mathrm{H} \qquad (n,p) $$

$$ {}^{89}_{39}\mathrm{Y} + {}^{1}_{0}n \rightarrow {}^{86}_{37}\mathrm{Rb} + {}^{4}_{2}\mathrm{He} \qquad (n,\alpha) $$

Another possible mode of formation of rubidium-86 is by slow-neutron fission of uranium. In the two former reactions the exact cross-sections for pile neutrons are not known, although they are small. In the fission reaction the yield[24] of rubidium-86 is only about $1\cdot6 \times 10^{-4}$, so that interference of this kind from any of these three elements would only arise when they were present to an extent of several orders of ten greater than the rubidium in the samples.

Similarly, caesium-134 might be formed by an $(n,p)$ reaction on barium-134, although it cannot be formed by an $(n,\alpha)$ reaction from a stable element, nor is it formed in uranium fission.

Other radionuclides of rubidium can also be formed from strontium and uranium, and those of caesium from barium and, in addition, from lanthanum and uranium; but these isotopes can usually be differentiated from the rubidium-86 and caesium-134 specifically used for the determination.

Although, as indicated above, interference due to nuclear reactions other than the $(n,\gamma)$ process being used in the determination occurs only rarely, even then a preliminary concentration of the rubidium and caesium from the elements mentioned will overcome any difficulties, but some of the advantages of the method are lost.

The natural radioactivity of potassium and rubidium may have to be considered when the ultimate sensitivity of the method is reached, but this was insignificant in the present work.

## CONCLUSIONS

The methods described in this paper have been applied to samples containing amounts of rubidium and caesium as small as $10^{-7}$ to $10^{-8}$ g and the ultimate sensitivity of the method has not been approached. Precision (standard deviation) has generally been better than $\pm 10$ per cent., which is usually adequate for this trace-element work, but, we believe, could be improved if necessary. The levels of rubidium and caesium have been fixed within narrow limits for sea-water from the Atlantic Ocean, and the ability of seaweeds to concentrate these elements from sea-water has been shown. The values of Borovik-Romanova[6,11,12] for rubidium in sea-water and seaweeds have been confirmed.

The major advantages of the present method over those methods previously used for determining rubidium and caesium are the improved sensitivity and specificity and the avoidance of reagent blanks; blanks only need to be measured for the ion-exchange concentration from sea-water before irradiation, and even then they are less than 1 per cent. of the rubidium determined and less than 2·5 per cent. of the caesium determined.

We are grateful to Dr. R. Scott of the Seaweed Research Institute, Inveresk, for supplying the samples of seaweed; to Dr. L. H. N. Cooper of the Marine Biological Laboratory, Plymouth, for the sea-water; to Dr. J. D. H. Wiseman of the British Museum (Natural History) for the marine sediments; and to Dr. B. W. Bradford of the Billingham Division of I.C.I. Ltd., for the coals, which were carefully sampled averages of a year's deliveries from the collieries and seams mentioned.

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# Determination of Acrylonitrile in Air

BY J. HASLAM AND G. NEWLANDS

A method has been developed for the determination of acrylonitrile in air at concentrations of about 0 to 150 mg per cubic metre. In the test a known volume of the air is passed through a solution of lauryl mercaptan in *iso*propanol. Ethanolic potassium hydroxide is then added to catalyse the reaction between acrylonitrile and the mercaptan. After acidification of the mixture with acetic acid, a volume of standard iodine solution equivalent to the lauryl mercaptan originally used is added. The excess of iodine, which is proportional to the amount of acrylonitrile present in the original sample of air, is then determined absorptiometrically.

THE increasing use of acrylonitrile in industrial operations and its highly toxic nature made it desirable to develop a method for the determination of small amounts of acrylonitrile in concentrations of about 0 to 150 mg per cubic metre of air.

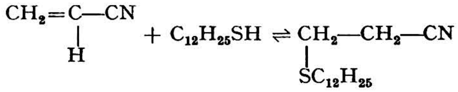
Peterson and Radke[1] developed a method in which the acrylonitrile is absorbed in sulphuric acid. The acid solution is then hydrolysed with sodium hydroxide solution in the presence of hydrogen peroxide and copper acetate, the copper acetate preventing polymerisation of the acrylonitrile. The ammonia liberated in the hydrolysis is distilled into a known volume of standard acid and the excess of acid is titrated with standard alkali.

This method is lengthy, although Clasper (unpublished communication) has succeeded in reducing the time required for the test by introducing direct Nesslerisation of the ammonia produced in the hydrolysis. Nevertheless, it was decided that a more rapid and specific test was desirable.

Beesing, Tyler, Kurtz and Harrison[2] determined acrylonitrile by making it react with a mercaptan followed by titration of the excess of mercaptan with standard iodine solution. It was thought that this principle might form the basis of a simple and rapid test for acrylonitrile in air. This test, it was suggested, would be more specific than previous tests and, moreover, would be capable of dealing with small concentrations. Such a method has been developed.

The method depends on the absorption of the acrylonitrile in a solution of lauryl mercaptan in *iso*propanol followed by addition of ethanolic potassium hydroxide to catalyse the reaction between the acrylonitrile and the mercaptan. After acidification of the solution with acetic acid, a volume of iodine solution equivalent to the amount of mercaptan originally present is added and the excess of iodine, which is proportional to the acrylonitrile, is determined absorptiometrically.

The relevant reactions are as follows—



$$\underset{\displaystyle \mathrm{H}}{\mathrm{CH_2{=}C{-}CN}} + C_{12}H_{25}SH \rightleftharpoons \underset{\displaystyle \mathrm{SC_{12}H_{25}}}{\mathrm{CH_2{-}CH_2{-}CN}}$$

$$2C_{12}H_{25}SH + I_2 \rightleftharpoons C_{12}H_{25}{-}S{-}S{-}C_{12}H_{25} + 2HI$$

The time required for a test is about 1 hour excluding the sampling time, which would be about 20 minutes for a 40-litre sample.

The reaction is fairly specific, although $\alpha\beta$-unsaturated nitriles, esters or aldehydes, if present, would react with the mercaptan under the conditions of the test. These substances, however, are not likely to be present in the atmosphere of factories in which acrylonitrile is being handled.

Full details of the test and the results of its application to atmospheres containing known concentrations of acrylonitrile are described below.

## METHOD

### APPARATUS—

*Absorbers*—Two absorbers of a type suitable for a gas flow of about 2 litres per minute.

*Flow meter*—A Rotameter covering the range of 1 to 5 litres per minute or a suitable gas meter.

### REAGENTS—

*Mercaptan solution*—Dissolve 2·5 g of lauryl mercaptan in *iso*propanol in a 250-ml calibrated flask and dilute to the mark with *iso*propanol.

*Potassium hydroxide solution*—Dissolve 5 g of analytical-reagent grade potassium hydroxide in 100 ml of aldehyde-free ethanol.

*Acetic acid, glacial*—Analytical-reagent grade.

*Iodine solution, approximately* 0·03 N—Dilute 75 ml of 0·1 *N* iodine solution to 250 ml with water.

iso*Propanol.*

*Standard acrylonitrile solution*—(*a*) Weigh accurately about 0·5 g of pure acrylonitrile into a 100-ml calibrated flask, dissolve it in *iso*propanol and dilute to the mark with *iso*propanol. (*b*) Transfer an aliquot of solution (*a*) equivalent to 0·05 g of acrylonitrile to a 100-ml calibrated flask and dilute to the mark with *iso*propanol. Then 1 ml of solution contains 0·5 mg of acrylonitrile.

### PREPARATION OF CALIBRATION CURVE—

A calibration curve relating the amount of acrylonitrile in mg to the final absorptiometer reading is prepared as follows.

Transfer seven 10-ml aliquots of the mercaptan solution by pipette to 50-ml calibrated flasks. To the flasks add 0·0, 1·0, 2·0, 3·0, 4·0, 5·0 and 6·0-ml aliquots of the standard acrylonitrile solution (*b*) and sufficient *iso*propanol to make the total volume 16 ml. Add 1 ml of 5 per cent. ethanolic potassium hydroxide solution to each flask from a pipette, mix the solution and set it aside for 4 minutes. To each flask add 2 ml of glacial acetic acid by pipette and mix the contents. Titrate the solution that does not contain acrylonitrile with the 0·03 *N* iodine solution to a faint yellow end-point. Record the volume of iodine solution required and transfer the same volume of 0·03 *N* iodine solution to each of the flasks containing acrylonitrile. Mix the solutions well, dilute to the mark with *iso*propanol and again mix them. Measure the optical density of the acrylonitrile solutions against the blank solution on a Spekker absorptiometer, with 1-cm cells and Ilford No. 601 spectrum violet filters. Plot the values for optical density against concentration of acrylonitrile in mg per 100 ml of solution.

This curve is usually a smooth curve, and typical results are as follows—

| | | | | | |
|---|---|---|---|---|---|
| Acrylonitrile, mg per 50 ml .. | 0·5 | 1·0 | 1·5 | 2·0 | 3·0 |
| Acrylonitrile, mg per 100 ml .. | 1·0 | 2·0 | 3·0 | 4·0 | 6·0 |
| Optical density .. .. .. | 0·149 | 0·315 | 0·441 | 0·566 | 0·788 |

### APPLICATION OF THE TEST TO ACRYLONITRILE - AIR MIXTURES—

Acrylonitrile - air mixtures were prepared by means of a fluid feed atomiser of the type described by Gage.[3] A solution of acrylonitrile in *iso*propanol was fed into the atomiser from a 0·5-ml "Agla" syringe, the plunger of which was driven at a known rate by means of a slow-injection apparatus. The air flow through the atomiser was about 11 litres per minute. The rate of injection of the solution per unit of time was calculated from the cross-section of the plunger. From the injection rate and air rate, the concentration of acrylonitrile in the gaseous mixture was calculated as mg per cubic metre of gas. The concentration of acrylonitrile in the gas mixture was varied by altering the rate of injection or the concentration of acrylonitrile in the *iso*propanolic solution or both.

If $X$ = concentration of acrylonitrile in *iso*propanolic solution, per cent. w/v,
$R$ = rate of injection, minutes per inch,
$y$ = rate of air flow, litres per minute, and
0·5108 ml = rate of injection per inch for the syringe used, then—

$$\text{Acrylonitrile in gas mixture} = \frac{0{\cdot}5108 \times X \times 10^3 \times 10^3}{R \times 100 \times y}$$

$$= \frac{0{\cdot}5108 \times X \times 10^4}{R \times y} \text{ mg per cubic metre.}$$

For instance, in an experiment the values were $X$, 9·03 per cent.; $R$, 80 minutes per inch; and $y$, 11·3 litres per minute. Then—

$$\text{Acrylonitrile concentration} = \frac{0{\cdot}5108 \times 9{\cdot}03 \times 10^4}{80 \times 11{\cdot}3}$$

$$= 51{\cdot}02 \text{ mg per cubic metre.}$$

The effects of acrylonitrile and *iso*propanol vapours on the concentration have been neglected, as these effects are not significant.

The test was next applied to acrylonitrile - air mixtures of known composition prepared as described above, the following procedure being used.

### PROCEDURE—

Transfer 10 ml of the mercaptan solution by pipette and 5 ml of *iso*propanol to each of the two absorbers. Support the absorbers in beakers and pack them with crushed solid carbon dioxide. Connect in series the two absorbers, the Rotameter (or gas meter) and the source of suction. Regulate the flow-rate to about 2 litres per minute by means of an air leak and draw about 40 litres of the atmosphere to be tested through the absorbers. Disconnect the absorbers and bring them to room temperature. To each absorber add by pipette 1 ml of 5 per cent. ethanolic potassium hydroxide solution, mix the solution and set it aside for 4 minutes. Then, with a pipette add 2 ml of glacial acetic acid to each absorber, mix the solution and to it add from a burette a volume of the 0·03 *N* iodine solution pre-determined as described below. Transfer the contents of each absorber to the same 100-ml calibrated flask, wash the absorber with *iso*propanol, transfer the washings to the flask, and dilute to the mark with *iso*propanol (solution *S*).

Transfer 10 ml of the mercaptan solution by pipette and 5 ml of *iso*propanol to a 50-ml calibrated flask, and with a pipette add 1 ml of 5 per cent. ethanolic potassium hydroxide solution, mix the contents and set it aside for 4 minutes. Add 2 ml of glacial acetic acid from a pipette, mix the solution and titrate it with the 0·03 *N* iodine solution to a faint yellow end-point and then dilute to 50 ml with *iso*propanol (solution *B*).

Note the volume of iodine solution required and add the same volume of iodine solution to the test solutions in the absorbers as indicated above.

Measure the optical density of the test solution (*S*) against the blank solution (*B*) on a Spekker absorptiometer, with 1-cm cells and Ilford No. 601 spectrum violet filters. From a previously prepared calibration curve relating optical density to concentration of acrylonitrile, determine the concentration of acrylonitrile in the sample solution. Calculate the amount of acrylonitrile absorbed from the volume of air passed and hence calculate the concentration of acrylonitrile in the atmosphere in mg per cubic metre.

### CALCULATION—

Let $W$ = concentration of acrylonitrile, mg per 100 ml, *i.e.*, the weight of acrylonitrile absorbed, mg, and

$V$ = volume of air passed, litres. Then—

$$\text{Acrylonitrile content of atmosphere} = \frac{W \times 10^6}{V \times 10^3}$$

$$= \frac{W \times 10^3}{V} \text{ mg per cubic metre.}$$

The results were as follows—

| Acrylonitrile concentration, mg per cubic metre | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Calculated .. | .. | 23 | 23 | 29 | 34 | 42 | 46 | 51 | 56 | 56 | 68 | 79 | 102 | 116 |
| Found .. | .. | 23 | 22 | 27 | 30 | 39 | 42 | 44 | 47 | 44 | 57 | 70 | 90 | 102 |

Most of the results are low, *i.e.*, they average about 90 per cent. of the theoretical, but this accuracy will be satisfactory for most purposes, especially as the test is rapid.

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# The Separation of Zinc from Cadmium

## With Special Reference to the Determination of Zinc in Cadmium Metal

BY E. R. BAGGOTT AND R. G. W. WILLCOCKS

Experiments on the behaviour towards an anion-exchange resin of cadmium and zinc in iodide solution are described. It is shown that cadmium and zinc can be separated by passing a mixture of their sulphates in mixed sulphate - iodide solution through an anion-exchange column. Evidence is presented that an anionic complex of iodide and zinc exists in solutions containing only iodide as the anion, but not when sulphates are also present. One part of zinc can be separated and recovered from 20,000 parts, or more, of cadmium. After separation, the zinc may be determined by a rapid dithizone method.

DURING work on the production of pure cadmium metal, a rapid method was needed for the determination of small amounts of zinc in the presence of large quantities of cadmium.

The method described by Scott[1] was found to be time-consuming and it involved three precipitations with hydrogen sulphide and five evaporations. The reliability of the results for small amounts of zinc was also suspect.

Bryson and Lenzer-Lowy[2] have summarised the difficulties to be encountered in the separation of zinc and cadmium and have presented a method for the separation of zinc from a moderate excess of cadmium, but this and other methods considered by them become increasingly unsatisfactory as the cadmium to zinc ratio in the sample increases. In the determination of zinc in commercially pure cadmium metal, a ratio of cadmium to zinc of 20,000 to 1 may be encountered and for this the conventional methods are quite unsuitable. Therefore it seemed necessary to examine more unusual methods of separation.

Ion-exchange methods have been used in the separation of similar ions, and it appeared likely that such a method would be useful for the separation of zinc and cadmium. Kozak and Walton[3] found that the complex ammine ions of zinc and cadmium were only partly separated when passed through a base ion-exchange resin (sulphonated coal). Experiments with various cation-exchange materials were unsuccessful, whether the zinc and cadmium were passed through the exchange column in the form of their simple ions or of their complex cations.

Anion exchange appeared to be more promising, as both cadmium and zinc form complex halide anions of the type $MX_4''$. According to the work of Stokes,[4] Stokes and Levien[5] and Leden[6] the order of stability of these anions is—

$$ZnCl_4'' > ZnBr_4'' > ZnI_4'' \quad \text{and} \quad CdI_4'' > CdBr_4'' > CdCl_4''.$$

These stabilities indicated that use might be made of the difference in stability between the complex halides of cadmium and zinc, in particular, the iodides.

## EXPERIMENTAL

### BATCH EXPERIMENTS—

Exploratory experiments showed that when a mixture of zinc and cadmium sulphates in potassium iodide solution was shaken with a strong base anion-exchange resin, there was a marked reduction in the cadmium content of the solution, but little or no reduction of the zinc content could be detected.

Batch experiments in which solutions containing cadmium sulphate, potassium iodide and sulphuric acid were agitated with a number of anion-exchange resins (in the hydroxide forms) indicated that the highest capacity for cadmium was exhibited by De-Acidite FF and, therefore, most of the subsequent work was done with this resin. Amberlite IR-4B (a weak base anion-exchange resin) and Amberlite IRA-410 (a strong base anion-exchange resin) had lower capacities, although it is possible that the capacity of these resins might be raised by suitable regeneration. In support of this, some difficulty was experienced with a new sample of De-Acidite FF, which exhibited a rather low capacity when first used, but increased in capacity considerably after several treatments with cadmium iodide and with intermediate regenerations.

Batch experiments also showed that iodide ions had a greater affinity for the resin than had sulphate ions and that if sufficient iodide was present in solution, sulphates were not absorbed on to the resin. For this reason, use of the resin in the iodide form facilitated the study of the effect of iodide concentration on the exchange of cadmium iodide. Fig. 1 shows the effect of the molar ratio of potassium iodide to cadmium in the sample solution on the absorption of cadmium on resin in the iodide form. The maximum absorption of cadmium occurs when the potassium iodide is present in approximately the stoicheiometric ratio, *i.e.*, potassium iodide to cadmium in the ratio 4 to 1.

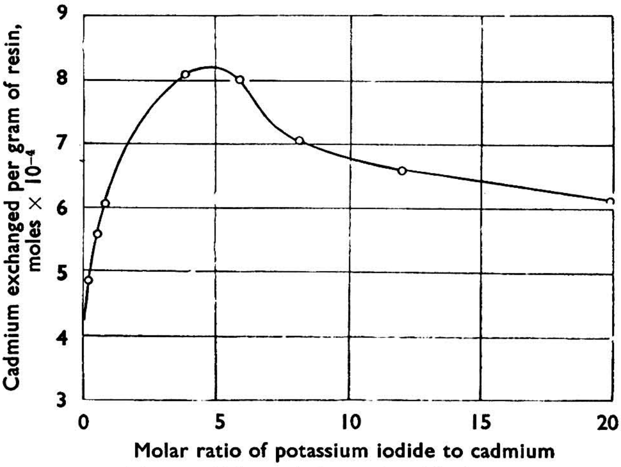

Fig. 1. Effect of the ratio of iodide to cadmium on the batch exchange of cadmium on De-Acidite FF

The preliminary experiments also indicated that the absorption of the cadmium iodide complex was independent of the sulphate-ion concentration in the sample solution.

The batch method used in the preliminary experiments, although useful in rapid exploratory work, would be unsuitable for continuous routine work, as batch methods with ion-exchange materials are seldom as efficient as is the use of columns and, furthermore, the mechanical shaking necessary in batch methods results in severe attrition of the resin. Attention was therefore turned to experiments with columns.

### EXPERIMENTS WITH ION-EXCHANGE COLUMNS—

A series of experiments was conducted to study the elution characteristics of cadmium, zinc, sulphate and iodide when the resin was prepared in various ways and when various eluting solutions were used. In this series of experiments, 40 g of air-dried De-Acidite FF resin was used in a column 16 mm in diameter. The individual experiments are set out in tabular form in Table I.

TABLE I

SEPARATION OF ZINC AND CADMIUM BY MEANS OF A COLUMN OF ION-EXCHANGE RESIN

| Experiment number | Pre-treatment of resin column | Influent solution | Eluting solution | Flow-rate, ml per minute | Fractions collected | Results |
|---|---|---|---|---|---|---|
| *C*1 | OH′ resin washed with KI solution until effluent is neutral | $Cd(SO_4)$, 1 g; KI, 5·9 g; $H_2SO_4$, 1 g in 250 ml | water | 25 | 20 × 30 ml | See Fig. 2 |
| *C*2 | OH′ resin washed with 2 bed volumes of 50 g per litre of KI in *N* $H_2SO_4$; then with water until effluent is neutral | As in *C*1 plus 1·00 mg of Zn as sulphate | water | 18 | 7 × 100 ml | See Fig. 3 |
| *C*3 | OH′ resin treated as in *C*2, then flooded with 1 bed volume of 50 g per litre KI solution | As in *C*2 | water | 20 | 14 × 50 ml | See Fig. 4 |
| *C*4 | As in *C*3 | As in *C*2 | 50 g per litre of KI | 20 | 2 × 300 | *1st fraction*<br>Zn, 1·186 mg<br>Cd, nil<br>*2nd fraction*<br>Zn, nil<br>Cd, nil |
| *C*5 | $SO_4''$ resin | As in *C*2 | 50 g per litre of KI | 25 | 1 × 300 | Zn, 1·190 mg<br>Cd, 0·650 mg |
| *C*6 | $SO_4''$ resin flooded with a solution containing 50 g per litre of KI and 25 g per litre of $H_2SO_4$ | As in *C*2 | 50 g per litre of KI | 25 | 1 × 300 | Zn, 1·225 mg<br>Cd, nil |
| *C*7 | As in *C*6 | As in *C*2, but without added Zn | 50 g per litre of KI | 25 | 1 × 300 | Zn, 0·196 mg<br>Cd, nil |

Column is 16 mm in diameter and contains 40 g of De-Acidite FF.
OH′ resin—Resin in the hydroxyl form.
$SO_4''$ resin—Resin in the sulphate form.

TABLE IA

RECOVERIES OF ZINC

| Experiment number | Zinc added, mg | Zinc found, mg | Recovery,* % |
|---|---|---|---|
| *C*4 | 1·000 | 1·186 | 99·0 |
| *C*5 | 1·000 | 1·190 | 99·4 |
| *C*6 | 1·000 | 1·225 | 102·9 |

* Zinc found less the zinc in experiment *C*7.

NOTES ON EXPERIMENTS *C*1 TO *C*7 IN TABLE I—

*C*1—From Fig. 2 it is evident that the pre-treatment of the hydroxyl form of the resin with potassium iodide solution does not convert it entirely to the iodide form, as indicated by the initial rise in the pH of the effluent. This pH rise caused precipitation of cadmium in the column. When the iodide content of the effluent falls to less than 1 g per litre of potassium iodide, cadmium begins to be eluted.

*C*2—Fig. 3 shows that pre-treatment of the hydroxyl form of the resin with acidified potassium iodide solution prevents the violent fluctuation of pH, but cadmium breaks through in the first fractions in which the potassium iodide content is low. Cadmium breakthrough recurs in the last fractions when the iodide content is again low.

*C*3—Fig. 4 shows that flooding the column with a solution of potassium iodide (containing 50 g per litre) before passing in the influent solution prevents the early breakthrough of cadmium. Use of a more concentrated influent solution does not adversely affect the retention of cadmium and allows all the zinc to be eluted in a smaller volume of effluent. However, the cadmium and zinc curves overlap, the cadmium breakthrough probably being caused by decrease of iodide concentration.

*C*4—Elution with a solution of potassium iodide (containing 50 g per litre) instead of with water prevents the breakthrough of cadmium entirely but allows all the zinc to pass.

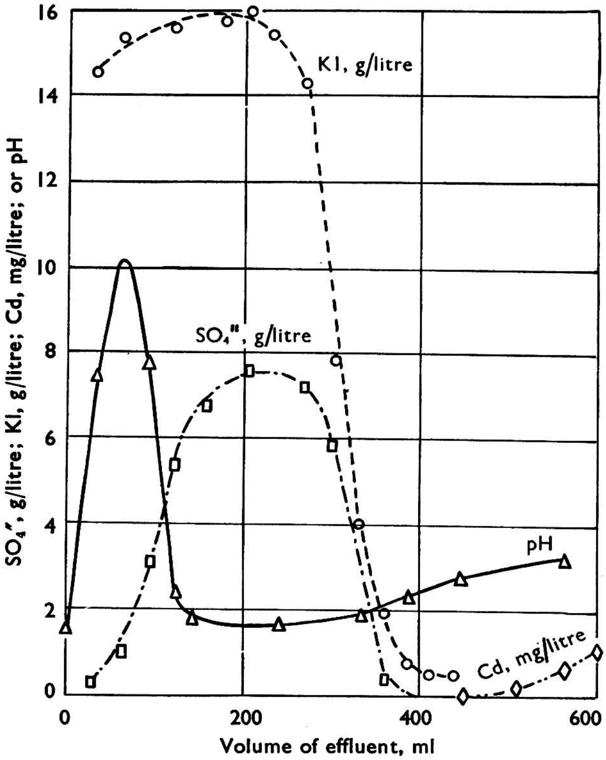

Fig. 2. Variation of the composition of the effluent with its volume: experiment *C*1 (Table I)

*C*5, *C*6 *and* *C*7—Resin in the sulphate form when pre-treated with an acid solution of potassium iodide almost prevents the breakthrough of cadmium. These three experiments were conducted to determine whether the cheaper regeneration of the resin (as sulphate form rather than as iodide form) would be effective. The untreated sulphate form does not retain cadmium sufficiently.

INFLUENCE OF SULPHATES ON THE FORMATION OF AN ANIONIC ZINC - IODIDE COMPLEX—

The sharp separation of cadmium and zinc in iodide solution on the resin column indicated a very low stability for the zinc - iodide complex. However, Stokes[4,5] has shown that zinc forms a complex iodide in iodide solutions above 0·5 *M*. Therefore it was considered desirable to determine whether the anionic zinc complex is formed under the conditions of the method described in this paper.

If no such complex is formed, the zinc elution curve should be of the same general shape and have a peak at the same point as that of any other non-absorbed ion. Any lag of the peak for zinc behind that of a non-absorbed ion would indicate the formation of a zinc anionic complex.

If it is assumed that ammonium ions do not form anionic complexes under the conditions of the exchange separation described and, further, that ammonium ions do not affect the equilibrium between zinc and iodide ions, then the introduction of a small amount of ammonium salt into the influent solution would permit the comparison of the elution curves for ammonium and zinc.

Experiments on ion exchange were therefore conducted on solutions similar in general composition to those used in the analytical separation, but to which an ammonium salt had been added. The elution curves shown in Fig. *5a* indicate that zinc and ammonium pass through the column at almost identical rates, implying that no anionic zinc complex is formed. However, when sulphate ions were excluded from the influent so that it contained only zinc, ammonium and iodide ions, the elution curves were those shown in Fig. *5b*. Therefore, in the absence of sulphate, there is a noticeable retention of zinc in the column. As the ionic strengths of the two types of solution were similar, it appears that sulphate prevents the formation of the zinc - iodide complex. In the absence of sulphate, Stokes' findings are confirmed.

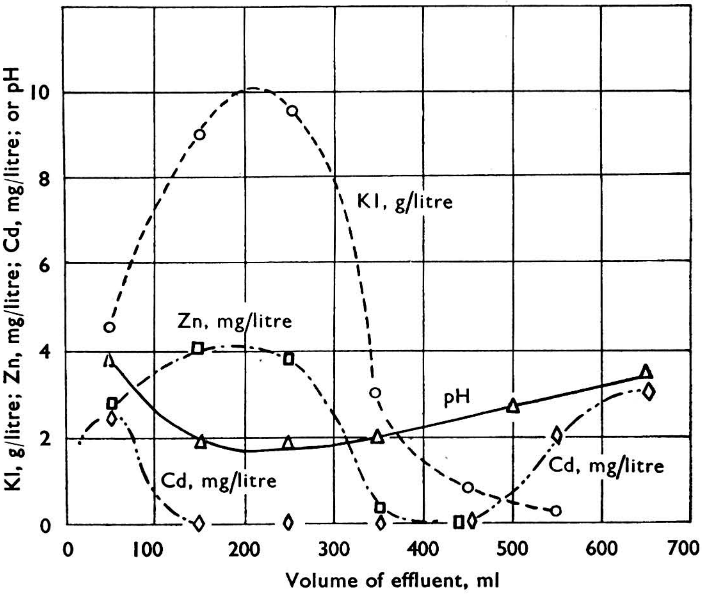

Fig. 3. Variation of the composition of the effluent with its volume: experiment *C*2 (Table I)

### ANALYTICAL METHODS USED FOR THE COLUMN EXPERIMENTS

In all the experiments described, the zinc content of the effluents was determined by a modification of the method of Fischer and Leopoldi,[7] in which zinc is determined colorimetrically by means of diphenylthiocarbazone (dithizone).

In selecting a method for the determination of small amounts of zinc in the effluents from ion-exchange columns, attention was concentrated on possible interference from iodide and cadmium, as iodide would be present in fairly large amounts and it was expected that some cadmium would pass through the column. The dithizone method appeared most likely to be suitable for the purpose and before embarking on the main experiments on ion exchange, the method was tested. After modification as described below, it was found to be satisfactory.

### EXAMINATION AND MODIFICATION OF THE DITHIZONE METHOD FOR ZINC—

Application of the usual procedures for the use of dithizone to pure zinc sulphate solutions containing iodide showed that iodide does not interfere with the determination of zinc. However, when cadmium was added, the values were high, as the cadmium - iodide complex is apparently not sufficiently stable to prevent the reaction of cadmium with dithizone.

Sodium thiosulphate has been used as a complexing agent for cadmium but, in this work, it was not found to be entirely satisfactory. Another procedure often recommended is to wash the carbon tetrachloride solution containing the dithizone complexes of zinc and cadmium with a dilute solution of sodium sulphide, so as to extract the cadmium complex preferentially.[7] At least five separate washes are required and this makes the method tedious and increases the chance of error. Furthermore, the instability of dilute sodium sulphide solutions makes both their pH and sulphide concentration uncertain and variations in both these factors can lead to erroneous results.

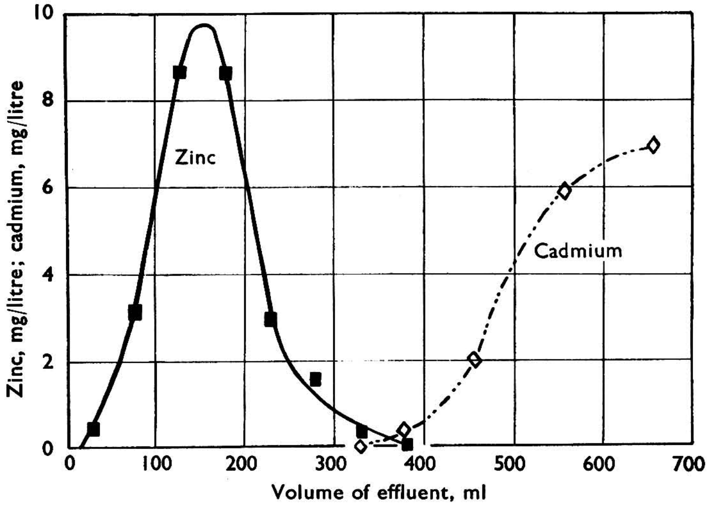

Fig. 4. Separation of cadmium and zinc on a column of ion-exchange resin: experiment $C3$ (Table I)

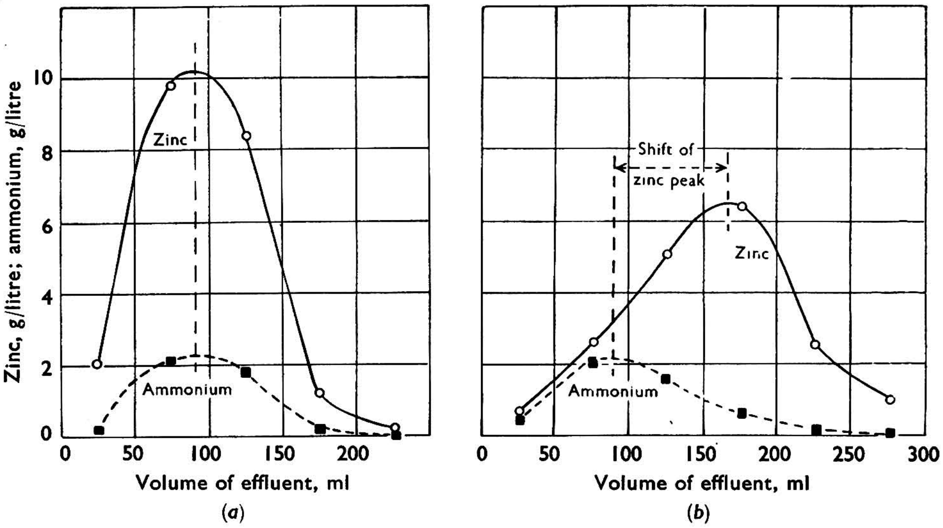

Fig. 5. Curves to show the influence of sulphate ions on the retention of zinc iodide on a column of ion-exchange resin, ammonium ions being used as marker.

(*a*) Sample solution containing 1 g of zinc (as sulphate), 1 g of ammonium sulphate ($\triangleq$ 0·26 g of ammonia), 6 g of potassium iodide and 1 g of sulphuric acid in 50 ml of water: wash solution, 50 g of potassium iodide per litre.

(*b*) Sample solution containing 1 g of zinc (as iodide), 2·2 g of ammonium iodide ($\triangleq$ 0·26 g of ammonia) and 4 g of potassium iodide in 50 ml of water: wash solution, 50 g of potassium iodide per litre

Under the climatic conditions in which this work was conducted, it has been found that the one-colour method for the use of dithizone is much more reliable than the two-colour method, probably because the metal - dithizone complexes appear to be more stable to heat than does dithizone itself. Of the various reagents available for the removal of excess of dithizone from carbon tetrachloride solutions, two were selected as being most likely to be useful. Dilute ammonium hydroxide (approximately 1·2 g of ammonia per litre)[8] and a phosphate buffer solution of pH 11·0[9] were tested, the latter solution being found to be more reliable.

It was also found that a combined buffer and sulphide solution would remove both excess of dithizone and the cadmium - dithizone complex in one extraction without affecting the colour of the zinc complex. Furthermore, the colour of the zinc - dithizone complex was stable for more than 30 minutes, even at an ambient temperature of 30° C.

As a result of the exploratory experiments and of past experience with dithizone methods, the following method was finally adopted.

## METHOD

### REAGENTS—

*Zinc-free distilled water*—All distilled water used must have a zinc content of less than 2 p.p.m. Purify contaminated water by acidifying it with pure sulphuric acid and re-distilling it in an all-glass still.

*Sodium acetate solution,* 0·5 M—Dissolve 68 g of the trihydrate in distilled water and dilute to 1 litre. Extract this solution with 0·01 per cent. dithizone solution until all the heavy metals have been extracted and then wash it with carbon tetrachloride until the bottom layer is colourless. Finally, filter the solution into a suitable storage bottle.

*Sodium thiosulphate solution,* 50 *per cent.*—Dissolve 50 g of the analytical-reagent grade salt, $Na_2S_2O_3.5H_2O$, in distilled water and dilute to 100 ml. Free the solution from heavy metals as described for sodium acetate.

*Bromocresol green indicator solution*—Dissolve 0·1 g of indicator in 2·9 ml of 0·05 *N* sodium hydroxide and 5 ml of ethanol and then dilute to 250 ml with 20 per cent. aqueous ethanol.

*Dithizone in carbon tetrachloride,* 0·01 *per cent.*—Dissolve 0·5 g of diphenylthiocarbazone in redistilled carbon tetrachloride. This solution is unstable above 30° C and in oxidising atmospheres. It may be preserved for 10 days by covering it with aqueous sulphurous acid in amber bottles.

*Dithizone in carbon tetrachloride,* 0·002 *per cent.*—The stock solution of dithizone (0·01 per cent.) is diluted with redistilled carbon tetrachloride. Only sufficient solution for immediate use is prepared.

*Zinc solution, standard*—Dissolve 0·1 g of analytical-reagent grade zinc metal (30 mesh) in a slight excess (5 ml) of *N* hydrochloric acid and dilute to 1 litre with distilled water.

*Zinc solution, working standard*—Dilute 10 ml of standard zinc solution to 100 ml with distilled water. This solution should be prepared as required, as its zinc content slowly decreases on standing. Then 1 ml of solution contains 10 µg of zinc.

*Buffered sulphide solution*—Dissolve 60 g of disodium hydrogen phosphate, $Na_2HPO_4.12H_2O$, in the minimum amount of water, and remove the heavy metals by extraction with dithizone and carbon tetrachloride as described above for sodium acetate. Add 2·5 g of sodium carbonate and dilute the solution to 1 litre with distilled water. Adjust the pH accurately, preferably with the aid of a pH meter, to 11·0 by the careful addition of 5 *N* sodium hydroxide solution. Any heavy metals that have been introduced by the carbonate and hydroxide are extracted as described above for sodium acetate.

While the phosphate solution is being prepared, pass a rapid stream of hydrogen sulphide through a 0·25 *N* sodium hydroxide solution until the pH of the solution falls below 8·0. This takes about 15 minutes.

To prepare the buffered sulphide solution, mix 90 ml of the phosphate buffer with 10 ml of the sodium hydrosulphide solution shortly before the reagent is required.

### PREPARATION OF THE CALIBRATION CURVE FOR ZINC

Into six 250-ml separating funnels introduce 0, 0·5, 1·0, 1·5, 2·0 and 2·5 ml (equivalent to 0, 5, 10, 15, 20 and 25 µg of zinc) of freshly prepared working-standard zinc solution.

Then treat the contents of each funnel as follows. Add 1 drop of zinc-free 5 *N* hydrochloric acid and 5 ml of sodium acetate buffer solution. Rinse down the inside of the funnel so that the total volume of liquid is about 15 ml. Add 2 ml of 50 per cent. sodium thiosulphate solution, followed by exactly 50 ml of 0·002 per cent. dithizone solution. Shake the mixture vigorously for exactly 2 minutes and allow the layers to separate.

Run off most of the lower layer into a clean separating funnel and add to it 10 ml of buffered sulphide solution. Add approximately 15 ml of distilled water and shake the funnel vigorously for 30 seconds. Dry the stem with a piece of filter-paper and run a few millilitres of the lower carbon tetrachloride layer to waste. Run most of the remaining carbon tetrachloride layer through a dry filter-paper into a 1-cm optical cell. Measure the optical density at a wavelength of 535 m$\mu$ on a spectrophotometer. Alternatively, a Spekker absorptiometer may be used, with 1-cm cells and the appropriate green filter.

It is desirable, particularly under adverse climatic conditions, to take each sample through the entire procedure separately. In any event, the extraction of the zinc - dithizone complex and the determination of its optical density should be accomplished with as little delay as possible.

Subtract the optical density reading of the blank (zinc absent) from each of the other readings and construct a graph of optical density against $\mu$g of zinc.

DETERMINATION OF ZINC—

Introduce into a 250-ml separating funnel, 10 to 50 ml of a solution containing 5 to 25 $\mu$g of zinc. The solution may also contain iodide, sulphate and not more than 80 $\mu$g of cadmium. Add a few drops of bromocresol green indicator solution and sufficient 0·5 *M* sodium acetate solution to cause the indicator to turn blue. Add 2 ml of 50 per cent. sodium thiosulphate solution and proceed exactly as described for the preparation of the calibration curve. A blank containing no zinc should be put through the entire procedure with each batch of determinations.

Subtract the optical density reading of the blank from that of the unknown and read on the calibration graph the number of $\mu$g of zinc equivalent to this resultant figure. The amount of zinc so determined will have been present in the original solution.

NOTE—

If only traces of zinc are present in a large volume of solution, add a few drops of 30 per cent. hydrogen peroxide solution and evaporate it to a small volume. Transfer the residual solution to a separating funnel, using the minimum amount of water for rinsing. Add bromocresol green indicator solution together with sufficient 0·5 *M* sodium acetate solution to change the indicator colour to blue. Then add 2 ml of 50 per cent. sodium thiosulphate solution and complete the determination as described above.

Alternatively, after the evaporation, neutralise the residual solution with redistilled ammonium hydroxide, make it just acid to bromocresol green and add 5 ml of 0·5 *M* sodium acetate solution. Then complete the determination as described above.

EVALUATION OF THE ANALYTICAL METHOD FOR ZINC—

In order to test the value of the method, it was applied to various synthetic solutions similar in composition to those that the exploratory experiments had shown could be expected from columns of ion-exchange resins. A blank determination was conducted for each group of tests and the figures quoted in Tables II, III and IV have been corrected for the blank value, which was very small, being about 0·5 $\mu$g of zinc. In all the work described in this paper, borosilicate glassware was used and, by means of blank determinations, was proved to be free from significant amounts of soluble zinc before use.

The potassium iodide used in this work was found to be substantially free from zinc, but a neutral solution of the impure salt could be freed from both zinc and cadmium by extraction with dithizone in the manner described for the purification of 0·5 *M* sodium acetate solution. The cadmium and zinc used in the evaluation were derived from spectrographically pure metals.

The results in Tables II, III and IV show that the method is satisfactory for the analysis of the effluents from the ion-exchange columns and that it covers a wider range of cadmium to zinc ratios than are normally encountered. Cadmium in excess of 80 $\mu$g per determination consumed all the available dithizone, as is shown by the complete disappearance of the green colour of free dithizone. It is possible that the addition of more dithizone would permit larger amounts of cadmium to be tolerated but, for the purpose for which the method was used, this was not necessary. With regard to the interference of heavy metals other than cadmium, the use of sodium thiosulphate in the method can be relied on to prevent interference by any metals likely to be present in the cadmium metal, with which this work was primarily concerned. Copper, lead and iron, for example, will not interfere under the conditions of the method. However, if interference by some other metal is encountered, there would seem to be no serious difficulty in introducing a further suitable reagent to obviate the interference.

TABLE II

INFLUENCE OF POTASSIUM IODIDE ON THE EXTRACTION OF ZINC BY DITHIZONE

| | | | | | |
|---|---|---|---|---|---|
| Potassium iodide added, g .. | 0 | 0·001 | 0·010 | 0·100 | 1·00 |
| Zinc added, µg .. .. .. | 20 | 20 | 20 | 20 | 20 |
| Zinc found, µg .. .. .. | 21 | 20 | 20 | 21 | 22 |

TABLE III

RECOVERY OF ZINC AS THE COMPLEX WITH DITHIZONE IN THE PRESENCE OF CADMIUM

| | | | | | | |
|---|---|---|---|---|---|---|
| Cadmium added, µg .. .. | 0 | 0 | 0 | 40 | 40 | 80 |
| Zinc added, µg .. .. .. | 10 | 20 | 25 | 10 | 20 | 25 |
| Zinc found, µg .. .. .. | 10 | 20 | 25 | 10·5 | 20 | 25 |

TABLE IV

RECOVERY OF ZINC AS THE COMPLEX WITH DITHIZONE IN THE PRESENCE OF POTASSIUM IODIDE AND CADMIUM

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Cadmium present, µg .. | 0·1 | 0·1 | 0·3 | 1·2 | 10·0 | 40·0 | 80·0 |
| Zinc added, µg .. .. | 10·0 | 5·0 | 5·0 | 10·0 | 0·5 | 20·0 | 25·0 |
| Zinc found, µg .. .. | 10·2 | 5·2 | 5·0 | 10·2 | 0·5 | 20·0 | 25·1 |

1 g of potassium iodide was present in each test

DETERMINATION OF CADMIUM IN THE PRESENCE OF ZINC AND POTASSIUM IODIDE—

The cadmium in the effluents was determined by the following method.

Prepare a solution of cadmium sulphate from the analytical-reagent grade salt so that 1 ml of the solution contains 0·010 mg of cadmium. Into six separating funnels introduce, respectively, 0·0, 0·5, 1·0, 1·5, 2·0 and 2·5 ml of the cadmium solution. Treat the contents of each funnel in the following manner.

Rinse down the sides of the funnel with distilled water and dilute the contents to between 10 and 15 ml. Add 3 ml of 20 per cent. sodium potassium tartrate solution and then a volume of 2·5 *N* sodium hydroxide solution equal to the volume of liquid in the funnel. Add approximately 10 ml of 0·002 per cent. solution of dithizone in carbon tetrachloride, shake the funnel vigorously for 1 minute and allow the layers to separate completely; run off the lower layer into a clean separating funnel. Add a further 10 ml of carbon tetrachloride to the original funnel and re-extract. The second carbon tetrachloride layer should be almost colourless.

Combine the two carbon tetrachloride extracts and wash the mixture once with 0·5 *N* sodium hydroxide solution to remove traces of the zinc - dithizone complex. Allow the two phases to separate, dry the stem of the funnel with a strip of filter-paper and run the lower layer into a 25-ml calibrated flask. Wash the aqueous liquid in the funnel with 5 ml of carbon tetrachloride and add the washing to the flask. Dilute to 25 ml with carbon tetrachloride, mix the contents of the flask thoroughly and filter them through a dry "fast" filter-paper into an optical cell. Determine the optical density in a 1-cm cell on either a spectrophotometer at a wavelength of 520 mµ or on a Spekker absorptiometer, using a green filter.

Subtract the reading of the blank from the other readings and construct a calibration curve in the usual manner.

For the determination of cadmium in the effluent from an ion-exchange column, take sufficient effluent to contain 0·005 to 0·020 mg in not more than 5 ml (evaporate the sample if necessary), and proceed as described above. From the optical density of the solution containing the cadmium - dithizone complex, determine the cadmium content of the sample by means of the calibration curve.

It is essential that the above method be applied in a room in which there is no possibility of hydrogen sulphide being present in the air, as traces of sulphides decompose the cadmium - dithizone complex. It is advisable that the buffered sulphide solution used in the determination of zinc be kept and used in a separate room.

### REGENERATION OF THE RESIN—

The foregoing experiments showed that an effective method could be devised for the complete separation of large amounts of cadmium from zinc. However, it had been noted that the cadmium - iodide complex has a strong affinity for the resin and, before deciding on the final procedure for the separation, it was necessary to examine methods for regeneration of the resin.

Considerable difficulty was at first encountered. The usual procedure of treating the resin column with sodium hydroxide solution was not satisfactory, as the cadmium - iodide complex decomposes in strongly alkaline solutions with the liberation of insoluble cadmium hydroxide. This chokes the pores of the resin and prevents complete regeneration. Attempts to regenerate with sodium hydroxide solution batchwise allowed the removal of suspended cadmium hydroxide by decantation, but the clogging of the resin pores still caused poor regeneration. Sulphuric acid in concentrations between 5 and 50 per cent. failed to effect any significant regeneration.

A practicable method for laboratory use was eventually devised, based on the readiness with which the cadmium - iodide complex is oxidised. Treatment of the column with an acidified dilute hydrogen peroxide solution resulted in the rapid liberation of iodine and the formation of cadmium sulphate; both these substances can be removed from the column without difficulty. The iodine liberated in the pores of the resin imparts to it a deep violet colour. A solution of a sulphite may be used to remove the iodine rapidly, but if the resin is to be re-used for the determination of zinc, all the sulphite must be removed, as it interferes in the determination. The regeneration technique finally adopted is as follows.

Accumulate 200 to 400 g of used resin and wash it by decantation with water in a beaker. Agitate the resin gently with 5 per cent. solution of sulphuric acid containing approximately 0·3 per cent. of hydrogen peroxide, the volume of acid used being twice that of the resin. After a few minutes, wash the resin with water by decantation until cadmium cannot be detected in the washings by a spot test with 2-naphthoquinoline.

Transfer the resin to a large column and drain off the free liquid. Run 2·5 *N* sodium hydroxide solution through the column at the rate of about 10 ml per minute until the effluent does not liberate iodine on acidification with dilute sulphuric acid. Wash the column thoroughly with water and re-treat it with the sulphuric acid - hydrogen peroxide mixture and repeat the water and sodium hydroxide solution washes as before.

After the second sodium hydroxide treatment, wash the resin with two bed volumes of 5 per cent. sulphuric acid and finally with distilled water to remove excess of acid.

The resin is now ready, in the sulphate form, for use in the separation of zinc and cadmium.

The recommended method of regeneration is effective and is not excessively expensive for a determination of the type described. For larger-scale application of the separation, alternative cheaper regeneration methods would be required whereby the iodide might be recovered. Further work on this problem is envisaged.

### RECOMMENDED PROCEDURES FOR THE SEPARATION OF ZINC FROM CADMIUM—

Weigh sufficient sample to contain up to 0·75 mg of zinc and not more than 1 g of cadmium. Dissolve the sample by the careful addition of 50 per cent. v/v nitric acid. Add sufficient 50 per cent. v/v sulphuric acid to convert all the cadmium to cadmium sulphate and to leave an excess of approximately 1·5 g of sulphuric acid. For a 1-g sample of cadmium metal, approximately 2·5 ml of 50 per cent. v/v sulphuric acid will be required.

Evaporate the mixture to fuming and continue heating for 5 minutes, cool the residue and to it add 100 ml of zinc-free water and then cool the solution. Dissolve potassium iodide in the solution at the rate of 6 g of potassium iodide per gram of cadmium. Copper, if present, will liberate iodine and form a precipitate of cuprous iodide, but this does not interfere.

Prepare a column of De-Acidite FF ion-exchange resin in the sulphate form. The column should be approximately 15 mm in diameter and the volume of the resin bed 80 ml. The bed must be free from air bubbles. Flood the column with a solution containing 50 g per litre of potassium iodide and 25 g per litre of sulphuric acid.

Run the solution of the sample through the column at a flow-rate of 10 to 12 ml per minute (this flow-rate has been found convenient when handling a battery of columns). When all the solution has entered the column, wash the column with a solution containing 50 g per litre of potassium iodide at the same flow-rate. Collect the effluent in a 500-ml graduated cylinder and continue to wash the column until 300 ml of effluent have been collected.

Mix the effluent thoroughly and transfer 5 to 50 ml (according to the expected zinc content) to a separating funnel. Add a few drops of bromocresol green indicator solution and proceed with the colorimetric determination of zinc as described above.

## RESULTS

The method was first applied to the analysis of synthetic solutions approximating in composition to solutions that would be produced by the dissolution in sulphuric acid of cadmium metal of various degrees of purity.

Table V shows the results for solutions containing various amounts of zinc and cadmium. The effects of the presence of comparatively large amounts of copper and of variation of column diameter are shown to be negligible, but the use of a weaker potassium iodide wash solution leads to greater cadmium breakthrough.

TABLE V

DETERMINATION OF ZINC IN SYNTHETIC MIXTURES OF CADMIUM AND ZINC

| Zinc added, µg | Copper added, mg | Flow-rate, ml per minute | Column diameter, mm | Cadmium in effluent, µg | Zinc found, µg | Zinc recovery, µg |
|---|---|---|---|---|---|---|
| — | — | 14·0 | 16 | 78 | 84* | — |
| 1000 | — | 12·5 | 16 | 12 | 1104 | 1020 |
| 500 | — | 12·0 | 16 | 12 | 600 | 516 |
| 500 | 3 | 10·0 | 16 | —† | 576 | 492 |
| 500 | 10 | 12·5 | 16 | —† | 585 | 501 |
| 500 | — | 6·5 | 30‡ | 30 | 585 | 501 |
| 1000 | — | 12·0 | 16 | 120§ | 1104 | 1020 |

Basal solution—1 g of cadmium (as $3CdSO_4.8H_2O$, AnalaR), 6 g of potassium iodide, 1 g of sulphuric acid, 100 ml of water

Volume of effluent collected for analysis, 300 ml

* Mean of three determinations.

† The cadmium in the effluent was not determinable owing to the presence of copper. The zinc determination was unaffected.

‡ Weight of resin was 40 g as in other experiments; approximate bed volume, 80 ml.

§ 20 g per litre potassium iodide solution used for washing instead of 50 g per litre solution.

Table VI shows the results found when the method is applied to samples of cadmium metal and to freshly precipitated cadmium sulphide. In all instances a satisfactory recovery of zinc is indicated.

The results indicate that zinc can be determined in cadmium metal at a concentration as low as 0·005 per cent. of zinc to within a 4 per cent. error or, stated differently, 1 part of zinc may be separated and recovered from 20,000 parts of cadmium. There is some indication that this ratio might be greater.

The results in Table V show that there is a small amount of cadmium in the effluent, but this might be due to the arbitrary collection of a fixed volume of effluent or to a slight leakage of cadmium through the column. However, the other experiments indicate that all the zinc can be collected free from cadmium if required, but as this would involve either closer fractionation or closer control of the flow-rate, it is not justified when the final analytical method used is insensitive to small amounts of cadmium.

TABLE VI

DETERMINATION OF ZINC IN CADMIUM METAL AND IN CADMIUM SULPHIDE

| Zinc added, µg | Cadmium in effluent, µg | Total zinc in effluent, µg | Zinc recovery, µg |
|---|---|---|---|
| — | 12 | 240 | —* |
| 500 | 12 | 750 | 510* |
| — | 12 | 30 | —† |
| 100 | 12 | 126 | 96† |
| 100 | 12 | 96 | 96‡ |
| 50 | 12 | 51 | 51‡ |

Volume of effluent collected for analysis, 300 ml
Flow-rate through column, 11 ml per minute
Diameter of column, 16 mm
Wash solution, 50 g per litre potassium iodide
Weight of cadmium taken in each instance, 1·000 g

* Cadmium metal prepared by the authors.
† Solution prepared from freshly precipitated cadmium sulphide.
‡ Spectrographically pure zinc-free cadmium metal (Johnson Matthey).

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# The Potentiometric Reduction of Uranyl Chloride Solutions

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The optimum conditions for the potentiometric reduction of uranyl chloride solutions have been studied. The results showed that uranium could be accurately determined potentiometrically by direct reduction with chromous chloride solution to the quadrivalent state. The titration could be performed at room temperature, but equilibria were attained more rapidly and the inflections indicating complete reduction became steeper at higher temperatures. The presence of hydrochloric acid had a similar effect and the fall of potential near the equivalence point was found to increase with the acidity and to reach a maximum in 8 *M* hydrochloric acid.

Titrations were performed at room temperature in presence of 8 *M* hydrochloric acid and complexing acids. Equilibria were attained instantaneously and the inflections were sharper and steeper; tartaric acid had the maximum effect. The addition of potassium chloride was found to be more effective and improved the titration curves even when 0·1 *M* hydrochloric acid was used at room temperature; increase of temperature or acidity improved the results considerably.

Most determinations of uranium depend on the potentiometric titration of reduced uranium solutions with strong oxidising agents, such as potassium permanganate or ceric sulphate. However, the literature on the reduction of sexavalent uranium contains many contradictory statements on the extent to which the reduction proceeds, especially when metallic reductors are used. Attention was therefore directed to the use of strong reducing agents, such as titanous or chromous salts, for direct titration.

According to Kolthoff and Tomiček,[1] uranyl salts can be directly reduced by titanous chloride to the quadrivalent state. The results were better when highly acidic solutions at 55° to 60° C were used. Steur[2] found that solutions of uranyl salts in strong hydrochloric acid could be completely reduced by titanous chloride at 60° C in the presence of tartrate. Flatt and Sommer[3] determined uranyl compounds by their potentiometric reduction to the quadrivalent state with chromous salts. Titrations were performed in hot 2 to 6 *N* hydrochloric acid and in 1 to 6 *N* sulphuric acid.

A perusal of the literature, even that of recent date, on the potentiometric reduction of uranium compounds shows that the subject needs further investigation. The optimum conditions for the reduction of uranyl chloride to the quadrivalent state by chromous salts in solutions containing hydrochloric acid are described in this paper. Various experimental conditions were used in a study of the factors affecting the procedure: these factors were the acidity of the solutions, their temperatures and the influence of complexing acids and neutral salts.

## METHOD

### REAGENTS—

*Chromous chloride solution*—The chromous chloride solution was prepared electrolytically and stored in the manner described by Flatt and Sommer.[4] AnalaR potassium dichromate was heated cautiously with concentrated hydrochloric acid and the mixture was boiled until the evolution of chlorine ceased. The chromic solution was then diluted with 0·5 *N* hydrochloric acid and transferred to the electrolytic cell. The anode compartment was made of thin porous material enclosing an anode element consisting of 4 carbon rods; the cathode was a cylindrical lead sheet covered with a thin layer of fine adherent lead dioxide prepared by Tafel's method.[5] The chromic solution was then reduced, a current density of 0·02 amp. per sq. cm of cathode being used. The electrolyte in the anode compartment was 2 *M* hydrochloric acid. The reduction usually required 8 to 10 hours and was complete when an aliquot of the reduced solution decolorised the theoretical volume of potassium permanganate solution.

*Standard uranyl chloride solutions*—These solutions were prepared either by dissolving pure uranyl chloride in distilled water or by converting recrystallised uranyl acetate to the chloride. The uranium content was determined as $U_3O_8$.

*Apparatus and procedures for titrations with chromous chloride*—The equipment and procedures used were, with some modifications, those described by Flatt and Sommer.[4] Five litres of about 0·1 *N* chromous chloride solution were prepared by siphoning a suitable volume of the blue chromous solution from the electrolytic cell in an atmosphere of carbon dioxide into a storage vessel containing oxygen-free distilled water. The solutions were thoroughly mixed by passing a stream of carbon dioxide through the liquid. The solution was kept in an atmosphere of hydrogen both before and during use. It was standardised against standard copper sulphate solution and the concentration did not alter during storage. After 90 days a 0·11275 *M* solution was found to be 0·11273 *M*.

The titrations were made in a 200-ml Pyrex-glass vessel fitted with a rubber stopper through which pass four glass tubes each having a ground-glass socket. Through each tube is fitted, by means of the ground-glass joint, one of the following four elements—

(*a*) The stirrer, which consists mainly of the two glass parts of a syringe and is moved by a d.c. motor to permit regular and easily controlled stirring.

(*b*) The indicator electrode, which is a platinum wire of diameter 0·3 mm and length 6 mm sealed into a narrow glass tube and fitting into the tube passing through the stopper in such a way that the larger tube forms an outer jacket; a gas inlet to a second narrow glass tube and an outlet from the outer jacket are fitted for the circulation of carbon dioxide.

(*c*) The salt bridge, which has a reservoir at the upper end of the limb dipping into the titration vessel to trap any bubbles of gas generated in experiments at high temperatures. The salt bridge is refilled before each experiment to minimise the diffusion of foreign ions into the potassium chloride solution.

(*d*) The tip of the burette, which is drawn down nearly to a capillary to minimise the formation of air bubbles or the outflow of the liquid owing to expansion when titrations are made at high temperatures, and also to restrict the delivery to small drops of about 0·02 ml.

The insertion of these elements through ground-glass joints facilitates their removal when required. A layer of mercury spread over the rubber stopper prevents ingress of atmospheric oxygen. The titration vessel is also provided with two extra tubes. One enters the vessel near the top and is placed at a suitable angle to take a thermometer if required; it is used for introducing solutions into the vessel. The other reaches to the bottom of the vessel and is closed by a tap; it is used for emptying the vessel without removing the rubber stopper. The carbon dioxide used was purified by passing it through leuco-indigo carmine and chromous sulphate solutions.

The potential difference between the indicator electrode and a saturated-calomel reference electrode connected through the salt bridge to the solution was measured directly on a sensitive potentiometer during the titration, sufficient time being allowed for constant conditions to be attained. Before the titration was started, purified carbon dioxide was bubbled through the solution and the issuing gases were tested for traces of oxygen by bubbling them through leuco-indigo carmine solution. The titration vessel was always kept in an adjustable constant-temperature bath.

The titrations were always made with 100 ml of hydrochloric acid solution containing 0·1572 g of uranyl chloride, *i.e.*, 0·1295 g of $U_3O_8$, and the acid concentration was varied between 0·1 *M* and 8 *M* hydrochloric acid; the temperature was varied between room temperature and 90° C. Experiments were also carried out in the presence of complexing acids, such as oxalic, tartaric or citric acid, and also in the presence of neutral salts, such as potassium chloride. To ensure an excess, the solutions were made about 0·1 *M* with respect to the reagents used.

## RESULTS AND DISCUSSION

The results are summarised in Table I and some examples are shown as curves I to VI in Figs. 1 and 2; they showed that uranium could be accurately determined by potentiometric titration with chromous chloride solution, when it was directly reduced to the quadrivalent state. The titration could be performed even in the cold, although then equilibria were attained but slowly and the curves were not sharp. The fall of potential near the end-point was always slow and small (curve I). Equilibria, however, were attained more quickly and the inflections indicating complete reduction became steeper with rise of temperature. As the temperature of solution increased, so the potential was attained more quickly and the fall of potential at the equivalence point was greater. The maximum change per 0·02 ml of titrant occurred when the titration was performed at 90° C (curve II).

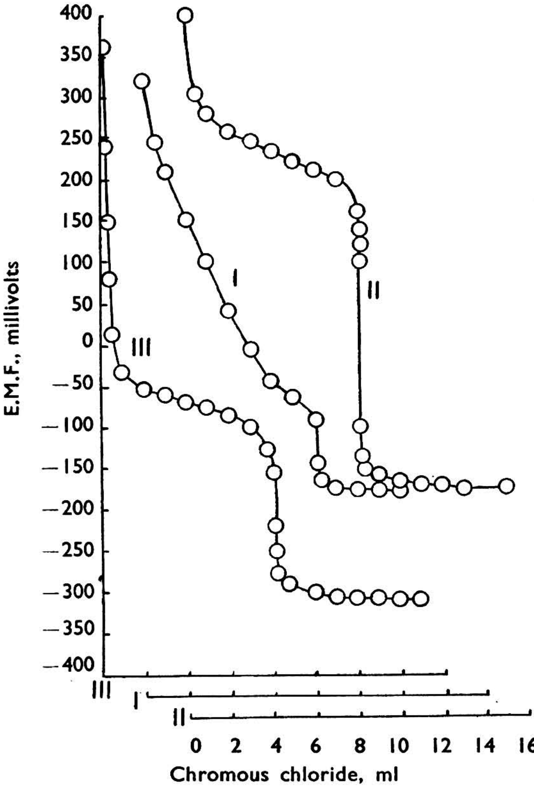

Fig. 1. Titration curves for sexavalent uranium in presence of: curve I, 8 *M* hydrochloric acid at room temperature; curve II, 8 *M* hydrochloric acid at 90° C; and curve III, 0·1 *M* hydrochloric acid at 90° C

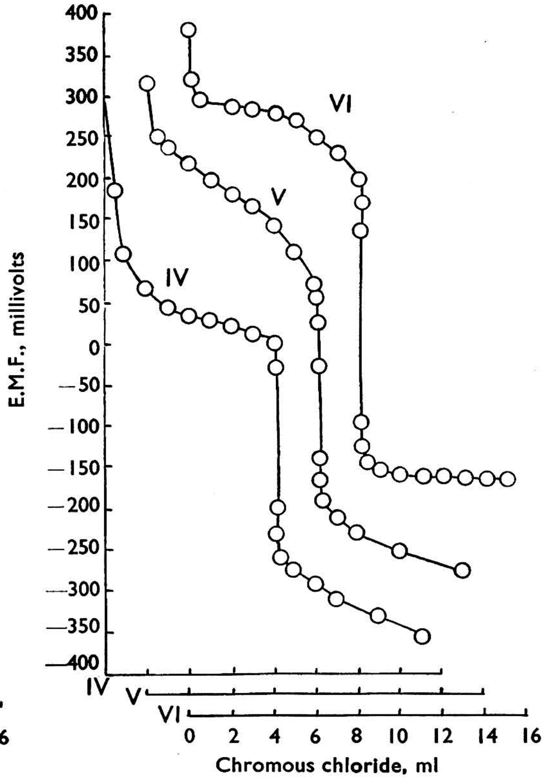

Fig. 2. Titration curves for sexavalent uranium at room temperature in presence of: curve IV, 8 *M* hydrochloric acid and 0·1 *M* tartaric acid; curve V, 8 *M* hydrochloric acid and 0·1 *M* oxalic acid; and curve VI, 8 *M* hydrochloric acid and 0·1 *M* potassium chloride

The presence of hydrochloric acid had a similar effect and the fall of potential near the equivalence point was found to increase with the acidity; it reached a maximum in 8 *M* hydrochloric acid but was much less in 0·1 *M* hydrochloric acid (curve III). It was always necessary to add a trace of a ferrous salt as a catalyst, otherwise the equilibria were attained but slowly. In all experiments the reduction proceeded quantitatively to completion, and the results were reproducible.

An investigation was made into the effect of adding a complexing acid or a neutral electrolyte, such as potassium chloride: for this, titrations were performed at room temperature (about 25° C) in the absence of ferrous iron, 8 *M* hydrochloric acid containing oxalic, citric or tartaric acid being used. Equilibria were attained instantaneously and the inflections were sharper and steeper than those produced under other conditions. Tartaric acid had the maximum effect (curve IV) and oxalic acid the least effect (curve V). The addition of potassium chloride was found to be more effective and the curves for titrations at room temperature, 8 *M* hydrochloric acid being used, were found to be the sharpest and steepest (curve VI). Even when 0·1 *M* hydrochloric acid was used, the addition of potassium chloride

TABLE I

THE POTENTIOMETRIC TITRATION OF URANYL CHLORIDE WITH CHROMOUS CHLORIDE

| Experimental conditions | Maximum $\Delta$E per 0·02 ml, mV per ml | $U_3O_8$ present, g per 100 ml | Error, % |
|---|---|---|---|
| 0·1 *M* hydrochloric acid at 90° C .. .. .. .. | 0·033 | 0·1290 | −0·39 |
| 2·0 *M* hydrochloric acid at 90° C .. .. .. .. | 0·056 | 0·1292 | −0·22 |
| 4·0 *M* hydrochloric acid at 90° C .. .. .. .. | 0·110 | 0·1291 | −0·3 |
| 6·0 *M* hydrochloric acid at 90° C .. .. .. .. | 0·143 | 0·1292 | −0·22 |
| 8·0 *M* hydrochloric acid at 90° C .. .. .. .. | 0·200 | 0·1293 | −0·15 |
| 8·0 *M* hydrochloric acid at 80° C .. .. .. .. | 0·140 | 0·1292 | −0·22 |
| 8·0 *M* hydrochloric acid at 70° C .. .. .. .. | 0·120 | 0·1291 | −0·3 |
| 8·0 *M* hydrochloric acid at 60° C .. .. .. .. | 0·115 | 0·1290 | −0·39 |
| 8·0 *M* hydrochloric acid at room temperature .. .. | 0·022 | 0·1288 | −0·54 |
| 8·0 *M* hydrochloric acid + 0·1 *M* oxalic acid at room temperature .. .. .. .. .. .. .. .. | 0·112 | 0·1292 | −0·22 |
| 8·0 *M* hydrochloric acid + 0·1 *M* citric acid at room temperature .. .. .. .. .. .. .. .. | 0·120 | 0·1291 | −0·3 |
| 8·0 *M* hydrochloric acid + 0·1 *M* tartaric acid at room temperature .. .. .. .. .. .. .. .. | 0·170 | 0·1292 | −0·22 |
| 8·0 *M* hydrochloric acid + 0·1 *M* potassium chloride at room temperature .. .. .. .. .. .. | 0·230 | 0·1293 | −0·15 |
| 0·1 *M* hydrochloric acid + 0·1 *M* KCl at room temperature | 0·049 | 0·1291 | −0·3 |

was found to improve the sharpness and steepness of the titration curves. Rise of temperature would further improve the results.

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# The Comparison of Inks and Writings by Paper Chromatography

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Methods are described for the examination by descending paper partition chromatography of fluid writing inks and dried ink deposits. These methods can provide convincing proof of the non-identity of two or more inks. Positive identification of dyestuffs present in small amounts of writing and stamp-pad inks is frequently possible by combining spectrophotometric analysis with paper chromatography.

INKS and ink writings can be characterised by both chemical and physical methods. In examinations of questioned documents, chemical tests are applied directly to the ink writing.[1,2,3,4,5,6] These methods have the disadvantages of seldom distinguishing between inks of the same type, of exposing the document to the risk of damage and of being difficult to demonstrate in court. Physical methods of examining ink and ink writings include visual, microscopic and photographic study with reflected, transmitted and oblique visible light; visual and photographic examination under reflected ultra-violet light or of the fluorescence induced by it[1,3,7]; infra-red photography[1,2,3,8,9,10]; infra-red photoscopy,[11] which is the process of converting the invisible infra-red image of an object into a visible image that can be seen instantly and continuously during the period when the object is subjected to infra-red radiation, this being accomplished by means of a specially designed apparatus utilising electronic valves; soft X-rays[12]; and reflection spectrophotometry.[13] These methods have the advantage that there is little risk of damaging the document, the results can often be demonstrated in court and differences between inks of the same type can sometimes be noted. The main disadvantages are that some of the techniques require expensive equipment that would not be available in many laboratories, and photographic methods of distinguishing colour differences, as well as reflection spectrophotometry, depend on the light-reflecting properties of the inks in the visible range; with many inks, especially blues, blacks and blue-blacks, nearly all the incident light is absorbed and the amount of light reflected in any narrow wavelength region is so small that direct comparison is difficult.

Owing to these difficulties, inherent in the application of these methods to forensic problems involving ink and ink writings, a new approach based on the separation and identification of individual constituents present in the inks was sought to provide more conclusive results. As most writing inks in common use contain synthetic dyestuffs, techniques for their separation, developed during the past 3 years, are described in this paper.

## EXPERIMENTAL

More than 60 samples of fountain-pen inks, 25 samples of ball-pen inks and 32 samples of stamp-pad inks in a wide range of colours and brands in common use were supplied by the courtesy of the manufacturers; 75 samples of dyestuffs used in ink formulation were donated by several dyestuff manufacturers and distributors. These were used as received without any attempt at purification.

### EXAMINATION OF FLUID INKS—

It appeared that ink dyestuffs might be separated from each other and from other ink components by paper partition chromatography. Other factors that influenced the selection of this technique for study were the small quantity of ink required, the visible record of the results, which permits photographic reproduction and presentation in court, and the relatively simple and inexpensive apparatus necessary.

Trial experiments were performed by the descending techniques successfully used in the separation of amino-acids[14] and sugars.[15] The following solvent systems were tested on several inks and dyestuffs—

(*i*) water;
(*ii*) *n*-butanol - ammonium hydroxide - water in the ratio of 4:1:5 parts by volume;
(*iii*) *n*-butanol - acetic acid - water in the ratio of 4:1:5 parts by volume;
(*iv*) *iso*butanol saturated with 1·25 *N* ammonium hydroxide;
(*v*) phenol - water in the ratio of 4:1 parts by weight;
(*vi*) phenol - water - acetic acid in the ratio of 75:24:1 parts by weight;
(*vii*) methanol - water - formic acid in the ratio of 95:48:3 parts by volume;
(*viii*) one per cent. ammonium hydroxide saturated with pentanol.

The separations of the ink dyestuffs were best with solvent systems (*iii*), (*v*) and (*vi*). Somerford,[16] who used an ascending technique, recommended that water should be used as the developing solvent, but the separations were found to be unsatisfactory with water and it caused excessive tailing of the spots. Brackett and Bradford,[17] who used the ascending method described by Tennent, Whitla and Florey,[18] found that the separation of ink dyestuffs with *iso*butanol and *n*-butanol, both saturated with 1·25 *N* ammonium hydroxide, was good.

## METHOD

### SOLVENTS—

Solvents should be of analytical-reagent grade, so that no further purification is necessary, with the exception of phenol. Solvent systems containing phenol develop a brown colour, but this reaction is retarded if the phenol is purified by vacuum distillation in the presence of 1 g of zinc dust per 500 g of phenol.

### APPARATUS—

Any chromatographic chamber capable of containing paper sheets 18 inches × 22 inches is suitable. The unit sold by the University Apparatus Company, Berkeley, California, has been used for large-scale work. For preliminary and exploratory work, 6-inch diameter glass cylinders, 18 inches high, with glass troughs on stainless-steel supports are quite satisfactory. Whatman No. 1 rectangular sheets of paper are used.

PROCEDURE—

Draw two parallel lines across the paper strip, one line three inches from the top and the other 1·5 inches from the top. Crease the paper strip along the upper line, so that it will hang evenly from the glass trough. The second line is the starting line of the chromatogram. Using a micropipette of capacity 0·005 ml, spot this volume of ink on the starting line. Larger volumes applied in one application cause diffused spots in the resulting chromatogram. The spots should be separated from each other by 2 to 3 cm. Their positions are conveniently marked on the starting line by pencil dots. It is advisable, when comparing two or more inks, to make chromatograms of each at several dilutions, *e.g.*, one spot of ink containing two applications of 0·005 ml, one spot containing one application of 0·005 ml of ink diluted 10-fold and a fourth spot of 0·005 ml of ink diluted 20-fold, on the same sheet of paper. Allow the spots to dry, then hang the paper sheet in the chamber and prepare chromatograms with solvents (*iii*), (*v*) or (*vi*). At approximately 25° C these solvents require 14 to 16 hours to descend 15 inches of paper. Remove the sheet from the chamber, mark the boundary of the solvent front and dry the paper in the fume hood at room temperature.

EXAMINATION OF INK FILMS AND RESIDUES—

The document examiner is frequently faced with the problem of determining whether two writings were made with similar or different inks. To make chromatograms of the ink in the writing line, it must be dissolved and transferred to the chromatographic paper. The procedure used should not mutilate the document to any appreciable extent. Distilled water has been found to be a good transfer solvent for fountain-pen inks and most stamp-pad inks. For the majority of ball-pen inks a satisfactory solvent mixture consisted of 2·6 parts of glycerol, 3·0 parts of acetone, 2·5 parts of acetic acid and 10 parts of water, all parts being by volume. This mixture will also dissolve stamp-pad inks that are insoluble in water. Certain ball-pen inks that were insoluble in the above solvent mixture were transferred successfully with 5 $N$ ammonium hydroxide. A few ball-pen inks were resistant to transfer. It is essential that the transfer solvent has a low evaporation rate, a surface tension sufficiently high to prevent diffusion into the paper and the ability to dissolve the ink.

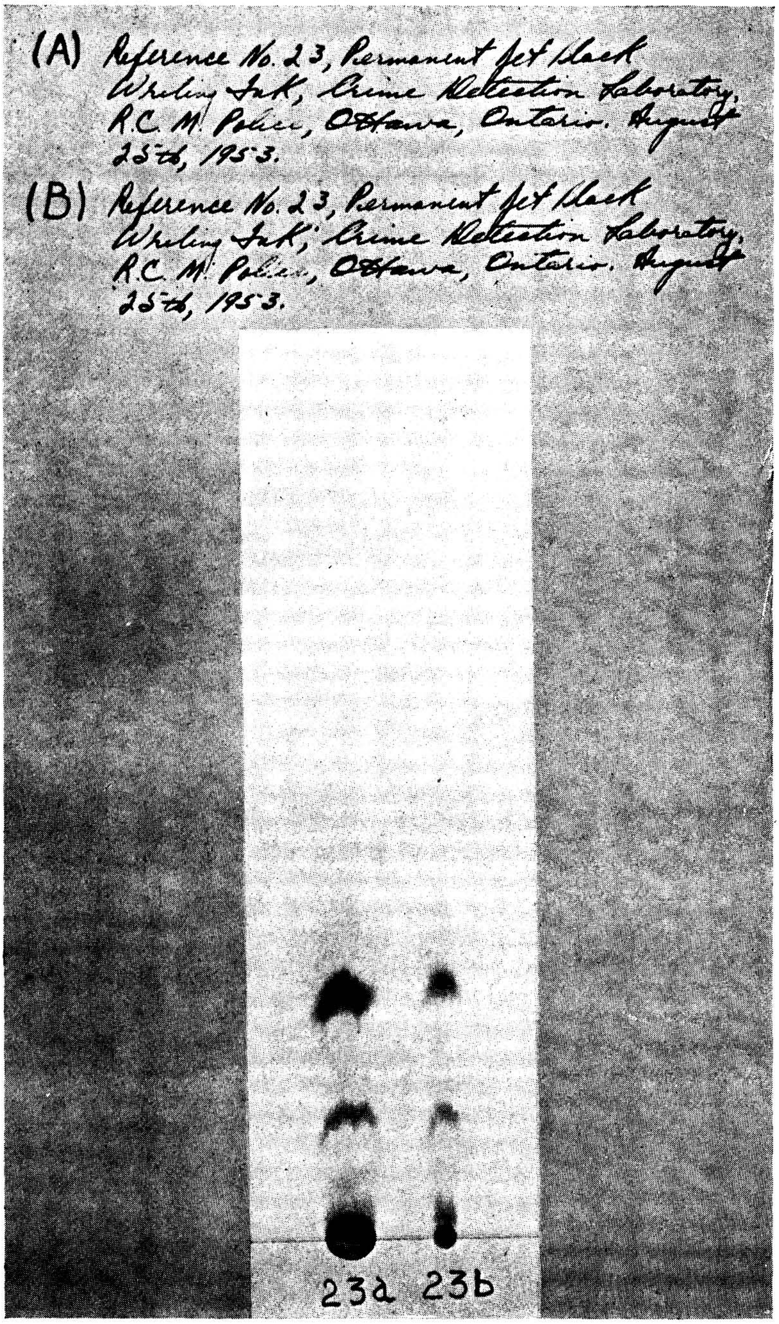
Somerford[16] used a pipette or small platinum wire loop, while Brackett and Bradford[17] used a glass rod with a fine point to apply and remove the transfer solvent from the ink line. The results were satisfactory when the following procedure was used. A tuberculin syringe of capacity 0·25 ml is fitted with a No. 26 needle. The tip of the needle is ground flat and the outside surface coated with a thin film of silicone grease to prevent creeping of the transfer solvent. The syringe is filled with transfer solvent and, while the ink stroke is being observed under a stereoscopic microscope or fingerprint magnifier, several drops of solvent are applied to the area under observation. The diameter of the drop should be less than the width of the ink stroke. After a short time, usually within two minutes, the drops of solvent are removed with a second syringe and transferred to the starting line of the chromatogram. The syringe collects the drops completely and cleanly. The area is then blotted and the procedure is repeated on successive portions of the writing until sufficient ink has been transferred to produce a chromatogram as described above. A blank area of the paper is treated in the same manner.

When this technique is used, there will be little indication that the writing has been altered. This is illustrated by Fig. 1. The chromatogram, 23*b*, was developed from ink transferred from the writing designated B. Writing A is the original writing before any ink was removed A chromatogram of the same ink taken from the bottle is shown in 23*a*.

Chromatograms of ink deposits on pen nibs and in ink wells can be produced in a similar manner. The dried deposit is dissolved in a few drops of the appropriate solvent and transferred to the starting line of the chromatogram with a syringe or micropipette.

IDENTIFICATION OF INK DYESTUFFS—

The ink dyestuffs can be qualitatively identified by comparing the ink chromatograms with chromatograms of known dyestuffs. More exact and positive identification can be made by extracting the dye from the chromatographic paper and examining it spectrophotometrically. The individual spots are cut from the air-dried chromatogram and fastened with a



(A) Reference No. 23, Permanent Jet Black
Writing Ink, Crime Detection Laboratory,
R.C.M. Police, Ottawa, Ontario. August
25th, 1953.

(B) Reference No. 23, Permanent Jet Black
Writing Ink, Crime Detection Laboratory,
R.C.M. Police, Ottawa, Ontario. August
25th, 1953.

Fig. 1. Chromatogram of ink writing, with water as transfer solvent and *n*-butanol - acetic acid - water as developing solvent

stainless-steel clip to the lower end of a condenser with a ground-glass joint. A small quantity of distilled water is placed in a test tube having a ground-glass joint to fit the condenser, to which it is then attached. The water is gently boiled and the condensed vapours flow over the paper, extracting the dye. Extraction is complete in two to five minutes. An unstained portion of the chromatogram is similarly extracted to produce the blank solution for use in the adjustment of the spectrophotometer. The absorption characteristics of the dye solutions are determined from 2400 A to 7500 A and the curves are compared with curves determined for known dyes treated in the same manner. The results are plotted so that log $A_S$ (log log $1/T_S$) values are ordinates and wavelength or log wavelength values are abscissae; this produces curves whose shapes are independent of the concentration of the absorbing material.[19] Hence if two dyes yield coincident curves, it is an indication of chemical identity. Further, if the curve of a standard is compared with the curve of a sample of unknown concentration plotted on the same graph, then the relative concentration of absorbing material in the latter can be readily determined from the vertical distance between the two curves along any one wavelength.

From the chromatographic and spectrophotometric results the identity of the dyestuff can be established. It should be noted that the dye solutions are available after the spectrophotometric examination for tests with various reagents if the identity of the dye is still in question, but this has seldom been necessary.

## RESULTS AND DISCUSSION

Many dyestuffs give several spots on the chromatogram, probably owing to impurities, unreacted constituents and isomeric forms of the dye in the commercial samples tested.[20] However, on most chromatograms one or two main spots appear; the position ($R_F$ value) and absorption properties of these spots are usually sufficient to characterise the dye. Dyes of similar structure, *e.g.*, C.I. 657 and 658; C.I. 677, 680 and 681; C.I. 706 and 707, produce nearly identical chromatograms. However, the structural differences are sufficient to alter the shade so that there is little probability of confusing such dyes with each other. For example, malachite green is made bluer by the introduction of a chlorine atom, when setoglaucine is formed. Similarly, the blue colour becomes more concentrated in the system magenta - methyl violet - crystal violet.

Fountain-pen and stamp-pad inks give chromatograms with well defined spots in contrast to chromatograms of ball-pen inks, which may be quite streaky. The dyestuffs present in an ink can usually be qualitatively identified by comparing the chromatogram of the ink with chromatograms of known dyes. It has been found, however, that the $R_F$ values of the dyes present in an ink are frequently greater than those given by the dyes separately. Further, many inks, especially the permanent blue and blue-blacks, contain two or more dyes each of which may give several spots, so that identification from a consideration of $R_F$ values alone is rather uncertain. By combining chromatographic separation with spectrophotometric examination, over thirty dyestuffs present in blue and blue-black inks have been identified. Green inks usually contain a green and a yellow dye; only three dyes of each colour have so far been identified in the green inks examined. No violet inks studied have contained more than one dyestuff. Red inks frequently contain two or more dyes and they are separated only with difficulty in the phenol and butanol solvents.

In many document problems that involve ink, it is only necessary to establish the degree of identity or non-identity of the questioned ink with one or more known inks; both questioned and known inks may be in the form of fluids or as residues on paper, pen nibs or in ink wells. For this purpose a comparison of the chromatograms of the questioned and known inks may be all that is necessary. The chromatograms should be prepared on the same paper and developed at the same time. They should be observed in visible light and under ultra-violet light. The chromatograms from inks containing different dyes have never been identical. However, two inks of different brands and containing the same dyes can give identical chromatograms. Hence different chromatograms indicate strongly that the inks under examination are dissimilar, but the reverse conclusion is not always true. When fluid inks are being examined and identification of the dye is not required, the circular-paper chromatographic technique described by Saifer and Oreskes[21] is convenient. But when the quantity of ink available for study is limited or if identification of the dyestuffs present is contemplated, the descending method recommended above is preferred. In laboratories where these methods are used, it is advisable to accumulate a reference file of ink and dye chromatograms and absorption curves of ink dyestuffs.

Experience has shown that ink chromatograms are reproducible over a considerable period of time. Chromatograms of inks two years old were identical with those produced from the fresh inks. Ink residues unprotected from dust and the laboratory atmosphere for a period of four months also gave chromatograms indistinguishable from those of the original fluid inks. Chromatograms of ink writings on untinted paper have never shown any spots not present in the chromatograms of the parent fluid inks. Sometimes the dye present in tinted paper may be transferred with the ink, therefore a chromatogram of a blank is always made at the same time. If insufficient ink is transferred from the writing line, some spots present on the chromatogram of the original ink may not appear in the chromatogram of the ink writing. This must be remembered when chromatograms of two or more writings are compared. Experiments are in progress to determine the effect of age of writing on the appearance of the chromatogram.

The forensic chemist will find the combination of paper chromatography and spectrophotometry useful for the separation, comparison and identification of colouring matter in a variety of materials other than inks. For example, in our laboratory these methods have been used in the examination of chips of stained varnish and for the comparison of a stain removed from the hood of an automobile with dyestuffs extracted from a piece of clothing. The limitations of these techniques for comparing and identifying dyes on fibres and colouring matter in various kinds of paint are being examined.

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# Notes

## STORAGE OF SEA-WATER SAMPLES FOR THE DETERMINATION OF SILICATE

THE study of the variation of the silicate content of ocean waters with depth, position and season is of growing importance to the oceanographer and marine biologist. Although it is desirable to examine water samples for silicate immediately after collection, this is not always possible. The samples must then be stored under conditions in which the contamination by extraneous silica is at a minimum. Atkins[1] has reported that the silicate content of a sea-water sample stored in a glass Winchester quart bottle increased at the rate of 0·2 mg per litre per month, and stated that the normal type of salinity bottles could be used without serious error for storage of samples for up to 5 days. Collins and Riffinburg[2] have studied the solubility of soda-glass bottles in distilled water. Noll, Maguire, Betz and Betz[3] after a comparison of containers made of soda and Pyrex glasses, hard rubber and metal lined with resin have recommended the use of the last type of container for the storage of boiler-feed samples. They also stated that acidification of the samples might reduce attack on glass vessels. Clelland, Cumming and Ritchie[4] have investigated the solubility of silica dusts in water at pH values from 2 to 11 and found a tenfold diminution of solubility between pH 8 and 4.

Armstrong[5] stored sea-water in the dark in polythene bottles and found rather erratic fluctuations in the silicate concentration over a storage period of 3 months; these ranged from a decrease of 18 per cent. with water containing 15 μg-atoms of silicon per litre, to an increase of 77 per cent. with 0·81 μg-atoms of silicon per litre.

### Experimental

The effect of pH on the rate of uptake of silicon by sea-water from soda-glass, Pyrex-glass and transparent-silica bottles has been investigated. Before use the bottles were cleaned in a (1 + 1) mixture of nitric and sulphuric acids, rinsed well with distilled water and allowed to drain for a short time. It was found that the rate of solution of silica was greatly increased if the bottles were allowed to become completely dry. Samples of filtered sea-water (chlorinity, 18·92 parts per thousand; silicon, 240 μg per litre), sterilised at 70° C, were stored in the dark in the bottles and examined weekly for silicate[6] over a period of 8 weeks. Similar tests were performed with the same bottles, sea-water that had been acidified with concentrated hydrochloric acid (0·05 ml per 100 ml) to give a pH of about 2·50 being used. The results of a typical series of tests are summarised in Table I. Both acidified and unacidified waters in all bottles showed fairly regular weekly increases in silicate content. The attack of unacidified sea-water on soda-glass was about thirteen times as rapid as on silica and about four times as rapid as on Pyrex glass, but the rate of attack varied from bottle to bottle and depended on the condition of its interior surface. Acidification markedly reduces the speed of solution of silica from both soda and Pyrex glasses, and bottles made of either material can be used for the storage of acidified samples (pH 2·5) for short periods.

TABLE I

STORAGE OF SEA-WATER SAMPLES IN SILICEOUS BOTTLES

| | Average increase in silicate concentration per week, μg of silicon per litre | | Rate of solution of surface of bottle, μg of silicon per sq. cm per week | |
|---|---|---|---|---|
| Bottle | pH 7·5 | pH 2·5 | pH 7·5 | pH 2·5 |
| Soda glass* (1) | 118 | 13 | 0·13 | 0·014 |
| Soda glass* (2) | 117 | 13 | 0·13 | 0·014 |
| Soda glass* (3) | 70 | 9·8 | 0·08 | 0·011 |
| Pyrex glass | 17 | 4·6 | 0·029 | 0·008 |
| Fused silica | 6·6 | 6·4 | 0·010 | 0·010 |

* 160-ml "salinity" bottles.

Polythene bottles present a considerable number of potential advantages over glass bottles for the collection of water samples at sea. It has been found that filtered and sterilised sea-waters enriched with silicate (above 15 mg of silicon per litre) showed very little change in silicate content (less than 2 per cent.) when stored for up to 3 months. Alternatively, similarly treated samples, containing concentrations of silicate normally encountered in sea-water (0·5 mg of silicon per litre) generally decreased considerably (up to 20 per cent.) in silicate concentration in the first week of storage and then remained fairly constant. This is in contradiction to the work of Armstrong,[5] who found that a general, but variable, increase in silicate content occurred with unfiltered samples during storage in polythene containers for 3 months; this was probably caused by solution of suspended siliceous matter.

Filtered sea-water samples acidified to pH 2·1 to 2·5 and stored in polythene bottles in the dark remained constant to within 1 per cent. for at least 5 weeks at silicate concentrations up to at least 15 mg of silicon per litre, as shown by the results in Table II.

TABLE II

VARIATION WITH TIME OF SAMPLES OF FILTERED ACIDIFIED SEA-WATER

| Storage time, weeks .. .. | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 11 |
|---|---|---|---|---|---|---|---|---|
| Sample A, mg of silicon per litre | 0·474 | 0·475 | 0·472 | 0·471 | 0·474 | 0·476 | — | — |
| Sample B, mg of silicon per litre | 2·58 | 2·60 | 2·60 | — | 2·58 | 2·55 | 2·55 | — |
| Sample C, mg of silicon per litre | 14·60 | — | 14·80 | — | — | — | — | 15·20 |

As suspended siliceous matter may dissolve gradually in sea-water, it is preferable to remove it by filtration before storage of the samples. The suitability of Whatman No. 2 and No. 41 filter-papers for this purpose has been tested and it has been found that provided the filter-paper is washed with sea-water before filtration of the main part of the solution uptake of silicon is inappreciable (less than 0·1 μg of silicon per 100 ml filtered). Acidified sea-water (pH 2·5) tends to pick up rather more silicon from the filter-paper (about 0·3 μg of silicon per 100 ml filtered).

For filtration at sea a serviceable apparatus consists of an 8·75-cm polythene funnel shaved down to fit tightly inside the rim of an inverted 8·75-cm polythene acid tray or petri dish, which serves as a lid. The latter has a 2-cm hole in its centre, which serves for the introduction of the sample. An 18-cm filter-paper slightly overlaps the edge of the funnel and acts as a seal when the lid is fitted. Even in very rough seas water does not slop out of the funnel provided that it is not more than three-quarters full. Both funnel and filtrate receiver are held in a rack by means of tool clips.

### PROCEDURE FOR USE AT SEA

Drain the sea-water sample (about 140 ml) from the water sampling bottle into a polythene bottle. Place a folded filter-paper (Whatman No. 2 or No. 41) in the polythene funnel and fit its lid. Pour about 20 ml of the sea-water sample into the funnel and allow it to run to waste. Filter the remainder of the sample into a polythene bottle containing 2 drops (0·05 ml) of concentrated hydrochloric acid. Stopper the bottle with a rubber bung or polythene cap and store it in the dark. The same filter-paper can be used for the filtration of several sea-water samples provided that it is rinsed with the next sample before use.

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DEPARTMENT OF OCEANOGRAPHY
THE UNIVERSITY
LIVERPOOL, 3

J. B. MULLIN
J. P. RILEY
*May 4th*, 1954

## AN IMPROVEMENT IN THE DETERMINATION OF URANIUM-235 BY RADIOACTIVATION

IN a recent paper[1] the determination of uranium-235 in mixtures of the naturally occurring uranium isotopes by radioactivation was described and it was indicated that the precision of the method (coefficient of variation of better than ±2 per cent.) could probably be improved by paying more careful attention to the weighing and counting procedures, particularly the latter. During the past 18 months the method has been successfully used as a check on mass spectrographic and spectrographic line-shift methods, but in order to be of greater value it was considered necessary to increase the precision of the activation method.

Weighings of the $U_3O_8$ irradiated and of the barium sulphate precipitates counted have been made to the nearest 0·05 mg so that with 100-mg quantities of each the weighing error is ±0·1 per cent. or less. There has been a significant increase in precision by paying stricter attention to the operation of the counting equipment and to the technique adopted for counting. The counting equipment used in this work consisted of: (*i*) a power unit (A.E.R.E. type No. 1082A), (*ii*) a scaling unit (A.E.R.E. type No. 1009A), (*iii*) a time assessory unit (A.E.R.E. type No. 1003B) and (*iv*) a probe unit (A.E.R.E. type No. 1014A). Time pulses were produced by a clock attached to the timing unit. The Geiger - Müller tube used (type GM4, 7 mg per sq. cm) was mounted in a lead castle with a Perspex lining.

Provided that the equipment was in good working order it should have been possible to verify that the variation between repeat counts, produced by a sensibly constant radioactive source, fell within the limits determined only by the statistical error due to the random nature of radioactive decay. The standard deviation, $\sigma$, of a number of counts, $N$, is given by $\sigma = \sqrt{N}$ and the coefficient of variation $= \pm\sigma \times 100/N$ per cent., from which it is seen that the precision, as measured by the coefficient of variation, is improved by increasing the number of counts recorded.

Check experiments showed that testing the reproducibility of the counting equipment by means of the "mains frequency test" control in the scaler was not always satisfactory, as variations of about 1 per cent. were observed between repeat counts and they were attributed to fluctuations in the mains frequency. When a pulse oscillator was used as a source of constant-spaced pulses, there was a big improvement in reproducibility provided that: (*i*) the timing unit had been switched on for several hours (preferably overnight), (*ii*) the clock had been wound and kept closed at least 30 minutes before counting and (*iii*) the Post Office register in the scaler was used and not the mechanical register in the timing unit, as the mechanical register was shown to be liable to jam or slip in an unpredictable manner, a trouble noted with more than one such register.

With these precautions, the equipment was capable of recording repeat counts from the pulse oscillator with a coefficient of variation of ±0·1 per cent. The probe unit was next adjusted by means of the pulse oscillator and a calibrated synchroscope so as to give a paralysis time of 300 ± 2 microseconds, which enabled accurate coincidence corrections to be made. Another effect noted in this and other work in which radioactive sources were counted was that when a counter had not been used for a few hours (the units being switched on during this period) the subsequent first count was nearly always low and its error was well outside the variations found in the following repeat counts. This effect, which has been noted by others and is probably due to the hysteresis effect of the Geiger tube,[2] was readily obviated by leaving the source in its counting position a few minutes before the counting was started.

A final check on the equipment was made with a source of $U_3O_8$ in equilibrium with $UX_1$ and counting it eight times for 40-minute periods. Each count consisted of approximately 242,000 pulses from the Geiger tube. The expected standard deviation, $\sigma_e$, on such a count when there were no sources of variation other than random decay was $\sigma_e = \sqrt{242{,}000}$, which gives a coefficient of variation of ±0·20 per cent. The observed coefficient of variation calculated from $\sigma_e = \sqrt{\Sigma d^2/n - 1}$ for the replicates was found to be ±0·24 per cent., which was taken as indicating that the equipment was working satisfactorily.

As conditions had been established for the counter, the precision of the activation method was re-determined. Seven accurately weighed portions of pure $U_3O_8$ of natural isotopic composition were irradiated and chemically processed as usual and counted under the conditions described above. The results were as follows—

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Observed count per 4 minutes .. .. | 51,477 | 52,660 | 53,968 | 49,739 | 51,408 | 50,524 | 50,652 |
| Corrected counts per minute per mg of $U_3O_8$ | 402·2 | 397·2 | 400·8 | 401·1 | 401·5 | 401·9 | 397·3 |

When the error was assumed to be due only to the random counting error and $\sigma_e = \sqrt{51{,}000}$, the expected coefficient of variation on a single result was ±0·44 per cent. The observed coefficient of variation on the replicates calculated as before was found to be ±0·53 per cent. This result indicated that most of the total error was due to the natural counting error and that the chemical procedure was still adequate at this level of precision. Therefore, if a sample together with a standard are each examined in triplicate and approximately 50,000 counts are recorded from each of the corresponding barium sulphate precipitates, then it can be calculated in conjunction with the above results that the mean result would have a coefficient of variation of ±0·44 per cent. (*i.e.*, a fivefold improvement over that previously reported).

In Table I are shown some typical results by the radioactivation method and by the mass spectrometer (Metropolitan-Vickers, type M.S.2) for some samples of uranium depleted in uranium-235. Both sets of results are normalised by taking the uranium-235 content of naturally occurring uranium as 0·715 per cent.,[3] and the samples and standard were only examined in duplicate by radioactivation. The precisions given for each set of results are for 3$\sigma$ limits.

TABLE I

DETERMINATION OF URANIUM-235 IN URANIUM

| Uranium-235 determined by | |
|---|---|
| Radioactivation, % | Mass spectrometer, % |
| 0·391 ± 0·006 | 0·388 ± 0·007 |
| 0·388 ± 0·006 | 0·392 ± 0·007 |
| 0·385 ± 0·006 | 0·390 ± 0·007 |
| 0·391 ± 0·006 | 0·390 ± 0·007 |
| 0·391 ± 0·006 | 0·391 ± 0·007 |
| 0·374 ± 0·006 | 0·373 ± 0·007 |
| 0·389 ± 0·008 | 0·395 ± 0·007 |
| 0·387 ± 0·008 | 0·388 ± 0·007 |
| 0·398 ± 0·008 | 0·396 ± 0·007 |

It is considered that a limit has now been reached for the precision of the method with the above equipment. To increase the precision further by a significant amount would necessitate the recording of a much larger number of counts, $10^6$ for a coefficient of variation of ±0·1 per cent., from each source. To achieve this with the equipment described above would require counting each barium sulphate source for approximately 2 hours, a period that is not only inconveniently long from a practical viewpoint, but would introduce an error owing to decay. As the decay of barium-140 is not simple, this isotope reaching transient equilibrium with lanthanum-140, a correction for decay would not be simple or accurate and would probably offset the increased precision due to the larger number of counts. To be able to record $10^6$ counts in 5 minutes could probably be managed by means of a suitable proportional or scintillation counter coupled to two scalers in series. By this or similar means the statistical counting error would be much reduced and it would then be necessary to check that the chemical part of the procedure was capable of giving a similar precision. Self-absorption and scattering errors of the precipitates counted might also be significant.[4] Consideration is also being given to the possibility of irradiating samples in an acid-soluble plastic tube, so that after irradiation the tube and its contents could then be dissolved, without any fear of loss in transferance.

The results of this investigation show, probably for the first time, that the precision of a radioactivation method of analysis can be made at least equal to the precision of many of the more established chemical and physical methods used for other purposes.

I thank Mr. C. H. Morris for assistance in checking the electronics of the equipment and the Managing Director, Department of Atomic Energy (I.G.), for permission to publish this Note.

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DEPARTMENT OF ATOMIC ENERGY (I.G.)
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A. P. SEYFANG

*July* 30*th*, 1954

# THE DETERMINATION OF GALLIUM

In a previous paper[1] procedures were described for the determination of gallium in alloys after its preliminary separation from chloride solutions with diethyl ether. For amounts of gallium less than 3·5 mg a volumetric method was used, with potassium ferrocyanide as the titrant and 3:3′-dimethylnaphthidine as the indicator, whereas larger amounts were determined gravimetrically after precipitation with camphoric acid from a formate buffer solution. During the development of volumetric procedures with ethylenediaminetetra-acetic acid for the determination of aluminium[2] and zirconium,[3] it was observed that gallium also formed a stable complex with EDTA, which could be used for the volumetric determination of the gallium. This observation has also been confirmed by the independent work of Patrovsky,[4] who reported a titration procedure in which the fluorescence of the complex formed by gallium with morin is used for the detection of the end-point.

Fritz and Fulda[5] have found that the coloured lakes formed by zirconium with certain organic dyes are valuable for the detection of the end-point in direct titrations of zirconium with EDTA. As gallium also forms coloured lakes[6] under suitable conditions, it was considered that the development of a titration procedure with a visual colour change at the end-point should be possible. A satisfactory procedure has been formulated and the coloured lake produced by gallium with gallocyanine is used to show the end-point of the titration. Moreover, this single procedure has proved suitable for the determination of gallium at all concentrations in the range given in the previous paper.[1] Preliminary experiments showed that the pH region for the formation of the gallium - gallocyanine lake was from about pH 1·5 and above, the gallium lake being blue in colour. However, on titration of gallium with EDTA, the discharge of the blue colour, which corresponds to the complete complexation of the gallium, could best be seen in solutions in the pH range from 2·5 to 3·0. It was therefore found desirable to buffer solutions in this range of pH before performing the titration. The final volume of the solution appeared to have no influence on the titration, but for convenience in this work all volumes were kept in the region of 50 to 100 ml.

## METHOD

### REAGENTS—

*Indicator solution*—Take 100 mg of powdered gallocyanine, mix it with 10 ml of glacial acetic acid and stir the mixture to dissolve as much of the solid as possible.

*Ethylenediaminetetra-acetic acid solution*—Prepare and standardise a 0·1 *M* solution of this reagent exactly as previously described.[2] Suitably dilute aliquots of the 0·1 *M* solution to give 0·02 *M* and 0·002 *M* solutions.

### PROCEDURE—

To the gallium solution contained in a 150-ml squat beaker, add 10 ml of glacial acetic acid followed by dropwise addition of ammonium hydroxide, sp.gr. 0·88, to adjust the pH of the solution to a value of 2·8 as shown by a direct-reading pH meter. Add 5 drops of the indicator solution and stir the mixture to assist the formation of the blue-coloured gallium lake. Then titrate the solution with a standard solution of ethylenediaminetetra-acetic acid, stirring it with a glass rod until the colour of the blue lake is completely discharged and the solution becomes red. Use the 0·02 *M* EDTA reagent for amounts of gallium greater than 2 mg and the 0·002 *M* reagent for smaller amounts of gallium.

Then 1 ml of 0·02 *M* EDTA solution ≡ 1·394 mg of gallium.

## RESULTS

The procedure was tested by applying it to aliquots of a standard gallium solution prepared by dissolving the Specpure metal in nitric acid and then diluting with water to give a solution containing 0·466 mg of gallium per ml. A weaker solution was prepared for testing the titration of the smaller amounts of gallium. The results in Table I show the good agreement between the amounts of gallium taken and those recovered.

Further experiments were performed to test that the titration procedure was also applicable after the extraction of gallium with diethyl ether under the experimental conditions previously reported.[1] Suitable aliquots of the standard gallium solution were taken, 40 ml of diluted sulphuric acid (1 + 1) were added to each aliquot and the solution was then evaporated to fumes of sulphur trioxide. After it had cooled, the solution was diluted with water to a volume of 100 ml, 20 g of ammonium chloride were added and the solution was stirred to dissolve the ammonium chloride.

TABLE I

RESULTS FOR THE TITRATION OF GALLIUM WITH EDTA

| Gallium taken, mg | Gallium found, mg | Error, % |
|---|---|---|
| 0·243 | 0·25 | +2·8 |
| 0·485 | 0·50 | +3·0 |
| 1·21 | 1·215 | +0·42 |
| 2·33 | 2·35 | +0·87 |
| 4·66 | 4·68 | +0·43 |
| 11·66 | 11·73 | +0·60 |
| 23·32 | 23·40 | +0·34 |
| 46·64 | 46·9 | +0·55 |

The solution was transferred to a 250-ml separating funnel and the gallium was extracted by shaking with three separate 50-ml portions of conditioned diethyl ether. The combined ether extracts were next washed with 10 ml of the 20 per cent. v/v sulphuric acid - 20 per cent. ammonium chloride solution used to condition the diethyl ether. The gallium was finally extracted from the ether into distilled water by shaking the ether extracts with three separate 50-ml portions of water. The aqueous extracts were combined together in a 250-ml squat beaker and boiled to remove ether and to reduce the volume to about 50 ml. The EDTA titration procedure was finally applied to determine the amount of gallium recovered. The good agreement between the amounts of gallium taken and the recovery is shown in Table II.

TABLE II

RECOVERY OF KNOWN AMOUNTS OF GALLIUM AFTER THE EXTRACTION WITH ETHER

| Gallium taken, mg | Gallium recovered, mg | Error, % |
|---|---|---|
| 2·33 | 2·40 | +3·0 |
| 4·66 | 4·74 | +1·7 |
| 11·66 | 11·75 | +0·77 |
| 23·32 | 23·39 | +0·30 |

The EDTA titration is much quicker than the gravimetric method in which camphoric acid is used. Moreover, this titration is suitable for the analysis of alloys after the separation of the gallium by ether extraction, as it allows the direct determination of amounts of gallium from 0·25 mg to at least 50 mg.

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G. W. C. MILNER
*August 3rd*, 1954

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# Book Reviews

TRAITÉ DE MICRO-ANALYSE MINÉRALE. QUALITATIVE ET QUANTITATIVE. Volume I. By C. DUVAL. Pp. 552. Paris: Presses Scientifiques Internationales. 1954.

Inorganic microchemistry can be regarded as being at least half a century old, and a journal devoted solely to microchemistry has appeared for more than half of that time. The literature of microchemistry is, however, much more widely scattered than the latter fact would suggest, and numerous contributions to it appear in all the journals dealing with analytical chemistry. Apart from this, isolated papers of microchemical interest may be found, almost by chance, in practically any scientific journal. There is therefore every justification for attempting to present a compendium of all inorganic micro-analytical procedures, although the task is indeed a formidable one. For such a labour, Professor Duval, with his wide experience and his numerous contacts, possesses the necessary qualifications.

When it is realised that the present volume is the first of four, the magnitude of the task becomes really apparent. And it requires very little examination of this volume to show that the complete work will form a notable contribution, not only to microchemical literature, but to the reference literature of analytical chemistry as a whole.

In this volume the elements dealt with are hydrogen (with special sections for the isotopes, water, hydrogen peroxide and deuterium and tritium oxides), the alkali metals, beryllium, magnesium, the alkaline-earth metals (including radium), scandium, yttrium, the lanthanons (treated both as a group and individually), actinium and its isotope, mesothorium-II.

The mode of treatment may best be illustrated by outlining the more important information included under the element potassium. First are given certain physical constants—atomic number, atomic weight and electrode potential. The mode of natural occurrence, the general properties of the element and its ion, the forms in which it may require detection or determination, preparation of a reference solution, dissolution of the sample and separation from other elements are all described in some detail. Methods of detection include flame coloration, emission spectrum and its analytical application, crystal tests (with illustrations of the characteristic crystal forms used for identification), spot tests and chromatography. Quantitative methods are divided into gravimetry (six methods in detail, with variants, and thermolysis curves of the weighing forms; further methods noted), titrimetry (eight methods in detail), polarography (two methods), colorimetry (seven methods), spark and arc spectrography and radioactive determination. The chapter closes with a full bibliography.

It is too much to expect that a monumental work of this nature should be without flaw. Thus, to continue reference to potassium, the chromatographic separation is not the most recent that has been described in the literature. And the spectrographic and radioactive determinations are included under the heading of colorimetry rather than in a separate miscellaneous section. The reviewer would be the last person to suggest, however, that such things lessen seriously the intrinsic value of the work.

It is claimed that the work is critical, and that the methods recommended can be used with confidence. This in itself is a first essential. Apart from this, however, the inclusion of so much

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information of general analytical importance will make the work a valuable source-book, not only for the inorganic micro-analyst, or even for the microchemist, but for the whole body of analytical chemists. Professor Duval and his co-workers, whose help he acknowledges in the preface, are to be congratulated on rendering an outstanding service to their colleagues in the widest sense. It is to be hoped that there will be no great delay in the publication of the remaining three volumes.

CECIL L. WILSON.

PAPER CHROMATOGRAPHY. By Dr. F. CRAMER. Second Edition translated by L. RICHARDS. B.Sc. Pp. xii + 124. London: Macmillan & Co., Ltd.; New York: St. Martin's Press Inc, 1954. Price 25s.

This book is a practical manual of paper chromatography, but it deals also very briefly with paper electrophoresis and mentions other chromatographic and solvent-extraction techniques.

The theory of the method is dealt with so shortly that it would help only to the understanding of the meaning of $R_F$, and some questionable comments are made on the underlying physical chemistry, all, it must be conceded, derived from published work. There are few references to work published since 1951.

An adequate description of experimental technique is given. The difficult subject of quantitative methods is handled so summarily as to be of little value.

Many useful tables of $R^F$ values of different groups of substances are given and methods of showing the presence of the substances on paper are considered at the same time. A transparent chart is provided for ready estimation of $R_F$ values. The book can be recommended as a useful compilation of data.

A. J. P. MARTIN

# Publications Received

BRITISH PHARMACEUTICAL CODEX, 1954. Published by direction of the Council of the Pharmaceutical Society of Great Britain. Pp. xxxii + 1340. London: The Pharmaceutical Press. 1954. Price 63s.

LEHRBUCH DER PHYSIOLOGISCHEN CHEMIE. By S. EDLBACHER and F. LEUTHARDT. Eleventh Edition. Pp. xvi + 813. Berlin: Walter de Gruyter & Co. 1954. Price DM42.

CALENDAR OF THE PHARMACEUTICAL SOCIETY OF GREAT BRITAIN, 1954–55. Pp. vi + 306. London: The Pharmaceutical Press. 1954. Price 12s. 6d.

ORGANIC ANALYSIS. Volume II. Edited by J. MITCHELL, jun., I. M. KOLTHOFF, E. S. PROSKAUER and A. WEISSBERGER. Pp. viii + 372. New York and London: Interscience Publishers Inc. 1954. Price $8.50; 68s.

ELEMENTS OF FOOD ENGINEERING. Volume II. UNIT OPERATIONS, 1. By M. E. PARKER with the collaboration of E. H. HARVEY and the late E. S. STATELER. Pp. viii + 360. London: Chapman & Hall Ltd.; New York: Reinhold Publishing Corporation. 1954. Price 68s.

ELEMENTS OF FOOD ENGINEERING. Volume III. UNIT OPERATIONS, 2. By M. E. PARKER with the collaboration of E. H. HARVEY and the late E. S. STATELER. Pp. viii + 241. London: Chapman & Hall Ltd.; New York: Reinhold Publishing Corporation. 1954. Price 54s.

PROTECTION AGAINST RADIATIONS FROM RADIUM, COBALT-60 AND CESIUM-137. National Bureau of Standards Handbook 54. Pp. vi + 60. Washington, D.C.: U.S. Government Printing Office. 1954. Price 25 cents.

PERMISSIBLE DOSE FROM EXTERNAL SOURCES OF IONIZING RADIATION. RECOMMENDATIONS OF THE NATIONAL COMMITTEE ON RADIATION PROTECTION. National Bureau of Standards Handbook 59. Pp. viii + 79. Washington, D.C.: U.S. Government Printing Office. 1954. Price 30 cents.

PRECISION LABORATORY STANDARDS OF MASS AND LABORATORY WEIGHTS. By T. W. LASHOF and L. B. MACURDY. National Bureau of Standards Circular 547, Section 1. Pp. iv + 24. Washington, D.C.: U.S. Government Printing Office. 1954. Price 25 cents.

FROM CLASSICAL TO MODERN CHEMISTRY. SOME HISTORICAL SKETCHES. By A. J. BERRY, M.A. Pp. xii + 251. Cambridge University Press. 1954. Price 25s.

# Erratum

DECEMBER (1954) ISSUE, p. 731, 5th line of synopsis. *For* "0·005 p.p.m." *read* "0·05 p.p.m."

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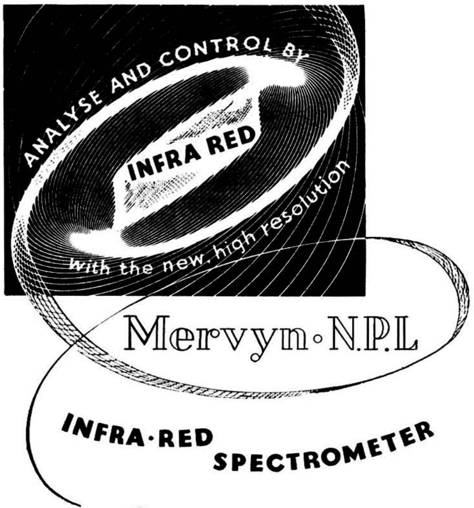

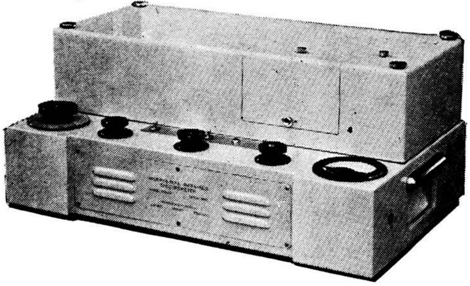

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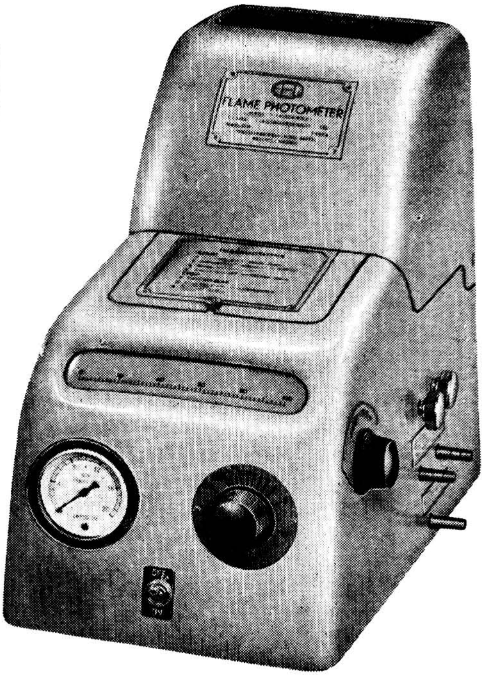
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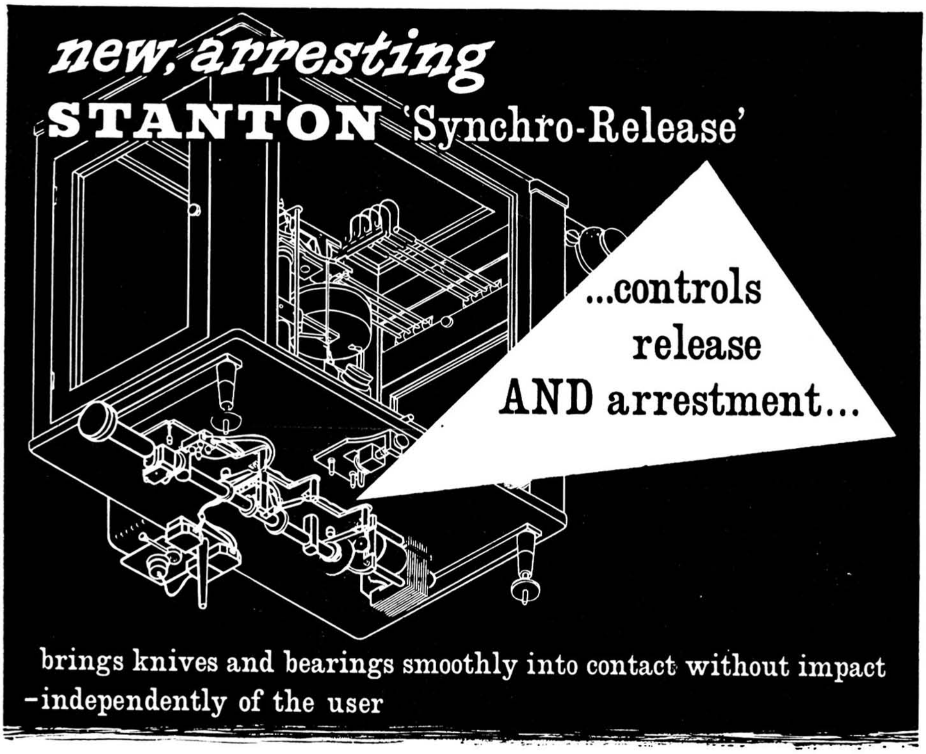
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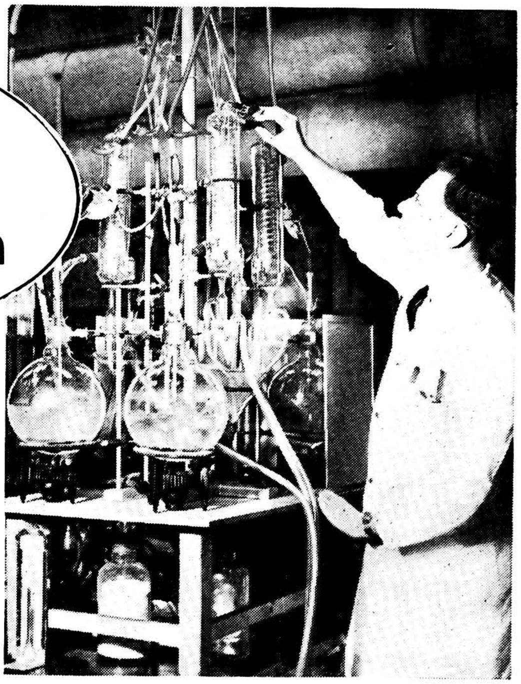

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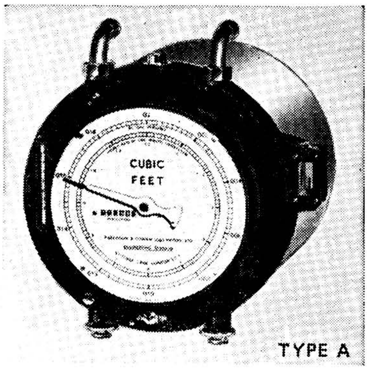
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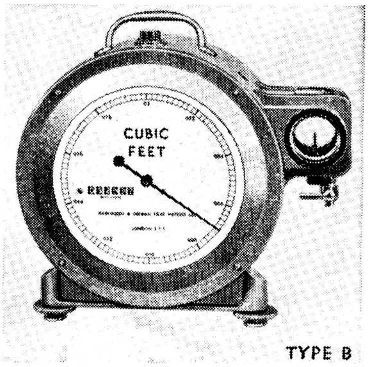
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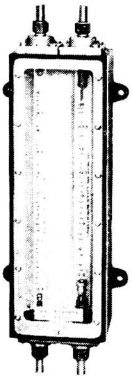
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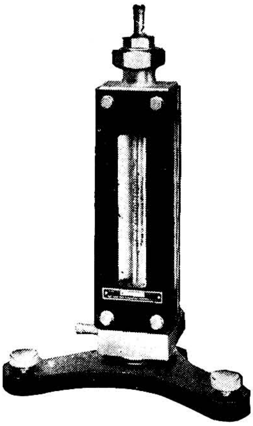
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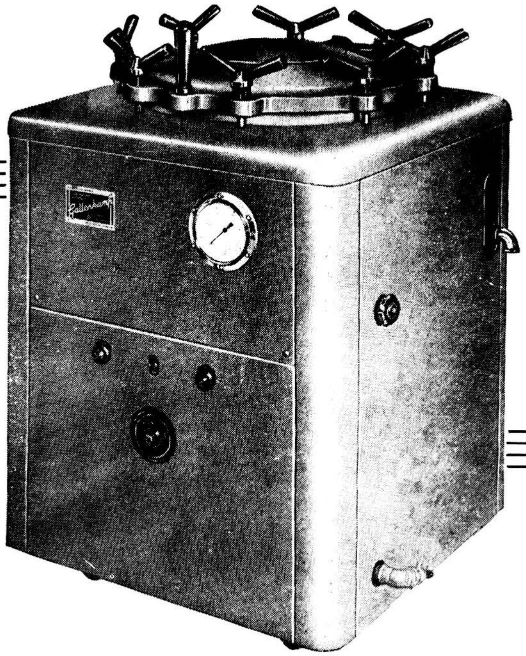

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