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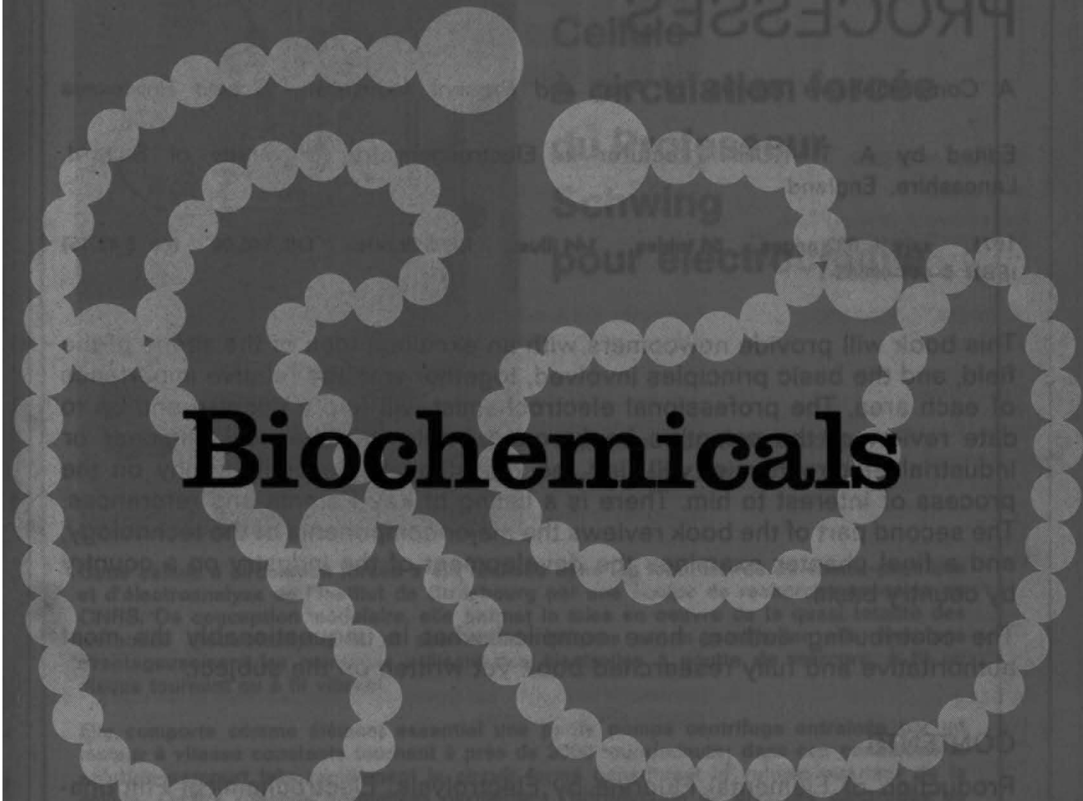

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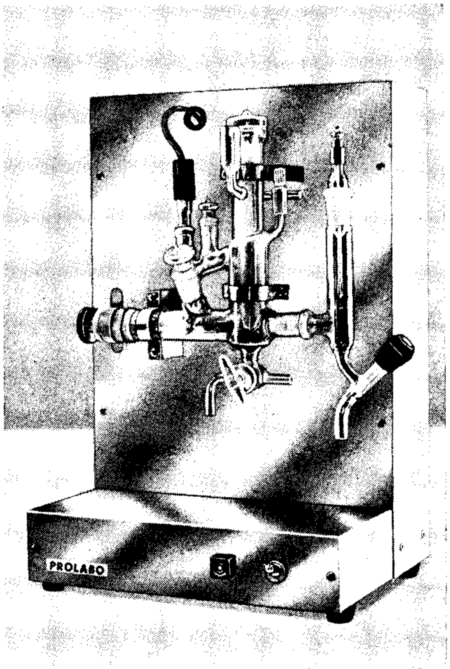
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FRITZ FEIGL

1891–1971

On January 23rd, 1971, Professor Dr. Fritz Feigl died in Rio de Janeiro after a long and severe illness. There passed away a great man, a man who established entirely new trends in analytical chemistry.

At the time of Feigl's 70th birthday, a great deal was written about his life and about his remarkable creation of spot-test analysis, which it is unnecessary to repeat here. At this time, it seems more appropriate to recall the great influence which Feigl exerted on the development of chemistry, and particularly of analytical chemistry.

In 1914, the year when Feigl decided to dedicate himself to the study of analytical chemistry, few of these developments were to be foreseen. What then remained to be done in the field of analytical chemistry? Qualitative analysis, in particular, seemed to be a closed field; few important developments or significant advances were to be expected. The prevalence of this attitude can be demonstrated by the fact that the classical textbook of F. P. Treadwell appeared in numerous, almost unaltered editions, during the period 1899 to 1943.

The schemes of classical qualitative analysis had, however, serious disadvantages. Many of the reactions used for detection were rather insensitive and the general technique of analysis required much time and material; the detection of anions was an unreliable and cumbersome process. Feigl attempted to lessen these disadvantages by the introduction of new methodology. He showed that when the detection reactions were carried out on single drops of test solution with single drops of reagent solutions, it became possible to achieve not only much more sensitive tests but also considerable savings of time and materials. These general ideas on technique were basically part of the general tradition of Austrian microchemistry as propounded by Emich. From these original spot tests on paper, a whole new system of qualitative analysis has been developed, much of the work involved in its creation being done by Feigl and his collaborators. His books about it, especially "*Qualitative Analyse mit Hilfe von Tüpfelreaktionen*", which appeared later in English as "*Spot Tests in Inorganic Analysis*", now in its 6th Edition, and the many editions of "*Spot Tests in Organic Analysis*", will long outlive their author.

At the time when this work was initiated, many obstacles remained to be overcome. Primarily, there were very few reagents available for the detection of ions by means of colour reactions. The first reagents such as alizarin and benzidine were only slightly selective so that prior separations were essential. In an attempt to solve this problem, Feigl re-examined some very old work which showed that the water of a solution diffuses on filter paper more rapidly than the solute, and that individual salts and ions show quite different rates of diffusion. Feigl proved that this pheno-

menon—the basis of modern paper chromatography—could be used to separate ions spatially on filter paper so that they could be detected in the presence of each other.

Yet even these techniques were not enough to solve all the problems which resulted from the application of spot methods to the detection of different ions. The reagents known at that time were completely inadequate; selective reagents were not available for a sufficient number of ions. Even at the present time, new directions in inorganic chemistry can be derived from the work of Werner who created the idea of "complex compounds". For Feigl, it was natural to seek new reagents among complex compounds, and this proved to be a very profitable approach. Inner complex compounds, a sub-group of Werner's complex compounds, were of particular interest. In these inner complex compounds, the metal ions are bound not only by their principal valences to an acidic group, but also by subsidiary bonds to other parts of the same molecule. The organic compounds which form inner complex salts show an affinity for particular metal ions; this affinity depends on the presence of a particular atomic grouping (now known as an analyticofunctional group) in the organic compound and it is common to all organic compounds with a particular grouping. The remaining portion of the organic molecule can be altered to cause variations in other properties of the compound, such as solubility in water and colour, and so it becomes possible to vary the sensitivity of a particular reagent. One of Feigl's major achievements was to realise that this variability could be used to produce a reagent with specially designed properties. Many of the dissertations produced under Feigl's guidance relate to this work, which appeared in the theoretical part of the earlier editions of his book, "*Qualitative Analyse mit Hilfe von Tüpfelreaktionen*". In 1948, Feigl wrote his classic book on this subject, "*The Chemistry of Specific, Selective and Sensitive Reactions*".

This concept of seeking and developing reagents according to analyticofunctional groupings has been found exceptionally fruitful, and is now a universally flourishing branch of analytical chemistry. It is this work, rather than spot tests—despite their great importance—which is the really notable result of Feigl's scientific activity. It was this work on the systematic development of new reagents with their finely tailored properties which made possible so many later developments in analytical chemistry.The great merits of Feigl's work in this field will remain, even when his special work on spot-test analysis has been superseded by the inevitable advance of chemistry, although there is no indication at the present time that spot tests will lose their value.

Fritz Feigl will be remembered as a great man who introduced many new concepts which have led to the rationalization of many fields of analytical chemistry. He could, with justice, have said: "*Exegi monumentum aere perennius*".

Vinzenz Anger (Vienna)

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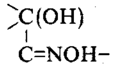
43 (mit G. SICHER UND O. SINGER) Über die kupfer-affine Wirksamkeit der Atomgruppe  $\begin{matrix} \rangle C(OH) \\ | \\ C{=}NOH- \end{matrix}$
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REVIEW

THE GAS CHROMATOGRAPH–MASS SPECTROMETER INTERFACE

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(Received 2nd October 1971)

The coupling of a gas chromatograph to a mass spectrometer provides the chemist with a valuable analytical technique. Complex mixtures can be separated by the gas chromatograph and each component individually analysed by the mass spectrometer, even when present in only small amounts.

There are, however, two major problems to be overcome in the combination of these two methods: first, the outlet of the gas chromatograph is normally at atmospheric pressure whereas a mass spectrometer operates under high vacuum conditions. Secondly, the chromatograph peak contains only a small concentration of the sample, being mainly carrier gas. An interface system is consequently required which will remove as much of the carrier gas as possible but will deliver the sample into the mass spectrometer without the mass spectrometer pressure rising above an acceptable level.

It is important to realize that mass spectrometers vary considerably in the pressure that they can accept without deleterious loss of spectral resolution. Factors such as the arrangement of the pumps, the pumping speeds and whether or not the ion source and analyser are differentially pumped, are important. Differential pumping in particular allows much higher ion-source pressures than could otherwise be tolerated.

The ideal properties for an interface are:

(*i*) all of the sample but none of the carrier gas enters the mass spectrometer;

(*ii*) the separation of the carrier gas is independent of its flow rate;

(*iii*) the separation of the carrier gas is independent of the operating temperature;

(*iv*) there is no discrimination against molecules with particular functional groups or molecular weight;

(*v*) no chemical change in the sample is caused by the interface;

(*vi*) the range of sample sizes leaving the chromatograph can be handled by the interface;

(*vii*) any carrier gas can be used;

(*viii*) no peak broadening results from the interface;

(*ix*) the interface has no memory effects;

(*x*) the interface system does not require separate pumping or heating.

The success of an interface in delivering all the sample into the mass spectrometer is given by the yield, Y (sometimes called the efficiency), which has been defined by Grayson and Wolf[1] as the percentage of the sample leaving the gas chromatograph which reaches the mass spectrometer. The enrichment factor, N, is defined as the ratio of sample concentration in the carrier gas entering the mass spectrometer to that leaving the gas chromatograph.

Three main types of interface system have so far been reported: the molecular jet, effusion types through various kinds of sinter, and diffusion types through semi-permeable membranes. The different systems and their various advantages and disadvantages are discussed below.

THE MOLECULAR JET

This interface is unique in that no physical barrier, through which either the sample or the carrier gas preferentially passes, is involved. The effluent from the gas chromatograph passes through a jet into an evacuated chamber (Fig. 1). Since the hydrogen or helium carrier gas molecules have a lower momentum and a higher diffusivity they tend to be removed, at right angles to the gas stream, to a much greater extent than the sample molecules. The enrichment process may be repeated before the gas enters the mass spectrometer.

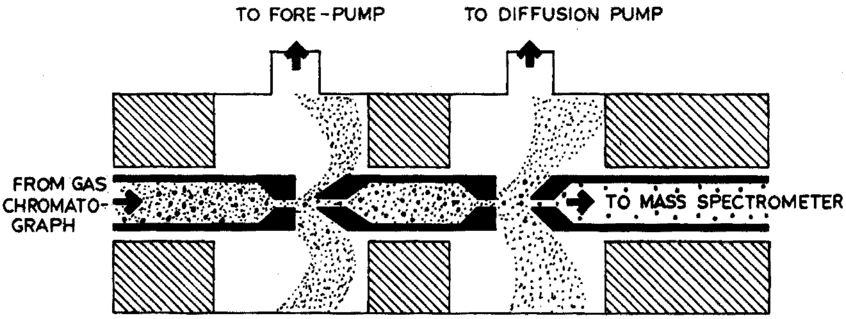

Fig. 1. The molecular jet interface.

This interface was developed by Ryhage[2] and Stenhagen[3] based on the isotope jet separator described by Becker[4]. Later Ryhage[5] published further details of its construction and performance. The first stage is maintained at a pressure of about 130 N m^{-2} (*ca.* 1 torr) by a fore-pump and the second stage at about 0.1 N m^{-2} (*ca.* 10^{-4} torr) by a diffusion pump. The orifices have diameters of 0.1–0.3 mm; the gaps between the orifices are 0.15 mm in the first stage and 0.5 mm in the second stage. The orifices and gap of the second stage are larger than those of the first, in order to maintain viscous flow conditions under the much reduced pressure and so prevent peak broadening. The dimensions of the orifices, the gaps between them and their accurate optical alignment have been found to be highly critical in obtaining the best performance from the interface, so that it is difficult to fabricate in the laboratory.

Using the two-stage design at 450° K and with a helium carrier gas flow of 500 nm^3 sec^{-1}, Ryhage[5] obtained a yield of 70% and an enrichment factor of 80 for methyl palmitate (m.w. 270) and a yield of 65% and an enrichment factor of 86 for tetramethylpyrazine (m.w. 136). Very few other yields and enrichment factors have been reported for this interface. Results with samples of low molecular weight would be particularly interesting, as they might be expected to give low yields. The yield was found to increase with increased carrier gas flow rate when the single-stage design was used but reached a maximum at a flow rate of 500 $nm^3 sec^{-1}$ with the two-stage design. The temperature of the interface was not found to be important[6] provided that it was above the boiling point of the sample passing through, otherwise low yields were caused by condensation.

The single-stage design is most suitable for use with the low carrier gas flow rates from capillary columns where the two-stage design would give very low yields. The higher flow rates from packed columns make the two-stage design essential in preventing too much carrier gas reaching the mass spectrometer, unless the latter is differentially pumped.

The performance of the molecular jet interface can be summarized as follows:

(*i*) it is capable of giving good yields and enrichments;

(*ii*) the performance varies with carrier gas flow rate though a wide range of flow rates may be used;

(*iii*) a wide range of operating temperatures may be used;

(*iv*) there is no discrimination against molecules with particular functional groups but its performance with low-molecular-weight samples requires investigation;

(*v*) catalytic degradation of samples on the hot metal surface is possible but the high gas flow rates through the interface make this unlikely;

(*vi*) a wide range of sample sizes may be used, though very small samples (*ca.* 10 ng) may give low yields due to adsorption;

(*vii*) only hydrogen or helium can be used as carrier gases;

(*viii*) there is a negligible time lag through the interface;

(*ix*) no memory effects have been reported;

(*x*) separate heating and pumping of the interface are required.

The interface is compact and robust. The jets may clog up, but the interface is easy to clean. Its critical dimensions make it impracticable to fabricate in the laboratory but commercial versions have proved satisfactory for many applications.

EFFUSION SYSTEMS

Various interface designs have been based on the preferential effusion of a low-molecular-weight carrier gas through a porous material leaving the enriched sample gas to flow into the mass spectrometer. Normally the gas leaving the chromatograph passes through an entrance constriction before reaching the interface. The constriction is designed to reduce the pressure so that molecular flow conditions exist through the pores of the interface. Molecular flow occurs when the mean free path of the gas molecules is some ten times greater at least than the pore diameter. Under these conditions the rate of gas flow, F, through the porous material is given by[7]:

$$F = \frac{\bar{v}A}{4kT}(P_1 - P_2) \qquad (1)$$

where $\bar{v}$ is the mean velocity of the gas molecules, A is the surface area, k is Boltzmann's constant, T is the absolute temperature, and P_1 and P_2 are the partial pressures on the high and low pressure sides of the porous barrier, respectively. Since the mean velocity is inversely proportional to the square root of the molecular weight, M, and since each gas will effuse independently, the ratio of flow rates is given by:

$$\frac{F_s}{F_c} = \left(\frac{M_c}{M_s}\right)^{\frac{1}{2}} \frac{P_{s1} - P_{s2}}{P_{c1} - P_{c2}}$$

where the subscripts s and c denote the sample and carrier gas, respectively. For the special case where P_1 is much greater than P_2, the equation reduces to:

$$\frac{F_s}{F_c} = \left(\frac{M_c}{M_s}\right)^{\frac{1}{2}} \frac{P_{s1}}{P_{c1}} \tag{2}$$

This equation shows that the light carrier gas will be preferentially lost through the porous barrier, leaving the remaining gas enriched in the heavier sample.

All the interfaces of this type have the inevitable disadvantage that some of the sample will be lost, particularly with low-molecular-weight compounds. The poor performance of effusion interfaces for samples of low molecular weight is illustrated in Fig. 2 which shows a plot of enrichment against molecular weight for a wide range of samples with a porous silver membrane interface[8]. The area of the porous barrier is important, since it must be sufficiently large for good enrichment to occur but not so large that poor yields will result.

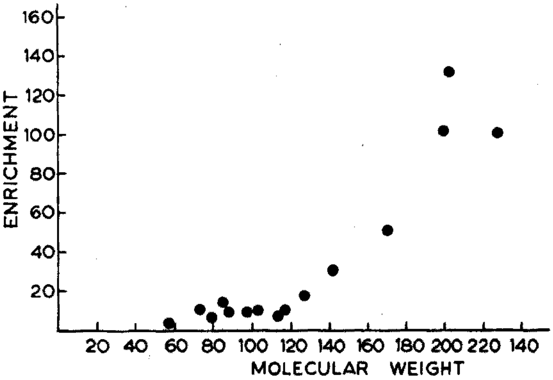

Fig. 2. Enrichment *versus* molecular weight by using a porous silver membrane interface. (Adapted from ref. 8).

Interfaces based on six types of porous material have been reported: glass, ceramic, stainless steel, nickel, silver and Teflon. These are discussed below. In addition, a variable slit device has been reported by Brunnée *et al.*[9] in which effusion occurs at the variable slit between two sharp edges of about 2 cm diameter. The slit width can be varied between 0 and 100 μm to accommodate flow rates from 17 to 1667 nm^3 sec^{-1}. The yield was found to vary with flow rate and with the slit width. Cholesterol (m.w. 386) gave a yield of 32% with a flow rate of 500 nm^3 sec^{-1}.

Porous glass and ceramic

An interface system based on a tube of fritted glass housed in an evacuated chamber was first reported by Biemann and Watson[10]. An improved design was reported by them in 1965[11]. The effluent from the gas chromatograph passes through an entrance constriction into the tube where the carrier gas is preferentially removed. The remaining gas, enriched in the sample and at a much lower pressure, passes out through an exit constriction into the mass spectrometer. This constriction curtails the flow of gas into the mass spectrometer. In later designs[1,12] this exit constriction is replaced by a needle valve. As an alternative to the tube designs used by the above and by Markey[13], Morin[14] uses an entirely different design where the chromatograph effluent flows into a chamber formed by a "sandwich" of two discs of fritted glass 1.3 mm apart, and evacuated from the outside. The enriched gas passes out through an exit tube into the mass spectrometer. Gold diaphragms, with a small central hole and housed in the inlet and exit tubes, perform the same functions as the constrictions previously described.

Markey *et al.*[15] have used a 1-cm length of porous ceramic tubing replacing a longer length of fritted glass tubing, and suggest that a more uniform and compact interface is obtained.

Operating temperatures of up to 625°K have been used with glass frit interfaces though Grayson and Wolf[1] found that increased yields of some 15–20% could be obtained by reducing the temperature from 573°K to 348°K. As in the case of the molecular jet interface, it is important that the operating temperature is above the sample boiling point to prevent condensation losses. Grayson and Wolf[1] obtained a significant increase in enrichment, though little change in the yield, by increasing the flow rate from 85 to 250 $nm^3\ sec^{-1}$. Ten Noever de Brauw and Brunnée[12] found that increasing the flow rate further ceased to affect the enrichment. The expected poor performance of effusion interface systems with low-molecular-weight samples was found for the glass frit by Grayson and Wolf[1], who obtained a yield of 15% and an enrichment of 3 for ethane (m.w. 30), but a yield of 52% and an enrichment of 10 for isononane (m.w. 128) under the same conditions. This effect was also reported by ten Noever de Brauw and Brunnée[12].

The performance of the glass frit interface can be summarized as follows:

(*i*) good yields and enrichments can be obtained;

(*ii*) the performance is independent of carrier gas flow rates above 250 $nm^3\ sec^{-1}$;

(*iii*) a wide range of operating temperatures may be used;

(*iv*) adsorption of polar compounds has been reported by MacLeod and Nagy[16], though a silanization procedure they used appeared to prevent this;

(*v*) the performance is poor with samples of low molecular weight;

(*vi*) a wide range of sample sizes can be handled;

(*vii*) only hydrogen or helium can be used as carrier gases;

(*viii*) no peak broadening or memory effects have been reported;

(*ix*) separate pumping and heating of the interface is required;

(*x*) the glass frit is fragile.

Porous nickel and porous stainless steel

An interface based on a tube of silanized porous stainless steel, similar in design to the fritted glass tube of Biemann and Watson[10] has been reported by Krueger and McCloskey[17]. With a helium carrier gas flow rate of 580 $nm^3\ sec^{-1}$ at an operating temperature of 523°K, a yield of 40% and an enrichment of 108 were obtained for cholestane (m.w. 372).

An interface with two discs of porous stainless steel in a design similar to that of Morin[14] has been reported by Yamauchi and Kamijyo[18]. When discs of 0.4-μm pore diameter were used with a helium flow rate of 333 $nm^3\ sec^{-1}$ at room temperature, a yield of 35% and an enrichment of 200 were obtained for *n*-hexane (m.w. 86). Temperatures up to 508°K could be used, though sample decomposition was noted at the higher temperatures. An interface utilizing a single disc of 20-μm porous stainless steel, inserted in the leg of a "T" piece, has been reported by Copet and Evans[19]. This was used with a helium carrier gas flow rate of 420 nm^3 sec^{-1} at 500°K. A performance superior to that of the molecular jet interface is claimed.

An interface based on a tube of porous nickel has recently been reported[20]. The tube (0.2–0.3 μm pore diameter), which is fitted inside an evacuated sheath, has stainless steel capillary tubes welded to each end to effect suitable pressure reduction. Inside the porous tube there is a cylindrical rod, centred by means of rings at each end, which enables the dead space to be reduced and makes the gas circulate as close as possible to the porous wall. The use of a central rod has not been otherwise reported and its effect requires further investigation. The interface was used with a helium carrier gas flow of 472 nm^3 sec^{-1}, with operating temperatures up to 523°K. Enrichments of 7 for ethylene (m.w. 28), 12 for butadiene (m.w. 54) and 20 for toluene (m.w. 92), show the expected change with molecular weight for an effusion-based interface.

These porous metal interfaces appear to have a very similar performance to the fritted glass interfaces with the added advantage of robustness; however, little actual testing of their performance has as yet been reported.

Porous silver membranes

An interface based on effusion through a porous silver membrane was first reported by Cree[8]. The design is similar to those of Morin[14] and of Yamauchi and Kamijyo[18], consisting of a chamber formed by two discs of membrane, evacuated from the outside. The gas chromatograph effluent flows through the chamber where the carrier gas is preferentially removed and enriched in the sample, on into the mass spectrometer. The enrichments obtained varied from 2 or 3 at low masses to over 100 with samples of molecular weight above 200 (Fig. 2). Flow rates up to 670 nm^3 sec^{-1} and operating temperatures upto 723°K were used.

Blumer[21] reported a design where a small membrane was installed in the leg of a "T" junction. The chromatograph effluent passes over the membrane, where the carrier gas preferentially effuses into the evacuated leg, leaving the enriched sample to pass into the mass spectrometer. Enrichments between 4 and 24 and yields between 33 % and 59 % were obtained with samples of *n*-pentane (m.w. 72), *n*-decane (m.w. 142) and *n*-hexadecane (m.w. 226). Flow rates up to 300 nm^3 sec^{-1} and operating temperatures up to 523° K were used. The interface was tested with a wide range of samples, and no chemical change, resulting from catalysis by the membrane, was found.

Grayson and Wolf[22] reported the use of a porous silver membrane as the second stage with a silicone rubber membrane as the first stage, in order to maintain a suitably low pressure in the mass spectrometer while using a relatively large area of silicone rubber membrane. A flow rate of less than 67 nm^3 sec^{-1} reached the silver membrane, which gave enrichments of around 1.5 and yields around 50 %.

The silver membrane interface is simple to make, robust and easy to clean or replace and though its performance needs further investigation, it may well prove particularly useful as a second stage.

Teflon membrane tube

An effusion-based interface based on a Teflon tube has been reported by Lipsky *et al.*[23]. It consists of a coil of 2 m of Teflon housed in an evacuation chamber. Stainless steel tubes at each end effect the necessary pressure reduction. The temperature of the tube has to be maintained within the 540–600°K region with an optimum around 560°K; below this range no effusion occurs and above it pin-hole leaks have been found to develop[1].

Evans[24] claimed an enrichment of 100 for this interface but this does not appear to have been verified by experiment. In practice, Grayson and Wolf[1] obtained enrichments of up to 6 only with yields of 46–95%. They found that an increase in the carrier gas flow rate from 85 to 250 $nm^3\ sec^{-1}$ led to a slight increase in enrichment but a decreased yield. Higher flow rates than this led to excessive pressure in the mass spectrometer. Lipsky *et al.*[25] did use flow rates of 330–500 $nm^3\ sec^{-1}$, as the resultant pressure of 0.013 $N\ m^{-2}$ was acceptable in their mass spectrometer.

Arnold and Fales[26] have reported that Teflon tubing, used in gas chromatography, interacts with both polar and non-polar compounds causing considerable tailing of the peaks. The Teflon was also found to cause loss of basic amines at 573°K by reaction. These effects are in addition to the normal discrimination against low-molecular-weight samples which occurs with effusion interfaces.

The performance of this interface can be summarized as follows:

(*i*) good yields but poor enrichments are obtained;

(*ii*) flow rates above 250 $nm^3\ sec^{-1}$ may not be possible;

(*iii*) the operating temperature must be between 540 and 600°K;

(*iv*) discrimination against low-molecular-weight samples and certain functional groups occurs;

(*v*) only hydrogen and helium can be used as carrier gases.

(*vi*) there is a long lag time (20–30 sec) before the sample reaches the mass spectrometer, which may cause peak broadening;

(*vii*) separate pumping and heating of the interface are required;

(*viii*) the interface is robust and relatively simple to construct.

The many disadvantages and limitations of this interface have resulted in its being very rarely used.

DIFFUSION SYSTEMS WITH SEMI-PERMEABLE MEMBRANES

The composition of the effluent from a gas chromatograph can be changed by passing it against a semi-permeable membrane. If the permeability of the carrier gas differs from that of the sample gas, then the gas mixture emerging from the membrane will be enriched in whichever gas has the larger permeability. Passage through the membrane results from the gas molecules dissolving in the high-pressure side, diffusing through and finally volatilizing on the low-pressure side.

Two types of interface have been based on this principle. The first utilizes a silicone rubber membrane which is highly permeable to organic molecules but virtually impermeable to the permanent gases. The second involves a tube of a palladium–silver alloy which is permeable only to hydrogen.

Silicone rubber membrane

It has been shown by Lucero and Haley[27] that the rate of flow of gas, F, through a semi-permeable membrane is given for each species i, by:

$$F_i = P_{mi} A \Delta P_i / d \qquad (3)$$

where P_{mi} is the permeability coefficient, A is the surface area, and $\Delta P_i/d$ is the pressure gradient through the membrane.

The yield of sample, in this case the percentage which passes through the membrane, also depends on these factors since if passage through the membrane is slow, only a small amount of sample will get through during the residence time of the sample against the membrane. The enrichment depends only on the relative permeabilities of the sample and carrier gases provided that the pressure on the gas chromatograph side of the membrane is significantly greater than that on the mass spectrometer side.

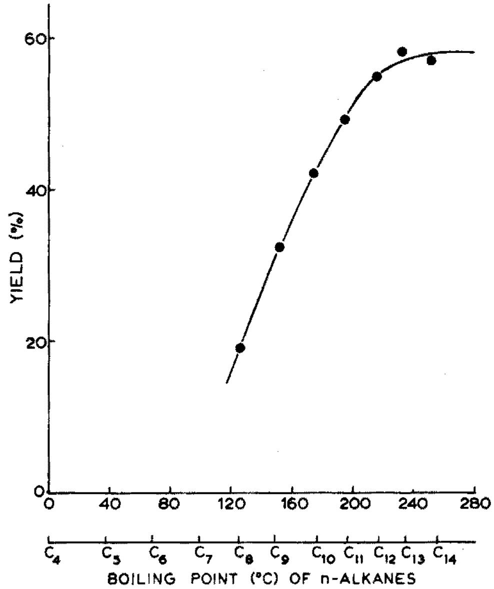

Fig. 3. Dependence of the yield through a silicone rubber membrane interface on the boiling point of the sample.

The dependence of yield on permeability can be seen indirectly from Fig. 3 which shows the results of Hawes *et al.*[28]. Using an interface of this type, temperature-programmed between 330 and 425°K, they found for a series of *n*-alkanes that as the boiling point increases through the series, the yield also increases to a maximum value. Clearly the permeability is increasing with the boiling point. This means that samples which are gaseous at ambient temperatures have too low a permeability to give a significant yield. This is a major limitation of this interface.

The second factor in eqn. (3), the area of the membrane, is important in the design of the interface. Increasing the area increases the yield of sample, but at the same time it allows more of the carrier gas to reach the spectrometer. Grayson and Wolf[22] overcame this problem by using a membrane of large surface area as the first stage, with a second stage of porous silver membrane to remove the excess carrier gas. A large surface area has the additional advantage of allowing a wide range of flow rates and sample sizes. If the area of membrane is small, it will be saturated by large samples. Watson[29] suggests that this will occur at sample flow rates above 100 μg sec^{-1} ($\simeq$0.1 nm^3 sec^{-1}) but does not specify an area of membrane.

The first design by Llewellyn and Littlejohn[30] had two stages each involving 500 μm^2 of membrane. Later designs used only one membrane; that of Hawes *et al.*[28] had only 15 μm^2 of membrane exposed, that of Grayson and Wolf[22] 150 μm^2, and that of Black *et al.*[31] 645 μm^2. The last two designs also involve porous silver membranes. In each case the chromatograph effluent is passed over the surface of the membrane. The portion which passes through goes into the mass spectrometer with the remainder going to the chromatograph detector. This obviates the need to obtain the chromatogram by splitting off part of the column effluent.

The operating temperature (°K) has been shown[27] to be inversely proportional to the logarithm of the enrichment. This was supported experimentally by Hawes *et al.*[28], who obtained a decreasing yield of dodecane as the operating temperature was increased. Grayson and Wolf[22] found that the helium transmission through the membrane increased with increased temperature. A low operating temperature is clearly advisable, provided that peak tailing does not result. Grayson and Wolf recommend an operating temperature some 50°K below the boiling point of the sample. Hawes *et al.* house the interface in the chromatograph oven.

The performance of this interface can be summarized as follows:

(*i*) high yields and very high enrichments have been claimed;

(*ii*) a wide range of carrier gas flow rates can be used;

(*iii*) the performance improves with decreasing temperature;

(*iv*) only organic samples which are liquid or solid at ambient temperature give good yields, but there is no discrimination against low-molecular-weight samples as such;

(*v*) there is no chemical effect on the sample;

(*vi*) large samples may saturate the membrane;

(*vii*) a wide range of carrier gases may be used, which is an important advantage over effusion-based interfaces;

(*viii*) peak broadening and memory effects may occur;

(*ix*) separate heating of the interface is recommended, though it may be situated in the chromatograph. Separate pumping is only necessary for two-stage designs.

Palladium–silver tube

An interface based on a palladium–silver tube was first proposed on a theoretical basis by Lucero and Haley[27] and developed by Simmonds *et al.*[32]. It utilizes the property of palladium foil, alloyed with 25% silver to give mechanical strength, and heated to 525°K, of being freely permeable to hydrogen and totally impermeable to all other molecules. If the chromatograph effluent, with hydrogen as the carrier gas, is passed through a sufficiently long tube of this alloy all the hydrogen will pass through the wall leaving the entire sample to pass into the mass spectrometer. This represents infinite enrichment and 100% yield.

Lucero and Haley[27] derived the following expression for the enrichment:

$$N = \left[1 - \frac{2LP_{\mathrm{mh}}(P_1^{\frac{1}{2}} - P_2^{\frac{1}{2}})}{F_1 \ln (r_0/r_i)}\right]^{-1} = \frac{1}{1-x} \tag{4}$$

where L is the tube length, r_0 and r_i are the external and internal radii of the tube, P_{mh} is the hydrogen permeability coefficient, P_1 and P_2 are the equilibrium hydrogen pressures at the gas chromatograph and mass spectrometer ends of the tube, respectively, and F_1 is the total gas flow rate into the tube.

From eqn. (4) one can see that the enrichment becomes infinite when x becomes equal to 1; thus by fixing the dimensions of the tube to accommodate the flow rate and permeability (this varies with temperature), infinite enrichment can be easily attained. Lucero and Haley[27] calculated that for a flow rate of 1670 nm^3 sec^{-1} at 525°K a tube 0.33 m long, 3.2 mm o.d. and 51 μm thick would give this result. Simmonds *et al.*[32] used a smaller tube than this but the maximum flow rate used in their work was only 83 nm^3 sec^{-1}. They heated the tube to the required temperature by simply passing a current along it.

The hydrogen passing through the tube is chemically removed by an external flow of air or oxygen. The chamber around the tube could be evacuated but this is less effective as the pressure gradient at the spectrometer end is likely to be quite small. It is also much easier to provide an air flow than a vacuum system. The use of oxygen rather than air, or an increase in the rate of flow, improves the efficiency of hydrogen removal, allowing operation at a lower temperature.

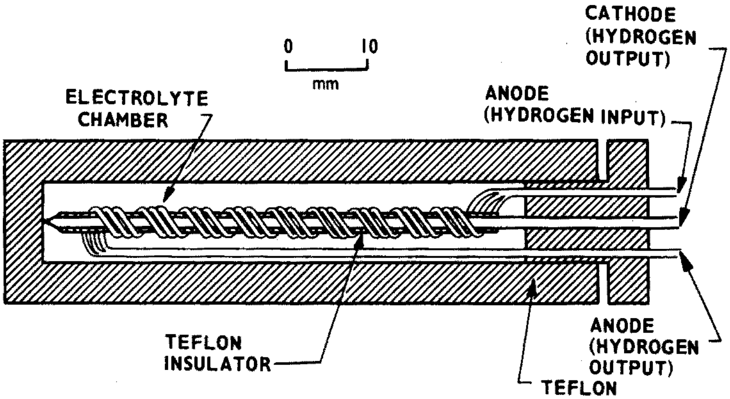

Fig. 4. Palladium–silver electrolytic interface. Reprinted from *J. Chromatogr. Sci.*, 8 (1970) 456 by courtesy of Preston Technical Abstracts Company.

In more recent work[33,34], oxidation is carried out electrolytically. The gas-chromatographic effluent flows into a palladium–silver tube which is now the anode of an electrolytic cell (Fig. 4). This is would helically round a second tube of the alloy which forms the cathode with Teflon spacers separating the two electrodes. The cell body is also made of Teflon, the electrolyte is fused potassium hydroxide–lithium hydroxide and the whole cell is operated at 475–515°K.

The operation of the cell is shown in Fig. 5. Hydrogen dissolves in the anode where it is oxidized to hydrogen ion which then diffuses through the anode to the electrolyte where it combines with a hydroxyl ion to give water. The reverse process occurs at the cathode; thus hydrogen is removed from the anode tube and regenerated at the cathode. It can then be recycled into the chromatograph.

A major advantage of this method of hydrogen removal is that the current flow in the cell drops when a sample compound is present in the hydrogen. The interface thus acts as its own gas chromatographic detector, obviating the need for part of the column effluent to be split off to a conventional gas chromatographic detector.

The major potential disadvantage of this interface is the possibility of catalytic hydrogenation of the sample. Simmonds *et al.*[32] investigated this for a number of types of compound and found that hydrogenation tended to be specific and essentially complete in compounds with conjugated unsaturation such as dienes, α,β-unsaturated aldehydes, ketones and nitriles, but otherwise did not occur at all. Certain compounds such as sulphur-containing gases and iodine compounds may cause temporary or permanent poisoning of the tube surface, allowing hydrogen to break through into the mass spectrometer.

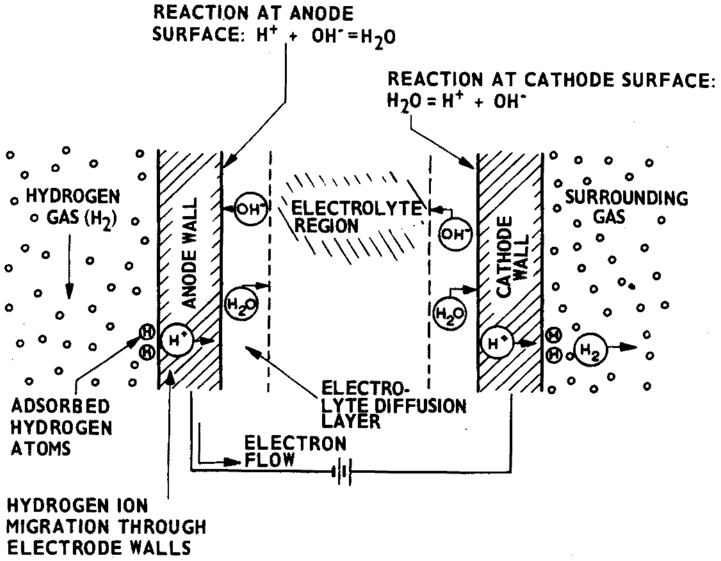

Fig. 5. Diffusion and electrolytic reactions in interface. Reprinted from ref. 34 by courtesy of Preston Technical Abstracts Company.

The performance of this interface can be summarized as follows:

(*i*) 100% yields and infinite enrichments can be achieved;

(*ii*) careful design will allow a wide range of hydrogen flow rates to be accommodated;

(*iii*) changing the external gas flow rate or using oxygen rather than air allows considerable variation in the operating temperature;

(*iv*) there is no discrimination against low-molecular-weight samples;

(*v*) certain samples may be hydrogenated by the interface, and certain others may poison it;

(*vi*) any sample size can be handled;

(*vii*) only hydrogen may be used as the carrier gas;

(*viii*) no peak broadening results from the interface and there are no memory effects;

(*ix*) separate pumping of the interface is unnecessary.

This interface is relatively simple and cheap to construct and may be ideal for many applications where the limitations of hydrogen as the carrier gas and the possibility of hydrogenation do not pose any problems. It is unique in being capable of giving 100% yields with samples of low molecular weight, and so may be particularly useful in analysis of the products from the pyrolysis of polymers.

CONCLUSIONS

It is clear from the previous discussion that there is no ideal interface for all applications. For a specific analytical problem one must consider the advantages and disadvantages of each and choose the most appropriate.

The molecular jet and glass frit interfaces are probably the most widely used in routine gas chromatograph–mass spectrometer applications as they were amongst the first to be developed. Porous metal interfaces are relatively new, and their performance has therefore not been extensively tested. The Teflon tube appears to have very little to commend it, and is not commonly used. All these interfaces are based on a molecular weight difference between the sample and the carrier gas. This can result in a significant portion of the sample being lost with the carrier gas, particularly if it has a low molecular weight. Further loss of sample occurs if some of the column effluent is split off before the interface to the chromatograph detector to give a chromatogram. As a further disadvantage all these interfaces require separate pumping and heating.

The silicone rubber membrane interface is based on the difference in permeability rather than in molecular weight between the sample and the carrier gas. This makes it the best system for separating a wide range of inorganic or low-boiling organic gases from organic samples of high boiling point ($>350^\circ$K).

The palladium–silver tube interface, in most cases, delivers the entire sample into the mass spectrometer whilst removing all the hydrogen carrier gas. It needs no external pumping and no oven and is relatively simple and cheap to construct. It is likely to be ideal for many purposes, particularly when samples of low molecular weight are involved, and could well become widely used in the future.

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SUMMARY

The performances of the various interface systems for combining a gas chromatograph with a mass spectrometer are reviewed.

RÉSUMÉ

On examine les possibilités de combinaison d'un chromatographe gazeux et d'un spectromètre de masse.

ZUSAMMENFASSUNG

Es wird eine Übersicht über die Leistungsfähigkeit der verschiedenen Interface-Systeme gegeben, die für den Anschluss eines Massenspektrometers an einen Gas-Chromatographen verwendet werden.

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DETERMINATION OF STABILITY CONSTANTS OF CHÈLATE COMPLEXES

PART I. THEORY

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The increasing use of chelating agents in analytical chemistry has created a demand for reliable values of equilibrium constants. Modern chelating agents often contain a large number of coordination centers, which means that, in addition to normal chelates, they may form also acid, basic and binuclear complexes. If an analytical chemist wants to select the optimal conditions and estimate the attainable accuracy in his analyses, he has to take the constants of all species into consideration.

The determination of these constants may at first sight seem a rather complicated problem. If we have an aqueous system where M is the metal ion and L a ligand, and disregard all complexes containing more than two of these components and more than two hydrogen or hydroxide ions, there still remain 15 species (if dimers are excluded): ML, MHL, MH_2L, MOHL, $M(OH)_2L$, M_2L, M_2HL, M_2H_2L, M_2OHL, $M_2(OH)_2L$, ML_2, MHL_2, MH_2L_2, $MOHL_2$, $M(OH)_2L_2$. Moreover, one must take into consideration the acidity constants of the many H_nL complexes—more than six dissociating protons in a chelating acid are not rare—and the often far from simple hydrolysis reactions of the metal ions. It is true that all of the species mentioned do not occur simultaneously, but, on the other hand, still other species may also be formed. Metal ions with a low coordination number may form trinuclear complexes, and if the coordination number of the central ion is high, complexes with more than two ligands can be formed. Consideration must also be paid to a possible dimerization (and even polymerization).

A superficial study of the literature may strengthen the impression of complexity. The mathematical and graphical methods which are employed utilize several concepts and parameters unfamiliar to analytical chemists. If many species are involved in the equilibria and the calculations are made by computers, the programs are mostly rather complicated. Very generalized programs are not simple to master as the generalization involves a great risk of making errors and greater difficulties in finding them. If the problems are solved in parts, the calculations will be simplified, but iterative procedures demand great care and with complicated systems it is difficult to estimate the weights of the various experimental data.

Most of the constants determined in recent decades were determined by means of pH measurements, whereas pM measurements were much less used. Protons are liberated when a metal ion replaces hydrogen ions in the ligand and the concentration of the ligand not bound to metal ions can be determined from the change in pH. The method gives good results for complexes of medium stability, but if very stable complexes are formed, the replacement of protons will be so complete that pH measurements cannot yield accurate values of stability constants. This fact and the neglect of existing species are mostly the reasons why various authors often report values that differ even in order of magnitude.

It is obvious that the problem of determining equilibrium constants in a system containing three components, M, L, and H (or OH) will be simplified, and more reliable results will be obtained, if the concentrations of not one, but two components are measured. Therefore, measurements of both pH and pM would seem advantageous.

Nowadays, there are plenty of ways of measuring pM values. Electrodes of the first, second and third order serve this purpose; also amalgam electrodes are often applicable. In recent times a large number of selective electrodes have become available: membrane electrodes, solid state electrodes, liquid state electrodes including ion-exchange electrodes and others. Besides, such electrodes can also be used for pL measurements. Finally, metal indicators permit very accurate pM determinations.

It may be objected that many of the techniques mentioned allow pM measurements only within a limited concentration range and within a certain pH range, or that they are rather sensitive to foreign ions. However, even if the possibilities of measuring pM values are restricted, just a few pM values in a limited range greatly facilitate the calculation of equilibrium constants. This is the case, for instance, if pM measurements are possible only in acidic solutions. When stability constants are determined, interfering ions can be avoided as a rule. Selective electrodes, although not yet ideal, work remarkably well in metal buffer solutions containing no interfering ions.

It is true that potentials indicate activities, not concentrations, which mainly interest the analyst. However, an activity correction can conveniently be included in the normal potential of a metal.

The authors believe it advantageous to determine the stability constants of chelate complexes in a way somewhat different from the ways commonly used in dealing with non-chelate complexes. The fact that the chelates mostly do not contain more than two metal atoms, ligands or dissociating protons (hydroxide ions) simplifies the calculations. Many concepts which are very useful in treating equilibria of non-chelate complexes—particularly when the number of ligands in a complex is high—are by no means indispensable when chelate equilibria are considered. Such concepts are formation functions, average ligand numbers, normalized curves and variables, F-functions, etc. (*cf.* the comprehensive monograph by Rossotti and Rossotti[1] or the book by Beck[2]). Our presentation lays particular emphasis on the requirements of analytical chemists. This is the reason why we have consistently operated with the concept of the α coefficient, *i.e.* the side-reaction coefficient, a concept widely used for analytical purposes and thus familiar to most analytical chemists. Actually, no other concept or parameter is used in the computations of stability constants presented below.

Even if the presented methods do not give very precise values, the accuracy is quite sufficient for most analytical work. The second decimal of a logarithmic constant is of little value to analysts who seldom work under very precisely defined experimental conditions; specific properties of the ions determining the ionic strength, or a small change in ionic strength, may affect even the first decimal of a logarithmic constant, particularly if the charges of the ions are high, as is often the case with anions of chelating agents. Incidentally, a refinement of the values obtained by means of the proposed method is often not difficult, which means that very accurate values are also attainable.

In the following paragraphs, the method is first presented in a general form. The method of calculation is applied to a hypothetical "ideal" case. Here "ideal" is considered to mean that pM measurements are possible over the whole pH region of interest, that no other species than the 15 mentioned at the beginning of this paper are formed, and that the metal complexes are sufficiently stable, which implies that the differences between the protonation constants of the metal complexes are sufficiently large. The validity of these assumptions will then be critically discussed and ways of applying corrections will be described. A few practical numerical examples will be given that elucidate the reliability and the simplicity of the proposed methods. Finally, some attention will be directed to the possible occurrence of other complexes and the determination of their stability constants.

It is important that the reader is familiar with all the used concepts. Therefore, the definitions of these concepts and the notation used are first reviewed.

It is assumed that the acidity constants of the complexing agent are known. Their determination is described in many textbooks.

CONCEPTS AND NOTATION

We start from a normal mononuclear complex, ML. If one or more of the species, L, M and ML, are involved in any side reactions—for instance with H or OH ions forming H_nL, $M(OH)_n$, MH_nL or $M(OH)_nL$—the sums of the concentrations of these species and all their side-reaction products are commonly denoted by primed symbols. Thus, $[L']$ denotes the sum of $[L]$ and all $[H_nL]$ terms, $[M']$ denotes the sum of $[M]$ and all $[M(OH)_n]$ terms. If ML forms acid or basic complexes, the primed term $[(ML)']$ denotes the sum of $[ML]$ and the concentrations of the formed acid and basic 1 : 1 complexes.

In the usual expression for the stability constant of ML

$$K_{ML}^{M,L} = \frac{[ML]}{[M][L]}$$

no attention is paid to any side reaction. By priming the symbols written as subscript and superscripts of the constant, one obtains a *conditional* constant. The subscript denotes the dissociating complex, the superscripts denote the dissociation products. Consequently, $K_{(ML)'}^{M',L'}$ means that the side reactions of all three species have been taken into consideration; $K_{ML}^{M,L'}$ means that only the side reactions of the ligand have been considered. Measures of the extents of the side reactions are the so-called *side-reaction coefficients* or α coefficients defined by the expressions

$$\alpha_M = \frac{[M']}{[M]}\,; \quad \alpha_L = \frac{[L']}{[L]}\,; \quad \alpha_{ML} = \frac{[(ML)']}{[ML]} \qquad (1)$$

If a reacting species does not participate in any side reaction, the α coefficient of the species is unity, but if side reactions interfere, then $\alpha > 1$. The relationship between the stability constant $K_{\mathrm{ML}}^{\mathrm{M,L}}$ and the conditional stability constant is

$$K_{(\mathrm{ML})'}^{\mathrm{M',L'}} = \frac{\alpha_{\mathrm{ML}}}{\alpha_{\mathrm{M}}\alpha_{\mathrm{L}}} K_{\mathrm{ML}}^{\mathrm{M,L}} \tag{2}$$

Corresponding equations are valid for other equilibria.

In the literature some superscripts are often omitted if no confusion seems possible. For instance, instead of $K_{\mathrm{ML}}^{\mathrm{M,L}}$, one writes K_{ML} and instead of $K_{\mathrm{MHL}}^{\mathrm{H,ML}}$, one writes $K_{\mathrm{MHL}}^{\mathrm{H}}$.

The α coefficients are, of course, functions of the equilibrium constants of the side reactions. If the reactions between L and hydrogen ions are considered, the value of the α coefficient is given by

$$\alpha_{\mathrm{L(H)}} = 1 + \sum_{n=1}^{N} [\mathrm{H}]^n \beta_n \tag{3}$$

where β_n is the cumulative protonation constant, *i.e.*

$$\beta_n = \frac{[\mathrm{H}_n\mathrm{L}]}{[\mathrm{H}]^n[\mathrm{L}]} \tag{4}$$

and N is the maximum number of bound protons.

The interfering species responsible for the side reaction is always given in parentheses in the subscript of the α coefficient.

Similar expressions are valid for other α coefficients.

If several competing side reactions occur, one must use an over-all α coefficient which can be calculated from the individual α coefficients by means of the equation

$$\alpha_{\mathrm{L}} = \alpha_{\mathrm{L(A_I)}} + \alpha_{\mathrm{L(A_{II})}} + \ldots + (1-p) \tag{5}$$

The various interfering species, A, are designated by Roman numbers. p is the number of these species. If the over-all α coefficient is high in value, the last term can be neglected. This means that the over-all α coefficient is approximately equal to the sum of the individual coefficients. Very often one of the individual α coefficients predominates and the other coefficients can be neglected.

Details of the calculations and more thorough explanations of the presented concepts and their use can be found in ref. 3.

GENERAL METHOD OF DETERMINING STABILITY CONSTANTS OF CHELATE COMPLEXES

Mononuclear monoligand complexes

This group includes ML and its acid and basic complexes. The constants of the five species possibly formed can be determined by conducting a series of pH and pM measurements on a solution containing the metal and ligand (in its acid form) in the molar ratio $C_{\mathrm{M}} : C_{\mathrm{L}}$ of 0.5 : 1, that is gradually neutralized by adding potassium hydroxide solution.

We consider an—at least approximately—"ideal" case and assume that the hypothetical complexing agent is a hexabasic acid with the following successive logarithmic acidity constants: 2.5, 3.0, 4.0, 6.0, 9.0, 10.0, *i.e.* $\log \beta_{\mathrm{HL}} = 10.0$, $\log \beta_{\mathrm{H_2L}} = 19.0$,

$\log \beta_{H_3L}=25.0$, $\log \beta_{H_4L}=29.0$, $\log \beta_{H_5L}=32.0$, $\log \beta_{H_6L}=34.5$.

Moreover, we assume that the unknown stability constants to be determined experimentally are $\log K_{ML}^{M,L}=16.0$, $\log K_{MHL}^{H,ML}=6.5$, $\log K_{MH_2L}^{H,MHL}=4.0$, $\log K_{MOHL}^{-H,ML}=-9.0$, $\log K_{M(OH)_2L}^{-H,MOHL}=-11.5$. The negative hydrogen symbol means that [OH] has been eliminated by inserting the ionic product of water. Hence,

$$=\frac{[\mathrm{MOHL}][\mathrm{H}]}{[\mathrm{ML}]} \tag{6}$$

This constant is thus the equilibrium constant of the reaction $ML+H_2O=MOHL+H$. Table I will clarify the method of calculating the constants.

The first two columns contain pH and pM values recorded when a solution with $C_M=1.0\cdot10^{-2}$ and $C_L=2.0\cdot10^{-2}$ (the C's denote total concentrations) was gradually neutralized with potassium hydroxide solution. The corresponding values of the $\alpha_{L(H)}$ coefficient are given in the third column. These values were calculated by means of eqn. (3). (For a simple method of calculating α coefficients, see the paper by Ringbom and Still[4].)

The problem is to determine the stability constants of ML, MHL, MH_2L, MOHL and $M(OH)_2L$ from the values in these three columns. Essential are the general principles, and logarithmic constants to only one decimal place suffice for the present purposes.

If, in a solution where the total molar concentration of the metal is half the

TABLE I

pH AND pM VALUES FOR THE DETERMINATION OF THE STABILITY CONSTANTS OF MONONUCLEAR MONOLIGAND COMPLEXES OF A COMPLEXING AGENT H_6L

($C_M=1.0\cdot10^{-2}\,M$; $C_L=2.0\cdot10^{-2}\,M$. Neutralized with KOH)

pH	*pM*	*log* $\alpha_{L(H)}$ (*eqn.* 3)	*log* $K_{(ML)'}^{M,L}$ *pM* + *log* $\alpha_{L(H)}$
3.0	3.22	17.38	20.60
3.5	4.41	15.21	19.62
4.0	5.48	13.32	18.80
4.5	6.49	11.63	18.12
5.0	7.47	10.08	17.55
5.5	8.41	8.63	17.04
6.0	9.32	7.30	16.62
6.5	10.18	6.12	16.30
7.0	11.08	5.04	16.12
7.5	12.01	4.03	16.04
8.0	13.02	3.04	16.06
8.5	14.00	2.12	16.12
9.0	14.98	1.32	16.30
9.5	16.24	0.62	16.86
10.0	16.75	0.32	17.07
10.5	17.50	0.12	17.62
11.0	18.08	0.04	18.12
11.5	18.80		18.80
12.0	19.62		19.62
12.5	20.54		20.54
13.0	21.51		21.51

total molar concentration of the ligand, ML were the only complex formed and its formation were practically complete, [ML] would equal [L]; the corresponding metal ion concentration, $[\mathrm{M}]_{0.5}$ would be very small compared to [ML], and the equilibrium expression

$$K_{\mathrm{ML}}^{\mathrm{M,L}} = \frac{[\mathrm{ML}]}{[\mathrm{M}][\mathrm{L}]} \tag{7}$$

would take the form

$$\log K_{\mathrm{ML}}^{\mathrm{M,L}} = \mathrm{pM}_{0.5} \tag{8}$$

In practice, however, side reactions of the ligand and complex with hydrogen and hydroxide ions must be taken into consideration, *i.e.* primed symbols have to be used for all species except [M], which is directly measured. Consequently,

$$\frac{[(\mathrm{ML})']}{[\mathrm{M}][\mathrm{L}']} = K_{(\mathrm{ML})'}^{\mathrm{M,L}'} = \frac{\alpha_{\mathrm{ML(H,OH)}}}{\alpha_{\mathrm{L(H)}}} K_{\mathrm{ML}}^{\mathrm{M,L}} \tag{9}$$

The constant $K_{\mathrm{ML}}^{\mathrm{M,L}}$ is hence given by

$$\log K_{\mathrm{ML}}^{\mathrm{M,L}} = \mathrm{pM}_{0.5} + \log \alpha_{\mathrm{L(H)}} - \log \alpha_{\mathrm{ML(H,OH)}} \tag{10}$$

The last term of eqn. (10), $\log \alpha_{\mathrm{ML(H,OH)}}$, is zero if no acid or basic complexes are formed by ML. For many chelates there exists a certain pH range where the sum of $\mathrm{pM}_{0.5}$ and $\log \alpha_{\mathrm{L(H)}}$ is constant and equal to $\log K_{\mathrm{ML}}^{\mathrm{M,L}}$. The values of $\mathrm{pM}_{0.5} + \log \alpha_{\mathrm{L(H)}} = \log K_{(\mathrm{ML})'}^{\mathrm{M,L}}$ are given in the fourth column of Table I and plotted as a function of pH in Fig. 1.

The curve has an almost horizontal course in the pH range from about 7.5 to 8.0, where obviously ML predominates. The ordinate at the minimum point gives the value of the stability constant, hence $\log K_{\mathrm{ML}}^{\mathrm{M,L}} = 16.0$. The rise of both the left and the right branches of the curve proves the existence of acid as well as basic complexes. The vertical distance between a point on the curve on the left and the horizontal line passing through the ordinate 16.0 equals $\log \alpha_{\mathrm{ML(H)}}$ at the pH in question; the vertical distance between a point on the curve on the right and the horizontal line DEF equals $\log \alpha_{\mathrm{ML(OH)}}$.

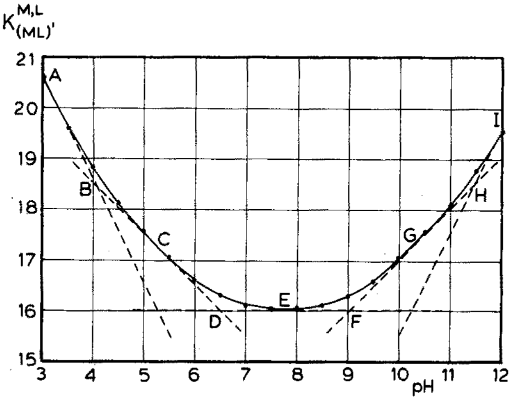


Fig. 1. $\log K_{(\mathrm{ML})'}^{\mathrm{M,L}}$ calculated from pM data as a function of pH.

The relationship between $\alpha_{ML(H)}$ and the protonation constants is

$$\alpha_{ML(H)} = 1 + [H]K^{H,ML}_{MHL} + [H]^2 K^{2H,ML}_{MH_2L} \tag{11}$$

The calculation of the two protonation constants from known values of [H] and $\alpha_{ML(H)}$ is thus a simple task. However, if the values are not too close to each other, they can be read directly from Fig. 1 without any calculations. One just extends the tangent of slope −1 to the rising curve to its point of intersection with the horizontal line passing through the ordinate log $K^{M,L}_{ML}$. One obtains log $K^{H,ML}_{MHL} = 6.5$. If two protons are taken up, the last term in eqn. (11) will predominate and the slope of the curve will be −2. This is the case at the extreme left and the constant can be determined in a similar way. The abscissa of the point of the intersection of the two extrapolated straight lines equals 4.0; hence log $K^{H,MHL}_{MH_2L} = 4.0$.

The formation constants of the basic complexes can be determined in an analogous way. From Fig. 1 the following values are obtained: log $K^{-H,ML}_{MOHL} = -9.0$ and log $K^{-H,MOHL}_{M(OH)_2L} = -11.5$.

The points of intersection of the horizontal line passing through ordinate 16.0 and the extrapolated tangents with the slopes −2 and +2 give the constants log $K^{2H,ML}_{MH_2L} = 2 \cdot 5.25 = 10.5$ and log $K^{-2H,ML}_{M(OH)_2L} = -2 \cdot 10.25 = -20.5$.

The assumed and the obtained values are in satisfactory agreement if values accurate to only one decimal are required.

Binuclear monoligand complexes

The many coordination centers of the hypothetical complexing agent discussed above make it likely that it forms also binuclear complexes. We will therefore consider the same reagent and assume the following fictive values for the constants of the binuclear complexes: log $K^{M,ML}_{M_2L} = 6.0$, log $K^{H,M_2L}_{M_2HL} = 4.5$, log $K^{H,M_2HL}_{M_2H_2L}$ very low in value, log $K^{-H,M_2L}_{M_2OHL} = -7.0$, log $K^{-H,M_2OHL}_{M_2(OH)_2L} = -9.0$.

These constants can also be determined by performing only one series of pM and pH measurements. One prepares a solution containing the metal and ligand in the ratio $C_M : C_L$ of 1.5 : 1. If ML and M_2L are formed quantitatively, a metal buffer solution is obtained where $[ML] = [M_2L]$. However, side reactions with hydrogen and hydroxide ions interfere and hence the symbols of both species must be primed. It follows that:

$$\frac{[(M_2L)']}{[M][(ML)']} = K^{M,(ML)'}_{(M_2L)'} = \frac{\alpha_{M_2L(H,OH)}}{\alpha_{ML(H,OH)}} K^{M,ML}_{M_2L} \tag{12}$$

or

$$\log K^{M,ML}_{M_2L} = pM_{1.5} + \log \alpha_{ML(H,OH)} - \log \alpha_{M_2L(H,OH)} \tag{13}$$

The constants can therefore be evaluated in the same way as those of mononuclear complexes. The only difference is that the coefficient $\alpha_{L(H)}$ has to be replaced by $\alpha_{ML(H,OH)}$ which can be computed from the equation

$$\alpha_{ML(H,OH)} = 1 + [H]10^{6.5} + [H]^2 10^{10.5} + \frac{10^{-9.0}}{[H]} + \frac{10^{-20.5}}{[H]^2} \tag{14}$$

The protonation constants are determined as described for mononuclear monoligand complexes.

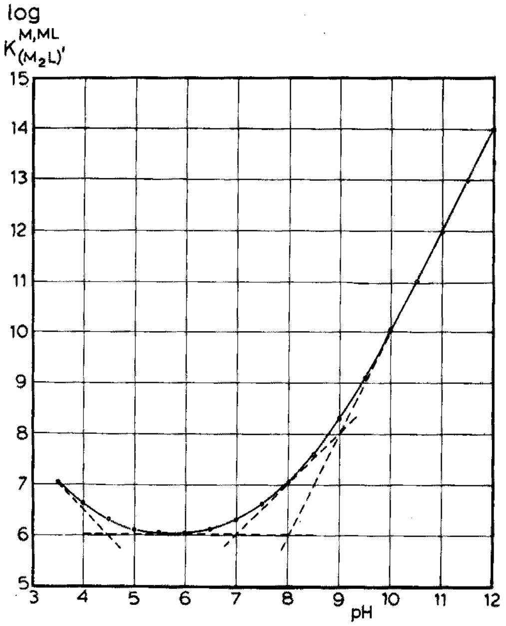
Table II is quite analogous to Table I. A number of pH and pM values are

TABLE II

pH AND pM VALUES FOR THE DETERMINATION OF THE STABILITY CONSTANTS OF BINUCLEAR COMPLEXES OF A COMPLEXING AGENT H_6L

($C_M = 3.0 \cdot 10^{-2}\,M$; $C_L = 2.0 \cdot 10^{-2}\,M$. Neutralized with KOH)

pH	*pM*	$\log \alpha_{ML(H,OH)}$ (*eqn.* 14)	$\log K^{M,ML}_{(M_2L)'}$ $pM + \log \alpha_{ML(H,OH)}$
3.5	3.42	3.62	7.04
4.0	3.82	2.80	6.62
4.5	4.18	2.12	6.30
5.0	4.57	1.55	6.12
5.5	5.00	1.04	6.04
6.0	5.43	0.62	6.05
6.5	5.82	0.30	6.12
7.0	6.18	0.12	6.30
7.5	6.59	0.04	6.63
8.0	7.02	0.06	7.08
8.5	7.50	0.12	7.62
9.0	8.00	0.30	8.30
9.5	8.50	0.62	9.12
10.0	8.99	1.05	10.04
10.5	9.39	1.62	11.01
11.0	9.88	2.12	12.00
11.5	10.20	2.80	13.00
12.0	10.38	3.62	14.00



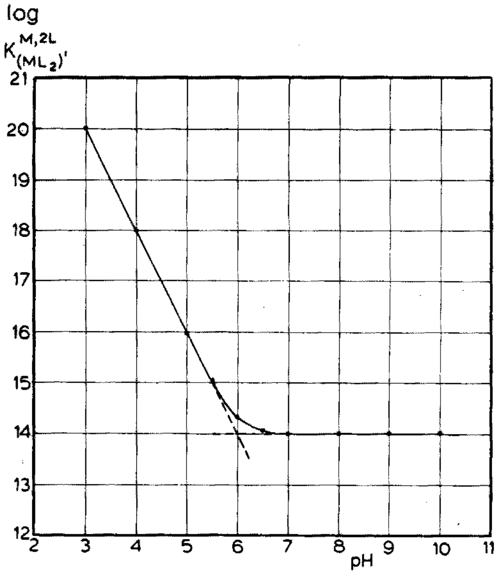


Fig. 2. log $K^{M,ML}_{(M_2L)'}$ calculated from pM data as a function of pH.

Fig. 3. log $K^{M,2L}_{(ML_2)'}$ calculated from pM data as a function of pH.

given in the first two columns and corresponding $\alpha_{ML(H,OH)}$ values obtained from eqn. (14) are given in the third column.

If one plots the sum of $pM_{1.5}$ and log $\alpha_{ML(H,OH)}$ as a function of pH, the curve given in Fig. 2 results. This curve plots values of the constant log $K^{M,ML}_{(M_2L)'}$ (*cf.* eqn. 13) and has an almost horizontal course between about pH 5.5 and pH 6.0. The corresponding ordinate is 6.0 and this is the value of log $K^{M,ML}_{M_2L}$. The stability constants of the acid and basic complexes can be determined graphically by the slope method described for mononuclear complexes. The results are log $K^{H,M_2L}_{M_2HL} = 4.5$, no appreciable formation of the M_2H_2L complex, log $K^{-HM_2L}_{M_2OHL} = -7.0$, and log $K^{-H,M_2OHL}_{M_2(OH)_2L} = -9.0$ in agreement with the initially assumed values.

Mononuclear biligand complexes

If the metal ion does not take up more than two ligands and the complex formed is not very weak, the constants are easily determined by measuring pM values of a solution containing a large excess of the ligand when the pH is varied by addition of a solution of potassium hydroxide.

In the general equation

$$\frac{[(ML_2)']}{[M][L']^2} = K^{M,2L'}_{(ML_2)'} \tag{15}$$

C_M can be substituted for $[(ML_2)']$ and $C_L - 2\,C_M$ for $[L']$. For instance, if one chooses $C_M = 10^{-4}$ and $C_L = 10^{-2}$, the measured pM value is a good estimate of the constant log $K^{M,2L'}_{(ML_2)'}$. If the values of 2 log $\alpha_{L(H)}$ are added to the pM values measured, the values of the constant log $K^{M,2L}_{(ML_2)'}$ are obtained and can be plotted as a function of pH.

The constants of the protonated biligand complexes can be determined from the slopes of the log $K^{M,2L}_{(ML_2)'}$–pH curve in an analogous way as in evaluation of the constants of the protonated monoligand complexes.

Chelating agents that form binuclear complexes do not generally form biligand complexes. The case of mononuclear biligand complexes can therefore be discussed by considering another complexing agent that contains fewer coordination centers. It may be noted that stable basic mononuclear biligand chelates are not common.

As a hypothetical example, we will consider a complexing agent with the logarithmic acidity constants $pk_1 = 4.0$, $pk_2 = 5.0$, $pk_3 = 8.0$. The cumulative constants are thus log $\beta_{HL} = 8.0$, log $\beta_{H_2L} = 13.0$ and log $\beta_{H_3L} = 17.0$.

We will assume that a metal, M, forms with the ligand L the following complexes with the given constants: log $K^{L,ML}_{ML_2} = 6{,}0$, log $K^{H,ML_2}_{MHL_2}$ very low, log $K^{2H,ML_2}_{MH_2L_2} = 12.0$.

The constants of the monoligand complexes, say, log $K^{M,L}_{ML} = 8.0$ and log $K^{H,ML}_{MHL} = 4.5$ can be determined as described for mononuclear monoligand complexes, although some corrections based on rules to be given later have to be applied at low pH values.

The constants of the biligand complexes can be calculated from the pH and pM values given in Table III, where values of log $\alpha_{L(H)}$ calculated from eqn. (3) are also tabulated.

The sum pM + 2 log $\alpha_{L(H)}$ = log $K^{M,2L}_{(ML_2)'}$ is plotted as a function of pH in Fig. 3. The curve has a horizontal course at pH values above about 7. The ordinate, *i.e.*

TABLE III

PH AND PM VALUES FOR THE DETERMINATION OF THE STABILITY CONSTANTS OF BILIGAND COMPLEXES OF A COMPLEXING AGENT H_3L

($C_M = 1.0 \cdot 10^{-4}\, M$; $C_L = 1.0 \cdot 10^{-2}\, M$. Neutralized with KOH)

pH	*pM*	$\log \alpha_{L(H)}$ (*eqn.* 3)	$\log K^{M,2L}_{(ML_2)'}$ $pM + 2 \log \alpha_{L(H)}$
3.5	5.76	6.62	19.00
4.0	7.36	5.32	18.00
5.0	9.36	3.32	16.00
5.5	9.80	2.62	15.04
6.0	10.22	2.04	14.30
6.5	11.02	1.51	14.04
7.0	11.92	1.04	14.00
8.0	13.92	0.04	14.00
9.0	14.00		14.00
10.0	14.00		14.00

$\log K^{M,2L}_{ML_2}$, is 14.0. Since $\log K^{M,L}_{ML} = 8.0$, it follows that $\log K^{L,ML}_{ML_2} = 6.0$. The curve to the left has a slope of -2 and intersects the $\log K^{M,2L}_{ML_2}$ line at pH 6.0. Considering that

$$\log \alpha_{ML_2(H)} = 1 + [H]^2 K^{2H,ML_2}_{MH_2L_2} \tag{16}$$

it follows that $\log K^{2H,ML_2}_{MH_2L_2} = 2 \cdot 6.0 = 12.0$, in agreement with the assumed value.

CORRECTION OF CONSTANTS OF "NON-IDEAL" SYSTEMS

The described method of evaluating constants consists of two steps: first, measured pM values are added to calculated log α values to obtain values of the conditional constant; second, the conditional constant values obtained are plotted as a function of pH and the desired (non-conditional) stability constants are determined graphically.

For "ideal" systems, this procedure leads to correct values. If the system is "non-ideal", the results are more or less incorrect and must be appropriately corrected. Errors may arise either in the first or in the second step described above. The two cases will now be discussed separately.

Correction of the preliminary conditional constants

It is necessary to treat the three types of complexes discussed in the foregoing section separately.

Mononuclear monoligand complexes. The method described above was based on the assumption that if $C_M : C_L = 0.5 : 1$, the quotient $[(ML)']/[L']$ is equal to unity. This assumption is justified only if the complexation is sufficiently complete. If considerable amounts of ML dissociate, [ML]—or, more correctly, $[(ML)']$—will decrease and $[L']$ will increase. Therefore, a correction may be necessary which can be applied by replacing unity by the value

$$\frac{[(ML)']}{[L']} = \frac{C_M - [M']}{C_M + [M']} = \frac{\frac{1}{2}C_L - [M']}{\frac{1}{2}C_L + [M']} \tag{17}$$

As a rule, this correction is necessary only for rather acidic solutions where the value of the conditional constant of ML is low.

The prime on M in the correction factor given in eqn. (17) deserves some comment. When the concentration of a metal ion is measured potentiometrically, [M] is obtained. (The influence of activity factors was mentioned on p. 34.) However, if the concentration of metal not complexed by L is required—and this is the problem above—the concentrations of the products of the side reactions of the metal must also be known. It is mostly a question of the influence of hydroxide ions, *i.e.* one must consider that $[M'] = \alpha_{M(OH)}[M]$. For many metals this interference occurs predominantly in alkaline solutions and can mostly be neglected. Tabulated $\alpha_{M(OH)}$ values as functions of pH can be found for most metals in ref. 3. In this way, the possible influence of the hydrolysis of a metal ion can conveniently be taken into consideration.

The equilibrium can also be affected by other side reactions. In some exceptional cases, it may happen that the binuclear complex M_2L is so stable that in sufficiently acidic solution it will predominate over ML even when an excess of the ligand is present. However, $K^{M,(ML)'}_{(M_2L)'}$ can be evaluated from the data of the series for binuclear monoligand complexes already described, and the values of this constant will tell us at what pM and pH limit the formation of binuclear complexes is considerable. If such a possibility is disregarded, a rise of the left part of curves similar to that in Fig. 1 can be incorrectly interpreted as being caused by acid mononuclear complexes (*cf.* the discussion by Harju[5]).

If ML_2 is formed, the ratio $[(ML)']/[L']$ is not affected in a solution where $C_M : C_L = 0.5 : 1$, and remains equal to unity as long as a considerable amount of the free metal ion (or M′ ion) is not present. A correction can be calculated by means of the equation

$$\frac{[(ML)']}{[L']} = \frac{\frac{1}{2}C_L - [M'] - [(ML_2)']}{\frac{1}{2}C_L + [M'] - [(ML_2)']} \tag{18}$$

Only if [M′] is considerable will this ratio differ from unity.

Binuclear monoligand complexes. The method based on pM and pH measurements on a solution where $C_M : C_L = 1.5 : 1$ demands a sufficiently complete reaction. In cases of incompleteness, the assumption that $[(M_2L)']/[(ML)']$ equals unity is not justified and a correction has to be applied to eqn. (12).

An expression for the correction can be derived from the two dissociation reactions

$$(M_2L)' = M' + (ML)' \tag{19}$$

$$(ML)' = M' + L' \tag{20}$$

It follows that

$$\frac{[(M_2L)']}{[(ML)']} = \frac{\frac{1}{2}C_L - ([M'] - [L'])}{\frac{1}{2}C_L + ([M'] - [L']) - [L']} = \frac{\frac{1}{2}C_L - [M'] + [L']}{\frac{1}{2}C_L + [M'] - 2[L']} \tag{21}$$

The prime on M is inserted in order to draw attention to the possibility of hydrolysis reactions. Mostly, there is no interference. [L′] is not measured, but can be derived from $K^{M,L'}_{(ML)'}$ which was determined as described for mononuclear monoligand complexes. Thus:

$$C_M = 1.5\,C_L = [M'] + [(ML)'] + 2[(M_2L)'] \tag{22}$$

$$C_L = [L'] + [(ML)'] + [(M_2L)'] \tag{23}$$

$$K^{M,L'}_{(ML)'} = \frac{[(ML)']}{[M][L']} \tag{24}$$

Combination of these equations gives

$$[L'] = \frac{\frac{1}{2}C_L + [M']}{2 + [M]\,K^{M,L'}_{(ML)'}} \tag{25}$$

It may be noted that the correction given by eqn. (21) is necessary only when the complexation is rather incomplete as often is the case in acidic solutions.

Mononuclear biligand complexes. If the stability constants of biligand complexes are to be evaluated by the method suggested in the preceding section, a rather large excess of the ligand must be present. Therefore, the assumption that $[(ML_2)'] \approx C_M$ is usually justified. If the formation of the biligand species is incomplete, a corrected expression must be used, *viz.*

$$[(ML_2)'] = C_M - [(ML)'] - [M'] \tag{26}$$

$[M]$ is measured. If the metal is involved in side reactions (usually with hydroxide ions), $[M]$ must be transformed into $[M']$ by $[M'] = \alpha_M[M]$. $[(ML)']$ can be calculated from $K^{M,L'}_{(ML)'}$ which was evaluated for mononuclear monoligand complexes.

Correction of the graphically determined (non-conditional) constants

It was previously mentioned that the graphical method based on extrapolated tangents gives correct values only if the differences between the values of successive protonation constants are sufficiently large. Now we will show how to correct the values when the differences are small.

Considering the part DEF of the curve in Fig. 1, it is obvious that if the distance between the two break points D and F were very short, no part of the curve would be horizontal. A fraction of the metal complex would exist in protonated form also at the minimum point. The correct value of log $K^{M,L}_{ML}$ would be a little less than the ordinate at the minimum point, *i.e.*

$$\log K^{M,L}_{ML} = pM_{min} - \log \alpha_{ML(H,OH)} \tag{27}$$

The formation of MHL and MOHL complexes must be taken into consideration. The α coefficient is given by

$$\alpha_{ML(H,OH)} = 1 + [H]\,K^{H,ML}_{MHL} + \frac{1}{[H]}\,K^{-H,ML}_{MOHL} \tag{28}$$

As an approximation, the two constants in eqn. (28) can be taken equal to the pH values at the points of intersection of the extrapolated tangents of the curve, *i.e.* at the points D and F. Therefore, if we consider $[H]$ at point E, *i.e.* the midpoint between D and F, we obtain

$$\alpha_{ML(H,OH)} \approx 1 + [H]_E\,10^{pH_D} + \frac{1}{[H]_E}\,10^{-pH_F} = 1 + 10^{-(pH_E - pH_D)} + 10^{-(pH_F - pH_E)} \tag{29}$$

or, generally,

$$\alpha = 1 + 2\cdot 10^{-\frac{1}{2}\Delta pH} \tag{30}$$

TABLE IV

LOG α AS A FUNCTION OF ΔpH
(Log $\alpha = \log(1+2\cdot 10^{-\frac{1}{2}\Delta \mathrm{pH}})$)

ΔpH	*log α*	*ΔpH*	*log α*
4.0	0.01	1.1	0.19
3.5	0.02	1.0	0.21
3.0	0.03	0.9	0.23
2.5	0.05	0.8	0.25
2.0	0.08	0.7	0.28
1.9	0.09	0.6	0.30
1.8	0.10	0.5	0.33
1.7	0.11	0.4	0.35
1.6	0.12	0.3	0.38
1.5	0.13	0.2	0.41
1.4	0.15	0.1	0.44
1.3	0.16	0	0.48
1.2	0.18		

where ΔpH is the difference between the abscissae of two intersection points (in the discussed example, D and F).

The use of eqn. (30) represents a very simple and rapid way of correcting values obtained by the graphical procedure described above. It may be emphasized that eqn. (30) is generally applicable to all curves of the type in Fig. 1 that arise when more than one protonated complex is formed.

To facilitate the evaluation of corrections, values of log α for various values of ΔpH calculated from eqn. (30) are collected in Table IV.

It can be seen that if ΔpH is larger than 2, the correction is less than 0.1 logarithmic unit; when $\Delta\mathrm{pH} = 1$, the correction is 0.21. However, if the difference between the (true) values of two successive logarithmic stability constants is less than about unity, iterative correction may be necessary.

Examples of the described method of correcting stability constants will be reported in Part II of this series.

CONCLUSION

A method for determining stability constants of chelate complexes in a system containing a large number of complexes has been proposed above. The character of the problem may vary and the method of calculating constants may have to be modified (*cf.*, for instance, Harju's method of measuring pL values by means of a mercury electrode[5]), but the basic principle is always the same: a consistent use of α coefficients.

The proposed treatment does not include complexes with three or more ligands and no attention has been paid to a possible occurrence of dimerized (or polymerized) complexes. Dimers are by no means rare among chelate complexes, and if there are reasons for suspecting the existence of dimers, several series of pM measurements at various C_M concentrations should be performed. The calculation of the constants is then a comparatively simple task.

According to the proposed method, stability constants are calculated by the addition of only a few data or read directly from simple graphs. The calculations do not require the introduction of any other parameters than α coefficients, but sometimes correction of the measured or calculated quantities are necessary. If the Tables presented in ref. 4 are used, not even a slide rule is needed for the calculations.

In these simplified calculations we have made no use of the amount of hydroxide ions consumed in the neutralization. For the determination of the stability constants of acid and basic complexes, inclusion of this variable would increase the attainable accuracy (*cf.* Harju[5]).

For the analytical chemist, graphical methods providing a survey of the equilibrium situations are particularly valuable. Computer methods are often considered a supplement to graphical methods and are useful for refining approximate values obtained in some other way. Incidentally, the writing of a computer program based on the principles presented in this paper is not very difficult. Of course, computers can also be used directly and our intention is by no means to dispute their great usefulness in analytical chemistry; they often offer invaluable help in the solution of many complicated problems, as can be seen from monographs that have been published in recent years. However, many problems which seem at first sight rather involved, can be solved surprisingly simply and rapidly without a computer. Examples from practice illustrating this fact are given in the following paper.

SUMMARY

A method for the calculation of the stability constants of chelate complexes from pH and pM values is presented. The method, which is based on a consistent use of side-reaction coefficients, is applicable also to systems containing a large number of complexes. The values of the constants are obtained graphically in a simple way, but in many cases corrections are necessary. Methods of correction are described.

RÉSUMÉ

Une méthode est proposée pour calculer les constantes de stabilité de chélates, à partir de pH et de pM. Elle est applicable également à des systèmes renfermant un grand nombre de complexes. Les valeurs des constantes sont obtenues directement à l'aide d'un graphique. Mais, dans de nombreux cas, des corrections sont nécessaires. Les méthodes de correction sont décrites.

ZUSAMMENFASSUNG

Es wird eine Methode für die Berechnung der Stabilitätskonstanten von Chelatkomplexen aus pH- und pM-Werten vorgelegt. Die Methode beruht auf der konsequenten Anwendung von Nebenreaktionskoeffizienten und ist auch auf Systeme anwendbar, die eine grosse Anzahl von Komplexen enthalten. Die Werte der Konstanten werden graphisch auf einfachem Wege erhalten; jedoch sind in vielen Fällen Korrekturen notwendig. Die Korrekturmethoden werden beschrieben.

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DETERMINATION OF STABILITY CONSTANTS OF CHELATE COMPLEXES

PART II. APPLICATIONS

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In the preceding Part I of this series, the theory of a method for the evaluation of the stability constants of chelate complexes from pH and pM values was formulated. In this Part, the theory is applied to systems of different types where pM measurements were performed with a copper amalgam electrode and a silver electrode.

CALCULATION OF THE STABILITY CONSTANTS OF COPPER *o*-PHOSPHORYLSERYLGLUTAMIC ACID COMPLEXES FROM MEASURED pCu VALUES

Österberg[1] has reported the results of a series of very thorough investigations on the equilibria of copper complexes of peptides and related compounds. He used a copper amalgam electrode as well as a glass electrode and based his calculations of constants on methods, partly graphical, developed by Sillén, Rossotti and others[2]. Integrated curves, curve-fitting methods, and a number of parameters commonly used in coordination chemistry were used. The obtained values were refined by the generalized least-square method with the program Letagrop. It was of interest to determine to what extent values of constants calculated by our simplified method on the basis of Österberg's experimental data would agree with his probably very accurate values.

In Österberg's paper are reported the results of one series of measurements where $C_{\text{Cu}} : C_{\text{L}}$ was exactly 0.5 : 1. If our method is used, a number of values of this series will suffice for the calculation of all stability constants of the monoligand complexes.

Some of Österberg's experimental data are given in the first three columns of Table V*. The fourth column contains values of log $\alpha_{\text{L(H)}}$ calculated from eqn. (3) (Part I) with the following cumulative protonation constants determined by Österberg: log $\beta_{\text{HL}} = 8.20$, log $\beta_{\text{H}_2\text{L}} = 13.89$, log $\beta_{\text{H}_3\text{L}} = 18.29$, log $\beta_{\text{H}_4\text{L}} = 21.33$.

By addition of pCu and log $\alpha_{\text{L(H)}}$ at different pH values, one obtains values of the conditional constant log $K^{\text{Cu,L}}_{(\text{CuL})'}$. The values at pH less than 5.2 require a small correction given by eqn. (17). (A way of simplifying such calculations is described in this issue[3].) The corrected values given in the last column are plotted as a function of pH in Fig. 4. The plot immediately gives a survey of the equilibria.

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* For convenience in cross-referencing, Tables, Figures and equations are numbered consecutively from Part I, *Anal. Chim. Acta*, 59 (1972) 33.

TABLE V

CALCULATION OF THE STABILITY CONSTANTS OF THE MONOLIGAND COPPER COMPLEXES OF *o*-PHOSPHORYLSERYLGLUTAMIC ACID FROM pCu DATA

(Data taken from a paper by Österberg[1]. $C_{Cu}=0.727\cdot10^{-3}\,M$. $C_L=1.454\cdot10^{-3}\,M$. $\mu=0.15(KNO_3)$.
$$\text{pCu} = \frac{E_m-312[H]-106.29}{29.58}+3.00)$$

pH	E_m (*mV*)	*pCu*	*log* $\alpha_{L(H)}$ (*eqn.* 3)	*log* $K^{Cu,L}_{(CuL)'}$ *pCu + log* $\alpha_{L(H)}$ *not corrected*	*log* $K^{Cu,L}_{(CuL)'}$ *corrected acc. to eqn.* (17)
3.013	111.07	3.151	9.57	12.72	10.87
3.090	111.10	3.154	9.30	12.45	10.69
3.194	111.19	3.159	8.94	12.10	10.47
3.298	111.35	3.166	8.61	11.78	10.27
3.410	111.64	3.177	8.24	11.42	10.07
3.484	111.89	3.185	8.01	11.20	9.95
3.687	113.12	3.229	7.38	10.61	9.63
3.874	115.21	3.300	6.83	10.13	9.39
4.080	118.75	3.420	6.25	9.67	9.17
4.266	123.25	3.573	5.75	9.32	8.98
4.466	129.35	3.780	5.25	9.03	8.83
4.673	137.23	4.046	4.75	8.80	8.69
4.873	145.85	4.337	4.32	8.66	8.60
5.101	156.74	4.706	3.85	8.56	8.54
5.296	166.55	5.037	3.48	8.52	8.51
5.399	171.74	5.212	3.30	8.51	8.50
5.497	176.85	5.385	3.13	8.52	8.52
5.683	186.46	5.710	2.83	8.54	8.54
5.871	196.19	6.042	2.56	8.60	8.60
6.031	204.7	6.327	2.33	8.66	8.66
6.253	216.4	6.723	2.05	8.77	8.77
6.468	228.0	7.114	1.80	8.91	8.91
6.685	239.9	7.516	1.56	9.08	9.08
6.878	250.4	7.884	1.35	9.23	9.23
6.978	256.1	8.063	1.26	9.32	9.32
7.091	262.3	8.274	1.16	9.43	9.43
7.208	268.4	8.480	1.04	9.52	9.52
7.398	278.8	8.832	0.87	9.70	9.70

The plot has a nearly horizontal course between about pH 5.2 and pH 5.7, and has its minimum value 8.50 at pH 5.40. The rise of the plot on both sides of the horizontal line proves that both acid and basic complexes exist. The curvature of the plot shows that complexes with one and two protons and with one hydroxide group are formed. When the principles presented in Part I are applied, the following approximate values of constants can immediately be read from the figure:

$$\log K^{Cu,L}_{CuL}=8.50;\ \log K^{H,CuL}_{CuHL}=4.73;\ \log K^{H,CuHL}_{CuH_2L}=3.61;$$
$$\log K^{2H,CuL}_{CuH_2L}=2\cdot4.17=8.34;\ \log K^{-H,CuL}_{CuOHL}=-6.20$$

However, the horizontal part of the curve is not very wide, because in this pH range a small fraction of the copper complex exists in protonated and hydrolyzed forms. The correct value of log $K^{Cu,L}_{CuL}$ is probably a little less than the minimum value 8.50 at pH 5.40, *i.e.*

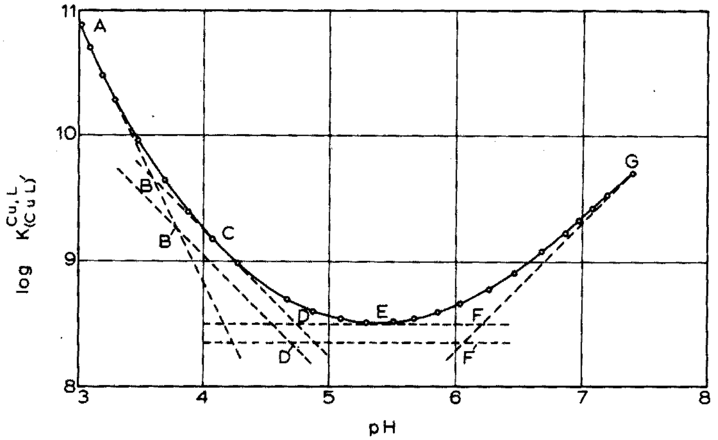


Fig. 4. log $K^{Cu,L}_{(CuL)'}$ of *o*-phosphorylserylglutamic acid calculated from pCu data of Österberg[1] as a function of pH.

$$\log K^{Cu,L}_{CuL} = 8.50 - \log \alpha_{CuL(H,OH)} \tag{31}$$

From Table IV (Part I) one immediately obtains values of the α coefficients needed for the correction of the approximate values taken from Fig. 4:

$$\Delta pH_{DF} = 6.20 - 4.73 = 1.47;\ \log \alpha_{CuL(H,OH)} = 0.14 \tag{32}$$

$$\Delta pH_{BD} = 4.73 - 3.61 = 1.12;\ \log \alpha_{CuHL(H,OH)} = 0.19 \tag{33}$$

To clarify the procedure, these log α values are drawn in Fig. 4 as lines (B'D' and D'F') parallel to the extrapolated tangents. The following corrected values of the constants are obtained:

$$\log K^{Cu,L}_{CuL} = 8.50 - 0.14 = 8.36 \tag{34}$$

$$-\log K^{-H,CuL}_{CuOHL} = 6.20 - 0.14 = 6.06 \tag{35}$$

$$\log K^{H,CuL}_{CuHL} = 4.73 + 0.14 - 0.19 = 4.68 \tag{36}$$

$$\log K^{H,CuHL}_{CuH_2L} = 3.61 + 0.19 = 3.80 \tag{37}$$

The tangents AB (the CuH_2L line) and FG (the CuOHL line) at the ends of the curve are not corrected in the Figure. A correction of the line FG will probably be superfluous because no sign of a new change in slope can be observed at the extreme right, *i.e.* almost 1.5 pH units from the break at F. The correctness of this conclusion can be checked by calculating the constant $K^{-H,CuL}_{CuOHL}$ algebraically from the α values. The term $[H]K^{H,CuL}_{CuHL}$ in eqn. (28), which accounts for the formation of CuHL complexes, can be omitted at pH values above about 6. Consequently,

$$K^{-H,CuL}_{CuOHL} = [H](\alpha_{CuL(OH)} - 1) \tag{38}$$

where $\log \alpha_{CuL(OH)}$ is the difference between the ordinate of a point on the curve on the right (*i.e.* $\log K^{Cu,L}_{(CuL)'}$) and the horizontal line at $\log K^{Cu,L}_{CuL} = 8.36$ (*cf.* Fig. 4). Table VI shows the result of such a calculation. The obtained value 6.06 is in excellent agreement with the value 6.06 at the corrected point of intersection (eqn. 35).

The pH difference between the points A and B is small, less than 0.8 pH unit. Therefore, in addition to CuH_2L, small amounts of CuHL probably exist in a solu-

TABLE VI

CALCULATION OF LOG $K^{-H,CuL}_{CuOHL}$ FROM pCu VALUES AT pH >6

pH	*log* $K^{Cu,L}_{(CuL)'}$ *from Table V*	*log* $\alpha_{CuL(OH)}$ *log* $K^{Cu,L}_{(CuL)'} - 8.36$	$-\log K^{-H,CuL}_{CuOHL}$ *log* $[H]$ $(\alpha_{CuL(OH)} - 1)$
6.031	8.66	0.30	6.03
6.253	8.77	0.41	6.05
6.468	8.91	0.55	6.06
6.685	9.08	0.72	6.06
6.878	9.23	0.87	6.07
6.978	9.32	0.96	6.07
7.091	9.43	1.07	6.06
7.208	9.52	1.16	6.08
7.398	9.70	1.34	6.08
			Average: 6.06

TABLE VII

CALCULATION OF LOG $K^{2H,CuL}_{CuH_2L}$ FROM pCu DATA AT pH 3–4

pH	*log* $K^{Cu,L}_{(CuL)'}$ *from Table V*	*log* $\alpha_{CuL(H)}$ *log* $K^{Cu,L}_{(CuL)'} - 8.36$	*log* $K^{2H,CuL}_{CuH_2L}$
3.013	10.87	2.51	(8.47)
3.090	10.69	2.33	(8.42)
3.194	10.47	2.11	8.38
3.298	10.27	1.91	8.35
3.410	10.07	1.71	8.32
3.484	9.95	1.59	8.31
3.687	9.63	1.27	8.27
3.874	9.39	1.03	8.27
			Average: 8.32

tion of pH 3. If we want to refine the value of $K^{H,CuHL}_{CuH_2L}$, it can be done similarly as was done for K^{-H}_{CuOHL} in Table VI. Table VII presents the results based on the equation

$$K^{2H,CuL}_{CuH_2L} = \frac{\alpha_{CuL(H)} - 1 - [H]10^{4.68}}{[H]^2} \tag{39}$$

which is derived from eqn. (11). Log $\alpha_{CuL(H)}$ is the vertical distance between a point on the horizontal line at the ordinate 8.36 and the log $K^{Cu,L}_{(CuL)'}$ curve at the pH in question.

The obtained average value, 8.32, corresponds to a value of log $K^{H,CuHL}_{CuH_2L} = 8.32 - 4.68 = 3.64$. This result is, as expected, a little smaller than the previously obtained value of 3.80 (eqn. 37).

At pH 3, less than 3% of the copper is complexed and the highest acidities are less reliable than the others. When the average value was calculated, the first two values were omitted. Incidentally, the larger value of the constant at pH 3 can be interpreted as being due to the existence of a complex with more than 2 protons.

If demands on accuracy are high, the obtained corrected values can serve as bases for new iterative corrections. Such a correction based on Table IV will take

TABLE VIII

COMPARISON OF CALCULATED VALUES OF STABILITY CONSTANTS OF THE MONOLIGAND COPPER COMPLEXES OF *o*-PHOSPHORYLSERYLGLUTAMIC ACID

	$\log \beta_{CuL}$	$\log \beta_{CuHL}$	$\log \beta_{CuH_2L}$	$\log \beta_{CuOHL}$
Calculated by Österberg	8.34 ± 0.01	13.04 ± 0.05	16.65 ± 0.12	2.29 ± 0.02
Calculated by the method presented here	8.35	13.02	16.69	2.30

only a few seconds. The equations (40)–(44) below illustrate the procedure.

$$\Delta pH_{D'F'} = 6.06 - 4.68 = 1.38;\ \log \alpha_{CuL(H,OH)} = 0.15 \text{ (Table IV)} \tag{40}$$

$$\Delta pH_{B'D'} = 4.68 - 3.64 = 1.04;\ \log \alpha_{CuHL(H,OH)} = 0.21 \text{ (Table IV)} \tag{41}$$

$$\log K_{CuL}^{Cu,L} = 8.50 - 0.15 = 8.35 \tag{42}$$

$$-\log K_{CuOHL}^{-H,CuL} = 6.20 - 0.15 = 6.05 \tag{43}$$

$$\log K_{CuHL}^{H,CuL} = 4.73 + 0.15 - 0.21 = 4.67 \tag{44}$$

A third iteration would not alter these results.

If the above values are used for recalculating Table VII, one obtains $\log K_{CuH_2L}^{2H,CuL} = 8.34$, *i.e.* $\log K_{CuH_2L}^{H,CuHL} = 8.34 - 4.67 = 3.67$.

All the constants of the monoligand complexes calculated on the basis of α coefficients and expressed as cumulative constants are presented in Table VIII together with the values of Österberg based on no less than 187 experimental points. The agreement is surprisingly good. As a matter of fact, all our values are within the 3σ error limits given by Österberg.

The advantages of methods based on a great number of data points over methods based on only a few data are sometimes a matter of controversy. We feel that numerous data are of limited value if one cannot exactly determine the relative weights of the various values measured under different conditions. It is true that constants based on only a few data can be misleading but if the data have been measured under experimental conditions not far from the optimal ones, they can claim a high degree of reliability.

Österberg also determined the stability constants of the biligand complexes. Unfortunately, he had only a limited amount of the complexing agent at his disposal and hence did not perform any measurements with a large excess of ligand present. The largest excess was in a solution where $C_{Cu} = 0.388 \cdot 10^{-3}$ and $C_L = 3.05 \cdot 10^{-3}$. If the stability constants reported by Österberg are correct, about 15% of the copper at most is present in the form of biligand complexes. At pH 3, the amount is less than 1%. Above pH 8, no pCu measurements could be performed.

It follows that even a small difference in the second decimal of the measured pCu and pH values, or in the logarithmic constants of the monoligand complexes, will markedly alter the values of the stability constants of the biligand complexes.

The proposed method of calculating values of constants was applied to the mentioned series in spite of the small excess of ligand. The values obtained agreed fairly well with the values of Österberg. However, because of the great influence of small experimental errors on the results, we consider the results uncertain and report no values.

CALCULATION OF THE STABILITY CONSTANTS OF SILVER–TTHA COMPLEXES FROM pAg MEASUREMENTS

TTHA (triethylenetetraminehexaacetic acid) is a decadentate complexing agent with four amino groups. Obviously, the existence of polynuclear and acid silver complexes is probable, whereas basic—at least mononuclear—complexes are scarcely formed. Considering that the predominant coordination number of silver is only two, the formation of biligand complexes is unlikely.

As an accuracy of about ±0.1 logarithmic unit is aimed at, corrections affecting only the second decimals are neglected in the following.

The general principles of the calculations were described in Part I. The results of a series of experiments to determine the constants of the mononuclear complexes are presented in Table IX. $C_{Ag} : C_L$ was 0.5 : 1.

TABLE IX

THE DETERMINATION OF THE STABILITY CONSTANTS OF MONONUCLEAR SILVER–TTHA COMPLEXES FROM pH AND pAg VALUES

(50 ml of solution A ($C_{Ag} = 0.5 \cdot 10^{-2}\,M$; $C_L = 1.0 \cdot 10^{-2}\,M$; $\mu = 0.1$ with KNO_3) titrated with 0.1 *M* NaOH)

pH	*pAg*	*log* $\alpha_{L(H)}$	*log* $K^{Ag,L}_{(AgL)'}$ $pAg + \log \alpha_{L(H)}$
4.60	2.72	12.08	(14.80) 14.45 (corr.)
5.00	3.04	10.83	(13.87) 13.71 (corr.)
5.50	3.43	9.49	(12.92) 12.86 (corr.)
6.00	3.94	7.98	11.92
7.00	5.02	5.65	10.67
8.00	5.96	3.61	9.57
9.00	7.10	1.74	8.84
10.00	8.23	0.47	8.70
11.00	8.62	0.06	8.68
11.45	8.70		8.70

The $\alpha_{L(H)}$ values were calculated from eqn. (3) on the basis of the following values of constants determined by Bohigian and Martell[4]:

$$\log \beta_{HL} = 10.19,\ \log \beta_{H_2L} = 19.59,\ \log \beta_{H_3L} = 25.75,\ \log \beta_{H_4L} = 29.91,$$
$$\log \beta_{H_5L} = 32.86,\ \log \beta_{H_6L} = 35.28\,.$$

By adding pAg to $\log \alpha_{L(H)}$, we obtain the conditional constant $\log K^{Ag,L}_{(AgL)'}$ which is plotted as a function of pH in Fig. 5. The values at pH 4.60, 5.00 and 5.50 were corrected with the aid of eqn. (17).

It can be seen that in the pH region investigated no basic complexes are obviously formed, whereas the curvature of the plot on the acid side shows that two complexes, AgHL and AgH_2L, exist. If the rules given for the "ideal" case are followed, the approximate values of the constants are $\log K^{Ag,L}_{AgL} = 8.7$, $\log K^{H,AgL}_{AgHL} = 8.9$, $\log K^{H,AgHL}_{AgH_2L} = 6.2$, $\log K^{2H,AgL}_{AgH_2L} = 2 \cdot 7.55 = 15.1$.

The difference between the protonation constants is so large that no corrections of the points of intersection of the extrapolated tangents are needed nor are any other corrections necessary.

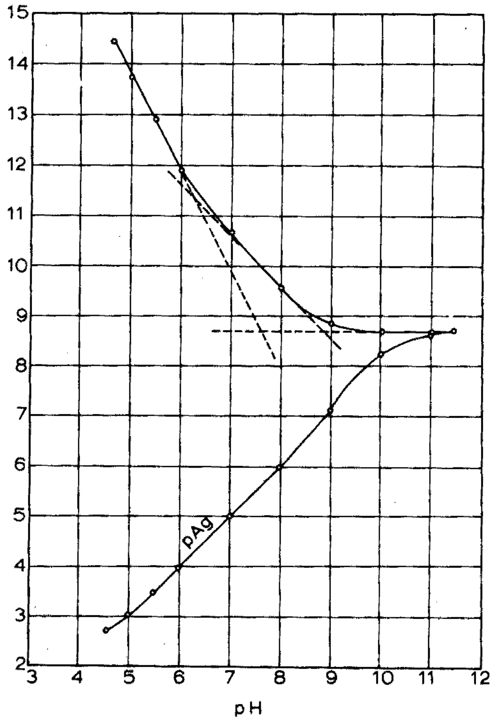
For the determination of the stability constants of the binuclear complexes,

TABLE X

THE DETERMINATION OF THE STABILITY CONSTANTS OF BINUCLEAR SILVER–TTHA COMPLEXES FROM pH AND pAg VALUES

(100 ml of solution B ($C_{Ag} = 6.0 \cdot 10^{-3}\ M$; $C_L = 4.0 \cdot 10^{-3}\ M$; $\mu = 0.1$ with KNO_3) titrated with 0.1 M NaOH)

pH	*pAg*	*log* $\alpha_{AgL(H)}$	*log* $K^{Ag,AgL}_{(Ag_2L)}$ *pAg* + *log* $\alpha_{AgL(H)}$
4.30	2.45	6.50	(8.95) 8.41 (corr.)
4.50	2.48	6.10	(8.58) 8.18 (corr.)
5.00	2.60	5.12	(7.72) 7.02 (corr.)
5.50	2.74	4.18	(6.92) 6.33 (corr.)
6.00	2.96	3.32	(6.28) 5.90 (corr.)
6.50	3.23	2.58	(5.81) 5.63 (corr.)
7.00	3.52	1.97	(5.49) 5.40 (corr.)
7.60	3.99	1.34	5.33
8.00	4.24	0.95	5.19
8.50	4.65	0.54	5.19
9.00	4.97	0.25	5.22
9.50	5.24	0.10	5.34
10.00	5.51	0.03	5.54
10.50	5.65	0.01	5.66



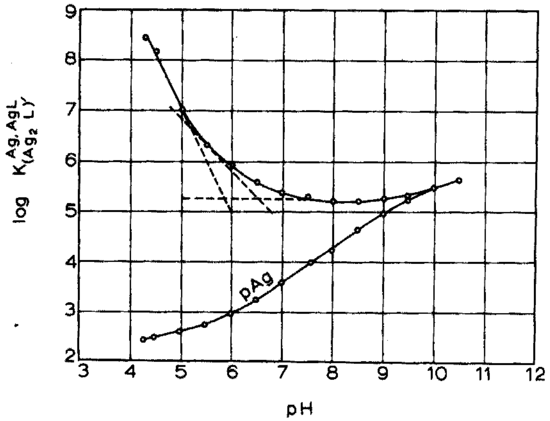


Fig. 5. Determination of the stability constants of mononuclear silver–TTHA complexes.

Fig. 6. Determination of the stability constants of binuclear silver–TTHA complexes.

the data given in Table X were collected. $C_{Ag}:C_L$ was 1.5 : 1.

The $\alpha_{AgL(H)}$ values in the third column were calculated on the basis of the constants of the acid mononuclear complexes determined above by means of the equation

$$\log \alpha_{AgL(H)} = 1 + [H]\ 10^{8.9} + [H]^2\ 10^{15.1} \tag{45}$$

The values of the conditional constant, $K^{Ag,AgL}_{(Ag_2L)'}$ at pH values below 7 were corrected according to eqns. (21) and (25). This logarithmic constant is plotted as a function of pH in Fig. 6. The following approximate values of the stability constants can be read from the figure:

$$\log K^{H,Ag_2L}_{Ag_2HL} = 6.5,\ \log K^{H,Ag_2HL}_{Ag_2H_2L} = 5.3,\ \log K^{2H,Ag_2L}_{Ag_2H_2L} = 2\cdot 5.9 = 11.8 \tag{46}$$

The two protonation constants differ relatively little from each other and hence the slope method is not very accurate. The constants can be corrected according to the principles outlined in Part I. One obtains (Fig. 6)

$$\Delta \text{pH} = 6.5 - 5.3 = 1.2;\ \log \alpha_{Ag_2HL(H,OH)} = 0.18 \text{ (Table IV)} \tag{47}$$

$$\log K^{H,Ag_2L}_{Ag_2HL} = 6.5 - 0.18 = 6.32 \approx 6.3 \tag{48}$$

$$\log {}^{H,Ag_2HL}_{Ag_2H_2L} = 5.3 + 0.18 = 5.48 \approx 5.5 \tag{49}$$

The slight rise of the curve at pH 10 in Fig. 6 could be interpreted as being due to the formation of some basic compounds. However, the measured potentials in this pH region are somewhat uncertain.

The many coordination centers of TTHA point to the possibility that trinuclear silver complexes are formed. Protonated species of appreciable stability are scarcely formed, and it is obvious that $K^{Ag,Ag_2L}_{Ag_3L}$ must be considerably smaller than $K^{Ag,AgL}_{Ag_2L} = 10^{5.3}$.

Although trinuclear complexes are not among the 15 species listed at the beginning of this paper when considering an "ideal" case, some words about them may be added.

Analogously as in the previous series, one can prepare a solution in which $C_{Ag}:C_L$ is 2.5 : 1, and measure pAg as a function of pH. An approximate value of the constant can be computed from the equation

$$\log K^{Ag,Ag_2L}_{Ag_3L} = \text{pAg}_{2.5} + \log \alpha_{Ag_2L(H)} \tag{50}$$

If the measurements are made at pH 7–10, the last term will be zero. Again, the incompleteness of the reaction demands a correction. An exact expression can be derived, but an estimation on the basis of the constants of the mono- and binuclear complexes shows that $[L']$ and $[(AgL)']$ will be negligibly small. Hence, the following equation will give a sufficiently accurate correction

$$\frac{[Ag_3L]}{[Ag_2L]} \approx \frac{\frac{1}{2}C_L - [Ag]}{\frac{1}{2}C_L + [Ag]} \tag{51}$$

The results of some measurements are given below:

$C_{Ag} = 5.0\cdot 10^{-3}$; $C_L = 2.0\cdot 10^{-3}$; pH = 9.0; pAg = 3.36.

The uncorrected constant $\log K^{Ag,Ag_2L}_{Ag_3L}$ would be 3.36. A correction based on eqn. (51) gives a value of 3.0.

Summarizing, the values of the silver–TTHA stability constants expressed as logarithmic cumulative constants are:

$\log \beta_{AgL} = 8.7$, $\log \beta_{AgHL} = 17.6$, $\log \beta_{AgH_2L} = 23.8$, $\log \beta_{Ag_2L} = 14.0$,
$\log \beta_{Ag_2HL} = 20.5$, $\log \beta_{Ag_2H_2L} = 25.6$, $\log \beta_{Ag_3L} = 17.0$

The following values of cumulative constants have been reported for the indicated species previously in the literature[5]:

$\log \beta_{AgL} = 8.67$, $\log \beta_{AgHL} = 17.78$, $\log \beta_{Ag_2L} = 13.89$

The agreement is fairly good.

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SUMMARY

The proposed simplified method for calculating the stability constants of chelate complexes from pH and pM measurements (Part I) is applied to two systems. On the basis of data reported by Österberg, the stability constants of copper *o*-phosphorylserylglutamic acid are calculated and good agreement is achieved. In addition, the stability constants of the mononuclear, binuclear and trinuclear silver complexes of TTHA (triethylenetetraminehexaacetic acid) were calculated from potentiometric pAg data. These calculations yielded the following values of the cumulative constants: $\log \beta_{AgL} = 8.7$, $\log \beta_{AgHL} = 17.6$, $\log \beta_{AgH_2L} = 23.8$, $\log \beta_{Ag_2L} = 14.0$, $\log \beta_{Ag_2HL} = 20.5$, $\log \beta_{Ag_2H_2L} = 25.6$, $\log \beta_{Ag_3L} = 17.0$.

RÉSUMÉ

La méthode de calcul de constantes de stabilité de chélates, à partir de pH et pM, décrite dans la première partie de ce travail, est appliquée à deux systèmes: cuivre–acide *o*-phosphorylsérylglutamique et les complexes mononucléaires, binucléaires et trinucléaires d'argent avec l'acide triéthylènetétraminohexacétique (TTHA). Les valeurs obtenues sont données.

ZUSAMMENFASSUNG

Die vorgeschlagene vereinfachte Methode zur Berechnung der Stabilitätskonstanten von Chelatkomplexen aus pH- und pM-Messungen (Teil I) wird auf zwei Systeme angewendet. Auf der Basis der von Österberg angegebenen Daten werden die Stabilitätskonstanten von Kupfer–*o*-Phosphorylserylglutaminsäure berechnet; es wird eine gute Übereinstimmung erzielt. Zusätzlich wurden die Stabilitätskonstanten der einkernigen, zweikernigen und dreikernigen Silberkomplexe von TTHA (Triäthylentetraminhexaessigsäure) aus potentiometrischen pAg-Werten berechnet. Diese Berechnungen ergaben die folgenden Werte für die kumulativen Konstanten: $\log \beta_{AgL} = 8.7$, $\log \beta_{AgHL} = 17.6$, $\log \beta_{AgH_2L} = 23.8$, $\log \beta_{Ag_2L} = 14.0$, $\log \beta_{Ag_2HL} = 20.5$, $\log \beta_{Ag_2H_2L} = 25.6$, $\log \beta_{Ag_3L} = 17.0$.

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THE DETERMINATION OF TRACES OF NICKEL BY GAS–LIQUID CHROMATOGRAPHY

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The determination of metals by the technique of gas–liquid chromatography was once considered a novelty. However, in the past ten years, the gas chromatography of metal complexes particularly with ligands of the β-diketone type, has received much attention, and the early work on this topic has been comprehensively reviewed[1]. Although over thirty metals can now be chromatographed directly as β-diketone complexes, analytical utility has been achieved only in a few cases, notably with beryllium and chromium(III); much of the recent work has been concerned with the determination of traces of these metals in substances as varied as human tissue and lunar material[2-12].

The application of gas chromatography in inorganic analysis has been limited by the problems involved in the quantitative conversion of metal ions in aqueous solution to a suitable metal chelate which must possess adequate volatility and thermal stability for quantitative elution from a gas-chromatographic column. Earlier attempts to develop a suitable nickel chelate based on a conventional β-diketone ligand have failed to provide these requisites for successful chromatography. Thus the nickel chelate of heptafluorobutanoylpivalylmethane (or 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione) has been found to exhibit unsatisfactory elution characteristics, and cannot be formed in quantitative yield[13]. Nickel has been determined by pyrolysis gas chromatography of the polychlorinated xanthate[14], but it was not an actual nickel compound that was chromatographed and determined.

The use of monothio-β-diketones has increased in recent years owing to their ability to form stable monomeric chelates with many metals which form hydrated or polymeric chelates with the usual β-diketones. These chelates are readily soluble in polar organic solvents. Studies, particularly of the nickel chelates of the monothio-β-diketones, have shown them to possess several desirable analytical properties. Their excellent thermal stability and volatility have resulted in favourable gas-chromatographic behaviour[15-18], whilst their solvent extraction properties have been exploited in a spectrophotometric determination of nickel[19]. The excellent solvent extraction properties of these sulphur-containing ligands have been confirmed in a recent report[20].

We have examined the analytical utility of gas chromatography for the determination of nickel(II) as the bis(monothiotrifluoroacetylacetonato)nickel(II) chelate, which was selected in order to take advantage of the extreme sensitivity of

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the electron capture detector to fluorinated compounds. This particular chelate has been found to be eminently suitable for the spectrophotometric determination of nickel, which, together with the solvent extraction properties of the chelate, has already been reported[19]. The present paper includes a description of the development of a gas chromatographic method for the determination of traces of nickel, as well as the results of some applications of the method to a variety of specimens selected to demonstrate the versatility of the method.

EXPERIMENTAL

Reagents

The extracting ligand, monothiotrifluoroacetylacetone, was prepared as described previously[16,18,19] and was stored as the lead chelate, which was stable for several months when kept in a refrigerator. Working strength solutions of the ligand were prepared by passing hydrogen sulphide (99.5%, B.O.C.) into a solution of the lead chelate (0.2 g) in diethyl ether (20 ml). The solvent was removed by simple distillation and the dark red ligand was diluted to 50 ml with *n*-hexane. This solution could be stored in the refrigerator for several weeks without adverse effects.

Bis(monothiotrifluoroacetylacetonato)nickel(II), $Ni(T\text{-}TFA)_2$, was synthesized by shaking an aqueous solution of a nickel salt with a solution of the ligand in *n*-hexane. The product was purified by vacuum sublimation[19]. Working strength solutions of $Ni(T\text{-}TFA)_2$ were prepared by appropriate dilution of a stock solution containing 100 p.p.m. Ni as the chelate in *n*-hexane. An aqueous stock standard (1000 p.p.m.) was prepared from AnalaR nickel nitrate hexahydrate, and other solutions were obtained by appropriate dilution of this stock solution.

Laboratory-grade solvents were used throughout and were found to be perfectly satisfactory.

AnalaR acids were used for the mineralisation of the specimens for analysis.

Buffer solutions were prepared according to the formulae of Clark and Lubs[21].

Instrumentation

A Philips PV4000 research gas chromatograph furnished with a Pye electron capture detector containing a 10-mCi ^{63}Ni radioactive source was used in all the work described here. The detector was used in the pulsed mode with a pulse interval of 5 μsec for general work, while an interval of 100 μsec was used where the maximum sensitivity was required. The pulse amplitude was maintained at 45 V and the pulse width at 0.8 μsec throughout.

Analytical chromatography was effected on a 4-ft. teflon column (3/16-in. o.d.) packed with "Universal B" (60–85 mesh) support material coated with 5% silicone gum rubber (E350). Substrate materials were obtained from Phase Separations Ltd., "Universal B" being a patented, silanised support. A 6-ft. stainless steel column ($\frac{1}{8}$-in. o.d.) was also used with a packing of 2.5% Apiezon L on "Universal B" (60–85 mesh).

The carrier gas was oxygen-free nitrogen (99.9%, B.O.C.) which was passed through a molecular sieve before entering the chromatograph. The flow-rate was 90 ml min^{-1} as measured with a soap film flowmeter. No scavenger flow was used.

For the analysis of aqueous solutions of nickel, the column temperature was maintained at 170°, while for the analysis of the tea and fat digests, the column temperature was programmed to give an initial isothermal period of 2 min at 140° followed by heating over 1 min to 170°, which was maintained until the analysis was complete. The injection port and detector oven temperatures were 170° and 200°, respectively.

Injections were made with a 10-μl syringe (Scientific Glass Engineering Pty. Ltd.) by a solvent flush technique in which *n*-hexane was used to flush the solution from the syringe.

Thermal analysis was carried out on a Perkin Elmer TGS-1 Thermobalance with 2-mg samples at a temperature scan rate of 20° $\min^{-1}$. Oxygen-free nitrogen was passed through the apparatus at about 20 ml $\min^{-1}$.

Ultraviolet spectra were measured on a Unicam SP800 recording spectrophotometer in silica cells of 10 mm path length.

Atomic absorption measurements were obtained with a Varian Techtron AA-5 atomic absorption spectrophotometer fitted with a 6-in. air–acetylene burner. A nickel hollow-cathode lamp was used with a current of 8 mA and the measurements were made at the most sensitive absorption line (232.0 nm). The spectral slit width was 50 μm.

Extraction procedure

The following procedure was used for the formation and extraction of $Ni(T\text{-}TFA)_2$ from the aqueous solutions of nickel(II).

Adjust the sample, usually containing 1–20 μg Ni in 10 ml of aqueous solution, to pH 4.6 by addition of an equal volume of buffer solution followed by the dropwise addition of dilute aqueous ammonia solution (about 0.1 *M*). Shake the mixture for 5 min in a separating funnel with 1 ml of the solution of the chelating agent, and, after allowing the phases to separate, discard the lower aqueous phase. Carefully dry the stem of the funnel with a tissue and run the organic phase into a vial containing 3–5 ml of 0.01 *M* sodium hydroxide solution. Shake the mixture for 30 sec to destroy residual chelating agent.

Analyse the extract by injecting 1–2 μl samples into the chromatograph and comparing the peak areas with those from alternate injections of standard $Ni(T\text{-}TFA)_2$ solutions. It is not necessary to separate the extract from the sodium hydroxide solution as no loss of chelate occurs.

Extraction volumes can be modified according to the nickel solution being analysed, and volume ratios varying from 10:1 to 250:1 were used. It was never necessary to dilute the extract to a known volume after equilibration.

Mineralisation procedures

Standard alloy. Dissolve a sample of the alloy in 10 ml of (1+1) hydrochloric acid and add 2 ml of concentrated nitric acid. Boil the mixture until no residue remains, and dilute the solution to 250 ml. Dilute a 2.5-ml portion further to 250 ml to give the working solution, and extract 50-ml aliquots of this with 5 ml of the solution of the chelating agent according to the above procedure.

Tea. The following wet and dry ashing procedures were evaluated in this study.

Wet ash. Accurately weigh the sample, containing 10–20 μg of nickel, into a

100-ml Pyrex beaker, add 10 ml of nitric acid and cover the vessel with a clock glass. Evaporate the solution on an electric hot-plate and bake the residue for a few minutes before allowing it to cool. Repeat this procedure three more times. Dissolve the final residue in a few drops of nitric acid and dilute to 25 ml with distilled water. Treat a 10-ml portion of this solution at pH 1–2 with hydrogen sulphide for a few minutes, and then extract as described previously.

Dry ash. Weigh the sample into a porcelain crucible, and heat for 20 h at 540° in a muffle furnace. Remove the crucible from the furnace and moisten the ash with dilute hydrochloric acid (3 *M*); cover the crucible with a watch glass, and evaporate to dryness on an electric hot-plate. After cooling, dissolve the residue in distilled water (adding a little hydrochloric acid if necessary) and dilute to 25 ml. Treat portions of this solution in the same way as those obtained by the wet ashing procedure.

Fats. Weigh a sample of the crude hydrogenated triglyceride (containing up to 10 μg of nickel) into a porcelain crucible and heat on an electric hot-plate for about 4 h to remove the more volatile components of the fat. Transfer the crucible containing the dark brown or black tarry residue to a muffle furnace and heat for 2–3 h at 540° until only a few carbon particles remain. Remove the crucible from the furnace and moisten the residue with a few drops of dilute hydrochloric acid (3 *M*). Warm the mixture on the hot-plate for a few minutes, dilute the contents of the crucible to 25 ml and extract portions of the solution as described previously.

RESULTS AND DISCUSSION

Gas chromatography of the nickel chelate

Thermogravimetric analysis of $Ni(T\text{-}TFA)_2$ indicated that the chelate is completely volatile and shows no sign of decomposition. In Fig. 1, the nickel thermogram is compared with those for the trifluoroacetylacetonates of beryllium and

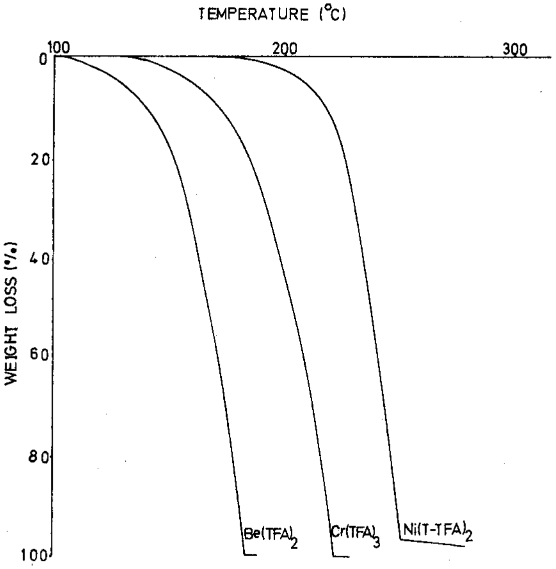


Fig. 1. Thermogravimetric analyses of metal chelates.

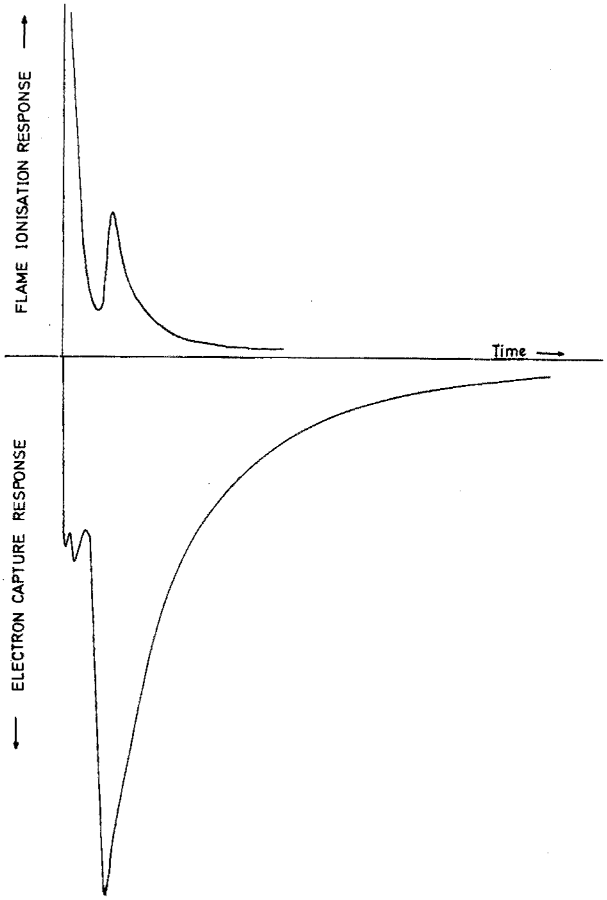


Fig. 2. A comparison of the responses of the flame ionisation and electron capture detectors: 6-ft. stainless steel column packed with 2.5% Apiezon L on "Universal B". Column temperature 170°; detector temperature 210°; injection port temperature 210°. Nitrogen flow rate 60 ml min^{-1}. Amplifier attenuation $5 \cdot 10^2$. Sample for FID, 2 μg; sample for ECD, 0.3 μg.

chromium(III) which show excellent chromatographic elution characteristics. These two chelates were prepared by standard methods[22,23]. It could therefore be predicted that Ni(T-TFA)$_2$ would show good chromatographic characteristics, and the first reports showed that this was indeed the case. However, this work[16,18] was carried out with a flame ionisation detector and a 6-ft. stainless steel column ($\frac{1}{8}$-in. o.d.) packed with 2.5% Apiezon L on "Universal B". When this work was repeated with the electron capture detector some decomposition was found; the decomposition products had been masked previously by the FID response to the solvent (Fig. 2). It was therefore necessary to establish the best chromatographic conditions for the elution as well as the detector conditions for maximal sensitivity. The use of the silicone gum stationary phase in a 4-ft. teflon column gave good chromatography under the conditions previously described, the optimal gas flow rate being 90 ml min^{-1} (Fig. 3). The use of a higher column temperature decreased the column efficiency.

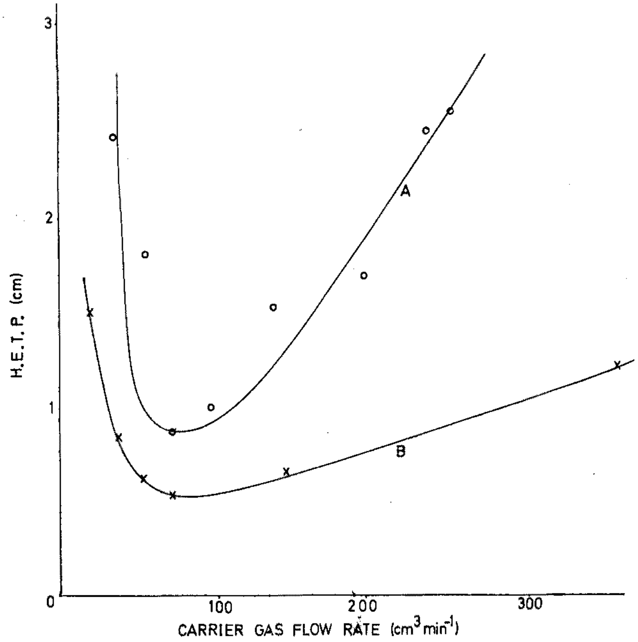


Fig. 3. Column performance curves. Column temperatures: (A) 190°; (B) 170°.

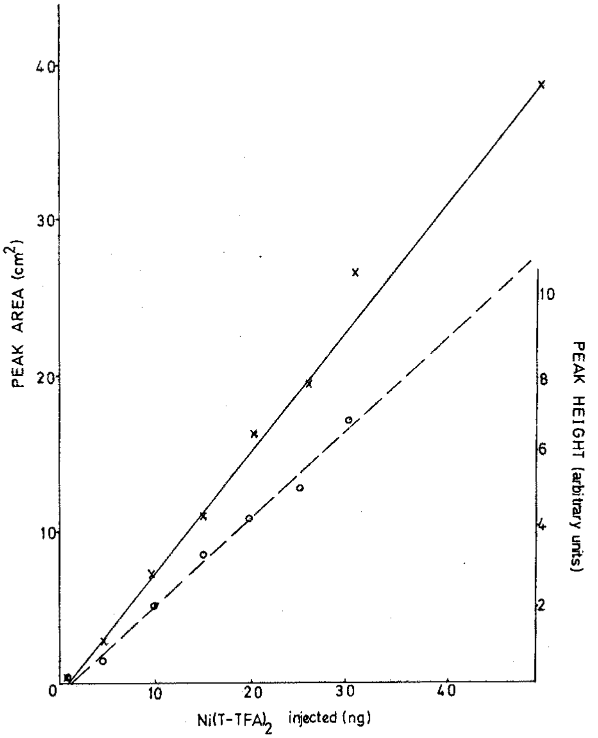


Fig. 4. The variation of the detector response to Ni(T-TFA)$_2$. Pulse period 100 μsec. Amplifier attenuation $1 \cdot 10^2$. (-----) Peak height; (——) peak area.

The detector operating conditions were also systematically examined; it was found that for general use a pulse period of 5 μsec was preferable, as this gave good sharp peaks. Maximal sensitivity was achieved with a pulse period of 100 μsec but the concomitant peak broadening and increased response to chelating agent residues did not favour the general use of this period.

When these chromatographic conditions were used, the variation of the detector response with sample size was found to be linear over short ranges as shown in Fig. 4. The fact that the graph does not pass through the origin suggests some sample loss by column adsorption and this was manifest in the slight increase in detector response over a period of use. This fact combined with day-to-day variations in the calibration graph made it preferable to make quantitative measurements by reference to alternate injections of standard solutions of $Ni(T\text{-}TFA)_2$. The limit of detection was found to be $5 \cdot 10^{-11}$ g of nickel. Mass spectral analysis of the eluted material showed that the $Ni(T\text{-}TFA)_2$ was eluted unchanged.

Extraction conditions

The small response factor of the electron capture detector to hydrocarbons makes these ideal solvents, because there is no interference from solvent tailing as has usually been found with the flame ionisation detector in these studies. *n*-Hexane was the solvent of choice because under the conditions of maximal sensitivity electron capturing impurities were well resolved from the chelate peak, which was not the case with benzene and toluene. Furthermore, *n*-hexane had no tendency to form emulsions with the aqueous phase, and the negligible volume change on partition enabled analyses to be made on the extracts without dilution. However, while the electron capture detector is insensitive to hydrocarbons, the response factor to halogenated compounds is very large with the result that the detector is extremely sensitive to the chelating agent. This was removed by washing the extracts with aqueous sodium hydroxide solution (0.01 *M*) before the determination; the breakdown products were eluted before the chelate and so did not interfere with its determination. No loss of $Ni(T\text{-}TFA)_2$ was observed after this treatment, and standard solutions of the chelate gave the same response when chromatographed directly and when prepared with ligand, which was removed as described above.

The results of a systematic investigation of the factors affecting the formation and extraction of $Ni(T\text{-}TFA)_2$, which have been reported more fully elsewhere[19], are summarised in Figs. 5 and 6. It can be seen that at pH 4.5–5.0 the chelation and extraction are essentially quantitative after a single 5-min extraction step. Although this corresponds only to about 95% conversion to the chelate, nevertheless this was perfectly acceptable for most purposes and further extractions did not improve the recoveries. However, if required, a correction factor could be applied.

Determination of nickel

Aqueous standard solutions of nickel nitrate were analysed by the method; Table I shows some typical recoveries. The precision of the results was quite acceptable as shown in Table II.

When the gas chromatograph was operated at the maximal sensitivity, it was possible to determine nickel in solutions down to 0.01 and 0.001 μg ml^{-1}, the results obtained being 0.009 and 0.0009 μg ml^{-1}, respectively.

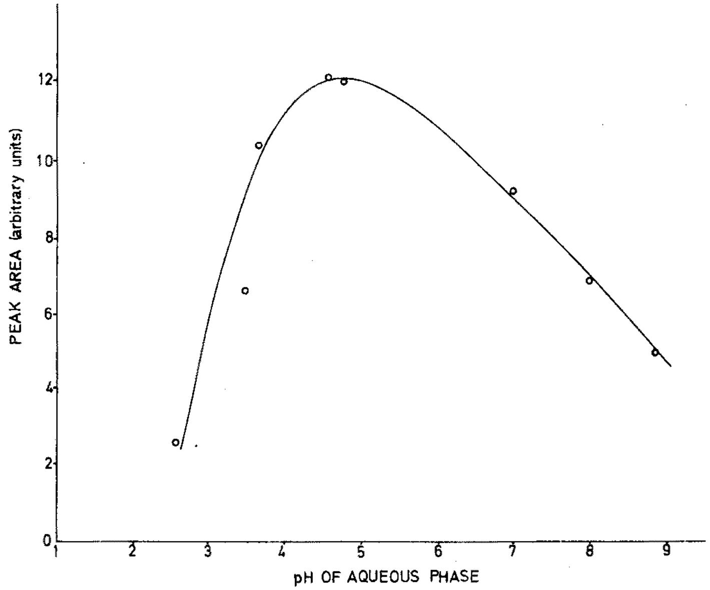


Fig. 5. The variation of the formation and extraction of Ni(T-TFA)$_2$ with the pH of the aqueous phase.

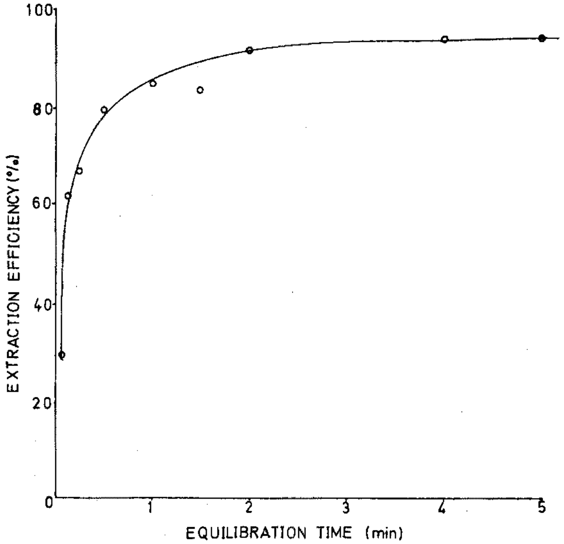


Fig. 6. The effect of the equilibration time on the distribution of nickel.

Interferences

Several ions were examined for interference in the determination of nickel. These ions were added in 100-fold amounts to solutions of nickel (1.0 μg ml^{-1}), which was then determined by the usual procedure. The results were expressed in terms of recovery compared to control solutions which contained no diverse ions and which were analysed simultaneously. Table III includes some of the results. It

TABLE I

ANALYSIS OF NICKEL NITRATE SOLUTIONS

Amount of Ni taken (g/50 ml)	*Yield of Ni(T-TFA)$_2$*		*Recovery (%)*
	Theoretical	*Found*	
$2.499 \cdot 10^{-4}$	$1.693 \cdot 10^{-3}$	$1.66 \cdot 10^{-3}$	98
$4.998 \cdot 10^{-5}$	$3.386 \cdot 10^{-4}$	$3.16 \cdot 10^{-4}$	93

TABLE II

PRECISION AND ACCURACY OF THE METHOD

Nickel concentration ($\mu g\ ml^{-1}$)	*Nickel found ($\mu g\ ml^{-1}$)*	*S*	*S_r*	*No. of detns.*
1.0	0.94	±0.07	± 7.2%	7
0.1	0.09	±0.014	±15.5%	5

TABLE III

INTERFERENCES IN THE DETERMINATION OF NICKEL

(1.0 μg Ni ml^{-1}; 100 μg ml^{-1} of diverse ion added)

Ion	*Recovery of Ni (%)*	*Ion*	*Recovery of Ni (%)*
Hg(I)	159	Cr(III)	87
Cd(II)	96	Al(III)	102
Zn(II)	92	Fe(III)	105
Mn(II)	103	Fe(III)+citrate (1:5)	100
Hg(II)	279	Sn(IV)	97
Co(II)	262	V(V)	101
Pt(II)	96		

was also found that magnesium(II), calcium(II) and barium(II) did not interfere[19].

In the case of copper(II) a very large peak, attributed to decomposition of a copper chelate formed in the extract, was eluted before the Ni(T-TFA)$_2$ peak and made it impossible to determine the nickel. This interference of copper(II) was easily eliminated by passing hydrogen sulphide into the aqueous solution (pH 1–2) before extraction; this procedure was subsequently used in the analysis of tea. Table III shows that significant interferences were also obtained in the presence of cobalt(II) and mercury(I,II).

Iron(III) did not interfere, although a broad peak was eluted before the Ni(T-TFA)$_2$ peak. Again this was attributed to the decomposition of a chelate formed in the extraction, but, unlike the case with copper(II), the elution was sufficiently rapid to allow resolution of the nickel chelate. The presence of citrate masked the iron(III), and so allowed greater resolution of the Ni(T-TFA)$_2$, but this could also be achieved by means of temperature programming of the column, which will be discussed later.

SOME APPLICATIONS OF THE METHOD

Nickel alloy

A sample of an alloy containing 2.89 % Ni (Sample No. 22a, Bureau of Analysed Samples Ltd., Newham Hall, Middlesbrough, Teesside) was analysed to show that the method was applicable to percentage levels of nickel, although it was first necessary to dilute the digested sample to a manageable concentration to avoid the use of large amounts of chelating agent, and to prevent overloading the detector. A value of 2.58 % was obtained for the nickel content of the alloy, the relative standard deviation being ±10.8 %.

Extensive dilution of the solution before analysis is not a recommended practice owing to the loss of accuracy, but it was not envisaged that the method would find use at such concentrations, and the following examples are applications at the trace level.

Tea

A sample of tea was considered to be a useful application of the method because natural nickel contents in the manufactured leaf are often about 10 μg g^{-1}. The specimen obtained was known to contain traces of nickel, copper and iron with larger amounts of manganese (Table IV, footnote). It was expected that after destruction of the organic matter, the only interference would be from copper, and this was found to be the case, but it was easily eliminated by treatment with hydrogen sulphide as described above. The organic matter in the sample was destroyed by wet and dry ashing methods, and analyses of ten samples in each case gave the results summarised in Table IV. For comparison the results obtained by spectrophotometric analysis of the extracts[19] and by atomic absorption spectrophotometry of the aqueous phases are also included.

TABLE IV

THE DETERMINATION OF NICKEL IN INSTANT TEA[a]

Method	*Ni found ($\mu g\ g^{-1}$)*	*S*	*S_r*
Wet ash			
G.l.c.	13.0	±1.4	±10.8%
Spectrophotometry	14.0	±1.4	±10%
A.a.s. on aq. phase	12.7	±2.5	±19.7%
Dry ash			
G.l.c.	12.8	±2.0	±15.6%
Spectrophotometry	12.6	±1.6	±12.7%

[a] Independent analysis of the sample by atomic absorption spectrophotometry gave the following results: 10–20 μg g^{-1} each of Cu, Fe, Ni, and 1000 μg g^{-1} of Mn.

Dry ashing has often been reported to cause losses by volatilisation or adsorption, while the advantages of wet ashing are often lost by contamination from the

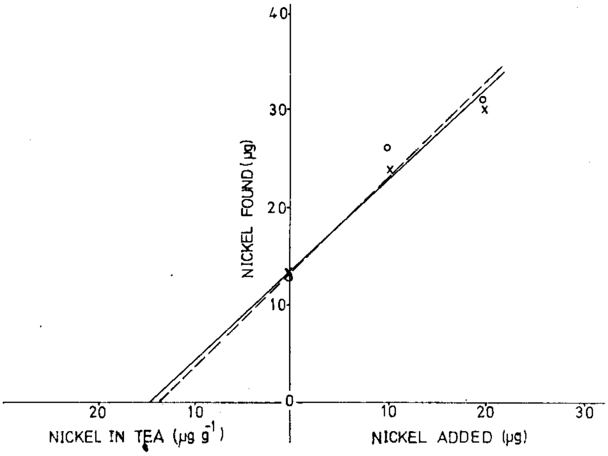


Fig. 7. The analysis of the tea sample by the method of standard additions. (○----○) A.a.s.; (× —— ×) g.l.c.

reagents. Burke and Albright[24] found both methods to be satisfactory, although they recommended wet ashing for instant teas. The above results show overall agreement, although the dry ashing method does seem to produce a wider variation in the results. Blank values showed that no contamination was produced from the reagents.

The results were checked by the use of standard additions to the tea sample before ashing, the resultant solutions being analysed by chromatography of the extracts and by atomic absorption spectrophotometry of the aqueous phases. These results are shown in Fig. 7, which proves the value for the nickel concentration to be 14.0 ± 1.5 µg g^{-1} and 13.5 ± 1.5 µg g^{-1} for the two respective techniques.

Figure 8 (B) shows a typical chromatogram for the extract from a sample of tea. This chromatogram was obtained by the use of a temperature programme. Figure 8 also shows chromatograms obtained under isothermal conditions; it is clear that temperature programming improves the resolution of the $Ni(T\text{-}TFA)_2$ peak, while retaining the optimal peak shape.

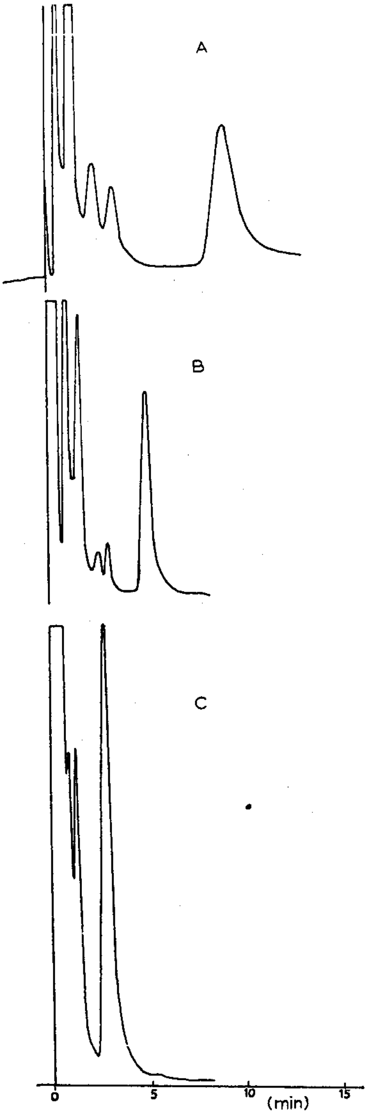
Fats

Samples of crude hydrogenated triglycerides containing traces of nickel were obtained for analysis, and these were mineralised by the dry ashing procedure. It was found that combustion of the samples in the furnace caused severe losses, and so

TABLE V

THE ANALYSIS OF FAT SAMPLES

Nickel content (µg g^{-1})		*No. of analyses*
Found	*Independent analysis (a.a.s.)*	
10.0 ± 0.9	9.5	5
3.7 ± 0.9	4.0	5



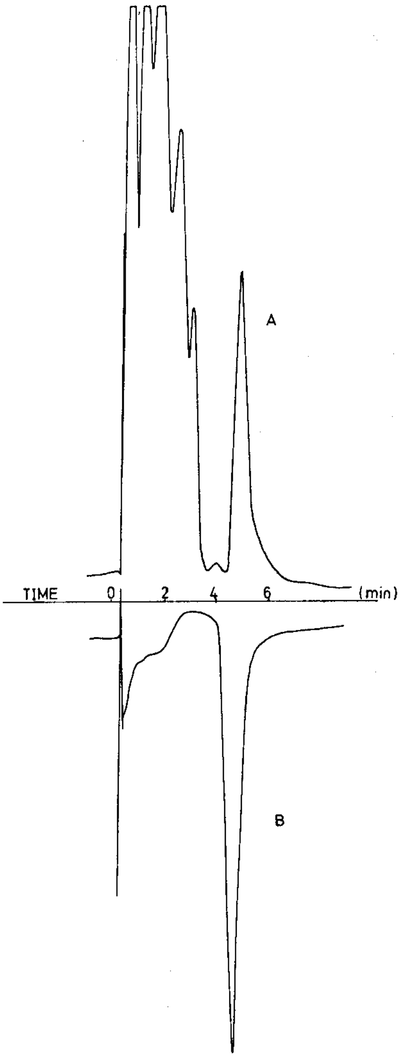


Fig. 8. The use of temperature programming in the analysis of nickel in tea. (A) Isothermal at 140°; (B) temperature programmed from 140° to 170°; (C) isothermal at 170°.

Fig. 9. Gas chromatogram of a fat extract. Amplifier attenuation $20 \cdot 10^2$. (A) 1.5 μl of fat extract; (B) 1.7 μl of standard $Ni(T\text{-}TFA)_2$ solution (5 p.p.m.).

the more volatile components of the fat were removed by preliminary heating on the hot-plate. Similarly it was found that ashing the sample to the extent that all of the carbon was removed also resulted in severe losses, and so the sample was removed from the furnace when a little carbon residue remained.

Analysis by gas chromatography according to the usual procedure gave the results shown in Table V. Once again, the temperature programme was used. These results again show reasonable agreement with the independent analyses for the samples, and Fig. 9 shows a typical chromatogram for an extract and for an authentic sample of $Ni(T\text{-}TFA)_2$. The uneven base-line is simply a consequence of the temperature programme.

CONCLUSIONS

The use of gas–liquid chromatography offers a sensitive method for the separation and determination of traces of nickel in a variety of samples.

A recent review[25] of the applications of non-flame cells in atomic absorption and atomic fluorescence spectroscopy lists the limits of detection for nickel by various modifications. The sensitivity of the present method appears to compare very favourably with these various modifications and in terms of practicality, the gas chromatographic method is equally convenient.

It is hoped that this work contributes in some way to the ultimate goal of metal analysis by gas chromatography, which must surely be the simultaneous determination of several metals.

We are indebted to International Nickel Ltd. for the provision of the sample of a Brooke Bond freeze-dried vending tea, to Van den Bergh and Jurgens Ltd. for providing the samples of crude hydrogenated fats, and to the University of Birmingham for the provision of a research grant to R.S.B.

SUMMARY

A rapid and sensitive method for the determination of trace amounts of nickel has been developed, in which a volatile nickel chelate is analysed by gas–liquid chromatography. The method involves extraction of the aqueous solution of nickel at pH 4.5–5.0 with a solution of monothiotrifluoroacetylacetone in *n*-hexane, the use of a single extraction giving recoveries in excess of 90%. The extract is washed with sodium hydroxide solution (0.01 *M*) to destroy residual chelating agent, and the bis(monothiotrifluoroacetylacetonato)nickel(II) is determined by gas chromatography on a 4-ft. teflon column packed with 5% silicone gum rubber (E350) on "Universal B" support. The extreme sensitivity of the electron capture detector enables $5 \cdot 10^{-11}$ g of nickel to be detected, while nickel concentrations down to 0.1 μg ml^{-1} have been determined in routine analyses. The effect of diverse metal ions is examined; the most significant interference, resulting from the presence of copper(II), is easily eliminated by preliminary treatment of the solution with hydrogen sulphide. The new method has been applied to the determination of nickel at the percentage level in an alloy, and at trace levels in tea and fat samples. The results show good agreement with independent analyses for the samples.

RÉSUMÉ

Une méthode rapide et sensible est proposée pour le dosage de traces de nickel; elle consiste à analyser un chélate volatil de nickel par chromatographie gaz–liquide. On procède à une extraction à l'aide d'une solution de monothiofluoroacétylacétone dans le n-hexane, à pH 4.5–5.0. On examine l'influence de divers métaux. L'interférence du cuivre(II) est la plus importante; on l'élimine facilement par traitement préliminaire à l'hydrogène sulfuré. Cette nouvelle méthode a été appliquée au dosage du nickel dans un alliage et au dosage de traces de nickel dans des échantillons de thé et de matières grasses.

ZUSAMMENFASSUNG

Es wurde eine schnelle und empfindliche Methode für die Bestimmung von Spurenmengen Nickel entwickelt, bei der ein flüchtiger Nickelchelat durch Gas–Flüssig-Chromatographie analysiert wird. Bei der Methode wird Nickel aus wässriger Lösung bei pH 4.5–5.0 mit einer Lösung von Monothiotrifluoracetylaceton in *n*-Hexan extrahiert, wobei mit einer einzigen Extraktion mehr als 90% erfasst werden. Der Extrakt wird zur Beseitigung des verbliebenen Chelatisierungsmittels mit 0.01 *M* Natronlauge gewaschen und das Bis(monothiotrifluoracetylacetonato)-nickel(II) durch Gas-Chromatographie an einer 4 ft.-Teflonsäule bestimmt, die mit 5% Silicongummi (E350) auf "Universal B"-Träger gefüllt ist. Die extreme Empfindlichkeit des Elektroneneinfang-Detektors ermöglicht den Nachweis von $5 \cdot 10^{-11}$ g Nickel, während Nickelkonzentrationen bis zu 0.1 μg ml^{-1} herab bei Routineanalysen bestimmt wurden. Der Einfluss verschiedener Metallionen wurde untersucht. Die grösste Störung wird durch die Gegenwart von Kupfer(II) verursacht; sie kann leicht durch vorhergehende Behandlung der Lösung mit Schwefelwasserstoff vermieden werden. Die neue Methode wurde auf die Bestimmung von Nickel im Prozentbereich in einer Legierung und im Spurenbereich in Tee- und Fettproben angewendet. Die Ergebnisse stimmen mit unabhängigen Analysen der Proben gut überein.

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SELECTIVE SEPARATION OF TIN(IV) BY SOLVENT EXTRACTION WITH N-BENZOYL-N-PHENYLHYDROXYLAMINE

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The determination of small amounts of tin in natural and industrial samples requires a preliminary separation of tin from the basic components and from a great number of other elements present in low concentrations. For this purpose several methods are used: distillation of tin(IV) halides[1], precipitation with hydrogen sulphide or ammonia in the presence of a suitable collector[2], solvent extraction with benzene, esters, ketones, amines or organophosphorus extractants[3], or solvent extraction of tin chelates of organic ligands[4]. The most suitable for practical applications are the solvent extraction methods, but these methods have relatively low selectivity.

In the present work, some new possibilities were investigated for a more selective and more effective extractive separation of tin. As the separation of small amounts was the main interest, the extraction of tin chelates was studied.

Tin may be present in solutions in the oxidation states tin(II) and tin(IV). Tin(II) is comparatively easily oxidized to tin(IV) under the action of air and light; hence, from a practical point of view, the behaviour of tin(IV) is more important than that of tin(II). Tin(IV) has the electronic configuration $4\,d^{10}$. The unoccupied 5 s and 5 p orbitals and the high positive charge of tin(IV) are the reason for its strong tendency towards hydrolysis. The same factors are responsible for the reactions of tin(IV) with organic reagents possessing functional groups containing oxygen or oxygen and nitrogen atoms, such as phenylfluorone, quinalizarin, purpurin, cupferron, pyrocatechol violet, oxine, N-benzyl-N-phenylhydroxylamine, phenylarsonic acid, etc. Tin(IV) forms five- or four-membered rings with these reagents.

Suitable reagents for the selective chelate extraction of tin(IV) are N-benzoyl-N-phenylhydroxylamine and phenylarsonic acid. Both reagents react with tin(IV) in a comparatively acidic medium. In the present paper, the selective solvent extraction of tin(IV) with N-benzoyl-N-phenylhydroxylamine (BPHA) is discussed. It is known that BPHA can extract several metals from 1–11 *M* hydrochloric acid solutions; in addition to tin(IV), it is possible to extract titanium(IV), zirconium(IV), hafnium(IV), niobium(V), tantalum(V), antimony(V), molybdenum(VI), tungsten(VI), vanadium(V), chromium(VI) and cerium(IV).

Lyle and Shendriker[6,7] found that the maximum distribution coefficient of tin(IV) in solvent extraction with 1% chloroform solutions of BPHA ($D_{\text{Sn}} = 17$) could be obtained at the acidity 0.8*M* hydrochloric acid. Rakovskii and Petrukhin[8] showed that it was possible to extract tin(IV) with BPHA from 10 *M* sulphuric acid medium.

From slightly hydrochloric acid medium, tin(IV) reacts probably with the deprotonated form of BPHA. BPHA is a weak acid ($pK_{HA} = 8.15$)[9] and a positively charged chelate complex of tin(IV) is formed having a metal–ligand ratio of 1:2.[6] The effective solvent extraction of such complexes can be carried out in the presence of an appropriate anionic partner[10-12].

EXPERIMENTAL

Standard solution of tin(IV)

Tin(IV) chloride solution was prepared by dissolving metallic tin (3N purity) in concentrated hydrochloric acid and hydrogen peroxide on a water bath. The solution was evaporated almost to dryness and the residue was dissolved and diluted to a measured volume with 2 *M* hydrochloric acid. The concentration of the resulting solution was determined by titration with DCTA[13].

The experiments were carried out with 10 ml of aqueous $2.52 \cdot 10^{-4}$ *M* tin(IV) solution (300 μg). The ratio of the aqueous and organic phases was 1:1.

BPHA solutions

An aqueous or chloroform 0.1% (w/v) solution of BPHA was used ($4.7 \cdot 10^{-3}$ *M*). BPHA was introduced in the aqueous phase by addition of acetic acid, chloroacetic acid or ethanol. The reagent was purified by recrystallization from hot water.

The reagents were of Merck p.a. quality. The chloroform was scrubbed several times with water and distilled before use.

Procedures

The experiments for the evaluation of the distribution coefficients were carried out in 50-ml Jena reaction vessels. The two phases were mixed in a shaking machine at 80 rev. min^{-1}. It was established that the extraction equilibrium was attained within 10 min.

The distribution coefficients were calculated from the results of spectrophotometric determinations of tin(IV) with pyrocatechol violet[14] both in the aqueous phase and in the extract after stripping for 10 min with 8 *M* hydrochloric acid.

RESULTS AND DISCUSSION

The extraction of the tin(IV)–BPHA complex with chloroform was plotted as a function of the hydrochloric acid concentration in the presence of acetic acid, chloroacetic acid and ethanol (Fig. 1); the curves are similar in character. The highest values for the distribution coefficients (D_{Sn}) were obtained in the interval 0.2–0.5 *M* hydrochloric acid. Much lower values of D_{Sn} were obtained at higher acidities. This finding may be explained either as a decreased dissociation of the reagent, or as the formation of more saturated, in respect to chloride ions, complexes of tin, which do not react with BPHA[15]. It can also be seen from the Figure that the presence of ethanol, acetic acid or chloroacetic acid increased the distribution coefficients. The D_{Sn} values for 0.5 *M* hydrochloric acid in the presence of various additions are given in Table I; the *S* values given in the third column represent the ratio of the distribution coefficients of tin(IV) in the presence and absence of additions to the aqueous phase.

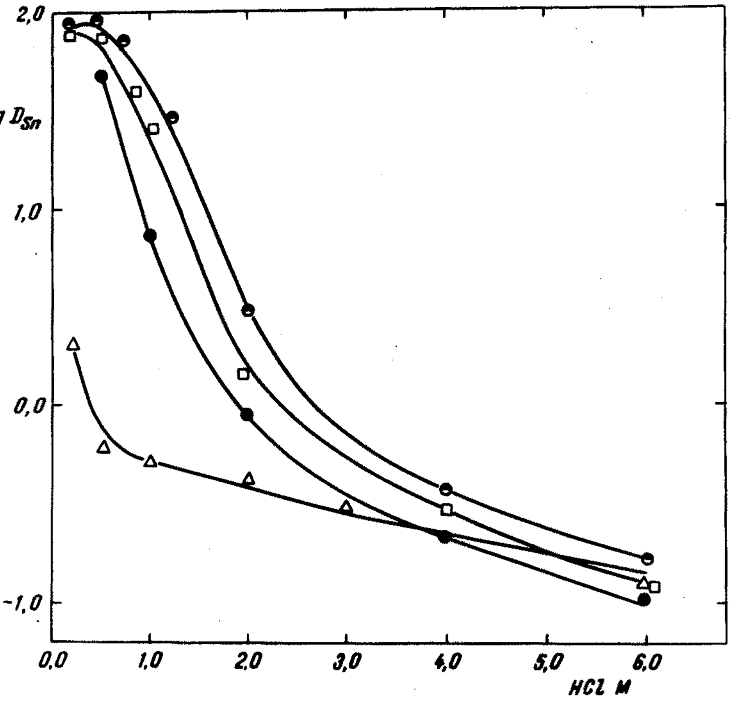

Fig. 1. Dependence of log D_{Sn} on the hydrochloric acid concentration in the aqueous phase when extracting the tin(IV)–BPHA complex. (△) BPHA introduced in the organic phase. BPHA introduced in the aqueous phase with (●) C_2H_5OH; (□) CH_3COOH; (◒) $CH_2ClCOOH$.

TABLE I

DISTRIBUTION COEFFICIENTS FOR TIN(IV) IN DIFFERENT MEDIA

Medium	D_{Sn}	*S*
0.5 *M* HCl	0.62	—
0.5 *M* HCl+1 ml 95% C_2H_5OH	49.00	79.3
0.5 *M* HCl+1 ml 50% CH_3COOH (0.8 *M*)	74.0	119.3
0.5 *M* HCl+1 ml 75% $CH_2ClCOOH$ (0.8 *M*)	99.0	160.0

The increase in D_{Sn} in the presence of acetic and chloroacetic acids may be explained on the assumption that a cationic complex of tin(IV) with BPHA is formed in the investigated system, which is extracted after neutralization of its charge with the anion of the respective acid. The infrared spectra of precipitates obtained from acetic and hydrochloric acid media were taken in Nujol and in Fluoro B; the stretching vibrations of C=O could not be observed, hence acetic acid is not a component of the complex. The spectra of chloroform solutions of precipitates showed a similar picture; there was, however, a band shifted by 100 cm^{-1} (from 1630 to 1530 cm^{-1}) which was also observed by Lyle and Shendriker[6] in the infrared spectrum of the tin(IV)–BPHA complex. This shift was explained by Lyle as due to a coordinate bond between C=O of BPHA and tin(IV). Micro-analytical results for the composition of the precipitate confirmed the data of Lyle and Shendriker, namely $Sn(BPHA)_2Cl_2$. Hence the increase in tin extraction with BPHA in the presence of acetic acid, chloroacetic acid or alcohol could not be explained by assuming participation of these compounds in the tin(IV) complex.

Investigating the solvent extraction of a number of metal ions with BPHA, Förster[16] found that the extraction was improved when an acetonic solution of the reagent was used. This finding was explained by Förster as being due to the increased solubility of the metal chelates in the chloroform–acetone mixture as well as to an increase in the reagent concentration present in the aqueous phase. It may be assumed that the observed increase in extraction coefficients, in the present case, caused by alcohol, acetic acid or chloroacetic acid is also due to the different distribution of the reagents between the two phases. The results shown in Table II are in agreement with this assumption.

TABLE II

DISTRIBUTION COEFFICIENTS OF BPHA IN DIFFERENT MEDIA

Composition of organic phase	*Composition of aqueous phase*	D_{BPHA}
	0.5 *M* HCl	181
0.1% BPHA	0.5 *M* HCl + 1 ml 95% C_2H_5OH	164
in $CHCl_3$	0.5 *M* HCl + 1 ml 50% CH_3COOH	117
	0.5 *M* HCl + 1 ml 75% $CH_2ClCOOH$	87.8

Separation of tin from interfering ions

The metal ions which are also extracted at the acidity optimal for the extraction of tin(IV) (0.5 *M* hydrochloric acid) were studied; these were titanium(IV), vanadium(V), zirconium(IV), hafnium(IV), tantalum(V), niobium(V), molybdenum(VI), tungsten(VI), antimony(V), chromium(VI) and cerium(IV). These ions were masked by complex-formation with tartaric acid or hydrogen peroxide and the resulting complexes were stable and soluble in water. In acidic medium chromium(VI) was reduced by the hydrogen peroxide to chromium(III) which was not extracted. Molybdenum(VI) and vanadium(V) were partially extracted but remained in the organic phase when tin(IV) was back-extracted with 8 *M* hydrochloric acid. Extractions were therefore carried out from 0.5 *M* hydrochloric acid medium in the presence of 1 ml of 2 *M* tartaric acid, 1 ml of 30% hydrogen peroxide and 1 ml of 1% solution of BPHA in acetic acid. The results are shown in Table III.

Extractions of 30 μg of tin were also carried out in the presence of 10-fold amounts of titanium(IV), vanadium(V), zirconium(IV), hafnium(IV), niobium(V), tantalum(V) and antimony(V); the average result was 32 μg tin.

The results obtained so far have shown that the investigated extraction system could be used for separation of tin in determinations of this element in rocks, minerals and industrial products.

TABLE III

EFFECT OF INTERFERING IONS

Metal ion	*Ratio Sn/M*	*Added Sn(μg)*	*Found Sn(μg)*	*Metal ion*	*Ratio Sn/M*	*Added Sn(μg)*	*Found Sn(μg)*
Ti(IV)	1: 10	30	29.5	Ta(V)	1: 1	30	30.0
	1: 50	30	29.0		1: 10	30	28.0
	1:100	30	31.0	Mo(VI)	1: 10	30	29.7
V(V)	1: 50	30	28.6		1: 50	30	29.3
	1:100	30	28.2	W(VI)	1: 10	30	29.8
Zr(IV)	1: 1	300	296.0		1:100	30	30.1
	1: 10	30	30.5	Sb(V)	1: 1	29.8	29.8
	1: 50	30	30.0		1: 10	30	31.0
	1:100	30	31.4		1: 50	30	28.7
Hf(IV)	1: 10	50	48.0		1:100	30	30.2
	1: 50	30	29.3	Cr(VI)	1: 50	30	29.9
	1:100	30	29.3	Ce(IV)	1: 1	300	296.0
Nb(V)	1: 1	30	30.0		1: 10	30	29.2
	1: 10	30	29.4		1: 50	30	28.5
	1:100	30	28.0		1:100	30	28.0

SUMMARY

The solvent extraction of tin(IV) with chloroform solutions of BPHA in hydrochloric acid medium is described. Maximum extraction was obtained from 0.2–0.5 *M* hydrochloric acid. The distribution coefficient of tin was increased 100 to 150 times when BPHA was introduced in the aqueous phase with ethanol, acetic acid or chloroacetic acid. Under the optimal conditions for extraction of tin(IV), Ti(IV), V(V), Cr(VI), Zr, Hf, Nb(V), Ta(V), Mo(VI), W(VI), Ce(IV) and Sb(V) interfered. When hydrogen peroxide and tartaric acid were added as masking reagents, tin(IV) could be separated from these ions in ratios from 1:50 to 1:100.

RÉSUMÉ

On décrit une extraction de l'étain(IV) dans un solvant, en utilisant des solutions de BPHA dans le chloroforme, en milieu acide chlorhydrique. Le coefficient de partage de l'étain est augmenté 100 à 150 fois lorsque BPHA est introduit dans la phase aqueuse, avec éthanol, acide acétique ou acide trichloracétique. Par addition de peroxyde d'hydrogène et d'acide tartrique comme réactifs de masquage, l'étain(IV) peut être séparé d'ions présentant des interférences tels que Ti(IV), V(V), Cr(VI), Zr, Hf, Nb(V), Ta(V), Mo(VI), W(VI), Ce(IV) et Sb(V).

ZUSAMMENFASSUNG

Es wird die Extraktion von Zinn(IV) mit BPHA-Lösungen in Chloroform aus salzsaurem Medium beschrieben. Maximale Extraktion wurde im Bereich 0.2–0.5 *M* Salzsäure erreicht. Der Verteilungskoeffizient von Zinn wurde um den Faktor 100 bis 150 erhöht, wenn BPHA in der wässrigen Phase mit Äthanol, Essigsäure oder Chloressigsäure eingesetzt wurde. Unter den optimalen Bedingungen für

die Extraktion von Zinn(IV) störten Ti(IV), V(V), Cr(VI), Zr, Hf, Nb(V), Ta(V), Mo(VI), W(VI), Ce(IV) und Sb(V). Bei Zugabe von Wasserstoffperoxid und Weinsäure als Maskierungsreagenzien konnte Zinn(IV) von diesen Ionen in den Verhältnissen 1:50 bis 1:100 abgetrennt werden.

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THE TOLUENE EXTRACTION OF SOME ELEMENTS AS IODIDES FROM SULPHURIC ACID–POTASSIUM IODIDE MEDIA. APPLICATION TO NEUTRON ACTIVATION ANALYSIS

PART I. EXTRACTION BEHAVIOUR OF As, Au, Bi, Br, Cd, Cu, Ga, Ge, In, Hg, Mo, Pb, Sb, Se, Sn, W AND Zn

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The extraction behaviour of many elements into various organic solvents from iodide systems has been studied by a number of investigators[1–3]. These studies were almost exclusively carried out with polar solvents such as ethers and ketones, and in general, the selectivity for any one element is not outstanding. However, with benzene or toluene as extractant, excellent selectivity has been reported in the case of tin[4] and for antimony[5,6]. The extraction of tin iodide into benzene or toluene from sulphuric acid–potassium iodide solutions has been developed into a sensitive spectrophotometric procedure by several workers[7–10]. Apart from tin and germanium[11], however, and a limited amount of information on antimony[12] and arsenic[13], the quantitative behaviour of other elements in this system is not well known (except for some extraction data[14] obtained at one particular value of acid and iodide concentrations). For this reason, and because of the practical advantages of benzene or toluene over polar solvents, it seemed worth investigating the quantitative extraction behaviour of other elements with toluene from sulphuric acid–potassium iodide solutions over a wide range of conditions, with a view to developing chemical separation methods (particularly for neutron activation applications) both for tin and antimony and for any other elements that might prove suitable.

Since the investigation was aimed ultimately at developing extractive radiochemical separation methods, especially for tin, antimony and arsenic, and to obtain information on possible interferences in these separations, in the first stage elements were studied which might be expected to extract at least partially or would represent important radiochemical interferences. The extraction data were obtained by using γ-emitting tracer solutions to obtain the distribution ratio of the two phases from activity measurements. Toluene was preferred to benzene, being less toxic (as well as less water-soluble and less dense). The elements studied so far in iodide–sulphuric acid media are: As, Au, Br, Cd, Cu, Ga, Ge, Hg, In, Mo, Sb, Se, Sn, W and Zn. In addition, the behaviour of bismuth and lead, though not of interest for activation analysis, was investigated for general chemical interest and possible classical applications.

EXPERIMENTAL

Apparatus

All extractions were performed in cylindrical 50-ml separating funnels with 10 ml of both aqueous and toluene phases. Vigorous hand shaking for 3 min was employed after the phases had equilibrated at 25° in a water bath.

Reagents

Analytical-grade sulphuric acid, toluene, potassium iodide and double-distilled water were used throughout.

Counting

Scintillation counting of γ-emitting radiotracers was used. Either a single-channel analyser with a well-type 1.5 × 1.5″ NaI(Tl) crystal or a multichannel analyser (256-channel) with a 3 × 3″ well-type NaI(Tl) crystal was used. The latter was used where discrimination was necessary against γ-rays from other elements (*e.g.* in the parent–daughter relationship ^{115}Cd–^{115m}In), or where only a higher γ-ray energy was counted to minimize absorption errors between the aqueous and toluene phase. Only 1–2 ml of each phase was measured and for such geometry, absorption errors are small; this was checked experimentally and the difference was found to be negligible.

Radiotracer solutions

These were prepared locally by irradiation in the Institute's TRIGA MARK II reactor. Only pure metals or oxides were used; these were dissolved in either sulphuric acid, sodium hydroxide, or water and the solutions were then diluted. Thus the only foreign ion introduced into the extraction vessel was a small amount of sodium in certain cases*. The purity of the tracer solutions was checked by γ-spectrometry. In the case of tin, purification from ^{125}Sb was first carried out by an iodide extraction method.

The following radionuclides were used:

^{76}As (26.4 h), ^{198}Au (64.8 h), ^{82}Br (35.4 h), ^{115}Cd (53.5 h), ^{64}Cu (12.8 h), ^{72}Ga (14.1 h), ^{75}Ge (83 min) and ^{77}Ge (11.3 h), ^{115}In (4.5 h) and ^{116}In (54 min), ^{203}Hg (47 d), ^{99}Mo (66 h), ^{122}Sb (64.3 h) and ^{124}Sb (60 d), ^{75}Se (120 d), ^{113}Sn (115 d) and ^{117m}Sn (14 d), ^{187}W (23.8 h) and ^{65}Zn (245 d).

^{212}Pb (10.6 h) and ^{212}Bi (60.6 min) tracers were prepared by extraction from ^{224}Ra(ThX) preparations; dithizone was used for lead and cupferron for bismuth. For ^{212}Pb, time was allowed after the toluene extraction experiments for radioactive equilibrium to be re-established before measurement.

The concentration of each element added for the extraction experiments is given in the appropriate section of the results.

Method

A suitable volume of 15 *N* sulphuric acid, previously volumetrically standardized, was pipetted into the extraction vessel followed by dropwise addition of the radiotracer solution from a 5-ml polythene vial with a drawn-out neck; generally

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* In the case of gold, a small amount of chloride ion was also introduced.

10–50 drops were added. Potassium iodide solution of either 5 *M* or 0.5 *M* concentration (or weaker in the case of antimony and mercury) was then added in the requisite amount by pipette and the volume was adjusted to 10.0 ml with water by pipette; 10.0 ml of toluene were then added and the vessel was placed in a water bath at 25° for 10 min. It was then removed, wiped and vigorously shaken for 3 min, and the phases were allowed to separate for some minutes. Finally 1- or 2-ml aliquots of each phase were pipetted into 5-ml measuring vials and the activities were measured as described above.

From the ratio of the activities, the distribution coefficient and the percentage extraction into toluene was calculated.

Extraction curves were obtained at 4 or more potassium iodide molarities for varying sulphuric acid normalities (3–15 *N*) for extractable elements, or negative data at high (1.0 *M*) and low (0.05 *M* or 0.1 *M*) potassium iodide molarities for non-extractable elements.

RESULTS

As mentioned above, the temperature was controlled at 25°. The extraction of some elements, *e.g.* antimony and germanium, was found to be very temperature-dependent, the extraction increasing with temperature.

The upper range of acidity that may be used at a particular potassium iodide molarity is limited by the formation of a $K_2SO_4 \cdot 2\,H_2O$ precipitate. The practical upper limits at 25° are 6 *N* H_2SO_4 for 1.5 *M* KI, 9 *N* H_2SO_4 for 1.0 *M* KI and 12 *N* H_2SO_4 for 0.5 *M* KI.

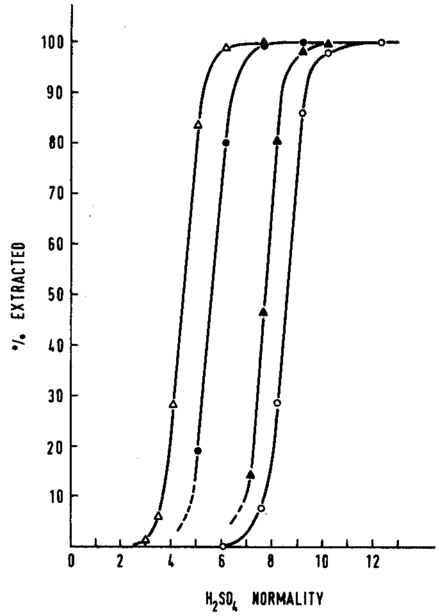
The potassium iodide solutions were made up freshly at least weekly during these studies. However, no evidence was obtained to suggest that yellow-coloured old solutions containing iodine gave different results. A few experiments were made on the extraction of arsenic with a solution of potassium iodide containing dissolved free iodine, with virtually identical extraction results. Storing in the dark slows the development of the colouration.

Extractable elements

Arsenic. The extraction behaviour of arsenic(III) is shown in Fig. 1. The concentration of arsenic used in the aqueous phase was *ca.* $5 \cdot 10^{-5}$ *M* for the construction of the curves. However, in subsequent separation experiments, arsenic(III) was used up to $7 \cdot 10^{-3}$ *M* at a number of points on the curves, with identical extraction behaviour.

Arsenic added as arsenic(V) will be reduced to arsenic(III) by the hydriodic acid present.

Germanium. The extraction behaviour of germanium(IV) is shown in Fig. 2. The full lines are the results obtained in this study, and the dashed lines are results reported by Tanaka[11]. The two sets of curves are parallel but displaced by approximately one unit of sulphuric acid normality. Details of Tanaka's method which might explain the discrepancy, such as the temperature, were not available; it is unlikely that the differences are due to the use of toluene instead of benzene. Apart from a single point at 9 *N* sulphuric acid (6% extraction), it was not possible to obtain the 1.0 *M* KI curve, which Tanaka shows, owing to potassium sulphate precipitation. Some points were duplicated, as shown in the curves, with a different radiotracer solution and fresh iodide and acid solutions, as a check.



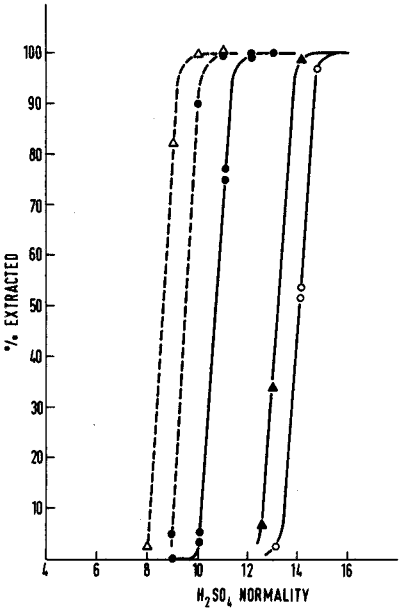


Fig. 1. Extraction of arsenic(III) into toluene as a function of H_2SO_4 and KI concentrations at 25°. (△) 1.0, (●) 0.5, (▲) 0.1, (○) 0.05 *M* KI.

Fig. 2. Extraction of germanium(IV) into toluene as a function of H_2SO_4 and KI concentrations at 25°. (——) This work; (----) results of Tanaka[11]. (△) 1.0, (●) 0.5, (▲) 0.1, (○) 0.05 *M* KI.

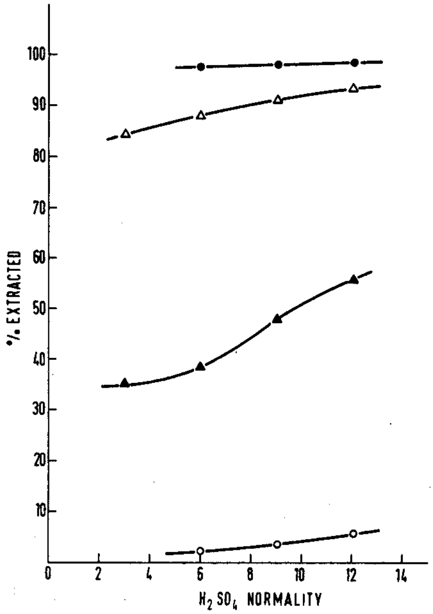


Fig. 3. Extraction of mercury(II) into toluene as a function of H_2SO_4 and KI concentrations at 25°. (○) 0.05, (▲) 0.01, (△) 0.002, (●) 0.0005 *M* KI.

The interpretation of the radiochemical results is more complex than for any other tracer used, because of the daughter nuclide ^{77}As formed from ^{77}Ge and ^{77m}Ge. This difficulty was overcome by using freshly irradiated germanium which is then mainly radioactive due to ^{75}Ge (83-min half-life). Fortunately, the γ-rays from ^{77}As are of low abundance. With older tracer solutions of ^{77}Ge, γ-spectrometry was used to evaluate the germanium extraction, by means of only the 0.63- and 0.71-MeV peaks. Since arsenic was extracted at lower acidities than germanium, any error from ^{77}As would make the apparent extraction higher, *i.e.* it would not explain the discrepancy.

Mercury. The extraction of mercury, added as mercury(II), is shown in Fig. 3. The extraction was appreciable only at very low iodide molarities. From 0.0005 *M* potassium iodide, the extraction was 97.5–98.5% in 6 *N*–12 *N* sulphuric acid. (The extraction found at 10 *N* H_2SO_4–0.01 *M* KI was, from the curve, 51 %, in exact agreement with the result of Grimanis *et al.*[14].) The concentration of mercury in the aqueous phase was $5 \cdot 10^{-4}$ *M* for curves at 0.05 *M* and 0.01 *M* and $5 \cdot 10^{-6}$ *M* for the curves at 0.002 *M* and 0.0005 *M*.

Antimony. The extraction curves for antimony(III) are shown in Figs. 4a and b. The extraction from 0.05 *M* iodide was 99.4–99.6 % in 6–12 *N* sulphuric acid; this is an important plateau for practical applications. Noticeable is the increasing tendency at low potassium iodide concentrations, to lower extraction, presumably owing to hydrolysis at a given acidity as the iodide concentration decreases (see Fig. 4b). On the other hand, because of the formation of the complex antimonate ion at high iodide concentrations, extraction tended to increase with falling iodide concentration (Fig. 4a). Thus for a given acidity there was a value of the iodide concentration giving

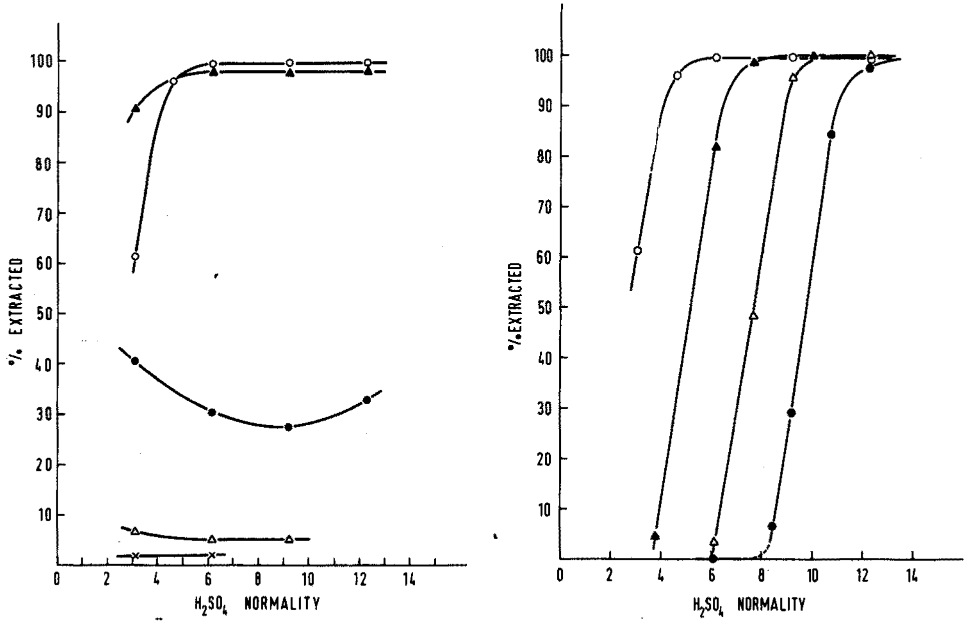


Fig. 4. (a) Extraction of antimony(III) into toluene as a function of H_2SO_4 and KI concentrations at 25°. (×) 1.5, (△) 1.0, (●) 0.5, (▲) 0.1, (○) 0.05 *M* KI. (b) Extraction of antimony(III) into toluene as a function of H_2SO_4 and KI concentrations at 25°, for low iodide concentrations. (○) 0.05, (▲) 0.01, (△) 0.002, (●) 0.0005 *M* KI.

maximum extraction. A specific instance of this was previously found by Ramette[12] who investigated the extraction at 10 N sulphuric acid.

The concentration of antimony in the aqueous phase was $4 \cdot 10^{-5}$ M for the curves between 1.5 and 0.05 M potassium iodide, and $5 \cdot 10^{-6}$ M for those between 0.01 and 0.0005 M potassium iodide. A number of points on the curves in Fig. 4a were shown to be the same at $4 \cdot 10^{-3}$ M antimony.

Higher oxidation states are reduced to antimony(III) by hydriodic acid.

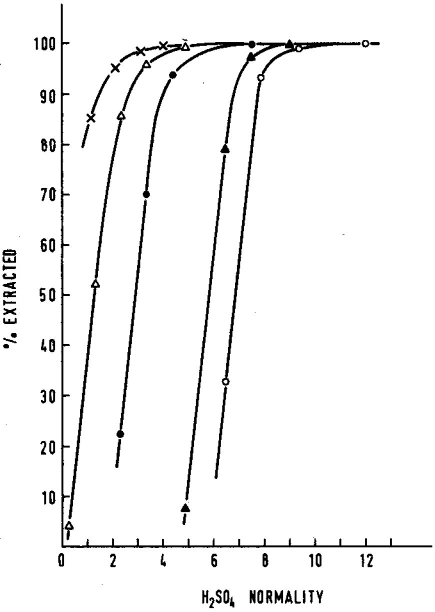


Fig. 5. Extraction of tin(IV) into toluene as a function of H_2SO_4 and KI concentrations at 25°. (×) 1.5, (△) 1.0, (●) 0.5, (▲) 0.1, (○) 0.05 M KI.

Tin. The extraction curves for tin, added as tin(IV), are shown in Fig. 5. Tanaka[11] has published similar curves for the benzene extraction of tin(IV) at potassium iodide molarities of 1.0, 0.5 and 0.1 M. The values found in the present work were virtually identical to those of Tanaka; in addition, the behaviour at 1.5 and 0.05 M KI is given.

The tin concentration used in the aqueous phase was 10–25 μg ml^{-1}, *i.e.*, $1\text{–}2 \cdot 10^{-4}$ M. For the preparation of ^{125}Sb-free active tin solutions, a concentration of 10^{-2} M tin(IV) was used with identical extraction results.

Other elements

Experiments were made at concentrations of about 10^{-5} M for these elements. The chemical forms of the elements added were as follows: Au(III), Bi(III), Br$^-$, Cd(II), Cu(II), Ga(III), In(III), Mo(VI), Pb(II), Se(IV), W(VI) and Zn(II).

The elements bromine, cadmium, copper, gallium, gold, molybdenum, tungsten and zinc were found to be non-extractable (< 0.1%) by toluene over the range of acidity 3–9 N sulphuric acid for 1.0 M potassium iodide, and 3–12 N sulphuric acid for 0.1 M or 0.05 M potassium iodide.

TABLE I

% EXTRACTION OF INDIUM BY TOLUENE AS A FUNCTION OF H_2SO_4 AND KI CONCENTRATIONS AT 25°

KI molarity (M)	*Normality of H_2SO_4*			
	3 *N*	6 *N*	9 *N*	12 *N*
0.05	—	0.2	—	1.7
0.1	0.0	—	1.3	3.1
1.0	0.0	1.8	2.5	—

In the case of indium, slight extraction was found, as shown in Table I. Bismuth and lead were investigated over the same acidity range in 1.0, 0.5, 0.1 and 0.05 *M* potassium iodide; extraction was small, decreasing to zero at the higher iodide concentrations. The maximum extraction found in 0.05 *M* potassium iodide at the higher acidities was around 2% for bismuth and 5% for lead.

Selenium is a special case, since on addition of selenium (IV) solution, a selenium precipitate is produced by reduction with hydriodic acid. The amorphous form is soluble in toluene and hence "extraction" occurs. When acidities from 12 *N* to as low as 0.2 *N* and potassium iodide molarities of 1.0 *M* and 0.05 *M* were used, the percentage of selenium found in the organic phase was always greater than 99.0%. This behaviour was followed for a selenium concentration of 20 μg ml^{-1} in the aqueous phase, *i.e.*, $2.5 \cdot 10^{-4}$ *M*. When larger quantities than 50 μg Se ml^{-1} were used, it partially or completely precipitated from the 10 ml of organic phase. The solution was unstable and tended to precipitate in the presence of foreign ions (*e.g.* from wet-ashed material) or on standing.

DISCUSSION

The toluene extraction of iodides from sulphuric acid solutions displays some notable differences from the behaviour of polar solvents. Thus Au, Cu, Cd, In, Mo, W and Zn are not extractable with toluene, while the extraction of bismuth and lead is small. West[6] has already drawn attention to the higher selectivity of benzene over polar solvents in the case of antimony, and found that benzene lacked the general tendencies to iodide or iodide complex extraction displayed by other solvents. The data presented in this paper confirm this trend, while quantifying the behaviour of the extractable elements. From the extraction curves presented for As, Ge, Hg, Sb and Sn, it is apparent that quantitative extraction of these elements under specific conditions provides useful separations from many other elements. The form of the curves is also such that these extractable elements may be readily separated from each other.

The sulphuric acid solutions of wet-ashed residues afford a convenient starting point for extraction separations as the iodides, particularly for activation analysis. Moreover, toluene is a favourable solvent owing to its relative freedom from contamination by the aqueous phase.

On the basis of the above results, a method for the determination of arsenic and antimony in irradiated biological material has been developed[15]. In addition, a simple solvent extraction method for the determination of tin in such materials has been worked out[16].

The behaviour of many other elements remains to be quantified, in particular, the group VIII elements. However, it is of interest to report that in extraction experiments on a number of neutron-irradiated materials, no γ-emitting radionuclide of any elements other than those above were observed. The possible interferences of foreign ions should also be checked in separations developed for real systems.

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SUMMARY

The solvent extraction with toluene of 17 elements as iodides from sulphuric acid–potassium iodide media has been investigated with a view to developing separation methods, particularly for neutron activation analysis. Extraction curves at four or more potassium iodide molarities are presented as a function of acidity for the extractable elements As, Ge, Hg, Sb and Sn. Information is given for the elements Au, Bi, Br, Cd, Cu, Ga, In, Mo, Pb, Se, W and Zn over a range of conditions. The extraction curves are characteristic and enable a number of clean and useful separations to be made.

RÉSUMÉ

On examine les possibilités d'extraction dans le toluène pour 17 éléments sous forme d'iodures, en milieu acide sulfurique–iodure de potassium, en vue de la mise au point de méthodes de séparation, en particulier pour l'analyse par activation neutronique. Des courbes d'extraction à diverses molarités sont données, en fonction de l'acidité, pour As, Ge, Hg, Sb et Sn. Des renseignements sont fournis pour les éléments suivants: Au, Bi, Br, Cd, Cu, Ga, In, Mo, Pb, Se, W et Zn.

ZUSAMMENFASSUNG

Die Extraktion der Jodide von 17 Elementen mittels Toluol aus Schwefelsäure–Kaliumjodid-Medium wurde im Hinblick auf die Entwicklung von Trennverfahren untersucht, die sich besonders für die Neutronenaktivierungsanalyse eignen. Für die extrahierbaren Elemente As, Ge, Hg, Sb und Sn werden die Extraktionskurven als Funktion der Acidität bei vier oder mehr Kaliumjodid-Molaritäten vorgelegt. Über das Verhalten der Elemente Au, Bi, Br, Cd, Cu, Ga, In, Mo, Pb, Se, W und Zn bei verschiedenen Bedingungen wird berichtet. Die Extraktionskurven sind charakteristisch und ermöglichen die Ausführung einer Reihe von sauberen und nützlichen Trennungen.

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THE TOLUENE EXTRACTION OF SOME ELEMENTS AS IODIDES FROM SULPHURIC ACID–POTASSIUM IODIDE MEDIA. APPLICATION TO NEUTRON ACTIVATION ANALYSIS

PART II. DETERMINATION OF ARSENIC AND ANTIMONY IN BIOLOGICAL MATERIALS AT SUBMICROGRAM LEVELS

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In Part I[1] curves were presented for the extraction behaviour of a number of elemental iodides, including arsenic and antimony, from sulphuric acid–potassium iodide media with toluene. The present paper reports the application of this extraction system to the development of a method for the simultaneous determination of arsenic and antimony with quantitative yield in biological materials at submicrogram levels by neutron activation.

Apart from the precipitation and distillation methods, which are time-consuming, various solvent extraction methods have been used for arsenic and antimony. Extraction from hydrochloric acid with a variety of solvents has been known for a long time, and the hydrobromic acid system has also been used[2]. Both these systems, especially when used in conjunction with solvents such as ketones or ethers, are rather unselective and further radiochemical purification is usually needed by precipitation or ion-exchange steps. Use of a high-resolution Ge(Li) detector naturally reduces the degree of decontamination required, but because of its low efficiency, very long counting periods are required at submicrogram levels. Moreover, the main γ-ray peaks of ^{76}As and ^{122}Sb, at 0.559 and 0.564 MeV[3], are not absolutely resolved even with a good crystal, so that chemical separation is desirable.

The extraction of arsenic triiodide with chloroform was used by Prestwood[4] as a stage in a lengthy radiochemical procedure for arsenic, while Tanaka[5] has published a spectrophotometric method for the determination of arsenic in steels based on the benzene extraction of the iodide from hydrochloric acid.

In the present extraction method, arsenic and antimony are together selectively extracted into toluene from sulphuric acid–iodide media[1], and then sequentially washed out of the organic phase in high enough purity for direct measurement. The only other element found to extract under the conditions used is tin. One advantage of using a sulphuric acid medium is that extraction can be applied directly to the solution resulting from wet ashing with sulphuric and nitric acids.

The proposed method was tested on samples of Bowen's standard kale[6,7], on human hair samples and on a proposed N.B.S. standard material, orchard leaves (SRM 1571). Many preliminary experiments with tracers of ^{76}As and ^{122}Sb were performed with several matrices to check for losses during wet ashing, to check the validity of the extraction steps and the chemical yield, and the complete procedure for both elements simultaneously.

EXPERIMENTAL

Reagents

The 15 *N* sulphuric acid used was prepared from A.R. grade concentrated sulphuric acid and standardized titrimetrically.

The wash solutions were prepared as follows:

15 ml 12 *N* H_2SO_4/0.05 *M* KI: from 12 ml 15 *N* H_2SO_4, 0.75 ml 1.0 *M* KI and 2.25 ml H_2O.

15 ml 6 *N* H_2SO_4/0.05 *M* KI: from 6 ml 15 *N* H_2SO_4, 0.75 ml 1.0 *M* KI and 8.25 ml H_2O.

15 ml 6 *N* H_2SO_4/1.4 *M* KI: from 6 ml 15 *N* H_2SO_4, 4.2 ml 5.0 *M* KI and 4.8 ml H_2O.

The iodide solution was added immediately before use.

Apparatus

Long-necked Kjeldahl flasks (100 ml) were used for wet ashing, and 50-ml cylindrical separatory funnels for the extractions.

Counting equipment was a T.M.C. 256-channel analyser used with a 3 × 3 in NaI(Tl) well-type crystal. For some experiments, an ORTEC co-axial Ge(Li) high-resolution detector, volume 28 ml, resolution 2.75 keV at 1.33 MeV, was used in conjunction with an ORTEC biassed amplifier and a Nuclear Data ND-180 512-channel analyser.

Irradiations

Samples of 0.1–1.0 g were irradiated in quartz in the Institute's TRIGA MARK II reactor at a flux of $1.8 \cdot 10^{12}$n cm^{-2} sec^{-1} for about 20 h. Standards in the form of solutions of As_2O_3 and Sb_2O_3 in nitric acid (0.2 *N*) and hydrochloric acid (2 *N*), respectively, at 10 μg ml^{-1} were irradiated alongside in quartz tubes. Samples were "cooled" for 1–3 days after irradiation depending on their dose emission.

Method

The procedure begins with the toluene extraction of both elements from 12 *N* sulphuric acid–0.05 *M* potassium iodide; after a clean-up stage, arsenic is then washed out the toluene phase with 6 *N* sulphuric acid–0.05 *M* iodide, followed by antimony removal into 6 *N* sulphuric acid–1.5 *M* iodide. The complete procedure is outlined schematically in Fig. 1. The procedure is essentially quantitative as can be calculated from the extraction curves as follows. At stage (3) of the procedure, 100% of the arsenic and 99.5% of the antimony are extracted; stage (4) removes 0.4% antimony. Stage (6) removes 100% of the arsenic into the aqueous phase together with 0.9% of the antimony (0.6% for the first 10-ml wash, and 0.3% for the second 5-ml wash). Stage (7) recovers the remaining 98% antimony into the aqueous phase. These recovery figures were verified experimentally in a number of trials as described below.

The quantitative nature of the procedure, which eliminates yield determinations, means careful working. The procedure can be simplified (*e.g.* only single

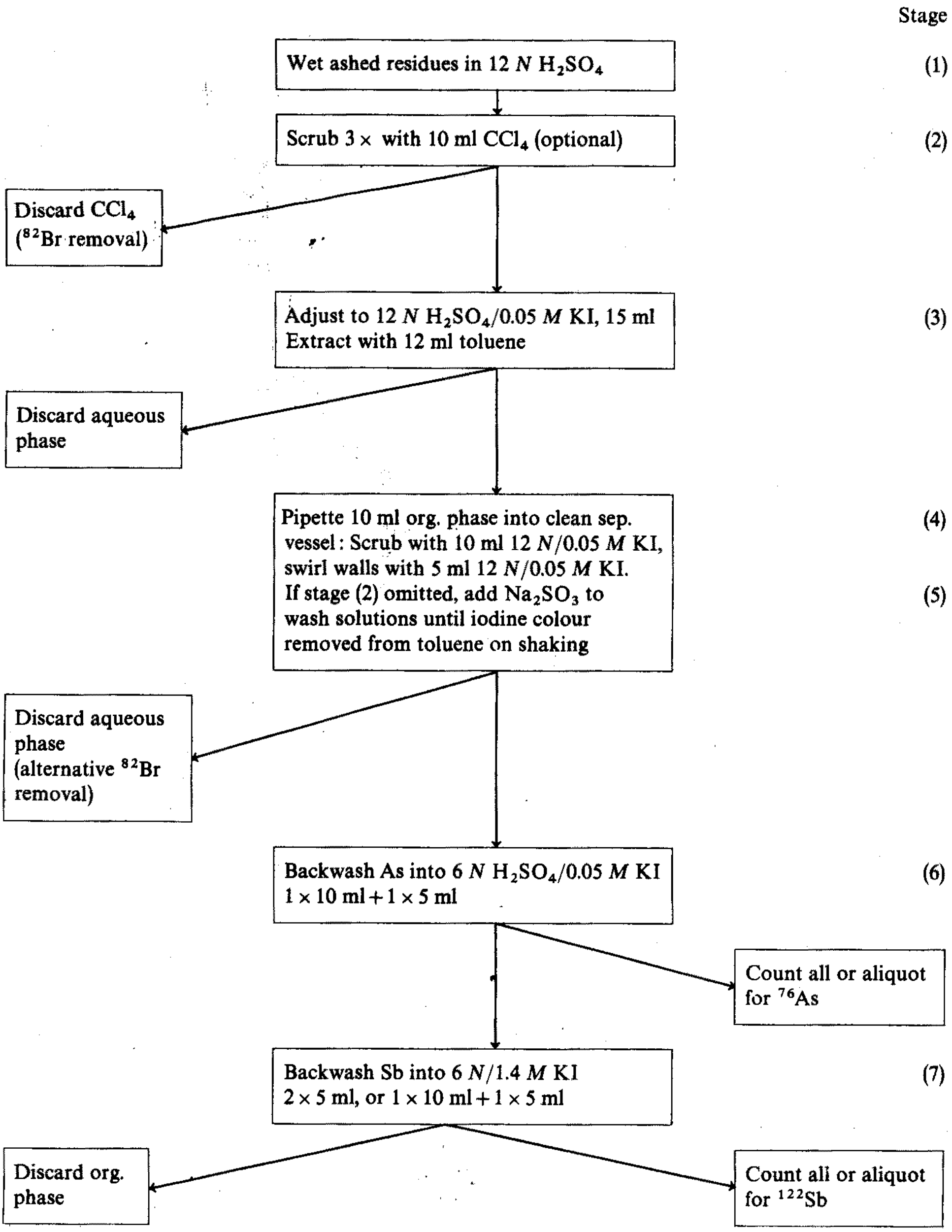

Fig. 1. Schematic flow sheet of arsenic and antimony separation.

stage back-extractions of arsenic and antimony, of small volume, say 5 ml) to be more rapid and semi-quantitative (and without loss of purity); chemical or re-irradiation yield determinations could then be applied if necessary. It should be noted that even if all the arsenic is not removed, it will not be extracted during the washing out of the antimony. Obviously also the method can be shortened to determine arsenic or antimony alone if required.

Procedure. Transfer the irradiated sample to the Kjeldahl flask; add 1–2 mg each of arsenic(III) and antimony(III) carriers, 4 ml of concentrated sulphuric and 2 ml of concentrated nitric acids. Boil the mixture cautiously over a flame. Add more nitric acid to effect oxidation if necessary, until only slight charring occurs on heating just to sulphuric acid fumes. Then add 30% hydrogen peroxide dropwise cautiously and reheat the solution. Repeat this step until the solution is quite colourless. This completes the oxidation and removes any nitric acid remaining. Finally add a few ml of water and boil to destroy excess of peroxide and to reduce the volume to below 10 ml. Transfer the cooled solution to a 50-ml separatory funnel with two rinsings, first with 1 ml of concentrated sulphuric acid plus a little water, and then with water alone. The volume should now be 13–14 ml. (The amount of sulphuric acid used, 5 ml, produces a 12 N solution when the volume is adjusted to 15 ml at stage (3).)

The rest of the procedure (Fig. 1) is self-explanatory. Note that for removal of traces of free bromine (^{82}Br), either stage (2) or stage (5) should be used; however, this may not be necessary with some samples. This is discussed further under *Interferences.*

Normally the aqueous fractions, as well as the standards, are made up to 25 ml in 6 N sulphuric acid, and either all are measured (flat top NaI(Tl) crystal or Ge(Li) crystal) or 10-ml aliquots are taken for the well-type detector. For samples with very low ^{76}As and ^{122}Sb activity, two 5-ml washes may be used for removing arsenic and antimony, so that all 10 ml may be measured, though a few percent of arsenic may be lost (see below). The antimony standard should also be made up to contain a concentration of potassium iodide equal to that in the sample to equalize self-absorption.

RESULTS

Losses during wet ashing, and recovery during first extraction

It was found that negligible loss of arsenic and antimony occurred during the ashing process. This is in agreement with the results of Hadzistelios and Grimanis[2], and the extensive experiments of Gorsuch[8]. To check possible losses, wet ashing was done as described above in the presence of weighed amounts of ^{76}As or ^{122}Sb (or ^{124}Sb) tracers, the wet-ashed solution was extracted at 12 N sulphuric acid–0.05 M iodide, and the activity of an aliquot of the extract was compared with a standard of the original radiotracer. For kale, which has a high calcium content, a calcium sulphate precipitate appeared on cooling and diluting the sulphuric acid solution. The extraction step was thus also checked for any possible losses by adsorption of this precipitate. The results are shown in Table I.

It is clear that complete recovery is obtained, except for antimony with 0.5-g quantities of kale; and complete recovery of antimony (with the expected 0.5% in the aqueous phase) can be obtained by using a 0.2-g kale sample.

Freedom of arsenic and antimony fractions from cross-contamination

Experiments were made to check whether the separation is in practice as good as the extraction curves[1] predict. The complete separation procedure was performed on an irradiated sample of N.B.S. standard orchard leaves, SRM 1571, which was found to have a high arsenic and antimony content, so that the Ge(Li) crystal could be used to check the purity of the fractions. The spectra of the individual fractions and of pure radiotracer standards are shown in Fig. 2. Clearly, the purity of the fractions is excellent.

TABLE I

PERCENTAGE RECOVERY OF ARSENIC AND ANTIMONY ON WET ASHING AND EXTRACTION AT 12 N SULPHURIC ACID–0.05 M IODIDE BY COMPARISON WITH STANDARDS

Element	*Matrix*	*Weight (g)*	*% in org. phase*	*% in aqueous phase*
As	Grass	0.5	100.1	0.05
	Kale	0.5	99.7	0.15
	Hair	0.5	100.9	0.1
Sb	Orchard leaves	0.5	99.8	0.6
	Orchard leaves	0.5	100.3	0.6
	Hair	0.5	99.9	—
	Blood serum	0.5	98.0	0.4
	Blood serum	0.5	99.4	0.5
	Kale	0.5	94.6	6 (on $CaSO_4$ppte)
	Kale	0.5	92.2	4 (on $CaSO_4$ppte)
	Kale	0.1	100.4	0.4
	Kale	0.2	100.1	0.4

Secondly, in the percentage yield experiments described below, which give an activity balance for both elements, the purity of the fractions was checked and found to be excellent. The activity balance obtained also in itself strongly suggested that the fractions must be pure.

For the procedure described, the arsenic fraction also contains 0.9% of the

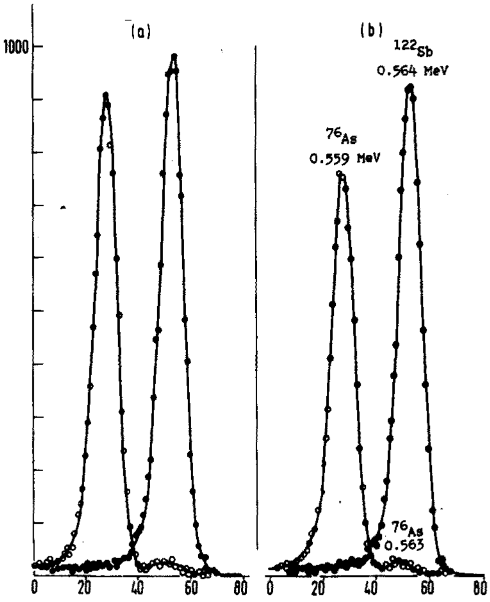

Fig. 2. γ-Spectra, Ge(Li) detector, of ^{76}As and ^{122}Sb. (a) Separated from 0.5 g of orchard leaves, (b) standards.

antimony. For most samples, the arsenic activity, and content, are greater so that the error is small, and can be allowed for up to moderate antimony levels. For samples with a much larger content of antimony than of arsenic, the arsenic fraction may be very simply purified by shaking the aqueous 6 *N* sulphuric acid–0.05 *M* iodide arsenic rinse solution once with toluene, which removes 99.4 % of the antimony into the organic phase. Alternatively, the antimony can be washed out of the organic phase before arsenic reversing the order of steps (6) and (7) in the Procedure (Fig. 1).

Percentage recoveries of arsenic and antimony

It was expected that recoveries of arsenic and antimony should be 100 and 98 %, respectively. Weighed amounts of ^{76}As and ^{124}Sb tracers were added to hair or kale and the complete procedure was performed; the recovered activities were then compared against weighed standards of each tracer. The results obtained are shown in Table II. (The values are of course normalized to allow for the 10/12 volume fractionation of the toluene phase.) It is clear that complete recovery of arsenic was indeed obtained, if arsenic is well washed out as described in the Procedure with one 10-ml and one 5-ml wash. For antimony the recovery with hair is in agreement with the expected 98 %, while with kale it is likely that the small 2 % loss is due to adsorption on calcium sulphate. This did not happen in the experiments in Table I, but slight adsorption may occur during the extra time of contact necessary for the carbon tetrachloride washing stages. For calculation of antimony results in kale, a recovery of 96 % was used.

TABLE II

RECOVERY OF ARSENIC AND ANTIMONY TRACERS IN COMPLETE METHOD

Matrix	*Recovery (%)*	*Notes on procedure*
0.5 g hair	As 96.5 Sb 97.7	only 1 × 10 ml As wash
0.5 g hair	As 101.1 Sb 97.7	as described
0.2 g kale	As 95.0 Sb 96.0	2 × 5 ml As washes
0.2 g kale	As 99.7 Sb 96.0	as described

Although it is clear from these recoveries that no losses occur during the carbon tetrachloride (bromine removal) scrubbing stage, this was also checked in separate experiments with ashed kale or hair with added tracers.

Results for kale and orchard leaves

For Bowen's kale the following results, per gram of dry material, were obtained; each result is the average of 6 determinations.

Arsenic 0.118 ± 0.004 μg g^{-1}
Antimony 0.050 ± 0.003 μg g^{-1}

These results are in good agreement with those most recently collected by Bowen[7], where the recommended value for arsenic is 0.14 p.p.m. (spread 0.11–0.22) and 0.07 for antimony (from 3 sets of results of 0.059_8, 0.065_6 and 0.099_4).

For the newer N.B.S. material, proposed orchard leaves standard SRM 1571, the following results were obtained; each result is the average of 3 determinations.

Arsenic $9.70 \pm 0.12\ \mu g\ g^{-1}$
Antimony $3.14 \pm 0.13\ \mu g\ g^{-1}$

For this sample, 2 independent values were obtained with a Ge(Li) crystal; these results were 10.3 and 10.3 μg As g^{-1}, and 3.14 and 3.16 μg Sb g^{-1}. The results obtained with the Ge(Li) crystal are not judged to be so accurate as the NaI(Tl) values, because the geometrical arrangement was less well defined.

Some values were obtained on hair samples, which are not recorded here as being rather meaningless in isolation, but clean ^{76}As and ^{122}Sb spectra were obtained by the separation procedure.

Sensitivity

For the irradiation conditions described, after two days cooling, 0.2 g of kale, *i.e. ca.* 25 ng of arsenic and 10 ng of antimony, each require 20–30 min counting in the well of the 3 × 3 NaI crystal for reasonable statistics, *i.e.* peak area integral >5000 counts.

Interferences and impurities in the spectra

The only elements known from previous extraction studies to co-extract are tin, and under certain conditions, selenium. Tin has such a low activation cross-section and its radionuclides such low γ-energies that no interference can occur. Selenium likewise has rather a small activation cross-section and ^{75}Se, the only isotope of importance, has γ-rays at lower energies than ^{76}As or ^{122}Sb. Moreover, selenium is generally present in biological material in low abundance.

Bromine, in particular ^{82}Br, was the only radionuclidic impurity detected in the spectra. Bromide ion does not extract and the interference is due to free bromine. For this reason, the scrubbing stage with carbon tetrachloride was introduced. In some experiments with ^{82}Br tracer, it was found that almost all bromine was removed during the wet ashing stage but the small percentage which remained could cause some interference. Comparative sets of spectra were obtained with the 3 × 3 in NaI(Tl) well-crystal for the ^{76}As and ^{122}Sb fraction isolated from irradiated kale, with and without, respectively, this scrubbing stage. No impurity peaks were visible in the former case, but slight peaks identifiable as ^{82}Br were seen in the latter case. In the case of the N.B.S. material, no special bromine removal stage was necessary as the relative amounts of arsenic and antimony are very large. This will probably be true for other materials with low, or relatively low, bromine contents. On the other hand, the method may prove to be inapplicable to matrices of very high bromine content.

As a quicker alternative to the carbon tetrachloride scrubbing stage, solid sodium sulphite can be added to the scrub solution at stage (5) of the procedure (see Fig. 1). This ensures removal of bromine from the toluene phase. Preliminary experimental work has shown that the recoveries of arsenic and antimony are not affected by the presence of the reductant, and the revised method has given results for kale in agreement with those reported above, with clean spectra.

In conclusion, the determination of arsenic and antimony in biological material by extraction of their iodides has been shown to be reliable by thorough checks and testing, and by giving results on a standard material in good agreement with other methods. The method is quick and eliminates the yield determination stage. Application of the separation scheme should be possible to other matrices such as metals or alloys, and geological material.

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SUMMARY

A method is described for the neutron activation analysis of arsenic and antimony simultaneously in biological materials at submicrogram level, based on the differences in the extraction behaviour of the iodides from sulphuric acid–potassium iodide medium with toluene. Both elements are first extracted from the sulphuric acid solution of the wet-ashed residues and then successively and selectively washed out of the organic phase in quantitative yield. Checks on losses during wet ashing, the validity of the extraction steps, and the complete procedure for both elements are reported. Results are presented for Bowen's standard kale and the N.B.S. standard, orchard leaves SRM 1571. Errors and interferences are discussed.

RÉSUMÉ

On décrit une méthode pour l'analyse par activation neutronique simultanée de l'arsenic et de l'antimoine, dans des substances biologiques; elle est basée sur l'extraction des iodures dans le toluène, en milieu sulfurique–iodure de potassium. On indique les erreurs et les interférences.

ZUSAMMENFASSUNG

Es wird eine Methode für die simultane Neutronenaktivierungsanalyse von Arsen und Antimon in biologischen Proben im Mikrogramm-Bereich beschrieben. Sie beruht auf dem unterschiedlichen Verhalten der Jodide bei der Extraktion mit Toluol aus Schwefelsäure–Kaliumjodid-Medium. Beide Elemente werden zunächst aus der schwefelsauren Lösung der nassveraschten Rückstände extrahiert und dann nacheinander und selektiv aus der organischen Phase mit quantitativer Ausbeute ausgewaschen. Es wurden Kontrolluntersuchungen bezüglich der Verluste während der nassen Veraschung, der Leistungsfähigkeit der Extraktionsschritte und des gesamten Verfahrens für beide Elemente durchgeführt. Es werden die Ergebnisse für Bowens Standard-Kohl und N.B.S.-Standard-Blätter SRM 1571 vorgelegt. Fehler und Störungen werden diskutiert.

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DISMUTATION REVERSIBLE DE UO_2(V) DANS L'EUTECTIQUE LiCl–KCl FONDU. II

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(Reçu le 22 octobre 1971)

Dans une première partie[1], nous avons examiné la réaction de dismutation–amphotérisation réversible de UO_2(V) dans l'eutectique LiCl–KCl fondu à 450° et nous avons montré que l'équilibre

$$2\,UO_2^+ + 4\,HCl \rightleftharpoons UO_2^{2+} + U^{4+} + 2\,H_2O + 4\,Cl^-$$

pouvait interpréter les données expérimentales de spectrophotométrie d'absorption visible et proche i.r. dans le domaine des pressions en HCl comprises entre 60 et 230 mm Hg.

Dans cette publication, nous allons examiner une autre interprétation possible.

GÉNÉRALITÉS

Nous avons vu que l'équilibre de dismutation–amphotérisation peut se formuler de la façon générale suivante[1]:

$$2\,UO_2^+ + n\,HCl \rightleftharpoons UO_2^{2+} + U^{4+} + 2\,W + n\,Cl^- \qquad (1)$$

W peut représenter OH^-, H_2O ou H_3O^+ et dans ce cas, n prend respectivement les valeurs 2, 4 et 6.

La constante d'équilibre de cette réaction est:

$$K = \frac{[UO_2^{2+}]\,[U^{4+}]\,[W]^2}{[UO_2^+]^2\,P_{HCl}^n} \qquad (2)$$

Or, dans nos conditions expérimentales[1]

$$[W] = 2\,[U^{4+}]$$

et si l'on pose

$$L = \frac{[UO_2^{2+}]\,[U^{4+}]^3}{[UO_2^+]^2} \qquad (4)$$

l'expression (2) devient

$$n \log P_{HCl} = \log L - \log \tfrac{1}{4}K \qquad (5)$$

En portant $\log P_{HCl}$ en fonction de $\log L$ dans le domaine des pressions en HCl

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comprises entre 60 et 230 mm Hg, nous avons obtenu une droite de pente $\frac{1}{4}$ et nous en avons conclu que l'espèce W était H_2O[1].

Cette conclusion n'est évidemment valable que dans le cas de l'existence d'une réaction unique de dismutation formant dans le bain une espèce W bien déterminée. Si les trois espèces W, à savoir OH^-, H_2O et H_3O^+, existent simultanément dans le bain, l'expression logarithmique (5) se modifie ; en effet :

$$2\,UO_2^+ + 6\,HCl \rightleftharpoons UO_2^{2+} + U^{4+} + 2\,H_3O^+ + 6\,Cl^- \tag{6}$$

$$K_1 = \frac{[UO_2^{2+}]\,[U^{4+}]\,[H_3O^+]^2}{[UO_2^+]^2\,P_{HCl}^6} \tag{7}$$

$$2\,UO_2^+ + 4\,HCl \rightleftharpoons UO_2^{2+} + U^{4+} + 2\,H_2O + 4\,Cl^- \tag{8}$$

$$K_2 = \frac{[UO_2^{2+}]\,[U^{4+}]\,[H_2O]^2}{[UO_2^+]^2\,P_{HCl}^4} \tag{9}$$

$$2\,UO_2^+ + 2\,HCl \rightleftharpoons UO_2^{2+} + U^{4+} + 2\,OH^- + 2\,Cl^- \tag{10}$$

$$K_3 = \frac{[UO_2^{2+}]\,[U^{4+}]\,OH^-]^2}{[UO_2^+]^2\,P_{HCl}^2} \tag{11}$$

Or, $[W] = [H_3O^+] + [H_2O] + [OH^-]$ (12)

En combinant les expressions (4), (7), (9), (11) et (12), on obtient :

$$\frac{L^{\frac{1}{2}}}{P_{HCl}} = \frac{K_1^{\frac{1}{2}}}{2}\,P_{HCl}^2 + \frac{K_2^{\frac{1}{2}}}{2}\,P_{HCl} + \frac{K_3^{\frac{1}{2}}}{2} \tag{13}$$

Cette expression peut aisément se transformer sous la forme logarithmique suivante :

$$\log L = \log\frac{K_2}{4} + 4\log P_{HCl} + 2\log\left[\left(\frac{K_1}{K_2}\right)^{\frac{1}{2}} P_{HCl} + 1 + \left(\frac{K_3}{K_2}\right)^{\frac{1}{2}} \frac{1}{P_{HCl}}\right] \tag{14}$$

dont la signification devient plus claire si on considère les réactions

$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^- \tag{15}$$

avec

$$K_4 = \frac{[H_3O^+]}{[H_2O]\,P_{HCl}} \tag{16}$$

et

$$HCl + OH^- \rightleftharpoons H_2O + Cl^- \tag{17}$$

avec

$$K_5 = \frac{[H_2O]}{[OH^-]\,P_{HCl}} \tag{18}$$

On calcule aisément que

$$K_4 = \left(\frac{K_1}{K_2}\right)^{\frac{1}{2}} \tag{19}$$

et

$$K_5 = \left(\frac{K_2}{K_3}\right)^{\frac{1}{2}} \qquad (20)$$

L'expression (14) devient

$$\log L = \log \frac{K_2}{4} + 4 \log P_{\mathrm{HCl}} + 2 \log \left(\frac{[\mathrm{H_3O^+}]}{[\mathrm{H_2O}]} + 1 + \frac{[\mathrm{OH^-}]}{[\mathrm{H_2O}]}\right) \qquad (21)$$

Si on porte log P_{HCl} en fonction de log L, on doit obtenir une courbe répondant aux équations (14) ou (21).

D'après l'équilibre (15), on peut s'attendre à ce que la forme H_3O^+ soit prépondérante aux fortes pressions en HCl. Dans ces conditions, 1 et $[\mathrm{OH}]/[\mathrm{H_2O}]$ sont négligeables devant $[\mathrm{H_3O^+}]/[\mathrm{H_2O}]$. L'expression (21) devient:

$$\log L = \log \frac{K_1}{4} + 6 \log P \qquad (22)$$

Cette dernière égalité est tout à fait analogue à l'expression (5) et elle est valable dans le cas où se produirait la seule réaction de dismutation (6). Aux fortes valeurs de P_{HCl}, la courbe log $P_{\mathrm{HCl}} = \mathrm{f}(\log L)$ pourrait présenter une portion rectiligne de pente $\frac{1}{6}$ illustrée par le domaine E sur la Fig. 1.

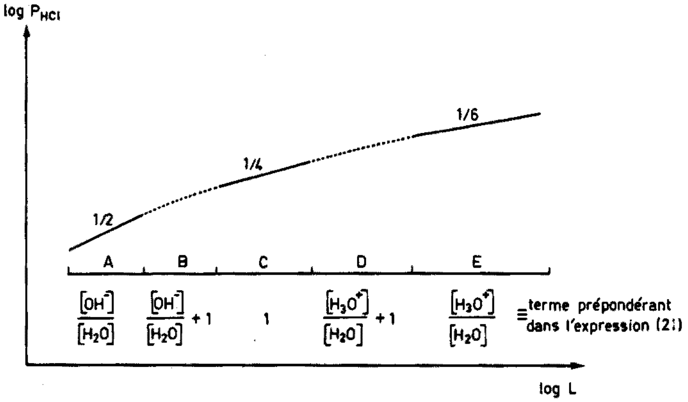

Fig. 1. Influence des rapports de concentrations en OH^-, H_2O et H_3O^+ sur l'équilibre de dismutation.

Au fur et à mesure que la pression en acide chlorhydrique diminue, H_3O^+ peut se transformer en H_2O. Si H_2O est la forme prépondérante, $[\mathrm{H_3O^+}]/[\mathrm{H_2O}]$ et $[\mathrm{OH^-}]/[\mathrm{H_2O}]$ sont négligeables devant 1. L'expression (21) prend la forme

$$\log L = \log \frac{K_2}{4} + 4 \log P_{\mathrm{HCl}} \qquad (23)$$

Cette expression est à nouveau analogue à (5) dans le cas où se produirait la seule réaction de dismutation (8). Dans un domaine de pression intermédiaire, la courbe log $P = \mathrm{f}(\log L)$ pourrait présenter une portion rectiligne de pente $\frac{1}{4}$ illustrée par le domaine C sur la Fig. 1. Cette expression (23) est à la base de l'interprétation donnée dans la première partie de cette publication.

Aux faibles pressions en HCl, OH^- peut devenir la forme prépondérante, auquel cas $[H_3O^+]/[H_2O]$ et 1 sont négligeables devant $[OH^-]/[H_2O]$; l'expression (21) devient

$$\log L = \log \frac{K_3}{4} + 2 \log P_{HCl} \qquad (24)$$

L'expression (24), caractéristique de la réaction de dismutation (10) est encore une fois analogue à l'expression (5). Aux faibles pressions en HCl, la courbe $\log P = f(\log L)$ pourrait présenter une portion rectiligne de pente $\frac{1}{2}$, illustrée par le domaine A sur la Fig. 1.

Sur cette même Figure, les domaines B et D seraient respectivement ceux où $[OH^-]/[H_2O]$ et $[H_3O^+]/[H_2O]$ ne seraient pas négligeables devant 1.

Si les termes $[H_3O^+]/[H_2O]$, 1 et $[OH^-]/[H_2O]$ ne sont négligeables l'un vis-à-vis de l'autre à aucun moment, la courbe expérimentale $\log P = f(\log L)$, tout en conservant l'allure de la Fig. 1, ne présentera aucune partie rectiligne. La pente des tangentes à cette courbe tendra vers $\frac{1}{2}$ aux faibles pressions en acide chlorhydrique, vers $\frac{1}{6}$ aux fortes pressions et sera comprise entre $\frac{1}{2}$ et $\frac{1}{6}$ aux pressions intermédiaires.

RÉSULTATS EXPÉRIMENTAUX

Les points expérimentaux publiés dans la première partie[1], ne sont pas incompatibles avec une courbe répondant à l'équation (14). Pour arriver à préciser la validité de cette équation, nous avons déterminé une série de points expérimentaux supplémentaires aux faibles pressions en HCl (< 80 mm Hg). Ces résultats montrent

TABLEAU I

Exp.	P_{HCl} *(mm Hg)*	$[U(IV)]$ *(mole $l^{-1} \cdot 100$)*	$[UO_2(V)]$ *(mole $l^{-1} \cdot 100$)*	*2ème série*	*3ème série*	
				$-\log L$	$[H_2O]$ *(mole $l^{-1} \cdot 100$)*	*$-\log L$*
22	62	0.27	2.11	5.05	1.06	4.48
	45.5	0.23	2.17	5.30	1	4.62
	29.5	0.15	2.28	5.85	0.89	4.94
	18	0.11	2.35	6.30	0.82	5.19
28	43	0.29	2.17	5.14		
	67.5	0.30	2.35	5.17		
41	76	0.26	1.43	5.22	1.32	4.43
	39	0.17	1.53	5.84	1.22	4.75
	16	0.12	1.60	6.39	1.15	4.99
	74	0.31	1.50	5.08	1.30	4.43
	35	0.21	1.56	5.62	1.24	4.66
	16	0.075	1.50	6.89		
	68.5	0.26	1.60	5.33	1.45	4.46
	28	0.20	1.70	5.77	1.35	4.70
	61	0.20	1.50	5.62		
	27	0.14	1.58	6.14		
	12.5	0.093	1.62	6.70		

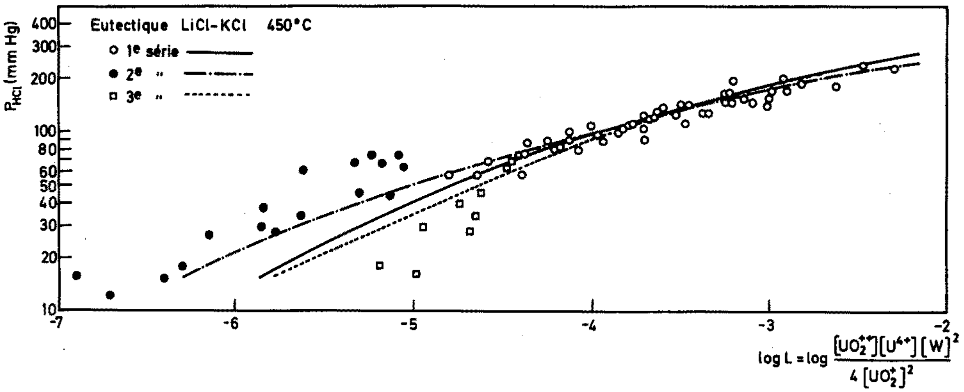

Fig. 2. Influence de la pression en HCl sur le degré d'avancement de la réaction de dismutation.

une importante dispersion provoquée par l'erreur dans la mesure spectrophotométrique (la concentration en U(IV) étant faible dans ce domaine de pressions) ainsi que vraisemblablement par une réaction parasite.

Si l'on calcule les valeurs de L de la façon déjà décrite[1], on obtient les valeurs reproduites dans le Tableau I (2ème série) et les points expérimentaux se situent assez bien dans le prolongement de la droite de pente $\frac{1}{4}$ obtenue dans le domaine de reproductibilité (Fig. 2, 1ère et 2ème séries). Si l'on s'en tient là, les conclusions tirées dans la première partie de cette publication[1] restent valables.

Il faut cependant faire remarquer l'existence d'une réaction parasite; en effet, en laissant évoluer le système en équilibre de dismutation sous une pression en HCl constante et faible pendant une nuit, on observe une diminution simultanée des concentrations en U(IV) et UO_2(V) avec $\Delta[U^{4+}] > \Delta[UO_2^+]$.

Ce fait pourrait être dû à l'oxydation de U(IV) par W (OH^-, H_2O ou H_3O^+) selon la réaction

$$U^{4+} + 2\,H_2O \rightarrow UO_2^{2+} + 2\,H^+ + H_2 \qquad (25)$$

Comme $[U^{4+}]$ et $[W]$ diminuent, le système fonctionne en consommant UO_2(V). D'après la constante d'équilibre (2) de la réaction de dismutation, la grandeur $[[UO_2^{2+}][U^{4+}][W]^2/[UO_2^+]^2]$ doit rester constante puisque K et P^n sont constants. En outre, puisqu'il faut 2 W pour oxyder un seul U(IV), la condition $[W] = 2[U^{4+}]$ reste valable à tout moment et la valeur de L devrait ne pas être influencée par la réaction parasite (25). Or, le calcul montre que la diminuton des concentrations en U(IV) et UO_2(V), observée lors de la réaction parasite, s'accompagne d'une diminution de la valeur de L. La réaction parasite n'est donc pas l'oxydation de U(IV) par W.

Il pourrait s'agir de l'oxydation de UO_2(V) par HCl selon

$$UO_2^+ + HCl \rightarrow UO_2^{2+} + \tfrac{1}{2}\,H_2 + Cl^- \qquad (26)$$

Cette réaction, qui est l'inverse de celle utilisée pour la préparation des solutions de UO_2(V), ne peut cependant expliquer que la diminution de la concentration en U(IV) soit supérieure à celle de la concentration en UO_2(V).

Un dégagement de vapeur d'eau ferait évoluer le système dans le sens de la dismutation, ce qui conduit à une augmentation de la concentration en U(IV).

D'ailleurs, après dégagement de vapeur d'eau, on a $[W] < 2\,[U^{4+}]$, ce qui signifie que la valeur calculée de L selon l'expression (4) en supposant que la condition (3) est respectée, serait supérieure à la valeur réelle, alors que dans le cas présent, on observe une diminution.

La seule explication plausible reste l'oxydation de U(IV) par l'oxygène résiduel. Chalkley[2] a montré que les bains de chlorure d'uranyle sont capables de consommer l'oxygène de l'air et de le retenir sous une forme soluble. Cet oxygène pourrait, dans notre cas, provenir de faibles rentrées d'air au cours des manipulations. Dans ces conditions, les expressions (3) et (4) ne sont plus valables; la quantité L est définie de façon plus correcte comme suit:

$$L = \frac{[UO_2^+]\,[U^{4+}]\,[W]^2}{4\,[UO_2^+]^2} \qquad (27)$$

On peut considérer tout d'abord que pendant l'évolution à la pression en HCl constante, c'est-à-dire pendant l'oxydation de U(IV) par l'oxygène, la concentration en l'espèce W reste constante; cette valeur étant connue, on peut dès lors calculer L d'après l'expression (27) et on obtient une valeur supérieure à celle obtenue la veille à la même pression en HCl, sans doute à cause d'un léger dégagement de vapeur d'eau.

Pour tenir compte de l'oxydation de U(IV) par l'oxygène et du dégagement de vapeur d'eau pendant les mesures très espacées, on considère qu'entre deux telles mesures effectuées à la même pression en HCl, la valeur de L reste constante. On peut dès lors calculer la nouvelle valeur de W d'après l'expression (27):

$$[W] = \left(\frac{4\,L}{[UO_2^{2+}]\,[U^{4+}]}\right)^{\frac{1}{2}} \cdot [UO_2^+] \qquad (28)$$

dans laquelle nous introduisons la valeur de L trouvée lors de la première mesure et celles de $[UO_2^{2+}]$, $[UO_2^+]$ et $[U^{4+}]$ lors de la seconde mesure.

Entre deux nouveaux équilibres de dismutation successifs, à des pressions en HCl différentes, la variation de la concentration en l'espèce W est de nouveau donnée par la relation:

$$\Delta[W] = 2\Delta[U^{4+}] = -\Delta[UO_2^+] \qquad (29)$$

Pour ne pas tenir compte de l'oxydation parasite de U(IV) par l'oxygène, on utilise de préférence la relation

$$\Delta[W] = -\Delta[UO_2^+].$$

Dans ce qui suit, les résultats sont groupés en trois séries:

—une première série représente uniquement les points expérimentaux obtenus dans le domaine de bonne reproductibilité ($P_{HCl} > 60$ mm Hg) et déjà décrits dans la première partie[1].

—une seconde série représente tous les points expérimentaux affectés d'aucune correction.

—une troisième série représente tous les points expérimentaux, les mesures à faible P_{HCl} étant corrigées de la façon qui vient d'être décrite.

Ces différentes séries de valeurs sont reprises dans le Tableau I (à l'exception de la 1ère série déjà décrite[1]) et reportées sur la Fig. 2.

Les points expérimentaux corrigés se disposent sur une courbe, ce qui signifie qu'au moins deux formes de W peuvent exister en solution.

Au moyen d'un programme FORTRAN (IBM 360) préparé par P. zur Nedden, nous avons calculé, par approximations successives, les valeurs des constantes K_1, K_2 et K_3 de l'expression (13). Les valeurs et les écarts-types obtenus pour les trois séries sont reproduits dans le Tableau II. Les valeurs de K_4 et K_5 sont déterminées au moyen des expressions (19) et (20).

TABLEAU II

	1ère série	*2ème série*	*3ème série*
K_1 (mole^2 l^{-2} atm^{-6})	10.9 ± 0.7	10 ± 0.6	7.8 ±0.6
K_2 (mole^2 l^{-2} atm^{-4})	$3.5 \cdot 10^{-4}$ ± $5.2 \cdot 10^{-4}$	$9.5 \cdot 10^{-2}$ ± 0.13	0
K_3 (mole^2 l^{-2} atm^{-2})	$1.3 \cdot 10^{-2}$ ± $0.8 \cdot 10^{-3}$	$3.55 \cdot 10^{-3}$ ± $3.7 \cdot 10^{-4}$	$1.9 \cdot 10^{-2}$ ± $1 \cdot 10^{-3}$
K_4 (atm^{-1})	175 ±130	10 ± 7	
K_5 (atm^{-1})	0.165 ± 0.12	5.2 ± 3.6	
K_6 (atm^{-2})	29.0 ± 1.8	54 ± 4.4	20.3 ± 1.3

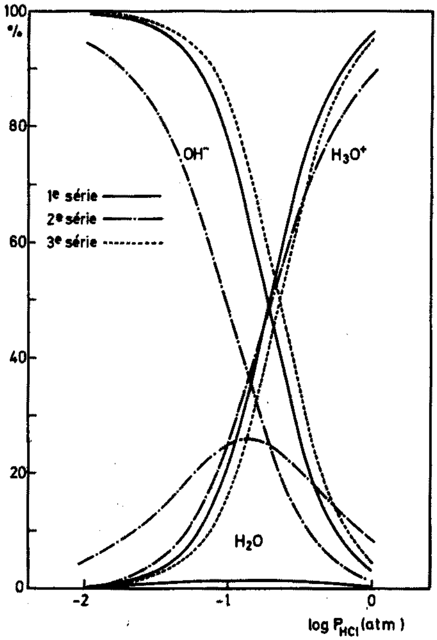

Fig. 3. Répartition des formes OH^-, H_2O et H_3O^+ en fonction de la pression en acide chlorhydrique.

Dans le cas de la 3ème série, la valeur de K_2 est nulle, ce qui signifie que la forme H_2O n'intervient pas dans l'équilibre de dismutation. Dans ce cas, il faut considérer l'équilibre

$$OH^- + 2\,HCl \rightleftharpoons H_3O^+ + 2\,Cl^- \tag{30}$$

avec

$$K_6 = \frac{[H_3O^+]}{[OH^-]\,P^2_{HCl}} = K_4K_5 = \left(\frac{K_1}{K_3}\right)^{\frac{1}{2}} \tag{31}$$

Les valeurs de K_4, K_5 et K_6 sont reprises dans le Tableau II. Au moyen de ces valeurs, on peut calculer la répartition des formes OH^-, H_2O et H_3O^+ en fonction de la pression en acide chlorhydrique (Fig. 3).

CONCLUSIONS

Les conclusions que l'on peut tirer du Tableau II et de la Fig. 3 sont les suivantes : alors que le premier examen des résultats expérimentaux dans le domaine de bonne précision nous avait fait conclure, sur la base de la pente de la courbe expérimentale, à l'existence de l'équilibre de dismutation donné par l'équation (8), l'extension des mesures aux plus basses pressions en HCl et l'analyse plus quantitative de l'ensemble des résultats sur ordinateur conduisent à des conclusions quelque peu différentes :

1. Tout d'abord, il faut bien constater que les valeurs des constantes d'équilibre ou encore la répartition de W entre ses trois formes varient assez fortement pour les trois séries ; néanmoins, on peut remarquer que dans les trois cas, l'importance de l'espèce H_2O reste toujours faible vis-à-vis des autres contrairement à notre conclusion de l'article précédent[1].

2. En ne considérant que les mesures de la première série, les résultats expérimentaux se laissent bien interpréter par les équilibres (6) et (10), ce qui revient à dire, comme le montre la Fig. 3, que dans ce domaine l'eau est peu stable et se dismute en H_3O^+ et OH^- suivant l'équilibre d'autoprotolyse

$$2\,H_2O \rightleftharpoons H_3O^+ + OH^-$$

avec

$$\frac{[H_3O^+]\,[OH^-]}{[H_2O]^2} = \frac{K_4}{K_5}$$

La constante d'autoprotolyse de l'eau est élevée et vaut environ 10^3.

3. Si l'on considère cependant l'ensemble des mesures de la 2ème série, les constantes auxquelles on aboutit indiquent plutôt l'intervention des trois équilibres (6), (8) et (10) c'est-à-dire un équilibre d'autoprotolyse de l'eau avec une constante de 2.

4. Enfin, dans le cas de la 3ème série, en tenant compte de la réaction parasite, on trouve à nouveau que la constante d'autoprotolyse de l'eau est élevée ($> 10^4$) ce qui signifie que H_2O est très instable dans ce milieu dans les conditions considérées.

Il semble donc se dégager de cette étude que contrairement à la conclusion énoncée précédemment, la proportion de H_2O dans W est faible ; les espèces H_3O^+ et OH^- sont plus abondantes. Néanmoins, l'imprécision sur la valeur de la constante d'autoprotolyse de l'eau reste très grande et pour tenter de cerner de plus près la réalité, nous avons effectué une étude de la dismutation de l'uranium pentavalent en fonction de la température d'une part et de la nature du bain fondu d'autre part. Ces résultats seront exposés dans une troisième partie.

Il est encore opportun de signaler que le traitement par un courant d'acide chlorhydrique gazeux est généralement utilisé par de nombreux chercheurs pour éliminer l'eau et les ions oxydes des bains de chlorures fondus. Il ressort des courbes de la Fig. 3 qu'il est possible d'améliorer ce traitement en faisant barboter non pas HCl, mais un mélange HCl–gaz inerte dont la pression partielle en HCl corresponde au maximum de la courbe % H_2O (P_{HCl} comprise entre 100 et 200 mm Hg dans l'eutectique LiCl–KCl à 450°).

Nous remercions vivement le F.N.R.S. et l'I.I.S.N. pour l'intérêt constant apporté à nos travaux et le soutien financier accordé à notre laboratoire. Nous tenons également à remercier Messieurs P. zur Nedden et J. F. Desreux pour l'aide appréciable qu'ils nous ont apportée lors des calculs sur ordinateur.

RÉSUMÉ

La réaction de dismutation–amphotérisation de l'uranium(V) en uranium(IV) et uranium(VI) dans un bain de chlorures fondus (eutectique LiCl–KCl) à 450° a été étudiée en fonction de la pression d'acide chlorhydrique gazeux par spectrophotométrie d'absorption visible et proche i.r. Etant donné les erreurs importantes qui affectent les mesures à basse pression, il est difficile de tirer des conclusions précises: alors que dans une publication antérieure limitée à un domaine de pression où la précision est satisfaisante, nous avions conclu à la réaction suivante:

$$2\,UO_2^+ + 4\,HCl \rightleftharpoons UO_2^{2+} + U^{4+} + 2\,H_2O + 4\,Cl^- \quad (1)$$

il semble maintenant, sur la base de l'ensemble des mesures, qu'il faille également faire intervenir les équilibres suivants:

$$2\,UO_2^+ + 2\,HCl \rightleftharpoons UO_2^{2+} + U^{4+} + 2\,OH^- + 2\,Cl^- \quad (2)$$

$$2\,UO_2^+ + 6\,HCl \rightleftharpoons UO_2^{2+} + U^{4+} + 2\,H_3O^+ + 6\,Cl^- \quad (3)$$

et il semble que l'intervention de la réaction (1) soit relativement faible.

SUMMARY

The disproportionation of UO_2(V) in LiCl–KCl eutectic at 450° has been studied as a function of the pressure of hydrogen chloride in a wide range by visible and near infrared absorption spectrophotometry. As important errors affect the measurements at low pressure, no precise conclusions can be drawn. A previous study limited to a pressure range where precision was satisfactory, indicated that the following reaction occurred:

$$2\,UO_2^+ + 4\,HCl \rightleftharpoons UO_2^{2+} + U^{4+} + 2\,H_2O + 4\,Cl^- \quad (1)$$

Now, on the basis of complementary measurements, the following equilibria must be taken into account:

$$2\,UO_2^+ + 2\,HCl \rightleftharpoons UO_2^{2+} + U^{4+} + 2\,OH^- + 2\,Cl^- \quad (2)$$

$$2\,UO_2^+ + 6\,HCl \rightleftharpoons UO_2^{2+} + U^{4+} + 2\,H_3O^+ + 6\,Cl^- \tag{3}$$

and it seems that the contribution of reaction (1) is relatively small.

ZUSAMMENFASSUNG

Die Disproportionierung von $UO_2(V)$ in LiCl–KCl-Eutektikum bei 450° wurde als Funktion des Chlorwasserstoff-Druckes in einem weiten Bereich durch Absorptionsspektrophotometrie im Sichtbaren und im nahen Infrarot untersucht. Da erhebliche Fehler die Messungen bei niedrigem Druck beeinflussen, können keine genauen Schlüsse gezogen werden. Eine vorhergehende Untersuchung, die sich auf einen Druckbereich beschränkte, in dem die Genauigkeit zufriedenstellend war, ergab Hinweise auf folgende Reaktion:

$$2\,UO_2^+ + 4\,HCl \rightleftharpoons UO_2^{2+} + U^{4+} + 2\,H_2O + 4\,Cl^- \tag{1}$$

Nach den jetzt zusätzlich durchgeführten Messungen müssen folgende Gleichgewichte berücksichtigt werden:

$$2\,UO_2^+ + 2\,HCl \rightleftharpoons UO_2^{2+} + U^{4+} + 2\,OH^- + 2\,Cl^- \tag{2}$$

$$2\,UO_2^+ + 6\,HCl \rightleftharpoons UO_2^{2+} + U^{4+} + 2\,H_3O^+ + 6\,Cl^- \tag{3}$$

Der Anteil von Reaktion (1) scheint relativ gering zu sein.

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THE DETERMINATION OF RUBIDIUM AND CAESIUM IN GEOLOGICAL MATERIALS BY ATOMIC EMISSION SPECTROPHOTOMETRY WITH A NITROUS OXIDE–ACETYLENE FLAME

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The determination of rubidium and caesium by atomic flame emission spectrophotometry has centered on the use of the air–acetylene flame. The high degree of ionization[1] of these two elements in flame spectroscopy has led to the use of potassium as an ionization buffer. Studies by Poluektov and Vitkun[2] suggested that complete suppression of ionization would often require too high a concentration of potassium. Therefore, in the determination of rubidium and caesium, potassium is simultaneously measured and then added to attain a high but definite concentration in the solution to be sprayed[3-6]. Even with the elimination of ionization, chemical interference still exists from several elements[5,7-9]. Spectral interferences illustrated by Buell[11] can be successfully eliminated by a simple scanning technique[11,12].

The present paper describes the use of a nitrous oxide–acetylene flame for the routine determination of rubidium and caesium in geological materials with a detection limit of 0.002% (in the solid). Its application to p.p.m. levels of rubidium and caesium is limited only by the availability of a scanning monochromator.

EXPERIMENTAL

Apparatus

A Techtron model AA5 atomic-absorption spectrophotometer fitted with a Jarrell Ash model 82-025 scanning monochromator, a 285-Hz chopper and the standard Techtron burner assembly was used. The monochromator was equipped with a variable, curved jaw slit assembly (10–400 μm aperture) and a grating blazed at 400 nm. The reciprocal dispersion was 1.6 nm in the first order.

Spectra were recorded on a Servoscribe potentiometric recorder.

A Wratten number 25A coloured glass filter was used to remove second-order interferences.

A Hamamatsu HTV-R446 photomultiplier tube was used for both elements.

Reagents

1000 *p.p.m. Primary standards.* For rubidium, dissolve 1.4148 g of rubidium chloride in water and dilute to 1 l. For caesium, dissolve 1.2667 g of caesium chloride (Halewood chemical 3N) in water and dilute to 1 l.

10% *Potassium buffer solution.* Dissolve 177 g of potassium carbonate (Riedelde Haen A. G., Hanover) in a minimum of dilute hydrochloric acid and dilute to 1 l. Any other high-purity potassium salt can be used but must contain < 1.0 p.p.m. rubidium and caesium.

Operating conditions

All work was carried out at the primary emission wavelengths of rubidium (780.0 nm) and caesium (852.1 nm). The instrumental conditions are listed in Table I.

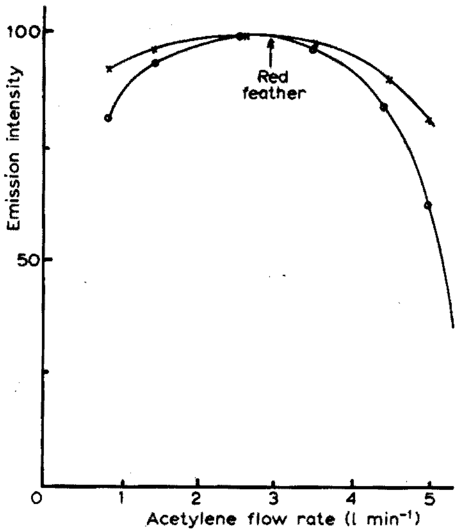
TABLE I

INSTRUMENTAL CONDITIONS FOR THE DETERMINATION OF RUBIDIUM AND CAESIUM WITH THE NITROUS OXIDE–ACETYLENE FLAME

Element	*Rubidium*	*Caesium*
Wavelength, nm	780.0	852.1
Photomultiplier tube	R 446	R 446
Spectral half band width, nm	0.08	0.24
Slit height, mm	20	20
Burner[a]	AB 50	AB 50
Burner height, mm	4	4
Flame adjustment[b] (red feather mm)	1	1
Typical gain setting	5 (high)	6 (high)
Typical working range (p.p.m.)	0–5	0–5

[a] Aligned parallel to light path.

[b] Adjusted to give maximum emission intensity when a standard solution was aspirated.



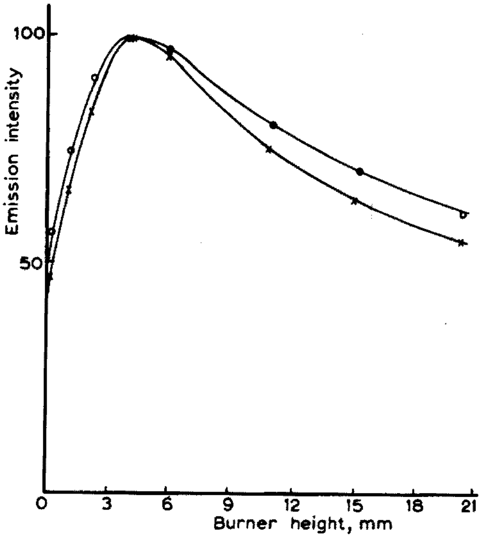


Fig. 1. The effect of acetylene flow rate on emission intensity. Other parameters as given in Table I. (o) Rubidium; (x) caesium.

Fig. 2. The effect of burner height on emission intensity. Other parameters as given in Table I. (o) Rubidium; (x) caesium.

Recommended procedure

Weight 0.5 g of sample into a PTFE beaker. Add 5 ml of concentrated nitric acid, 0.5 ml of concentrated sulphuric acid and 5 ml of 40% hydrofluoric acid and heat until fumes of sulphur trioxide appear. Cool, and add the same quantities of acids again. Take to fumes and then add the acids for a third time and leave on a hotplate overnight. Cool, add 10 ml of concentrated hydrochloric acid and 10 ml of distilled water, and heat to dissolve soluble salts. Transfer direct to a 100-ml flask, add 10 ml of 10% potassium buffer solution and dilute to volume. After shaking transfer to a plastic container. Aspirate under the conditions listed in Table I.

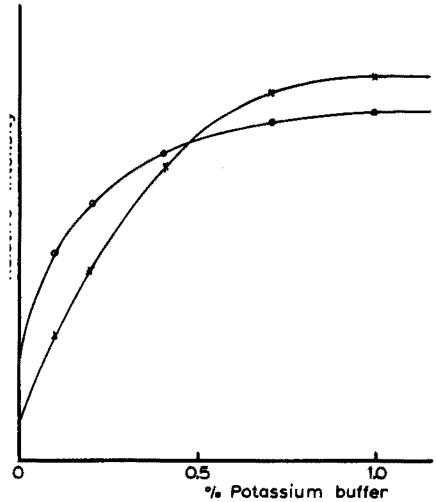
Rubidium and caesium standards, containing 1% potassium buffer and 10% hydrochloric acid, are prepared by dilution of the 1000-p.p.m. primary solutions.

RESULTS AND DISCUSSION

Flame composition and burner height

The effects of flame adjustment and burner height for both elements are given in Figs. 1 and 2. The burner heights are measured in millimeters, where the zero corresponds to a position when the burner top is in the centre of the light path. For the burner height study, the flame was adjusted to give maximal sensitivity. In all work a nebulization pressure of 175 kNm^{-2} (25 p.s.i.) was used which produced a nitrous oxide flow of 7–8 l min^{-1}. For the flame adjustment study the burner height was optimized as in Fig. 2.

The flame showing the highest emission intensity had a trace of red feather in each case.



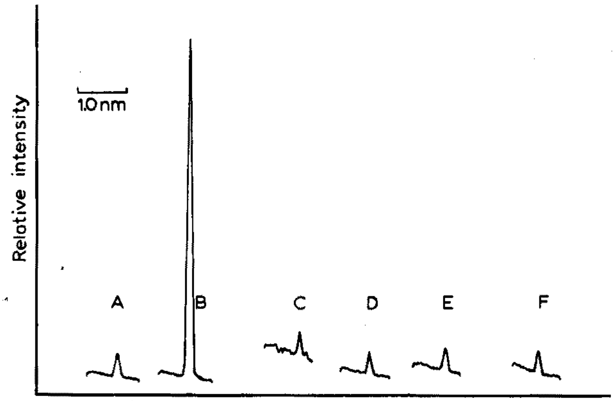


Fig. 3. The effect of potassium buffer solution on the relative emission of rubidium (o) and caesium (x). Instrumental conditions as given in Table I.

Fig. 4. Spectral interference on rubidium. All solutions contain 1% potassium buffer and 10% hydrochloric acid. (A) Water; (B) 1.0 p.p.m. rubidium; (C) 2000 p.p.m. calcium; (D) 2000 p.p.m. strontium; (E) 2000 p.p.m. barium; (F) 1000 p.p.m. potassium.

Effect of buffer

The use of potassium as an ionization buffer is well known[1-3] and the spectrochemical technique of addition of excess is documented for the air–acetylene flame[4-6]. In the nitrous oxide–acetylene flame it is shown in Fig. 3 that with increasing amounts of potassium buffer solution, the transmission of a solution containing 5 p.p.m. rubidium or caesium reaches a definite plateau. This indicates that suppression of ionization is complete with a solution containing 1% potassium, hence the need for a standard addition technique as suggested by Fabrikova and others[2-6] is unnecessary.

Interference studies

Spectral interference was investigated by aspirating a 2000 p.p.m. solution of most common cations and scanning the wavelength for each analyte.

Chemical and ionization interferences were investigated by preparing sets of solutions containing the same concentration of analyte and interferents at the 1000 and 2000 p.p.m. levels.

Rubidium.

When a solution containing 1 p.p.m. rubidium and 1% potassium buffer was used, the gain was adjusted to give 100% transmission. No detectable increase in background was observed for the following elements: sodium, lithium, caesium, aluminium, magnesium, manganese, iron, cobalt, nickel, copper, zinc, lead, cerium and lanthanum. Calcium, strontium, barium and potassium gave slight increases in background (Fig. 4), calcium having the largest effect in that a sample with no rubidium would be found to contain 0.001% (on a 0.5% w/v sample concentration).

Chemical and ionization effects were studied at the 5 p.p.m. rubidium level for those elements listed above (Table II) and all results were within 5.0±0.1 p.p.m. when the recommended instrument conditions in Table I were used.

Caesium. With a solution containing 1 p.p.m. caesium and 1% potassium buffer, the instrument was set to 100% transmission. No detectable increase in background

TABLE II

INTERFERENCE STUDY—RUBIDIUM

(All interference solutions contain 1% potassium buffer, 10% hydrochloric acid, 2000 p.p.m. interferent and 5 p.p.m. rubidium)

Interferent 2000 p.p.m.	*Time scan*[a]	*Wavelength scan*[b]	*Interferent 2000 p.p.m.*	*Time scan*[a]	*Wavelength scan*[b]
—	5.00	Nil	Iron	5.02	Nil
Lithium	4.92	Nil	Cobalt	5.03	Nil
Sodium	4.95	Nil	Nickel	5.02	Nil
Potassium	5.11	0.05	Copper	4.98	Nil
Caesium	5.04	Nil	Zinc	5.04	Nil
Magnesium	5.02	Nil	Aluminium	4.90	Nil
Calcium	4.95	0.05	Lead	4.98	Nil
Strontium	4.93	0.03	Cerium	4.92	Nil
Barium	4.90	0.03	Lanthanum	4.98	0.03
Manganese	4.98	Nil			

[a] Calculated rubidium content (p.p.m.) (not corrected for spectral interference).
[b] Spectral interference (p.p.m. rubidium).

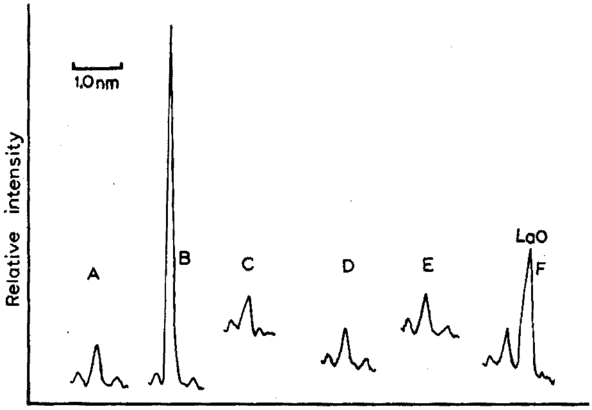


Fig. 5. Spectral interference on caesium. All solutions contain 1% potassium buffer and 10% hydrochloric acid. (A) Water; (B) 1 p.p.m. caesium; (C) 2000 p.p.m. calcium; (D) 2000 p.p.m. strontium; (E) 1000 p.p.m. barium; (F) 1000 p.p.m. lanthanum.

TABLE III

INTERFERENCE STUDY—CAESIUM

(All interference solutions contain 1% potassium buffer, 10% hydrochloric acid, 2000 p.p.m. interferent and 5 p.p.m. caesium)

Interferent 2000 *p.p.m.*	*Time scan*[a]	*Wavelength scan*[b]	*Interferent* 2000 *p.p.m.*	*Time scan*[a]	*Wavelength scan*[b]
—	5.00	Nil	Calcium	4.98	Nil
Lithium	4.95	Nil	Strontium	4.95	Nil
Sodium	4.94	Nil	Barium	5.11	0.16
Potassium	5.07	Nil	Lanthanum	4.99	0.07
Rubidium	4.99	Nil			
Magnesium	4.93	Nil			
Calcium	5.13	0.11			
Strontium	5.12	0.07			
Barium	5.40	0.35			
Manganese	4.95	Nil			
Iron	5.00	Nil			
Cobalt	4.98	Nil			
Nickel	5.00	Nil			
Copper	4.95	Nil			
Zinc	4.94	Nil			
Aluminium	4.94	Nil			
Lead	5.01	Nil			
Cerium	4.95	Nil			
Lanthanum	5.13	0.15			

[a] Calculated caesium content (p.p.m.) (not corrected for spectral interference).

[b] Spectral interference (p.p.m. caesium).

was observed for the following elements: lithium, sodium, potassium, aluminium, magnesium, rubidium, manganese, iron, cobalt, nickel, copper, zinc, lead and cerium. Calcium, strontium, barium and lanthanum showed increases in background level (Fig. 5), such that if a pure limestone were analysed for caesium without a wavelength scan an apparent 0.003% caesium would be found.

Chemical and ionization effects were studied at the 5-p.p.m. caesium level for those elements listed above. All elements other than calcium, strontium, barium and lanthanum (at levels greater than 1000 p.p.m. in solution) gave results of 5.0 ± 0.1 p.p.m. (Table III).

These interference studies indicate that the determination of rubidium and caesium at levels as low as 0.002% can be achieved in a routine laboratory on a wide range of samples.

Application to standard samples

A limited number of NBS standards were analysed by the above procedure; the results are contained in Table IV. In Fig. 6, time and wavelength scans are shown for rubidium and caesium on sample NBS 1016 which contains 65% calcium oxide (equivalent to 2500 p.p.m. calcium in solution). Table III indicates that spectral interference should be present with NBS 1016 especially in the determination of caesium. This was found to be so, in that without correcting for spectral interference the result was 0.0018% (18 p.p.m.) caesium oxide, but after allowing for spectral interference less than 0.001% (4 p.p.m.) caesium oxide was found. The utilization of wavelength scanning on this sample clearly illustrates the versatility of the technique at the p.p.m. level.

TABLE IV

APPLICATION TO STANDARD SAMPLES

(The results are means of triplicates and are quoted as per cent metal oxide)

Description	*Rubidium*		*Caesium*	
	This method	*Certified*	*This method*	*Certified*
NBS 70a Potassium Feldspar	0.059	0.06	0.001_1	—
NBS 99a Soda Feldspar	0.011	—	0.001	—
NBS 181 Lithium Ore	0.008_1	—	0.006_6	—
NBS 1016 Portland Cement	<0.001	<0.001	<0.001	—
Pollucite	0.17	0.19	26.3	26.0

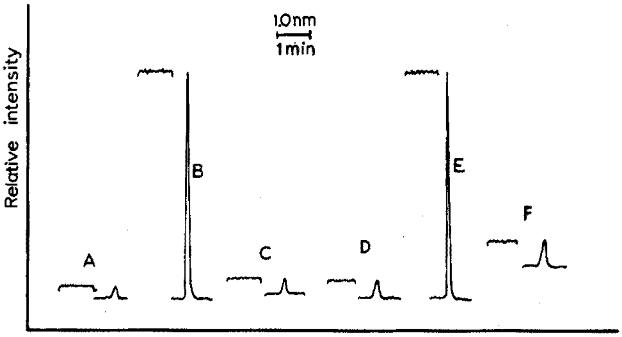


Fig. 6. Time and wavelength scan on sample NBS 1016. All solutions contain 1% potassium buffer and 10% hydrochloric acid. (A) '0' p.p.m. rubidium standard; (B) 0.5 p.p.m. rubidium; (C) NBS 1016 (for rubidium); (D) '0' p.p.m. caesium standard; (E) 0.5 p.p.m. caesium; (F) NBS 1016 (for caesium).

For correlation at higher levels, a sample of pollucite ore was analysed; the results were found to be in a very good agreement with a wet chemical separation procedure[10].

SUMMARY

An atomic emission spectrophotometric procedure is presented for the determination of rubidium and caesium at the per cent and p.p.m. levels. A nitrous oxide–acetylene flame and a potassium ionization buffer are used. There is no need for prior separation, pre-concentration or general matrix matching of standards.

RÉSUMÉ

On propose une méthode spectrophotométrique par émission atomique pour le dosage du rubidium et du césium. On utilise une flamme oxyde nitreux–acétylène et un tampon d'ionisation potassium. Il n'est pas nécessaire d'effectuer un traitement préalable de séparation ou de pré-concentration.

ZUSAMMENFASSUNG

Es wird ein Verfahren der Atomemissions-Spektrophotometrie zur Bestimmung von Rubidium und Cäsium im Prozent- und p.p.m.-Bereich beschrieben. Es werden eine Lachgas–Acetylen-Flamme und ein Kalium-Ionisationspuffer verwendet. Eine vorausgehende Abtrennung, Anreicherung oder eine Angleichung der Vergleichslösungen an die Matrix sind nicht nötig.

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THE ANALYSIS OF TUNGSTEN CARBIDES BY OPTICAL EMISSION SPECTROMETRY

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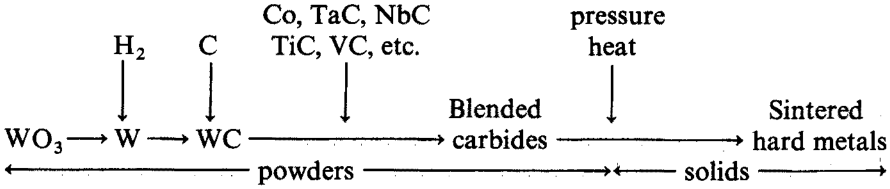
Tungsten carbide hard metals constitute a group of industrially important alloys applied in industries such as engineering, agriculture, appliance, textile and construction, where the extreme hardness and wear resistance of these materials can be used to advantage[1]. Development and maintenance of optimal properties in the alloys requires precise testing and control of composition, to ensure best performance and avoid wastage of the expensive materials involved in manufacture.

The literature on the analysis of tungsten carbide hard metals and powders is relatively sparse. Classical chemical methods[2-4] have been described for Al, C, Co, Cr, Fe, Nb, Mn, Mo, Ni, Si, Ta, Ti, and W; Shanahan[5] removed tungsten by chlorination before the chemical determination of aluminium, calcium and silicon. Molecular spectrophotometry[6] has been used for cobalt, iron and titanium, and atomic absorption spectrophotometry for cobalt[7] and iron[8]. X-ray fluorescence spectrometry has been applied to the determination of the major alloying elements in cemented[9,10], and powdered carbides[10], and solutions[11]. Maeda *et al.*[10] discuss the difficulties caused by surface inhomogeneities and the complex inter-element effects which require extensive suites of standards for each alloy type. Kántor *et al.*[12] described an optical emission spectrographic solution method for the determination of W, Co, Ti, Ta, Nb, Fe, Ni, Cr, Mn, Mg and Ca in hard metals. Spark excitation and the rotating disc electrode were used, the coefficients of variation ranged from 3–7%, and the detection limits were adequate for all elements excepting niobium; the method of sample solution preparation and the excitation technique are time-consuming.

Adequate d.c. and a.c. arc techniques[13-18] have been presented for the analysis of tungsten metal and tungstic oxide. These methods have been developed for trace element analyses and much attention has been given to suppression of the complex tungsten spectrum by inducing carbide formation in the heated electrode. However, poor reproducibility is obtained when spark excitation is used[16] because of erratic "*in situ*" formation of tungsten carbide.

The manufacturing process, which is briefly outlined below.



requires rapid analyses of oxide, carbide and intermediate powders as well as residues, rejects and the final cemented carbide products. The physical form of some sintered samples such as chips and fracture pieces, makes them unsuitable for direct analysis. However, these samples can be oxidized[6,14,17-19] and therefore a method for oxide analysis is required; an oxide method would also be suitable for controlling the input tungstic oxide and as a calibration method for cemented and powdered carbide reference standards. Rapid direct reading optical emission spectrometric methods have been investigated and developed for all of these products.

EXPERIMENTAL

Spectrometer

Jarrell-Ash 2-m direct-reading model 66-105; dispersion, 0.42 nm mm^{-1}; wavelength ranges 175–210 and 220–420 nm; pressure 0.65 N m^{-2}.

Electrical parameters

High voltage spark; 23 kV peak (briquettes), 27 kV peak (sintered solids); 40 μH (briquettes), residual μH (sintered solids); 5.5 r.f.A (briquettes), 9 r.f.A (sintered solids); 7.5 nF; 30 ohms primary; < 1 ohm secondary; 300 discharges sec^{-1}.

Electrode system

Graphite 6.5 mm dia. ASTM C5A tip; gap 4 mm; argon flow 7.5 l min^{-1}; sample preparation, hand rubbed on 400 grit SiC (briquettes), machine finished on 60 grit SiC (sintered solids).

Exposure conditions

Pre-flush 5 sec; pre-spark 10 sec (briquettes), 30 sec (sintered solids); integration 25 sec, terminated on La 379.08 nm (briquettes), and background (sintered solids).

Slit widths (μm) and wavelengths (nm)

Entrance slit, 25; W, 75, 400.88; Al, 50, 396.15; La, 35, 379.08; background, 100, 363.05; Co, 50, 345.35; Ni, 75, 341.48; Ti, 50, 324.20; Nb, 35, 319.50; V, 75, 310.23; Cr, 75, 267.72; Ta, 50, 263.69; Fe, 50, 259.84; Si, 100, 251.61.

Reagents

Graphite powder, briquetting grade; lithium nitrate, anhydrous; fusion mixture (64% lithium tetraborate–36% lanthanum tetraborate).

Recommended procedure

Briquetted oxides. Hand-crush solid and chip carbides to < 500 μm in a tungsten carbide mortar and further crush to < 125 μm in a 10-cm^3 tungsten carbide grinding barrel on a Siebtechnik swing mill. Grind tungstic oxides to < 63 μm in a tungsten carbide grinding barrel and dry at 110°. Weigh 85 mg (carbides) or 100 mg (oxides) into a 95/5, Pt/Au crucible containing 2 g of fusion mixture and 500 mg of lithium nitrate, and mix with a platinum wire; also prepare calibration standards from appropriate pure oxides. Pre-heat tungsten carbide mixes at 800° for 15 min to convert carbides to oxides, and then fuse all samples at 950° for 10 min. Cool, recover the fused bead, weigh the bead and add graphite powder (1.5 × recovered bead weight). Mill the fusion bead and graphite powder for 3 min in a 100-cm^3 tungsten carbide grinding barrel. Press the milled powder to a 25-mm dia. briquette at 45 kN.

Briquetted powder carbides. Weigh 200 mg of carbide powder samples or calibration standards into a phial containing 2 g of fusion mixture and 3.3 g of graphite powder. Mix by shaking, transfer to a 100-cm^3 tungsten carbide grinding barrel, mill for 3 min on a Siebtechnik swing mill and press to a 25-mm dia. briquette at 45 kN.

Excite the oxide or carbide briquettes, or solid samples under the indicated experimental parameters, and calculate the results.

RESULTS AND DISCUSSION

National standard samples of tungsten carbide to cover the range of cemented and powdered carbides produced (50–90% WC, 4–25% Co, 0–20% TiC, 2–12% TaC, 0–4% NbC, 0–0.1% VC, 0–0.5% Fe and < 0.1% Cu, Mn, Ni, and Cr) are not available and it was necessary to manufacture suitable reference standards. Synthetic oxide calibration standards made by precise weighing and fusion of pure materials and which contain some thirty major and trace elements are adequate for the briquetted oxide technique. However, the preparation of powdered and cemented carbide standards required a major effort. A small-scale commercial technique was used to blend and homogenize the appropriate carbides and trace metals to give six powdered carbide standards with a complete coverage for eleven major and minor elements. In turn, these powders were compacted to 33 mm dia. pieces and sintered to yield cemented standards. These powdered and cemented standards were analysed by the briquetted oxide technique by X-ray fluorescence and optical emission spectrometry, and by atomic absorption spectrophotometry, to confirm that the results predicted from the blended weights had been achieved and to assign a standard result.

Wybenga[9] indicated that a variety of compositional changes can occur in the outer layers of cemented carbide during the vacuum sintering process, especially cobalt within 0.2 mm of the surface. Since homogeneity is essential in cemented carbide standards several checks were carried out. First, 0.5 mm was removed from all surfaces in 0.1-mm layers and it was confirmed that a constant Co/W ratio had been re-established. Electron probe microanalysis scans were then carried out at high and low resolution; inhomogeneities were evident between 4 μm (dia.) areas which are below the size of the original blended particles, but no inhomogeneities were detected between 100 μm (dia.) areas along sections 4 mm deep.

The briquetted oxide technique described in the recommended procedure has its origin in the work of Hasler[20] and subsequent developments[21-24]. Factors which were considered in establishing a suitable briquetted oxide composition included sample-to-flux ratio, type of fusion mixture, choice of internal standard element and a requirement that the briquettes be suitable also for X-ray fluorescence spectrometry. A sample-to-flux ratio of 1:20 was considered to be a suitable compromise between adequate sensitivity for minor elements and sufficient dilution to minimize matrix effects. The investigation of several fusion mixture formulations indicated that a lanthanum-containing flux would serve as a heavy element absorber in X-ray fluorescence analysis and lanthanum could be used as the internal standard element in optical emission spectrometry.

Platinum–gold crucibles are superior to graphite crucibles because "memory" contamination is much less, in-fusion oxidations can be carried out, and no elemental reductions take place[21]. Platinum–gold crucibles must be protected against reducing conditions and this requirement leads logically to the use of in-fusion techniques to oxidize carbides and sulphides. Of the various in-fusion oxidizing agents which have been recommended, lithium nitrate[22] is preferred to sodium nitrate[22] and barium peroxide[24], because of maximal oxygen availability per unit weight, and because the excess of nitrate is destroyed, and no extraneous element is added to the flux.

Although the briquettes are tetraborate in character compared with the more basic metaborate of many workers, nevertheless it was observed that a long-term tendency to pick up water and carbon dioxide was exhibited. This effect resulted in a gradual drift in calibration curves derived from calibration briquettes which had been exposed to the atmosphere, compared to curves obtained with new briquettes. The effect could be avoided by storing briquettes at 110° and surfacing freshly before each group of excitations.

No difficulties were experienced with the preparation and excitation of briquetted powder carbides.

The cemented carbides are extremely hard (>1200 DPH) and the relative abrasion resistance decreases from SiC to BC to diamond[1]. Quality control situations involving large numbers of solid samples would require specialized surfacing equipment, such as diamond grinding wheels or electrolytic polishing. For limited sample throughput, satisfactory surfaces were obtained by using commercially available silicon carbide floor sanding discs. The hard surface required a more energetic discharge (9 r.f. A) and a relatively long pre-burn (30 sec) to ensure that adequate burn penetration was achieved.

The major elements present in tungsten carbide hard metal alloys, particularly tungsten, titanium and cobalt, possess complex atomic emission spectra, and consequently line interferences are almost inevitable. The major elements are not seriously affected by interfering lines, but significant interferences exist for many wavelengths normally used for the determination of minor elements, and corrections must be applied. The wavelengths used in this investigation represent the best choice of the available lines with a general-purpose spectrometer used for analyses of various metals and oxides. For briquetted oxides and powder carbides, under the conditions outlined in the recommended procedure, 1% of the interfering elements stated caused the following positive interferences: with Ta, 0.006% Si, 0.017% Fe, and 0.004% Nb; with W, 0.001% Si, 0.035% Cr and 0.0002% V; with Co, 0.001% Ca, 0.006% Ni; with Nb, 0.0007% Al.

Typical calibration graphs for determinations of the more important elements in tungsten carbide hard metals are shown in Fig. 1 and a comparison of reproducibilities obtained by the three methods is shown in Table I. Greater elemental coverage and highest precision were attained by means of the oxidation–fusion procedure but results obtained on unfused briquettes and sintered solids are quite satisfactory for commercial analyses.

While published literature indicates that X-ray fluorescence is the preferred method for direct reading analysis of tungsten carbides, this investigation has shown that optical emission spectrometry can be applied successfully.

Appreciation is expressed to the Broken Hill Proprietary Company Limited for permission to publish this work.

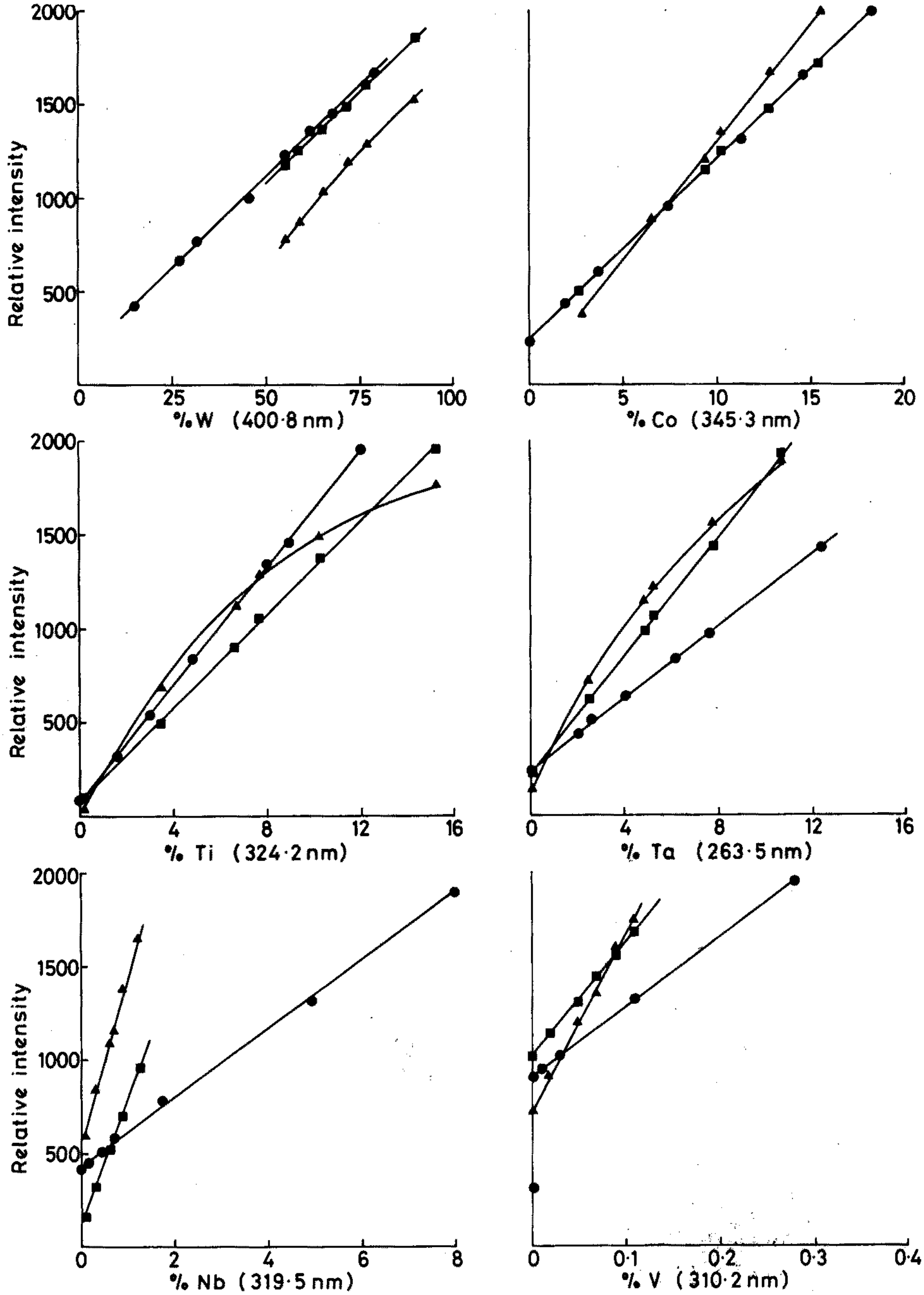


Fig. 1. Calibration graphs for tungsten carbide analysis. (●) Fused oxide, (■) unfused powder, (▲) sintered solid.

TABLE I

REPRODUCIBILITY DATA FOR ONE STANDARD BY THREE METHODS

Method		*W*	*Co*	*Ti*	*Ta*	*Nb*	*V*	*Ni*	*Cr*	*Fe*	*Si*	*Al*
Briquetted oxides	d^a	0.1	0.3	0.1	0.4	0.04	0	0.01	0.01	0	0	0
	1s	0.28	0.11	0.21	0.19	0.031	0.005	0.006	0.009	0.011	0.005	0.011
	S_r	0.005	0.011	0.014	0.018	0.025	0.071	0.105	0.087	0.033	0.035	0.26
Briquetted powder carbides	d	0.4	0.3	0	0.2	0	0					
	1s	0.54	0.17	0.20	0.26	0.039	0.005	nd	nd	nd	nd	nd
	S_r	0.010	0.017	0.013	0.024	0.032	0.071					
Cemented carbides	d	0.3	0.2	0.3	0.3	0.06	0.01					
	1s	0.49	0.26	0.26	0.34	0.068	0.005	nd	nd	nd	nd	nd
	S_r	0.009	0.025	0.017	0.031	0.056	0.071					
Calibrated result	$\bar{x}$	55.4	10.3	15.1	10.8	1.22	0.07	0.07	0.12	0.33	0.14	0.04

[a] d = Deviation. $S_r = 1s/\bar{x}$. $\bar{x}$ = Mean. *nd* = Not determined.
The deviations and mean refer to 12 results.

SUMMARY

Three direct reading, optical emission spectrometric techniques which use spark excitation are described for the analysis of tungsten carbide alloys in powder and compacted forms. The techniques cover oxidized samples which are fused with lithium–lanthanum tetraborate and briquetted with graphite, powdered carbide samples which are briquetted with lithium–lanthanum tetraborate and graphite, and cemented carbide metal samples. The preparation of reference standard samples and spectral interferences are described. The relative standard deviations are 0.005–0.031 for major and 0.02–0.26 for minor elements, and the best precision is obtained with oxide briquettes.

RÉSUMÉ

On décrit trois techniques spectrométriques d'émission pour l'analyse de carbures de tungstène, soit en poudre, soit sous forme compacte. On indique la préparation d'échantillons de référence et les interférences spectrales. Les déviations standards relatives sont 0.005–0.031 pour les éléments majeurs et 0.02–0.26 pour les éléments mineurs.

ZUSAMMENFASSUNG

Es werden drei emissionsspektrometrische Verfahren im optischen Bereich mit Funkenanregung und direkter Ablesung beschrieben für die Analyse von Wolframcarbid-Legierungen in Pulver- und kompakter Form. Die Verfahren verwenden oxidierte Proben, die mit Lithium–Lanthan-Tetraborat geschmolzen und mit Graphit gepresst werden, gepulverte Carbid-Proben, die mit Lithium–Lanthan-Tetraborat und Graphit gepresst werden, oder gesinterte Carbid–Metall-Proben. Die Herstellung der Vergleichs-Standardproben und die spektralen Störungen werden beschrieben. Die relativen Standardabweichungen sind 0.005–0.031 für Elemente in grösseren Mengen und 0.02–0.26 für Elemente in geringeren Mengen; die beste Reproduzierbarkeit wird mit Oxid-Presslingen erzielt.

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ELECTROREDUCTION AND POLAROGRAPHIC DETERMINATION OF NITRAZEPAM IN SERUM

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Nitrazepam (1,2-dihydro-7-nitro-2-oxo-5-phenyl-3H-1,4-benzodiazepine, "Mogadon") is a rapidly acting hypnotic drug and procedures have been outlined for determination of the drug in various materials by spectrophotometry and chromatography[1-3]. However, these methods involve time-consuming separations and are very inconvenient for routine analysis.

According to Senkowski *et al.*[4] the drug is polarographically active and is reduced in two steps at the dropping mercury electrode. Oelschläger *et al.*[2] claimed that the current is diffusion-controlled and proportional to the concentration in the range 10^{-5}–10^{-3} *M*; they recommended acetate buffer pH 4.7 containing 10–20% dimethylformamide as supporting electrolyte for determination of nitrazepam in tablets.

The present work was carried out in order to study the electroreduction of nitrazepam in detail and to investigate the application of polarography to rapid analysis of the drug in biological materials.

EXPERIMENTAL

Polarograms were recorded with a Metrohm E 261 R Polarecord connected to a Metrohm E 393 a.c. modulator. An Ag/AgCl/saturated KCl electrode served as reference electrode and a tungsten electrode was employed as auxiliary electrode. All a.c. polarograms were obtained with an amplitude of 10 mV r.m.s. The capillary characteristics of the dropping mercury electrode, measured in 0.1 *M* potassium nitrate (open circuit) at a mercury height of 38.4 cm, were $m = 2.230$ mg sec^{-1} and $t = 2.95$ sec. All experiments were performed at $25 \pm 0.1°$. Dissolved air was removed from the solutions by bubbling oxygen-free nitrogen through the cell for 10 min and passing it over the solution during the electrolysis.

Cyclic voltammetry, chronopotentiometry and coulometry experiments were performed with a versatile solid-state instrument constructed in this laboratory following the design of Goolsby and Sawyer[5]. A Mosely 7030 AM X–Y recorder and a Honeywell Electronic 194 stripchart recorder were used in conjunction with the instrument. A three-electrode assembly was used for all measurements. A Metrohm E 410 hanging mercury drop was used as working electrode for the cyclic voltammetry experiments and a mercury pool was employed for the controlled potential coulometric measurements. The reference electrode was an aqueous Ag/AgCl and a platinum coil served as auxiliary electrode. These electrodes were isolated in glass tubes with fine-

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porosity fritted glass discs. The shield tubes were filled with the supporting electrolyte used in the sample solution. The solution was stirred with a magnetic stirrer and a Teflon stirring bar.

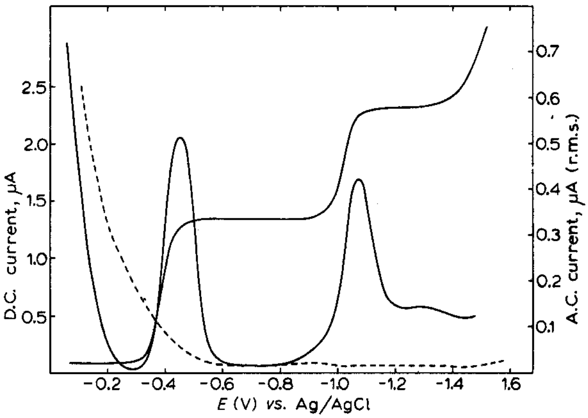
RESULTS

Polarograms of nitrazepam recorded from 0.1 *M* sulphuric acid, acetate, citrate or phosphate buffers exhibit two well-defined waves at all pH values. In acidic solutions a maximum is observed on the first wave but it is easily suppressed by addition of small amounts of decylamine. Preliminary experiments showed that the drug is decomposed in aqueous solutions. Polarograms recorded from acidic and from alkaline solutions showed that the first wave was shifted to more negative potentials and that the height of the second wave decreased with the time elapsed after mixing the solution. However, the drug appeared to be more stable in neutral solutions and no shift in potentials or decrease in wave height was observed five hours after mixing the solution when phosphate buffer pH 6.9 was used as supporting electrolyte. Because the drug is only slightly soluble in phosphate buffers, the stock solutions were prepared by dissolving the appropriate amount of nitrazepam in sodium hydroxide and immediately diluting the solution with phosphate buffer to pH 6.9. In the following experiments a new stock solution was prepared each day and discarded after 5 h.

Polarography

Polarograms of nitrazepam recorded from phosphate buffer pH 6.9 exhibit two waves with half-wave potentials $E_{\frac{1}{2}} = -0.38$ V and -1.02 V (Fig. 1). The d.c. polarographic steps are followed by a.c. polarographic waves with summit potentials about 40 mV more negative than the half-wave potentials.

As shown in Fig. 1 the base current is greatly depressed at potentials more positive than the first a.c. wave indicating that the oxidized form of the depolarizer is strongly adsorbed on the electrode[6]. The adsorption of the drug was verified by drop



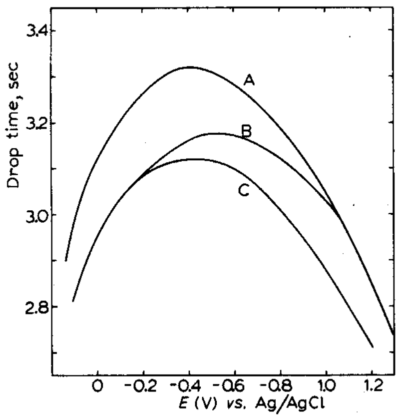


Fig. 1. A.c. and d.c. polarograms of 0.1 m*M* nitrazepam in phosphate buffer pH 6.9. Dashed line represents the a.c. polarographic base current.

Fig. 2. Electrocapillary curves of phosphate buffer pH 6.9 in the absence (curve A), in the presence of 0.25 m*M* nitrazepam (curve B) and in the presence of 20% serum (curve C).

time measurements. As indicated in Fig. 2, the presence of $2.5 \cdot 10^{-4}$ M nitrazepam causes a large decrease in the drop time over a considerable potential range, indicating that the drug is surface-active and is strongly adsorbed on the electrode at potentials more positive than -1 V *vs.* Ag/AgCl.

The effect of drop time on the limiting current was investigated by recording polarograms of 10^{-4} M nitrazepam in phosphate buffer pH 6.9 at various heights of the mercury column. The value $ih^{-\frac{1}{2}}$, where h is the height of the column after correction for the "back-pressure", was constant, indicating that the current is diffusion-controlled. However, the height of the a.c. wave increased linearly with increasing height of the column, which implies that the concentration of the depolarizer responsible for the a.c. current is time-dependent and that the a.c. current is partly controlled by the rate of a slow reaction[7,8].

The temperature coefficient (determined in the range 16–40°) of the d.c. current, 1.3% per degree, also implies that the rate of adsorption must be fast and that the current is controlled essentially by diffusion.

The effect of pH on the current–voltage curves was investigated by recording polarograms of 10^{-4} M nitrazepam in citrate and phosphate buffers. The half-wave potentials of both waves shifted to more negative values with increasing pH of the electrolyte, indicating that hydrogen ions are consumed in both electrode reactions. In the pH range 4–11 the half-wave potentials of the two waves may be expressed by the equations:

First wave: $E_{\frac{1}{2}} = -0.030 - 0.050 \cdot \mathrm{pH}$

Second wave: $E_{\frac{1}{2}} = -0.770 - 0.037 \cdot \mathrm{pH}$

The number of hydrogen ions, Z, consumed in the electrode reaction is given by

$$\Delta E_{\frac{1}{2}}/\Delta \mathrm{pH} = -0.059 \cdot Z/\alpha n_a$$

where α is the transfer coefficient and n_a the number of electrons in the rate-controlling step of the reduction process. The values αn_a calculated from the equation

$$E_{\frac{3}{4}} - E_{\frac{1}{4}} = \frac{0.0517}{\alpha n_a}$$

where $\alpha n_a = 2.1$ (first wave) and $\alpha n_a = 1.3$ (second wave), which gives the values $Z = 1.8$ and $Z = 0.81$ for the first and the second wave, respectively. Consequently, two hydrogen ions probably take part in the rate-controlling step of the first electrode reaction and one hydrogen ion in that of the second electrode reaction.

Polarograms recorded from phosphate buffer pH 6.9 and various amounts of nitrazepam present, showed that the height of both waves increases linearly with the concentrations. As indicated in Fig. 3 the diffusion current of the first d.c. polarographic step is higher than the current of the second step and considerably greater than the peak height of the corresponding a.c. wave. Hence, the first d.c. step is most useful for the determination of small amounts of the drug. The height of this wave is proportional to the concentration in the entire range 10^{-6}–$2.5 \cdot 10^{-4}$ M, the value $i_d/C = 11.4$ μA l mmole^{-1}, and the diffusion current constant $I = 5.4$ μA l mmole^{-1} mg$^{-\frac{2}{3}}$ sec$^{\frac{1}{2}}$.

Coulometry

Coulometric reductions at controlled potential of nitrazepam in phosphate

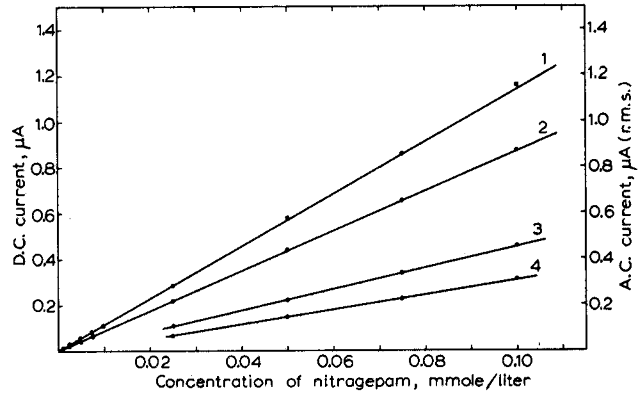


Fig. 3. Diffusion current of the first (curve 1) and of the second (curve 2) d.c. polarographic step and the peak height of the first (curve 3) and of the second (curve 4) a.c. polarographic wave of nitrazepam in phosphate buffer pH 6.9.

buffer pH 6.9 were performed to determine the number of electrons involved in the overall electron-transfer reactions. The experiments were carried out in the absence of air with a small electrolysis cell and a mercury pool as working electrode.

The potential of the mercury pool was first controlled at -0.70 V *vs.* Ag/AgCl. After 40 min of electrolysis, 0.99 coulomb was consumed in the reduction of $2.5 \cdot 10^{-6}$ mole of nitrazepam, which yields the value $n = 3.98$ for the first polarographic wave. The potential of the mercury pool was then increased to -1.2 V and the electrolysis continued for 50 min; 0.48 coulomb was consumed in this reduction, which yields the value $n = 1.95$ for the second polarographic wave. The experiment was repeated with a new solution containing the same amount of nitrazepam and with the potential of the working electrode controlled at -1.2 V; 1.425 coulomb was consumed in the complete reduction of nitrazepam, corresponding to a value of $n = 5.94$. These experiments clearly demonstrate that four electrons are involved in the first polarographic step and that the second step involves two electrons.

Cyclic voltammetry

Voltammetric experiments were performed at a hanging mercury drop electrode. Two cathodic peaks at potentials corresponding to the two polarographic steps were obtained (Fig. 4). If the potential sweep was repeated at the same mercury drop, the peak heights decreased and the peak potentials were shifted to more negative values, even though the solution was well stirred between each cyclic sweep. This is probably the result of the adsorption of nitrazepam on the electrode surface. However, reproducible voltammograms were obtained for the first potential sweep on each mercury drop. Hence, in the following experiments the mercury drop was exchanged between each experiment and just before the next potential sweep.

No anodic peak resulting from reoxidation of the reduction product was observed at any scan rate or any switching potential, indicating a highly irreversible electrode reaction.

Voltammograms of nitrazepam in phosphate buffer pH 6.9 were recorded from several solutions in the concentration range $5 \cdot 10^{-6}$–$2.5 \cdot 10^{-4}$ *M*. A few data are given in Table I. The current function, $i_p/Cv^{\frac{1}{2}}$, appeared to be very dependent on both the

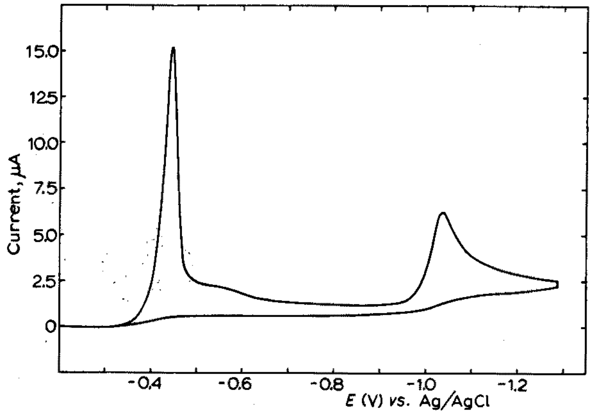


Fig. 4. Cyclic voltammogram of 10^{-4} M nitrazepam in phosphate buffer pH 6.9. Scan rate 0.1 V $\sec^{-1}$.

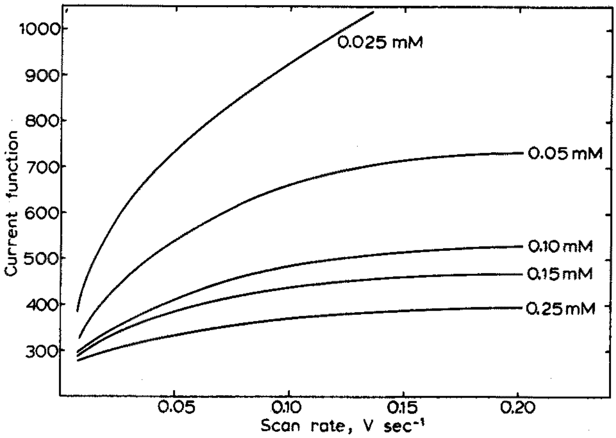


Fig. 5. Current function ($i_p/Cv^{\frac{1}{2}}$) of the first voltammetric peak of nitrazepam in phosphate buffer pH 6.9 as a function of scan rate. Bulk concentrations of nitrazepam are indicated on the curves.

scan rate and the bulk concentration of nitrazepam. However, as indicated in Fig. 5, the current function approaches a constant "diffusion-controlled" value at slow scan rates and at high bulk concentrations. This is a characteristic feature for surface-active depolarizers[9]. At sufficiently fast scan rates, the amount of diffusing material is small compared to the amount of adsorbed material at the electrode surface. On the other hand, when the bulk concentration is increased, the adsorption has a lesser relative influence on the peak current.

As a result of the adsorption the peak potentials are shifted cathodically and become dependent on the bulk concentration (Table I). Hence, the value αn_a cannot be calculated from the shift of peak potential with increasing scan rate.

Chronopotentiometry

The reduction of nitrazepam in phosphate buffer pH 6.9 gives rise to two-step chronopotentiograms. No reverse wave is observed, which indicates a highly irreversible process. The potential–time relationship for such processes is given by[10]

TABLE I

VOLTAMMETRIC DATA FOR THE REDUCTION OF NITRAZEPAM IN PHOSPHATE BUFFER pH 6.9

Scan rate ($V\ sec^{-1}$)	*First wave*			*Second wave*		
	$-E_p$ (V)	i_p (μA)	$i_p/Cv^{\frac{1}{2}}$ ($\mu A l mmole^{-1}\ V^{-\frac{1}{2}} sec^{\frac{1}{2}}$)	$-E_p$ (V)	i_p (μA)	$i_p/Cv^{\frac{1}{2}}$ ($\mu A l mmole^{-1}\ V^{-\frac{1}{2}} sec^{\frac{1}{2}}$)
0.25 *mM nitrazepam*						
0.200	0.490	44.5	398	1.050	12.5	112
0.100	0.472	29.5	373	1.042	7.93	100
0.033	0.452	14.4	316	1.039	4.07	90
0.0167	0.443	9.40	291	1.035	2.80	87
0.0083	0.435	6.35	279	1.035	1.98	87
0.10 *mM nitrazepam*						
0.200	0.464	23.7	530	1.045	8.13	182
0.100	0.445	15.3	483	1.037	5.02	159
0.033	0.426	6.80	374	1.025	2.51	138
0.0167	0.415	4.28	332	1.019	1.65	128
0.0083	0.407	2.72	299	1.013	1.06	116
0.025 *mM nitrazepam*						
0.200	0.440	13.6	1.217	1.043	5.43	486
0.100	0.420	7.27	920	1.034	2.73	346
0.033	0.398	2.94	646	1.018	1.14	251
0.0167	0.384	1.62	502	1.006	0.66	205
0.0083	0.374	1.00	440	0.995	0.41	180

$$E = \frac{0.059}{\alpha n_a} \log \frac{nFC^0 k^0_{fh}}{i_0} + \frac{0.059}{\alpha n_a} \log \frac{\tau^{\frac{1}{2}} - t^{\frac{1}{2}}}{\tau^{\frac{1}{2}}}$$

where E is the potential of the working electrode, α the transfer coefficient, n_a the number of electrons in the rate-controlling step, F the faraday, k^0_{fh} the forward heterogeneous rate constant, i_0 the current density, C^0 the concentration of the active species in the bulk of the solution, τ the transition time and t the time after the electrolysis is started. At $t=0$ the equation reduces to:

$$E_{t=0} = \frac{0.059}{\alpha n_a} \log \frac{nFC^0 k^0_{fh}}{i_0}$$

By applying a constant current and recording the potential of the working electrode as a function of time, $E_{t=0}$ can be obtained by extrapolation of the potential–time curve to zero.

A plot based on this equation for the first chronopotentiometric wave of nitrazepam showed a straight line. The slope of the line was 0.049 which gives the value $\alpha n_a = 1.20$, and indicates that the rate-determining charge-transfer step involves two electrons.

DISCUSSION

It is evident from the experimental results that a slow electron-transfer is involved in the first electrode reaction of nitrazepam. The galvanostatic experiments established that two electrons are involved in the rate-determining step, and the shift in the half-wave potential with increasing pH indicates that two hydrogen ions are consumed in the reaction. However, the coulometry experiments established that four electrons are consumed in the overall reduction and hence, the following reduction mechanism may be postulated for the first polarographic wave.

$$\text{R–NO}_2 + 2\text{H}^+ + 2e \xrightarrow{\text{slow}} \text{R–NO} + \text{H}_2\text{O}$$

$$\text{R–NO} + 2\text{H}^+ + 2e \xrightarrow{\text{fast}} \text{R–NHOH}$$

The fast reduction of the nitroso group is probably responsible for the appearance of an a.c. polarographic wave and the preceding slow reduction of the nitro group explains the drop-time dependence of the a.c. current.

The second reduction wave of nitrazepam involves two electrons. In strongly acidic solutions the half-wave potential is -0.67 V which is exactly the same value as that reported for the single wave of diazepam[11]. Consequently, this wave is probably due to reduction of the azomethine group:

$$>\text{C=N–} + 2\text{H}^+ + 2e \rightarrow\ >\text{CH–NH–}$$

The shift of the half-wave potential with increasing pH indicates that only one hydrogen ion is involved in the rate-determining step. Hence, this electrode reaction might also proceed in two steps.

Analytical applications

Cyclic voltammetry experiments and drop-time measurements showed that nitrazepam is adsorbed at the electrode surface. Hence, it should be possible to determine the drug in biological materials in the presence of surface-active proteins without any preceding separation, as has been done for chlordiazepoxide[12].

Various amounts of nitrazepam were added to 5 ml of horse serum, the serum was diluted to 25 ml with phosphate buffer pH 6.9 and after removal of dissolved air with nitrogen, the polarogram was recorded. The half-wave potentials were shifted to more negative values and the limiting current was depressed by the presence of serum. However, the first polarographic wave of nitrazepam was well-defined even in the presence of 20% serum. Moreover, the height of the wave was proportional to the concentration of nitrazepam in the range 10^{-6}–10^{-4} *M*, corresponding to 1.5–140 μg ml^{-1} in the serum.

Because serum is more strongly adsorbed than nitrazepam at high negative potentials (Fig. 2), the second polarographic wave of nitrazepam was seriously distorted and not suitable for quantitative work.

Further experiments showed that serum contains a sufficient amount of salts to act as supporting electrolyte. Moreover, the best pH region for polarographic determination of this drug happens to be the pH of serum. Hence, the dilution of the sample with phosphate buffer can be omitted and nitrazepam can be determined polarographically in serum without any separation and without addition of any supporting electrolyte. Only dissolved air must be removed before the polarogram is recorded.

As shown in Fig. 6, the first wave of nitrazepam in serum is measurable even at concentrations below 1 μg ml^{-1}. The half-wave potential in this medium is -0.51 V *vs.* Ag/AgCl.

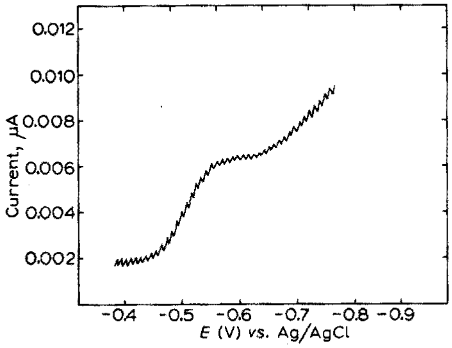


Fig. 6. Polarogram of 0.8 μg ml^{-1} nitrazepam in serum.

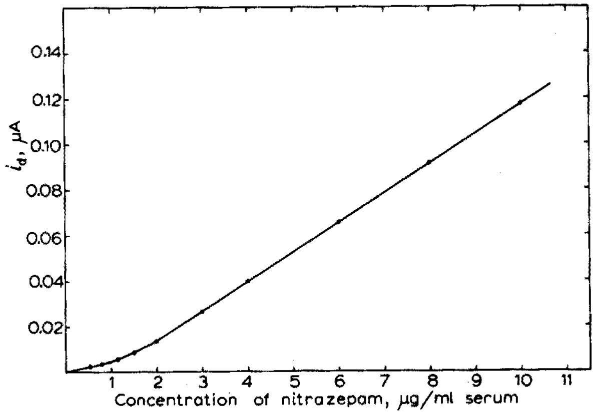


Fig. 7. Calibration curve for nitrazepam in serum.

The results obtained in determinations of nitrazepam in serum are given in Fig. 7. The height of the wave is proportional to the concentration of the drug in the range 2–80 μg ml^{-1}. At lower concentrations the limiting current is depressed and a deviation from the straight line is obtained. However, the polarograms are perfectly reproducible and by using a standard curve, the drug can be estimated in the entire range 0.5 to 80 μg ml^{-1} serum with a relative deviation of a few percent.

The proposed method is very selective. Other diazepine derivatives with similar chemical structures such as chlordiazepoxide and diazepam are reduced at considerably more negative potentials and do not interfere in the determination. Moreover, these experiments indicate that nitrazepam can be determined also in other biological fluids provided that the sample is diluted with phosphate buffer pH 6.9. However, it is often desirable to determine nitrazepam in serum at concentrations below 0.5 μg ml^{-1} and work is now in progress to investigate the application of more sensitive electrochemical methods, such as single sweep voltammetry at fast scan rates, for the determination of smaller amounts of nitrazepam in serum.

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SUMMARY

The electroreduction of nitrazepam has been investigated by polarography, cyclic voltammetry, chronopotentiometry and controlled potential coulometry. The drug is decomposed in acidic and alkaline solutions but is fairly stable in neutral media. In phosphate buffer pH 6.9 the reduction occurs in two steps. The first step is a 4-electron reduction of the nitro group to the hydroxylamine and the second step is a 2-electron reduction of the azomethine ($>C=N-$) group. The first polarographic wave probably involves a rate-determining 2-electron reduction of the nitro group. This wave is well defined and suitable for determination of the drug in the range 10^{-6}–$5 \cdot 10^{-4}$ *M*. The half-wave potential is −0.38 V *vs.* Ag/AgCl, and the current is diffusion-controlled. The oxidized form of nitrazepam is strongly adsorbed at the electrode surface, hence the drug can be determined in the presence of surface-active substances like proteins. A procedure has been developed for the direct polarographic determination of microgram quantities of the drug in serum. The proposed method is very rapid and accurate and permits determination of 0.5–80 μg per ml of the drug in serum.

RÉSUMÉ

On examine l'électroréduction du "nitrazepam" ("Mogadon") par polarographie, voltammétrie cyclique, chronopotentiométrie et coulométrie à potentiel contrôlé. La drogue est décomposée en solutions acides ou alcalines, mais elle est stable en milieu neutre. Une méthode est proposée pour le dosage polarographique direct de microquantités de cette substance dans le sérum. Elle est très rapide et précise et permet le dosage de quantités de l'ordre de 0.5 à 80 μg par ml de sérum.

ZUSAMMENFASSUNG

Die elektrochemische Reduktion von Nitrazepam wurde mittels Polarographie, cyclischer Voltammetrie, Chronopotentiometrie und Coulometrie mit kontrolliertem Potential untersucht. Die Droge zersetzt sich in sauren und alkalischen Lösungen, ist jedoch in neutralem Medium einigermassen beständig. In Phosphatpuffer pH 6.9 verläuft die Reduktion in zwei Stufen. Die erste Stufe ist eine 4-Elektronenreduktion der Nitrogruppe zum Hydroxylamin und die zweite eine 2-Elektronenreduktion der Azomethin-($>C=N-$)-Gruppe. Bei der ersten polarographischen Welle findet wahrscheinlich eine geschwindigkeitsbestimmende 2-Elektronenreduktion der Nitrogruppe statt. Diese Welle ist sehr gut definiert und eignet sich für die Bestimmung der Droge im Bereich 10^{-6}–$5 \cdot 10^{-4}$ *M*. Das Halbwellenpotential ist −0.38 V gegen Ag/AgCl, und der Strom ist diffusionskontrolliert. Die oxidierte Form von Nitrazepam wird an der Elektrodenoberfläche stark adsorbiert; deshalb kann die Droge in Gegenwart von oberflächenaktiven Substanzen wie Proteinen bestimmt werden. Es wurde ein Verfahren für die direkte polarographische Bestimmung von Mikrogramm-Mengen der Droge in Serum entwickelt. Die vorgeschlagene Methode ist sehr schnell und genau und ermöglicht die Bestimmung von 0.5–80 μg der Droge pro ml Serum.

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ORGANIC RADICAL-ION SALTS AS SELECTIVE ELECTROCHEMICAL SENSORS

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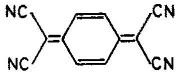
Earlier measurements have suggested that semiconducting organic radical-ion salts may be used profitably as the active components of solid-state ion-selective electrodes[1]. As a natural extension of those studies several further materials have been investigated in the hope that the important electrode properties of operational activity range and selectivity could be improved.



I

Weidenthaler and Pelinka[2] have shown that the observed potential response of electrodes incorporating 7,7,8,8-tetracyanoquinodimethan (TCNQ, I) or its salts towards changes in ionic activity of certain metal ions, M^+, in solution results from an equilibrium between solid MTCNQ and its ions at the electrolyte–electrode interphase. The response equation may be written:

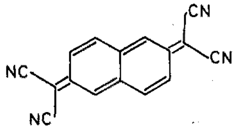
$$E = \text{const} - \frac{RT}{F} \ln K_{sp}(\text{MTCNQ}) + \frac{RT}{F} \ln a_{M^+}$$

where K_{sp}(MTCNQ) is the solubility product of MTCNQ. The electrode thus behaves essentially as an electrode of the second kind. If this explanation is correct, then the lower limit of the activity range of M^+ to which the electrode responds will be fixed by the finite solubility of the salt reflected by the solubility product. Further, if interference is assumed to occur through an ion-exchange process then the selectivity coefficient characteristic of a definite pair of ions may be related to differences in the values of the corresponding solubility products[3]. A certain amount of qualitative evidence in favour of this mode of behaviour has been obtained during studies with TCNQ-based electrodes and it appears reasonable to use solubility characteristics as a guide in choosing other systems for study. Measurements are in progress to provide a more quantitative basis for these assumptions.

With regard to extending the range of activity, the basic problem seemed to be one of finding compounds with properties similar to those of TCNQ, in particular, with the ability to form sufficiently stable radical-anion salts with a variety of metallic, organometallic or organic cations, but with much lower solubilities in aqueous solutions than the corresponding salts of TCNQ. The relative order of solubilities shown by the salts of a given starting compound would not be expected to differ greatly from that of the TCNQ salts, in view of the similarities in structure and electrostatic interactions. Nevertheless, for a particular electrode material, improved selectivity with regard to a specified reference–interference cation pair might be obtained. This would result primarily from an increased difference in the solubilities of the salts corresponding to the reference and interfering cations in comparison with the solubility difference found for the relevant TCNQ salts.

Organic radical-ion salts, possessing open-shell electronic configurations, may exhibit acceptably low electrical resistivity in the solid-state through favourable broadening of these shells to produce a partially filled electronic conduction band. In addition, effectively planar radical-ions like $TCNQ^{\overline{\cdot}}$, tend to form face-to-face stacks in the crystal where appreciable π-orbital overlap between neighbouring molecules further enhances electron mobility. In some cases the resistivities of TCNQ salts approach values characteristic of metals through a combination of these two effects[4]. Other organic complexes and closed-shell salts, which might have provided excellent choices from their solubility and selectivity characteristics, are generally good insulators and are consequently unsuitable for use in solid-state electrodes.

In the light of these criteria, three compounds were chosen for further study. These were 11,11,12,12-tetracyanonaphtho-2,6-quinodimethan (TNAP; II), 9-dicyanomethylene-2,4,7-trinitrofluorene (DTF; III), and 2,4,5,7-tetranitrofluoren-$\Delta^{9,\alpha}$-malononitrile (TFM; IV). All possess planar, aromatic molecules which are heavily substituted with the electron-attracting groups $-CN$ and $-NO_2$. Each molecule consequently shows high electron affinity, and π-delocalization of an acquired electron over the entire atomic framework lends stability to the resulting radical-anion.



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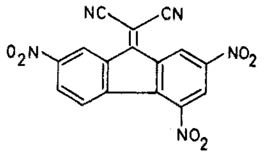

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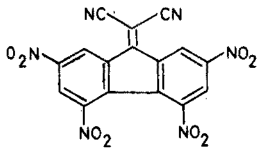


IV

TNAP resembles TCNQ very closely but half-wave reduction potentials show it to be a much stronger π-acid. Details of its preparation and properties have been reported[5]. Both simple and complex radical-ion salts may be prepared by techniques applicable to TCNQ[6]. DTF and TFM are readily prepared from the corresponding nitrofluorenones[7]. TFM, containing an additional nitro group, is a substantially stronger electron acceptor than DTF[8]. Radical-ion salts may be obtained by procedures appropriate to TCNQ and TNAP. The lithium salts of all three radical-anions are sufficiently soluble in methanol or water to allow the synthesis of other cation salts by direct metathesis, the required product being precipitated. Although detailed measurements of the electrical properties of the salts used in the present studies were not undertaken, adequately low electrical resistivities for electrode use were encountered in all cases.

EXPERIMENTAL

Materials

TNAP was obtained partly by total synthesis according to an established procedure and partly by oxidation of its precursor, 2,6-naphthalenedimalononitrile[5]. DTF and TFM were prepared from the corresponding nitrofluorenones (K&K Laboratories Inc. and Aldrich Chemical Co., Inc., respectively) as described by Mukherjee and Levasseur[7]. Reaction with lithium iodide in hot acetonitrile solution afforded the lithium salts of the respective radical-anions. Metatheses of these latter salts with suitable salts of lead, copper(II) and tetraphenylarsonium ions in aqueous or methanolic solution yielded the corresponding radical-ion salts. Recrystallizations were carried out from acetonitrile.

Preparation of electrodes

Electrodes were constructed from the lead, copper and tetraphenylarsonium salts of all three radical-anions (a total of nine different materials) as described earlier[1]. A minimum of three electrodes was prepared from each material. Alternative methods of fabrication, *e.g.*, dispersion of the active material in an inert plastic membrane, have not been examined although such procedures may be advantageous for salts which are difficult to obtain in an acceptable compacted form.

Measurements

Response characteristics were determined in unbuffered aqueous solutions of lead nitrate, copper(II) nitrate and tetraphenylarsonium chloride. Approximate selectivity parameters were derived from measurements made in aqueous 0.1 *M* solutions of suitable salts of the interfering cation. Variations in cell potential were measured at 25° with an Orion model 701 digital pH-meter. The reference was an Orion model 90–02 double liquid-junction electrode with an outer-chamber filling of aqueous 10% potassium nitrate. Single ion activities were evaluated from the extended Debye–Hückel relation using the ion-size parameters of Kielland[9]. Mean activity coefficients for tetraphenylarsonium chloride in aqueous solution[10] were used to obtain the single ion activity of $(C_6H_5)_4As^+$ by assuming chloride ion activities equal to those found in potassium chloride solutions of the same ionic strength.

In general, the salt preparations were performed with excess of the cation-containing reagents. In this respect the conditions favoured simple salt formation; complex salts containing neutral molecules of TNAP, DTF or TFM were unlikely to be formed in appreciable amounts. Closer examination of the stoichiometry of the various salts was not undertaken in this instance. The electrodes functioned almost immediately on initial immersion in the test solutions. The response times were usually less than 3 min and pre-soaking was not required. Some difficulties were caused by the appearance of cracks in some of the pressed-powder pellets with consequent loss of acceptable electrode function. Further studies aimed at alleviating such complications are in progress and alternative methods of construction have yielded much improved behaviour both from stability and reproducibility viewpoints.

Few detailed studies of long-term stability have, as yet, been carried out but examples of $(C_6H_5)_4$AsDTF electrodes have been stored dry for periods up to 3 months without serious deterioration in electrode properties. Reproducibility appears to be within ±2 mV for series of measurements with a given test solution. The salts themselves appear quite stable in the solid-state for periods of several months.

RESULTS AND DISCUSSION

In all cases the three salts containing a given cation, *e.g.*, $Pb(TNAP)_2$, $Pb(DTF)_2$ and $Pb(TFM)_2$, showed similar behaviour; essentially Nernstian response curves over the cation activity ranges studied (typically 10^{-1}–10^{-6} *M*) were obtained. Representative plots are shown for electrodes prepared from $Pb(TNAP)_2$, $Cu(DTF)_2$ and $(C_6H_5)_4As(TFM)$ in Fig. 1. In comparison a $Pb(TCNQ)_2$ electrode showed a lower limit in its linear range at 10^{-4} *M* lead(II). This result supports the original assumption that by employing salts of a radical-anion with a higher molecular weight as electrode sensors, lower solubility and a consequent improvement in operational activity range would result.

Marked variations in the standard potential values were obtained with different examples of a given electrode. This most probably arises from differences in contact potential between the graphite paste and the sensor pellet. Such differences between individual electrodes necessitate separate calibrations but do not affect the selectivity parameters. Preliminary studies showed the electrodes to be appreciably selective for a reference ion. More detailed measurements are needed for complete evaluation of a given electrode but the orders of magnitude shown in Table I for three of the electrodes examined serve as a guide to the expected performance. Values of *K* below 1 reflect selectivity for the reference ion for which $K=1$. The heavy metal ions silver(I) and mercury(II) were found to interfere strongly in all cases by formation of the corresponding insoluble salts upon the electrode surface. Again for comparison purposes, the selectivity shown by a $Cu(TCNQ)_2$ electrode for copper(II) over nickel(II) was of the order $K_{Cu-Ni}=10^{-2}$. The sequence of approximate selectivity coefficients, with the exception of that of hydrogen ion, follows closely the same order for each of the materials. The relative position of the hydrogen ion selectivity coefficient differs for the various materials; in particular, hydrogen ion interference is much less pronounced for the $Cu(TCNQ)_2$ electrode than for that incorporating $Cu(TFM)_2$. At the same time, however, the latter electrode shows much better selectivity for copper(II) ions over Ni(II) ions than is found in the case of the TCNQ salt, reflecting the wider difference in solubilities which has been obtained. For cations other than hydrogen ion, interfer-

TABLE I

APPROXIMATE SELECTIVITY COEFFICIENTS $K_{ref.-inter.}$

Cation	*Electrode sensor*			
	$Pb(TNAP)_2$	*$Cu(TFM)_2$*	*$(C_6H_5)_4As(DTF)$*	*$Cu(TCNQ)_2$*
Pb^{2+}	1	10^{-3}	10^{-4}	—
Li^+, Na^+, K^+	10^{-4}	10^{-5}	$<10^{-6}$ [a]	—
H^+	1	10^{-2}	10^{-3}	10^{-4}
Cu^{2+}	10^3	1	—	1
Ni^{2+}	—	10^{-4}	—	10^{-2}
$(C_6H_5)_4As^+$	—	—	1	—
Ca^{2+}, $(CH_3)_4N^+$	—	—	10^{-5}	—
$(C_4H_9)_4N^+$	—	—	10^{-1}	—

[a] Below lower limit of detection of reference ion.

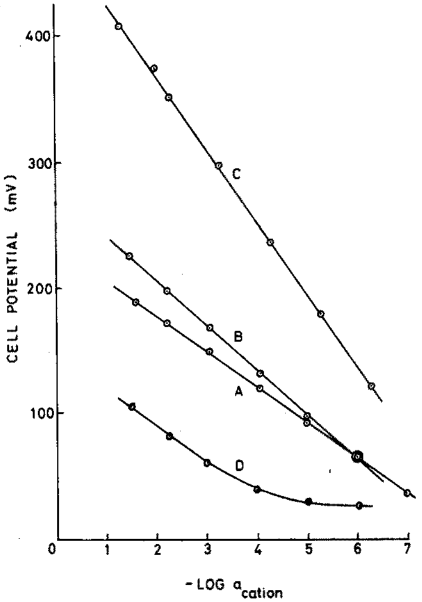
ence involves an ion-exchange process, whereby the interfering cation replaces the reference ion in the radical-ion salt sensor. As a first approximation, the extent of interference will follow the order of solubilities of the different salts. Hydrogen ion interferes by an entirely different mechanism which involves initial attack on the organic radical-anion followed by radical disproportionation:

$$2A^{\cdot -} + 2H^{+} \rightleftharpoons 2AH^{\cdot} \rightleftharpoons A + AH_2$$

The factors which determine the ease of hydrogen ion attack are difficult to define clearly but undoubtedly the electron density distributions of the different radical anions as well as steric influences are involved.

A possible application of electrodes selective to $(C_6H_5)_4As^+$ cations as indicators in the potentiometric titration of perchlorate solutions with solutions of $(C_6H_5)_4$-AsCl was considered. As an example, Fig. 2 shows a titration curve obtained with a $(C_6H_5)_4$As(DTF) electrode. Further detailed studies aimed at an assessment of this method for determining perchlorate concentrations are in progress.

Although many fundamental questions dealing with the most suitable conditions under which such electrochemical sensors can be used, the factors determining



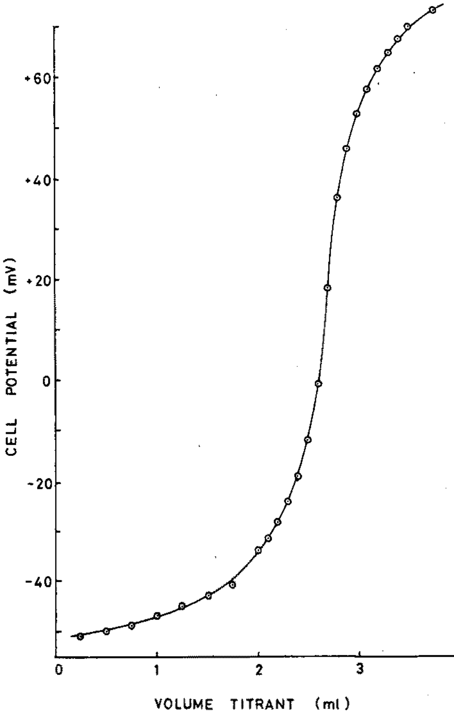


Fig. 1. Response curves for electrodes made from (A) $Pb(TNAP)_2$, 28 mV decade^{-1}; (B) $Cu(DTF)_2$, 33 mV decade^{-1}; (C) $(C_6H_5)_4$As(TFM), 58 mV decade^{-1}; (D) $Pb(TCNQ)_2$, 30 mV decade^{-1} towards Pb^{2+}, Cu^{2+}, $(C_6H_5)_4As^+$ and Pb^{2+} cations, respectively.

Fig. 2. Potentiometric titration of 25.0 ml of aqueous $NaClO_4$ (0.005 *M*) with aqueous $(C_6H_5)_4AsCl$ (0.0466 *M*), for a $(C_6H_5)_4$As(DTF) electrode. The calculated equivalent volume of titrant = observed equivalent volume = 2.68 ml.

selectivity, the long-term stability and possible alternative methods of fabrication (*e.g.*, heterogeneous or liquid membrane types) remain to be answered, it appears that further efforts with this class of materials are justified.

The author wishes to thank Kerstin Edström for carrying out the measurements, Dr. W. R. Hertler for generous gifts of TNAP and its precursor, and Prof. Gillis Johansson for valuable discussions. Financial support by the Swedish Board for Technical Development is gratefully acknowledged.

SUMMARY

A series of semiconducting organic radical-ion salts has been studied with regard to the potential use of such compounds in solid-state ion-selective electrodes. Improvements in working activity ranges and selectivities were obtained in comparison with previously investigated salts of TCNQ; excellent calibration graphs were obtained for lead(II), copper(II) and tetraphenylarsonium ions.

RÉSUMÉ

On examine les possibilités d'utilisation de sels à radicaux ioniques organiques comme composants actifs d'électrodes ioniques sélectives. D'excellents graphiques d'étalonnage sont obtenus pour le plomb(II), le cuivre(II) et les ions tétraphénylarsonium.

ZUSAMMENFASSUNG

Es wurde eine Reihe von halbleitenden organischen Radikalion-Salzen im Hinblick auf die mögliche Verwendung solcher Verbindungen in ionenselektiven Festkörperelektroden untersucht. Es wurden Fortschritte in den Aktivitätsbereichen und Selektivitäten erzielt im Vergleich zu den vorher untersuchten Salzen von TCNQ; es wurden ausgezeichnete Eichkurven erhalten für Blei(II)-, Kupfer(II)- und Tetraphenylarsonium-Ionen.

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SHORT COMMUNICATIONS

The calculation and use of α coefficients

Side-reaction coefficients—usually called α coefficients—are nowadays widely used in analytical chemistry to simplify equilibrium calculations. The concept of the α coefficient was originally introduced by Schwarzenbach[1], but several authors have later extended its use. Ringbom[2] has suggested that the influence of practically all occurring side reactions on a certain main reaction should be taken into account by means of such coefficients. The net influence of several side reactions is given by an "over-all α coefficient", which is often approximately equal to the sum of the individual α coefficients.

If a metal ion M and a ligand L form a complex ML, hydrogen or hydroxide ions may affect the reaction in three ways. The reactions of the ligand with hydrogen ions are taken into account by the coefficient $\alpha_{L(H)}$, the reactions of M ions with hydroxide ion by the coefficient $\alpha_{M(OH)}$ and the reactions of ML with hydrogen and hydroxide ions by the coefficient $\alpha_{ML(H,\,OH)}$. Analogously, reactions between L and interfering cations, M_I, M_{II}, ..., are taken into account by the coefficients $\alpha_{L(M_I)}$, $\alpha_{L(M_{II})}$, ... and reactions between M and interfering ligands, A_I, A_{II}, ..., by the coefficients $\alpha_{M(A_I)}$, $\alpha_{M(A_{II})}$, ... The interfering species responsible for a side reaction is always given in parentheses in the subscript of α.

The calculation of α coefficients is, of course, based on equilibrium constants. For instance,

$$\alpha_{L(H)} = 1 + \sum_{n=1}^{N} [H]^n \beta_n \tag{1}$$

where β_n is the cumulative protonation constant and N is the maximum number of bound protons.

Similar expressions can be written for other α coefficients. On the basis of these coefficients, conditional stability constants of numerous complexes can be calculated[2-4].

An α coefficient is thus the sum of a number of exponential terms, and its calculation is actually a very simple mathematical operation. For calculating α coefficients, (*e.g.* $\alpha_{L(H)}$ as a function of pH for a polybasic acid), modern desk calculators and computers are particularly appropriate and are commonly used.

Nevertheless, the analyst often meets problems demanding α coefficients which are not tabulated in any textbook, and suitable calculators or computers are not always immediately available. Moreover, if many side reactions occur, computers do not always represent the most rapid and practical means of estimating the values of individual and over-all α coefficients. The reason is that, as a rule, the final result is affected by only a few of the numerous side equilibria.

We have noticed that many chemists waste time by performing calculations with α coefficients in a far from rational way and are not aware of the fact that additions (or subtractions) of exponential terms can be performed by reference to short tables often included in tables of logarithms.

Tables I and II are given in a form particularly appropriate for chemists, who generally are not interested in logarithmic α values accurate to more than two decimal places. The tables hardly need any explanation, but a few comments may be appropriate. If the sum of two exponential terms or their difference is to be calculated with a precision of two decimals in the exponent, the smaller term can be neglected if the difference between the exponents exceeds 2. When the exponents differ by more than one unit, the exponent of the larger term will change at most 0.04. This means that several terms can be neglected in calculations of individual or over-all α coefficients.

The use of the tables can best be illustrated by means of a few examples.

Example 1. Calculate $\alpha_{L(H)}$ for the complexing agent TTHA at pH 6.50. The cumulative protonation constants are[5] $\log\beta_1 = 10.19$, $\log\beta_2 = 19.59$, $\log\beta_3 = 25.75$, $\log\beta_4 = 29.91$, $\log\beta_5 = 32.86$, $\log\beta_6 = 35.28$.

The complete expression for $\alpha_{L(H)}$ is

$$\begin{aligned}\alpha_{L(H)} = 1 + 10^{-6.5}\ 10^{10.19} + 10^{-13.0}\ 10^{19.59} + 10^{-19.5}\ 10^{25.75} + \\ + 10^{-26.0}\ 10^{29.91} + 10^{-32.5}\ 10^{32.86} + 10^{-39.0}\ 10^{35.28} \qquad (2)\end{aligned}$$

It is immediately seen that the third term, $10^{6.59}$, and the fourth term, $10^{6.25}$, are the two largest ones. The difference between their exponents is 0.34 and, accord-

TABLE I

ADDITION OF EXPONENTIAL TERMS $10^a + 10^b = 10^{a+x}$ $(a \geq b)$

$a-b$	x									
	0	1	2	3	4	5	6	7	8	9
0.0	0.301	0.296	0.291	0.286	0.281	0.277	0.272	0.267	0.263	0.258
0.1	0.254	0.250	0.245	0.241	0.237	0.232	0.228	0.224	0.220	0.216
0.2	0.212	0.209	0.205	0.201	0.197	0.194	0.190	0.187	0.183	0.180
0.3	0.176	0.173	0.170	0.167	0.163	0.160	0.157	0.154	0.151	0.148
0.4	0.146	0.143	0.140	0.137	0.135	0.132	0.129	0.127	0.124	0.122
0.5	0.119	0.117	0.115	0.112	0.110	0.108	0.106	0.104	0.101	0.099
0.6	0.097	0.095	0.093	0.091	0.090	0.088	0.086	0.084	0.082	0.081
0.7	0.079	0.077	0.076	0.074	0.073	0.071	0.070	0.068	0.067	0.065
0.8	0.064	0.063	0.061	0.060	0.059	0.057	0.056	0.055	0.054	0.053
0.9	0.052	0.050	0.049	0.048	0.047	0.046	0.045	0.044	0.043	0.042
1.0	0.041	0.040	0.040	0.039	0.038	0.037	0.036	0.035	0.035	0.034
1.1	0.033	0.032	0.032	0.031	0.030	0.030	0.029	0.028	0.028	0.027
1.2	0.027	0.026	0.025	0.025	0.024	0.024	0.023	0.023	0.022	0.022
1.3	0.021	0.021	0.020	0.020	0.019	0.019	0.019	0.018	0.018	0.017
1.4	0.017	0.017	0.016	0.016	0.015	0.015	0.015	0.014	0.014	0.014
1.5	0.014	0.013	0.013	0.013	0.012	0.012	0.012	0.012	0.011	0.011
1.6	0.011	0.011	0.010	0.010	0.010	0.010	0.009	0.009	0.009	0.009
1.7	0.009	0.008	0.008	0.008	0.008	0.008	0.007	0.007	0.007	0.007
1.8	0.007	0.007	0.007	0.006	0.006	0.006	0.006	0.006	0.006	0.006
	1.90–1.98	0.005	1.99–2.09	0.004	2.10–2.23	0.003	2.24–2.46	0.002	2.47–2.94	0.001

TABLE II

SUBTRACTION OF EXPONENTIAL TERMS $10^a - 10^b = 10^{a-y}$ $(a \geqq b)$

$a-b$	y									
	0	1	2	3	4	5	6	7	8	9
0.0	∞	1.643	1.347	1.176	1.056	0.964	0.889	0.827	0.774	0.728
0.1	0.687	0.650	0.617	0.587	0.560	0.535	0.511	0.490	0.469	0.451
0.2	0.433	0.416	0.401	0.386	0.372	0.359	0.346	0.334	0.323	0.312
0.3	0.302	0.292	0.283	0.274	0.265	0.257	0.249	0.242	0.234	0.227
0.4	0.220	0.214	0.208	0.202	0.196	0.190	0.185	0.180	0.175	0.170
0.5	0.165	0.160	0.156	0.152	0.148	0.144	0.140	0.136	0.133	0.129
0.6	0.126	0.122	0.119	0.116	0.113	0.110	0.107	0.104	0.102	0.099
0.7	0.097	0.094	0.092	0.089	0.087	0.085	0.083	0.081	0.079	0.077
0.8	0.075	0.073	0.071	0.070	0.068	0.066	0.065	0.063	0.061	0.060
0.9	0.058	0.057	0.056	0.054	0.053	0.052	0.050	0.049	0.048	0.047
1.0	0.046	0.045	0.044	0.043	0.042	0.041	0.040	0.039	0.038	0.037
1.1	0.036	0.035	0.034	0.033	0.033	0.032	0.031	0.030	0.030	0.029
1.2	0.028	0.028	0.027	0.026	0.026	0.025	0.025	0.024	0.023	0.023
1.3	0.022	0.022	0.021	0.021	0.020	0.020	0.019	0.019	0.018	0.018
1.4	0.018	0.017	0.017	0.016	0.016	0.016	0.015	0.015	0.015	0.014
1.5	0.014	0.014	0.013	0.013	0.013	0.012	0.012	0.012	0.012	0.011
1.6	0.011	0.011	0.011	0.010	0.010	0.010	0.010	0.009	0.009	0.009
1.7	0.009	0.009	0.008	0.008	0.008	0.008	0.008	0.007	0.007	0.007
1.8	0.007	0.007	0.007	0.006	0.006	0.006	0.006	0.006	0.006	0.006
1.9	0.006									
	1.91–1.98	0.005	1.99–2.09	0.004	2.10–2.24	0.003	2.25–2.46	0.002	2.47–2.94	0.001

ing to Table I, the sum of the two terms is $10^{6.59+0.16} = 10^{6.75}$. The other five terms of eqn. (2) have exponents more than 2 units smaller than the exponent of this sum and can thus be neglected.

Example 2. What is the conditional constant of the zinc–DCTA complex at pH 10 in the presence of free ammonia, $[NH_3] = 0.1$ M, and sodium ions, $[Na] = 0.2 = 10^{-0.70}$ M? Calculate pZn_{eq} if a 10^{-3} M zinc salt solution is titrated.

The answer requires knowledge of the over-all α coefficients. The expressions for the individual coefficients are given below; the values of the constants needed were taken from the collection in ref. 2, except $K_{NaL} = 10^{4.40}$ and $\beta_1 = K_{HL} = 10^{13.17}$ of DCTA (H_4L), which are from a recent paper by Carr and Swartzfager[6]. K_{ZnL} corrected by noting their new value of K_{HL} is $10^{20.14}$.

$$\alpha_{L(H)} = 1 + 10^{-10}\ 10^{13.17} + 10^{-20}\ 10^{19.37} + 10^{-30}\ 10^{22.97} + \\ + 10^{-40}\ 10^{25.48} = 10^{3.17}\ .$$

$$\alpha_{L(Na)} = 1 + 10^{-0.70}\ 10^{4.40} = 10^{3.70}.$$

$$\alpha_{Zn(NH_3)} = 1 + 10^{-1}\ 10^{2.27} + 10^{-2}\ 10^{4.61} + 10^{-3}\ 10^{7.01} + 10^{-4}\ 10^{9.06} = 10^{5.10}.$$

$$\alpha_{Zn(OH)} = 1 + 10^{-4}\ 10^{4.4} + 10^{-12}\ 10^{14.4} + 10^{-16}\ 10^{15.5} = 10^{2.4}.$$

No constants of basic or mixed ammonia ZnL complexes are given in the literature.

It follows that the over-all α coefficient $\alpha_{\mathrm{L(H,Na)}} = 10^{3.17} + 10^{3.70} - 1$, *i.e.*, according to Table I, $\alpha_{\mathrm{L}} = 10^{3.70+0.11} = 10^{3.81}$. The over-all coefficient $\alpha_{\mathrm{Zn(NH_3,OH)}} = 10^{5.10}$. The conditional constant $\log K_{\mathrm{ZnL}}^{\mathrm{Zn}',\mathrm{L}'} = 20.1 - 3.8 - 5.1 = 11.2$, and if a $10^{-3}\,M$ solution is titrated, $\mathrm{pZn_{eq}} = \frac{1}{2}(3 + 11.2) + 5.1 = 12.2$. If the transition point of the used indicator, $\mathrm{pZn_{trans}}$, is known, the attainable accuracy expressed as per cent error can be directly read from an error diagram (ref. 2, p. 80).

Note. If the equilibrium constants valid at $\mu = 0.1$ were corrected to values valid at the ionic strength of the solution (about 0.2–0.25), the $\mathrm{pZn_{eq}}$ value would be about 0.1 unit lower.

It may also occur that other mathematical operations including the subtraction of exponential terms have to be performed. The following formula may sometimes be useful:

$$\frac{10^a + 10^b}{10^a - 10^b} = \frac{10^{a+x}}{10^{a-y}} = 10^{x+y} \tag{3}$$

Example 3. In a paper from this laboratory[4], the stability constants of the mononuclear silver–TTHA complexes were determined from pAg values. The value of the stability constant at pH 4.60 when pAg = 2.72 (given in Table IX, Part II) was corrected by means of the expression:

$$\text{Correction factor} = \frac{\frac{1}{2}\,C_{\mathrm{L}} - [\mathrm{Ag}]}{\frac{1}{2}\,C_{\mathrm{L}} + [\mathrm{Ag}]} = \frac{10^{-2.30} - 10^{-2.72}}{10^{-2.30} + 10^{-2.72}} = 10^{-0.35}$$

$a - b = 0.42$ and, according to Tables I and II, $x = 0.140$ and $y = 0.208$. Consequently, we obtain $10^{-(0.14+0.21)} = 10^{-0.35}$.

A chemist familiar with the use of Tables I and II, can easily and mentally make such corrections in a few moments.

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Gas chromatography of rare earth chelates of isobutyrylpivalylmethane

It has been recognized that the gas chromatography of metal chelates could be a useful technique for the rapid separation and the determination of micro amounts of metal ions, and some reports have already been published. Beryllium[1] has been sensitively determined, as has chromium[2,3] in alloys or biological materials. Methods for other metals such as aluminum, iron, copper, etc. have also been proposed[4-8]. Application of gas chromatography to the determination of rare earth elements, of which the separation is usually troublesome and time-consuming, would be particularly attractive. The rare-earth chelates with 2,2,6,6-tetramethyl-3,5-heptanedione[9], 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione[10], and 1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedione[11,12] have been successfully gas-chromatographed. Utsunomiya and Shigematsu[13] have also made systematic investigations on this interesting problem using a number of β-diketones synthesized[13]. In the course of the study, it was found that the rare-earth chelates with 2,2,6-trimethyl-3,5-heptanedione (isobutyrylpivalylmethane, IBPM) are sufficiently volatile and thermally stable to permit their gas chromatography, like the β-diketone chelates described above.

In the present work, scandium, yttrium and the rare-earth IBPM chelates were prepared and their thermogravimetric and gas chromatographic behaviors were investigated. The possibility of direct determinations by measuring the peak height was also surveyed, although complete separation and simultaneous determination have still not been achieved.

Experimental

Preparation of rare-earth chelates. Isobutyrylpivalylmethane (IBPM) was synthesized by the Claisen condensation[14] of pinacolone and ethyl isobutyrate with sodium amide. The purified product has a b.p. of 77–78° at 13 mm Hg.

Scandium, yttrium or the rare earth oxide (99.9%) was dissolved in the minimal quantity of concentrated nitric acid and the solution was evaporated almost to dryness. After the residue had been dissolved in a small volume of water–ethanol (1 + 1), a stoichiometric amount of IBPM was added with stirring and the pH of the mixture was maintained at *ca.* 6 with a 1 *M* ammonia solution. The solution was then diluted with a large amount of water, and then precipitate formed was filtered off, washed and dried in a vacuum desiccator. Finally the product was recrystallized from benzene and dried in a vacuum desiccator. The melting points and the results of the elemental analyses of these IBPM chelates are summarized in Table I.

Gas chromatography. Gas chromatograms were obtained with a Yanagimoto gas chromatograph GCD-5DH with a thermal conductivity detector. Chromosorb W AW DMCS (60–80 mesh) coated with 5% (w/w) Dow Corning high-vacuum silicone grease was packed into a stainless steel column (75 cm × 3 mm i.d.). The injection temperature was kept at 300°, the column was heated from 210 to 280° at various rates, and the detector temperature was 310°. Helium was used as the carrier gas.

Thermogravimetry. The thermogravimetric analyses were made with a Shimadzu thermo balance. A portion (*ca.* 20 mg) of a chelate in a platinum dish was heated at a rate of 10° min^{-1} in a nitrogen stream at a flow rate of 50 ml min^{-1}.

TABLE I

MELTING POINTS AND ANALYTICAL RESULTS FOR IBPM CHELATES

Chelate	*Color*	*M.p.* (°)	*Calcd.* (%)		*Found* (%)	
			C	*H*	*C*	*H*
$Sc(C_{10}H_{17}O_2)_3$	White	88.0	65.20	9.30	63.26	9.31
$Y(C_{10}H_{17}O_2)_3$	White	180–184	60.39	8.62	58.60	8.60
$La(C_{10}H_{17}O_2)_3$	White	116–118	55.72	7.95	53.01	7.96
$Pr(C_{10}H_{17}O_2)_3$	Green	166–167	55.55	7.93	52.00	7.73
$Nd(C_{10}H_{17}O_2)_3$	Blue	188–190	55.27	7.88	52.88	7.74
$Sm(C_{10}H_{17}O_2)_3$	Yellow	176–177	54.75	7.81	51.69	7.63
$Eu(C_{10}H_{17}O_2)_3$	Yellow	182–183	54.62	7.79	51.56	7.59
$Gd(C_{10}H_{17}O_2)_3$	White	192–193	54.19	7.73	51.54	7.58
$Tb(C_{10}H_{17}O_2)_3$	White	195–198	54.05	7.71	51.08	7.47
$Dy(C_{10}H_{17}O_2)_3$	White	190–193	53.76	7.67	49.81	7.45
$Ho(C_{10}H_{17}O_2)_3$	Yellow	190–192	53.57	7.64	49.62	7.30
$Er(C_{10}H_{17}O_2)_3$	Pink	142–144	53.38	7.62	51.21	7.69
$Tm(C_{10}H_{17}O_2)_3$	White	180–181	53.25	7.60	46.75	7.11
$Yb(C_{10}H_{17}O_2)_3$	White	178–179	52.93	7.55	46.44	7.19
$Lu(C_{10}H_{17}O_2)_3$	White	162–165	52.78	7.53	46.21	6.95

Results and discussion

Thermogravimetric analysis. TGA curves of scandium, yttrium and the rare-earth IBPM chelates are shown in Fig. 1. All the chelates, except praseodymium and lanthanum chelates, sublime almost quantitatively at temperatures between 150 and 260°. Praseodymium and lanthanum chelates are also volatile, but they leave a small residue indicating thermal degradation. Figure 1 shows that the volatility of the rare-earth IBPM chelates increases with increase in the atomic number, *i.e.* with decrease

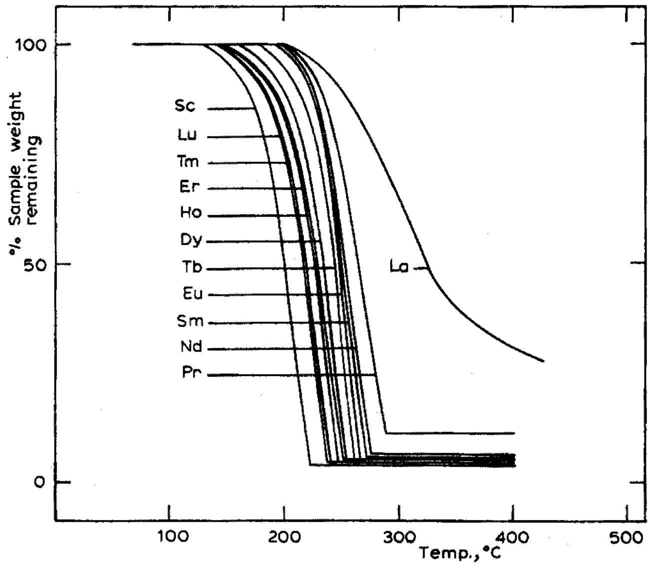

Fig. 1. Thermogravimetric curves of rare earth IBPM chelates.

in the ionic radius of the central rare-earth ion. This tendency has been reported for other β-diketone chelates[11,12,15].

Gas chromatography. Figure 2 shows chromatograms of scandium, lutetium and erbium chelates. Usually, 1–10 μl of 4–5% (w/v) benzene solution was injected, and the temperature was programmed from 210 to 250° at a rate of 4° min^{-1}. The infrared spectrum of the lutetium portion obtained from the collection gas chromato-

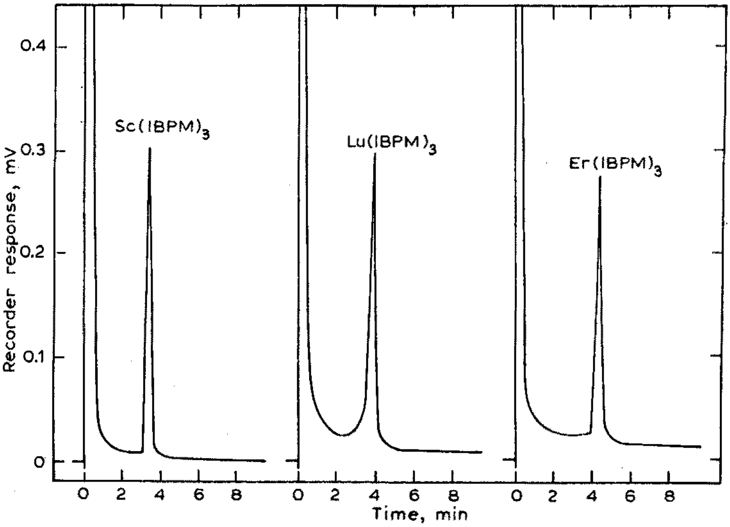

Fig. 2. Chromatograms of 59 μg of $Sc(IBPM)_3$ in 10 μl of benzene, 190 μg of $Lu(IBPM)_3$ in 5 μl, and 221 μg of $Er(IBPM)_3$ in 5 μl. Stainless steel column filled with 5% DC HV silicone grease on Chromosorb-W AW DMCS. Column temp.; programmed from 210 to 250° at 4° min^{-1}; injection temp. 300°, and detector temp. 310°. Helium flow rate: 46 ml min^{-1}.

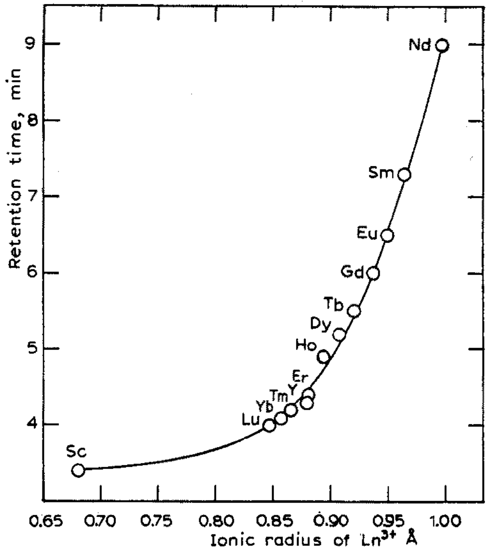

Fig. 3. Retention data as a function of ionic radius. Conditions same as those in Fig. 2.

TABLE II

LINEAR RANGES OF CALIBRATION GRAPHS FOR RARE-EARTH CHELATES
(Peak heights *vs.* weight plots)

IBPM chelate	*Metal* (μg)	*Column temp.* (°)
Sc	1– 6.5	220
Y	10– 60	232
Lu	10–130	220
Yb	10–100	220
Tm	10–100	220
Er	25–110	232
Ho	15–100	240
Dy	15–100	240
Tb	15– 95	240
Gd	15– 95	244
Eu	15– 90	244
Sm	15– 90	250

graph was compared with that of pure lutetium chelate. Both spectra were the same, hence most of the chelate was eluted without decomposition. Figure 3 indicates the dependence of the retention times for the scandium, yttrium and rare-earth chelates on the ionic radius of the central trivalent metal ions. The retention time increases with the increase in the ionic radius, and praseodymium and lanthanum chelates are hardly eluted under the conditions used.

These results are just what would be expected from the TGA curves (Fig. 1), and similar correlations have been observed with other β-diketonates[9–12]. Analytical curves of scandium, yttrium and the rare-earth elements were obtained by injecting varying amounts of benzene solutions of the chelates on to an isothermal column. The peak heights were proportional to the amounts of the chelates over useful ranges (Table II). The terbium chelate showed curious behavior; when terbium chelate solutions were repeatedly injected, the peak height decreased gradually. Injection of a large quantity of solvent (benzene) after the chelate gave no measurable elution of the terbium chelate, but when a solution of IBPM in benzene was injected to wash the column, a peak corresponding to that of terbium chelate appeared in addition to the reagent peak; this peak decreased and finally faded out when the IBPM injection was repeated. A further injection of the terbium sample reproduced a reasonable peak height.

The phenomena indicate appreciable decomposition of the terbium chelate in the column. Other rare-earth chelates tested did not show similar phenomena, and the behavior of terbium may be caused by its tendency to tetravalence.

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The determination of microgram quantities of sulphur in molten tin

In 1968, a method for the determination of traces of sulphur in tin was described[1]; the method was based on the Wösthoff sulphur analyser and has since proved satisfactory in routine use.

However, the previous work[1] was concerned only with the analysis of solid tin samples, and it became necessary to perfect a suitable sampling technique for the molten metal and also to investigate the effect of sample handling to ensure that no sulphur was lost during these operations. It was established that the Sulmhograph gives precise results in the range 1–100 p.p.m. and comparison to colorimetric results (methylene blue) indicated that the method is accurate. However, although the colorimetric method is reliable enough to detect gross errors, it is not precise enough to detect more subtle ones. More recent work[2] has provided a means of standardising the Sulmhograph with sulphur dioxide gas, enabling a more exact assessment to be made.

Apparatus

Instrumentation included the Wösthoff Sulmhograph 12 sulphur analyser, Wösthoff electrostatic precipitator, Carbolite furnace, type CFM4/1450/VT4, and unglazed porcelain boats and lids.

Standardisation equipment included the Wösthoff gas forwarding pump, type M22aX, and Wösthoff gas dosing devices, types DS2 and DS10.

Procedure

Flush the silica sample probe (Fig. 1) with nitrogen and preheat it to remove any adsorbed gases and moisture. Suck the molten tin slowly into the probe to reduce the possibility of degassing. Quickly withdraw the probe and rapidly quench it in water; to prevent the entry of contaminants eject a fine stream of droplets until the tin has solidified.

Crack away the silica and remove any surface contamination by unlubricated turning. Cut into pellets of about 1 g and clean off the cut ends.

Burn off all porcelain boats and lids. Place each pellet on to an inverted lid and place it in turn on the boat (in this way the boats are not shattered during combustion). Insert the boat into the cooler part of the furnace tube until the tin is molten and transfer to the combustion zone. Carry out the combustion under oxygen in a furnace temperature of 1350°. Compare the step heights of the samples with those of the standards.

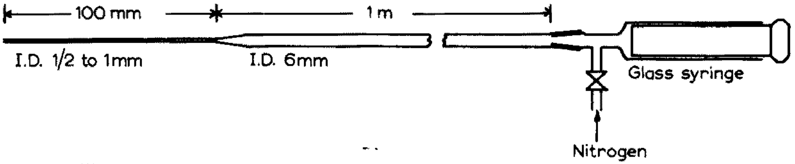

Fig. 1. Silica sample probe.

Discussion

Sampling. The sampling technique was devised originally for the determination of oxygen in molten tin in view of the inadequacy of the British Standard Method[3] for this purpose. It was examined for its suitability for the analysis of sulphur.

About 5 cwt (*ca.* 250 kg) of molten tin under an inert atmosphere was doped with 12 g of tin(II) sulphide to bring the tin to about 10 p.p.m. sulphur. This low level was chosen in order that the amount of tin(II) sulphide volatilised from the melt should be insignificant during the period of sampling. The precision of the sampling technique was determined by taking a number of samples. Each sample was analysed ten times, three pellets being cut from the forward end of each sample, four from the centre and three from the rear end. It was assumed that any loss of sulphur would show itself by inhomogeneity in the samples.

The results are given in Table I. The slight downward drift in the mean figures probably indicates a slight volatilisation of tin(II) sulphide. It will be observed that there is no noticeable imhomogeneity in these samples and pellets can therefore be used for analysis.

Sample preparation. The early work was carried out in the absence of the above data. Then, the samples were milled and well mixed to ensure homogeneity. A comparison was made of millings and pellets prepared from the same samples. The pellets were cut as before, the rest of the sample being milled. In each case the millings gave a lower result than the pellets (Table II). All arguments based on contamination would seem to be inapplicable since millings have a high surface area and would be more likely to come into contact with contaminating materials.

Two experiments were devised; in the first a number of pellets were rolled in assay rolls to about 0.1 mm thickness. These strips were folded to the approximate dimensions of the original pellet. There was no significant difference between the results for the rolled pellets ($\bar{x} = 13.1$ p.p.m., $s = 0.4$ p.p.m.) and the unrolled pellets ($\bar{x} = 12.9$ p.p.m., $s = 0.5$ p.p.m.).

In the second experiment, pellets were compared to millings and millings were

TABLE I

PRECISION AND HOMOGENEITY OF SAMPLING

Sample	$\bar{x}$ *(p.p.m.)*	*s (p.p.m.)*
1	9.8	0.1
2	9.8	0.3
3	9.5	0.1
4	9.3	0.2
5	9.1	0.2
6	9.2	0.2
7	9.0	0.2

TABLE II

COMPARISON OF PELLETS AND MILLINGS

Sample	*Pellets*		*Millings*	
	$\bar{x}$ *(p.p.m.)*	*s (p.p.m.)*	$\bar{x}$ *(p.p.m.)*	*s (p.p.m.)*
1	5.3	0.2	4.9	0.3
2	12.0	0.5	10.1	0.9
3	44.9	0.6	43.2	0.6

pressed into pellets. There was no significant difference between pellets and pressed millings (Table III) but the millings showed the usual deficiency. It would appear therefore that the form of the sample is critical to the analysis and that pellets are more satisfactory than millings. These findings are in agreement with the studies of v.d. Geest *et al.* on iron and steel[4].

TABLE III

COMPARISON OF PELLETS, MILLINGS AND PRESSED MILLINGS

Sample	$\bar{x}$ *(p.p.m.)*	*s (p.p.m.)*
Pellets	9.4	0.2
Millings	7.8	0.3
Pressed millings	9.7	0.2

Standardisation. The technique of standardising the instrument with sulphur dioxide[2] was checked against standard sulphur in tin samples. Since, as far as is known, there are no standards commercially available, these were made by weighing small amounts of tin(II) sulphide into tin capsules. After the sulphide had been weighed in, the capsule was plugged with tin and analysed in the usual way. Since the premelting was carried out in the furnace tube, any sulphide not dissolving was monitored as a secondary combustion step. The sulphur content of tin(II) sulphide can be determined by chemical methods to a better precision and accuracy than can p.p.m. amounts of sulphur in tin. This, and the fact that tin(II) sulphide is readily soluble in molten tin, led to this means of preparing the more accurately known samples. Thus

TABLE IV

ANALYSIS OF TIN(II) SULPHIDE

Sample		*Standardisation*					*S*	
Weight	*Form*	*Dilution*	*Injection*				$\bar{x}$ (%)	*s*
			No. of doses	*Wt. of* ≡ *S*	*Injection rate* (*ml min*$^{-1}$)	*Rate of dosage*		
600–800 μg	SnS	Nil	1	150 μg	100	—	19.9	0.6
600–800 μg	Melt	× 16	4	150 μg	100	Continuous	20.0	0.3
5–6 mg	SnS	Nil	1	1.3 mg	100	—	20.4	0.3
5–6 mg	Melt	Nil	5	0.7 mg	100	Continuous	20.4[a]	—

[a] These analyses were not satisfactory; in most, some sulphide floated to the surface of the melt without dissolving and the combustions were therefore in two stages, sulphide and melt. 20.4% is the mean of the most probable results.

the tin(II) sulphide can be determined as the free sulphide (short combustion) and as a sulphur-in-tin melt (combustion time about 20 sec). As each procedure requires its own standardisation technique, it follows that if the sulphide can be determined in both ways to give good agreement with the chemical analysis, then the standardisation procedures are correct. The results were found to be in agreement (Table IV), confirming the suitability of pellets for this analysis.

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The spectrofluorimetric determination of sulphide

The fluorimetric determination of sulphide by its quenching action on the fluorescein mercuriacetate complex has been described by Wronski[1] and also by Grünert *et al.*[2]. More recently, Bark and Rixon[3] have described a method based on the liberation by sulphide ions of fluorescent 2,2′-pyridylbenzimidazole from its non-fluorescent mercury(II) complex. 2-(*o*-Hydroxyphenyl)benzoxazole (HPB) has been reported[4] as a reagent exhibiting bright green fluorescence in acetone solution, the fluorescence being attenuated in the presence of copper(II) ions, and has been used as a luminescent indicator in the titration of copper. The fluorescent properties of HPB and its copper complex together with the effects of sulphide ions on solutions of the complex have been examined and have resulted in the analytical method for sulphide determination presented here.

Equipment

All spectra and fluorescence intensity measurements were obtained on an Aminco-Bowman Spectrofluorimeter employing xenon arc and off-axis ellipsoid mirror system.

Reagents

HPB in ethanol, 10^{-3} *M*. Dissolve 0.0219 g of reagent in 100 ml of ethanol.

Copper(II) solution, 10^{-3} *M*. Dissolve 0.0241 g of copper(II) nitrate in 100 ml of water.

Sodium sulphide solution, 10^{-4} *M*. Dissolve 0.2402 g of sodium sulphide nonahydrate in water, add 4 ml of *M* sodium hydroxide and adjust the volume to 100 ml. Dilute 5 ml to 500 ml for the working solution.

Procedure

Add 0.2–1.0 ml volumes of 10^{-4} *M* sulphide solution to 0.4-ml aliquots of copper(II) solution diluted to about 50 ml. Add 1 ml of *M* sodium hydroxide followed by 1 ml of HPB solution and adjust the final volume to 100 ml with water. Treat the unknown sulphide sample in an identical manner. Using an excitation wavelength of 355 nm, measure the fluorescence emission intensity of standards and unknown at 439 nm.

Over this range of sulphide concentration a linear plot which passes through the origin is obtained as a calibration curve. The working range of sulphide concentration is 0–100 ng ml^{-1} with a limit of detection of 1 ng.

Discussion

The green fluorescence of HPB, reported[4] to occur in buffered solutions below pH 6 was investigated and such solutions were found to be weakly fluorescent in the pH range 3.2–6.0. This fluorescence was too weak to form the basis of a spectrofluorimetric method; furthermore, precipitation occurred on the addition of a copper(II) solution. The fluorescent properties of the reagent were examined over the whole pH range and an intense blue fluorescence was found with a constant emission over the pH range 10.7–12.5. This intense fluorescence decreased markedly below pH 10, however, and had disappeared at pH 8. As this blue fluorescence was quenched by copper(II) ions, this was made the basis of the method with 1 ml of *M* sodium hydroxide being added to maintain the pH above 10; at this pH, no precipitation occurred. The order of addition was found to be important, if copper(II) ions and HPB are interacted, a large quantity of sulphide is required to regenerate the fluorescence of the reagent. The method of addition ensures that interaction of sulphide with copper ions is complete before the excess of copper is reacted with HPB. Cyanide was found to interfere, the formation of a stable cyanocuprate preventing the copper from interacting with the reagent. This cyanide reaction is such that, in the absence of sulphide, the method may be used for cyanide determination, giving a linear calibration curve over the concentration range 0–200 ng CN ml^{-1}.

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Ring-colorimetric determination of trace metals in milk

Trace metals in milk (Cu, Fe, Zn and Mn) have been determined by various workers[1-4] by colorimetric and atomic emission or absorption methods. All these methods involve more or less expensive instrumentation, which is better avoided as a matter of economic interest, for routine analysis when very high accuracy is not required. In the present communication a very simple procedure based on ring colorimetry[5] is described which not only is economical and rapid but also affords sufficient sensitivity in the micro and sub-micro region.

Milk contains a large amount of phosphate as calcium and magnesium salts which interfere with the classical methods of analysis for zinc and manganese. Prior removal of such phosphate is essential in the classical methods; these inconvenient and lengthy procedures have been avoided by adopting the present scheme of analysis.

Apparatus

A Weisz Ring Oven (National Appliance Co., Portland, Oreg.) was used, with a Hamilton syringe of minimum 1 μl capacity for application of test solutions.

Filter paper circles (Whatman No. 41, 55 mm diameter) were washed free from iron with 0.1 *M* hydrochloric acid on the ring oven. These papers were then thoroughly washed with double distilled water, dried and used.

Reagents

Double distilled water, and analytical-grade reagents were used throughout.

Standard solutions. (i) Copper sulphate, (ii) iron(III) alum, (iii) zinc sulphate, and (iv) manganese sulphate were used to prepare solutions containing 1 mg ml^{-1} of the particular metal ion. These solutions were diluted as required.

Milk samples

Samples of milk from two local dairies in Delhi (India) were employed.

Procedure

Ash the milk as described by Schilt and Taylor[6] taking 100 ml as the total volume. Expel nitric acid from the final residue by adding a minimal amount of concentrated hydrochloric acid. Dry on the water-bath and dissolve in water to give 1 ml as the total volume.

Punch out a disc (6 mm diam.) from the iron-free Whatman filter paper, place in the glass holder and transfer a known volume (20 μl is sufficient) of the milk solution in small lots. Add 2 drops of 0.1 *M* hydrochloric acid to the disc, dry and place on a circle of Whatman No. 41 filter paper (55 mm diam. and free from iron) already set on the ring oven at 70–80°. Wash with di-isopropyl ether so that all the iron moves towards the ring zone. Retain the disc for copper, manganese and zinc and develop iron with aqueous 0.1% potassium hexacyanoferrate(II) solution[5].

Add a drop of aqueous 1% potassium thiocarbonate solution to the disc and fume over hydrochloric acid to fix copper as copper sulphide. Dry the disc and place on another filter paper circle set on the ring oven at 100–110°. Wash zinc and manganese ions into the ring zone by applying a drop of 0.1 *M* hydrochloric acid and then washing with water. Retain the disc for copper. To determine zinc and manganese individually cut the filter paper circle into two halves. Develop zinc[7] in the first half by spraying with an alcoholic 1% solution of diethylaniline and then immersing it in a bath of aqueous 1% potassium hexacyanoferrate(III). Remove the paper after 5 min, wash well with water and dry; a sharp red line indicates the presence of zinc ions.

For manganese immerse the second half in a 10-ml bath of (1:1) ammonia solution containing 1 g of diammonium hydrogen-phosphate. Remove the paper after 1 min, wash well with water, dry and spray first with a saturated solution of potassium periodate in water and then with 0.1% "tetrabase" (tetramethyldiaminodiphenylmethane) dissolved in 1 *M* acetic acid; a blue line for manganese ions appears. This blue line was found to be visually comparable for nearly 10 min.

To estimate copper, place the disc containing copper sulphide in the glass holder, moisten with water, and fume over ammonia and then over bromine. Dry the disc and place on another filter paper circle set on the ring oven. Apply a drop of 0.1 *M* hydrochloric acid and then wash the copper ions into the ring zone with water. Discard the disc. Add a drop of aqueous 0.1% zinc sulphate solution, wash with water, dry and finally develop with ammonium mercury thiocyanate[5]. A violet ring indicates the presence of copper ions.

For semiquantitative evaluation, compare visually the intensities of the colored rings obtained with the different metal ions with standard rings. Prepare suitable standard scales separately by taking 1, 3, 5, 7, 9 and 11 μl of each of the standard copper(II), iron(II), zinc(II) solutions (each 0.1 mg ml^{-1}) and manganese (II) solution

(0.01 mg ml^{-1}) through the entire procedure.

Typical results are given in Table I.

TABLE I

TRACE METAL CONTENT (P.P.M.)
(Average of five readings)

Milk	*Cu*	*Fe*	*Zn*	*Mn*
Cow	0.25	0.36	3.2	0.18
Buffalo	0.20	0.30	2.2	0.12
Goat	0.28	0.37	3.0	0.20

Discussion

Interference from phosphate in the simultaneous determination of zinc and manganese in milk was obviated by incorporating diethylaniline and "tetrabase" as developing agents. The only care that is needed is in the determination of manganese; after spraying the "tetrabase", visual comparison must be made quickly because the reagent itself imparts a blue background when the paper starts to dry.

The method described is not only useful in the rapid determination of trace metals in milk but can also prove advantageous in rapid checking of the quality of animal feeds.

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New spot test for hydrazines

Hydrazine compounds can be detected by developing coloured products through four different classes of reactions: (*a*) condensation with aldehydic or nitro compounds: (*b*) oxidation to diazonium salts followed by coupling with amines or naphthols to give azo dyes; (*c*) reduction of some heavy metals; and (*d*) reactions with some complex compounds[1,2]. In more recent work, condensation of hydrazines with 2,4,6-trinitrobenzene sulphonic acid[3] or 1-fluoro-2,4-dinitrobenzene[4] has been described. Oxidation of hydrazines with selenium[5] or bromate[4] to give diazonium salts which can be coupled with aromatic amines or naphthols to give coloured azo dyes has been also advocated. Reduction of silver(I) salts in basic media has been utilized[6].

In the present communication *peri*-naphthindan-2,3,4-trione hydrate is described as a new sensitive and selective organic reagent for hydrazines. It is shown to be suitable for many hydrazine salts, and substituted and unsubstituted aryl and alkyl hydrazines, the lower limit of identification being 0.3 μg.

Experimental

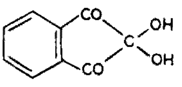
Reagents. Twice-distilled water was used throughout. The reagents used were of analytical grade except where otherwise stated. The citrate buffer solution contained 1 g of citric acid monohydrate and 1 g of potassium citrate monohydrate in 250 ml of water.

Peri-naphthindan-2,3,4-trione hydrate was prepared and purified as described by Errera[7]. A freshly prepared aqueous 0.01% (w/v) solution of the reagent was used.

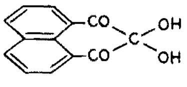
Procedure. Treat 1 drop of the alcoholic or aqueous test solution in a micro test tube with 2 drops of the reagent solution and 1 drop of citrate buffer. Warm the mixture gently. If hydrazines are present, a more or less intense red colour develops within a few seconds. With high concentrations of hydrazines, the colour develops immediately at room temperature.

Results and discussion

Detection of hydrazines. Organic and inorganic hydrazines react with cyclic triketo compounds in a citrate buffer medium to yield coloured products. Reaction of hydrazine sulphate with 1,2,3-indenetrione hydrate (I) gives a green colour; the lower limit of identification is 1 mg. However, *peri*-naphthindan-2,3,4-trione hydrate (II) reacts under the same conditions to give a stable red colour or precipitate, the lower limit of identification being 1 μg.

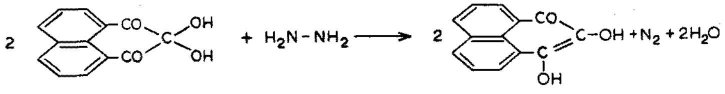


(I)



(II)

The reaction of hydrazine with *peri*-naphthindan-2,3,4-trione hydrate involves reduction of the colorless trione to the corresponding red dihydroxy *peri*-naphthindenone (III) and oxidation of the hydrazine to nitrogen.



(II) (III)

It was found that one mole of nitrogen was evolved per mole of hydrazine. The formation of the dihydroxy compound (III) was confirmed by its chemical and physical identity with an authentic specimen prepared by the action of ascorbic acid on the trione[8].

Sensitivity and selectivity. The reaction with *peri*-naphthindan-2,3,4-trione hydrate detects: 1 μg of hydrazine sulphate, 0.3 μg of hydrazine hydrate, 0.8 μg of hydrazine oxalate, 0.7 μg of hydrazine hydrochloride, 0.3 μg of *p*-nitrophenylhydrazine hydrochloride, 2 μg of phenylhydrazine, 1.8 μg of hydrazine picrate, 0.8 μg of methylhydrazine sulphate and 3 μg of 2,4-dinitrophenylhydrazine.

Many organic functions having a reducing character were tested. Amino compounds (aminobenzoic acid, sulphanilic acid, diphenylamine, dichloroaniline and anthranilic acid), amides (benzamide and acetamide), acids (citric acid, oxalic acid, glycolic acid, dihydroxybenzoic acid, salicylic acid, crotonic acid, maleic acid, and formic acid), hydroxy compounds (hydroquinone, β-naphthol, 2,2′-dihydroxydiphenyl and glycerol), carbonyl compounds (*p*-nitro-acetophenone, formaldehyde and salicylaldehyde), carbohydrates (glucose and maltose) and thiols (2-mercaptobenzimidazole and 2-mercaptobenzothiazole) did not interfere. However, milligram amounts of benzidine, semicarbazide hydrochloride, pyrogallol and ascorbic acid interfered.

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Solvent extraction of germanium(IV) with mesityl oxide

Mesityl oxide, 4-methyl-3-penten-2-one, can quantitatively extract germanium(IV) from solutions containing 5 *M* hydrochloric acid and 2 *M* lithium chloride as the salting-out agent. Germanium is stripped from the organic phase with water and determined photometrically as its complex with phenylfluorone at 510 nm.

Germanium is usually separated either by distillation or by extraction into carbon tetrachloride from strongly hydrochloric acid[1,2]. 8-Hydroxyquinoline[3] and N-phenyl-N-benzoylhydroxylamine[4] in chloroform have been used for its extraction. The synergic extraction with oxine and trioctylamine[5] can be useful in weakly acidic solutions. Diantipyrinylmethane in chloroform[6] and 2,2′-dipyridyl-catecholate[7] have also been applied for extraction of germanium. 2-Ethylhexanol[8] has been used for the extraction of the molybdogermanate complex, and octylmethylene diphosphonic acid in ligroin[9] has served for separation from arsenic; the extraction with bis-2-(ethylhexyl)phosphoric acid[10] is not quantitative. Attempts have been made to extract germanium from iodide[11] and fluoride[12] media with benzene or carbon tetrachloride, but extraction from chloride media and subsequent photometric determination with phenylfluorone[13,14] seems to be the most favoured method.

The method proposed in this communication is very rapid and permits clean-cut separation of germanium in microgram concentrations from many elements.

TABLE I

EXTRACTION AS FUNCTION OF ACIDITY AND MESITYL OXIDE CONCENTRATION
(Ge = 27.5 μg; 2 *M* LiCl salting-out agent)

Mesityl oxide	*HCl (initial) (M)*	*% Extraction*	*Distribution ratio D*
100%	1	29.2	1.02
(8.70 *M*)	2	29.2	1.02
	3	39.6	1.60
	4	89.6	21.34
	5	100.0	∞
75%	1	—	—
(6.53 *M*)	2	—	—
	3	10.52	0.2939
	4	52.6	2.774
	5	84.16	13.28
50%	1	—	—
(4.35 *M*)	2	—	—
	3	2.63	0.0675
	4	36.62	1.44
	5	73.64	6.98
25%	1–3	—	—
(2.17 *M*)	4	10.52	0.2939
	5	47.34	2.239
19%	1–4	—	—
(1.62 *M*)	5	36.82	1.455

Experimental

Stock solution of germanium(IV). Dissolve 3.605 g of germanium dioxide in a minimum volume of 0.1 *M* sodium hydroxide and acidify with hydrochloric acid. Dilute to 500 ml with distilled water. Standardization[15] showed the solution to contain 5.5 mg Ge ml^{-1}. Solutions containing 27.5 μg Ge ml^{-1} were prepared by suitable dilution.

Phenylfluorone (E. Merck). Dissolve 0.100 g in 50 ml of methanol and 1 ml of hydrochloric acid, and dilute to 500 ml with methanol.

Gum arabic (B.D.H.). Dissolve 0.5 g in 50 ml of hot water.

Mesityl oxide (B.D.H.; b.p. 125–132°) was used.

General procedure. To an aliquot of solution containing 3–90 μg of germanium, add hydrochloric acid and lithium chloride to give concentrations of 5 *M* and 2 *M*, respectively, in a volume of 25 ml. Shake with 10 ml of mesityl oxide for about 2 min. Strip germanium from the organic phase with two 10-ml portions of water. To the aqueous phase, add 5 ml of gum arabic and 5 ml of 12 *M* hydrochloric acid. Dilute to

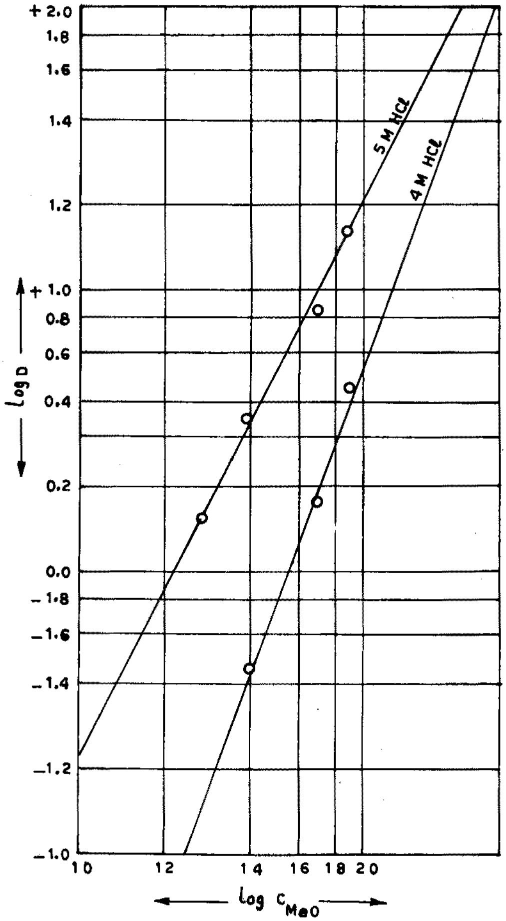

Fig. 1. Relationship between log *D* and the concentration of mesityl oxide at different acidities in presence of 2 *M* lithium chloride.

30 ml, add 5 ml of phenylfluorone solution and make the total volume up to 50 ml. Leave the solution for 20–30 min and measure the absorbance at 510 nm against the reagent blank[16].

Results and discussion

Effect of acidity and mesityl oxide concentration. Germanium(IV) was extracted from 1–5 *M* hydrochloric acid in the presence of 2 *M* lithium chloride with 19–100% (1.62–8.70 *M*) mesityl oxide in toluene (Table I). Extraction was quantitative only with pure mesityl oxide from 5 *M* hydrochloric acid. Plots of log *D* *versus* log C_{MeO} (Fig. 1) at 4 *M* and 5 *M* acid concentration showed slopes of 2.75 and 2.15, indicating that the probable composition of the extractable species is $GeCl_4 \cdot 3MeO$. Benzene, chloroform, carbon tetrachloride and methyl isobutyl ketone were avoided as diluents.

Effect of salting-out agents. The chloride salts of lithium, sodium, potassium, ammonium, calcium and aluminum (1–2 *M*) were tested as salting-out agents, in

TABLE II

EFFECT OF DIVERSE IONS[a]

(Ge = 27.5 μg, 5 *M* HCl + 2 *M* LiCl; 100% mesityl oxide)

Substance added	*Tolerance limit (μg)*	*Substance added*	*Tolerance limit (μg)*
Pb^{2+}	250	Sr^{2+}	1000
Hg^{2+}	None	Ba^{2+}	1000
Tl^{3+}	250	Mg^{2+}	10,000
Ag^{+}	None	Rb^{+}	5000
Cu^{2+}	500	Cs^{+}	5000
Cd^{2+}	250	SeO_3^{2-}	125
Sn^{2+}	None	TeO_3^{2-}	125
Sb^{3+}	1000	ReO_4^{-}	150
Bi^{3+}	1000	VO_3^{-}	100
Ru^{3+}	200	WO_4^{2-}	None
Rh^{3+}	None	$Mo_7O_{24}^{6-}$	None
Pd^{2+}	125	Oxalic acid	1000
Pt^{6+}	None	Citric acid	1000
Fe^{3+}	100	Tartaric acid	1000
Cr^{3+}	150	Malonic acid	1000
Al^{3+}	10,000	Ascorbic acid	1000
Ti^{4+}	125	CH_3COO^-	1000
Be^{2+}	1000	EDTA (disodium)	1000
Th^{4+}	150	PO_4^{3-}	1000
Zr^{4+}	500	$S_2O_3^{2-}$	1000
U^{6+}	250[b]	F^-	1000
Ce^{3+}	None	SCN^-	1000
Zn^{2+}	1000	CN^-	500
Mn^{2+}	1000	ClO_3^-	1000
Co^{2+}	1000	SO_4^{2-}	10,000
Ni^{2+}	1000	NO_3^-	10,000
Ca^{2+}	10,000		

[a] Cations were added as their chloride, nitrate or sulphate salts, and anions as their sodium, potassium or ammonium salts.

[b] Extracted from 1 *M* HNO_3 + 0.5 *M* NH_4NO_3 with mesityl oxide[17].

presence of 3–5 *M* hydrochloric acid, with 100% mesityl oxide as the extractant. For quantitative extraction, 5 *M* hydrochloric acid was essential, and 2 *M* lithium chloride or 1 *M* calcium or aluminum chloride could be used as the salting-out agent. Lithium chloride was preferred for further work.

Period of extraction. The extraction was carried out for varying times (1–15 min). An equilibration time of 2 min was adequate.

Effect of diverse ions. Various diverse ions were tested for interferences (Table II). The tolerance limit was taken as the amount required to cause ±2% error in germanium recovery. Ions showing strong interferences are silver, tin, platinum, rhodium, mercury, cerium, tungstate and molybdate. The interference of certain ions can be mitigated by selective extraction[17].

From ten runs with 27.5 μg of germanium, the average recovery was 99.8 ± 0.2% with a standard deviation of ± 1.0%. As little as 3 μg of germanium could be extracted and determined by the proposed method.

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Mesityl oxide as an extractant for gallium(III)

Mesityl oxide (4-methyl-3-penten-2-one) has been used for the solvent extraction separation of various transition metals[1]. These studies have been extended to gallium(III) which can be extracted with 19% mesityl oxide in methyl isobutyl ketone, from 0.5 *M* hydrochloric acid solution containing 8 *M* lithium chloride as salting out agent. The metal from the organic phase is stripped with water and determined in the aqueous phase by titration with EDTA[2].

Several oxygen-containing solvents have been used for the solvent extraction of gallium; diethyl ether allows extraction of the chloro and bromo complexes of gallium[3,4], as well as the thiocyanate complex[5]. Isopropyl ether[6] extracts gallium from 7 *M* hydrochloric acid. Incomplete extraction of gallium(III) from hydrochloric acid with tributyl phosphate has been reported[7-9], as well as quantitative extraction[10]. Tetraphenylarsonium chloride[11] and triphenylphosphine oxide[12] have been employed for the extraction of gallium, as have various dyes[13] and β-diketones, such as acetylacetone[14,15], benzoylacetone[15] and dibenzoylmethane[15].

In contrast to some of these methods, the proposed extraction of gallium(III) with mesityl oxide is quantitative at low acidity even for shaking times of only 30 sec; a clean-cut separation of gallium from many cations and anions is possible.

Experimental

Reagents. Mesityl oxide (B.D.H.) was used after double distillation.

A stock solution of gallium(III) (12 mg ml^{-1}) was prepared by dissolving 7.7487 g of gallium trichloride (Koch-Light Company) in 250 ml of (1 + 1) hydrochloric acid. The solution was standardized by titration with EDTA.

General procedure. To an aliquot of solution containing 12.0 mg of gallium(III), add hydrochloric acid and lithium chloride to make their concentrations 0.5 *M* and 8 *M*, respectively, in a total volume of 25 ml. Extract with 10 ml of 19% mesityl oxide in methyl isobutyl ketone for 30 sec. Allow the layers to separate, remove the aqueous layer, and then strip gallium from the organic phase with two 10-ml portions of water. Titrate the metal in the aqueous phase with EDTA[2].

Effect of acidity and mesityl oxide concentration

The concentration of hydrochloric acid was varied from 0.1 to 6.0 *M*, and that of mesityl oxide from 19–100% by dilution with methyl isobutyl ketone. The results (Table I) showed that quantitative extraction of gallium(III) is possible from 3.0–6.0 *M* hydrochloric acid with undiluted mesityl oxide. In presence of 8 *M* lithium chloride, extraction was quantitative from 0.5 *M* hydrochloric acid solution even with 19% mesityl oxide. Various other solvents such as benzene, toluene, xylene, chloroform, carbon tetrachloride, *n*-butanol; nitrobenzene and amyl acetate were also tried as diluents; extraction was always complete except with chloroform and carbon tetrachloride. However, methyl isobutyl ketone was preferred, as it gave clear separation of the layers. The plot of log *D* *vs.* log *c* (mesityl oxide concentration) for 2 *M* hydrochloric acid (Fig. 1) gave a slope of 1.53, indicating that the probable extracted species is $[\text{H GaCl}_4 \cdot 2\ \text{MeO}]$.

TABLE I

DISTRIBUTION RATIO AS A FUNCTION OF ACIDITY
(Ga(III) = 12.0 mg)

Concn. of MeO (%)	*Initial HCl* (*M*)	% *Extraction*	*D*	*Concn. of MeO* (%)	*Initial HCl* (*M*)	% *Extraction*	*D*
19% (1.65 *M*)	0.5	1.74	0.04	75% (6.52 *M*)	0.5	2.61	0.06
	1.0	3.05	0.07		1.0	12.23	0.34
	1.5	13.1	0.37		1.5	38.86	1.58
	2.0	30.12	1.07		2.0	74.66	7.36
	2.5	72.93	6.73		2.5	97.36	92.19
	3.0	83.39	12.55		3.0–4.0	99.13	284.80
	4.0	98.24	139.50		5.0–6.0	100.00	∞
	5.0–6.0	98.68	186.80				
25% (2.17 *M*)	0.5	1.74	0.04	100% (8.70 *M*)	0.5	4.8	0.12
	1.0	3.05	0.07		1.0	23.14	0.75
	1.5	15.71	0.46		1.5	57.23	3.34
	2.0	43.66	1.93		2.0	88.18	18.60
	2.5	75.53	7.71		2.5	97.36	92.19
	3.0	85.13	14.31		3.0–4.0	99.13	284.30
	4.0	98.24	139.50		5.0–6.0	100.00	∞
	5.0	98.68	186.60				
	6.0	100.00	∞				
50% (4.35 *M*)	0.5	2.18	0.05				
	1.0	7.42	0.20				
	1.5	24.88	0.82				
	2.0	60.68	3.85				
	2.5	90.80	24.67				
	3.0	98.24	139.50				
	4.0	98.68	186.80				
	5.0–6.0	100.00	∞				

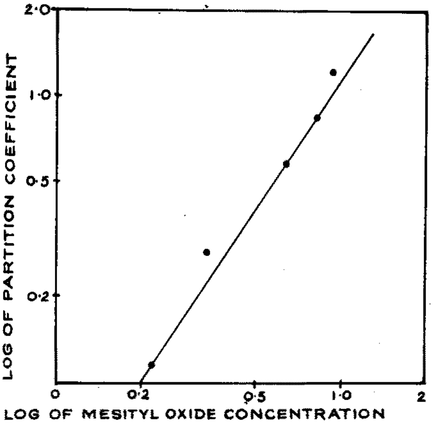

Fig. 1. Partition coefficient as a function of mesityl oxide concentration (aqueous phase 2 *M* HCl).

Effect of salting-out agent

The chlorides of lithium and ammonium were tried as salting-out agents (Table II). For quantitative extraction of gallium(III) at low acidity, it was necessary

TABLE II

EFFECTS OF LITHIUM CHLORIDE AND AMMONIUM CHLORIDE AS SALTING-OUT AGENT

(Ga(III) = 12.0 mg. Shaking period = 30 sec)

Salting-out agent	*HCl (M)*	*% Extraction*	*D*	*Salting-out agent*	*HCl (M)*	*% Extraction*	*D*
Lithium chloride with 19% mesityl oxide in MIBK				*Ammonium chloride with 100% mesityl chloride*			
2 *M*	0.1	2.20	0.05	2 *M*	0.5	58.93	3.588
	0.5	13.22	0.38		1.0	90.82	24.74
	1.0	54.19	2.95		2.0	98.56	171.10
	2.0	94.26	41.06				
4 *M*	0.1	45.37	2.07	3 *M*	0.5	78.85	9.309
	0.5	82.81	12.04		1.0	95.66	55.09
	1.0	84.59	13.72		2.0	99.04	257.80
	2.0	96.03	60.46				
6 *M*	0.1	91.62	27.33	4 *M*	0.5	93.24	34.48
	0.5–1.0	96.92	78.65		1.0–2.0	100.00	∞
	2.0	97.79	110.60				
8 *M*	0.1–0.2	97.79	110.60				
	0.5–2.0	100.00	∞				

to use 8 *M* lithium chloride or 4 *M* ammonium chloride as the salting-out agent. Aluminium or magnesium chloride could not be used as they interfered in the final determination.

TABLE III

EFFECT OF DIVERSE IONS

(Ga(III) = 12.0 mg in presence of 0.5 *M* HCl and 8 *M* LiCl. Mesityl oxide = 19% in MIBK)

Diverse ion[a]	*Tolerance limit (mg)*	*Diverse ion*[a]	*Tolerance limit (mg)*
Co^{2+}	20	Tl^{3+}	10
Mn^{2+}	20	In^{3+}	None
Al^{3+}	20	V^{5+}	10
Mo^{6+}	5	W^{6+}	5
Hg^{2+}	15	Cr^{6+}	5
Cu^{2+}	20	Fe^{3+}	None
UO$_2^{2+}$	5	Tartaric acid	10
Pd^{2+}	16	Citric acid	10
Pt^{4+}	16	Fluoride	20
Au^{3+}	20	SCN$^-$	None
Ti^{2+}	20	HPO$_4^{2-}$	10
Ni^{2+}	20	Ascorbic acid	20
Sn^{2+}	5	Borate	20
Bi^{3+}	20	Peroxide	5 ml of 20 volume
Sb^{3+}	5	EDTA	10
Tl$^+$	20		

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[a] Cations were used as their chloride or nitrate salt, and anions as their sodium, potassium or ammonium salt.

Time of extraction

The extraction was carried out for times varying from 30 sec to 10 min. Extraction was quantitative on shaking for 30 sec or 1 min, but longer extraction times reduced the percentage extraction slightly (96.9% after 10 min).

Effect of diverse ions

Many diverse ions were tested for interference (Table III). The tolerance limit was set at the amount required to cause an error of less than 2%. Moderate amounts of many ions are tolerable. The ions showing strong interference include iron, indium an thiocyanate. Large amounts of tungsten could be masked with tartaric acid. The interferences of chromium(VI) and vanadium(V) could be eliminated by reduction with ascorbic acid.

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ERRATUM

N. H. Clark and J. G. Pyke, The determination of uranium in exploration samples by X-ray emission spectrometry, *Anal. Chim. Acta*, 58 (1972) 234–237.

On page 236, under the heading *Matrix effects*, the phrase: "One sample was high in antimony" should be replaced by: "One sample showed unusually strong absorption of both the ULα line and the scattered tube radiation".

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BOOK REVIEWS

C. E. Crouthamel, *Applied Gamma-ray Spectrometry*, 2nd Edn. completely revised and enlarged by F. Adams and R. Dams, Pergamon Press, 1970, 753+xviii pp., price £12.00.

The collection of γ-ray spectra, and the tables, in the rear half of the first edition of this book were probably consulted more frequently than the excellent and informative text. To some users, it was therefore regretful that, as high-resolution semiconductor detectors became increasingly used during the last ten years, some of the compilations of data in "Crouthamel" became less useful.

Clearly, Adams and Dams have recognised this growing need to revise the original text and tables. The second edition of *Applied Gamma-ray Spectrometry*—greatly enlarged and extensively revised—contains a valuable new chapter on semiconductor detectors and concomitant equipment and another on the determination of identity, purity and quantity of radionuclides. Experimentalists will be pleased to find that more than 170 pages are devoted to an impressive collection of germanium-detector spectra.

The appendix of sodium iodide detector spectra, which was such a popular feature of the First Edition, remains. Indeed, it has been enlarged. For example, spectra of several neutron-deficient nuclides have now been included. Another appendix, consisting of tabulations of photon energy, atomic number and half-life sequences, has also been retained; but readers are warned that these tables (Appendix VI) have not been revised. Not surprisingly, they contain some information which is now unnecessarily imprecise and the existence of nuclides discovered since about 1959 is not indicated. The editors provide a few references from which more recent evaluations of half-life and photon energies may be sought; nevertheless it is disappointing that such a potentially useful section of the book should suffer from this irritating fault. It is only fair to add, however, that in a new appendix (Appendix VII), up-to-date information of the type just referred to *has* been provided, but only for those nuclides formed by neutron capture.

According to the Preface, the book is "primarily meant for experimentalists". To these it can be commended without reservation. But the text covers almost every conceivable aspect of γ-ray spectrometry, and the book should also be of considerable value to any who teach the subject.

The one misgiving that the reviewer does have concerns the price. The book is well-produced and one can appreciate that it must be costly, but that having been said, the fact is that many post-graduate students and research workers will, in all probability, deny themselves a personal copy of *Applied Gamma-ray Spectrometry*, simply because it appears to be so expensive. Make no mistake about it, this book is much too good to be restricted to library collections and the Publishers might benefit a substantial number of people by introducing a paperback edition as soon as possible.

C. L. Graham (Birmingham)

Analytical Chemistry of Nitrogen and its Compounds. Parts 1 and 2, Edited by C. A. Strueli and P. R. Averell, Chemical Analysis, Vol. 28, Part 1: vii+429 pp., Part 2: vii+332 pp., Wiley–Interscience, New York, 1971, price £16.50 (both parts).

This volume (in two separate parts) is the latest addition to the well-known Interscience Chemical Analysis series and sets out to cover the analytical chemistry of nitrogen in organic and inorganic compounds. The entire work is composed of sixteen chapters each contributed by a specialist on the particular subject and divided in such a way that all the inorganic material is contained in Part 1 along with some of the organic material; Part 2 deals exclusively with organic aspects. This division is purely for convenience; it is not possible to purchase the one or other part of this volume separately. Part 1 begins with an account of the determination of total nitrogen. This subject has a particularly wide interest and it is disappointing to find it dealt with rather superficially in a mere 22 pages. Surprisingly, the now well-established CHN analysers are collected together in a section headed "Future Direction" containing all of five and a half lines of text. It is unfortunate that the book begins with such a cursory account of what might well have been considered one of the main aspects of the work.

The remaining fifteen chapters cover specialised topics and include the n.m.r. of nitrogen, inorganic nitrogen compounds associated with hydrogen, oxygen, carbon, silicon, boron, halogens, sulphur and phosphorus, amines, amides, nitro- and nitroso-compounds, urea and related compounds, compounds with $-\mathrm{C{\equiv}N}$ linkages, $-\mathrm{N{=}N}-$ linkages, heterocyclic nitrogen compounds, aminoacids, polypeptides and proteins, and finally synthetic nitrogen-containing polymers.

Whilst one might sympathise with the editors in their endeavours to produce a comprehensive account of the analytical chemistry of nitrogen in all its various organic and inorganic forms (the alkaloids being a deliberate exception), nevertheless the present volume falls short of expectations. The individual chapters on organic material are simply attenuated accounts of well-established methods of organic functional group analyses which are much better discussed in existing monographs devoted to this aspect of organic analysis. Of much greater value are the chapters on the inorganic nitrogen functions, the analyses of which are much less well documented; more information on these compounds of nitrogen, particularly in combination with analytically troublesome elements would have been welcomed by the analyst. Indeed, more comprehensive accounts of the analysis of the commoner inorganic nitrogen functions would not be amiss, especially when one discovers that the section on the determination of, for example, the nitrate ion, is far from complete.

On the whole, this volume leaves one with the impression of what it might have been, rather than what it is—a somewhat uninspired and unsuccessful attempt to cover a very wide field of analytical chemistry. It has the advantage of doing this within the confines of a single volume (in two separate parts), but it seems to lack the authority which has been the hallmark of most of the previous volumes in this hitherto excellent series.

W. I. Stephen (Birmingham)

Morris W. Lerner, *The Analysis of Elemental Boron*, U. S. Atomic Energy Commission: Division of Technical Information, National Technical Information Service, Springfield, Va. 22151, TID-25190, 1971, ix+125 pp., price $3.00.

This paperback is one of the A.E.C. Critical Review Series, which covers a very wide range of scientific topics. The analysis of boron and boron carbide is of considerable importance in nuclear technology, and large cooperative efforts have been made to establish reliable procedures and techniques. Most of the methods described arose from this program, though other information is also included.

After a brief discussion of standards, dissolution of boron and boron carbide, methods of separation, losses and contamination, and determinations of boron are described. The greater part of the book deals with the determination of impurities by all types of instrumental analysis. This is essentially a practical manual, and will be very useful to all concerned with boron analysis.

Topics in Organic Mass Spectrometry, Edited by A. L. Burlingame, Advances in Analytical Chemistry and Instrumentation, Vol. 8, Interscience–J. Wiley, New York, 1970, xi+471 pp., price £10.55.

This volume contains nine reviews of various aspects of mass spectrometry: Techniques of Molecular Ionization (H. D. Beckey and F. J. Comes); Correlation of Fragment Ion Structures with Energetics of Formation (A.G. Harrison); Gas-liquid Chromatography–Mass Spectrometry Combination (S. Ställberg-Stenhagen and E. Stenhagen); High-resolution Mass Spectrometry (K. Biemann); Mechanisms of Ion-decomposition Reactions (F. W. McLafferty); Mass Spectrometry of Complex Natural Compounds (B. C. Das and E. Lederer); Applications of Mass Spectrometry in Flavor and Aroma Chemistry (W. H. McFadden and R. G. Buttery); Applications of Mass Spectrometry to Organic Geochemistry (H. K. Schnoes and A. L. Burlingame).

F. Helfferich and G. Klein, *Multicomponent Chromatography: Theory of Interference*, Chromatographic Science Series Vol. 4, M. Dekker, Inc., New York, 1970, viii+419 pp., price £11.65 ($24.50).

This book describes a unified theory of chromatography of all types for which the normal assumption of independent behavior of sorbable species cannot be made. It contains much previously unpublished work. The material is divided into 6 chapters: Introduction; Definitions and Basic Concepts; Theoretical Basis; Column Response; Relaxation of Simplifying Premises; Assessment and Outlook. Appendices describe H-function roots and responses to square-wave influent composition pulses, as well as selectivity reversals.

RECENT PUBLICATIONS FROM THE NATIONAL BUREAU OF STANDARDS

Journal of Physical and Chemical Reference Data

This new journal, edited from N.B.S., will make available reliable reference data and is organized jointly by N.B.S., the American Institute of Physics and the American Chemical Society. Further information can be obtained from American Chemical Society, 1155 16th Street, N. W., Washington, D. C. 20006, U.S.A.

R. S. Gorozhanina, A. Y. Freedman and A. B. Shaievitch, *Standard Reference Materials: Standard Samples issued in the U.S.S.R.*, Translated from the Russian by M. C. Selby, N.B.S. Spec. Publ. 260-30, NTIS, Springfield, Va. 22151, 86 pp., price $1.00.

B. C. Keysar, *Specifications and Tolerances for Reference Standards and Field Standard Weights and Measures. 3. Specifications and Tolerances for Metal Volumetric Field Standards*, N.B.S. Handbook 105/3, NTIS, Springfield, Va. 22151, 8 pp., price $0.25.

D. D. Wagman, *Selected Values of Chemical Thermodynamic Properties: Tables for Elements 54–61 in the Standard Order of Arrangement*, N.B.S. Technical Note 270-5, NTIS, Springfield, Va. 22151, 49 pp., price $0.55.

J. F. Martin, *Standard Reference Materials: National Bureau of Standards–U. S. Steel Corporation Joint Program for Determining Oxygen and Nitrogen in Steel*, N.B.S. Spec. Publ. 260-26, NTIS, Springfield, Va. 22151, 40 pp., price $0.50.

PUBLICATIONS RECEIVED

Absorption Spectra in the Ultraviolet and Visible Region, Edited by L. Lang, Vol. XV, Akademiai Kiado, Budapest, 1971, 407 pp., price £7.00.

Absorption Spectra in the Ultraviolet and Visible Region, Edited by L. Lang, Cumulative Index (XI–XV), Akademiai Kiado, Budapest, 1971, 103 pp., price £0.75.

L. Rougeot, *Les Alcools*, Que-Sais-Je? Le point des Connaissances Actuelles No. 1446, Presses Universitaires de France, Paris, 1971, 126 pp.

R. Schaal, *La Cinétique Chimique Homogène*, Collection SUP. Le Chimiste, 2, Presses Universitaires de France, Paris, 1971, 166 pp.

H. Breidenbach, *Prüfprogramme zur organischen Chemie*, Berufskundliche Reihe zur Fachzeitschrift Chemie für Labor und Betrieb, Band 13, Umschau Verlag, Frankfurt/Main, 1971, 136 S., Kartoniert DM 7.80.

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