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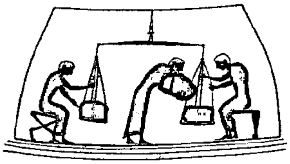

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3. R. J. Winterton in C. L. Wilson and D. W. Wilson, *Comprehensive Analytical Chemistry*, Vol. IB, p. 238. Elsevier, Amsterdam, 1960.
4. A. B. Smith, *The Effect of Radiation on Strengths of Metals.* A.E.R.E., M/R 6329, 1962.
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DETERMINATION OF GOLD BY X-RAY FLUORESCENCE METHODS

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(*Received* 8 *October* 1965. *Accepted* 10 *December* 1965)

Summary—X-ray fluorescence methods for the determination of gold in silver beads and in hydrochloric acid solutions are described. These techniques may be applied to silver containing 0·2–5% of gold and to solutions containing 0·004–0·1% of gold. Platinum, palladium, rhodium and iridium do not interfere.

THE use of X-ray fluorescence methods for the determination of metals is well established for all but the lightest elements.[1] These techniques are rapid, and because the sample is not destroyed a comparison of accuracy and precision with other methods can be made. Furthermore, accuracy and precision can be increased by repeated or prolonged counting intervals.

Although gold has been determined by the complete range of analytical techniques, very little has been reported on its determination by X-ray fluorescence methods. Strasheim and Wybenga[2] determined platinum, gold and iridium in small quantities in solutions of matte, using a correction factor for platinum and a ratio method for gold and iridium. Although the results obtained agreed with values obtained by chemical methods, the latter are not described.

This report describes procedures used for the determination of gold, and gold in the presence of platinum metals in hydrochloric acid solutions and of gold in silver assay beads. The determination of gold in acidic solution provides a rapid and accurate alternative to spectrophotometric and titrimetric methods and there is the significant advantage that platinum metals do not interfere appreciably.

The determination of gold in silver beads is of particular interest to those using fire assay procedures. A common method for determining milligram amounts of gold in silver beads includes parting with acids, filtration and heating before weighing. For microgram amounts of gold in silver, dissolution and spectrophotometric determinations are usually required. A necessary condition for the application of X-ray fluorescence to silver-gold beads is the homogeneous distribution of gold in the silver. In general, gold–silver alloys are considered to be solid solutions, but because of the specific conditions required for the preparation of assay beads the homogeneity of the latter was investigated by irradiating several locations on both surfaces of a few foils produced by rolling the beads.

EXPERIMENTAL

Apparatus

Philips Universal Vacuum X-ray spectrograph equipped with a tungsten target X-ray tube
Beckman Model B spectrophotometer
William and Wilson 20 KW electric furnace
Cupels supplied by A. P. Green Co. (Weston, Ontario, Canada)

Reagents

Gold foil (Johnson Matthey)
Gold, precipitated powder (Fisher purified)
Silver, precipitated powder (Fisher certified reagent)
Lead foil (Matheson Coleman and Bell reagent)

All acids used were commerically pure reagent grade except the hydrobromic acid which was the colourless fraction obtained by distillation of reagent-grade acid. All other chemicals were reagent grade.

Standard gold solutions. Approximately 1 g of gold foil was dissolved in *aqua regia* and the nitrous oxides removed by repeated evaporations with hydrochloric acid in the presence of a few milligrams of sodium chloride. The solution was filtered and the residue ignited, dissolved by the same procedure and added to the original filtrate. The final solution was diluted to 1 l. with $0{\cdot}12M$ hydrochloric acid. Dilute gold solutions were prepared by dilution with $0{\cdot}12M$ hydrochloric acid. The concentrated stock solution was standardised with hydroquinone.[3]

Procedure

For the determination of gold in dilute hydrochloric acid solution, the gold $L\beta_1$ line ($31{\cdot}19°$, 2θ) (lithium fluoride crystal) was used because of lower interference from the tungsten-scattered spectral lines compared to that found for the other analytical lines. The tungsten tube was operated at 40 kV and 22 mA, and the scintillation detector at 800 V.

Because the setting of the goniometer is crucial for accurate readings, once it had been adjusted to the gold peak it was not changed until a complete series of results had been obtained. The blank was determined by counting at the same angle a solution containing the same constituents as the samples with the exception of gold. This method allowed for any trace gold or impurity present in the reagents.

To avoid any change in path-length, the same acid-resistant PVC liquid-sample holder in the same position and alignment was used for all measurements; the sample holder was left assembled with the same Mylar film bottom until a complete series of samples had been treated. The cell was inverted to remove the sample, rinsed twice with water and dried with a tissue, care being taken not to distort the Mylar film.

Infinite layer thickness was found to be given by about 10 ml of sample solution. Although consistent results could be obtained with the cell three-quarters full, this volume was inconvenient to use. If the same volumes of sample solutions were added to the dry sample holder, a constant level was maintained and consistent results were obtained. Any volume seems suitable provided the solution covers the bottom of the holder, and the use of smaller aliquots permits the determination of smaller amounts of gold.

Gold solutions are easily decomposed by ultraviolet light[4] and it was found that prolonged exposure to X-rays also causes the formation of a reddish precipitate of gold. Attempts were made to stabilise the gold solution by the addition of gelatin but were unsuccessful. In order to avoid decomposition of the gold solution, a fixed irradiation time of 10·0 sec was maintained and the Mylar film was examined for any gold precipitate by the frequent counting of blank solutions in the same cell. Short irradiation times produced no precipitate. At least five aliquots of each sample were counted and the average deviation was always less than 1%.

Large variations in the concentration of hydrochloric acid significantly affected the counting rate; an increase from 0·25 to $0{\cdot}50M$ in hydrochloric acid decreased the counting rate by 7%. The acid concentration was easily maintained within the permissible limits.

RESULTS AND DISCUSSION

The results for 5·0 ml and 2·0 ml of dilute standard gold solutions in $0{\cdot}12M$ hydrochloric acid are given in Table I. These show good consistency for the range 40–1000 ppm. The addition of various platinum metal chlorides to gold samples introduced only a slight error; equal concentrations of platinum metal and gold gave results which were 0–5% low. The results obtained when platinum, palladium, rhodium, iridium, or a combination of the four platinum metals were added to gold are also given in Table I.

Pulse height analysis with a base-line level of 5·0 V and a window width of 12·5 V reduces the high background more than the gold peak so that the difference is increased by approximately 7%. Results obtained with 5·0 ml of gold solution by pulse height analysis are included in Table I.

Table I.—Determination of gold in solution

Concentration of gold, *ppm*	Aliquot used, *ml*	P.H.A. used	Pt metals added	Intensity, *cps*	*A**	Average, *A*†
0	2·0	No	No	1958		
100	2·0	No	No	2241	2·83	
200	2·0	No	No	2513	2·78	
300	2·0	No	No	2727	2·56	
400	2·0	No	No	2967	2·52	
500	2·0	No	No	3255	2·59	2·66 ± 0·12
0	5·0	No	No	2685		
40	5·0	No	No	2799	2·85	
80	5·0	No	No	2904	2·74	
120	5·0	No	No	3028	2·86	
160	5·0	No	No	3149	2·90	
200	5·0	No	No	3246	2·81	2·83 ± 0·046
0	5·0	No	No	2620		
200	5·0	No	No	3260	3·20	
400	5·0	No	No	3890	3·18	
600	5·0	No	No	4495	3·13	
800	5·0	No	No	5100	3·10	
1000	5·0	No	No	5695	3·08	
2000	5·0	No	No	8520	2·95	3·11 ± 0·063
0	5·0	Yes	No	1899		
40	5·0	Yes	No	2026	3·18	
80	5·0	Yes	No	2135	2·95	
120	5·0	Yes	No	2259	3·00	
160	5·0	Yes	No	2382	3·02	
200	5·0	Yes	No	2488	2·95	3·02 ± 0·064
0	15·0	No	No	2371		
400	15·0	No	No	3371	2·50	
400	15·0	No	Pt	3369	2·49	
400	15·0	No	Pd	3341	2·43	
400	15·0	No	Rh	3356	2·46	
400	15·0	No	Ir	3316	2·36	
400	15·0	No	Pt, Pd Rh, Ir	3365	2·49	2·45 ± 0·04

* *A* is the difference in count rate between sample and blank, divided by concentration.
† Average value of *A* ± average deviation.

Gold in silver beads was determined under conditions similar to those used for gold in solution. The $L\beta_1$ gold line at (31·19°, 2θ) (lithium fluoride crystal) was used for counting and the same power settings were used. The use of a blank eliminated changing the goniometer setting for a set of samples, and avoided adjustment errors and interference from impurities in the reagents.

Gold-silver beads weighing 100, 25, 12 and 8 mg were prepared. For the larger amounts of gold, gold powder was weighed directly on a microbalance and transferred to a boat made from 6 × 6 in. lead foil. For smaller amounts of gold, an aliquot of gold solution was added to the lead boat and the liquid was evaporated in a steam cabinet. For all samples, silver powder was added and the lead boat carefully folded. The artificial lead buttons containing gold and silver were cupelled at 980° on preheated #8 S.A. cupels. Preliminary cupellation tests showed no loss of gold powder and only insignificant losses for low concentrations of evaporated gold solution. Silver losses on cupellation were appreciable and varied because of differences in temperature within the furnace and variations in the silver content of the lead. The final concentrations of gold in the gold-silver alloys were calculated from the amount of gold added and the weight of the silver bead after cupellation. Blanks were prepared from silver powder added to lead foil and also by evaporating 0·12M hydrochloric acid in lead foil.

Because the X-ray path-length must be constant for consistent results, the hemispherical silver bead produced by cupellation is not suitable for the determination of gold. The beads were, therefore, rolled to a thickness of 0·02–0·03 mm after adhering cupel material had been gently removed with a spatula. To facilitate rolling and prevent splitting, the alloys were intermittently annealed[5] several times by heating them to red heat in porcelain crucibles over a Meker burner for 2–3 min. After sufficient rolling and annealing the silver foil was flattened between two steel blocks. This procedure provides a much larger surface area for irradiation and thus gives a higher counting rate.

To obtain a constant surface area for irradiation a metal disk with a central hole was used as a shield. Copper foil was the best of several metals tried because it gave the lowest background. The size of hole used was the largest that was just smaller than the smallest rolled bead of a particular set. Different diameters of openings were used for different weights of beads, but the same shield was used for any one set. The number of counts for gold per unit area was found to be a constant within experimental error. Any variation in the irradiation of the sample caused by a change of position was avoided by using the same copper shield held firmly in position in the sample holder, in the same orientation and holder position. The sample was kept flat and in the proper position by a brass weight which fitted inside the sample holder. No Mylar film was necessary with this arrangement.

Pulse height analysis was used to eliminate some of the interference from silver although the background was still significant. The base-line level was set at 2·5 V and the window width at 8·5 V. Because no appreciable gain in precision was obtained by longer fixed counting times, 50·0 or 100·0 sec were used. The homogeneity of several beads was checked by irradiating several locations on both sides of the foil. The average deviation in count rate was no more than 1%. Repeated counting of the same area showed an average deviation of less than 0·5%. The slight difference in count rates may be caused by slight irregularities on the surface of the foil caused by rolling or adhering cupel material. Because some of the X-rays penetrate the thin foil and are reflected by the brass block, the thickness of the foil could be of significance. Fortunately for the ease of preparation, this does not appear to be the case. A difference of 50% in thickness does not affect the count rate appreciably. A plot of results from samples of about the same thickness shows a similar deviation to a plot for samples of random thickness.

The results in Table II indicate that silver beads weighing 5–100 mg may be used, provided a constant surface area is irradiated. The useful concentration range is 0·2–5% or 20–500 μg of gold in a 10-mg silver bead.

Several of the gold-silver beads used for these experiments were parted in nitric acid (1 + 2) and the gold filtered off. The paper was carefully burned and the gold annealed. The larger amounts of gold were weighed, then dissolved in *aqua regia*. After removal of nitrous oxides by several evaporations in the presence of hydrochloric acid and a few milligrams of sodium chloride, the gold solution was diluted

TABLE II.—DETERMINATION OF GOLD IN SILVER

						Determination of gold		
Weight of bead, *mg*	Weight of gold, *mg*	Gold, %	Intensity, *cps*	*A**	Average, *A*†	Gravi-metric, *mg*	Colorimetric, *mg*	Liquid X-ray, *mg*
110·0	0	0	195·6					
88·3	0·080	0·091	206·8	123‡			0·080	
124·1	0·202	0·163	226·0	186‡			0·195	
127·0	0·276	0·217	243·6	221			0·276	
82·4	0·412	0·500	310·0	228			0·412	
159·0	0·534	0·336	273·4	231			0·504	
123·4	0·583	0·472	298·0	217			0·563	
117·9	0·711	0·603	327·0	218			0·709	
86·6	0·775	0·895	401·4	230			0·770	
122·4	0·912	0·745	358·2	218			0·893	
107·5	1·070	0·995	433·8	239		1·07	1·12	1·10
139·7	1·258	0·901	409·0	237			1·25	—
109·2	1·640	1·50	553·2	238			1·61	—
95·9	2·100	2·19	713·6	237		1·88	2·09	1·87
137·7	3·512	2·55	799·2	237		3·41	3·56	3·53
86·9	4·273	4·92	1379·2	241		4·03	4·27	4·15
114·5	5·180	4·52	1239·6	231		4·58	4·71	4·76
158·3	7·444	4·70	1274·4	230		7·44	7·38	7·18
115·1	9·470	8·23	2048·2	225	230 ± 6·5	10·32	9·35	9·63
101·9§	0·740	0·726	370·6	241				
109·9‖	1·020	0·928	417·7	239				
112·4¶	0·909	0·809	409·5	264‡				
103·7**	0·804	0·775	368·2	223	234 ± 8			
12·3	0	0	159·8				—	
11·0	0·021	0·191	176·1	85·3			0·0209	
14·1	0·021	0·149	171·3	77·2			0·0233	
12·1	0·042	0·347	195·7	103·5			0·0433	
13·1	0·042	0·321	185·9	81·3			0·0433	
13·8	0·063	0·457	204·8	98·5			0·0625	
11·9	0·063	0·529	211·8	98·3			0·0630	
11·5	0·084	0·730	223·1	86·7			0·0840	
11·5	0·084	0·730	226·4	91·2			0·0830	
12·7	0·126	0·992	249·0	89·9			0·123	
11·4	0·126	1·11	258·6	89·4			0·122	
12·6	0·189	1·50	297·3	91·7			0·181	
11·9	0·189	1·59	300·6	88·6	90·1 ± 5·4		0·179	
8·01	0	0	159·5					
6·46	0·042	0·650	220·6	94·0			0·0415	
8·80	0·084	0·955	255·6	100·6			0·0810	
8·72	0·126	1·444	298·6	96·3	97·0 ± 2·4		0·120	
29·8	0	0	193·0	—				
25·7	0·042	0·163	234·6	255			0·0402	
26·3	0·084	0·319	275·4	258			0·0805	
27·3	0·126	0·462	312·0	257	257 ± 1·0		0·126	

* *A* is the difference in count rate between sample and blank, divided by the concentration.
† Average value of *A* ± average deviation.
‡ This value of *A* not included in average.
§ Contains 1 mg of Pt.
‖ Contains 1 mg of Pd.
¶ Contains 1 mg of Rh.
** Contains 1 mg of Ir.

with $0{\cdot}12M$ hydrochloric acid, and aliquots were taken for determination by liquid X-ray fluorescence and for spectrophotometric determination as bromaurate.[6] The smaller amounts of gold were determined only spectrophotometrically. The results of these analyses are given in Table II.

Samples of gold-silver beads containing platinum metals were prepared by evaporating 1 mg of platinum metal as chloride solution in a lead boat. After addition of gold and silver powder, the lead boat was folded and cupelled as before. Rhodium and iridium are not fully soluble in silver and during cupellation may appear as black particles on the surface of the silver bead. This prevents the determination of either rhodium or iridium by this technique because mechanical losses will occur during rolling and in any case the beads are not homogeneous. The results in Table II show that platinum, palladium and iridium do not interfere with the determination of gold.

The use of vacuum in the sample chamber increases the count rate of the gold samples by approximately 10%. This is a slightly more sensitive technique provided the vacuum is reproducible, but it is more time-consuming.

Accurate and reproducible results are obtainable for gold in hydrochloric acid solution and for gold in silver beads. It is not improbable that the use of X-ray tubes with other target materials might eliminate the high background found with both techniques and produce more intense gold lines. Higher energy applied to the X-ray tube would also increase sensitivity. Despite the restrictions imposed by the available equipment, quantitative results were obtained quickly and without difficulty. The data obtained by the recommended techniques were confirmed by comparisons with known compositions and by chemical determinations.

Zusammenfassung—Röntgenfluoreszenzmethoden zur Bestimmung von Gold in Silberperlen und in salzsauren Lösungen werden beschrieben. Die Vorschriften sind anwendbar auf 0,2–5% Gold enthaltendes Silber und auf Lösungen mit 0,004–0,1% Gold. Platin, Palladium, Rhodium und Iridium stören nicht.

Résumé—On décrit des méthodes de fluorescence aux rayons X pour le dosage de l'or dans les perles d'argent et les solutions en acide chlorhydrique. On peut appliquer ces techniques à de l'argent contenant 0,2–5% d'or at à des solutions contenant 0,004–0,1% d'or. Le platine, le palladium, le rhodium et l'iridium n'interfèrent pas.

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VANADIUM COMPOUNDS IN REDUCTIMETRIC TITRATIONS—II*

STANDARDISATION OF VANADIUM(II) SULPHATE WITH COMMON OXIDISING AGENTS AND DETERMINATION OF BINARY MIXTURES

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Summary—Methods for the standardisation of vanadium(II) sulphate are described. With weak oxidising agents, e.g., Fe(III)/Fe(II) in phosphoric acid, vanadium(II) undergoes a one-electron change, which is satisfactorily indicated by Neutral Red, Phenosafranine or Safranine T, or by potentiometry. Stronger oxidising agents oxidise vanadium(II) to vanadium(IV); Variamine Blue, Methylene Blue, *o*-dianisidine, cacotheline, ferroin, bis(α,α'-bipyridyl)iron(II) and ammonium molybdate are satisfactory indicators. Binary mixtures of oxidising agents can be determined.

INTRODUCTION

THE continuation of our work on the standardisation of vanadium(II) sulphate and its applications in reductimetric titrations has now shown that in the presence of 8–10M phosphoric acid iron(III) oxidises vanadium(II) to vanadium(III) only. The formal redox potentials of the Fe(III)/Fe(II) system in varying concentrations of phosphoric acid have already been studied in detail by Gopala Rao and Sagi[1] and they have shown that the potentials fall steeply with increasing phosphoric acid concentration (formal redox potential +0·438 V in about 8M phosphoric acid). This enabled Rao and coworkers to develop methods of determination of uranium(VI),[1] molybdenum(VI),[2] vanadium(IV) and vanadium(V).[3]

In the present investigations the one-electron change in the case of vanadium(II) with iron(III) in the presence of phosphoric acid has been indicated visually, by Neutral Red, Phenosafranine and Safranine-T, and potentiometrically, and the titre values have been shown to agree fairly well. With stronger oxidising agents (oxidation potential $\geqslant$ +0·76 V) vanadium(II), however, undergoes a two-electron change and the end-point has been indicated by a number of visual indicators not employed earlier.

Ellis and Vogel[4] used Phenosafranine as an indicator for the one-electron change of vanadium(II) on the addition of iron(III) solution to vanadium(II) sulphate. It has now been found that the one-electron change can be indicated by the conventional and more convenient method of adding vanadium(II) sulphate to iron(III) solution in the presence of 8–10M phosphoric acid.

The two-electron change was also noted by Ellis and Vogel[4] by titrating vanadium(II) sulphate against cerium(IV), chromium(VI) and vanadium(V). They, however,

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* Part I—*Talanta*, 1965, **12**, 665.

used *N*-phenylanthranilic acid as visual indicator. Earlier, Banerjee[5] used diphenylamine for the standardisation with cerium(IV). In the present investigations vanadium(II) has been standardised against cerium(IV) visually using Methylene Blue, Variamine Blue, *o*-dianisidine, cacotheline and ferroin, against chromium(VI) using Variamine Blue, *o*-dianisidine, cacotheline and ferroin and against vanadium(V) using Variamine Blue, *o*-dianisidine, cacotheline, ferroin, bis(α,α'-bipyridyl)iron(II) and ammonium molybdate as internal indicators. The two-electron change with iron(III) has also been indicated by cacotheline as internal indicator in the presence of copper sulphate as catalyst. Methods for the determination of binary mixtures of the oxidising agents with iron(III) have been devised.

Erdey and Bodor[6] described the use of Variamine Blue as internal indicator in the titration of iron(III) against ascorbic acid; Bergmann[7] employed cacotheline in the titrimetric determination of tin(II) with iodine. Szarvas and Lantos[8] used cacotheline as a redox indicator in the titration of iron(III), chromium(VI), cerium(IV) or vanadium(V) against tin(II) chloride. Weeks[9] proposed the use of *o*-dianisidine as oxidation-reduction indicator. Szabo and Sugar[10] used ammonium molybdate as internal indicator in the reductimetric titration of iron(III) with tin(II) chloride.

EXPERIMENTAL AND RESULTS

Reagents

Vanadium(II) sulphate solution. Prepare approximately 0·05 to 0·1*M* solution and standardise as described in the earlier communication.[11]

Iron(III) sulphate solution. Prepare approximately 0·1*M* solution and standardise as described previously.[11]

Cerium(IV), chromium(VI) and vanadium(V) solutions. Prepare approximately 0·1*N* solutions from analytical-grade samples.

Copper(II) sulphate solution, 0·1M.

Phosphoric acid. Use syrupy phosphoric acid of E. Merck quality.

Neutral Red, Phenosafranine and Safranine-T, 0·1% aqueous solutions.

Variamine Blue, 1% aqueous solution.

Cacotheline and ammonium molybdate. Prepare saturated aqueous solutions.

o-Dianisidine. Dissolve 0·5 g of the compound in 200 ml of water, add 2 ml of hydrochloric acid and dilute to 500 ml.

Bis-(α,α'-bipyridyl)iron(II). Dissolve 1·17 g of the base in 100 ml of water containing 0·695 g of iron(II) sulphate heptahydrate.

Ferroin, 0·025M solution.

Apparatus

Apparatus used was the same as described previously[11] except that the potentials were measured with the help of a Student's Potentiometer (Pye) using a Cambridge Spot Galvanometer, and a magnetic stirrer was used for stirring the solutions.

Standardisation of vanadium(II) sulphate against iron(III) solution using Neutral Red, Phenosafranine and Safranine-T as visual indicators (one-electron change)

Place 2 to 5 ml of iron(III) solution, 5 to 15 ml of syrupy phosphoric acid, 2 to 3 drops of the indicator in the titration vessel and bubble carbon dioxide through the solution for about 10 min. Titrate the solution slowly with vanadium(II) solution to a yellowish green colour. The indicators are reversible and the indicator correction is almost negligible. The titre corresponds to a one-electron change *i.e.*, V(II) to V(III). A few typical results are given in Table I.

Standardisation of vanadium(II) sulphate against iron(III) solution potentiometrically

The procedure followed was the same as described above except that the titrations were carried out potentiometrically (see Fig. 1, curve A). A few typical results are given in Table II.

TABLE I.—VISUAL INDICATORS FOR TITRATION OF IRON(III) WITH VANADIUM(II)

Indicator used	Vanadium(II), *mmoles*	
	Present	Found
Neutral Red	0·1998	0·1989
	0·3996	0·3997
	0·4994	0·4999
Phenosafranine	0·1998	0·1989
	0·3996	0·3997
	0·4994	0·4999
Safranine-T	0·1998	0·1989
	0·3996	0·3997
	0·4994	0·4999

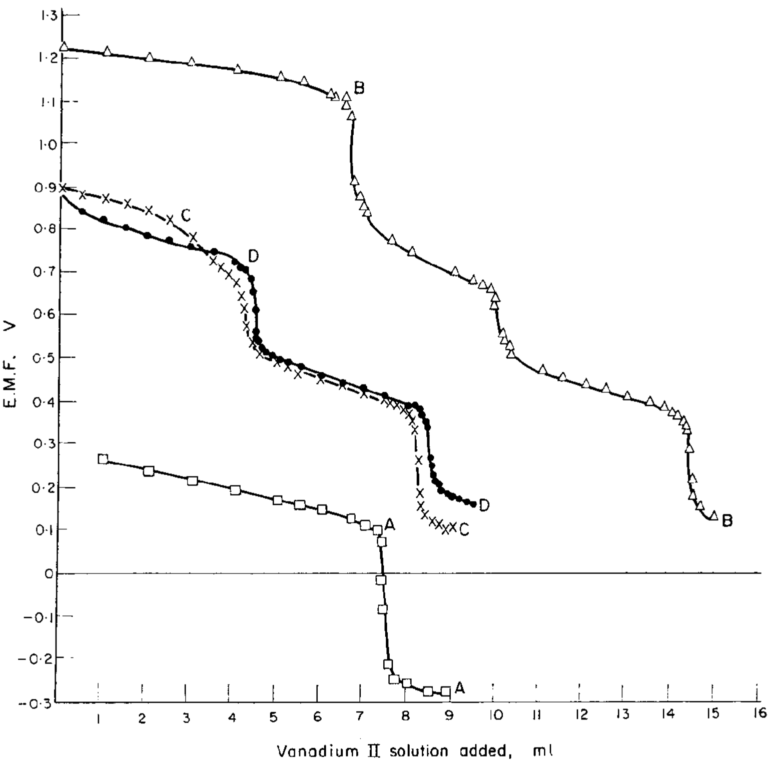

FIG. 1.—Potentiometric titrations with vanadium(II) solution, using platinum and calomel electrodes:—

A—iron(III)
B—iron(III) + cerium(IV)
C—iron(III) + chromium(VI)
D—iron(III) + vanadium(V)

TABLE II.—POTENTIOMETRIC TITRATION OF IRON(III) WITH VANADIUM(II) IN PRESENCE OF 8–10*M* PHOSPHORIC ACID

Vanadium(II), *mmoles*	
Present	Found
0·1999	0·1998
0·3988	0·3996
0·4988	0·4984

Standardisation of vanadium(II) sulphate against cerium(IV), chromium(VI), vanadium(V) and iron(III) solution using visual indicators (two-electron change)

Place 5 to 10 ml of the oxidising agent in the titration vessel, add sulphuric acid (12*N*) so as to make the overall acidity about 6*N* except for the standardisation with iron(III) solution and also when Methylene Blue is used as indicator. In these cases the acidity is that due to the solutions taken, which for iron(III) is approximately 1*N*. Add 2 to 3 drops of the indicator, in the case of Variamine Blue, adding it near the end-point. Deoxygenate the solution by bubbling carbon dioxide through it for about 10 min and titrate slowly till a sharp colour change is obtained. All the indicators are reversible and the indicator correction is almost negligible. The titre corresponds to a two-electron change in the case of vanadium(II), *i.e.*, V(II) to V(IV). A few typical results are given in Table III.

TABLE III.—VISUAL INDICATORS FOR TITRATION OF CERIUM(IV), VANADIUM(V), CHROMIUM(VI) AND IRON(III) WITH VANADIUM(II)

Oxidising agent used	Indicators used	Vanadium(II), *mmoles*	
		Present	Found
Cerium(IV)	Methylene blue	0·4803	0·4800
	Variamine blue	0·4779	0·4779
	o-Dianisidine	0·4400	0·4400
	Cacotheline	0·2222	0·2222
	Ferroin	0·8216	0·8215
Vanadium(V)	Variamine blue	0·5204	0·5205
	o-Dianisidine	0·4600	0·4600
	Cacotheline	0·2111	0·2100
	Ferroin,	0·4600	0·4600
	Bis(α,α′-bipyridyl)iron(II)	0·5204	0·5205
	Ammonium molybdate	0·4600	0·4600
Chromium(VI)	Variamine blue	0·4991	0·5000
	o-Dianisidine	0·5000	0·5000
	Cacotheline	0·4999	0·5000
	Ferroin	1·0002	0·1000
Iron(III)	Cacotheline	0·4999	0·4995
		0·4730	0·4755

Determination of mixtures of cerium(IV) and iron(III), chromium(VI) and iron(III) and vanadium(V) and iron(III) with vanadium(II) solution

Visually. As shown earlier cacotheline can be used satisfactorily as an internal indicator for the standardisation with iron(III), cerium(IV), chromium(VI) or vanadium(V) solution. When these oxidising agents are present together the colour transition of the indicator takes place only when they are reduced completely. The titre, therefore, corresponds to the sum of the components. Cerium(IV), chromium(VI) or vanadium(V) can, however, be estimated visually in the presence of *N*-phenylanthranilic acid as indicator and iron(III) does not interfere. Titrations under these conditions provided the methods of estimation of such binary mixtures. The detailed procedure follows:

Place 5 to 10 ml of iron(III) and 5 to 10 ml of other oxidising agent in the titration vessel and add 1 to 2 ml of 0·1*M* copper(II) sulphate and 2 to 3 drops of the indicator. Bubble carbon dioxide through for about 10 min and titrate the solution slowly with vanadium(II) sulphate to a distinct blue colour. The titre corresponds to the simultaneous reduction of iron(III) and the other oxidising agent and to a two-electron change in the case of vanadium(II). Take another aliquot of the mixture and add sulphuric acid (12*N*) so as to make the overall acidity to about 6*N*. Now add 2 to 3 drops of *N*-phenylanthranilic acid indicator and bubble carbon dioxide through for about 10 min. Titrate the solution slowly to the green colour. The end-point corresponds to the reduction of cerium(IV), chromium(VI) or vanadium(V) only and to a two-electron change in the case of vanadium(II). A few results are given in Table IV.

TABLE IV.—VISUAL AND POTENTIOMETRIC TITRATIONS OF MIXTURES OF CERIUM(IV) AND IRON(III), CHROMIUM(VI) AND IRON(III) AND VANADIUM(V) AND IRON(III) WITH VANADIUM(II)

Mixture	First component, *mmoles*			Second component, *mmoles*		
	Taken	Found		Taken	Found	
		Visually	Potentiometrically		Visually	Potentiometrically
Cerium(IV) and iron(III)	1·0960	1·0980	1·0890 (by first break) 1·0920 (by second break)	0·4755	0·4783	0·4750
Cerium(IV) and iron(III)	0·5545	0·5544	0·5511 (by first break) 0·5522 (by second break)	0·9510	0·9511	0·9479
Cerium(IV) and iron(III)	0·5545	0·5544	0·5576 (by first break 0·5565 (by second break)	0·4755	0·4783	0·4783
Chromium(VI) and iron(III)	0·0833	0·0833	0·0836	0·4755	0·4760	0·4760
Chromium(VI) and iron(III)	0·1666	0·1666	0·1666	0·4755	0·4760	0·4784
Vanadium(V) and iron(III)	0·5355	0·5355	0·5331	0·9510	0·9520	0·9570
Vanadium(V) and iron(III)	0·5355	0·5355	0·5331	0·4755	0·4760	0·4760

Potentiometrically. When the mixture of cerium(IV) and iron(III) was titrated against vanadium(II) solution potentiometrically, three potential breaks were obtained, the first corresponding to the oxidation of vanadium(II) to vanadium(V) by the cerium(IV) present, the second to the reduction of vanadium(V) formed to vanadium(IV) and the third to the reduction of iron(III). The potential break in the first case was about 140 mV, in the second case about 30 mV and in the third case about 80 mV per 0·05 ml of vanadium(II) solution. When the mixtures of chromium(VI) and iron(III) and vanadium(V) and iron(III) were titrated, only two breaks were obtained, the first corresponding to the reduction of chromium(VI) or vanadium(V) and the second to the reduction of iron(III) and to the two-electron change in the case of vanadium(II). The potential breaks in the reduction of chromium(VI) and vanadium(V) were about 30 mV and 50 mV per 0·05 ml of vanadium(II), respectively. It was thus possible to estimate both the components of these binary mixtures with one titration in each case (Fig. 1). The procedure followed was as given above except that sulphuric acid (6*N*) was added to make the overall acidity about 1*N* in chromium(VI) and iron(III) and vanadium(V) and iron(III) mixtures. In the absence of the acid the first break in the potential was not well defined. A few results are given in Table IV.

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Résumé—On décrit des méthodes d'étalonnage du sulfate de vanadium(II). Avec des agents d'oxydation faibles, par exemple fer(III)/fer(II) en acide phosphorique, le vanadium subit une transformation à un seul électron, indiquée de façon satisfaisante par le rouge neutre, la phénosafranine, la safranine T ou par potentiométrie. Des agents oxydants plus forts oxydent le vanadium(II) en vanadium(IV); le bleu variamine, le bleu de méthylène, l'*o*-dianisidine, la cacothéline, la forroïne, le bis(α,α-bipyridyl)fer(II) et le molybdate d'ammonium sont des indicateurs satisfaisants. On peut doser des mélanges binaires d'agents d'oxydation.

Zusammenfassung—Methoden zur Einstellung von Vanadin(II)-sulfat werden beschrieben. Mit schwachen Oxydationsmitteln, z. B. Eisen(III)/Eisen(II) in Phosphorsäure, verliert Vanadin(II) ein Elektron; befriedigende Indikatoren sind Neutralrot, Phenosafranin, Safranin T oder die Potentiometrie. Stärkere Oxydationsmittel oxydieren Vanadin(II) zu Vanadin(IV); Variaminblau, Methylenblau, *o*-Dianisidin, Kakothelin, Ferroin, Bis(α,α′-bipyridl)Eisen(II) und Ammonmolybdat sind brauchbare Indikatoren. Es können binäre Gemische von Oxydationsmitteln bestimmt werden.

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PRECIPITATION OF NICKEL AND PALLADIUM DIMETHYLGLYOXIMATES FROM HOMOGENEOUS SOLUTION

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Summary—A comparison of the reaction mechanisms by which nickel or palladium dimethylglyoximate is precipitated from homogeneous solution by the reactions of biacetyl and hydroxylamine discloses many differences. Knowledge of the kinetics and mechanism of the reactions can be used to avoid formation of excess dimethylglyoxime, a limitation of the conventional methods of precipitation.

SINCE the introduction of dimethylglyoxime in 1905 by Tschugaeff[1] as a qualitative test for nickel and its subsequent application to quantitative determination, it has become universally accepted as the most important and most widely used analytical reagent for the gravimetric determination of nickel and palladium. Despite impressive reasons for the universal acceptance of dimethylglyoxime, and these can be found in any comprehensive text on analytical chemistry, there are some disadvantages. Among these are the insolubility of the dimethylglyoxime itself, the bulkiness of the precipitates which limits the quantity of metal ion which can be readily handled, some undesirable coprecipitation effects and, in the case of low concentrations of metal ions, some difficulties arising from the solubility of the metal chelates.

The disadvantages can be greatly alleviated by the use of PFHS (precipitation from homogeneous solution). This involves the reaction of biacetyl and hydroxylamine[2,3] in the presence of either nickel(II) or palladium(II) as shown by the simplified scheme of Fig. 1. To cite but one advantage obtained by the use of PFHS, a chemical technician can easily handle 200 mg of nickel whereas 30 mg is the upper limit when conventional precipitation is utilised.

The reactions of biacetyl and hydroxylamine in the presence of either nickel or palladium have been the subject of considerable investigation in our laboratories. A comparison of these reactions, at ~pH 7 where nickel is precipitated and at ~pH 0·4 where palladium is precipitated, discloses some significant differences in the mechanisms involved. Furthermore, the results of these studies have suggested possibilities for improvement in existing methods of PFHS.

Precipitation of Nickel Dimethylglyoximate

In the investigation of the kinetics and mechanism of the precipitation of nickel dimethylglyoximate by Hileman and Gordon,[4] studies were first made of the reaction

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of biacetyl and hydroxylamine at pH 7 in the absence of nickel. A partial summary of the reactions is as follows:

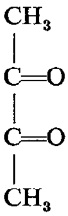
$$B + Hx \underset{k_{-1}(\text{fast})}{\overset{k_1(\text{fast})}{\rightleftarrows}} I_1 \quad (\text{where } I_1 \text{ is a carbinolamine intermediate}) \tag{4}$$

$$I_1 \xrightarrow[\text{slow}]{k_2} HM + H_2O \tag{5}$$

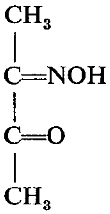
$$HM + Hx \underset{k_{-3}(\text{fast})}{\overset{k_3(\text{fast})}{\rightleftarrows}} I_2 \quad (I_2 \text{ is also a carbinolamine intermediate}) \tag{6}$$

$$I_2 \xrightarrow[\text{slow}]{k_4} HD + H_2O \tag{7}$$

where

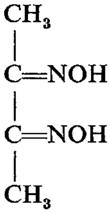


$$B = \begin{array}{c} CH_3 \\ | \\ C{=}O \\ | \\ C{=}O \\ | \\ CH_3 \end{array}$$

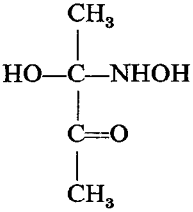


$$HM = \begin{array}{c} CH_3 \\ | \\ C{=}NOH \\ | \\ C{=}O \\ | \\ CH_3 \end{array}$$

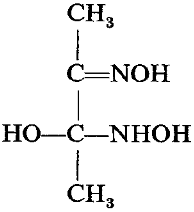
$Hx = H_2NOH$



$$HD = \begin{array}{c} CH_3 \\ | \\ C{=}NOH \\ | \\ C{=}NOH \\ | \\ CH_3 \end{array}$$



$$I_1 = \begin{array}{c} CH_3 \\ | \\ HO{-}C{-}NHOH \\ | \\ C{=}O \\ | \\ CH_3 \end{array}$$

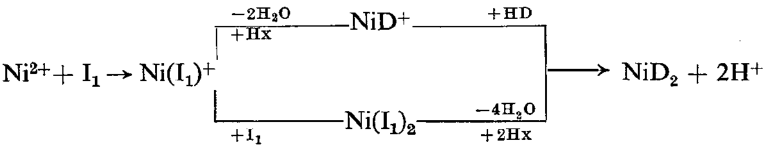


$$I_2 = \begin{array}{c} CH_3 \\ | \\ C{=}NOH \\ | \\ HO{-}C{-}NHOH \\ | \\ CH_3 \end{array}$$

With the exception of k_3 and k_{-3}, the rate constants for the above reactions have been measured in the absence of nickel; spectral evidence for the intermediates has also been obtained.

Further studies of the reactions in the presence of nickel indicate that there are at least two independent paths by which nickel is precipitated as the solid red chelate. One path involves the precipitation of nickel with dimethylglyoxime formed by the above sequence of equations. Another *faster* path involves the formation of complexes of nickel with the intermediate I_1 followed by subsequent dehydration of the nickel complexes to form the solid phase; the complexes are possibly NiI_1^+ and $Ni(I_1)_2$. The two paths are

$$Ni^{2+} + 2HD \xrightarrow{\text{fast}} NiD_2 + 2H^+ \tag{8}$$



(9)

There are two sub-paths in reaction (9), because of the dehydration of some $Ni(I_1)^+$ to NiD^+ which must then wait for dimethylglyoxime to be produced by the slow reaction sequence [reactions (4)–(7)] before being converted into nickel dimethylglyoximate.

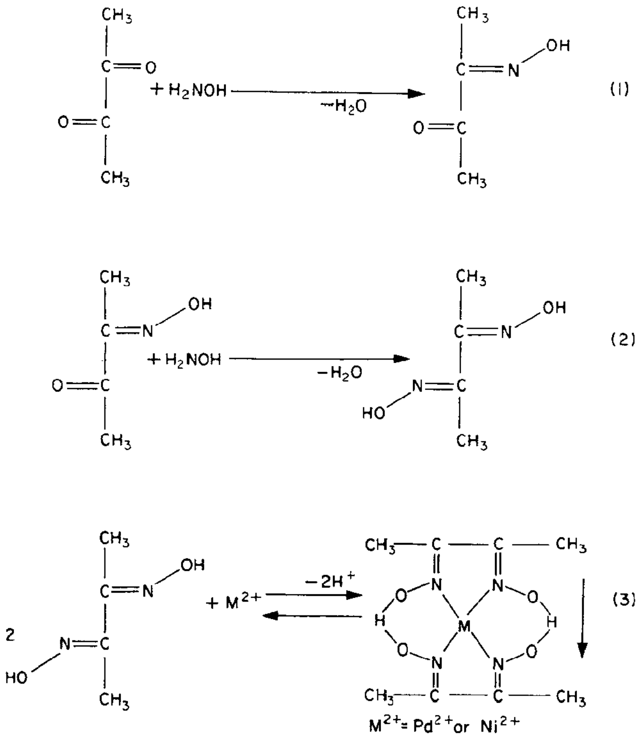


FIG. 1.—The precipitation of palladium and nickel dimethylglyoximates from homogeneous solution—a simplified mechanism.

Because there are two major independent paths by which nickel dimethylglyoximate is produced, one observes two nucleation bursts. [If one starts with biacetyl monoxime instead of biacetyl, *i.e.*, the reaction sequence numbers (6)–(7), one observes but one nucleation burst because there is only one path by which nickel dimethylglyoximate is formed. The intermediate I_2 apparently does not react with nickel so that the mechanism is simpler in the previous case.]

Analytical method for nickel

In devising the analytical method for the PFHS of nickel, Salesin and Gordon[2] suggested adding an amount of biacetyl equal to 6 × the weight of nickel (but never less than 0·12 g of biacetyl) and an amount of hydroxylamine hydrochloride equal to 4 × the weight of biacetyl (but never less than 0·5 g of hydroxylamine hydrochloride). In addition, the following was specified:

Ni present, *mg*	Solution volume, *ml*
0·5–5	100
5–50	200
50–100	300
100–200	400

The solution containing all the reactants is (a) allowed to stand at room temperature for at least 1 hr (or longer) after precipitation begins, (b) heated at 80–90° for 2 hr, then (c) cooled to room temperature before filtration. The solution is allowed to stand at room temperature so that a slow reaction will occur, thus allowing minimum supersaturation in order for nucleation and initial crystal growth to proceed under conditions leading to a precipitate with favourable analytical characteristics. The heating process then results in virtually complete conversion of biacetyl into dimethylglyoxime.

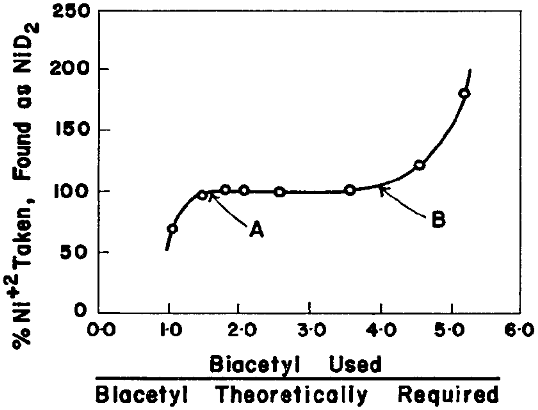


FIG. 2.—Salesin's study of the amount of biacetyl required to precipitate completely nickel as NiD_2 in a reaction time of 48 hr.

Most of the nickel will be precipitated by the faster path [*cf.* reaction (9)] in which the metal ion is complexed by the carbinolamine intermediate. However, dimethylglyoxime will still continue to be formed by the slow path of reactions (4)–(7). If one utilises the rate constants and other information obtained by Hileman and Gordon[4], one finds that only a small fraction (~5%) of the residual biacetyl is converted into dimethylglyoxime by the slow path in the 1-hr standing period at room temperature. Further approximations show that the 2-hr heating period converts over 99% of the residual biacetyl into dimethylglyoxime. In the procedure of Salesin and Gordon[2] this will result in a final supersaturation of 1·3 to 4× the equilibrium solubility of dimethylglyoxime over the range of conditions used. It is strange and indeed fortuitous that excess of dimethylglyoxime is not coprecipitated with the red chelate under these conditions.

In other experiments, Salesin[5] also found that coprecipitation of the free reagent did not begin until the supersaturation is somewhat higher than the upper limit in the 1·3 to 4 range. Salesin's[5] results are shown in Fig. 2; in obtaining the data for this figure Salesin allowed the precipitation reactions to continue at room temperature for 48 hr. Subsequent calculations by means of the rate data of Hileman and Gordon show (a) that the conversion of the residual biacetyl into dimethylglyoxime is 90% complete, (b) that at point A on the curve of Fig. 2, where the precipitation of nickel dimethylglyoximate just begins to be quantitative, the supersaturation is 1·35 and (c) that at point B on the curve, where coprecipitation of the free reagent becomes evident, the supersaturation is 7·3. Again, it is not obvious why excess of dimethylglyoxime does not coprecipitate in 48 hr when the solution is so supersaturated.

Although the procedure of Salesin and Gordon[2] gives very satisfactory results, it is now possible to design a revised procedure wherein one does not encounter a solution supersaturated with dimethylglyoxime. This requires the rate data of Hileman and Gordon for the reaction of biacetyl and hydroxylamine and, in addition, rate data for the precipitation of nickel dimethylglyoximate. The latter were obtained from Fig. 3, the data for which were obtained from precipitation reactions in which the following were present in a 250-ml final volume: 6·4 g of hydroxylamine hydrochloride, 48·8 mg of nickel, and biacetyl from 1·86 × 10^{-2} to 7·44 × $10^{-2}M$. The solutions were adjusted to pH 7·1 and allowed to stand at room temperature for 15 min after which the red precipitate was quickly filtered off, dried and weighed. The rate constant for the precipitation sequence, which is first order with respect to biacetyl, was approximately 3 × 10^{-2} min^{-1}. From this rate constant and the rate data of Hileman and Gordon,[4] the theoretical time values of Table I were obtained.

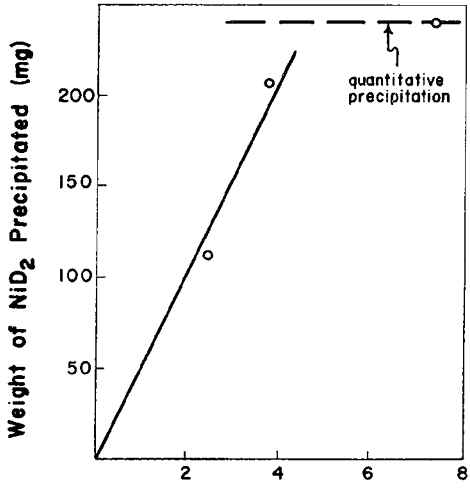


FIG. 3.—Weight of nickel dimethylglyoximate obtained in 15 min as a function of initial biacetyl concentration.

TABLE I.—THEORETICAL TIMES REQUIRED TO PRECIPITATE NiD_2 AND TO SATURATE SOLUTION WITH HD

	Initial concentration of biacetyl, $M \times 10^{-2}$			
	7·44	3·72	1·86	1·40*
Time required for quantitative precipitation of NiD_2, *min*	8	17	39	61*
Additional time for solution to become saturated with HD at equilibrium value, *min*	60	181	516	1060

* The value 1·40 × 10^{-2} corresponds to the amount of biacetyl recommended in the procedure of Salesin and Gordon.[2]

Table I indicates that, at a value of initial biacetyl concentration equal to $1{\cdot}40 \times 10^{-2}M$ and all other conditions as shown for the experiments of Fig. 3, it requires 61 min for quantitative precipitation of the red nickel chelate and an additional 1060 min just to saturate the solution with dimethylglyoxime. To test this, several precipitation reactions were allowed to proceed and at various time intervals, nickel dimethylglyoximate was filtered off, dried and weighed. The results, shown in Table II, generally confirm the predictions in that quantitative precipitation of the red chelate was complete in 30–60 min and that coprecipitation of dimethylglyoxime had not taken place even after a total of 2880 min had elapsed.

TABLE II.—WEIGHT OF NICKEL FOUND AS A FUNCTION OF TIME
(Ni taken: 47·1 *mg*)

Time of reaction, *min*	Nickel found, *mg*
30	45·8
60	47·0
90	47·1
120	47·1
180	47·0
240	47·1
360	47·3
960	47·3
1440	47·1
2880	47·0

Precipitation of Palladium Dimethylglyoximate

In the palladium investigation[6] the reaction of biacetyl and hydroxylamine was also studied initially with palladium absent. In contrast to the nickel reaction which was carried out at pH 7, the palladium reaction was carried out at ~pH 0·4. The reactions of biacetyl and hydroxylamine proceeded as follows:

$$\mathrm{B} + \mathrm{Hx} + \mathrm{H}^+ \rightleftharpoons \mathrm{HMH}^+ + \mathrm{H_2O} \tag{10}$$

$$\mathrm{HMH}^+ \rightleftharpoons \mathrm{HM} + \mathrm{H}^+ \tag{11}$$

$$\mathrm{HM} + \mathrm{Hx} + \mathrm{H}^+ \rightleftharpoons \mathrm{HDH}^+ + \mathrm{H_2O} \tag{12}$$

$$\mathrm{HDH}^+ \rightleftharpoons \mathrm{HD} + \mathrm{H}^+ \tag{13}$$

where HMH^+ = conjugate acid of HM, HDH^+ = conjugate acid of HD, and H^+ = hydrogen ion.

No evidence was found for the presence of detectable quantities of carbinolamine intermediates at pH 0·4; rather, as the reaction sequence shows, the synthesis of dimethylglyoxime proceeds *via* the formation of protonated biacetyl monoxime and protonated dimethylglyoxime. It is to be noted that reaction (13) for the formation of dimethylglyoxime is reversible at pH 0·4. This is in contrast to reaction (7) where the formation at pH 7 is irreversible.

It was found that palladium does not play a role similar to nickel in that the formation of dimethylglyoxime proceeds by reactions (10)–(13) unaffected by the presence of palladium (present as $\mathrm{PdCl_4}^{2-}$).

Analytical method for palladium

Ellefsen's data[6] for the investigation of the PFHS of palladium predict that 0–200 mg of palladium can be quantitatively precipitated in 5 hr under appropriate analytical conditions without free dimethylglyoxime also being precipitated. To test this prediction, several precipitation reactions were carried out with 200 ml of solution (pH 0·4) containing 520 mg of biacetyl, 830 mg of hydroxylamine hydrochloride, 6·8 ml of concentrated hydrochloric acid and 0–200 mg of palladium. In this reaction medium, in the absence of palladium, the quantity of dimethylglyoxime formed is sufficient just to saturate the solution. The solutions were filtered after a 6-hr reaction period, thus allowing one additional hour beyond the 5-hr theoretical period. Part I of Table III shows the results obtained. They indicate, first of all, the absence of free dimethylglyoxime. However, some palladium remains in solution particularly in the case of large initial amounts of palladium. In an attempt to remedy this effect, other experiments were performed with suitable alterations as shown in part II of Table III. A longer reaction time, rather than stirring to relieve supersaturation, seems necessary to effect quantitative precipitation.

TABLE III.—WEIGHT OF PALLADIUM FOUND

I. By procedure described in text[a]		II. By alteration of procedure	
Pd taken, *mg*	Pd found, *mg* difference	Pd taken, *mg*	Pd found, *mg* difference
1·4	−0·1	207·1	−8·4[b]
3·4	−0·1	207·1	−7·2[c]
13·7	−0·3	207·1	−7·3, −6·9[d]
34·5	−0·4	207·1	−6·4[e]
69·0	−0·5	207·1	−6·1[f]
138·1	−0·9	207·1	−0·3[g]
207·1	−4·6, −11·7	207·1	−0·5[h]

[a] Stirring was not used in any of the experiments.
[b] 7-hr reaction time without stirring.
[c] 8-hr reaction time without stirring.
[d] 5·5-hr reaction time followed by 0·5-hr stirring period.
[e] 6-hr reaction time with continuous stirring.
[f] 8-hr reaction time with continuous stirring.
[g] 14-hr reaction time without stirring.
[h] 13-hr reaction time with 1-hr stirring period.

DISCUSSION

One of the great advantages of PFHS is that it affords a method of controlling the rate of a precipitation reaction. By obtaining information about the kinetics and mechanism of the generation reactions, it is possible to design gravimetric methods on a non-empirical basis. Two possible examples of how this might be done have been demonstrated: (a) in the case of nickel dimethylglyoximate where the formation of free dimethylglyoxime by an irreversible process is avoided by utilising kinetic information about the rate of production of the reagent, and (b) in the case of palladium dimethylglyoximate where the formation of free dimethylglyoxime is avoided by utilising equilibria information.

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Zusammenfassung—Ein Vergleich der Reaktionsmechanismen, nach denen Nickel- oder Palladiumdimethylglyoximat aus homogener Lösung durch Reaktion von Biacetyl und Hydroxylamin gefällt werden, zeigt viele Unterschiede. Die Kenntnis von Kinetik und Mechanismus der Reaktionen kann dazu verwendet werden, die Bildung von überschüssigem Dimethylglyoxim zu vermeiden, was eine Begrenzung derüblichen Fällungsmethoden darstellte.

Résumé—Une comparaison des méchanismes réactionnels selon lesquels les diméthylglyoximates de nickel ou de palladium sont précipités à partir d'une solution homogène par réaction du biacéryle et de l'hydroxylamine révèle de nombreuses différences. On peut utiliser la connaissance de la cinétique et du mécanisme des réactions pour éviter la formation d'un excés de diméthylglyoxime, qui est une limitation des méthodes ordinaires de precipitation.

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USE OF ASYMMETRICALLY-POLARISED DROPPING-MERCURY ELECTRODES IN CONTROLLED-POTENTIAL POLAROGRAPHY

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Summary—It is shown that uncompensated cell resistance in controlled-potential polarography can be decreased by the use of asymmetrical polarisation of the dropping-mercury electrode.

INTRODUCTION

IN polarographic studies with solutions of very high specific resistance or with relatively high cell-currents, controlled-potential polarography is generally used. In this case, a three-electrode polarographic cell is employed, the potential of the dropping-mercury electrode being measured against a reference electrode, while the polarographic current is conducted through a counter-electrode.[1–12] This technique yields strikingly favourable results as long as solutions of moderately high specific resistance are used, and the high cell resistance is either simulated by means of a resistor connected in series with the cell[5,11] or it is the result of special cell geometry with relatively long and narrow current paths.[1,9,10] However, as has been demonstrated by Schaap and McKinney,[13,14] a certain amount of the cell resistance cannot be compensated, the uncompensated part being the greater, the higher is the specific resistance of the solution. The resistance of the polarographic cell (R) has been considered to be the sum of an "internal" (R_i) and an "external" (R_e) resistance.[15,16] The value of R_i is given by the formula $R_i = \rho/4\pi r$ if the distance between the dropping-mercury electrode and counter-electrode is large, where ρ is the specific resistance of the solution and r the radius of the mercury drop. Accordingly, it is independent of the geometry of the polarographic cell; the latter affects only the value of R_e. Schaap and McKinney[14] have found that "potentiostats used in connection with three-electrode polarographic cells do not effect compensation for R_i if the tip of the reference electrode is more than about 0·5 cm from the dropping-mercury electrode" and "although R becomes small when the reference electrode probe is placed very close to the dropping-mercury electrode surface, it was not possible experimentally to position the probe so that R was reduced to zero".

The authors have come to the conclusion that the above limitation is the result of the fact that the usual electrode arrangement is unfavourable as regards resistance compensation. In the three-electrode cells, as well as in every conventional polarographic cell, the counter-electrode is placed at a distance from the dropping-mercury electrode which is greater by at least one order of magnitude than the radius of the mercury drop at its maximum size. Accordingly, every point on the surface of the

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dropping-mercury electrode is practically equidistant from the counter-electrode. This results in a symmetrical current distribution in the vicinity of the dropping-mercury electrode with a current flow in a radial direction.[17] This accounts for the fact that a relatively high current density prevails at the surface of the dropping-mercury electrode, and a large potential drop is built up in its immediate vicinity. Consequently, the tip of the reference electrode cannot be placed near enough to the surface of the dropping-mercury electrode neither can it be placed out of the path of the cell current, even if it is on the opposite side with respect to the counter-electrode.

A substantial decrease in uncompensated resistance was obtained by establishing a highly asymmetrical current distribution at the dropping-mercury electrode. For this purpose, a polarographic cell was used (Fig. 1) in which the counter-electrode (C) was a micro-electrode placed in close proximity to the dropping-mercury electrode.

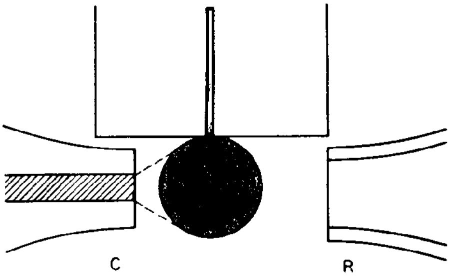

FIG. 1

Current was thus conducted almost completely to the nearer side of the mercury drop and the reference electrode (R) was out of its path. The effectiveness of this arrangement can be judged from Fig. 2, which shows the polarograms of 8 × $10^{-3}M$ Cd^{2+} in butyl alcohol containing 0·01M lithium chloride. The curves were recorded with a controlled-potential polarograph, type OH-102, of Hungarian make. The counter-electrode was a platinum wire, 0·6 mm dia. fused into a glass capillary and ground,

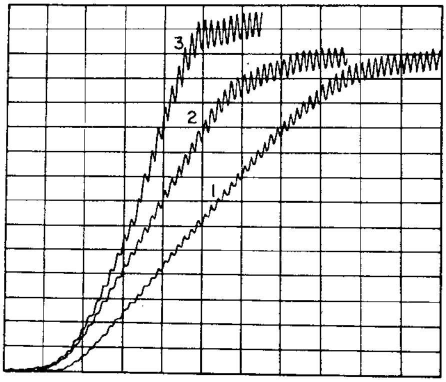

FIG. 2

together with the glass envelope, in a plane perpendicular to its axis. Both reference and counter-electrodes could move along a common axis, the latter intersecting the middle of the dropping-mercury electrode at maximum drop size. The cell also contained a mercury pool electrode.

RESULTS

Curve 1 in Fig. 2 is a normal polarogram recorded with two electrodes, a dropping-mercury electrode and a pool. Curve 2 was taken with three electrodes and symmetrical polarisation, the mercury pool serving as counter-electrode, whereas curve 3 was recorded with asymmetrical polarisation, using the micro-electrode as counter-electrode. The apparent cell resistances can be estimated from the slopes of the polarograms.[18] On the basis of the equation of the polarographic curve, an approximate cell resistance of 77·3 kΩ was calculated for curve 1, while for curves 2 and 3 values of 47·7 kΩ and 31·4 kΩ, respectively, were obtained. (For a more precise resistance determination, the question of reversibility of the electrode reaction should be taken into consideration; this has been neglected in estimating the above values.) It is apparent that the decrease in cell resistance brought about by i.R compensation was further enhanced by the use of asymmetrical polarisation. While recording curve 3, both reference- and counter-electrodes were in close proximity to the surface of the dropping mercury electrode. With increasing distance of the counter-electrode, the polarograms approximated to curve 2, and became identical to it if the distance was higher than 7 to 10 mm. On the other hand, the distance of the reference electrode tip had practically no effect on the curve slope, provided that the counter-electrode was close to the dropping-mercury electrode.

On the basis of the above considerations, the concept of R_i appears in a different light: it is not an intrinsic property of the dropping-mercury electrode, as is suggested by the term "internal resistance", but rather the contribution of the small electrode surface to the total resistance of the system. Any other micro-electrode should behave in very much the same manner. Thus, in the case of the above-mentioned micro-electrode, when placed in a solution of specific resistance $\rho = 2{\cdot}94 \times 10^5$ ohm.cm, and measured against a counter-electrode of large surface area placed near to it, a resistance value of $3{\cdot}14 \times 10^4\,\Omega$ was obtained, while by the use of the Brdička equation,[15] an "internal resistance" of

$$R_i = \frac{\rho}{\pi r} = \frac{2{\cdot}94 \times 10^5}{3{\cdot}14 \times 0{\cdot}03} = 3{\cdot}12 \times 10^4\,\Omega$$

was calculated. (The formula $\rho/\pi r$ instead of $\rho/4\pi r$ was used to account for the fact that the electrode surface was a circular plane and not a sphere.)

It must be borne in mind that the geometry shown in Fig. 1 prevails only at maximum drop size. At the earlier stages of drop life, the distance dropping-mercury electrode–counter-electrode is larger, resulting in a smaller degree of asymmetry in polarisation and in a lower performance of the compensation circuit. Consequently, the use of intermittent scanning (tast-polarography) is likely to bring about a further decrease in the uncompensated cell resistance in controlled potential polarography with asymmetrically polarised dropping-mercury electrodes.

Résumé—On montre que la résistance non compensée de la cellule en polarographie à potentiel contrôlé peut être abaissée par l'emploi d'une polarisation asymétrique de l'électrode à goutte de mercure.

Zusammenfassung—Es wird gezeigt, daß der unkompensierte Zellwiderstand bei der Polarographie mit geregelter Spannung durch asymmetrische Polarisation der Quecksilbertropfelektrode herabgesetzt werden kann.

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EINE MANOMETRISCHE METHODE ZUR BESTIMMUNG VON CARBONATEN IN MINERALIEN UND GESTEINEN

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Zusammenfassung—Es wird eine Methode zur Bestimmung von Carbonaten in Mineralien und Gesteinen vorgeschlagen, die auf der Zersetzung der Probe mit 20-proz. Schwefelsäure im Vakuum beruht. Die Bestimmung erfolgt in einer Apparatur von verhältnismässig einfacher Konstruktion. Der Kohlendioxidgehalt wird nach dem Grad der Druckveränderung im System bestimmt und von einer geeichten Skala abgelesen. Die Methode ist für die Analyse von Proben mit 0,1 bis 40% Kohlendioxidgehalt anwendbar. Die Genauigkeit der Bestimmung beträgt 0,75 bis 10%.

DIE verbreitetste, in verschiedenen Varianten vorgeschlagene Methode zur Bestimmung von Carbonaten beruht auf deren Zersetzung mit Säuren.[1–7] Das freigewordene Kohlendioxid wird von einem geeigneten Absorptionsmittel aufgefangen und nach der Gewichtsveränderung des letzteren die Menge des freigewordenen Gases beurteilt.

Zuverlässige Ergebnisse kann diese Methode aber nur dann liefern, wenn die Carbonatzersetzung, das Vertreiben des Kohlendioxids und die Absorption vollständig sind. Um diesem Erfordernis zu genügen, muss man das Reaktionsgemisch erwärmen und indifferentes Gas durchströmen lassen. Dies alles erfordert eine komplizierte Apparatur, verlängert die Bestimmungsdauer und schafft neue Fehlerquellen.

Um das Vertreiben des Kohlendioxyds durch andere Gase zu vermeiden, haben Pentscheff und Jordanov[8] vorgeschlagen, das Zersetzen des Carbonats im Vakuum auszuführen. Zu diesem Zweck wurde ein spezieller Apparat konstruiert, dessen Schema in Abb. 1 gezeigt ist. Die zu untersuchende Probe wird mit Phosphorsäure (2:1) zersetzt, das freigewordene Kohlendioxid über Phosphorpentoxid getrocknet und mit Hilfe einer modifizierten Töplerpumpe abgesaugt und gesammelt. Die geringen Wassermengen verdunsten unter diesen Bedingungen und werden im Absorber festgehalten, wobei das in ihnen gelöste Kohlendioxid frei wird.

Dieser Apparat ermöglicht die bequeme Bestimmung von Carbonaten in Mineralien und Gesteinen mit einer Genauigkeit von ungefähr 0,5%. Sein Nachteil ist jedoch, dass mit Quecksilber gearbeitet werden muss.

Es wird daher hier eine neue Methode vorgeschlagen, bei der das Zersetzen des Carbonats ebenfalls im Vakuum geschieht, aber die Menge des entweichenden Kohlendioxids nach dem Grad der Druckveränderung im System bestimmt wird. Hierzu dient der in Abb. 2 gezeigte Apparat.

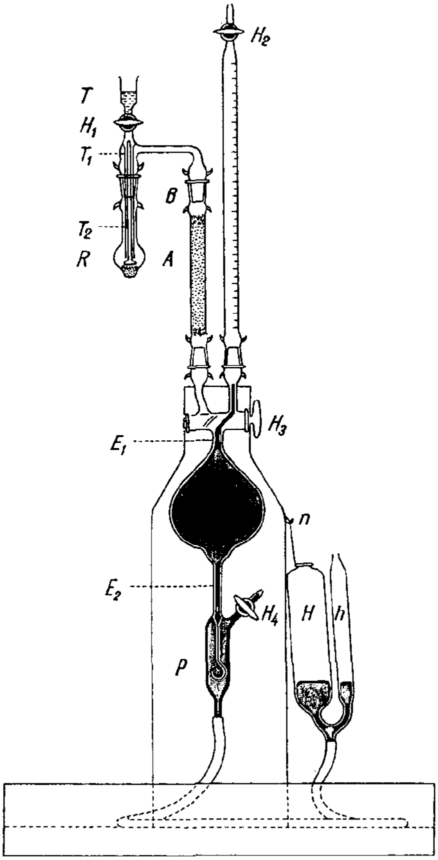

ABB. 1

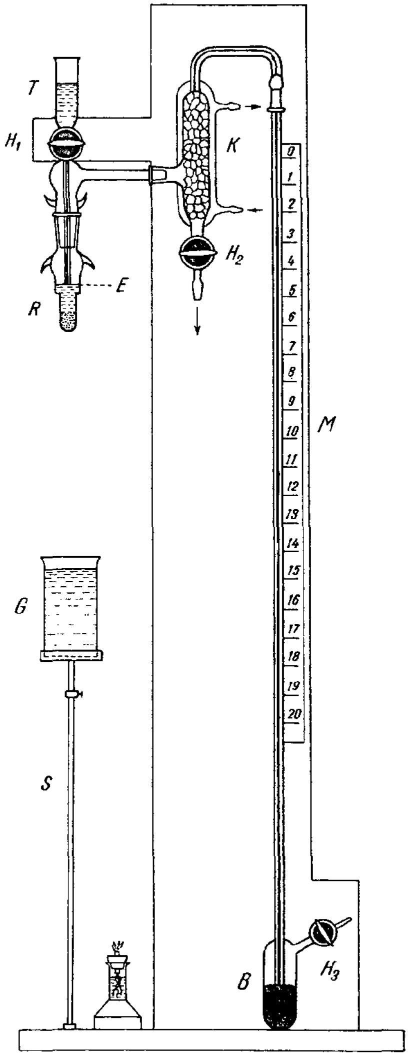

ABB. 2

Das Probestück befindet sich im Reaktionsgefäss R. Der Apparat wird über den Hahn H_2 evakuiert bis die Quecksilbersäule im Manometerrohr das als Null angenommene Niveau erreicht. Man bringt das Reaktionsgefäss durch Eintauchen in ein Becherglas mit Wasser und das Absorptionsgefäss über den Kühler auf Temperatur konstanz. Druckbestimmend in dem Apparat ist das in ihm verbliebene Gas und der Gleichgewichtsdruck des Wasserdampfes bei gegebenen Temperatur. Auf die Probe lässt man Schwefelsäure aus dem Hahn H_1 in das Reaktionsgefäss tropfen. Zur vollständigen Zersetzung der Probe und Vertreibung des in der Lösung befindlichen Kohlendioxyds wird das Reaktionsgefäss leicht angewärmt. Nach Abkühlen auf die Arbeitstemperatur liest man den neuen Stand der Quecksilbersäule ab.

Beschreibung des Apparates

Der Apparat besteht aus folgenden Hauptteilen (s. Abb. 2): Reaktionsgefäss R, Absorptionsgefäss mit Wasserkühlmantel K und Manometerrohr M. Diese drei Teile des Apparates sind durch Schliffe miteinander verbunden und auf einen Plexiglasständer montiert.

Das Reaktionsgefäss hat eine besondere Form. Sein unterer Teil, in den die zu untersuchende Probe gebracht und die Reaktion mit der Säure ausgeführt wird, ist schmaler. Die Säure wird in den Trichter T gegossen und durch Öffnen des Hahns H_1 über das innen angeschmolzene Kapillarrohr (lichte Weite 1 mm) ins Reaktionsgefäss abgelassen.

Das Absorptionsgefäss K ist mit kupfersulfatgetränktem Bimsstein gefüllt und hat die Aufgabe, den evtl. entweichenden Schwefelwasserstoff abzufangen. Im Mantel des Gefässes zirkuliert Wasser mit konstanter Temperatur aus einem Thermostaten, oder noch einfacher, aus der Wasserleitung.

Als Manometerrohr wird eine Kapillare von 1,5 mm Innendurchmesser und 780 mm Länge verwendet. Ihr unteres Ende ist mit einem kleinen Quecksilberbehälter verbunden. Zur Ablesung dient eine Millimeterskala.

Der gesamte freie Raum im Reaktions- und im Absorptionsgefäss beträgt während der Arbeit ungefähr 20 cm^3. Er ist so gewählt, dass bei einer Ausgangsprobe von 0,5 g mit 0,1% Kohlendioxidgehalt sich der Druck im Apparat um ungefähr 10 mm Hg ändert.

Vorbereiten für die Inbetriebnahme des Apparates

Die einzelnen Teile des Apparats werden mittels eingefetteter Schliffe verbunden. Der Behälter B wird bis zur Hälfte mit Quecksilber gefüllt. Der Apparat wird über den Hahn H_2 evakuiert. Es muss gewissenhaft (mehrere Stunden) kontrolliert werden, ob der Apparat luftdicht ist.

Zu den Vorarbeiten gehört auch das Eichen der Millimeterskala in Gewichtsprozenten entweichendes Kohlendioxid. Diese Eichung ist für alle weiteren Bestimmungen gültig, vorausgesetzt, dass der freie Raum im Apparat, die Quecksilbermenge und die Arbeitstemperatur in bestimmten, von der Genauigkeit der Methode geforderten Grenzen, konstant bleiben.

Die Eichung der Skala erfolgt durch 0,1 g Ausgangsprobe mit 1 bis 20% Kohlendioxidgehalt. Ist der Kohlendioxidgehalt der Probe höher oder niedriger, dann nimmt man von der Probe 0,5, 0,2 oder 0,05 g und multipliziert die von der Skala abgelesene Zahl mit einem entsprechenden Faktor.

Das Eichen der Skala geschieht am einfachsten mit Natriumcarbonatlösung einer Konzentration, bei der 1% Kohlendioxid 0,1 ml Lösung entspricht. Eine derartige Lösung erhält man durch lösen von 2,4100 g wasserfreien Natriumcarbonats in 100 ml Wasser. Wird die Skala für Kohlendioxidgehalte von 10 bis 20% geeicht, so ist es empfehlenswert, die Konzentration der Lösung auf das Doppelte zu erhöhen.

Eine bestimmte Menge der obigen Lösungen wird mit einer entsprechenden Pipette in das Reaktionsgefäss eingemessen, das ein Stückchen Bimsstein enthält. Beim Anschliessen des Gefässes an den Apparat muss darauf geachtet werden, dass der Schliff gut eingefettet ist. Der Apparat wird mit Hilfe einer Wasserstrahlpumpe evakuiert und auf Temperaturkonstanz gebracht, bis sich der Quecksilberstand in dem Manometerrohr nicht mehr verändert. Dann wird das Quecksilberniveau genau auf Null eingestellt. Man öffnet sodann vorsichtig den Hahn H_1 und lässt soviel 20-proz. Schwefelsäure in das Reaktionsgefäss eintropfen, bis das Niveau in letzterem bis zum Unterrand des Kapillarrohrs gestiegen ist. Die Lösung wird vorsichtig erwärmt, damit das darin gelöste Kohlendioxid entweicht. Nach Einstellung konstanter Temperatur wird das Niveau der Quecksilbersäule abgelesen.

Die Druckänderung im Apparat, die das von 0,1 ml Na_2CO_3 Lösung mit obenerwähnter Konzentration freigesetzte Kohlendioxid bewirkt, lässt sich abschätzen, wenn der freie Raum im Apparat bekannt ist. Da das Volumen des Kohlendioxids bei Normalbedingungen 0,506 cm^3 und der freie Raum im Apparat ungefähr 20 cm^3 beträgt, ist die entsprechende Druckänderung etwa 20 mm Hg.

Arbeitsvorschrift und Genauigkeit der Methode

Die Menge der Ausgangsprobe wählt man je nach ihrem vermutlichen Carbonatgehalt aus folgender Tabelle:

CO_2-Gehalt, %	Probe, *g*
0,1–1	0,5000
1,0–10	0,2000
2,0–20	0,1000
20,0–40	0,0500

Die Probe wird direkt in das Reaktionsgefäss eingewogen und mit einigen Tropfen Wasser benetzt. Nach Eingabe der notwendigen Säuremenge wartet man 1–2 Minuten, bis der grössere Teil des Carbonats aufgeschlossen ist.* Sonst wird wie oben beschrieben verfahren.

Zur Vorbereitung des Apparats für die nächste Bestimmung gleicht man den Unterdruck durch Öffnen des Hahns H_2 aus, nimmt das Gefäss R ab, säubert und trocknet es.

Eine Bestimmung dauert etwa 30–40 Minuten.

Die kleinste, noch nachweisbare Carbonatmenge entspricht etwa 0,01 % Kohlendioxid. Bequem und mit befriedigender Genauigkeit lässt sich bei einen Kohlendioxidgehalt höher als 0,1 % arbeiten.

Die Genauigkeit der Methode hängt von der Temperatur konstanz ab. Unter Berücksichtigung des Gleichgewichtsdrucks des Wasserdampfs über 20-proz. Schwefelsäure bei verschiedenen Temperaturen weicht bei Temperaturschwankungen von ±1°C der im Apparat ermittelte Druck um etwa 0,75 mm Hg ab. Der relative Fehler der Bestimmung ist somit durch die Probemenge und ihren Carbonatgehalt, d.h. durch den Grad der Druckänderung im Apparat bedingt. So wird zum Beispiel bei 0,5 Ausgangsprobe und 0,1 % CO_2-Gehalt der relative Fehler 7,5 % und bei 0,1 g Probe und 10 % CO_2-Gehalt der relative Fehler 0,75 % betragen,

Summary—A method of determining carbonates in minerals and ores is suggested, based on decomposition of the sample with 20 % sulphuric acid in vacuum. The determination is carried out in an apparatus of relatively simple construction. The carbon dioxide content is determined by the alteration in pressure of the system and read off from a graduated scale. The method is applicable for the analysis of samples with 0·1–40 % carbon dioxide content; the accuracy of the determination is 0·75–10 %.

Résumé—On suggère une méthode de dosage des carbonates dans les minéraux et minerais, basée sur la décomposition de l'échantillon au moyen d'acide sulfurique à 20 % sous vide. Le dosage est mené dans un appareil de construction relativement simple. La tenuer en gaz carbonique est déterminée par la modification de pression du système et lue sur une échelle graduée. La méthode est applicable à l'analyse d'échantillons contenant 0,1 à 40 % de gaz carbonique; la précision du dosage est de 0,75–10 %.

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* Wenn die zu untersuchende Probe Sulfide enthält, ist es zur vollständigeren Bindung des entweichenden Schwefelwasserstoffs empfehlenswert, der Schwefelsäurelösung einige Tropfen Quecksilber-II-sulfat zuzusetzen.

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ERRORS OF KINETIC DATA OBTAINED FROM THERMOGRAVIMETRIC CURVES AT INCREASING TEMPERATURE*

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Summary—Errors of kinetic data obtained from thermogravimetric curves at increasing temperature are discussed.

INTRODUCTION

THERMOANALYTICAL METHODS,[27,28] such as thermogravimetry, differential thermal analysis, dilatometry and thermovolumetry, are currently being used to investigate the kinetics of chemical processes at increasing temperature in heterogeneous systems with some success. These methods measure, in a continuous and usually automatic way, the changes of some physical property, such as weight, enthalpy, length or volume, of the investigated system with temperature under a chosen temperature programme. If this programme is a linear function of time

$$\frac{\mathrm{d}T}{\mathrm{d}t} = \phi, \textit{ i.e.} \qquad T = T_0 + \phi t \tag{1}$$

where T is the temperature, t is the time and ϕ is the heating rate, then one is dealing with thermographic methods and, in particular, *with thermogravimetric weight analysis at increasing temperature;* it is the particular nature of these methods which is the subject of the present paper.

It was in 1932 that Škramovský[1] pointed out the advantages of these methods; however, the experimental techniques being imperfect in these times, these methods helped only in the quantitative and qualitative determination[37] of substances. Though remarkable successes were declared, it was only the commercial production of various modern apparatus (especially thermobalances and temperature regulators) and last, but not least, the basic theoretical essays of the applicability of thermogravimetric curves for mathematical evaluation of kinetic data by van Krevelen, van Heerden and Hutjens[2] and by Freeman and Carroll,[3] that proved the main advantages of this approach, consisting of the determination of kinetic data by a single decomposition curve. Though the development of the above-mentioned method is evident, preference is given to slow isothermal measurements, which generally are considered more precise. Šatava and Šesták[4] obtained by both isothermal and non-isothermal methods (with the same apparatus and under the same experimental conditions for the heat decomposition of α-$CaSO_4 . 0{\cdot}5H_2O$) kinetic results corresponding to each other, by which the applicability of the non-isothermal method was confirmed. Of course, this does concern the accuracy of kinetic data measurement, but does not inform us

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about the nature of the process which becomes the rate-controlling process of the investigated reaction, *e.g.*, surface chemical reaction, diffusion or nucleation,[5,22,26] *etc.* If it is the question of accuracy of kinetic data, it is important to maintain the possibility of reproducing the conditions of the investigated reaction. However, when one tries to determine the particularity of mechanism of the investigated process, one has to arrange the conditions of reaction in order to isolate the investigated reaction from disturbances (the disturbing effects are, for example, diffusion of gaseous products or heat exchange, that might, in certain cases, become the rate-controlling process, *i.e.*, the slowest effect). The arrangement of conditions of the reaction is specific for each investigated reaction.

The error of computed kinetic data is influenced by:

1. *The accuracy of determining directly measured data* (weight, temperature of sample, time, *etc.*).
2. *The accuracy of maintaining conditions defined in advance during the reaction* (linearity of temperature increase, constancy of aerodynamic conditions and composition of gaseous medium) *and removing the influence of disturbing effects.*
3. *The accuracy of mathematical evaluation of experimental curves.*

Many authors[6–18] have described the errors, the nature of which was various; however, their explanations estimated purely the qualitative aspects of the problem.

OUTLINE OF ACCURACY OF COMPUTED KINETIC DATA

1. *Errors of directly measured data*

Accuracy of weight-change measurements. This depends on the perfection of the apparatus used, *i.e.*, sensitivity of balances, width of recording chart, linearity of weight scale, reliability of recording chart motion, *etc.* In addition, it depends on the removal of the buoyancy variations and aerodynamic forces[7,12] (which, usually, are negligible in given temperature ranges) and of aerodynamic noises.[14] These two phenomena are given by the arrangement (*i.e.*, by the kind of thermobalances, by the size and geometry of both the heated space and the crucible) and the heating rate and either by the pressure or the controlled motion of the medium. Buoyancy and aerodynamic noises are also a part of the accuracy mentioned below in maintaining the conditions of the reaction.

Accuracy of temperature measurements. Thermocouples are used as detectors for temperature measurement by means of the e.m.f. compensation method. Error arising from measurements of "cold-side" temperature (if zero temperature is not maintained) is negligible provided that the temperature level is constant during decomposition. However, the setting of the thermocouple welded junction is much more important. When the usual way of setting outside the sample is used, the differences between the measured and correct temperature range from 5 to 20°K depending on temperature and heating rate, the thermocouple junction being placed some 2 mm from the crucible[6,7] [similar to Fig. 5(5)].

2. *Accuracy in maintaining reaction conditions and reducing disturbances*

The arrangement of the experiment is most important for accuracy. The rate of the investigated process must be kept from distortion by the slow rate of disturbing effects. The slowest disturbing effects are usually found to be those of transport, which consist of heat and mass transfer.

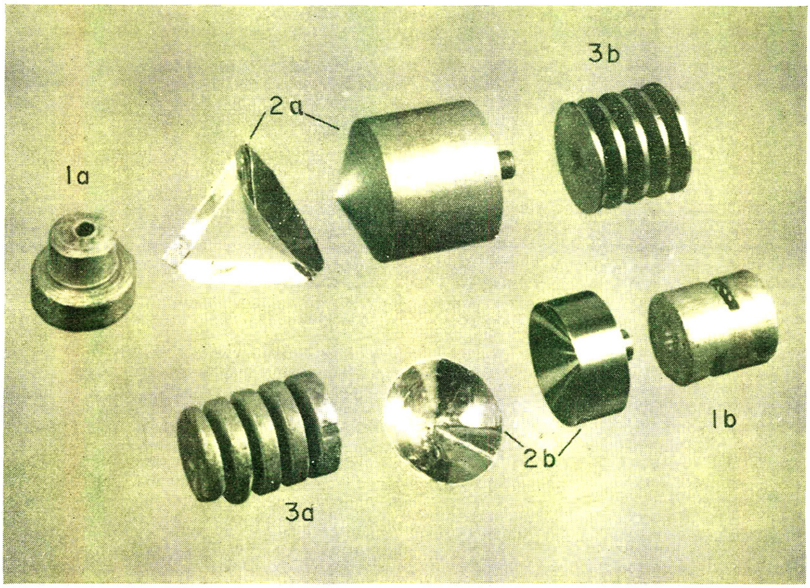

FIG. 1.—Different kinds of crucible-holder suitable for the decomposition of solid substances:

(1a) Perforated silver block (hollows containing the investigated sample in the outer-wall). The hollow in the inner wall serves for the setting in of the corund twice-capillary with a thermocouple for the purpose of temperature measurement by contact of the thermocouple welded junction inside the metal block (the setting of all other types of crucible holder is the same).

(1b) Perforated silver block with hollows (capillaries) of 1 mm diameter and of 3 different depths, intended for investigating the problem of diffusion through a layer of the sample

(2a) Aluminium block with a very light lid holder (on which the investigated sample is spread out in a thin layer) is set on the conical top of a metal heating block fixed in a furnace with stabilised temperature. This arrangement is convenient for isothermal decomposition when rapid attainment of decomposition temperature of the investigated sample is wanted (for detailed information see reference 4).

(2b) The same as in the preceding type of block holder but made out of platinum (the cone in reverse position).

(3a) Silver ribbed holder intended for non-isothermal decomposition. A thin layer of the investigated sample is spread on the ribs of the ribbed holder.

(3b) The same as the preceding type of crucible holder but made out of platinum.

When the *heat transfer* (heat exchange between the reaction interface and the source of heat) turns into a disturbing effect, non-linearity of temperature increase occurs. Linearity of temperature increase apparently depends on the kind of programme equipment chosen and on the heat situation inside the furnace (heat capacity, system of regulation of heating, aerodynamic conditions). However, the most complicated problem appears to be the removal of the non-linearity of temperature increase which is determined by the geometry and the sample mass. The errors from heat transfer are described as follows.

Influence of temperature gradient in sample. Taking into account some simplified premises, the author[6] deduced that the maximal temperature gradient between the wall of the sample holder and the centre of the sample (Ym) considered as a disk (or a cylinder), is proportional to the thickness (s) [diameter (r)] and the constant of proportionality equal to the square root of the product of the enthalpy change of reaction (ΔH), of the heat capacity of the sample (G) and the heating rate (ϕ), and of the reciprocal of its heat conductivity (λ).* For example, with a cylindrical sample of diameter 1 mm, placed in a silver block, the temperature increase of which was 5°K/min, the maximal temperature gradient found was as follows: 4·8°K for the dehydration of kaolin; 13·2°K for the decarbonisation of magnesite and 3·1°K for the dehydration of α-$CaSO_4.0{\cdot}5H_2O$ (computed for powdery and compressed samples).

The amount of sample influences the enthalpy change during the reaction in the sample and is able to slow down (or speed up) the temperature increase with a view to the original programme. In that case, one has to handle *the errors from self cooling of the sample*[18] which is a function of sample load, and of the enthalpy change of the reaction, in addition to the heat inertia of the crucible [depending on its weight, heat capacity and conductivity, *e.g.*, for the decomposition of 0·15 g of kaolin in a silver crucible of 27 g, see Fig. 1(1a), with a heating rate of 5°K/min, the temperature increase will be slowed down by about 1°K/min]. It is possible to estimate the optimum amount of sample by means of a semi-empirical method[6] under given experimental conditions (*i.e.*, taking the dependence of the maximum rate of decomposition on the heating rate).

When one wants to choose a suitable heating rate, it is necessary to consider not only its influence in removing the above stated factors (for that purpose the value of the heating rate should be as small as possible), but also its influence on the temperature range in which the reaction will be accomplished (the temperature range increases at rising heating rate and thus the field of temperatures for mathematical evaluation will be extended; *e.g.*, for decomposition of kaolin the temperature range is about 85°K for a heating rate of 2·0°K/min and about 180°K for 20°K/min). The most convenient heating rate seems to be from 3 to 6°K/min.

The influence of heat phenomena may be limited in the following ways in accordance with the above-mentioned considerations. The temperature is measured by contact of the thermocouple welded junction inside a metal holder of suitable heat conductivity and capacity (*e.g.*, silver, platinum or aluminium or sintered corundum, *etc.*) slipped onto the corundum dual-capillary thermocouple tube (the crucible is placed above the balance beam to diminish the influence of aerodynamic noises but it imposes the problem of its considerable weight). The load of the investigated

* For a disk $Ym = \sqrt{\frac{\Delta H \cdot G \cdot \phi}{\lambda}} \cdot \frac{s}{2}$; for a cylinder $Ym = \sqrt{\frac{\Delta H \cdot G \cdot \phi}{2\lambda}} \cdot r$.

substance is either put into a perforated crucible[8] [see Fig. 1(1a)] or mixed with granular metal material whose surface is covered by the powdered sample (granules allow good heat conductivity and capacity).[10] The most convenient experimental arrangement seems to be as follows.[4,6] A thin layer of the investigated sample is spread on the ribs of a ribbed crucible [see Fig. 1(3a and 3b)] for better heat exchange between sample and holder (and environment). In this way, the disturbing effect of the diffusion of gaseous products through the sample layer are reduced (see the following paragraph).

The influence of *mass transfer* cannot be eliminated in a simple way, because it is very hard to find out in advance how important this influence will be and, consequently, general conclusions cannot be formulated. The most frequent disturbing transport effect is the removal of gaseous reaction product from the reaction interface.[22] For simplification, this effect can be imagined as two consecutive effects: first, migration of gaseous products through the solid phase (*internal diffusion*) and secondly, the removal of gaseous products from the surface of the sample (*external diffusion*). When the diffusion rate is small, it is evident that local concentration of gaseous products may occur, thus changing the equilibrium conditions. By migration of gaseous products through the solid product (or by contact with the surface of the solid product) recombination (or adsorption on the surface) takes place.

Mass transfer is undoubtedly the source of the majority of phenomena reported by different authors. These phenomena concern the diffusion[9,15] (shape, size and size distribution of sample) or the influence of environment[4,14–17,29–32] (constancy of gaseous environment composition, influence of pressure of vacuum, dynamic conditions in the case of a circulating gaseous medium, and especially the effect of the aerodynamic conditions on the gaseous film sticking to the surface of the sample). Therefore, it is very important to choose experimental conditions so as to minimise the influence of mass transfer (and the reverse reaction). These experimental conditions will be found out by means of semi-empirical tests in apparatus intended for kinetic analysis (in this way, for example, it is possible to decide whether a stream of inert gas may adequately prevent the influence of the reverse reaction or whether the use of vacuum is necessary).

The importance of mass transfer is proved by a set of decomposition thermogravimetric curves of kaolin obtained under various experimental conditions (Fig. 2). The influence of the transport of reaction product from the surface of the sample is the cause of variation in the shape of curves 1 and 2 of Fig. 2. The substance is spread in a thin layer on the ribs of a ribbed silver crucible [see Fig. 1(3a)] under a static (curve 2) and dynamic (curve 1) air environment. The influence of diffusion in the sample is the cause of variation in the shape of curves 3, 4 and 5 of Fig. 2, obtained by decomposition of a kaolin sample placed in 1-mm capillaries of different length in the perforated silver crucible [see Fig. 1(1b)]. The above-mentioned experiments will result in reducing the thickness of the sample layer and, in this particular case, in speeding up the gaseous stream (or in decreasing the pressure) conditions should be established to prevent distortion of the investigated reaction from mass transfer within the limits of uncertainty of directly measured quantities.*

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* These phenomena are closely connected with the nature of the rate controlling process and therefore are important for the physico-chemical interpretation of the measured data (equally as the nature of the starting material, *e.g.*, size and shape of its crystals and its mechanical and thermal history, *etc.*).[29]

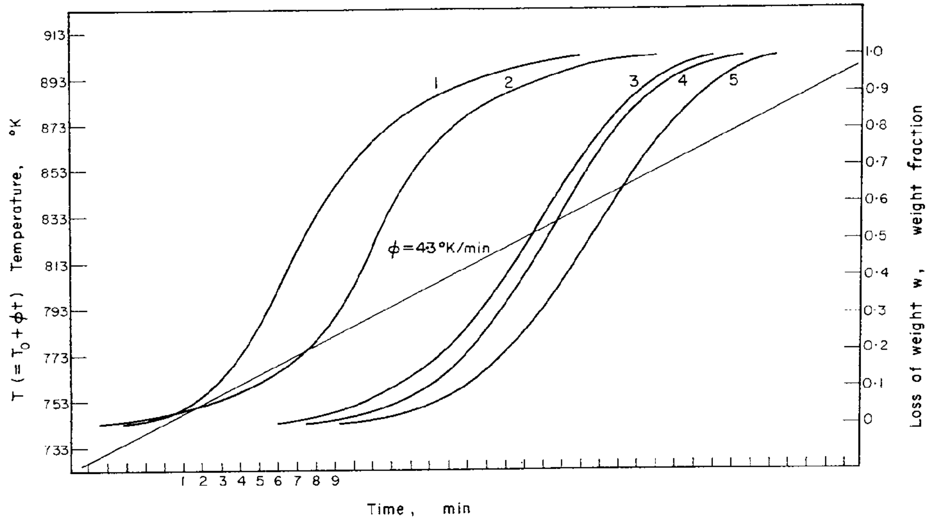

FIG. 2.—Experimental curves for the decomposition of kaolin under various experimental conditions (heating rate: 4·3°K/min; sample load: 0·04 g; specific weight of sample from 1·2 to 1·3 g/cm³; size distribution of kaolin: 1–2μ):

(1) Decomposition accomplished on a ribbed holder [see Fig. 1(3a)] in a dynamic environment (circulating air).
(2) Same arrangement as in (1) but in a static environment (static air).
(3) Decomposition accomplished in a perforated silver block [see Fig. 1(1b); length of capillaries: 3mm].
(4) Same arrangement as in (3) but length of capillaries 6 mm.
(5) Same arrangement as in (3) but length of capillaries 10 mm.

3. *Accuracy of mathematical evaluation of curves*

With isothermal methods one assumes several mechanisms and by substitution of experimental data one determines the most convenient one. However, this procedure is much more complicated when the method of rising temperature is used and, therefore, the evaluation of thermogravimetric curves will be founded on the formal kinetic equation

$$-\frac{\mathrm{d}X}{\mathrm{d}t} = k\,X^{n} \tag{2}$$

where X is the amount of substance under reaction, n is the order of reaction and k is the specific rate of reaction. Equation (2) describes very well the course of the heat decomposition of solids, such as the endothermal decomposition of hydrates, sulphates, carbonates, or the exothermal decomposition of oxalates, permanganates, perchlorates, metal azides and further the combination of metals with oxygen or hydratation and, finally even sublimation and evaporation. The temperature dependence of the specific rate k, may be expressed, according to Arrhenius, by the relationship

$$k = Ze^{-E/RT} \tag{3}$$

where Z is the frequency factor, E is the activation energy and R is the gaseous constant, for these processes pass in a narrow temperature range. A mathematical treatment of thermogravimetric curves is given by the preceding equation, making possible three methods of evaluation:

(i) differential,
(ii) integral,
(iii) approximate.

Because the value of the weight loss is known it will be suitable to transfer the quantity X to the weight loss w by the following equation:

$$-\mathrm{d}X = \frac{m_0}{w_\infty}\,\mathrm{d}w \tag{4}$$

where m_0 is the initial amount of substance and w_∞ is the maximal weight loss. By integration of the left-hand side of equation (4) from m_0 to X and by integration of the right-hand side from zero to w, the following relationship is obtained:[8]

$$X = \frac{m_0}{w_\infty}(w_\infty - w) \tag{5}$$

By substitution of equations (5) and (3) into equation (2) and by differentiating the logarithmic form, one obtains the evaluating equation for the *differential method* according to Freeman and Caroll[3] (see Table I). By means of this equation one obtains both the value of the activation energy and the order of reaction. The latter can only be presumed when using the other two methods or it can be determined through many laborious computations.

Integral methods use the integrated form of equation (2) after a preceding transposition of the weight loss w of equations (4) and (5)

$$\left(\frac{m_0}{w_\infty}\right)^{1-n}\int_0^w (w_\infty - w)^{-n}\,\mathrm{d}w = \frac{Z}{\phi}\int_{T_1}^{T_2} e^{-E/RU}\,\mathrm{d}T \tag{6}$$

The right-hand side of equation (6) will be solved by per-partes method and the solution of equation (6) consists of an infinite series of which, usually, the first two terms serve for all calculations of interest to us. These methods were used by Doyle[11] and by Coats and Redfern[19] (see Table I), as well as by Turner and associates,[20] who deduced the semi-empirical equation, and finally by van Krevelen and associates,[2] who reported their solution in the form of a nomogram.

With *approximation methods* the integral on the right-hand side of equation (5) is solved by approximation using the temperature T_i (corresponding to maximal rate of decomposition, *i.e.*, to the inflection point of the curve). This method was used by Horowitz and Metzger,[21] by van Krevelen and associates[2] (see Table I), by Fuoss and associates,[32] by Berlin and Robinson[34] and by Reich[24] and associates.[25]*

Every mathematical method is more or less subject to some inexactitude that influences the accuracy of the results.[25] We felt that due interest had not been paid

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* The latter authors have been studying the evaluation of the kinetic data from several traces obtained at different heating rates as well as Friedman[35] and Anderson.[36] (We shall be concerned with the detailed mathematical description of the individual methods in a report which will appear in *Silikáty* probably at the end of 1966.)

to this fact and our work tried to bring herewith the contribution of our own experience. In order to determine the errors from mathematical evaluation it is necessary to introduce theoretical curves, because it is impossible to avoid all the errors from experimental arrangement. That is why the thermogravimetric curves, computed from chosen kinetic data, will serve for the following considerations.

THEORETICAL CALCULATIONS OF THERMOGRAVIMETRIC CURVES

According to Šatava,[8] if one solves the right-hand side of equation (6) by exponential integral:

$$E_i(-x) = \int_x^\infty \frac{e^{-u}}{u}\,\mathrm{d}u \qquad (7)$$

(where u is variable and x is the integral limit which in this case equals E/RT) and one transfers equation (5) to the form, used further to theoretical calculations of curves, for $n = 1$

$$* \; 2{\cdot}3 \log \frac{w_\infty}{w_\infty - w} =$$

for $n \neq 1$

$$\left[1 - \left(\frac{w_\infty - w}{w_\infty}\right)^{1-n}\right]\frac{1}{1-n} = \frac{ZE}{\phi R m_0^{1-n}}\left[\left|\frac{e^{-u}}{u}\right|^{x} - E_i(-x)\right] = K\left[\int\right] \qquad (8)$$

where K is a multiplying constant equal to the fraction on the right-hand side of equation (8) and $[\int]$ is the term in square brackets on the right-hand side.

The values of $[\int]$ were taken from Akahira's tables,[23] where values of x from 20 to 50 are listed in steps of 0·02.

The following kinetic data were chosen for calculations of curves:

$$E = 2{\cdot}7 \times 10^4$$
$$Z = 7 \times 10^{11}$$
$$n = \tfrac{1}{3};\ \tfrac{1}{2};\ \tfrac{2}{3};\ 1;\ 2$$
$$m_0 = 8{\cdot}4 \times 10^{-4}$$
$$\phi = 3{\cdot}18/60$$

(kinetic data correspond to the dehydration of α-$CaSO_4.0{\cdot}5\ H_2O$ in a static environment).

Theoretical thermogravimetric curves and their derivative curves [the latter obtained by numerical derivation equation (9)] are plotted in Fig. 3

$$\left(\frac{\mathrm{d}w}{\mathrm{d}t}\right)_{w_0} = \frac{1}{h}\left[\frac{\Delta_0 + \Delta_{-1}}{2} - \ldots\right] \qquad (9)$$

where h is a step of derivation, the equidistant ordinate of the temperature is chosen, and $\Delta_0 = w_1 - w_0$; $\Delta_{-1} = w_0 - w_{-1}$. The numerical derivation is much more precise than any usual graphical method, and is more suitable with respect to further procedure (especially differential method).

COMPARISON OF DIFFERENT MATHEMATICAL METHODS

The values of weight loss and temperature were taken from the thermogravimetric curves drawn in Fig. 3 by the same procedure as in the case of elaboration of

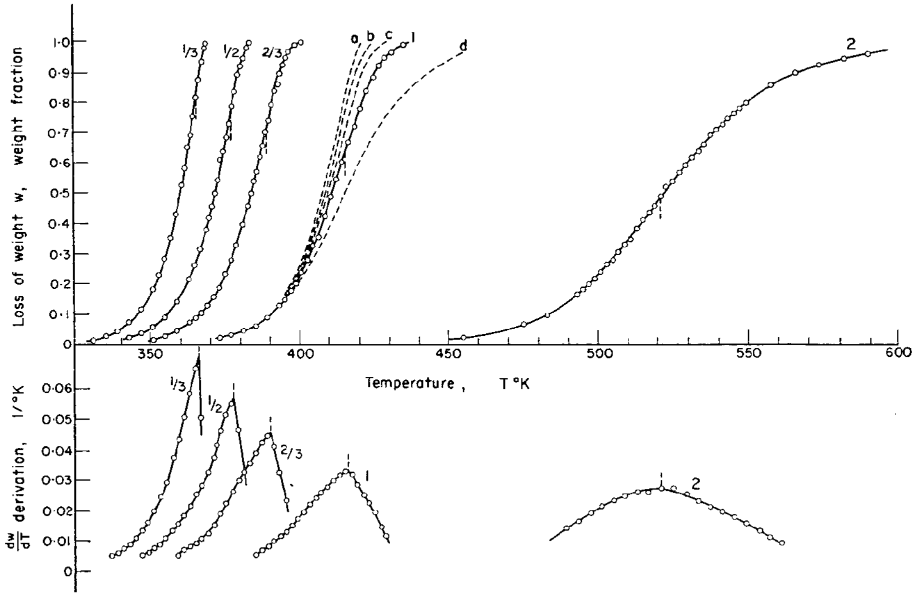

Fig. 3.—Theoretical thermogravimetric curves at increasing temperature plotted (using the equation and chosen kinetic constants see Table I) with their corresponding derivative curves. $\frac{1}{3}$, $\frac{1}{2}$, $\frac{2}{3}$, 1 and 2: these symbols indicate the values of the reaction order taken for computation of the given curves. Dashed lines indicate the situation of theoretical thermogravimetric curves if the load of sample is 1 mol. The symbols correspond to the following values of reaction order: a = $\frac{1}{3}$, b = $\frac{1}{2}$, c = $\frac{2}{3}$, 1 = 1 and d = 2.

experimental curves and the values were then treated by different evaluation methods.[2,3,11,19,21]

A comparison of the values obtained is given in Table I.

DISCUSSION

1. *Errors of mathematical treatment*

In Table I are shown the deviations of computed values of E from the originally chosen real values. They do not differ by more than 10%, so that all the methods seem to be satisfactory for the computation of kinetic data within the limits of required accuracy.

Let us have a look at the sensitivity of the mathematical treatment with regard to occasional errors due to inaccuracy of visual deduction of values from the automatically-recorded decomposition curves. For the purpose of rough determination let us consider the curve for $n = \frac{1}{2}$ (see Fig. 3) and according to the rule of the transfer of errors it is possible to calculate the uncertainty ε_E of the value of E, if one subtracts the weight loss w with uncertainty $\varepsilon_W = 0{\cdot}5\,\%$ and the temperature with one $\varepsilon_T = 1$°K. (Equations used for the calculation of errors will not be explained because of their extensitivity.) For the Freeman-Caroll derivation method is $\varepsilon_E = 4\,\%$ ($\varepsilon_n = 12\,\%$), for the Doyle integration method $\varepsilon_E = 4\,\%$ and for the Horowitz-Metzger approximative method $\varepsilon_E = 9\,\%$ (when the right value of n is assumed). However, the

TABLE I.—COMPARISON OF THE RESULTS OF KINETIC ANALYSIS (THE CURVES FROM FIG. 3) OBTAINED BY DIFFERENT MATHEMATICAL METHODS

	The theoretical shape of the thermograms (of the values w/w_∞) was computed by the equation $\left(1-\frac{w}{w_\infty}\right) = \left\{1-\frac{ZE(1-n)}{\phi R m_0^{1-n}}\left[\int\right]\right\}^{1-n}$ $\quad ^*\log\left(\frac{w_\infty}{w_\infty - w}\right) = \frac{ZE}{2{\cdot}3\phi R}\left[\int\right]$ using the arbitrarily chosen values of $E = 2{\cdot}7 \times 10^4$, $Z = 7 \times 10^{11}$, $\phi = 3{\cdot}18/60$, $m_0 = 8{\cdot}4 \times 10^{-4}$ and several values of the order of reaction n.	n	$\frac{1}{3}$ (0·333)	$\frac{1}{2}$ (0·500)	$\frac{2}{3}$ (0·666)	1	2
	The values of w/w_∞ obtained, through applying the usual experimental procedure from the plotted (Fig. 3) theoretical thermograms, were evaluated by kinetic analysis using the following methods:						
	Theoretically computed inflection points according to the equation $\left(1-\frac{w}{w_\infty}\right) = n^{1/1-n}$	$\sqrt[1-n]{n}$	0·192	0·250	0·298	0·368	0·500
	Experimentally obtained inflection points	$\left(1-\frac{w}{w_\infty}\right)_i$	0·184	0·237	0·272	0·350	0·515
	Frequency factor Z obtained by inserting the values w/w_∞ from the thermograms into the equation: $Z = \frac{\phi R m_0^{1-n}}{E(1-n)\left[\int\right]}\left[1-\left(1-\frac{w}{w_\infty}\right)^{1-n}\right]$ $\quad ^*Z = \frac{\phi 2{\cdot}3R\log\left(\frac{w_\infty}{w_\infty - w}\right)}{E\left[\int\right]}$	Z	6·98 $\times 10^{11}$	6·75 $\times 10^{11}$	7·08 $\times 10^{11}$	7·17 $\times 10^{11}$	7·11 $\times 10^{11}$
Differential method	Freeman and Caroll[3] (graphically) $\frac{\Delta\log(dw/dt)}{\Delta\log(w_\infty - w)} = -\frac{E}{2{\cdot}3R}\frac{\Delta^1/T}{\Delta\log(w_\infty - w)} + n$	n	0·28	0·46	0·73	1·01	1·90
		E	26·6 $\times 10^3$	25·6 $\times 10^3$	26·0 $\times 10^3$	27·6 $\times 10^3$	25·7 $\times 10^3$
Integral methods	Doyle[11] (numerically) $E = \frac{RT_a^2(1-n)(dw/dT)_a}{\left(\frac{w_\infty - w}{w_\infty}\right)_a^n\left[1-\left(\frac{w_\infty - w}{w_\infty}\right)^{1-n}\right]_a w_\infty}$ $\quad ^*E = \frac{RT_a^2(dw/dT)_a}{\left(\frac{w_\infty - w}{w_\infty}\right)_a 2{\cdot}3\log\left(\frac{w_\infty}{w_\infty - w}\right)_a w_\infty}$	E	28·2 $\times 10^3$	28·1 $\times 10^3$	27·8 $\times 10^3$	29·2 $\times 10^3$	—
	$q(x) = \frac{\left(\frac{w_\infty - w}{w_\infty}\right)_a^n\left[1-\left(\frac{w_\infty - w}{w_\infty}\right)^{1-n}\right]_a w_\infty}{T_a(1-n)(dw/dT)_a}$ $\quad ^*q(x) = \frac{\left(\frac{w_\infty - w}{w_\infty}\right)_a 2{\cdot}3\log\left(\frac{w_\infty}{w_\infty - w}\right)_a w_\infty}{T_a(dw/dT)_a}$ For the computed values of $q(x)$ tabulated in Doyle's table ($q(x) = x_a[\int]_{x_a}e^{x_a}$) one finds the corresponding x_a and computes E by the equation $x_a = E/RT_a$.	E	26·5 $\times 10^3$	26·8 $\times 10^3$	26·6 $\times 10^3$	27·2 $\times 10^3$	—
	Coats and Redfern[19] (graphically) $\left\{^*\log\frac{2{\cdot}3\log\left(\frac{w_\infty}{w_\infty - w}\right)}{T^2} = \right\}\log\frac{\left[1-\left(\frac{w_\infty - w}{w_\infty}\right)^{1-n}\right]}{(1-n)T^2} = \log\frac{ZR}{\phi E}\left[1-\frac{2RT}{E}\right] - \frac{E}{2{\cdot}3R}\cdot\frac{1}{T}$	E	25·5 $\times 10^3$	26·8 $\times 10^3$	26·8 $\times 10^3$	27·6 $\times 10^3$	—
Approximate methods	Horowitz and Metzger[21] (graphically) $\log\left[1-\left(\frac{w_\infty - w}{w_\infty}\right)^{1-n}\right] = \log(1-n) + \frac{E}{2{\cdot}3RT_i^2}.\theta$ $\quad ^*\log\log\left(\frac{w_\infty - w}{w_\infty}\right) = -\log 2{\cdot}3 + \frac{2{\cdot}3RT_i^2}{E}.\theta$	E	30·4 $\times 10^3$	29·8 $\times 10^3$	29·8 $\times 10^3$	30·9 $\times 10^3$	—
	Van Krevelen, van Heerden and Hutjens[2] (graphically) $\left\{^*\log 2{\cdot}3\log\left(\frac{w_\infty}{w_\infty - w}\right) = \right\}\log\left[1-\left(\frac{w_\infty - w}{w_\infty}\right)^{1-n}\right]$ $= \log\left[\frac{Z}{\phi}\left(\frac{0{\cdot}368}{T_i}\right)^{E/RT_i}\frac{1}{E/RT_i + 1}\right] + \left(\frac{E}{RT_i}+1\right)\log T$	E	28·5 $\times 10^3$	26·9 $\times 10^3$	28·4 $\times 10^3$	28·8 $\times 10^3$	—

Symbols used:

E = activation energy (cal. mol^{-1}),
n = order of reaction,
Z = frequency factor (sec^{-1}, mol^{1-n}),
R = gas constant (1·987 cal. mol.$^{-1}$ deg^{-1}),
X = number of moles (mol) (respective amount of component, concentration, *etc.*)

w = loss of weight (mol; g; *etc.*),
w_∞ = maximal loss of weight (mol; g; *etc.*),
m_0 = sample load (mol; g; *etc.*),
T = temperature (°K),
ϕ = (dT/dt) = rate of heating (deg. min^{-1}),
Δ = difference,

t = time (sec),
$\theta(= T - T_i)$ = difference of given temperature T and temperature T_i corresponding to maximal decomposition rate (°K),
dw/dt = rate of loss of weight (mol. sec^{-1}),

Indexes used:

i = values of the symbol corresponding to point of inflection (to the highest rate of the decomposition process),
a = value of the symbol for a defined (usually chosen) point,
* those symbols are valuable only for the order $n = 1$

$\left[\int\right] = \left\{\left|\frac{e^{-u}}{u}\right|^{x} - \int_{x}^{\infty}\frac{e^{-u}}{u}\,du\right\}_i \left(x = \frac{E}{RT}\right)_i$ (taken from Akahira's tables).

magnitude of this error depends considerably on the position of the point on the thermogravimetric curve, in which the kinetic analysis is being performed. The analysis of errors proves that in the case of the derivation method the most precise kinetic data are obtained when medium steep parts of the thermogravimetric curves are taken for computation, these being more convenient for a precise determination of the instantaneous rate of reaction (the same absolute ε_W is far more perceptible in a small value Δ_w for the initial and the final parts than at the steep medium part). The same is true with Doyle's method. The accuracy of the approximation method depends considerably on the accuracy of determination of the inflection point temperature (especially with the Horowith-Metzger method).

However, the reverse of the coin of evaluation methods is the work consumption. From this point of view, Doyle's method seems to be very simple because kinetic data may be obtained from a single point on the decomposition curve. The necessity to know beforehand the value of the reaction order appears to be a disadvantage, which, partially, finds a remedy in the Coats-Redfern method. Whether the supposed reaction is suitable will be further proved by the linearity of dependence resulting from their evaluating equation (a similar application with the methods in references 2 and 21 is possible). These methods are time consuming but a knowledge of the theoretical inflection point position with different reaction orders[21] (see Table I) will, however, be useful because the approximate value of the reaction order can be deduced from the inflection point position of the experimental curve. The van Krevelen method seems to be the most rapid one, even though the derivative method should not be omitted because of the possibility of parallel determination of reaction order. The Coats-Redfern method seems to be more accurate but considerably work consuming.

2. *Theoretical influence of variation of kinetic constant on shape and position of theoretical thermogravimetric curves*

Consider equation (8) and vary the values of E, n and Z so that either the value of the exponent $(1 - n)$ on the left-hand side or the value of term $K[\int]$ on the right-hand side is changed.

A change in the reaction order n reveals merely a change of shape of the thermogravimetric curve, as shown in Fig. 3 (curves a, b, c, 1 and d) if $m_0 = 1$.

Changes in the frequency factor Z and the activation energy E induce either a change in the multiplying constant K or a change in the term $[\int]$. To maintain the real sense of the left-hand side of equation (8), the value of the product $K[\int]$ must approach one; if the value of Z is decreased by one order, *i.e.*:

$$\text{from} \qquad \frac{7 \times 10^{11}}{m_0^{(1-n)}} \rightarrow \frac{7 \times 10^{10}}{m_0^{(1-n)}}$$

the value of K is decreased. If the value of the term $K[\int]$ is to be maintained comparable to one, the value $[\int]$ must increase by one order (if kinetic constants are maintained), this being possible only by a change of integral limits and thus by a decrease of the value

$$x = \frac{E}{RT} \text{ to } x' = \frac{E}{E/(T + \Delta T)} \tag{10}$$

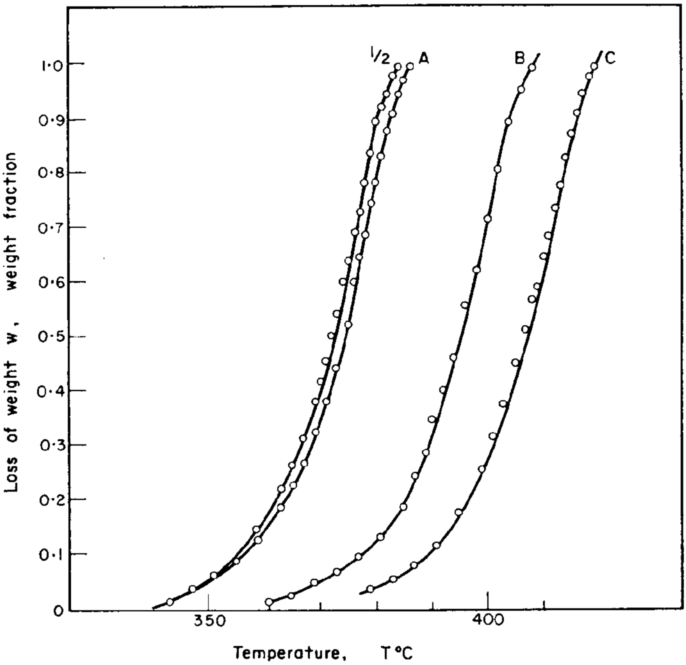

Fig. 4.—Influence of kinetic constants on the position and shape of theoretical thermogravimetric curves of order ½.

(½) Original theoretical thermogravimetric curve (see Fig. 3 and Table I).

(A) Theoretical thermogravimetric curve taken at 10% declination from the original heating rate.

(B) Theoretical thermogravimetric curve calculated at 90% reduction of the original frequency factor

(C) Theoretical thermogravimetric curve calculated at 10% reduction of the original activation energy.

this coming into action by shifting of curves by ΔT ($\simeq$23°K) to the region of high temperatures (see Fig. 4, curve B). This proves that a decrease of frequency factor shifts the decomposition of substance to the high temperatures region.

If the value of the activation energy is increased by 10%, *i.e.*

$$\text{from } 2{\cdot}7 \times 10^4 \quad \text{to} \quad 2{\cdot}97 \times 10^4$$

(and the original value of Z is maintained), the change in the value of the multiplying constant is small but with respect to the change of integral limits, the value of $[\int]$ decreases considerably. This may be compensated by an increase of the value of the temperature T

$$\frac{E}{RT} = \frac{E + \Delta E}{R(T + \Delta T)} \tag{11}$$

The compensation will reshift the curves to the region of high temperatures by ΔT($\simeq$35°K) characterising the increase of decomposition temperature due to a higher activation energy (see Fig. 4, curve C).

A conclusion can be drawn from the above reported consideration. The reaction order theoretically influences only the shape of curves, the values of activation energy and the frequency factor (as well as the load and the heating rate) influences the position of curves in temperature scale [and, partly, the steepness of curves] (see Fig. 4).

3. *Theoretical influence of variables T and ϕ on kinetic data obtained from thermogravimetric curves*

With experimental *temperature* T measurements a higher temperature will usually be found. This means that the value of the integral limits [$\int$] is decreased to the value:

$$\frac{E}{R(T+\Delta T)} \quad \left(\text{which is equivalent to } \frac{E-\Delta E}{RT}\right) \tag{12}$$

when the decreasing integral limit of value [$\int$] increases. To maintain the right-hand side of equation (8) close to one, the multiplying constant K must be decreased in this way: the value of the product EZ is decreased. Hence, if a higher temperature than the real one was taken, lower values of E and Z should be obtained.

This is confirmed by experiments (see Fig. 5). The theoretical curve 1, computed

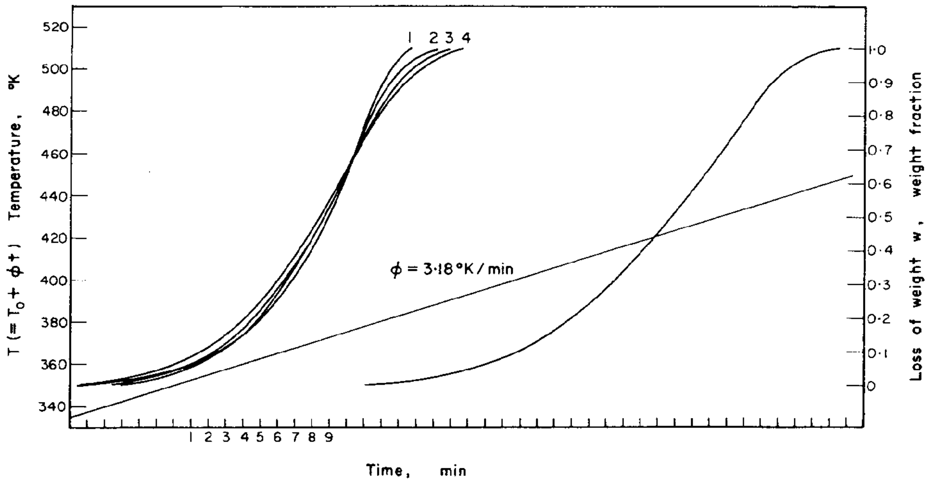

FIG. 5.—Experimental thermogravimetric curves for the decomposition of α-$CaSO_4.0{\cdot}5\ H_2O$ in static air environment.

(1) Theoretical decomposition curve (computed by means of kinetic analysis of experimental curves obtained under optimal condition of the case in question) [see Table I].

(2) (3), (4) Experimental thermogravimetric curves obtained through decomposition on a ribbed silver holder [see Fig. 1(3a)].

(5) Experimental thermogravimetric curves obtained through decomposition in a perforated crucible [see Fig. 1(1a); temperature taken outside the crucible].

The sketched curves in this figure are evaluated according to the Freeman-Caroll kinetic analysis method:

Thermograv. curves	Heating rate	Sample load, *g*	Inflex. point	Activation energy	Reaction order	Frequency factor
1	3·18	0·13	0·237	$25{\cdot}6 \times 10^3$	0·46	$7{\cdot}6 \times 10^{11}$
2	3·04	0·13	0·333	$26{\cdot}6 \times 10^3$	0·67	$6{\cdot}7 \times 10^{11}$
3	3·26	0·128	0·317	$25{\cdot}5 \times 10^3$	0·65	$6{\cdot}5 \times 10^{11}$
4	3·18	0·135	0·381	$26{\cdot}0 \times 10^3$	0·97	$7{\cdot}9 \times 10^{11}$
5	3·17	0·18	0·343	$19{\cdot}5 \times 10^3$	0·67	$0{\cdot}3 \times 10^{11}$

from values obtained under the optimal experimental arrangement,[4] is compared with curves 5 obtained experimentally for the decomposition α-$CaSO_4.0{\cdot}5\,H_2O$ in a perforated silver crucible [Fig. 1(1a)] in a static environment, if the temperature is measured by means of thermocouples placed between the crucible and the furnace wall. In this case the values of E and Z are really lower than those obtained under the optimal experimental arrangement (change of temperature by some 50°K and a slight decrease of the steepness of the curves decreases the value of E by approximately 30% and that of Z by approximately 100%).

Consider when the value of the *heating rate* ϕ is changed in consequence of self cooling (for example the value ϕ becomes lower by 10%). Suppose that ϕ decreases from an original value of 3·18°K/min to 2·86°K/min. This means that one obtains the values of $\phi_{\text{meas.}}$ and $T_{\text{meas.}}$ (providing a precise direct measurement of temperature, *e.g.*, inside the metal holder) but, in fact, the decomposition in the sample takes place at the temperature $T_{\text{real.}}$ and at the heating rate $\phi_{\text{real.}}$, *i.e.*:

$$T_{\text{meas.}} = T_{\text{real.}} - (\phi_{\text{real.}} - \phi_{\text{meas.}})t \tag{13}$$

Curve A modified in this way is plotted in Fig. 4 (weight loss w is plotted *vs.* $T_{\text{meas.}}$ and when $T_{\text{real.}}$ and $\phi_{\text{real.}}$ are used for computation). This modification influences either the multiplying constant K (slightly) or the value of $[\int]$. In Fig. 5 the deformation of shape (and the slight decrease of steepness) is shown. These deformations bring about a considerable change of n and a slight change of E and Z (see Fig. 4, curve A; by evaluation of curve A according to Freeman-Caroll the values $E = 24{\cdot}2 \times 10^3$ and $n = 0{\cdot}23$ are obtained).

A similar conclusion will be found if one compares the experimental curves of α-$CaSO_4.0{\cdot}5\,H_2O$ decomposition in Fig. 5, curves 2, 3, 4 (in a static environment on the ribbed silver crucible) with the theoretical curve 1. The positions of all these curves are virtually the same, their shapes being slightly different, which probably is due to self cooling (even though the influence of non-constancy of aerodynamic conditions would have a similar effect). In addition, the deformation will mostly appear as a change of the value of the reaction order.

Experimental conditions influence not only the accuracy of the values of T and ϕ but even the values of *weight loss* (as mentioned above). According to equation (8) modification of all the kinetic quantities E and Z and even n may be expected but no generalisation was found.

CONCLUSIONS

The error of mathematical treatment of reported methods is found to range from 5 to 10%. With current experimental procedure these errors are usually found to be less than those due to false determining of directly measured quantities, incorrect definition and to inconstancy of experimental conditions.

However, if it is possible to reduce the errors caused by the experimental arrangement it is necessary to have an accurate mathematical evaluation in view. A preference should be given to derivative and integral methods for the purpose of accurate mathematical evaluation.

A theoretical analysis of errors proves that faulty measurements of temperature must distort, in the first place, the value of the activation energy, while non-linearity of heating rate distorts, predominantly, the value of the reaction order.

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Zusammenfassung—Die Fehler von aus thermogravimetrischen Kurven bei steigender Temperatur ermittelten kinetischen Daten werden diskutiert.

Résumé—On discute des erreurs sur les données cinétiques obtenues à partir des courbes thermogravimétriques à température croissante.

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DETECTION AND DETERMINATION OF CHLOROPHENOLS AND CHLOROPHENOXYACETIC ACIDS BY INSTRUMENTAL ANALYSIS

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Summary—A quantitative method for the determination of chlorophenols and chlorophenoxyacetic acids in aqueous solutions is described. The samples investigated contained 2-chlorophenol, 2,4-dichlorophenol, 2,6-dichlorophenol, 2,4,6-trichlorophenol and their phenoxyacetic acid derivatives. The total amount of chlorophenols is determined by spectrophotometry, the ratio of individual chlorophenols by gas chromatography and the total quantity of phenoxyacetic acids by acidimetric titration. The determinations are carried out after extraction with diethyl ether, carbon tetrachloride and petroleum ether, respectively.

THE chlorophenoxyacetic acids produced by reacting chlorophenols with monochloroacetic acid are very effective herbicides. Among the isomers of dichlorophenoxyacetic acid, 2,4-dichlorophenoxyacetic acid is the most effective, and therefore the chlorination of the phenol is directed so as to obtain a product consisting mainly of 2,4-dichlorophenol. The proportion of other isomers formed depends on the degree and conditions of chlorination. Information about the ratio of the isomers formed is important for the promotion of the desired main reaction. An accurate and rapid method of analysis, supplying data of this kind, may also provide important help for the factory management.

For the control of the efficiency of acylation with monochloroacetic acid, knowledge of the chlorophenol content and chlorophenoxyacetic acid content of the product is required.

For the quick detection of chlorophenols Kanazawa[1] has converted the chlorophenols into methyl ethers, to be investigated successively by vapour phase chromatography.

Barry *et al.*[2] have determined the optimum conditions of gas chromatography on a column packed with three stationary phases [silicone oil, Dow Corning No. 200, silicone grease for high vacuum and di(2-methylnonyl)phthalate], using helium as the carrier gas. The results obtained were checked by infrared spectroscopy. Kolloff *et al.*[3] obtained satisfactory results on a Carbowax 20M stationary phase containing phosphoric acid in the gas-chromatographic investigation of a mixture containing 2,4-dichlorophenol, 2,6-dichlorophenol, *o*-chlorophenol and 2,4,6-trichlorophenol.

Polish authors[4] have determined by acidimetry the total quantity of the chlorophenols. Faust and Aly[5] reported on a colorimetric method using 4-aminoantipyrin as the reagent.

Aly[6] and Faust determined 2,4-dichlorophenoxyacetic acids in aqueous solution after extraction with ether plus chloroform and chromotropic acid. Bevenue *et al.*[7,8] determined traces of chlorophenoxyacetic acid in potato and other agricultural produce.

After extraction with benzene, the extract was investigated at 200° by gas-chromatography on a column packed with silicone grease as the stationary phase. Yip[9] determined 2,4-dichlorophenoxyacetic acid and its esters by gas chromatography at 225° on silicone grease as the stationary phase, using a micro-coulometric detector. Erne[10] employed paper chromatography for the detection of chlorophenoxyacetic acids in water. The process involves the extraction of the corresponding parts on the paper chromatogram and the colorimetic determination of the extract of the various chlorophenoxyacetic acid derivatives with chromotropic acid. An acidimetric method is reported by Gribova[11] for the determination of chlorophenoxyacetic acids, using potentiometric indication. The determination of dichlorophenoxyacetic acids is described by Wudzinska and Lefter;[4] the determination is carried out titrimetrically in isopropyl alcohol, with a solution of tetramethylammonium hydroxide in isopropyl alcohol.

The samples examined by authors contained 2-chlorophenol, 2,4-dichlorophenol, 2,6-dichlorophenol, 2,4,6-trichlorophenol and their phenoxyacetic acid derivatives in aqueous solution. Depending on the phase of manufacture from which the samples had been taken, the individual components were present in the form of free phenols or phenoxyacetic acids or their sodium salts.

The total quantity of the chlorophenols has been determined by spectrophotometry, the amount of the individual chlorophenols by gas-chromatography, in conjunction with the spectrophotometric results. This combination of methods proved more rapid and simple than performing the total analysis by gas chromatography with the available equipment.

For the determination of the total quantity of phenoxyacetic acids an acidimetric method has been employed. Before the determination, contaminants, water and interfering components were removed by extraction.

EXPERIMENTAL

Reagents

Chlorophenols. 2-Chlorophenol, 2,4-dichlorophenol, 2,6-dichlorophenol and 2,4,6-trichlorophenol of analytical purity and 2,4-dichlorophenoxyacetic acid, obtained by the acylation of 2,4-dichlorophenol, were used.

Apparatus

Gas chromatography. Gas-chromatographic determinations were carried out with a Carlo Erba Fractovap, Type B apparatus, with detection of the heat conductivity by a thermistor. The results were registered by a potentiometric line-recorder. Chromatographic peak areas were measured with an electronic integrator. The column was an acid-proof steel tube of 2 m length and of 6 mm internal diameter. The packing was Celite carrier, of mesh size 40–60, containing 25% of Carbowax 1000 and 2% of phosphoric acid. Tests were carried out at 150°; the temperature of the evaporating zone was 220°. The flow rate of the hydrogen carrier gas was 2 l./hr.

The Celite carrier was dehydrated by drying at 160°. The Carbowax 1000 stationary phase was dissolved in carbon tetrachloride at about 40°, and after the addition of the concentrated phosphoric acid was admixed with the carrier. The solvent was evaporated on a water-bath, and the packing was stabilised in a drying-oven at 160°.

Spectrophotometer. Unicam SP 700.

Automatic titrator. Orion OP 501.

Gas-chromatographic investigations

The gas-chromatographic investigation of aqueous solutions containing chlorophenols, or chlorophenols and chlorophenoxyacetic acids, cannot be carried out directly. Though the difference between the boiling points of the investigated components and of water is sufficient to permit satisfactory separation, the tailing of the water peak appearing in the chromatograms of the aqueous

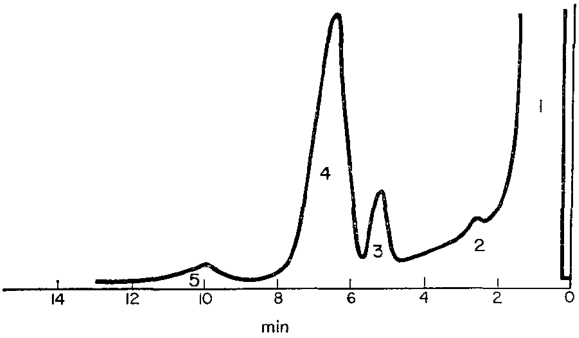

FIG. 1.—Gas chromatogram of aqueous chlorophenol solutions:—1: Water; 2: 2-chlorophenol; 3: 2,6-dichlorophenol 4: 2,4-dichlorophenol; 5: 2,4,6-trichlorophenol.

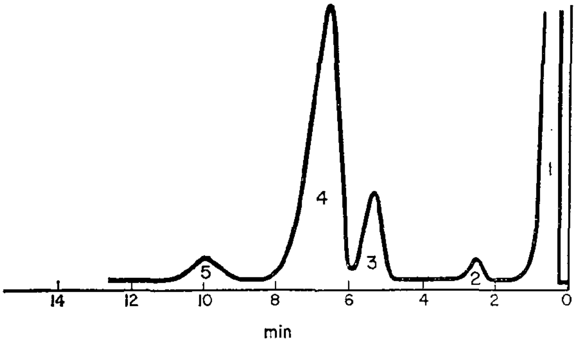

FIG. 2.—Gas chromatogram of chlorophenol solutions in ether:—1: ether; 2: 2-chlorophenol; 3: 2,6-dichlorophenol; 4: 2,4-dichlorophenol; 5: 2,4,6-trichlorophenol.

chlorophenol solutions will interfere considerably with the quantitative determination, and in some cases, even with the detection of 2-chlorophenol and 2,6-dichlorophenol (Fig. 1).

The chlorophenols are separated from the water by extraction with ether. It has been established that by extracting the acidified solutions twice, the total quantity of the chlorophenols will be transferred to the solvent phase. The chromatogram was recorded on the ether extract (Fig. 2) on a column packing containing 25% of Carbowax 1000 + 2% of phosphoric acid.

The quantitative evaluation was carried out on the basis of the single peak areas and referred to the total areas of the chlorophenol peaks. In this way, the ratio of the chlorophenols in the sample was obtained. The total chlorophenol content of the aqueous solutions was determined by spectrophotometry.

Spectrophotometric investigations

The absorption spectra of 2-chlorophenol, 2,4-dichlorophenol, 2,6-dichlorophenol and 2,4,6-trichlorophenol were investigated, using carbon tetrachloride as the solvent, in the ultraviolet and the near infrared range. The absorption spectra show that the individual chlorophenols cannot be determined simultaneously, because their absorption maxima occur at almost identical wavelengths (Fig. 3).

The molar extinction coefficients of these chlorophenols were determined and were found to differ slightly from each other. Hence, if it is desired to determine spectrophotometrically the total amount of the chlorophenols, a chlorophenol mixture, containing the individual chlorophenols in a ratio similar to that of the sample to be tested, will be prepared for the plotting of the

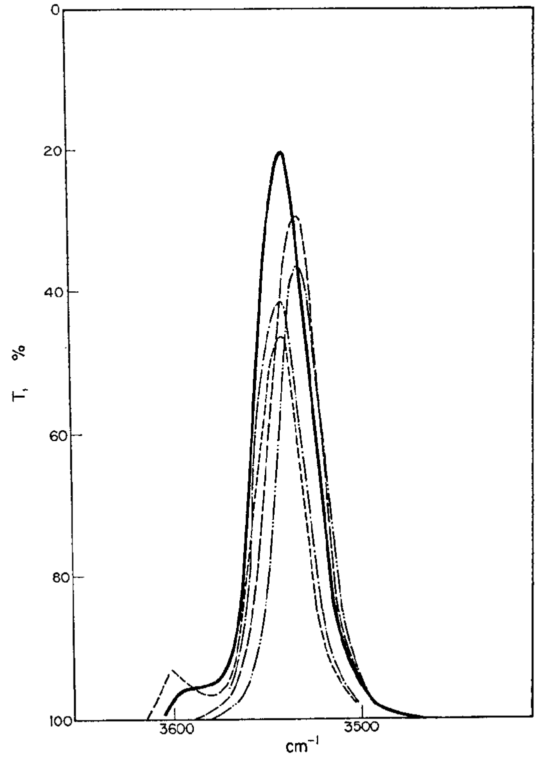

FIG. 3.—Absorption spectra of chlorophenols in carbon tetrachloride:
– – – 2-chlorophenol
·—·—· 2,4-dichlorophenol
—··— 2,6-dichlorophenol
–– –– 2,4,6-trichlorophenol
——— standard chlorophenol mixture.

calibration curve (Fig. 3, standard). The chlorophenol ratio to be expected in practice was determined with the help of previously recorded gas chromatograms, on the basis of which the proportion of the chlorophenols in the standard mixture was fixed as follows:

2-chlorophenol: 1·3% 2,4-dichlorophenol: 78·1%
2,6-dichlorophenol: 12·8% 2,4,6-trichlorophenol: 7·7%

The chlorophenols, or rather the aqueous solutions containing their sodium salts, were acidified with hydrochloric acid and extracted with carbon tetrachloride. The transmission of the chlorophenols in the extract was measured at a frequency of 3,540 cm^{-1}, and the chlorophenol concentration of the aqueous solutions was determined with the aid of a transmission-concentration diagram, plotted for the standard mixture. The optimum concentration range of chlorophenol was found to be $1 \cdot 0 - 4 \cdot 0 \times 10^{-3}M$ (Table I).

In the course of the carbon tetrachloride extraction one part of the chlorophenoxyacetic acids will pass into the solvent phase, but their presence does not interfere with the determination of the chlorophenols.

Acidimetric investigations

The total quantity of the chlorophenoxyacetic acids was determined by potentiometric titration with $0 \cdot 1M$ sodium hydroxide solution in an acetone medium.

According to our investigations, chlorophenols interfere with the titrimetric determination of chlorophenoxyacetic acids, and, therefore, after acidification, they were removed from the aqueous

Table I.—Accuracy of the spectrophotometric determination of chlorophenols and efficiency of the extraction

Test No.	Chlorophenol mixture			
	Taken, *g*	Found, *g*	Deviation, *g*	Recovery, %
1	0·1165	0·1161	0·0004	99·6
2	0·2330	0·2330	0·0000	100·0
3	0·3495	0·3457	0·0038	98·9
4	0·4660	0·4646	0·0014	99·7
5	0·5825	0·5773	0·0052	99·1

Table II.—Accuracy of the titrimetric determination of chlorophenoxyacetic acids and chlorophenols after preliminary extraction

	Taken, *g*	Found, *g*	Deviation, *g*
Chlorophenoxyacetic acids	0·1909	0·1897	0·0012
	0·1755	0·1731	0·0024
	0·1310	0·1292	0·0018
Chlorophenols	0·2017	0·2227	0·0210
	0·1419	0·1479	0·0060
	0·2380	0·2350	0·0030

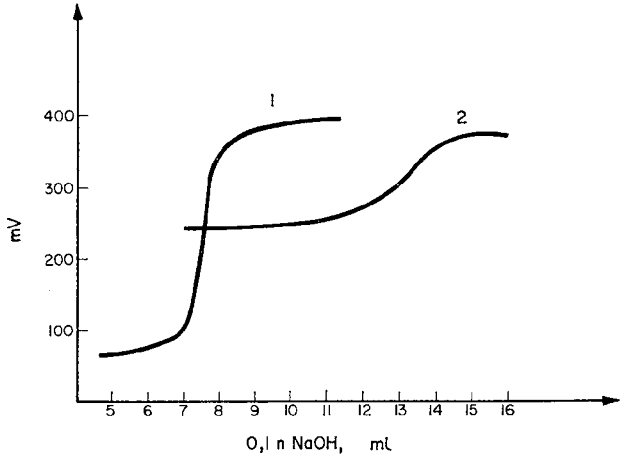

Fig. 4.—Potentiometric titration curves:—
1: Dichlorophenoxyacetic acid and mixture
2: Dichlorophenol mixture.

solution of the samples by extraction with petroleum ether. It has been established that chlorophenoxyacetic acids are insoluble in petroleum ether, while chlorophenols can be removed quantitatively from the aqueous phase. The chlorophenoxyacetic acids were extracted with diethyl ether, the solvent was evaporated, the residue taken up in acetone and the acids were determined titrimetrically (Table II; Fig. 4, Curve 1).

The titration curve for the chlorophenoxyacetic acid mixture obtained from the sample is identical with that of the curve for pure 2,4-dichlorophenoxyacetic acid. According to gas-chromatographic determinations, the product obtained in the chlorination of phenol contains more than 85% of the 2,4-dichlorophenol. The phenoxyacetic acid mixture is formed in the course of the acylation of the chlorophenol mixture. Trichlorophenoxyacetic acids are not significantly noticeable. Thus, no substantial error is incurred if the results of titration are calculated as dichlorophenoxyacetic acid.

TABLE III.—COMPOSITION OF PROCESS SAMPLES AS DETERMINED BY THE PROPOSED METHOD

Sample No.	Total chlorophenol content, *weight %*		Proportion of chlorophenols, %	Concentration of chlorophenols, *weight %*	Concentration of chlorophenoxyacetic acids, *weight %*
1	2-chlorophenol	69·6	1·5	1·0	—
	2,4-chlorophenol		75·7	52·7	
	2,6-chlorophenol		15·3	10·6	
	2,4,6-chlorophenol		7·5	5·2	
2	2-chlorophenol	28·3	1·5	0·4	10·4
	2,4-chlorophenol		76·0	18·7	
	2,6-chlorophenol		16·6	4·7	
	2,4,6-chlorophenol		6·0	1·7	
3	2-chlorophenol	15·9	1·0	0·2	39·8
	2,4-chlorophenol		81·5	12·9	
	2,6-chlorophenol		7·1	1·1	
	2,4,6-chlorophenol		10·4	1·7	
4	2-chlorophenol	37·0	1·5	0·5	15·9
	2,4-chlorophenol		79·3	28·3	
	2,6-chlorophenol		12·5	4·6	
	2,4,6-chlorophenol		6·9	2·6	

The titration curve of the chlorophenol mixture is protracted (Fig. 4, Curve 2), and is therefore unsuitable for the determination of chlorophenols.

The composition of the samples from the plant was calculated from the results of the spectrophotometric, gas-chromatographic and acidimetric determinations (Table III).

Parallel tests show the relative error, referred to the mean value of the results obtained by the described methods, to be less than ±5%.

Procedure

Gas-chromatographic determination of ratio of chlorophenols. Add a weighed amount (about 2 g) of the substance to be tested to a 50-ml separating funnel, add 2 ml of distilled water, acidify with concentrated hydrochloric acid, add 5 ml of diethyl ether, and shake the mixture. Separate the aqueous phase, and re-extract with a further 5-ml portion of diethyl ether. Reduce the volume of the combined ethereal phases to about 2 ml.

Record the chromatogram from 50 µl of the ethereal solution. The sequence of the peaks appearing on the chromatogram is the following: 2-chlorophenol, 2,6-dichorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol. The relative quantity of the individual chlorophenols is evaluated from the total of the area of the chlorophenol peaks.

The percentage of the individual chlorophenols in the samples investigated was established by consideration of the results of the spectrophotometric and gas-chromatographic tests.

Spectrophotometric determination of chlorophenols. Add a weighed amount (0·1–0·5 g, depending on the chlorophenol content of the sample) of the sample to a separating funnel. Acidify the sample with 0·5 ml of concentrated hydrochloric acid, add 2 ml of distilled water, and from a pipette 10 ml of carbon tetrachloride. Shake the mixture for 3 min and allow to stand for a few hours. After this period, drain about 5–6 ml of the carbon tetrachloride phase into a dry closed vessel, and discard the rest; ensure that the total volume of the aqueous phase shall remain in the separating funnel. Repeat the extraction with another 10-ml portion of carbon tetrachloride.

Transfer 0·5 to 5·0 ml from each of the two extracts to dry 25-ml flasks, and fill to the mark with carbon tetrachloride. Measure the transmission of the prepared samples in 1-cm quartz cells at a frequency of 3,540 cm^{-1}. Add the results obtained for the two extracts. Prepare a calibration curve by putting standard amounts through the procedure.

The optimum concentration range of chlorophenol was found to be 1·0 to 4·0 × $10^{-3}M$.

Titrimetric determination of chlorophenoxyacetic acids. Place a weighed amount (0·2–0·5 g) of the sample in a 50-ml separating funnel, and add 0·5 ml of concentrated hydrochloric acid and 2 ml of distilled water. Extract the solution with three 3-ml portions of petroleum ether. The petroleum ether phase, containing the chlorophenols, is not required and may be discarded. Extract the aqueous phase with three 3-ml portions of diethyl ether. Drain the ether extract into a 100-ml Erlenmayer flask and evaporate the ether at room temperature. Dissolve the dry residue in 50 ml of undried acetone.

Titrate the solution in acetone with 0·1*M* sodium hydroxide solution. The chlorophenoxyacetic acid content is calculated from the titration curve.

The determination is carried out with an automatic titrimeter, using a glass electrode as the measuring electrode and a calomel electrode as the reference electrode.

Zusammenfassung—Eine Methode zur quantitativen Bestimmung von Chlorphenolen und Chlorphenoxyessigsäuren in wäßrigen Lösungen wird beschrieben. Die untersuchten Proben enthielten 2-Chlorphenol, 2,6-Dichlorphenol, 2,4,6-Trichlorphenol und die davon abgeleiteten Phenoxyessigsäuren. Die Gesamtmenge an Chlorphenolen wird spektrophotometrisch, das Verhältnis der einzelnen Chlorphenole gaschromatographisch und die Gesamtmenge an Phenoxyessigsäuren durch acidimetrische Titration bestimmt. Die Bestimmungen werden nach Extraktion mit Diäthyläther, Tetrachlorkohlenstoff und Petroläther ausgeführt.

Résumé—On décrit une méthode quantitative de dosage des chlorophénols et des acides chlorophénoxyacétiques en solutions aqueuses. Les échantillons étudiés contenaient: 2-chlorophénol, 2,4-dichlorophénol, 2,6-dichlorophénol, 2,4,6-trichlorophénol et leurs dérivés phénoxyacétiqueacides. La quantité totale de chlorophénols est déterminée par spectrophotométrie, les taux des chlorophénols individuels par chromatographie en phase vapeur et la quantité totale d'acides phénoxyacétiques par titrage acidimétrique. Les dosages sont menés après extraction à l'éther diéthylique, au tétrachlorure de carbone et à l'éther de pétrole respectivement.

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SPECTROPHOTOMETRIC EXTRACTIVE TITRATIONS—II*

DETERMINATION IN GALLIUM ARSENIDE OF THE SUM OF METALS EXTRACTABLE WITH DITHIZONE

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Summary—A procedure for the determination of the sum of metals, which are extractable with dithizone, in gallium arsenide is given. After the dissolution of the sample the impurities are extracted with several portions of $10^{-4}M$ dithizone in carbon tetrachloride, gallium being screened by tartrate ion. The excess of the reagent is extracted into $0{\cdot}1M$ aqueous ammonia and after stripping into carbon tetrachloride the dithizone is determined by spectrophotometric extractive titration. The effect of pH is considered. The limit of detection, based on the evaluation of twenty blanks, is $2{\cdot}30 \times 10^{-8}$ mole, the equivalent of $1{\cdot}50$ μg of zinc.

INTRODUCTION

THE semiconductor industry needs sensitive, reliable and simple methods for the determination of trace impurities in a variety of high-purity materials. Hitherto spectrographic, spectrophotometric or polarographic methods have proved most convenient. Neutron-activation analysis and mass spectrometry are seldom applied, though they are advantageous. Most of the methods offer either information about the concentration of a single element, or semiquantitative information in the case of the simultaneous determination of several elements. This latter is true in the case of spectrography and mass spectrometry. When a more precise determination of trace metal content is required, lengthy and laborious calibration is necessary.

In some cases, especially when raw materials are to be evaluated, it is sufficient to know the general degree of purity of the material. This requirement may be fulfilled by the methods of group determinations, such as those reported by various workers in the last few years. Häberli[1] determined the sum of metals forming complexes with dithizone in antimony of high purity, Marczenko *et al.*[2] used the same reagent for determination of the impurity content in reagent-grade chemicals. Both these authors used direct or indirect extractive titration. Blank *et al.*[3] developed the spectrophotometric procedure using diethyldithiocarbamate for the determination of the sum of lead, bismuth, cadmium, zinc, manganese and iron. As far as is known to us, no such method has been applied to the analysis of gallium arsenide. The present paper deals with this problem.

Determination of the sum of elements using spectrophotometric extractive titration

In the methods of group determination the impurity content is most conveniently expressed in terms of a single element, *e.g.*, zinc or copper. But there is the question

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which element should be chosen as a representative. This problem is solved, however, when the content is expressed in moles. For this purpose, among others, spectrophotometric extractive titration[4] can be used. When titrating the sum of metals by this technique, there are at least two possibilities: first, direct titration at the wavelength of the maximum absorbances of chelates; second, titration at the wavelength of the maximum absorbance of the chelating agent. Both these possibilities are treated in this paper.

Dithizone was chosen as an extractive chelating agent because it is able to extract the metal impurities most frequently found in gallium arsenide. At the same time, metals which form extractable complexes with dithizone are the most interesting from the point of view of the electrical properties of the material investigated.

EXPERIMENTAL

Apparatus

Absorbance was measured using a Unicam SP 600 spectrophotometer. Titrations were performed using the cells and cell-attachment described before.[4]

Reagents

All reagents were of G.R. purity.

Water. Water was deionised and then twice distilled from an all-quartz apparatus; its conductivity was lower than 1×10^{-6} ohm^{-1} cm^{-1}.

Acids and bases. Hydrochloric acid and aqueous ammonia were prepared by isopiestic distillation. Nitric acid was twice distilled from an all-quartz apparatus.

Dithizone. Dithizone solution in carbon tetrachloride was purified in the way described by Iwantscheff[5] using twice distilled carbon tetrachloride as solvent.

Masking agents. Ammonium citrate solution (30% w/v) and sodium-potassium tartrate solution (40% w/v) were purified by extraction with a solution of dithizone in carbon tetrachloride at pH 10. The excess of dithizone was extracted with several portions of chloroform until the last extract was colourless. This manner of purification, based on the different extraction capability of the solvents mentioned above, was chosen to avoid the addition of any acid which might contaminate the resulting solution.

Preliminary experiments

Effect of bulk constituent. This effect is most important in trace analysis. At the beginning of the investigation it was supposed that the chosen reagent, dithizone, does not react with any of the bulk constituents, *i.e.*, arsenic and gallium. But recently it has been found by Pierce and Peck[6] that gallium is extracted by dithizone. The extraction constant is, however, small and extraction occurs only in the presence of a large excess of reagent. Furthermore, in the presence of citrate or tartrate ions, the most convenient agents for preventing the hydrolysis of gallium, the extraction should be substantially diminished. Our experiments have shown that at pH higher than 9 no extraction of gallium from citrate or tartrate solution occurs, when extracting with a $10^{-5}M$ solution of dithizone in carbon tetrachloride.

Effect of pH. Extraction of most of the metals extracted by dithizone is markedly affected by the presence of citrate or tartrate ions. It was necessary to find a pH range over which the efficiency of dithizone extraction is at a maximum. For this reason extraction curves of metal dithizonates in the presence of the anions mentioned above were investigated. Solutions of metal ions $0{\cdot}27M$ in citrate or $0{\cdot}285M$ in tartrate were extracted with a $10^{-5}M$ solution of dithizone in carbon tetrachloride at various pH values, the ratio of dithizone to metal content being one half of the stoichiometric one. Amounts of the extracted metal ions were determined using the monocolour or mixed colour method.[5] Results of these experiments given in Fig. 1a and in Table I show that in the presence of tartrate ion the region of maximum efficiency is at pH 9·4–9·9. In the case of nickel the efficiency is less than 99%. This is perhaps due to the short time of extraction (2 min). In the case of citrate no pH region suitable for the simultaneous extraction of the elements of interest was found.

The results here obtained are in disagreement with those of Häberli,[1] who titrates the sum of metals with dithizone in the presence of tartrate ion at pH 7–9. He does not consider the point explicitly so it is possible that he overlooked the influence of tartrate ion on the formation and extraction of dithizonates and did not verify the conditions experimentally.

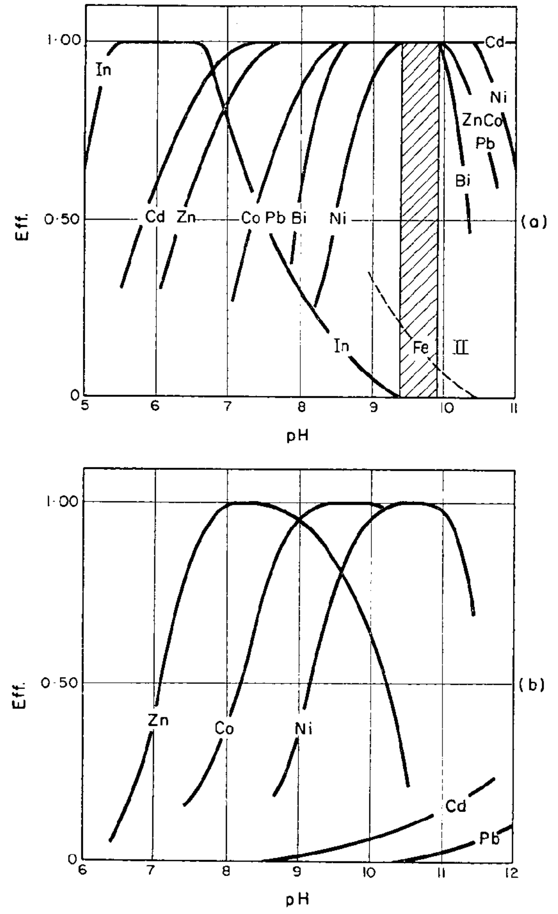

FIG. 1.—Efficiency of the consumption of dithizone as a function of pH of the aqueous phase:

a—aqucous phase 0·285*M* in tartrate (except for In and Fe)
b—aqueous phase 0·27*M* in citrate.

The direct titration. At the beginning of the investigation titrations at the wavelength of absorption maxima of individual dithizonates were used. It was established that the efficiency of consumption of dithizone is near to unity for most of the dithizone metals and that at best it is possible to titrate the sum of them at 520–525 mμ. Figure 2 shows the typical shape of the titration curve in such a titration. It was observed that larger amounts of dithizone metals give too high values of absorbance to yield precise end-point estimation. Therefore the indirect method of determination was developed, based on the estimation of excess dithizone not consumed by the extracted metals.

Recovery of dithizone. The indirect method based on the titration of excess of dithizone might be applied provided that the free dithizone is fully recovered after the extraction of metals. This assumption was checked in a series of experiments when the known amount of dithizone was extracted from carbon tetrachloride into 0·01*M* ammonia or ammoniacal 0·0285*M* tartrate solution. Dithizone was back-extracted, after acidification with sulphuric acid, with three 5-ml portions of carbon tetrachloride. The amount of dithizone was then established by titration with a standard solution of mercuric ion. Titrations were performed at 620 mμ. The shape of the titration curve is shown in Fig. 3. From Table II which shows the results of the experiments described it can be concluded that dithizone is quantitatively recovered from ammoniacal and tartrate solutions.

TABLE I.—CALCULATED* AND EXPERIMENTAL pH-BOUNDARIES FOR CONSUMPTION OF DITHIZONE

Element	Lower pH, calc.	Lower pH, found	Medium
Cu	4·02	—	0·285M sodium potassium tartrate
Cd	8·08	7·2	
Zn	7·71	7·7	
Bi	8·38	8·6	
Pb	8·59	8·5	
Co	9·12	8·5†	
Ni	10·74	9·4†	
Cd	>12	>12	0·27M ammonium citrate
Zn	—	8·0	
Pb	—	>12	
Co	—	9·3	
Ni	—	10·3	

* Calculated according to data of Charlot[10] and Yatsimirski and Vasil'ev[11] using the equation of Růžička and Starý.[12]

† Efficiency lower than 1.

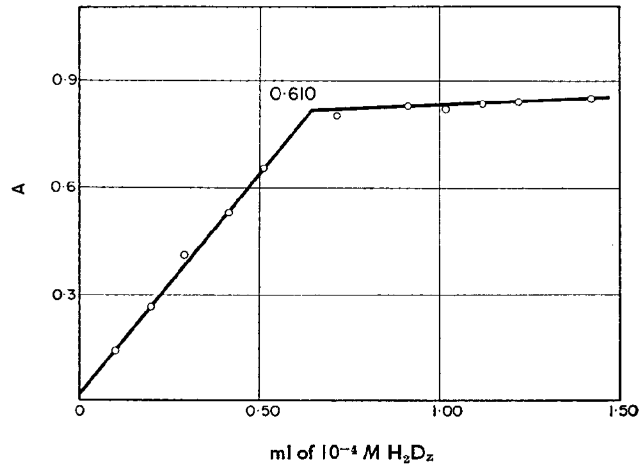

FIG. 2.—Direct titration of the sum of dithizone metals in the presence of 50 mg of Ga(III) (3·04 × 10^{-8} mole of Me(II) present, λ = 525 mμ).

After these preliminary experiments the following procedure for the determination of the sum of dithizone metals in gallium arsenide was devised and used.

Procedure

Dissolution and pretreatment of the sample. Transfer not more than 1 g of powdered sample into a 50-ml quartz beaker, and add 2 ml of hydrochloric and 2 ml of nitric acid. When the reaction has ceased, place the beaker under the infrared lamp and evaporate the excess of acids. Add 2 ml of hydrochloric acid and evaporate to syrupy consistency. Add 5 ml of sodium potassium tartrate solution (40 %), adjust the pH to 9 with ammonia using PHAN paper strips. Mix well so that the precipitate, which may be present, dissolves. Finally adjust the pH of the solution to 9·4–9·9 using a pH meter. The total volume of the solution should be *ca.* 25 ml.

Extraction. Transfer the sample solution into a 50-ml separatory funnel (A), add precisely 2·00 ml of $10^{-4}M$ dithizone solution in carbon tetrachloride and shake for 2 min. Transfer the organic

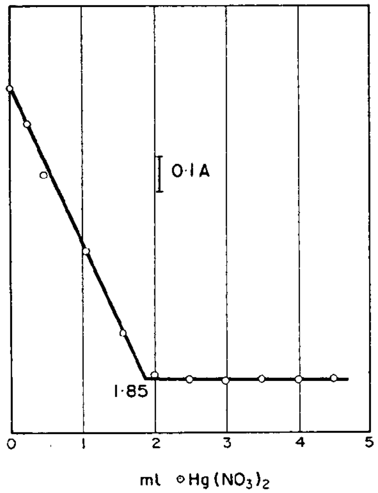

FIG. 3.—Titration of 1·00 ml of *ca.* $10^{-4}M$ H_2Dz with a solution containing 5·00 μg of Hg(II)/ml at 620 mμ.

TABLE II.—RECOVERY OF DITHIZONE FROM AQUEOUS PHASE

Amount of dithizone taken, *μmole*	Amount of dithizone found, *μmole*
0·100*	0·1008
0·100*	0·0995
0·100*	0·0970
0·100†	0·0995
0·100†	0·1003
0·100†	0·0991

* Extraction from 0·01M aqueous ammonia.
† Extraction from 0·285M ammoniacal sodium potassium tartrate solution (pH 9·5–10).

layer into the second separatory funnel (B). Repeat the extraction using 2-ml portions of dithizone till a colourless or slightly green extract is obtained. Wash the organic extracts collected in separatory funnel B with 10 ml of 0·01M ammonia. Join the aqueous layer to the sample solution in separatory funnel A, acidify it using a few drops of sulphuric acid (1 + 1), till the blue-green turbidity due to the dithizone appears. Then extract three times with 5-ml portions of carbon tetrachloride shaking each time for 1 min. Collect the extracts in the titration cell.

Titration and calculation of the results. Into the titration cell containing 15 ml of dithizone solution recovered in the previous stage, pipette say 0·5 ml of standard mercuric solution of pH 3, containing 5·00 μg/ml. Shake vigorously for 20–30 sec. Let the phases separate and measure the absorbance at 620 mμ against 15 ml of pure solvent shaken for the same time with *ca.* 5 ml of water (pH 3). Repeat the addition till the whole titration curve (Fig. 3) is obtained. Titrate 1·00 ml of $10^{-4}M$ dithizone, diluted to 15 ml with carbon tetrachloride, in the same manner (to check the concentration of the dithizone solution). To obtain the blank value carry out the whole procedure using the same amount of acids as when dissolving the test samples.

Calculate the amount of impurities present in the sample using the relation:

$$X = \left(a - a_B - \frac{b - b_B}{c}\right) \cdot \frac{1}{n} \cdot c_{H_2D_z} \cdot 10^{-3}$$

where X is the amount of impurities in moles, a and a_B are the volumes of $10^{-4}M$ dithizone solution in ml used when extracting impurities from the sample and the blank, respectively, b and b_B are the volumes in ml of standard mercuric solution used in titrating the excess of dithizone in the sample and blank, respectively, c is the titre in ml of mercuric solution of known concentration, obtained when checking the concentration of the dithizone solution, $c_{H_2D_z}$ is the molar concentration of dithizone calculated from the c-value and n is the valency of the metal ion.

RESULTS

The proposed procedure was applied to samples of gallium arsenide and checked by the method of standard addition (the standard amounts were added before the dissolution of the samples). Results of these experiments given in Table III indicate sufficient reliability of the procedure for nearly all the metals extracted by dithizone. Under the conditions of the procedure low recoveries were obtained only in the case of silver, because this element is not quantitatively extracted at the chosen pH. A "mixed n" was used to take into account the effect of tervalent and bivalent metals; "n" $= 2(m_{sum} - m_{Bi}) + 3m_{Bi}/m_{sum}$ where the m_i's are the additions in moles.

Table III.—Analysis of gallium arsenide*†

Amount present, *μmole*	Added, *μmole*	Found, *μmole*	Recovery,	
			μmole	%
0·0625	0·0250 Hg	0·0866	0·0241	96·3
0·0664	0·0955 Cu	0·1576	0·0912	95·6
0·0942	0·0955 Bi	0·1802	0·0860	91·4
0·1690	0·0955 Cd	0·2810	0·1120	108·6
0·1167	0·0955 Pb	0·2300	0·1133	109·4
0·0625	0·1490 Co	0·2010	0·1385	93·2
0·0664	0·1490 Ni	0·2009	0·1345	90·3
0·1690	0·2450 Zn	0·4050	0·2360	96·1
0·2250	0·2820 Zn, Bi, Co, Ni	0·5045	0·2795	99·3
0·0794	0·3440 Hg, Cu, Cd, Bi	0·4296	0·3502	101·7
0·0812	0·1775 Ag	0·1987	0·1175	66·2
0·1197	0·2023 In	0·1201	essentially zero	

* Average results from duplicate or triplicate determinations. Blank subtracted.
† Sample weight of 1 g.

For real samples n was taken to equal 2 because it is the most frequent value. The metals extracted with dithizone but not included in Table III, *e.g.*, iron, manganese, platinum, palladium, selenium, tellurium and thallium, should not be extracted under the conditions used.[5,7,8] Similarly, indium is not included in the sum (Fig. 1a).

On the basis of twenty blank values the standard deviation of a single determination of the blank was found to be $5{\cdot}24 \times 10^{-9}$ mole. Consequently the sensitivity limit is $2{\cdot}30 \times 10^{-8}$ mole, which represents 1·50 μg of zinc. This value, which seems rather high at first sight, is understandable, because it represents the sum of nine metals.

DISCUSSION

The procedure developed is very rapid; results may be obtained within 2 hr, including the dissolution of the sample. It offers general information about the purity of gallium arsenide but is unable to give any idea about the concentration of individual impurities. This disadvantage may be overcome, however, by a convenient spectrographic treatment of the collected extracts containing metal impurities.

In the present paper the procedure for gallium arsenide only is described but there are no obstacles in its application to the analysis of gallium or arsenic. In the case of gallium the sample weight should not be higher than 0·5 g, but when analysing arsenic no difficulties should appear with much larger samples. Furthermore, there is no need of tartrate and consequently a much wider pH range is admissible. Generally, the proposed procedure may be applied to the analysis of a variety of materials successively sequestered by tartrate ion.

Higher sensitivity might be achieved by using nitric acid of higher purity for the dissolution of the sample and also by omitting the addition of sulphuric acid when re-extracting the free dithizone. The latter method is dependent on the use of chloroform instead of carbon tetrachloride. When omitting the tartrate in the analysis of arsenic it should be also possible to titrate directly the sum of dithizone metals at lower pH, measuring the absorbance at 620 mμ after each addition. The shape of the titration curve should be such as was given for silver or bismuth in the previous paper.[4]

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Zusammenfassung—Es wird eine Arbeitsvorschrift zur Bestimmung der Summe aller mit Dithizon extrahierbaren Metalle in Galliumarsenid angegeben. Nach Lösen der Probe werden die Verunreinigungen mit mehreren Portionen einer 10^{-4} molaren Lösung von Dithizon in Tetrachlorkonlehstoff extrahiert, wobei Gallium durch Tartrat maskiert wird. Das überschüssige Reagens wird in 0,1*M* wäßrigen Ammoniak extrahiert; nach Zerlegen der Komplexe durch Extraktion in Tetrachlorkohlenstoff wird das Dithizon durch spektralphotometrische extraktive Titration bestimmt. Der pH-Einfluß wird erörtert. Die Nachweisgrenze beträgt auf Grund von zwanzig Blindbestimmungen $2{,}30 \cdot 10^{-8}$ Mol entsprechend 1,50 μg Zink.

Résumé—On donne une technique de dosage de la somme des métaux extractibles à la dithizone dans l'arséniure de gallium. Après dissolution de l'échantillon, les impuretés sont extraites par plusieurs portions de dithizone $10^{-4}M$ en tétrachlorure de carbone, le gallium étant protégé par l'ion tartrique. L'excès de réactif est extrait en solution aqueuse d'ammoniaque 0,1*M* et, après passage en tétrachlorure de carbone, on dose la dithizone par titrage spectrophotométrique par extraction. On considère l'effet du pH. La limite de détection, basée sur l'évaluation de vingt essais témoins, est de $2{,}30 \times 10^{-8}$ mole, l'équivalent de 1,50 μg de zinc.

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CERATE OXIDIMETRY OF ALPHA-HYDROXY AND ALPHA-KETO CARBOXYLIC ACIDS IN ACETIC ACID

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Summary—Methods for the preparation and use of a solution of ammonium hexanitratocerate(IV) in acetic acid as a titrant for the oxidation of alpha-hydroxy and alpha-keto carboxylic acids in acetic acid are presented. The applicability of this reagent with respect to the stoichiometry, products and reaction times obtained is discussed.

INTRODUCTION

THE first systematic study of cerium(IV) oxidation of organic compounds in aqueous solution was presented by Smith and Duke.[6] They were able to establish concise rules for the products and stoichiometry to be expected by using severe conditions, *e.g.*, 4M perchloric acid, excess oxidant, extended reaction times and often elevated temperatures, to ensure the complete oxidation of the organic molecule to formic acid and carbon dioxide. Subsequent investigators[2,3] have been able to effect cerium(IV) oxidation of organic compounds under less severe conditions by utilising non-aqueous solvents. The oxidations previously reported in the literature[4,5] have been of structurally unrelated compounds and of little prognostic value. Consequently, a study of cerium(IV) oxidation of alpha-hydroxy carboxylic acids and some related compounds in acetic acid was undertaken to ascertain the extent to which knowledge of the stoichiometry, products and reaction times would be analytically useful.

EXPERIMENTAL

Reagents

Cerium(IV) *reagent* (0·05M). Nine hundred and fifty ml of acetic acid, which is 1M in water, are heated to 60° in a 1-litre round-bottom flask and 26 g of ammonium hexanitratocerate(IV) are added. The solution, which is constantly stirred and protected from light, is allowed to cool to room temperature, then transferred to an amber bottle for storage.

Sodium oxalate. 4·6904 g of dried sodium oxalate (0·0700N) are dissolved in 1 litre of glacial acetic acid which is 1M in perchloric acid.

Organic compounds. Glycolic acid, lactic acid and pyruvic acid were used without further purification and the purity was established by titration with standard base. Mandelic acid was recrystallised twice from benzene. Phenyllacetic acid was recrystallised from benzene and the purity established by titration with standard base. Reagent-grade citric acid and tartaric acid were used without further purification. Sodium benzoyl formate was recrystallised from dioxan-water. Sodium glyoxylate was recrystallised from acetone-water. Phenylcyclopentylglycolic acid and mesitoylformic acid were organic research preparations and were used without further purification.

Procedures

Standardisation of cerium reagent. Four ml of concentrated perchloric acid (70%) are added to 50 ml of the cerium reagent and the resultant solution immediately titrated with standard sodium oxalate either to the disappearance of the yellow colour of cerium(IV) or to a biamperometric end-point using a Sargent "Model III" manual polarograph equipped with platinum-platinum electrodes at an applied potential of 400 mV.

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Oxidation of organic compounds. The organic sample is dissolved in 50 ml of glacial acetic acid and 8 ml of concentrated perchloric acid are added. The solution is immediately titrated with the cerium reagent, preferably using an amber burette, to a biamperometric end-point. An alternate procedure is to add an excess of the cerium reagent to the organic sample dissolved in glacial acetic acid. After a suitable interval, the solution is made 1*M* in perchloric acid and the excess cerium(IV) immediately titrated with a solution of standard sodium oxalate. All oxidations are performed at room temperature.

RESULTS AND DISCUSSION

The alpha-hydroxy acids studied can be divided into two groups. One group, including glycolic, lactic, phenyllactic, mandelic and tartaric acids, produces an aldehyde as a result of the two-electron change and an acid as a result of a four-electron change. The other group, including phenylcyclopentylglycolic acid and citric acid, produces ketones as a result of a two-electron change. The alpha-keto acids (pyruvic, benzoylformic and glyoxylic acids), which can be readily represented as reacting in their hydrated forms to give acids, are in the second group.

Glycolic acid, lactic acid and phenyllactic acid

These compounds are slowly oxidised to the corresponding aldehyde and carbon dioxide; the resultant aldehyde is oxidised somewhat slowly to the acid:

$$\mathrm{RCHOHCO_2H + 2Ce^{4+} \rightarrow RCHO + 2Ce^{3+} + 2H^+ + CO_2}^*$$

$$\mathrm{RCHO + H_2O + 2Ce^{4+} \rightarrow RCO_2H + 2Ce^{3+} + 2H^+.}$$

The overall reaction proceeds so slowly that the stability of the reagent becomes the limiting factor in precisely determining the stoichiometry.

Mandelic acid

The cerium reagent rapidly oxidises the mandelic acid to benzaldehyde and carbon dioxide:

$$\mathrm{C_6H_5CHOHCO_2H + 2Ce^{4+} \rightarrow C_6H_5CHO + 2Ce^{3+} + 2H^+ + CO_2.}$$

The benzaldehyde was identified with 2,4-dinitrophenylhydrazine and the carbon dioxide was quantitatively recovered by means of standard solutions of barium hydroxide. As seen from Table I, the milliequivalents of cerium(IV) per millimole, of acid for the direct titration are a little over two, probably as a result of the reaction of benzaldehyde with the cerium reagent. The values by the excess method average 2·00. Apparently, under these conditions, the benzaldehyde is very much less reactive than the mandelic acid.

Tartaric acid

Not only is tartaric acid an alpha-hydroxy acid, but it is also a diol, so that there is a possibility of a diol cleavage competing with the decarboxylation. Four equivalents of cerium(IV) produce 2 moles of carbon dioxide, which was determined by sweeping the reaction mixture with nitrogen and collecting the carbon dioxide in solutions of standard barium hydroxide. Tartronaldehydic acid ($\mathrm{CO_2HCHOHCHO}$) was identified *via* the *p*-nitrophenylhydrazone after 2 equivalents of cerium(IV) had been consumed. Glyoxal (CHOCHO) was detected *via* a spot test using dianisidine[1] after 4 equivalents of cerium(IV) had been consumed. The amount of formic acid present

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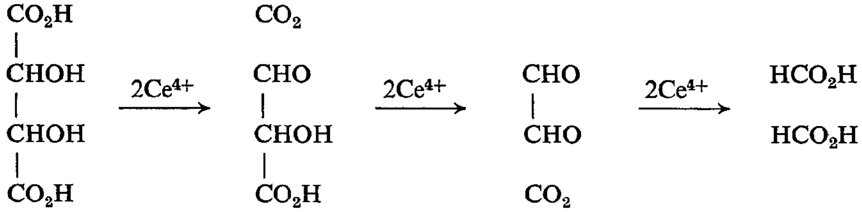
* Because the exact nature of the cerium species in solution is unknown, no attempt will be made to present a balanced system.

TABLE I.—STOICHIOMETRY OF CERATE OXIDATIONS

Acid	Mmole	Reaction times	Mequiv of Ce(IV)/ mmole organic
Glycolic	0·500	4·8 hr	1·12
		9·0	1·53
		12·0	1·91
		22·0	2·08
Lactic	0·620	57·0 hr	2·55
			2·60
Phenyllactic	0·595	1·5 hr	0·93
		10·0	1·11
Mandelic	0·100	Immed.*	2·03
			2·04
			2·04
	0·200	5 min†	1·99
	0·429		2·01
	0·475		1·99
	0·476		2·01
Tartaric	0·1327	Immed.	4·56
			4·59
	0·1335		4·45
			4·45
			4·45
	0·1661	80 min	6·23
		90 min	6·50
		95 min	6·21
Phenylcyclopentylglycolic	1·032	Immed.	1·98
			1·98
			1·98
		5 min	2·02
			2·00
			2·01
			1·99
			2·00
			2·01
Pyruvic	0·644	5 min	2·01
			1·99
			2·00
Benzoylformic	0·487	5 min	1·99
	0·477		1·99
	0·464		1·98
Glyoxylic	0·756	5 min	2·00
	0·773		2·00
	0·839		2·00
Citric	0·0250	Immed.	3·95
			3·97
			4·00
	0·115	25 min	13·1
	0·0645	85 min	12·6
			12·5
			11·6

* Direct titration
† Indirect titration

after the addition of 6 equivalents of cerium(IV) was estimated *via* the reduction of mercuric chloride. Consequently, the oxidation of tartaric acid can be represented as proceeding in the following manner:



$$\begin{array}{c}\mathrm{CO_2H}\\|\\\mathrm{CHOH}\\|\\\mathrm{CHOH}\\|\\\mathrm{CO_2H}\end{array} \xrightarrow{2\mathrm{Ce}^{4+}} \begin{array}{c}\mathrm{CO_2}\\ \\\mathrm{CHO}\\|\\\mathrm{CHOH}\\|\\\mathrm{CO_2H}\end{array} \xrightarrow{2\mathrm{Ce}^{4+}} \begin{array}{c}\mathrm{CHO}\\|\\\mathrm{CHO}\\ \\\mathrm{CO_2}\end{array} \xrightarrow{2\mathrm{Ce}^{4+}} \begin{array}{c}\mathrm{HCO_2H}\\ \\\mathrm{HCO_2H}\end{array}$$

Tartaric acid is rapidly oxidised, but the stoichiometry obtained in the direct titration does not correspond to any well defined stage in the oxidation sequence and is not analytically valuable. Nevertheless, it is apparent that the reagent will preferentially react with the alpha-hydroxy carboxyl functional group rather than the diol functional group.

Phenylcyclopentylglycolic acid

This acid is rapidly oxidised to phenylcyclopentyl ketone and carbon dioxide.

$$\mathrm{C_6H_5C(C_5H_9)OHCO_2H} + 2\mathrm{Ce}^{4+} \rightarrow \mathrm{C_6H_5COC_5H_9} + 2\mathrm{Ce}^{3+} + \mathrm{CO_2} + 2\mathrm{H}^+.$$

The ketone was identified *via* the 2,4-dinitrophenylhydrazone and the carbon dioxide was quantitatively recovered with solutions of standard barium hydroxide. Here again, even though the direct titration is more precise, the average value of 2·01 for the stoichiometry from the excess method is more consistent with the oxidation reaction.

Citric acid

The cerium reagent rapidly oxidises citric acid. Four equivalents of cerium(IV) produce 1·4 mole of carbon dioxide per mole of citric acid. The initial product is probably acetone dicarboxylic acid ($\mathrm{CO_2HCH_2COCH_2CO_2H}$), which is also rapidly oxidised by the cerium reagent. The stoichiometry as indicated by the direct titration is probably not valid and is merely a psuedo end-point occurring at an integral number of equivalents of cerium(IV) per mole of citric acid due to the cummulative effect of reactive intermediates.

Pyruvic acid, benzoylformic acid and glyoxylic acid

These compounds are all rapidly oxidised by the cerium reagent to carbon dioxide and the corresponding acid with one less carbon. Benzoic acid was isolated by carbon disulphide extraction:

$$\mathrm{RCOCO_2H} + \mathrm{H_2O} \rightarrow \mathrm{RC(OH)_2CO_2H} + 2\mathrm{Ce}^{4+} \rightarrow \mathrm{RCO_2H} + 2\mathrm{Ce}^{3+} + \mathrm{CO_2} + 2\mathrm{H}^+.$$

Direct titrations with the cerium reagent resulted in values slightly less than those provided by the excess method.

Mesitoylformic acid

This acid consumes 3·9 equivalents of cerium(IV) per mole by the excess method. Variable results caused by decarboxylation of the compound in the presence of acid were obtained for the carbon dioxide recoveries. The values approached 1·8 mole of carbon dioxide per mole of acid. It was possible to identify mesitol as a product by isolation of the dibromo derivative, so that the reaction could be represented as:

$$C_6H_2(CH_3)_3COCO_2H + 2H_2O + 4Ce^{4+} \rightarrow C_6H_2(CH_3)_3OH + 2CO_2 + 4Ce^{3+} + 4H^+.$$

Apparently, the steric effect of the ortho methyl groups on the benzene ring obviate the formation of mesitoic acid, which is fairly stable to the cerium reagent, and enables the oxidation to proceed further.

CONCLUSIONS

It is readily apparent that molecules with similar functional groups are oxidised by the cerium reagent at radically different rates. Factors such as the steric and electronic environment of the functional group oxidised and the stability of the products play their usual prominent roles. The low mineral acid content and low dielectric constant of the solvent no doubt contribute to the selectivity of the cerium reagent. Integral stoichiometry, which does not always indicate stable oxidation products, is best obtained by use of the excess method with compounds that are rapidly oxidised. Generalisations which can be made on the basis of the compounds studied are:

(1) Alpha-keto acids are rapidly oxidised and amenable to accurate determination.

(2) Aliphatic alpha-hydroxy acids are slowly oxidised and not amenable to accurate determination.

(3) Alpha-hydroxy acids with an alpha-phenyl group are rapidly oxidised and amenable to accurate determination.

(4) Polycarboxylic hydroxy-acids are rapidly oxidised but are not amenable to accurate determination.

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Zusammenfassung—Methoden zu Herstellung und Gebrauch einer Lösung von Ammoniumhexanitratocerat(IV) in Essigsäure als Titrierlösung zur Oxydation von alpha-Hydroxy- und alpha-Keto-Carbonsäuren in Essigsäure werden angegeben. Die Anwendbarkeit des Reagens bezüglich Stöchiometrie, Produkten und Reaktionszeiten wird diskutiert.

Résumé—On présente des méthodes pour la préparation et l'emploi d'une solution d'hexanitratocérate (IV) d'ammonium en acide acétique comme agent de dosage pour l'oxydation des acides α-hydroxy et α-céto carboxyliques en acide acétique. On discute des possibilités d'application de ce réactif des points de vue stoechiométrie, produits et temps de réactions obtenus.

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AMPEROMETRY WITH TWO POLARISABLE ELECTRODES—XI*

DETERMINATION OF BISMUTH BY EDTA TITRATION

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Summary—Optimum conditions have been found for a highly selective determination of bismuth *via* EDTA titration with biamperometric indication of the end-point. The influence of the applied potential, pH and stirring on the accuracy and selectivity of the determination has been studied. In a medium of 0·4*M* nitric acid only high concentrations of iron(III) and copper(II) interfere with the determination of bismuth. Zirconium, thallium(III) and indium interfere even in small concentrations. The average error of the determination of 5–100 mg of bismuth (when titrated with 0·05*M* EDTA solution) is ±0·1% rel. and for the determination of 0·5–10 mg it is ±0·3% rel. (0·005*M* EDTA). The method has been verified by the analysis of a Wood's metal of known composition.

INTRODUCTION

IN THE titration of some metals with EDTA biamperometric indication of the end-point is satisfactory in acidic media. The limited pH range of the titration is influenced only by the stability and rate of formation of the complex formed during the titration. The determination of the metal can be carried out in an acidic medium where the determination is most selective and visual indicators fail.[1]

Up to now optimum conditions for the determination of iron(III),[2] thallium(III),[3] thorium,[4] indium[5] and gallium[6] have been found by using chelometric titration in a strongly acidic medium with biamperometric indication of the end-point. In the present paper conditions for the determination of macro amounts of bismuth are given.

EXPERIMENTAL

Reagents

0·05*M EDTA solution.* Prepared by dissolving Chelaton III (Lachema, Brno, Czechoslovakia) in water and standardising by titration with lead nitrate solution using Xylenol Orange as indicator.

0·05*M Bismuth nitrate solution.* Prepared by dissolving bismuth nitrate pentahydrate in dilute nitric acid (0·1*M*) and standardised chelometrically using Xylenol Orange as indicator.

Buffer solutions (pH 1·5–2·5). Prepared from 1*M* trichloroacetic acid by neutralisation with aqueous ammonia, under potentiometric control of pH with a glass electrode.

Apparatus

The same instruments as described in a previous paper were used.[7] The electrodes were two platinum plates (5 × 6 × 0·2 mm) fused in glass tubes. As detector a micro ammeter (0–200 μA) was used.

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* Part X: J. Vorlíček and F. Vydra, *Collection Czech. Chem. Commun.*, in press.

Procedure

To a suitable amount of 0·05*M* bismuth nitrate solution a measured amount of 7*N* nitric acid (or 10 ml of 1*M* buffer solution) was added. When the selectivity of the determination was studied, the chosen amount of the substance to be examined was added. The solution was diluted to 100 ml. In the absence of this information the titrations must be carried out in 0·5*M* nitric acid 2 or 3 min after the potential has been applied on the electrodes. The applied potential was 1·5V and the rate of stirring 1500 rpm. After each addition of the titrant the value of the current was read on the micro ammeter. In the neighbourhood of the equivalence point the titration curve is linear. All data given in this paper are arithmetical means of three determinations.

RESULTS

As in previous papers it has been found that the magnitude of the applied potential does not influence the accuracy of the determination when a sufficiently sensitive detector is used. Using a micro ammeter a suitable value of applied potential is 1·5V.

The influence of the rate of stirring and of temperature on the course of the titration with biamperometric end-point detection is the same as in the determination of other metals carried out in an acidic medium. If the rate of stirring is higher than 600 rpm the course of the titration is independent of stirring.

An increase in temperature gives a small increase of current. Because higher temperatures increase the hydrolysis of bismuth salts, titration of bismuth at a higher temperature is not recommended.

Passivation of the electrodes during the titrations does not occur in practice. To prevent passivation phenomena, it is quite sufficient to wash the electrodes with water after each titration, and occasionally to wash them with a warm mixture of sulphuric acid and potassium dichromate solution, then immerse the electrodes in distilled water for 2–3 hr.

TABLE I.—INFLUENCE OF pH ON THE ACCURACY OF THE DETERMINATION OF BISMUTH

Medium	Bismuth, *mg* Taken	Bismuth, *mg* Found	Error, % *rel.*
1*N* HNO_3	22·80	16·2	−29·0
0·7*N* HNO_3	22·80	20·75	−9·0
0·6*N* HNO_3	22·80	22·63	−0·7
0·5*N* HNO_3	22·80	22·69	−0·5
0·4*N* HNO_3	22·80	22·85	+0·2
0·2*N* HNO_3	22·80	22·75	−0·2
0·1*N* HNO_3	22·80	22·80	0·0
pH 1·5	22·80	22·75	−0·2
pH 2·1	22·80	22·63	−0·7
pH 2·5	22·80	21·43	−6·0

The biamperometric titration of bismuth was examined in more acidic solutions because of the great stability of the bismuth-EDTA chelate and because solutions of bismuth salts hydrolyse easily in slightly acidic media.

A series of titrations was carried out at various concentrations of nitric acid and in various buffer solutions; the corresponding titration curves are given in Fig. 1. From these curves it is clear that the error is ±0·2% rel. in the range from 0·4*N* nitric acid to pH 2. At higher concentrations of nitric acid the corresponding curves are not sharp enough in the neighbourhood of the equivalence point and the results of the titrations under these conditions have a large negative error. Above pH 2 hydrolysis effects influence the course of the titration and the results are lower.

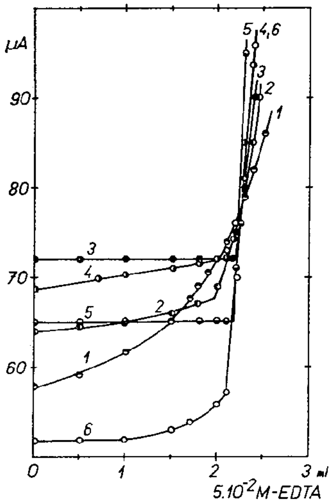

FIG. 1.—Influence of concentration of nitric acid and pH on the course of the titration curves in the biamperometric titration of bismuth with EDTA [2 ml of 0·05*M* $Bi(NO_3)_3$; Pt-Pt electrodes; applied potential: 1·5V; total volume: 100 ml]: (1) 1*N* HNO_3; (2) 0·7*N* HNO_3; (3) 0·4*N* HNO_3; (4) pH 1·5; (5) pH 2·1; (6) pH 2·5.

Concentration range and accuracy

Using 0·05*M* EDTA solution as titrant and biamperometric indication it is possible to determine 5·22–104·2 mg of bismuth with an average error of ±0·1% rel. in 0·4*N* nitric acid. This accuracy is better than that obtained in the visual titration of bismuth with EDTA. Using a micro ammeter 0·005*M* EDTA can be used as titrant. The identification of the equivalence point is not so precise in this case (see Fig. 2), but the consumption of the titrant can be read with sufficient accuracy. Under identical conditions as in the titration with 0·05*M* EDTA, bismuth in the range 0·52–10·4 mg can be determined with 0·005*M* EDTA with an average error not exceeding ±0·3% rel.

The results obtained show that even more dilute solutions of EDTA could be used for biamperometric titration of bismuth.

Selectivity

The determination of bismuth described above is not altered by any concentration of magnesium, cobalt, strontium, barium, beryllium, uranium(VI), manganese(II), silver, aluminium, thallium(I), fluoride, perchlorate and sulphate. The determination of 5·22 mg of bismuth in the presence of 1500 mg of lead, 2240 mg of cadmium, 1300 mg of zinc, 1160 mg of cobalt, 1170 mg of nickel, 175 mg of lanthanum and 290 mg of thorium has been carried out with an error not exceeding ±0·3% rel. Under certain conditions bismuth may also be determined in the presence of 45 mg of scandium, 70 mg of gallium, 55 mg of iron(III), 6·2 mg of copper and 300 mg of sodium chloride. Even small concentrations of indium, zirconium and thallium(III) interfere with the determination of bismuth.

These data show that the described biamperometric titration of bismuth should be successfully applicable in analytical practice because of its high selectivity.

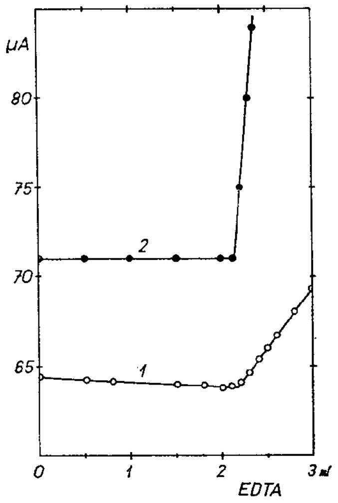

Fig. 2.—Influence of the titrant concentration on the course of the titration curves in the biamperometric titration of bismuth with EDTA [2 ml of 0·005*M* or 0·05*M* $Bi(NO_3)_3$; 0·4*N* HNO_3; Pt-Pt electrodes; applied potential: 1·5V; total volume: 100 ml]: (1) 0·005*M* EDTA; (2) 0·05*M* EDTA.

Determination of bismuth in Wood's metal

As an example of the application of the described titration the determination of bismuth in low-melting alloys has been chosen. The procedure given describes the course of the determination of bismuth in Wood's metal.

Treat 0·2 g of sample with 20 ml of conc. nitric acid and evaporate almost to dryness. Evaporate five times with 10-ml portions of 40% hydrobromic acid. Dissolve the final residue in 10 ml of conc. nitric acid, transfer to a 100-ml volumetric flask and dilute to the mark with water. Twenty-five ml of this final solution are transferred to a beaker, diluted to 50 ml with water and titrated under biamperometric control with 0·05*M* EDTA solution at an applied potential of 1·5V. For calculating the end-point, plot the current readings against ml of EDTA added.

Using the above procedure 50·02% of bismuth (average of three titrations) was found for an alloy sample of composition 49·92% of bismuth, 36·60% of lead, 4·50% of cadmium and 8·98% of tin (control analysis carried out chelometrically[8]).

Résumé—On a trouvé les conditions optimales d'un dosage hautement sélectif du bismuth par titrage au moyen d'EDTA avec indication biampérométrique du point final. On a étudié l'influence du potentiel appliqué, du pH et de l'agitation sur la précision et la sélectivité du dosage. Dans un milieu acide nitrique 0,4*M*, seules des concentrations élevées en fer(III) et cuivre(II) interfèrent avec le dosage du bismuth. Le zirconium, le thallium(III) et l'indium interfèrent même à faibles concentrations. L'erreur moyenne du dosage de 5–100 mg de bismuth (lorsqu'on titre par une solution 0,05*M* d'EDTA) est de ±0,1% rel. et pour le dosage de 0,5–10 mg elle est de ±0,3% rel. (EDTA 0,005*M*). On a vérifié la méthode par l'analyse d'un métal de Wood de composition connue.

Zusammenfassung—Die günstigsten Bedingungen für eine hochselektive Bestimmung von Wismut durch EDTA-Titration mit biamperometrischer Endpunktsanzeige wurden ermittelt. Untersucht wurden der

Einfluß der angelegten Spannung, des pH und der Rührung auf Genauigkeit und Selektivität der Bestimmung. In $0{,}4M$ Salpetersäure stören die Wismutbestimmung nur hohe Eisen(III)- und Kupfer(II)-Konzentrationen. Zirkon, Thallium(III) und Indium stören auch in kleinen Konzentrationen. Der mittlere Fehler der Bestimmung von 5–100 mg Wismut (titriert mit $0{,}05M$ EDTA-Lösung) beträgt ±0,1% relativ und bei der Bestimmung von 0,5–10 mg ±0,3% relativ ($0{,}005M$ EDTA). Die Methode wurde durch Analyse eines Woodschen Metalles bekannter Zusammensetzung geprüft.

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SPECTROFLUORIMETRIC DETERMINATION OF SUBMICROGRAM AMOUNTS OF ALUMINIUM USING SALICYLIDENE-*o*-AMINOPHENOL

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Summary—Salicylidene-*o*-aminophenol provides a sensitive spectrofluorimetric reagent for the determination of aluminium down to 27 ng (or $2{\cdot}7 \times 10^{-4}$ ppm in the final solution). The most suitable conditions of pH (5·6), reagent concentration and development time (>20 min) have been established. Extraction with sodium diethyldithiocarbamate into ethyl acetate at the pH of the determination renders the method highly selective; out of 46 foreign cations examined only chromium(III), scandium and thorium interfere. Anions which form complexes with aluminium, such as citrate, tartrate and fluoride, also cause interference, but none of the common anions interferes. A 1:1 stoichiometry of the complex has been established and some conclusions have been drawn concerning its nature.

INTRODUCTION

THE standard fluorimetric methods for the determination of aluminium utilise Morin (3,5,7,2′,4′-pentahydroxyflavone)[1], Pontachrome Blue Black R (4-sulpho-2-hydroxy 1-naphthalene-azo-2′-naphthol)[2] or 8-hydroxyquinoline.[3] In a recent communication from this laboratory, 2-hydroxy-3-naphthoic acid[4] has been described as an alternative reagent which possesses several advantages.

The first two reagents listed necessitate the use of highly coloured solutions and the fluorescence emission is, therefore, measured in a region where most detectors are less sensitive. Furthermore, there is considerable overlap of absorption and emission bands with both these reagents and hence an internal screening effect on the fluorescence of the aluminium complex. Morin is a highly unselective reagent and the Pontachrome BBR method, although reported to be specific for aluminium is, in fact, vitiated by the precipitation of the hydroxides of many metals; it also requires a development time of nearly 1 hr. 8-Hydroxyquinoline forms fluorescent complexes with very many cations, and consequently more than one extractive separation is usually necessary, often at different pH values. The 2-hydroxy-3-naphthoic acid reagent, which was developed principally as a reagent for beryllium, provides a method for aluminium which is basically more selective than the Morin and 8-hydroxyquinoline methods and relies on the use of masking agents to overcome the difficulties arising from the precipitation of metal hydroxides. However, many ions still cause serious interference.

The present paper describes a method based on the use of salicylidene-*o*-aminophenol, which is considerably more sensitive than the previous methods, requires only a short development time and which, by incorporation of a simple and rapid extractive separation, achieves much higher selectivity.

In his studies on the fluorescence reactions of Schiff bases with metal ions,[5–7] Holzbecher found that salicylidene-*o*-aminophenol gave a very sensitive fluorescence reaction with aluminium. This reaction has been used[8] to determine aluminium in some simple compounds. The reagent is conveniently prepared from readily available materials[9] and can be easily purified. Many cations interfere with the reaction, but the majority may be removed by extraction as their diethyldithiocarbamates into ethyl acetate at the pH of the determination, without adverse effect on the subsequent spectrofluorimetric determination of aluminium. Out of 46 cations examined, the only interferences which could not be removed readily were those due to chromium(III), scandium and thorium.

The method provides a rapid, sensitive and selective determination of nanogram to microgram quantities of aluminium using virtually colourless solutions.

EXPERIMENTAL

Apparatus

A Farrand Optical Co. Spectrofluorimeter (Cat. No. 104244) fitted with a 150-W d.c. xenon arc lamp (Hanovia Division Cat. No. 901 C-1) and RCA 1P 28 photomultiplier. Both excitation and emission beams are passed through monochromators with 10-mμ half-bandwidth slits, the effective optical path lengths in solution being 5 mm for excitation and 10 mm for emission. Fused quartz cells (10 × 20 × 50 mm) were used throughout.

Vibron pH meter, model 39A (Electronic Instruments Ltd., Richmond, Surrey, England).

Volumetric flasks were periodically coated with silicone "Repelcote", 2% dimethyldichlorosilane in carbon tetrachloride (Hopkin and Williams Ltd.), to minimise adsorption of metal ions on the glass.

Reagents

0·1% *Salicylidene-*o*-aminophenol solution.* Prepared from salicylaldehyde (General Purpose Reagent, B.D.H. Ltd., Poole, England) and *o*-aminophenol (Technical Grade, B.D.H. Ltd.) by the method of Freeman and White.[9]

The microanalytical results obtained for the analyses of two different preparations of the reagent corresponded to:

Found:	C: 73·2, 72·9%;	H: 5·63, 5·08%;	N: 6·47, 6·77%.
Calculated:	C: 73·3%;	H: 5·16%;	N: 6·58%.

Dissolve 0·5 g of the solid reagent in 500 ml of acetone. This reagent solution is stable for several weeks.

Buffer solution (pH 5·6) Add sufficient glacial acetic acid (*ca.* 10 ml) to 50 g of ammonium acetate in 400 ml of water to give pH 5·60 ± 0·05.

$10^{-2}M$ *Aluminium solution.* Dissolve 0·4744 g of potassium alum, [$AlK(SO_4)_2 \cdot 12\,H_2O$], in 100 ml of water. Dilute this stock solution as required before use for the preparation of calibration curves. Solutions more dilute than $10^{-3}M$ should not be stored for any length of time, even in siliconed flasks because of the tendency for aluminium to be adsorbed strongly on glassware. 1 ml of $10^{-6}M$ solution = 0·027 μg of aluminium.

0·2% *Sodium diethyldithiocarbamate solution.* Dissolve 1 g of sodium diethyldithiocarbamate (Hopkin and Williams Ltd.) in 500 ml of water. This solution is subject to oxidation and should be made up daily.

Ethyl acetate. (General Purpose Reagent, Hopkin and Williams Ltd.)

All other reagents were of analytical reagent quality. Distilled water from an all-glass distillation apparatus was used.

Procedure

Add a 10-ml aliquot of standard aluminium solution, containing 2·7 × 10^{-2} μg to 2·7 μg of aluminium, to a 250-ml separatory-funnel containing 10 ml of pH 5·6 buffer and 30–35 ml of ethyl acetate. Add 10 ml of 0·2% sodium diethyldithiocarbamate solution and shake for 30 sec. Reject the organic phase, which contains the undesired foreign ions, and transfer the aqueous extract to a 100-ml standard flask. Add 5 ml of 0·1% salicylidene-*o*-aminophenol reagent and dilute to 100 ml with water. Measure the fluorescence of the solution after 20 min at 520 mμ using an excitation wavelength of 410 mμ.

The calibration curves should be prepared as above, using aliquots of $10^{-4}M$ to $10^{-6}M$ aluminium solutions freshly prepared by dilution of the $10^{-2}M$ or 10^{-3} M stock solution. The curves pass above the origin because of the blank value.

RESULTS AND DISCUSSION

Spectral characteristics

The uncorrected emission and excitation spectra are given in Fig. 1. The excitation spectrum has maxima at 410 and *ca.* 340 mμ, in agreement with the absorption spectrum of the reagent, while the fluorescence emission maximum occurs at 520 mμ.

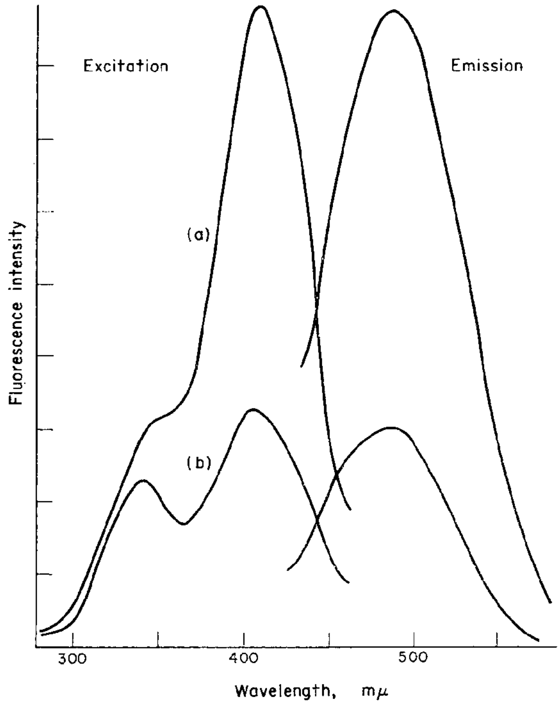


FIG. 1.—Uncorrected excitation and emission spectra of (a) 0·005% reagent with 2·7 × 10^{-3} μg/ml aluminium; (b) 0·005% reagent alone.

The correction curves for variations of photomultiplier response (Fig. 2a) and source intensity with wavelength (Fig. 2b) have been obtained using a standard tungsten lamp. The corrected spectra have been published elsewhere.[10]

The peak at 340 mμ was found by spectrophotometry to be characteristic of the reagent, and contributes little towards the fluorescence of the complex.

Influence of pH

The intensity of fluorescence was measured over a range of pH values obtained by adjusting the pH of the solution with ammonia or acetic acid (Fig. 3b). The aluminium complex shows a sharp pH dependence with a maximum at pH 5·6 in agreement with other work.[8] It is, therefore, advisable to check the pH before measurement;

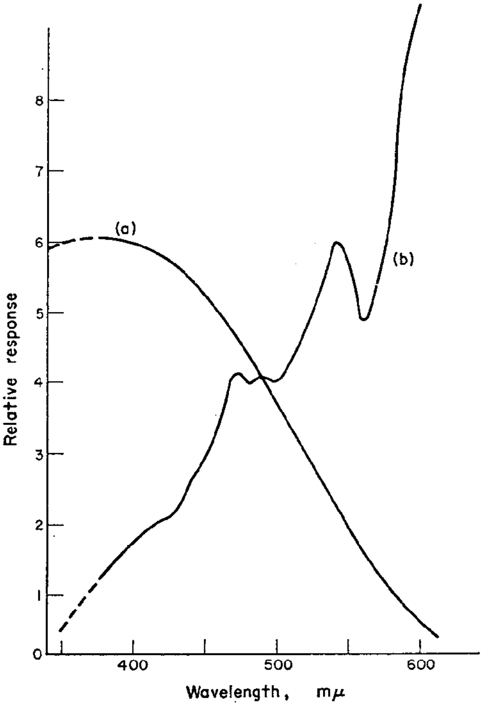


FIG. 2.—(a) Relative quantum response of IP 28 photomultiplier plus analysing monochromator against wavelength. (b) Relative quantum distribution of 150-W d.c. Xenon arc lamp plus excitation monochromator.

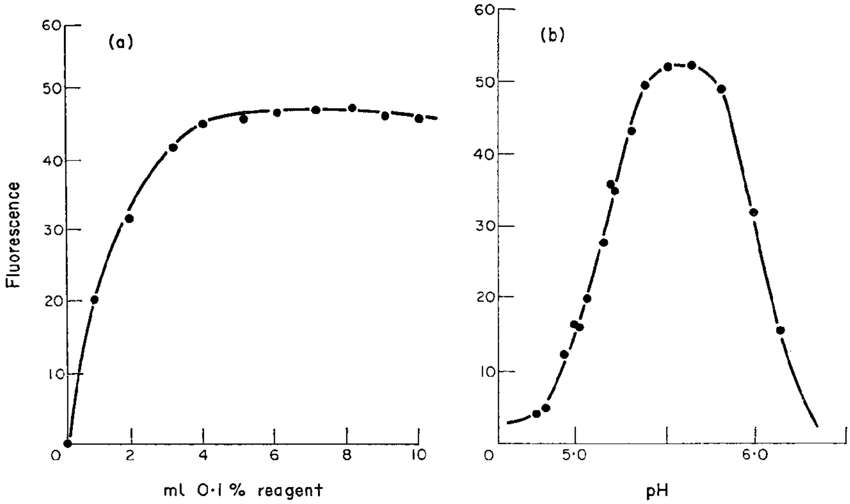


FIG. 3.—(a) Variation of intensity of fluorescence of a solution containing 2·7 μg of aluminium with concentration of reagent. (b) Variation of intensity of fluorescence with pH, for a solution containing 0·005% reagent and 0·27 μg of aluminium.

the tolerance is ±0·1 pH unit, but in this respect the proposed method does not demand closer limits than other fluorimetric procedures.[2,4]

Reagent concentration

The effect of variation of the reagent concentration on the fluorescence intensity of the aluminium complex is shown in Fig. 3a. In the recommended procedure, 5 ml of 0·1% reagent are used, corresponding to a 1000-fold excess over the upper limit of aluminium used in this investigation.

Influence of time

The fluorescence intensity of a 10^{-6} M (0·027 ppm) aluminium test solution was measured and found to be steady 15 min after mixing. A constant ratio was obtained thereafter when measured against a quinine sulphate standard throughout the next 4 hr; on standing overnight the ratio had dropped by only 3%.

On addition of the reagent, a yellow colour is first observed both in the absence and presence of aluminium, which gradually fades after dilution. The fading process takes 10–15 min, after which measurements can be made. The fading is independent of lighting conditions, because a reagent blank, freshly diluted and kept in a dark cupboard, fades at the same rate as one exposed to normal laboratory illumination. Because the fading process is rapid in solutions of low pH, it is thought that the reagent, but not the aluminium complex, is hydrolysed in the acid solution. Although aluminium reacts with salicylaldehyde, one of the hydrolysis products, to give a green fluorescence, the reaction is not as sensitive as with the Schiff base reagent.

Limits of determination

A linear relationship between fluorescence intensity and concentration of the final solution exists for aluminium in the range 10^{-8} M ($2{\cdot}7 \times 10^{-4}$ ppm) up to $10^{-6}M$, *i.e.*, for amounts ranging from 27 ng to 2·7 μg in 100 ml. The linearity probably extends above this range. If due allowance is made for the volume of reagents to be added in the procedure, this corresponds to a working concentration range of 4×10^{-4} to 4×10^{-2} ppm for the original aluminium test solution. The blank value corresponds to 0·1 μg of aluminium.

The limit of determination of aluminium using the 2-hydroxy-3-naphthoic acid reagent previously investigated in this laboratory[4] was *ca.* 270 ng so that the present procedure is approximately 10 times more sensitive.

Attempts were made to reduce the value of the blank of the present reagent by preparing it in the presence of EDTA, to remove trace metals from the starting materials, and by repeated recrystallisation of the reagent from various solvents to remove fluorescent impurities. The use of appropriate filters on emission and excitation beams to minimise second-order diffraction and the variation of monochromator slit-widths was also examined. None of these approaches caused any significant reduction of the residual fluorescence. Reduction of the amount of reagent also reduced the metallofluorescence from a given amount of aluminium, and it was not felt necessary to sacrifice sensitivity because the blank value was reproducible. The blank is due to salicylaldehyde produced by hydrolysis of reagent. This also accounts for the relatively large excess of reagent required.

Interferences

Five ml of 10^{-5} *M* aluminium solution ($1{\cdot}35 \times 10^{-1}$ μg) were used with a 100-fold molar excess of foreign ion. The limiting error was taken empirically as ±5% of the pure aluminium solution. Marginal interferences were examined in more detail. The following 34 cations did not interfere beyond the diethyldithiocarbamate extraction stage: Li, Na, K, NH_4, Be, Mg, Ca, Sr, Ba, Ga, In, Tl(I), Tl(III), Sn(IV), Pb, As(III), Se(IV), Te(IV), V(IV), Mn, Fe(II), Fe(III), Co, Ni, Cu(II), Zn, Cd, Hg(II), Y, La, Mo(VI), Ag, Ce(III).

Antimony(III), bismuth and uranium(VI) were quantitatively removed after two or more extractions and did not subsequently interfere. It was more convenient to use carbon tetrachloride for these multiple extractions and ethyl acetate only for the final extraction.

Tungsten formed a yellow product with the reagent which gave low results, but only when present in greater than a 10-fold excess. A similar interference caused by vanadium(V) and cerium(IV) could be eliminated completely by reduction with ascorbic acid before extraction. Reduction with ascorbic acid also improved the extraction of iron and the stability of the reagent to oxidation at pH 5·6. Tin(II) was best removed by extraction of tin(IV) diethyldithiocarbamate following oxidation with hydrogen peroxide and removal of the peroxide. Zirconium gave low results because of precipitation, but this interference could be almost entirely removed by the addition of large excesses of mandelic acid after the diethyldithiocarbamate extraction. A 100-fold excess of platinum gave a turbidity which yielded high results; the addition of cyanide masked this interference.

The remaining cations were thorium, scandium and chromium(III). Thorium gave slightly low results (*ca.* 10% with 100-fold excess) with no visible signs of interference. Scandium appeared to form a fluorescent complex, and chromium(III) gave very low results. The effects of niobium and tantalum were not examined because these cations could only be obtained in fluoride or tartrate solutions which are mentioned below as anionic interferences.

An extensive study of anionic interferences was not made, but it was confirmed that small quantities of fluoride, tartrate, citrate and oxalate interfered seriously by diminishing the fluorescence due to aluminium, while acetate, chloride, bromide, iodide, sulphate, nitrate, perchlorate, cyanide and carbonate showed no interference.

Members of the complexan series, *e.g.*, EDTA, CDTA, NTA and IDA, and the diketone acetylacetone reduced the fluorescence of the complex. The metal complexes, zinc-EDTA, manganese(II)-EDTA and cadmium-EDTA, did not affect the fluorescence, but proved ineffective as masking agents.

Beryllium, even in 1000-fold excesses, did not interfere with the determination as it does with most other methods for aluminium. It is, however, noteworthy that at higher ph values (*ca.* 9–10), beryllium gives a blue fluorescence with salicylidene-*o*-aminophenol. Because beryllium is not extracted as its diethyldithiocarbamate,[11] this could form the basis of a sequential determination of beryllium and aluminium. The reagent is, however, not very sensitive for beryllium.

Structure of complex

Slope–ratio plots (Fig. 4) indicate a metal:ligand ratio of 1:1, but no solid complex could be isolated for further examination. It is probable that the complex formed is polynuclear and similar to those proposed for the aluminium complexes of Pontachrome BBR and 2-hydroxy-3-naphthoic acid. This is supported by the following observations:—

1. Although no aluminium complex could be isolated, a green fluorescence was produced when a 0·1 % solution of salicylidene-*o*-aminophenol was dropped on to a sample of alumina which had been converted to the inert form by heating strongly. Simultaneously, the surface of the alumina was stained yellow, the colour of the reagent, and the colour was not removed at all by washing with water, alcohol or acetone.
2. The pH of formation of the complex is pH 5·6, which is considerably higher than the pH at which aluminium hydroxide precipitates (approximately pH 4·1).

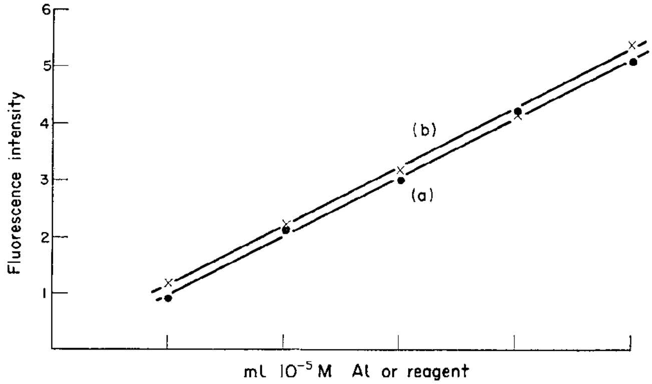


Fig. 4.—Slope–ratio plot showing variation of intensity of fluorescence of (a) aliquots of $10^{-5}M$ aluminium solution with 5 ml of 0·1 % reagent solution at pH 5·6 in 100 ml; (b) aliquots of $10^{-5}M$ reagent solution with 5 ml of $10^{-3}M$ aluminium solution in 100 ml.

3. The fluorescent aluminium complex of salicylidene-*o*-aminophenol has several properties similar to the complexes of aluminium with 2-hydroxy-3-naphthoic acid and Pontachrome BBR. The pH range for formation is narrow in all three instances and occurs over a similar range: Pontachrome BBR, pH 5; 2-hydroxy-3-naphthoic acid, pH 5·8; salicylidene-*o*-aminophenol, pH 5·6. The pH of formation for these aluminium complexes would, therefore, seem to be dependent more on the degree of hydrolysis of the aquo complex of aluminium than on the state of ionisation of the ligand.

The above evidence suggests that the aluminium:reagent adduct may exist as an entity in which the reagent molecules are adsorbed chemically on to the surface of colloidal aluminium hydroxide by replacement of surface hydroxyl groups.

There is other evidence, however, which favours the formation of a more definite chemical compound. For example, it is possible to extract the aluminium-salicylidene-*o*-aminophenol complex into water-immiscible solvents, such as n-butanol, isopentanol, n-pentanol and n-hexanol. This behaviour is more characteristic of a true aluminium complex, such as aluminium 8-hydroxyquinolate, rather than a simple adsorption compound. It is relevant to note that only alcohols were effective extracting solvents, and it is possible that these molecules substitute for solvated water molecules to form the extractable species. This is also supported by the partial extraction of the aluminium complex into methyl isopropyl ketone (to the extent of 50%) and the very low extraction into methyl isobutyl ketone (*ca.* 5%). The difference in extraction is possibly due to the steric effects of the isobutyl and isopropyl groups in the solvated complex; the donor properties of the carbonyl group are unlikely to be substantially different for the two ketones.

The 1:1 stoichiometry found for the compound also favours the existence of a true complex rather than an adsorption compound.

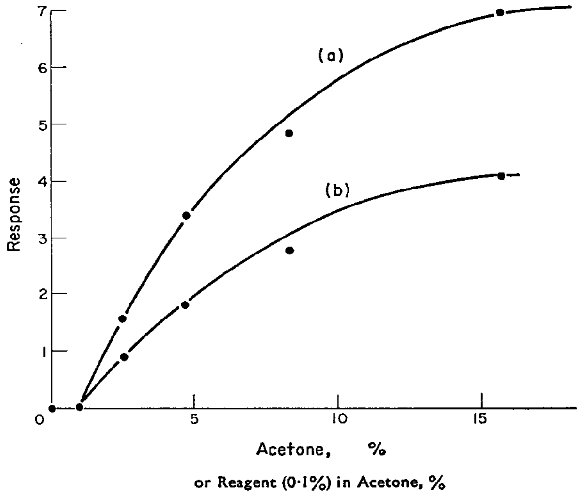
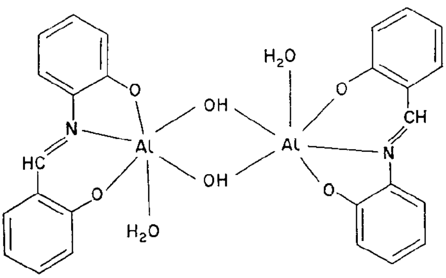


FIG. 5.—Scatter produced by 2·7 × 10^{-2} μg/ml aluminium solution with (a) varying acetone content of solution; (b) varying reagent content of solution.

To investigate the solubilising effect of the reagent on the aluminium solution at pH 5·6, light scattering experiments were carried out using the spectrofluorimeter. Inner-filter and fluorescence effects were minimised by setting both monochromators at 550 mμ. It was found that the addition of reagent produced a higher degree of scatter than was obtained from the aluminium solution. Subsequently, it was observed that the acetone in which the reagent was made up was responsible for at least some of the increased light scattering. This can be attributed to the aggregation of aluminium hydroxide caused by the reduced dielectric constant of the medium. When the experiments were repeated and the same amount of acetone was added to a blank solution, it was found that correspondingly less scatter was obtained in the presence of larger excesses of reagent (Fig. 5). Although it is not possible to interpret these results unequivocally, it would appear that the reagent definitely opposes the formation of insoluble aluminium hydroxide species. It probably does so by the suggested mechanism, whereby chemical combination of the ligand through replacement of a hydroxyl group in the hydrated alumina unit terminates the possibility of further aggregation of these units through cross-linking.

With this evidence in mind it appears that the complex is neither a simple mononuclear one, nor an adsorption of reagent on to polymeric alumina, but most probably resembles a low order polynuclear species such as the binary one suggested below



The properties of such a body should be consistent with the observed resistance to precipitation; 1:1 stoichiometry; degree of light scattering; narrow pH zone of stability; extractability into water-immiscible, oxygen donor solvents.

Acknowledgement—One of us (R. S.) thanks the Science Research Council for the award of a research studentship. We are also grateful to the S.R.C. for the award of a special research grant to T. S. W. for the purchase of the spectrofluorimeter and to the Mond Division of I.C.I. Ltd. (Runcorn) for the loan of similar apparatus.

Zusammenfassung—Salicyliden-*o*-aminophenol ist ein empfindliches Reagens zur spektrofluorimetrischen Bestimmung von Aluminium bis 27 ng (oder $2{,}7 \cdot 10^{-4}$ ppm in der Endlösung). Die am besten geeigneten Bedingungen in pH (5,6), Reagenskonzentration und Entwicklungszeit (über 20 min) wurden ermittelt. Extraktion mit Natriumdiäthyldithiocarbamat in Essigester beim pH der Bestimmung macht die Methode hochselektiv; aus 46 untersuchten Fremd-Kationen stören nur Chrom(III), Scandium und Thorium. Mit Aluminium Komplexe bildende Anionen wie Citrat, Tartrat und Fluorid stören, nicht dagegen die gebräuchlichen Anionen. Der Komplex hat die Zusammensetzung 1:1; bezüglich seiner Natur wurden einige Schlüsse gezogen.

Résumé—Le salicylidène *o*-aminophénol est un réactif spectrofluorimétrique sensible pour le dosage de l'aluminium en quantité aussi faible que 27 ng (ou $2{,}7 \times 10^{-4}$ ppm dans la solution finale). On a établi les conditions les plus convenables de pH (5,6), concentration du réactif et temps de développement (>20 mn). L'extraction au moyen de diéthyldithiocarbamate de sodium en acétate d'éthyle au pH du dosage rend la méthode hautement sélective; des quarante six cations étrangers examinés, seuls le chrome (III), le scandium et le thorium interfèrent. Les anions qui forment des complexes avec l'aluminium, tels que citrate, tartrate et fluorure provoquent aussi une interférence, mais aucun des anions communs n'interfère. On a établi une stoechiométrie 1:1 du complexe, et dégagé quelques conclusions concernant sa nature.

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USE OF GAS-LIQUID AND THIN-LAYER CHROMATOGRAPHY IN CHARACTERISING AIR POLLUTANTS BY FLUOROMETRY

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Summary—Relatively large amounts of alkylated derivatives of the polynuclear aromatic hydrocarbons are present in some urban atmospheres. These compounds are believed to be derived from industrial sources. Because alkylation of the tetracyclic aromatic hydrocarbons can confer carcinogenic activity on the derivatives, the presence of substantial amounts of these alkylated compounds in the air needs thorough study. The R_F value and the retention time, by themselves, are inadequate for characterisation of the polynuclear compounds. Gas-liquid chromatography followed by fluorometric examination of the eluent bands, and mixed-adsorbent two-dimensional thin-layer chromatography followed by direct fluorometric examination are very useful in characterising all types of organic compound in the organic fractions of airborne particulates and effluents from air pollution sources.

INTRODUCTION

THE identification of large conjugated compounds in polluted air has been expedited and simplified by recently introduced separation and spectral methods. The two separation methods that show the most promise for this application are two-dimensional thin-layer chromatography and gas-liquid chromatography.

The greatest value of two-dimensional thin-layer chromatography with mixed adsorbents is that it allows quick separation, characterisation, and assay of complicated molecules. Even with two-dimensional thin-layer chromatography on one adsorbent, polynuclear ring-carbonyl compounds collected from the urban atmosphere have been separated and assayed satisfactorily.[1]

To date, the most important property of gas-liquid chromatography is its resolving power, which is sometimes far superior to that of other methods. The type of separation possible with this technique has been exemplified by Solo and Pelletier[2] in their separation of phenanthrene and ~60 of its alkylated derivatives.

We have found that identifying unequivocally the large conjugated molecules in polluted air requires more than the R_F value or the retention time. Consequently, research has been concentrated on methods of spectral characterisation. This work has shown that the quickest and most satisfactory methods of characterising unknown compounds separated by paper or thin-layer chromatography consists of direct fluorometric[3–5] and phosphorimetric[6] examinations of the chromatogram. In some cases the elution of a spot on to glass-fibre paper before spectral examination gives more useful results, especially when the spot is to be treated with a caustic reagent or solvent before spectral examination.

The techniques of high-temperature gas-liquid chromatography, mixed-adsorbent two-dimensional thin-layer chromatography, and spectrophotofluorometry have been combined in a co-ordinated study of the composition of the urban atmosphere in terms of its particulate matter. Such qualitative studies are a necessary preliminary to the more thorough investigation of the quantitative composition of air pollution source effluents and the polluted urban atmosphere.

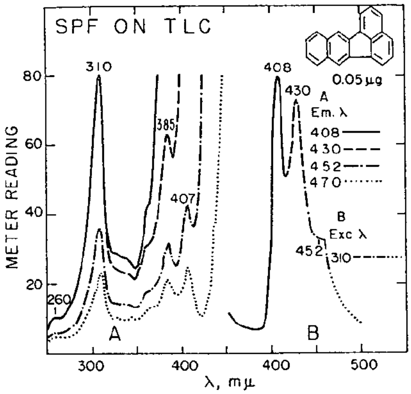

Fig. 1.—Fluorometric excitation (A) and emission spectra of benzo[k]fluoranthene on an alumina-cellulose acetate (2:1) thin-layer plate.

Abbreviations—SPF on TLC = direct spectrophotofluorometric examination of the thin-layer plate. Exc. λ (Em. λ) = excitation (emission) wavelength at which the emission (excitation) spectrum was obtained.

EXPERIMENTAL*

Reagents and apparatus

All standards were obtained from commercial sources and were crystallised to a constant melting point when they were found to be chromatographically impure.

Spectrophotometry. Spectrophotometric examination of column chromatographic effluents was done with a Cary Model II recording spectrophotometer with 1-cm path-length cells; fluorometric work, with an Aminco-Bowman spectrophotofluorometer with a solid-state attachment and a 1P21 phototube; phosphorimetric work, with an Aminco-Keirs spectrophotophosphorimeter with a 1P21 phototube.

Gas chromatography. For column chromatographic fractions 14 and 16 a Perkin-Elmer Model 800 chromatograph was used at temperatures of 240° in the column, 400° at the injection port, and 300° in the detector; helium flow was 40 ml/min at the vent and 80 ml/min through the column; air flow was 400 ml/min, and hydrogen flow, 20 ml/min. For column chromatographic fraction 11, the column temperature was kept at 210°. The column was 10% Apiezon L (W/W) on 60- to 80-mesh Chromasorb W (HMDS) in a stainless steel tube 2 m long and 1/8-in. O.D.

Gas chromatographic bands were collected by holding an alumina thin-layer plate as close as possible to the column vent without allowing it to touch the vent. The spots on the plate were then examined directly with the fluorometer.

Fluorometric examination of thin-layer plates

Thin-layer chromatograms and alumina thin-layer plates containing the collected gas chromatographic bands were treated and examined in a Chromato-Vue cabinet (Kensington Scientific Corp., Berkeley 10, Calif.) under the short and the long ultraviolet lights. Exposure to light and chemicals was kept at a minimum until the material was examined fluorometrically. A preliminary visual examination can be of help in ascertaining the type of compound present.

Fluorescence excitation and emission spectra of the spot in neutral, acid, and alkaline solution can be obtained by direct fluorometric examination of the spot. The experimental directions were given in previous papers.[7,8]

* Mention of commercial products does not constitute endorsement by the Public Health Service.

Scatter bands can interfere with the measurement of the complete excitation and emission spectra of an unknown directly from a chromatogram. The resolution of this type of interference is shown in Fig. 1. With the instrument set at the strongest emission wavelength, 408 mμ for benzo[k]fluoranthene, only the 310 mμ band of the excitation spectrum is obtained. By use of emission wavelengths farther away from the excitation bands, the entire excitation spectrum can be obtained.

DISCUSSION

Alkyl derivatives of polynuclear aromatic hydrocarbons in the urban atmosphere

The research in this paper was undertaken to answer several questions. The first question was whether large amounts of alkylated polynuclear aromatic hydrocarbons are present in the atmosphere and in effluents from air pollution sources. Because large amounts (relative to benzo[a]pyrene) of compounds containing a tetracyclic ring are present in the atmosphere and especially in source effluents, the question has arisen whether any of these compounds are alkylated.

It is well known that methylation of tetracyclic aromatic hydrocarbons and aza heterocyclic compounds can enhance their carcinogenic activity or can make inactive compounds carcinogenic.[9,10] Thus, chrysene is inactive on the subcutaneous tissue of mice, whereas its 4-, 5- and 6-methyl derivatives yield activities rated as +, +++, and +, respectively.[10] Benz[a]acridine and benz[c]acridine show no carcinogenic effect on mouse skin, whereas 7-methyl derivatives yield +++ activity and many of their other methyl derivatives show carcinogenic activity.[10] The relatively large amounts of alkylated tetracyclic compounds in some types of air pollution could be of some significance in the etiology of lung cancer.

To test whether alkylated hydrocarbons are present in urban atmospheres, we assembled a large composite organic sample for study. This sample was a benzene-extracted fraction of airborne particulates collected in 1963 and 1964 from approximately 100 large American cities. Quantitative analytical data indicated that some of the collection points were in or near industrial areas contributing large amounts of pollutants to the surrounding air.

The mixture was column chromatographed and then examined absorptiometrically by standard procedure.[11] The spectra indicated the presence of alkyl derivatives of the polycyclic aromatic hydrocarbons. Spectral examination of samples from industrial sources shows the same phenomenon while a similar examination of most urban samples gives no indication of the presence of alkyl derivatives.

Fraction 11, whose absorption spectra showed no evidence of alkyl derivatives, was examined more thoroughly by gas-liquid chromatography (Fig. 2). On the basis of fluorometric and phosphorimetric spectra and retention times, phenanthrene, anthracene, two alkyl phenanthrenes, and 2-methylpyrene were identified in the sample. Many unknown compounds were present in smaller amounts. In addition, a large amount of material came out at 60 min. This band contained a small amount of aromatic compound(s) and a large amount of saturated compound(s).

The absorption spectrum of fraction 14 (Fig. 3) indicated the presence of anthracene, phenanthrene, pyrene, and unknown compounds. Two-dimensional thin-layer chromatography indicated the presence of at least eight compounds. Gas chromatography indicated the presence of anthracene, phenanthrene, alkylphenanthrene, 4H-cyclopenta[d e f]phenanthrene, fluoranthene, pyrene and 2-methylpyrene. The presence of these compounds was confirmed by direct phosphorimetric and fluorometric examination of the collected material, as shown for phenanthrene,

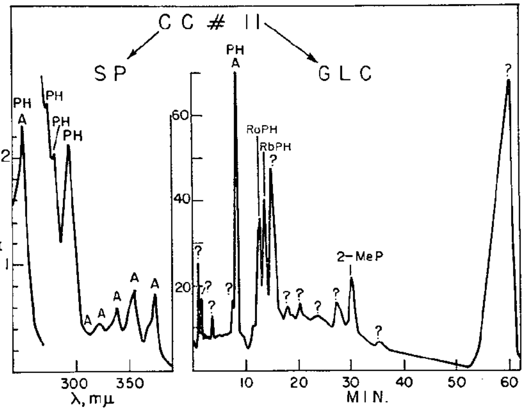

FIG. 2.—Alumina column chromatographic tricyclic subfraction (11) of the benzene-extracted fraction of a composite sample of airborne particulates from American cities. Absorption spectrum in pentane and a gas-liquid chromatogram.

Abbreviations—CC No. 1 = Column chromatographic tube No. 1.
SP = Spectrophotometric ultraviolet absorption spectrum.
GLC = Gas-liquid chromatography.
A = Anthracene.
PH = Phenanthrene.
RaPH = Alkylphenanthrene.
RbPH = Another alkylphenanthrene.
2-MeP = 2-Methylpyrene.

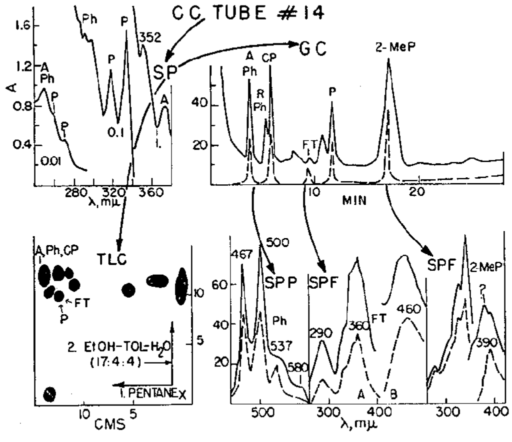

FIG. 3.—Alumina column chromatographic subfraction 14 of same run as in Fig. 2. Absorption spectrum in pentane at dilutions of 1, 0·1, and 0·01. Gas-liquid chromatogram. Two-dimensional thin-layer chromatogram on alumina-cellulose acetate (2:1). Phosphorimetric and fluorometric spectra obtained from the spectral examination of the appropriate gas chromatographic bands.

Abbreviations—CC Tube No. 14 = Column chromatographic tube No. 14.
GC = Gas chromatography
TLC = Thin-layer chromatography.
SPP = Spectrophotophosphorimetric spectra.
SPF = Spectrophotofluorometric spectra.
P = Pyrene.
FT = Fluoranthene.
CP = 4H-cyclopenta[def]phenanthrene.

fluoranthene and 2-methylpyrene. Spectral examination indicated that some of the bands were not pure, but contained other fluorescing or phosphorescing material.

Fraction 16 was the least complicated (Fig. 4). The absorption spectra showed the presence of pyrene and fluoranthene and indicated no alkyl derivatives of unknown compounds. Gas chromatographic examination indicated the presence of fluoranthene, pyrene and 2-methylpyrene. Direct fluorometric examination of the collected bands confirmed the presence of these compounds.

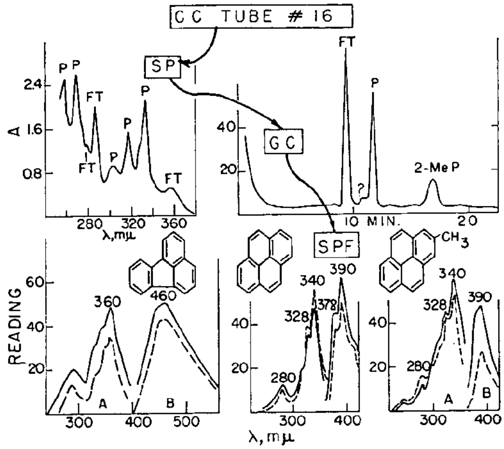

Fig. 4.—Alumina column chromatographic subfraction 16 of same run as in Fig. 2. Gas-liquid chromatogram. Fluorometric spectra obtained from the spectral examination of the appropriate gas chromatographic eluates.

Other column chromatographic fractions examined in the same way also contained alkylated derivatives of polynuclear aromatic hydrocarbons. Because we lack supply of alkylated derivatives of many of these compounds, identification of these compounds, except as to parent ring structure, is not satisfactory.

Examination of effluents from industrial sources of pollution, such as oil refineries and asphalt plants, disclosed a very high proportion of alkylated hydrocarbons. In these samples even the absorption spectra clearly indicated the presence of alkylated hydrocarbons.

The evidence indicates that the composition of the column chromatographic fractions is much more complicated than is indicated by absorption spectrometry, and sometimes is even more complicated than is indicated by two-dimensional thin-layer chromatography or gas chromatography. Results show that neither R_F values obtained by thin-layer chromatography nor retention times obtained by gas chromatography can be used, by themselves, to characterise the large aromatic compounds unequivocally. Gas chromatography is superior to two-dimensional thin-layer chromatography for separating the tricyclic and tetracyclic polynuclear aromatic hydrocarbons.

Two-dimensional thin-layer chromatographic separation of urban atmospheric samples

Another question in this investigation was whether two-dimensional thin-layer chromatography could be used to accelerate the identification of air pollutants

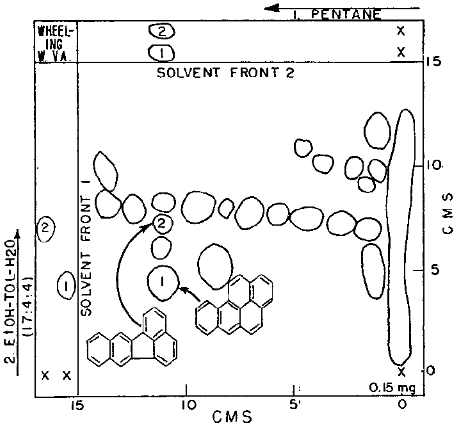

FIG. 5.—Two-dimensional thin-layer chromatogram on alumina-cellulose acetate (2:1) of 0·15 mg of benzene-soluble fraction of the airborne particulates from the downtown area in Wheeling, West Virginia. One-dimensional runs of standards.

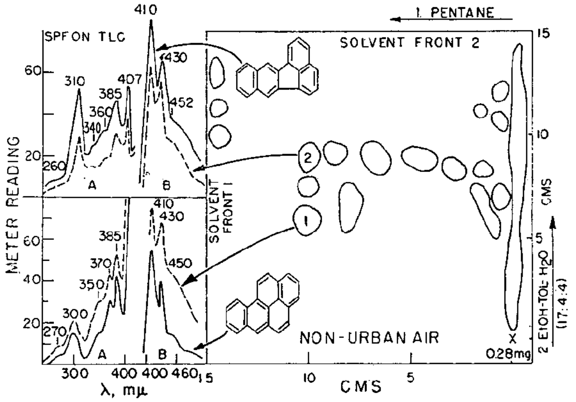

FIG. 6.—Two-dimensional thin-layer chromatogram on alumina-cellulose acetate (2:1) of 0 28 mg of a benzene-soluble fraction of the airborne particulates from a non-urban atmosphere. Fluorometric excitation (A) and emission spectra of two separated spots (– – –) and of benzo[a]pyrene and benzo[k]fluoranthene on the plate (———).

present in the benzene-soluble fractions of urban airborne particulates and effluents from air pollution sources. Separation of a sample from Wheeling, West Virginia, (Fig. 5) indicated the presence of benzo[a]pyrene and benzo[k]-fluoranthene. These two compounds were readily characterised, as shown for a non-urban sample (Fig. 6). In these samples the compounds were characterised by R_F values obtained in two different solvent systems and by the identity of the fluorometric spectra of the unknown with spectra of the standard.

Benzo[a]pyrene and benzo[e]pyrene are readily and completely separated by this method. Such a separation has not yet been achieved in gas chromatography.[12,13]

Only very small amounts of sample are needed for analysis—0·15 mg for the Wheeling sample and 0·28 mg for the non-urban sample. Even lesser amounts can be used.

The composite urban benzene-soluble fraction was examined by two different thin-layer chromatographic methods. By separation of 0·49 mg of the sample on an alumina-cellulose layer followed by direct fluorometric examination acridine, pyrene, and benz[c]acridine were identified readily (Fig. 7). The same sample was separated two-dimensionally on an alumina-cellulose acetate system. Through R_F values and direct fluorometric examination the following compounds were identified: anthracene benz[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, carbazole, chrysene, and pyrene (Fig. 8).

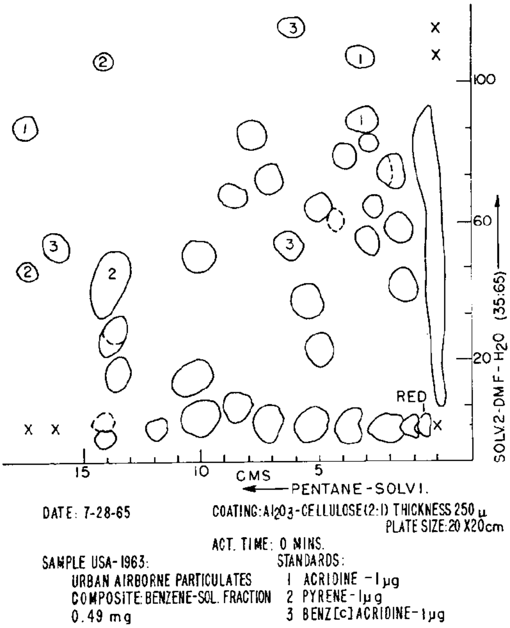

Fig. 7.—Record of a two-dimensional thin-layer chromatographic separation and the characterisation of three spots on alumina-cellulose (2:1).

Two dimensional thin-layer chromatographic separation of samples from air pollution sources

The benzene-extracted fraction of an airborne particulate sample collected near the open burning of auto tyres, floor mats and seat covers was very readily separated into a large number of spots (Fig. 9). 7H-Benz[de]anthracen-7-one and phenalen-1-one were characterised by their R_F values as compared to standards, by fluorescence colours in the neutral and acidic state, and by the identity of their fluorometric spectra in neutral and acid solution with the comparable spectra of standards. Only 36 *µg* of sample were needed for these characterisations.

A basic fraction of coal-tar pitch was analysed two-dimensionally on an alumina-cellulose plate (Fig. 10). Although this mixture was extremely complicated, six compounds were readily characterised by use of R_F values and fluorometric examination. These compounds were acridine, benz[a]acridine, benz[c]acridine, benzo[f]quinoline, benzo[h]quinoline, and dibenz[a,h]acridine.

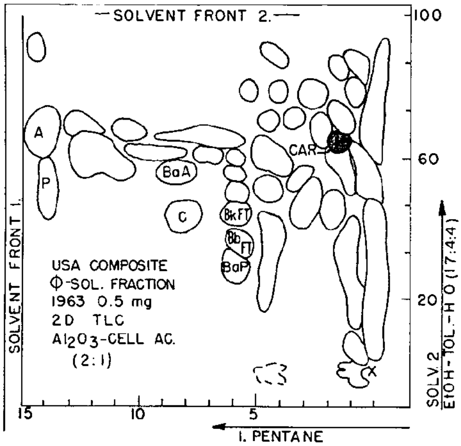

Fig. 8.—Two-dimensional thin-layer chromatographic separation and characterisation of anthracene, benz[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, carbazole, chrysene and pyrene. Carbazole is located by the blue colour it gives with trifluoroacetic acid and ultra-violet light.

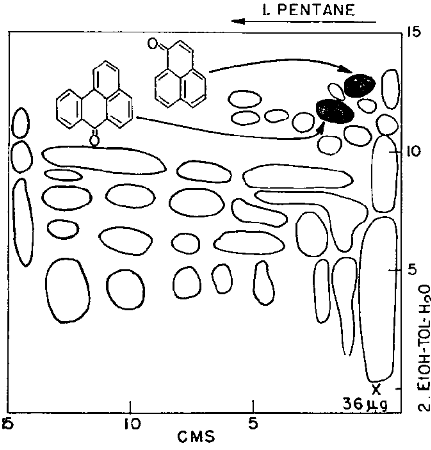

Fig. 9.—Two-dimensional thin-layer chromatographic separation on alumina-cellulose acetate (2:1) of a non-basic subfraction of the benzene-soluble fraction of the airborne particulates collected from the open burning of auto tyres, floor mats, and seat covers. Separation of phenalen-1-one and 7H-benz[de]anthracen-7-one shown.

The corresponding non-basic fraction of coal-tar pitch was separated two-dimensionally on alumina (Fig. 11). A large proportion of the sample was found at the solvent fronts in the system used. This material, mainly hydrocarbons, was ignored. Three compounds were characterised: carbazole and 4H-benzo[d e f]carbazole, which gave blue visible colours with trifluoroacetic acid, and 7H-benz[de]anthracen-7- one.

CONCLUSION

Substantial amounts of alkylated polynuclear hydrocarbons are present in the atmosphere, especially in areas where a special form of industrial pollution is heavy

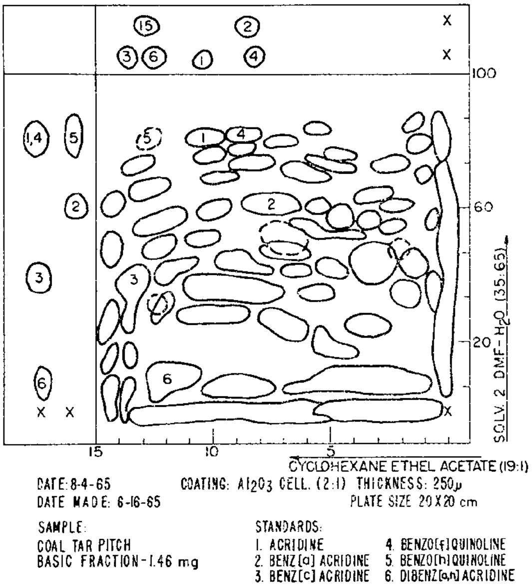

FIG. 10.—Record of the two-dimensional separation of 1·46 mg of the coal-tar-pitch basic fraction. Characterisation of six compounds.

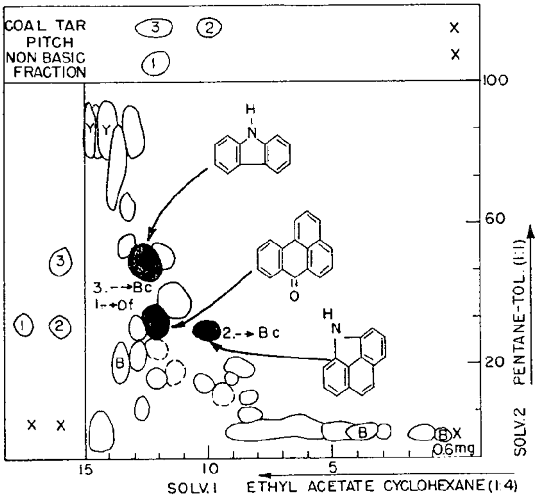

FIG. 11.—Two-dimensional thin-layer chromatographic separation of 0·6 mg of the coal-tar-pitch non-basic fraction on alumina. One dimensional separations of carbazole, 7H-benz[de]anthracen-7-one, and 4H-benzo[def] carbazole.

Abbreviations—BC = Blue colour.
Of = Orange fluorescence.
——— = No fluorescence.
B = Blue fluorescence.
Y = Yellow fluorescence.

(*e.g.*, asphalt and petroleum industries). Because of the presence of these alkylated compounds in some polluted atmospheres, a direct gas chromatographic analysis for polynuclear aromatic hydrocarbons could be highly erroneous unless the components of the analysed bands were identified completely. In addition, the presence of alkylated tetracyclic hydrocarbons warrants a thorough investigation of the possible cancer peril from these compounds.

Separation of tricyclic and tetracyclic aromatic hydrocarbons by gas chromatography was superior to that obtained by two-dimensional thin-layer chromatography, at least in the investigated systems. Gas chromatography allied with spectrophotofluorometry has shown the complexity of some of the column chromatographic fractions of organic airborne particulates in terms of the tricyclic and tetracyclic aromatic hydrocarbons. All the fractions are much more complicated than their absorption spectra indicate; fluorometric and phosphorimetric analysis show that most of the fractions are more complicated than is indicated by gas chromatography or two-dimensional thin layer chromatography. Neither R_F values nor elution times are sufficient by themselves to characterise the large organic compounds.

Two-dimensional thin-layer chromatography, especially with mixed adsorbents, followed by direct fluorometric examination is invaluable in characterising a large variety of polynuclear air pollutants. By the thin-layer chromatographic and spectrophotofluorometric methods described in this and previous papers investigators should be able to develop methods to scan automatically and selectively an entire two-dimensional plate and to assay for the compounds of interest. Meanwhile the gas and thin-layer chromatographic procedures described should be applicable to the development of a wide variety of methods for the assay of benzo[a]pyrene and other air pollutants.

Acknowledgements—The authors express appreciation for the technical assistance of W. C. Elbert in some of the thin-layer chromatographic separations and to J. Pfaff for the phosphorimetric measurements.

Résumé—Des quantités relativement importantes de dérivés alkylés d'hydrocarbures aromatiques polynucléaires sont présentes dans certaines atmosphères urbaines. On pense que ces composés proviennent de sources industrielles. L'alkylation des hydrocarbures aromatiques tétracycliques pouvant conférer aux dérivés une activité carcinogène, la présence de quantités substantielles de ces composés alkylés dans l'air nécessite une étude complète. La valeur du R_F et le temps de rétention sont par eux-mêmes insuffisants pour caractériser les composés polynucléaires. La chromatographie gaz-liquide suivie de l'examen fluorométrique des fractions d'éluant et la chromatographie en couche mince bi-dimensionnelle avec absorbant mixte suivie de l'examen fluorométrique direct sont très utiles pour la caractérisation de tous les types de composés organiques dans les fractions organiques des particules en suspension dans l'air et des dégagements des sources de pollution de l'air.

Zusammenfassung—In einigen Stadtatmosphären sind relativ große Mengen alkylierter Derivate von mehrkernigen aromatischen Kohlenwasserstoffen vorhanden. Es wird angenommen, daß sie aus der Industrie stammen. Da Alkylierung tetracyclischer aromatischer Kohlenwasserstoffe den Derivaten carcinogene Eigenschaften verleihen kann, bedarf die Anwesenheit beträchtlicher Mengen dieser Alkylverbindungen in der Luft eingehender Untersuchung. R_F-Wert und Retentionszeit allein sind zur Charakterisierung der mehrkernigen

Verbindungen ungeeignet. Gaschromatographie mit nachfolgender fluorometrischer Untersuchung der Eluatbanden und zweidimensionale Dünnschichtchromatographie auf gemischtem Adsorbens und anschließende direkte fluorometrische Untersuchung sind sehr nützlich bei der Charakterisierung aller Arten organischer Verbindungen in den organischen Anteilen in Luft suspendierter Festteilchen und Emissionen aus den Quellen der Luftveruneinigung.

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SHORT COMMUNICATIONS

Determination of free acid in antimony(III) and bismuth(III) solutions

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Because of the great hydrolytic tendency of antimony(III) and bismuth(III) in aqueous solution it is necessary to add excess of free acid (up to $2N$) to prevent hydrolysis of their stock solutions. In the course of our investigations on the stability of some complexes of these elements, it was found necessary to know the free acid content in these solutions. Pavlinova[1] used potassium hexacyanoferrate(III) as a precipitant for the removal of antimony and bismuth before determining the free acid titrimetrically.

Antimony(III) and bismuth(III) form stable complexes with EDTA, a detailed study of which has already been reported.[2] It is shown here that this property can be conveniently utilised for determining the free acid content in the salt solution. The method is simple, convenient and reliable.

EXPERIMENTAL

Stock solutions

Antimony trichloride solution ($\sim 0{\cdot}4M$) was prepared by dissolving the analytical reagent grade salt in $2M$ hydrochloric acid. Bismuth perchlorate solution ($0{\cdot}3M$) was prepared by dissolving a known weight of powdered bismuth trioxide in $2M$ perchloric acid. The antimony solution was standardised by the bromate method[3] and for bismuth the oxide was taken as primary standard. In the case of bismuth, the free acid content was calculated assuming that 3 equivalents of acid were used in dissolving every gram atom of bismuth. EDTA solution was prepared by dissolving pure Titriplex III (E. Merck, metal titration grade) in deionised water and standardised by titration against zinc sulphate solution using Erio T as indicator.

A mixed indicator was prepared by dissolving 0·1% w/v of Methyl Orange and 0·05% w/v of Bromocresol Green in water.

Procedure

A known amount of the antimony or bismuth solution, containing about $0{\cdot}5$ to 1×10^{-3} mole of the metal, is added with constant stirring to about 2% excess over the theoretical amount of $0{\cdot}01M$ disodium EDTA solution and titrated against standard $0{\cdot}1N$ sodium hydroxide solution. Potentiometric titrations were carried out with a Beckmann model G pH meter using a glass electrode and a calomel reference electrode to a pH of 4·5. In the indicator method the end-point is determined by a colour change from orange to blue-green.

RESULTS AND DISCUSSION

In $2N$ acid solution, both antimony and bismuth exist as triply charged ions, so that the reaction with EDTA can be represented by the equation

$$M^{3+} + YH_2^{2-} \rightleftharpoons MY^- + 2H^+ \qquad (1)$$

In the presence of an equivalent amount or excess of EDTA, the hydrolysis of the bismuth complex occurs only at pH > 8 and that of the antimony complex at pH > 5.[2] Therefore, the amount of free acid can be determined by titrating against standard alkali potentiometrically. Some typical potentiometric titration curves with the complexes, 1 : 1 metal : EDTA solutions, and in the presence of excess of EDTA, are shown in Fig. 1, from which it is clear that the inflection point observed at pH $\sim 4{\cdot}5$ is not appreciably altered by the presence of excess of disodium EDTA.

The free acid content is obtained by subtracting the acid liberated in reaction (1) (equal to twice the concentration of the metal ion) from the titre. The results obtained in the presence of various amounts of metal and free acid, by potentiometric and visual indicator methods, are summarised in Table I. The values found by the visual indicator method compare favourably with those obtained

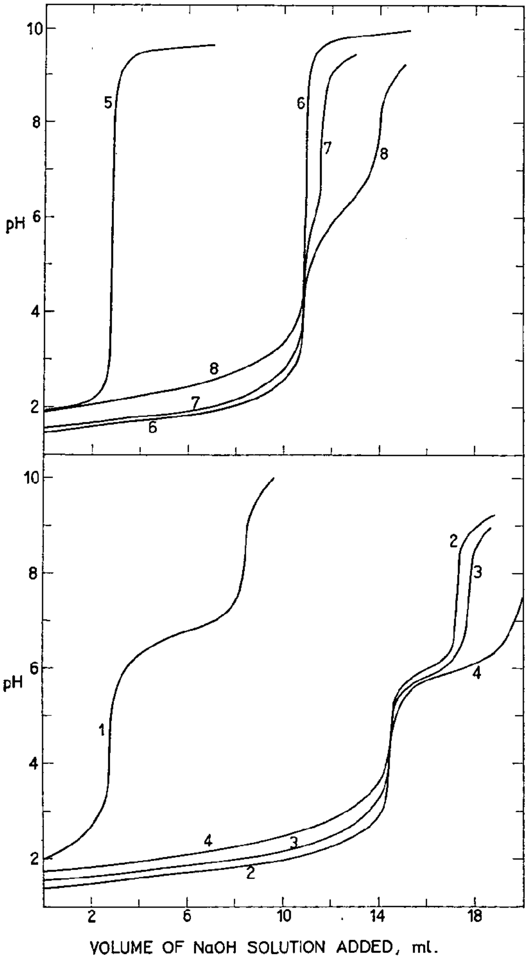

FIG. 1.—Potentiometric titration curves for Sb- and Bi-EDTA solutions against NaOH:

(1) 100 ml of 0·01*M* Sb-EDTA solution;
(2) 5 ml of 0·1*M* $SbCl_3$ solution in HCl + 5 ml of 0·1*M* EDTA;
(3) 5 ml of 0·1*M* $SbCl_3$ solution in HCl + 7 ml of 0·1*M* EDTA;
(4) 5 ml of 0·1*M* $SbCl_3$ solution in HCl + 15 ml of 0·1*M* EDTA;
(5) 10 ml of 0·1*M* Bi-EDTA solution;
(6) 10 ml of 0·0932*M* bismuth perchlorate solution in $HClO_4$ + 29·35 ml of 0·1*M* EDTA;
(7) 10 ml of 0·0932*M* bismuth perchlorate solution in $HClO_4$ + 11·35 ml of 0·1*M* EDTA;
(8) 10 ml of 0·0932*M* bismuth perchlorate solution in $HClO_4$ + 19·4 ml of 0·1*M* EDTA.

TABLE I.—DETERMINATION OF FREE ACID IN ANTIMONY AND BISMUTH SALT SOLUTIONS AT HIGH ACIDITIES ($>1N$)

	Metal present, *mole* × 10^{-3}	Free acid added, *mequiv*	Free acid found, *mequiv* Potentiometric method	 Indicator method
Antimony	1	5	4·98	4·97
	1	10	10·02	9·97
	1	15	15·00	15·05
	1	5 + 10% excess of EDTA	4·98	4·97
	1	5 + 30% excess of EDTA	4·97	4·96
	1	5 + 50% excess of EDTA	4·95	4·94
	2	10	9·95	9·94
	2	15	15·05	14·97
	3	15	15·00	15·05
	3	20	19·95	20·05
Bismuth	0·5	3	2·99	3·00
	0·5	7	7·00	6·98
	0·5	10	10·02	10·00
	0·5	3 + 10% excess of EDTA	2·99	2·99
	0·5	3 + 30% excess of EDTA	2·99	2·98
	0·5	3 + 50% excess of EDTA	2·97	2·96
	1·0	4	4·00	3·98
	1·0	7	6·95	6·97
	1·0	10	9·95	10·02
	2	10	10·05	10·00
	2	15	14·95	15·05

potentiometrically, the error in all cases being less than 1 %. The values obtained in the presence of an excess of EDTA greater than the 1:1 stoichiometric ratio are also given in Table I. From these data it can be seen that the addition of excess of EDTA tends to lower the experimental values. However, even in the presence of a 50% excess of EDTA the maximum error is only about 1·5%.

When the acidity of the salt solution is $<1N$ for antimony and $<0{\cdot}5N$ for bismuth, the average charge of the ions is known to be one, corresponding to MO^+.[4,2] Under these conditions the reaction with EDTA results in the formation of a complex without the liberation of protons

$$MO^+ + YH_2^{2-} \rightleftharpoons MY^- + H_2O \qquad (2)$$

Therefore, the titre gives the free acid content of the solution directly.

Though reactions of the type represented by equation (2) are uncommon, its validity in the case of antimony and bismuth can be readily proved by dissolving the corresponding oxychlorides (MOCl) in equimolar amounts of disodium EDTA. These complexes are soluble and the pH of the solution is about 5, indicating the non-liberation of protons. Further, the identity of the spectra of the complexes obtained from the normal and oxysalts proves that the same complex is formed in both cases.

The applicability of the present titration methods under conditions where MO^+ exists has been checked by determining the free acid by an ion-exchange method as follows. The stock solution of

TABLE II.—DETERMINATION OF FREE ACID IN BISMUTH SOLUTION AT LOW ACIDITIES ($<0{\cdot}2N$)

Bismuth, *M*	Free acid, *N*	Concentration of acid Ion exchange, *N*	 EDTA titration, *N*
0·025	0·1417	0·1413	0·1420
0·020	0·1134	0·1130	0·1135
0·015	0·0850	0·0854	0·0850
0·010	0·0567	0·0564	0·0568

bismuth perchlorate was diluted to an acidity of about 0·1–0·2*N*. A known amount of this solution was passed through a cation-exchange resin column (5 g of Dowex-50W for about 1 mequiv of bismuth) in the hydrogen form, when the bismuth is absorbed as BiO^+. The resin was then washed with acid-free water and the total acid in the effluent and washings titrated against standard alkali. The free acid was calculated by subtracting from the titre the acid liberated from the resin due to absorption of BiO^+. In Table II are compared some experimental values obtained by this method with those obtained by the EDTA titration method. The values obtained by the two methods agree within the limits of experimental error.

The 'true' free acid content of the solution can be accurately determined by the present method only if the ions are present completely in one form, either M^{3+} or MO^+. When a mixture of M^{3+} and MO^+ exists in appreciable amounts, the concentrations of each species should be known through hydrolytic or other data to enable a correct determination of the free acid content.

Acknowledgement—The authors wish to thank Dr. Jagdish Shankar for his interest in the work.

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Summary—A method for the determination of free acid in antimony(III) and bismuth(III) solutions is given. A solution of the disodium salt of EDTA, 2–3% in excess of the stoichiometric amount, is added to the metal salt solution and titrated with sodium hydroxide solution potentiometrically or visually using a mixed indicator. The error in the method is less than 0·5%.

Résumé—On donne une méthode de dosage de l'acide libre dans des solutions d'antimoine(III) et de bismuth(III). A la solution de sel métallique, on ajoute une solution de sel disodique d'EDTA, 2–3% en excès par rapport à la quantité stoechiométrique, et titre au moyen d'une solution de soude par potentiometrie ou visuellement au moyen d'un indicateur mixte. L'erreur par cette méthode est inférieure à 0,5%.

Zusammenfassung—Eine Methode zur Bestimmung freier Säure in Antimon(III)- und Wismut(III)-Lösungen wird angegeben. Eine Lösung des Dinatriumsalzes von EDTA wird in 2–3% Überschuß über die stöchiometrische Menge zur Metallsalzlösung gegeben und potentiometrisch oder visuell mit einem Mischindikator mit Natriumhydroxydlösung titriert. Der Fehler der Methode ist geringer als 0,5%.

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Einige kritische Bemerkungen zur quantitativen ultrarotspektrographischen Analyse von Metallen über ihre Chelatverbindungen

(*Eingegangen am* 29 *November* 1965. *Angenommen am* 8 *December* 1965)

ULTRAROTSPEKTROGRAPHISCHE Messungen sind gelegentlich auch in der anorganisch-chemischen Analyse anwendbar. Neben der qualitativen und quantitativen Auswertung der im Ultrarotgebiet liegenden Eigenschwingungen verschiedener Anionen[1-12] können diese bzw. auch Kationen in Form geeigneter meist schwerlöslicher metallorganischer Verbindungen, bei Kationen vorwiegend als Chelate, bestimmt werden. Aus Messung der UR-Extinktion der Präparate (meist als KBr-Preßling) läßt sich dann die im Preßling enthaltene Menge des Ions bestimmen.[13-17] Aus dem Extinktionsverhältnis zweier charakteristischer Chelatbanden* kann man auch das Konzentrationsverhältnis der Metallionen im Preßling und in Verbindung mit einer weiteren chemischen Bestimmung die Menge der Einzelkomponenten ermitteln.[18-20] Einige im wesentlichen zwar bekannte Gesichtspunkte der UR-Analyse sollen hinsichtlich ihrer Besonderheiten bei der Analyse von Metallchelaten kurz aufgeführt werden, da sie bislang nicht oder nur ungenügend hierbei berücksichtigt wurden.

(1) Die aus Extinktionsmessungen von Chelatpräparaten unmittelbar erhaltenen linearen oder gekrümmten Eichkurven erlauben die Bestimmung geringer Metallionenmengen, bei Verwendung von Halbmikropreßlingen (*ca.* 100 mg KBr; $\phi = 11$ mm; Dicke = 0,3 mm) sogar im μg-Bereich, wie Abb. 1 zeigt.

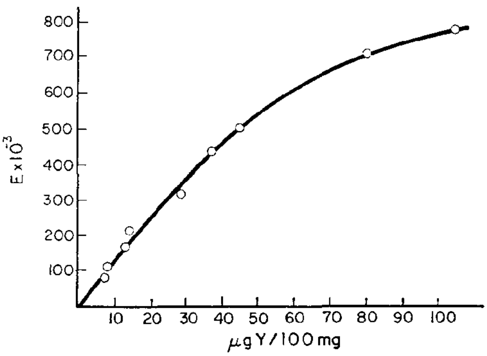

ABB. 1.—Eichkurve: Yttrium-Oxinat (Analysenbande: 12,21 μ; Auswertung: "basic-line"-Verfahren; Pressverluste gewichtskorrigiert) (Aufnahme mit Mikropressling, Halterung und Reflektionsansatz des Leitz—UR-Spektrographen)

Diese hohe Empfindlichkeit läßt sich aber nur bei vollständiger und reproduzierbarer Überführung der Niederschlagsmengen vom Fällungsgefäß in den KBr-Preßling ausnutzen. Deis ist bisher für kleine Niederschlagsmengen nur schlecht möglich. (Zu der bei der ultrarotspektrographischen Analyse der Anionen[2,3,8] erfolgreich benutzten Gefriertrocknung von Lösungen liegen ebenfalls keine Erfahrungen vor.) Die Anwendbarkeit derartiger Verfahren in der praktischen Analyse wird dadurch erheblich eingeschränkt. Lediglich die Bestimmung des Mischungsverhältnisses ist von einer quantitativen Überführung des Niederschlages in den Preßling unabhängig.

(2) Bei der Ermittlung des Mischungsverhältnisses zweier schwerlöslichen Metallchelate im Preßling zeigte sich als Ergebnis zahlreicher eigener Versuche, daß die mit synthetischen Gemischen und mit Präparaten aus gemeinsamer Ausfällung erhaltenen Eichkurven in der Regel nicht übereinstimmen (siehe Abb. 2).

Bei gemeinsamen Ausfällungen erhält man häufig, vor allem bei Neigung zur Mischkristallbildung, Abweichungen sowohl der Intensität als auch der Wellenlänge von den für die einzelnen Chelate charakteristischen Banden.[18] Eine Prüfung dieser Verhältnisse, besonders auch hinsichtlich des Einflusses der Fällungsbedingungen, dürfte daher in der Regel notwendig sein.

(3) Ebenfalls kurz hingewiesen sie auf einige in diesem Zusammenhang interessierende Fehlermöglichkeiten bei der Herstellung der KBr-Preßlinge. Für quantitative Bestimmungen ist bekannt-

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* In Wellenlänge und Intensität vom Metallion abhängige Bande in einer gleichartigen Reihe von Chelatverbindungen (z.B. Oxinate, Anthranilate, *etc.*).

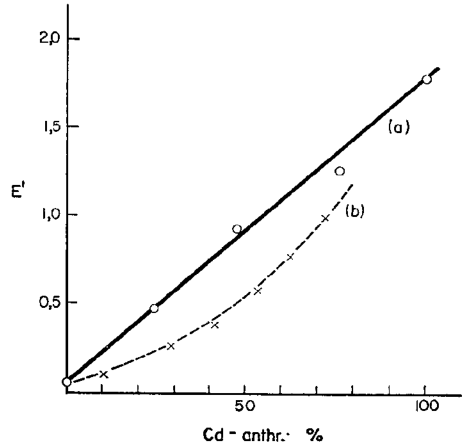

Abb. 2.—Eichkurve von Cd/Zn-anthranilatmischungen

$$E' = \frac{E_{10,0} - E_{12,0}}{E_{9,45} - E_{12,0}} \quad \text{(Näheres s. 18).}$$

(a) mechanische Mischung (b) gemeinsame Ausfällung

lich eine sorgfältige Mischung und Trocknung des Präparates vor dem Pressen notwendig. Ein einfaches Verreiben in einer Porzellan- oder Achatschale gibt aber wegen der dabei erhaltenen ungleichmäßigen Korngröße der Chelatniederschläge nur unbefriedigende Ergebnisse bei quantitativen Messungen.[21] Die Probe + KBr wird daher auch zur Erreichung einer besseren Homogenität meist in kleinen Mischern (nach v. Ardenne[22]) vibriert. Mit wachsender Vibrationszeit erhält man dabei bekanntlich infolge der Abnahme der Korngröße eine Zunahme der Extinktion[23,24] der sich bei längeren Vibrationszeiten oft eine durch die Zersetzung der Substanz bedingte Abnahme überlagert. Diese Erscheinungen zeigten auch fast alle bisher von uns untersuchten Chelatverbindungen. Eine typische Kurve enthält Abb. 3, aus der auch das häufig zu beobachtende unterschiedliche Verhalten im NaCl- und CsBr-Bereich hervorgeht.

Die Vibrationsbeständigkeit ist dabei in vielen Fällen der Stabilität der Chelatverbindung proportional. In Abb. 4 wurde jeweils das Extinktionsverhältnis einer charakteristischen Chelatbande gegen eine bei allen Verbindungen gleichartig auftretende Bande des Reagenzes gebildet.

Man erkennt deutlich, daß die relative Abnahme dieses Extinktionsverhältnisses von der Stellung des Metalles in der Mellor-Malley-Reihe[25,26] und damit von der Chelatbeständigkeit abhängt.

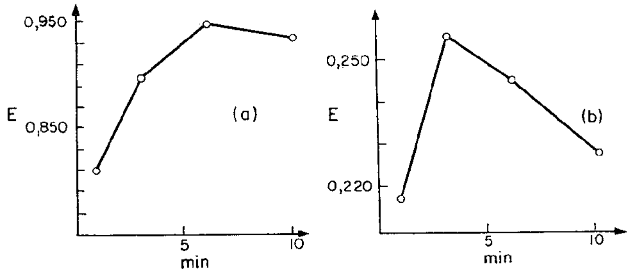

Abb. 3.—Abhängigkeit der Extinktion der Chelatbanden von der Vibrationsdauer
Probe: Y-oxinat; *ca.* 14 mg/700 mg KBr;
(a) NaCl-Bereich (12,21 μ)
(b) CsBr-Bereich (20,35 μ)

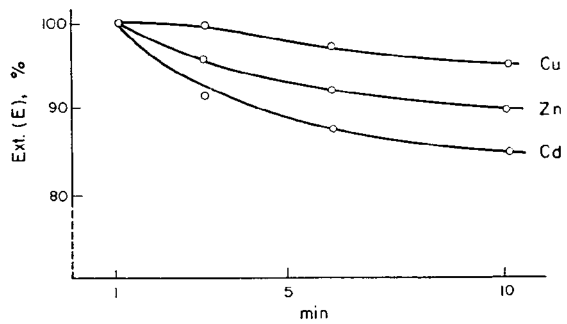

ABB. 4.—Chelatbeständigkeit und Vibrationsabhängigkeit Proben: Cu-, Zn-, Cd-anthranilat, je *ca.* 15 mg/700 mg KBr. (Mischen im Vibrator)

$$\text{Auswertung: Cu-anthranilat: } E = \frac{E_{8,95} - E_{10,75}}{E_{11,5} - E_{10,75}}$$

$$\text{Zn-anthranilat: } E = \frac{E_{9,45} - E_{10,75}}{E_{11,6} - E_{10,75}}$$

$$\text{Cd-anthranilat: } E = \frac{E_{8,75} - E_{12,00}}{E_{11,6} - E_{10,75}}$$

Diese Ergebnisse zeigen die Bedeutung konstanter Mischungs- und Zerkleinerungsverhältnisse auch für die UR-spektrographische Analyse metallorganischer Verbindungen.

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Summary—Attention is drawn to some points (measurement, mixing, calibration curve) regarding the applicability of infrared spectrographic procedures in the analysis of metals by means of their chelates.

Zusammenfassung—Auf einige Gesichtspunkte (Überführung, Mischung, Eichkurve) zur Anwendbarkeit ultrarotspektrographischer Verfahren bei der Analyse von Kationen über Chelatverbindungen wird hingewiesen.

Résumé—On attire l'attention sur quelques points (mesure, mélange, courbe d'étalonnage) concernant les possibilités d'application des méthodes spectrographiques infra-rouges dans l'analyse des métaux au moyen de leurs chélates.

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Talanta, 1966, Vol. 13, pp. 639 to 640. Pergamon Press Ltd. Printed in Northern Ireland

PRELIMINARY COMMUNICATION

Automatic scanning of chromatoplates by multi-scaling using a gamma-ray spectrometer

(*Received* 13 *December* 1965. *Accepted* 13 *December* 1965)

EXISTING radiochromatogram scanners are generally special equipment designed just for application to chromatography.[1] Some of them are based on twin Geiger-Müller tubes, between which the chromatographic strips are driven; they require a special attachment for reading a thin layer, and they are good enough for locating a radioactive spot but insufficient for analysis, especially in the case of gamma-ray spectrometry. The Packard Model 460 uses a typewriter to transport the actual chromatogram and to print the data on a sheet of paper which is taped to the chromatogram. Other scanners move the counter upon the chromatographic plates: the Desaga scanner moves a scintillation detector in connection with a strip chart recorder, but the detector is not satisfactorily shielded.

EXPERIMENTAL

Some new models of gamma-ray spectrometers, such as the 128-channel Nuclear Data ND-110 contain an internal multi-scaling device which permits a study of the variation of the radiation intensity as a function of time: it was elaborated in order to draw the decay curves of short-lived radioisotopes. The multi-scaling measure time can be of 1 msec up to 10 sec per channel.

We have seen that this instrument can be used to locate and analyse a radioactive spot on a thin chromatographic layer or on a chromatographic paper strip. In fact, when the spectrometer is used on multi-scaling, impulses can be collected to drive an X–Y plotter. The plotter is placed close to the detector's shield, with its surface at the level of the lead plate where the window is cut. Two cotton threads are attached to the extremities of the bar that holds the pen, and to the chromatographic paper. When the recorder is at the zero position, the starting chromatographic mark on the paper should be on the window: the direction is set by two lead bars.

By turning the "analyse" knob the spectrometer and the recorder are started simultaneously; the recorder draws the paper, step by step, synchronously with the multi-scaling measure times, on the window upon the scintillation detector.

For standard chromatoplates 200 mm long, a window 9 mm long in a 40-mm thick sheet of lead is used.

The spectrometer can read out the results as 128 numbers on a Teletype, or 128 points on the graph previously used. This graph locates different radioactive spots in a very precise way.

Moreover, the plate can be driven back to centre the spot on the window, and the spectrometer set to give a gamma-ray spectrum to identifiy the substance from which the spot originated. Following the general rules of quantitative analysis by gamma-ray spectrometry, the amount of radioelement can be estimated by comparison with a standard.

If several chromatographic spots were evaluated on the same plate, it can be manually positioned on the window at the subsequent point of application by moving the two lead bars.

This technique presents the great advantages over the commercially available scanning devices, that the detector is constantly shielded and no equipment is needed to read out and to draw the chromatogram other than the gamma-ray spectrometer itself. The spectrometer, in fact, performs functions which are unavailable in any other instrument: namely, examining a bidimensional chromatogram and presenting digital and tape informations relative to the location, zone shape and amount of radioactivity thereon, for every radioelement.

This technique will be applied to our future studies of chromatography and the results reported in due course.

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Summary—The location of radioactive tracers on chromatographic thin layers or papers is realised, together with the qualitative and quantitative analysis, using only a gamma-ray spectrometer.

Résumé—On peut procéder à la localisation des traceurs radioactifs sur les chromatogrammes en couches minces et sur papier, conjointement aux analyses qualitative et quantitative, en utilisant seulement un spectromètre à rayons gamma.

Zusammenfassung—Radioaktive Tracer auf Dünnschicht- oder Papierchromatogrammen werden nur mit Hilfe eines Gamma-Spektrometers lokalisiert sowie qualitativ und quantitativ analysiert.

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Talanta, 1966, Vol. 13, pp. i to ii. Pergamon Press Ltd. Printed in Northern Ireland

NOTICES

DEUTSCH DEMOKRATISCHE REPUBLIK

Der Fachverband analytische Chemie der Chemischen Gesellschaft in der Deutschen Demokratischen Republik veranstaltet am 31. Oktober und 1. November 1966 in Leipzig eine Vortragstagung

Adsorption und Verteilung in der analytischen Chemie

Um die Thematik in übersehbaren Grenzen zu halten, sollen im wesentlichen nur die folgenden Arbeitsgebiete behandelt werden:

Extraktionsverfahren
Papierchromatographie
Dünnschichtchromatographie
Säulenchromatographie
Ionenaustauschverfahren

Interessenten werden gebeten sich mit dem Sekretariat der Chemischen Gesellschaft in der DDR, 108 Berlin 8, Clara-Zetkin-Straße 105 in Verbindung zu setzen.

Vortragsanmeldungen werden bis zum 15. Mai 1966 von Herrn Prof. Dr. G. Ackermann, 92 Freiberg (Sachs), DDR, Institut für anorgan. und analyt. Chemie der Bergakademie, Leipziger Straße, entgegen genommen.

FRANCE

Wednesday–Friday 2–4 *November* 1966: **Scientific Symposia on Automation in Analytical Chemistry 1966:** *Technicon Instruments Co., Ltd.* Salon de la Chemie, 27, bis, Rue Saint Dominique, Paris VIIe, France.

UNITED STATES OF AMERICA

Monday–Friday 22–26 *August* 1966: **Gordon Research Conference on Analytical Chemistry.** New Hampton School, New Hampton, New Hampshire.

The programme is as follows:

Monday, 22 *August*

Mass Transport in Electroanalytical Methods; a Comparative Treatment.	David K. Roe
Chronocoulometry: Recent Applications of Current Integration Methods.	Robert A. Osteryoung
Techniques for Elucidation of Organic Electrode Processes in Polarography.	Petr Zuman

Tuesday, 23 *August*

Computers in Analytical Chemistry, (1) *Basic and Special Purpose Languages* (2) *System Design Considerations* (3) *Importance of Time-Sharing to the Analytical Chemist* (4) *The Computer and the On-Stream Analyzer.*	N. Rasmussen, M. Silberg, R. A. Edwards and V. G. Poll

Wednesday, 24 *August*

Analytical Chemistry of Living Systems.	Ross U. Robinson
Intercorrelations with NMR, Infrared and Mass Spectrometry.	W. Donald Cooke
Panel Discussion	

Thursday, 25 *August*

Uses of Pulse Techniques in NMR.	Erwin L. Hahn
Open session	

Friday, 26 *August*

Spectroscopic Applications of Gas Lasers. A. JAVAN and M. FELD
Gas Absorption Spectroscopy in the Infrared using a Laser Light Source.

Further information may be obtained from Dr. W. GEORGE PARKS, University of Rhode Island, Kingston, Rhode Island.

Sunday–Tuesday 23–25 *October* 1966: **Sixth Informal Conference on Vacuum Microbalance Techniques.**

The conference will take place at Newporter Inn, Newport Beach, California.

Appropriate topics include original use, design and construction of vacuum microweighing systems and components, in such fields as adsorption studies, surface chemistry and thin film deposition, including both experimental and theoretical work.

Interested parties are invited to submit titles and abstracts to the following address before 1st August, 1966: 7500 Jefferson Street, Paramount, California 90723, U.S.A.

Wednesday–Friday 16–18 *November* 1966: **Eastern Analytical Symposium:** *Sponsored jointly by American Chemical Society, American Microchemical Society and Society for Applied Spectroscopy.* Statler-Hilton Hotel, New York, U.S.A.

The symposium will consist of selected invited papers on topics of current interest in chemical analysis and closely related fields. Suggestions for programme topics and speakers are invited from all interested persons; these should be submitted to the Program Chairman, Dr. MICHAEL CEFOLA, Department of Chemistry, Fordham University, New York 58, U.S.A.

For further information on the Symposium contact the Publicity Chairman, Mr. IVOR L. SIMMONS, M & T Chemicals, Inc., P.O. Box 471, Rahway, N. J. 07065, U.S.A.

Talanta, 1966, Vol. 13, pp. iii to iv. Pergamon Press Ltd. Printed in Northern Ireland

PAPERS RECEIVED

New colorimetric reagents for determination of trace amounts of oxidants and reductants: A. A. Schilt and A. M. Cresswell (4 *December* 1965)

Moisture characteristics of banded ingredients in coal and their influence on preparation of analysis samples: O. W. Rees (12 *December* 1965)

Acid-base indicator transition ranges in pyridine: J. S. Fritz and F. E. Gainer (21 *December* 1965)

Inorganic chromatography with phenylbenzohydroxamic acid-impregnated paper: J. Sherma and J. S. Fritz (3 *January* 1966)

Titrimetric determination of hydrogen peroxide in alkaline solution: W. H. McCurdy, Jr. and H. F. Bell (5 *January* 1966)

Some new chromogens for iron, cobalt and copper: Substituted hydrazidines and as-triazines containing the ferroin group: A. A. Schilt (5 *January* 1966)

Rapid complexometric analysis of brass with CDTA: C. A. Goetz and T. C. Loomis (6 *January* 1966)

The $K_2S_2O_7$-K_2SO_4, AgCl-KCl electrochemical cell: C. L. Bissell and F. R. Duke (7 *January* 1966)

Determination of iron in cadmium and cadmium telluride: D. H. Wilkins and G. E. Smith (15 *January* 1966)

Acid-base titrations in non-aqueous solvents: Analysis of dimethyl sulphate: W. M. Banick, Jr. and E. C. Francis (17 *January* 1966)

Borate complexes of benzohydroxamic acid and some of its derivatives: A spectrophotometric study: A. R. Fields, B. M. Daye and R. Christian (18 *January* 1966)

Determination of microgram quantities of metal ions by chelometric titration with amperometric end-point detection: F. Freese and G. Den Boef (24 *January* 1966)

Comparative study of methods for precipitating calcium oxalate from homogeneous solution: A. Bashar and A. Townshend (24 *January* 1966)

Ultrapurity analysis of zone-melted organic compounds—(A new quantitative differential thermal analysis method): R. Friedenberg and P. J. Jannke (24 *January* 1966)

Effect of salts on the partition of 8-quinolinol: John G. Mason and Irving Lipschitz (25 *January* 1966)

Determination of magnesium in pure iron with 2-thenoyltrifluoroacetone extraction: O. Kammori, I. Taguchi and K. Yoshikawa (27 *January* 1966)

Automatic neutron-activation unit and its application to oxygen determination in metals: I. Fujii and H. Muto (28 *January* 1966)

Anion-exchange separation techniques with methanol-aqueous solutions of hydrochloric and nitric acid: Richard J. Morrow (28 *January* 1966)

Inorganic chromatography on impregnated ion-exchange papers: J. Sherma (31 *January* 1966)

Spectrophotofluorometric determination of terbium and europium in potassium carbonate solution: T. Taketatsu, M. A. Carey and C. V. Banks (31 *January* 1966)

Hydrolysis study of organic acid anhydrides by differential thermal analysis—I: Pyromellitic dianhydride J. M. Rosenfeld, D. F. Loncrini and C. B. Murphy (1 *February* 1966)

L'application des radioisotopes a là chromatographic sur colonnes de celluloses substituées: R. A. A. Muzzarelli (1 *February* 1966)

Thermal analysis of some analogous thiols and their palladium complexes: B. C. Bera and M. M. Chakrabartty (3 *February* 1966)

Determination of indium in "Standard Rocks" by neutron-activation analysis: O. Johansen and E. Steinnes (3 *February* 1966)

Complexes de l'acide anthranil-diacétique, "anda", avec des métaux trivalents—I: Sur les complexes gallium-anda et indium-anda: C. Drăgulescu, Septimia Policec and T. Simonescu (4 *February* 1966)

Complexes de l'acide anthranil-diacétique, "anda", avec des métaux trivalents—II: Sur les complexes scandium-, yttrium-, lanthane-anda: C. Dragulescu, Septimia Policec and T. Simonescu (4 *February* 1966)

Separation of strontium from large amounts of calcium with application to radiostrontium analysis: Victor E. Noshkin and Norman S. Mott (4 *February* 1966)

Wet ashing of coal with perchloric acid plus periodic acid for determination of sulphur and other minor components: Gerald I. Spielholtz and Harvey Diehl (7 *February* 1966)

Scheme of analysis for separation and accurate determination of iron and aluminium in a single sample of silicate rock: J. C. Van Loon (7 *February* 1966)

Analysis of peracetic acid solutions: W. T. Dixon (7 *February* 1966)

Carminic acid as a reagent for spectrofluorimetric determination of molybdenum and tungsten—I: Development of procedures: G. F. Kirkbright, T. S. West and Colin Woodward (7 *February* 1966)

Carminic acid as a reagent for spectrofluorimetric determination of molybdenum and tungsten—II: Determination of molybdenum in mild steel: G. F. Kirkbright, T. S. West and Colin Woodward (7 *February* 1966)

Polarography of B_{12} coenzyme: B. Kratochvil and Harvey Diehl (7 *February* 1966)

Determination of fluorine in bones and teeth with Xylenol Orange: J. A. Růžička, H. Jakschová and L. Mrklas (8 *February* 1966)

Selective EDTA titration of gallium and aluminium in presence of other metals: K. L. Cheng and B. L. Goydish (8 *February* 1966)

Kinetic analysis of glycol mixtures: D. Benson and N. Fletcher (9 *February* 1966)

Study of factors which affect the reaction of ferrous ions with tripyridyl-s-triazine: E. B. Buchanan Jr., D. Crichton and J. R. Bacon (11 *February* 1966)

Reversible complex formation in organic chemical microscopy: A simple test for HMX: H. J. Scullion and Jeffrey Lewis (11 *February* 1966)

Oxidation of phosphorothioic acid by chloramine-T: T. Jose Jacob and C. G. R. Nair (11 *February* 1966)

Vanadatometric determination of thioacetamide: Miss S. Gita, P. T. Joseph and C. G. R. Nair (11 *February* 1966)

Mercurimetric determination of thiocyanates and isothiocyanates: Mieczyslaw Wroński (15 *February* 1966)

Talanta, 1966, Vol. 13, p. v. Pergamon Press Ltd. Printed in Northern Ireland

PUBLICATIONS RECEIVED

International Series of Monographs on Nuclear Energy, Division VIII, Materials, Volume 2: Rubidium and Caesium: F. M. PEREL'MAN. Pergamon Press, Oxford. Pp. vii + 145. 60s.

Introduction. The discovery and natural occurrence of rubidium and caesium. Properties of rubidium and caesium and their compounds. Systems formed by rubidium and caesium salts. The analytical chemistry of rubidium and caesium. The extraction of rubidium and caesium from minerals and ores. The preparation of the metals and various compounds of rubidium and caesium. References. Additional references (1960–64).

Talanta, 1966, Vol. 13, p. vii. Pergamon Press Ltd. Printed in Northern Ireland

PUBLISHER'S ANNOUNCEMENT

REPRINTS OF REVIEW PAPERS

Reprints of the following reviews published in Talanta are available from Journals Department Pergamon Press Ltd., Headington Hill Hall, Oxford, England, at 7s. or $1 per copy, on a cash with order basis only:

"Precipitation of Metal Chelates from Homogeneous Solution" by F. H. Firsching.

"Recent Developments in the Ring Oven Technique" by H. Weisz.

"Adsorption Indicators in Precipitation Titrations" by R. C. Mehrotra and K. N. Tandon.

"Radiometric Titrations" by T. Braun and J. Tölgyessy.

"Recent Uses of Liquid Ion Exchangers in Inorganic Analysis" by H. Green.

"Applications of Nuclear and Electron Magnetic Resonance in Analytical Chemistry" by B. D. Flockhart and R. C. Pink.

"A Critical Evaluation of Colorimetric Methods for Determination of Noble Metals—III: Palladium and Platinum" by F. E. Beamish.

"A Critical Evaluation of Colorimetric Methods for Determination of the Noble Metals—III: Rhodium, Iridium, Ruthenium, Osmium and Gold" by F. E. Beamish.

"Present State of Complexometry—I: Determination of Quadrivalent and Tervalent Metals" by Rudolf Přibil.

"Some Recent Developments in Radioactivation Analysis: A Review of Improvements in the Analytical Technique" by F. Girardi.

"Separation of Transplutonium Elements" by J. Starý.

Single copies of the **Heyrovský Honour Issue of Talanta,** December 1965, may be obtained from Journals Dept., Pergamon Press Ltd., Headington Hill Hall, Oxford, England, at £2 or $6.50 per copy on a cash with order basis only.

SUMMARIES FOR CARD INDEXES

Determination of gold by X-ray fluorescence methods: A. Chow and F. E. Beamish, *Talanta*, 1966, **13**, 539 (Department of Chemistry, University of Toronto, Toronto 5, Canada).

Summary—X-ray fluorescence methods for the determination of gold in silver beads and in hydrochloric acid solutions are described. These techniques may be applied to silver containing 0·2–5% of gold and to solutions containing 0·004–0·1% of gold. Platinum, palladium, rhodium and iridium do not interfere.

Vanadium compounds in reductimetric titrations—II: Standardisation of vanadium(II) sulphate with common oxidising agents and determination of binary mixtures: K. L. Chawla and J. P. Tandon, *Talanta*, 1966, **13**, 545 (Department of Chemistry, University of Rajasthan, Jaipur, India).

Summary—Methods for the standardisation of vanadium(II) sulphate are described. With weak oxidising agents, e.g., Fe(III)/Fe(II) in phosphoric acid, vanadium(II) undergoes a one-electron change, which is satisfactorily indicated by Neutral Red, Phenosafranine or Safranine T, or by potentiometry. Stronger oxidising agents oxidise vanadium(II) to vanadium(IV); Variamine Blue, Methylene Blue, *o*-dianisidine, cacotheline, ferroin, bis(α,α'-bipyridyl)iron(II) and ammonium molybdate are satisfactory indicators. Binary mixtures of oxidising agents can be determined.

Precipitation of nickel and palladium dimethylglyoximates from homogenous solution: Louis Gordon, P. R. Ellefsen, George Wood and Orville E. Hileman, Jr., *Talanta*, 1966, **13**, 551 (Department of Chemistry, Case Institute of Technology, Cleveland, Ohio, 44106, U.S.A.).

Summary—A comparison of the reaction mechanisms by which nickel or palladium dimethylglyoximate is precipitated from homogeneous solution by the reactions of biacetyl and hydroxylamine discloses many differences. Knowledge of the kinetics and mechanism of the reactions can be used to avoid formation of excess dimethylglyoxime, a limitation of the conventional methods of precipitation.

ОПРЕДЕЛЕНИЕ ЗОЛОТА МЕТОДАМИ РЕНТГЕНОВСКОГО ФЛУОРЕСЦЕНТНОГО АНАЛИЗА:

A. Chow and F. E. Beamish, *Talanta*, 1966, **13**, 539.

Резюме—Описаны методы рентгеновского флуоресцентного анализа для определения золота в зернах серебра и солянокислых растворах. Этими методами можно пользоваться в анализе серебра содержающего 0,2–5% золота и в анализе растворов содержающих 0,004–0,1% золота. Платина, палладий, родий и иридий не мешают определению.

СОЕДИНЕНИЯ ВАНАДИЯ В РЕДУКТОМЕТРИЧЕСКИХ ТИТРОВАНИЯХ—II: УСТАНОВКА ТИТРА СУЛЬФАТА ВАНАДИЯ(II) С ОБЫКНОВЕННЫМИ ОКИСЛИТЕЛЯМИ И АНАЛИЗ ДВОЙНЫХ СМЕСЕЙ:

K. L. Chawla and J. P. Tandon, *Talanta*, 1966, **13**, 545.

Резюме—Описываются методы для установки титра сульфата ванадия(II). В случае слабых окислителей, на пример железа(III)/железа(II) в фосфорнокислом растворе, ванадий(II) меняет один электрон; эта перемена удовлетворительно индицирована нейтральным красным, феносафранином, сафранином Т или потенциометрическим методом. Боле сильные окислители окисляют ванадий(II) до ванадия(IV); в качестве индикатора могут служить вариаминсиний, метиленсиний, *o*-дианизидин, какотелин, ферроин, бис(α,α-дипиридил)железо(II) и молибдат аммония. Можно анализировать двойные смеси окислителей.

ОСАЖДЕНИЕ ДИМЕТИЛГЛИОКСИМАТОВ НИКЕЛЯ И ПАЛЛАДИЯ ИЗ ГОМОГЕННЫХ РАСТВОРОВ:

Louis Gordon, P. R. Ellefsen, George Wood and Orville E. Hileman, Jr., *Talanta*, 1966, **13**, 551.

Резюме—Сравнением механизма реакции осаждения диметилглиоксимата никеля или палладия из гомогенного раствора на основании реакций диацетила и гидроксиламина обнаруживаются многие разницы. Сведения о кинетике и механизме реакций могут быть использованы чтоб избечь образование избытка диметилглиоксима, представляющего недостаток обыкновенных методов осаждения.

Use of asymmetrically-polarised dropping-mercury electrodes in controlled-potential polarography: T. Damokos and E. Juhász, *Talanta*, 1966, **13**, 559 (Institute for Physical Chemistry, Technical University, Budapest, Hungary).

Summary—It is shown that uncompensated cell resistance in controlled-potential polarography can be decreased by the use of asymmetrical polarisation of the dropping-mercury electrode.

A manometric method for determination of carbonates in minerals and ores: N. Jordanov, *Talanta*, 1966, **13**, 563 (Institut für Allgemeine und Anorganische Chemie an der Bulgarischen Akademie der Wissenschaften, Sofia, Bulgarien).

Summary—A method of determining carbonates in minerals and ores is suggested, based on decomposition of the sample with 20% sulphuric acid in vacuum. The determination is carried out in an apparatus of relatively simple construction. The carbon dioxide content is determined by the alteration in pressure of the system and read off from a graduated scale. The method is applicable for the analysis of samples with 0·1–40% carbon dioxide content; the accuracy of the determination is 0·75–10%.

Errors of kinetic data obtained from thermogravimetric curves at increasing temperature: J. Šesták, *Talanta*, 1966, 13, 567 (Institute of Solid State Physics, Czechoslovak Academy of Sciences, Prague 6, Cukrovarnická 10, Czechoslovakia).

Summary—Errors of kinetic data obtained from thermogravimetric curves at increasing temperature are discussed.

Detection and determination of chlorophenols and chlorophenoxyacetic acids by instrumental analysis: Mrs. L. Lechner, Mrs. A. Somogyi and Mrs. L. Biró, *Talanta*, 1966, **13**, 581 (Research Institute for Heavy Chemical Industries, Budapest XI, Hungary).

Summary—A quantitative method for the determination of chlorophenols and chlorophenoxyacetic acids in aqueous solutions is described. The samples investigated contained 2-chlorophenol, 2,4-dichlorophenol, 2,6-dichlorophenol, 2,4,6-trichlorophenol and their phenoxyacetic acid derivatives. The total amount of chlorophenols is determined by spectrophotometry, the ratio of individual chlorophenols by gas chromatography and the total quantity of phenoxyacetic acids by acidimetric titration. The determinations are carried out after extraction with diethyl ether, carbon tetrachloride and petroleum ether, respectively.

ИСПОЛЬЗОВАНИЕ НЕСИММЕТРИЧЕСКИ ПОЛЯРИЗИРОВАННЫХ РТУТНЫХ КАПЕЛЬНЫХ ЭЛЕКТРОДОВ В ПОЛЯРОГРАФИИ ПРИ КОНТРОЛИРОВАННОМ ПОТЕНЦИАЛЕ:

T. Damokos and E. Juhász, *Talanta*, 1966, **13**, 559.

Резюме—Показано что некомпенсированное сопротивлсние клетки в полярографии при контролированном напряж уменьшается несимметрической поляризацией ртутного капельного злектрода.

МАНОМЕТРИЧЕСКИЙ МЕТОД ДЛЯ ОПРЕДЕЛЕНИЯ КАРБОНАТОВ В МИНЕРАЛАХ И РУДАХ.

N. Jordanov, *Talanta*, 1966, **13**, 563.

Резюме—Предложен метод для определения карбонатов в минералах и рудах, основывающийся на разложении пробы с 20% тной серной кислотой в вакууме. Определение проводится в сравнительно несложном приборе. Содержание двуокиси углерода определяют из перемены давления в системе и отсчитывают на градуированной шкале. Методом можно пользоваться в анализе проб содержающих 0,1–40% двуокиси углерода; точность определения равна 0,75–10%.

ОШИБКИ В КИНЕТИЧЕСКИХ ДАННЫХ ПОЛУЧЕННЫХ ИЗ ТЕРМОГРАВИМЕТРИЧЕСКИХ КРИВЫХ ПРИ РАСТУЩЕЙ ТЕМПЕРАТУРЕ:

J. Šesták, *Talanta*, 1966, **13**, 567.

Резюме—Обсуждены ошибки в кинетических данных полученных из термогравиметрических кривых при растущей температуре.

ОБНАРУЖЕНИЕ О ОПРЕДЕЛЕНИЕХЛОРФЕНОЛОВ И ХЛОРФЕНОКСИУКСУСНЫХ КИСЛОТ С ИСПОЛЬЗОВАНИЕМ ИНСТРУМЕНТАЛЬНЫХ МЕТОДОВ АНАЛИЗА:

L. Lechner, A. Somogyi and L. Biró, *Talanta*, 1966, **13**, 581.

Резюме—Описан количественный метод для определения хлорфенолов и хлорфеноксиуксусных кислот в водных растворах. Исследованные пробы содерживали 2-хлорфенол, 2,4-дихлорфенол, 2,6-дихлорфенол, 2,4,6-трихлорфенол и их феноксикислые производные. Общее содержание хлорфенолов определено спектрофотометрическим методом, отношение индивидуальных хлорфенолов методом газовой хроматографии и общее содержание феноксиуксусных кислот ацидиметрическим титрованием. Определения проведены после экстрагирования этиловым эфиром, тетрахлорметаном или петролейным эфиром, соответственно.

Spectrophotometric extractive titrations—II: Determination in gallium arsenide of the sum of metals extractable with dithizone: AFTANAS GALÍK and MIROSLAV KNÍŽEK, *Talanta*, 1966, **13**, 589 (A. S. Popov's Research Institute for Radio and Telecommunications, Prague, Czechoslovakia).

Summary—A procedure for the determination of the sum of metals, which are extractable with dithizone, in gallium arsenide is given. After the dissolution of the sample the impurities are extracted with several portions of $10^{-4}M$ dithizone in carbon tetrachloride, gallium being screened by tartrate ion. The excess of the reagent is extracted into $0{\cdot}1M$ aqueous ammonia and after stripping into carbon tetrachloride the dithizone is determined by spectrophotometric extractive titration. The effect of pH is considered. The limit of detection, based on the evaluation of twenty blanks, is $2{\cdot}30 \times 10^{-8}$ mole, the equivalent of $1{\cdot}50\ \mu g$ of zinc.

Cerate oxidimetry of alpha-hydroxy and alpha-keto carboxylic acids in acetic acid: JOHN T. GATTO and KENNETH G. STONE, *Talanta*, 1966, **13**, 597 (Chemistry Department, Michigan State University, East Lansing, Michigan, U.S.A.).

Summary—Methods for the preparation and use of a solution of ammonium hexanitratocerate(IV) in acetic acid as a titrant for the oxidation of alpha-hydroxy and alpha-keto carboxylic acids in acetic acid are presented. The applicability of this reagent with respect to the stoichiometry, products and reaction times obtained is discussed.

Amperometry with two polarisable electrodes—XI: Determination of bismuth by EDTA titration: F. VYDRA and J. VORLÍČEK, *Talanta*, 1966, **13**, 603 (Analytical Laboratory, Polarographic Institute of J. Heyrovský, Czechoslovak Academy of Sciences, Prague 1, Jilská 16, Czechoslovakia).

Summary—Optimum conditions have been found for a highly selective determination of bismuth *via* EDTA titration with biamperometric indication of the end-point. The influence of the applied potential, pH and stirring on the accuracy and selectivity of the determination has been studied. In a medium of $0{\cdot}4M$ nitric acid only high concentrations of iron(III) and copper(II) interfere with the determination of bismuth. Zirconium, thallium(III) and indium interfere even in small concentrations. The average error of the determination of 5–100 mg of bismuth (when titrated with $0{\cdot}05M$ EDTA solution) is $\pm 0{\cdot}1\%$ rel. and for the determination of 0·5–10 mg it is $\pm 0{\cdot}3\%$ rel. ($0{\cdot}005M$ EDTA). The method has been verified by the analysis of a Wood's metal of known composition.

СПЕКТРОФОТОМЕТРИЧЕСКИЕ ЭКСТРАКТИВНЫЕ ТИТРОВАНИЯ—II: ОПРЕДЕЛЕНИЕ СУММЫ ЭКСТРАГИРУЕМЫХ ДИТИЗОНОМ МЕТАЛЛОВ В АРСЕНИДЕ ГАЛЛИЯ.

A. Galík and M. Knížek, *Talanta*, 1966, **13**, 589.

Резюме—Приведена процедура для определения суммы зкстрагируемых дитизоном металлов в арсениде галлия. После растворения пробы зкстрагируют примеси с $10^{-4}M$ раствором дитизона в тетрахлорметане, маскируя галлий тартратионом. Избыток реагента зкстрагируют $0{,}1M$ водным раствором аммияка и после перевода в тетрахлорметан дитизон определяют спектрофотометрическим зкстрактивным титрованием. Рассмотрено влияние pH. Предел обнаружения, определен на основании 20 слепых опытов, равен $2{,}30 \times 10^{-8}$ молей, зквивалентно 1,50 мкг цинка.

ОКСИДИМЕТРИЯ АЛЬФА-ГИДРОКСИ И АЛЬФА-КЕТОКАРБОНОВЫХ КИСЛОТ В УКСУСНОЙ КИСЛОТЕ С ИСПОЛЬЗОВАНИЕМ ЦЕРАТИОНА:

John T. Gatto and Kenneth Stone, *Talanta*, 1966, **13**, 597.

Резюме—Сообщены методи для приготовления и использования раствора гексанитратоцерата(IV) в уксусной кислоте в качестве титрованного раствора для окисления альфа-гидрокси и альфа-кетокарбоновых кислот в уксусной кислоте. Обсуждена применимость этого реагента учитывая стехиометрию, продукты и длительность реакций.

АМПЕРОМЕТРИЯ С ДВУМЯ ПОЛЯРИЗИРУЮЩМИИСЯ ЭЛЕКТРОДАМИ—XI:

ОПРЕДЕЛЕНИЕ ВИСМУТА ТИТРОВАНИЕМ С ЭДТА:

F. Vydra and J. Vorlíček, *Talanta*, 1966, **13**, 603.

Резюме—Определены оптимальные условия для высоко избирательного определения висмута титрованием с ЭДТА, пользуясь биамперометрическим обнаружением конца титрования. Изучено влияние приложенного напряжения, pH и перемешивания на точность и избирательность определения. В растворе $0{,}4M$ азотной кислоты определению висмута мешают только большие концентрации железа(III) и меди(II). Цирконий, таллий(III) и индий мешают даже в небольших концентрациях. Средняя ошибка в определении 5–100 мг висмута (при титровании с $0{,}05M$ раствором ЭДТА) равна $\pm 0{,}1\%$, а в определении 0,5–10 мг равна $\pm 0{,}3\%$ (0,005M ЭДТА). Метод был испытан в анализе Вуда металла знакомого состава.

Spectrofluorimetric determination of submicrogram amounts of aluminium using salicylidene-*o*-aminophenol: R. M. Dagnall, R. Smith and T. S. West, *Talanta*, 1966, **13**, 609 (Department of Chemistry, Imperial College, London S.W.7, England).

Summary—Salicylidene-*o*-aminophenol provides a sensitive spectrofluorimetric reagent for the determination of aluminium down to 27 ng (or $2{\cdot}7 \times 10^{-4}$ ppm in the final solution). The most suitable conditions of pH (5·6), reagent concentration and development time (>20 min) have been established. Extraction with sodium diethyldithiocarbamate into ethyl acetate at the pH of the determination renders the method highly selective; out of 46 foreign cations examined only chromium(III), scandium and thorium interfere. Anions which form complexes with aluminium, such as citrate, tartrate and fluoride, also cause interference, but none of the common anions interferes. A 1:1 stoichiometry of the complex has been established and some conclusions have been drawn concerning its nature.

Use of gas-liquid and thin-layer chromatography in characterising air pollutants by fluorometry: E. Sawicki, T. W. Stanley, S. McPherson and M. Morgan, *Talanta*, 1966, **13**, 619 (Laboratory of Engineering and Physical Sciences, Division of Air Pollution, Robert A. Taft Sanitary Engineering Center, Public Health Service, U.S. Department of Health, Education and Welfare, Cincinnati, Ohio 45226, U.S.A.)

Summary—Relatively large amounts of alkylated derivatives of the polynuclear aromatic hydrocarbons are present in some urban atmospheres. These compounds are believed to be derived from industrial sources. Because alkylation of the tetracyclic aromatic hydrocarbons can confer carcinogenic activity on the derivatives, the presence of substantial amounts of these alkylated compounds in the air needs thorough study. The R_F value and the retention time, by themselves, are inadequate for characterisation of the polynuclear compounds. Gas-liquid chromatography followed by fluorometric examination of the eluent bands, and mixed-adsorbent two-dimensional thin-layer chromatography followed by direct fluorometric examination are very useful in characterising all types of organic compound in the organic fractions of airborne particulates and effluents from air pollution sources.

СПЕКТРОФЛУОРОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ СУБМИКРОГРАММОВЫХ КОЛИЧЕСТВ АЛЮМИНИЯ С ИСПОЛЬЗОВАНИЕМ САЛИЦИЛИДЕН-*о*-АМИНОФЕНОЛА:

R. M. Dagnall, R. Smith and T. S. West, *Talanta*, 1966, **13**, 609.

Резюме—Салицилиден-*о*-аминофенол представляет собой чувствительный спектрофлуорометрический реагент для определения алюминия все до 27 нг (или 2,7 $\times 10^{-4}$ мг)л в конечном растворе). Определены оптимальные условия для pH (5,6), концентрации реагента и времени проявления окраски (>20 мин.). Метод становится высоко избирательный экстрагированием образца диэтилдитиокарбаматом натрия в этиловый эфир уксусной кислоты при pH 5,6; между испытанными 46 катионами только хром(III), скандий и торий мешают определению. Анионы образующие комплексы с алюминием как на пример цитрат, тартрат и фторид тоже влияют на определение, но обыкновенные анионы не мешают. Определено стехиометрическое отношение комплекса 1:1 и сделаны ссилки на его строение.

ИСПОЛЬЗОВАНИЕ МЕТОДОВ ГАЗО-ЖИДКОСТНОЙ И ТОНКОСЛОЙНОЙ ХРОМАТОГРАФИИ ДЛЯ ХАРАКТЕРИЗОВАНИЯ ЗАГРЯЗНЯЮЩИХ ВЕЩЕСТВ В ВОЗДУХЕ ПТУЕМ ФЛУОРОМЕТРИИ:

E. Sawicki, T. W. Stanley, S. McPherson and M. Morgan, *Talanta*, 1966, **13**, 619.

Резюме—Сравнительно большие количества алкилзамещенных многоядерных ароматических углеводородов находятся в атмосфере некоторых городов. Предполагается что эти соединения происходят из промишленных источников. Присутствие больших количеств этих алкилдериватов в воздухе изискует тщательное изучение, потому что алкилирование четырехядерных ароматических углеводородов может произвести раковызывающее действие. Значение R_F и время удерживания сами собой не достаточны для характеризования этих многоядерных соединений. Газо-жидкостная хроматография с последующим флуорометрическим исследованием элюированных фракций и хвухдимензиональная тонкослойная хроматография с смешанными адсорбентами с последующим прямым флуорометрическим исследованием представляют очень полезные методы для характеризования всех типов органических соединений, находящихся в воргаинческих фракциях частиц в воздухе и в веществах, происходящих из источников загрязнения воздуха.

Determination of free acid in antimony(III) and bismuth(III) solutions: R. KRISHNA IYER and T. R. BHAT, *Talanta*, 1966, **13**, 631 (Atomic Energy Establishment Trombay, Chemistry Division, Bombay-28, India).

Summary—A method for the determination of free acid in antimony(III) and bismuth(III) solutions is given. A solution of the disodium salt of EDTA, 2–3% in excess of the stoichiometric amount, is added to the metal salt solution and titrated with sodium hydroxide solution potentiometrically or visually using a mixed indicator. The error in the method is less than 0·5%.

Some critical comments on the quantitative infrared spectrographic analysis of metals by means of their chelates: R. NEEB, *Talanta*, 1966, **13**, 635 (Institut für Anorganische Chemie und Kernchemie der Johannes Gutenberg-Universität Mainz, Bundesrepublik Deutschland).

Summary—Attention is drawn to some points (measurement, mixing, calibration curve) regarding the applicability of infrared spectrographic procedures in the analysis of metals by means of their chelates.

Automatic scanning of chromatoplates by multi-scaling using a gamma-ray spectrometer: R. A. A. MUZZARELLI, *Talanta*, 1966, **13**, 639 (Faculty of Sciences, University of Sherbrooke, Sherbrooke, P.Q., Canada.)

Summary—The location of radioactive tracers on chromatographic thin layers or papers is realised, together with the qualitative and quantitative analysis, using only a gamma-ray spectrometer.

ОПРЕДЕЛЕНИЕ СВОБОДНОЙ КИСЛОТЫ В РАСТВОРАХ СУРЬМЫ(III) И ВИСМУТА(III):

R. Krishna Iyer and T. R. Bhat, *Talanta*, 1966, **13**, 631.

Резюме—Сообщен метод для определения свободной кислоты в растворах сурьмы(III) и висмута(III). Раствору соли металла добавляют раствор динатриевой соли ЭДТА—2-3% сверх стехиометрического количества—и титруют с раствором гидроокиси натрия, с использованием потенциометрического метода или визуально, пользуясь смешанным индикатором. Ошибка метода меньше чем 0,5%.

НЕКОТОРЫЕ КРИТИЧЕСКИЕ ЗАМЕЧАНИЯ К КОЛИЧЕСТВЕННОМ ОПРЕДЕЛЕНИЮ МЕТАЛЛОВ ПУТЕМ ИХ ХЕЛАТОВ МЕТОДОМ ИНФРАКРАСНОЙ СПЕКТРОСКОПИИ:

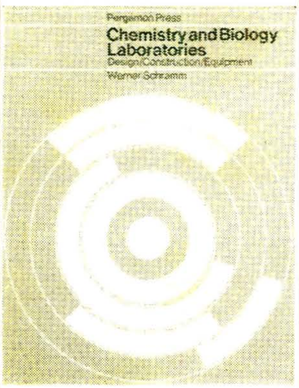
R. Neeb, *Talanta*, 1966, **13**, 635.

Резюме—Обращается внимание на некоторые пункты (измерение, перемешивание, стандартная кривая) в связи с применимостью метода инфракрасной спектроскопии в анализе металлов в форме их хелатов.

АВТОМАТИЧЕСКАЯ ОЦЕНКА ХРОМАТОГРАММ С ИСПОЛЬЗОВАНИЕМ СПЕКТРОМЕТРА ГАММА ЛУЧЕЙ.

R. A. A. Muzzarelli, *Talanta*, 1966, **13**, 639.

Резюме—Определение местоположения радиоактивных индикаторов на тонкослойных и бумажных хроматограммах получено, вместе с количественным и качественным анализом, только с использованием спектрометра гамма лучей.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