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## Aims and Scope

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## DETERMINATION OF INDIUM AND TIN BY ACTIVATION ANALYSIS USING REPLACEMENT SUBSTOICHIOMETRY

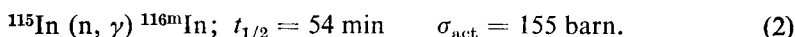
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(Received 1 July 1968. Accepted 10 September 1968)

**Summary**—A new method for the determination of indium by activation analysis has been developed. It is based on the replacement of indium from indium dithizonate (in carbon tetrachloride) by a sub-stoichiometric amount of aqueous mercury(II) solution. Preliminary steps are the extraction of indium from alkaline cyanide solution with an excess of dithizone solution and washing the extract with buffer solution. The time necessary for the separation is 10–20 min. With this method indium can be determined by using either short ( $^{116m}\text{In}$ ,  $t_{1/2} = 54$  min) or long-lived radioisotopes ( $^{114m}\text{In}$ ,  $t_{1/2} = 50$  d). As by the reaction  $^{112}\text{Sn}(n, \gamma)^{113}\text{Sn}(119\text{d}) \xrightarrow{ec} ^{113m}\text{In}(104\text{min})$ , indium- $^{113m}\text{In}$  is formed, which has a different  $\gamma$ -spectrum from that of indium- $^{114m}\text{In}$ , the determination of both indium and tin is possible. The proposed method has been applied to the determination of indium and tin in granite and gallium.

NATURAL indium consists of two isotopes,  $^{113}\text{In}$  (4.23%) and  $^{115}\text{In}$  (95.77%). On irradiation with thermal neutrons the nuclides give the following nuclear reactions:<sup>1</sup>



The short-lived isotopes  $^{114}\text{In}$  and  $^{116}\text{In}$  ( $t_{1/2} = 72$  sec and 13 sec) are also formed. Reactions (1) and (2) are, however, preferable for activation analysis. In a tin matrix, indium isotopes formed from the tin by (n, p) reactions will interfere. Errors can also arise from self-shielding in comparison samples.<sup>1</sup>

Indium has been determined<sup>2</sup> by activation, solvent extraction of indium with dithizone from alkaline cyanide solution, stripping into the aqueous phase, and final substoichiometric separation of indium-EDTA complex on a cation-exchange resin.

As shown in our previous work,<sup>3</sup> a replacement substoichiometric method can sometimes be more suitable for the separation of metals having relatively low extraction constants, this being the case with indium dithizonate, for which direct substoichiometric extraction from cyanide media is not sufficiently quantitative, and extraction in the absence of cyanide is not selective.

As by the reaction  $^{112}\text{Sn}(n, \gamma)^{113}\text{Sn}(119\text{d}) \xrightarrow{ec} ^{113m}\text{In}(104\text{min})$ ,  $^{113m}\text{In}$  is formed<sup>1</sup> (with a  $\gamma$ -spectrum different from that of  $^{114m}\text{In}$ ) the determination of traces of tin and the simultaneous determination of traces of indium ( $^{114m}\text{In}$ ) and tin ( $^{113m}\text{In}$ ) by means of one separation procedure is possible. The sensitivity for tin is determined by that of the  $^{112}\text{Sn}(n, \gamma)^{113}\text{Sn}$  reaction, since  $^{113m}\text{In}$  will reach radioactive equilibrium with its parent nuclide  $^{113}\text{Sn}$  in 17 hr. There are numerous (n,  $\gamma$ ) reactions with the various tin isotopes,<sup>1</sup> but they do not interfere. The method proposed is more

rapid but slightly less sensitive than that of Hamaguchi *et al.*<sup>4</sup> based on the reaction  $^{120}\text{Sn} (n, \gamma) ^{121}\text{Sn}$  (27.5 hr), the sensitivity of which was 0.2  $\mu\text{g}$  of tin. The use of radiotin isotopes, however, is complicated by the necessity to separate the tin chemically, a notoriously difficult problem. The method described here is much simpler.

## EXPERIMENTAL

### Reagents

All reagents used were analytical grade.

*Indium carrier solution.* Contains 300  $\mu\text{g}$  of In per ml of 0.1M nitric acid.

*Tin carrier solution.* Contains 500  $\mu\text{g}$  of Sn per ml of 5M nitric acid. Freshly prepared before use.

*Dithizone solution,*  $7.7 \times 10^{-4}\text{M}$ . In carbon tetrachloride.

*Mercury solution.* Contains 200  $\mu\text{g}$  of Hg(II) per ml of 0.1M nitric acid.

*Tartrate solution.* Sodium tartrate, 0.2M, containing enough ammonia to give a pH of 7.5 when 4 ml of tartrate solution are added to 2 ml of mercury solution.

### Development of the method

The pH range for substoichiometric replacement with chloroform as solvent was calculated and checked experimentally,<sup>3</sup> and found to be 6–9; the same range holds for carbon tetrachloride as solvent.

The extraction of indium from solutions containing cyanide and thiosulphate was studied. With 100% excess of dithizone indium was extracted in the pH range 7–9 from a medium containing 2% potassium cyanide and 4% sodium thiosulphate. At pH values below 7.5 and lower concentrations of cyanide, zinc was partly extracted, but not from 3% cyanide–4% thiosulphate solution at pH 8–9.

For removal of excess of free dithizone from the organic phase 0.01M borax (pH 9.2) was used. Two or three washes are sufficient. The loss of indium carrier during washing does not exceed 20%.

### Irradiation

For  $^{114\text{m}}\text{In}$  in the test samples (2–3 g) of granite powder were sealed in glass ampoules and irradiated in a nuclear reactor with a flux of  $7.5 \times 10^{10} \text{ n.mm}^{-2}.\text{sec}^{-1}$  for 200 hr. The indium standard (1.15  $\mu\text{g}$  of In) was sealed in a quartz ampoule and irradiated simultaneously with the test samples.

For  $^{116\text{m}}\text{In}$  in the granite samples (0.1 g) sealed in polyethylene ampoules were irradiated for 10 min at  $5 \times 10^{10} \text{ n.mm}^{-2}.\text{sec}^{-1}$  (at the bottom of the sample holder) in a nuclear reactor by means of a pneumatic tube device. The standard (indium solution in polyethylene ampoule—0.575  $\mu\text{g}$  of In) was irradiated simultaneously with two samples.

For  $^{113\text{m}}\text{In}$  (from Sn) and  $^{114\text{m}}\text{In}$  in the samples were sealed in aluminium capsules (granite powder) or quartz ampoules (gallium). The standards of indium (11.5  $\mu\text{g}$ ) and tin (96.6 mg of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ) were sealed in quartz ampoules. The irradiation was carried out in a nuclear reactor at a neutron flux of  $7.5 \times 10^{10} \text{ n.mm}^{-2}.\text{sec}^{-1}$  for 160 hr; the cooling time was about 20 days. After irradiation the standards were dissolved in hydrochloric acid and 0.23  $\mu\text{g}$  of In and 50.7  $\mu\text{g}$  of Sn were used in each analysis. The volumes and irradiation positions of samples and standard were kept as equal as possible, especially for  $^{116\text{m}}\text{In}$ .

### Dissolution of the samples

Before dissolution of the samples carrier solutions (300  $\mu\text{g}$  of In + 500  $\mu\text{g}$  of Sn) were added (tin was omitted if only indium was to be determined). The volatility of tin compounds must be taken into account, especially that of the chlorides ( $\text{SnCl}_2$ , b.p. 623°;  $\text{SnCl}_4$ , b.p. 114°).<sup>5</sup> The dissolution of the granite must therefore be carried out with the mixture of hot hydrofluoric and sulphuric acids in the absence of hydrochloric acid. The dissolution of tin(II) chloride from the standard in hydrochloric acid must be carried out with utmost care. The samples of gallium were dissolved in hot nitric acid.

### Procedure

In order to keep the same conditions of radioactive equilibrium between the parent  $^{113}\text{Sn}$  and the daughter  $^{113\text{m}}\text{In}$ , the same chemical operations with standard and sample must be carried out simultaneously.

The sample solution was neutralized with aqueous ammonia. Then 5 ml of sodium tartrate solution and a few mg of ascorbic acid were added [reduction of iron(III) to iron(II)], followed by 20% potassium cyanide and 20% sodium thiosulphate solutions to give final concentrations of 3 and 4% respectively. The pH was then made 8–9, and indium extracted with two portions of dithizone solution (15 and 5 ml). The combined extract was washed three times with 40 ml 0.01 M borax. After washing, the organic extract must be red. Then tartrate buffer (4 ml) and

mercury solution (2 ml) were added and the mixture shaken for 30 sec. The activity of indium in the aqueous phase was then measured. A similar procedure was applied to the standards.

Quantitative measurements were made by means of a multichannel  $\gamma$ -spectrometer with NaI(Tl) crystal. The content of indium and tin was calculated from peak areas estimated by Covell's method.<sup>6</sup> The content of indium was calculated in the usual way from the 191-keV peak area ( $^{114m}\text{In}$ ) and that of tin from the 392-keV peak area ( $^{113m}\text{In}$ , 104 min). All corrections for the decay of  $^{113m}\text{In}$  were made.

### RESULTS AND DISCUSSION

In alkaline cyanide media only indium, tin(II), bismuth, lead and thallium(I) can be extracted with dithizone.<sup>7</sup> Bismuth and lead will not interfere, because of their nuclear properties. Tin is removed by washing the dithizone extract. Thallium can partly accompany indium during the separation procedure. As radioisotopes of thallium are pure  $\beta$ -emitters, thallium will seriously interfere only with  $\beta$ -measurements of indium activity. A gamma spectrum showed the radioindium obtained by this method was radiochemically pure. Only in one case, where the separation procedure had not been carried out quite correctly (the cyanide solution was added after the dithizone) did cobalt get into the substoichiometric extract, and that can be explained by the formation of the inert cobalt complex with dithizone, which once formed is very stable towards mineral acids and cyanide solution.<sup>7</sup> When the proposed conditions of separation are strictly kept the extracts should be radiochemically pure.

Typical results for granites were:  $^{114m}\text{In}$  method (3-g samples, 192-keV peak for activity measurement), In 27 ppm, standard deviation 1 ppm (5 variates);  $^{116}\text{In}$  method (0.1-g samples, 406-keV peak, measured 3 hr after irradiation), In 0.67 ppm, standard deviation 0.07 ppm (10 variates);  $^{113}\text{In}/^{114m}\text{In}$  method (1-g samples, 191-keV peak for  $^{114m}\text{In}$ , 392-keV peak for  $^{113m}\text{In}$ ), In 52 ppm, standard deviation 3 ppm (6 variates), Sn 3.6 ppm, standard deviation 0.2 ppm (6 variates). Results for tin in a gallium sample (0.5 g) are Sn 61 ppm, standard deviation 3 ppm (6 variates). The sensitivities, under the conditions described, are 0.01  $\mu\text{g}$  for indium and 0.5  $\mu\text{g}$  for tin, based on the condition that the minimum peak-height is twice the average background at the foot of the peak.

The precision with the short-lived isotope is less than that with the long-lived one, probably on account of the gradient of neutron flux in the pneumatic tube device used. Self-shielding in the standards was not taken into consideration, as the amounts used were very small, and in the case of  $^{116m}\text{In}$  were irradiated in aqueous medium.

*Acknowledgements*—The author would like to express his thanks to Drs. M. Křivánek and J. Rais for their critical discussion and for their interest in this work.

**Résumé**—On a élaboré une nouvelle méthode de détermination de l'indium par analyse par activation. Elle est basée sur le remplacement de l'indium du dithizonate d'indium (en tétrachlorure de carbone) par une quantité substochiométrique de solution aqueuse de mercure(II). Les stades préliminaires sont l'extraction de l'indium d'une solution alcaline de cyanure avec un excès de solution de dithizone et le lavage de l'extrait avec une solution tampon. Le temps nécessaire pour la séparation est de 10–20 mn. Avec cette méthode on peut utiliser pour doser l'indium, des radioisotopes de courte ( $^{116m}\text{In}$ ,  $t_{1/2} = 54$  mn) ou longue vie ( $^{114m}\text{In}$ ,  $t_{1/2} = 50$  j). Comme dans la réaction  $^{112}\text{Sm}$  ( $n, \nu$ )  $^{113}\text{Sn}$  (119 j)  $\xrightarrow{\text{ec}}$   $^{113m}\text{In}$  (104 mn) il se forme de l'indium 113 m, qui a un spectre  $\gamma$  différent de celui de l'indium 114 m, les dosages de l'indium et de l'étain sont tous deux possibles. On a appliqué la méthode la proposée à la détermination de l'indium et del 'étain dans le granit et le gallium.

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## A CELL FOR HIGH-PRECISION CONSTANT-CURRENT COULOMETRY WITH EXTERNAL GENERATION OF TITRANT

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**Summary**—A cell has been designed for the high-precision coulometric titration, with externally generated titrant, of materials which otherwise undergo undesirable reactions at the working electrodes. With this cell potassium dichromate has been titrated, *via* its hydrolysis reaction, with hydroxyl ion generated at the cathode, cathodic reduction of the chromium(VI) being circumvented. In this cell 99.9% of the titrant required is generated in one chamber and transferred to another for reaction; the titration is then completed with titrant generated at a second, drip-type electrode working at much lower current. By means of commercially available Leeds and Northrup coulometric titration electrical equipment, titration of NBS 136b Potassium Dichromate gave a purity of 99.976%, standard deviation 0.005%, and of NBS 84d Potassium Acid Phthalate (done as a check) 99.991%, standard deviation 0.005%, both values being in excellent agreement with other work.

Two high-precision assays of NBS 136b Potassium Dichromate by coulometric titration with electrogenerated iron(II) have now been made, by Marinenko and Taylor<sup>1</sup> and by Knoeck and Diehl,<sup>2</sup> the results being 99.977 and 99.975% respectively with relative standard deviations in both cases of 2 parts in 10<sup>5</sup>.

Potassium dichromate can be titrated as an acid, for reaction with water yields the hydrogen chromate, and although the idea of using it as a primary standard acid is an old one, dating back to 1882,<sup>3</sup> potassium dichromate has not been widely used in this way, largely because the yellow colour of the chromate obscures the visual endpoint, and perhaps also because the reaction was reported to be slow.<sup>4</sup>

Preliminary work showed that the hydrolysis actually proceeds swiftly enough for a normal titration, and within the limits of error of volumetric glassware (1 part in 1000), identical results were obtained in the standardization of 0.1*N* sodium hydroxide by titration of potassium dichromate and potassium hydrogen phthalate. Moreover, with thymolphthalein as indicator the colour change from yellow to green (thymolphthalein colourless in acid form, blue in alkaline form) is sharp and distinct although not striking.

In a coulometric titration, hydroxyl ion is of course generated at the cathode, and because reduction of chromate would occur in preference to reduction of water, internal generation of hydroxyl ion cannot be used to titrate the hydrogen chromate ion or any other acid with oxidizing properties (*e.g.*, potassium hydrogen iodate). External generation cells for coulometric titration are based on flow of electrolyte past the generating electrode; for the long titrations necessary to obtain high accuracy, the

continual flow of solution into the cell leads to such a large volume that precise end-point detection is impossible. Reduction of flow is not a solution to the problem, because loss of titrant by back diffusion becomes serious. In the present work this problem has been met by designing a new cell, one in which the major part of the hydroxyl ion is generated internally but in a chamber separated from that containing the sample. After >99.9% of the hydroxide necessary has been generated, the electrogeneration is stopped and sample and hydroxide are brought together. The titration is then completed with hydroxide generated by a second, conventional, external, dripping generation cathode operating with low current. This new cell has been used for the assay of NBS 136b Potassium Dichromate and NBS 84d Potassium Acid Phthalate.

## EXPERIMENTAL

### Apparatus

*Measurement of mass, current and time.* The Leeds and Northrup coulometric titration apparatus described by Eckfeldt and Shaffer<sup>5</sup> and used in our earlier work<sup>2</sup> was used in the present work except that the cell of new design was used. All of the precautions and frequent checks on the calibration and functioning of the apparatus mentioned in the earlier paper were continued.

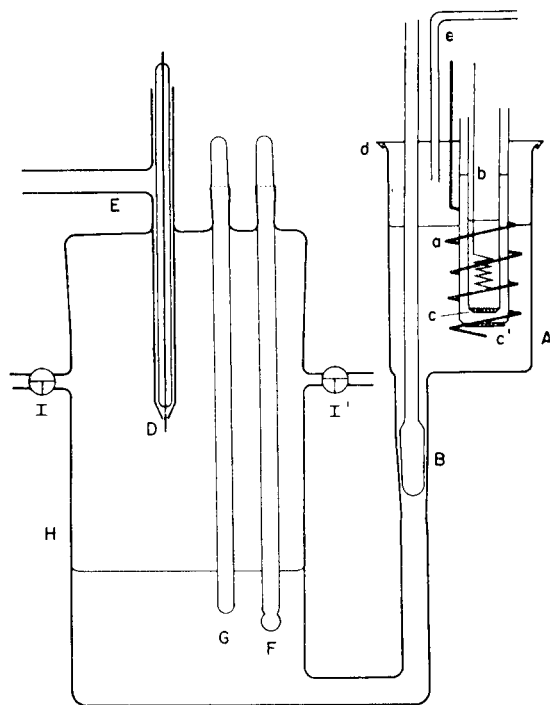


FIG. 1.—Two-chambered cell for coulometric titration with external generation of titrant.

*A*, Generation chamber (for bulk of titrant); *B*, polished ground-glass valve; *H*, reaction chamber; *I* and *I'*, 3-way stop-cocks for introduction and release of nitrogen; *D*, platinum wire working electrode for completing titration; *E*, portion of electro-generation assembly for completing titration (remainder shown in Fig. 2); *F* and *G*, glass and reference electrodes; *a*, platinum working cathode; *b*, platinum or silver working anode; *c* and *c'*, shield tubes with ultrafine glass frits at ends; *d*, polyethylene cover; *e*, nitrogen inlet.

*Two-chambered cell for generation of titrant out of contact with sample.* The cell used, Fig. 1, consisted of two chambers, *A* and *H*, interconnected by glass tubing carrying the ground and polished glass valve *B*. Chamber *A*, volume 300 ml, in which the bulk of the titrant was generated internally but separately from the sample, was otherwise of the same general construction as the cell used in the earlier work,<sup>2</sup> the electrical generating assembly consisting of concentric shield tubes *c* and *c'* with fritted glass ends, and the working electrodes *a* and *b*. Although not shown in Fig. 1, the cover of chamber *A* was pierced so that glass and S.C.E electrodes could be inserted during the preliminary treatment of the catholyte and later withdrawn and the openings sealed. Chamber *H*, in which the main reaction was effected and the titration completed, was fitted with the indicator electrodes *G* and *F* inserted through ground-glass joints, and the external, dripping, generating electrode assembly used to complete the titration. Solution in chamber *H* was moved to chamber *A* by pressure of nitrogen gas introduced through stop-cock *I* and returned by gravity on release of the gas pressure through *I'*. The external dripping electrode assembly, shown in Fig. 2, consisted of the working platinum cathode *D* and a silver wire anode *M*, the fritted glass disc *J*, and the connection *K* to the reservoir of electrolyte. Flow of electrolyte to the cathode was controlled by stop-cock *L*. The liquid level in the reservoir was maintained higher than the level in the tube carrying the anode *M*, so that the flow through the glass frit was toward *M*.

*Electrodes and electrolytes.* The working cathode, *a* in Fig. 1, was a helix of platinum wire with a surface area of 26 cm<sup>2</sup>. The anode, *b* in Fig. 1, was a helix of either silver or platinum with a surface area of about 8 cm<sup>2</sup>. When the platinum anode was used an additional shield tube terminating in an ultrafine glass frit was inserted between *c* and *c'* to ensure separation of anode and cathode products.

The catholyte used in chamber *A* was 1.0*M* sodium perchlorate. The anolyte was 1.0*M* potassium chloride when the silver wire anode was used, or 1.0*M* sodium perchlorate when the platinum wire anode was used. The bridging electrolyte, filling the space between *c* and *c'*, was 1.0*M* potassium

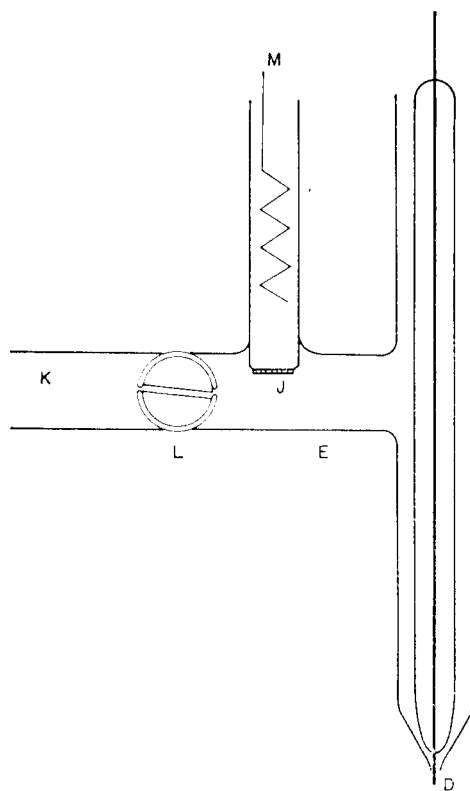


FIG. 2.—Detail of external generation assembly for completing titration. *E*, Tube for flowing electrolyte (continued in Fig. 1); *D*, working platinum electrode; *J*, ultrafine glass frit; *K*, tube leading to reservoir of electrolyte; *L*, stop-cock for flow adjustment; *M*, silver wire anode.

perchlorate. The catholyte fed from the reservoir connected at *K* to the dripping cathode used to complete the titration was 1.0*M* sodium perchlorate previously titrated coulometrically to pH  $7.00 \pm 0.05$  (see below). The electrolyte in the compartment surrounding the silver wire anode *M* was 1.0*M* potassium chloride.

Electrolyte for the reservoir *K* was conditioned before use, in the following manner. About 2 l. of 1.0*M* sodium perchlorate were placed in a 3-l. beaker. The beaker was fitted with a polyethylene cover through which were passed a large platinum gauze electrode, a shield tube containing 1.0*M* sodium perchlorate and a 1-cm<sup>2</sup> platinum foil electrode, a reference electrode and a glass electrode. The working electrodes were connected to the constant-current source and the solution was electrolysed at 64.3 mA with the platinum electrode in the solution serving as anode. The solution thus became more acidic as electrolysis progressed. At pH 5.5 the electrolysis was discontinued and nitrogen gas was passed over the stirred solution for several hours to remove dissolved carbon dioxide. The polarity of the generating electrode was reversed and electrolysis resumed until the pH of the solution rose to  $7.00 \pm 0.05$ . The solution was then transferred to reservoir *K* and kept under nitrogen free from carbon dioxide.

*Materials.* Potassium Acid Phthalate NBS 84d and Potassium Dichromate NBS 136b were dried for 24 hr at 110° and stored *in vacuo* over anhydrous magnesium perchlorate until analysed.

Commercial "prepurified" cylinder nitrogen was passed successively through a tube containing "Ascarite" and through two scrubbers containing a solution identical to the catholyte.

All solutions were prepared with distilled and demineralized water, redistilled from alkaline permanganate.

*End-point detection.* End-points were determined electrometrically with an expanded scale pH-meter (Corning Scientific Instruments, Model 10) with a glass-reference combination electrode. The glass electrode was soaked in supporting electrolyte when not in use. The pH-meter was standardized with commercial buffers of pH 10 and 7. Response times of the pH-meter were about 2 min after which the instability was only a few thousandths of a pH unit.

The end-point was determined by calculating the inflection point in the curve of pH *vs.*  $\mu$ equiv generated, by the differential method of Yan,<sup>6</sup> points very near to and bracketing the inflection point being used. In practice the titration data need not be plotted when the Yan method is used. Because the calculation makes use of only four sets of data, the inflection point was calculated several times from different sets, the average being taken as the end-point. The differences between this average and individual points calculated were less than 4 parts in 10<sup>5</sup> of the total number of equivalents passed. In practice it was possible to locate the end-point from inspection of the plot with about equal precision and in fact about the same precision is obtained by simple titration to a specified end-point as calculated theoretically from the acid dissociation constant.

*Manipulation.* A volume of 150 ml of 1.0*M* sodium perchlorate, designated solution 1, was introduced into chamber *A* and titrated coulometrically to pH 5.5, as determined with a glass-reference combination electrode inserted through the cover. Carbon dioxide-free nitrogen was passed over the solution for 1 hr to remove dissolved carbon dioxide. The polarity of the generating electrodes was then reversed and the acid solution titrated to pH 8.5. This procedure, that is alternate oxidation and reduction, was repeated three times to ensure the removal of electroactive impurities. The final step was to titrate the acid solution to pH  $7.00 \pm 0.02$ . Valve *B* was then opened and solution 1 allowed to flow into chamber *H*. A crystal of the substance to be subsequently titrated, potassium dichromate or potassium acid phthalate, was added to this solution and the resulting solution was titrated to the end-point with hydroxide generated at *D* with a current of 0.643 mA from the constant-current source. This pretitration was carried out by passing current for short intervals and, after each interval, measuring the pH. The final counter reading,  $Q_2$ , was recorded. The end-point was calculated and the counter reading,  $Q_1$ , corresponding to it recorded. The quantity,  $Q_2 - Q_1$ , then represented alkali added beyond the end-point and was taken into consideration in the final calculation. Solution 1, in chamber *H*, was then ready for introduction of the sample.

With valve *B* closed, 150 ml of the pretreated 1.0*M* sodium perchlorate were transferred from reservoir *K* (see preceding section on preparation of electrolytes) to chamber *A*; this solution is designated solution 2. Carbon dioxide was removed and solution 2 titrated to pH  $7.00 \pm 0.02$  by the procedure given in the preceding paragraph. The counter of the constant current source was set at zero and 99.9% of the hydroxide ion theoretically required was generated at 64.3 mA. The counter reading,  $Q_3$ , was recorded.

Meanwhile, the sample, weighed by difference into a glass boat, was lowered into the titration chamber *H* and dissolved in solution 1. Valve *B* was then opened and solution 2 (containing the hydroxide) allowed to flow into chamber *H*. The combined liquid in *H* was then forced into chamber *A* by nitrogen introduced through stop-cock *I* and then brought back into *H* by releasing the nitrogen through *I'*. In this way chamber *A* was rinsed and the transfer of hydroxide made quantitative. After five such transfers, the titration was resumed with use of the small generating cathode *D* and

the 0.643-mA current, and starting with the counter reset at zero. The titration was completed by passing current in small increments and measuring the pH of the solution after each small increment. Before each pH measurement, chamber *A* was rinsed three times with solution from *H*, using nitrogen pressure and stop-cocks *I* and *I'*. The final end-point was calculated and the corresponding reading,  $Q_4$ , of the counter recorded.

The weights of potassium dichromate and potassium acid phthalate taken for titration were chosen so that about 20000  $\mu$ equiv were titrated.

The total number of coulombs passed was calculated from the counter reading (time) and the *IR* drop across the standard resistance in series with cell; the latter term was the average of the *IR* drop recorded at every 15-min interval during the generation step (see earlier paper). The final calculation then took the form

$$\text{equiv} = [(Q_2 - Q_1)(IR)_1 + Q_3(IR)_2 + Q_4(IR)_3 - c]F$$

$(IR)_1$  and  $(IR)_3$  being 0.643 mA and  $(IR)_2$  an exact value close to 64.3 mA. The term *c* was a correction of 0.44  $\mu$ equiv, the amount of electricity needed to bring solution 2 (electrolyte only, 150 ml of 1M sodium perchlorate) from pH 7.0 to 8.5 as calculated (0.44  $\mu$ equiv) and as determined in separate experiments (0.43, 0.46, 0.44  $\mu$ equiv). The value used for *F*, the faraday, was  $96487.0 \pm 1.2$  coulombs per equivalent, as determined by Craig, Hoffman, Law and Hamer<sup>7</sup> and corrected to the C<sup>12</sup> atomic weight scale.<sup>8</sup> The equivalent weights used, 147.096 for potassium dichromate and 204.229 for potassium acid phthalate, were calculated from the values of the 1961 Report of the International Commission on Atomic Weights.<sup>9</sup>

The precision and error in the measurements of time, mass and current have been discussed in the previous paper.<sup>2</sup>

## RESULTS

Results of six titrations of NBS 84d Potassium Acid Phthalate are given in Table I. The average purity based on acid content, 99.991%, is in excellent agreement with the results of Taylor and Smith,<sup>10</sup> 99.989%; Eckfeldt and Shaffer,<sup>5</sup> 99.999%; and Bates and Wichers,<sup>11</sup> 99.987%. The satisfactory operation of the external generation cell was thus confirmed.

TABLE I.—COULOMETRIC ASSAY OF NBS 84d POTASSIUM ACID PHTHALATE

Found, %	Found in other work, %
99.984	99.999* Eckfeldt and Shaffer, <sup>5</sup> coulometric
99.986	99.989† Taylor and Smith, <sup>10</sup> coulometric
99.992	99.987 Bates and Wichers, <sup>11</sup> titrimetric
99.993	
99.995	
99.996	
Average 99.991	
Standard deviation 0.005	

\* 100.002 when corrected to most recent value of the faraday.<sup>5</sup>

† 99.992 when corrected to most recent value of the faraday.<sup>5</sup>

Results of six titrations of NBS 136b Potassium Dichromate are given in Table II. The average purity based on acid content, 99.976%, is in excellent agreement with the purity of this material found by coulometric titration with iron(II), 99.977% (Marinenko and Taylor<sup>1</sup>) and 99.975% (Knoeck and Diehl<sup>2</sup>).

## DISCUSSION

### Current efficiency

The electrogeneration of hydroxide ion from a sodium perchlorate solution proceeds with 100% current efficiency inasmuch as there are no species present more easily reduced than water. It is clear from the balanced equations that a hydrogen ion is consumed for every electron used in the reduction of such species as chlorate

TABLE II.—COULOMETRIC ASSAY OF NBS 136b POTASSIUM DICHROMATE AS AN ACID

Found, %	Found in Other work, %
99-968	99-98 Certificate value, National Bureau of Standards
99-974	99-977 Marinenko and Taylor, <sup>1</sup> coulometric with Fe(II)
99-975	99-975 Knoeck and Diehl, <sup>2</sup> coulometric with Fe(II)
99-977	
99-982	
99-981	
Average 99-976	
Standard deviation 0.005	

or perchlorate so that even if traces of chlorate were present or traces of perchlorate were reduced overall current efficiency would be maintained.

#### *Potassium Acid Phthalate*

Although the four values for the purity of 84d, reported by different workers, see Table I, are in agreement, it must be noted that in view of the accuracy and precision inherent in the coulometric method, better agreement might have been expected; the precision in each of the four independent assays is a few parts in  $10^5$  but the range of results is 12 parts in  $10^5$ . The Taylor and Smith,<sup>10</sup> and Eckfeldt and Shaffer<sup>5</sup> results were obtained by coulometric titration. Recalculation of these results using the more recent value of the faraday gives 99-992 and 100-002% respectively.<sup>5</sup> The Bates and Wichers<sup>11</sup> value, 99-987%, was obtained by differential potentiometric titration, single-crystal benzoic acid being used as a reference material. While the agreement between the values of Bates and Wichers, Taylor and Smith and the present work is excellent, for some other materials, notably the Bates and Wichers b-series benzoic acid, the agreement between the Taylor and Smith coulometric assay and the Bates and Wichers value is somewhat poorer<sup>10,11</sup> (about 15 parts in  $10^5$ ). It is therefore difficult to choose any one assay of Potassium Acid Phthalate as the best value. The discrepancies between the four reported assays of 84d appear to lie outside the error of the analysis and although Eckfeldt and Shaffer<sup>5</sup> have discussed these discrepancies in some detail, they remain for the present unresolved and deserving of future attention.

The standard deviation of the results reported in the present work, 0-005%, is somewhat greater than the 0-003% standard deviation reported by Taylor and Smith and by Eckfeldt and Shaffer. Relatively large volumes, about 600 ml at the end-point, are required in the operation of the external generation cell, the break in the titration curve is not as sharp as might be obtained with smaller volumes, and the end-point is less precisely located.

#### *Potassium Dichromate*

The results of the titrations of NBS 136b as an acid are in excellent agreement with the results obtained by coulometric titration with iron(II).<sup>1,2</sup> Thus potassium dichromate is suitable for use as a primary standard acid as well as a primary standard oxidizing agent.

The standard deviation reported in this work, 0.005%, is appreciably greater than that found in titrations with iron(II), 0.002%.<sup>1,2</sup> Again the poorer precision is probably a reflection of a less precise method of end-point detection.

Although small amounts of metallic impurities have been found<sup>12</sup> in NBS 136b, it was shown in our previous work<sup>2</sup> that the difference between the coulometric assay of 136b and 100.000% is due largely to occluded water.

**Zusammenfassung**—Eine Zelle zu sehr genauen coulometrischen Titrationsen wurde entwickelt, die mit außerhalb erzeugtem Titranten arbeitet. Sie eignet sich für Stoffe, die sonst an den Arbeitselektroden unerwünschte Reaktionen eingehen. Mit dieser Zelle wurde Kaliumdichromat über seine Hydrolysenreaktion mit kathodisch erzeugtem Hydroxylion titriert, wobei die kathodische Reduktion des Chrom(VI) umgangen wurde. In dieser Zelle werden 99,9% des benötigten Titranten in einer Kammer erzeugt und für die Reaktion in eine andere überführt; die Titration wird dann zu Ende geführt mit Titrant, der an einer zweiten Elektrode vom Tropfentyp erzeugt wird; diese arbeitet mit viel niedrigerem Strom. Mit Hilfe handelsüblicher coulometrischer Titrationsausrüstung von Leeds und Northrup ergab Kaliumdichromat NBS 136b eine Reinheit von 99,976% mit der Standardabweichung 0,005% und (als Probe) Kaliumhydrogenphthalat NBS 84d 99,991% mit der Standardabweichung 0,005%. Beide Werte stimmen mit anderen Arbeiten ausgezeichnet überein.

**Résumé**—On a conçu une cellule pour le titrage coulométrique de haute précision, avec agent de titrage engendré extérieurement, de produits qui autrement subissent des réactions indésirables aux électrodes de travail. Avec cette cellule on a titré le bichromate de potassium, *via* sa réaction d'hydrolyse, avec l'ion hydroxyle engendré à la cathode, la réduction cathodique du chrome(VI) étant éliminée. Dans cette cellule, 99,9% de l'agent de titrage nécessaire est engendré dans un compartiment et transféré dans un autre pour la réaction; le titrage est alors terminé avec l'agent de titrage engendré par une seconde électrode du type à goutte travaillant avec une intensité beaucoup plus faible. Au moyen de l'équipement électrique de titrage coulométrique commercialement disponible Leeds et Northrup, le titrage du bichromate de potassium NBS 136b donne une pureté de 99,976%, écart type 0,005%, et celui du phthalate acide de potassium NBS 84 d (effectué comme recoupement) donne 99,991%, écart type 0,005%, les deux valeurs étant en accord excellent avec un autre travail.

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## ALKALINE EARTH SEPARATIONS ON MICROCRYSTALLINE CELLULOSE COLUMNS\*

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**Summary** Magnesium, calcium, strontium and barium may be separated quantitatively from each other on a column of microcrystalline cellulose. Barium and radium are also separated from each other. The metal ions are eluted from the column by methanol-hydrochloric acid in varying proportions. The separated metal ions can be titrated with EDTA. Trace amounts of metal ions may be determined by neutron activation.

ALTHOUGH paper chromatography has been widely used for the separation of metal ions as well as organic substances, most of such work has been qualitative and has dealt with the separation of minute quantities. Around 1950 Burstall and co-workers demonstrated the quantitative separation of macro amounts of uranium, thorium, niobium, tantalum and a few other metals on columns filled with activated cellulose.<sup>1,2</sup> Fouarge<sup>3,4</sup> used a cellulose column for the separation of calcium, strontium, barium and radium, but he worked mostly with microgram quantities of radioisotopes. Good separations of the alkaline earths from each other have been obtained on ion-exchange columns with eluents such as ammonium lactate,<sup>5</sup> diaminocyclohexane-tetra-acetic acid and,<sup>6</sup> or  $\alpha$ -hydroxyisobutyrate; however the complexing eluents complicate subsequent measurement of the separated metals.

In the present work, macro or micro quantities of magnesium, calcium, strontium and barium are separated on a column of microcrystalline cellulose. After separation, the eluent is easily volatilized, and the amounts of metal ions separated are sufficient for quantitative titration with 0.01M EDTA. The method also quantitatively separates traces of magnesium or alkaline earth from  $\sim 10^6$  times as much of another alkaline earth.

### EXPERIMENTAL

#### *Reagents and equipment*

Metal chloride stock solutions were prepared. The radioisotopes barium-133, strontium-85, beryllium-7 and radium-226 were obtained commercially. Macro amounts of separated metal ions were titrated with 0.01M EDTA, by standard procedures.

Conventional glass chromatographic columns were used. The conical column was 7 mm in diameter at the base and 24 mm in diameter 200 mm up from the base. For columns requiring pressure, compressed air was used with a Johnson regulator and a Koby air filter.

The gamma emissions of the radioisotopes were counted with an RIDL anti-walk single-channel analyser, model No. 27351, and an NaI(Tl) crystal. An RIDL model 34-26 256-channel gamma-analyser was used to record gamma spectra after production of the radioisotope by thermal neutrons at the Ames Laboratory Research Reactor.

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### Procedures

**Column separations.** The microcrystalline cellulose, FMC Corp. Avicel grade, was slurried with the eluent, and fines were removed. This slurry was added to the column and the cellulose was then worked with 100 ml of the eluent. The eluent level was dropped to that of the cellulose and the sample mixture was added.

The sample mixture was prepared by mixing portions of the metal ion stock solutions in a 10-ml beaker and evaporating to 1.0–3.0 ml. This metal mixture was transferred quantitatively to the cellulose column with a dropping pipette. After the sample was sorbed onto the cellulose, eluent was added and the elution begun.

**Metal-ion determinations.** All the metal ions, except the radioisotopes, were determined by EDTA titration. Barium was titrated spectrophotometrically at pH = 10 with arsenazo I as the indicator at 555 nm.

**Radiometric procedures.** Radioactive effluents were collected in test-tubes and the gamma-emissions measured. Elution curves were drawn and the recovery determined from the ratio of total sample activity to activity of a standard.

For neutron-activation determinations the procedure was as follows: the effluent containing the metal fraction was concentrated by evaporation, nitric acid was added, and the solution was concentrated again to remove chloride. This solution was quantitatively transferred to a volumetric flask, diluted to the mark and an aliquot transferred into a polyethylene vial. Standards and sample vials were irradiated with thermal neutrons at a flux of  $3.5 \times 10^{11}$  n. mm<sup>-2</sup> sec<sup>-1</sup>. Gamma-emissions were measured directly without further sample preparation for barium and strontium concentrations at the mg-level. For the determination of barium at tracer-level concentrations the solution in the irradiated vials was transferred to a beaker, barium and sulphate were added, the precipitate was filtered off and the <sup>139</sup>Ba gamma-emissions were recorded. Unknown concentrations were then determined from a plot of activity *vs.* concentration.

### CONDITIONS FOR SEPARATION

The eluent for our column separations, methanol–hydrochloric acid, was suggested primarily by the work of Sommer<sup>8,9</sup> on qualitative paper chromatography. The proportions of the eluent components were varied until satisfactory separations were obtained on microcrystalline cellulose columns. In general a methanol–hydrochloric acid ratio of 70:30 seems best for separations of magnesium, calcium and strontium, and 95:5 for strontium–barium separations.

Burstall,<sup>1,2</sup> Fouarge<sup>3,4</sup> and others found it necessary to activate cellulose powder by boiling with acid in order to obtain satisfactory chromatographic separations. However, the newer microcrystalline cellulose<sup>10</sup> requires no such treatment. The American Viscose product works better than microgranular Whatman CC-31, which produced tailing (see Fig. 1). Also, columns packed with the American Viscose product had better flow characteristics.

Slahr *et al.*<sup>11</sup> have shown that conical chromatographic columns produce sharper elution bands than cylindrical columns. To test this, the elution band for strontium was compared in conical and cylindrical columns containing the same weight of cellulose. As shown in Fig. 1, the elution band is sharper for the conical column. In the separation of strontium and barium, there is a greater volume between the strontium and barium curves with the conical column.

### RESULTS AND DISCUSSION

Table I shows results for separations of magnesium and the alkaline earths from each other. Methanol–hydrochloric acid (70:30) is used for the separation of magnesium and calcium, and may be used for the separation of strontium also. However, changing to a 95:5 eluent after all the calcium has been eluted sharpens the strontium elution curve considerably. Although barium can be rapidly eluted from the column with water, an eluent such as 80:5:15 methanol–hydrochloric acid–water facilitates conditioning of the column for another separation without repacking.

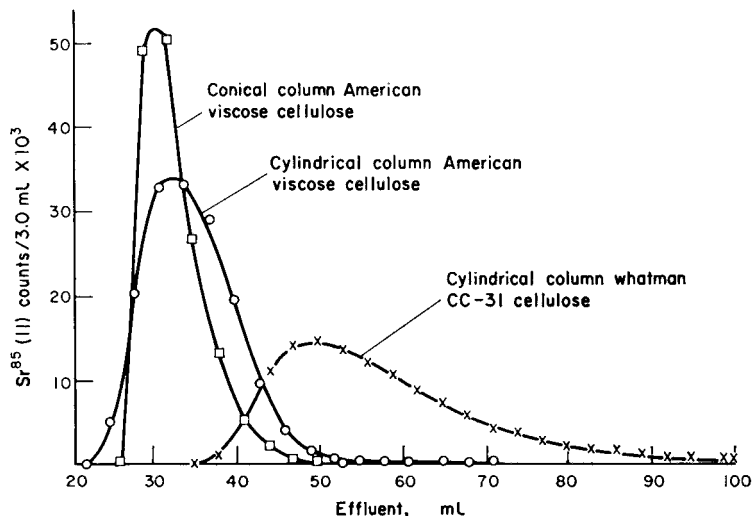


FIG. 1.—Elution of  $^{85}\text{Sr}$  from various cellulose columns. The same weight of cellulose was used in each experiment. Eluent is methanol-hydrochloric acid (95:5).

Further evidence of the efficiency of the method used is the low HETP of 0.6 mm, calculated from the magnesium elution curve in Fig. 2.

Some of the mixtures in Table I contained strontium or barium at tracer-level concentrations. The weight ratio (total metal mixture weight/weight of trace metal) of  $^{133}\text{Ba}$  in experiment 4 and  $^{85}\text{Sr}$  in another experiment was approximately  $10^6$ .

TABLE I.—SEPARATIONS ON MICROCRYSTALLINE CELLULOSE COLUMNS

Sepr. no.	Metal	Eluent, MeOH—HCl—H <sub>2</sub> O	Bandwidth, ml	Taken, $\mu\text{mole}$	Found, $\mu\text{mole}$	Recovery, %	Column length, mm
1	Mg	70-30-0	17-22	74.6	74.6	100.0	250
	Ca	70-30-0	27-34	37.4	37.4	100.0	
2	Mg	70-30-0	20-28	66.0	65.9	99.8	270
	Ca	70-30-0	32-42	37.4	37.2	99.5	
	Sr	70-30-0	49-77	18.0	18.1	100.4	
3	Sr	95-5-0	16-32	37.5	37.2	99.2	260
	Ba	95-5-0	33-64	34.0	34.2	100.6	
4*	Sr	95-5-0	40-96	115	120	104.3	190*
	Ba	0-0-100	165-190	$1.26 \times 10^{-4}$	$1.22 \times 10^{-4}$	96.8	
5	Mg	70-30-0	56	109.0	109.0	100.0	490
	Ca	70-30-0	65-103	79.3	79.5	100.3	
	Sr	95-5-0	116-169	37.5	37.9	101.1	
	Ba	95-0-5	200-243	34.0	33.5	98.5	
6	Mg	20-30-0	25-63	97.1	96.4	99.3	490
	Ca	20-30-0	68-106	74.1	71.1	96.0	
	Sr	90-10	112-202	11.5	11.5	100.0	
	Ba	80-5-15	205-325	10.1	10.3	102.0	

\* Conical column.

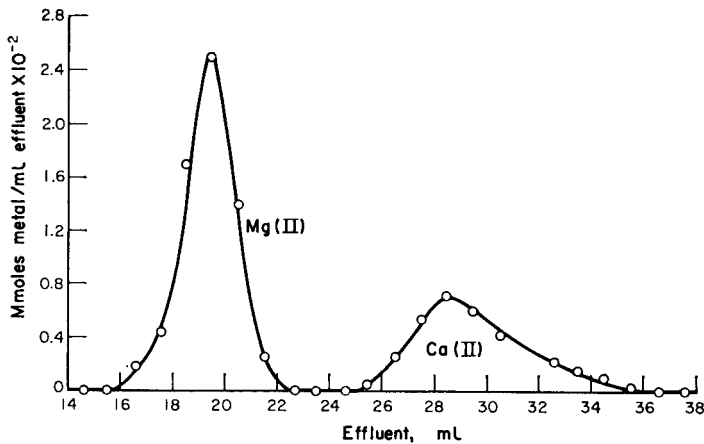


FIG. 2.—Curves for elution of 74.6  $\mu$ mole of magnesium and 37.4  $\mu$ mole of calcium from a 230  $\times$  10 mm cellulose column. Eluent is methanol–hydrochloric acid (70:30); flow-rate 0.5 ml/min.

These experiments not only demonstrate the range of concentrations of metals which can be separated, but also show that the microcrystalline cellulose does not irreversibly retain any of the radioisotopes at the carrier-free concentration level (1  $\mu$ g).

Experiment 6 shows an alkaline earth separation with the strontium and barium concentration determined by neutron activation. The strontium fraction was irradiated for 1.0 min and the barium fraction for 20 sec. The results show that a clean and accurate separation was accomplished.

Determination of very small amounts of barium by chromatographic separation and neutron activation was attempted in the analysis of 10 mg of reagent grade strontium chloride with a barium concentration stated to be 0.002%. After chromatographic separation and activation of the barium fraction, inactive barium chloride was added and all the barium was precipitated and isolated as barium sulphate. Although the amount of barium found was close to that expected, the sensitivity of the neutron-activation method is limited by a blank equivalent to 1.7  $\mu$ g of active barium.

In order to make the alkaline earth separation study more complete, the last in the series,  $^{226}\text{Ra}$  was studied. Results for separations of  $^{133}\text{Ba}$  from  $^{226}\text{Ra}$  are presented in Table II. The recovery of  $^{226}\text{Ra}$  was low in all experiments, owing to the separation of a short-lived radioisotope from the  $^{226}\text{Ra}$  which appears in the effluent before the  $^{133}\text{Ba}$  peak. An elution curve for a barium–radium separation is shown in Fig. 3.

TABLE II.—SEPARATION OF BARIUM, RADIUM AND RARE EARTHS

Sepn. no.	Metal	Eluent, MeOH—HCl—H <sub>2</sub> O	Bandwidth, ml	Taken, $\mu$ mole	Found, $\mu$ mole	Column length, mm
1	Ba	85–5–10	24–57	9.97	9.63	140
	Ra	0–0–100	42–	$7.1 \times 10^{-4}$	$6.6 \times 10^{-4}$	
2	Ba	85–5–10	30–81	9.97	10.05	140
	Ra	0–0–100	85–130	$7.1 \times 10^{-7}$	$6.2 \times 10^{-4}$	
3	Er	4M HNO <sub>3</sub> —EtOH	25–45	87.0	87.0	270
	Ba	1:2	58–90	$1.26 \times 10^{-4}$	$1.22 \times 10^{-4}$	

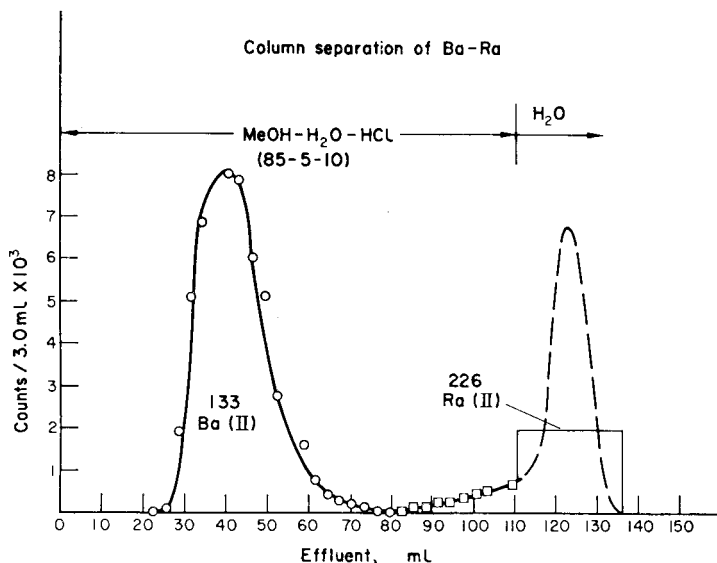


FIG. 3.—Separation of  $^{133}\text{Ba}$  and  $^{226}\text{Ra}$  on a  $150 \times 10$  mm microcrystalline cellulose column. Eluent is methanol-hydrochloric acid-water (85:10:5); flow-rate 0.1 ml/min.

The separation of  $^7\text{Be}$ -Mg was studied on a  $270 \times 11$  min cellulose column with a methanol-hydrochloric acid (70:30) eluent. Only a partial separation was achieved, with considerable overlap of peaks. The  $^7\text{Be}$  peak preceded the Mg peak.

Because the alkaline earths and rare earths often appear together, results for separation of some of the alkaline earths from some of the rare earths are presented in Table II. The representative rare earth, europium, was separated from all the alkaline earths except calcium which appeared with the europium in the effluent.

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**Zusammenfassung**—Magnesium, Calcium, Strontium und Barium können an einer Säule aus mikrokristalliner Cellulose quantitativ voneinander getrennt werden. Auch Barium und Radium werden getrennt. Die Metallionen werden von der Säule mit Methanol-Salzsäure in wechselnden Verhältnissen eluiert. Die getrennten Metallionen können mit EDTA titriert werden. Spuren von Metallionen können durch Neutronenaktivierung bestimmt werden.

**Résumé**—On peut séparer quantitativement les magnésium, calcium, strontium et baryum l'un de l'autre sur une colonne de cellulose microcristalline. Le baryum et le radium sont aussi séparés l'un de l'autre. On élue les ions métalliques de la colonne par le méthanol-acide chlorhydrique en proportions variables. On peut titrer les ions métalliques séparés à l'EDTA. On peut déterminer des traces d'ions métalliques par activation de neutrons.

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## RESOLUTION OF RACEMIC SUBSTANCES BY LIQUID ION-EXCHANGE

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**Summary**—Two optically active liquid anion-exchangers have been synthesized. The separation factors of the enantiomers of sodium ( $\pm$ )-mandelate and sodium-*N*-acetyl-( $\pm$ )-alanate have been determined by batchwise equilibration of aqueous solutions of the salts with chloroform solutions of each of the exchangers. Sodium mandelate has been resolved by Craig countercurrent extraction with one of these exchangers. Optically pure products can be obtained even though the liquid ion-exchanger is not optically pure.

PREVIOUS papers from this laboratory have described the resolution of mandelic acid by chromatography with an optically active anion-exchange resin<sup>1</sup> or Sephadex<sup>2</sup> as the stationary phase, also the separation of diastereoisomeric esters by chromatography on optically inactive ion-exchange resins.<sup>3,4</sup> Dashkevich<sup>5</sup> equilibrated water with solutions of ( $\pm$ )-mandelic acid in several optically active organic liquids. In most cases, a partial resolution resulted. His most favourable results were obtained with (–)-menthone; the separation factor of the enantiomers, calculated from the results, is 1.055. This is much better than the factor (1.005) found for Lott's anion-exchange resin<sup>1</sup> although not so good as the factors found for the resolution of the diastereoisomeric esters<sup>3,4</sup> (1.07–1.15). However, a repetition in this laboratory of Dashkevich's experiments yielded a separation factor of 1.010 for (–)-menthone,<sup>6</sup> although better agreement was obtained with (–)-carvone and other optically active liquids.

An attempt was made<sup>6</sup> to resolve mandelic acid chromatographically with a stationary phase of equal volumes of (–)-carvone and tetrachloroethylene supported by beads (100–200 mesh) of polystyrene cross-linked with 2% of divinylbenzene. The resin was superficially sulphonated<sup>8</sup> and the eluent was water. A slight resolution was obtained, and the separation factor was found to be 1.010, in agreement with Dashkevich's results. However the height of one theoretical plate was 10 mm, too large for a satisfactory resolution. Siliconed diatomaceous earth<sup>9</sup> was also used as support for the (–)-carvone, but no resolution was observed.

Since liquid ion-exchangers generally have greater selectivity coefficients than the analogous ion-exchange resins, it was hoped that an optically active liquid anion-exchanger would have a greater separation factor for the enantiomers of mandelate ion than does Lott's ion-exchange resin.

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## EXPERIMENTAL

*Synthesis of optically active liquid ion-exchangers*

(-)-*N*-(1-naphthyl)methyl- $\alpha$ -methylbenzylamine,  $C_{16}H_{17} \cdot CH_2 \cdot NH \cdot CH(C_6H_5)CH_3$ , hereafter denoted S-amine or Sa, was prepared as follows: (-)-*N*-methylbenzylamine was obtained by resolving the racemic reagent-grade chemical with (+)-tartaric acid<sup>10</sup> or was purchased from Norse Chemical Co., Cudahy, Wisconsin. The products from both sources were usually 99% optically pure or better, never less than 97%.

To prepare S-amine, equimolar quantities of the active  $\alpha$ -methylbenzylamine and chloro(1-naphthyl)methane (Eastman, practical grade, distilled) were dissolved in toluene and heated in an oil-bath at 110° until the mixture was apparently solid. The mixture was filtered with suction, and the filtrate was heated again in the oil-bath. This process was repeated a few times until no further crystallization occurred. Aqueous sodium hydroxide was added to the crystals to liberate the S-amine. This was dissolved in twice its volume of ether. The solution was dried with sodium sulphate and filtered. The ether was evaporated, and the residual brown liquid was distilled at low pressure.

The properties of S-amine are: b.p. 175–177° at 2.5–4 mbar;  $d_{25}^{25}$  1.063,  $n_D^{25}$  1.6175,  $[\alpha]_D^{25}$  -17.80 (neat); insoluble in water but soluble in most organic liquids. A potentiometric titration in glacial acetic acid with standard perchloric acid showed 5.15% N (theory 5.36).

S-amine hydrochloride, SaHCl, was prepared by passing dry hydrogen chloride into a solution of S-amine in dichloromethane and filtering off the resulting crystals;  $[\alpha]_D^{25}$  -5.74 (4.53 mg/ml in water); solubilities at 25°, 0.20M in chloroform, 0.061M in water, 0.03M in dichloromethane, less soluble in most common organic solvents; molar absorptivities in water  $2520 \pm 20$  at 257 nm,  $6600 \pm 80$  at 283 nm, the wavelength of maximum absorption.

The hydrochloride of (-)-*N*-(*n*-octadecyl)- $\alpha$ -methylbenzylamine, hereafter denoted K-amine or Ka, was prepared analogously to S-amine hydrochloride.<sup>11</sup> 1-Chloro-*n*-octadecane (Eastman, m.p. 18–20°) was substituted for chloro(1-naphthyl)methane, and the quantity of toluene was adjusted so that the reaction mixture refluxed at 140°. Since the free K-amine could not be distilled without decomposition, the pure hydrochloride was not prepared from the distilled amine, but the crude hydrochloride was recrystallized. Crude hydrochloride was dissolved in boiling 95% ethanol (6.7 ml of ethanol per g of hydrochloride). Then water was added, 3.3 ml per g of hydrochloride. The mixture was cooled to 10° and filtered. The crystals were 99.3% pure as judged by potentiometric titration with standard silver nitrate solution.

The specific rotations of K-amine hydrochloride were -21.80 at 589 nm and -70.0 at 365 nm (0.050 g/ml in chloroform). Solubilities at 24° were 0.454M in chloroform, 0.00824M in carbon tetrachloride, 0.00340M in benzene, 0.000305M in *n*-decane and  $<7 \times 10^{-3}M$  in water.

*Batchwise equilibration experiments*

The chloroform and water used in these experiments were saturated with each other before the solutes were dissolved. Equal volumes of 0.1519M S-amine hydrochloride in chloroform, and aqueous solutions containing sodium chloride and sodium ( $\pm$ )-mandelate in various known concentrations, were shaken together in separatory funnels for 3 min. (Preliminary experiments had indicated that equilibrium is reached in 0.5 min.) After separation of the phases, an aliquot of the chloroform solution was evaporated to dryness. The residue was dissolved in 50% acetic acid and titrated potentiometrically with silver nitrate to determine the concentration of chloride in the organic phase.

Total mandelate in the aqueous phase was determined as follows: the entire aqueous phase was made alkaline with a few drops of 8M sodium hydroxide and extracted three times with an equal volume of chloroform to remove the small but appreciable amount of S-amine hydrochloride. Then total mandelate was determined by measuring the absorbance of a diluted aliquot at 257 nm. The molar absorptivity of sodium mandelate was taken<sup>12</sup> as 189.5. The equilibrium concentration of chloride in the water was calculated as the sum of the original chloride concentrations in both phases minus the concentration of chloride in the organic phase as found by the titration. The equilibrium concentration of mandelate in the organic phase was calculated as the difference between the initial and equilibrium concentrations of mandelate in the aqueous phase.

The rotation of the purified aqueous phase was measured within 0.002° at the sodium D line with a Perkin-Elmer polarimeter, model 141. The results were used to calculate the concentration of each enantiomer in each phase and hence the distribution ratios *C* and the selectivity coefficients *E*. In these calculations, -104 was used as the specific rotation of sodium (-)-mandelate.

Similar batchwise extraction experiments were performed with S-amine hydrochloride and sodium *N*-acetyl-( $\pm$ )-alanate and with K-amine hydrochloride and sodium ( $\pm$ )-mandelate and sodium *N*-acetyl-( $\pm$ )-alanate.

*Chromatography*

Attempts were made to find a suitable support for the chloroform solution of S-amine hydrochloride in reversed-phase partition chromatography. The following supports were investigated: cross-linked polystyrene beads, 2% divinylbenzene, 100–200 mesh (Dow Chemical Co.) superficially sulphonated<sup>8</sup>; Amberlite XAD-2, a macroreticular polystyrene resin (Rohm and Haas); silica gel, 100 mesh, treated with dichlorodimethylsilane; Aeropack-30, 100–200 mesh, diatomaceous earth treated with dichlorodimethylsilane (Wilkins Instrument and Research); Tee-6, Teflon-6, 100–110 mesh (Analabs); Kel-F, 50 mesh (3M Co.); vulcanized rubber, 30 mesh (Uniroyal); cellulose, 45% acetylated, 124 mesh (Schleicher and Schuell).

*Craig countercurrent extraction*

The apparatus was fully automated and consisted of 200 tubes, each of 80-ml capacity. The liquid phases were 0.151M S-amine hydrochloride in chloroform and 5.00M sodium chloride in water, mutually saturated before the experiment. Into each of the tubes were put 40.0 ml of the chloroform solution of S-amine hydrochloride. Into the first tube were put 12.1 mmole of sodium ( $\pm$ )-mandelate dissolved in 40 ml of 5.00M aqueous sodium chloride. The phases were equilibrated by 10 strokes of the machine, a number that had proved to be sufficient in preliminary tests. After a settling period of 2 min, the upper phase was transferred to the next tube and 40.0 ml of fresh 5.00M aqueous sodium chloride were added to the first tube. These steps were repeated in the conventional manner. At appropriate intervals, the aqueous phase issuing from the last tube of the apparatus was analysed as described under *Batchwise equilibration experiments*.

The Craig countercurrent extractor was also used in an experiment analogous to displacement chromatography. Into each of the 200 tubes were put 40.0 ml of 0.100M S-amine hydrochloride in chloroform. Then 67 40.0-ml portions of 0.100M aqueous sodium ( $\pm$ )-mandelate were fed into the first tube and distributed among the first 67 tubes by the usual operation of the machine. Thereafter, 40.0-ml portions of 0.100M aqueous sodium hydroxide were fed into the first tube. Analysis of the effluent fractions from the last tube were performed as above.

## RESULTS AND DISCUSSION

*Batchwise equilibration*

Representative results of these experiments with sodium mandelate and S-amine hydrochloride are given in Table I.  $C_n$  is the distribution ratio of the (–)-mandelate, *i.e.*, the ratio of the amount of this species in the organic phase to the amount in the aqueous phase.  $E_n$  is the selectivity coefficient of (–)-mandelate relative to chloride

$$E_n = C_n \cdot \frac{\text{amount of chloride in H}_2\text{O}}{\text{amount of chloride in CHCl}_3} \quad (1)$$

TABLE I.—BATCHWISE EXTRACTIONS OF ( $\pm$ )-MANDELATE BY (–)-S-AMINE HYDROCHLORIDE  
All organic phases were initially 0.1519M (–)-S-amine hydrochloride in chloroform.

No.	Initial molarity of aqueous phase		$C_p$	$C_n$	$E_p$	$E_n$	$\epsilon$
	NaC <sub>8</sub> H <sub>7</sub> O <sub>3</sub>	NaCl					
1	0.05146	3.000	2.35	1.74	62.8	46.5	0.35
2	0.09960	3.000	1.90	1.43	68.8	51.8	0.33
3	0.2002	3.000	1.02	0.805	64.1	50.6	0.27
4	0.3017	3.000	0.639	0.519	60.1	49.4	0.23
5	0.3996	3.000	0.455	0.372	60.0	48.7	0.22
6	0.0500	0.9636	3.81	2.79	35.2	25.8	0.37
7	0.0500	1.995	2.78	2.09	50.6	38.1	0.33
8	0.0500	3.980	2.22	1.58	76.2	54.2	0.41
9	0.0500	4.998	2.17	1.53	92.5	65.2	0.42
Mean					63	48	0.33



$C_p$  and  $E_p$  are defined analogously for the (+)-mandelate.  $E$  is the selectivity coefficient of (+)-mandelate relative to (–)-mandelate.  $\epsilon$  is defined by equation (2)

$$\epsilon = E - 1 = (C_p/C_n) - 1 = (E_p/E_n) - 1. \quad (2)$$

It is to be expected that the values of  $C_p$  and  $C_n$  will vary with changes in the concentrations of the initial solutions. If both solutions are ideal,  $E_p$  and  $E_n$  should be constants. Actually, they are subject to relative standard deviations of about 20%. Variations in activity coefficients, probably aggravated by dimerization of the solutes in the chloroform, are the likely causes of these large deviations. On the other hand, the mean value of  $E$ , 1.33, is subject to a relative standard deviation of only 5.5%.

Table II shows the results of similar experiments with (–)-K-amine hydrochloride and sodium ( $\pm$ )-mandelate. Here the relative standard deviations of  $E_p$  and  $E_n$  exceed 20% while that for  $E$  is only 1.1%.

One batchwise extraction experiment was done with the sodium salt of *N*-acetyl-( $\pm$ )-alanine and S-amine hydrochloride and another with the same sodium salt and

TABLE II.—BATCHWISE EXTRACTIONS OF ( $\pm$ )-MANDELATE BY (–)-K-AMINE HYDROCHLORIDE

In all cases, the initial concentration of sodium mandelate in the water was 0.05029*M* and that of the amine hydrochloride in the chloroform was 0.3500*M*.

No.	Initial molarity of NaCl in water	$C_p$	$C_n$	$E_p$	$E_n$	$\epsilon$
1	1.000	6.84	5.93	23.3	20.2	0.15
2	2.000	4.23	3.75	27.8	24.7	0.13
3	3.000	3.28	2.92	31.9	28.4	0.12
4	4.000	2.96	2.61	39.4	34.8	0.13
5	5.000	2.51	2.25	40.1	36.0	0.12
Mean				32	27	0.13

K-amine hydrochloride. In order to maintain  $E > 1$  in these experiments,  $E$  is defined as the selectivity coefficient of the (+)-enantiomer relative to the (–). The observed values of  $\epsilon$  were 0.064 and 0.007.

Since  $\epsilon$  is a good measure of the ease with which a desired resolution can be accomplished, it must be concluded that neither S-amine nor K-amine offers an efficient method for the resolution of *N*-acetylalanine. On the other hand the value of  $\epsilon$  for S-amine and mandelate is unusually large for the separation of enantiomers. Therefore the chromatographic work and the countercurrent extractions were done only with this pair of compounds.

### Chromatography

Reversed-phase chromatography with the chloroform solution of S-amine hydrochloride as the stationary phase supported by a suitable porous solid would be a much more efficient method of resolution than batchwise extraction. None of the supports was satisfactory. Polystyrene and Amberlite XAD-2 had plate heights of about 10 mm. Although siliconed silica gel can absorb 7% of its weight of chloroform and still remain apparently dry, when this material is placed in water, droplets of chloroform are formed. After absorption of the chloroform the siliconed Aeropack, Teflon and Kel-F floated on water. Therefore the columns were dry-packed, and water was forced through the columns under pressure. None of these columns was

satisfactory for chromatography. Rubber and acetylated cellulose became tacky on contact with chloroform.

### Craig countercurrent elution

When the Craig countercurrent extraction apparatus is used by the method of continuous withdrawal, the process is analogous to elution chromatography. Therefore the equations of ion-exchange elution chromatography<sup>13</sup> are applicable:

$$U^* = CV + V \quad (3)$$

$$M^* = \frac{J}{V} \sqrt{\frac{p}{2\pi C(1 + C)}} \quad (4)$$

$$\log M = \log M^* - 0.217 p \left( \frac{C + 1}{C} \right) \left( \frac{U - U^*}{U^*} \right)^2 \quad (5)$$

where  $p$  is the number of tubes in the apparatus exclusive of the first (199);  $V$  is the total volume of mobile phase in these tubes (7960 ml);  $U$  is the volume (ml) of effluent from the apparatus;  $M$  is the molarity of a sample constituent in a fraction of the effluent; the asterisk denote the values at the peak of the graph;  $J$  is the amount (mmole) of a sample constituent.

Before the countercurrent experiment was performed, the ideal graphs of  $M$  vs.  $U$  were calculated for each enantiomer as follows. Since the original concentrations of sodium chloride and amine hydrochloride were the same as in experiment 9 of Table I,  $E_p$  was taken as 92.5 and  $E_n$  as 65.2. Then  $C_p$  and  $C_n$  were calculated (2.794 and 1.969, respectively) by equation (1) with the assumption that the extent of the ion-exchange reactions caused only negligible changes in the concentrations of chloride in the two phases. Finally, equations (3)–(5) were used to calculate  $M$  at assumed values of  $U$  for each isomer. These are the full-line curves of Fig. 1. It is clear that 200 plates or tubes are not sufficient to give a quantitative resolution of mandelate ion; nevertheless the calculations indicate that 3.0 mmole of each enantiomer, *i.e.*, half of the quantities taken, should theoretically be obtained in an optical purity of 99.96%.

The dashed-line curves of Fig. 1 are the experimental plots of  $M$  vs.  $U$  for the two enantiomers. Two discrepancies between the theoretical and experimental curves are clearly visible. First, the peak of each experimental curve precedes that of the ideal curve by about 2000 ml. According to equation (3), this means that the  $C$  values for the experimental curves are less than those calculated from the values of  $E_n$  and  $E_p$  of experiment 9 of Table I. The  $\epsilon$  value calculated from the experimental peaks is 0.52. Secondly, the experimental peaks are wider than the theoretical peaks. An increase in the width of a peak in elution chromatography is associated with a decrease in the number of plates in the column. However, there can be no uncertainty or variation in the number of tubes in a countercurrent extraction. The apparent decrease in the number of tubes may be due to failure to reach equilibrium in each tube although the preliminary experiments indicated that sufficient time was allowed for equilibration. Other causes of the greater spreading may be (1) variations in  $E_n$ ,  $E_p$ ,  $C_n$  and  $C_p$  as compositions of both phases were changed, (2) the wall effect or failure of all of the upper phase to be transferred to the next tube and (3) imperfect functioning of the apparatus so that more or less than 40.0 ml of 5.00M sodium chloride was added to

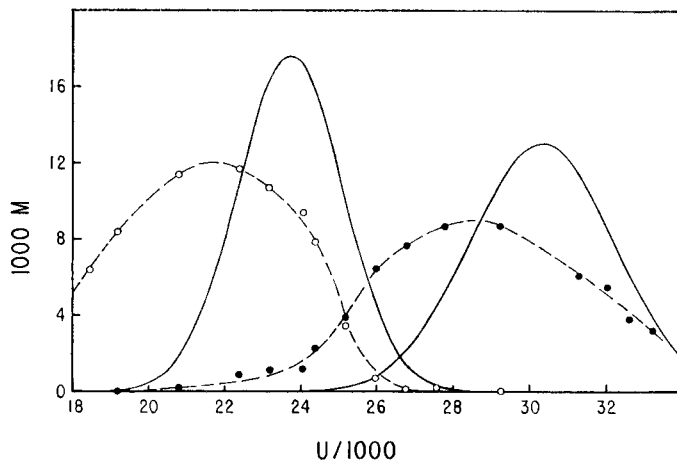


FIG. 1.—Ideal (full line) and experimental (dashed line) curves for the resolution of sodium mandelate by countercurrent extraction, elution method.

the first tube. It is probable that all three of these considerations contributed to the spreading of the peaks.

#### *Craig displacement*

It is well known that a larger yield can be obtained by displacement chromatography than by elution chromatography. Analogously, larger yields of the enantiomers are to be expected if racemic sodium mandelate is resolved with S-amine by the displacement method of countercurrent extraction. If a binary mixture, consisting of equal concentrations of the two constituents [such as sodium ( $\pm$ )-mandelate] is to be separated and if the front between these solutes is to emerge from the apparatus in its steady state, the maximum number of tubes,  $r$ , into which the sample may be put, is related<sup>14</sup> to the total number of tubes,  $p$ , by

$$r = 2pe/(2 + \epsilon) \quad (6)$$

(The notation of this paper rather than Trémillon's is used.) The value of  $p$  is 200, and  $\epsilon$  was assumed to be 0.40; then  $r$  is 67.

Expected breakthrough points were calculated from the original contents of the Craig tubes with the assumption that each tube contained 40.00 ml of upper phase. The expected values were 13320, 14660 and 16000 ml for (–)-mandelate, (+)-mandelate and hydroxide respectively.

The circles in Fig. 2 show the experimental results. The breakthroughs of (–)- and (+)-mandelate occurred at 13460 and 14890 ml. The differences from the expected results are due to the failure of the Craig apparatus to deliver exactly 40.00 ml of sodium hydroxide to the first tube at each step and to failure to make the various solutions exactly 0.1000M. The experiment was stopped at 15880 ml, before the breakthrough of the sodium hydroxide.

Curve A is drawn to fit the experimental points of the breakthrough of (–)-mandelate. Although the curve is not symmetrical, its steepness indicates that  $E_n$  is large. Curve B shows the concurrent decrease in chloride. Ideal breakthrough

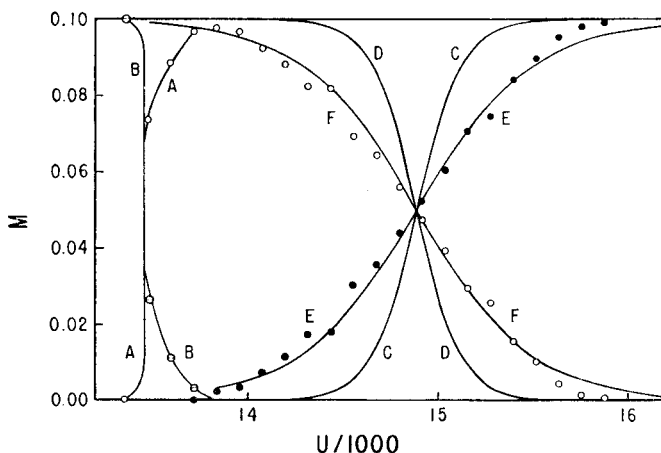


FIG. 2.—Resolution of sodium mandelate by countercurrent extraction, displacement method.  $\ominus$  chloride;  $\circ$  (–)-mandelate;  $\bullet$  (+)-mandelate. See text for the significance of curves A, B, C, D, E and F.

graphs of (+)-mandelate were calculated by the equation<sup>15</sup>

$$M = M_i / (1 + E^n) \quad (7)$$

where  $M_i$  denotes the total concentration in the upper phase,  $0.1000M$ , and  $n$  is the number of transfer steps between any given abscissa and the breakthrough, taken as negative after the breakthrough. Curves C and D were calculated with  $\varepsilon = 0.40$ . The experimental points lie very far from these graphs. However, the assumption that  $\varepsilon = 0.14$  yields curves E and F in fairly good agreement with the experimentally determined points. This approximate agreement does not indicate that  $\varepsilon$  was 0.14 under the conditions of this experiment. If it had been so small, the front between the isomers would have been very far from the steady state on emergence from the apparatus; and this fact would have made the curve even more flat. The correct value of  $\varepsilon$  for the conditions of this experiment lies between 0.14 and 0.40.

The results indicate that 36 mmole of each enantiomer were obtained with an optical purity of 99% or better.

#### *Effect of optical purity of the resolving agent*

Let us now consider the effect of the presence of some of the (+)-isomer in the (–)-S-amine hydrochloride that is used in a resolution of sodium mandelate by countercurrent elution extraction. Let the subscripts 1, 2 and 3 refer respectively to the pure (–)-exchanger, to the exchanger consisting of  $y$  mole-fraction of (+)- and  $(1 - y)$  mole-fraction of (–)-isomer, and to the pure (+)-exchanger. Let the subscripts  $n$  and  $p$  refer to the two mandelate enantiomers. Then

$$C_{1n} = \frac{v_0 M_0 X_{1n}}{v_w [(-)\text{-Ma}^-]_w} \quad (8)$$

where  $M_0$  is the total concentration of S-amine in the organic phase,  $X_{1n}$  is the fraction of it combined with (–)-mandelate, and  $v_0$  and  $v_w$  are the volumes of the organic and aqueous phases respectively.

In one tube of exchanger 2, there are  $(1 - y)v_0M_0$  mmole of (–)-exchanger and  $yv_0M_0$  mmole of (+)-exchanger. The quantity of (–)-S-amine (–)-mandelate in this tube is  $(1 - y)v_0M_0X_{1n}$  and the quantity of (+)-S-amine (–)-mandelate is  $yv_0M_0X_{3n}$ . The total amount of (–)-mandelate in the organic phase of this tube is  $v_0M_0X_{2n}$ . Therefore

$$v_0M_0X_{2n} = (1 - y)v_0M_0X_{1n} + yv_0M_0X_{3n}$$

Substitution of equation (8) and analogous equations in this yields

$$C_{2n} = C_{1n}(1 - y) + yC_{3n}$$

and since

$$C_{3n} = C_{1p},$$

$$C_{2n} = C_{1n}(1 - y) + yC_{1p}. \quad (9)$$

An analogous derivation yields

$$C_{2p} = C_{1p}(1 - y) + yC_{1n}. \quad (10)$$

Thus if the  $C$  values of both enantiomers of the sample with respect to an optically pure stationary phase are known, the  $C$  values with an optically impure resolving agent can readily be calculated.

To consider the effect of an optically impure stationary phase on a displacement experiment, it is necessary only to note that  $E = C_p/C_n$ . Therefore, for the optically impure exchanger

$$E_2 = \frac{C_{1p}(1 - y) + yC_{1n}}{C_{1n}(1 - y) + yC_{1p}}. \quad (11)$$

Table III shows the effect of (+)-S-amine hydrochloride in the (–)-isomer when this exchanger is used to resolve sodium mandelate by both the elution and displacement methods of countercurrent extraction. The values in columns 3, 4 and 5 were calculated by equations (9), (10) and (11) respectively, with the assumptions that  $C_{1n} = 1.980$  and  $C_{1p} = 2.810$ . In the 6th column,  $p$  represents the number of tubes in the Craig apparatus necessary for a quantitative resolution (0.05% cross-contamination) by the elution method. It was calculated from the equation

$$\sqrt{p} = 3.29(C_n + C_p + 1)/(C_p - C_n).$$

In the 7th column,  $r$  represents the maximum number of tubes in a 200-tube apparatus into which racemic mandelate may be put if the front is to attain the steady state; it was computed by equation (6) with the same assumptions for  $C_{1n}$  and  $C_{1p}$  as above. In the last column,  $w$  represents the quantity (mmole) of each mandelate enantiomer that is obtained with an optical purity of 99% or better. The same assumptions as above were made; also it was assumed that 40.0 ml of racemic mandelate were put into each of  $r$  tubes (column 6), that  $v_0 = v_w$  and that all solutions were 0.100M. To calculate  $r$ , equation (7) was used to calculate the limiting values of  $n$  for the overlap region ( $0.01 < M/M_t < 0.99$ ). Subtraction of  $n$  for the overlap region from  $r$  and division of this difference by 2 yields the number of tubes containing 40.0 ml of 0.100M solution of each pure enantiomer. When  $y \geq 0.20$ , the overlap region is greater than  $r$  and no pure enantiomers are obtained.

Although this section deals specifically with the resolution of sodium mandelate by optically impure S-amine hydrochloride by countercurrent extraction, the equations

TABLE III.—THE EFFECT OF THE OPTICAL PURITY OF THE STATIONARY PHASE

$y$	Optical purity of exchanger, %	$C_{2n}$	$C_{2p}$	$E$	$p$	$r$	$w$ , mmole
0.000	100.0	1.980	2.810	1.419	527	69	84
0.050	90.0	2.021	2.769	1.370	649	62	68
0.100	80.0	2.063	2.727	1.322	824	55	44
0.150	70.0	2.105	2.688	1.276	1079	48	24
0.200	60.0	2.146	2.644	1.232	1464	41	0
0.250	50.0	2.187	2.603	1.190	2097	34	0
0.300	40.0	2.229	2.561	1.149	3293	27	0
0.400	20.0	2.312	2.478	1.072	13170	13	0
0.500	0.0	2.395	2.395	1.00			

and principles are also applicable to the resolution of other racemic substances by other optically impure stationary phases by either countercurrent extraction or chromatography. This is a potential advantage of these methods in comparison with the classical method that depends on the differences in the solubilities of diastereoisomeric salts. Another such advantage is that chromatography and countercurrent extraction yield in one operation both enantiomers in equal amounts and purities. In contrast, a recrystallization procedure that yields one enantiomer in the desired purity often yields the other in much smaller amount and in much lower purity.

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**Zusammenfassung**—Zwei optisch aktive flüssige Anionenaustauscher wurden synthetisiert. Durch portionsweise Gleichgewichtseinstellung wässriger Lösungen der Salze mit Chloroformlösungen der Austauscher wurden die Trennfaktoren der Antipoden von Natrium( $\pm$ )mandelat und Natrium-*N*-acetyl( $\pm$ )alanat bestimmt. Natriummandelat wurde durch Gegenstromextraktion nach Craig mit einem der Austauscher in seine Antipoden gespalten. Man kann optisch reine Produkte erhalten, auch wenn der flüssige Ionenaustauscher nicht optisch rein ist.

**Résumé**—On a synthétisé deux échangeurs d'anions liquides optiquement actifs. On a déterminé les facteurs de séparation des énantiomères du ( $\pm$ )-mandélate de sodium et du *N*-acétyl ( $\pm$ )-alanate de sodium par mise en équilibre par portions des solutions aqueuses des sels avec des solutions chloroformiques de chacun des échangeurs. On a dédoublé le mandélate de sodium par extraction à contre-courant de Craig avec l'un de ces échangeurs. On peut obtenir des produits optiquement purs même si l'échangeur d'ions liquide n'est pas optiquement pur.

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## DETERMINATION OF PALLADIUM AND PLATINUM BY ATOMIC ABSORPTION\*

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**Summary**—Palladium and platinum are determined by atomic absorption after fire-assay concentration into a gold bead. The limit of determination is  $\sim 0.06$  ppm in a 20-g sample. Serious depressive interelement interferences are removed by buffering the solutions with a mixture of cadmium and copper sulphates with cadmium and copper concentrations each at 0.5%. Substantial amounts of Ag, Al, Au, Bi, Ca, Co, Cr, Fe, Hg, K, La, Mg, Mn, Mo, Na, Ni, Pb, Te, Ti, V, Y, Zn, and the platinum metals do not interfere in the atomic-absorption determination.

IN THE determination of platinum by atomic absorption serious depressive interelement interferences are found, particularly from other noble metals, as illustrated in Fig. 1. These effects cannot be eliminated by the use of addition, dilution, or other related techniques. Strasheim and Wessels,<sup>1</sup> who first noted these interferences, were able to overcome the depressive effects of these and other elements by determining platinum in strongly buffered solutions of copper sulphate at a total salt concentration of 5%. Although effective, this high salt concentration leads to some problems such as burner clogging.

We have tested other salts that might be as effective as copper sulphate but at a lower concentration. The greatest reduction of interference was obtained with mixtures of cadmium and copper sulphates, and one containing 0.5% each of cadmium and copper was selected. In addition to lowering the total salt content required, this mixed reagent enhances the sensitivity for the determination of both palladium and platinum.

A procedure is proposed in which palladium and platinum are preconcentrated in a gold bead resulting from fire-assay fusion and cupellation. After dissolution of the bead in *aqua regia* the palladium and platinum are determined in a cadmium-copper sulphate solution by atomic absorption. The limit of determination is  $\sim 0.06$  ppm in a 20-g sample.

### EXPERIMENTAL

#### Reagents

*Gold wire* for fire-assay, 99.999% pure and 0.1 mm diameter. Prepare in lengths weighing 2.5 mg.

*Gold solution.* Prepare from the same stock of gold wire a gold chloride solution containing 2.5 mg of gold per ml in 1% v/v hydrochloric acid.

*Mixed cadmium-copper solution.* Dissolve 57.0 g of cadmium sulphate ( $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ ) and 98.2 g of copper sulphate pentahydrate in a mixture of 500 ml of hydrochloric acid and 300 ml of water. Dilute to 1 litre with water.

*Standard stock solutions of platinum metals.* Prepare from the metals or the ammonium chloro-salts, stock solutions containing 1.000 mg of metal per ml in 2% v/v hydrochloric acid. Prepare other solutions by diluting these stock solutions by factors of ten, with 2% v/v hydrochloric acid.

\* Publication authorized by the Director, U.S. Geological Survey.



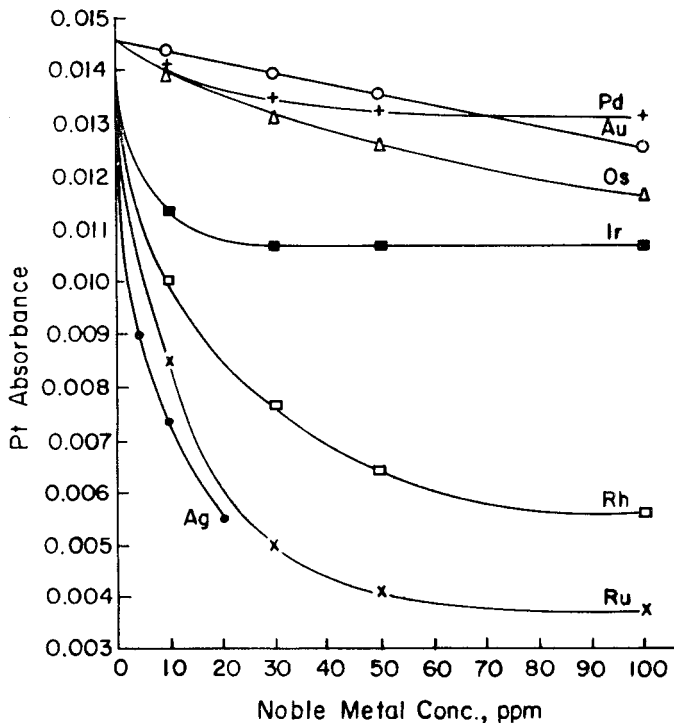


FIG. 1.—Effect of noble metal concentration on the absorbance of 10 ppm Pt in 10% v/v hydrochloric acid.

#### Instrument parameters and settings

A Perkin-Elmer Model 303 instrument was used with the following operating conditions.

	Palladium	Platinum
Wavelength	340.5 nm	265.9 nm
Slit	0.3 mm	0.3 mm
Hollow-cathode current	30 mA	25 mA
Acetylene flow-setting	6	6
Air flow-setting	6.8	6.8
Flame	oxidizing	oxidizing
Burner	standard head	standard head
Aspirator	adjusted for optimum uptake	adjusted for optimum uptake

#### Procedure

The fire-assay fusion and cupellation follow accepted practices as described by Bugbee.<sup>2</sup> The specific procedure adopted, including recommended flux compositions for acid and basic rocks, is that described by Haffy and Riley<sup>3</sup> except that 2.5 mg of gold are used as carrier instead of 1. A 15–30-g sample and a blank are taken for the assay.

Transfer to a small beaker the gold bead obtained on cupellation. Add 2 ml of *aqua regia* and allow the mixture to stand overnight at room temperature. Heat the solution to ensure complete dissolution of the bead. Repeat the treatment with hot *aqua regia* if necessary. Evaporate the solution to dryness on a steam-bath. Add 1 ml of hydrochloric acid (1 + 1) and again evaporate the solution to dryness on a steam-bath. Repeat. Add 1 ml of the cadmium-copper solution, warm briefly to dissolve salts, and transfer the solution to a 5-ml volumetric flask. Dilute to the mark with water. Prepare palladium and platinum standards and blanks each containing 2.5 mg of gold and 1 ml of the cadmium-copper solution in 5 ml total volume. Determine palladium and platinum on all solutions by atomic absorption.

## RESULTS

The determination of palladium by atomic absorption is accompanied by few, if any, interferences. For this reason all tests were made with a view to establishing the best conditions for the determination of platinum. These conditions were then tested and adopted for the determination of palladium.

*Effect of various acids*

The atomic absorption by platinum decreases with increase in concentration of hydrochloric, nitric or perchloric acid. The relative decrease is approximately the same with the first two, but more serious for the latter. The absorbance from 100 ppm platinum in 10% v/v hydrochloric acid is about 8% less than that for a solution containing no acid. A 10% v/v hydrochloric acid concentration was used to provide for a silver solubility of up to 20 ppm. The solubility of silver, an element not uncommonly isolated in a fire assay, increases with increase in hydrochloric acid concentration. Increased acidities can be used, but at reduced platinum sensitivity, when more than 20 ppm of silver are encountered.

*Interference studies*

To overcome the depressive interferences from various metals, Strasheim and Wessels<sup>1</sup> recommended that platinum be determined in the presence of sufficient copper sulphate to maintain the copper concentration at 2%. They also noted that depressive effects remained marked even at concentrations up to 1.5% of copper. We examined a number of other compounds, and of those tested, cadmium sulphate, lanthanum chloride, lanthanum sulphate, lead nitrate, zinc sulphate and mixtures of cadmium and copper sulphates, all showed varying degrees of interference reduction in 10% v/v hydrochloric acid. From the standpoint of low total salt concentration, least interference with platinum absorbance from other noble metals was obtained with mixtures of cadmium and copper sulphates, followed closely by lanthanum sulphate. Differences were too slight to make the choice of the mixed cadmium-copper system other than arbitrary. These mixtures proved to be effective over a wide range of cadmium-copper concentration ratios, from 5:1 to 1:5. Tolerances for interfering metals were found to increase with increase in cadmium and copper concentrations. A final concentration of 0.5% each of cadmium and copper was selected for the operating conditions.

The causes of depressive interelement effects are not understood. The apparent reduction of the number of platinum atoms in the normal state may be due to excitation (including collisions of the second kind), ionization or chemical (condensed phase type) interference. It is also not known why copper sulphate or mixtures of cadmium and copper sulphates are effective in minimizing interference. But the co-presence of sulphate is necessary as other salts of these metals such as acetate, nitrate and chloride, or sulphuric acid alone, act as serious depressants.

*Tolerances for other elements*

In determination of 10 or 100 ppm of platinum the atomic absorption procedure tolerates separately (error less than 2%) 1000 ppm each of Al, Bi, Co, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Te, Ti, V, Zn, and 200 ppm each of Ir, Os, Pd and Ru, the maximum tested. Unless higher concentrations of cadmium and copper sulphate are

used, rhodium should be restricted to 150 ppm. At the 10-ppm level of platinum, 1000 ppm each of Hg, La and Y, and 400 ppm of Cr do not interfere; at the 100 ppm level of platinum only half the concentration noted for each of these elements is tolerated. In determination of palladium at the 10 or 100 ppm level, 200 ppm each of Ir, Os, Pt, Rh and Ru, and 1000 ppm each of the other metals listed above are tolerated separately. In determining palladium or platinum, silver does not interfere up to 20 ppm, the limit of solubility under conditions provided. As noted earlier, more silver can be tolerated at higher acidities; alternatively, small amounts of silver chloride can be removed by filtration. Gold depresses the absorbance of platinum by 1% for each 100 ppm of gold present, but this is easily compensated for by adding gold to the standards. The palladium determination is not affected by at least 500 ppm of gold. Although it is possible to tolerate up to 1000 ppm of Ca in determining Pd or Pt, the calcium concentration is best limited to less than 200 ppm because of the formation of calcium sulphate and attendant burner difficulties.

Mixtures of platinum metals were also tested. Negligible interference was obtained in the determination of 10, 50, 100 or 200 ppm of platinum in solutions also containing mixtures of 100 ppm each of Rh, Ru, Os, Pd and Ir, and 20 ppm of Ag. No interference was found in the determination of 10, 50, 100 or 200 ppm of palladium in solutions containing mixtures of 100 ppm each of Rh, Ru, Os, Pt and Ir, and 20 ppm of Ag.

#### *Standard curves for platinum and palladium*

The standard curve relating net absorbance to concentration of platinum at 265.9 nm is linear up to a concentration of 200 ppm of platinum, the maximum tested. The low concentration region up to 10 ppm of platinum was examined in detail, and after allowing for a small reagent blank, no deviation from linearity was found. The sensitivity is 1.7 ppm Pt for 1% absorption. While platinum can be detected in solution at a concentration of 0.04 ppm, the lower determination limit if the error is not to exceed 15% is 0.25 ppm. Thus 0.06 ppm is determinable in 20 g of original sample.

The standard curve for palladium at 340.5 nm is also linear up to 200 ppm. The sensitivity is 0.8 ppm Pd, the detection limit is 0.04 ppm in solution, and the determination limit is 0.25 ppm in solution or 0.06 ppm in 20 g of original sample.

#### *Dissolution of the gold bead from cupellation*

Sometimes the gold bead obtained on cupellation dissolves with difficulty in *aqua regia*. This occurs especially when the weight ratio of silver to gold in the bead lies between 1:3 and 3:1. When this occurs, the ratio can be changed, within limits, by adding more gold in a repeat fire assay. Compensating amounts of gold are then added to the standards in the atomic-absorption determination.

#### *Test of total procedure*

Samples of which the palladium and platinum contents had been determined either chemically or by emission spectroscopy were used to test the proposed atomic-absorption procedure. The chemical determinations were made on completely decomposed samples by the procedure of Grimaldi and Schnepfe<sup>4</sup> and the other

determinations were made on fire-assay beads by the solution-spectrochemical procedure of Haffty and Riley.<sup>3</sup> The results, shown in Table 1, are in good agreement. Some of the scatter in repeat determinations is undoubtedly due to heterogeneity of the palladium and platinum distribution in the samples.

TABLE I.—COMPARISON OF RESULTS BY VARIOUS METHODS

Sample location	Palladium, ppm					Platinum, ppm					
	Atomic absorption		Chemical		Spectro-chemical	Atomic absorption		Chemical		Spectro-chemical	
Rhodesia	0.83	0.83	0.81	0.80	—	1.80	1.80	1.73	1.80	—	
1	0.81	0.82	0.78	0.83		1.95	1.90	1.80			
Rhodesia	1.15	1.15	1.15	1.15	—	3.43	3.33	3.50	3.41		
2	1.12	1.12	1.05	1.10	—	3.20	3.80			—	
La Plata district;	0.35	0.35	—		0.37	0.42	0.43	0.43	—	0.36	0.43
Colorado-1	0.26	0.33			0.45		0.39	0.48		0.37	
La Plata district;	2.70	2.71	—		2.7		1.33	1.30	—	1.3	
Colorado-2											
Keystone district;	3.21	2.94	—		3.2		0.65	0.68	—	0.67	
Wyoming											

**Zusammenfassung**—Nach Schmelzanreicherung in einer Goldperle werden Palladium und Platin durch Atomabsorption bestimmt. Die Nachweisgrenze beträgt in einer 20 g-Probe etwa 0,06 ppm. Grobe Fehler nach unten durch Fremdelemente unterdrückt man durch Puffern der Lösungen mit Cadmium- und Kupfersulfat von je 0,5%. Wesentliche Mengen Ag, Al, Au, Bi, Ca, Co, Cr, Fe, Hg, K, La, Mg, Mn, Mo, Na, Ni, Pb, Te, Ti, V, Y, Zn und Platinmetalle stören bei der Atomabsorptionsbestimmung nicht.

**Résumé**—On détermine le palladium et le platine par absorption atomique après concentration par fusion dans une perle d'or. La limite de dosage est ~0,06 ppm dans un échantillon de 20 g. On élimine de sérieuses interférences dépressives entre éléments en tamponnant les solutions avec un mélange de sulfates de cadmium et de cuivre, avec des concentrations de cadmium et de cuivre de 0,5% chaque. Des quantités substantielles de Ag, Al, Au, Bi, Ca, Co, Cr, Fe, Hg, K, La, Mg, Mn, Mo, Na, Ni, Pb, Te, Ti, V, Y, Zn et les métaux de la mine du platine n'interfèrent pas dans la détermination par absorption atomique.

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## CATALYTIC ACTIVITY AND COMPLEXATION—IV\*

### 2,2'-BIPYRIDYL AS ACTIVATOR FOR THE CATALYTIC ULTRAMICRO DETERMINATION OF SILVER

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**Summary**—The activation of the catalytic persulphate oxidation of sulphanilic acid when the catalyst, silver(I), is suitably complexed, is discussed. 2,2'-Bipyridyl is proposed as activator as it accelerates the rate-determining step of the process—the oxidation of silver(I) to silver(II). The mechanism of activation is investigated and discussed in detail. On the basis of these investigations a catalytic method has been developed for the determination of silver(I), with a sensitivity of  $4 \times 10^{-4}$   $\mu\text{g/ml}$  and  $\pm 7.6\%$  relative error.

ON THE basis of some theoretical considerations we have predicted that the oxidation of sulphanilic acid by persulphate could serve as an indicator reaction for the determination of silver(I) by its catalytic action.<sup>1</sup> Experiments have confirmed this assumption. During the course of the reaction an orange-red colour develops which makes possible photometric kinetic measurements. The reaction has good selectivity but its sensitivity is low—amounts of 50  $\mu\text{g}$  can be determined in a total volume of 25 ml. For this reason it was decided to select a suitable activator which could increase the sensitivity of the reaction.

Investigations of the reaction kinetics showed<sup>1</sup> that the probable mechanism of the catalytic reaction is persulphate oxidation of silver(I) to a higher oxidation state which reacts with the substrate sulphanilic acid (*Sulph*) to give an orange-red product *P* and silver(I).

The question of which higher oxidation state of silver is involved—Ag(II) or Ag(III)—is still discussed in the literature, many authors being inclined to believe that Ag(II) is formed.<sup>2</sup> Our results<sup>1</sup> lead to the same conclusion.

Kinetic data<sup>1</sup> have shown that the rate-determining step of the reaction is the oxidation of Ag(I) to Ag(II). It was necessary, therefore, to find an activator capable of accelerating this step. Such an activator might be a substance which can decrease the oxidation potential of the couple Ag(II)/Ag(I).

Scrocco *et al.*<sup>3</sup> found that the standard oxidation potential of the system Ag(II)/Ag(I) in the presence of 2,2'-bipyridyl is 1.453 V, whereas in 2M nitric acid and 4M perchloric acid it is 1.914 V and 2.00 V respectively<sup>4,5</sup>. The relative stability of Ag(II) complexes with bipyridyl would be expected because of the higher charge being spread over a larger ion, and because of the extra binding energy of bipyridyl to the bivalent silver.

That bipyridyl could serve as an activator for the oxidation of Ag(I) to Ag(II) and therefore for the catalytic process in question was proved experimentally.

\* Part III: *Inorg. Chim. Acta*, 1967, **1**, 432.

## EXPERIMENTAL

The reaction rate was followed by the change in the absorbance at 535 m $\mu$  of the reaction system, due to the formation of the orange-red reaction product. The solutions of the reagents were placed in three separate sections of the glass reaction vessel<sup>6</sup> and kept for 15 min in a thermostat. The reagents were then mixed by vigorous shaking and the solution was transferred to the photometer cell.

In all the experiments the reagent solutions—persulphate and sulphanilic acid—were prepared in buffer solutions and the total volume made up to 25 ml in the reaction vessel with the same buffer solution. Thus the ionic strength was kept constant, even when the reagent concentrations were varied.

The molar absorptivity of the reaction product is very high permitting the reaction kinetics to be followed during the initial period of the reaction, when the fraction  $x$  of the substrate used is negligible compared to its initial concentration  $C_0$ . In this case the kinetic equation

$$\frac{dx}{dt} = k \cdot f(C)(C_0 - x)^n \quad (1)$$

can be simplified to

$$\frac{dx}{dt} = k \cdot f(C) \cdot C_0^n \quad (2)$$

which on integration gives

$$x = k \cdot f(C) \cdot C_0^n \cdot t. \quad (3)$$

In equations (1)–(3)  $f(C)$  stands for the terms which take into account the concentrations of persulphate and the catalyst. Potassium persulphate was used in a large excess compared with the sulphanilic acid concentration, and therefore, during the course of the reaction its concentration remained practically constant, as did that of the catalyst. Under these conditions equation (3) can be represented as

$$x = k' \cdot t. \quad (4)$$

The constant  $k'$  can be determined from the slope of the graph of  $x$  against the time  $t$ , *i.e.*,

$$k' = \tan \alpha' = \frac{\Delta x}{\Delta t} \quad (5)$$

and  $x$  can be determined from the Lambert-Beer law and substituted in equation (5), which then becomes

$$k'' = \tan \alpha = \frac{\Delta A}{\Delta t} \quad (6)$$

Equation (6) was used for the determination of the reaction rate in the initial period of the reaction.

The stock reagent solutions of 0.01M sulphanilic acid, and 0.1M potassium persulphate, were made from reagent grade substances dissolved in water that had been twice distilled in a Jena glass vessel.

The stock solution of silver(I) nitrate was 10<sup>-3</sup>M. Working solutions (10<sup>-6</sup>M) were prepared by dilution each day, because such concentrations change on prolonged storage. The solutions of silver nitrate were stored in dark vessels.

## RESULTS

The dependence of the reaction rate on the acidity of the solution was studied in the pH range 1.0–8.5. The acidity in the pH range 1.0–2.4 was adjusted by the addition of a suitable amount of sulphuric acid. In the pH range 2.4–8.5 the buffers were made from acetic, phosphoric and boric acids (0.4M, 1:1:1) and suitable volumes of 0.2M sodium hydroxide. The acidity was checked with a pH-meter. The results are shown in Fig. 1. It can be seen that the reaction rate has a maximum value in the pH range 4.2–4.4.

The temperature dependence of the reaction rate was studied in the range 20–60° at pH 4.35. From the results plotted in Arrhenius co-ordinates the activation energy was calculated and found to be 10.75 kcal/mole and 7.30 kcal/mole for the uncatalysed and catalysed reactions respectively.

The influence of 2,2'-bipyridyl, persulphate and sulphanilic acid on the reaction rate was studied at 30° and pH 4.35. The results for 2,2'-bipyridyl are given in Fig. 2.

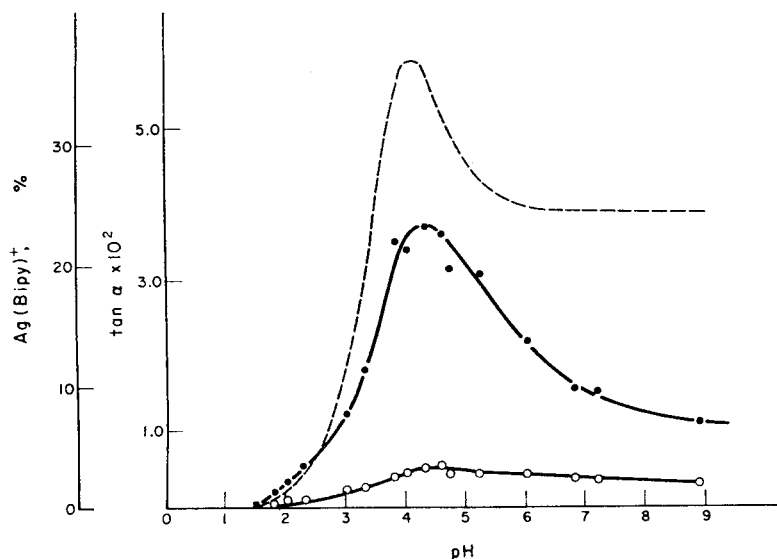


FIG. 1.—Dependence of the reaction rate on the acidity.  
 ○—Uncatalysed reaction; ●—in the presence of catalyst. Dotted line shows the formation curve of  $\text{Ag}(\text{bipy})^+$ . Sulphanilic acid  $2 \times 10^{-3}M$ , potassium persulphate  $2 \times 10^{-2}M$ , silver nitrate  $4 \times 10^{-7}M$ , 2,2'-bipyridyl  $9.6 \times 10^{-4}M$ ; temperature  $20.0 \pm 0.1^\circ\text{C}$ .

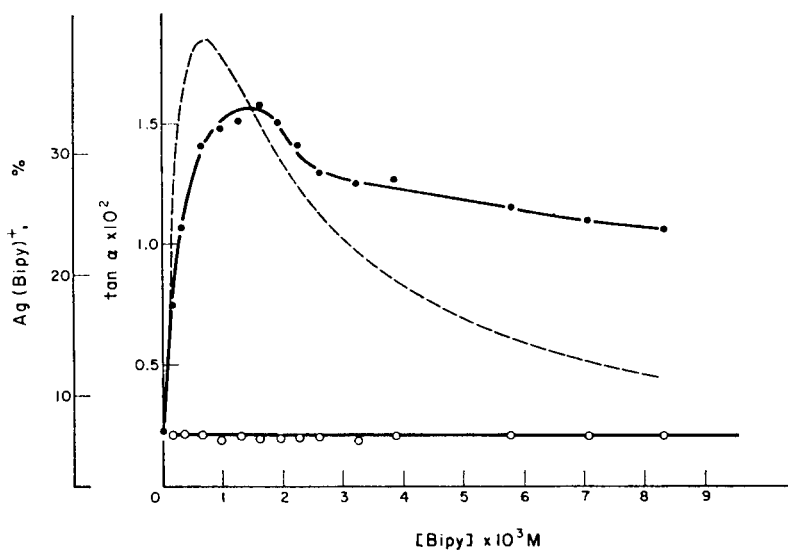


FIG. 2.—Dependence of the reaction rate on 2,2'-bipyridyl concentration.  
 ○—Uncatalysed reaction; ●—in the presence of catalyst. Dotted line shows the formation curve of  $\text{Ag}(\text{bipy})^+$ . Sulphanilic acid  $2 \times 10^{-3}M$ , potassium persulphate  $2 \times 10^{-2}M$ , silver nitrate  $4 \times 10^{-7}M$ ; pH 4.35; temperature  $30.0 \pm 0.1^\circ\text{C}$ .

The rate increases linearly with persulphate concentration in the range  $0.2 \times 10^{-3}$ – $8 \times 10^{-3}M$  for both catalysed and uncatalysed reactions. The concentration of sulphanilic acid shows a similar influence on the reaction rate, but only up to concentrations of about  $10^{-4}M$ , after which the catalytic reaction gradually becomes independent of sulphanilic acid concentration.

#### DISCUSSION

The experimental results show that the kinetic equation of the uncatalysed reaction can be written as

$$v = k \cdot [S_2O_8^{2-}][Sulph] \quad (7)$$

where  $v$  is the reaction rate and  $k$  represents the reaction rate constant.

The catalysed reaction is also first order with respect to persulphate and sulphanilic acid. These data combined with those of a calibration curve lead to the kinetic equation

$$v_c = \chi [S_2O_8^{2-}][Sulph][Ag^+] \quad (8)$$

where  $\chi$  is the apparent rate constant, which includes also the concentration of the activator, 2,2'-bipyridyl.

However, first order reaction with respect to sulphanilic acid is followed at low concentrations of the substrate ( $0.1 \times 10^{-4}$ – $1.0 \times 10^{-4}M$ ); at concentrations over  $2 \times 10^{-3}M$  the kinetic equation becomes of the type

$$V_c = \chi \cdot [S_2O_8^{2-}][Ag^+] \quad (9)$$

which is usual for silver-ion catalysed oxidation reactions of persulphate.<sup>2</sup>

The transformation of equation (8) into equation (9) at substrate concentrations still very low compared with that of the oxidant (1:20) also confirms the fact that the rate determining step of the reaction is the oxidation of silver(I).

The kinetic equations (7) and (8) are of the same type as for the unactivated reaction,<sup>1</sup> indicating that the activator does not change the reaction mechanism but only accelerates the rate-determining step of the reaction.

The graph of the dependence of reaction rate of 2,2'-bipyridyl concentration has a maximum (Fig. 2), which can be explained by complex formation between the catalyst and the activator.

As reduction of Ag(II) to Ag(I) is faster than oxidation of Ag(I) to Ag(II) most of the catalyst is present in the system as Ag(I), which forms two complexes with the activator— $Ag(bipy)^+$  and  $Ag(bipy)_2^+$ . The formation of the co-ordinatively saturated complex  $Ag(bipy)_2^+$ , however, prevents the interaction of the catalyst with the other reagents, *i.e.*, the oxidant and the substrate, this decreasing the reaction rate.

If the activation effect is really connected with the formation of an unsaturated complex of the catalyst with the activator, a correlation must exist between the reaction rate and the extent of formation of  $Ag(bipy)^+$ . We calculated the fraction of the silver bound as  $Ag(bipy)^+$  for the reaction conditions stated for Fig. 2. These data are plotted as the dotted line on the same figure. The formation of silver(I) complexes with sulphanilic acid and the protonation of 2,2'-bipyridyl were also taken into account by means of side-reaction coefficients  $\alpha_M$  and  $\alpha_L$ .<sup>7</sup> All data for the stability constants of the complexes were taken from Sillén and Martell's tables.<sup>8</sup>

The similarity of the two curves is striking, with a sharp increase at small activator



concentrations and a gradual decrease after the maximum. The maximum of the formation curve is slightly displaced to lower activator concentrations compared with that of the kinetic curve, probably because the formation curve is calculated on the assumption that silver is present in the solution entirely as Ag(I). The fact that part of the silver exists as Ag(II) would increase the value of  $\alpha_M$  and would therefore displace the maximum to the right.

The slope of the kinetic curve after the maximum is less than that of the formation curve of Ag(bipy)<sup>+</sup> and the maximum is not so sharp. Possibly the second molecule of 2,2'-bipyridyl can be displaced from the co-ordination sphere of silver(I), which would account for the considerable reaction rate even under conditions where Ag(bipy)<sub>2</sub><sup>+</sup> is the dominant silver(I)-bipyridyl species.

Further evidence for the role of Ag(bipy)<sup>+</sup> in the process is given by the dependence of the reaction rate on the acidity, shown in Fig. 1. We calculated the formation curve of Ag(bipy)<sup>+</sup> for the reaction conditions stated for Fig. 1. The formation curve is shown in the same figure as a dotted line. Again, the close resemblance is striking. The formation curve has a plateau in the pH range 6–8, while the kinetic curve keeps on going down, though with a changed character. This difference could be connected with the dependence of the rate of the uncatalysed reaction on the acidity. It is well known that the rates of oxidation reactions with persulphate decreases when the acidity of the solution diminishes.<sup>2</sup> The rate of oxidation of silver(I) to silver(II) in alkaline solution therefore decreases, accounting for the lower overall reaction rate.

#### ANALYTICAL PROCEDURE

The investigations described above were used to decide that the following optimal conditions for the determination of micro amounts of silver would be  $2 \times 10^{-3}M$  sulphanilic acid and  $2 \times 10^{-2}M$  potassium persulphate in pH 4.35 buffer solution;  $1.6 \times 10^{-3}M$  2,2'-bipyridyl; temperature  $30.0 \pm 0.1^\circ$ ; dilution to 25 ml with pH 4.35 buffer solution; measurement at 535 nm.

The calibration curve for silver was prepared by using these conditions with silver(I) concentrations in the range  $4 \times 10^{-4}$ – $3 \times 10^{-3}\mu\text{g/ml}$ .

The influence of some other metal ions which usually accompany silver in its ores and minerals was also studied. The experiments were carried out under the same conditions as for the calibration curve. The silver(I) concentration was  $1.07\mu\text{g}/25\text{ ml}$ . The maximum permissible amounts of these ions (in  $\mu\text{g}/25\text{ ml}$ ) are shown in Table I.

The results for the calibration curve were also used to calculate the standard deviation  $s$  and the 95% confidence limit relative error  $\Delta x$  of the method.<sup>9</sup> The values are  $1.38 \times 10^{-3}\mu\text{g}$  and  $\pm 7.6\%$  respectively.

The absence of a systematic error in the method was demonstrated by means of

TABLE I.—INFLUENCE OF OTHER METAL IONS

Interfering ion	Tolerance $\mu\text{g}$	Interfering ion	Tolerance, $\mu\text{g}$
Ir(IV)	2.5	Pt(IV)	100
Hg(II)	5	Ru(III)	100
Au(III)	10	Os(VIII)	100
Pd(II)	10	Fe(III)	100
Cu(II)	10	Zn(II)	100
Cd(II)	50	Te(IV)	100
Ni(II)	50	Tl(I)	1000
As(V)	50	Pb(II)	1000
Mn(II)	55		

Student's  $t$ -test. The  $t$ -values were 1.35 for the results and 2.37 from the  $t$ -table, i.e.,  $t_{\text{table}} > t_{\text{found}}$ .

**Zusammenfassung**—Die Aktivierung der katalytischen Persulfatoxidation von Sulfanilsäure, wenn der Katalysator Silber(I) komplex gebunden ist, wird diskutiert. 2,2'-Bipyridyl wird als Aktivator vorgeschlagen, da es den geschwindigkeitsbestimmenden Schritt des Prozesses, die Oxidation von Silber(I) zu Silber (II), beschleunigt. Der Mechanismus der Aktivierung wird erforscht und im Detail diskutiert. Auf Grund dieser Versuche wurde ein katalytisches Verfahren zur Bestimmung von Silber(I) entwickelt, mit einer Empfindlichkeit von  $4 \cdot 10^{-4} \mu\text{g/ml}$  und  $\pm 7,6\%$  relativem Fehler.

**Résumé**—On discute de l'activation de l'oxydation catalytique au persulfate de l'acide sulfanilique lorsque le catalyseur, l'argent(I), est convenablement complexé. On propose le 2,2'-bipyridyle comme activateur étant donné qu'il accélère le stade déterminant la vitesse du processus l'oxydation de l'argent(I) en argent(II). On étudie et discute en détail le mécanisme d'activation. Sur la base de ces recherches on a élaboré une méthode catalytique pour le dosage de l'argent(I), avec une sensibilité de  $4 \times 10^{-4} \mu\text{g/ml}$  et une erreur relative de  $\pm 7,6\%$ .

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## ADVANTAGES OF A TWO-DETECTOR SYSTEM IN AUTOMATED SUBSTOICHIOMETRIC RADIOISOTOPE DILUTION ANALYSIS

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**Summary**—Automation widens the scope of substoichiometric radioisotope dilution analysis. This is because the very strict requirement of the manual method—chemical separation of exactly equal quantities of the test substance—need no longer be fulfilled: reproducibility of the determination is reached by means of automated operation and activity measurement. The theory given in this paper shows how the choice of suitable chemical reactions is widened and why the reliability and the advantages of isotope dilution analysis are secured by the use of a two-detector system.

ISOTOPIC tracer methods involve heterogeneous chemical equilibria and can be described by the radioactivity–mass balance equilibrium

$$\frac{y + x}{y} = \frac{A_y}{m_y} \cdot \frac{m_x}{A_x}$$

where  $x$  is the quantity of the non-active species to be determined,  $y$  is the quantity of the radioactive species added (serving as a standard and chemically identical with the non-active species), and  $A_y$  and  $A_x$  denote the activities of the amounts  $m_y$  and  $m_x$  chemically separated from the radioactive standard and from the mixture of it with the test substance.

There are two related cases.

1. Isotope dilution analysis<sup>1</sup> which is based on measurement of the *change of specific activity* (from  $A_y/m_y$  to  $A_x/m_x$ ).
2. Radiometric analysis<sup>2</sup> which is based on measurement of the *change of distribution of the radioactive species* between two phases.

Although in both cases the radioactivity of the separated chemical compound reflects the presence of a non-active species to be determined, only isotope dilution analysis possesses the unique advantage that irreproducible losses of the species to be determined (which have occurred after isotopic equilibrium has been reached, *e.g.*, during some preliminary separation steps) have no influence on the analytical result.

The application of substoichiometric separation to isotope dilution renders the determination of specific activities unnecessary and enhances the value of this method in trace analysis.<sup>3</sup> In order to ensure reproducible isolation of equal amounts, very strict requirements must be met, including the one that no more than 0.1% of the reagent may remain unreacted at chemical equilibrium. This, of course, limits the

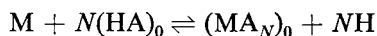
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choice of reagents to those having high equilibrium constants. In order to overcome this limitation De Voe *et al.*<sup>4</sup> and Kyrš<sup>5</sup> suggested the use of calibration curves. However, as  $m_x$  became inevitably a function of  $(x + y)$  the methods were no longer those of isotope dilution, but less favourable radiometric procedures and are therefore referred to as substoichiometric radiometric analysis<sup>4</sup> or concentration dependent distribution.<sup>5</sup> A further disadvantage of these methods is that the reproducibility is critically dependent on the reproducibility of the chemical separation, which in turn depends on small changes of acidity, volumes of phases, temperature, time, *etc.*,<sup>5</sup> and is no longer controlled by the amount of reagent consumed.

A commercial instrument (Technicon AutoAnalyzer) is already available, which permits strict control of all reaction conditions (including time and temperature) in a simple way. Our experience with this instrument<sup>6-8</sup> convinced us that the strict requirements imposed on substoichiometric separation when performed manually are not needed in the case of automated operation. In order to automate *isotope dilution analysis* a two-detector system is proposed, whereby the activities before and after substoichiometric separation are simultaneously recorded and used for evaluation.

#### THEORY

Solvent extraction of the metal ion M with the reagent HA dissolved in the organic phase may be described by the equilibrium



where subscript 0 refers to the organic phase. All charges are omitted for simplicity. The extraction constant corresponding to this equilibrium is

$$K = \frac{[\text{MA}_N]_0 [\text{H}]^N}{[\text{M}] [\text{HA}]_0^N}$$

Introducing the total metal concentration  $C_M$  and total reagent concentration  $C_{\text{HA}}$  and assuming the volumes of the water and organic phases to be equal, we obtain

$$\frac{(C_M - [\text{MA}_N]_0)(C_{\text{HA}} - N[\text{MA}_N]_0)^N}{[\text{MA}_N]_0} = \frac{[\text{H}]^N}{K}$$

This equation gives an  $(N + 1)$ th order equation for  $[\text{MA}_N]_0$  as a function of  $C_M$ ,  $C_{\text{HA}}$  and  $[\text{H}]^N/K$ . Of the possible  $(N + 1)$  solutions, however, only one corresponds to reality.

Considering the simplest case, when  $N = 1$  and the dissociation of the reagent in the aqueous phase can be neglected,

$$[\text{MA}]_0^2 - [\text{MA}]_0 \left( C_M + C_{\text{HA}} + \frac{[\text{H}]}{K} \right) + C_M \cdot C_{\text{HA}} = 0 \quad (1)$$

When substoichiometric isolation is carried out,  $[\text{H}]/K$  (ideally) approaches zero, giving

$$[\text{MA}]_0 = C_M \quad \text{for} \quad C_M < C_{\text{HA}}$$

and

$$[\text{MA}]_0 = C_{\text{HA}} \quad \text{for} \quad C_M > C_{\text{HA}} \quad (\text{see Fig. 1}).$$

When the chemical conditions of separation are less favourable, as reflected by an increase in the value of  $[H]/K$ , deviations from the straight-line relationship will occur. With  $[MA]_0$ ,  $C_M$  and  $[H]/K$  expressed in units of  $C_{HA}$ , the substoichiometric extraction curves have been calculated for values of  $[H]/K$  equal to  $0.1C_{HA}$ ,  $C_{HA}$  and  $10C_{HA}$ , Fig. 1. Clearly the substoichiometrically isolated amounts (*i.e.*, for  $C_M > C_{HA}$ ) depend on the total amount of metal present.

Substoichiometric radioisotope dilution analyses are always based on the substoichiometric separation of an amount  $m_y$  from a standard solution of the labelled material; this is followed by the separation under identical conditions of an amount,

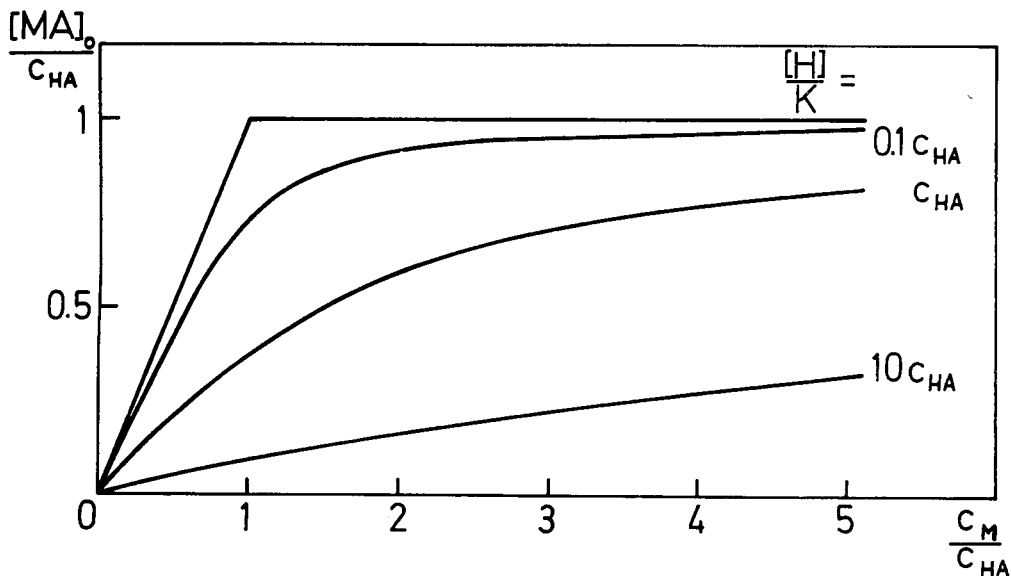


FIG. 1.—The amount of metal substoichiometrically extracted, as a function of  $C_M$ , acidity and  $K$ -value.

$m_x$ , of a mixture of amounts  $x$  of the element being determined and  $y$  of the tracer used. For the standard solution  $C_M = y$  and for the mixture  $C_M = x + y$ .

The isotope-dilution equation

$$x = y \left( \frac{A_y m_x}{A_x m_y} - 1 \right) \quad (2)$$

then reduces to

$$x = y \left( \frac{A_y}{A_x} - 1 \right) \text{ only if } \frac{[H]}{K} \text{ approaches } 0.$$

This limits the choice of chemical reagents to those having very high values of  $K$ .

The measured value of the total activity added,  $A^T$ , and the isolated activity in the organic phase,  $A$ , are related to the original specific activity  $S$  of the labelled metal ions added, by the equations

$$A_y^T = k' S y \quad \text{and} \quad A_y = k'' S m_y$$

where  $k'$  and  $k''$  are constants depending on the measurement geometry, amplification, detector dead-time and radioactive decay. Within certain limits these constants can be electronically controlled.

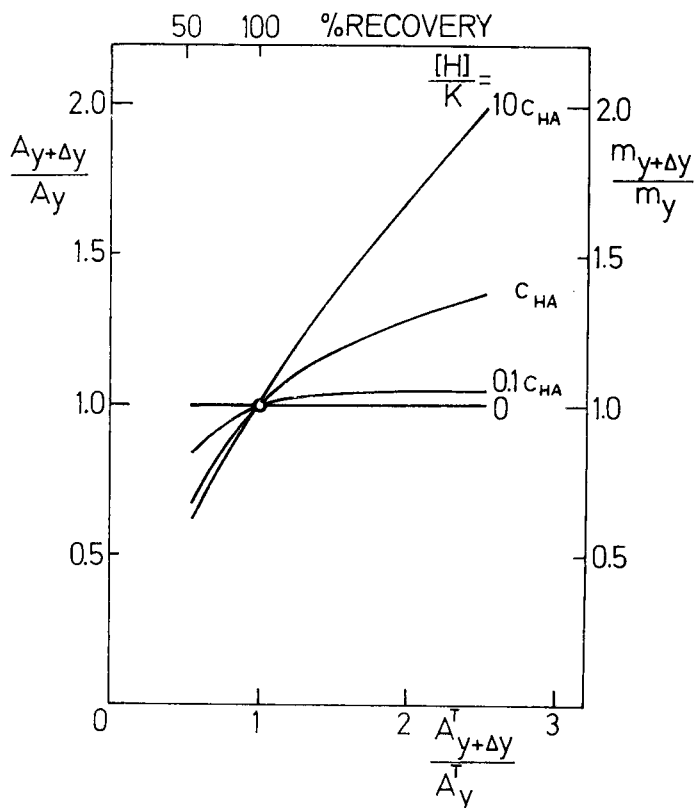


FIG. 2.—The height of a standard peak as a function of acidity,  $K$ -value and various yields of preliminary separation ( $y = 2C_{HA}$ , constant specific activity,  $A_{y+\Delta y}^T/A_y^T = 1$  for 100% recovery).

In the proposed method the activities  $A^T$  and  $A$  are continuously measured by flow-cell detectors (1 and 2 in Fig. 4) and recorded by means of a twin-pen recorder attached to the ratemeters. The activities can be conveniently expressed as peak heights,<sup>6-8b</sup> because  $A^T$  and  $A$  are measured virtually simultaneously and the geometry of the cells and the amplification factors remain constant. The ratios of  $A^T$  and  $A$  are, under those conditions, independent of radioactive decay.

Variation in the added amount of labelled metal,  $\Delta y$ , for  $x = 0$ , is reflected in the values of  $A_y^T$ ,  $m_y$  and consequently  $A_y$ . Thus

$$\frac{A_{y+\Delta y}^T}{A_y^T} = \frac{y + \Delta y}{y} \quad \text{and} \quad \frac{A_{y+\Delta y}}{A_y} = \frac{m_{y+\Delta y}}{m_y}$$

As  $m_{y+\Delta y}/m_y$  is related to  $(y + \Delta y)/y$  through equation (1), where  $m_{y+\Delta y}$  and  $m_y$  correspond to the values of  $[MA]_0$  for  $C_M = y + \Delta y$  and  $y$ , respectively, one obtains

$$\frac{m_{y+\Delta y}}{m_y} = \frac{A_{y+\Delta y}}{A_y} = f\left(\frac{A_{y+\Delta y}^T}{A_y^T}\right).$$

This relationship is shown in Fig. 2 for  $y = 2C_{HA}$  and for  $[H]/K = 0, 0.1C_{HA}, C_{HA}$

and  $10C_{\text{HA}}$ . The condition  $y = 2C_{\text{HA}}$  corresponds to 50% stoichiometry, and is chosen as the most favourable. (If  $y > 2C_{\text{HA}}$  too much activity is lost, and if  $C_{\text{HA}} < y < 2C_{\text{HA}}$  the selectivity of separation becomes lower.<sup>3,9</sup>) Figure 2 is characteristic for each chemical system and important in practical evaluation of losses or "gains" and will be discussed below; it is sometimes known as the "activity-activity curve." In the ideal case  $A_{y+\Delta y}/A_y = 1$  for any  $A_{y+\Delta y}^T/A_y^T$ . This corresponds to complete fulfilment of the substoichiometric condition that equal amounts of metal ion are extracted from standard and sample,  $m_x = m_y$ , i.e., to the curves of Figs. 1 and 3 when  $[\text{H}]/K = 0$ . When this ideal condition is not met  $m_x \neq m_y$  and the amount of metal separated depends solely upon the amount present in the aqueous phase (Fig. 1). This is reflected in deviations from the zero slope shown in Fig. 2,

When an unlabelled amount of metal,  $x$ , is present beside the labelled amount,  $y$ , ( $C_M = y + x$ ), then

$$A_x^T = k'Sy \quad \text{and} \quad A_x = k''Sm_x \frac{y}{y+x}.$$

In practice determinations of  $x$  are based on the peak height ratio,  $A_y/A_x$ , and it is seen that

$$\frac{A_y}{A_x} = \frac{m_y}{m_x} \cdot \frac{y+x}{y} \quad (3)$$

Thus, this ratio is a function of  $y$  and  $C_M$ , because  $m_y$  and  $m_x$  corresponds to the values of  $[\text{MA}]_0$  [equation (1)] for  $C_M$  equal to  $y$  and  $(y+x)$ , respectively. With  $y = 2C_{\text{HA}}$  as above, Fig. 3 shows this peak height ratio as a function of  $x$  (calibration graph) expressed in units of  $C_{\text{HA}}$  for values of  $[\text{H}]/K$  of 0,  $0.1C_{\text{HA}}$ ,  $C_{\text{HA}}$  and  $10C_{\text{HA}}$ . As in Figs. 1 and 2 it is noted that deviations from ideality occur as  $[\text{H}]/K$  increases.

If, during the course of analysis, losses (or gains) of  $C_M$  take place (losses during preconcentration and preseparation procedures performed manually) although an initial isotopic equilibrium is established, the peak height ratio  $A_y/A_x$  will only remain unaffected when  $m_y = m_x$ . For all other cases, when the chemical conditions are less favourable, corrections are necessary.

Equation (3) shows that as long as the losses or gains occur after establishment of isotopic equilibrium, the value of  $(y+x)/y$  remains constant. Therefore the peak height ratio depends only on the ratio  $m_y/m_x$ . This is illustrated in Fig. 3, where peak height ratios are calculated as a function of the original value of  $x$  (expressed in units of  $C_{\text{HA}}$ ) for  $y = 2C_{\text{HA}}$  assuming 25% loss (or gain) for the cases  $[\text{H}]/K = 0, 0.1C_{\text{HA}}, C_{\text{HA}}$  and  $10C_{\text{HA}}$ , respectively. The relationships are seen to be nearly rectilinear within the given ranges.

Calculations based on Fig. 3 and assuming the most favourable case of  $A_y/A_x = 2$  and  $x = y = 2C_{\text{HA}}$  indicate that if  $A_y/A_x$  can be determined with a maximal error of 2.5%, then  $x$  can be determined with errors of approximately 5, 6, 10 and 20%, for the  $[\text{H}]/K = 0, 0.1C_{\text{HA}}, C_{\text{HA}}$  and  $10C_{\text{HA}}$  respectively. In practice, where submicrogram quantities are to be automatically determined within, say, a maximum error of 10%, the value of  $[\text{H}]/K$  for any particular reaction should never be higher than  $C_{\text{HA}}$ .

Calculations for  $N > 1$  are analogous to those above, although they are more

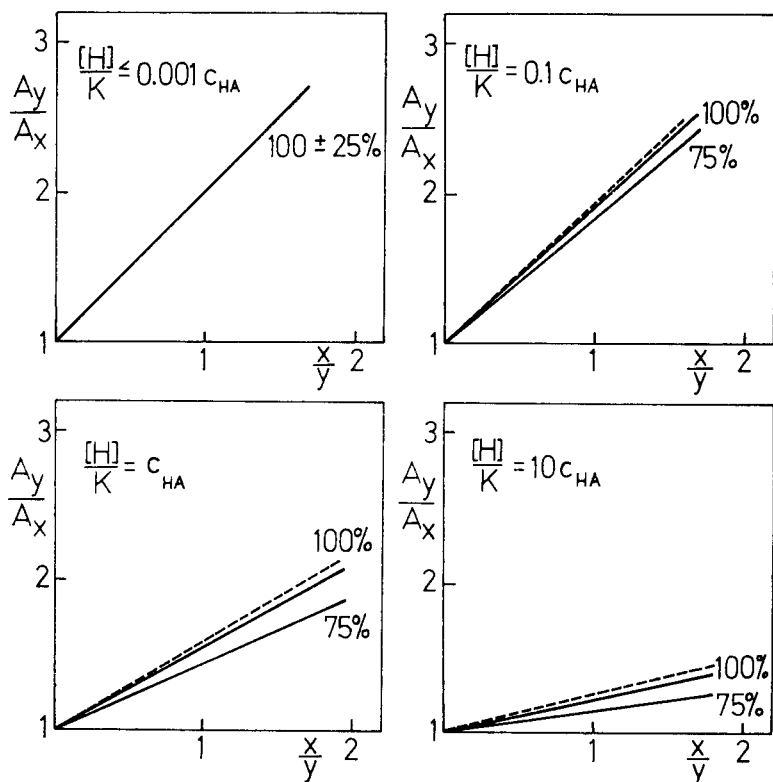


FIG. 3.—Calibration graphs as calculated for various chemical equilibria and various yields of the preliminary separation ( $y = 2C_{HA}$ , variable specific activity). The broken curve shows 25% gain.

complicated. However, a general conclusion may be drawn that the limiting condition for manual substoichiometry, namely  $[H]/K^{1/N} \leq 0.001 C_{HA}$  (for  $C_M = 2C_{HA}$ ),<sup>3</sup> changes in the automated method to  $[H]/K^{1/N} \leq C_{HA}$ .

#### DISCUSSION

The improvement on the manual method basically derives from the superior reproducibility of the automatic method. The stringent chemical requirements in the manual method provide for inevitable between-sample variations in temperature, time and vigour of shaking, pH *etc.* Lack of chemical control cannot be compensated for entirely by the AutoAnalyzer, because in the extreme limit, approached when  $[H]/K > 10C_{HA}$  (Figs. 1–3), no separation takes place and the analysis fails completely. However, as shown above, the chemical conditions can be relaxed when an AutoAnalyzer is used. The two-detector system allows deviations from the ideal chemical case to be noted and corrected for readily, so that substoichiometric analyses can be easily performed with the accuracy and precision usually associated with the method.

All cases considered above are valid for the equilibrium state, which need not necessarily be reached in a continuous flow system, where kinetic parameters play a more important role in manual batch analysis.



### Outline of procedure

In practice the suitability of a chemical reaction which has been chosen from theoretical data can be tested by the following experiment. A series of solutions, containing increasing quantities of  $y$  are automatically analysed as shown diagrammatically in Fig. 4. The recorded values of  $A_y^T$ ,  $A_{y+\Delta y}^T$ ,  $A_y$  and  $A_{y+\Delta y}$  are plotted as in Fig. 2. If the slope of the resulting curve (for values of  $A_{y+\Delta y}^T/A_y^T \geq 1.5$ ) is the same or smaller than that for  $[H]/K = C_{HA}$ , a calibration graph may be prepared. For that

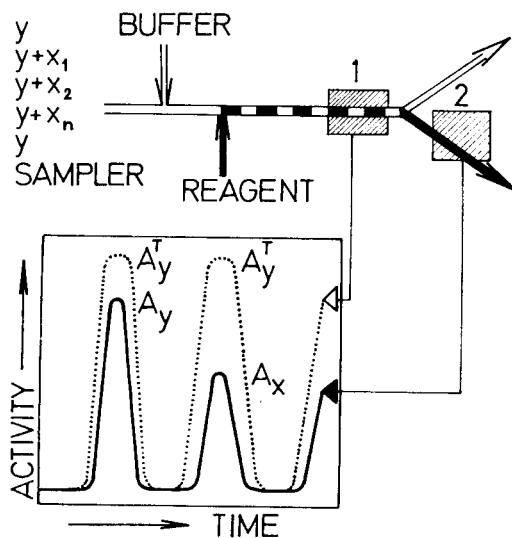


FIG. 4.—Principle of the two-detector system.

Samples ( $y + x_1, y + x_2 \dots$ ) bracketed with standards (containing only  $y$ ) are sampled, mixed with buffer and then with a substoichiometric amount of reagent, dissolved in an organic solvent. The resulting mixture is pumped through a detector 1, then the phases are separated and the one containing substoichiometrically separated amounts is pumped through detector 2. The amplified and integrated signals from both detectors are simultaneously registered on a two-pen recorder.

purpose a series of dilution experiments for  $y, y + x_1, y + x_2 \dots y + x_n$  are carried out in order to obtain calibration curves for 100%, 90% and, say, 75% recoveries (the curves for "gains" are usually not recorded, being of small practical importance). In an actual analysis the samples are always bracketed by standards  $A_y, A_y^T$  (containing  $y$  but no  $x$ ) in order to check the "standard level" (*i.e.*, constancy of  $C_{HA}$  and the efficiency of counting  $-k', k''$ ). As long as the ratio  $A_{x+y}^T/A_y^T = 1$ , the value of  $x$  is found from the ratio  $A_y/A_x$  by means of the calibration curve for 100% recovery. If  $A_{x+y}^T/A_y^T < 1$ , then losses in both  $y$  and  $x$  occurred during preliminary separation. Therefore the corrected value of standard  $A_y$ , *i.e.*,  $A_{y+\Delta y}$ , must be found from Fig. 2 and also the recovery. The  $A_{y+\Delta y}/A_x$  ratio obtained can now be used for determining  $x$  by means of that calibration curve which corresponds to the calculated recovery. It is worth noticing (Fig. 2) that the heights of the standard peak  $A_y$  (and of the sample peaks  $A_x$  for  $x < y$ ) are relatively more affected by losses than those belonging to samples where  $x > y$ . Preliminary results confirm the correctness of the theory and

a comprehensive experimental proof is being obtained which will be published at the earliest opportunity.

### CONCLUSION

The two-detector system was originally considered as an additive means of increasing the reliability of the routine method for determining traces of mercury in biological samples.<sup>8</sup> Its further evaluation led us to a more general concept, which will undoubtedly widen the possibilities of substoichiometry in trace analysis.

Still greater possibilities seem to lie unexplored in the field of biochemical analysis. Examples are (a) the radiometric method for determination of traces of insulin (called saturation analysis<sup>13</sup> or radioimmunoassay<sup>14</sup>) which if automated as suggested here would be more reliable and practical, and (b) the substoichiometric determination of the amounts of radioactive substances and measurement of their specific activities. The second possibility has been suggested in connection with the studies of plant nutrient availability.<sup>15</sup>

The limiting conditions theoretically derived for substoichiometric extraction of co-ordinately unsaturated salts (Alimarin and Perezhgin<sup>10</sup>), substoichiometric EDTA complexation followed by solvent extraction of unreacted metal ion (Briscoe and Dodson<sup>11</sup>), and replacement substoichiometry (Obrusnik and Adámek<sup>12</sup>), as well as for precipitation and ion-exchange methods<sup>9</sup> should also be reconsidered. However, the extraction systems noted above, together with substoichiometric extraction of metal chelates, are most promising because separation of two immiscible liquids is easily automated on a continuous flow basis.

**Zusammenfassung**—Die Automation erweitert den Anwendungsbereich der unterstöchiometrischen Radioisotopenverdünnungsanalyse. Das liegt daran, daß die sehr kritische Forderung des manuellen Verfahrens, daß genau gleiche Mengen der Testsubstanz chemisch getrennt werden, nicht mehr erfüllt werden muß: man erreicht die Reproduzierbarkeit der Bestimmung mit Hilfe automatischer Operationen und der Aktivitätsmessung. Die in dieser Arbeit entwickelte Theorie zeigt, wie die Auswahl geeigneter chemischer Reaktionen erweitert und die Zuverlässigkeit sowie die Vorteile der Isotopenverdünnungsanalyse beibehalten wird, wenn man ein System mit zwei Detektoren verwendet.

**Résumé**—L'automatisation étend le champ d'application de l'analyse substoéchiométrique par dilution isotopique. Ceci est dû au fait que l'exigence très stricte de la méthode manuelle—séparation chimique de quantités exactement égales de la substance-essai—n'a plus besoin d'être remplie: la reproductibilité de la détermination est atteinte au moyen d'opération et de mesure d'activité automatisées. La théorie donnée dans ce mémoire montre combien le choix de réactions chimiques convenables est étendu et pourquoi l'exactitude et les avantages de l'analyse par dilution isotopique sont assurés par l'emploi d'un système à deux détecteurs.

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## SHORT COMMUNICATIONS

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### Determination of small amounts of TBP and DBP in uranyl nitrate solutions

(Received 29 July 1968. Accepted 4 November 1968)

AT THE Japan Atomic Energy Research Institute spent fuel is reprocessed by a modified Purex method. Uranium is extracted with 30% tri-*n*-butyl phosphate (TBP) in dodecane from 2*M* nitric acid, and after further purification is back-extracted into dilute nitric acid. The aqueous solution of uranyl nitrate thus obtained is separated from the organic phase by decantation, and is then concentrated by evaporation. If the concentration of TBP or its decomposition products in the uranyl nitrate solution becomes high, there is an increased risk of explosion in the evaporator.<sup>1</sup> Therefore, it is necessary to determine these organic solvents in a concentrated aqueous solution of uranyl nitrate, and infrared spectrometry<sup>2</sup> and titration<sup>3</sup> have been used for this although neither is quite sensitive enough.

A very low concentration of tri-*n*-butyl phosphine oxide in an aqueous solution has been determined by a solvent-extraction method, in which the extractant is collected in an organic diluent and its concentration is then determined by measuring the distribution ratio of a radioactive tracer between the organic phase and an aqueous phase of definite composition.<sup>4</sup>

This work describes similar techniques for determining both TBP and di-*n*-butyl phosphate (DBP). These methods are much more sensitive than the spectrometric or titrimetric methods, do not need any special apparatus and are simple and rapid.

### EXPERIMENTAL

#### Reagents

*Tri-n-butyl phosphate, TBP.* The reagent was used after being purified by the conventional method.<sup>5</sup>

*Di-n-butyl phosphate, DBP.* The commercial reagent grade was used as received.

*Dodecane.* 2,4,5,7-Tetramethyldecane with b.p. 212° was used.

*Zirconium-95.* Suitable amounts were separated from niobium-95 by an ion-exchange procedure.<sup>6</sup> The tracer was added in hydrochloric acid for the TBP determination and in nitric acid for the DEP determination.

Other reagents were of analytical grade.

#### Procedures

All the experiments in this work were carried out at room temperature, 25 ± 2°.

*Determination of TBP in 2*N* uranyl nitrate solution.* Shake known amounts of undiluted TBP with 0.1*M* nitric acid containing 2*N* uranyl nitrate, to give standard TBP solutions. Shake 10 ml of the solution with 10 ml of dodecane in order to collect TBP in the organic phase. Because in practice the dodecane solution of TBP obtained at this stage contaminated with uranyl and nitrate ions and DBP, shake the solution with an equal volume of 1% sodium bicarbonate solution. This almost quantitatively removes DBP, but small amounts of TBP are also lost. Shake the dodecane layer with 10 ml of 10*M* hydrochloric acid.

Take 1.5 ml of the dodecane solution of TBP thus obtained, and equilibrate with 1.5 ml of zirconium-95 solution in 10*M* hydrochloric acid. Measure the activity of the two phases and calculate the distribution ratio of the zirconium. Prepare a calibration curve (Fig. 1) by putting known amounts of TBP through the procedure in the absence of uranium.

*Determination of TBP in processed fuel solutions.* In a 200-ml separating funnel take 100 ml of the sample solution containing 0.1–10 mg of TBP, and shake vigorously with 5 ml of dodecane for 10 min. Collect the organic phase and repeat the extraction with another 5 ml of dodecane. A third extraction is not usually necessary. The TBP in the combined extract is then determined by the procedure above.

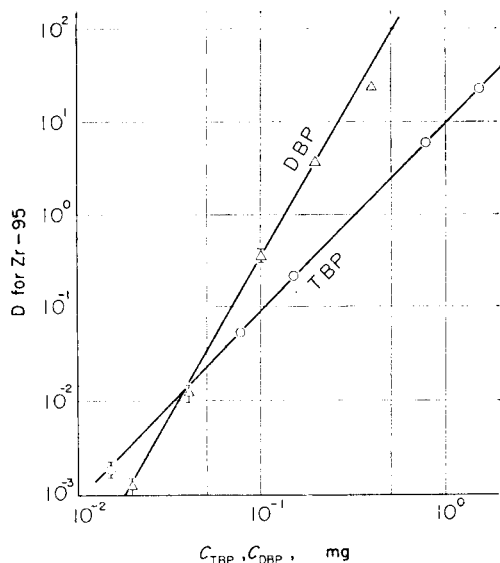


FIG. 1.—Calibration curves for TBP and DBP Temp.  $25 \pm 2^\circ$ .

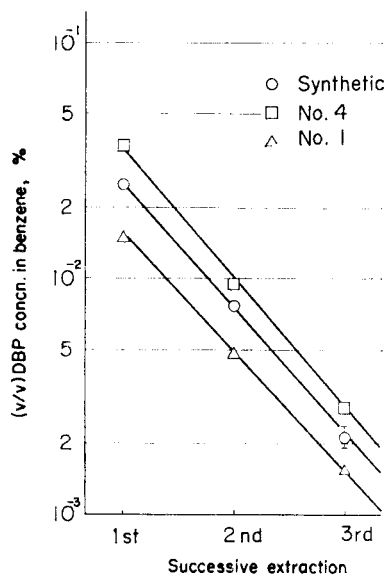


FIG. 2.—Determination of  $p$ . Successive extraction of DBP from a synthetic solution of DBP is uranyl nitrate solution and two solutions from the reprocessing plant.

*Determination of DBP in processed fuel solutions.* Shake vigorously 50 ml of uranyl nitrate sample solution with 50 ml of benzene for 10 min. Centrifuge and separate the phases and then shake the benzene phase with 5 ml of 1% sodium bicarbonate solution for 10 min and allow the layers to settle out. Take 0.1 ml of the bicarbonate phase and acidify it with 0.1 ml of 2.0M nitric acid and dilute to 2 ml with 1.0M nitric acid. Determine the distribution ratio for zirconium by spiking with zirconium-95 and equilibrating with 2 ml of dodecane. Prepare calibration curve (Fig. 1) by determining the distribution ratio of zirconium between 2 ml of 1M nitric acid and 2 ml of dodecane

containing known amounts of DBP. Calculate the concentration of DBP,  $C_{DBP}$ , in the 1% sodium bicarbonate extract, and relate this to the amount of DBP in the original solution with the aid of the equation

$$\text{mg of DBP/50 ml of sample solution} = 50 \cdot C_{DBP} \cdot p^{-1}$$

here  $p$  is the degree of extraction of DBP, defined as  $p = C_{org}/(C_{aq} + C_{org})$ . If the DBP in the aqueous phase is extracted with an equal volume of benzene and the equilibrium concentrations of DBP are  $C_{aq(1)}$  and  $C_{org(1)}$  respectively,  $p = C_{org(1)}/[C_{aq(1)} + C_{org(1)}]$ . If the aqueous phase is extracted with a fresh equal volume of benzene and the new equilibrium concentrations are  $C_{aq(2)}$  and  $C_{org(2)}$  then

$$\begin{aligned} p &= C_{org(2)}/[C_{aq(2)} + C_{org(2)}] \\ &= C_{org(2)}/C_{aq(1)}. \end{aligned}$$

Hence  $p = 1 - [C_{org(2)}/C_{org(1)}]$

The ratio of  $C_{org(1)}$  and  $C_{org(2)}$  can be determined experimentally by the procedure given, and  $p$  calculated. Results shown in Fig. 2 yield a value of  $p$  of  $0.68 \pm 0.08$ .

## RESULTS AND DISCUSSION

### Determination of TBP

The distribution ratio,  $D = C_{Zr(org)}/C_{Zr(aq)}$ , for zirconium-95 was measured in the system 10M hydrochloric acid-TBP in dodecane as a function of TBP concentration (Fig. 1).

Log  $D$  varies linearly with log  $C_{TBP}$  in the range 0.01–1.0 mg of TBP per ml of dodecane, with slope 2. The relative standard deviations of the measurements vary with the value of  $D$  but do not exceed 8%.

The recovery of TBP from uranyl nitrate solution is quantitative within the limits of experimental error. It was also found that the concentration of TBP in dodecane is unaffected if the solution is shaken with uranyl nitrate solution.

### Determination of DBP

Benzene extracts DBP from uranyl nitrate solution more efficiently than does dodecane, but the extraction is not quantitative. However, if the distribution ratio is known, the amount of DBP in the initial aqueous solution can be calculated from that in the benzene extract.

TBP is also extracted with DBP but DBP can be back-extracted with 1% sodium bicarbonate solution leaving most of the TBP in the benzene solution. The back-extraction is quantitative for 0.05–0.2 mg/ml of solution for benzene:aqueous phase from 5:1 to 1:1. The small amount of TBP extracted into the aqueous phase does not affect the zirconium distribution if the TBP concentration is below 0.05% v/v (Table I). The slope of log  $D$  vs. log  $C_{DBP}$  is 3 (Fig. 1).

TABLE I.— $D$  VALUES FOR ZIRCONIUM IN THE SYSTEMS 1M HNO<sub>3</sub> DODECANE CONTAINING BOTH DBP AND TBP

Dodecane containing		$D$
DBP, mg	TBP, mg	
0.2	0.98	3.8
0.2	0.74	3.5
0.2	0.49	3.6
0.2	0.23	3.2
0.2	0	3.5

TABLE II.—DETERMINATION OF TBP AND DBP IN URANYL NITRATE SOLUTIONS

Sample	TBP found, mg/l.	DBP found, mg/l.
1	28 ± 1	220 ± 20
2	25 ± 1	210 ± 20
3	9 ± 1	300 ± 20
4	16 ± 1	560 ± 40
5	73 ± 2	47 ± 4

*TBP and DBP contents of uranyl nitrate solutions*

Four uranyl nitrate solutions, 1-4, were taken from the evaporator of the reprocessing plant just after the end of the operation with non-irradiated uranium. Another sample solution was taken from the evaporator during the stationary operation. Each sample was analysed for TBP and DBP; typical results are shown in Table II.

*Acknowledgement*—The authors wish to express their sincere thanks to Dr. T. Aochi and his co-workers of the JAERI laboratory for sample solutions of uranyl nitrate.

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**Summary**—Tri- and dibutylphosphate (TBP and DBP) in concentrated uranyl nitrate solution are determined by a method based on the solvent extraction of zirconium-95. The distribution ratio of zirconium-95 between dilute solutions of TBP and DBP in dodecane and 10M hydrochloric acid and 1M nitric acid respectively is measured. There is a logarithmic relationship between the distribution ratio and concentration of TBP and DBP, which enables them to be determined rapidly and with an error of  $\pm 10\%$  over the range 1-100 ppm of TBP and 40-600 ppm of DBP. The lower limit is 0.5 ppm for TBP and 10 ppm for DBP.

**Résumé**—On dose les tri- et dibutylphosphate (TBP et DBP) dans une solution concentrée de nitrate d'uranyle par une méthode basée sur l'extraction par solvant du zirconium-95. On mesure le rapport de partage du zirconium-95 entre des solutions diluées de TBP et de DBP dans le dodécane et l'acide chlorhydrique 10M et l'acide nitrique 1M respectivement. Il y a une relation logarithmique entre le rapport de partage et la concentration en TBP et DBP, qui rend possible leur détermination rapide avec une erreur de  $\pm 10\%$  dans le domaine 1-100 ppm de TBP et 40-600 ppm de DBP. La limite inférieure est 0,5 ppm pour le TBP et 10 ppm pour le DBP.

**Zusammenfassung**—Tri- und Dibutylphosphat (TBP und DBP) werden in konzentrierter Uranylnitratlösung mit Hilfe der Solventextraktion von Zirkonium-95 bestimmt. Das Verteilungsverhältnis von Zirkonium-95 zwischen verdünnten Lösungen von TBP und DBP in Dodekan und 10M Salzsäure bzw. 10M Salpetersäure wird gemessen. Es besteht eine logarithmische Beziehung zwischen Verteilungsverhältnis und Konzentration an TBP und DBP, die ihre schnelle Bestimmung gestattet, mit einem Fehler von  $\pm 10\%$  im Bereich 1-10 ppm TBP und 40-600 ppm DBP. Die untere Grenze liegt bei 0,5 ppm für TBP und 10 ppm für DBP.

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## Argentometric titration of chloride with dichlorofluorescein as an adsorption indicator: A useful modification

(Received 24 October 1968. Accepted 18 December 1968)

DICHLOROFUORESCEIN was first used as an adsorption indicator in the argentometric titration of chloride ion by Kolthoff.<sup>1</sup> Common practice<sup>2</sup> is to watch the coagulated precipitate (flocs appear about 0.5% before the equivalence point) for the sharp colour change from yellow-green to pink. The sensitivity of the end-point therefore depends on the amount of precipitate, *i.e.*, on the chloride concentration in the solution being titrated.

If the colloidal precipitate can be kept dispersed at the end-point, the colour change is observed throughout the whole volume of suspension rather than on a small amount of flocculated precipitate. This was realized by Kolthoff,<sup>3</sup> who used "protective colloids" such as dextrin, a degraded form of starch, to maintain stability of the suspension beyond the end-point. According to a recent review by Napper<sup>4</sup> these "protective colloids" stabilize the particles by mechanisms such as steric stabilization. Mehrotra<sup>5</sup> also used this technique but with Congo Red as indicator to improve the end-point for the same titration.

This investigation stemmed from an attempt to use the adsorption indicator technique for the titration of butylammonium chloride,  $\text{CH}_3(\text{CH}_2)_3\text{NH}_3^+\text{Cl}^-$ , solutions; premature flocculation of the silver chloride and deterioration of the end-point colour change occurred.

### EXPERIMENTAL

#### Reagents

**Butylammonium chloride.** Prepared by passing dry hydrogen chloride through a concentrated solution of butylamine in diethyl ether. The precipitated butylammonium chloride was recrystallized twice from dry acetone. Its melting point was sharp and its NMR spectrum had the expected proton distribution.

**Indicator solution.** A 0.1% solution of dichlorofluorescein (DCF) in 60% ethyl alcohol.

Water was doubly distilled, the second time from alkaline permanganate solution.

#### Procedure

It was found that in the presence of the butylammonium cation the simple argentometric titration technique with DCF as indicator<sup>2</sup> was inadequate because the precipitate flocculated well before the end-point. Consequently detection of an end-point depended solely on a colour change that was at best rather limited in extent and certainly less sharp than in the absence of butylammonium ions.

The modified technique consisted simply of diluting the solution with three times its volume of ethyl alcohol before addition of the indicator.

### DISCUSSION

Premature flocculation presumably occurs because of preferential adsorption of the butylammonium ion onto the negative silver chloride particle,<sup>6</sup> causing early neutralization of the particle's charge and concomitant destabilization. This was confirmed by mobility measurements made with microelectrophoresis apparatus of the Alexander and Siggers<sup>7</sup> type. At constant ionic strength (*ca.* 0.1M) replacement of  $\text{K}^+$  by  $\text{BuNH}_3^+$  caused the particle mobility to be increased from  $-5.2 \times 10^{-2}$  to  $-2.4 \times 10^{-2}$   $\text{mm}^2.\text{V}^{-1}.\text{sec}^{-1}$ . Deterioration or even total absence (depending on electrolyte concentration) of the colour change at the end-point is somewhat more difficult to explain. Mehrotra and Tandon,<sup>8</sup> in a comprehensive review of the theories of adsorption indicators, favour the existence of a definite compound between the silver cation and the DCF anion. This compound, which they have isolated, has the same colour as is seen in the titrated solution after the end-point and is more soluble than silver chloride. These workers suggest that the compound co-precipitates with the silver chloride after the end-point is reached so that the colour change is confined to the precipitate. To test this, a sample of freshly precipitated and well-washed silver chloride was prepared with a slight excess of  $\text{Ag}^+$  ions adsorbed on the surface. After centrifugation, a small quantity of DCF was added to the supernatant liquid, whereupon the precipitate rapidly turned pink whilst the supernatant liquid remained green, the colour of the simple dye. Addition of more  $\text{Ag}^+$  ions had no effect on this system, which is



further evidence for a simple adsorption mechanism and renders the invoking of a co-precipitation mechanism unnecessary. The most likely explanation for the poor colour change is that specific adsorption of the  $\text{BuNH}_3^+$  ion displaces or masks the  $\text{Ag}^+$  ion on the surface, preventing formation of the coloured complex.

With the addition of ethyl alcohol the precipitate remained stable even after the end-point, which was marked by a colour change from colourless to pink throughout the solution. This colour change was sharper than in the simple case of chloride titration by silver ions in the absence of interfering ions.

In the absence of interfering ions such as butylammonium the original technique<sup>8</sup> can be used reasonably successfully but addition of excess of ethyl alcohol still improves the sharpness of the end-point considerably.

It would seem, therefore, that addition of alcohol produces two effects. First, when butylammonium ion is present, reduction of the solution's dielectric constant reduces the specific adsorption of this ion. Secondly the solubility of silver chloride is less by a factor of about ten in a 1:3 water-alcohol mixture<sup>9</sup> than in water, probably resulting in smaller silver chloride particles with greater total surface area and a greater observable colour change at the end-point. The possibility that the addition of ethyl alcohol increases the solubility of the silver complex causing colour change in the homogeneous phase as well as at the solid-liquid interface can be discarded because centrifugation of the suspension after the end point showed that the colour change was confined to the particles.

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**Summary**—The addition of excess of ethyl alcohol renders more useful the argentometric titration of chloride with dichlorofluorescein as adsorption indicator by improving the end-point, both when simple counter-ions are present and also when the presence of adsorbable and/or complexing counter-ions renders the normal technique inadequate.

**Zusammenfassung**—Die Zugabe von überschüssigem Äthanol erhöht den Nutzen der argentometrischen Titration von Chlorid mit Dichlorfluorescein als Adsorptionsindikator, da sie den Endpunkt verbessert. Dies gilt sowohl, wenn nur einfache Gegenionen anwesend sind, als auch, wenn die Gegenwart adsorbierbarer und/oder komplexbildender Gegenionen das normale Verfahren unbrauchbar macht.

**Résumé**—L'addition d'un excès d'alcool éthylique rend plus utile le titrage argentométrique du chlorure avec la dichlorofluorescéine comme indicateur d'adsorption en améliorant le point de virage, tant lorsque des ions antagonistes simples sont présents que lorsque la présence d'ions antagonistes adsorbables et/ou complexants rend la technique normale inadéquate.

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## Vacuum system for the semi-automatic degassing of solvents

(Received 19 November 1968. Accepted 18 December 1968)

THE need to degas solvents arises from the fact that oxygen dissolved in the solvent at normal temperatures is sufficient to disturb measurement of transient species produced in some photochemical and electrochemical experiments.<sup>1</sup>

Two methods have generally been used for degassing solutions, both of which have disadvantages. The first is bubbling a suitable inert gas, usually nitrogen, through the solution and then sealing off the solution on a vacuum line with or without a small number of "freeze-thaw" cycles. The second method uses repeated "freeze-thaw" cycles until the pressure over the frozen solution reaches an appropriate low value, usually  $10^{-5}$ – $10^{-6}$  mbar. The primary disadvantage of the first method is that the amount of oxygen remaining in the solution after the treatment remains unknown. Thus inconsistencies may develop when oxygen-sensitive systems are under study. The main disadvantage of the second technique is the large amount of time that must be devoted to the degassing of individual reaction mixtures to obtain the desired consistency of results.<sup>2</sup>

In order to overcome both of these disadvantages a procedure based on the "freeze-thaw" method has been developed for degassing large volumes of solvent.

### EXPERIMENTAL

The apparatus is shown in Fig. 1. *A* and *B* are Teflon vacuum stop-cocks; *C* is a 1000-ml in-line trap which contains liquid nitrogen; *D* is an O-ring seal; *E* contains the liquid to be degassed (about 100 ml).

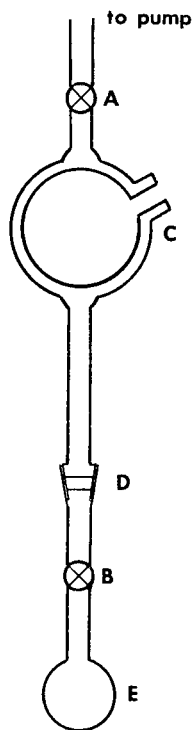


FIG. 1.—Apparatus used for degassing solvents.

The entire apparatus is attached to a vacuum manifold above stop-cock *A*. Operation of the system is as follows. With the trap *C* empty and *B* closed, *A* is opened and the space between the two stop-cocks is evacuated. While this is being done the solvent in *E* is being frozen in the normal freeze-thaw cycle. With the solvent frozen, *B* is opened and the whole system is allowed to pump down to a

suitable pressure. With the liquid in *E* still frozen, *C* is filled with liquid nitrogen. With *A* and *B* remaining open, the liquid in *E* is slowly allowed to warm up to room temperature. As the liquid warms, enough dissolved gas is given off to raise the pressure to about 1  $\mu$ bar. When the liquid is warm enough vapour will begin to condense on the bottom of *C* while almost all of the dissolved gases will pass through to the pumps. Eventually, a sufficient amount of liquid will condense on the trap so that it will start dripping down to the bulb *E*. An equilibrium will be set up between the condensation on *C* and the flow back to *E*. During this time the pressure in the system as a whole will continue to decrease until the vacuum gauge reading is between 1 and 6 nbar while the degassing apparatus is open to the vacuum pumps. The only precaution that must be taken during the process is that the level of the coolant in the trap does not fall sufficiently to allow escape of the liquid being degassed (refill about every 30 min). Since the liquid flowing back to *E* is quite cold it is also necessary to heat the system between *C* and *B* as well as to heat the liquid in *E* with warm air at suitable intervals (about 30 min) in order to speed up the circulation between *C* and *E*. When the cycle is finished *A* is closed and the liquid in *E* is frozen as the coolant in *C* is removed (best with a stream of nitrogen gas). *B* is then closed and the liquid can be stored in *E* until it is to be used, at which time it can be distilled into a cell which can be attached to another portion of the vacuum system. A similar although less elaborate system has been proposed for degassing individual small samples.<sup>3</sup>

## RESULTS

The system described has been used to degas methylcyclohexane, benzene and isopropanol. Excellent results have been obtained for all of these. Maintenance of the degassing cycle for from 2 to 3 hr leads to a pressure over the frozen solvent of less than 10 nbar. Continuing the cycle for another hour leads to pressures over the frozen liquids of less than about 6 nbar. This system has the further advantage that the bulb *E* can be removed with the liquid under vacuum and stored until needed. If storage is prolonged, the degassing may have to be repeated but will be much shorter in duration since the liquid will not be saturated with dissolved gases. Depending on the care used during degassing, liquid losses can be held to considerably less than 10% during any run. Occasionally, when a large volume of liquid was being degassed, so much would condense on the bottom of the trap that some would escape into the system. This could be easily controlled by noting any large pressure increases, shutting stop-cock *A* for a moment and heating the area round the bottom of the trap with warm air.

The reproducibility of the process is illustrated by the lifetime of the triplet state of phenazine has a value of approximately 50  $\mu$ sec both with a number of samples of methylcyclohexane degassed as described and with samples completely degassed by the old, much less efficient, "freeze-thaw" method.

Liquids to be degassed should be tested in case they attack the O-ring seals or taps.

*Acknowledgement*—The authors would like to thank Dr. E. W. Abrahamson for his continual encouragement and support. The apparatus was designed for research sponsored by the Atomic Energy Commission, Contract No. At-11-1-904.

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**Summary**—A semi-automatic system capable of quickly degassing large amounts of solvent is described.

**Zusammenfassung**—Ein halbautomatisches System wird beschrieben, mit dem man schnell große Lösungsmittelmengen entgasen kann.

**Résumé**—On décrit un système semi-automatique capable de dé gazer rapidement de grandes quantités de solvant.

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## Gas-chromatographic display of the polycyclic aromatic hydrocarbon fraction of cigarette smoke

(Received 17 September 1968. Accepted 14 November 1968)

THE presence of compounds, in addition to benzo[*a*]pyrene (BaP), with high electron-affinities, in the polycyclic aromatic hydrocarbon fraction of cigarette smoke, was sought by gas chromatography with a sensitive electron-capture detector. Also, smoke condensates from different tobacco types were examined to learn whether or not each isolated polycyclic hydrocarbon fraction yielded a distinguishable gas chromatographic "fingerprint."

An electron-capture detector with a radioactive source, tritium, was found to have certain deficiencies for this study—there were operating temperature limitations and loss of sensitivity and response due to fouling. Therefore, a new and different commercial electron-capture detector was used. It is basically an ionization detector utilizing a helium glow discharge as the electron source and is capable of operating with high sensitivity up to 400°. The extreme sensitivity of this detector allowed an analysis to be made with as few as 15–20 cigarettes.

### EXPERIMENTAL

#### Reagents

Pre-equilibrated solvents and reagents have been previously described.<sup>1,2</sup> Standard solutions of BaP, perylene and other polycyclic aromatic hydrocarbons were prepared in hexane.

#### Apparatus

Beckman GC-5 gas chromatograph equipped with electron-capture detector and dual flame-ionization detectors, used with a 2.75 m × 3.2 m stainless-steel column containing 3% SE-30 on 60/80 mesh Chromosorb W.

TABLE I.—RETENTION TIMES AND ELECTRON AFFINITIES OF POLYCYCLIC HYDROCARBONS RELATIVE TO BENZO[*a*]PYRENE (BaP)

Compound	Column temp., °C	Relative retention time (BaP = 1)	Relative response per ng (BaP = 100)
1. Fluorene	225	0.10	1
2. Anthracene	225	0.10	2
3. Phenanthrene	225	0.12	1
4. Fluoranthene	225	0.17	1
5. Pyrene	225	0.19	1
6. Benzo[ <i>b</i> ]fluorene	225	0.24	1
7. Benzo[ <i>ghi</i> ]fluoranthene	225	0.35	10
8. Benz[ <i>a</i> ]anthracene	225	0.40	10
9. Chrysene	225	0.40	1
10. Benzo[ <i>b</i> ]fluoranthene	225	0.83	13
11. Benzo[ <i>a</i> ]pyrene	225, 250, 260	1	100
12. Benzo[ <i>e</i> ]pyrene	250	1	25
13. Perylene	250	1	1
14. Dibenz[ <i>a, c</i> ]anthracene	250	1.9	60
15. Dibenz[ <i>a, h</i> ]anthracene	250	1.9	20
16. Benzo[ <i>ghi</i> ]perylene	250	2.1	50
17. Dibenzo[ <i>a, l</i> ]pyrene	260	3.6	30
18. Coronene	260	4.0	15
19. Dibenzo[ <i>a, e</i> ]pyrene	260	4.2	100

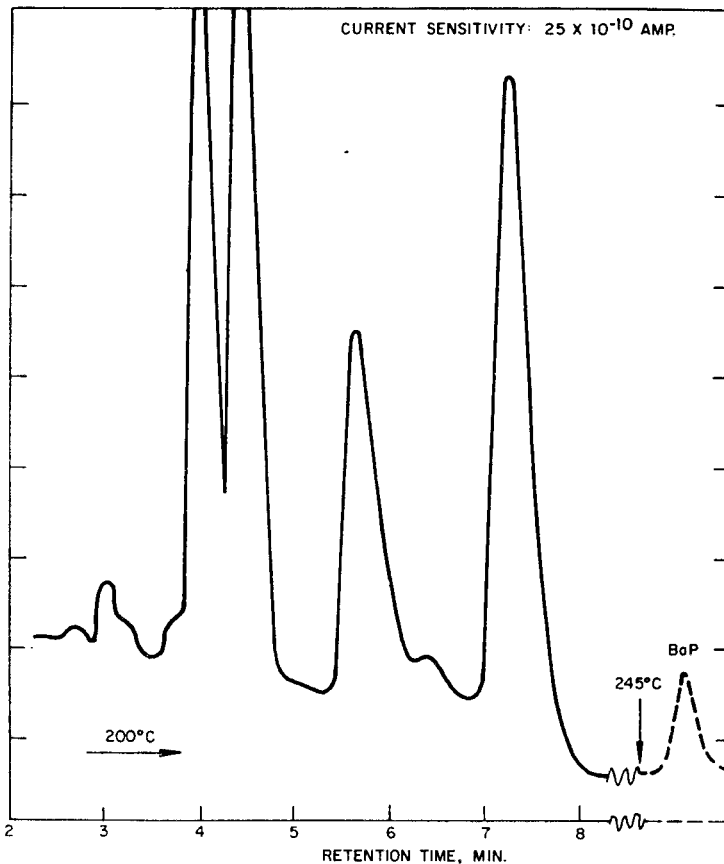


FIG. 1.—(—) Gas chromatogram of polycyclic hydrocarbon fractions 1-5 from silica gel column for all-burley tobacco cigarette. (---) Corresponding benzo[*a*]pyrene (BaP) peak, fractions 6-9.

#### Procedure

The fractionation of cigarette smoke condensate and the isolation of the polycyclic aromatic hydrocarbon fraction have been described.<sup>1,2</sup> A summary of the analysis scheme is as follows.

1. Smoke condensate collection
2. Partitioning between solvent pairs
3. Silica gel column chromatography (hexane)
  - (a) Fractions 1-5, preceding BaP
  - (b) Fractions 6-9, containing BaP
  - (c) Fractions 10-15
4. Acid treatment of fractions
5. Gas chromatographic analysis

#### RESULTS AND DISCUSSION

Retention times and electron-capture (EC) detector responses for some polycyclic aromatic hydrocarbons relative to benzo[*a*]pyrene (BaP) were determined and are listed in Table I. All except possibly nos. 14 and 19 are present in cigarette smoke.<sup>3,4</sup> Equal weights of each compound, *e.g.*, 30 ng, were injected into the GC-5 and the area of each peak was measured to obtain the equal weight response values. These values, Table I, are a measure of the electron affinities relative to that of BaP. The weight response ratios were obtained for a specific set of operating conditions and are subject to some change as conditions vary. A wide range of electron affinities is noted, with BaP

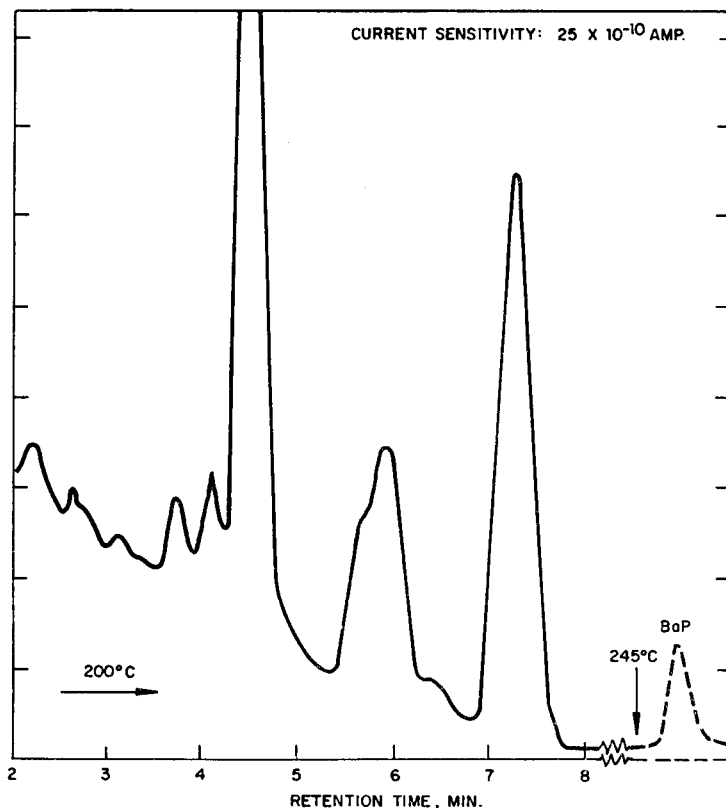


FIG. 2.—(—) Gas chromatogram of polycyclic hydrocarbon fractions 1-5 from silica gel column, for oriental tobacco cigarette. (---) Corresponding benzo[a]pyrene, fractions 6-9.

among the highest. Very small quantities of the polycyclics could be measured with this EC detector. For example, as little as 0.5 ng of benzo[a]pyrene was determined. This is less than the amount found in one puff. These small quantities were not detectable by flame-ionization detection.

The polycyclic fractions from different tobacco-type cigarettes were examined. The combined fractions preceding BaP off the silica gel column yielded particularly interesting chromatograms. An aliquot equivalent to about half of a puff was injected. Chromatograms at 200° of these fractions for (1) an all-burley tobacco cigarette (2) an oriental tobacco cigarette and (3) a blended tobacco cigarette (American) are reproduced in Figs. 1, 2 and 3 respectively. Figure 3 was obtained at a lower carrier gas flow-rate; hence, retention times in Fig. 3 are lower by almost a minute. The corresponding BaP peak obtained separately at 245° is sketched in for comparison in each figure. Benzo[e]pyrene does not contribute more than ~2% to the observed BaP peak.<sup>2</sup> The amount of BaP is about 0.5 ng in Figs. 1 and 2 and about 1 ng in Fig. 3. BaP was quantitatively measured at optimum conditions for its analysis.<sup>2</sup> The presence of peaks much larger than that of BaP is an obvious feature of these chromatograms. These peaks, as yet unidentified, cannot be ascribed to compounds such as pyrene and chrysene, which are present in larger quantities than BaP, because their response values are much too low, or their relative retention times do not fit. These compounds are also more volatile than BaP and apparently present in much smaller quantities. The latter might explain in part why they have not yet been identified. The chromatograms in Figs. 1-3 contain relatively few, well-resolved, peaks. Carrugno and Rossi<sup>5</sup> in their study of polynuclear hydrocarbons in cigarette smoke used a different fractionation scheme and obtained many more peaks from a much larger sample size.

There are similarities as well as differences among the three chromatograms. For example, the blended cigarette, Fig. 3, was easily distinguishable from the other two. These chromatograms were reproducible "fingerprint" chromatograms. It was established that the observed peaks were not artifacts arising from the fractionation scheme and acid treatment. Control analyses on the reagents and solvents were carried out to verify this. Also, the chromatograms of fractions 1-5 for the blended

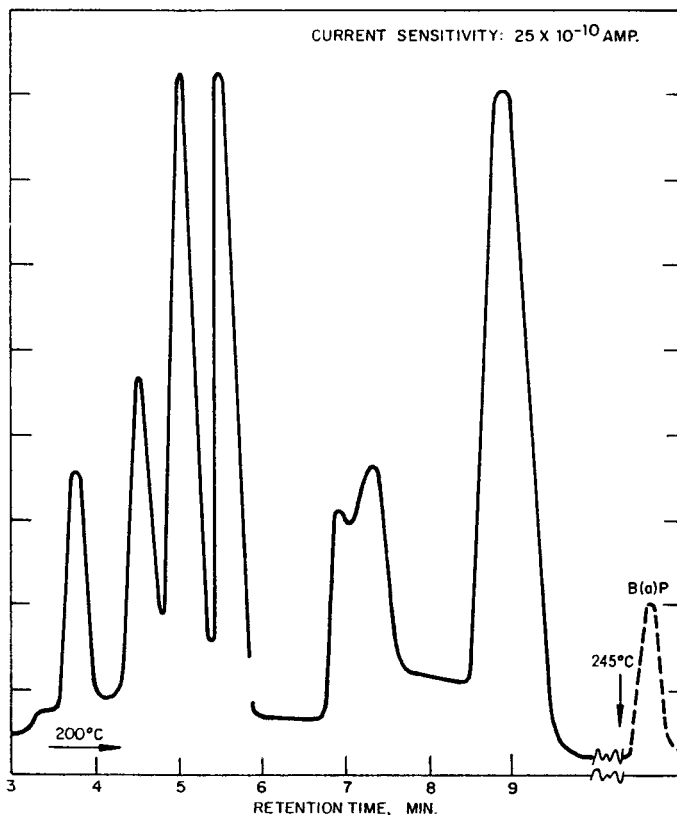


FIG. 3.—(—) Gas chromatogram of polycyclic hydrocarbon fractions 1-5 from silica gel column for blended tobacco cigarette. (---) Corresponding benzo[*a*]pyrene (BaP) peak fractions 6-9.

cigarette were nearly identical, except for some "background" material, to those obtained without acid treatment. Overall recoveries, based on the recovery of the internal standard, were about 70%.

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**Summary**—High electron-affinity polycyclic aromatic hydrocarbons in cigarette smoke are detected by gas chromatography. The resulting gas chromatograms can be used for "fingerprint" identification of the hydrocarbon fractions in cigarette smoke.

**Zusammenfassung**—Polycyclische aromatische Kohlenwasserstoffe mit großer Elektronenaffinität werden in Zigarettenrauch gaschromatographisch nachgewiesen. Die erhaltenen Gaschromatogramme können zur "Fingerabdruck"-Identifizierung der Kohlenwasserstofffraktionen in Zigarettenrauch verwendet werden.

**Résumé**—On détecte des hydrocarbures aromatiques polycycliques à haute affinité électronique dans la fumée de cigarette par chromatographie en phase gazeuse. On peut utiliser les chromatogrammes de gaz qui en résultent pour l'identification "par empreinte" des fractions d'hydrocarbures dans la fumée de cigarette.

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4. E. L. Wynder and D. Hoffmann, *Tobacco and Tobacco Smoke Studies in Experimental Carcinogenesis*, Academic Press, New York, 1967.
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Talanta, 1969, Vol. 16, pp. 625 to 626. Pergamon Press. Printed in Northern Ireland

### Use of radioactive kryptonate of thallium in the determination of oxygen dissolved in water or other liquids

(Received 22 July 1968. Accepted 22 October 1968)

THE determination of small amounts of oxygen dissolved in water or other liquids is usually one of the most difficult analytical problems. The determination of dissolved oxygen is of great importance in biological studies as well as in the prevention of corrosion.

Richter and Gillespie<sup>1</sup> have worked out a method for the determination of the concentration of oxygen dissolved in water, based on the quantitative oxidation of labelled (<sup>204</sup>Tl) metallic thallium with dissolved oxygen. The radioactivity of water due to thallium ions passed into the solution is measured. The disadvantage of this method is that it involves radioactive hazards and waste disposal problems.

These disadvantages are eliminated by our method,<sup>2</sup> which is a combination of that due to Richter and Gillespie and of the technique of using radioactive kryptonates.

The radioactive krypton used for labelling the metallic thallium is a noble gas. It does not generally form genuine chemical compounds or enter metabolic systems, and therefore from the biological point of view is very safe. As the reactive product is gaseous, it is relatively easy to separate it from the components of the system analysed and to measure the radioactivity of the active product or the residual activity of the radioactive kryptonate.

In water and in other liquids the dissolved oxygen is determined with the aid of the radioactive kryptonate of thallium, Tl[<sup>86</sup>Kr]. The thallium carrier is prepared by coating a copper (or platinum) plate or copper cutting with thallium electrolytically. A carrier prepared in this way is kryptonated by bombardment with ions of <sup>86</sup>Kr or by the diffusion technique.<sup>3</sup>

The determination of oxygen is based on the reaction:  $4\text{Tl}[\text{}^{86}\text{Kr}] + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{Tl}^+ + 4\text{OH}^- + \text{}^{86}\text{Kr}$ , where the radioactive <sup>86</sup>Kr is released and the activity of the radioactive kryptonate of thallium in solution decreases. This reaction is stoichiometric.

Radioactive kryptonate of thallium is placed in the liquid to be analysed or the liquid is passed through a column of radioactive kryptonate of thallium. The radioactive krypton released or the decrease of radioactivity of the Tl[<sup>86</sup>Kr] is measured. This analysis can be made automatic.

With distilled water samples the measured decrease of radioactivity of the kryptonate of thallium was found to be linear with the concentration of dissolved oxygen down to the lowest investigated concentration (0.3 ppm).

Distilled water saturated with air was used for calibration, the oxygen concentration being calculated from the atmospheric pressure and the temperature of the water. It is sufficient to calibrate with one standard solution.

#### Method

Submerge radioactive kryptonate of thallium (in the form of an electrolytic layer on a 10 × 10 mm copper plate and of known activity) for 15 min in 20 ml of sample. Dry the plate in a vacuum desiccator under reduced pressure and remeasure the activity of the plate. Calculate the oxygen concentration by simple proportion from the relative decrease in activity for the sample and for a standard of known oxygen content.

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Š. VARGA



**Summary**—Radioactive kryptonate of thallium is placed in the liquid sample. Oxygen dissolved in the sample reacts with the surface layer of radioactive kryptonate of thallium, and releases radioactive krypton in amount proportional to the amount of oxygen.

**Zusammenfassung**—Das radioaktive Kryptonat von Thallium wird in die flüssige Probe gegeben. In der Probe gelöster Sauerstoff reagiert mit der Oberflächenschicht des Kryptonates und setzt eine der Sauerstoffmenge proportionale Menge radioaktives Krypton frei.

**Résumé**—On place le kryptonate de thallium radioactif dans l'échantillon liquide. L'oxygène dissous dans l'échantillon réagit avec la couche superficielle du kryptonate de thallium radioactif et libère le krypton radioactif en quantité proportionnelle à la quantité d'oxygène.

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## LETTER TO THE EDITOR

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### Determination of sulphur in nickel-iron alloys

SIR,

In an investigation of the effect of composition on the properties of nickel-iron alloys a need arose for a method to determine sulphur in these alloys in amounts much less than the 0.005% which is considered the lower limit of the combustion procedure.

The method routinely used here for trace amounts of sulphur in iron-base alloys<sup>1</sup> could not be used because of the insolubility of nickel in dilute hydrochloric acid. Luke<sup>2</sup> found that the dissolution of nickel in hydrochloric acid can be greatly accelerated by the addition of a small amount of platinum(IV) chloride. By combination of these two techniques in a procedure in which 0.005% platinum(IV) chloride in 1:1 hydrochloric acid is used as the dissolving agent, trace amounts of sulphur in nickel and nickel-iron alloys can be determined.

Analysis of several cobalt-iron alloys which can be dissolved in dilute hydrochloric acid with or without the addition of platinum(IV) chloride served as a check on the reliability of the method (five samples: H<sub>2</sub>PtCl<sub>6</sub> added; A 0.017, B 0.012, C 0.017, D 0.0034, E 0.00011% S; H<sub>2</sub>PtCl<sub>6</sub> omitted; A 0.018, B 0.011, C 0.021, D 0.0031, E 0.00018% S).

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16 September 1968

MARY LOUISE THEODORE

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- Eine verbesserte Apparatur zur kontinuierlichen trägerfreien Durchflußionophorese:** W. PREETZ and H. L. PFEIFER. (19 February 1969)
- Determination of yttrium in rare earths by photon activation analysis:** G. J. LUTZ and P. D. LAFLEUR. (21 February 1969)
- On the atomic weight of potassium:** GEORGE MARINENKO. (3 March 1969)
- Determination of deuterium in heavy water by secondary deuterium activation induced by 14 MeV neutrons:** R. PRETORIUS and R. E. WAINERDI. (3 March 1969)
- Spectrophotometric determination of traces of arsenic:** VERA STARÁ and JIŘI STARÝ. (4 March 1969)
- Gleichzeitige spektrophotometrische Bestimmung des Zirkoniums und Hafniums:** SEPTIMIA POLICEC, T. SIMONESCU and C. DRĂGULESCU. (4 March 1969)
- Photometric titration of small quantities of metals with ethylenediaminetetra-acetic acid:** R. BELCHER, BARBARA CROSSLAND and T. R. F. W. FENNELL. (6 March 1969)
- Determination of europium in minerals and rocks by neutron activation and  $\gamma\gamma$ -coincidence spectrometry:** O. B. MICHELSEN and E. STEINNES. (6 March 1969)
- Untersuchungen zur Optimierung der Reaktionsbedingungen für die katalytische Jodwirkung auf das System Ce(IV)-arsenige Säure—(Eine modifizierte Sandell-Kolthoff-Reaktion):** GUNTER KNAPP and HANS SPITZY. (6 March 1969)
- Eine Apparatur zur automatischen Jodbestimmung im Nanogrammbereich:** GUNTER KNAPP and HANS SPITZY. (6 March 1969)
- Selective complexometric determination of mercury, with thiourea as masking agent:** RAJINDER PAL SINGH. (7 March 1969)
- Carrying-out of emission spectral analyses with the help of spectral photographic plates treated in a phenidone developer:** A. PETRAKIEV and G. DIMITROV. (17 March 1969)
- Ronald Belcher:** M. WILLIAMS. (18 March 1969)
- Publications of Ronald Belcher:** M. WILLIAMS. (18 March 1969)
- Chitin and chitosan as chromatographic supports and adsorbents for collection of metal ions from organic and aqueous solutions and sea-water:** RICCARDO A. A. MUZZARELLI and OTTAVIO TUBERTINI. (18 March 1969)
- Sulphur in foodstuffs—I. Determination as sulphate:** G. BESWICK and R. M. JOHNSON. (19 March 1969)

## PUBLICATIONS RECEIVED

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**Computer Calculation of Ionic Equilibria and Titration Procedures with Specific Reference to Analytical Chemistry:** DAVID DYRSSEN, DANIEL JAGNER and FREDRIK WENGELIN. Almquist and Wiksell, Stockholm; Wiley, London, 1969. Pp. 250. 85s.

The preface to this book states that the aim in Sweden is that by 1970 every science graduate should be able to use computer techniques within his special branch. The authors consider it easier for a chemist to learn programming than for a mathematician to learn to avoid chemical errors in programs devised. This valuable book supplies the necessary material for the chemist (especially the analyst) to write his own programmes for problem solving, and at the same time manages to teach a great deal of basic chemistry as well. Each chapter has a set of problems for the neophyte to test his learning. The book is strongly recommended to all interested in computer programming, analytical chemistry and complexation chemistry.

**Decomposition Techniques in Inorganic Analysis:** J. DOLEŽAL, P. POVONDRA and Z. ŠULCEK. Iliffe, London; SNTL, Prague; Elsevier, New York, 1968. Pp. 224. 55s.

This unique book compiles methods of "opening-out" samples for wet analysis, and is therefore extremely useful to the practising analyst suddenly confronted with a new problem of sample decomposition. All the methods given have been tested by the authors for reliability—a feature which enhances the value of the book. There is a wealth of information on the decomposition of minerals and other traditional "insolubles". The authors are to be warmly thanked for bringing together material that is as often wanted as it is scattered through the literature.

**The Determination of Epoxide Groups:** B. DOBINSON, W. HOFMANN and B. P. STARK. Pergamon, Oxford, 1969. Pp. viii + 79. 42s. \$6.00.

This is the first volume of a new series of monographs in organic functional group analysis under the general editorship of Prof. Belcher and Dr. D. M. W. Anderson.

**Modern Methods in Organic Microanalysis:** J. P. DIXON. Van Nostrand, London, 1968. Pp. xvii + 301. 70s.

This is a general account of methods of organic microanalysis, reflecting the author's personal experience and preferences. Where details of methods are not given, there is usually enough literature coverage for the reader to find the necessary details for himself.

**Ekstraktsiya vnutrikompleksnykh soedinenii:** YU. A. ZOLOTOV. Izdat. Nauka, Moscow, 1968. Pp. 313. 1R.47K.

This book (in Russian) is a general account of solvent extraction methods, together with a survey of their applications. There are some useful ancillary features such as a table of masking agents and numerous summarizing tables.

**Analytical Methods for Atomic Absorption Spectrometry:** Perkin-Elmer, Norwalk, Connecticut 06852, 1968. Pp. x + 60 + 226 procedures. \$25.00.

This loose-leaf compilation is issued free with Perkin-Elmer atomic-absorption spectrophotometers or may be purchased separately. It is the fourth revision of the original printing made in 1964, and contains a bibliography listing 891 references to atomic-absorption methods, and details of 226 procedures for individual elements either alone or in a variety of matrices.

**Fibrous Proteins:** edited W. G. CREWTER. Butterworths, London, 1969. Pp. 432. £10.

**Organic Photochemistry—2: IUPAC.** Butterworths, London, 1968. 25s.

**The Determination of Particle Size, I. A Critical Review of Sedimentation Methods:** The Society for Analytical Chemistry, London, 1968. Pp. iv + 42. 30s.

This is a critical review of sedimentation methods of particle size analysis. Both sedimentation under gravity and under the influence of centrifugal forces are discussed and the discussion includes descriptions of the various techniques available for determining the rate of sedimentation. There is a short theoretical introduction and a comprehensive list of references.

**Analysis in the Chemical Industry:** L. A. HADDOCK. Pergamon, Oxford, 1968. Pp. xii + 220.

This is an analytical textbook with a difference, written by a chemist with a very wide experience of the British chemical industry. It is not a collection of analytical recipes but a description of how to organize an industrial analytical laboratory. There are sections which deal with sampling problems, with automatic and on-line analysis, with instrumentation and administration. The book will be useful for a wide range of students who may be entering the chemical industry, and to potential plant and factory managers.

**Chemical Applications of Potentiometry:** HAZEL S. ROSSOTTI. Van Nostrand, London, 1969. Pp. xiv + 229. 75/-

This book presents a thermodynamically rigorous approach to the uses of potentiometry for studying real systems and can be said to take over where most books leave off, while at the same time introducing the reader to the subject from scratch. Many examples from the literature are quoted, and the book will be of great help to anyone concerned with the interpretation of potentiometric data. The IUPAC (Stockholm) Convention is used throughout. A little over half the book contains material suitable for undergraduate reading (General and Honours Degree), the remaining chapters covering recent work on gradients in cells, and potentiometry in non-aqueous solvents, in fused salts, and with solid electrolytes.

## NOTICES

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### UNITED STATES OF AMERICA

The Association of Official Analytical Chemists will hold its 83rd Annual Meeting on 13-16 October 1969 at Marriott Motor Hotel, Twin Bridges, Washington, DC 20001. Further information can be obtained from L. G. Ensminger, Executive Secretary, AOAC, Box 540, Benjamin Franklin Station, Washington, DC 20044, U.S.A.

The Gordon Research Conferences for 1969 include Analytical Chemistry (11-15 August), Separation and Purification (18-22 August), Ion Exchange (18-22 August), Chemical Oceanography (14-18 July), Environmental Sciences—Air (30 July-4 July), Chemistry of Molten Salts (25-29 August) and Laser Interaction with Matter (25-29 August). Further details and the full programme can be obtained from Dr. Alexander M. Cruickshank, Director, Gordon Research Conferences, Pastore Chemical Laboratory, University of Rhode Island, Kingston, Rhode Island 02881, U.S.A.

### EAST GERMANY

The third International Symposium on Reinststoffe in Wissenschaft und Technik will be held in Dresden 4-8 May 1970, under the auspices of the Deutsche Akademie der Wissenschaften zu Berlin. Details are obtainable from Institut für Metallphysik und Reinstmetalle—Reinststoffsymposium, DDR—8020 Dresden, Winterbergstraße 28.

## SUMMARIES FOR CARD INDEXES

**Determination of indium and tin by activation analysis using replacement substoichiometry:** IVAN OBRUSNÍK, *Talanta*, 1969, **16**, 563. (Institute of Nuclear Research, ČSAV, Rež near Prague, Czechoslovakia.)

**Summary**—A new method for the determination of indium by activation analysis has been developed. It is based on the replacement of indium from indium dithizonate (in carbon tetrachloride) by a substoichiometric amount of aqueous mercury(II) solution. Preliminary steps are the extraction of indium from alkaline cyanide solution with an excess of dithizone solution and washing the extract with buffer solution. The time necessary for the separation is 10–20 min. With this method indium can be determined by using either short ( $^{116m}\text{In}$ ,  $t_{1/2} = 54$  min) or long-lived radioisotopes ( $^{114m}\text{In}$ ,  $t_{1/2} = 50$  d). As by the reaction  $^{112}\text{Sn} (n, \gamma) ^{113}\text{Sn} (119\text{d}) \xrightarrow{ec} ^{113m}\text{In} (104\text{min})$ , indium-113m is formed, which has a different  $\gamma$ -spectrum from that of indium-114m, the determination of both indium and tin is possible. The proposed method has been applied to the determination of indium and tin in granite and gallium.

**A cell for high-precision constant-current coulometry with external generation of titrant. High-precision assay of potassium hydrogen phthalate and potassium dichromate:** JOHN KNOECK and HARVEY DIEHL, *Talanta*, 1969, **16**, 567. (Department of Chemistry, Iowa State University, Ames, Iowa 50010, U.S.A.)

**Summary**—A cell has been designed for the high-precision coulometric titration, with externally generated titrant, of materials which otherwise undergo undesirable reactions at the working electrodes. With this cell potassium dichromate has been titrated, *via* its hydrolysis reaction, with hydroxyl ion generated at the cathode, cathodic reduction of the chromium(VI) being circumvented. In this cell 99.9% of the titrant required is generated in one chamber and transferred to another for reaction; the titration is then completed with titrant generated at a second, drip-type electrode working at much lower current. By means of commercially available Leeds and Northrup coulometric titration electrical equipment, titration of NBS 136b Potassium Dichromate gave a purity of 99.976%, standard deviation 0.005%, and of NBS 84d Potassium Acid Phthalate (done as a check) 99.991%, standard deviation 0.005%, both values being in excellent agreement with other work.

ОПРЕДЕЛЕНИЕ ИНДИЯ И ОЛОВА МЕТОДОМ  
РАДИОАКТИВАЦИОННОГО АНАЛИЗА С  
ПРИМЕНЕНИЕМ ЗАМЕСТИТЕЛЬНОЙ  
СУБСТЕХИОМЕТРИИ:

IVAN OBRUSNIK, *Talanta*, 1969, **16**, 563.

**Резюме**—Разработан новый метод радиоактивационного анализа для определения индия. Метод основывается на замещении индия в дитизонате индия (в растворе тетрахлорметана) субстехиометрическим количеством водного раствора ртути(II). Предварительно извлекают индий из щелочного раствора цианида с избытком раствора дитизона и промывают экстракт с буферным раствором. Время выполнения разделения 10–20 мин. Этот метод позволяет определять индий с использованием радиоизотопов короткого ( $^{116m}\text{In}$ ,  $t_{1/2} = 54$  мин) или долгого ( $^{114m}\text{In}$ ,  $t_{1/2} = 50$  дней) полупериода. Потому что в реакции  $^{112}\text{Sn}(n, \gamma) ^{113}\text{Sn}(119 \text{ дн.}) \xrightarrow{\text{ac}} ^{113m}\text{In}(104 \text{ мин.})$  образуется индий-113m спектр гамма лучей которого различный от спектра индия-114m, дана возможность определения индия и олова. Предложенным методом пользовались для определения индия и олова в граните и галлии.

ЯЧЕЙКА ДЛЯ ВЫСОКОПРЕЦИЗИОННОЙ  
КУЛОНОМЕТРИИ ПРИ ПОСТОЯННОЙ СИЛЕ ТОКА  
С ВНЕШНИМ ГЕНЕРИРОВАНИЕМ ТИТРАНТА.  
ВЫСОКОПРЕЦИЗИОННОЕ ОПРЕДЕЛЕНИЕ КИСЛОГО  
ФТАЛАТА КАЛИЯ И БИХРОМАТА КАЛИЯ:

JOHN KNOESK and HARVEY DIENL, *Talanta*, 1969, **16**, 567.

**Резюме**—Сконструирована ячейка для высокопрецизионного кулонометрического титрования, с внешним генерированием титранта, материалов при которых являются нежелательные реакции на рабочих электродах. Пользуясь этой ячейкой титровали бихромат калия, путем его реакции гидролиза, с гидроксидом генерированным на катоде, избегая восстановления хрома(VI) на катоде. В этой ячейке 99,9% потребного титранта генерируется в одной камере и переводится в другую камеру для реакции; титрование затем проводят до конца с титрантом генерированным на другом электроде капельного типа, работающем при гораздо ниже-силы тока. В анализе бихромата калия NBS 136b с коммерческим прибором для кулонометрического титрования Дидс и Нортруп получена чистота 99,976% с стандартной ошибкой 0,005%, в анализе кислого фталата калия NBS 84d (в качестве эталона)—99,991%, с стандартной ошибкой 0,005%; обе величины отлично соглашаются с результатами других методов.



**Alkaline earth separations on microcrystalline cellulose columns:** JAMES S. FRITZ and MARK A. PETERS, *Talanta*, 1969, **16**, 575. (Institute for Atomic Research and Department of Chemistry, Iowa State University, Ames, Iowa 50010, U.S.A.)

**Summary**—Magnesium, calcium, strontium and barium may be separated quantitatively from each other on a column of microcrystalline cellulose. Barium and radium are also separated from each other. The metal ions are eluted from the column by methanol-hydrochloric acid in varying proportions. The separated metal ions can be titrated with EDTA. Trace amounts of metal ions may be determined by neutron activation.

**Resolution of racemic substances by liquid ion-exchange:** S. J. ROMANO, K. H. WELLS, H. L. ROTHBART and W. RIEMAN III, *Talanta*, 1969, **16**, 581. (School of Chemistry, Rutgers—The State University, New Brunswick, N.J., U.S.A.)

**Summary**—Two optically active liquid anion-exchangers have been synthesized. The separation factors of the enantiomers of sodium ( $\pm$ )-mandelate and sodium-*N*-acetyl-( $\pm$ )-alanate have been determined by batchwise equilibration of aqueous solutions of the salts with chloroform solutions of each of the exchangers. Sodium mandelate has been resolved by Craig countercurrent extraction with one of these exchangers. Optically pure products can be obtained even though the liquid ion-exchanger is not optically pure.

**Determination of palladium and platinum by atomic absorption:** M. M. SCHNEPPE and F. S. GRIMALDI, *Talanta*, 1969, **16**, 591. (U.S. Geological Survey, Washington, D.C., U.S.A.)

**Summary**—Palladium and platinum are determined by atomic absorption after fire-assay concentration into a gold bead. The limit of determination is  $\sim 0.06$  ppm in a 20-g sample. Serious depressive interelement interferences are removed by buffering the solutions with a mixture of cadmium and copper sulphates with cadmium and copper concentrations each at 0.5%. Substantial amounts of Ag, Al, Au, Bi, Ca, Co, Cr, Fe, Hg, K, La, Mg, Mn, Mo, Na, Ni, Pb, Te, Ti, V, Y, Zn, and the platinum metals do not interfere in the atomic-absorption determination.

РАЗДЕЛЕНИЕ ЩЕЛОЧНОЗЕМЕЛЬНЫХ  
ЭЛЕМЕНТОВ НА КОЛОНКАХ МИКРОКРИСТАЛЛИЧЕСКОЙ ЦЕЛЛЮЛОЗЫ:

JAMES S. FRITZ and MARK A. PETERS, *Talanta*, 1969, 16, 575.

**Резюме**—Магний, кальций, стронций и барий разделяли количественно одного от другого на колонке микрокристаллической целлюлозы. Барий и радий также разделяются. Ионы металлов элюируют из колонки смесью метанола и соляной кислоты в различных отношениях. Разделенные ионы титруют с ЭДТА. Следовые количества ионов металлов определяют методом нейтронно-активационного анализа.

РАЗДЕЛЕНИЕ РАЦЕМИЧЕСКИХ ВЕЩЕСТВ  
МЕТОДОМ ЖИДКОФАЗНОГО ИОННОГО ОБМЕНА:

S. J. ROMANO, K. H. WELLS, H. L. ROTHWART and W. RIEMAN III, *Talanta*, 1969, 16, 581.

**Резюме**—Синтезированы два оптически активных жидкофазных анионита. Определены факторы разделения ехантиомеров натрий-(±)-манделата и натрий-*N*-ацетил-(±)-аланата периодической эквilibрацией водных растворов солей с хлороформовыми растворами каждого из ионообменников. Манделат натрия разделили противоточным извлечением с одним из этих ионообменников по методу Крейга. Получены продукты оптической чистоты даже в случае если жидкофазный ионообменник не является оптически чистым.

ОПРЕДЕЛЕНИЕ ПАЛЛАДИЯ И ПЛАТИНЫ МЕТОДОМ  
АТОМНО-АБСОРБЦИОННОЙ СПЕКТРОСКОПИИ:

M. M. SCHNEPFE and F. S. GRIMALDI, *Talanta*, 1969, 16, 591.

**Резюме**—Палладий и платину определили методом атомно-абсорбционной спектроскопии после их концентрирования сухим путем в зерне золота. Чувствительность определения— $\sim 0,06$  мкг/г в 20 г пробы. Серьезное взаимодействие элементов удалено буферированием растворов смесью сульфатов кадмия и меди, содержащей 0,5% каждого элемента. Значительные количества Ag, Al, Au, Bi, Ca, Co, Cr, Fe, Hg, K, La, Mg, Mn, Mo, Na, Ni, Pb, Te, Ti, V, Y, Zn и платиновых металлов не мешают определению методом атомно-абсорбционной спектроскопии.

**Catalytic activity and complexation—IV. 2,2'-Bipyridyl as activator for the catalytic ultramicrodetermination of silver:** P. R. BONTSHEV, A. ALEXIEV and B. DIMITROVA, *Talanta*, 1969, **16**, 597. (Department of Analytical Chemistry, Sofia University, Bulgaria.)

**Summary**—The activation of the catalytic persulphate oxidation of sulphanilic acid when the catalyst, silver(I), is suitably complexed, is discussed. 2,2'-Bipyridyl is proposed as activator as it accelerates the rate-determining step of the process—the oxidation of silver(I) to silver(II). The mechanism of activation is investigated and discussed in detail. On the basis of these investigations a catalytic method has been developed for the determination of silver(I), with a sensitivity of  $4 \times 10^{-4}$   $\mu\text{g/ml}$  and  $\pm 7.6\%$  relative error.

**Advantages of a two-detector system in automated substoichiometric radioisotope dilution analysis:** C. G. LAMM and J. RŮŽIČKA, *Talanta*, 1969, **16**, 603. (Chemistry Laboratory A, Technical University of Denmark, Lyngby, Denmark.)

**Summary**—Automation widens the scope of substoichiometric radioisotope dilution analysis. This is because the very strict requirement of the manual method—chemical separation of exactly equal quantities of the test substance—needs no longer be fulfilled: reproducibility of the determination is reached by means of automated operation and activity measurement. The theory given in this paper shows how the choice of suitable chemical reactions is widened and why the reliability and the advantages of isotope dilution analysis are secured by the use of a two-detector system.

**Determination of small amounts of TBP and DBP in uranyl nitrate solutions:** TOMITARO ISHIMORI and KAORU UENO, *Talanta*, 1969, **16**, 613. (Chemistry Division, Japan Atomic Energy Research Institute, Tokai, Ibaraki, Japan.)

**Summary**—Tri- and dibutylphosphate (TBP and DBP) in concentrated uranyl nitrate solution are determined by a method based on the solvent extraction of zirconium-95. The distribution ratio of zirconium-95 between dilute solutions of TBP and DBP in dodecane and 10M hydrochloric acid and 1M nitric acid respectively is measured. There is a logarithmic relationship between the distribution ratio and concentration of TBP and DBP, which enables them to be determined rapidly and with an error of  $\pm 10\%$  over the range 1–100 ppm of TBP and 40–600 ppm of DBP. The lower limit is 0.5 ppm for TBP and 10 ppm for DBP.

КАТАЛИТИЧЕСКАЯ АКТИВНОСТЬ И  
КОМПЛЕКСООБРАЗОВАНИЕ—IV. 2,2'-ДИПИРИДИЛ  
В КАЧЕСТВЕ АКТИВАТОРА ДЛЯ КАТАЛИТИЧЕСКОГО  
УЛЬТРАМИКРООПРЕДЕЛЕНИЯ СЕРЕБРА:

P. R. BONTSCHEV, A. ALEXIEV and B. DIMITROVA, *Talanta*, 1969, **16**, 597.

**Резюме**—Обсуждено каталитическое окисление персульфатом сульфаниловой кислоты с катализатором—серебром (I)—в форме подходящего комплекса. 2,2'-Дипиридил предложен в качестве активатора так как он ускоряет определяющую скорость процесса фазу—окисление серебра(I) в серебро(II). Детально исследован и обсужден механизм активации. На основе этих исследований разработан каталитический метод определения серебра(I), чувствительность которого— $4 \times 10^{-4}$  мкг/мл, а относительная ошибка— $\pm 7,6\%$ .

ПРЕИМУЩЕСТВА СИСТЕМ С ДВУМЯ ДЕТЕКТОРАМИ  
В АВТОМАТИЧЕСКОМ СУБСТЕХИОМЕТРИЧЕСКОМ  
АНАЛИЗЕ МЕТОДОМ РАЗБАВЛЕНИЯ  
РАДИОИЗОТОПОВ:

C. G. LAMM and J. RŮŽIČKA, *Talanta*, 1969, **16**, 603.

**Резюме**—Автоматизация расширяет поле применения субстехиометрического анализа методом разбавления изотопов. Это основывается на факте что не надо исполнять очень строгое требование ручного метода—химическое разделение точно равных количеств анализируемого вещества: воспроизводимость определения получается автоматической работой и измерением активности. Приведена в статье теория показывает как расширяется выбор подходящих химических реакций и почему двухдетекторная система обеспечивает надёжность и преимущества анализа методом разбавления изотопов.

ОПРЕДЕЛЕНИЕ НЕБОЛЬШИХ КОЛИЧЕСТВ ТБФ  
И ДБФ В РАСТВОРАХ НИТРАТА УРАНИЛА:

TOMIYARO ISHIMORI and KAORU UENO, *Talanta*, 1969, **16**, 613.

**Резюме**—Трибутилфосфат (ТБФ) и дибутилфосфат (ДБФ) в концентрированном растворе нитрата уранила определяют методом основанным на экстракции циркония-95 растворителями. Измеряют отклонение распределения циркония-95 между разбавленными растворами ТБФ и ДБФ в додекане и 10М соляной кислоте и 1М азотной кислоте, соответственно. Существует логарифмическое отношение между распределением и концентрацией ТБФ и ДБФ, на основе которого удается определять их быстро и с ошибкой  $\pm 10\%$  в диапазоне 1–100 мг (л ТБФ и 40–600 мг) л ДБФ. Чувствительность определения—0,5 мг/л ТБФ и 10 мг/л ДБФ.

**Argentometric titration of chloride with dichlorofluorescein as an adsorption indicator: A useful modification:** JOHN P. FRIEND, *Talanta*, 1969, **16**, 617. (Department of Physical Chemistry, University of Sydney, Australia.)

**Summary**—The addition of excess of ethyl alcohol renders more useful the argentometric titration of chloride with dichlorofluorescein as adsorption indicator by improving the end-point, both when simple counter-ions are present and also when the presence of adsorbable and/or complexing counter-ions renders the normal technique inadequate.

**Vacuum system for the semi-automatic degassing of solvents:** JOHN R. WIESENFELD and STEVEN M. JAPAR, *Talanta*, 1969, **16**, 619. (Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106, U.S.A.)

**Summary**—A semi-automatic system capable of quickly degassing large amounts of solvent is described.

**Gas-chromatographic display of the polycyclic aromatic hydrocarbon fraction of cigarette smoke:** HOWARD J. DAVIS, *Talanta*, 1969, **16**, 621. (Celanese Research Company, Summit, New Jersey, U.S.A.)

**Summary**—High electron-affinity polycyclic aromatic hydrocarbons in cigarette smoke are detected by gas chromatography. The resulting gas chromatograms can be used for "fingerprint" identification of the hydrocarbon fractions in cigarette smoke.

**Use of radioactive kryptonate of thallium in the determination of oxygen dissolved in water or other liquids:** J. TÖLGYESSY and Š. VARGA, *Talanta*, 1969, **16**, 625. (Department of Radiochemistry and Radiation Chemistry, Slovak Technical University, Bratislava, Jánska 1, Czechoslovakia.)

**Summary**—Radioactive kryptonate of thallium is placed in the liquid sample. Oxygen dissolved in the sample reacts with the surface layer of radioactive kryptonate of thallium, and releases radioactive krypton in amount proportional to the amount of oxygen.

АРГЕНТОМЕТРИЧЕСКОЕ ТИТРОВАНИЕ ХЛОРИДА  
С ДИХЛОРФЛУОРЕСЦЕИНОМ В КАЧЕСТВЕ  
АДСОРБЦИОННОГО ИНДИКАТОРА: ПОЛЕЗНАЯ  
МОДИФИКАЦИЯ:

JOHN P. FRIEND, *Talanta*, 1969, **16**, 617.

**Резюме**—Аргентометрическое титрование хлорида в присутствии избытка этилового спирта с использованием дихлорфлуоресцеина в качестве адсорбционного индикатора дает лучший конец титрования в присутствии простых противных ионов, а также в случаях в которых обыкновенный метод неприменимый вследствие присутствия адсорбируемых и/или комплексообразующих противных ионов.

СИСТЕМА ПОЛЬЗУЮЩАЯСЯ ВАКУУМОМ ДЛЯ  
ПОЛУАВТОМАТИЧЕСКОЙ ДЕГАЗАЦИИ РАСТВОРИ-  
ТЕЛЕЙ:

JOHN R. WIESENFELD and STEVEN M. JAPAR, *Talanta*, 1969, **16**, 619.

**Резюме**—Описана полуавтоматическая система для быстрой дегазации больших количеств растворителей.

ГАЗОВО-ХРОМАТОГРАФИЧЕСКАЯ КАРТИНА  
ФРАКЦИИ МНОГОЯДЕРНЫХ АРОМАТИЧЕСКИХ  
УГЛЕВОДОРОДОВ В ДЫМЕ ПАПИРОС:

HOWARD J. DAVIS, *Talanta*, 1969, **16**, 621.

**Резюме**—Обладающие высоким электронным аффинитетом многоядерные ароматические углеводороды обнаружены методом газовой хроматографии. Полученными хроматограммами можно пользоваться для «фингерпринт» идентификации фракций углеводородов в дыме папирос.

ИСПОЛЬЗОВАНИЕ РАДИОАКТИВНОГО  
КРИПТОНАТА ТАЛЛИЯ ДЛЯ ОПРЕДЕЛЕНИЯ  
РАСТВОРЕННОГО В ВОДЕ И ДРУГИХ  
ЖИДКОСТЯХ КИСЛОРОДА:

J. TÖLGYESSY and S. VARGA, *Talanta*, 1969, **16**, 625.

**Резюме**—Радиоактивный криптонат таллия помещали в жидкую пробу. Растворенный в пробе кислород взаимодействует с поверхностным слоем радиоактивного криптоната таллия освободит количество радиоактивного криптона пропорциональное количеству кислорода.

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