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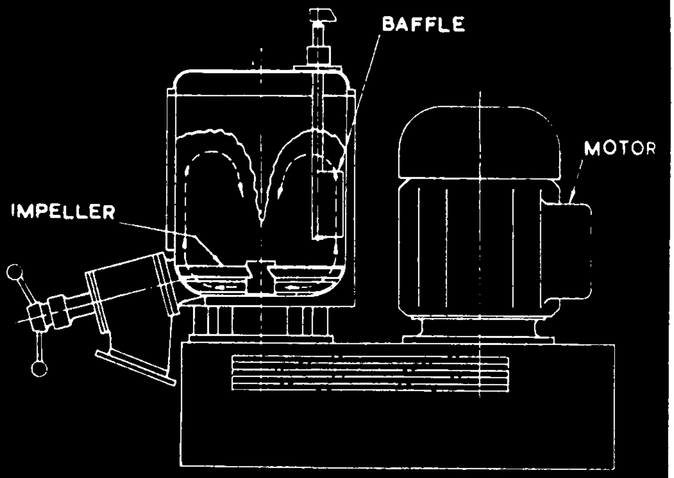
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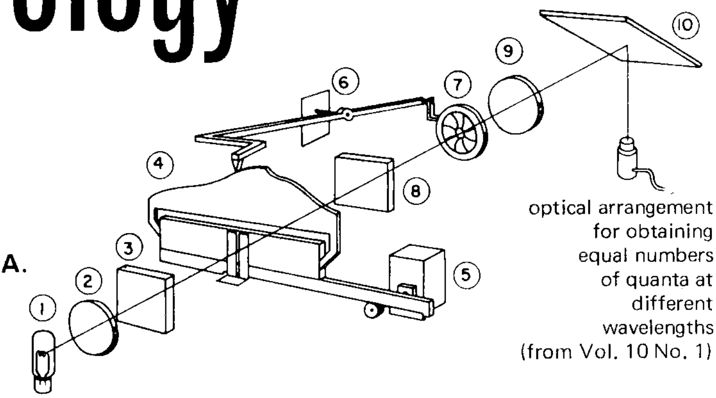

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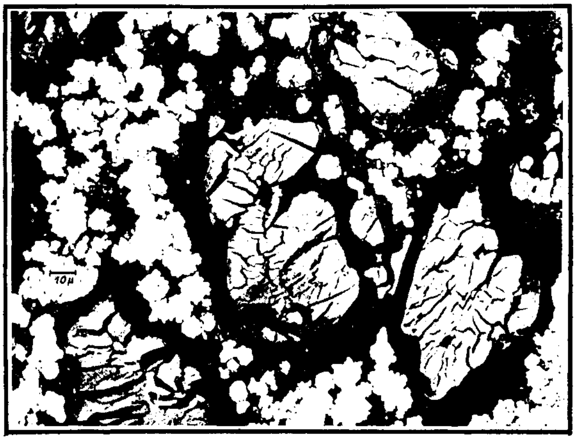

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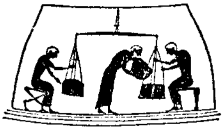

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TALANTA REVIEW*

RADIOACTIVE KRYPTONATES AND THEIR USES IN CHEMICAL ANALYSIS

J. TÖLGYESSY and Š. VARGA
Department of Radiochemistry and Radiation Chemistry, Slovak Technical University, Bratislava, Czechoslovakia

(*Received* 6 *June* 1969. *Accepted* 28 *October* 1969)

Summary—A review is presented of the uses of radioactive kryptonates in chemical analysis.

A NEW GROUP of radioactive tracers became available to analytical chemists in 1957, as a result of the pioneering work of Chleck and his co-workers[1–5] on the preparation, properties and possible uses of radioactive kryptonates. From this work it would seem that radioactive krypton-85 can be incorporated into such a variety of materials that it can be considered a universal radioactive tracer. Subsequent theoretical and practical studies have shown that kryptonates have applications in several areas of science and technology, but this review is concerned solely with their applications to analysis.[6–12]

DEFINITION AND CLASSIFICATION OF RADIOACTIVE KRYPTONATES

The term "radioactive kryptonates" is used for substances into which atoms or ions of the radioactive nuclide krypton-85 are incorporated, regardless of the structure of the substance. The process of incorporating the krypton into the solid carrier is called *kryptonation*. "Radioactive kryptonate" is the generic term for krypton carriers, regardless of the steric distribution of atoms or ions of the krypton in the kryptonate.

Radioactive kryptonates of solid systems with an ionic, atomic, molecular or metal crystalline lattice, amorphous substances and mixed amorphous–crystalline systems have been prepared. Almost 200 chemical substances have been kryptonated and this number is steadily increasing.[9,10,14–22]

We will use as a symbol for radioactive kryptonates $A[^{85}Kr]$, where A is the carrier substance.

The possibilities of incorporating radioactive krypton atoms into the carrier substance are mainly dependent upon the lattice structure. Solid crystalline substances show many defects in the lattice, and it is the defects of the carrier which are the most advantageous sites for the hetero krypton atom.

Thus, during formation of the radioactive kryptonate, the krypton-85 atoms can be incorporated into the carrier in the positions[13,22,23] of lattice vacancies, where the krypton atoms will have a structural substitutional function; between planes of the structural elements of the lattice, with an interstitial function; of cavities in the crystalline lattice of the carrier's clathrate structure; of other types of dislocation defects in the carrier lattice; of microbubbles in the carrier material.

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PREPARATION OF RADIOACTIVE KRYPTONATES

For the preparation of radioactive kryptonates there are several methods known, which can be divided into two groups: kryptonation of the carrier during formation of the solid phase; kryptonation of the carrier in the solid phase.

The carrier can be kryptonated during formation of the solid phase by crystallization of the carrier substance from a melt or solution in an atmosphere of radioactive krypton or by sublimation of the carrier substance in an atmosphere of radioactive krypton.

Solid phase carriers can be kryptonated by bombardment of the solid carrier substance with accelerated radioactive krypton ions, or by diffusion of radioactive krypton into the solid carrier substance at high pressure and temperature.

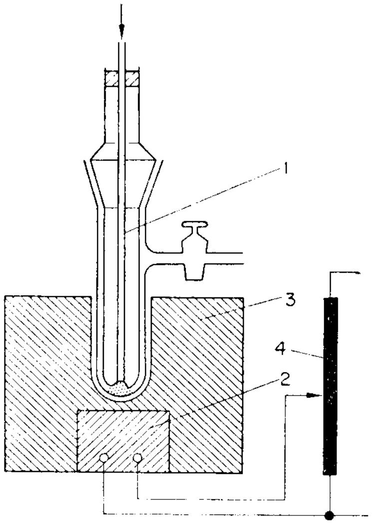

Fig. 1.—Scheme of apparatus for sublimation kryptonation.[25]
1—Sublimation apparatus; *2*—electrical heating; *3*—aluminium block; *4*—transformer.
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The kryptonation technique employed depends mainly upon the character of the carrier and how the radioactive kryptonate is to be used.

Kryptonation during the formation of the carrier's solid phase is of value mainly for the preparation of radioactive kryptonates of the clathrate type. Chleck[1,2] prepared radioactive clathrates of hydroquinone with krypton by slow crystallization of hydroquinone from a melt in an atmosphere of krypton-85 at high pressures. The method of crystallization from a melt is more advantageous than that of crystallization from solution, because it does away with the need for filtration, washing and drying of the kryptonate. It has been modified for the preparation of radioactive hydroquinone kryptonates with high specific activity.[24]

The condensation of the carrier substance during sublimation offers very favourable conditions for incorporation of radioactive krypton atoms into the crystalline lattice of the carrier, mainly in those cases when the subliming carrier forms a clathrate type crystalline lattice,[23,25] and the apparatus is very simple (Fig. 1).

Solid state carrier kryptonation methods represent the most widespread procedure for the preparation of radioactive kryptonates.

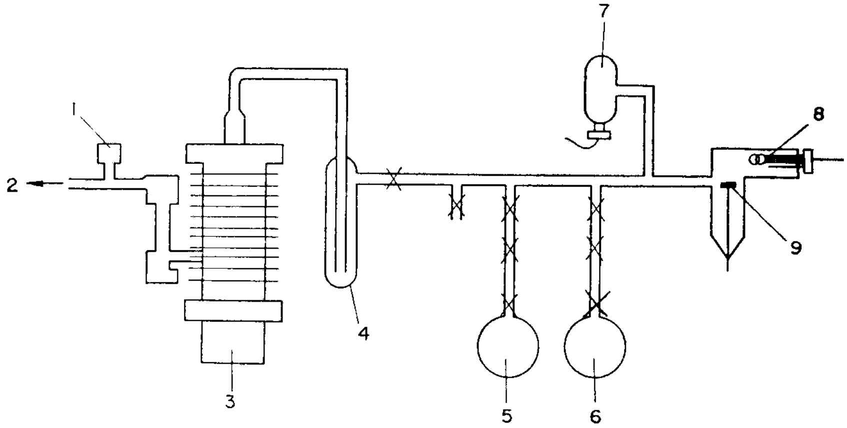

FIG. 2.—Apparatus for ion bombardment.[5]
1—Thermocouple gauge; *2*—forepump; *3*—diffusion pump; *4*—cold trap; *5*—krypton; *6*—^{85}Kr; *7*—ion gauge; *8*—electron gun; *9*—target.
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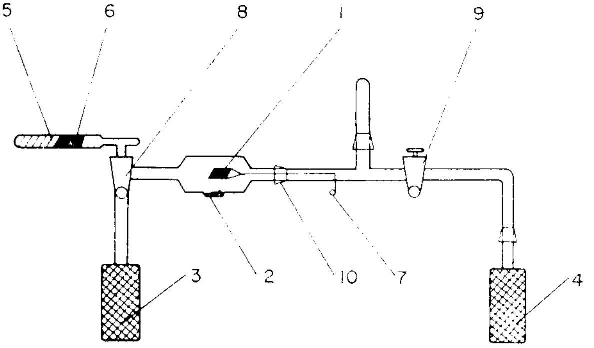

FIG. 3.—Equipment for the preparation of radioactive kryptonates by ion bombardment according to Č. Jech.[27]
1—Anode, *2*—cathode; *3*, *4*—active carbon; *5*—tube with metallic calcium; *6*—glass wool; *7*—platinum eye; *8*, *9*—vacuum valves; *10*—ground joint.
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The technique of kryptonation by bombardment of solid carriers is based on the generation of krypton-85 ions and their acceleration in an electrostatic field to different energies (5-160 keV). The beam of accelerated ions is focused towards the solid carrier target, connected with the negative electrode. Solid carriers with low vapour pressure are regularly kryptonated by this method.

Figure 2 is a diagram of the apparatus for bombardment kryptonation of a target with ^{85}Kr ions at a potential of about 10 kV.[5]

The apparatus may also have an electromagnetic separator,[26] which separates ions according to their specific charge and permits the focusing of krypton-85 ions on the solid target.

Jech[27,28] worked out an instrumentally simple method for kryptonation with accelerated krypton ions. The kryptonated target is inserted between the electrodes of a Tesla transformer. The high-voltage high-frequency discharge ionizes the krypton and accelerates the krypton ions, which are then captured in the crystalline lattice of the target substance. The scheme of the apparatus is shown in Fig. 3. The adsorption

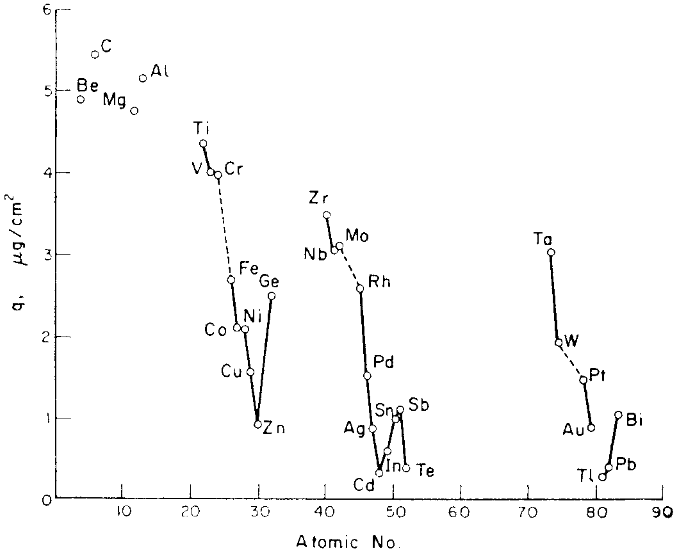

FIG. 4.—Saturation values (q) of Kr in different targets.[26]
0·1 μA . mm^{-2}; 45 keV energy.
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properties of active carbon are utilized for the preparation of the vacuum in the bombardment apparatus and also for binding of the radioactive gas. The adsorption and release of the gas is carried out by changing the temperature of the active carbon.

The sample is placed in the sample chamber. The apparatus is connected by the ground joint *10*, the vacuum stop-cock *9* is opened and the ampoule with active carbon is immersed in liquid nitrogen. Air is adsorbed on the active carbon and the vacuum measured with the Tesla instrument. When a sufficient vacuum has been attained, stop-cock *9* is closed and stop-cock *8* opened, so that krypton-85 fills the anodic space. The anode *1* is formed by an aluminium plate fixed on a platinum wire, which is sealed in the glass vacuum apparatus in such a way that a little eye *7* sticks out. The krypton ions are accelerated by the high-frequency discharge of the Tesla instrument. One pole is attached to the eye forming the anode, the other—fitted with an aluminium plate to give a bigger surface—forms the cathode *2*, and is placed accurately under the sample. Discharge is made in short bursts (a few seconds) to prevent the glass and the sample from preheating. Then the ampoule *3* is immersed in liquid nitrogen and krypton-85 is adsorbed on the active carbon. Stop-cock *8* is closed and stop-cock *9* opened, the pressure rises and the sample is taken out. Ampoule *3*, filled with active carbon carrying the adsorbed krypton, is connected with a little tube filled with metallic calcium, *5*, which serves for the capture of air residues from the gaseous krypton. The ground joint *10* allows the apparatus to be filled with krypton.

When kryptonation is carried out by the method of ionic bombardment a krypton-85 saturation value is reached which is a periodic function of the atomic number of the kryptonated element (Fig. 4).[26]

Solid carriers are often kryptonated by diffusion of the krypton into the solid substance at high pressure and temperature. Pressure bombs are used and a drawback of the method is that after kryptonation the residue of krypton-85 is lost, when the pressure bomb is opened.

Losses of radioactive krypton are markedly lowered by use of microdiffusion techniques,[29,30] which are advantageous for powder samples. This method is very important for the preparation of radioactive kryptonates utilized in analytical applications.

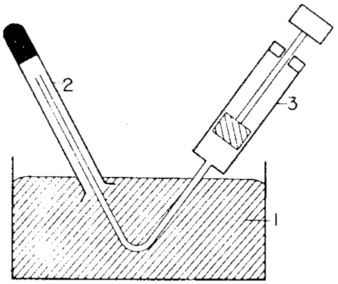

FIG. 5.—Filling of capillaries with radioactive krypton.[29]
1—Vessel with mercury; *2*—sample in capillary; *3*—syringe.
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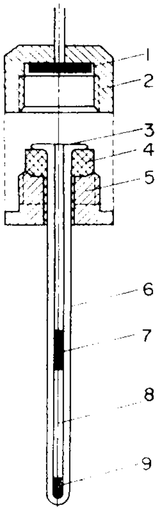

FIG. 6.—Diffusion kryptonation.[29]
1—Matrix sealing; *2*—matrix; *3*—ground part of capillary; *4*—rubber sealing; *5*—screw with opening; *6*—glass capillary; *7*—movable mercury plug; *8*—gaseous ^{85}Kr; *9*—sample.
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Kryptonation is carried out in thick-walled glass capillaries of 0·24 m length. The mouth of the capillary, with the sample, *2*, is immersed in a beaker containing mercury, *1*. With an injection syringe *3*, air is exhausted and the whole capillary filled with mercury (Fig. 5). The needle is taken out and the needle of another injection syringe, filled with krypton-85 is put in. By injection of krypton, mercury is pushed out from the capillary until only a 4–8 mm length is left at the mouth of the capillary.

The capillary is mounted with a rubber seal and attached to a holder (Fig. 6). Then the capillary is attached to a nitrogen bomb through a copper spiral tube. The pressure is accurately set by an incorporated needle valve, and after the necessary kryptonation time the valve on the bomb is closed and the sealing screw between the bomb and the needle valve is released. Then the needle valve is opened, so that the pressure reaches atmospheric. The capillary is taken out, the mercury removed and the end of the capillary is cut off. The radioactive kryptonate is put into a beaker fitted with a ground joint.

The amount of radioactive krypton incorporated into the carrier by diffusion techniques depends upon the pressure, time and temperature of kryptonation.

PROPERTIES OF RADIOACTIVE KRYPTONATES

The kryptonate can be viewed either as a carrier of krypton-85 or as a chemical labelled with krypton-85 tracer. In chemical analysis the krypton-85 nuclide plays the role of a radioactive tracer.

Krypton-85 has a half-life of 10·27 yr and decays almost entirely by 0·672-MeV β-emission. Krypton-85m has a half-life of 4·36 hr and the decay is associated with 0·305-MeV γ-radiation and 0·830-MeV β-emission. Thus the nuclear characteristics of the isotope make it well suited for the uses described below.

The general properties of the radioactive kryptonates are determined by the properties of the carrier and by the method and conditions of kryptonation. An important requirement in using radioactive kryptonates for chemical analysis is stability with respect to temperature, time and chemical composition of the medium in which the radioactive kryptonate is stored.

The basis of the use of radioactive kryptonates in analytical chemistry is that during the chemical reaction, the crystalline lattice of the kryptonated carrier is destroyed, the carrier consumed and the radioactive krypton released.

If the radioactive kryptonate is to function as an analytical reagent, the amount of krypton-85 released during the reaction must be proportional to the amount of the substance or component to be determined by analysis, *i.e.*, krypton is homogeneously distributed throughout the carrier. If the kryptonate is to function as an titrimetric indicator, krypton-85 must be released at the equivalence point.

Homogeneous distribution of krypton in the carrier substance can be expected in kryptonates prepared by kryptonation of the carrier during formation of the solid phase, *viz.*, during crystallization and sublimation. Kryptonates prepared by these methods are sufficiently stable for analytical use at laboratory temperature. Chemical and kinetic properties of the carrier are only slightly influenced by changes of its lattice characteristics by the presence of the krypton-85 atom in the crystalline lattice.

Radioactive kryptonates with a clathrate crystalline structure also have homogeneous krypton distribution throughout the clathrate cage.[31,32] Hydroquinone seems to be a very advantageous carrier component, because it has an open crystalline structure and cavities of favourable dimensions, and $[C_6H_4(OH)_2]_3[^{85}Kr]$ has been found useful.

The krypton in kryptonates prepared by diffusion technique and by bombardment with ions is distributed inhomogeneously. The krypton atoms are concentrated near to the surface, the depth of their penetration being about 10–10^2 μm. Radioactive kryptonates prepared by diffusion techniques confirm dependences derived from the theory of diffusion phenomena, but according to Chleck[4] the release of krypton—the dekryptonation process—does not occur by a normal diffusion mechanism. For a certain carrier the amount of krypton released from the kryptonate is a function of temperature. During the bombardment of carrier with accelerated krypton ions, the surface layers of the lattice may be disturbed, depending on the energy of the ions.

For analytical purposes the amount of krypton released during the analytical reaction can be determined by standard radiochemical measurement of the activity of the released gas or the residual kryptonate.

Work with radioactive kryptonates needs a minimum of safety precautions, because noble gases do not enter into metabolic systems. Another advantage in working with kryptonates is that krypton-85 is bound to a solid carrier, so work with it is easier and more convenient than with gaseous radioactive krypton.

USES OF RADIOACTIVE KRYPTONATES IN CHEMICAL ANALYSIS

Analytical methods which use radioactive kryptonates are typical examples of "radio-release" methods, *i.e.*, a group of analytical methods based on the release and measurement of radioactive reaction products.[8,11,33–35]

Radio-release methods depend on the selective reaction of the non-radioactive component being determined or the auxiliary reagent (for example the titration solution) with the radioactive agent (in our case with the radioactive kryptonate). During reaction the radioactive component is released, mostly in gaseous form. The determination can be made, (*i*) with a calibration curve, (*ii*) by comparison with a standard, or (*iii*) by titration.

The following are examples of the analytical uses of radioactive kryptonates.

Analysis of gases

Work with radioactive kryptonates has been directed mainly towards the determination of gaseous components and traces of impurities in air. Methods have been developed for the determination of: ozone, oxygen, sulphur dioxide, fluorine, chlorine, chlorine trifluoride, nitrogen dioxide, nitric oxide, amines and hydrogen. Some of these methods are intended for the determination of these components in the atmosphere of other planets (*e.g.*, Mars and Venus). These methods are also of great importance in industrial hygiene for the determination of components in the atmosphere of various hazardous work places.

Oxygen.[3] Krypton-85 is released from radioactive kryptonates during their oxidation, owing to the chemical destruction of the surface layers, the amount being proportional to the degree of oxidation and thus to the concentration of oxygen. The oxidation rate of a substance is generally a function of the temperature and oxygen concentration. Most substances are coated with an oxide film, or in the presence of oxygen an oxide film is quickly formed. This surface film prevents further oxidation. The oxidation rate becomes in practice independent of oxygen concentration and approaches a reaction of zero order. Because of this phenomenon, it was assumed from the start that carbon would be a suitable material for the determination of oxygen. Tests with kryptonated spectroscopically pure graphite rods at various temperatures, pressures and oxygen concentrations proved the applicability of this method.

Figure 7 shows these dependences. It is obvious that as the oxygen concentration changes so the activity of the kryptonate decreases. In large concentrations of oxygen the activity decrease with time is not linear.

The rate of activity decrease of pyrolytic graphite kryptonate as a function of the log of the oxygen concentration was found to be linear at constant temperature for various temperatures. The rate at 1050° is sufficient for the determination of oxygen in the range usually required (0·1 vol. % and total pressure 13–130 mbar, which corresponds to 0·01–0·13 mbar partial pressure of oxygen). The relation $\mathrm{d}(S/S_0)/\mathrm{d}t$, *i.e.*, the rate of loss of kryptonate activity and decrease in oxygen concentration, is given by the equation

$$\frac{\mathrm{d}(S/S_0)}{\mathrm{d}t} = K_1[\mathrm{O}_2]^{1/2}. \qquad (1)$$

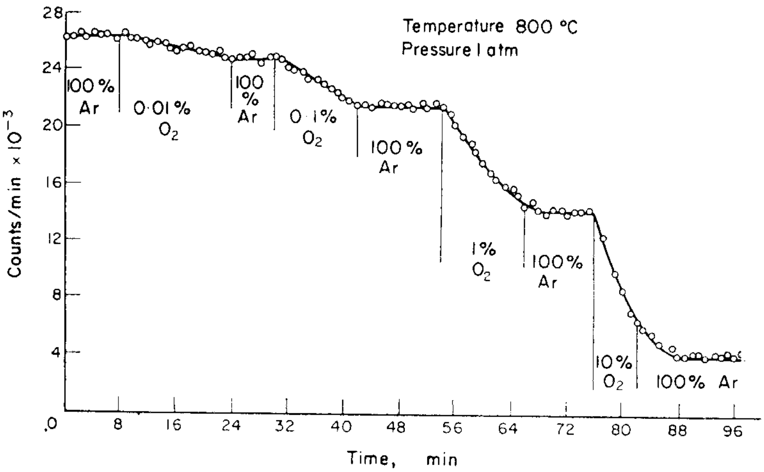

Fig. 7.—Decrease in activity of pyrolytic graphic kryptonate at various O_2 concentrations.[3]
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By use of the radioactive pyrolytic graphite kryptonate it proved possible to determine 2·2 ppm of oxygen in argon.

By the use of radioactive copper kryptonates, at different temperatures, oxygen can be determined in the concentration range 10^{-5}–10^{5} ppm. This kryptonate reacts faster with oxygen than the pyrolytic graphite kryptonate.

The percentage loss of activity of the copper kryptonate is also linearly dependent on the log of the oxygen concentration over the range of 10^{-2}–10^{4} ppm oxygen.[3] The curves [equation (1)] for 250, 300 and 1050° were calculated from the Arrhenius temperature dependence, and, as with the curves for pyrolytic graphite the slope of log % O_2 *vs.* log $d(S/S_0)/dt$ is 0·5, indicating that the slow oxidation stage will be the dissociation of oxygen molecules, *i.e.*,

$$O_2 \rightleftharpoons 2O \tag{2}$$

The temperature dependence of the oxidation process is given by

$$\frac{d(S/S_0)}{dt} = -K[O_2]^{1/2}\, e^{-24\cdot 2/RT} \tag{3}$$

where the value of the coefficient K is 0·085 %/min.ppm$^{1/2}$, when ln $[O_2] = 0$ (*i.e.*, $O_2 = 1$ ppm) and $T = 773K$. By means of this equation the loss of activity of the copper kryptonate at various oxygen concentrations and source temperatures can be predicted.

The originators of the method, Chleck and co-workers,[3] proposed copper kryptonate for the determination of the oxygen content in the atmosphere of Mars and other planets. Results of experiments showed that other components of the earth's atmosphere (carbon dioxide and nitrogen) which may also occur in the atmosphere of Mars, do not interfere, nor does the density of the Mars atmosphere. The device monitors the activity of a kryptonate by means of a sodium iodide crystal connected to a photomultiplier, power-supply and read-out.

Hydrogen.[6,36–38] Hydrogen as reducing agent reacts with many oxidizing agents. Of the radioactive kryptonates of metal oxides investigated the best hydrogen sensor seems to be platinum(IV) oxide. Chleck and co-workers[37] have found that the kinetics of the process are described by

$$\frac{\mathrm{d}(S/S_0)}{\mathrm{d}t} = -3{\cdot}29\,.\,10^6[\mathrm{H}]\,.\,e^{-7{\cdot}18\times 10^3/T} \tag{4}$$

During the investigations the reaction vessel containing the radioactive kryptonate of platinum(IV) oxide was filled with gases of differing hydrogen content, at room temperature as well as at higher temperatures. For work at higher temperatures the kryptonate was preheated in an oven. During preheating the kryptonate becomes thermally stable at the oven temperature and lower temperatures. The activity of the kryptonate will decrease only when reaction takes place. By measurement of activity losses of the kryptonate, the rate of krypton-85 loss was determined. The work was carried out with milligrams of metal oxide kryptonates with specific activities 1–5 μCi/mg.

The log of the rate of activity loss of the kryptonate in %/min is directly proportional to the log of the concentration of hydrogen above the $PtO_2[^{85}Kr]$, when the measurements are made at room temperature in an atmosphere of nitrogen. With air as the diluting gas, no decrease of activity was detected, because the hydrogen was oxidized by oxygen on the surface of the oxide. During this oxidation the surface of the oxide is not disturbed and so no krypton is released. For measurement of the hydrogen concentration in its mixtures with oxygen (*e.g.*, in air), this catalytic oxidation must be avoided. For this purpose various powdered materials are added to platinum(IV) oxide, the best seeming to be aluminium oxide powder. These powdered additives probably function by hydrogen diffusion through them to the surface of the kryptonate $PtO_2[^{85}Kr]$, where the reaction then takes place.[36] The catalytic hydrogen oxidation will be prevented by the inability of oxygen to reach this surface. In this case, to ensure the same sensitivity as with $PtO_2[^{85}Kr]$ alone, the temperature should be increased during the experiments. With a mixture of $PtO_2[^{85}Kr]$ and Al_2O_3 at the maximum working temperature of 435° (given by the thermal stability of PtO_2) 1% hydrogen can be determined within 0·5 sec and 10^{-3}% within 10 min. The higher the specific activity of the kryptonate used, the higher the sensitivity of the determination.

The influence of other gases on the determination of hydrogen was also investigated. Small amounts of hydrogen sulphide, sulphur dioxide, hydrochloric and hydrofluoric acid and water, all present in the laboratory atmosphere, did not measurably interfere with the determination. Water vapour up to saturation, carbon dioxide up to 1% and sulphur dioxide up to 0·5% had no influence on the determination. Hydrogen sulphide did not interfere up to a concentration of 100 ppm; at higher concentrations it does not react with the mixture of kryptonated PtO_2–Al_2O_3, but it prevents the reaction of hydrogen. Methane reacted with the solid carrier only at high concentrations and temperatures.

Chleck designed the prototype of the hydrogen analyser (Fig. 8), the basic part of which consists of an end-window Geiger–Müller counter and a sensor element (a mixture of kryptonated PtO_2–Al_2O_3 on a nichrome wire, fixed on a ceramic ring). The radiation detector is aimed directly at the kryptonate and the reaction of the

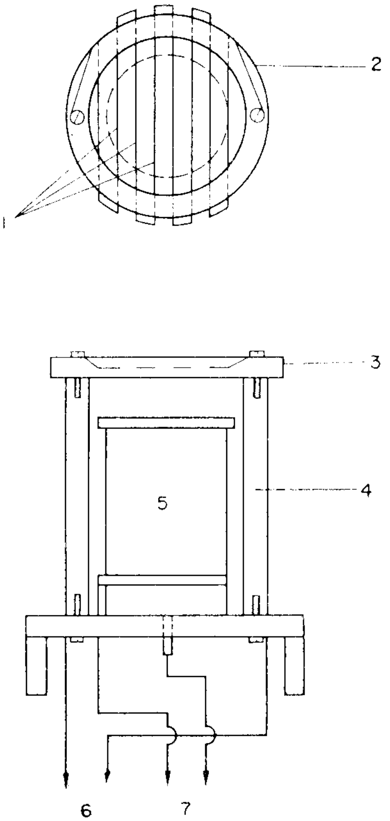

FIG. 8.—Prototype of hydrogen sensor.[36]
1—$PtO_2[^{85}Kr]$ – Al_2O_3 source on nichrome wire; *2*—ceramic insulator; *3*—ceramic insulator; *4*—brass conducting and support rods; *5*—Geiger tube; *6*—source power supply; *7*—ratemeter and recorder.
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hydrogen with the kryptonate is shown by the activity loss. The counter is connected to a ratemeter, which in turn is coupled to a recorder.

Ozone.[3,24,39–42] Determination of ozone is required for monitoring of the atmosphere of workplaces where it is used to bleach fats, oils, waxes, flour, starch, *etc.*, for control of the sterilization of drinking water, and for atmospheric studies.

In ozone determinations with the radioactive hydroquinone kryptonate the following reaction is used

$$[C_6H_4(OH)_2]_3[^{85}Kr] + O_3 \rightarrow 3C_6H_4O_2 + 3H_2O + {}^{85}Kr\uparrow \qquad (5)$$

The log of the activity of the released krypton-85 is linearly proportional to the log of the ozone concentration over a concentration range of 10^{-10}–10^{-6} g of ozone per litre of air. This sensitivity was achieved with a kryptonate the specific activity of which was about 100 mCi/g. Naturally, a higher specific activity proportionally increases the sensitivity value.

The measuring arrangement is that the gas containing the substance to be determined is carried through a dust filter to the reaction cell, where it comes into contact with the radioactive kryptonate. During the reaction with ozone the kryptonate

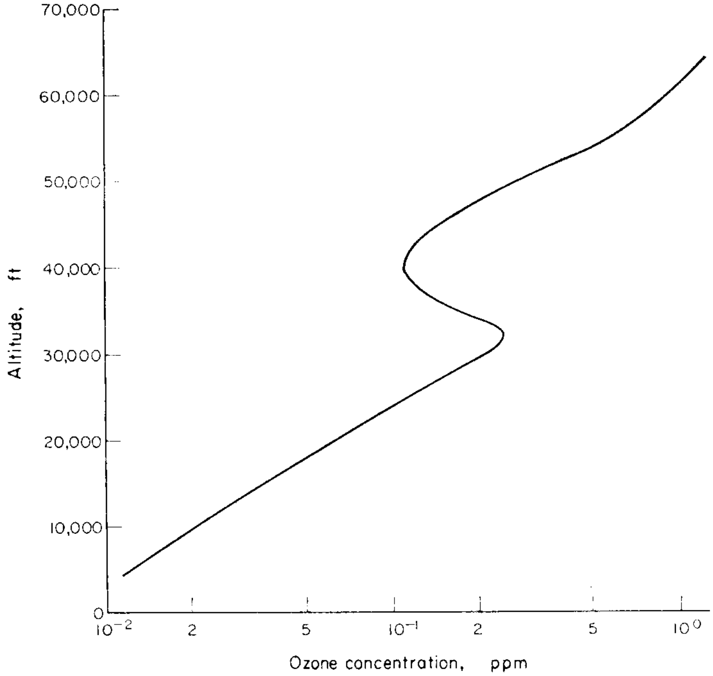

FIG. 9.—Vertical profile of atmospheric ozone.[39]
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releases krypton-85, which is transported by the carrier gas to the measuring cell, where the radioactivity is measured by a Geiger–Müller counter and recorded.

To simulate conditions in the upper layers of the atmosphere, Chleck and Ziegler[41] designed an apparatus in which the ozone was generated by an ultraviolet lamp; by lowering the pressure in the reaction cell it was possible to produce conditions which exist at the maximum height reached by weather balloons.

The general requirements for analysers of air composition in the upper layers of the atmosphere are high sensitivity, low weight, small dimensions and low price. These requirements are met in an ozone analyser which consists of the radioactive kryptonate, a measuring cell with an end-window Geiger–Müller counter, and a little pump.[41] The analyser, in a plastic case, is attached to the upper part of a normal weather radiosonde. The detected activity is recorded directly, and Fig. 9 shows the vertical profile of atmospheric ozone, measured by the analyser.[39]

Chleck and Cucchiara[3] also investigated the possibility of determining ozone by means of radioactive copper kryptonate, since ozone reacts with it at markedly lower temperature than molecular oxygen does. Experiments were made at 200 and 100°, when no reaction with oxygen was found, and it was shown that this kryptonate can be used at temperatures below 100°.

Sulphur dioxide.[40–45] Sulphur dioxide has been determined with the radioactive hydroquinone kryptonate. The determination is based on the mechanism of double release. In the first stage sulphur dioxide releases chlorine dioxide, which is a strong oxidizing agent. The chlorine dioxide oxidizes the radioactive kryptonate and gaseous

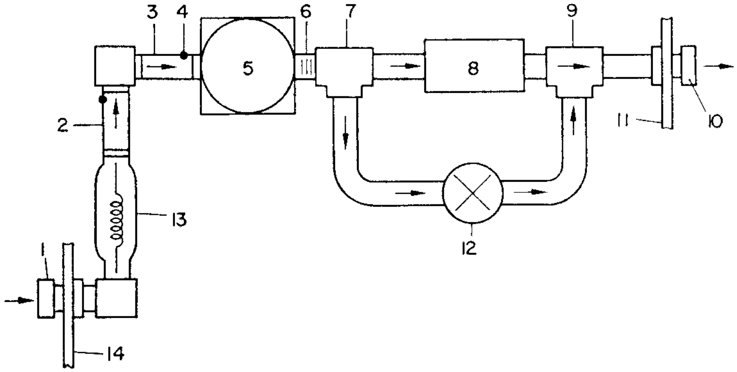

FIG. 10.—The flow diagram for the UDMH monitor.[47]
1—Input; *2*—NaClO$_2$ cell; *3*—clathrate cell; *4*—red dot or arrow; *5*—counting chamber; *6*—flow-meter; *7*—tee; *8*—pump; *9*—tee; *10*—exhaust; *11*—panel; *12*—flow control; *13*—cracking oil; *14*—panel.
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krypton-85 is released. The following reactions are involved:

$$SO_2 + 2NaClO_2 \rightarrow 2ClO_2 + Na_2SO_2 \qquad (6)$$

(this equation is an oversimplification since experimentally it was found that 1 molecule of sulphur dioxide releases between 4 and 8 molecules of chlorine dioxide)

$$ClO_2 + [C_6H_4(OH)_2]_3[^{85}Kr] \rightarrow {}^{85}Kr\uparrow \qquad (7)$$

The activity of the released krypton-85 is linearly dependent on the concentration of sulphur dioxide, which can be determined down to 0·001 ppm.

The only gases that should interfere with the operation of this analyser are those which can oxidize either sodium chlorite or the hydroquinone in the clathrate. The oxides of nitrogen and ozone are the only commonly occurring atmospheric gases that should cause any trouble.

Fluorine.[46] Fluorine can be determined by means of the radioactive hydroquinone kryptonate. In the apparatus described by Hommel and co-workers[46] a radioactive kryptonate with a specific activity of 450 mCi/g was used. The measuring cell contained an amount corresponding to about 50 mCi. One of these measuring cells has a lifetime of many months when traces of fluorine (less than 2 ppm) are measured. However, it is necessary to recalibrate the apparatus from time to time.

Analysers[32,47,48]

Two types of apparatus for determination of atmospheric impurities (F_2, Cl_2, ClF_3, SO_2, NO_2, NO, RNH_2, O_3), of oxidizing or reducing nature, in concentrations of the order of ppm, have been developed in the research institute of Tracerlab. These are the nitrogen dioxide detectors which represents one of the simplest devices and the UDMH (unsymmetrical dimethylhydrazine) unit which is much more complicated. By these instruments gases which can react directly or indirectly (by chemical, catalytic or thermal reaction) with the radioactive kryptonate are measurable.

The flow diagrams for the nitrogen dioxide and UDMH monitors are similar; that of the latter is shown in Fig. 10. The basic system contains a sampling pump, flow adjustment valve, counting chamber and radioactive kryptonate (clathrate). Chemical and catalytic cells are included when necessary (Fig. 10). The sample gas is pulled through the system by the pump. As the gas of interest enters the instrument, it immediately comes into contact with the chemical and catalytic cells, if they are required, and then reacts with the radioactive kryptonate. The krypton-85 released enters a counting chamber of known volume where its concentration per unit volume is determined. This concentration can be related directly to the volume concentration of the gas of interest entering the system.

Experience has shown that a multi-gas system has much poorer operational characteristics than the single-gas units.

With this apparatus the most widely used rocket fuels and oxidizing agents can be analysed. The output from the apparatus is a simple electric signal, which can be used not only for the control of the measuring device and recorder but also for the starting of a control and safety warning device.

A detection limit of 0·5 ppm has been observed regularly on a routine basis, and for special situations 0·1 ppm has been detected. The upper limit depends on the cell-life required and on the saturation characteristics of the Geiger tube.

Analysis of solutions

Radioactive kryptonates can also be used for the analysis of solutions by the direct reaction of the substances determined or reagents used with the radioactive kryptonate. A special position is held by titration methods, which will be treated separately.

With methods described in this part of the review analytical results were gained by the use of calibration curves. Either the activity drop of the radioactive kryptonate or the radioactivity of the krypton-85 released can be measured.

Water in organic solvents.[36–38,49] Determination of water in organic solvents is based on the reaction

$$2H_2O + CaC_2[^{85}Kr] \rightarrow Ca(OH)_2 + C_2H_2 + {}^{85}Kr\uparrow \tag{8}$$

The total activity of the krypton-85 released is measured, and is directly proportional to the amount of water reacting with the radioactive kryptonate of calcium carbide added to the solution investigated. The method is applicable for the determination of 0·25–2·0% H_2O in methanol.[49]

Hydrochloric acid. The determination of acids is based on following their reaction with an appropriate kryptonate by tracing the rate of krypton-85 release. Thus aqueous solutions of 10^{-1}–$10^{-3}M$ hydrochloric acid were analysed by the use of radioactive kryptonates of magnesium.[37,49,50] At constant temperature and under constant reaction conditions rate of release of krypton is directly proportional to acid concentration.

For the determination of the concentration 10^{-1}–$10^{-4}M$ hydrochloric acid, radioactive silver kryptonate has been used with success.[51]

Iron.[34,52] Rotariu, Hoskins and Hattori[52] tried to determine iron(III) in aqueous solution by the use of the radioactive kryptonate of hydroquinone. They assumed that it would be possible to determine iron in ppM concentrations, but at present the range is 2–20 ppm.

In the method proposed, iron(III) was extracted into trifluorotoluene by thenoyltrifluoroacetone (TTA) at pH 2–3 and the organic phase containing iron(III) was transferred to a closed system. For 8 sec gaseous hydrogen chloride was bubbled through the solution and the surplus of gas was removed by nitrogen. One mg of radioactive hydroquinone was added to the solution, which was mixed for 15 min. The reactants were frozen out with a mixture of solid carbon dioxide and acetone and krypton-85 pumped into the ionization cell, where its activity was measured. Although it was possible to determine 2–20 ppm of iron in the trifluorotoluene-TTA solution, the results, after investigation of the distribution coefficient of iron(III) between water and the organic solvent, showed that for quantitative extraction it would be necessary to repeat the extraction three or four times.

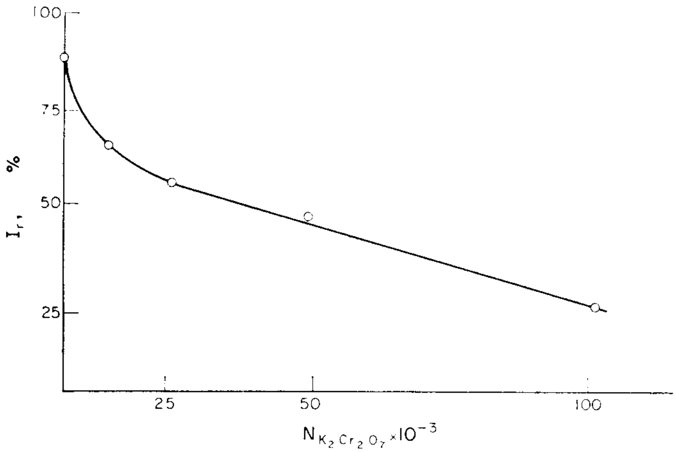

FIG. 11.—Calibration curve from determination of dichromate.[51] (Reprinted by permission of the copyright holder, Elsevier).

Dichromate.[51] For the determination of dichromate ions the reaction with the radioactive silver kryptonate Ag[^{85}Kr] is used.

$$Cr_2O_7^{2-} + 6Ag[^{85}Kr] + 14H^+ \rightarrow 6Ag^+ + 2Cr^{3+} + 7H_2O + {}^{85}Kr\uparrow \qquad (9)$$

Thus, dichromate in the concentration range from 0·0125 to 0·1*N* was determined. Figure 11 shows the calibration curve. It has been shown that iron(III), chloride and nitrate interfere.[53]

Vanadate.[51] Vanadate ions can be determined by a procedure similar to that used for dichromate. The following reaction is carried out in the presence of fluoride:

$$V(OH)_4^+ + 2H^+ + Ag[^{85}Kr] \rightarrow VO^{2+} + Ag^+ + 3H_2O + {}^{85}Kr\uparrow \qquad (10)$$

The sensitivity of Ag[^{85}Kr] to $V(OH)_4^+$ is great. A solution of the order of $10^{-7}N$ is still able to decrease measurably the radioactivity of Ag[^{85}Kr]. At the $10^{-5}N$ level the reproducibility is ±3%.

The comparison of both foregoing determinations shows that the vanadate reacts more sensitively than the dichromate with Ag[^{85}Kr], although the difference in normal potentials is greater for the dichromate. The probable cause of this is the different reaction medium: with dichromate a neutral solution is involved, with vanadate the medium is strongly acid.

Oxygen.[54,55] The determination of small amounts of oxygen dissolved in water or other liquids is one of the most difficult analytical problems, but can be solved by means of the radioactive thallium kryptonate. The determination is based on the reaction

$$4\mathrm{Tl}[^{85}\mathrm{Kr}] + \mathrm{O}_2 + 2\mathrm{H}_2\mathrm{O} \rightarrow 4\mathrm{Tl}^+ + 4\mathrm{OH}^- + {}^{85}\mathrm{Kr}\uparrow \qquad (11)$$

The radioactive kryptonate of thallium is added to the solution to be analysed or the solution is passed through the thallium kryptonate. The oxygen present in the liquid reacts with the surface layer of thallium, and krypton-85 is released, the amount of which is proportional to the amount of oxygen dissolved in the liquid.

The fall in radioactivity of the thallium kryptonate, measured in distilled water, is linear with the concentration of oxygen dissolved, down to 0·3 ppm.

The analyser used for determination was calibrated with distilled water saturated with air. The oxygen concentration in pure water at atmospheric pressure and room temperature was determined. The linearity of the calibration curve was such that it was sufficient to calibrate the analyser with one standard solution.

By this method oxygen concentration in potable water, water samples from lakes, rivers, sea-water, *etc.*, can be determined.

Radioactive kryptonates in titrimetric analysis

Titrimetric analysis with radiometric end-point indication (so-called radiometric titration) has assumed greater importance recently, owing to the working out of new methods for separating titration components and to new titration procedures.[56–58] Possibilities of further development are presented by radioactive kryptonates.[36,37,59] This area is being intensively developed in our Institute.[14–22,61–62]

Essence of the method. In the application of radioactive kryptonates to end-point indication, an auxiliary reaction of the radioactive kryptonate with an excess of titrant is used in which radioactive krypton is released. As the reaction product is a gas it is relatively easy to separate it from the other components of the reaction, which are in the solid (kryptonate indicator) and liquid (titrant and titrand) phases.

Radioactive kryptonates can only be used as end-point indicators if the kryptonated solid material does not react with the solution being titrated.

Substances reacting with the kryptonate indicator could interfere with the end-point by releasing krypton-85 prematurely. If this interfering reaction is slow, it will increase the background count but the end-point will be detectable. If the interfering reaction is so fast that it is impossible to determine the exact start of the krypton-85 release during titration, either the interfering ion must be removed, or a different kryptonate must be used.

Amongst the properties of radioactive kryptonates used as indicators dekryptonation of the proper kryptonate in different conditions is of great importance. Therefore, before application of a certain radioactive kryptonate as an indicator, investigation must be made of the radioactivity decrease of the kryptonate in air under laboratory conditions and the influence of the titration medium and of the titrant.

The greater the stability of a given radioactive kryptonate in the air and in the titration medium and the easier the release of incorporated krypton-85, the better it is for titrimetric use. Table I lists radioactive kryptonates which have been used as indicators.

TABLE I.—SOME RADIOACTIVE KRYPTONATED INDICATORS

Radioactive kryptonate	Relative specific activity	Titrand	Titrant	Titration type	References
$Mg[^{85}Kr]$*		$1{\cdot}75M$ NaOH $0{\cdot}10M$ NaOH	$1{\cdot}75M$ HCl $0{\cdot}10M$ HCl	neutralization	59
$Zn[^{85}Kr]$*		$0{\cdot}01M$ NaOH	$0{\cdot}01M$ HCl	neutralization	59
$Zn[^{85}Kr]$*		F^-	$0{\cdot}01M$ $Th(NO_3)_4$	precipitation	36, 59
$AgIO_3[^{85}Kr]$*	$1{\cdot}7 \times 10^6$§	Ca^{2+}, Sr^{2+}, Mg^{2+}	$10^{-2}M$ EDTA	complexometric	16, 17
$Y_2(C_2O_4)_3[^{85}Kr]$†	$7{\cdot}7 \times 10^6$§	Fe^{3+}	$10^{-2}M$ EDTA	complexometric	16, 62
$AgI[^{85}Kr]$*	$1{\cdot}9 \times 10^6$§	Ni^{2+}	$0{\cdot}1M$ KCN	complexometric	18
Glass$[^{85}Kr]$†	0·3–400‡	Ca^{2+}, Cd^{2+}	$0{\cdot}2M$ NaF	precipitation	19
Glass$[^{85}Kr]$†	0·3–400‡	Th^{4+}	$0{\cdot}2M$ NaF	precipitation	61
Glass$[^{85}Kr]$†	250‡	H_2SO_4, HCl HNO_3	$0{\cdot}1M$, $0{\cdot}5M$ NaOH	neutralization	20
$Ag[^{85}Kr]$†	0·25–300‡	Ba^{2+}	$10^{-3}N$ $K_2Cr_2O_7$	precipitation	15, 51

* Prepared by diffusion technique.
† Prepared by bombardment with accelerated ions.
§ Specific activity in cpm/g.
‡ Specific activity in cpm/mm^2.

Radiometric titrations using radioactive kryptonates as end-point indicators may be performed discontinuously or continuously.

Discontinuous titration. During discontinuous titrations the radioactivity of the solid indicator or of the krypton released is measured after each addition of the titrant solution. The titration curve is plotted as count rate *vs.* volume of titrant. The radioactivity of the krypton released only can be measured if the radioactive kryptonate has high specific activity. The following methods have been used to date.

1. Solid radioactive kryptonate ($AgIO_3[^{85}Kr]$; $Y_2(C_2O_4)_3[^{85}Kr]$; $AgI[^{85}Kr]$) is added to the solution in the titration vessel.[14] The kryptonate forms a continuous layer at the bottom of the narrowed part of the titration vessel. Titration is begun 5 min after addition of the radioactive kryptonate. During titration a steady flow of nitrogen is bubbled through the solution, which carries off the released krypton-85. The activity of the radioactive kryptonate is measured regularly 2 min after each addition of titrant. From the measured activity a titration curve is plotted. Activity is expressed relative to the activity measured at the start of the titration.

2. Two types of titration using a radioactive glass kryptonate (kryptonated cover glass) or a silver kryptonate (kryptonated silver plate) have been employed.[15,20,51]

(*a*) The solution investigated and the radioactive silver or glass kryptonate are placed in the titration vessel, fitted with a bubbling tube. During titration, nitrogen is bubbled through, which carries off the released krypton-85. After each addition of titrant the radioactive kryptonate is left in the solution for 3 min and then removed and dried for a fixed time and its radioactivity measured under equal geometric conditions with an end-window counter.

(*b*) The radioactivity of the silver or glass kryptonate is measured directly in the solution, by making use of a cylindrical beta-counter, fitted with a plexiglass ring. The radioactive kryptonate is placed in the ring. Three min after each addition of the titrant solution the kryptonate activity is measured during 2 min, and then the titrant solution is added during 1 min. Continuous titration is also suitable for this method.

Continuous titrations. The titrant solution is added continuously to the test solution and the released krypton-85 is carried off by nitrogen or other suitable carrier gas into a flow-through detector of radioactivity, joined to a ratemeter and recorder.[18]

Figure 12 shows the titration curve for the determination of nickel by continuous titration with 0·1*M* potassium cyanide.

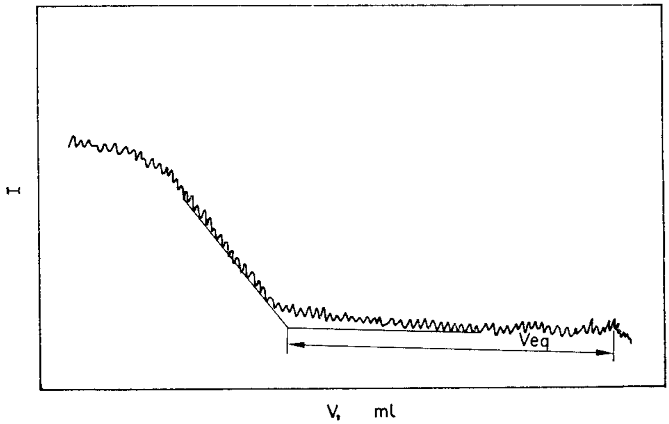

FIG. 12.—Titration curve of nickel determination by continuous titration.[18] (Reprinted by permission of the copyright holder, Akademie Verlag).

Radiocomplexometric titration

Radioactive kryptonates are used with advantage as end-point indicators in complexometric titrations.[16,17] The titration of cation M with complex-forming agent (titrant) C is considered in terms of the reaction

$$M + C \rightarrow MC \tag{12}$$

The end-point is determined by means of the solid radioactive kryptonate AB[^{85}Kr]. After the termination of reaction (12) the complex-forming titrant reacts with the indicator and forms a soluble compound according to the reaction

$$AB[^{85}Kr] + C \rightarrow AC + B + {}^{85}Kr\uparrow \tag{13}$$

whereby gaseous radioactive krypton is released. The equilibrium of reaction (12) is characterized by the stability constant of the MC complex and by the solubility product of the solid radioactive kryptonate AB[^{85}Kr].

Titration can be carried out if the following conditions are satisfied.

(*a*) If the formation constant for MC is much greater than that for AC.

(*b*) If the ratio between the stability constant of AC and the solubility product of the kryptonate AB[^{85}Kr] allows the dissolution of the kryptonate by the complex-forming agent according to reaction (13).

During titration to the end-point, reaction (12) takes place. The radioactivity of the kryptonate is constant. After the end-point is passed the excess of the complex-forming agent C reacts with component A and simultaneously dissolves the radioactive kryptonate AB[^{85}Kr] and releases krypton-85. According to this, the radioactivity

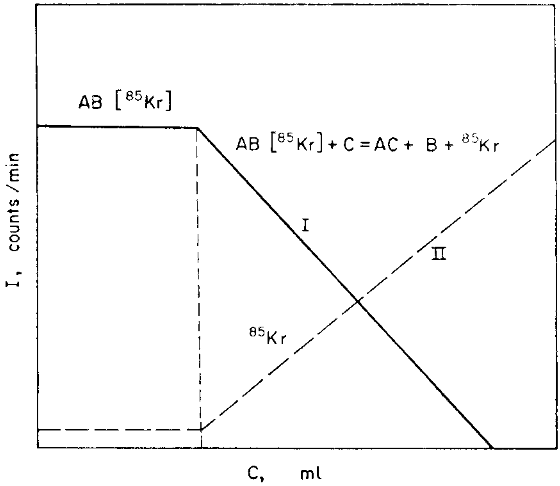

FIG. 13.—Theoretical titration curves of complexometric titration.[60] I—measurement of indicator activity; II—measurement of released ^{85}Kr activity. (Reprinted by permission of the copyright holder, Akadémiai Kiadó).

of the kryptonate proportionally decreases with the amount of the agent C added in excess (curve I, Fig. 13). As already mentioned, during titration the activity of the krypton released can also be measured (curve II, Fig. 13).

On this principle radiocomplexometric titration can be realized by a suitable complex-forming agent, which reacts quantitatively with the ions of the element determined, and a suitable radioactive kryptonate.

The theory of radiocomplexometric titration, the mechanism of indicator action during titration and the choice of suitable radioactive kryptonate as end-point indicator have been studied in detail.[60]

Determination of calcium, strontium, magnesium. In the determination of calcium (and similarly of strontium and magnesium) the pH of the solution is adjusted to 9·0–10·0 with 0·1M sodium hydroxide. The radioactive kryptonate $AgIO_3[^{85}Kr]$ is added and discontinuous titration carried out with $10^{-2}M$ EDTA. Up to the end-point the reaction is

$$Ca^{2+} + Y^{4-} \rightleftharpoons CaY^{2-} \qquad (15)$$

After the end-point, the reaction taking place is

$$AgIO_3[^{85}Kr] + Y^{4-} \rightarrow AgY^{3-} + IO_3^- + {}^{85}Kr\uparrow \qquad (16)$$

The reproducibility of the determination is good but there is a negative bias which suggests that krypton is released just before the equivalence point. This agrees with the results of Liebermann and co-workers[63] who determined calcium by titration with a 0·05M EDTA solution and the solid indicator $^{110m}AgIO_3$. Probably this is caused by the relatively close values of the stability constants ($\log K_{CaY^{2-}} = 10{\cdot}7$; $\log K_{AgY^{3-}} = 7{\cdot}3$), so that silver begins to react with the EDTA before complete complexation of calcium.

Strontium and magnesium can also be determined by this method. For the determination of calcium and magnesium (*e.g.*, in dolomite, glass, pharmaceutics,

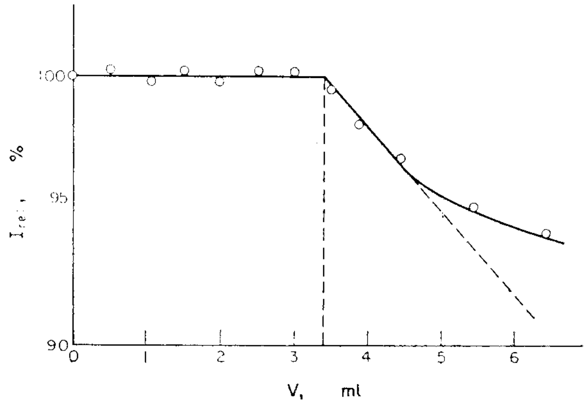

FIG. 14.—Titration curve for titration of nickel with 0·1*M* KCN, radioactive silver iodide kryptonate being used as end-point indicator.[18]
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water) two aliquots are used, one for the sum of calcium and magnesium determined, the other for titration of magnesium in the filtrate after calcium is precipitated as molybdate.

Determination of iron.[62] Iron has been determined by the discontinuous method. The radioactive kryptonate $Y_2(C_2O_4)_3[^{85}Kr]$ is added to the solution tested, which is titrated with $10^{-2}M$ EDTA. Up to the end-point the reaction is

$$Fe^{3+} + EDTA \rightarrow Fe(EDTA) \tag{17}$$

and after the end-point

$$Y_2(C_2O_4)_3[^{85}Kr] + 2EDTA \rightarrow 2Y(EDTA) + 3C_2O_4^{2-} + {}^{85}Kr\uparrow \tag{18}$$

As the log of the conditional stability constant of the iron/EDTA chelate, 9·1, and that of the yttrium/EDTA chelate, 17·8–18·1, are appreciably different, the accuracy of titration can be high enough. The system is buffered with sodium acetate (pH 5·0) and tartaric acid is added to keep iron in solution. The method is suitable for the determination of iron in cement.

The determination of iron and aluminium in one solution is possible by radiochelatometric titration. First, iron(III) is titrated at pH 5·0 with EDTA and the indicator $Y_2(C_2O_4)_3[^{85}Kr]$. Then the indicator is filtered off, the pH is adjusted to 9·0 and aluminium is titrated with EDTA and the indicator $AgIO_3[^{85}Kr]$.

Determination of nickel.[18] For the determination of nickel the radioactive kryptonate $Ag[^{85}Kr]$ has been used as indicator and 0·1*M* potassium cyanide as titrant. The titration was carried out in ammoniacal medium by the discontinuous and continuous methods. Up to the end-point the reaction is

$$Ni^{2+} + 4CN^- \rightleftharpoons [Ni(CN)_4]^{2-} \tag{19}$$

After the end-point the reaction which takes place is

$$AgI[^{85}Kr] + 2CN^- \rightarrow [Ag(CN)_2]^- + I^- + {}^{85}Kr\uparrow \tag{20}$$

the solid kryptonated indicator dissolves and its activity decreases with increasing volume of titrant added (Fig. 14). This increase is not always linear, especially with kryptonates of low specific activity. According to the diffusion theory there exists a certain concentration gradient in the kryptonated substance. Probably this gradient will cause the non-linear decrease of the activity when the titrant is added, but in practice this is without importance, as it is the relative activity change of the indicator after the end-point that is involved.

Precipitation titration

The sensitivity limit of precipitation titrations is generally of the order of 1 mg depending on the solubility product of the precipitate formed during titration. In spite of this, precipitation reactions are often used in titration. Several types of radioactive kryptonates have been used as indicators in precipitation titrations. Use is made of the dissolution of the surface of a radioactive kryptonate of a metal, or of disturbance of the surface of the radioactive kryptonate of glass, or of redox reactions on the surface of the radioactive kryptonate, caused by the titrant after the end-point.

Use of radioactive kryptonates of metals. At present only one radioactive metal kryptonate has been used in a precipitation titration.

Fluorides have been determined by titration with thorium(IV) with kryptonated zinc foil as the indicator.[36,37,59] After the equivalence point the excess of thorium ion is hydrolysed and the hydrogen ions formed react with $Zn[^{85}Kr]$, releasing krypton-85. Readily evaluated end-points were obtained for concentrations up to $10^{-4}M$ and even 2 μg of fluoride per ml could be determined.

It is known that the end-point in this titration is not stoichiometric. Therefore a calibration curve of moles of fluoride *vs.* ml of standard thorium consumed was used. It was reproducible and gave satisfactory results over the range 0·001–0·1*M* fluoride concentrations.

Use of radioactive kryptonates of glass. The destruction of the glass surface to release krypton is complete and varies according to the action of atmospheric moisture, acids, bases, the composition of the glass *etc.* The loss is initially high but decreases to a stable value, as the surface particles become exhausted to such an extent that decomposition is stopped. The extraction with bases is 200 times as great as that with acids, so radioactive glass kryptonate can be used with advantage as indicator in the titration of acids with bases. Hydrofluoric acid readily attacks glass and this has been exploited in precipitation titrations where the precipitate is a sparingly soluble fluoride.

Cadmium and calcium,[19] and thorium,[61] have been titrated with 0·2*M* sodium fluoride with radioactive fused silica kryptonate as indicator, at pH 6·0, pH 7·0 and in 0·5*M* sulphuric acid respectively. The solubility products of calcium and cadmium fluoride are such that mg amounts can be determined. After the end-point hydrofluoric acid strongly attacks the glass, with the consequent release of krypton-85 and decrease in the radioactivity of the glass. A calibration curve was used to determine the thorium concentration.

Use of redox indicators.[15,51] Some radioactive kryptonates, as for instance $Ag[^{85}Kr]$, may be used as redox indicators. Their surface is decomposed by oxidizing agents after the end-point, with consequent release of krypton-85. For example, barium has been titrated with 0·001*N* potassium dichromate with radioactive silver kryptonate as indicator. Up to the end-point the precipitation reaction is

$$2Ba^{2+} + Cr_2O_7^{2-} + H_2O \rightleftharpoons 2BaCrO_4 + 2H^+ \tag{21}$$

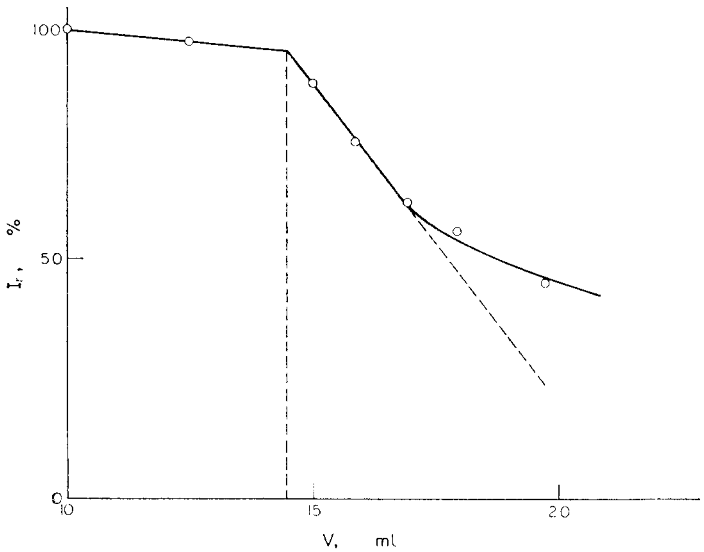

FIG. 15.—Titration curve for titration of Ba^{2+} with 0·001N $K_2Cr_2O_7$, using radioactive silver kryptonate as indicator.[15]
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and after the end-point, redox reaction (9) is going on. The activity decrease of the silver kryptonate is measured after each addition of the titrant. The titration curve for such a titration is illustrated on Fig. 15.

Neutralization titration

Radiometric neutralization titrations can now be realized with the advent of radioactive kryptonates.

Use of radioactive kryptonates of metals.[59] Radioactive kryptonates of magnesium and zinc have been used as indicators in the titration of a strong base (1·75, 0·1 and 0·01M sodium hydroxide) with a strong acid (hydrochloric acid of the same molarity). The krypton-85 released was determined after each addition of titrant. Figure 16 shows the titration curves obtained during these titrations.

Use of radioactive kryptonates of glass.[20] The radioactive kryptonate of glass is a suitable indicator in the titration of acids with strong bases. Here, after the equivalence point the excess of base decomposes the surface layers of glass, with the consequent release of radioactive krypton and decrease in the radioactivity of the glass. The end-point can be readily determined and coincides with the equivalence point.

CONCLUSION

This review presents a picture of the uses of radioactive kryptonates in chemical analysis. They can be used to determine substances of various character in gaseous and liquid samples by a relative method using calibration curves, by comparison with standards, or by titration methods.

Although one of the most recent areas of nuclear analytical chemistry (belonging to the group of "radio-release" methods) is involved, the analyses already carried out show the wider possibilities which radioactive kryptonates offer in resolving various

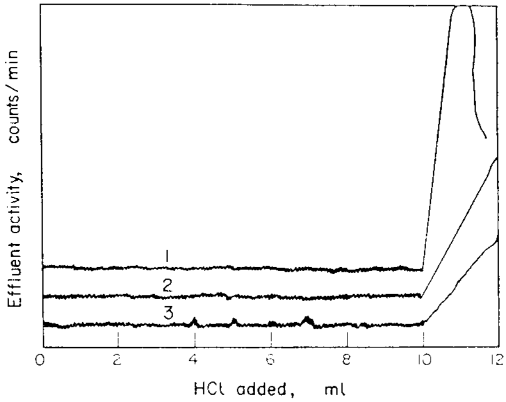

FIG. 16.—Acid–base titration curves.[59]
1—1·75*M* NaOH, Mg-kryptonate; *2*—0·10*M* NaOH, Mg-kryptonate; *3*—0·01*M* NaOH, Zn-kryptonate; for all titrations—10 ml taken.
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problems of chemical analysis. Experimental studies showed that other radio-release methods, using agents labelled with radionuclides, can be advantageously changed to methods using radioactive kryptonates. The importance of analytical methods using radioactive kryptonates is underlined by the fact that leading firms pay great attention to the design and construction of analysers, working on the principles mentioned.

Radioactive kryptonates, besides being of direct analytical application, are also helpful in resolving important problems of physical chemistry, closely related to analytical chemistry (study of kinetics and mechanism of chemical reactions, study of catalysis, adsorption and chemical reactivity, study of structural and surface changes and phase transformations, *etc.*)[9,10] which are, however beyond the scope of this paper. Future work in this field should be of theoretical interest and practical importance.

Zusammenfassung—Es wird eine Übersicht über die Anwendungen von radioaktiven Kryptonaten in der chemischen Analyse gegeben.

Résumé—On présente une revue des emplois des kryptonates radioactifs en analyse chimique.

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VERSATILE INSTRUMENT FOR DIRECT OR DIFFERENTIAL A.C. RESISTANCE OR CONDUCTANCE MEASUREMENTS ON SOLUTIONS

EUGENE D. OLSEN and ROBERT J. MARTIN
Chemistry Department, University of South Florida, Tampa, Florida 33620, U.S.A.

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Summary—A simple but versatile instrument with an electronic (non-servo) measuring circuit is described which is capable of making direct or differential measurements of the resistance or conductance of solutions over an absolute resistance range from 0·1 Ω to 1 MΩ, in six linear ranges. Linearity is better than 2% on all ranges, and reproducibility is better than 1%. Drift is less than 1% over 12 hr. Less than 0·01% change in resistance can be measured in the differential modes, permitting more sensitive measurements than can be made in direct conductance measurements. Applications of the instrument for monitoring ion-exchange separations and conductometric titrations are illustrated.

THERE are many advantages to the automatic, continuous recording of solution conductance or resistance. Kinetic studies become more convenient and applicable over a greater range of conditions than is possible manually, titrations are facilitated, and flowing streams can be continuously monitored. Several types of conductance- or resistance-recording instruments have been reported,[1–9] but all lack certain features of sensitivity, versatility or speed of response. Holm-Jensen[1] has designed an electronic measuring circuit suitable for conductometric titrations, but the circuit requires elaborate adjustments to achieve linearity even over a narrow range of conductances, and the sensitivity is insufficient for most solution chromatographic studies. All of the other instruments that have been reported[2–9] use a servo system in the measuring circuit, whereby any change in conductance in a bridge-type circuit activates a servo-driven potentiometer which restores the balance in the bridge and simultaneously gives recorder read-out. The sensitivity of such bridge circuits is inherently limited by the resistance of the servo slidewire.[2] Additional disadvantages of such servo-balancing systems are "hunting" and/or slow response time, these two characteristics being interdependent and requiring a compromise.[3] The above-mentioned limitations of servo-balanced measuring circuits were confirmed in this laboratory, with circuits similar to those of DeVerdier and Sjöberg[2] and James, Martin and Randall.[4]

The previously reported instruments[1–9] lack versatility in that the available read-out is linear in either resistance or conductance, but not both, and most[1,3,4,6–9] only make direct measurements on a single cell. The designs by DeVerdier and Sjöberg[2] and Wickbold[5] measure the difference in conductivity between two cells, but there is no provision for measuring the absolute conductance of either cell, and servo systems are used in the measuring circuits. This paper describes a simple but versatile instrument with an electronic measuring circuit for making direct or differential measurements of the resistance or conductance of solutions, over a large range of resistances or conductances. Either one or two conductance cells can be used, and a switch selects a read-out which is linear in each of the following functions: (*a*) direct resistance of cell 1 or 2; (*b*) direct conductance of cell 1 or 2; (*c*) differential resistance between the two cells; (*d*) differential conductance between the two cells. The differential functions can be made extremely sensitive by null-balancing the signal from each of the two cells, and amplifying the difference signal by a factor of up to 1000. Applications of the instrument for monitoring ion-exchange effluents and conductometric titrations are illustrated.

EXPERIMENTAL

Apparatus

Conductance resistance instrument. Figure 1 shows a block diagram of the instrument in the differential conductance mode and Fig. 2 shows a complete schematic diagram of the instrument. The voltage source in Fig. 1 is a signal having a constant voltage (E) of about 1·25 V rms and a frequency of either 60 Hz or 2 kHz (selectable by means of switch $S1$ in Fig. 2). The 2-kHz signal is used for solutions of high conductance where electrolysis could be significant, and is provided by the Hartley-type oscillator shown in Fig. 2. The 60-Hz signal is used for solutions of low conductance where capacitive reactance may be important, and is provided by the filament supply winding of power transformer $T3$ (Fig. 2). Potentiometer $R5$ allows the voltage of the 60-Hz and 2-kHz sources to be matched in an initial calibration so that the signal frequency can be switched at any time without significantly disturbing the measurement in process.

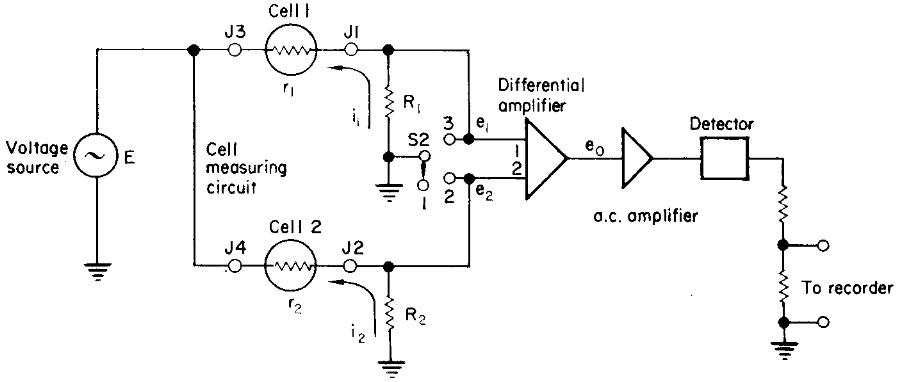

FIG. 1.—Block diagram of the instrument in the differential conductance mode.

The signal voltage is applied to the cell measuring circuit consisting of cells 1 and 2 and a set of range resistors. The range resistors are symbolized in Fig. 1 as R_1 and R_2, and their counterparts in Fig. 2 are the conductance range resistors selectable with switches $S3C$ and $S3D$, respectively. The a.c. voltages e_1 and e_2 generated in the cell measuring circuit are directly proportional to the conductance of cells 1 and 2, respectively, which may be shown as follows. First consider what happens when only the conductance of cell 1 is being measured (function switch $S2$ is in position 2, which amounts to grounding the second input to the difference amplifier at terminal $J2$). It can be seen that

$$i_1 = \frac{E}{R_1 + r_1}. \tag{1}$$

If the range resistor R_1 is chosen to be much smaller than r_1 (in practice R_1 is made one-tenth the full-scale value of r_1), then equation (1) reduces to

$$i_1 \sim \frac{E}{r_1}, \tag{2}$$

and voltage e_1 is given by

$$e_1 = i_1 R_1 \cong \frac{ER_1}{r_1}. \tag{3}$$

Since E and R_1 are constants, e_1 is directly proportional to $1/r_1$, the conductance of cell 1. In the same way, when only the conductance of cell 2 is being measured (function switch $S2$ is in position 3),

$$e_2 = i_2 R_2 \sim \frac{ER_2}{r_2}, \tag{4}$$

and thus e_2 is directly proportional to $1/r_2$, the conductance of cell 2. When function switch S_2 is in position 1, equations (3) and (4) are simultaneously valid, and if R_1 equals R_2, the differential amplifier generates a voltage (e_0 in Fig. 1) which is directly proportional to the difference in conductivity between cells 1 and 2, namely

$$e_0 = k\left(\frac{1}{r_1} - \frac{1}{r_2}\right), \tag{5}$$

where k is a constant which depends on the gain of the difference amplifier, the source voltage, and the range resistance.

To measure the difference in resistance of cells 1 and 2, function switch $S2$ is turned to position 4, which amounts to interchanging the position of each cell and its range resistor (*i.e.*, interchange r_1 and R_1, as well as r_2 and R_2). Again R_1 is made equal to R_2, but in this case the range resistors are chosen to be much larger than the cell resistances (in practice R_1 and R_2 are made ten times the full-scale value of the cell resistances). Under these conditions equation (1) reduces to

$$i_1 \sim \frac{E}{R_1} = I_1, \tag{6}$$

where I_1 is a constant current. Voltage e_1 is now directly proportional to the resistance of cell 1, as follows:

$$e_1 = I_1 r_1. \tag{7}$$

Similarly, voltage e_2 is now directly proportional to the resistance of cell 2, as follows:

$$e_2 = I_2 r_2. \tag{8}$$

Since R_1 is made equal to R_2, I_1 equals I_2 [equation (6)], and the differential amplifier generates a voltage (e_0) which is directly proportional to the difference in resistance of cells 1 and 2, as follows:

$$e_0 = k'(r_1 - r_2), \tag{9}$$

where k' is a constant which depends on the same factors as k. To measure the resistance of cell 1 only, function switch $S2$ is left in position 4 and a jumper wire is inserted between terminals 2 and 4, thus shorting cell 2 out of the circuit. Similarly, the resistance of cell 1 alone is measured with function switch $S2$ in position 4 and a jumper wire between terminals 1 and 3.

The differential amplifier in Figs. 1 and 2 is a cathode-coupled twin triode fed by a constant-current source to achieve a very high common-mode rejection ratio. The constant-current source is a fixed bias pentode with a dynamic plate resistance of about 1·36 MΩ. The source current is adjusted in an initial calibration with a screwdriver-type potentiometer ($R10$) in order to obtain an optimum rejection ratio, and once adjusted need not be changed. The single-ended output of the differential amplifier is fed into an RC coupled amplifier with a gain of about 10. The gain is adjusted with potentiometer $R14$ each time the instrument is calibrated.

The amplifier circuit was designed to compensate for the non-linearity of the cell-measuring circuit. For example, in the conductance-measuring mode, reference to equations (1) and (2) would indicate that as the solution resistance (r_1) decreases, the non-linearity should increase, causing the current to be up to 10% low at full-scale. However, the operating point of the 12AT7 amplifier tube was chosen to take advantage of the increasing convexity of the 12AT7 characteristic curves as the grid voltage decreases (becomes more positive), thereby compensating almost exactly for the non-linearity of the resistance-divider network.

The a.c. output of the amplifier is rectified with a voltage-doubler type detector having an RC output filter. The resistance portion of the filter is used as a voltage divider to provide full-scale outputs of 10, 1, 0·1 and 0·01 V respectively. Thus, almost any servo-recorder could be used to measure the output voltage. A Heath Model EUW-20A recorder was used in this study.

An added feature of the circuit shown in Fig. 2 is the drop counter, which is used to impose a voltage pulse on the recorder chart each time an increment of solution "shorts" between terminals $J5$ and $J6$. The actual solution contacts consisted of two platinum wires, separated by approximately 3 mm, mounted horizontally and parallel to each other, and positioned immediately below the discharge point of the fraction collector (used in separations), or capillary flow restrictor (used in titrations). Approximately 40-mm lengths of thin platinum wire were used, with electrical connections made to insulated copper wire by twisting and taping, and these copper wires were connected to terminals $J5$ and $J6$. As each increment of solution fell, it momentarily made contact across the two platinum wires, thereby imposing a voltage signal on the detector output. To prevent the retention of any droplets on the platinum wires, a 6-mm tip on each wire was bent downward through 90°. Any liquid adhering to the platinum wires indicated that they were dirty; they were conveniently cleaned by heating in a flame. The size of the pulse could be adjusted with potentiometer $R25$, and the polarity of the pulse could be selected with toggle switch $S5$.

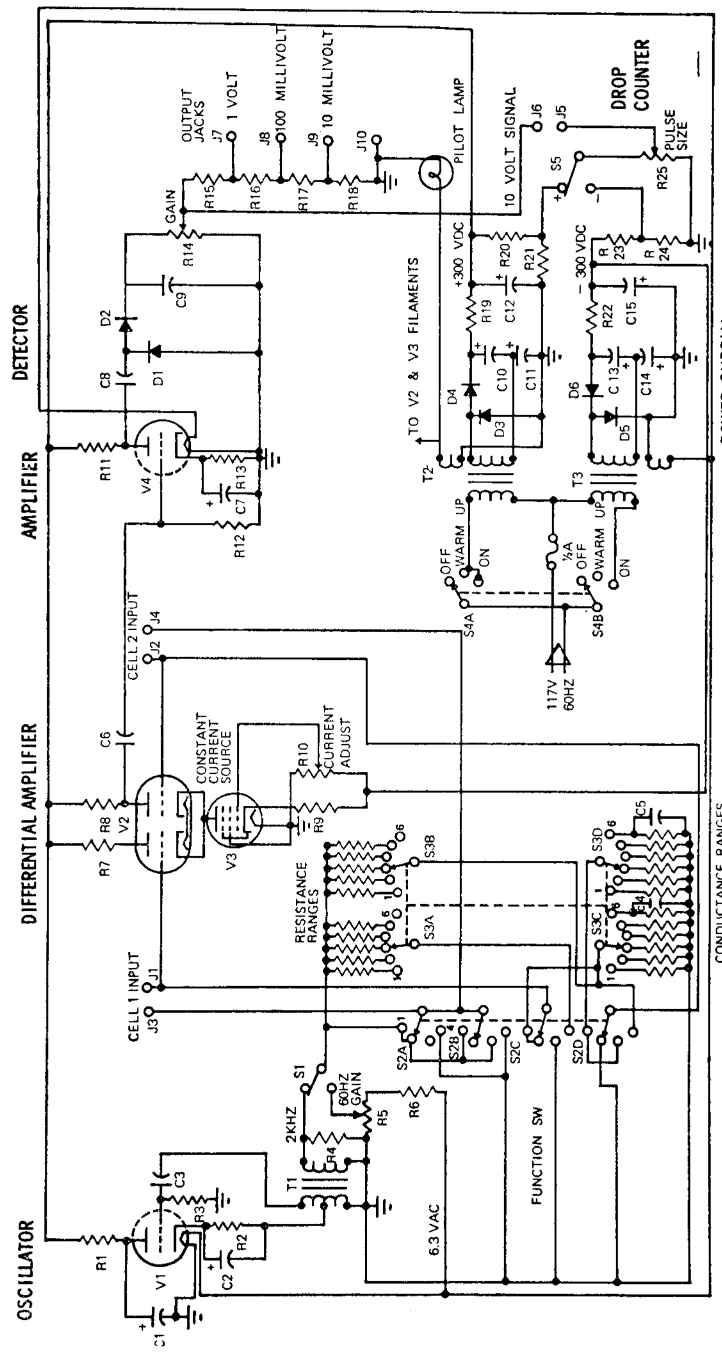

FIG. 2.—Complete schematic of the conductance-resistance instrument.

Legend Key for Figure 2

Tubes, V

1	1/2 12AT7
2	12AU7
3	6BH6
4	1/2 12AT7

Diodes, D

1, 2	1N 34A
3–6	1N438S, 0·1 A, 600 PIV

Resistors, R (all ±10%, 1/2 W unless noted otherwise)

1	22 K
2	470
3, 12	1 M
4	10
5	500 Pot Lin
6	1 K
7–9, 20, 23	100 K ± 5%
10	500 K Pot Lin
11	47 K
13	3·9 K
14	1 M Pot Lin
15	909 K ± 1%
16	90·9 K ± 1%
17	9·09 K ± 1%
18	1 K ± 1%
19, 22	27 K 1 W
21, 24	10 K ± 5%
25	10 K Pot Lin

Pilot Lamp No. 47 filament lamp, 6·3 V, 0·35 A, bayonet fitting

Transformers, T

1	Audio output transformer (Stancor TA-8U)
2, 3	Power transformer, 150 V a.c., 100 mA, and 6·3 V a.c., 1 A

Resistors for Resistance Ranges (All ±1%)

(One set each for switches 3A and 3B)

Switch Position	*Resistor*
1	100
2	1 K
3	10 K
4	100 K
5	1 M

Resistors for Conductance Ranges (All ±1%)

(One set each for switches 3C and 3D)

Switch Position	*Resistor*
1	1
2	10
3	100
4	1 K
5	10 K
6	100 K

Capacitors, C

1, 10–15	50 mF, 450 V d.c.
2, 7	10 mF, 25 V d.c.
3	470 pF, ± 10%, 500 V d.c.
4, 5	220 pF
6	0·1 mF, ± 10%, 400 V d.c.
8, 9	0·22 mF, ± 10%, 200 V d.c.

Switches, S

1, 5	SPDT Toggle, 1/2 A, 125 V a.c.
2	4P4T NS, Rotary
3	4P6T NS, Rotary
4	DP3T, Rotary, 1/2 A, 125 V a.c.

Equipment for ion-exchange separation. The ion-exchange column consisted of a glass tube 0·15 m long by 6 mm inside diameter, closed at the lower end by a coarse sintered-glass disk upon which the resin bed rested, and fitted at the top with a bowl 90 mm in diameter, to hold the eluent. A side-arm funnel, attached to the column and connected to a common outlet through a three-way stop-cock, provided a means of calibration or check on the response of the conductance monitor. A resin (H^+-form) volume of 2·0 ml was used to give a bed height of about 68 mm.

The conductance cells consisted of a flow-cell of fixed cell constant in the effluent stream, and a dip-type cell of variable cell constant dipping into eluent contained in the bowl at the top of the column. The flow-cell was fabricated by sealing two 25-gauge platinum wires about 20 mm in length through the centre of a 2 mm i.d. capillary tube, 25 mm in length, with the second wire 8 mm downstream from the first. After platinizing, the flow cell had a cell constant of 0·61 mm^{-1}, measured by using a solution of known specific conductance. Ball joints were used to attach the flow cell to the column outlet. A pair of dip-type electrodes was fabricated by sealing a 25-gauge platinum wire in the end of each of two 150-mm lengths of glass tubing so that 3 mm protruded. A bead of glass about 3 mm in diameter was then sealed to the protruding wire, nearly covering all of the wire except for a small length of exposed wire between the glass bead and the end of the glass tubing. The exposed wire was barely discernible, but became clearly defined upon platinizing. The pair of electrodes was mounted in a two-holed cork stopper and the cell constant could be varied from about 0·5 to 0·7 mm^{-1} by sliding one or the other of the electrodes up or down (coarse adjustment), or by twisting or rotating one or both electrodes (fine adjustment).

For making differential measurements of solutions of higher resistance, thin sheets of platinum foil were used instead of platinum wires, and connecting wires were shielded. Dip-type cells with variable cell constants were prepared similar to the previously described cell, except that the platinum foil protruding from each piece of glass tubing was bent at right angles to the tubing, so that each foil was horizontal and parallel to the other, allowing the spacing between cell plates to be varied by sliding one or the other of the electrodes up or down.

Equipment for conductometric titrations. The conductance instrument was used in the direct conductance mode (one cell only) for various conductometric titrations. A dip-type conductivity cell (similar to Industrial Instruments Model CEL-BB05) with a cell constant of 0·140 mm^{-1} was used. To automate the addition of titrant increments, a titrant delivery system similar to one described earlier[10] was used, with minor modifications. Instead of addition of titrant in large increments from a siphon pipe,[10] drop-sized increments from a capillary flow-restrictor were used. To mark the addition of each titrant increment on the recorder chart, the drop counter described above was used.

Reagents

The resin was Baker Analyzed Dowex 50W-X8, 100–200 mesh. All other chemicals were reagent grade. The resin was cleaned as described previously.[11]

Procedure

Ion-exchange separation of lithium, sodium and potassium. Two ml of the resin (in the hydrogen-ion form) were washed with 10 ml of 0·100*M* hydrochloric acid. After about 5 ml of 0·100*M* hydrochloric acid had passed, the cell constant of the dip-type cell immersed in the influent solution was precisely "nulled" against the effluent flow-cell of fixed cell constant. This null-balance adjustment was made by first making a direct reading of the absolute conductance of the effluent stream (switch *S*2 in position 2, so that the conductance of only cell 1 was being read) and then, while making a direct reading of the conductance of the influent stream (switch *S*2 in position 3, so that the conductance of only cell 2, was being read), adjusting the cell constant of the dip-type cell in the influent until the influent conductance reading agreed exactly with the effluent reading. To null the cells more precisely, the instrument was switched to the differential conductance mode (switch *S*2 in position 1), and the dip-type cell was fine-tuned to give a minimum differential reading at successively higher gains until a gain of 1000 was achieved. [In practice, the gain was increased in steps of 10, by first moving the positive recorder lead from terminal *J*8 (the 100-mV full-scale output) to terminal *J*7 (the 1-V full-scale output); the next factor of 10 gain was achieved by switching the module range to the next more sensitive range (*e.g.*, from the 10^4-μmho full-scale range to the 10^3-μmho full-scale range); a final factor of 10 gain was achieved by switching the Heath recorder range from 100 mV to 10 mV. After each increment of gain the dip-type cell was renulled more precisely.]

A 0·70-ml sample that was 0·286*M* in lithium nitrate, 0·0286*M* in sodium chloride, and 0·0428*M* in potassium chloride was put on the column at a flow-rate of about 0·5 ml/min, and eluted with 250 ml of 0·100*M* hydrochloric acid at a flow-rate of 1 ml/min. The effluent conductance was monitored continuously with respect to the influent conductance, the difference being amplified by a factor of 1000. To verify the composition of the effluent, 2-ml fractions were occasionally collected and analysed for lithium, sodium and potassium by flame spectrophotometry.

Conductometric titration. Forty ml of 0·025*M* hydrochloric acid were titrated with 0·85*M* sodium hydroxide, with a capillary flow-restrictor giving a flow-rate of 0·5 ml/min and a drop size of 0·040 ml. A nitrogen atmosphere was maintained to minimize carbon dioxide absorption during the course of the titration.

RESULTS AND DISCUSSION

Characteristics of instrument

Table I shows the various resistance and conductance ranges of the instrument. The instrument is capable of making direct measurements of resistances from 0·1 Ω to 1 MΩ in six ranges, with each range linear to within 2% of full-scale. Reproducibility is within 1%. The resistance and conductance ranges listed in Table I cover the entire range of solution conductances normally encountered, from 30% sulphuric acid to high-grade distilled water, for an ordinary cell with a 0·100-mm^{-1} cell constant. Since conductance cells can be purchased or constructed with cell constants ranging from 10^{-4} to 10 mm^{-1}, the range of the instrument could be extended, by proper choice of cells, to cover specific resistances ranging from 10^{-2} Ω.mm to 10 GΩ.mm.

TABLE I.—RESISTANCE AND CONDUCTANCE RANGES

Full-scale resistance, Ω	10	100	1000	10000	—	—
Resistance range, Ω	0–10	0–100	0–1000	0–10000	—	—
Full-scale conductance, *μmho*	—	10000	1000	100	10	1
Conductance range, *μmho*	—	0–10000	0–1000	0–100	0–10	0–1
Resistance corresponding to full-scale conductance, Ω	—	100	1000	10000	100000	10^6

It should be noted from Table I that intermediate ranges of resistance can be measured equally well in terms of either resistance or conductance, whereas low resistance (below 10 Ω) should be measured only on the resistance scale, and high resistances (above 10 kΩ) should be measured only on the conductance scale. For resistances below 10 Ω the conductance mode becomes non-linear because of excessive current drain on the source, whereas for resistances above about 10 kΩ the resistance mode becomes non-linear because currents in the measuring circuit are too low. It was demonstrated that another conductance range of 0–0·1 μmho corresponding to a full-scale resistance of 10 MΩ, could be added with no significant loss of linearity or response, but this was not included in the final design because of the severe shielding requirements that are necessary at such high resistances, and because the availability of cells with small cell-constants makes this range unnecessary.

The sensitivity or detectability of the instrument may be arbitrarily defined as the resistance change necessary to cause a chart deflection of two divisions. Thus, in direct resistance or conductance measurements the sensitivity was about 2% of the full-scale resistance or conductance. In differential resistance or conductance measurements at a gain of 1000, however, it was found that a change of resistance of 0·01% or less caused a deflection of 2 or more divisions from balance. For example, with decade resistance boxes in place of cells 1 and 2 and with about 10 kΩ carefully balanced against each other at a gain of 1000, a 1-Ω change of the decades caused about 2·5 divisions deflection. Similarly, after null-balancing two resistances of about 100 kΩ against each other, a 10-Ω change caused about 3 divisions deflection. In all cases linearity of the differential measurements was within 3% without recalibrating.

The accuracy of the instrument for measuring solution conductances was checked by comparing the conductance of five different concentrations of hydrochloric acid, ranging from 0·050*M* to $1{\cdot}0 \times 10^{-4}M$, using both an Industrial Instrument Model RC-16B2 conductivity bridge, accurate to ±1%, and the instrument described here, with the same conductivity cell. In all cases the conductivities agreed within 3%. After a 30-min warm-up the stability of the instrument was excellent, with a drift of less than 0·5%/hr and less than 1% drift over 12 hr.

Ion-exchange separation

Figure 3 shows an automatically recorded differential conductance curve for the elution of lithium, sodium and potassium ions from Dowex 50W-X8 with 0·10*M* hydrochloric acid as eluent. Shortly after the sample was put on the column the conductivity changed sharply, necessitating a decrease in gain from 1000 to 40. This conductance change is due to the slight difference in anion composition and solute concentration between the sample solution and the 0·10*M* hydrochloric acid eluent which had been used to balance the differential conductance monitor. When the effluent volume had reached about 46 ml, after the sharp lithium peak had emerged,

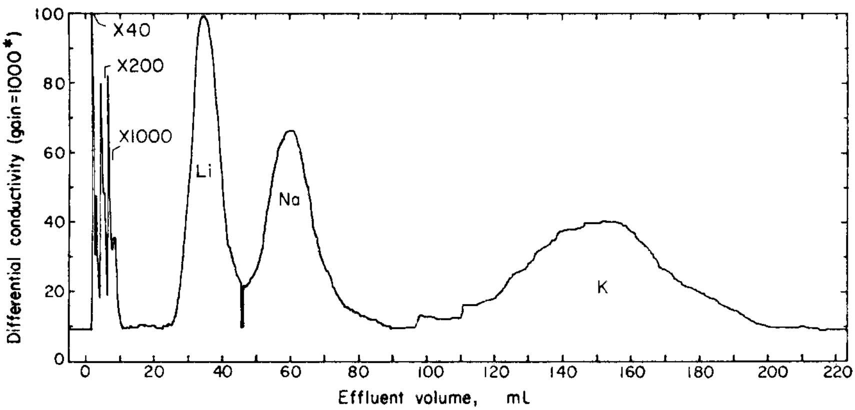

FIG. 3.—Automatically recorded differential conductance elution curve for the separation of lithium, sodium and potassium by ion-exchange.
Chart speed, 2·5 mm/min; flow-rate, 1·0 ml/min.
* Except in initial region, where gain was changed as indicated.

the three-way stop-cock below the column was used to switch the 0·10*M* hydrochloric acid eluent in the side-arm funnel momentarily into the effluent conductance cell, in order to check on response of the instrument, base-line drift, or hold-up in the conductance cell. As can be seen from Fig. 3, the conductance returned immediately to the base-line level, indicating fast response and negligible drift or cell hold-up. The composition of each peak was verified by collecting occasional fractions and analysing with a flame spectrophotometer.

The reproducibility of Fig. 3 was checked by repeating the elution three times, each peak volume being reproducible within ± 3 ml, and all peak heights being reproducible to within 6%. No special precautions were taken to maintain constant temperature, except that all solutions were prepared the day before use in order to reach complete temperature equilibrium and the instrument and cells were shielded from draughts. The separation shown in Fig. 3 is not necessarily optimum, as the separation between lithium and sodium could be improved with a slightly longer column or slower flow-rate, but at the expense of a longer total elution time.

The elution curve illustrates the value of differential conductance monitoring, because it would be impossible to locate the peak volumes in this separation with direct measurements of conductance, as the total change in conductance was less than 1% in each peak region. Thus, when this same elution was monitored with direct conductance measurements, a straight line resulted, with no observable changes in conductance in any of the peak regions.

The drop counter provided by the instrument proved very useful when the differential conductance instrument was used to monitor chromatographic effluents while fractions were collected. The drop counter registers a pulse on the conductance chart for each drop, thereby making it a simple matter to correlate precisely the collected fractions and recorded conductance.

Conductometric titrations

Figure 4 illustrates the automatically recorded conductometric titration of 0·025*M* hydrochloric acid with 0·85*M* sodium hydroxide. As each drop was added the drop

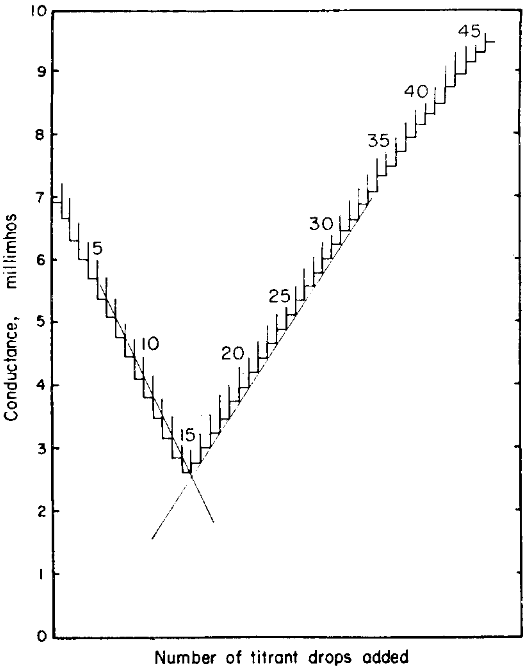

FIG. 4.—Automatically recorded conductometric titration of 40 ml of 0·025*M* HCl with 0·85*M* NaOH.
Drop size, 0·080 ml; flow-rate, 0·60 ml/min; recorder speed, 25 mm/min; cell constant, 0·140 mm^{-1}.

counter provided a sharp vertical pulse enabling the number of drops to be easily counted. The end-point was determined by extrapolation of the straight line portions before and after the end-point, with the location of the intersection indicating the drop within which the end-point occurred, and even the precise fraction of the drop needed to reach the end-point.[12] Thus, in Fig. 4, the end-point occurred after the addition of 15·0 drops. The average of seven such titrations had an error of +0·5% with a relative standard deviation of 0·6%. Triplicate titrations of 0·01*M* potassium hydroxide with 0·10*M* hydrochloric acid had an error of +0·5% with a relative standard deviation of 0·3%.

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Zusammenfassung—Ein einfaches, aber vielseitiges Instrument mit elektronischem Meßkreis (ohne Servo) wird beschrieben, das direkte oder Differenzmessungen des Widerstandes oder der Leitfähigkeit von Lösungen von 0,1 Ω bis 1 MΩ in sechs linearen Meßbereichen ermöglicht. Die Linearität ist in allen Bereichen besser als 2% und die Reproduzierbarkeit besser als 1%. Die Drift ist in 12 h kleiner als 1%. Im Differenzbetreib konnen kleinere Widerstandsänderungen als 0,01% gemessen werden; das erlaubt empfindlichere Messungen als bei der direkten Leitfähigkeitsmessung. Anwendungen des Instruments bei der Überwachung von Ionenaustauschtrennungen und konduktometrischen Titrationen werden beschrieben.

Résumé—On décrit un instrument simple mais universel avec un circuit électronique de mesure (non-servo) qui est capable de faire des mesures directes ou différentielles de la résistance ou de la conductance dans un domaine de résistance absolu allant de 0,1 Ω à 1 MΩ, en six gammes linéaires. La linéarité est meilleure que 2% dans toutes les gammes et la reproductibilité est meilleure que 1%. Le décalage est inférieur à 1% sur 12 h. On peut mesurer un changement inférieur à 0,01% dans la résistance dans les méthodes différentielles, permettant des mesures plus sensibles que celles pue l'on peut faire dans les mesures de conductance directes. On donne comme exemples des applications de l'instrument aux contrôles de séparations par échange d'ions et de titrages conductimétriques.

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POTENTIOMETRISCHE KIESELSÄUREBESTIMMUNG UNTER VERWENDUNG EINER TITANELEKTRODE—I

DAS VERHALTEN DER TITANELEKTRODE

GERHARD ACKERMANN
Lehrstuhl für Analytische Chemie, Sektion Chemie, Bergakademie Freiberg, 92 Freiberg, (sachen) D.D.R.

und

JOACHIM LANGE
VEB Spezialglaswerk Einheit, 758 Weißwasser, D.D.R.

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Zusammenfassung—Es wird die Empfindlichkeit einer Titanelektrode gegenüber Fluoridionen in Anwesenheit von Fluorosilicationen untersucht. In $3M$ Salzsäure, die etwas Eisen(III) enthält, kann die Elektrode für die Indizierung einer Titration von Kieselsäure mit Fluorid verwendet werden. Da die Reaktionen ziemlich langsam verlaufen, ist die Anwendung eines potentiometrischen Titrators erforderlich.

DIE MEISTEN volumetrischen Bestimmungsmethoden für Kieselsäure beruhen auf der Hydrolyse des Kaliumhexafluorosilicats. Der Umsetzung zwischen löslichen Kieselsäuren und Fluoridionen, d.h. der Bildungsreaktion des Hexafluorosilications, wurde bisher für analytische Untersuchungen wenig Bedeutung beigemessen, da für die Indizierung der Reaktion

$$SiO_3^{2-} + 6F^- + 6H^+ \rightarrow [SiF_6]^{2-} + 3H_2O \quad (1)$$

in dem zur quantitativen Umsetzung erforderlichen stark sauren Medium kein geeignetes Indikatorsystem bekannt war. Im Rahmen der vorliegenden Arbeit wurde nach einer Elektrode gesucht, die es gestattet, die nach Ablauf der Reaktion (1) auftretenden freien Fluoridionen zu indizieren.

Die Titanelektrode

Bei der Suche nach geeigneten, in sauren Lösungen beständigen Festelektroden wurde im Titan ein geeignetes Elektrodenmaterial gefunden, welches in Verbindung mit der ges.Kalomelelektrode (KE) den gewünschten Forderungen hinsichtlich Empfindlichkeit gegenüber Fluoridionen bei gleichzeitiger Beständigkeit gegenüber Hexafluorosilicondionen entsprach.

Um die zu bestimmenden Kieselsäuremengen in saurem Medium in Lösung zu halten, erwies sich eine $3M$ salzsaure Lösung, gesättigt mit Kaliumhexafluorosilicat und Kaliumchlorid (Grundlösung), als besonders geeignet. Für ihre Verwendung sprechen ferner folgende Argumente.

1. Titan ist in salzsaurer, chloridgesättigter Lösung sehr korrosionsbeständig.[2]
2. Um die Eignung der Titanelektrode für die Umsetzung nach (1) zu prüfen, muß eine Modell-Lösung geschaffen werden, die die Verhältnisse während des gesamten Titrationsverlaufes und am Äquivalenzpunkt eindeutig wiedergibt. Das aber erfordert die Sättigung einer solchen Lösung mit Kaliumhexafluorosilicat.

3. Die Löslichkeit des Kaliumhexafluorosilicats in $3M$ Salzsäure geht nach Sättigung der Lösung mit Kaliumchlorid von $0{,}1M$ auf *ca.* $2.10^{-3}M$ zurück, was die Verschiebung des Gleichgewichts der Reaktion nach (1) fördert. Die Löslichkeit ist in diesem Medium allerdings stark temperaturabhängig. Deshalb ist für eine gute Reproduzierbarkeit eine hohe Temperaturkonstanz erforderlich.

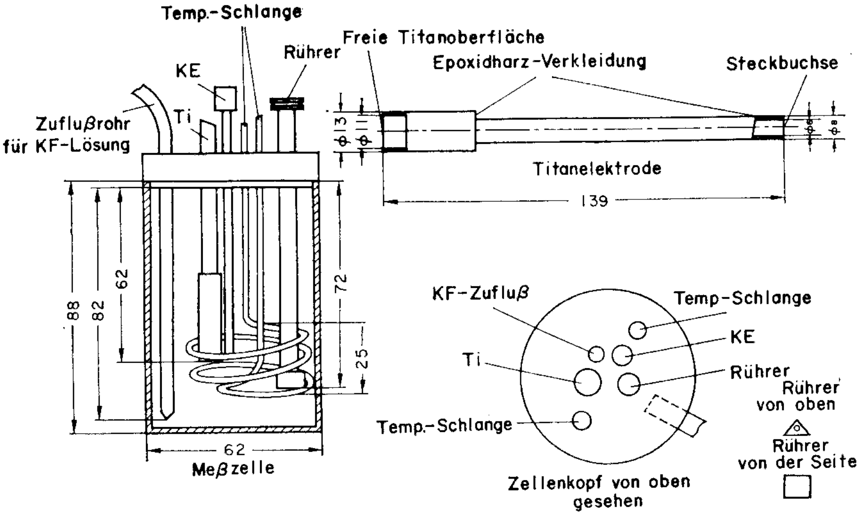

ABB. 1.—Konstruktionszeichnung der Meßzelle und der Titanscheibenelektrode.

In Abb. 1 ist der Aufbau der verwendeten Meßzelle dargestellt, gesondert dazu die in Epoxidharz vergossene Titanscheibenelektrode von 100 mm^2 Oberfläche, hergestellt aus technischem Titanrundmaterial. Das Epoxidharz wurde so abgedreht, daß nur die 100 mm^2 große Grundfläche des Titanzylinders mit der Lösung in Berührung kommt. In der Meßzelle ist ferner eine Temperierschlange erkennbar, die in Verbindung mit einem Thermostaten die Lösung konstantauf 20°C hält. Als Maßflüssigkeit fand eine $1M$ Kaliumfluoridlösung Verwendung. Die Titanelektrode wurde vor jeder neuen Messung mechanisch poliert. Hierzu wurde die Oberfläche der Titanscheibe mit einer gummigebundenen Korundpolierscheibe solange bearbeitet, bis sie einen gleichmäßigen matten metallischen Glanz aufwies. Diese Behandlung ist notwendig, um für jede Messung frische und reproduzierbare Oberflächenbedingungen zu schaffen.

Das Elektrodenpotential und seine Stabilisierung

Beim Einsetzen der Meßkette Ti-KE in die Grundlösung stellt sich nach wenigen Sekunden ein Potential von —600 bis —700 mV ein, das auch erhalten wird, wenn eine hexafluorosilicationen-freie Lösung mit einer Fluoridionenkonzentration von $0{,}01M$ verwendet wird. Nach Straumanis[3] entspricht dies dem Auflösungspotential des Titans.

In einer an Hexafluorosilicat- und Fluorid-Ionen freieen $3M$ salzsauren Lösung, ges. mit Kaliumchlorid, steigt das Potential allmählich zu positiveren Werten an, was auf die bekannte besondere Stabilität des Titans in chloridhaltigen Lösungen zurückzuführen ist. Setzt man nach einigen Minuten derartigen Lösungen festes

Kaliumhexafluorosilicat zu, so sinkt das Potential rasch zu stark negativen Werten ab, weil sich das Titan auflöst.

Da die Entstehung und Anwesenheit von Hexafluorosilicationen bei der Durchführung einer Titration nach (1) jedoch unumgänglich ist, muß dafür Sorge getragen werden, daß die Titanoberfläche wohl dem Angriff durch Hexafluorosilicationen widersteht, durch Fluoridionen jedoch meßbare Potentialänderungen hervorgerufen werden. Dies gelingt durch Zusatz geringer Eisen(III)-chlorid-Mengen, deren Konzentration so bemessen sein muß, daß die Empfindlichkeit gegenüber Fluoridionen gewahrt bleibt.

Es wird hierbei die Tatsache ausgenutzt, daß für die Aufrechterhaltung eines passiven Zustandes des Titans ein Oxydationsmittel genügender Stärke und Konzentration zugegen sein muß, wodurch das Korrosionspotential des Titans infolge Bildung schwerlöslicher Deckschichten in den sogenannten oxidpassiven Bereich gehoben wird.[4,5]

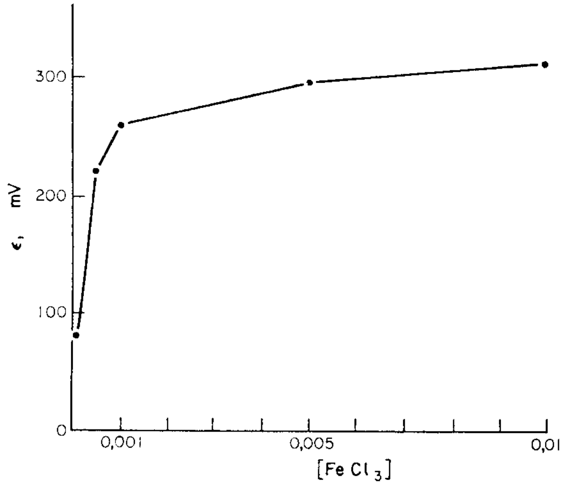

Abb. 2.—Abhängigkeit des Potentials der Titanelektrode in $3M$ Salzsäure, gesättigt mit Kaliumchlorid und Kaliumhexafluorosilicat, von der Eisen(III)-Konzentration, gemessen gegen ges. KE

Abbildung 2 zeigt das Potential der Titanelektrode bei steigender Eisen(III)-chlorid-Konzentration in der Grundlösung. Das Potential strebt einem Grenzwert zu, in gleichem Maße wie die Deckschichtenbildung voranschreitet. Das Potential-Zeit-Verhalten der Titanelektrode in der Grundlösung in Gegenwart von $5.10^{-4}M$ Eisen(III)-chlorid nach Zusatz von $10^{-3}M$ Fluoridionen zeigt die Abb. 3. Der zeitabhängige Potentialanstieg wird beim Auftreten freier Fluoridionen in der Grundlösung solange unterbrochen, bis diese durch Reaktion mit der Titanoberfläche verbraucht sind. Der auf Fluoridzusatz einsetzende geringe Potentialrückgang bildet die Grundlage des entwickelten Verfahrens zur potentiometrischen Kieselsäurebestimmung.

Die Elektroden-Reaktion mit Fluorid

Nach Straumanis und Ballas[6] ist eine Titanoberfläche im oxidpassiven Zustand mit einer Schutzschicht aus Oxiden und Salzen des Titans bedeckt, die in Säure nicht

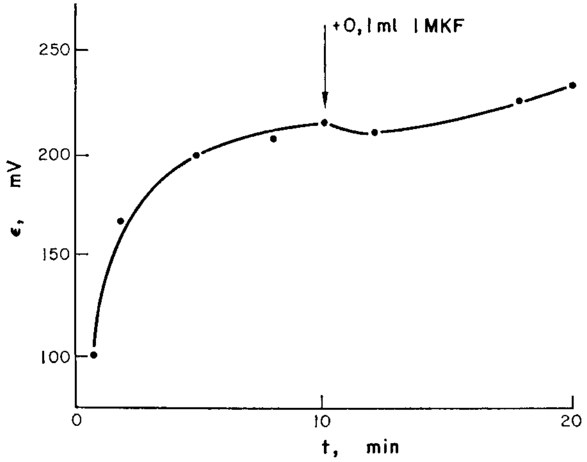

ABB. 3.—Potential-Zeit-Verhalten der Titanelektrode nach Zusatz von Fluoridionen.

oder nur schwer löslich sind. In fluoridhaltigen sauren Medien jedoch lösen sich diese Schutzschichten je nach Konzentration mehr oder weniger rasch unter Bildung von Fluorokomplexen des 3- und 4-wertigen Titans auf. Die dadurch freigelegte Metalloberfläche wird dann sowohl durch die Flußsäure wie auch durch die in der Lösung enthaltene Salzsäure angegriffen. Für den potentialbestimmenden Vorgang kann im vorliegenden Fall angenommen werden:

$$\mathrm{Ti} \rightleftharpoons \mathrm{Ti}^{3+} + 3e^{-}. \qquad (2)$$

Es war nun notwendig zu erfahren, wie die Reaktionsgeschwindigkeit der Umsetzung zwischen Fluoridionen und der Elektrodenoberfläche von der Eisen(III)-Konzentration abhängt. Hierzu wurde als Maß die Potentialänderung pro Zeiteinheit gewählt. Abbildung 4 zeigt diese Geschwindigkeit in Abhängigkeit von der Fluoridkonzentration. Sie nimmt erwartungsgemäß mit steigender Fluoridkonzentration zu und mit steigender Eisenkonzentration ab. Bei einer Eisen(III)-Konzentration von $5.10^{-4}M$ und einer Fluoridkonzentration von $10^{-3}M$ ist aus dem Diagramm eine dem Reaktionsablauf proportionale Spannungsänderung von etwa 0,1 mV/sec entnehmbar.

Der Reaktionsablauf an der Titanoberfläche ist aber auch von der Salzsäurekonzentration abhängig, wie Abb. 5 zeigt. Bei konstanter Eisen(III)-Ionenkonzentration nimmt die Empfindlichkeit mit steigender H^{+}-Konzentration zu. Orientierende Kieselsäuretitrationen mit $1M$ Kaliumfluoridlösung haben jedoch ergeben, daß in $3M$ salzsäure der potentiometrische Kurvenverlauf am gleichmäßigsten ausgebildet ist.

Daß mit steigender Eisen(III)-Konzentration die Empfindlichkeit der Titanelektrode in $3M$ Salzsäure gegenüber Fluoridionen abnimmt, zeigt die Potential-Zeit-Kurve in Abb. 6. Hier ist bei einer Konzentration von $5.10^{-3}M$ Eisen(III)-chlorid nach Zusatz von 0,1 ml $1M$ Kaliumfluoridlösung auf 100 ml Grundlösung kein Potentialrückgang mehr feststellbar. Die Elektrodenoberfläche ist unter diesen Umständen zu stark passiviert.

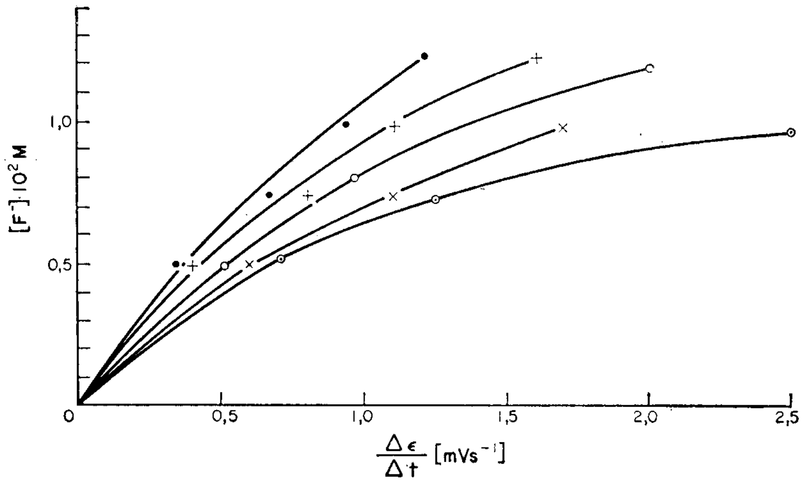

ABB. 4.—Potentialänderungsgeschwindigkeit bei verschiedenen Eisen(III)-Konzentrationen und Fluoridkonzentration. Die Kurven entsprechen nachstehenden Eisen(III)-chlorid-Konzentrationen:

● $10^{-2}M$
+ $5 \cdot 10^{-3}M$
○ $10^{-3}M$
× $5 \cdot 10^{-4}M$
⊙ $2{,}5 \cdot 10^{-4}M$

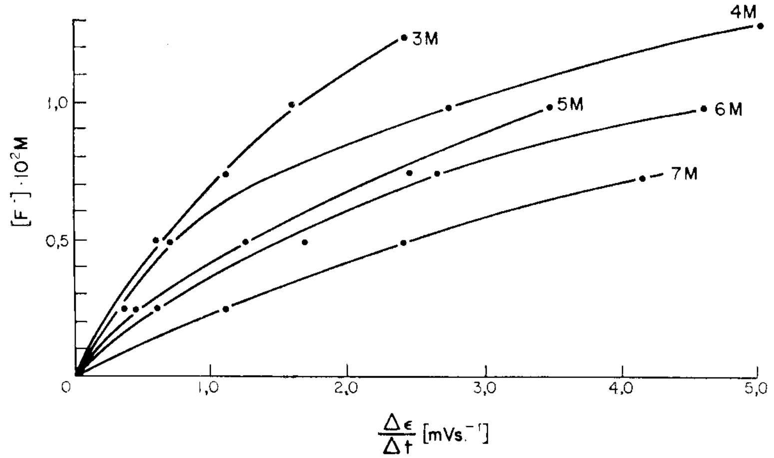

ABB. 5.—Potentialänderungsgeschwindigkeit bei verschiedenen Salzsäurekonzentrationen.

Der Blindwert

Da die Umsetzung zwischen den Fluoridionen und der Titanoberfläche zeitlich gehemmt ist (vgl. Abb. 3) und da zur komplexen Bindung der passivierend wirkenden Eisen(III)-Ionen ebenfalls Fluoridionen benötigt werden, muß angenommen werden, daß kieselsäurefreie Lösungen bei einer Titration ebenfalls Maßlösung verbrauchen, deren Größen in ml im folgenden als Blindwert bezeichnet wird. Aus dem gleichen Grund muß für die Durchführung einer Titration eine automatische Titriereinrichtung eingesetzt werden, die es ermöglicht, den Zufluß an Kaliumfluoridlösung umso langsamer zu gestalten, je mehr sich die Reaktion ihrem Endpunkt nähert. Andernfalls erfolgt eine Übertitration, da man ja im allgemeinen den Endpunkt nicht kennt.

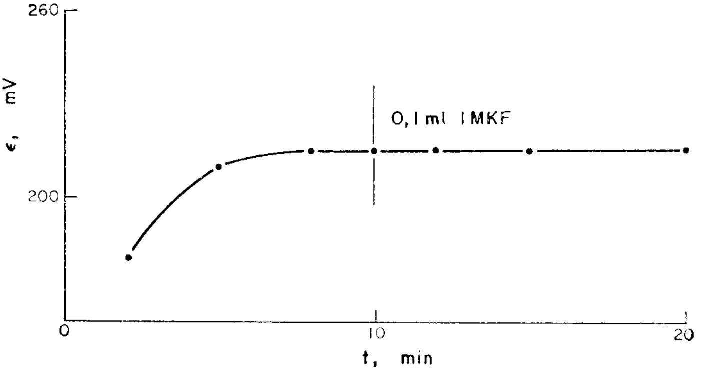

ABB. 6.—Potential-Zeit-Verhalten in der Grundlösung bei einer Eisen(III)-Konzentration von $5 \cdot 10^{-3}M$.

Für den vorliegenden Zweck ist z.B. ein Gerät der Firma Radiometer, Kopenhagen, geeignett, das sich aus der automatischen Bürette ABU 1, dem Potentialmeßgerät PHM 28, dem Steuerglied TTT 11 und dem Schreiber SBR 2 zusammensetzt. Der Schreiber registriert die Potentialänderung pro Zeit als Funktion des Kaliumfluorid-Verbrauches. Der Papiervorschub wurde entsprechend der oben erwähnten Spannungsänderung bei $10^{-3}M$ Kaliumfluorid und $5.10^{-4}M$ Eisen(III)-chlorid auf 0,1 mV/sec eingestellt. Der Zufluß an $1M$ Kaliumfluoridlösung aus der automatischen Bürette wird dann sofort gestoppt, wenn die Potentialänderungsgeschwindigkeit größer als 0,1 mV/sec geworden d.h. wenn der Umschlagspunkt erreicht ist.

Zur Ermittlung des Blindwertes wurden folgende apparative Einstellungen vorgenommen: Schreiber SBR 2 Papiervorschub 1,25 mm/min, Papiereichung −5 mV/mm; Titrator TTT 11 Downscale, Prop. Band 0,1; Autobürette ABU 1, 25 ml; Potentialmeßgerät PHM 28 Skala −200 mV bis +800 mV.

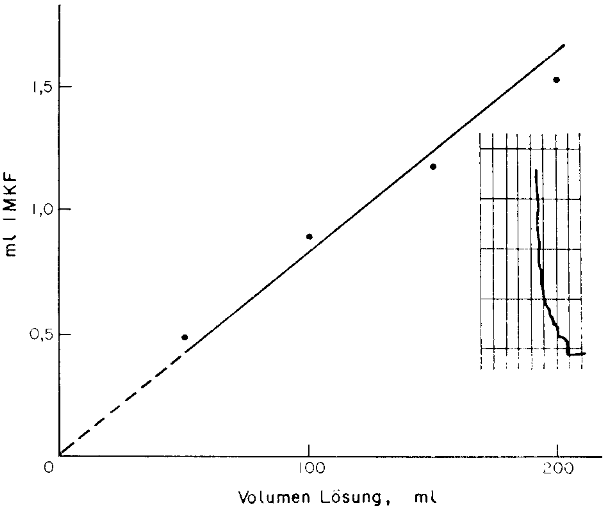

ABB. 7.—Abhängigkeit des Blindwertes vom Gesamtvolumen der Grundlösung.

Als erstes wurde die Abhängigkeit des Blindwertes vom Gesamtvolumen der Grundlösung bei 20°C ermittelt. Bei einer Eisen(III)-Konzentration von $5.10^{-4}M$ in der Grundlösung ergibt sich die in Abb. 7 dargestellte Abhängigkeit. Mit eingezeichnet ist der Kurvenverlauf bei einer Blindwertbestimmung. (Die Kurven des Schreibers SBR 2 werden von rechts nach links aufgezeichnet. Das Potential nimmt von unten nach oben ab. Im vorliegenden Fall lag das Anfangspotential gegen ges. KE bei + 210 mV. Die Titration wurde bei + 25 mV abgebrochen).

Der Blindwert ist erwartungsgemäß auch von der Eisen(III)-Konzentration, der Salzsäurekonzentration und von der Temperatur abhängig. Eine Erhöhung der Eisen(III)-Konzentration von $10^{-3}M$ auf $10^{-1}M$ läßt den Blindwert von *ca.* 1 ml $1M$ Kaliumfluorid auf *ca.* 4 ml ansteigen. Bei Steigerung der Salzsäurekonzentration von $3M$ auf $6M$ sinkt der Blindwert um *ca.* 0,5 ml ab. Ein Kelvin Temperaturerhöhung schließlich bewirkt eine Abnahme des Blindwertes von *ca.* 0,05 ml $1M$ Kaliumfluorid. Für 100 ml Grundlösung entspricht der Blindwert einer Konzentration von *ca.* $0{,}8.10^{-2}M$ an Kaliumfluorid die notwendig ist, um die Eisen(III)-Ionen komplex zu binden und das Potential endgültig aus dem oxidpassiven Bereich herauszulösen.

Die oben erwähnte Mindestkonzentration von $10^{-3}M$ Kaliumfluorid (vgl. Abb. 3) bewirkt zwar eine vorübergehende Unterbrechung des Kaliumfluorid-Zuflusses aus der automatischen Bürette; die passivierende Wirkung des Systems ist aber noch zu groß, um bei dieser Konzentration bereits eine restlose Zerstörung der Passivschicht zu ermöglichen. Somit holt nach einer gewissen Zeit das Kontrollpotentiometer am Schreiber SBR 2 dieses geringfügig in negative Richtung abgewanderte Potential wieder ein, die Titration wird fortgesetzt, wieder gestoppt, fortgesetzt usw. bis der oxidpassive Bereich schließlich durchschritten ist. Nur durch diese Automatik ist es überhaupt möglich, sich an den Endpunkt heranzutasten.

Versuchsauswertung im Hinblick auf die analytische Anwendung

Für die analytische Verwendung des Elektrodensystems Titan—ges.KE zu potentiometrischen Kieselsäurebestimmungen ergeben sich aus den bisherigen Versuchsergebnissen folgende Erkenntnisse.

1. Zur Einstellung eines positiven Potentials gegen die ges.KE in $3M$ Salzsäure, gesättigt mit Kaliumchlorid und Kaliumhexafluorosilicat, ist die Anwesenheit geringer Eisen(III)-Mengen erforderlich, vorteilhaft $5.10^{-4}M$. Bei höherer Konzentration wird die Empfindlichkeit gegen Fluoridionen zu gering; bei geringeren Gehalten ist die Potentialkonstanz nicht mehr gewährleistet und das Potential schwankt unregelmäßig.
2. Für die Einstellung eines relativ konstanten Potentials muß mit dem Titrationsbeginn nach Einsetzen des Elektrodensystems in die Lösung eine gewisse Zeit, am besten 10 min, gewartet werden.
3. Die Elektrodenoberfläche muß vor jeder neuen Messung mechanisch poliert, d.h. erneuert werden, sonst ergeben sich unreproduzierbare Potentialverhältnisse und die Ansprechempfindlichkeit auf Fluoridionen wird gestört.
4. Zweckmäßigerweise wird in salzsaurer, kaliumchloridhaltiger Lösung gearbeitet, da hier das Titan eine besonders hohe Korrosionsbeständigkeit aufweist, und außerdem Störungen durch schwerlösliche Niederschläge kaum zu erwarten sind.
5. Zur Verringerung der Löslichkeit des Kaliumhexafluorosilicats müssen die Lösungen mit Kaliumchlorid gesättigt werden. Einsatz von Kaliumchlorid ist günstiger als das Arbeiten mit organischen Lösungsmitteln, da bei letzteren notwendigerweise eine Verdünnung der zu untersuchenden Silicatlösungen eintritt. Die Kaliumhexafluorosilicat-Konzentration muß aber niedrig gehalten werden, da die Titanelektrode ebenfalls auf Fluorosilicationen anspricht.

6. Es muß für eine gute Temperaturkonstanz gesorgt werden, da eine starke Temperaturabhängigkeit der Löslichkeit des Kaliumhexafluorosilicats in der Grundlösung besteht.
7. Obwohl bei höheren Salzsäurekonzentrationen die Empfindlichkeit gegen Fluoridionen zunimmt, empfiehlt sich ein Arbeiten in 3*M* Salzsäure, denn höhere Salzsäuregehalte bewirken wiederum stärkere Verdünnung der Silicatlösungen, deren Ausgangskonzentration durch den alkalischen Aufschluß begrenzt ist.
8. Da die Titanelektrode nicht augenblicklich auf Fluoridionen anspricht, muß gegen Ende der Titration außerordentlich langsam titriert werden, wozu bei unbekannter Lage des Endpunktes, d.h. bei unbekanntem Kieselsäuregehalt, eine Titrierautomatik notwendig wird.
9. Die Zeitabhängigkeit der Umsetzung zwischen Fluoridionen und der Titanoberfläche bedingt einen Blindverbrauch an Fluoridmaßlösung, der bei Titrationen kieselsäurehaltiger Lösungen zu berücksichtigen ist.

Auf die Anwendung dieser Ergebnisse zur potentiometrischen Kieselsäurebestimmung wird im zweiten Teil der Arbeit eingegangen.

Die Verfasser danken Herrn Prof. Dr. habil. W. Forker, Direktor des Instituts für Chemie an der Technischen Hochschule Karl-Marx-Stadt, für seine nützlichen Ratschläge.

Summary—The response of a titanium electrode to fluoride in the presence of fluosilicate has been investigated. In 3*M* hydrochloric acid containing a small amount of iron(III) the electrode can be used to follow potentiometrically the titration of silicate with fluoride. As the reactions and response are rather slow, an automatic potentiometric titrator must be used.

Résumé—On a étudié la réponse d'une électrode de titane au fluorure en la présence de fluosilicate. En acide chlorhydrique 3*M* contenant une petite quantité de fer(III), on peut utiliser l'électrode pour suivre potentiométriquement le titrage du silicate avec le fluorure. Comme les réactions et la réponse sont assez lentes, il faut utiliser un appareil de titrage potentiométrique automatique.

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POTENTIOMETRISCHE KIESELSÄUREBESTIMMUNG UNTER VERWENDUNG EINER TITANELEKTRODE—II

DAS BESTIMMUNGSVERFAHREN

GERHARD ACKERMANN
Lehrstuhl für analytische Chemie, Sektion Chemie, Bergakademie Freiberg,
92 Freiberg (Sachsen), D.D.R.
und
JOACHIM LANGE
VEB Spezialglaswerk Einheit, 758 Weißwasser, D.D.R.

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Zusammenfassung—Die Bedingungen für die automatische potentiometrische Titration von Kieselsäure mit 1*M* Kaliumfluorid unter Verwendung einer Titanelektrode werden beschrieben. Die Wirkung einer Temperatureänderung und anderer Faktoren wird diskutiert. Die Standardabweichung für die Bestimmung von Proben bis zu 240 mg beträgt 1 mg Aluminium, Eisen, Borat, Nitrat, Sulfat und Phosphat stören dabei.

IM ERSTEN TEIL dieser Arbeit[2] wurde das Verhalten einer Titanelektrode in salzsaurer Lösung gegenüber Fluoridionen bei gleichzeitiger Anwesenheit von Hexafluorosilicat-Ionen im Hinblick auf ihre Verwendung zur Indikation der Umsetzung von Silicat- und Fluoridionen nach

$$SiO_3^{2-} + 6F^+ + 6H^+ \rightleftharpoons [SiF_6]^{2-} + 3H_2O$$

untersucht. Über ihre Eignung bei der potentiometrischen Kieselsäurebestimmung soll nachstehend berichtet werden.

Titrationen von reinen Kieselsäurelösungen

Im Nickeltiegel werden 4 mal 1,000 g auf eine Korngröße von 0,06 mm gepulverter, mit konz. Salzsäure eine Stunde am Rückflußkühler ausgekochter, dann bei 1150° geglühter Quarzsand (SiO_2-Gehalt >99,95%, ermittelt durch Abrauchen mit Flußsäure) mit je 8 g Kaliumhydroxid aufgeschlossen. Hierbei wird zunächst das Kaliumhydroxid allein im Tiegel eingeschmolzen, dann erst die Sandeinwaage auf die erkaltete Schmelze gegeben und erneut aufgeschmolzen. Die vier wiederum erkalteten Schmelzen werden nach Lösen in heißem Wasser gemeinsam in einen 500-ml Meßkolben filtriert und so von ausgeschiedenem Nickelhydroxid befreit. Nach Abkühlen, Auffüllen mit dest. Wasser und Durchmischen entspricht 1 ml dieser Lösung 8,0 mg SiO_2.

Diese Kieselsäurelösung dient als Urtiterlösung. Aliquote Teile dieser Lösung (5 bis 25 ml) werden in den Titrierbecher gegeben, mit dest. Wasser auf 50 ml aufgefüllt und mit soviel ml konz. Salzsäure versetzt, daß die Lösung nach Auffüllen auf 100 ml 3*M* an freier Salzsäure ist (unter Berücksichtigung der für die Neutralisation des Kaliumhydroxids notwendigen Salzsäuremenge je nach aliquotem Teil 24,5 bis 26 ml Salzsäure).

Dann werden aus einer Mikrobürette 0,5 ml 0,1*M* Eisen(III)-chlorid, gelöst in 1*M* Salzsäure, zugesetzt und nach Abkühlen auf Zimmertemperatur auf 100 ml ± 2 ml mit dest. Wasser aufgefüllt (Marke am Titrierbecher). Schließlich werden mit einem Eichmaß *ca.* 25 g Kaliumchlorid und *ca.* 0,5 g Kaliumhexafluorosilicat zugegeben, die Meßkette Titan–ges. Kaliumelektrode (KE) eingesetzt, Rührer und Thermostat eingeschaltet (20°) und nach 10 Minuten mit der automatischen Titration unter Verwendung einer *ca.* 1*M* Kaliumfluoridlösung entsprechend den Ausführungen im ersten Teil dieser Arbeit begonnen.

Die Verwendung einer genau 1*M* Kaliumfluoridlösung, deren Einstellung analytisch sehr aufwendig wird, ist nicht erforderlich, wenn die Lösung gegen bekannte Kieselsäuremengen faktorisiert wird. Wie bei der Titration von kieselsäurefreien Lösungen, d.h. bei der Ermittlung des Blindwertes, tastet sich der Titrator an den

Endpunkt der Reaktion heran und schaltet den Zufluß an Fluoridlösung vorübergehend ab, wenn die Potentialänderungsgeschwindigkeit größer als 0,1 mV/sec wird.

Als Beispiel zeigt die Abb. 1 Titrationskurven von 40 bis 300 mg SiO_2 pro 100 ml Grundlösung. Die Originallänge des Papierstreifens, auf dem die Kurven aufgenommen wurden, beträgt 0,33 m, 10 mm entsprechen eine Potentialänderung von 50 mV. Die Originalbreite des Papierstreifens beträgt 0,25 m, 10 mm entsprechen 1 ml Kaliumfluoridlösung. (1 ml 1*M* Kaliumfluorid entspricht *ca.* 10 mg SiO_2). Die Anfangspotentiale liegen bei 200–250 mV, die Endpotentiale bei 50–100 mV gegen ges. KE. Hier wurde dann der Titrator ausgeschaltet. Trägt man den Verbrauch an 1*M* Kaliumfluoridlösung für verschiedene Kieselsäure-Mengen in ein Koordinatensystem ein, so erhält man eine Gerade die nicht durch den Ursprung geht, sondern die Abszisse bei 0,9 ml schneidet. Dieser Abschnitt ist identisch mit dem früher diskutierten Blindwert.

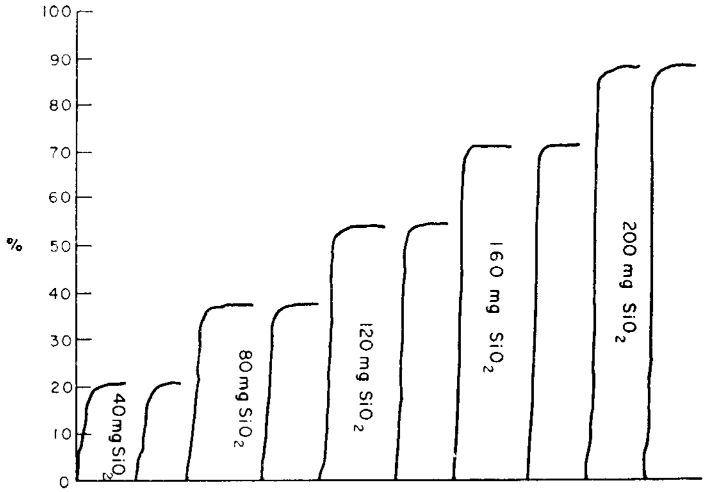

Abb. 1.—Titrationskurven verschiedener SiO_2-Mengen, aufgenommen an aliquoten Teilen homogener Kieselsäurelösungen.

Die sehr guten Ergebnisse automatischer Kieselsäurebestimmungen mit potentiometrischer Indizierung an der Titanelektrode bei Verwendung aliquoter Teile einer homogenen Aufschlußlösung lassen sich jedoch an Lösungen aus individuellen Aufschlüssen nicht bestätigen. Ursache hierfür ist das bekannte Polymerisationsbestreben der Kieselsäure in saurer Lösung, wodurch es selbst unter peinlichster Einhaltung aller experimentellen Bedingungen nicht möglich wird, exakt reproduzierbare Kieselsäuresole zu erhalten. Welche Bedeutung beispielsweise die Standzeit eines sauren Kieselsäuresols auf den Kaliumfluoridverbrauch hat, ergibt sich aus der Tatsache, daß mit zunehmender Wartezeit vor Titrationsbeginn auch der Kaliumfluoridverbrauch zunimmt (Abb. 2). Hierbei wurden jeweils aliquote Teile der oben angeführten homogenen Kieselsäure-Urtiterlösung titriert. Die relativ geringe Löslichkeit der entstehenden Kieselsäuresole begrenzt die Größe der Einwaage bei individuellen Sandproben mit max. 250 mg SiO_2/100 ml Grundlösung.

Zur Bereitung individueller Kieselsäure-Lösungen wurde nachstehender Arbeitsgang eingehalten.

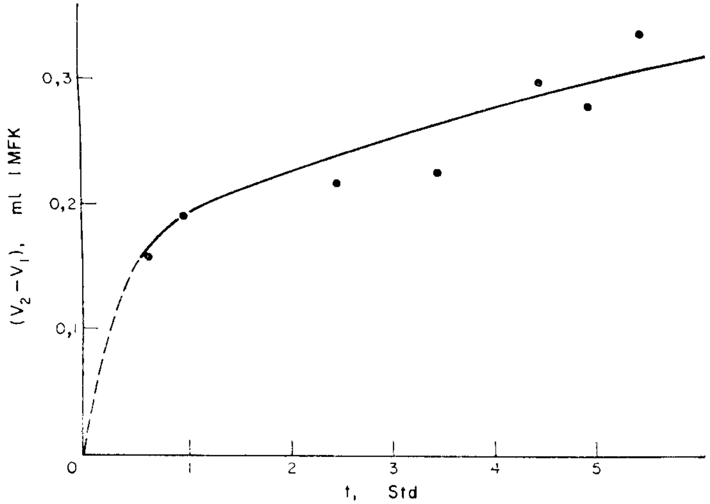

ABB. 2.—Abhängigkeit des Verbrauches an 1*M* Kaliumfluorid vom Alterungszustand des Kieselsäuresols.
V_1 = Verbrauch zur Zeit t_1
V_2 = Verbrauch zur Zeit t_2
$t_2 > t_1$.

Jeweils 0,2100 g Quarzsand (<0,06 mm) werden im Nickeltiegel mit 5 g Kaliumhydroxid—wie oben beschrieben—aufgeschlossen. Die Schmelze wird mit heißem Wasser im Tiegel selbst ausgelaugt, anschließend in den Titrierbecher gespült und mit Wasser auf 50 ml verdünnt. Nach Abkühlen auf Zimmertemperatur wird die alkalische Lösung unmittelbar vor Beginn der Titration mit 30 ml konz. Salzsäure in einem Guß unter kräftigem Rühren versetzt. Man füllt mit Wasser auf 100 ml auf, läßt 15 Minuten bedeckt im siedenden Wasserbad stehen und kühlt dann unter fließendem Wasser auf 20° ab. Schließlich werden aus einer Mikrobürette 0,5 ml 0,1*M* Eisen(III)-chlorid-Lösung, *ca.* 25 g Kaliumchlorid und *ca.* 0,5 g Kaliumhexafluorosilicat zugegeben, wonach die Lösung wie oben beschrieben titriert wird.

Experimentelle Besonderheiten, die den Kurvenverlauf bestimmen

Unter Berücksichtigung der im ersten Teil dieser Arbeit gemachten Ausführungen zum Blindverbrauch an 1*M* Kaliumfluoridlösung für kieselsäurefreie Lösungen, setzt die Präzision der in Abb. 1 gezeigten Kurven die exakte Einhaltung folgender Parameter voraus:

Sättigung der Lösung mit Kaliumhexafluorosilikat und Kaliumchlorid, Temperaturkonstanz von 20 ± 0,5°, Volumenkonstanz, Konstanz und Anpassung der Titriergeschwindigkeit an die Umsetzungsgeschwindigkeit, Konstanz der Geometrie des Zellenaufbaues und damit Konstanz der Diffusionsstromverhältnisse an der Titanoberfläche, sowie hinreichende Reproduzierbarkeit der Titanoberfläche durch mechanische Politur vor Beginn jeder Messung. Welchen Einfluß diese Parameter auf den Kurvenverlauf ausüben, darüber geben die folgenden Abbildungen Auskunft.

In Abb. 3 ist eine Titrationskurve dargestellt, bei der die Grundlösung zu Beginn der Titration wohl mit Kaliumchlorid, nicht aber mit Kaliumhexafluorosilicat gesättigt war. Offensichtlich tritt dadurch unmittelbar nach Beginn der Titration eine vorübergehende Übersättigung der Lösung, d.h. erhöhte Hexafluorosilicat-Ionenkonzentration auf, die einen zeitweiligen Potentialrückgang auslöst und die Titration solange unterbricht, bis sich die Hexafluorosilicat-Konzentration in der Grundlösung wieder stabilisiert hat. Unterbleibt die Sättigung der Lösung mit Kaliumhexafluorosilicat und Kaliumchlorid, so ergeben sich Kurven ohne ausgeprägten Potentialsprung, die nicht verwertbar sind.

Die starke Temperaturabhängigkeit des Verbrauchs an 1*M* Kaliumfluoridlösung von *ca.* 0,05 ml pro Grad Celsius ist in Abb. 4 dargestellt. Mit eingezeichnet sind 2 Kurven für je 165 mg SiO_2, aufgenommen bei verschiedenen Temperaturen. Man erkennt, daß höhere Temperaturen einen stärkeren Potentialrückgang bei gleichzeitig geringerem Kaliumfluoridverbrauch hervorrufen.

Da der Blindwert vom Gesamtvolumen der Grundlösung abhängt,[2] ist der Verbrauch von 1*M* Kaliumfluoridlösung auch bei Kieselsäuretitrationen vom Volumen der zu titrierenden Lösung

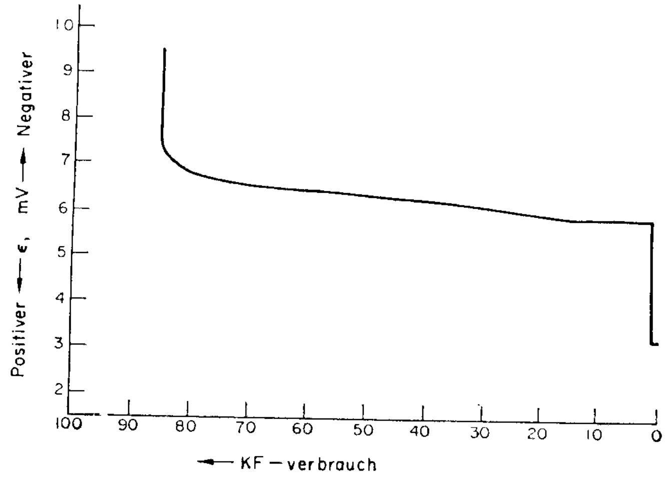

ABB. 3.—Automatisch-potentiometrische Titrationskurve von 200 mg SiO_2 aufgenommen in einer Grundlösung ohne Kaliumhexafluoro silicat.

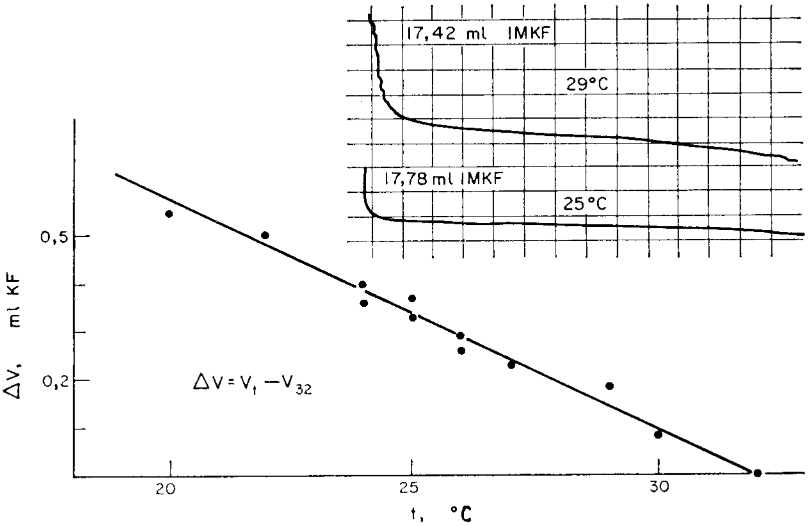

ABB. 4.—Abhängigkeit des Kaliumfluoridverbrauchs von der Temperatur.
V_t = Verbrauch an 1*M* Kaliumfluorid bei der Temperatur *t*
V_{32} = Verbrauch an 1*M* Kaliumfluorid bei 32°C.

abhängig. Eine Volumenvergrößerung von 10 ml bedingt einen Mehrverbrauch von *ca.* 0,1 ml 1*M* Kaliumfluorid.

Besondere Aufmerksamkeit muß der Geometrie des Zellenaufbaues und der Konstanz der Diffusionsstromverhältnisse gewidmet werden. So wird beispielsweise der Einfluß der Rührrichtung in Abb. 5 offensichtlich. Im vorliegenden Falle befinden sich Zulauföffnung und Elektrodenoberfläche in gleicher Höhe in der Mitte der Zelle. Während jedoch bei der oberen Kurve die zufließende Kaliumfluorid-Lösung von der Elektrodenoberfläche weggerührt wurde (Verbrauch 12,63 ml), wurde sie bei der unteren Kurve auf die Oberfläche zugerührt. Dabei wurden nur 12,40 ml für eine vorgegebene Kieselsäure-Konzentration von 110 mg SiO_2 pro 100 ml Grundlösung verbraucht, weil hier die lokale Fluoridionenkonzentration der an die Titanoberfläche anströmenden Lösungspartien zeitweilig größer ist als im ersten Fall. Die Rührgeschwindigkeit selbst ist von untergeordneter Bedeutung, sofern nur der Bodenkörper gründlich aufgewirbelt wird.

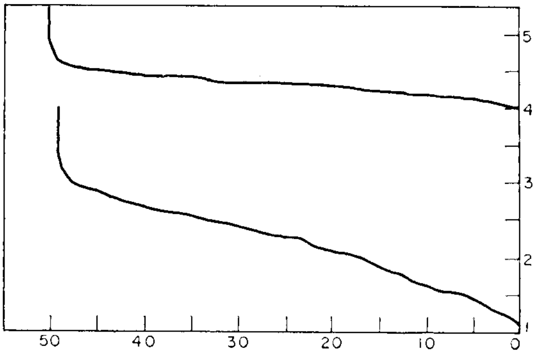

Abb. 5.—Titrationskurvenverlauf und Rührrichtung.

DISKUSSION DES TITRATIONSKURVENVERLAUFES

Neben der maßanalytische verwertbaren Umsetzung nach (1) müssen die nachstehend aufgezeigten Reaktionen für die Deutung des Titrationsverlaufes in Betracht gezogen werden.

$$SiO_3^{2-} + 6F^- + 6H^+ \longrightarrow [SiF_6]^{2-} + 3H_2O \qquad (1)$$

$$SiO_3^{2-} \xrightarrow{H^+} (SiO_2 \cdot xH_2O)_y \qquad (2)$$

$$Fe^{3+} + xF^- \longrightarrow [FeF_x]^{(3-x)} \qquad (3)$$

$$K_2[SiF_6] \longrightarrow 2K^+ + [SiF_6]^{2-} \qquad (4)$$

$$Fe^{3+} + Ti^{3+} + H_2O \longrightarrow Fe^{2+} + TiO^{2+} + 2H^+ \qquad (5)$$

$$Ti + 4OH^- + 4Fe^{3+} \longrightarrow TiO_2 + 2H_2O + 4Fe^{2+} \qquad (6)$$

$$4H^+ + TiO_2 + xF^- \longrightarrow [TiF_x]^{(4-x)} + 2H_2O \qquad (7)$$

$$Ti \longrightarrow Ti^{3+} + 3e \qquad (8)$$

$$2Ti + 6H^+ \longrightarrow 2Ti^{3+} + 3H_2 \qquad (9)$$

Da die Stabilitätskonstanten der Fluorokomplexe in der Grundlösung nicht bekannt sind, müssen die Ergebnisse empirisch erklärt werden. Im einzelnen läßt sich folgendes ableiten.

Reaktionen in der Lösung

Polymerisation der Kieselsäure unter Bildung von Kieselsäuresolen unterschiedlicher Aggregationszustände nach (2) und dadurch Verringerung der Umsetzungsgeschwindigkeit der Ionenreaktion nach (1).

Umsetzung der Fluoridionen mit dem Potentialstabilisator Eisen(III) nach (3) und dadurch Schwächung der Oxydationskraft des Stabilisators.

Temperaturabhängigkeit der Löslichkeit des Kaliumhexafluorosilicats nach (4) und dadurch Veränderung der Konzentration freier Hexafluorosilicat-Ionen bei Temperaturänderung.

Umsetzung in Lösung gegangener Titan(III)-Ionen mit dem Potential-Stabilisator nach (5) und dadurch Verringerung der Stabilisierungswirkung des dreiwertigen Eisens.

Reaktion an der Elektrodenoberfläche

Deckschichtenbildung durch Umsetzung mit Hydroxid-Ionen selbst in stark saurer Lösung[3] nach (6) und dadurch Aufbau und fortschreitende Verstärkung einer Passivschicht.

Auflösung der Schutzschicht durch Fluoridionen nach (7) und dadurch Verringerung der Passivierung.

Auflösung der freigelegten Oberfläche nach (8) als potentialbestimmender Vorgang und schließlich Umsetzung mit Protonen nach (9) und dadurch Auflösung des Titans nach Abtragung der Schutzschicht.

Hierbei verlaufen die Reaktionen nach (2), (6) und (7) nicht augenblicklich, sondern benötigen eine gewisse Zeit.

Unter Berücksichtigung dieser 9 Reaktionen kann nun der Kurvenverlauf bei einer automatisch-potentiometrischen Titration folgendermaßen gedeutet werden:

Der mit Beginn der Titration einsetzende allmähliche Potentialrückgang kommt dadurch zustande, daß wohl die Hauptmenge der Fluoridionen mit der Kieselsäure nach (1) reagiert, ein Teil aber auch nach (7) die Schutzschicht auf der Elektrode abbaut. Da die Reaktionsgeschwindigkeiten zwischen Fluorid- und Silicat-Ionen bzw. Fluoridionen und Titanoberfläche von unterschiedlicher Größenordnung sind, hängt es von den experimentellen Bedingungen, insbesondere von den Diffusionsverhältnissen ab, ob dieser erste Teil der Kurve stark geneigt ist oder flach verläuft, ob ein starker oder mäßiger Potentialrückgang erfolgt.

Maßgebend für die Steigung in diesem Kurventeil sind weiterhin die zeitabhängigen Reaktionen der Kieselsäurepolymerisation sowie der Deckschichtenaufbau durch das Redoxsystem nach (2) und (6).

Als Beweis hierfür kann die Zunahme an Fluoridionenverbrauch bei gealtertem Kieselsäuresol dienen. Die Umsetzungsgeschwindigkeit zwischen den durch Alterung wachsenden Teilchen des Kieselsäuresols und den Fluoridionen wird langsamer, während die Geschwindigkeit nach (7) nicht verändert wird. Als Ergebnis dessen steigt der Kaliumfluoridverbrauch an.

Der immer stärker werdende Potentialrückgang in der Nähe des Endpunkts erklärt sich aus der nunmehr verstärkt einsetzenden Umsetzung zwischen Fluoridionen und Eisen(III) nach (3). Dadurch wird schließlich die Oxydationskraft derart geschwächt, daß das Potential aus dem oxidpassiven Bereich herauswandert und schließlich Auflösung gem. (7), (8) und (9) erfolgt. Die Kurve verläuft dann senkrecht, der Endpunkt ist erreicht.

Mit dieser Deutung des Kurvenverlaufs verknüpft ist die Deutung des schon erwähnten Blindwertes, d.h. des Kaliumfluoridverbrauchs der in kieselsäurefreien Lösungen benötigt wird, um ein eindeutiges Abtreiben des Potentials bis zum Auflösungspotential des Titans von *ca.* —600 mV gegen ges. KE auszulösen. Infolge der zeitabhängigen Reaktion nach (7) steigt der Blindwert mit steigender Titrationsgeschwindigkeit an. Natürlich wird dieser Blindverbrauch nicht allein durch die Titrationsgeschwindigkeit und damit durch die Diffusionsgeschwindigkeit freier Fluoridionen an die Titanoberfläche bestimmt, sondern auch durch Umsetzung dieser Ionen zu Eisenfluorokomplexen nach (3).

In die Deutung des Titrationskurvenverlaufes fügt sich die Abnahme des Kaliumfluoridverbrauchs mit steigender Temperatur gut ein, wenn man annimmt, daß die durch Temperatursteigerung ausgelöste höhere Konzentration an freien Hexafluorosilicat-Ionen ebenfalls zur Auflösung der Schutzschicht beiträgt. Zweifellos spielen hierbei auch die Dissoziationsgleichgewichte der Hexafluorosilicat-Komplexe in saurer Lösung unter Abspaltung von Fluoridionen eine Rolle.

Wird die Schutzschicht jedoch durch Hexafluorosilicat-Ionen angegriffen, dann kann ein äquivalenter Fluoridanteil eingespart werden und der Verbrauch an Kaliumfluorid geht zurück. Dieser durch Temperaturerhöhung ausgelöste Effekt ist infolge der Linearität der Kurve in Abb. 4 ganz sicher nicht auf Vergrößerung der Reaktionsgeschwindigkeit zurückzuführen, da dann ein logarithmischer Kurvenverlauf erwartet werden müßte.

Unter Berücksichtigung des Blindwertes läßt sich zeigen, daß die Umsetzung gem. (1) bei reinen Kieselsäure-Lösungen stöchiometrisch verläuft, d.h. sie entspricht dem atomaren Verhältnis $Si:F = 1:6$.

KONZENTRATIONSBEREICH UND REPRODUZIERBARKEIT

Der Konzentrationsbereich des entwickelten Verfahrens wird nach oben vor allem durch die Kieselsäuresolkonzentration bestimmt, sowie apparativ durch das Volumen der automatischen Bürette von 25 ml. Ein Nachfüllen der Bürette, d.h. Titrationen mit größeren Verbrauchen als maximal 25 ml, führt apparativ bedingt zu einer Verminderung der Genauigkeit. Bei Verwendung einer 1*M* Kaliumfluoridlösung ergibt sich so eine maximale Konzentration von 240 mg SiO_2/100 ml.

Nach unten ist der Konzentrationsbereich durch die Ansprechempfindlichkeit der Titanelektrode, d.h. durch die Größe des Blindwertes begrenzt, der *ca.* 10 mg SiO_2/100 ml Grundlösung entspricht. Das Verfahren bedarf wie bereits erwähnt prinzipiell einer Eichung mit Lösungen von bekanntem Kieselsäure-Gehalt. Über die Reproduzierbarkeit des Verfahrens bei Untersuchungen aliquoter Teile einer homogenen Kieselsäurelösung und Lösungen aus individuellen Aufschlüssen sowie über die Streubereiche der Einzelmessungen gibt die nachstehende Zusammenstellung Auskunft.

Charakteristische Fehlergrößen

Wiederholstandardabweichung für den geprüften Bereich von 40–200 mg SiO_2 und für 10 aliquote Teile einer homogenen Lösung:

$$S_h = \pm 0{,}19 \text{ mg } SiO_2$$

Vergleichsstreubereich hierfür:

$$\Delta x_h = 0{,}76 \text{ mg } SiO_2$$

Wiederholstandardabweichung für 13 individuelle Aufschlüsse von je 210 mg Sand

$$S_i = \pm 1{,}1 \text{ mg } SiO_2$$

Vergleichsstreubereich hierfür:

$$\Delta x_i = 3{,}3 \text{ mg } SiO_2$$

Störungen

In der nachstehend gegebenen Zusammenstellung sind die überprüften Ionen und ihre Störeinflüsse wiedergegeben.

Unter Berücksichtigung, daß Eisen(III) nicht über das für die Potentialkonstanz notwendige Maß vorhanden sein darf, sind es wie ersichtlich neben den Anionen, Nitrat, Sulfat und Phosphat vor allem die Fluorokomplexbildner wie Aluminium und Bor, die das Verfahren erheblich stören. Sie lassen sich durch Abtrennung des Aluminium bzw. Bor nach bekannten chemischen bzw. physikalisch-chemischen Verfahren nicht beseitigen, da hierbei in jedem Fall der Polymerisationszusatand des Kieselsäuresols verändert wird. Gleichzeitig zeichnen sich damit jedoch für die gegenüber Fluoridionen empfindliche Titanelektrode prinzipielle Einsatzmöglichkeiten zur Indizierung von Fluorokomplexbildungen ab.

TABELLE I. STÖREINFLÜSSE

Kation bzw. Anion	Konzentration, *M*	Zunahme des Verbrauches an 1*M* Kf
Na^+	0,01–0,05	keine signifikante Zunahme
Ca^{2+}	0,01–0,05	
$Mg^{2}c$	0,01–0,05	
Ba^{2+}	0,01–0,05	
Zn^{2+}	0,01–0,05	
Pb^{2+}	0,001–0,01	
Ti^{4+}	0,001–0,005	
Al^{3+}	0,005–0,015	*ca.* 2,5 ml
B^{3+}	0,005–0,015	*ca.* 2,5 ml
NO_3^-	0,1–0,5	*ca.* 0,5 ml
SO_4^{2-}	0,02–0,25	*ca.* 3,5 ml
PO_4^{3-}	0,02–0,25	*ca.* 10 ml

LITERATUR

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Summary—The conditions for the automatic potentiometric titration of silica with 1*M* potassium fluoride, using a titanium electrode, are described. The effect of temperature and other factors on the blank value is reported. The standard deviation is 1 mg for samples up to 240 mg of SiO_2. Aluminium, iron, borate, nitrate, sulphate and phosphate interfere.

Résumé—On décrit les conditions pour le titrage potentiométrique automatique de la silice avec le fluorure de potassium 1*M* en utilisant une électrode de titane. On rapporte l'influence de la température et d'autres facteurs sur la valeur du témoin. L'écart type est de 1 mg pour des échantillons allant jusqu'à 240 mg de SiO_2. L'aluminium, le fer, le borate, le nitrate, le sulfate et le phosphate gênent.

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SULPHUR IN FOODSTUFFS—I
DETERMINATION AS SULPHATE

G. Beswick® and R. M. Johnson
Department of Applied Biology and Food Science, Borough Polytechnic,
Borough Road, London, S.E.1

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Summary—Sulphate formed by the oxygen-flask combustion of foodstuffs may be determined colorimetrically with barium chloranilate, titrimetrically with barium perchlorate, or turbidimetrically with barium chloride. The difficulties encountered in each method, including interferences, have been investigated. The turbidimetric procedure is recommended if high precision is not required and due account is taken of interference from phosphate, iron, calcium and magnesium; the other two methods are unsuitable for routine work.

In recent years evidence has been presented that the protein values of most human diets are limited by their sulphur-containing amino-acid content.[1,2] Frequently the sulphur content of foods (often used as an index of the sulphur-containing amino-acids) has been calculated by the application of a factor to the nitrogen content. This is obviously unsatisfactory, especially for mixed diets. In most investigations where sulphur has been determined directly,[2] a simple oxygen-flask combustion[3,4] has been followed by a turbidimetric procedure. The effect of interferences from substances likely to occur in foods has not, however, previously been thoroughly investigated.

Of the methods available for the combustion of foodstuffs before sulphur determinations the oxygen-flask method has undoubted advantages, being simple, inexpensive, quick and, with care, quantitative and reliable. One disadvantage is that the moisture content of the food must be low and many foodstuffs must be dried before combustion.

Most spectrophotometric methods for the determination of sulphate depend on the displacement of a chromogenic molecule from an insoluble complex.[5] The barium chloranilate method is the most widely investigated as it is alleged to be relatively free from interferences from small quantities of many common anions.[6–8] Strict control of pH is essential, however, and several buffers have been suggested to replace the original phthalate buffer, which is frequently incapable of maintaining the desired pH after cation-exchange removal of interfering ions.[9–12] The need to prepare the reagent in a suitable form[13] and of sufficient purity to give a low blank,[14] together with the relative insensitivity of the method when measurements are carried out in the visible region and at pH 4–6, has given rise to several comments and investigations.[14–16] The molar absorptivity of the chloranilate ion is much greater at 280–350 nm than in the visible region.[15]

Titration of sulphate usually involves precipitation with barium or lead.[5] Barium perchlorate is generally preferred to barium chloride as titrant because it gives less co-precipitation error, in accord with the Paneth-Fajans rule.[17,18] Of the many indicators proposed, Thorin has advantages,[19,20] particularly when screened with Methylene Blue.[21,22] The sensitivity has been extended by spectrophotometric detection of the end-point.[23] Many cations interfere by co-precipitation or by forming coloured complexes and must be removed by ion-exchange. It is claimed that addition of excess of potassium bromide eliminates much of this interference.[24] Phosphate is the only common anion that causes serious interference, and standardization of the amount present,[25] or prior removal with zinc oxide,[26] magnesium carbonate,[20,27] magnesium oxide,[23,28] or silver oxide[29] have been suggested.

Sulphate is commonly determined turbidimetrically after the addition of barium chloride to an acidified solution of the sulphate. Several stabilizing agents have been proposed, including gum acacia,[30] gelatin,[31] starch,[32] dextran,[33] peptone, gum-ghatti[34,35] and glycerol.[36] Many other factors influence the precipitation, *e.g.*, pH, temperature, whether the reagent is in solution or solid form, in large or small crystals.[36,37] Garrido[38] has recently suggested the use of "Tween 80" as a stabilizing agent. Several workers claim that their methods are free from interference by more common ions, *e.g.*, ammonium, sodium, potassium, calcium, aluminium, magnesium, chloride, nitrate, silicate and phosphate.[30,39,40]

EXPERIMENTAL

Apparatus

Ion-exchange column. A 15-mm bore tube packed to a depth of 100 mm with Zeo-Carb 225 (H^+-form) 100–200 mesh. The resin was obtained from the Na^+-form by washing 200 g first with four 500-ml portions of 2·5*M* hydrochloric acid and then with distilled water until the washings reached pH 6.

Centrifuge tubes, 50-ml. Graduated by means of a grade A 10-ml burette, and fitted with rubber caps.

Oxygen flask. A 500-ml iodine-flask was fitted with a B24 ground-glass stopper and a 25-mm platinum wire hook (0·6 mm thickness). A detachable platinum spiral made from 90–100 mm of the same wire was fitted with a saucer shaped base made of 0·025-mm thick platinum foil.

Materials

Barium chloranilate. Barium chloride solution (2 l., 5%) was slowly added, with stirring, to chloranilic acid solution (2 l., 0·1%). After one week the aged precipitate was separated (by centrifuge), washed with water until the washings were free from chloride, and then with ethanol (three times) and diethyl ether (once) and finally dried in a desiccator. The commercial salt was unsuitable for analytical work.

Magnesium oxide. Analytical grade reagent was washed with hot water and dried.

Screened Thorin solution. Thorin solution (1 ml, 0·2%) and Methylene Blue solution (1·5 ml, 0·0125%) were added to isopropanol (100 ml). This mixture must be freshly prepared.

Barium chloride–Tween 80 reagent. Tween 80 (20 ml, polyoxyethylene sorbitan mono-oleate, Honeywill Atlas Ltd.) was dissolved in barium chloride solution (80 ml, 10%) with steady stirring, and stored for at least 24 hr before use.

Combustion paper for oxygen flask. Of the papers tested, Whatman No. 541 had the lowest sulphur content (0·004%).

Procedures

Spectrophotometric finish. The method is based on that described by Bertolacini and Barney.[7] An aliquot of sulphate solution was diluted to 10 ml in a test-tube and shaken with about 0·3 g of ion-exchange resin. After 5 min the solution was filtered (sintered-glass Hirsch funnel, porosity 4) and the funnel and resin washed with three 2-ml portions of water. The filtrate and washings were collected in a 50-ml graduated centrifuge tube and diluted to 16 ml; phthalate buffer (4 ml, pH 4·0), absolute ethanol (20 ml) and barium chloranilate (0·1 g) were added and the mixture was stirred for about 3 min. The tube was capped and after at least 15 min, centrifuged (M.S.E. Minor Model, setting 8) for at least 15 min. The absorbance was measured against a blank prepared from distilled water, buffer solution and ethanol.

Calibration curves prepared with aliquots of 0·01*N* sulphuric acid were concave (Table I) and differed for different batches of reagent. On variation of the quantity of barium chloranilate from 0·70 to 0·29 g the absorbance for 8·0 ml of 0·01*N* sulphuric acid remained practically constant,

TABLE I.—EFFECT OF SOME ANIONS ON THE CHLORANILATE METHOD

Sulphate, *μequiv*	Anion, *μequiv*	Absorbance (40-mm cell)	Change in absorbance caused by anion, %
0	—	0·009	—
20	—	0·090	—
40	—	0·230	—
60	—	0·395	—
80	—	0·593	—
20	CO_3^{2-} 213	0·085	—
60	106	0·421	+7
80	53	0·629	+6
0	Cl^- 225	0·131	—
20	180	0·233	+160
60	90	0·603	+50
80	45	0·697	+18
0	NO_3^- 129	0·064	—
20	103	0·213	+140
60	52	0·579	+45
80	26	0·639	+7
0	PO_4^{3-} 338	0·043	—
20	270	0·238	+160
40	203	0·417	+80
60	135	0·587	+50
80	68	0·708	+20

confirming that the excess of reagent was adequate. The interference of several anions was investigated by adding measured quantities to standard sulphate solutions and following the procedure. The results (Table I) indicate interference by chloride nitrate and phosphate.

Titrimetric finish. The method was based on that described by Fritz and Yamamura.[20] A distinct end-point was obtained when aliquots of 0·01*N* sulphuric acid were diluted to 10 ml and titrated against 0·004*N* barium perchlorate after addition of isopropanol (30 ml) and screened Thorin solution (10 ml). No systematic error was found in titration of 5–100 μequiv of sulphate, and the relative mean deviation was 0·2% (12 replicates, 100 μequiv). Phosphate was found to interfere seriously (>10% positive error) when present in more than about equivalent ratio.

To remove phosphate, the sample was diluted to 10 ml, boiled gently with 0·3 ± 0·01 g (or with 0·03 ± 0·005 g) of magnesium oxide for 5 min, cooled in ice and kept at 0° for 30 min, then filtered into the ion-exchange column. The filter and column were washed with water (twice with 1 ml, once with 0·5 ml), the column being sucked dry each time. The filtrate and washings were transferred to a 100-ml conical flask with isopropanol (40 ml) and titrated with 0·004*N* barium perchlorate, with 10 ml of screened Thorin solution as indicator. Recoveries were low but could be somewhat improved by adding sodium hydroxide solution before the magnesium oxide (Table II). Tests on solution

TABLE II.—RECOVERY OF SULPHATE IN PERCHLORATE METHOD AFTER TREATMENT FOR REMOVAL OF PHOSPHATE

Sulphate, *μequiv*	NaOH, *μequiv*	Recovery, %	
		0·30 g MgO	0·03 g MgO
20	0	83	93
	100	96	100
	200	97	102
	300	—	99
80	0	83	95
	100	93	99
	200	96	99
	300	—	99
	400	97	—

Blanks for 100–400 μg of NaOH amounted to 0·3–0·4 ml of 0·004*N* $Ba(ClO_4)_2$ for 0·3 g of MgO added, and 0·1–0·2 ml for 0·03 g of MgO.

containing known amounts of phosphate showed that phosphate removal was incomplete, even with sodium hydroxide added, and that sulphate was retained by the residue, especially if ammonia was used instead of sodium hydroxide. These observations were confirmed when solutions labelled with sulphur-35 and phosphorus-32 were treated according to the procedure and the activities of the residues and filtrates were measured.

With certain phosphate: sulphate ratios, the effect of unremoved phosphate fortuitously compensated almost exactly for the loss of sulphate by retention on the magnesium oxide, but the magnesium oxide method was found to be generally unreliable.

Turbidimetric method. An aliquot of sulphate solution (2·5–25 μequiv) plus concentrated hydrochloric acid (1 ml) was diluted to about 40 ml in a 50-ml standard flask. Barium chloride–Tween 80 reagent (5 ml) was added and the mixture diluted to the mark and mixed. After 1 hr the contents were mixed again and the absorbance of the mixture measured against water in a 40-mm cell, a neutral density filter being used. A blank was prepared at the same time. There must be enough hydrochloric acid to dissolve the products of the oxygen-flask combustion, especially iron. The optimum period of standing was determined by transferring the mixture immediately to the 40-mm cell and measuring the absorbance at intervals and by testing samples kept for various times. The results showed that 60–80 min is a suitable development period.

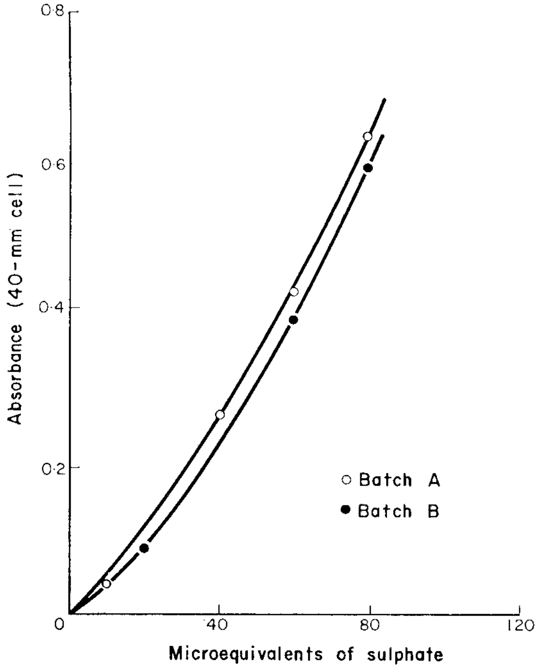

Fig. 1.—Calibration curves for turbidimetric method; different Tween 80 samples.

Calibration curves were steeper if an Ilford 601 filter was used instead of the neutral density (ND) filter, and were linear over most of their length but concave at low sulphate concentrations (Fig. 1). A new calibration curve must be made when a fresh batch of Tween is used (Fig. 1). The relative mean deviation (10 replicates) was 5·6% at the 10-mequiv sulphate level and 1·1% at the 30-mequiv level (ND filter), the values for the 601 filter being 4·6 and 1·8% respectively. Several elements present in foods give rise to ions likely to interfere. Measured quantities of aluminium, calcium, iron, magnesium, phosphate and nitrate were added to test solutions containing 10 μequiv of sulphate and tested: the results are presented in Table III.

Procedure for food analysis

If the food contains a high proportion of moisture (above 15–20%), dry it in a vacuum oven and powder it in a high-speed blender. Fit the platinum spiral to the stopper of the oxygen flask, heat it to redness and allow it to cool. Wrap the weighed sample in a Whatman No. 541 filter paper "flag"[4] and place this in the platinum spiral.

TABLE III.—INTERFERENCE BY COMMON ANIONS AND CATIONS IN THE TURBIDIMETRIC DETERMINATION OF 10 μequiv OF SULPHATE

Ions added, *μequiv*	Recovery of sulphate, %	Ions added, *μequiv*	Recovery of sulphate, %
Al 20	99	Mg 20	103
50	99	Ca 20	
Ca 20	107	Fe(III) 20	100
50	105	Ca 20	
100	93		
		Fe(III) 50	132
		PO_4^{3-} 50	
Fe(III) 10	97		
20	100		
50	103	Mg 20	
100	103	Ca 20	113
		Al 20	
Mg 20	106	Fe 20	
50	97		
		Ca 50	
PO_4^{3-} 10	88	Fe 50	
20	98	Mg 50	110
50	89	NO_3^- 50	
100	99	PO_4^{3-} 50	
NO_3^- 50	108	Ca 50	
100	102	Mg 50	101
		Fe(III) 50	
		PO_4^{3-} 50	

Mix 0·1*N* sodium hydroxide (1 ml), 100-vol hydrogen peroxide (3 drops) and water (4 ml) in the iodine-flask and carry out the combustion as usual.[4] When the flask is shaken to ensure absorption of combustion products the platinum spiral becomes detached, facilitating the dissolution of any residual ash. Leave the flask unopened for at least 15 min after combustion, then add concentrated hydrochloric acid (1 ml) and heat the flask on a boiling water-bath for 15 min with the stopper loosely inserted and 5 ml of water in the wide neck of the flask. Take the flask from the water-bath and remove the stopper so that the water in the neck washes the stopper and neck of the flask. Cool the flask to room temperature and transfer the contents to a 50-ml graduated flask, washing with water to give a volume of about 40 ml. Continue as described under turbidimetric finish. Prepare a blank at the same time and measure sample and blank against water.

RESULTS AND DISCUSSION

The calibration curves obtained for the chloranilate method were in good agreement with earlier results[6,7] and the sensitivity varied with batch of barium chloranilate as previously reported.[9] The interference of chloride and nitrate is greater than that of phosphate or carbonate. This may be a pH effect,[11] however, arising from the use of the ion-exchange resin, and a more effective buffer coupled with the use of an ammonium-form resin may improve results. Sensitivity is the main problem, but measurement at 328 nm may give some improvement.

For pure sulphate solutions, titration with barium perchlorate (screened Thorin as indicator) is satisfactory, but both anions and cations interfere. Magnesium carbonate, suggested for the removal of phosphate,[20] contained impurities that gave rise to serious interference. Magnesium oxide[23,28] could be obtained in a higher state of purity, but removal of phosphate was incomplete and sulphate ions were adsorbed.

The turbidimetric method described lacks precision (in common with other barium sulphate turbidimetric procedures[31,34,38]) and some ions commonly present

TABLE IV.—SULPHUR CONTENT OF FOODS (TURBIDIMETRIC METHOD)

Food	Moisture content, % *w/w*	Sample, *mg*	Net absorbance,	Sulphur content *mg/g*		
				As received	On dry weight (average)	Literature value
Wheat flour	11·8	51·4	0·030	1·0	1·0	1·28
		47·8	0·019	0·7		
Ground rice	13·7	56·0	0·020	0·6	0·6	0·89
		60·0	0·020	0·5		
Whole ground rye	10·9	38·0	0·020	0·9	1·1	—
		45·9	0·030	1·2		
Soya (diastatic)	6·8	50·1	0·174	4·2	4·5	4·56
		53·6	0·183	4·1		
Broad beans (Seville long pod)	9·9	44·6	0·041	1·6	1·8	1·66
		44·6	0·042	1·7		
French beans	11·4	55·3	0·120	2·7	2·9	1·6
		38·4	0·065	2·5		
Pea beans	13·5	43·6	0·055	1·8	2·2	1·87
		56·6	0·085	2·0		
Peas (Kelvedon Wonder)	11·1	68·2	0·122	2·4	2·6	2·32
		54·4	0·080	2·2		
Arachis nuts	5·21	56·0	0·092	2·4	2·1	3·95
		50·2	0·060	2·0		
Coconut (desiccated)	3·02	48·6	0·025	1·0	1·0	0·76
		48·0	0·024	1·0		
Coffee (Brazil)	5·27	50·3	0·028	1·1	1·1	1·15
		40·7	0·023	1·1		
Coffee (Jamaica)	7·29	38·2	0·028	1·4	1·4	1·15
		43·2	0·027	1·2		
Celery (stem)	0	50·2	0·110	2·9	2·9	3·0
		41·9	0·090	2·9		
Horseradish	0	48·3	0·513	7·3	7·7	8·4
		45·9	0·561	8·1		
Mustard seed (white)	7·14	42·7	0·70	12·9	13·6	13·7
		54·4	0·90	12·4		
Onion powder	6·33	37·6	0·118	4·3	4·4	7·04
		43·5	0·142	3·9		
Pepper (green, edible portion)	0	48·9	0·105	2·4	2·3	—
		44·9	0·082	2·2		
Tarragon (leaf)	11·0	44·4	0·095	2·5	2·9	—
		48·2	0·136	2·6		
Milk (National Dried)	2·63	47·8	0·086	2·7	2·7	2·37
		53·0	0·091	2·5		
Milk (skimmed, dried)	4·71	41·0	0·119	3·9	4·1	3·16
		29·4	0·074	3·9		
Egg (dried)	5·9	52·1	0·409	7·2	8·1	6·78
		37·5	0·285	8·0		
Sugar dried egg	5·93	24·8	0·095	5·5	5·7	4·5
		36·8	0·150	5·2		
Beef (cooked, A.F.D.*)	2·37	40·0	0·284	7·4	7·4	—
		53·0	0·409	7·0		
Chicken (cooked, A.F.D.*)	4·3	43·0	0·409	8·6	8·6	7·5
		57·3	0·537	7·9		
Cod (raw, A.F.D.*)	0	42·4	0·60	11·5	11·1	10·1
		46·8	0·61	10·6		
Herring (raw, A.F.D.*)	0	46·0	0·356	7·4	7·5	5·25
		46·8	0·381	7·6		

* A.F.D. = Accelerated freeze-dried.

in foods cause positive interference (Table III). Tween 80 is a suitable stabilizing agent but different batches of reagent may give different results. The neutral density filter gives a lower sensitivity than the 601 filter but a more useful working range.

Although all three methods were found satisfactory for pure organic compounds containing C, H, O and S, in the case of foodstuffs the inorganic ions remaining in solution after the oxygen-flask procedure give rise to interferences. If these interfering ions are to be removed, the chloranilate and perchlorate methods become laborious and unsuitable for routine work. If high precision is not required, however, the interference in the turbidimetric method is not generally serious and this technique may be used for routine analysis.

The agreement of the experimental results on foods with the literature values (Table IV) is satisfactory in view of the uncertain history of certain samples cited in the literature and the inherent lack of precision of the method. Some high results, *e.g.*, for dried egg, skimmed milk and herring may be due to the presence of interfering ions (phosphorus, calcium, iron and magnesium) in these foods, but the results for arachis nuts and onion powder are anomalous.

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Zussammenfassung—Durch Verbrennen von Nahrungsmitteln in Sauerstoff gebildetes Sulfat kann man kolorimetrisch mit Bariumchloranilat, titrimetrisch mit Bariumperchlorat und turbidimetrisch mit Bariumchlorid bestimmen. Die bei jedem Verfahren auftretenden Schwierigkeiten sowie die Strörungen wurden untersucht. Falls keine hohe Genauigkeit notwendig ist und die Störungen durch Phosphat, Eisen, Calcium und Magnesium angemessen berücksichtigt werden, ist das turbidimetrische Verfahren zu empfehlen; die anderen beiden sind für Routinezwecke ungeeignet.

Résumé—Le sulfate formé par la combustion d'aliments en fiole d'oxygène peut être dosé colorimétriquement au chloranilate de baryum, titrimétriquement par le perchlorate de baryum ou turbidimétriquement avec le chlorure de baryum. On a étudié les difficultés rencontrées avec chaque méthode, y compris les interférences. La technique turbidimétrique est recommandée si une haute précision n'est pas nécessaire et l'on tient compte des interférences du phosphate, du fer, du calcium et du magnésium; les deux autres méthodes ne conviennent pas au travail de routine.

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NAPHTHO[2,3-*d*]-2-SELENA-1,3-DIAZOLE AS A REAGENT FOR THE DETERMINATION OF MACRO TO SUBMICRO QUANTITIES OF PALLADIUM

HERBERT K. Y. LAU and PETER F. LOTT
Department of Chemistry, University of Missouri-Kansas City
Kansas City, Missouri 64110, U.S.A.

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Summary—Five analytical procedures, gravimetric, spectrophotometric, radiometric, fluorometric and atomic-absorption, have been developed for the determination of macro to submicro amounts of palladium. The methods are based on the reaction of $PdCl_2$ with naphtho[2,3-*d*]-2-selena-1,3-diazole. Analytical conditions such as the reaction time, concentration ranges, effect of pH and of 68 foreign ions, and solvent extraction were studied. Information relating to the structure and formula of palladium–piazselenol reaction products is included.

ONLY a few organic compounds containing selenium have been reported as forming compounds with metals, and these have been reviewed by Livingstone.[1] Recently a number of these selenium donor-type ligands[2,3] and benzo[*d*]-2-selena-1,3-diazole[4] have been investigated, and interest has been generated because of the high selectivity of these reagents for palladium. The piazselenol benzo[*d*]-2-selena-1,3-diazole was first reported as a gravimetric reagent for palladium by Ziegler and Glemser.[5] Recently, Bunting and Meloan[4] employed this reagent for a selective, simple, indirect spectrophotometric determination of palladium. The superiority of 2,3-diaminonaphthalene as a selenium reagent,[6] the high molar absorptivity ($4{\cdot}10 \times 10^3$ l. mole^{-1}. mm^{-1} at 480 nm) and the favourable fluorescence properties[7,8] led to the investigation of naphtho[2,3-*d*]-2-selena-1,3-diazole (DanSe) as a possible reagent for palladium. Furthermore, the kinetics of the reaction and the properties of DanSe have been studied.[9] By use of radioactively labelled DanSe,[8,10] a radiometric method for palladium is possible.

The present paper is a detailed study of the determination of macro and submicro amounts of palladium with DanSe in the presence of foreign ions.

EXPERIMENTAL

Reagents

A standard palladium(II) chloride solution was prepared by dissolving 1·1276 g of the reagent grade chemical in a litre of 0·01*M* hydrochloride acid and standardized by precipitation with nioxime. Other palladium solutions were prepared by dilution of this stock solution with 0·01*M* hydrochloric acid.

A standard selenium solution was prepared by dissolving 8·1680 g of selenous acid in a litre of water and standardized with 2,3-diaminonaphthalene.[6]

The procedure of Lott *et al.*[6] was used to prepare DanSe from 2,3-diaminonaphthalene and selenous acid. Ethanolic solutions of DanSe (about $10^{-3}M$) were prepared by dissolving in volumetric flasks freshly prepared moist precipitates of DanSe with 95% ethanol. More dilute solutions were prepared by dilution with 95% ethanol.

A selenium-75 solution, as selenous acid, was diluted to a specific activity of about $5{\cdot}8 \times 10^7$ cpm/ml and 0·2 ml was added to 2·4 ml of the standard selenium solution and diluted to prepare 100 ml of $1{\cdot}525 \times 10^{-3}M$ radioactive DanSe solution. More dilute solutions were prepared by dilution with 95% ethanol.

For the interference studies, reagent grade chemicals were used to make 0·01M aqueous solutions except where otherwise specified.

Analytical procedures

Preliminary experiments showed that two different precipitates were formed from the reaction of palladium(II) chloride with DanSe, depending on the molar ratio of palladium to DanSe. With DanSe in excess, a purple precipitate is formed. This reaction takes place in acidic solution and is relatively pH independent over the pH range 1–6 (Fig. 1). The reaction is rapid and highly insensitive to the interference of foreign metal ions. Furthermore, the purple precipitate is stable and insoluble in organic solvents such as ethanol, acetone and diethyl ether. However when palladium is in excess, the purple precipitate that is first formed is gradually converted into a green precipitate.

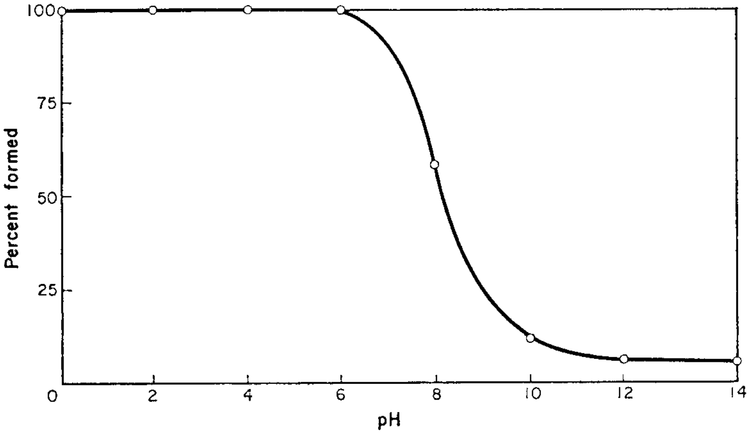


FIG. 1.—Effect of pH on the formation of the purple $Pd(DanSe)_2Cl_2$ complex.

Gravimetric procedure. To 20–80 ml of solution 1M in hydrochloric acid and containing from 5 to 20 mg of palladium, 100–400 ml of $2 \times 10^{-3}M$ DanSe are added. After stirring, the reaction mixture is allowed to stand at room temperature for 30 min and then filtered (medium-porosity sintered-glass crucible). The purple precipitate is washed first with 50 ml of acetone, then with 50 ml of water and finally with 30 ml of acetone. The precipitate is dried for 1 hr at 110°. The gravimetric factor for palladium is 0·1653.

Spectrophotometric procedure. A 4-ml aliquot containing up to 5 ppm of palladium and 0·1M in hydrochloric acid is added to 4 ml of $1{\cdot}525 \times 10^{-4}M$ ethanolic DanSe solution in a 15-ml centrifuge tube. After thorough mixing, the mixture is allowed to stand at room temperature for 30 min. Then the mixture is centrifuged at high speed for 3 min, and the supernatant liquid decanted into a 10-mm quartz cell and the absorbance measured at 380 nm against a reagent blank. The decrease in the absorbance is a measure of the palladium concentration in the sample. To avoid instrumental errors associated with high absorbance measurements, the supernatant liquid can be diluted before the absorbance measurements. Linear calibration curves are obtained over the range up to 5 ppm of palladium.

Radiometric procedure. A radioactive piazselenol solution is added to the palladium sample. The experimental conditions are similar to those for the spectrophotometric procedure, except that stock $1{\cdot}525 \times 10^{-4}M$ radioactive ethanolic DanSe solution is used. After the 3-min centrifugation, 2 ml of the supernatant liquid are accurately transferred into a 5-ml calibrated plastic tube and counted for 3 min. The decrease in the radioactivity, relative to a reagent blank, is a measure of the palladium concentration and a linear calibration curve up to 5 ppm of palladium is obtained.

Atomic-absorption procedure. About 30 ml of sample solution containing approximately 0·2 ppm of palladium and adjusted to pH 2·5 are introduced into a 60-ml separatory funnel. To this solution are added 5 ml of approximately $2 \times 10^{-4}M$ ethanolic DanSe solution (a minimum 5-fold stoichiometric excess). The reaction mixture is briefly shaken, then allowed to stand for 30 min. Exactly 5 ml of n-butyl acetate are added and the palladium–DanSe reaction product is extracted by shaking for 3 min. To remove droplets of water, the organic layer is filtered into the cuvette through a cotton plug in the stem of the separatory funnel. The organic layer is aspirated directly into the burner of the instrument and the absorption measured at 244·8 nm. The calibration curve is linear over the range 0–0·33 ppm of palladium.

Fluorometric procedure. Two procedures were developed, one suitable for 0–5 ppm of palladium and the other for 0–1 ppm. For the former the experimental conditions are similar to the spectrophotometric procedure except that the palladium solution is adjusted to pH 3·5–4·5 before addition of the DanSe solution. After centrifugation, the fluorescence intensity of the supernatant solution is measured. A linear calibration curve is obtained. For the concentration range 0–1 ppm, exactly 4 ml of $1{\cdot}15 \times 10^{-5}M$ ethanolic DanSe are added to a 4-ml palladium sample. After stirring, the mixture is allowed to stand for 20 min before the solution is transferred to the fluorometer cuvette. The fluorescence intensity is measured at an excitation wavelength of 375 nm and a fluorescence wavelength of 520 nm. The decrease in the fluorescence intensity relative to a reagent blank is a measure of the palladium content. A non-linear calibration curve is obtained (Fig. 2) in this range, probably because of dissociation of $Pd(DanSe)_2Cl_2$ at low concentrations.

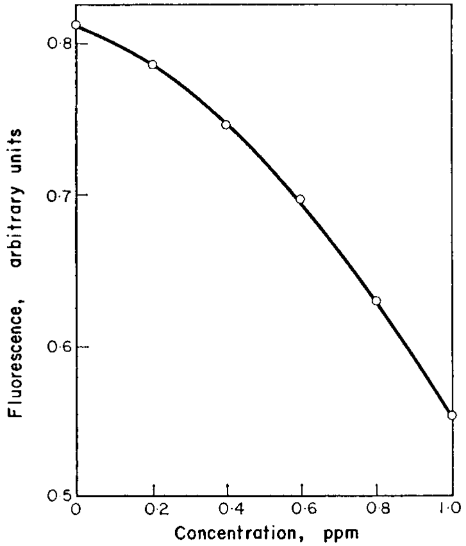


FIG. 2.—A standard curve for the fluorometric determination of Pd(II) with DanSe.

RESULTS

Reaction of DanSe *and palladium*

The reaction of ethanolic DanSe with palladium(II) in acidic solution is greatly influenced by the anion of the palladium salt as well as the palladium(II) concentration. In a strongly acidic hydrochloric acid solution, with excess of DanSe, a stable purple precipitate is formed quantitatively, but on addition of excess of palladium(II) chloride to this reaction mixture, the purple precipitate is gradually converted into a stable green precipitate. Analysis of the purple precipitate confirms the formula $Pd(C_{10}H_6N_2Se)_2Cl_2$: calculated—C 37·33%, H 1·87%, N 8·71% Cl 11·02%, Pd 16·53%; found—C 37·1%, H 1·9%, N 5·4%, Cl 11·5%, Pd 16·5%.

The green complex is also formed quantitatively in acid medium when palladium(II) is in excess. The ratio of Pd(II) to DanSe in the green complex was studied by atomic-absorption spectrophotometry. A Yoe-Jones plot suggested a molar ratio of 1:1 in the green precipitate; elemental analysis, though not giving conclusive results, tended to confirm this.

The anion of the palladium(II) salt enters into formation of the palladium–DanSe precipitate. In a study of nineteen common anions with palladium(II) nitrate and ethanolic DanSe solution at pH 0 and 4, only bromide, chloride, and to a small extent fluoride, precipitated Pd-DanSe (Table I). These precipitates were purple. A yellowish-white precipitate formed with thiosulphate.

TABLE I.—EFFECT OF ANIONS ON THE PRECIPITATION OF PALLADIUM WITH DanSe

Anion	Reaction*	
	pH 0	pH 4
NO_3^-	†	†
$H_2PO_4^-$	†	†
CNS^-	†	†
$S_2O_3^{2-}$	trace white ppte	trace yellow ppte
HPO_4^{2-}	†	†
NO_2^-	†	†
Citrate	†	†
SO_3^{2-}	†	†
$C_2O_4^{2-}$	†	†
Tartrate	†	†
CN^-	†	†
HCO_3^-	†	†
Acetate	†	†
ClO_3^-	†	†
SO_4^{2-}	†	†
F^-	purple ppte	purple ppte
Cl^-	purple ppte	purple ppte
Br^-	purple ppte	purple ppte
I^-	red soln	red soln

* 4·0 ml of $7·6 \times 10^{-4}M$ ethanolic DanSe and 2 ml of $0·01M$ anion and 0·5 ml of $3·09 \times 10^{-3}M$ $Pd(NO_3)_2$ in HNO_3. pH values were adjusted with HNO_3 or NaOH.

† No observable change or a trace amount of black, brown or purple precipitate observed after a day.

Properties of DanSe *and* $Pd(DanSe)_2Cl_2$

Dried DanSe is hard to dissolve in ethanol but DanSe will readily dissolve while still damp immediately after preparation and purification. Concentrated ethanolic DanSe solutions are unstable, because of a tendency toward polymerization;[6,7] however, a $1·5 \times 10^{-3}M$ DanSe stock solution could be stored for 2 days at room temperature without effect on the determination of palladium. A $1·5 \times 10^{-4}M$ solution was stable for at least one month. Though strong light slowly causes the polymerization or decomposition of ethanolic DanSe solutions, the only precaution taken was to store the stock DanSe solution in darkness. All work was performed in daylight, without deaeration of solutions or purifying of reagents.

Although microgram quantities of palladium could be extracted by butyl acetate and 2-heptanone for the atomic-absorption measurement, no organic solvent was found that would dissolve large quantities of the purple complex. Ziegler and Glemser[4] also observed the insolubility of Pd–piazselenol precipitates in common solvents. From the atomic-absorption measurements, the solubility of both the purple and green precipitates in ethanol-water mixture is estimated to be below $5 \times 10^{-7}M$. Both precipitates are stable to air-drying at 110° and will not decompose below 300°. Both complexes give rise to almost identical infrared spectra (4000–200 cm^{-1}) that are different from the infrared spectrum of DanSe.

Spectral characteristics

Although the absorbance and fluorescence spectra of DanSe have been reported,[6,8] spectra of DanSe in ethanolic solution at various pH values have not. The absorbance spectrum of the ethanol–water solution of DanSe at 380 nm was pH-independent from pH 0 to 12. The fluorescence at 520 nm was, however, sharply quenched by hydrogen ions below pH 3, but remained constant from pH 3 to 12.

Optimum conditions for atomic-absorption spectrophotometry

The optimum acetylene-air ratio and burner position were investigated and it was found that a fuel flow-rate of 3 l./min and air flow-rate of 21 l./min with a burner height setting at 45 mm below the incident beam gave optimum results. Other optimum instrumental settings were a gain of 5, slitwidth 0·3 mm and meter response 2 or 5 (setting numbers refer to the Perkin–Elmer model 303 used for these experiments).

Effect of pH and time

The formation of the purple Pd–DanSe precipitate is pH-dependent (Fig. 1). The effect of pH on the extraction of the palladium complex with *n*-butylacetate is shown in Fig. 3. As indicated, the palladium complex is best extracted between pH 2 and 3.

To study the time required for the completion of the reaction, solutions of DanSe and palladium(II) chloride were mixed in centrifuge tubes and allowed to stand for various times before centrifugation for 3 min. The supernatant liquid was decanted into a quartz cell for measurement at 380 nm. The reaction was found to reach completion in 6 min. However, in all analytical procedures, a 20–30 min reaction time was allowed.

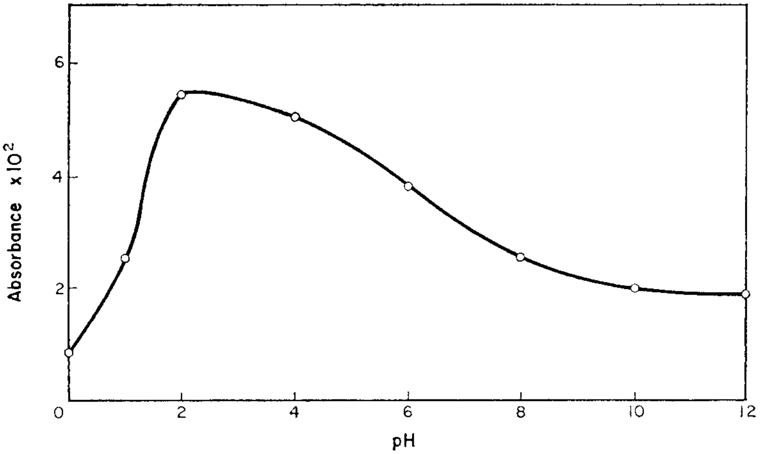


FIG. 3.—Effect of pH on the extraction of palladium with n-butylacetate.

Interference studies

DanSe is highly selective for palladium(II) chloride. Of fifty metal ions studied in 1*M* hydrochloric acid, only palladium complexed with ethanolic DanSe to give a stable purple precipitate. Cerium(IV) gave a white decomposed product; silver gave silver chloride. Bunting and Meloan[5] observed that mercury(II), titanium(IV) and cadmium interfered in the indirect spectrophotometric determination of palladium with benzo[*d*]-2-selena-1,3-diazole; no such interference was observed with DanSe under our reaction conditions. The primary interferences which prevented the precipitation of Pd(DanSe)$_2$Cl$_2$ were from anions such as iodide, cyanide, thiocyanate and thiosulphate that form stable palladium complexes, and the ions cerium(IV), gold(III) and nitrite which destroy DanSe. The additional interference noted in the spectrophotometric procedure is due to the natural colour of the diverse ions, since they are present at more than a 65-fold molar excess. In the fluorometric procedure, antimony(III), thorium, tin(IV), iron(III), bismuth and beryllium interfered owing to hydrolysis, because of the necessity of using a pH above 3·5. In the presence of arsenic(III) and osmium(VIII), lower results for palladium were observed in the spectrophotometric, fluorometric and radiometric procedures but not in the gravimetric and atomic-absorption procedures. The interference of zirconium in the atomic-absorption procedure was probably due to the formation of an emulsion at the interface of the organic layer. Emulsions did not form with the other ions. The effect of foreign cations and anions is summarized in Table II.

TABLE II.—FOREIGN ION EFFECT

Ion	DanSe*	Pd				
		Gravimetric†	Spectro-photometric§ *Absorbance*	Radio-metric‡ *cpm*	Fluoro-metric¶ *Arbitrary units*	Atomic absorption‖ *% Absorption*
Pd(II)	purple ppte	purple ppte	0·36	982	0·61	29·1
Blank	**	—	0·73	1597	1·13	1·4
Ag(I)	white ppte	white ppte	††	††	††	††
Al(III)	**	‡‡	0·33	828	0·59	30·8
As(III)	**	‡‡	0·61	1477	1·06	27·6
Au(III)	**	§§	0·80	937	0·0	12·6
Ba(II)	**	‡‡	0·33	891	0·57	29·1
Bi(III)	**	‡‡	0·47	980	††	29·0
Be(II)	**	‡‡	0·36	925	††	27·8
Ca(II)	**	‡‡	0·33	861	0·66	27·2
Ce(IV)	white ppte	white ppte	††	††	††	††
Cd(II)	**	‡‡	0·47	891	0·49	27·0
Co(II)	**	‡‡	0·44	891	0·56	29·1
Cr(III)	**	‡‡	0·44	891	0·49	29·1
Cu(II)	**	‡‡	0·44	982	0·53	27·0
Dy(III)	**	‡‡	0·37	1150	0·58	29·1
Eu(III)	**	‡‡				
Fe(III)	**	‡‡	1·90	916	0·0	28·2
Ga(III)	**	‡‡	0·33	982	0·59	29·0
Hg(II)	**	‡‡	0·32	842	0·47	29·1
In(III)	**	‡‡	0·31	927	0·68	27·7
Ir(III)	**	‡‡	0·44	905	0·49	23·2
K(I)	**	‡‡	0·36	980	0·62	29·1
La(III)	**	‡‡	0·36	1016	0·49	23·0
Lu(III)	**	‡‡	0·48	1074	0·49	30·8
Mg(II)	**	‡‡	0·31	861	0·66	27·2
Mn(II)	**	‡‡	0·31	882	0·56	26·2
Mo(VI)	**	‡‡	0·31	882	0·61	26·2
Na(I)	**	‡‡	0·36	982	0·61	29·1
Ni(II)	**	‡‡	0·36	1012	0·56	28·4
Nd(III)	**	‡‡				
Os(VIII)	**	§§	0·47	1513	1·10	29·3
Pt(IV)	**	§§	0·58	1090	0·0	23·8

TABLE II (*Continued*)

Ion	DanSe*	Pd				
		Gravimetric†	Spectro-photometric§ *Absorbance*	Radio-metric‡ *cpm*	Fluoro-metric¶ *Arbitrary units*	Atomic absorption‖ *% Absorption*
Pb(II)	**	‡‡	0·31	904	0·59	31·8
Rh(III)	**	‡‡	0·44	951	0·0	23·2
Ru(III)	**	‡‡	0·72	830	0·40	31·6
Rb(I)	**	‡‡	0·36	982	0·61	29·1
Re(IV)	**	‡‡	0·35	951	0·64	29·1
Sm(III)	**	‡‡				
Sn(IV)	**	‡‡	0·36	904	0·66††	27·0
Sr(II)	**	‡‡	0·35	861	0·66	27·2
Se(IV)	**	‡‡	0·36	828	0·61	29·1
Sb(III)	**	‡‡	0·47††	1227††	††	23·0††
Tb(III)	**	‡‡	0·32	885	0·68	29·0
Ti(IV)	**	‡‡	0·19	861	0·73	22·9
Th(IV)	**	‡‡	0·31	1016	††	28·6
Te(IV)	**	‡‡	0·32	828	0·57	27·7
UO_2(II)	**	‡‡	0·40	1074	0·55	36·2
V(V)	**	‡‡	0·43	894	0·11	36·2
Zr(IV)	**	‡‡	0·31	882	0·68	9·6
Zn(II)	**	‡‡	0·35	891	0·68	27·0
NO_3^-	**	‡‡	0·35	1005	0·71	29·1
$H_2PO_4^-$	**	‡‡	0·35	1005	0·71	29·1
CNS^-	**	no ppte	0·72	1560	1·08	2·3
$S_2O_3^{2-}$	less orange	white ppte	0·73	1562	1·03	6·2
HPO_4^{2-}	**	‡‡	0·37	1005	0·78	29·1
NO_2^-	**	§§	0·51	1375	1·08	22·3
Citrate	**	‡‡	0·37	1005	0·64	29·1
SO_3^{2-}	**	‡‡	0·36	983	0·63	26·2
$C_2O_4^{2-}$	**	‡‡	0·42	1144	0·93	27·2
Tartrate	**	‡‡	0·37	980	0·67	26·2
CN^-	**	no ppte	0·73	1560	1·08	0·0
HCO_3^-	**	‡‡	0·34	980	0·59	26·7
Acetate	**	‡‡	0·34	980	0·63	26·7
ClO_3^-	**	‡‡	0·32	1206	0·60	27·2
SO_4^{2-}	**	‡‡	0·34	980	0·61	27·7
F^-	**	‡‡	0·34	885	0·64	27·5
Cl^-	**	‡‡	0·35	980	0·61	29·0
Br^-	**	‡‡	0·32	845	0·69	27·2
I^-	red soln	red soln	0·73	1580	0·98	7·2

* 2 ml of 2·5 × $10^{-3}M$ ethanolic DanSe + 4 ml of 1*M* HCl + 1 ml of 0·01*M* diverse ion.

† Same as * except 0·2 ml of stock 6·17 × $10^{-3}M$ $PdCl_2$ was added.

§ 4 ml of 1·3 × $10^{-4}M$ ethanolic DanSe + 2 ml of 0·01*M* diverse ion and 4 ml of 8 ppm $PdCl_2$, both in 0·1*M* HCl.

‡ 4 ml of 2·5 × $10^{-4}M$ radioactive ethanolic DanSe + 2 ml of 0·01*M* diverse ion and 4 ml of 10 ppm $PdCl_2$, both in 0·1*M* HCl.

¶ 3 ml of 1·3 × $10^{-4}M$ ethanolic DanSe + 2 ml of 0·01*M* diverse ion and 4 ml of 2 ppm $PdCl_2$, both at pH 4.

‖ 5 ml of 4 × $10^{-4}M$ ethanolic DanSe + 20 ml of 2 ppm $PdCl_2$ in 0·1*M* HCl + 2 ml of 0·01*M* diverse ion; extracted with 5 ml of butyl acetate.

** No observable change.

†† Hydrolysis.

§§ Less purple ppte was formed or slower reaction.

‡‡ Purple ppte of Pd–DanSe.

Analysis of samples

A series of twelve solutions was prepared that contained equal volumes of 0·01*M* solutions of four diverse ions taken as the sulphate, chloride or nitrate salts; foreign anions were added as their potassium or sodium salts. Each solution was adjusted to the appropriate pH with concentrated hydrochloric acid or sodium hydroxide. A known amount of palladium(II) chloride was added, and then the sample was analysed for palladium by all five methods. The results are presented in Table III.

TABLE III.—PALLADIUM DETERMINATION BY DIFFERENT METHODS

	Palladium added				
	6·70 *mg*	2·00 *ppm*	3·00 *ppm*	0·60 *ppm*	0·167 *ppm*
	Palladium found				
Solution number	Gravimetric*	Spectro-photometric†	Radiometric§	Fluorometric‡	Atomic absorption¶
1	6·70 *mg*	1·80 *ppm*	3·02 *ppm*	0·56 *ppm*	0·164 *ppm*
2		2·04	3·27	0·53	0·155
3	6·65	2·02	3·00	0·53	0·165
4		**	3·25	**	0·163
5	6·70	**	3·25	**	0·168
6		2·02	2·75	0·56	0·168
7	6·74	2·01	3·20	0·62	0·169
8		1·80	2·93	0·60	0·162
9	6·61	1·90	2·70	0·53	0·171
10		2·15	2·77	0·53	0·166
11		2·20	2·81	0·55	0·161
12	6·71	2·01	2·83	0·56	0·159

Solution number	Foreign ions			
1	Mn(II)	Ca	Sr	Na
2	K	La	Th	Sn(IV)
3	Sn(II)	UO_2(II)	Cu(II)	Ga
4	Fe(III)	Ni	Al	Lu
5	V(V)	Dy	K	Ba
6	Mg	Co(II)	Hg(II)	Li
7	Cd	Rh(III)	Ir(III)	Cr(III)
8	Mo(VI)	Re(IV)	Ti(IV)	As(III)
9	NO_3^-	HPO_4^{2-}	Citrate	Na
10	Tartrate	HCO_3^-	Acetate	SO_4^{2-}
11	$C_2O_4^{2-}$	ClO_3^-	Br^-	Cl^-
12	Sr	In(III)	Te(IV)	Be

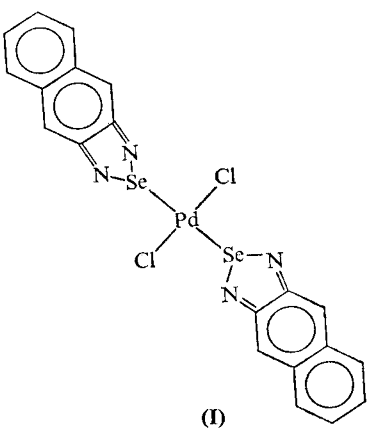
Each solution contains equal volumes of the four foreign ions initially at 0·01*M*.

* 10·00 ml of 6·2920 × $10^{-3}M$ $PdCl_2$ and 5 ml of stock foreign ion solution, both in 1*M* HCl.
† 1 ml of stock foreign ion solution added to a total of 4·00 ml of 2·00 ppm in $PdCl_2$ in 0·1*M* HCl.
§ 1 ml of stock foreign ion solution added to a total of 4·00 ml of 3·00 ppm of $PdCl_2$ in 0·1*M* HCl.
‡ 1 ml of stock foreign ion solution added to a total of 4·00 ml of 0·60 ppm of PdC_{62} at pH 3·5.
¶ 30·00 ml of 0·167 ppm $PdCl_2$ and 1 ml of stock foreign ion solution, both at pH 2·5.
** Interference caused by natural colour of foreign ion, or quenching or hydrolysis.

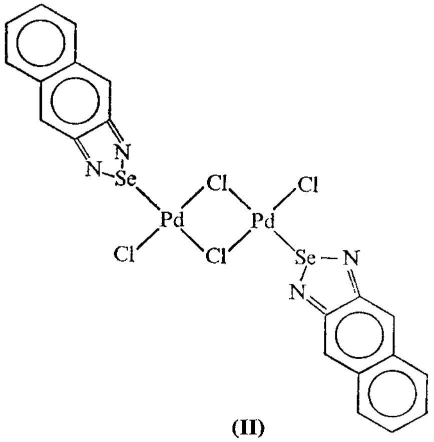
DISCUSSION

Palladium(II) complexes with a d^8 electronic configuration commonly have square planar configurations and Pd–Se metal-to-metal bonding has long been recognized to exist in compounds such as PdSe, $PdSe_2$, Pd_4Se_5 and Pd_4Se.[11] As a general rule, palladium(II) compounds have great affinity for nitrogen (amines and nitro compounds), halogens, cyanide and heavy atoms such as phosphorus, arsenic, sulphur and selenium. Cotton[12] explained that the strong bonding of heavy atoms is due to the formation of π-bonds formed by the overlap of the filled d_{xz}, d_{xy} and d_{yz} orbitals of palladium with empty d_π orbitals in the valence shells of the heavy atoms. Also, the delocalization of the metal electron density by π-bond formation between palladium and selenium atoms was reported by Bark and Brandon[2] as a major factor in determining the stability of their $PdCl_2$-2-(2-pyridyl)benzo[*b*]selenophene chelated complex. Further evidence for this π-bonding and hence the Pd–Se bonding is obtained by considering the inertness of the chlorine atoms in the two complexes towards boiling silver nitrate solution. Delocalization of the electron density cloud around the palladium atom should increase the polarity of the palladium–chlorine bond, and therefore its strength.[2] Regarding the structure of the green complex, palladium(II) chloride is known to react with ligands, *L*, such as amines, phosphines and sulphides to give complexes of the type $[LPdCl_2]_2$ and such complexes have bridging chlorine atoms.[13,14]

Because the *cis*-configuration is generally less symmetrical than the *trans*-configuration, and because both complexes give rise to almost identical infrared spectra, the two complexes are therefore expected to have either both *cis*- or both *trans*-configurations. Ignoring the question of *cis*- and *trans*-configuration, the structure of the two complexes, $Pd(DanSe)_2Cl_2$ **(I)** and $Pd_2(DanSe)_2Cl_4$ **(II)**, is believed to be:



(I)



(II)

The reagent DanSe had been shown to be extremely selective for palladium in moderately concentrated hydrochloric acid solution. Out of 50 metal ions studied, only palladium appeared to complex with DanSe, as judged by the colour change and precipitate formation. Because of the very high selectivity of DanSe for palladium and the fact that two different coloured precipitates are formed in sequence, DanSe may be a very superior reagent for the spot-test identification of palladium. Since selenium is difficult to determine directly by atomic-absorption spectroscopy[15] and since DanSe contains selenium, an indirect atomic-absorption procedure for the determination of selenium, utilizing the high selectivity of DanSe for palladium, is now being investigated.

Other advantages of DanSe as a palladium reagent are the simplicity of the analytical procedures and the diversity of the methods. Because the reaction is remarkably free from interference and very insensitive to pH changes as long as the solution is acidic, neither masking agents or buffers need be added.

With the exception of the gravimetric, atomic-absorption and to some extent the fluorometric method, the limiting factor in the sensitivity of the palladium determination is not due to the reagent itself, but is the degree of separation of the reagent from the Pd–DanSe precipitate. Very high-speed centrifugation offered only a slight improvement in sensitivity over conventional centrifugation. The Perkin–Elmer sampling boat atomizing system was also tested for the atomic-absorption determination, but a decrease rather than an enhancement in sensitivity was observed.

Precision and accuracy

The recovery of known amounts of palladium was satisfactory. Based on the results in Table III, obtained in the presence of a large excess of foreign ions, the gravimetric procedure shows a relative standard deviation of 0·7%, the spectrophotometric method 6·0%, the radiometric method 7·2%, the fluorometric method 8·7% and the atomic-absorption method 3·2%.

Sensitivity and detection limit

The criterion of Mandel and Stiehler[16] for the evaluation of the sensitivity (γ) of different methods was adopted, *i.e.*,

$$\gamma = \mathrm{d}I/s_{\mathrm{I}}\,\mathrm{d}C.$$

The main advantage of this criterion is that it takes into account not only the reproducibility of the testing procedure, but also its ability to discern small changes in concentration or amount. In addition, the unit used is amount or concentration, C, and is independent of the scale, I, on which the measurement is expressed. Thus, a direct comparison of the sensitivity of one method with another is made possible. The least-squares method was used to obtain the slope of the linear calibration curve, $\mathrm{d}I/\mathrm{d}C$, and the standard deviation, s_{I}, of points from the regression line. In the case of the fluorometric calibration curve (range 0–1 ppm Pd), the slope of the non-linear curve was measured at the mid-concentration range and the standard deviation was calculated from data in Table III.

TABLE IV.—SENSITIVITY OF THE DIFFERENT ANALYTICAL METHODS FOR PALLADIUM

Method	Sensitivity, *ppm*$^{-1}$	Detection limit,* *ppm*
Gravimetric	—	—
Spectrophotometric	18·5	0·172
Radiometric	23·2	0·137
Atomic absorption	164·4	0·019
Fluorometric (0–5 *ppm*)	25·2	0·126
(0–1 *ppm*)	33·5	0·095

* Conservative estimate of the detection limit. Values obtained represent a confidence level of 95%.

The reciprocal of the sensitivity is directly indicative of the minimum concentration required to produce a discernible change in the signal intensity. To obtain a conservative and objective evaluation for the detection limit (D.L.), the method of Skogerboe *et al.*[17] was used, *i.e.*,

$$\text{D.L.} = \frac{t(n-1, 1-\alpha)}{\gamma}$$

which takes into account the number of measurements (n) for the calibration curve and the confidence level, $100(1-\alpha)\%$, required. The use of 3·18 for t to obtain the data in Table IV represents a confidence level of 95% for six measurements. The pertinent sensitivity and detection limit data foı the five analytical methods for the determination of palladium are presented in Table IV.

Acknowledgement—One of the authors (H. K. Y. L.) wishes to acknowledge the receipt of a University of Missouri-Kansas City summer research fellowship for support of this work. The authors wish to express their appreciation to Miss Claudia Shepard for assistance in the atomic-absorption work.

Zusammenfassung—Fünf analytische Verfahren, je ein gravimetrisches, spektrophotometrisches, radiometrisches, fluorometrisches und ein Atomabsorptionsverfahren wurden für die Bestimmung von Palladium in Makro- bis Submikromengen entwickelt. Sie beruhen auf der Reaktion von $PdCl_2$ mit Naphtho[2,3-*d*]-2-selena-1,3-diazol. Die analytischen Bedingungen wie Reaktionszeit, Konzentrationsbereiche, Einfluß von pH und 68 Fremdionen sowie Extraktion wurden untersucht. Angaben über Struktur und Formel des Reaktions-produktes von Palladium und Piazselenol werden ebenfalls gemacht.

Résumé—On a élaboré cinq techniques analytiques, gravimétrique, spectrophotométrique, radiométrique, fluorimétrique et d'absorption atomique pour la détermination des quantités macro et submicro de palladium. Les méthodes sont basées sur la réaction de $PdCl_2$ avec le naphto (2,3-*d*)2-séléna 1,3-diazole. On a étudié les conditions analytiques telles que le temps de réaction, les domaines de concentration, l'influence du pH et de 68 ions étrangers, et l'extraction par solvant. On présente également des données relatives à la structure et la formule des produits de réaction palladium-piazselenol.

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HYDROCARBURES ET POLLUTION ATMOSPHÉRIQUE

Denise Halot
Laboratoire de Chimie Analytique, Faculté de Médecine et de Pharmacie, 37-Tours, France

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Résumé—Après avoir envisagé la provenance des hydrocarbures trouvés dans l'atmosphère, nous étudions brièvement leur toxicité, puis nous décrivons les diverses méthodes d'analyse des hydrocarbures aromatiques polycycliques, c'est-à-dire des hydrocarbures cancérigènes.

On sait que la pollution atmosphérique a trois origines principales:
—les foyers domestiques,
—les foyers et les émissions industrielles,
—les gaz d'échappement des automobiles.

NATURE ET PROVENANCE DES HYDROCARBURES TROUVÉS DANS L'ATMOSPHÈRE

Hydrocarbures aliphatiques et aromatiques

L'atmosphère des villes permet de déceler des hydrocarbures aliphatiques et aromatiques légers à des concentrations variant de 0,1 à 1 ppm.

Ces hydrocarbures proviennent de l'évaporation des produits pétroliers au niveau des réservoirs et des carburateurs des automobiles et de leur combustion incomplète pendant le fonctionnement du moteur. On les appelle des "imbrûles".

Hydrocarbures polyaromatiques

Les poussières atmosphériques contiennent des goudrons provenant de la décomposition pyrogénée de la houille, du bitume, des schistes, du pétrole *etc.* Ces goudrons renferment, à côté d'autres substances chimiques des hydrocarbures paraffiniques et surtout des hydrocarbures polyaromatiques, parmi lesquels des hydrocarbures cancérigènes.

Ces hydrocarbures polynucléaires rencontrés dans l'atmosphère proviennent des foyers domestiques et industriels,[1] et également des échappements de moteurs. A l'opposé de ce qui a lieu pour d'autres polluants comme l'anhydride sulfureux, ce sont les conditions de marche et non les produits d'alimentation qui jouent un rôle prépondérant. Par un réglage convenable des facteurs de combustion (en particulier de l'excès d'air), on peut diminuer considérablement l'émission des polynucléaires par un foyer.

Les moteurs en régime normal émettent beaucoup moins de polyaromatiques que lors des démarrages et des ralentis.[2–4]

TOXICITÉ DE CES DIFFÉRENTS HYDROCARBURES

Hydrocarbures aliphatiques et aromatiques

Il ne faut pas oublier le rôle très important des oléfines dans les réactions photochimiques qui conduisent, lorsque les conditions climatiques sont favorables à la formation d'ozone et également à l'apparition de vésicules liquides qui constituent le "smog" oxydant de Californie.[5]

Dans nos régions, il est peu probable qu'on ait à craindre de tels phénomènes; toutefois, la prudence voudrait que l'on surveillât les teneurs en oxydants, en nitrate de peracétyle ou PAN et en hydrocarbures imbrûlés dans les villes où se conjuguent un trafic automobile important, un ensoleillement intense et une inversion de températures qui emprisonne les gaz d'échappement des automobiles dans les couches basses et moyennes de l'atmosphère.

Hydrocarbures aromatiques polynucléaires

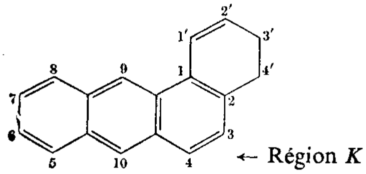
La source principale de toxicité des goudrons provient essentiellement de la présence des hydrocarbures aromatiques polynucléaires en raison de leur activité cancérigène. Rappelons brièvement l'historique de ce problème biologique.

En 1775 Pott constate, chez les ramoneurs, la fréquence anormale du cancer du scrotum. En 1915 Yamagiwa et Ichikawa obtiennent le premier cancer expérimental par application de goudron de houille sur l'oreille d'un lapin. L'école anglaise avec Cook et ses collaborateurs a fait beaucoup progressé la question: ils constatèrent d'abord que les goudrons cancérigènes pouvaient être obtenus à partir de produits contenant uniquement du carbone et de l'hydrogène. Ceci amena à penser que les principes actifs se rattachaient au groupe chimique des hydrocarbures.

Puis on découvrit que les fractions actives présentaient un spectre de fluorescence typique comparable à celui de certains hydrocarbures polycycliques déjà connus. Il s'agissait de trois bandes dans le violet, avec des maximums à 400, 418 et 440 nm environ. Ce test orienta les recherches vers des hydrocarbures aromatiques polycycliques.[6]

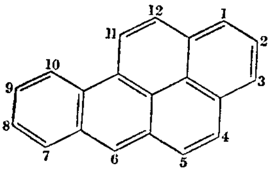
Effectivement en 1930, Kennaway et Hieger démontrent l'activité cancérigène du dibenzo[*ah*]anthracène. En 1933, Cook et ses collaborateurs[7] isolent le benzo-[*a*]pyrène du goudron de houille et montrent son action hautement cancérigène. Depuis de nombreux chercheurs ont pu prouver le pouvoir cancérigène sur l'animal d'un grand nombre d'hydrocarbures polycycliques. En 1948, Pullman[8,9] expose sa théorie de l'activité cancérigène: un produit cancérigène doit présenter une affinité pour la cellule vivante. Cette affinité s'explique par l'existence de "régions actives" de la molécule, c'est-à-dire de régions où il se produit une accumulation d'électrons.

Ainsi, le benzanthracène-1,2 n'est pas cancérigène. Par contre, on obtient des dérivés de plus en plus cancérigènes par substitution d'un radical méthyl en 5, en 9 ou en 10. La région active, ou région *K* est celle de la double liaison 3–4 où la concentration électronique augmente d'autant plus que le substituant en est plus rapproché.

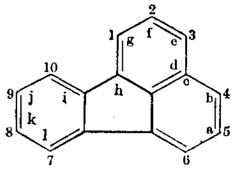


Benzanthracène-1,2

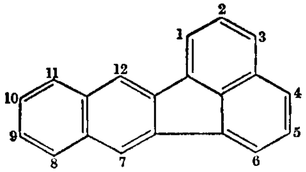
Actuellement, les seuls hydrocarbures cancérigénes couramment rencontrés dans l'atmosphère sont: le benzo[*a*]pyrène, le benzo[*e*]fluoranthène, le benzo[*k*]fluoranthène et le dibenzo[*a*,*h*]anthracène[10] ainsi que certains dérivés méthylés.



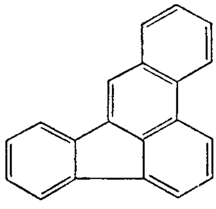
Benzo[*a*]pyrène



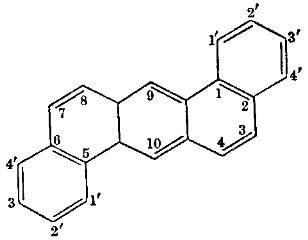
Fluoranthène



Benzo[*k*]fluoranthène



Benzo[*e*]fluoranthène



Dibenzo[*a*,*h*]anthracène

Remarque: nous avons choisi la nomenclature du 'Ring Index'' adoptée par les "Chemical Abstracts''. Il faut signaler que le benzo[*a*]pyrène est souvent appelé benzo-3,4 pyrène dans l'ancienne numérotation.

MÉTHODES D'ANALYSE DES HYDROCARBURES AROMATIQUES POLYCYCLIQUES

Les principales méthodes d'analyse des hydrocarbures aromatiques polycycliques vont être passées en revue. Nous étudierons successivement les méthodes d'extraction, de séparation et de dosage.

Il importe:

—de doser les goudrons dans leur ensemble,

—de doser les hydrocarbures cancérigènes.

Méthodes d'extraction

Nous prendrons ici le terme extraction au sens large et nous parlerons ègalement des techniques de concentration.

Extraction par filtration. Le procédé habituel en pollution atmosphérique consiste à faire passer par pompage un volume déterminé d'air sur un papier-filtre[11–13] ou de la fibre de verre.

Quel que soit le système utilisé, il est important de vérifier:

—que les plus petites particules pouvant contenir des polycycliques sont arrêtées; pour cela, il est bon de placer un deuxième filtre en aval du filtre principal,

—que les polynucléaires adsorbés par le filtre peuvent être remis ensuite quantitativement en solution.

Extraction par les solvants. (*a*) *Avec l'appareil Soxhlet;* on utilise l'appareil Soxhlet avec comme solvant le benzène ou le mélange benzène-méthanol. (*b*) *Extraction liquide-liquide;* l'échantillon à analyser est dissous dans un solvant convenable et on extrait les hydrocarbures polycycliques par un solvant non miscible au premier. (*c*) *Extraction à contre-courant;* l'extraction à contre-courant d'un mélange de polycycliques a été étudiée en se servant de l'ppareil de Craig.[14] Les solvants consistaient en un mélange de cyclohexane méthanol à 90% contenant 0,83% d'acide tétraméthylurique. La séparation est excellente mais la méthode est laborieuse. (*d*) *Sublimation;* des essais d'extraction ont été effectués par sublimation. Les auteurs utilisent un tube chauffé permettant un gradient de température décroissant à partir de 250° et un vide variant de 1,3 à 33 mbar.[15–17] Par cette technique, seul le chrysène, pour l'instant, est récupéré intégralement à partir d'un mélange complexe. (*e*) *Remarques;* Monkman[18] recommande d'éviter l'extraction au Soxhlet pour l'examen des poussières atmosphériques: car il pourrait y avoir destruction par chauffage en présence d'air et de lumière d'une fraction des hydrocarbures polycycliques. Le solvant de choix est le cyclohexane:[19,20] on agite 100 mg de poussière dans 100 ml de cyclohexane pendant trois heures dans un erlenmeyer, puis on filtre sur verre fritté.

La solution provenant de l'extraction des poussières est évaporée à siccité et le résidu est pesé. Il constitue l'extractible, on lui donne le nom de goudron. On reprend par l'éther de pétrole pour pouvoir éliminer les acides, les phénols et les bases lorsque ceux-ci se trouvent en grande quantité.

Méthodes de séparation

Pour séparer les hydrocarbures polyaromatiques entre eux on a recours essentiellement aux méthodes chromatographiques: chromatographie en phase liquide ou chromatographie en phase gazeuse. La chromatographie en phase gazeuse, servant de méthode de séparation mais également de méthode de dosage, sera étudiée en même temps que les procédés quantitatifs. Dans la chromatographie en phase liquide, il faut distinguer la chromatographie d'adsorption sur colonne ou sur couches minces, et la chromatographie de partage sur papier ou sur colonne.

Chromatographie d'adsorption sur colonne. Elle se fait, en général, sur alumine activée ou sur silicagel. On élue par le cyclohexane ou avec des mélanges hexane-diéthyléther.[3,21–23] Le silicagel permet de séparer assez rapidement les hydrocarbures aromatiques des autres hydrocarbures paraffiniques, des cyclanes et des oléfines. Par contre, seule l'alumine permet un fractionnement des aromatiques entre eux.

Chromatographie sur couches minces. Elle permet des séparations du même ordre que celles de la chromatographie sur colonne, mais elles sont beaucoup plus rapides. Le support est constitué par des plaques de verre recouvertes d'un mélange plâtre–silicagel.[24] On utilise également la poudre de cellulose acétylée. Köhler emploie un mélange alumine–acéthylcellulose, il travaille en chromatographie à deux dimensions avec comme solvants: hexane/pentane/toluène et méthanol/éthanol/eau.[25]

Sawicki[26] a comparé l'efficacité de trois méthodes sur couches minces sur un couple particulièrement difficile à séparer: le benzo[*a*]pyrène et le benzo[*k*]fluoranthène. Ces corps sont séparés sur cellulose acétylée avec élution par le mélange: éthanol/toluène/eau (17/4/4). Par contre, ils ne sont pas séparés sur cellulose non acétylée en éluant par le mélange diméthylformamide/eau (1/1), ni sur alumine avec le mélange pentane/éther (19/1).

Chromatographie de partage sur papier. En général on utilise le papier Whatman n° 1 ou Arches 304 et comme solvant le mélange diméthylformamide–éther de pétrole. Malý[27] imprègne le papier avec de l'huile blanche médicinale en le plongeant dans une solution d'huile dans l'éther de pétrole, et en laissant ensuite évaporer l'éther. Il réussit ainsi très bien la séparation du mélange benzo[*a*]pyrène–benzo[*k*]fluoranthène–pérylène des autre hydrocarbures. La phase stationnaire est constituée par de l'huile de vaseline et la phase mobile par du méthanol.

Chromatographie de partage sur colonne. Phases stationnaires: glycols, polyéthylèneglycols *etc.* Phase mobile: iso-octane. L'adjonction de trinitrobenzène sym. améliore beaucoup la séparation des différents constituants par suite de la formation de complexes entre les hydrocarbures et le dérivé nitré.[28]

Déterminations qualitatives et quantitatives

Il faut distinguer:

—les contrôles de routine où le but est d'obtenir des résultats rapides avec des moyens peu onéreux,

—l'analyse approfondie où l'on utilise les techniques les plus précises même si elles sont très longues.

Déterminations qualitatives. On examine directement les chromatogrammes en lumière de Wood ($\lambda = 365$ nm) et l'on mesure le R_f. Il est possible également de mesurer la surface des spots[29] ce qui permet une évaluation très approximative de la teneur. Certains hydrocarbures polycycliques sont fluorescents, d'autres le deviennent à la température de l'azote liquide ou en solution dans l'acide sulfurique ou l'acide trifluoracétique.

Déterminations quantitatives. Les méthodes les plus importantes sont: la spectrophotométrie d'absorption dans l'ultra-violet, la fluorimétrie, la chromatographie en phase gazeuse, et les méthodes biologiques.

(*a*) *Spectrophotométrie dans l'ultra-violet.* Tous les hydrocarbures polyaromatiques absorbent dans l'ultra-violet, et la mesure de l'absorption dans l'ultra-violet reste la méthode quantitative la plus sûre pour doser un polycyclique dont la nature est bien déterminée.

Les maximums d'absorption et les coefficients d'extinction sont donnés dans la littérature.[30,31] Mais il faut se servir de ces données avec circonspection si l'on ne connaît pas les conditions exactes dans lesquelles elles ont été établies.

Quels sont les inconvénients de cette technique? Tout d'abord le rayonnement ultra-violet est actif sur les polycycliques: il modifie leur structure si bien que l'absorption diminue avec le temps. Il est donc nécessaire d'opérer rapidement. Ce changement serait dû à une réaction des hydrocarbures avec l'ozone.[32] De plus, elle manque de sélectivité. Toutefois les travaux d'Haenni[33–37] ont montré que l'on peut établir des limites supérieures d'absorption ultra-violette à des longueurs d'onde convenablement choisies. Si ces limites ne sont pas dépassées, on est assuré qu'aucun hydrocarbure cancérigène ne se trouve dans l'échantillon analysé à une dose supérieure à 0,3 ppm.

On a cherché à appliquer la spectrophotométrie ultra-violette à des solutions contenant plusieurs polynucléaires. Il s'agit, selon un procédé classique en spectrophotométrie, de choisir des longueurs d'onde convenables, de déterminer les coefficients d'extinction respectifs et de résoudre un système de n équations à n inconnues. Ce procédé si imparfait qu'il soit est très utile pour doser des substances difficiles à séparer par chromatographie.[31,38–41] La principale difficulté vient du fait qu'en pollution atmosphérique, il faut toujours redouter la présence de corps non identifiés susceptibles de fausser le dosage. Korotkov a résolu avec succès le problème du mélange benzo[*a*]pyréne–dibenzanthracène.[39]

D'autre part, il a été montré[42] que le pouvoir cancérigène des poussières atmosphériques est proportionnel à leur teneur en benzo[*a*]pyrène. Et il est admis que le benzo[*a*]pyrène se trouve en proportion assez constante par rapport aux autres polycycliques. Ces deux faits ont amené les auteurs à porter leurs efforts sur la séparation du benzo[*a*]pyrène par chromatographie et son dosage par mesure de l'absorption dans l'ultra-violet.[43–46] Toutefois, il faut signaler que, contrairement à l'opinion de Mme Héros et de M. Amy, le pouvoir cancérigène des diverses poussières atmosphériques est seulement partiellement lié à leur teneur en benzo[*a*]pyrène. C'est ce qui a été démontré par Hueper et ses collaborateurs d'une part[47,48] et par Epstein et ses collaborateurs d'autre part.[49] Dans ces conditions, il est difficile, à partir d'un dosage de benzo[*a*]pyrène, de déduire le pouvoir cancérigène des poussières atmosphériques.

(*b*) *Fluorimétrie.* La fluorimétrie très employée présente un certain nombre d'avantages.

—Tous les hydrocarbures cancérigènes sont fluorescents.

—Elle est extrêmement sensible.

Par contre elle présente quelques difficultés:

—Elle est moins précise que la spectrophotométrie UV.

—Les traces de substances étrangères interviennent intensément par absorption ou inhibition de la fluorescence. Il est donc indispensable qu'un étalonnage préalable soit effectué dans des conditions opératoires strictement identiques.

—La fluorescence dépend de la nature du solvant.

C'est pourquoi, il faut distinguer des méthodes semi-quantitatives et des méthodes précises.

Les procédés semi-quantitatifs concernent surtout le benzo[*a*]pyrène, il est possible d'évaluer grossièrement sa teneur sans séparation préalable, grâce à une méthode par dilution successive et surcharge.[50,51] On effectue les spectres de fluorescence de dilutions successives de solutions de benzo[*a*]pyrène à doser jusqu'à disparition presque totale des bandes ultimes de fluorescence (403 et 427 nm). Ceci a pour but d'éviter les inhibitions éventuelles d'une part et les parties non linéaires de la courbe intensité de fluorescence-concentration. On ajoute alors des quantités connues de benzo[*a*]pyrène ce qui permet une évaluation approximative de la concentration cherchée.

Ce procédé a été perfectionné par Mme Héros[50,51] en l'appliquant après chromatographie.[52] La limite de sensibilité de la méthode est de 10 ng dans une cuve de 1 cm^3. Le benzo[*k*]fluoranthène interfère. Il est possible de résoudre le problème benzo[*a*]-pyrène–benzo[*k*]fluoranthène de la manière suivante:[42]

—dans un premier temps, on détermine la fluorescence du mélange,

—dans un deuxième temps, on élimine la fluorescence du benzo[*a*]pyrène par action du brome et l'on mesure celle du benzo[*k*]fluoranthène qui n'est pas modifiée.

En travaillant à $-190°$, il est possible d'améliorer de beaucoup la sensibilité et le grand nombre des bandes du spectre permet d'identifier le benzo[*a*]pyrène avec une plus grande certitude. On peut déceler, dans ces conditions, 100 ng par mm^3.

Pour les mélanges d'hydrocarbures autres que le benzopyrène, l'excitation par la raie de Wood $\lambda = 365$ nm ou la raie $\lambda = 253{,}7$ nm du mercure provoque l'apparition de la plupart des spectres de fluorescence. Pour n'en exciter qu'un seul, il faut profiter du fait que l'intensité de fluorescence est maximale ou minimale selon que la raie excitatrice se trouve à un maximum ou à un minimum d'absorption.

Pour un corps donné, il faut donc choisir une raie excitatrice à l'aide d'un monochromateur, de manière qu'elle coincide avec un maximum d'absorption de cette substance et un minimum pour tous les autres corps. Il faut également disposer d'une source suffisamment intense pour la détection par les phototubes. C'est ce qui a été réalisé avec les lampes au xénon.

Une autre technique est celle des spectres d'activation. Les spectres d'activation reprèsentent la variation d'intensité d'une bande fluorescente mesurée à longueur d'onde constante, en fonction de la lumière excitatrice supposée d'intensité constante. Pour réaliser un spectre d'activation, il faut un appareillage plus compliqué:

—une source émettant dans un vaste domaine,

—deux monochromateurs indépendants, un pour la lumière excitatrice, l'autre pour l'émission de fluorescence.

Il est possible de combiner les deux méthodes pour analyser un mélange complexe: on enregistre successivement des spectres de fluorescence avec, comme longueurs d'onde excitatrices, celles qui correspondent à un maximum du spectre d'activation pour chaque substance recherchée. Il est possible de faire apparaître chaque spectre de fluorescence séparément presque sans interférences.

Sawicki,[53] van Duuren,[54] Dubois et Monkman[55] ont réussi à doser, par fluorimétrie, des mélanges de polycycliques. Voici le principe pour le mélange benzo[*a*]pyrène–benzo[*k*]fluoranthène:

—à 308 nm il y a excitation de la fluorescence du benzofluoranthène uniquement,

—à 381 nm il y a, à la fois, excitation de la fluorescence des deux composés.

Pour terminer signalons des méthodes qui utilisent la spectrophotométrie dans l'ultra-violet et la spectrofluorimétrie. Ainsi il est possible de doser d'une part un certain nombre d'hydrocarbures par mesure de l'absorption dans l'ultra-violet et d'autre part le benzo[*a*]pyrène et le benzo[*k*]fluoranthène par fluorescence en solution dans l'hexane au moyen de deux longueurs d'onde excitatrices (308 nm et 384 nm).

(*c*) *Chromatographie en phase gazeuse.* Elle est encore peu utilisèe, mais c'est une méthode d'avenir. Elle présente un certain nombre de difficultés:

—multiplicité des produits contenus dans les poussières,

—points d'ébullition élevés des hydrocarbures cancérigènes (benzo[*a*]pyrène: 496°). Si la chambre d'injection du chromatographe est à une température trop élevée pour permettre la volatilisation des substances, on risque une décomposition ou une polymérisation. De plus le choix des phases stationnaires se trouve restreint. Pour remédier à ces inconvénients on effectue un fractionnement préliminaire par extractions successives des solutions de cyclohexane avec le mélange méthanol-eau et ensuite avec le nitrométhane.[56]

Voici les conditions opératoires:

—colonne capillaire en verre de 35 m de longueur et 0,35 mm de diamètre intérieur, chauffée à 200° (les parois internes sont enduites de caoutchouc au silicone),

—température d'injection: 250°.

Les déterminations quantitatives sont faites par la méthode de l'étalon interne avec comme étalon le triphényl-1,3,5 benzène. L'efficacité de la colonne mesurée pour le *n*-hexacosane est de 10^4 plateaux théoriques.

On utilise aussi la chromatographie à température programmée de 150 à 350°,[57] les auteurs se servent d'un dispositif à deux colonnes et deux détecteurs ce qui permet d'annuler la dérive de la ligne de base. La sensibilité est à peu près la même qu'en spectrophotométrie UV, la méthode est assez rapide, elle dure deux heures. Signalons également que, pour obtenir de meilleures séparations on s'est servi à la fois de la chromatographie sur chouches minces et de la chromatographie en phase gazeuse.

(*d*) *Méthodes biologiques*. Dans de nombreux cas, il n'est pas possible de se passer de l'analyse biologique bien qu'elle dure plusieurs mois parfois. On ne peut garantir, par exemple, qu'un échantillon n'est pas cancérigène, même si l'on est sûr qu'il ne renferme ni benzo[*a*]pyrène, ni dibenzanthracène, ni méthyl-cholanthrène. Pour avoir une certitude absolue il est nécessaire de faire un essai sur l'animal.

L'animal de choix est la souris, car le cancer apparaît après deux ou trois mois. Le pourcentage de souris contaminées renseigne sur l'activité cancérigène du produit.

CONCLUSION

Nous avons essayé de donner une idée aussi juste que possible du problème des hydrocarbures cancérigènes en pollution atmosphérique vu sous l'angle analytique.

Les méthodes quantitatives les plus utilisées actuellement sont la spectrophotométrie ultra-violette et la fluorimétrie. Il semble que, dans l'avenir, la chromatographie en phase gazeuse jouera un rôle très important à la fois en tant que méthode de séparation et de dosage.

Summary—A survey is given of the source of hydrocarbons found in the atmosphere, of their toxicity, and of the methods of analysis available for polycyclic aromatic hydrocarbons.

Zusammenfassung—Es handelt sich un eine Übersicht über den Ursprung der in der Atmosphäre gefundenen Kohlenwasserstoffe und ihre Toxizität sowie über die Analysenmethoden für polycyclische aromatische Kohlenwasserstoffe.

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ENTHALPIMETRIC DETERMINATION OF FLUORIDE

CARL E. JOHANSSON
Department of Analytical Chemistry, Chemical Center, University of Lund, Lund, Sweden

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Summary—An injection calorimeter used for analytical and thermochemical purposes is described. Amounts of sodium fluoride between 6 and 8 mg are determined with an error of ±0·04 mg. The calorimeter is also used in determining ΔH for the precipitation of lead chlorofluoride from water solutions with an ionic strength of $1M$. $\Delta H = 36{\cdot}6 \pm 0{\cdot}3$ kJ/mole. Quantitative analysis is made by flow microcalorimeter with amounts of sodium fluoride between 40 and 400 μg and an error of $\pm 4\ \mu$g. An ion-exchange system for separation of fluoride from phosphate, sulphate, nitrate and chloride is also described.

CALORIMETRIC methods are of importance not only in thermodynamics but also in the field of analytical chemistry. Enthalpy titration methods have been shown to be of value in both these areas. With this technique a constant flow of reagent is added to the calorimetric vessel, or the reagent is rapidly injected into the vessel containing the sample solution.[1–5]

In this paper results are reported from the enthalpimetric determination of fluoride in water solution. Both complexation and precipitation reactions could be considered.[6] In this work the precipitation reaction

$$\mathrm{Pb^{2+}_{(aq)} + F^{-}_{(aq)} + Cl^{-}_{(aq)} \rightarrow PbFCl_{(s)}} \qquad (1)$$

was used. This reaction is fast and is accompanied by a fairly large heat effect which makes it suitable for the analytical technique used here.

EXPERIMENTAL

Injection Calorimetry

Reagents

The sample solutions were made from sodium fluoride, phosphate, sulphate, chloride and nitrate, all of *pro analysi* quality. The eluent in the anion-exchange was sodium hydroxide solution made from a carbon dioxide-free concentrated solution. The anion-exchange resin was regenerated with sodium hydroxide solution. The cation-exchange resin was regenerated with $3M$ hydrochloric acid. The precipitant was $4{\cdot}9M$ lead(II) perchlorate, prepared from lead(II) oxide and 70% reagent grade perchloric acid. To lower the heat of solution of the reagent, the lead(II) perchlorate solution was diluted with 2% w/v water.

Ion-exchange procedure

If a sample contains other anions it is not possible to measure the fluoride content directly since the presence of these anions influences the enthalpy of reaction. Therefore ion-exchange steps had to be included in the procedure. The ion-exchange arrangement, shown in Fig. 1, consisted of a glass column with 5 g of ion-exchange resin Dowex 1 × 8, 200–400 mesh in OH form and a Teflon column containing 5 g of cation-exchange resin Dowex 50 W × 8, 20–50 mesh. In the analytical experiments with the injection calorimeter, samples containing 6–8 mg of fluoride and usually a 20-fold excess of chloride, nitrate, sulphate or phosphate were put on the anion-exchange column. Flow-rate in the absorption step was 1 ml/min.

If the sample also contained carbonate this ion had to be removed before the ion-exchange step. This was done by blowing carbon dioxide-free nitrogen through the sample solution after its pH had been adjusted to 5·5. After the absorption the resin was washed with distilled water until the effluent was neutral. The fluoride was eluted by $0{\cdot}2M$ sodium hydroxide at a flow-rate of 1·5 ml/min. The

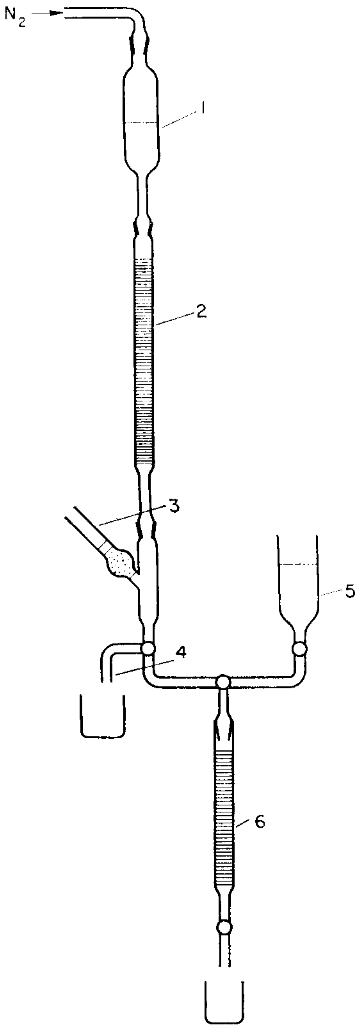

FIG. 1.—Ion-exchange arrangement.
1—Holder for sample solution, water, eluent and regeneration solution. 2—Anion-exchange column with Dowex 1 × 8. 3—Ascarite protection tube. 4—Discharge tube. 5—Holder for water and regeneration solution. 6—Teflon cation-exchange column with Dowex 50 W × 8.

first 60 ml of effluent did not contain any fluoride and were rejected. The following 100 ml contained all the fluoride, but no other anions, as was shown by spot tests[8] performed on the next few drops eluted. The anion-exchange resin was regenerated with 4*M* sodium hydroxide and was washed with distilled water.

The fluoride effluent was alkaline and could not be used directly in the calorimetric experiments. Neutralization with acid would give too high an ionic strength, which would interfere with the calorimetric measurements. The fluoride solution was therefore passed through the cation-exchanger. The hydrofluoric acid coming from the cation-exchanger was absorbed in 5 ml of solution that was 0·117*M* in sodium acetate, 0·033*M* in sodium hydroxide and 0·15*M* in sodium chloride, in a Teflon beaker. After evaporation to 6–7 ml the solution was cooled to room temperature. One ml of 0·915*M* acetic acid was added to the solution to give a pH of 4·4. This solution was diluted to 25 ml and added to the calorimetric cell.

Calorimeter

The reaction cell consisted of a 25-ml Dewar vessel made of Pyrex glass, placed in a polyethylene cover (Fig. 2). The temperature changes were measured with a Veco 32 A 12 2000-Ω thermistor, connected to a Wheatstone bridge. The signal from this was amplified with a Hewlett-Packard Null Voltmeter 491 A, the output signal of which was connected to a Servogor Re 511 recorder. The input signal to the amplifier was usually about 500 μV and was measured on the 1-mV range. The reagent was delivered through a glass spiral which was housed in the sample solution to obtain the same initial temperature for both solutions. The tip of the spiral ended 3 mm above the surface of the solution. The volume of the spiral was 0·83 ml and it was filled directly from a burette. By pressing air into the spiral the reagent was injected into the sample solution. The stirrer was made from Teflon attached to a glass shaft. Temperature was adjusted by means of a 50-Ω manganin heater which also was used for the electrical calibration of the calorimeter.

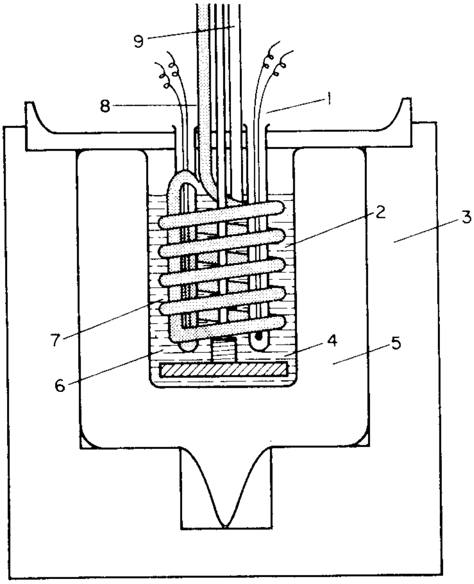

FIG. 2.—Calorimetric cell.
1—Thermistor. 2—Glass spiral. 3—Polyethylene cover. 4—Teflon stirrer. 5—Dewar vessel. 6—Heater. 7—Sample solution. 8—Tube to burette. 9—Tube to air syringe.

Calorimetric procedure

The temperature was adjusted with the heater to 25·0° and the calorimeter was allowed to equilibrate during 5 min, after which a linear voltage–time curve was obtained on the recorder. The reagent was then injected into the sample solution. After 1·5 min a steady state was established and the voltage again changed linearly with time. The distance between the two straight lines on the recorder chart was measured. In the analytical experiments the instrument was calibrated by measurements on known amounts of sodium fluoride, which had been passed through the cation-exchange step.

Flow Microcalorimetry

Reagents

The sample solutions, with a pH of 4·6, were 0·5–4 m*M* in sodium fluoride, 0·06*M* in acetic acid–sodium acetate and 0·03*M* in sodium chloride. The reagent was 0·49*M* lead perchlorate.

Calorimeter

A commercial instrument, the LKB 10700-1 was used.[7] This calorimeter is a twin heat-leakage calorimeter utilizing semiconducting thermocouple plates for measurements of the heat flow. The mixing cell was made of a gold spiral and had an internal volume of 1 ml. The signal from the thermopiles was amplified with a Keithley 150 B Amplifier, with the input signal measured in the 100-μV range. The amplified signal was recorded in the 50-mV range on the Servogor RE 511 recorder. Two LKB 102000 Perspex pumps were used to pump the reagent and sample solutions through the reaction cell. At steady state the calorimetric signal is proportional to the heat effect from the reaction in the cell. Thus the baseline displacement measured on the recorder is, for a given flow-rate, proportional to the concentration of the flouride in the sample.

Procedure

A blank solution, without fluoride, and the reagent were first pumped into the calorimeter. The flow-rate was 27·8 ml/hr for the sample solution and 15 ml/hr for the reagent. After some minutes a steady potential was obtained and the signal from the amplifier was adjusted to zero. The blank solution was then replaced by the sample solution. After 3–7 min, depending on the amount of fluoride, the potential became stable. The sample was then replaced by the blank solution and the potential returned to zero, Fig. 3.

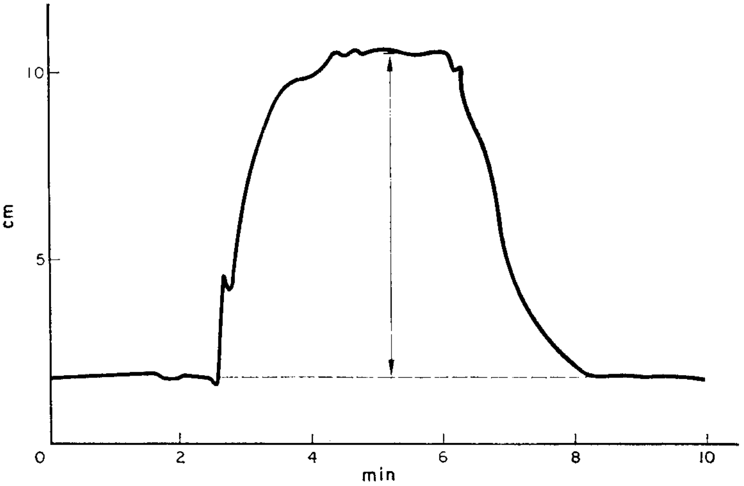

FIG. 3.—Response-time curve for precipitation of lead chlorofluoride in the flow microcalorimeter. The fluoride concentration is ~2·5 m*M*. The arrow shows the deflection read off.

Determination of the Enthalpy Change for the Precipitation Reaction

In a separate series of experiments the enthalpy change of precipitation reaction (1) was determined. These experiments were made with the injection calorimeter. The performance of this calorimeter was tested by measurement of the enthalpy of neutralization of dilute hydrochloric acid by sodium hydroxide solution.

Calorimeter equipment

In order to improve the precision of the recorder reading, 50–80% of the amplified signal was balanced out by a known external voltage signal. To achieve this, the amplifier was switched over to a preset negative off-balance value at the same time as the reagent was injected into the calorimeter. The measurement range of the amplifier was 300 μV and the recorder range was 0·5 V. The calorimeter was calibrated electrically in these experiments. A precision resistance of 10·00 ± 0·005 Ω was connected in series with the heater. Electrical energy evolved in the heater was calculated from measurements of the current through the 10-Ω resistance for the known time of 5·000 ± 0·002 sec.

Reagents

In the test experiments the sample solution was 0·004963*M* hydrochloric acid prepared from a 0·1*M pro analysi* standard in an ampoule, and boiled-out distilled water. The reagent solution consisted of 0·30*M* sodium hydroxide prepared from a carbon dioxide-free 1*M pro analysi* standard in an ampoule, and boiled-out distilled water. Both solutions were stored in bottles fitted with Ascarite protection tubes. In the precipitation reaction the sample solution consisted of 6–8 mg of sodium fluoride in a buffer solution of 0·060*M* acetic acid–sodium acetate and 0·030 *M* sodium chloride. The reagent was 4·9*M* lead(II) perchlorate. The cation-exchange resin was Dowex 50 W × 8, which was kept in a Teflon column.

Calorimetric procedure

In the test experiments 0·83 ml of 0·30*M* sodium hydroxide was reacted with 20–25 ml of the hydrochloric acid. One min after the injection a steady state was reached and the temperature–time curve became linear. After a period of about 3 min the system was calibrated electrically by the addition of 6·368 J.

The enthalpy change for the precipitation is a function of pH because of the partial ionization of the hydrofluoric acid initially present. Therefore a correction must be applied for the enthalpy of dissociation of hydrofluoric acid. In order to avoid systematic errors different amounts of fluoride and different pH values were used in the experiments. Some of the sample solutions were prepared by diluting different amounts of sodium fluoride to 25 ml in an acetate buffer solution and some were prepared by first passing the same amount of fluoride through a cation-exchange resin. The first solutions had a pH of about 4·6 and the others about 4·4.

The enthalpy of dilution of lead(II) perchlorate was measured and was also found to depend on the pH. Therefore, injections of the reagent were made into blank solutions with pH between 4·35 and 4·65 and an acetic acid–sodium acetate concentration of 0·06*M* and sodium chloride concentration of 0·03*M*. As in the test experiments, electrical calibrations were performed immediately after the reaction. In all the calorimetric experiments the injection was made at 25·0°. The temperature rise was about 0·05° both in the test experiments and in the precipitation reaction.

RESULTS AND DISCUSSION

Injection calorimetry

Usually the quantity of fluoride in the sample was adjusted to between 6 and 8 mg of sodium fluoride. Under these conditions the calibration curve was a straight line. With below 5 mg the reaction became slower and the reproducibility was not as good. By regression analysis of the calibration values, it was calculated that the amount of sodium fluoride could be determined within ±0·04 mg for an unknown sample run in duplicate (95% confidence limit). The results in Table I from analysis of solutions which had passed through the ion-exchange process show that the fluoride passes quantitatively through the columns.

TABLE I.

NaF added, *mg*	Other anion 0·5*M*, *ml*	NaF calc. from calibration curve, *mg*	Error, *mg*
6·300	PO_4^{3-} 4	6·296	−0·004
6·800	Cl^- 4	6·763	−0·037
7·000	NO_3^- 6	7·008	+0·008
7·250	Cl^- 6	7·254	+0·004
7·600	Cl^- 6	7·597	−0·003
7·800	Cl^- 4	7·843	+0·043
8·000	SO_4^{2-} 4	8·015	+0·015

Flow calorimetry

A linear relationship between the recorder signal and the fluoride concentration was obtained. By regression analysis it was calculated that for a duplicate sample the fluoride concentration could be determined within ±0·08 m*M* (95% confidence limit). However, the line does not pass through the origin, which indicates that the blank experiments did not completely account for zero effects. In analytical experiments, however, where the instrument can be calibrated with known solutions, such discrepancies are of little importance. The precipitation of lead chlorofluoride is thus shown to be useful for the determination of very low concentrations of fluoride by flow calorimetry. The results from the regression analysis imply that amounts of between 20 and 400 μg of sodium fluoride can be determined within ±4 μg with a duplicate sample. When the fluoride concentration was greater than 4 mM the amount of precipitate became so large that the increasing heat of friction caused irreproducible results. In some cases the flow was stopped by the precipitation. In the injection method the reagent had to be prepared to give a small heat dilution. This is not necessary in the flow calorimeter experiments because the heat of dilution can always be compensated electrically. The constancy of the heat of dilution can also be checked over a long period before the precipitation reaction is started, which is not possible in the injection method.

Determination of ΔH

Test experiments. The recorder signal (equal to the applied negative voltage and plus the value read on the recorder) was taken to be proportional to the heat, $Q_c = 6{\cdot}368$ J, at the calibration and to Q_n in the chemical experiments, respectively. Q_n consists of the heat of dilution and heat of reaction between acid and base. The heat of solution was measured by injecting reagent into a blank solution of boiled-out distilled water. These values were subtracted from Q_n and the remaining value was corrected to infinite dilution.[9,10] By dividing by the number of moles in the sample and changing the sign, the heat of ionization of water was obtained. The value from 13 experiments (95% confidence interval) was 55·79 ± 0·06 kJ/mole. This value is in excellent agreement with values in the literature,[1,9] showing that the calorimetric method is not impaired by any significant systematic errors.

The values obtained were used in regression analysis and showed that when the calorimeter is being used as an analytical instrument it is possible to determine a strong acid to within ±0·4 μmole (95% confidence limits).

Precipitation reaction. The quantity determined Q_p consists of three different heats.

$$Q_p = Q_1 + Q_2 + Q_3 \qquad (2)$$

Q_1 = Heat of dilution of lead(II) perchlorate
Q_2 = Heat of dissociation of hydrofluoric acid
Q_3 = Heat of precipitation of lead chlorofluoride

Q_1 was calculated from values obtained when the reagent solution was injected into blank solutions. Q_2 was calculated from the relation:

$$Q_2 = [\mathrm{HF}] \times \Delta H_{\mathrm{diss}} \qquad (3)$$

ΔH_{diss} = heat of dissociation of 1 mole of hydrofluoric acid (13·3 kJ/mole).[11] [HF] was calculated from:

$$[\mathrm{HF}] = \frac{[\mathrm{H}^+]\,.\,[\mathrm{F}^-]\,.f_+\,.f_-}{K_{\mathrm{diss}}}\,; \qquad K_{\mathrm{diss}} = 10^{-3{\cdot}17}$$ [11]

$Q_1 + Q_2$ lies between 0·04 and 0·33 J and depends on the pH. The results are summarized in Table II.

Each value given in Table II is the mean value for 4 determinations performed under identical conditions. The ΔH values derived all refer to the process

$$\mathrm{Pb}^{2+}_{(aq)} + \mathrm{F}^-_{(aq)} + \mathrm{Cl}^-_{(aq)} \rightarrow \mathrm{PbFCl}_{(s)}$$

at an ionic strength of 1M and at 25°. The mean ΔH-value (95% confidence limit) is calculated to be 36·6 ± 0·24 kJ/mole.

TABLE II.

Fluoride, *mole*	pH	Q_3, *J*	ΔH, *kJ/mole*
0·1471	4·61	5·402	36·7
0·1568	4·61	5·772	36·5
0·1680	4·62	6·167	36·3
0·1471	4·41	5·435	36·9
0·1568	4·40	5·830	36·7
0·1680	4·38	6·196	36·5

Acknowledgement—I wish to thank Dr Ingemar Wadsö for his valuable help during this work and the preparation of this report. I also wish to thank Dr K. J. Karrman and Ingvar Pettersson for their helpful advice.

Zusammenfassung—Ein Injektionskalorimeter für analytische und thermochemische Zwecke wird beschrieben. Natriumfluoridmengen zwischen 6 und 8 mg werden mit einem Fehler von ±0,04 mg bestimmt. Das Kalorimeter wird auch bei der Bestimmung von ΔH bei der Fällung von Bleichlorfluorid aus wäßrigen Lösungen der Ionenstärke 1*M* verwendet. $\Delta H = 36{,}6 \pm 0{,}3$ kJ/Mol. Quantitative Analysen werden in einem Mikro- Durchflußkalorimeter mit Natriumfluoridmengen zwischen 40 und 400 μg und einem Fehler von ±4 μg durchgeführt. Es wird auch ein Ionenaustauschsystem beschrieben, mit dem man Fluorid von Phosphat, Sulfat, Nitrat und Chlorid abtrennen kann.

Résumé—On décrit un calorimètre à injection utilisé dans des buts analytiques et thermochimiques. On dose des quantités de fluorure de sodium compris entre 6 et 8 mg avec une erreur de ±0,04 mg. On utilise aussi le calorimètre dans la détermination de ΔH pour la précipitation du chlorofluorure de plomb à partir de solutions aqueuses avec une force ionique de 1*M*. $\Delta H = 36{\cdot}6 \pm 0{\cdot}3$ kJ/mole. L'analyse quantitative est effectuée au moyen d'un microcalorimètre à écoulement avec des quantités de fluorure de sodium comprises entre 40 et 400 μg et une erreur de ±4 μg. On décrit aussi un système d'échange d'ions pour la séparation du fluorure des phosphate, sulfate, nitrate et chlorure.

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ETUDE POLAROGRAPHIQUE ET PHYSICOCHIMIQUE DE *N*-OXYDES—II

MÉCANISME DE RÉDUCTION ET PHÉNOMÈNES D'HYDRATATION DES ACÉTYL ET BENZOYL PYRIDINES *N*-OXYDES

E. Laviron, R. Gavasso et M. Pay*
Laboratoire de Polarographie organique associé au CNRS, Faculté des Sciences, Dijon, France

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Résumé—Une étude polarographique des acétyl et benzoyl pyridines *N*-oxydes fait apparaître des anomalies identiques à celles déjà signalées dans le cas des dérivés formylés correspondants: lorsque le substituant est en position 2 ou 4, il y a réduction simultanée des fonctions carbonyles et *N*-oxydes; en position 3 la réduction a lieu normalement à tous les pH. Une étude par spectroscopie U.V. a permis de mettre en évidence une hydratation du carbonyle, moins intense toutefois que dans le cas des dérivés formylés.

Nous avons examiné, dans l'article précédent de cette série,[1] le comportement polarographique et spectroscopique des formylpyridines *N*-oxydes. Cette étude nous avait permis de mettre en évidence deux phénomènes. (*a*) Un mécanisme de réduction anormal pour les dérivés 2 et 4, avec réduction simultanée des fonctions carbonyle et *N*-oxyde, le dérivé 3 se comportant normalement. (*b*) Une hydratation importante du carbonyle pour les trois isomères.

Le présent travail, consacré aux acétylpyridines *N*-oxydes et aux benzoylpyridines *N*-oxydes, nous a permis de conclure également à une hydratation du carbonyle, ainsi qu'au même type de réduction anormal pour les dérivés 2 et 4.

ETUDE POLAROGRAPHIQUE

*Acétyl-*3 *et benzoyl-*3 *pyridines* N-*oxydes*

Comme dans le cas du formyl-3 pyridine *N*-oxyde, on observe deux types de vagues (Fig. 1 et 2): une vague *A* à 2F, correspondant à la réduction du carbonyle, et une vague *B* à 2F correspondant à la réduction du groupe *N*-oxyde. La vague *A* se scinde en milieu alcalin en deux vagues à 1F chacune. Dans le cas du dérivé benzoylé, on observe en milieu alcalin une vague B_1 à des potentiels très négatifs; cette vague est peut-être due à la réduction de la fonction *N*-oxyde non protonisée. La réduction conduit donc à l'alcool *N*-oxyde sur la vague *A* et à l'alcool simple sur la vague *B*.

Ce mécanisme a été vérifié par électrolyse à potentiel contrôlé dans le cas du dérivé acétylé. Une électrolyse sur nappe de mercure sur la vague *A* conduit à l'hydroxyéthylpyridine *N*-oxyde. Ce produit ne semble pas avoir été décrit jusqu'ici dans la littérature (voir partie expérimentale).

Part I—*Talanta*, 1969, **16**, 293.

[*] Adresse permanente: Department of Chemistry, University of Cape Town, South Africa.

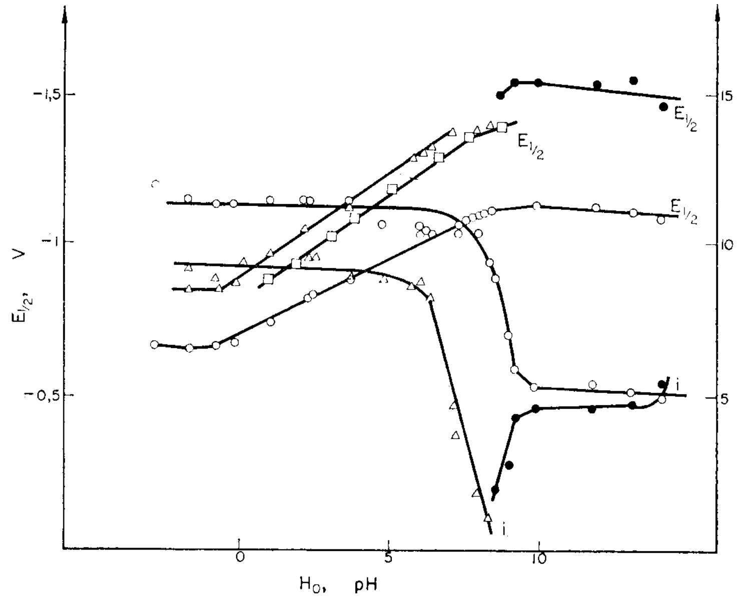

FIG. 1.—Variation de $E_{1/2}$ et du courant limite en fonction du pH pour l'acétyl-3 pyridine *N*-oxyde.
○: vague *A* ou A_1; ●: vague A_2; △: vague *B*; □: (α-hydroxyéthyl)-3 pyridine *N*-oxyde.

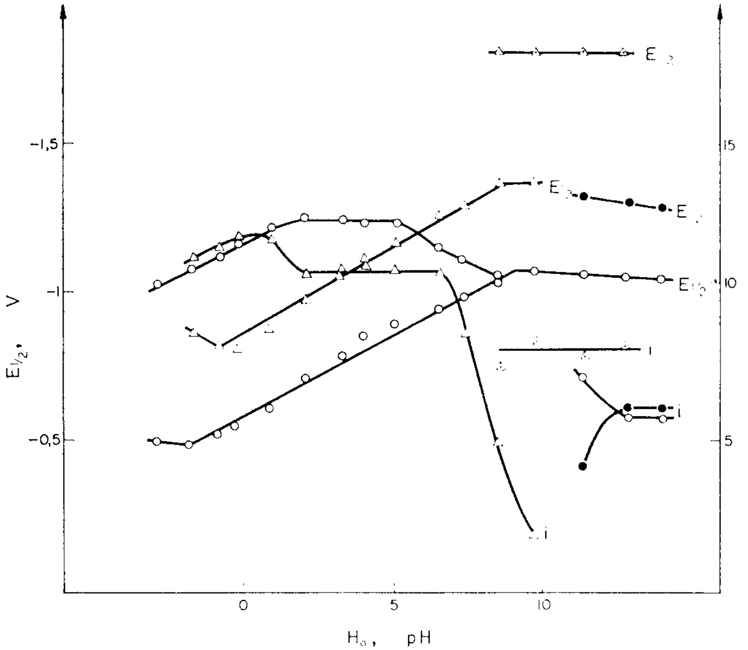

FIG. 2.—Variation de $E_{1/2}$ et du courant limite en fonction du pH pour le benzoyl-3 pyridine *N*-oxyde.
○: vague *A* ou A_1; ●: vague A_2; △: vague *B*; △: vague B_1.

Acétyl-2 et -4 et benzoyl-2 et -4 pyridines N*-oxydes*

Les benzoyl-2 et -4 pyridines *N*-oxydes présentent une vague à 4F dans tout le domaine de pH, avec, pour le dérivé 2, une légère diminution de la hauteur pour des pH supérieurs à 6 (Fig. 3).

L'acétyl-2 pyridine *N*-oxyde présente un comportement assez complexe. La hauteur totale du polarogramme correspond toujours à 4F sauf en milieu très alcalin. En milieu acide et à $pH > 6$ la vague A se scinde en deux vagues de hauteur égale A_1 et A_2; vers pH 6 la vague A_1 se scinde elle-même (apparition d'une vague A_3), et sa hauteur diminue en forme de courbe de dissociation (Fig. 4 et 5), à la suite sans doute d'un phénomène de recombinaison avec un proton.

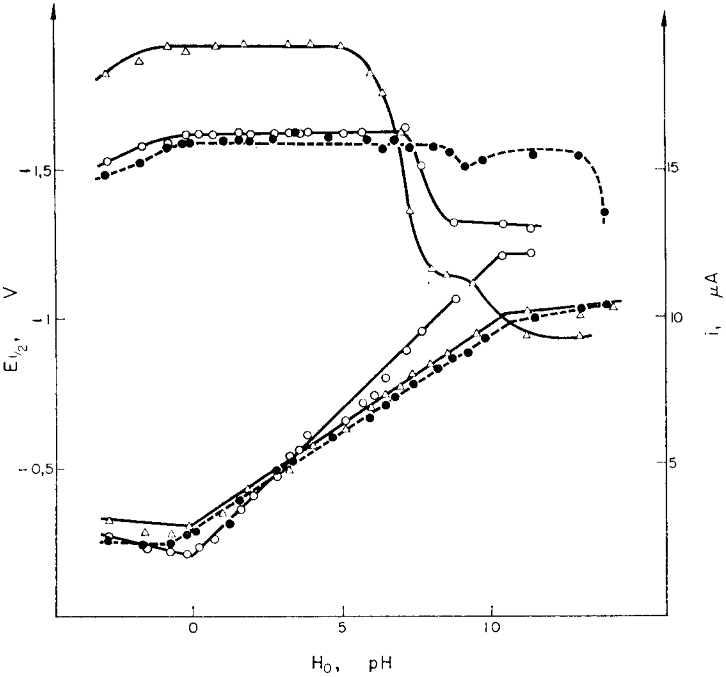

FIG. 3.—Variation de $E_{1/2}$ et du courant limite en fonction du pH pour l'acétyl-4 et les benzoyl-2 et -4 pyridines *N*-oxydes.
○: benzoyl-2 pyridine *N*-oxyde; ●: benzoyl-4 pyridine *N*-oxyde; △: acétyl-4 pyridine *N*-oxyde.

L'acétyl-4 pyridine *N*-oxyde présente une vague à 4F en milieu acide et neutre (la hauteur de vague plus grande que pour les dérivés benzoylés est due à une valeur plus grande du coefficient de diffusion); sa hauteur diminue vers pH 5 et correspond à un processus à 2F en milieu alcalin (Fig. 3).

Ces résultats permettent de conclure que comme dans le cas des formylpyridines *N*-oxydes, il y a réduction simultanée des fonctions carbonyle et *N*-oxyde, du moins en milieu acide et neutre. Le cas de l'acétyl-2 pyridine *N*-oxyde, plus complexe et pour lequel il est peut-être possible de distinguer les deux stades, sera examiné ultérieurement.

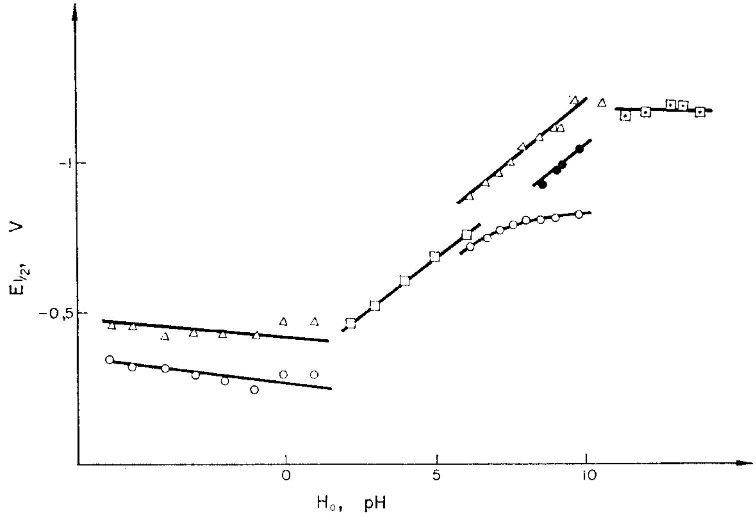

Fig. 4.—Variation de $E_{1/2}$ en fonction du pH pour l'acétyl-2 pyridine *N*-oxyde. ○: vague A_1; △: vague A_2; □: vagues $A_1 + A_2$; ●: vague A_3; ⊡: vagues $A_2 + A_3$.

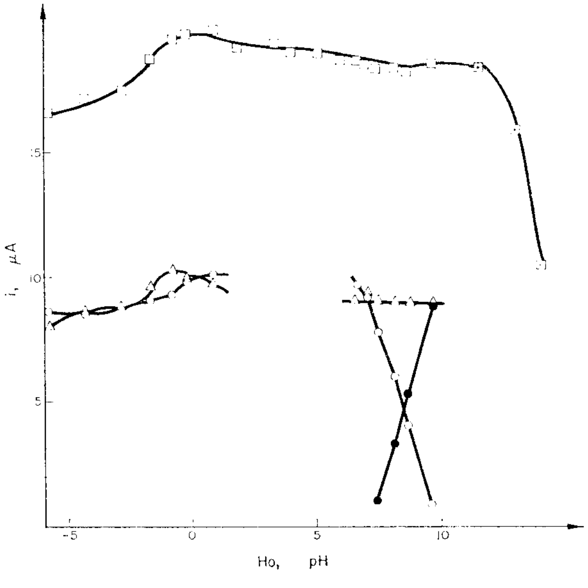

Fig. 5.—Variation du courant limite en fonction du pH pour l'acétyl-2 pyridine *N*-oxyde. Mêmes symboles que pour la Fig. 4.

En milieu alcalin le comportement devient plus compliqué, comme pour les formylpyridines *N*-oxydes. Une électrolyse à potentiel contrôlé de l'acétyl-4 pyridine *N*-oxyde à pH 13, sur le palier de la vague à 2F, a permis d'isoler le di(pyridyl-4',4")-2,3 butanediol-2,3 en quantité importante, et une très faible quantité d'hydroxyéthyl-4 pyridine. Dans ces conditions, malgré le processus apparent à 2F de la polarographie, le groupe *N*-oxyde est donc réduit. Les courbes donnant le nombre d'électrons participant à la réaction au cours de l'électrolyse sont d'ailleurs anormales. Au début, la réaction consomme 2F/Mole, puis après un certain temps 4F. Une étude détaillée du phénomène sera reprise ultérieurement.

Comme on peut le remarquer, la hauteur des polarogrammes en milieu neutre est toujours normale, au contraire de ce que l'on observait dans le cas des dérivés formylés correspondants. Ceci montre que l'hydratation dans ce milieu est négligeable.

SPECTROSCOPIE U.V. ET HYDRATATION DU CARBONYLE

Les équilibres entre le diverses formes hydratées ou ionisées ont été donnés dans l'article précédent.[1]

Les spectres U.V. présentent le même type de bandes que pour les formylpyridines simples[2] ou *N*-oxydes[1] (Fig. 6, 7et 8): une bande *K* à des longueurs d'onde inférieures à 240 nm; une bande *B* d'absorption benzénoïde dont le maximum est situé entre 250 et 300 nm suivant le composé et le milieu; la bande *R* d'absorption du carbonyle. La bande *B* est plus intense et plus large pour les dérivés benzoylés que pour les dérivés acétylés ou formylés; ceci est lié à la présence du noyau benzénique (conjugaison, absorption propre du noyau benzénique). La bande *R* n'est visible que dans le cas des acétyl-2 et -3 pyridines *N*-oxydes; pour les autres composés elle est sans doute plus ou moins masquée par la bande *B*.

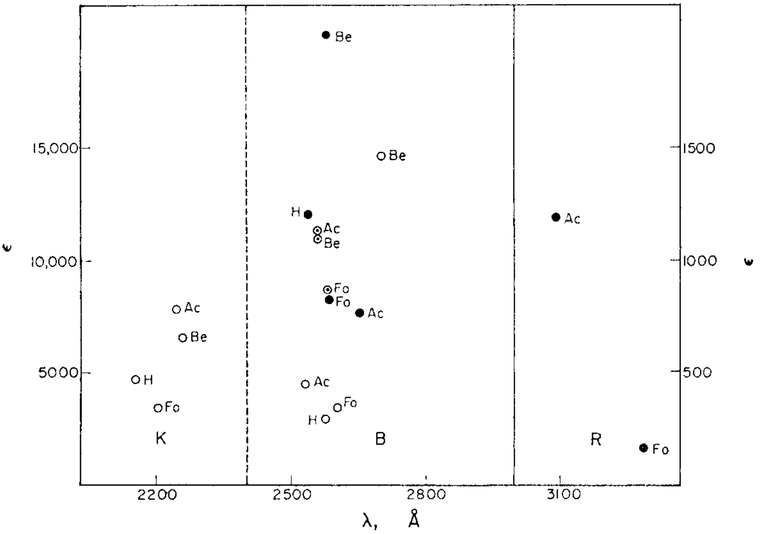

FIG. 6.—Position et intensité du maximum des bandes *K*, *B* et *R* pour les acétyl-2 benzoyl-2 et formyl-2 pyridines *N*-oxydes.
○: milieu acide; ●: milieu neutre; ⊙: milieu alcalin. Ac: acétyl; Be: benzoyl; Fo: formyl; H: pyridine *N*-oxyde non substitué.

Bande B

Milieu neutre. Pour l'acétyl-4 et la benzoyl-4 pyridines *N*-oxydes, on observe une bande *B* unique, dont le maximum se situe vers 290 nm; cette bande correspond donc à la bande B_2 d'absorption du noyau sous l'influence du carbonyle que l'on observait pour la formyl-4 pyridine[2] et le formyl-4 pyridine *N*-oxyde.[1] La bande B_1

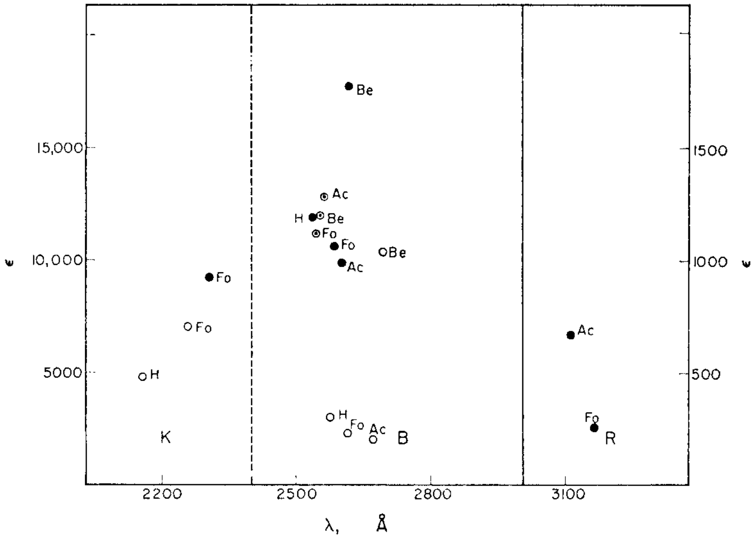

FIG. 7.—Position et intensité du maximum des bandes *K*, *B* et *R* pour les acétyl-3, benzoyl-3 et formyl-3 pyridines *N*-oxydes. Mêmes symboles que pour la Fig. 6.

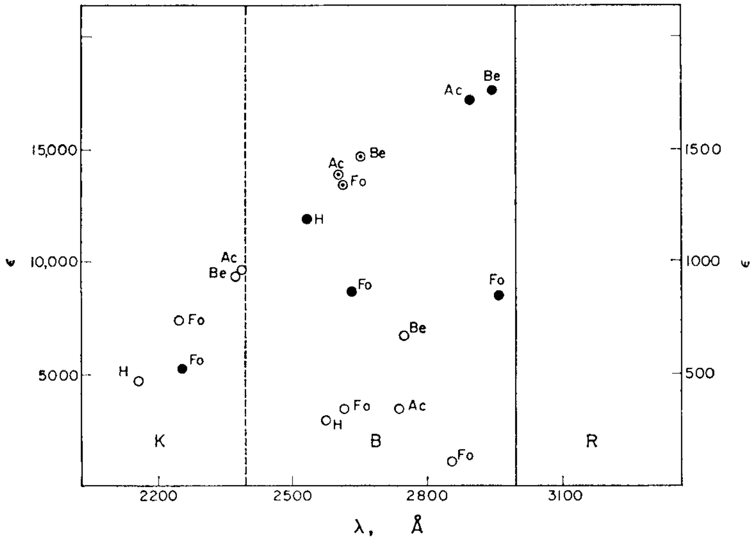

FIG. 8.—Position et intensité du maximum des bandes *K*, *B* et *R* pour les acétyl-4, benzoyl-4 et formyl-4 pyridines *N*-oxydes. Mêmes symboles que pour la Fig. 6.

correspondant[1,2] à l'absorption du noyau sous l'influence du groupement carbonyle hydraté n'existe pas. On en conclut que l'hydratation est pratiquement négligeable en milieu neutre pour les deux composés examinés, ce qui confirme les résultats polarographiques.

Pour les dérivés 2 et 3, la bande a une position normale (cf. dérivés formylés).

Milieu acide. La bande *B* est très diminuée pour tous les composés, conformément à ce que l'on observe normalement pour les *N*-oxydes de la pyridine.[3]

Milieu alcalin. On observe une évolution de la bande *B*. Pour les dérivés 4, la bande B_2 située vers 290 nm disparaît progressivement quand le pH augmente, tandis qu'apparaît une nouvelle bande B_1 vers 260 nm. On observait un comportement analogue pour la formyl-4 pyridine et le formyl-4 pyridine *N*-oxyde.[1] Cette évolution est attribuable à l'ionisation de l'hydrate et au déplacement de l'équilibre d'hydratation[1,4] (voir référence 1 pour les équilibres).

Pour les dérivés 2 et 3 la longueur d'onde du maximum ne varie pratiquement pas, mais on observe une variation de l'intensité, attribuable également à l'ionisation de l'hydrate.

Une étude en fonction du temps nous a permis de constater que les acétyl et les benzoylpyridines *N*-oxydes sont stables en milieu alcalin: par exemple une solution d'acétyl 4 pyridine *N*-oxyde dans la soude $10M$, abandonnée une heure et ramenée ensuite en milieu acide donne un spectre normal.

Bande R *du carbonyle*

La bande *R* des acétyl-2 et -3 pyridine *N*-oxydes apparaît nettement en milieu neutre. Son intensité, comme dans le cas des dérivés formylés, est très importante pour une bande de carbonyle. L'intensité est d'ailleurs nettement plus forte que celle observée pour les dérivés formylés, ce qui est en accord avec une hydratation négligeable en milieu neutre.

En milieu acide et alcalin, l'intensité de la bande diminue et pour de fortes acidités ou de fortes basicités la bande disparaît. Ceci montre que dans ces milieux il y a une forte hydratation du carbonyle.

Dans le cas de l'acétyl-4 pyridine *N*-oxyde, l'hydratation en milieu acide ne peut être directement mise en évidence, puisque la bande du carbonyle n'apparaît pas. Cependant l'analogie avec les dérivés 2 et 4 permet de conclure à une hydratation extrêmement probable.

Dans le cas des dérivés benzoylés, la bande du C=O n'apparaît pas non plus, et il n'est pas possible d'étudier l'hydratation en milieu acide. Mais étant donné que ces composés présentent en milieu alcalin une hydratation analogue à celle des dérivés acétylés, il est très vraisemblable qu'ils sont également hydratés en milieu acide.

*Etude des p*K

Les valeurs des pK apparents, pK_A (milieu acide) et pK_A' (milieu alcalin) figurent au tableau I. (Pour la définition des pK apparents, voir réf. 1 et 2.)

Les valeurs de pK_A sont du même ordre de grandeur que pour les formyl pyridines *N*-oxydes.[1] Ces valeurs dépendent[2] de la constante d'ionisation de la forme carbonyle libre et des constantes d'hydratation de la forme neutre et de la forme hydratée.

TABLEAU I.—pK DES ACETYL ET DES BENZOYLPYRIDINES *N*-OXYDES

	Position du substituant	pK_A	pK_A'
$COCH_3$	2	−0,1	13,2
	3	+0,2	13,7
	4	−0,6	14,2
COC_6H_5	2	−0,8	13,9
	3	+0,3	14,3
	4	−0,2	14,2

L'ignorance des valeurs des constantes d'hydratation ne permet pas de procéder à une étude quantitative. Cependant on a montré précédemment[2] que le pK_A doit être compris entre le pK de la forme carbonyle libre et celui de la forme hydratée (pK_3 et pK_4, voir réf. 2); comme d'autre part la valeur de ρ de la loi de Hammett appliquée aux pK correspondant à la protonisation du *N*-oxyde n'est pas extrêmement élevée[5] ($\rho \sim 2$), il est normal que les pK_A soient peu différents de ceux des formylpyridines *N*-oxydes.

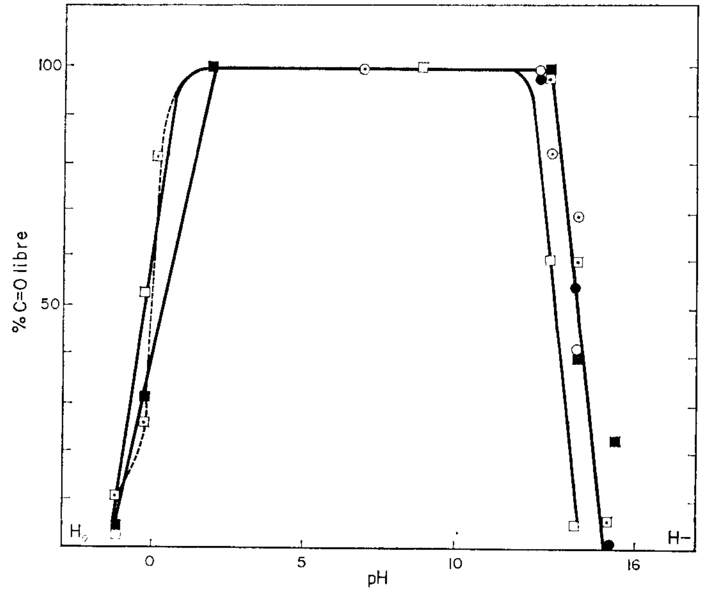

FIG. 9.—Graphique donnant le taux de carbonyle libre en fonction du pH pour les acétyl et benzoylpyridines *N*-oxydes.
□: acétyl-2; ■: acétyl-3; ⊡: acétyl-4; ○: benzoyl-2; ●: benzoyl-3; ⊙: benzoyl-4.

Les valeurs de pK_A' sont en revanche nettement plus élevées que celles obtenues dans le cas des formylpyridines *N*-oxydes. On peut rendre compte de ce fait de la façon suivante.

Si on suppose que la valeur de K_a (constante d'ionisation de l'hydrate)[1] varie peu d'une série à l'autre, on peut facilement calculer, à partir des données du travail précédent,[1] une formule qui permet de comparer les constantes d'un dérivé acétylé ou benzoylé et celles du dérivé formylé dans la même position:

$$1 + K_{1,x} = (1 + K_{1,f}) \frac{K''_{A,f}}{K''_{A,x}} .$$

Les indices x étant affectés aux constantes relatives aux acétyl et benzoylpyridines *N*-oxydes et les indices f à celles relatives aux dérivés formylés correspondants. L'hydratation étant beaucoup moins forte pour les dérivés acétylés et benzoylés, $K_{1,x}$ est grand ($K_{1,x} \gg K_{1,f}$), d'où la valeur plus faible de $K''_{A,x}$ ($K''_{A,x} \ll K''_{A,f}$), ce qui justifie le résultat trouvé pour les pK (p$K''_{A,x}$ > p$K''_{A,f}$). Les valeurs des constantes du membre de droite de l'équation précédente étant connues, on peut en tirer une valeur de $K_{1,x}$ qui permet de calculer le taux de carbonyle libre en milieu neutre. Le calcul donne pour tous les composés des valeurs comprises entre 99,5 et 100 %. Ces valeurs, bien que très approximatives, étant donné l'hypothèse faite sur les valeurs de K_a, confirment les résultats donnés plus haut en montrant que l'hydratation est très faible en milieu neutre.

Le graphique 9 qui donne le taux approximatif de carbonyle libre, résume les résultats obtenus. Ce taux a été déterminé en prenant 100 % pour le milieu neutre, conformément aux résultats obtenus, et en suivant la variation de la bande *R* pour les acétyl-2 et -3 pyridines *N*-oxydes, et de la bande *B* pour les autres dérivés.

PARTIE EXPERIMENTALE

Polarographie, spectroscopie U.V. et potentiel contrôlé

Les conditions expérimentales sont les mêmes que celles utilisées dans le travail précédent.[1] En milieu très alcalin nous avons utilisé lors des mesures spectroscopiques, la fonction d'acidité H_0.[6]

L'acétyl-4 pyridine *N*-oxyde a été électrolysé à pH 13, à −1,1 V (palier de la vague). Un abondant précipité blanc se forme rapidement; il est isolé par filtration et a été identifié par son spectre I.R. comme étant le di(pyridyl-4',4")-2,3 butane diol-2,3 (décomposition ~210°). Du filtrat on extrait par le chloroforme de faibles quantités d'hydroxyéthyl-4 pyridine, identifié par son spectre I.R.

L'acétyl-3 pyridine *N*-oxyde a été électrolysé dans l'acide sulfurique 0,1*N* à −1,0 V (vague *A*). Après le fin de l'électrolyse, la solution, neutralisée, est évaporée à sec, puis reprise par de l'alcool. Une deuxième évaporation à sec permet d'isoler un produit semi-solide brun; après séchage à la cloche à vide et recristallisation dans un mélange benzène–hexane, on obtient un solide blanc cristallisé, F = 110°, dont l'analyse correspond à la formule de l'alcool *N*-oxyde correspondant, 1'(α-hydroxyéthyl)-3 pyridine *N*-oxyde.

Analyse:				
	Calculé	C: 60,40 %	H: 6,53 %	N: 10,07 %
	Trouvé	C: 60,6 %	H: 6,7 %	N: 10,3 %

Synthèse des produits étudiés

Ont été préparés d'après les données de la littérature les acétyl-3 et 4 pyridines *N*-oxydes[7] et le benzoyl-2 pyridine *N*-oxyde.[8]

Pour l'acétyl-2 pyridine *N*-oxyde, on a employé la même méthode que pour les isomères 3 et 4, mais après évaporation du chloroforme, on a chassé par distillation sous pression réduite l'acétylpyridine qui n'avait par réagi et le résidu a été recristallisé dans le pentane. L'analyse montre que l'acétyl-2 pyridine *N*-oxyde ainsi obtenu cristallise avec une demi-molécule d'eau. F = 32°.

Le benzoyl-3 pyridine *N*-oxyde a été mentionné dans la littérature,[9] mais sa préparation et ses caractéristiques n'on pas été signalées. On a procédé comme pour le benzoyl-2 pyridine *N*-oxyde, mais l'huile obtenue après évaporation du chloroforme a été distillée sous pression réduite. La benzoyl pyridine qui n'a pas réagi passe d'abord; le benzoyl-2 pyridine *N*-oxyde passe ensuite vers 185° sous 0,13 mbar; ce composé fond vers 27° et est plus ou moins hydraté.

Le benzoyl-4 pyridine *N*-oxyde a été préparé comme le benzoyl-2 pyridine *N*-oxyde. F = 128–130°.

Summary—The polarographic behaviour of the acetyl- and benzoyl pyridine *N*-oxides shows the same type of anomalies as those which have previously been mentioned in the case of the corresponding formyl pyridine *N*-oxides: when the substituent lies in the 2 or 4 position, the *N*-oxide group and the carbonyl group are simultaneously reduced, the 3-isomers being normally reduced at all pH values. From the ultraviolet spectra, one concludes that the carbonyl group is hydrated, but not so strongly as in the case of the formyl pyridine *N*-oxides.

Zusammenfassung—Das polarographische Verhalten der Acetyl- und Benzoyl-pyridin-*N*-oxide zeigt dieselbe Art von Anomalien, wie sie früher bei den entsprechenden Formylpyridin-*N*-oxiden erwähnt wurden: bei Substitution in 2- oder 4-Stellung werden *N*-Oxidgruppe und Carbonylgruppe gleichzeitig reduziert, die 3-Isomeren werden bei allen pH-Werten normal reduziert. Aus den Ultraviolettspektren kann man schließen, daß die Carbonylgruppe hydratisiert ist, aber nicht so stark wie bei den Formylpyridin-*N*-oxiden.

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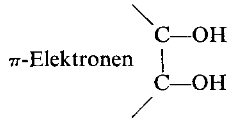
SHORT COMMUNICATIONS

Untersuchungen an Reagenzien für Niob und Tantal—VI Spektrophotometrische Bestimmung von Niob(V) und Tantal(V) mit Dibromgallussäure

(*Eingegangen am* 15 *Dezember* 1969. *Angenommen am* 31 *Januar* 1970)

In einer früheren Mitteilung[1] konnten wir zeigen, daß durch Substitution an einem organischen Grundkörper, welcher die analytisch-funktionelle Gruppe für Niob(V) und Tantal(V) enthält, die analytischen Eigenschaften der Komplexbildungsreaktionen beeinflußt werden können. Als Ergebnis systematischer Untersuchungen wurde die Dibromgallussäure als neues Reagens für die photometrische Bestimmung der Erdsäuren vorgeschlagen.

Von Nachteil ist, daß das System



wenig selektiv reagiert,[2,3] deshalb war zu erwarten, daß auch die Dibromgallussäure mit einer großen Zahl von Elementen farbige Reaktionsprodukte liefert. Im einzelnen wurden in saurer Lösung mit folgenden Ionen Reaktionen beobachtet: Ag(I), As(V), Au(III), Bi(III), Cd(II), Ce(IV), Co(II), Cr(VI), Cu(II), Fe(III), Ga(III), Hg(II), In(III), Ir(IV), Mn(II), Mo(VI), Nb(V), Os(VI), Pd(II), Pt(IV), Ru(IV), Sb(V), Ta(V), Ti(IV), Tl(III), U(VI), V(III), V(IV), V(V), W(VI), Zn(II).

In der analytischen Praxis können jedoch die Störungen bei der Bestimmung der Erdsäuren vielfach durch geeignete Trennungen (Ionenaustausch, Extraktion, Fällung) verringert werden. Die hier beschriebenen Methoden zur Bestimmung von Niob und Tantal sind unter Verwendung von Hilfskomplexbildnern ausgearbeitet, die unerwünschte Nebenreaktionen der Erdsäuren ausschalten und die Selektivität erhöhen. Über die Bildungsreaktionen und die Zusammensetzung der entstehenden Koordinationsverbindungen wurde bereits ausführlich berichtet.[4,5]

Bestimmungsmethoden

Der Einsatz der mitgeteilten Methoden richtet sich nach der jeweiligen analytischen Problematik (geforderte Genauigkeit und Empfindlichkeit, Gegenwart von Fremdelementen). Die angegebenen Bedingungen (Meßwellenlänge, pH-Wert, Reagenzkonzentration und s-Wert*) ergeben eine maximale Empfindlichkeit der Verfahren. Bei der Tantalbestimmung wurde besonders der Störung durch Niob(V) und bei der Niobbestimmung dem Einfluß von Tantal(V) Beachtung geschenkt. Daneben wurde versucht, die Komplexbildung von Dibromgallussäure mit Titan(IV), Wolfram(VI), Vanadin(V) und Molybdän(VI) auszuschalten, da diese Ionen ebenfalls intensiv gefärbte Reaktionsprodukte liefern. Von den üblichen anorganischen Ionen setzen Phosphat bzw. Sulfat in hohen Konzentrationen die Extinktion herab. Neutralsalze wie NaCl, $NaNO_3$ usw. wirken dagegen farbvertiefend. Die Standardabweichungen der einzelnen Verfahren wurden in Abwesenheit von Störelementen nach einer Methode von Dean und Dixon[6] bei $n = 4$ abgeschätzt. Als Störung sind Elementgehalte angegeben, welche die Extinktionen von Niob bzw. Tantal außerhalb der statistischen Schwankung beeinflussen.

Allgemeiner Arbeitsgang

Die Probe wird mit Kaliumdisulfat aufgeschlossen, die Schmelze in einer Hilfskomplexbildnerlösung in der Wärme gelöst und auf ein definiertes Volumen aufgefüllt. Einen aliquoten Teil pipettiert man in einen 50-ml-Meßkolben, erhöht—falls nötig—die Konzentration an Hilfskomplexbildner und bereitet die Lösung nach einer der angegebenen Arbeitsvorschriften vor. Gemessen wird nach dem Auffüllen auf 50 ml in Glas-bzw. Quarzküvetten geeigneter Schichtdicke gegen eine

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$$* \, s = \frac{\text{Konzentration an Hilfskomplexbildner}}{\text{Konzentration an Nb bzw. Ta}}\,; \text{ Konzentration in Mol/l.}$$

Blindprobe. Die Extinktionswerte sind bis zu einer Stunde konstant. Zur Auswertung dient eine Eichgerade, die unter gleichen Bedingungen aufgestellt wird.

Lösungen

Dibromgallussäure,[7] 10%ige wäßrige Lösung.
Ammoniumoxalat, 40 g/1.
Ammoniumtartrat, 15 g/1.
Natriumsulfit, 10%ige Lösung (täglich frisch bereiten)
ÄDTA, 0,1*M*
Salzsäure, 2*M*
Ammoniak, 2*M*

Niob

Methode 1. Die vorbereitete Probelösung mit Tartrat als Hilfskomplexbildner ($s < 100$) wird mit 10 ml Reagens versetzt, sofort 25 ml 2*M* Salzsäure zugegeben und bei 440 nm gemessen. $\varepsilon = 540$ $l.Mole^{-1}.mm^{-1}$. Das Lambert-Beer'sche Gesetz ist von 0 bis 36 μg Nb/ml erfüllt; Standardabweichung 1,5% (rel.) für 12 μg Nb/ml; Störungen (für 0,6 mg Nb) >1 mg Ta, >0,1 mg Ti, >0,6 mg W, >0,5 mg V, >0,05 mg Mo.

Methode 2. Die vorbereitete Probelösung mit Tartrat als Hilfskomplexbildner ($s < 500$) wird mit 5 ml Reagens versetzt, nach 15 Minuten 10 ml Natriumsulfitlösung zugegeben, der pH-Wert auf 4,5 eingestellt und nach 10 Minuten bei 380 nm gemessen. $\varepsilon = 1{,}08 \times 10^3$ $l.Mole^{-1}.mm^{-1}$. Das Lambert-Beer'sche Gesetz ist von 0 bis 60 μg Nb/ml erfüllt; Standardabweichung 1,4% (rel.) für 6 μg Nb/ml; Störungen (für 0,3 mg Nb) >0,3 mg Ta, >0,004 mg Ti, >0,1 mg W, >0,01 mg V, >0,1 mg Mo.

Methode 3. Die vorbereitete Probelösung mit Oxalat als Hilfskomplexbildner ($s < 150$) wird mit 5 ml Reagens sowie 10 ml Natriumsulfitlösung versetzt, der pH-Wert auf 5,3 eingestellt und nach 10 min bei 380 nm gemessen. $\varepsilon = 1{,}08 \times 10^3$ $l.Mole^{-1}.mm^{-1}$. Das Lambert-Beer'sche Gesetz ist von 0 bis 60 μg Nb/ml erfüllt; Standardabweichung 0,9% (rel.) für 6 μg Nb/ml; Störungen (für 0,3 mg Nb) >0,2 mg Ta, >0,1 mg Mo, >0,1 mg W, >0,005 mg V, >0,005 mg Ti.

Methode 4. Die vorbereitete Probelösung mit Tartrat als Hilskomplexbildner ($s < 200$) wird mit 2 ml ÄDTA-Lösung sowie 5 ml Reagens versetzt, der pH-Wert auf 2,4 eingestellt und nach 30 min bei 470 nm gemessen. $\varepsilon = 510$ $l.Mole^{-1}.mm^{-1}$. Das Lambert-Beer'sche Gesetz ist von 0 bis 36 μg Nb/ml erfüllt; Standardabweichung 1,8% (rel.) für 6 μg Nb/ml; Störungen (für 0,3 mg Nb) >5 mg Ta, >0,02 mg Ti, >10 mg W, >3 mg V, >0,1 mg Mo.

Tantal

Methode 1. Die vorbereitete Probelösung mit Oxalat als Hilfskomplexbildner ($s < 800$) wird mit 5 ml Reagens sowie 10 ml Natriumsulfitlösung versetzt, der pH-Wert auf 4,6 eingestellt und nach 10 min bei 320 nm gemessen. $\varepsilon = 1{,}62 \times 10^3$ $l.Mole^{-1}.mm^{-1}$. Das Lambert-Beer'sche Gesetz ist von 0 bis 100 μg Ta/ml erfüllt; Standardabweichung: 5,8% (rel.) für 10 μg Ta/ml; Störungen (für 0,5 mg Ta) >0,03 mg Nb, >0,01 mg Ti, >0,1 mg W, >0,01 mg V, >0,1 mg Mo.

Methode 2. Die vorbereitete Probelösung mit Oxalat als Hilfskomplexbildner ($s > 800$) wird mit 5 ml Reagens versetzt, der pH-Wert auf 2,0 eingestellt und bei 400 nm gemessen. $\varepsilon = 420$ $l.Mole^{-1}.mm^{-1}$. Das Lambert-Beer'sche Gesetz ist von 0 bis 200 μg Ta/ml erfüllt; Standardabweichung 0,3% (rel.) für 20 μg Ta/ml; Störungen (für 1 mg Ta) >30 mg Nb, >0,05 mg Ti, >2 mg W, >0,1 mg V, >0,2 mg Mo.

Bergakademie Freiberg
Sektion Chemie
Lehrstuhl für analytische Chemie
92 *Freiberg* (*Sachs*) *DDR*

GERHARD ACKERMANN
SIEGFRIED KOCH

Zusammenfassung—Es werden Arbeitsvorschriften zur spektrophotometrischen Bestimmung von Nb(V) und Ta(V) mit Dibromgallussäure in Gegenwart verschiedener Hilfskomplexbildner mitgeteilt. Neben der Empfindlichkeit und Standardabweichung der einzelnen Verfahren wird der Störeinfluß von Nb(V), Ta(V), Ti(IV), Mo(VI), W(VI) und V(V) angegeben.

Summary—Procedures are given for the spectrophotometric determination of Nb(V) and Ta(V) with dibromogallic acid, in the presence of various masking reagents. The sensitivities and standard deviations for the procedures are given, and the interfering elements in each case are listed.

Résumé—On donne des techniques pour le dosage spectrophotométrique de Nb(V) et Ta(V) avec l'acide dibromogallique, en la présence de divers agents de dissimulation. On donne les sensibilités et les écarts types pour les techniques, et l'on énumère dans chaque cas les éléments gênants.

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Separation of rhenium from molybdenum, tungsten, vanadium, platinum metals and other elements by reduction and solvent extraction

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THE SEPARATION of rhenium from molybdenum is often required[1] for its determination in molybdenites, concentrates and flue dusts, and the increasing use of rhenium as a minor constituent in alloys[2] of potential importance in rocketry, defence and atomic energy calls for rapid and simple methods for its determination in the presence of major constituents which are usually transition elements.

From acid solutions, separation from molybdenum is easily achieved by extracting either molybdenum[3–6] or rhenium[7–9] into organic solvents. The latter method has the advantage of separating rhenium from the alkali salts arising in a fusion, and from the bulk of other elements. Sulphuric acid solution is preferable[8] as many elements then accompany rhenium but little into the organic solvent. Isopentanol and isobutyl methyl ketone are two convenient solvents because of their high extractive power for rhenium, ready availability, low cost, quick separation of the phases and easy recovery of rhenium and the solvent. The former is preferable as it permits use of lower acidities. Small amounts of molybdenum, however, always accompany rhenium into the solvent and have to be removed by extraction as the xanthate,[10] the oxinate[11] or the thiocyanate.[8]

Sequestering, or lowering the oxidation state, might be expected to decrease the co-extraction of molybdenum and other elements; the acid concentration for optimum extraction of rhenium is still too high to permit their stable complexation, and decreasing the oxidation state remains the only alternative. However, the usually attainable stable lower oxidation state, Re(IV), is much less extracted[7] than Re(VII) at the same acidity. In sulphuric acid solution, hydrazine sulphate was found useful,[8] reducing Mo(VI) but not Re(VII). Many ions can be removed from solution or prevented from being extracted, by reduction to a very low oxidation state by zinc amalgam. Under these conditions Re(VII) is reduced to Re(−I)[13] which is found to be extractable from sulphuric acid by isopentanol, and this forms the basis of the following simple and rapid method for its separation from other elements.

EXPERIMENTAL

Reagents

Standard stock solutions were prepared by dissolving exact amounts of "Specpure" potassium perrhenate (Johnson Matthey, London) in known volumes of water, and diluting to yield lower concentrations. Solutions of the other elements were prepared from pharmacopoeia or analytical grade chemicals. Zinc amalgam, 2% w/w, was prepared[14] from zinc metal and pure mercury. Isopentanol and other solvents were used without purification.

Synthetic samples, composed as shown in Table II, were made by dissolving a commonly available compound of the element in 1M sulphuric acid. Tungstic acid precipitated but was not filtered off; it was transferred into the separating funnel along with the solution, and dissolved on reduction to W(III) by the amalgam.

Decomposition of natural samples

Reverberatory flue dust. Fuse about 1 g with sodium peroxide–carbonate mixture (3:2), leach with water and adjust to 1M in sulphuric acid.

Molybdenite. Fuse 0·5 g with sodium peroxide, cool, leach with water and acidify to 1M in sulphuric acid, or dissolve 0·5 g in conc. nitric acid, evaporate to 2 ml, neutralise and adjust to 1M sulphuric acid.

Separation procedure

A cold 1M sulphuric acid solution containing less than 200 μg of Re(VII) per ml and severa hundred mg of other elements was shaken with 15 ml of 2% zinc amalgam in a separating funnel for 3 min, the pressure being gently released at short intervals through the stop-cock. The aqueous layer was quickly covered with an equal volume of isopentanol and the amalgam run off and kept under 1M hydrochloric acid for further use. The aqueous phase was made 3M in sulphuric acid by careful dropwise addition of the concentrated acid, with strong cooling, and then shaken with the solvent for 3 min. The stem of the funnel was filled with solvent and the aqueous phase run off into another separating funnel containing an equal volume of the solvent, with which it was then shaken for 3 min. The end of the stem was immersed in the fresh solvent during the separation. After four such extractions in which contact of the aqueous layer with atmospheric oxygen was avoided as far as possible, the combined extracts were filtered free from any black particles of the elements. The rhenium was stripped by shaking for 2 min each time with two portions of equal volumes of water, after neutralization of the extracted acid with ammonia and oxidation of the reduced states with hydrogen peroxide. The back-extracts were evaporated to a suitable volume (and the peroxide simultaneously decomposed). The small amount of molybdenum, *etc* still accompanying rhenium was completely removed by the thiocyanate–pentyl acetate[8] or the oxine–chloroform[11] method. The aqueous solution was then free from all the elements likely to interfere in the determination of rhenium.

Microgram amounts of rhenium in the extract were determined colorimetrically by the tin(II) chloride–thiocyanate method,[15] the complex being extracted with isopentanol. Standard methods[12,15] were used to test for extraction of other elements.

RESULTS AND DISCUSSION

Mo(VI) is reduced to Mo(III) in sulphuric and hydrochloric acid solutions by zinc amalgam. At 2–8N acidity the extraction of Mo(III) by rhenium-extracting solvents (isopentanol, tributyl phosphate, isobutyl methyl ketone) is less than 1% from sulphuric and 2–10% from hydrochloric acid. Hence sulphuric acid is the preferred medium. The extent to which rhenium is reduced by zinc amalgam depends on its concentration and the acidity.[16] From 1M sulphuric acid and at <250 μg/ml it is reduced to Re(−I).[13,17] On the basis of the results in Table I, reduction in 1M sulphuric acid and extraction from the 3M acid were chosen. Concentrations of rhenium up to 200 μg/ml give similar results but higher concentrations result in black particles, probably of Re(0). SO_4^{2-}, PO_4^{3-}, Cl^-, F^- (as sodium salts in gram amounts) do not affect (±1%) the rhenium extraction.

TABLE I.—REDUCTION AND EXTRACTION OF RHENIUM AT DIFFERENT ACID CONCENTRATIONS

[H_2SO_4] for reduction, M	[H_2SO_4] for extraction, M	Extraction of Re, %
1	1	61
1	2	67
1	3	72
2	2	65
3	3	70
5	3	74
5	5	66
6*	3	8

* Black particles, probably of Re(0), appeared.

By shaking with zinc amalgam in 1M sulphuric acid[12,18] Pb(II), Hg(II), Tl(III), As(V), Se(VI), Te(VI), Ag(I), Cu(II), Au(III), Pt(IV and VI), Pd(II), Rh(III), Ir(III), Co(II), Ni(II) and perhaps Ru(III) and Os(VIII) are reduced to the elements and partly removed into the amalgam. Ce(IV), Ti(IV), V(V), W(VI), Cr(III and VI), Mn(VII) and Os(VIII) are reduced wholly or partially to Ce(III), Ti(III), V(II), W(III), Cr(II), Mn(II) and Os(?) respectively, which are not extracted by isopentanol from 3M sulphuric acid. Mo(VI), U(VI), Fe(III) and Ru(III) are reduced to Mo(III), U(III), Fe(II), Ru(?) and are extracted 0·7, 0·3, 2·0 and 0·04% respectively by isopentanol. Nitrate is reduced if in high concentration. Bi(III) is not extracted.

Except for small amounts of Mo, U, Fe and Ru, all elements of any importance are separated from rhenium by the reduction and subsequent extraction. These remaining elements can be completely separated from rhenium by thiocyanate–pentyl acetate[8] or the oxine–chloroform[11] extraction at a suitable pH. The rhenium in aqueous solution can be determined by any convenient method.

The wide applicability of the method is shown (Table II) by the analysis of molybdenites, flue dusts and synthetic samples containing alloying elements, with satisfactory results. The separation is simple, requiring cheap reagents commonly available in all laboratories, and rapid, taking only 20 min.

TABLE II.—ANALYSIS OF SOME SAMPLES BY THE PROPOSED METHOD

Composition of synthetic sample*				Re found, *μg*
Mo, *mg*	V, *mg*	W, *mg*	Re added, *μg*	
500	—	—	10·0	10·0
100	—	—	50·0	49·0
200	100	50	15·0	15·0
100	50	24	50·0	49·0
Os(15), Ru(15), Pt(14), Pd(15)			18·0	17·5
Os(6), Ru(5), Pt(6), Pd(5)			40·0	38·0
W(50), V(20), Cu(10), Cd(10), Ni(10), Mn(10), Cr(10), Se(10)			24·0	23·0
W(100), V(40), Cu(20), Cd(20), Ni(20), Mn(20), Cr(20), Se(20)			60·0	58·0
Reverberatory flue dust			70·0	69·5
Reverberatory flue dust			25·0	24·5
Molybdenite (Canada)			0·0020%†	0·0018%
Molybdenite (Norway)			0·0036%†	0·0039%

* Figures in brackets are the amount of the element, in mg.
† Reported values.

Under the same conditions, isobutyl methyl ketone extracts 70% Re and can also be used, but tributyl phosphate, isopentyl acetate and ether extract only 22, 16 and 2% Re respectively.

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Department of Chemistry
Kurukshetra University
Kurukshetra, India

V. YATIRAJAM
L. R. KAKKAR

Summary–Reduction in 1M H_2SO_4 with liquid zinc amalgam and extraction with isopentanol from 3M H_2SO_4, separates rhenium from almost all the interfering elements of importance in rhenium determination. The small amounts of Mo, U, Fe and Ru still accompanying rhenium are removed by the thiocyanate–pentyl acetate or the oxine-chloroform extraction. The method is simple, rapid and of very wide applicability. It is particularly useful in the determination of rhenium in various alloys and tungsten-containing samples.

Zusammenfassung—Die Reduktion mit flüssigem Zinkamalgam in 1 *M* Schwefelsäure und die Extraktion mit Isopentanol aus 3 *M* Schwefelsäure trennt Rhenium von fast allen wichtigen Störelementen. Die kleinen Mengen Mo, U, Fe und Ru, die das Rhenium noch begleiten, werden durch Thiocyanat-Pentylacetat- oder Oxin–chloroform-Extraktion entfernt. Das Verfahren ist einfach, schnell und sehr vielseitig anwendbar. Besonders nützlich ist es bei der Bestimmung von Rhenium in verschiedenen Legierungen und wolframhaltigen Proben.

Résumé—La réduction en H_2SO_4 $1M$ avec l'amalgame de zinc liquide et l'extraction par l'isopentanol de H_2SO_4 $3M$ séparent le rhénium de presque tous les éléments gênants qui sont d'importance dans la détermination du rhénium. Les petites quantités de Mo, U, Fe et Ru qui accompagnent encore le rhénium sont éliminées par extraction au thiocyanate-acétate de pentyle ou oxine-chloroforme. La méthode est simple, rapide et de très large possibilité d'application. Elle est particulièrement utile dans la détermination du rhénium dans divers alliages et dans les échantillons contenant du tungstène.

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Application of low-cost operational amplifiers to electrical detection in spark-source mass spectrometry*

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SPARK SOURCE mass spectrometer signals consist of repetitive ion-current pulses. Pulse-width and recurrence rate follow exactly the spark duty-cycle parameters. Figures 1 and 2 show reproductions of oscilloscopic displays of typical signals for a single mass peak in which the time variation of the ion-current is indicated. Heights of the individual pulses vary by approximately one order of magnitude as is shown in Fig. 1, although the average height is dependent upon the intensity of the specific spectral line focussed at the collector slit. Erratic fluctuation within pulses is common as is illustrated

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[*] Work was performed in the Ames Laboratory of the US Atomic Energy Commission. Contribution No. 2662.

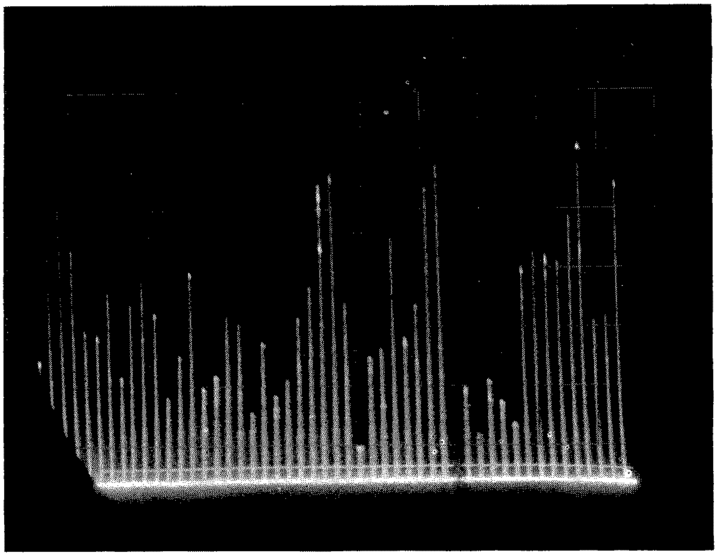

Fig. 1.—Photograph of oscilloscope traces of ion-current pulses. Spark pulse length 3·2 μsec and repetition rate 100 pulses/sec. Oscilloscope sensitivity 2V/cm and sweep rate 50 msec/cm (cm-spacings are the large blocks). The height of the fourth pulse from the right exceeded the maximum amplifier output voltage of 12·5V.

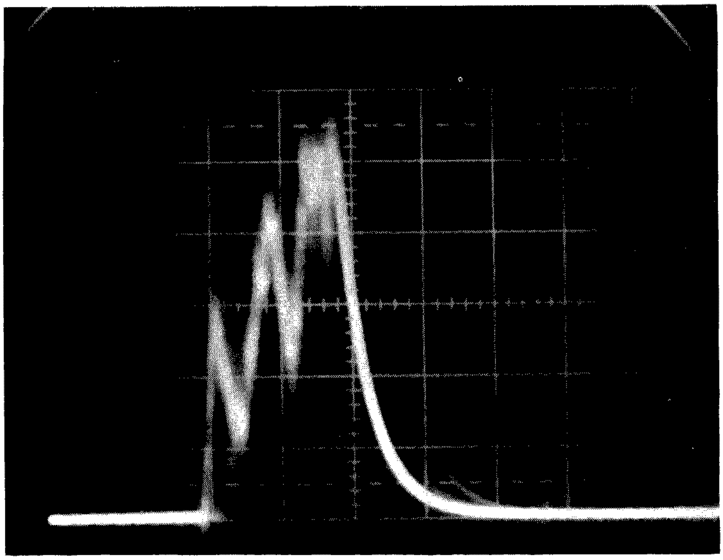

Fig. 2.—Photograph of oscilloscope trace of ion-current pulse. The pulse length was 100 μsec and repetition rate 10 pulses/sec. Oscilloscope sensitivity 10 mV/cm and sweep 50 μsec/cm.

in Fig. 2. A third feature of the signal is that the average ion-current intensity can vary by approximately an order of magnitude.

Owing to these fluctuations, signals detected at the spectrometer slit must be continuously measured as a function of the total ion current. This is accomplished by measuring the ratio of the signal at the main collector slit to the signal obtained from a beam monitor which is normally positioned in the field-free region between the electrostatic analyser and the magnetic analyser. Thus the detection system is required to handle two very erratic d.c. signals. Figure 3 is a schematic drawing of the original equipment used to measure this ratio. When a predetermined charge has accumulated on the monitor capacitor, the spark is shut off and the values of capacitor voltage are read from strip chart recordings of the vibrating reed electrometer (VRE) outputs. Although this system has been used with good accuracy,[2] it is difficult and time-consuming to use on a routine basis.

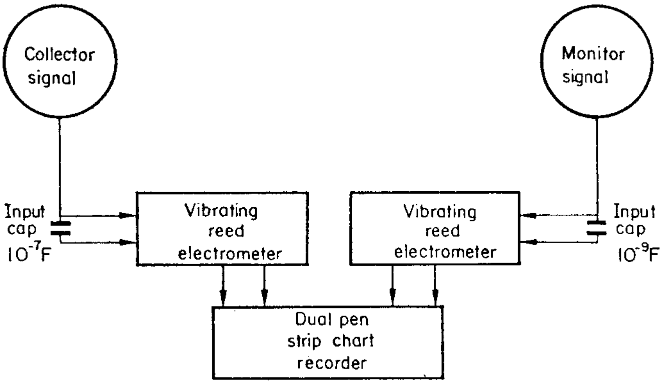

FIG. 3.—Schematic drawing of the original circuit for electrical detection.

An alternative to the capacitor system was assembled in which the input capacitors were replaced by resistors.[3] Input capacitances were adjusted to give time constants of about 0·2 sec. The VRE outputs were converted into frequencies and a ratio measurement was made with a ratio count meter. Again good accuracy was achieved and ease of data accumulation was considerably improved. However closer investigation of the actual operating conditions indicated two principal disadvantages: limited dynamic range and long amplifier time-constant. A long time-constant prevents observation of low-level non-homogeneities in a continuous measuring system since short-term variations will be averaged out. It also means that an error will be incorporated into the measurement, as illustrated in Fig. 4, which shows the voltage at the amplifier input rising very rapidly (*i.e.*, the initial voltage is determined by the size of the input capacitance and the coulombic charge in the initial portion of each pulse). The input voltage will fall according to the input circuit time-constant. As the time-constant for the input circuit becomes much smaller than the amplifier response-time, the area under the amplifier response curve will become less representative of the area under the input voltage curve. This is a source of potentially large systematic error.

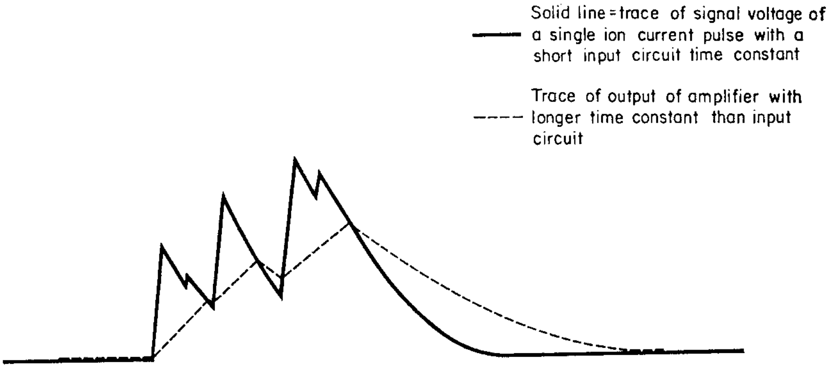

FIG. 4.—Illustration of possible source of systematic error for an amplifier with response time longer than the time-constant of the input signal voltage.

Recently, commercial operational amplifiers have become readily available. They have many desirable features but of principal interest here is their broad frequency response (down to d.c.), high input impedance, low noise and drift, low cost and small dimensions. At the time this work was initiated, Fairchild ADO-26 operational amplifiers were chosen. Since then, Analog Devices Model 147C operational amplifiers have also been tested. Both models have been satisfactory. It is the specific advantage of applying such amplifiers in conjunction with other equipment to the detection of spark-source ion-currents that we wish to stress. A schematic diagram of the circuit is shown in Fig. 5. The circuitry can be constructed to allow a choice of various input-resistances, capacitances or amplifier gain settings with a small space requirement. Optimum parameter settings will be discussed after the input capability of the voltage-to-frequency converters has been considered.

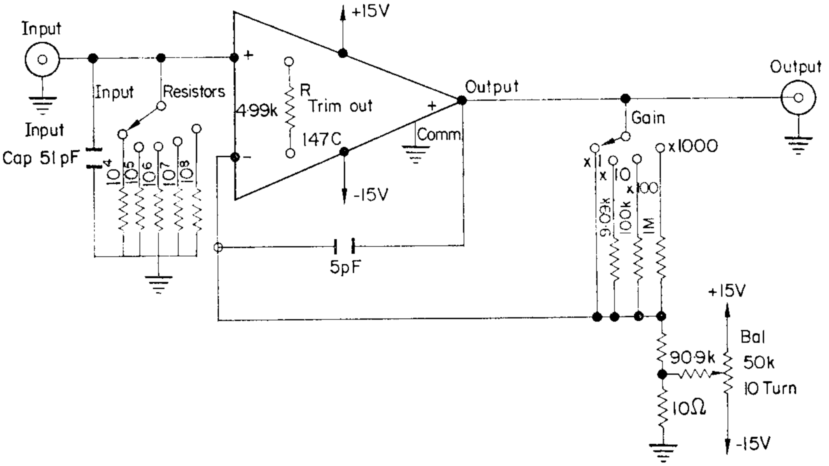

FIG. 5.—Operational amplifier circuit.

Voltage-to-frequency converter input capability

The voltage-to-frequency converters (Hewlett Packard, Model DY-2211/B) were tested for accuracy with pulsed inputs in which the pulse height (0–10 V), width (1–150 μsec), and rate (1–1000 Hz) were controlled. Output accuracy was within ±0·5% throughout all the ranges except for pulse heights greater than 5 V in which case the error rose to several per cent. This accuracy is retained when the maximum average input of 1·2 V-sec is maintained.

EXPERIMENTAL

Choice of operational amplifier operating parameters

Input capacitance and resistance of the amplifiers should be easily altered since optimum conditions will change under different sparking conditions. Maximum useful input resistance is limited by amplifier input resistance, input leakage paths, and amplifier zero stability. It was observed experimentally that the maximum input voltage was determined by the input capacitance. Thus the minimum capacitance must be determined either experimentally or by calculation from signal parameters. Normally an oscilloscope is connected at the amplifier output to display pulse shapes and the maximum amplifier output voltage. Another important condition is maintenance of the RC time-constant of the input circuit at some maximum value which should not exceed approximately $\frac{1}{3}$ of the repetition period. This assures a maximum signal-to-noise ratio while minimizing the possibility of amplifier overload from step-charge accumulation of several large sequential pulses. Typical signal conditions and representative calculations are given below.

$$\frac{\text{Signal (after electron multiplier)}}{\text{Concentration in sample}} = \frac{5 \times 10^{-13}\ \text{VF}}{\text{ppm}} = \text{unit sensitivity}$$

$$\text{Maximum amplifier output voltage} = 5\text{V}$$

$$\text{Minimum stray capacitance} = 20\,\text{pF}$$

$$\text{Maximum repetition rate of signal} \sim 320\ \text{pulses/sec}$$

$$\text{Maximum allowed RC time-constant} = \tfrac{1}{3} \times \tfrac{1}{320} \sim 10^{-3}\ \text{sec}$$

$$\text{Maximum resistance} := 10^{-3}/2 \times 10^{-11} = 5 \times 10^{7}\ \text{ohm}$$

Maximum concentration measurable, limited by overload considerations (assuming charges arrive simultaneously and with minimum stray capacitance in the input circuit) =

$$\frac{2 \times 10^{-11}\mathrm{F} \times 5\mathrm{V}}{5 \times 10^{-13}\,\mathrm{VF/ppm}} = 200\,\mathrm{ppm}.$$

With a resistance of 10^7 ohm and the same time-constant, the maximum concentration measurable would be 1000 ppm.

The overall circuit may best be considered as one which measures charge on a capacitor as it is discharged rapidly through a resistor. As mentioned earlier, the voltage-to-frequency converter output is directly proportional to the area under this decay curve. This combination of equipment provides some specific advantages. (*a*) The error illustrated in Fig. 4 is now negligible since the amplifier has sufficient speed of response to follow the input voltage pulse. (*b*) The output of the system can now reflect low-level sample inhomogeneities if this is desirable or these real variations can be averaged out by increasing the measuring period. (*c*) A good signal-to-noise ratio over a large dynamic range is obtained. An experimentally determined signal-to-noise ratio of 1000 is obtained between the signal due to an impurity present at 50 ppm and the standard deviation of the noise level with the spark running. An upper concentration limit of 500 ppm has been used without the amplifier overload voltage being exceeded (*cf.* maximum of 1000 ppm calculated above). This range of sensitivity can be achieved with the VRE only if ranging is employed. (*d*) Changing of circuit parameters is convenient and fast though normally not required during a given experiment.

It is generally recognized that capacity measurements can provide good accuracy when ratios of erratic low-level signals are measured. The work described here attempts to take advantage of this fact as well as permitting continuous monitoring of the signal. The system described provided good and variable time resolution for the observation of sample-inhomogeneities, retains the accuracy of capacity measurements, and uses convenient digital handling of data. If ion-counting is to be used at the collector (not feasible at the monitor), then a rapid analogue-to-digital conversion of the monitor signal would allow a more realistic short-term ratio measurement.

Since the advantages of electrical detection in spark-source mass spectrometry are now becoming apparent,[4-6] this work should be of interest to those laboratories considering upgrading photoplate mass spectrographs to allow electrical detection as well as photographic detection. The development of other systems which utilize logarithmic response amplifiers to provide good dynamic range capabilities presents a chance to compare advantages and disadvantages.

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Institute for Atomic Research and
Department of Chemistry
Iowa State University
Ames, Iowa 50010, *U.S.A.*

L. B. FURGERSON
R. J. CONZEMIUS
H. J. SVEC

Summary—An electrical detection system for spark-source mass spectrometry has recently been developed. This brief addendum describes an improvement in the signal amplification and its conversion to digital output which has important implications in the future development of electrical detection

Zusammenfassung—Ein elektrisches Nachweissystem für die Massenspektrometrie mit Funkenquelle wurde kürzlich entwickelt. Dieser kurze Zusatz beschreibt eine Verbesserung bei der Signalverstärkung und die Umsetzung des verstärkten Signals in einen digitalen Ausgang; die Verbesserungen haben wichtige Konsequenzen bei der zukünftigen Entwicklung des elektrischen Nachweises.

Résumé—On a élaboré récemment un système de détection électrique pour la spectrométrie de mass à source d'étincelle. Ce bref additif décrit une amélioration dans l'amplification du signal et sa conversion en sortie digitale qui a d'importantes incidences sur le développement futur de la détection électrique.

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Determination of silicone fluid surfactants in polyurethane/polyether blends by atomic-absorption spectroscopy

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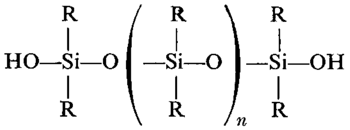
Silicone fluids are widely used as surfactants in foam manufacture, their function being to stabilize the foaming action and the cell size. The concentration of fluid used is critical and for most polyurethane blends is within the range 0·4–1·0 g/100 g of polyurethane polyol. Consequently, for purposes of quality control, costing, *etc*, a quick and accurate method for the determination of the silicone fluid content is desirable. Previous methods for the determination of silicone fluids have involved the decomposition of the silicone to silicate[1,2,3] which could then be estimated by conventional methods. Grantham and Hastings[4] have reported the determination of silicone resin by piperidine extraction but this method is lengthy and not considered suitable for many of the recently developed fluids. A method for the determination of some phenyl-substituted fluids by photoluminescence analysis has recently been described[5] but luminescence yields and hence sensitivities are low.

Atomic-absorption spectroscopy has recently been used for the determination of silicon in steels and similar materials.[6] With a pre-mixed nitrous oxide/acetylene flame, silicon concentrations of less than 1% could be rapidly determined. A fuel-rich flame was employed to suppress oxidation of the silicon to the non-absorbing oxide.

The present work describes the application of atomic-absorption spectroscopy to the determination of the silicone fluid content of some mixtures used in the manufacture of rigid polyurethane foams. By aspirating solutions of these fluids into the flame, attempts were made to measure the absorption of any atomic silicon released from the silicone fluid, the silicon line at 251·6 nm being used. The highly organic nature of the fluid should act to suppress oxidation of the silicon in the flame and so increase the sensitivity.

Two silicone fluids, A and B, have been investigated, together with their respective polyurethane blends, *i.e.*, polyurethane blend (1) was used in conjunction with silicone A and polyurethane blend (2) was used in conjunction with silicone B. Both silicone fluids may be represented by the general formula



$$HO\text{—}\underset{R}{\overset{R}{|\atop Si}}\text{—}O\left(\text{—}\underset{R}{\overset{R}{Si}}\text{—}O\right)_n\text{—}\underset{R}{\overset{R}{Si}}\text{—}OH$$

The blends were of the following composition

Polyether/polyurethane blend (1). (*I.C.I. Ltd.*). Polyether/polyurethane resin, water, foam cell modifier, tertiary amine catalyst. Viscosity 0·20 N.sec/m^2 at 25°.

Polyether/polyurethane blend (2). (*I.C.I. Ltd.*). Polyether/polyurethane resin, water, triethanolamine, tertiary amine catalyst. Viscosity 0·06 N.sec/m^2 at 25°.

The optimum experimental and instrumental conditions have been established and calibration graphs both for the pure silicone fluids and for mixtures of the fluids with their respective polyurethane blends have been prepared and compared.

EXPERIMENTAL

Apparatus

Unicam SP 90A Atomic Absorption Spectrophotometer, fitted with a 50-mm path-length nitrous oxide burner, and a high spectral-output hollow-cathode silicon lamp.

Reagents

Analytical grade reagents and distilled, demineralized water were used.

Stock solutions were made of silicones A and B (20 g/l.) in ethanol–water (1:1).

Establishment of optimum conditions

Although the silicone-polyol blends are fluid at room temperature, they must be diluted with a suitable solvent to ensure efficient nebulization into the flame. Therefore 1% w/w mixtures of silicones A and B in polyether blends (1) and (2) respectively, were diluted (5 g/50 ml) with the following solvents: water, 1% aqueous sodium chloride, 1% aqueous ferric alum, ethanol–water (1:1), ethanol and acetone. These solutions were sprayed into the flame under the optimum instrumental conditions described below. The results are given in Table I.

TABLE I.—THE EFFECT OF SOLVENT ON THE ABSORPTION BY SILICONE/POLYETHER BLENDS (1% w/w)

Solvent (blank set to zero)	Absorbance Silicone A/polyether (1) (scale expansion × 2)		Absorbance Silicone B/polyether (2) (scale expansion × 2)	
Water	0·210	0·211	0·200	0·200
1% Sodium chloride	0·240	0·241	0·229	0·231
1% Ferric alum	0·230	0·230	0·220	0·221
Ethanol–water (1:1)	0·200	0·202	0·199	0·198
Ethanol	0·201	0·202	0·200	0·199
Acetone (scale expansion × 1)	0·011	0·006	0·008	0·006

The various instrumental parameters were then investigated, the ethanol–water solution of silicone A/polyether blend (1) being used as sample. The best conditions are shown, together with those recommended by Price and Roos,[6] in Table II.

TABLE II.—OPTIMUM INSTRUMENTAL CONDITIONS FOR THE DETERMINATION OF SILICONE FLUIDS

	Our work	Price and Roos
Wavelength, *mm*	251·6	251·6
Slitwidth, *nm*	1·0	1·0
Observation height, *mm*	10	10
Nitrous oxide flow-rate, *l./min* at 207 kN/m^2 (30 psi)	5·0	5·0
Acetylene flow-rate, *l./min* at 104 kN/m^2 (15 psi)	5·0	4·0–4·5
Scale expansion	×2	—

Calibration graphs were prepared by taking 0–10 ml of stock solution of silicone fluid in 100-ml standard flasks, diluting to the mark with ethanol–water (1:1), mixing, and then measuring the atomic absorption under the conditions given in Table II, and were found to be linear for both fluids A and B. Linear plots were also obtained for the silicone/polyether blends: the standards were prepared by mixing 0–0·2 g of pure silicone with 10 g of polyether blend and diluting 5 g of each prepared standard to 50 ml in a graduated flask, with ethanol–water. Samples for analysis were similarly diluted (5 g to 50 ml).

DISCUSSION

Choice of solvent

In agreement with the findings of Price and Roos,[6] sodium and iron were found to enhance the absorption by silicon in the flame. However, in all the purely aqueous solvents, the silicone B/polyether blend (2) solution was very turbid. Acetone as solvent gave a very high blank reading and an alarming increase in the height of the flame. Furthermore, with both the purely organic solvents, carbon deposited on the burner slit was troublesome and had to be removed at frequent intervals. Ethanol–water proved to be the most convenient solvent and since it gave clear solutions and absorbance values only 10% below the maximum values obtained, it was used for further investigations.

The solution of silicone A containing iron(III) became dark brown on standing for 15 min. Obviously, if the sample to be measured contains appreciable amounts of iron or sodium, then allowances should be made for these in preparing the calibration graphs.

Choice of instrumental conditions

The instrumental conditions used in the present work are similar to those recommended by Price and Roos[6] except for the acetylene flow-rate which in our work is higher. Two advantages are gained here. First, the signal-to-noise ratio was greatest for the flow-rate range 4·8–5·0 l./min (*N.B.*, these flow rates are uncorrected) and secondly, once the flame had been established for about 20 min, carbon build-up on the burner was much less troublesome than at flow-rates between 4 and 4·5 l./min. At the latter flow-rates, a hard, brittle carbon deposit rapidly built up at the burner slit and quickly restricted gas flow; however, at 5·0 l/min, a soft carbon deposit formed which became negligible after 20 min.

Effect of time

For the reasons just given, the burner and lamp should be allowed to warm up for 20 min before any measurements are taken. The effect of time on the signal-to-noise ratio is shown in Fig. 1.

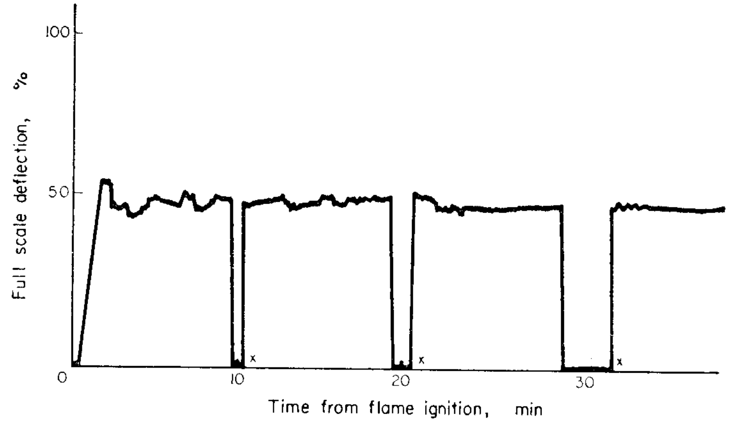


FIG. 1.—Effect of time on the signal-to-noise ratio for a solution containing 0·1 g of silicone A in polyether (1), in ethanol–water (1:1) as solvent (100 ml.). At position 'X', the recorder is on stand-by whilst any carbon deposit is removed.

Examination of the capillary tube, nebulizer chamber and all tubes up to and including the burner head showed no appreciable deposit of the viscose polyol after a long series of experiments, though this was first expected. Carbon build-up was troublesome only during the initial warm-up period and thereafter diminished considerably.

Sensitivity and detection limits

The sensitivity for 1% absorption, *viz.* the concentration of solution having an absorbance of 0·0044,[7] was calculated from each of the calibration graphs. For silicone A both as a solution of the pure fluid and in the presence of the polyurethane blend, it was 20 ppm and for silicone B 23 ppm.

The detection limit, defined as the concentration giving a reading equal to twice the standard deviation of a series of ten determinations at or near blank level, was 40 ppm for silicone A containing 10% of polyether blend (1). A scale expansion of ×4 was used to determine the detection limits.

Accuracy and reproducibility

The accuracy of the method was checked on the basis of the silicon content of fluids A and B, determined gravimetrically[1] and found to be 5·6% for A and 5·3% for B. These values are in agreement with those quoted by the manufacturers. Three random samples of each fluid, mixed with their respective polyether blends, were prepared by one of us and analysed by the other. The results are given in Table III.

TABLE III

Silicone A/Blend (1)		Silicone B/Blend (2)	
Si taken, *g*	Si found, *g*	Si taken, *g*	Si found, *g*
0·25	0·25	0·35	0·35
0·73	0·74	0·85	0·87
1·25	1·27	1·75	1·77

When 20 replicate dilutions of each stock silicone blend were measured under optimum conditions, all absorbance values obtained were within 1·2% of the mean.

The calibration graphs for silicone alone and in the presence of polyether blend had the same slope.

Department of Chemistry and Biology
John Dalton Faculty of Technology
Manchester Polytechnic
Chester St., Manchester 1, *U.K.*

G. DUNCAN*®
R. J. HERRIDGE

Summary—A method for the atomic-absorption determination of silicone fluid surfactants present in some polyurethane/polyether blends is described. The silicone fluid in the pure state, or in the presence of polyurethane blend, is diluted with a solvent and sprayed into the nitrous oxide/acetylene flame. The effects of solvent, instrumental conditions, time and presence of the polyurethane blends were investigated. Polyurethane/polyether blends do not interfere with the silicon absorption when the samples are dissolved in aqueous ethanol (1:1) and sprayed into a fuel-rich flame.

Zusammenfassung—Ein Atomabsorptions-Verfahren zur Bestimmung flüssiger oberflächenaktiver Substanzen auf Silikon-basis wird beschrieben, die in einigen Polyurethan-Polyäther-Verschnitten vorkommen. Die Silikonflüssigkeit wird allein oder in Gegenwart des Polyurethanverschnitts mit einem Lösungsmittel verdünnt und in die Lachgas-Acetylen-Flamme gesprüht. Die Einflüsse von Lösungsmittel, Einstellungen am Gerät, Zeit und Gegenwart der Polyurethanverschnitte wurden untersucht. Polyurethan-Polyäther-Verschnitte stören die Silicium-Absorption nicht, wenn die Proben in wäßrigem Äthanol (1:1) gelöst und in eine fette Flamme gesprüht werden.

Résumé—On décrit une méthode pour la détermination par absorption atomique d'agents surfactifs à liquide de silicone présents dans quelques mélanges polyuréthanne–polyéther. Le liquide de silicone à l'état pur ou en la présence de mélange de polyuréthanne est dilué par un solvant et pulvérisé dans la flamme protoxyde d'azote–acétylène. On a étudié les influences du solvant, des conditions instrumentales, du temps et de la présence des mélanges de polyuréthanne. Les mélanges polyuréthanne–polyéther n'interfèrent pas avec l'absorption du silicium lorsque les échantillons sont dissous en éthanol aqueux (1:1) et pulvérisés dans une flamme riche en combustible.

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* Present address: Chemical Technology Department, Northern College of Applied Arts and Technology, Kirkland Lake Campus, Kirkland Lake, Ontario, Canada.

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Stability characteristics of aqueous chloramine-T solutions

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THE PRESENT state of knowledge on the stability of chloramine-T has been critically reviewed by Bishop and Jennings.[1] Both the solid $CH_3C_6H_4SO_2NClNa\cdot 3H_2O$ and its aqueous solution (pH 7·7 for 0·05*M* solution) are quite stable in absence of other reagents if they are protected from direct sunlight, the titre decreasing by only 0·02% per month.

Most of the earlier work on chloramine-T in analytical chemistry involved its use as an oxidant in sulphuric or hydrochloric acid media, but recently thiourea,[2] thioacetamide[3] and dimethylsulphoxide[4] have been quantitatively oxidized in neutral, alkaline and weakly acidic media respectively by addition of excess of chloramine-T, the excess being determined iodometrically. It therefore became necessary to investigate the stability of aqueous chloramine-T solutions in various media.

EXPERIMENTAL

Chloramine-T of initial purity 98·5% was thrice recrystallized from conductivity water. An approximately 0·05*M* aqueous solution was prepared in triply distilled water and standardized iodometrically. The stability of aqueous chloramine-T solutions under different conditions was tested by comparing the titres before and after conditioning. The reproducibility in the titrations was generally ±0·1%.

RESULTS AND DISCUSSION

Results obtained for the very low pH media are presented in Table I. Solutions of chloramine-T are quite stable for short periods (at least 20 min) in 0·2–2*M* sulphuric acid or perchloric acid. This result is in agreement with the observations made by Nair.[5] In hydrochloric acid up to ~0·3*M*, chloramine-T is as stable as in sulphuric and perchloric acid media, but with higher hydrochloric acid concentrations, it decreases in stability probably because it oxidizes chloride to chlorine (tested for with starch-iodide paper and found to be evolved).

TABLE I.—STABILITY OF AQUEOUS CHLORAMINE-T SOLUTION (~0·05*M*) IN STRONGLY ACIDIC SOLUTIONS AT 25–30°C

		Iodometric titre value,* *ml* of thiosulphate (± 0·02), after	
		5 min	20 min
Perchloric acid	0·3*M*	21·75	21·75
	0·5*M*	21·75	21·75
	2·0*M*	21·75	21·75
Sulphuric acid	0·1*M*	21·75	21·75
	0·5*M*	21·75	21·75
	2·0*M*	21·75	21·75
Hydrochloric acid	0·1*M*	21·75	21·75
	0·3*M*	21·75	21·75
	0·5*M*	21·62	21·50
	1·0*M*	21·60	21·45
	1·8*M*	21·06	20·32

* Standard titre 21·75 ml.

Results for media of pH > 2·65 are presented in Table II. At pH 7·7 and above there was no deterioration in 1 hr in the strength of chloramine-T solution at room temperature. However, a slight but significant decrease in titre occurred at pH values between 2·65 and 5·65. The decrease in titre was rapid at first (during approximately 20 min) and then slowed down appreciably. Hence blank experiments must be made if chloramine-T is to be used in this pH range for indirect (back-titration) procedures. This loss in titre may be correlated mechanistically with Higuchi's recent observation on the rate of formation of dichloramine-T on varying the pH of chloramine-T solutions.

TABLE II.—STABILITY OF AQUEOUS CHLORAMINE-T SOLUTION (~0·05*M*) AT pH 2·65 AT 25–30°C

pH*	Iodometric titre value,† *ml* of thiosulphate (± 0·02), after		
	60 sec	20 min	60 min
2·65	21·75	21·66	21·66
3·14	21·75	21·66	21·66
3·44	21·75	21·66	21·66
3·74	21·75	21·61	21·61
4·00‡	21·71	21·52	21·52
4·15	21·71	21·47	21·47
4·45	21·61	21·23	21·23
4·75	21·61	21·23	21·23
5·00	21·61	21·23	21·23
5·65	21·66	21·48	21·48
7·7§	21·75	21·75	21·75
9·18¶	21·75	21·75	21·75
2*M* NaOH	21·75	21·75	21·75

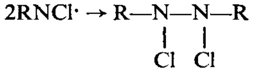
* Sodium acetate–acetic buffer system used unless otherwise stated.
† Standard titre 21·75 ml.
‡ Potassium acid phthalate buffer.
§ No buffer, pH of aqueous chloramine-T solution.
¶ 0·05*M* Borax buffer.

The behaviour of the rate of decrease in titre is similar to that of the rate of disproportionation of monochloramine-T ($CH_3C_6H_4SO_2NHCl$) into *p*-toluenesulphonamide and dichloramine-T[6] ($CH_3C_6H_4SO_2NCl_2$) as a function of pH. This indicates that the kinetics of the side-reaction closely follow those of the disproportionation reaction, and the loss in oxidative titre may be ascribed to minor side-reactions accompanying the major disproportionation reaction. The formation of dichloramine-T is reported[6] to involve the formation and eventual combination of free radicals:

$$R\dot{N}Cl + Cl\cdot \rightarrow RNCl_2$$

where $R = CH_3C_6H_4SO_2$.
The minor side-reactions occurring, namely,

$$2Cl\cdot \rightarrow Cl_2$$



$$2RNCl\cdot \rightarrow \underset{Cl}{\underset{|}{R{-}N}}{-}\underset{Cl}{\underset{|}{N{-}R}}$$

would cause a small loss in oxidative titre as the product $R_2N_2Cl_2$ will not oxidize iodide.

The rate of evolution of chlorine was evaluated from the relative intensities of the blue colour developed on starch–iodide paper. From sulphuric and perchloric acid media and media of pH > 7·7, there was no evolution of chlorine within 1 hr. However, in the pH range 2·65–5·65 the rate of evolution increased with increase in pH from 2·65, reaching a maximum at pH 4·7 and then decreasing again. In hydrochloric acid media, there was perceptible evolution of chlorine only when the acid concentration exceeded 0·5*M*. When chloramine-T solution was mixed with 4*M* hydrochloric acid, the starch-iodide paper first turned blue and then was rapidly bleached. This was ascribed to the oxidation of iodine to iodate by the large amount of chlorine evolved under these conditions. Hardy and Robson[7] reported a slow loss of chlorine from alkaline *N*-chloro-*N*-methylbenzamide solutions as a result of unidentified non-reversible reactions.

At higher temperatures (60–80°), chloramine-T solutions are stable only in highly acid (in absence of large concentrations of chloride, *e.g.*, in sulphuric acid) or alkaline conditions. We do not recommend the reagent for quantitative oxidations at higher temperatures in the pH range 2·0–5·65, as the blank values are very high and not reproducible.

Department of Chemistry
Indian Institute of Technology
Madras 36, *India*

V. R. S. RAO
D. VENKAPPAYYA
G. ARAVAMUDAN

Summary—Aqueous chloramine-T solutions in strongly alkaline medium are quite stable even up to 60°. In 0·2–2M sulphuric or perchloric acid at 25–30°, there is no loss in titre, but in hydrochloric acid solutions $>0·5M$, there is a loss in titre which increases with increase in hydrochloric acid concentration. This is ascribed to oxidation of chloride to chlorine. In the pH range 2·65–5·65 there is a small but reproducible loss in oxidative titre which is maximal at pH 4·7. This is ascribed to side-reactions occurring during partial disproportionation of monochloramine-T to dichloramine-T and *p*-toluenesulphonamide.

Zusammenfassung—Wäßrige Chloramin-T-Lösungen sind in stark alkalischem Medium bis 60° stabil. In 0,2–2 M Schwefel- oder Überchlorsäure bei 25–30° erfolgt kein Titerverlust; in salzsauren Lösungen über 0,5 M fällt der Titer mit steigender Salzsäurekonzentration ab. Dies wird einer Oxidation von Chlorid zu Chlor zugeschrieben. Im pH-Bereich 2,65–5,65 fällt der Oxidationstiter schwach, aber reproduzierbar, am meisten bei pH 4,7. Dies wird Nebenreaktionen zugeschrieben, die neben teilweisen Disproportionierung von Monochloramin-T zu Dichloramin-T und *p*-Toluosulfonamid herlaufen.

Résumé—Les solutions aqueuses de chloramine-T en milieu fortement alcalin sont tout à fait stables même jusqu'à 60°. En acide sulfurique ou perchlorique 0,2–2 M à 25–30°, il n'y a pas de perte en titre, mais en solutions d'acide chlorhydrique $>0,5$ M, il y a une perte en titre qui croît avec l'augmentation de la concentration en acide chlorhydrique. Ceci est attribué à l'oxydation du chlorure en chlore. Dans le domaine de pH 2,65–5,65, il y a une perte petite mais reproductible dans le titre d'oxydation, qui est maximale à pH 4,7. Ceci est attribué à des réactions secondaires se produisant durant la dismutation partielle de la monochloramine-T en dichloramine-T et *p*-toluènesulfamide.

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Spectrophotometric determination of ruthenium(III) and iridium(IV) with 8-hydroxyquinoline *N*-oxide

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ANALYTICAL applications and metal complexes of 8-hydroxyquinoline *N*-oxide were reported earlier.[1–10] During further investigations we have observed that platinum metal chloro-complexes heated with excess of oxine *N*-oxide at 100° for 30–60 min gave yellow to brown complexes, soluble in 30% v/v ethanol and having molar composition 1:1 and 1:2 (metal:ligand). We have found that oxine *N*-oxide can be used as a spectrophotometric reagent for determination of ruthenium(III) and iridium(IV).

EXPERIMENTAL

Reagents

Oxine *N*-oxide, prepared from oxine,[1] was used as the fresh aqueous solution. Stock solutions of the metals were prepared by dissolving ruthenium trichloride, sodium hexachlororhodate(III), palladium(II) chloride, potassium hexachloro-osmate(IV), sodium hexachloroiridate(IV) and chloroplatinic acid in 1*M* hydrochloric acid, and standardized spectrophotometrically[11] and gravimetrically.[12]

A 0·1*M* sodium chloride solution in 30% v/v aqueous ethanol was used as constant ionic strength medium.

RESULTS

Properties

Heating a 10-fold excess of oxine *N*-oxide with 1 ml of 0·004*M* platinum metal chloro-complex solution in a boiling water-bath for about 1 hr resulted in formation of the complex. The absorption spectra of the complexes thus obtained (and diluted to yield 25 ml of solution containing 30% v/v ethanol to make the solution homogeneous, and adjusted to suitable pH) were measured against a reagent blank, and are shown in Figs. 1–6. From the spectra it was concluded that under the conditions used each platinum metal forms two complexes with oxine *N*-oxide.

For complete colour development the initial pH proved important, and should be 1·5–3·0 for ruthenium(III), 4·0–6·0 for rhodium(III), 4·0–7·0 for palladium(II), 4·5–7·0 for osmium(IV), 5·0–7·0 for iridium(IV) and 4·0–6·5 for platinum(IV). The effect of pH on the absorbance of the complexes after formation is also given in Table I.

The complexes were found to be extractable to various extents in a variety of organic solvents (Table II).

The complex formation is slow at room temperature, but at 100° is complete in 30 min. To ensure complete formation the test solutions were all heated for 90 min. Once formed, the complexes were stable for 24 hr at room temperature and for 2 hr at 100°

For complete colour development, at least a 4:1 ligand:metal ratio was necessary. A 10-fold molar excess of reagent was therefore used, and the measurements were made against a reagent blank.

Procedures

Ruthenium(III). To 1 ml of chlororuthenate(III) solution add excess of oxine *N*-oxide solution, adjust the pH to between 1·5 and 3·0, and heat in a boiling water-bath for 60–90 min. Cool, adjust the pH to 3–5, and dilute to give a known volume containing 30% v/v ethanol and 2–20 ppm ruthenium. Measure the absorbance at 400 nm against a reagent blank.

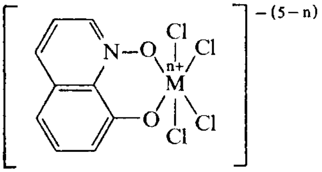
Iridium(IV). Heat the solution containing iridium(IV) and excess of oxine *N*-oxide at pH 4·0–7·0 in a boiling water-bath for 1 hr, cool, adjust the pH to >13, dilute to give a known volume containing 30% v/v ethanol and 1–7 ppm iridium, and measure the absorbance at 400 nm against a reagent blank.

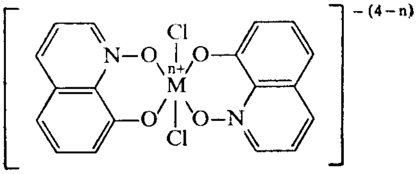
The interferences in the spectrophotometric determination of ruthenium(III) and iridium(IV) are reported in Table III. Chloroaurate(III) does not form a strongly coloured complex with the reagent.

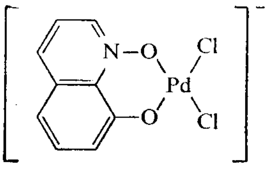
The metal:ligand ratio in the complexes was determined by Vosburgh and Cooper's method,[13] and found to be 1:1 and 1:2 for all the platinum metals.

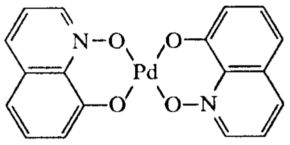
The ruthenium(III) and rhodium(III) complexes were found to be exchanged by IRA 410 anion-exchanger but not by IRC 50 or IRA 120 cation-exchangers. The palladium(II), osmium(IV), iridium(IV) and platinum(IV) complexes were partially exchanged by IRA 410(OH⁻) and the exchanged complexes were partially eluted with dilute hydrochloric acid (*ca.* 3*M*), but there was no exchange by IRC 50. The species formed are therefore either anionic or neutral complexes.

Tentative structures are shown below.









$M^{n+} = Ru^{3+}, Rh^{3+}, Os^{4+}, Ir^{4+}$ and Pt^{4+}.

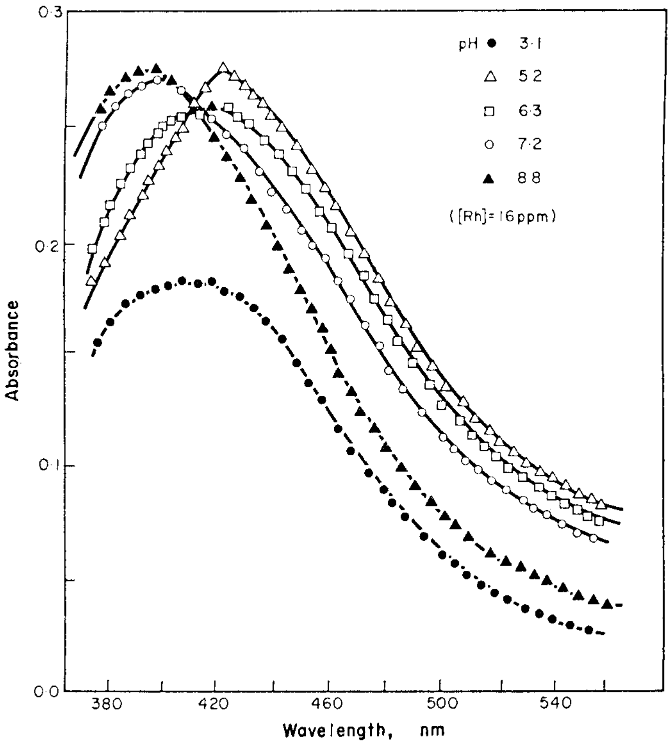


FIG. 1.—Absorption spectra of Rh(III) systems at different pH values.

TABLE I.—SPECTRAL CHARACTERISTICS OF THE PLATINUM METAL COMPLEXES IN 30% v/v AQUEOUS ETHANOL

Ion	Wavelength, *nm*	Molar absorptivity, *l.mole*$^{-1}$*.mm*$^{-1}$	pH range for constant absorbance	Conc. range for Beer's law, *ppm*
Ruthenium(III)	400*	486	3·0–5·0† 7·8–12·5§	1·8–20·0
	620‡	51	5·0–7·8	
Rhodium(III)	422*	183	4·7–5·7	4·0–50·0
	408‡	146	6·1–8·0	
	400*	185	8·2–8·9	
Palladium(II)	390*	253	7·5–8·2	3·5–35·0
	410*	228	9·0–10·0	
Osmium(IV)	420*	280	3·6–5·2	5·0–65·0
	412‡	252	6·0–9·2	
	400*	279	9·6–10·2	
Iridium(IV)	420*	362	2·5–5·0	4·0–48·0
	408‡	312	6·5–12·0	
	398*	1670	>13	1·0–7·0
Platinum(IV)	430*	72	2·3–6·1	20–200
	415‡	70	6·8–8·4	
	408*	75	9·1–10·0	

* Absorption maximum. § For the yellow solution.
† For the green solution. ‡ Isosbestic point.

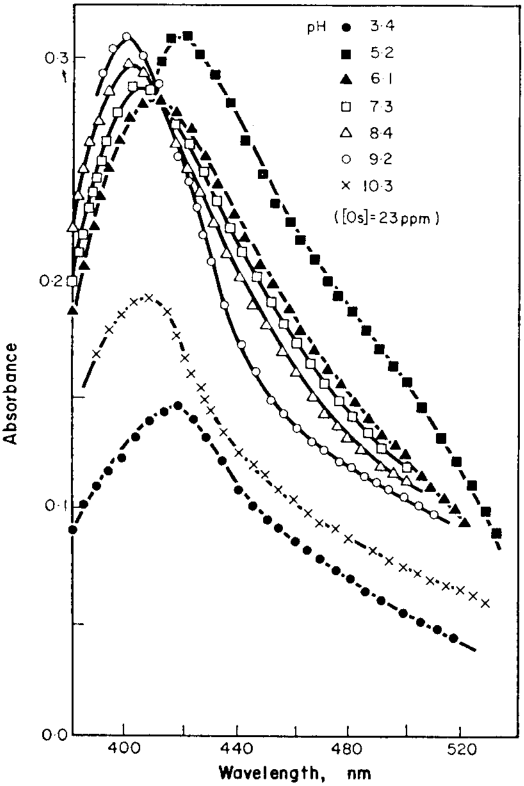


FIG. 2.—Absorption spectra of Os(IV) system at different pH values.

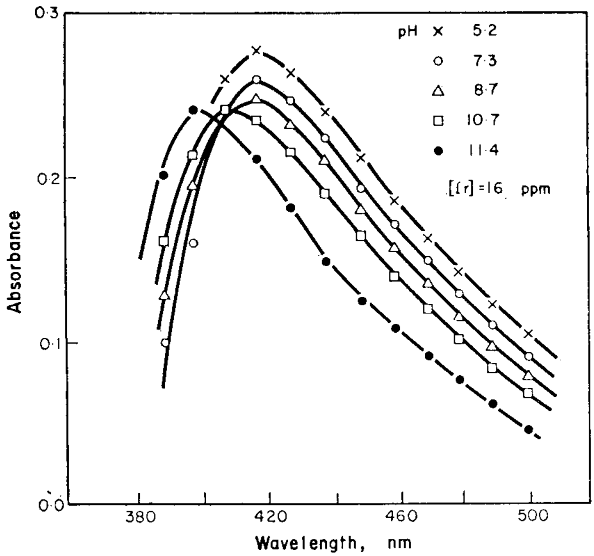


FIG. 3.—Absorption spectra of Ir(IV) system at different pH values.

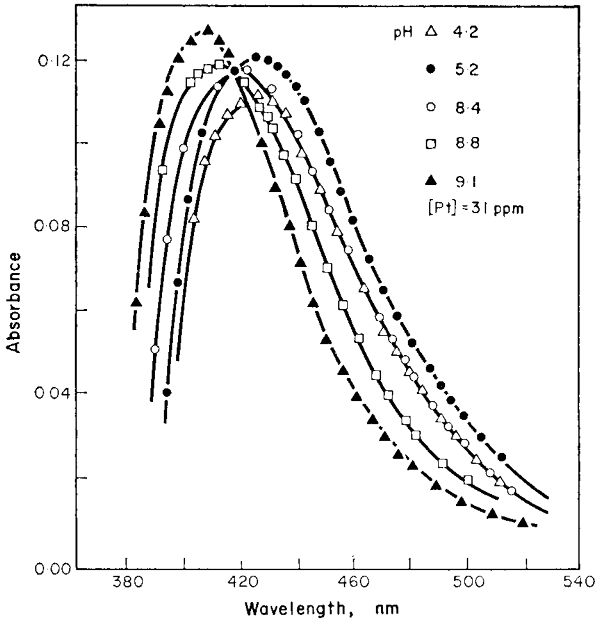


FIG. 4.—Absorption spectra of Pt(IV) system at different pH values.

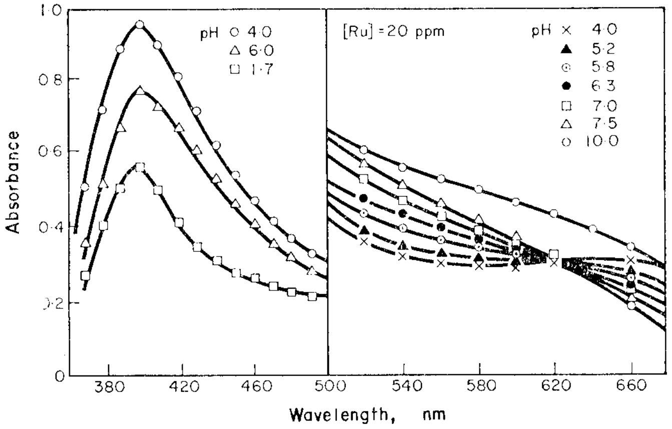


FIG. 5.—Absorption spectra of Ru(III) system at different pH values.

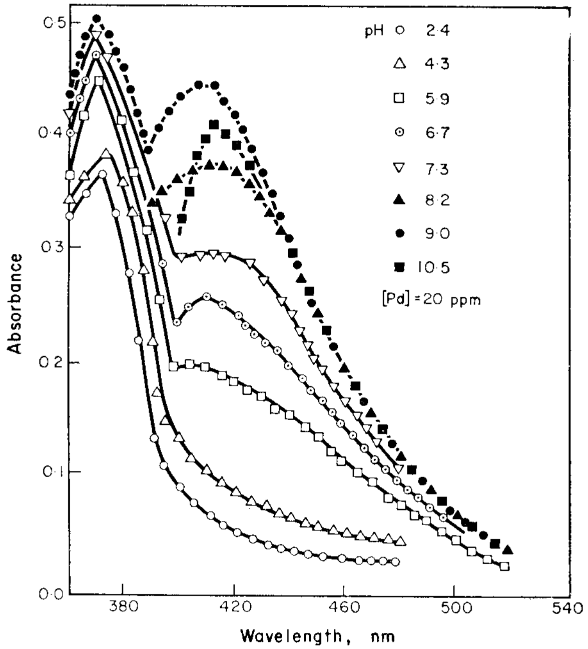


FIG. 6.—Absorption spectra of Pd(II) system at different pH values.

TABLE II.—EXTRACTABILITY OF THE PLATINUM METAL COMPLEXES

Solvent	Ru(III)	Rh(III)	Pd(II)	Os(IV)	Ir(IV)	Pt(IV)
Benzene	0	0	3	2	3	3
Toluene	0	0	3	2	3	3
Xylene	0	0	3	2	3	3
Petroleum ether	0	0	2	1	1	2
Butanol	3	1	3	3	3	3
Isobutanol	2	1	3	3	4	3
Pentanol	2	1	3	3	3	3
Isopentanol	2	1	3	3	3	3
Cyclohexanol	4	2	3	4	4	4
Chloroform	1	1	3	4	3	3
Carbon tetrachloride	0	0	2	1	2	2
o-Dichlorobenzene	2	3	4	2	3	3
Chlorobenzene	1	3	4	2	3	2
Bromobenzene	1	3	4	2	3	3
2-Butanone	4	0	3	2	3	2
Isobutyl methyl ketone	4	2	4	3	4	4
Nitrobenzene	2	2	3	3	3	2
Ethyl acetate	0	0	2	2	3	2
Diethyl ether	0	0	1	2	2	2
Tricresyl phosphate	0	2	3	2	3	2

Key: 0: not extractable; 1: the organic layer is just coloured yellow; 2: the solubility in the organic phase is less than that in the aqueous phase; 3: solubility in the organic phase is more than that in the aqueous phase; 4: extraction of the complex into the organic phase is nearly quantitative.

TABLE III.—INTERFERENCE DUE TO FOREIGN IONS IN THE SPECTROPHOTOMETRIC DETERMINATION OF RUTHENIUM(III) (4 ppm) AND IRIDIUM(IV) (1·2 ppm)

Ion and species	Tolerance *ppm*, for Ru(III)	Tolerance *ppm*, for Ir(IV)	Ion and species	Tolerance *ppm*, for Ru(III)	Tolerance *ppm*, for Ir(IV)
Ru(III) as $RuCl_6^{3-}$	—	8·0	Cl^- as NaCl	2000	4000
Rh(III) as $RhCl_6^{3-}$	2·8	9·0	NO_3^- as $NaNO_3$	2000	2000
Pd(II) as $PdCl_4^{2-}$	2·0	8·0	SO_4^{2-} as $Na_2SO_4\cdot10H_2O$	2000	2000
Os(IV) as $OsCl_6^{2-}$	4·0	15·0	Boric acid	1000	1000
Ir(IV) as $IrCl_6^{2-}$	0·5	—	Citric acid	300	300
Pt(IV) as $PtCl_6^{2-}$	13·0	50·0	Tartaric acid	500	500
Ni(II) as $NiSO_4\cdot7H_2O$	24·0	60·0	Oxalic acid, dihydrate	100	1000
Co(II) as $CoSO_4\cdot7H_2O$	14·0	16·0	Acetate as CH_3COONa	1000	1000
Fe(III) as $FeCl_3$	4·0	8·0	Au(III) as $AuCl_4^-$	2·0	3·0
Cu(II) as $CuSO_4\cdot5H_2O$	1·5	2·0	Ag(I) as $AgNO_3$	12·5	35·0
Cr(III) as $Cr(NO_3)_3\cdot9H_2O$	200	200			

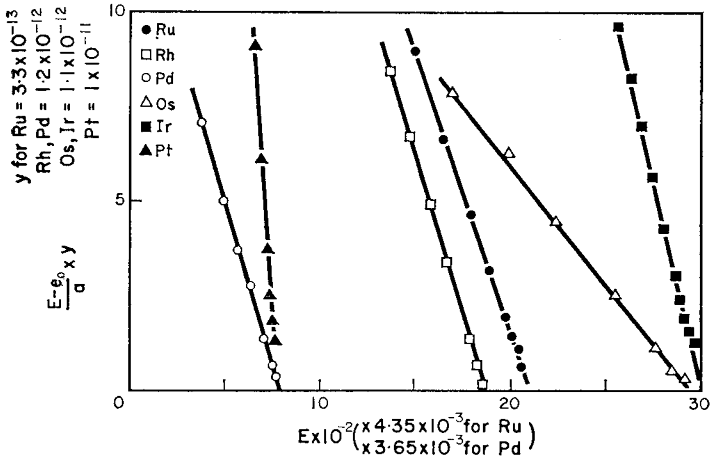


FIG. 7.—Plots of $(E - e_0)/a$ *vs.* E for the 1:1 complexes, at 420 nm.

TABLE IV.—THE STABILITY CONSTANTS OF THE PLATINUM METAL COMPLEXES WITH 8-HYDROXYQUINOLINE *N*-OXIDE

Ion	Wave-length, *nm*	log K_1	log K_2	log β_2	Ion	Wave-length, *nm*	log K_1	log K_2	log β_2
Ru(III)	400	11·48	5·40	16·88	Os(IV)	400	11·11	5·51	16·62
	420	11·34	5·32	16·68		420	11·11	5·56	16·67
	440	11·43	5·42	16·84		430	11·13	5·61	16·74
	460	11·40	5·45	16·85		440	11·12	5·45	16·57
	480	11·48	5·26	16·74		Average	11·12	5·53	16·65
	540	11·40	5·35	16·75					
	600	11·48	5·20	16·88	Ir(IV)	400	12·57	5·28	17·85
	Average	11·46	5·32	16·88		420	12·67	5·35	18·02
						440	12·57	5·28	17·85
Rh(III)	400	10·23	6·08	16·31		460	12·74	5·31	18·05
	420	10·26	5·93	16·49		480	12·58	5·26	17·84
	440	10·17	6·07	16·24		Average	12·62	5·30	17·92
	460	10·23	6·13	16·36					
	Average	10·22	6·05	16·27	Pt(IV)	400	12·85	4·06	16·82
						420	12·78	3·62	16·40
Pd(II)	390	10·40	6·92	17·32		440	12·82	3·88	16·70
	400	10·46	6·96	17·42		460	12·86	4·02	16·88
	410	10·45	6·93	17·38		Average	12·83	3·94	16·77
	420	10·46	6·85	17·31					
	Average	10·44	6·92	17·36					

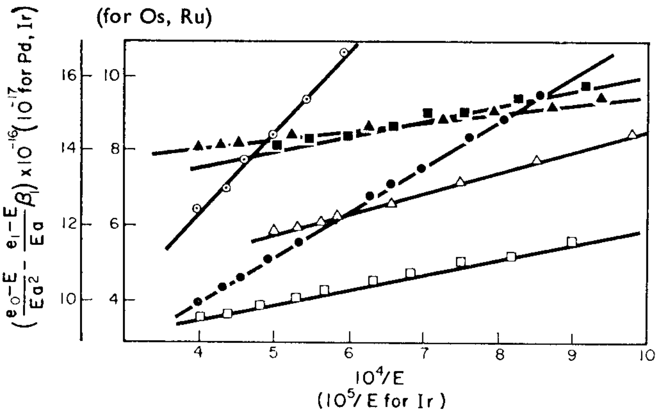


FIG. 8.—Plots of $[(e_0 - E)/a - (e_1 - E)\beta_1]/Ea$ *vs.* $1/E$ for the mixture of 1:1 and 1:2 complexes, at 420 nm.

Determination of stability constants

In the platinum metal–oxine *N*-oxide systems, besides the free metal ions, two coloured species ML_n ($n = 1$ or 2) are present (the number of chloride ions attached to the metal being ignored, as a constant excess of chloride is present, $0\cdot1M$). The stability constants were therefore determined by the following methods.[14]

The molar absorptivity E of a solution containing the complexes ML_n ($n = 0, 1, 2$) at equilibrium is given by

$$\frac{e_0 + e_1\beta_1 a + e_2\beta_2 a^2}{1 + \beta_1 a + \beta_2 a^2} = E, \tag{1}$$

where e_n is the molar absorptivity of the species ML_n, a is the equilibrium concentration of the free ligand, E is measured against a reagent blank, and β_n is the overall formation constant for the *n*th complex. The values of e_1 and β_1 were calculated by assuming the formation of only a 1:1 complex at low concentrations of free ligand; equation (1) can then be rearranged to

$$\frac{E - e_0}{a} = \beta_1 . e_1 - \beta_1 . E \tag{2}$$

so that plots of $(E - e_0)/a$ against E are straight lines with slope $-\beta_1$ and intercept $\beta_1 . e_1$. Figure 7 shows such plots at 420 nm and the values of β_1 obtained at different wavelengths are given in Table IV.

The values of the second stability constants were then calculated by plotting the left-hand side of equation (3) [which can be readily derived from equation (1)] against $1/E$ for values of a where both

$$\frac{e_0 - E}{Ea^2} + \frac{e_1 - E}{Ea}\beta_1 = \beta_2 - e_2 . \beta_2/E \tag{3}$$

1:1 and 1:2 complexes coexist, *e.g.*, at the isosbestic points, the resulting straight lines having slope $-e_2 . \beta_2$ and intercept β_2. Figure 8 shows such plots at 420 nm and the stability constants determined at different wavelengths are given in Table IV.

Department of Chemistry
The University
Delhi-7, India

R. D. Gupta
G. S. Manku
A. N. Bhat
B. D. Jain

Summary—The spectrophotometric characteristics and the stability constants of the yellow to brown 1:1 and 1:2 complexes of platinum metals with oxine *N*-oxide (existing as chloro mixed-ligand complexes) have been investigated. Oxine *N*-oxide can be used as a spectrophotometric reagent for ruthenium(III) and iridium(IV).

Zusammenfassung—Die spektrophotometrischen Eigenschaften und die Stabilitätskonstanten der gelben bis braunen 1:1-und 1:2-Komplexe von Platinmetallen mit Oxin-*N*-oxid (gemischte Chloro-Ligand-Komplexe) wurden untersucht. Man kann Oxin-*N*-oxid als spektrophotometrisches Reagens für Ruthenium(III) und Iridium(IV) verwenden.

Résumé—On a étudié les caractéristiques spectrophotométriques et les constantes de stabilité des complexes jaune à brun 1:1 et 1:2 des métaux du platine avec le *N*-oxyde d'oxine (existant à l'état de complexes chloro-ligand mixtes). Le *N*-oxyde d'oxine peut être utilisé comme réactif spectrophotométrique pour le ruthénium(III) et l'iridium(IV).

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Talanta, 1970, Vol. 17, pp. 783 to 784. Pergamon Press. Printed in Northern Ireland

LETTERS TO THE EDITOR

Use of $LiBO_2$ flux for K–Ar dating

SIR,

Purified vacuum-fused lithium metaborate ($LiBO_2$) has been tested as a flux in the vacuum melting of mineral samples for K–Ar dating and has been found to be completely compatible with typical argon extraction and analysis equipment. It has been tested with gold, molybdenum, and tungsten crucible material. The technique apparently produces no adverse gaseous products to interfere with gettering materials in the argon extraction train or with mass spectrometric measurements.

There are several advantages in using a flux. (1) Melting of even highly refractory samples can be accomplished at a relatively low temperature (~900°) with a greater assurance of complete melting and degassing of the sample. This might be useful in cases such as those reported by Webb and McDougall[1] in which extreme heating was necessary to release all of the radiogenic argon. (2) Power requirements (in this case from a radiofrequency generator) are greatly reduced. In fact, low temperature fusions could easily be produced by resistance heating, eliminating the high costs and safety hazards involved in radiofrequency heating. (3) Previous experiments suggest that lower-temperature fusions result in lower contamination by atmospheric argon, arising from heating of crucibles and fusion chambers. (4) The use of a low-temperature flux might inhibit the volatilization of potassium, allowing potassium determination on the fused residue.

The results of one such experiment with the Pennsylvania State University standard orthoclase Or-1* are shown in the Table. First, the sample was run by standard methods, wherein argon and potassium determinations were made on separate portions of sample. In a second run, 0·5 g of orthoclase was placed in an open thick-walled gold crucible containing 3·5 g of $LiBO_2$. This, in turn, was placed at the bottom of a silica test-tube. After fusion and argon extraction, a potassium determination was made on all the material left in both containers (some of the potassium having been deposited on the walls of the test-tube). Results for both the argon and potassium in this run are comparable to those obtained by the conventional methods. The low value of $14{\cdot}8_2\%$ K_2O obtained in the experiments reported here may or may not be due to slight potassium loss.

Sample	Experimental conditions	Total atmospheric argon, *mole*	K_2O, %	Radiogenic ^{40}Ar, *mole/g*
Or-1 (as received)	0·1-g sample in molybdenum and alundum crucibles, RF heated to 1400°.	$2{\cdot}6_5 \pm 0{\cdot}0_5 \times 10^{-10}$	$14{\cdot}9_2 \pm 0{\cdot}0_2$	$3{\cdot}5_4 \pm 0{\cdot}1_0 \times 10^{-10}$
Or-1A (sieved to + 325-mesh)	0·5-g sample in gold crucible and 0·15-m silica test-tube, with 3·5 g of vacuum-fused, crushed $LiBO_2$; RF heated to 893°.	$1{\cdot}8_6 \pm 0{\cdot}0_6 \times 10^{-10}$	$14{\cdot}8_2 \pm 0{\cdot}0_2$	$3{\cdot}5_0 \pm 0{\cdot}1_1 \times 10^{-10}$

Although much work remains to be done to prove the method for various types of samples, this experiment indicates that it may be possible to analyse the same portion of a sample for both potassium and argon. This would be most helpful in reducing errors arising from dividing samples, which, in some cases, may be very large.[2]

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* Chosen for this experiment because it is known to be a reliable potassium standard. Repetitive analyses have established its homogeneity at the 0·1-g sample level, and it varies by no more than $0{\cdot}0_2\%$ K_2O. Or-1 was washed through a 325-mesh sieve to prepare Or-1A. Then the original sample, the fines, and the 325-mesh material were compared; they differed by no more than $0{\cdot}0_2\%$ K_2O. While nothing was known of the argon content of Or-1A, it was hoped that it might be demonstrated to be a useful argon standard as well. The results indicate that, although it has a fairly young apparent age (16×10^6 y), it could, with further work, prove useful as an argon standard.

We are indebted to Dr. Oliver Preston, of the Intracast Division of Macronetics, Inc., of East Palo Alto, California, for assistance in the preparation of the vacuum-fused lithium metaborate used in these experiments.

U.S. Geological Survey
Menlo Park, Calif. 94025, U.S.A.
4 *March* 1970

JOAN C. ENGELS
C. O. INGAMELLS

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Talanta, 1970, Vol. 17, p. 784. Pergamon Press. Printed in Northern Ireland

Oxidation state of selenium dissolved in pure sulphuric acid

SIR,

Pure sulphuric acid, analytical reagent grade, always contains an ultramicro amount of selenium. The oxidation state of the selenium has not hitherto been established. The oxidation numbers of selenium are—II, 0, IV and VI. The existence of Se(—II) in pure sulphuric acid is highly unlikely, because H_2Se boils at $-42°$ and has a very low oxidation potential.

When 4-nitro-*o*-phenylenediamine is added to pure sulphuric acid, no 5-nitropiaselenol is produced. This indicates that selenium does not exist as Se(IV) in pure sulphuric acid. The oxidation state of selenium in pure sulphuric acid can be determined by comparing the results obtained when the previously described method[1] for determination of selenium [by oxidation of Se(0) to Se(IV) with bromine–bromide buffer and subsequent formation of 5-nitropiaselenol, which is determined by gas chromatography] is used with and without a preliminary reduction step with titanium(III). The results below show that when 0·053 μg of Se(0) is dissolved in carbon disulphide and the solution evaporated to dryness, recovery is quantitative when the 5-nitropiaselenol method[1] is used. Experiment 2 implies that pure sulphuric acid contains selenium only as Se(0). In experiment 3, 0·1 μg of Se(IV) deliberately added was determined quantitatively by the 5-nitropiaselenol method, along with selenium originally present in the sulphuric acid. Experiment 4 reveals that Se(VI) can only be determined if it is first reduced to Se(0). Experiment 5 indicates that the method with a preliminary reduction can be used to determine both Se(IV) and (VI). From these results, only elemental selenium exists in pure sulphuric acid.

Experiment	Se found, μg No reduction	Reduced with Ti(III)
(1) 0·053 μg of Se(0) in CS_2	0·054	
(2) pure H_2SO_4 (1 ml)	0·035	0·036
(3) pure H_2SO_4 (1 ml) + Se(IV) (0·1 μg)	0·133	
(4) pure H_2SO_4 (1 ml) + Se(VI) (0·1 μg)	0·040	0·136
(5) H_2SO_4 (Se-free) (1 ml) + Se(IV) (0·05 μg) + Se(VI) (0·1 μg)	0·080	0·156

For determination of Se(VI) the sample (1 ml of conc. sulphuric acid) is heated at ~90° on a water-bath with 5 ml of 0·03*M* titanium(III) chloride for 10–20 min. Then 3 ml of distilled water and 1·8 ml of 0·1*M* bromine–bromide buffer[1] are added and the solution is heated at 85° for 20 min, and is then processed by the method already described.[1]

Department of Chemistry
Faculty of Science
Okayama University
Okayama, Japan
17 *February* 1970

YASUAKI SHIMOISHI

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Talanta, 1970, Vol. 17, pp. i to ii. Pergamon Press. Printed in Northern Ireland

PUBLICATIONS RECEIVED

Microanalysis by the Ring Oven Technique: HERBERT WEISZ. 2nd Ed. Pergamon, Oxford, 1970. Pp. ix + 170. 60s. $8.00.

The success of the ring oven and of the first edition of this monograph is evidenced by the number of publications that have appeared since 1961 on applications of the technique. Users of the method will welcome having all the applications brought together.

Chemical Methods of Rock Analysis: PAUL G. JEFFERY. Pergamon, Oxford, 1970. Pp. xv + 509.

As a practical guide to the chemical analysis of rocks, this book represents the fruits of many years experience by a well known worker in the field. Methods are given for the determination of over 50 elements, and there are useful chapters on sample preparation and decomposition, statistics, and various schemes of analysis. The work seems likely to become a standard text for rock analysts for many years to come.

The Destruction of Organic Matter: T. T. GORSUCH. Pergamon, Oxford, 1970. Pp. viii + 152.

This little book gives a most useful compilation of information on the fate of various elements during destruction of organic matter by various means, particular attention being paid to the losses that may occur if an injudicious choice of conditions is made. The author is well known for his pioneering work in this field, during his tenure of the first Society for Analytical Chemistry research fellowship. As he points out, all too often little or no attention is paid to these matters, and they are glossed over-or not mentioned at all in many papers on trace analysis. This book will help to redress the balance and remove the excuse of ignorance.

Communications in Soil Science and Plant Analysis: J. BENTON JONES, JR., editor. Dekker, New York, 1970. $20.00 per annum (6 issues).

A new journal intended to give rapid publication of papers on soil science and crop production.

British Ceramic Abstracts: British Ceramic Research Association, Stoke on Trent, 1970. £10 per annum (6 issues); £2 per single issue.

A new abstracts journal dealing with all aspects of ceramics from raw materials to finished products.

Teoría y Práctica de la Cromatografía en Fase Gaseosa: L. GASCÓ. Publicaciones Cientificas de la Junta de Energia Nuclear, Madrid, 1970. Pp. XXIV + 549. 715 Pesetas.

For those who read Spanish, this is a useful exposition of the theory and practice of gas chromatography, with documentation up to 1969. The main emphasis is perhaps on theory and instrumentation, but there is fair coverage of applications to industrial, organic, inorganic and physical chemistry. Thanks to the habit of taking over scientific terminology from one language to another, the text is fairly readily interpreted even by someone who does not speak Spanish.

Quantitative Analytical Chemistry: Vol. I Introduction to Principles, Vol. II Short Introduction to Practice: H. A. FLASCHKA, A. J. BARNARD, JR. and P. E. STURROCK, Barnes & Noble, New York, 1969. Vol. I pp. xiii + 594, 52s. Vol. II pp. ix + 290, 27s.

The authors' aims are to present the fundamentals of the subject so that students of limited background can gain a good grounding in quantitative analytical chemistry. Classical and instrumental methods are dealt with. Small basic points, often skipped over in more advanced texts are dealt with clearly and simply. Worked or illustrative examples appear on nearly every page. In the practical directions the student is told what the procedure is all about, how to follow the procedure and then how to deduce what went wrong. Some may find it a bit pedantic but few, if honest, will not find some long-puzzling point explained, and the students for whom it is intended will offer thanks to the authors for their clarity.

Analytical Chemistry in Space: edited RICHARD E. WAINERDI. Pergamon, Oxford, 1970. Pp. vii + 277 £7.

One of the most exciting future projects for scientific research is the analysis of extraterrestrial material. The results of such analyses will provide new insights into problems connected with the origin of the solar system. This book describes progress in this fascinating new extension of analytical chemistry. Since many of the operations may be carried out by remote control in space or on other planets there is a concentration on instrumental techniques. The results of determinations using these techniques must be transmitted to earth by radio signals. Examples of these techniques which are described in the various chapters include mass spectrometry, neutron activation and neutron scattering. In addition to such descriptions, however, the book contains a considerable amount of material of cosmochemical interest with details of the structure and atmospheres of planets. This book will be of interest not only for the analytical chemist but also to students interested in astronomy and astro-physics. There is an excellent foreword by Sir Bernard Lovell.

Periodate Oxidation of Diol and Other Functional Groups. Analytical and Structural Applications: GLENN DRYHURST. Pergamon, Oxford, 1970. Pp. xii + 191. 70s. $9.50.

This book is a comprehensive review of one of the most valuable reactions encountered in carbohydrate chemistry, namely periodate oxidation. The material includes an account of preparative and analytical procedures and outlines the application of the method to structural chemistry. There are also details of anomalous periodate oxidations and of the use of the reaction in preparative organic chemistry. There is an extensive bibliography and the book will be of value to both analytical chemists and those involved in the study and practice of carbohydrate chemistry.

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SUMMARIES FOR CARD INDEXES

Radioactive kryptonates and their uses in chemical analysis: J. TÖLGYESSY and Š. VARGA, *Talanta*, 1970, **17**, 659. (Department of Radiochemistry and Radiation Chemistry, Slovak Technical University, Bratislava, Czechoslovakia.)

Summary—A review is presented of the uses of radioactive kryptonates in chemical analysis.

Versatile instrument for direct or differential a.c. resistance or conductance measurements on solutions: EUGENE D. OLSEN and ROBERT J. MARTIN, *Talanta*, 1970, **17**, 683. (Chemistry Department, University of South Florida, Tampa, Florida 33620, U.S.A.)

Summary—A simple but versatile instrument with an electronic (non-servo) measuring circuit is described which is capable of making direct or differential measurements of the resistance or conductance of solutions over an absolute resistance range from 0·1 Ω to 1 MΩ, in six linear ranges. Linearity is better than 2% on all ranges, and reproducibility is better than 1%. Drift is less than 1% over 12 hr. Less than 0·01% change in resistance can be measured in the differential modes, permitting more sensitive measurements than can be made in direct conductance measurements. Applications of the instrument for monitoring ion-exchange separations and conductometric titrations are illustrated.

Potentiometrische Kieselsäurebestimmung unter Verwendung einer Titanelektrode—I. Das Verhalten der Titanelektrode: GERHARD ACKERMANN und JOACHIM LANGE, *Talanta*, 1970, **17**, 693. (Lehrstuhl für Analytische Chemie, Sektion Chemie, Bergakademie Freiberg, 92 Freiberg (sachen) D.D.R.)

Summary—The response of a titanium electrode to fluoride in the presence of fluosilicate has been investigated. In 3*M* hydrochloric acid containing a small amount of iron(III) the electrode can be used to follow potentiometrically the titration of silicate with fluoride. As the reactions and response are rather slow, an automatic potentiometric titrator must be used.

РАДИОАКТИВНЫЕ КРИПТОНАТЫ И ИХ ПРИМЕНЕНИЕ В ХИМИЧЕСКОМ АНАЛИЗЕ:

J. Tölgyessy and Š. Varga, *Talanta*, 1970, **17**, 659.

Резюме—Приведеи обзор применений радиоактивных криптонатов в химическом анализе.

МНОГОСТОРОННЫЙ ПРИБОР ДЛЯ НЕПОСРЕДСТВЕННОГО ИЛИ ДИФФЕРЕНЦИАЛЬНОГО ИЗМЕРЕНИЯ ПЕРЕМЕННОТОЧНОГО СОПРОТИВЛЕНИЯ ИЛИ ПРОВОДИМОСТИ РАСТВОРОВ:

Eugene D. Olsen and Robert J. Martin, *Talanta*, 1970, **17**, 683.

Резюме—Описан онеслжный и многосторонный с электронной (не-серво) измерительной цепью которым можно проводить непосредственные или дифференциальные измерения сопротивления или проводимости растворов в диапазоне абсолютных сопротивлений от 0,1 Ω до 1 Ω, в шесть линейных диапазонов. Линейность больше чем 2 % во всех диапазонах, а воспроизводимость больше чем 1 %. Дрейф меньше чем 1 % в течение 12 ч. Можно измерить меньше чем 0,01 % перемены сопротивления дифференциальным способом, позволяя более чувствительные измерения чем в непосредственном измерении проводимости. Иллютрированы применения прибора в разделении ионообменным методом и в кондуктометрических титрованиях.

ПОТЕНЦИОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ ОКИСИ КРЕМНИЯ С ИСПОЛЬЗОВАНИЕМ ТИТАНОВОГО ЭЛЕКТРОДА—I. ХАРАКТЕРИСТИКА ТИТАНОВОГО ЭЛЕКТРОДА:

Gerhard Ackermann and Joachim Lange, *Talanta* 1970, **17**, 693.

Резюме—Изучен ответ титанового электрода на фторидион в присутствии фторосиликата. В 3 *M* соляной кислоте, содержащей небольщое количество железа(III), электродом можно пользоваться для потенциометрического титрования силиката с фторидом. Надо использовать автоматический прибор для потенциометрической титрации потому что реакции и ответ довольно медлены.

Potentiometrische Kieselsäurebestimmung unter Verwendung einer Titanelektrode—II. Das Bestimmungsverfahren: GERHARD ACKERMANN und JOACHIM LANGE, *Talanta*, 1970, **17**, 701. (Lehrstuhl für analytische Chemie, Sektion Chemie, Bergakademie Freiberg, 92 Freiberg (Sachsen), D.D.R.)

Summary—The conditions for the automatic potentiometric titration of silica with $1M$ potassium fluoride, using a titanium electrode, are described. The effect of temperature and other factors on the blank value is reported. The standard deviation is 1 mg for samples up to 240 mg of SiO_2. Aluminium, iron, borate, nitrate, sulphate and phosphate interfere.

Sulphur in foodstuffs—I. Determination as sulphate: G. BESWICK and R. M. JOHNSON, *Talanta*, 1970, **17**, 709. (Department of Applied Biology and Food Science, Borough Polytechnic, Borough Road, London, S.E.1.)

Summary—Sulphate formed by the oxygen-flask combustion of foodstuffs may be determined colorimetrically with barium chloranilate, titrimetrically with barium perchlorate, or turbidimetrically with barium chloride. The difficulties encountered in each method, including interferences, have been investigated. The turbidimetric procedure is recommended if high precision is not required and due account is taken of interference from phosphate, iron, calcium and magnesium; the other two methods are unsuitable for routine work.

Naphtho(2,3-*d*)-2-selena-1,3-diazole as a reagent for the determination of macro to submicro quantities of palladium: HERBERT K. Y. LAU and PETER F. LOTT, *Talanta*, 1970, **17**, 717. (Department of Chemistry, University of Missouri-Kansas City, Kansas City, Missouri 64110, U.S.A.)

Summary—Five analytical procedures, gravimetric, spectrophotometric, radiometric, fluorometric and atomic-absorption, have been developed for the determination of macro to submicro amounts of palladium. The methods are based on the reaction of $PdCl_2$ with naphtho[2,3-*d*]-2-selena-1,3-diazole. Analytical conditions such as the reaction time, concentration ranges, effect of pH and of 68 foreign ions, and solvent extraction were studied. Information relating to the structure and formula of palladium–piazselenol reaction products is included.

ПОТЕНЦИОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ ОКИСИ КРЕМНИЯ С ИСПОЛЬЗОВАНИЕМ ТИТАНОВОГО ЭЛЕКТРОДА—II. МЕТОД ОПРЕДЕЛЕНИЯ:

Gerhard Ackermann and Joachim Lange, *Talanta,* 1970, **17**, 701.

Резюме—Даны условия для автоматического потенциометрического титрования окиси кремния $1M$ фторидом калия с использованием титанового электрода. Определены влияния температуры и других факторов на фон. Стандартная ошибка составляет 1 мг для образцев до 240 мг SiO_2. Алюминий, железо, борат, нитрат, сульфат, и фосфат мешают определению.

СЕРА В ПИЩАХ—I. ОПРЕДЕЛЕНИЕ В ФОРМЕ СУЛЬФАТА:

G. Beswick and R. M. Johnson, *Talanta* 1970, **17**, 709.

Резюме—Сульфат образован сожжением пищевих веществ в колбе наполненной кислородом определяют колориметрически хлоранилатом бария, титриметрически перхлоратом бария или турбидиметрически с хлоридом бария. Изучены трудности встречающиеся в каждом из этих методов, включая мешающие действия. Рекommендован турбидиметрический метод если не требуется высокая воспроизводимость и если учитывать эффект фосфата, железа, кальция и магния. Два других метода неподходящие для серийного анализа.

НАФТО(2,3-*d*)-2-СЕЛЕНА-1,3-ДИАЗОЛ В КАЧЕСТВЕ РЕАГЕНТА ДЛЯ ОПРЕДЕЛЕНИЯ МАКРО-ДО СУБМИКРОКОЛИЧЕСТВ ПАЛЛАДИЯ:

Herbert K. Y. Lau and Peter F. Lott, *Talanta* 1970, **17**, 717

Резюме—Разработано пять аналитических методов–весовой, спектрофотометрический, радиометрический, флуорометрический и атомно-абсорбционный—для определения макро—до субмикроколичеств палладия. Методы основаны на реакции $PdCl_2$ с нафто (2,3-*d*)-2-селена-1,3-диазолом. Изучены аналитические условия, на пример продолжительность реакции, пределы концентраций, эффект pH и 68 странных ионов и экстрагирование растворителями. Приведены данные касающиеся строения и формулы продуктов реакции палладия с пиазселенолом.

Hydrocarbures et pollution atmosphérique: Denise Halot, *Talanta*, 1970, **17**, 729. (Laboratoire de Chimie Analytique, Faculté de Médecine et de Pharmacie, 37-Tours, France.)

Summary—A survey is given of the source of hydrocarbons found in the atmosphere, of their toxicity, and of the methods of analysis available for polycyclic aromatic hydrocarbons.

Enthalpimetric determination of fluoride: Carl E. Johansson, *Talanta*, 1970, **17**, 739. (Department of Analytical Chemistry, Chemical Center, University of Lund, Lund, Sweden.)

Summary—An injection calorimeter used for analytical and thermochemical purposes is described. Amounts of sodium fluoride between 6 and 8 mg are determined with an error of ±0·04 mg. The calorimeter is also used in determining ΔH for the precipitation of lead chlorofluoride from water solutions with an ionic strength of $1M$. $\Delta H = 36{\cdot}6 \pm 0{\cdot}3$ kJ/mole. Quantitative analysis is made with a flow microcalorimeter with amounts of sodium fluoride between 40 and 400 μg and an error of $\pm 4\ \mu$g. An ion-exchange system for separation of fluoride from phosphate, sulphate, nitrate and chloride is also described.

Etude polarographique et physicochimique de *N*-oxydes—II. Mécanisme de réduction et phénomènes d'hydratation des acétyl et benzoyl pyridines *N*-oxydes: E. Laviron, R. Gavasso et M. Pay, *Talanta*, 1970, **17**, 747. (Laboratoire de Polarographie organique associé au CNRS, Faculté des Sciences, Dijon, France.)

Summary—The polarographic behaviour of the acetyl- and benzoyl pyridine *N*-oxides shows the same type of anomalies as those which have previously been mentioned in the case of the corresponding formyl pyridine *N*-oxides: when the substituent lies in the 2 or 4 position, the *N*-oxide group and the carbonyl group are simultaneously reduced, the 3-isomers being normally reduced at all pH values. From the ultraviolet spectra, one concludes that the carbonyl group is hydrated, but not so strongly as in the case of the formyl pyridine *N*-oxides.

УГЛЕВОДОРОДЫ И ЗАГРЯЗНЕНИЕ АТМОСФЕРЫ:

Denise Halot, *Talanta* 1970, **17**, 729.

Резюме—Приведен обзор источников углеводородов обнаруживаемых в атмосфере, их токсичности и аналитических методов для определения многоядерных ароматических углеводородов.

ЭНТАЛЬПИМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ ФТОРИДА:

Carl E. Johansson, *Talanta*, 1970, **17**, 739.

Резюме—Описан инжекционный калориметр применимый в анализе и в термохимии. Прибор позволяет определять фторид натрия в диапазоне 6–8 мг с ошибкой ±0,04 мг. Калориметр также использован для определения ΔH в осаждении хлорофторида свинца из водных растворов имеющих ионную силу 1 M. $H = 36{,}6 \pm 0{,}3$ кдх/моль. Количественные анализы проведены проточным микрокалориметром на 40–400 мкг фторида натрия с ошбкой ±4 мкг. Также описан метод ионообменного отделения фторида от фосфата, сульфата, нитрата и хлорида.

ИЗУЧЕНИЕ *N*-ОКИСЕЙ ПОЛЯРОГРАФИЧЕСКИМ И ФИЗИКОХИМИЧЕСКИМ МЕТОДАМИ—II. МЕХАНИЗМ ВОССТАНОВЛЕНИЯ И ЯВЛЕНИЯ ГИДРАТАЦИИ АЦЕТИЛ- И БЕНЗОИЛПИРИДИН-*N*-ОКИСЕЙ:

E. Laviron, R. Gavasso and M. Pay, *Talanta* 1970, **17**, 747.

Резюме—Полярографические характеристики ацетил- и бензоилпиридин-*N*-окисей показывают те же неправилности как и упомянутые раньше соответственные формилпидин-*N*-окиси: группа *N*-окиси и карбонильная группа восстанавливаются одновременно в случае заместителя в положении 2 или 4; 3-изомеры восстанавливаются нормально при всех значениях pH. Ультрафиолетовые спектры позволяют сделать вывод о гидратации карбонильной группы, но не так сильной как в случае формилпиридин-*N*-окисей.

Untersuchungen an Reagenzien für Niob und Tantal—VI. Spektrophotometrische Bestimmung von Niob(V) und Tantal(V) mit Dibromgallussäure: GERHARD ACKERMANN und SIEGFRIED KOCH, *Talanta*, 1970, **17**, 757. (Bergakademie Freiberg, Sektion Chemie, Lehrstuhl für analytische Chemie, 92 Freiberg (Sachsl), DDR.)

Summary—Procedures are given for the spectrophotometric determination of Nb(V) and Ta(V) with dibromogallic acid, in the presence of various masking reagents. The sensitivities and standard deviations for the procedures are given, and the interfering elements in each case are listed.

Separation of rhenium from molybdenum, tungsten, vanadium, platinum metals and other elements by reduction and solvent extraction: V. YATIRAJAM and L. R. KAKKAR, *Talanta*, 1970, **17**, 759. (Department of Chemistry, Kurukshetra University, Kurukshetra, India.)

Summary—Reduction in $1M$ H_2SO_4 with liquid zinc amalgam and extraction with isopentanol from $3M$ H_2SO_4 separates rhenium from almost all the interfering elements of importance in rhenium determination. The small amounts of Mo, U, Fe and Ru still accompanying rhenium are removed by the thiocyanate–pentyl acetate or the oxine–chloroform extraction. The method is simple, rapid and of very wide applicability. It is particularly useful in the determination of rhenium in various alloys and tungsten-containing samples.

Application of low-cost operational amplifiers to electrical detection in spark-source mass spectrometry: L. B. FURGERSON, R. J. CONZEMIUS and H. J. SVEC, *Talanta*, 1970, **17**, 762. (Institute for Atomic Research and Department of Chemistry, Iowa State University, Ames, Iowa 50010, U.S.A.)

Summary—An electrical detection system for spark-source mass spectrometry has recently been developed. This brief addendum describes an improvement in the signal amplification and its conversion to digital output which has important implications in the future development of electrical detection.

ИЗУЧЕНИЕ РЕАГЕНТОВ ДЛЯ НИОБИЯ И ТАНТАЛА—VI. СПЕКТРОФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ НИОБИЯ(V) И ТАНТАЛА(V) ДИБРОМГАЛЛОВОЙ КИСЛОТОЙ:

GERHARD ACKERMANN and SIEGFRIED KOCH, *Talanta* 1970, **17**, 757.

Резюме—Приведены методы спектрофотометрического определения Nb(V) и Ta(V) с использованием дибромгалловой кислоты, в присутствии разных маскирующих агентов. Даны чувствительности и относительные ошибки методов и перечислены мешающие элементы.

ОТДЕЛЕНИЕ РЕНИЯ ОТ МОЛИБДЕНА, ВОЛЬФРАМА, ВАНАДИЯ, ПЛАТИНОВЫХ МЕТАЛЛОВ И ДРУГИХ ЭЛЕМЕНТОВ ВОССТАНОВЛЕНИЕМ И ЭКСТРАГИРОВАНИЕМ РАСТВОРИТЕЛЯМИ:

V. YATIRAJAM and L. R. KAKKAR, *Talanta* 1970, **17**, 759.

Резюме—Восстановление в 1 *M* H_2SO_4 с жидкой амальгамой цинка с последующим экстрагированием изопентанолом из 3 *M* H_2SO_4 отделяет рений от почти всех мешающих элементов важных в определении рения. Небольшие количества Mo, U, Fe и Ru до сих пор сопровождающих рений исключают экстрагированием с тиоцианатом- пентил- ацетатом или оксином- хлороформом. Метод является несложным, быстрым и широко применимым. Он особенно полезен для определения рения в разных сплавах и вольфрамсодержащих пробах.

ПРИМЕНЕНИЕ ДЕШЁВЫХ ОПЕРАТИВНЫХ УСИЛИТЕЛЕЙ В ЭЛЕКТРИЧЕСКОМ ОБНАРУЖЕНИИ В МАСС-СПЕКТРОМЕТРИИ С ИСКРОВЫМ ИСТОЧНИКОМ:

L. B. FERGUSON, R. J. CONZEMIUS and H. J. SVEC, *Talanta*, 1970, **17**, 762.

Резюме—В настоящее время разработана электрическая система обнаружения для масс-спектрометрии с искровым источником. Описано улучшение усиления сигнала и его превращения в цифровой выпуск. Это улучшение важно для будущего развития электрических систем обнаружения.

Determination of silicone fluid surfactants in polyurethane/polyether blends by atomic-absorption spectroscopy: G. Duncan and R. J. Herridge, *Talanta*, 1970, **17**, 766. (Department of Chemistry and Biology, John Dalton Faculty of Technology, Manchester Polytechnic, Chester St., Manchester 1, U.K.)

Summary—A method for the atomic-absorption determination of silicone fluid surfactants present in some polyurethane/polyether blends is described. The silicone fluid in the pure state, or in the presence of polyurethane blend, is diluted with a solvent and sprayed into the nitrous oxide/acetylene flame. The effects of solvent, instrumental conditions, time and presence of the polyurethane blends were investigated. Polyurethane/polyether blends do not interfere with the silicon absorption when the samples are dissolved in aqueous ethanol (1 : 1) and sprayed into a fuel-rich flame.

Stability characteristics of aqueous chloramine-T solutions: V. R. S. Rao, D. Venkappayya and G. Aravamudan, *Talanta*, 1970, **17**, 770. (Department of Chemistry, Indian Institute of Technology, Madras 36, India.)

Summary—Aqueous chloramine-T solutions in strongly alkaline medium are quite stable even up to 60°. In 0·2–2*M* sulphuric or perchloric acid at 25–30°, there is no loss in titre, but in hydrochloric acid solutions >0·5*M*, there is a loss in titre, which increases with increase in hydrochloric acid concentration. This is ascribed to oxidation of chloride to chlorine. In the pH range 2·65–5·65 there is a small but reproducible loss in oxidative titre which is maximal at pH 4·7. This is ascribed to side-reactions occurring during partial disproportionation of monochloramine-T to dichloramine-T and *p*-toluenesulphonamide.

Spectrophotometric determination of ruthenium(III) and iridium(IV) with 8-hydroxyquinoline *N*-oxide: R. D. Gupta, G. S. Manku, A. N. Bhat and B. D. Jain, *Talanta*, 1970, **17**, 772. (Department of Chemistry, The University, Delhi-7, India.)

Summary—The spectrophotometric characteristics and the stability constants of the yellow to brown 1 : 1 and 1 : 2 complexes of platinum metals with oxine *N*-oxide (existing as chloro mixed-ligand complexes) have been investigated. Oxine *N*-oxide can be used as a spectrophotometric reagent for ruthenium(III) and iridium(IV).

ОПРЕДЕЛЕНИЕ ПОВЕРХНОСТНОАКТИВНЫХ ВЕЩЕСТВ НА ОСНОВЕ СИЛОКСАНА В СМЕСЯХ ПОЛИУРЕТАНА И ПОЛИЭФИРА МЕТОДОМ АТОМНО-АБСОРБЦИОННОЙ СПЕКТРОСКОПИИ:

G. Duncan and R. J. Herridge, *Talanta* 1970, **17**, 766.

Резюме—Описан метод атомно-абсорбционной спектроскопии для определения поверхностноактивных веществ на основе силоксана, присутствующих в некоторых смесях полиуретана и полиэфира. Силоксан в чистом состоянии или в присутствии смеси полиуретана разбавляют растворителем и вбрызгивают в пламя закиси азота и ацетилена. Исследованы эффекты растворителя, условий прибора, времени и присутствии полиуретановых смесей. Смеси полиуретана и полиэфира не влияют на поглощение кремния если пробы растворяют в водном спирте (1:1) и вбрызгивают в пламя с большим отношением ацетилена.

ХАРАКТЕРИСТИКИ УСТОЙЧИВОСТИ ВОДНЫХ РАСТВОРОВ ХЛОРАМИНА Т:

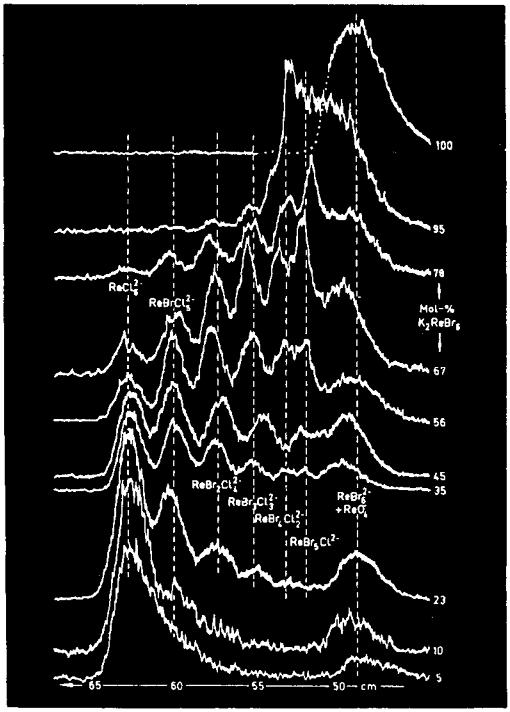
V. R. S. Rao, D. Venkappayya and G. Aravamudan, *Talanta*, 1970, **17**, 770.

Резюме—Водные растворы хлорамина Т в сильнощелочной среде довольно устойчивы даже до 60°. В 0,2–2 М растворах серной или хлорной кислот при 25–30° титр растворов не изменяется, но в растворах соляной кислоты $>0{,}5$ М титр изменяется с растущей концентрацией соляной кислоты. Этот факт приписывается окислению хлорида в хлор. В области рН 2,65–5,65 появляется небольшое но воспроизводимое снижение окислительного титра, которое достигает максимум при рН 7,7. Это приписывается бочными реакциями появляющимися в течении частичного диспропорционирования хлорамина Т в дихлорамин Т и п-толуолсульфонамид.

СПЕКТРОФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ РУТЕНИЯ(III) И ИРИДИЯ(IV) С *N*-ОКИСЬЮ 8-ОКСИХИНОЛИНА:

R. D. Gupta, G. S. Manku, A. N. Bhat and B. D. Jain, *Talanta* 1970, **17**, 772.

Резюме—Изучены спектрофотометрические характеристики и константы устойчивости желтых до коричневых 1:1 и 1:2 комплексов платиновых металлов с *N*-окисью оксина (существующих в форме хлоркомплексов с смешанными лигандами). *N*-окисью оксина можно пользоватся в качестве спектрофотометрического реагента для рутения(III) и иридия(IV).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