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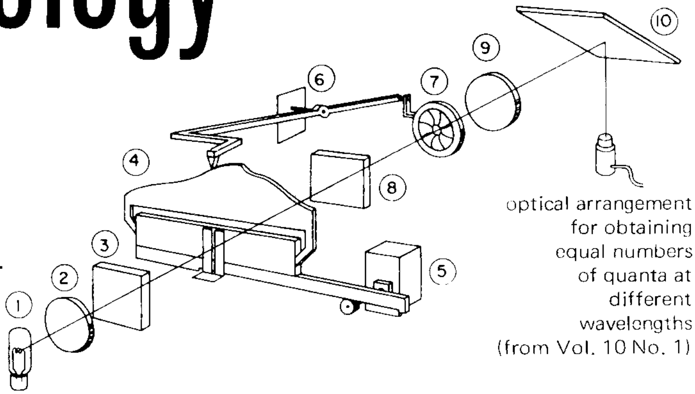

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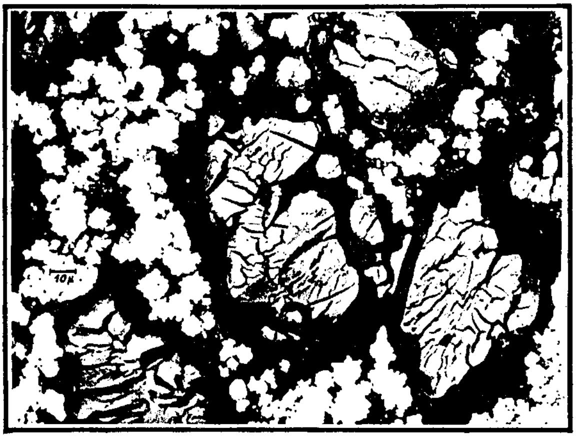

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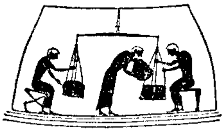

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ATOMIC-FLUORESCENCE SPECTROSCOPY OF LEAD

VÁCLAV SYCHRA and JAROSLAV MATOUŠEK
Department of Analytical Chemistry, Technical University, Prague 6, Czechoslovakia

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Summary—The fluorescence spectrum of lead excited with a high-intensity hollow-cathode lamp has been investigated and the probable mechanism of fluorescence transitions is suggested. It is confirmed experimentally that the most intense fluorescence line at 405·78 nm is mostly due to direct-line fluorescence. The premixed air–hydrogen flame, the separated air–acetylene flame, and the oxy-hydrogen flame diluted with argon have been used, the last mentioned giving a detection limit of 0·02 ppm with the line at 405·78 nm.

THE DETERMINATION of lead by atomic-fluorescence spectroscopy has already been reported by several authors, who have used either continuous excitation sources[1–3] or line excitation sources.[3–8] The best detection limit of 0·0035 ppm was obtained by Massmann,[6] who used a special hollow-cathode lamp as source, and evaporated the sample in an electrically heated graphite in an argon atmosphere.

In this study, a lead high-intensity hollow-cathode lamp of the Sullivan-Walsh design[9] was used as a fluorescence excitation source. This type of lamp has recently been used successfully for the atomic-fluorescence determination of silver,[10] beryllium,[11] arsenic,[5] copper,[5] magnesium,[12] iron,[5,13] cobalt[5,13] and nickel.[5,13,14] Atomic fluorescence of lead excited with a high-intensity hollow-cathode lamp was mentioned very briefly by Manning and Heneage.[5]

This paper reports the detailed investigation of the complete fluorescence spectrum of lead excited by a high-intensity hollow-cathode lamp and the determination of lead by atomic-fluorescence spectrophotometry in various premixed flames.

EXPERIMENTAL

Apparatus

A Techtron AA-4 atomic-absorption spectrophotometer equipped with a lead high-intensity hollow-cathode lamp and ultraviolet-sensitive HTV R 106 photomultiplier was coupled to a Hitachi Perkin–Elmer Model 165 recorder. The lamp and detector were square-wave modulated at 285 Hz. The instrument was adapted for fluorescence measurements in practically the same manner as described in our previous paper.[13] The optical arrangement is shown diagrammatically in Fig. 1. The mirror in the optical path of the exciting beam increased the fluorescence emission by 100%, but the mirror in the optical path of the fluorescence radiation enhanced the signal by only 70%, and also increased the background emission of the flame, and was not always found to be advantageous. The instrumental settings were adjusted to the maximum values:[13] primary lamp current, 15 mA; booster current, 300 mA; slit-width, 300 μm (band-width 0·99 nm).

Reagents

A stock lead solution was prepared by dissolving 1·000 g of spectrally pure metal in nitric acid (1 + 1) and diluting to 1000 ml with twice distilled water. More dilute solutions were prepared with the same concentration of nitric acid. All other solutions were prepared from reagent-grade chemicals.

Flame conditions

An air–hydrogen flame, an oxy-hydrogen flame diluted with argon, and a separated air–acetylene flame were used. The Techtron FE-1 emission burner head for the air–acetylene flame was fitted with a chamber with five concentric rows of holes and tangential nitrogen inlet to facilitate separation of the flame[15] (Fig. 2). For the air–hydrogen and hydrogen–oxygen–argon flames, a specially manufactured Meker-type brass burner head with 97 holes 0·5 mm diameter was also fitted with the chamber described.

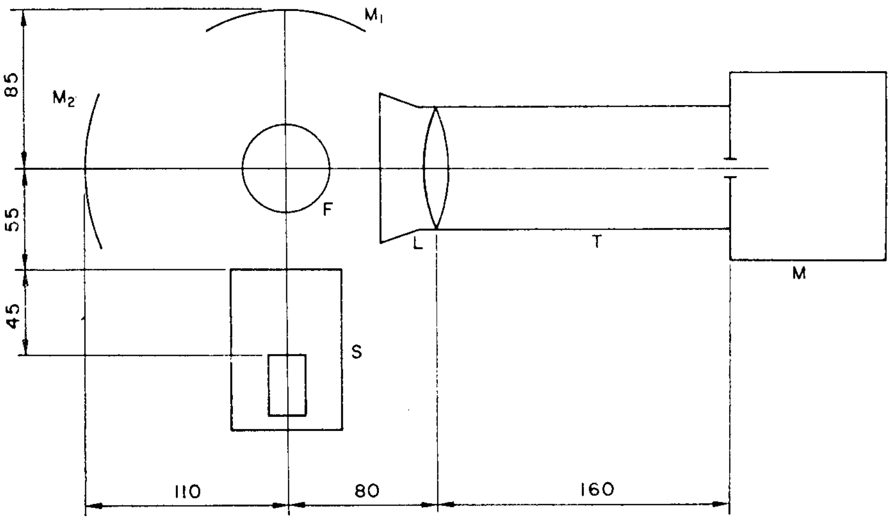

FIG. 1.—Optical arrangement for atomic-fluorescence measurements.
S—excitation source M$_1$, M$_2$—mirrors
F—flame T—selective radiation gathering tube
L—condensing lens M—monochromator

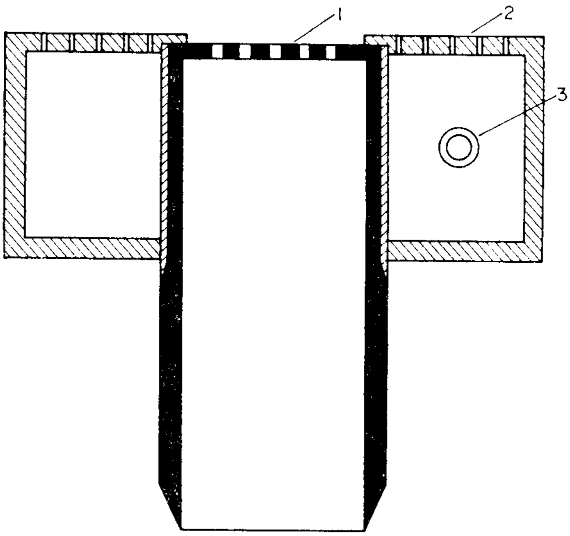

FIG. 2.—Burner for a nitrogen-separated air–acetylene flame.
(1) Burner head, (2) chamber, (3) nitrogen inlet

The dependence of background emission of the flames and of the fluorescence signal on the fuel to oxidant ratio was investigated to find the optimum gas flow-rates. From Fig. 3 it is apparent that the fluorescence signal in the hydrogen–oxygen–argon flame at a given oxygen flow-rate is strongly dependent on the hydrogen flow-rate, whereas the fluorescence signal in the air–hydrogen flame is practically independent of the hydrogen flow-rate. For the separated air–acetylene flame, the dependence of the fluorescence signal on the acetylene flow-rate exhibits a flat maximum. The resulting optimum gas flow-rates are listed in Table I.

The height of measurement in the flame was not critical, but to avoid emission from the primary reaction zone, the measurements on all flames were taken at 15–25 mm above the burner top.

The solution uptake rate was set to 4·7 ml/min for the air–hydrogen and hydrogen–oxygen–argon flame, and to 5·2 ml/min for the air–acetylene flame.

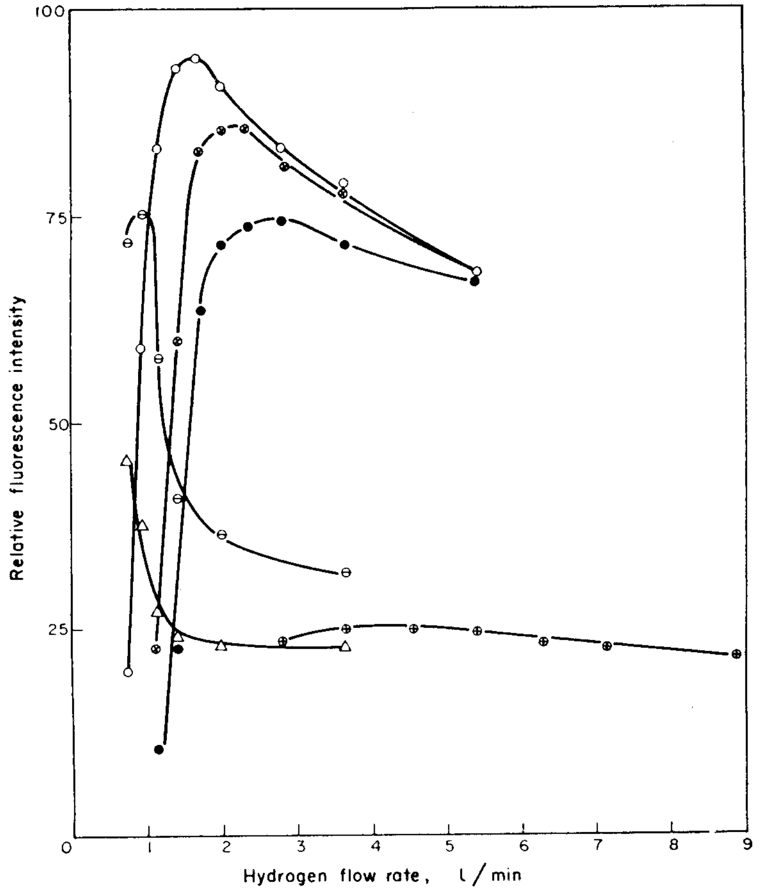

FIG. 3.—Variation of relative fluorescence intensity for lead at 405·78 nm in air–hydrogen, argon–hydrogen, and hydrogen–oxygen–argon flames.

⊕—air–hydrogen hydrogen–oxygen–argon, oxygen flow
△—argon–hydrogen ⊖—0·10 l./min
○—0·35 l./min
⊗—0·65 l./min
●—0·75 l./min

TABLE I.—BURNER OPERATING CONDITIONS

Flame	Flow-rate, *l./min*				
	H_2	C_2H_2	Air	O_2	Ar
H_2–air	4·55	—	6·35	—	—
H_2–O_2–Ar	1·70	—	—	0·35	5·70
C_2H_2–air	—	0·95	6·25	—	—

Emission and fluorescence spectra of lead

To choose the most sensitive fluorescence lines, the relative intensities of lines emitted by the excitation spectral source and of corresponding fluorescence lines in all the flames were determined. In scanning the fluorescence spectrum, a 10-ppm solution of lead was sprayed into the flame under the optimum conditions and at a slit-width of 50 μm. The emission spectrum of the lamp was scanned at the maximum lamp operating currents and at a slit-width of 10 μm. The relative emission and fluorescence intensities measured were corrected for the detector response.

Atomic-absorption measurements

To compare the atomic fluorescence and atomic absorption of lead, the same equipment was used, but with a 100-mm long air-acetylene flame. The instrumental settings were: primary lamp current, 6 mA; booster current, 300 mA; slit-width, 50 μm. The gas flow-rates and solution uptake rate were the same as for the fluorescence measurements.

RESULTS AND DISCUSSION

Atomic-fluorescence lines

Spectral characteristics of lead lines which exhibit atomic fluorescence in the three flames studied are listed in Table II. All fluorescence lines correspond to the transition to the $6p^2\ {}^3P$ level. As expected from atomic-absorption measurements, both resonance lines at 217·00 and 283·31 nm give relatively high fluorescence signals due to resonance fluorescence; in the case of the line at 283·31 nm a contribution from stepwise-line fluorescence cannot be excluded. The additional intense signals at 261·37 and 261·42, 280·20, 363·96, 368·35 and 405·78 nm must be mostly due to direct-line fluorescence; for example, for the lines at 405·78 and 363·96 nm, excitation by the 283·31 nm line to the $7s\ {}^3P_1{}^0$ state followed by radiative transition to the metastable $6p^2\ {}^3P_2$ and $6p^2\ {}^3P_1$ states, respectively, seems to be the most probable. This was assumed because of the great energy difference between the ground state of the atom and the two other components of the triplet $6p^2\ {}^3P$ state, and also because of the weak atomic absorption of these lines (see Table III). The fluorescence emission at 368·35 nm is the result of stepwise fluorescence, with the lower term of the fluorescence transition not being the ground state of the atom, *i.e.*, excitation with the 283·31 nm line to the $7s\ {}^3P_1{}^0$ state followed by a radiationless transition to the $7s\ {}^3P_0{}^0$ state, and then fluorescence transition to the metastable $6p^2\ {}^3P_1$ state. The energy which the excited atom must lose by a radiationless transition to the $7s\ {}^3P_0{}^0$ state is very small. For the most intense fluorescence line at 405·78 nm and for the lines at 368·35 and 363·96 nm this mechanism was confirmed experimentally by filtering off both resonance lines with a glass filter. Contributions of only 5 and 34% of the resonance fluorescence were found for the 405·78 and 368·35 nm lines, respectively. The fluorescence emission at 363·96 nm is completely direct-line fluorescence.

TABLE II.—RELATIVE EMISSION AND FLUORESCENCE INTENSITIES OF LEAD LINES

Line,[16] *nm*	Oscillator strength	Energy levels, *eV*	Transition[17,18]	Relative lamp emission intensity,	Relative fluorescence intensity		
					Air–H_2	H_2–O_2–Ar	Air–C_2H_2
217·00	0·048	0–5·712	$6p^2\ {}^3P_0$–$6d\ {}^3D_1{}^0$	15	18	16	26
261·37*	0·19	0·969–5·712	$6p^2\ {}^3P_1$–$6d\ {}^3D_1{}^0$	49	15	13	22
261·42*	2·7	0·969–5·711	$6p^2\ {}^3P_1$–$6d\ {}^3D_2{}^0$				
280·20	5·1	1·320–5·744	$6p^2\ {}^3P_2$–$6d\ {}^3F_3{}^0$	55	8	5	10
283·31	0·22	0–4·375	$6p^2\ {}^3P_0$–$7s\ {}^3P_1{}^0$	79	76	68	69
363·96	0·26	0·969–4·375	$6p^2\ {}^3P_1$–$7s\ {}^3P_1{}^0$	47	42	33	35
368·35	0·64	0·969–4·334	$6p^2\ {}^3P_1$–$7s\ {}^3P_0{}^0$	65	19	25	11
405·78	2·3	1·320–4·375	$6p^2\ {}^3P_2$–$7s\ {}^3P_1{}^0$	100	100	100	100

* Lines unresolved in emission and fluorescence spectra.

TABLE III.—SENSITIVITIES OF LEAD DETERMINATION BY ATOMIC-FLUORESCENCE AND ATOMIC-ABSORPTION SPECTROSCOPY IN VARIOUS FLAMES

Line, *nm*	Detection limit, *ppm*			
	AFS			AAS
	H_2–O_2–Ar	Air–H_2	Air–C_2H_2 (separated)	Air–C_2H_2
405·78	0·02*	0·10	0·20	15†
283·31	0·05	0·12	0·15	0·12
363·96	0·05	0·15	0·40	15
217·00	0·06	0·20	0·12	0·08
368·35	0·07	0·30	1·5	12
261·37 261·42	0·15	0·45	0·30	6
280·20	0·30	0·80	1·0	>100

* Signal to noise ratio = 2.

† Values obtained with the same instrument and the same spectral source.

The same confirmation could be made for the unresolved 261·37 and 261·42 nm lines and the 280·20 nm line, by filtering off the radiation of the 217·00 nm resonance line. In the case of the 280·20 nm line, the upper energy level of which lies 0·032 eV higher than the energy level of the 217·00 nm resonance line, thermally assisted direct-line fluorescence, postulated by Dagnall and co-workers for the explanation of some fluorescence transitions of antimony[19] and bismuth[20] must be assumed.

Analytical working curves and detection limits

In Fig. 4, the analytical working curves for the most sensitive lead line at 405·78 nm in various flames are shown, and in Fig. 5 for all the lead fluorescence lines observed in the hydrogen–oxygen–argon flame. In Fig. 4 the 217·00 nm line, which exhibits the best detection limit in the separated air–acetylene flame, is also included. The dependence of the relative fluorescence intensity on the concentration of lead is linear over a range of up to three orders of magnitude. Despite the fact that there are a number of factors causing analytical curves to have shapes differing from the theoretical growth curves,[21] the shapes of the working curves for the resonance lines are in very good agreement with those derived by Hooymayers[22] for the case when the source-line half-width is narrow compared to the absorption line half-width.

From theoretical results[22] it can be concluded that differences in the shapes and positions of the analytical curves for the same line excited in various flames by the same spectral source and with use of the same optical arrangement, are caused by differences in the ground-state atom concentration, fluorescence yield factor and the *a*-parameter. For the 405·78 nm line (see Fig. 4), the fluorescence signal obtained from the separated air–acetylene flame is higher than that from the air–hydrogen flame for all lead concentrations. This is evidently due to a higher efficiency of atomization in the hotter air–acetylene flame. The highest signal was obtained in the oxy-hydrogen flame diluted with argon, as might be expected,[13,23,24] owing to the higher fluorescence yield factor than for the air–hydrogen flame because of the quenching cross-section of argon being smaller than that of nitrogen. A 4·0-fold increase in the fluorescence signal was observed. For the other fluorescence lines, 3·1, 3·7, 2·5, 3·4, 3·0 and 5·0-fold increases, resulting from using the hydrogen–oxygen–argon flame in place of the air–hydrogen flame were found for the 217·00, 261·37 and 261·42, 280·20, 283·31, 363·96 and 368·35 nm lines, respectively. Since the noise of measurement for both flames is practically the same, the higher signal in the hydrogen–oxygen–argon flame results in lower detection limits. The use of the nitrogen sheath makes both air–hydrogen and hydrogen–oxygen–argon flames steadier and produces a further improvement (approximately 2-fold) in the detection limits. In the case of the separated air–acetylene flame, the relatively high background, especially at longer wavelengths, causes a deterioration in the detection limits in most cases compared with the air–hydrogen flame. Therefore, the best signal-to-noise ratio in the separated air–acetylene flame was obtained for the line at 217·00 nm.

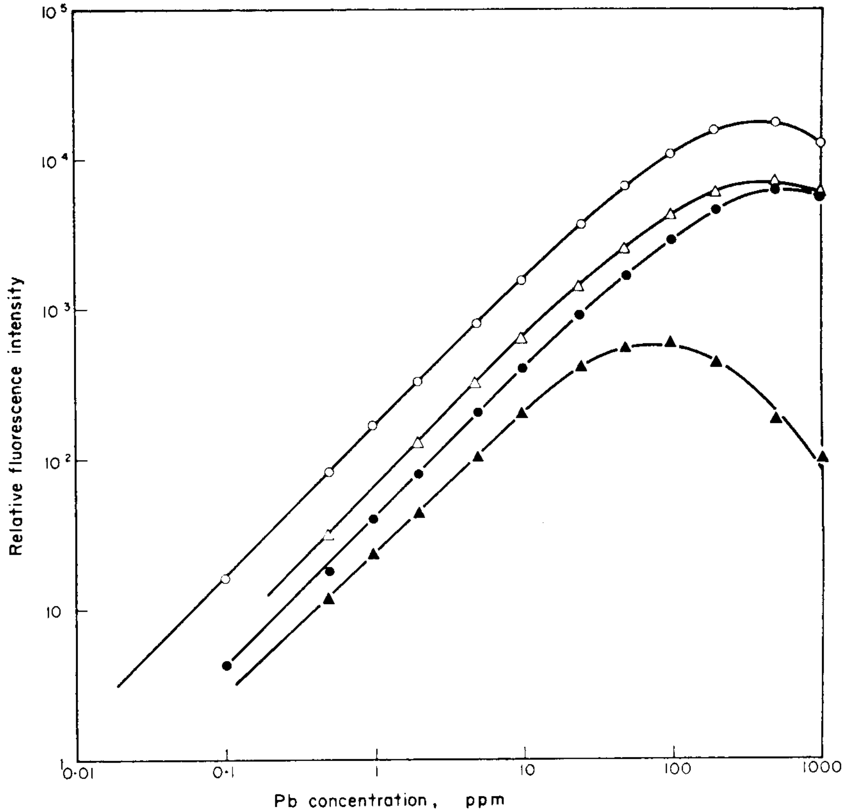

Fig. 4.—Analytical working curves for the Pb 405·78 nm line with various premixed flames.
●—air–hydrogen △—air–acetylene (separated)
○—hydrogen–oxygen–argon ▲—air–acetylene (separated, Pb 217·00 nm)

A comparison of detection limits for atomic fluorescence with various flames and atomic absorption, using the same instrument and the same spectral source, is made in Table III. In atomic fluorescence, there are seven sensitive analytical lines giving detection limits below 1 ppm. In atomic absorption only, two sensitive (resonance) lines are available while the absorption of the other lines which exhibit atomic fluorescence is considerably weaker. When the hydrogen–oxygen–argon flame is used, five fluorescence lines give better detection limits than the most sensitive atomic

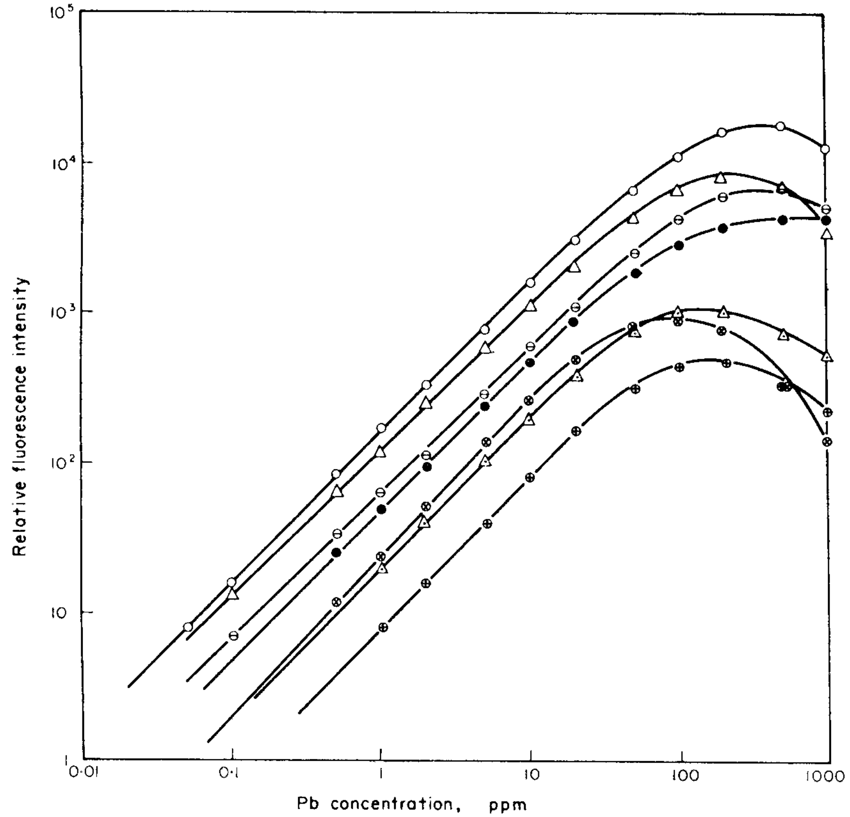

Fig. 5.—Analytical working curves for all fluorescence lines observed in the hydrogen–oxygen–argon flame.

○—405·78 nm ●—368·35 nm
△—283·31 nm ⊗—217·00 nm
⊖—363·96 nm ◬—261·37 and 261·42 nm
⊕—280·20 nm

absorption line at 217·00 nm (0·08 ppm). The best detection limit of 0·02 ppm was obtained for the 405·78 nm line.

Chemical interferences

The effect of hydrochloric, sulphuric, phosphoric, nitric, perchloric and hydrofluoric acids in concentrations of 0·01, 0·1 and 0·5*M* and of a 100-fold excess of Na, K, Cu, Mg, Ca, Zn, Al, V, Bi, Cr, Mo, W, Mn, Fe, Co and Ni on the fluorescence signal produced by a 5-ppm lead solution was investigated. In all the three flames studied, only 0·1 and 0·5*M* hydrofluoric acid and molybdate caused a significant interference ($>50\%$ decrease in fluorescence signal from a 5-ppm lead solution). Among the other ions, copper and tungsten slightly decrease the fluorescence signal ($<10\%$) in the air–hydrogen flame, while aluminium shows the same effect in the hydrogen–oxygen–argon flame. The chemical interference of hydrofluoric acid was considerably lowered by the addition of EDTA (final concentration 0·005*M*). The effects of the interfering cations were eliminated in the same manner. Similar interferences from hydrofluoric acid and molybdate were found for lead determined by atomic absorption in a 100-mm air–acetylene flame, as would be expected.

Zusammenfassung—Das mit einer intensiven Hohlkathodenlampe angeregte Fluoreszenzspektrum von Blei wurde untersucht und der wahrscheinliche Mechanismus der Fluoreszenzübergänge angegeben. Es wird experimentell bestätigt, daß die intensivste Fluoreszenzlinie bei 405,78 nm hauptsächlich als Resonanzfluoreszenz zustande kommt. Verwendet wurden die vorgemischte Luft-Wasserstoff-Flame, die getrennte Luft-Acetylen-Flamme und die mit Argon verdünnte Sauerstoff-Wasserstoff-Flamme. Die zuletzt genannte gibt mit der Linie bei 405,78 nm eine Nachweisgrenze von 0,02 ppm.

Résumé—On a étudié le spectre de fluorescence du plomb excité avec une lampe à cathode creuse de haute intensité et l'on suggère le mécanisme probable des transitions de fluorescence. Il est confirmé expérimentalement que la raie de fluorescence la plus intense à 405,78 nm est principalement dûe à la fluorescence de raie directe. On a utilisé la flamme prémélangée air–hydrogène, la flamme séparée air–acétylène et la flamme oxy–hydrogène diluée à l'argon la, dernière mentionnée donnant une limite de détection de 0,02 ppm avec la raie à 405,78 nm.

REFERENCES

1. C. Veillon, J. M. Mansfield, H. L. Parsons and J. D. Winefordner, *Anal. Chem.*, 1966, **38,** 204.
2. R. M. Dagnall, K. C. Thompson and T. S. West, *Anal. Chim. Acta*, 1966, **36,** 269.
3. D. C. Manning and P. Heneage, *Atomic Absorption Newsletter*, 1968, **7,** 80.
4. J. I. Dinnin, *Anal. Chem.*, 1967, **39,** 1491.
5. D. C. Manning and P. Heneage, *Atomic Absorption Newsletter*, 1967, **6,** 124.
6. H. Massmann, *Spectrochim. Acta*, 1968, **23B,** 215.
7. K. E. Zacha, M. P. Bratzel, Jr., J. D. Winefordner and J. M. Mansfield, Jr., *Anal. Chem.*, 1968, **40,** 1733.
8. M. P. Bratzel, Jr. and J. D. Winefordner, *Anal. Letters*, 1967, **1,** 43.
9. J. V. Sullivan and A. Walsh, *Spectrochim. Acta*, 1965, **21,** 727.
10. T. S. West and X. K. Williams, *Anal. Chem.*, 1968, **40,** 335.
11. J. W. Robinson and C. J. Hsu, *Anal. Chim. Acta*, 1968, **43,** 109.
12. T. S. West and X. K. Williams, *ibid.*, 1968, **42,** 29.
13. J. Matoušek and V. Sychra, *Anal. Chem.*, 1969, **41,** 518.
14. D. N. Armentrout, *ibid.*, 1966, **38,** 1235.
15. R. S. Hobbs, G. F. Kirkbright, M. Sargent and T. S. West, *Talanta*, 1968, **15,** 997.
16. C. H. Corliss and R. Bozman, *Experimental Transition Probabilities for Spectral Lines of Seventy Elements*, N.B.S., Washington, 1962.
17. C. E. Moore, *Atomic Energy Levels as Derived from the Analyses of Optical Spectra*, Vol. I-III, N.B.S., Washington, 1952.
18. R. Mavrodineanu and H. Boiteux, *Flame Spectroscopy*, Wiley, New York, 1964.
19. R. M. Dagnall, K. C. Thompson and T. S. West, *Talanta*, 1967, **14,** 1151.
20. *Idem*, *ibid.*, 1967, **14,** 1467.
21. P. J. T. Zeegers, R. Smith and J. D. Winefordner, *Anal. Chem.*, 1968, **40,** 26A.
22. H. P. Hooymayers, *Spectrochim. Acta*, 1968, **23B,** 567.
23. C. T. J. Alkemade, *Proc. Xth Colloq. Spectr. Intern.*, Univ. of Maryland, 1962.
24. D. R. Jenkins, *Spectrochim. Acta*, 1967, **23B,** 167.

Talanta, 1970, Vol. 17, pp. 371 to 380. Pergamon Press. Printed in Northern Ireland

SUBSTOICHIOMETRIC DETERMINATION OF TRACES OF PALLADIUM BY NEUTRON-ACTIVATION ANALYSIS

G. B. Briscoe and S. Humphries
Department of Chemistry, The University of Aston in Birmingham, Gosta Green,
Birmingham 4, England

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Summary—A highly selective, rapid one-step radiochemical separation procedure for palladium has been developed. It is based on the solvent extraction of palladium diethyldithiocarbamate from a 5*M* hydrochloric acid solution with a substoichiometric amount of copper diethyldithiocarbamate in chloroform. The separation has been applied to the determination of traces of palladium by neutron-activation analysis, in platinum, the rocks W-1 and PCC-1 and a biological material (kale). Amounts of palladium down to 10^{-8} g have been determined.

Neutron-activation analysis has been used to determine traces of palladium in rocks,[1,2] ores,[3] meteorites[4–6] and various metals.[7–10] Most of the previously reported methods of separation of palladium involve either precipitation or solvent extraction of the dimethylglyoximate, and, owing to the incompleteness of the process, involve many successive separation steps and therefore are complicated and time consuming. By use of the substoichiometric principle, the chemical separation has been greatly simplified and, because of the very high selectivity of this separation, a procedure has been developed which we would expect to be applicable to almost any type of matrix.

Table I.

Stable palladium isotope	Abundance %	Cross-section, *barn*	Product of (n, γ) reaction	Half-life	Major radiations
102	0·96	4·8	103	17 days	EC, Rh X-ray
106	27·33	0·29	107m	21·3 sec	IT, Pd X-ray
108	26·71	12	109	13·6 hr	β^-, Ag X-ray
108	26·71	0·2	109m	4·7 min	IT, Pd X-ray
110	11·81	0·2	111	22 min	β^-, γ
110	11·81	0·04	111m	5·5 hr	β^-, Pd X-ray

EC = electron capture; IT = internal transition.

The stable isotopes and the nuclear reactions resulting from thermal neutron irradiation of palladium are shown in Table I. The irradiation facilities available have thermal neutron fluxes of (1–6) × 10^{-10} n.mm^{-2}.sec.$^{-1}$ Under these conditions and from the data given in Table I, it can be shown that the most suitable isotope for the determination of palladium is palladium-109, which can be detected either by the beta or the gamma radiation and silver X-ray (22 keV) associated with the decay. It follows that under suitable conditions (irradiation in a flux of 10^{20} n.mm^{-2}.sec^{-1} to saturation activity followed by radiochemical separation) it is theoretically possible to determine down to 10^{-10} g of palladium.

For a substoichiometric separation by solvent extraction it is necessary to have a chelating agent which forms a very strong, readily extractable complex with the metal concerned. Diethyldithiocarbamic acid is known to form a strong complex with palladium. Exchange data, for carbon tetrachloride as solvent, have been reported to give the following order of decreasing extractability of metal diethyldithiocarbamates:[12] Hg(II), Pd(II), Ag, Cu, Tl(III), Ni, Bi, Pb, Co(III), Cd, Tl(I), Zn, In, Sb(III), Fe(III), Te(IV) and Mn. However, the order varies somewhat with the solvent used and the content of the aqueous phase. In a previous paper[13] the investigation of the extraction of palladium with a solution of copper diethyldithiocarbamate in chloroform was reported. This extractant was chosen because solutions of diethyldithiocarbamic acid and its sodium salt are not very stable, whereas a stock solution of the copper(II) complex in chloroform ($10^{-2}M$) keeps for months. The palladium complexes formed are more soluble in chloroform than carbon tetrachloride.

It was shown that under substoichiometric conditions two reactions occur:

$$\mathrm{Pd^{2+}_{(aq)} + Cu(DDC)_{2(org)} \rightleftharpoons Pd(DDC)_{2(org)} + Cu^{2+}_{(aq)}} \tag{1}$$

$$\mathrm{Pd(DDC)_{2(org)} + Pd^{2+}_{(aq)} + 2Cl^{-}_{(aq)} \rightleftharpoons 2PdCl(DDC)_{(org)}} \tag{2}$$

where DDC is the diethyldithiocarbamate ion and the subscripts "aq" and "org" indicate an aqueous and an immiscible organic phase respectively.

The extraction constant of the first complex, palladium diethyldithoicarbamate, into chloroform was found to be about 10^{70}, indicating that a substoichiometric determination using this complex is likely to be very selective. But at equilibrium the chloride complex (2) will be completely formed under substoichiometric conditions from solutions containing palladium chloride and hydrochloric acid only. However, the rates of the two reactions are affected by the hydrogen ion and chloride ion concentrations of the aqueous phase. Where both are high, *e.g.*, in $5M$ hydrochloric acid, palladium diethyldithiocarbamate is formed rapidly while the formation of palladium chloride diethyldithiocarbamate does not take place for several hours. Thus conditions can be chosen such that palladium diethyldithiocarbamate is formed on extraction with a substoichiometric amount of copper diethyldithiocarbamate.

EXPERIMENTAL

Reagents

All reagents were prepared from analytical reagent grade chemicals.

Copper diethyldithiocarbamate solution. Sodium diethyldithiocarbamate was recrystallized by dissolution in the minimum volume of ethanol and addition of a large excess of ether. After drying under vacuum, the crystals (0·45 g) were dissolved in distilled water, excess of copper sulphate solution was added and the resulting precipitate of copper diethyldithiocarbamate was extracted with several portions of chloroform. The extracts were combined and diluted to 100 ml with chloroform to give an approximately $10^{-2}M$ stock solution. This was diluted further with chloroform as required to give an approximately $5 \times 10^{-4}M$ solution. The exact concentration was determined by measuring the absorbance at 436 nm and assuming the molar absorptivity to be the same in chloroform as in carbon tetrachloride ($1{\cdot}3 \times 10^{3}$ mole.l^{-1}.mm^{-1}).[12]

Palladium carrier solution. Prepared by dissolving finely divided palladium metal in *aqua regia.* The resulting solution was evaporated to dryness with hydrochloric acid, several times, to remove oxides of nitrogen. The final solution in hydrochloric acid was diluted to approximately $10^{-2}M$ with distilled water.

Palladium-103 solution. Irradiated palladium metal was dissolved as above. The ^{111}Ag (active decay product of ^{111}Pd) was removed, before dilution, by the addition of inactive silver nitrate solution to the solution of palladium in hydrochloric acid, the resulting precipitate of silver chloride being centrifuged off. This procedure was repeated once and the final solution diluted to $10^{-2}M$ with distilled water as before. Because of the low specific activity of the palladium-103, this solution was used alone, *i.e.*, without the addition of palladium carrier solution.

Both the palladium carrier solution and the palladium-103 solution were standardized against $3 \times 10^{-3}M$ EDTA by the back-titration method developed by MacNevin and Kriege.[14]

Radiotracer solutions. Used for direct interference studies and prepared by irradiating the elements or their oxides in a flux of 10^{10} n.mm^{-2}sec^{-1} for 8 hr (Universities of Manchester and Liverpool Research Reactor).

Apparatus

Scintillation counter. The detector used was a 76 × 76 mm NaI(Tl) well-type crystal. For activity measurements this was associated with a single-channel gamma-ray spectrometer. For experiments using palladium-103 as a tracer, counting was carried out in a 10–50 keV channel; for experiments with palladium-109 (test analyses) counting was carried out in a 10–30 keV channel, and for the direct interference studies a discriminator voltage setting corresponding to 10 keV was used. Gamma-spectra were recorded by means of a 400-channel pulse-height analyser.

Chloroform solutions of palladium-103 and -109 had to be evaporated to dryness before counting, as the rhodium and silver X-rays used to detect these isotopes are strongly absorbed by solvents containing chlorine.

Filter paper. Dry Whatman No. 41 was used.

Irradiation

The test samples were weighed (see Table IV), sealed in quartz ampoules and irradiated in a reactor simultaneously with an appropriate amount of palladium chloride standard. Times of irradiation were 12 hr or 7 days at thermal neutron fluxes of 10^{10} or 6×10^{10} n.mm^{-2}.sec^{-1}. For irradiations the Harwell DIDO and the Universities of Manchester and Liverpool Research Reactor were used.

Development of method

All preliminary experiments were carried out with about $10^{-2}M$ palladium-103 and about $5 \times 10^{-4}M$ copper diethyldithiocarbamate in chloroform.

Extraction time. The time to reach the extraction equilibrium of palladium diethyldithiocarbamate from 5*M* hydrochloric acid was investigated by extraction of palladium for different times from 10 ml of 5 ± 1*M* hydrochloric acid containing 1·0 ml of palladium-103 solution, 5·0 ml of copper diethyldithiocarbamate solution being used as the extractant. The organic phase was filtered, a 3·0-ml aliquot was evaporated to dryness and the activity measured. From Fig. 1 where the activities of the organic phase are plotted *vs.* time of shaking, it can be seen that extraction equilibrium is reached in under 1 min and that the extract is unaffected by up to 2 hr shaking. This shows that the chloride complex is not formed. For all further experiments an extraction time of about 5 min was chosen.

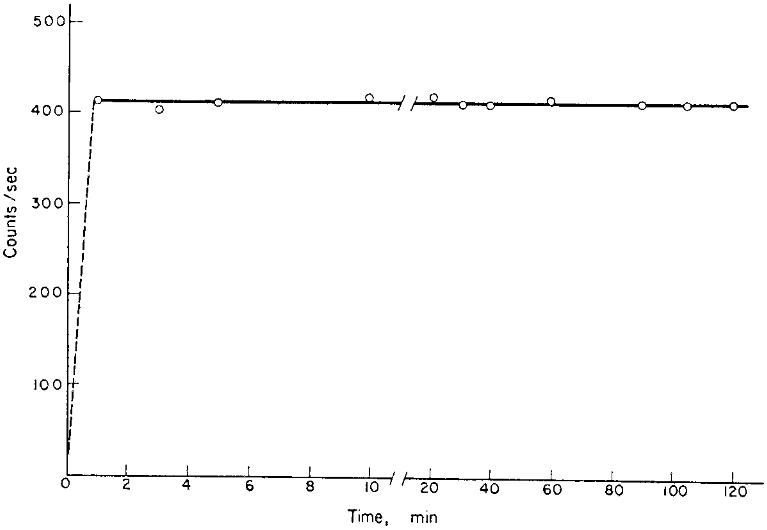

FIG. 1.—Extraction time of palladium from 5*M* hydrochloric acid with copper diethyldithiocarbamate ($10^{-2}M$ palladium-103; $5 \times 10^{-4}M$ copper diethyldithiocarbamate).

Reproducibility. To test that under the conditions above, exactly equal amounts of palladium could be extracted from solutions of varying palladium concentration, a series of solutions of 5 ± 1M hydrochloric acid containing increasing amounts of palladium-103 solution were extracted with 5·0 ml of copper diethyldithiocarbamate solution for about 5 min. The activity of the extracts was measured as before and plotted against the amount of palladium originally present in the aqueous phase. From the graph obtained (Fig. 2) it can be seen that after the equivalence point was reached, very good substoichiometric reproducibility was achieved.

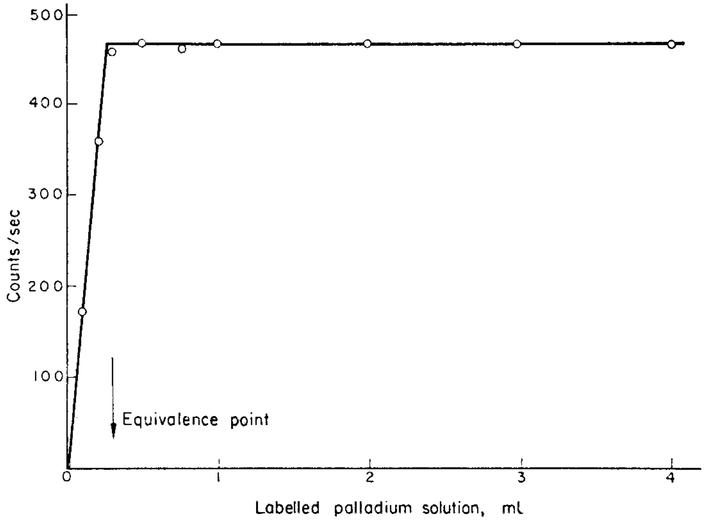

Fig. 2.—Substoichiometric reproducibility of the extraction of palladium from 5M hydrochloric acid with copper diethyldithiocarbamate ($10^{-2}M$ palladium-103; $5 \times 10^{-4}M$ copper diethyldithiocarbamate).

Selectivity

Indirect interference studies. These were based on the detection of any depression of the palladium activity extracted as the diethyldithiocarbamate, caused by the presence of various species in the original aqueous solution. Palladium-103 solution was mixed with the appropriate amounts of foreign species (Table II) in 5 ± 1M hydrochloric acid and the extraction carried out as before.

The species investigated in this way included most of the metals in the oxidation states most likely to be present after normal dissolution procedures, and the more common non-metal anionic species that are stable in fairly concentrated hydrochloric acid solution. Where groups of metals were known to be chemically similar, *e.g.*, lanthanides, alkali metals, alkaline earth metals, only a few members of the group were tested.

Where possible the aqueous solution contained the foreign species in 1000-fold molar excess over palladium. (This was based on the principle of the addition of mg amounts of palladium carrier to a matrix being analysed in gram quantities containing a high proportion of the species.) When the species being examined was only sparingly soluble in hydrochloric acid, a saturated solution was used.

From the results it can be seen that certain oxidizing substances significantly decrease the activity extracted. This is due to oxidation of the reagent and is prevented, except in the case of Se(IV) and Se(VI) by the addition of an excess of sodium sulphite (5 ml of a freshly prepared saturated solution). The continued interference of selenium is due to the reduction of Se(IV) and Se(VI) to selenium metal by the sulphite. This in turn reduces Pd(II) to the metal. Sulphite itself will reduce Pd(II) but the reduction is normally so slow as to be unimportant.

The only other interference with the extraction is that of Au(III) which appears to form a more readily extractable diethyldithiocarbamate than palladium.

Direct interference studies. The purpose of this investigation was to detect small quantities of highly radioactive species which might be extracted into the organic phase (possibly by some mechanism other than complexing with the diethyldithiocarbamate ion) without significantly depressing the palladium extraction. A labelled solution of the ion to be investigated was mixed with a non-active palladium carrier solution in 5 ± 1M hydrochloric acid and the substoichiometric extraction carried out as before. All the platinum metals (except rhodium, which produces only a very short-lived

TABLE II.

Foreign ion added	^{103}Pd extracted, % (compared with standard)	^{103}Pd extracted, in the presence of excess Na_2SO_3, %
Aluminium	97·0	
Antimony(III)	97·7	
Antimony(V)	1·5	100·0
Arsenic(III)	97·3	
Arsenic(V)	99·7	
*Barium	98·6	
Beryllium	100·0	
Bismuth	97·5	
Borate	98·5	
Bromide	99·4	
Cadmium	97·8	
Calcium	101·9	
Cerium(III)	101·0	
Cerium(IV)	0·5	101·5
Perchlorate	99·0	
Chromium(III)	98·4	
Cobalt(II)	99·4	
Copper(II)	99·4	
Gallium	98·4	
*Germanium	101·9	
Gold(III) (100 mg)	0·7	5·6
Indium(III)	99·7	
Iodide	101·2	
Iridium(IV) (10 mg)	—	103·0
Iron(II)	97·5	
Iron(III)	25·5	97·2
Magnesium	101·2	
Manganese(II)	97·0	
*Mercury(I)	103·1	
Mercury(II)	99·0	
Molybdenum(VI)	65·8	99·5
Nickel	98·8	
*Niobium(V)	98·6	
Nitrate	4·0	101·1
Osmium(IV) (50 mg)	—	94·8
Orthophosphate	98·8	
Platinum(IV) (10 mg)	98·1	
Potassium	100·0	
Rhenium(VII)	—	101·0
Rhodium(III) (40 mg)	—	104·0
Ruthenium(IV) (10 mg)	—	98·5
Selenium(IV)	66·6	25·9
Selenium(IV) (1 mg)	—	93·9
Selenium(VI)	5·6	53·5
Selenium(VI) (10 mg)	—	95·2
*Silicate	95·0	
*Silver	99·5	
Sodium	100·0	
Strontium	104·5	
Sulphate	101·5	
Sulphite	97·9	
Tellurium(IV)	101·1	
Tellurium(VI)	75·4	102·9
*Thallium(I)	101·2	
Thorium(IV)	99·4	
Tin(II)	103·3	
Tin(IV)	96·9	
Titanium(IV)	96·9	
*Tungsten(VI)	97·6	
Uranium(VI)	84·4	98·0
Vanadium(V)	55·2	100·6
Vanadium(VI)	1·5	99·3
Zinc	103·0	
*Zirconium(IV)	102·4	
*Lead(II)	101·0	
Hydrogen peroxide	1·6	99·0
Ammonium	100·0	
Acetate	97·4	

1 mg (10^{-5} mole) of palladium present in all cases.
10^{-2} mole of foreign ion present unless otherwise stated.
* Solution saturated with respect to this species.

isotope on thermal neutron irradiation) and those metals known to form fairly strong diethyldithiocarbamates were examined.

The results (Table III) show that a small amount of activity may appear in the organic phase, because of incomplete separation of the phases by filtration. This can be removed by washing the organic phase with 5*M* hydrochloric acid. The only isotopes extracted to a significant extent are ^{198}Au and ^{197}Pt. Gold(III), as in the indirect interference studies, completely replaces palladium from the diethyldithiocarbamic acid. Platinum(IV) also appears to form a more readily extractable diethyldithiocarbamate than palladium, but the reaction is so much slower than that with palladium that even with excess of platinum not enough is extracted to depress the palladium extraction significantly.

These experiments show that the separation is very selective for palladium. The only elements which interfere in any way are gold, selenium and platinum.

Elimination of interferences

Gold. As gold is likely to be present in trace quantities in most matrices, often in similar quantities to palladium, and its nuclear characteristics result in a considerably higher specific activity than that of palladium under the same irradiation conditions, it will nearly always be necessary to remove gold

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TABLE III.

Foreign ion added		Labelling radioisotope	Total activity added, *cps*	Activity of substoichiometric extract, *cps*	Radioactivie ion extracted, %
Mercury(II)	2·0 g	^{203}Hg	7340	1·30	0·02
Cerium(IV)	0·14 g	^{144}Ce	3330	0·36	0·01
Silver*		^{111}Ag	1050	0·30	0·03
Cobalt(II)	0·6 g	^{60}Co	13070	0·38	0·003
Thallium(I)*		^{204}Tl	10460	0·003	3×10^{-5}
Iodine(−I)	1·3 g	^{131}I	18600	10·4	0·05
Copper(II)	0·6 g	^{64}Cu	29000	1·0	0·003
Gold(III)	0·02 g	^{198}Au	23390	166·3	0·7
Ruthenium(IV)	0·01 g	^{97}Ru	7780	1·4	0·02
Osmium(IV)	0·05 g	^{193}Os	5233	1·1	0·02
Iridium(IV)	0·01 g	^{194}Ir	72777	1·0	0·0014
Platinum(IV)	0·10 g	^{197}Pt	800000	16000	0·2

1 mg of palladium present in all cases.
* Solution saturated with respect to this species.

before the substoichiometric separation is carried out. This is achieved quickly and simply by extracting the gold as gold(III) chloride from the solution in 5 ± 1*M* hydrochloric acid, with diethyl ether.

When 10 mg of gold (labelled with ^{198}Au) in 1·0 ml of palladium carrier solution in 5 ± 1*M* hydrochloric acid, were extracted with three 50-ml portions of diethyl ether before the substoichiometric extraction of palladium, a decontamination factor of about 2000 resulted. This decreased somewhat on lowering of the gold concentration and, for a solution containing 0·01 mg of gold, the decontamination factor was only about 200. In the test analyses, where the sample contained only trace quantities of gold, three ether extractions with no addition of carrier were found to be quite sufficient. A few more extractions may be needed for a matrix containing a high proportion of gold. For the platinum sample however, where a large quantity of carrier free ^{199}Au is produced from the decay of the 30-min half-life ^{199}Pt, the concentration of gold was too low for the ether extraction to give a large enough decontamination factor and so the addition of gold carrier was necessary.

Selenium and platinum. The reduction by selenium is insignificant if it is present only in mg amounts, while the extraction of platinum is so slow that it will not extract significantly in a shaking time of 5 min unless it is present in high concentrations.

In the test analysis of the platinum sample it was found that a preliminary separation of palladium by dimethylglyoxime precipitation, reduced the platinum concentration sufficiently to prevent its interference. We would also expect this method to be suitable for high selenium content samples.

Dissolution procedures

The procedures detailed below were tested by adding 1·0 ml of palladium-103 solution to the non-irradiated matrix. After dissolution the palladium was extracted with a substoichiometric amount of copper diethyldithiocarbamate solution. No significant losses of palladium were observed.

Rocks. To the test matrix in a 50-ml Teflon beaker, 1·0 ml of palladium carrier solution was added and the matrix dissolved in a mixture of hydrofluoric (10 ml), hydrochloric (2 ml) and nitric (10 ml) acids. After the silicon had been fumed off, four evaporations to dryness were carried out with 5-ml portions of hydrochloric acid, to remove oxides of nitrogen. The final residue was dissolved in 5 ml of concentrated hydrochloric acid.

Biological material (*kale*). To the test matrix in a 150-ml beaker, 1·0 ml of palladium carrier solution was added. After dissolution in 5 ml of nitric acid, the solution was evaporated to dryness. This was repeated several times until all the carboniferous material had been oxidized. Four evaporations to dryness were carried out with 5-ml portions of hydrochloric acid, to remove oxides of nitrogen, before dissolution of the final residue in 5 ml of concentrated hydrochloric acid.

Platinum. To the test matrix in a 150-ml beaker, 1·0 ml of palladium carrier solution and 1·0 ml of gold carrier solution (1 mg/ml) were added. The matrix was dissolved in 10 ml of *aqua regia* and the resulting solution diluted to about 100 ml with distilled water before addition of 2 ml of a 1% solution of dimethylglyoxime in ethanol. The solution was warmed and stirred. The palladium dimethylglyoxime formed was filtered off and washed first with dilute hydrochloric acid and then with distilled water. This precipitate was then dissolved off the paper by the addition of hot, concentrated nitric acid. A further 1·0 ml of gold carrier solution was added, the resulting solution evaporated to dryness, and the residue dissolved in 5 ml of hydrochloric acid. Four evaporations to dryness were carried out with 5-ml portions of hydrochloric acid to remove oxides of nitrogen, and the final residue dissolved in 5 ml of concentrated hydrochloric acid.

Extraction procedures

The dissolved samples were diluted with 5 ml of distilled water and extracted with three 50-ml portions of diethyl ether for 1–2 min. The ether layers were discarded and the aqueous phase shaken with 20 ml of chloroform for 30 sec (to remove any chloroform soluble substances). The separated aqueous phase was warmed to remove final traces of the organic solvents. After addition of 5 ml of freshly prepared, saturated sodium sulphite solution and 5 ml of concentrated hydrochloric acid, extraction was carried out with 5·0 ml of copper diethyldithiocarbamate solution for about 5 min. The organic phase was washed with two 10-ml portions of 5*M* hydrochloric acid (to remove traces of highly active aqueous phase), filtered, and a 3·0-ml aliquot evaporated to dryness and counted. This extraction was repeated once as a check.

The irradiated palladium standard (weight of palladium y_S) was dissolved in 5 ml of concentrated hydrochloric acid after the addition of 1·0 ml of palladium carrier solution. Freshly prepared, saturated sodium sulphite solution (5 ml) was added to this solution and extraction with a substoichiometric amount of copper diethyldithiocarbamate solution carried out as for the test samples. Washing of the aqueous phase was omitted. The activities of equal aliquots of the organic extracts from the test (a) and standard (a_S) samples were measured and the amount of palladium present in the test sample (y) calculated from the equation:

$$y = y_S \, . \, a/a_S.$$

RESULTS AND DISCUSSION

The results of the test sample analyses are summarized in Table IV. It can be seen that in all cases the reproducibility is very good. The mean values are slightly

TABLE IV.

Sample	Sample weight, *g*	Palladium standard activity, *cps*	Palladium sample activity, *cps*	Palladium found, *µg*	Palladium found, *ppm*	Mean, *ppm*	Results of other authors, *ppm*
W-1*	1·0059	870	3·4	$3{\cdot}9 \times 10^{-2}$	$3{\cdot}9 \times 10^{-2}$		
	1·0006	1320	4·8	$3{\cdot}6 \times 10^{-2}$	$3{\cdot}6 \times 10^{-2}$	$3{\cdot}9 \times 10^{-2}$	$1{\cdot}9 \times 10^{-2}$
	0·5404	450	1·0	$2{\cdot}2 \times 10^{-2}$	$4{\cdot}1 \times 10^{-2}$		(ref. 15)
	0·6672	1950	5·4	$2{\cdot}8 \times 10^{-2}$	$4{\cdot}1 \times 10^{-2}$		$1{\cdot}4 \times 10^{-2}$
							(ref. 16)
PCC-1*	1·0052	870	2·8	$3{\cdot}2 \times 10^{-2}$	$3{\cdot}2 \times 10^{-2}$		
	1·0033	1320	3·2	$2{\cdot}4 \times 10^{-2}$	$2{\cdot}4 \times 10^{-2}$		
	0·5062	1130	1·7	$1{\cdot}5 \times 10^{-2}$	$2{\cdot}9 \times 10^{-2}$	$2{\cdot}9 \times 10^{-2}$	$0{\cdot}7 \times 10^{-2}$
	0·5687	1130	1·9	$1{\cdot}7 \times 10^{-2}$	$3{\cdot}0 \times 10^{-2}$		(ref. 16)
	0·6948	1950	4·0	$2{\cdot}1 \times 10^{-2}$	$2{\cdot}9 \times 10^{-2}$		
Kale†	1·0031	450	1·3	$2{\cdot}8 \times 10^{-2}$	$2{\cdot}8 \times 10^{-2}$		
	0·4919	1950	2·8	$1{\cdot}4 \times 10^{-2}$	$2{\cdot}9 \times 10^{-2}$	$2{\cdot}6 \times 10^{-2}$	
	0·4894	1950	2·1	$1{\cdot}1 \times 10^{-2}$	$2{\cdot}2 \times 10^{-2}$		
	0·4730	1950	2·5	$1{\cdot}3 \times 10^{-2}$	$2{\cdot}6 \times 10^{-2}$		
Pt§	0·2615	240	8·4	0·350	1·34		
	0·2510	240	7·1	0·296	1·18	1·29	2·13
	0·2541	940	35·0	0·373	1·46		(ref. 7)
	0·2514	940	28·2	0·300	1·20		

* Provided by U.S. Geological Survey, Washington D.C. U.S.A.

† Provided by H. J. M. Bowen, The University, Reading, England.

§ Sample Pt3 (Ref. 7) provided by D. F. C. Morris, Brunel University, London, England.

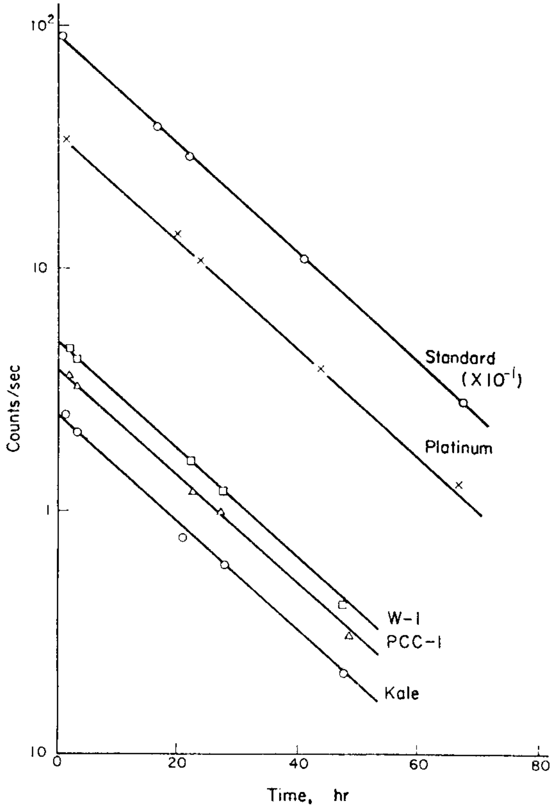

FIG. 3.—Decay curves of palladium diethyldithiocarbamate extracts.

higher than those obtained by other authors in the case of rocks[15-17] and slightly lower for the platinum.[7] Variation of sample size indicated that there were no self-shielding effects in the rocks or the kale. The radiochemical purity of the palladium diethyldithiocarbamate extracts was confirmed both by decay measurements, Fig. 3, and by comparison of their gamma-ray spectra with that of the standard, Fig. 4. It can be seen from the spectra that the extracts from the platinum sample contained a very small amount of ^{199}Au, but as only the 22-keV peak was counted, this would have very little effect on the results.

The standard rock W-1 contains trace amounts of some 40 elements and large amounts of 6 other elements, the main constituents being SiO_2 and Al_2O_3;[17] PCC-1 contains trace amounts of 10 elements and large amounts of 6 other elements with the main constituents being SiO_2 and MgO.[18] The platinum sample contains trace amounts of Se, Te, Os, Ir, Fe, Au, Ru, Co, As and Sb,[19] and the kale is a complicated organic matrix.[20] The fact that satisfactory results were obtained with all these materials, including the platinum matrix which must be one of the most difficult materials to analyse for trace palladium, shows the versatility of the method. The results of the preliminary experiments, together with the radiochemical purity of the palladium extracts from the test analyses, clearly indicate as predicted, that this substoichiometric copper diethyldithiocarbamate extraction is highly selective for palladium.

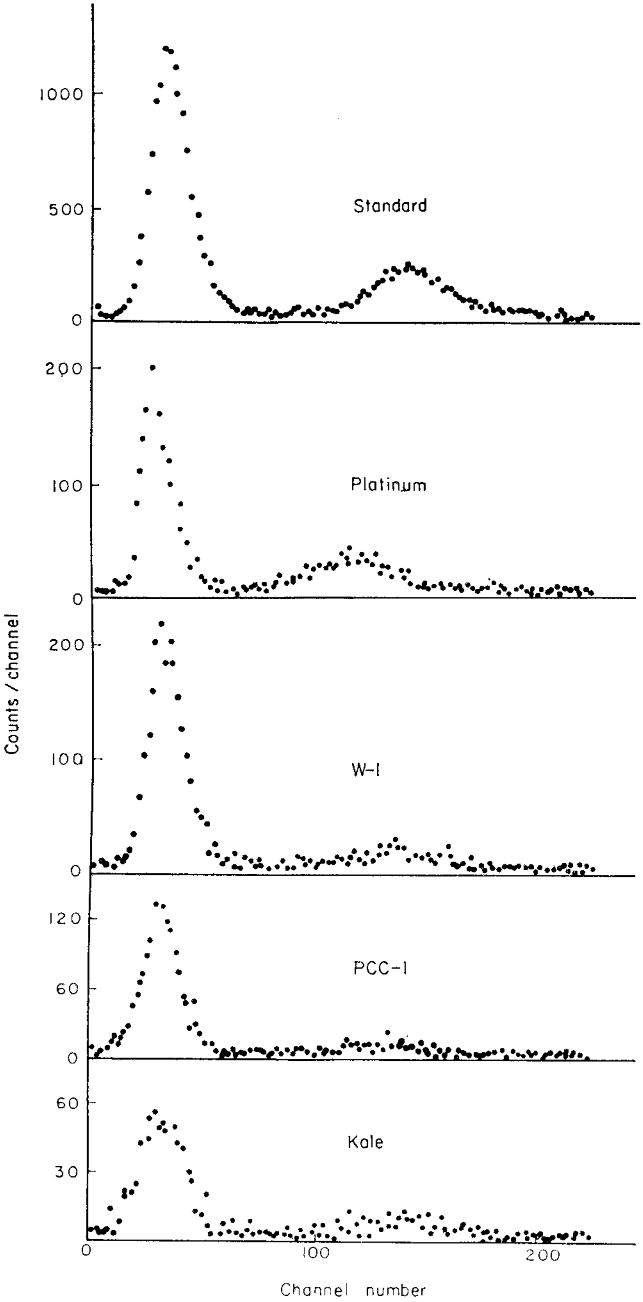

FIG. 4.—Gamma-ray spectra of palladium diethyldithiocarbamate extracts.

CONCLUSION

As has been shown before, metallic salts of diethyldithiocarbamic acid are very suitable for substoichiometric separations by solvent extraction. Methods for arsenic[21] and gold[22] have been developed, and now palladium. Although a few extraction constants have been determined, insufficient are known for prediction of the conditions for the substoichiometric separation of many metals and, as our kinetic studies have shown, this is not the only factor involved, especially with the so-called inert metals such as palladium and platinum.

Zusammenfassung—Ein hochselektives, schnelles, einstufiges radiochemisches Abtrennverfahren für Palladium wurde entwickelt. Es beruht auf der Extraktion von Palladium-diäthyldithiocarbamat aus $5M$ salzsaurer Lösung mit einer unterstöchiometrischen Menge Kupferdiäthyldithiocarbamat in Chloroform. Das Abtrennverfahren wurde auf die Bestimmung von Palladiumspuren durch Neutronenaktivierung in Platin, den Gesteinen W-1 und PCC-1 und einem biologischen Material (Kohl) angewandt. Bis herunter zu 10^{-8} g Palladium wurden bestimmt.

Résumé—On a élaboré, pour le palladium, une technique de séparation radiochimique hautement sélective, rapide et en un stade. Elle est basée sur l'extraction par solvant du diéthyldithiocarbamate de palladium d'une solution en acide chlorhydrique $5M$ avec une quantité substoechiométrique de diéthyldithiocarbamate de cuivre en chloroforme. On a appliqué la séparation à la détermination de traces de palladium par analyse par activation de neutrons dans le platine, les roches W-1 et PCC-1 et une substance biologique (chou vert). On a dosé des quantités de palladium descendant jusqu'à 10^{-8} g.

REFERENCES

1. E. A. Vincent and A. A. Smales, *Geochim. Cosmochim. Acta*, 1956, **9**, 154.
2. J. H. Crocket and G. B. Skippen, *ibid.*, 1966, **30**, 129.
3. D. F. C. Morris, N. Hill and B. A. Smith, *Mikrochim. Acta*, 1963, 962.
4. H. Brown and E. Goldberg, *Science*, 1949, **109**, 347.
5. E. Goldberg, A. Uchiyama and H. Brown, *Geochim. Cosmochim. Acta*, 1951, **2**, 1.
6. H. Hamaguchi, T. Nakai and Y. Kamemoto, *Nippon Kagaku Zasshi*, 1961, **82**, 1489.
7. R. A. Killick and D. F. C. Morris, *Talanta*, 1961, **8**, 601.
8. J. Gaittet, *Compt. Rend.*, 1958, **247**, 1861.
9. D. E. Zvygintsev and A. I. Kulak, *Zh. Neorgan. Khim.*, 1957, **2**, 1687.
10. V. N. Zamyatnina and L. A. Chikisheva, *Radiokhimiya*, 1963, **5**, 294.
11. C. M. Lederer, J. M. Hollander and I. Perlman, *Table of Isotopes*, 6th Ed., Wiley, 1967.
12. J. Starý, *The Solvent Extraction of Metal Chelates*, Pergamon, Oxford, 1964.
13. G. B. Briscoe and S. Humphries, *Talanta*, 1969, **16**, 1403.
14. W. M. MacNevin and O. H. Kreige, *Anal. Chem.*, 1955, **27**, 535.
15. L. H. Ahrens and M. Fleischer, *U.S. Geol. Survey Bull.* No. 1113, 83.
16. J. Haffty and L. B. Riley, *Talanta*, 1968, **15**, 111.
17. M. Fleischer and R. E. Stevens, *Geochim. Cosmochim. Acta*, 1962, **26**, 525.
18. F. J. Flanagan, *ibid.*, 1967, **31**, 289.
19. D. F. C. Morris and R. A. Killick, *Talanta*, 1961, **8**, 129, 793; 1962, **9**, 349, 879; 1963, **10**, 279, 987, 1153.
20. H. J. M. Bowen, *Analyst*, 1967, **92**, 124.
21. A. Zeman, J. Růžička, J. Starý and E. Klecková, *Talanta*, 1964, **11**, 1143.
22. D. A. Beardsley, G. B. Briscoe, J. Růžička and M. Williams, *ibid.*, 1965, **12**, 829.

Talanta, 1970, Vol. 17, pp. 381 to 390. Pergamon Press. Printed in Northern Ireland

FURTHER STUDY OF INDIVIDUAL ION ACTIVITIES IN PURE AQUEOUS SODIUM CHLORIDE SOLUTION

ADAM SHATKAY
Isotope Department, Weizmann Institute of Science, Rehovot, Israel

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Summary—The e.m.f. values between a chloride electrode and a reference electrode were measured in aqueous NaCl solutions between 10^{-5} and 6 m, saturated KCl and $1M$ KNO_3 bridges being used. The effect of the various liquid junctions is calculated and discussed. The consistency of the results is inspected, assuming either the MacInnes or the Guggenheim convention. The choice of different reference points for the standardization of the e.m.f.'s and for the activity coefficients is discussed. A comparison is made between the results obtained with an Ag/AgCl electrode of the second kind and a solid membrane chloride electrode.

IN A RECENT paper[1] the individual activities of Na^+ and Cl^- in pure aqueous solutions of sodium chloride were studied. The activity of Cl^- was calculated on the basis of measurements made with a standard calomel electrode and a saturated potassium chloride bridge against an Ag/AgCl electrode of the second kind. The range of concentrations studied was from 10^{-3} to 6 m. In the present paper the study has been extended by (*a*) lowering the concentrations of sodium chloride down to 10^{-5} m; (*b*) use of a potassium nitrate bridge in addition to the chloride bridge, and (*c*) use of a solid membrane chloride electrode. The implications of these extensions and the results obtained are discussed.

EXPERIMENTAL

The experimental details have already been described previously.[1] Additional particulars are as follows. In addition to the electrodes previously described, the Orion Analyzer Chloride Ion Activity Electrode Model 94-17 was employed. This electrode will be referred to as the solid membrane chloride electrode. In addition to the saturated potassium chloride bridge a $1M$ potassium nitrate bridge was employed. The bridges were connected with the test solutions through an asbestos fibre sealed in glass. The rate of diffusion is discussed below.

RESULTS AND DISCUSSION

The effect of the liquid junctions

A summary of the results obtained is given in Table I. The experimental e.m.f.'s tabulated in columns *b* and *c* include the problematic liquid junction potentials (E_j) between the bridge and the test solutions of sodium chloride.

The calculation of E_j for the sodium chloride junction with the saturated potassium chloride bridge (by using the Henderson equation) has already been discussed.[1] In a similar way the E_j between sodium chloride and the $1M$ potassium nitrate solution has been calculated. The results are plotted in Fig. 1.

It can be seen that the use of conductivities calculated for the real concentrations yields (in the case of the nitrate bridge) results significantly different from those obtained by using the limiting conductivities (unlike the case of the chloride bridge). In the following discussion E_j will be taken from the values obtained from the conductivities corresponding to the real concentrations.

TABLE I.—EXPERIMENTAL e.m.f.'S BETWEEN A SOLID MEMBRANE CHLORIDE ELECTRODE AND A SATURATED CALOMEL ELECTRODE

NaCl *mole/kg*	E_{Cl^-}, *mV*		ΔE_j, *mV*	
	KCl bridge	KNO_3 bridge	experimental	from Fig. 1
a	*b*	*c*	*d*	*e*
10^{-5}	—	259·0		
2×10^{-5}	—	249·4		
5×10^{-5}	—	234·0		
10^{-4}	213·1	217·5	11·9	12·1
2×10^{-4}	199·1	202·1	10·5	11·2
3×10^{-4}	187·9	191·8	11·2	10·7
5×10^{-4}	177·1	176·6	10·0	10·0
7×10^{-4}	168·5	170·9	9·9	9·6
10^{-3}	157·5	161·4	11·4	9·1
3×10^{-3}	131·4	134·2	10·3	7·7
7×10^{-3}	111·4	113·3	9·4	6·7
10^{-2}	102·1	104·2	9·6	6·5
3×10^{-2}	76·3	77·2	8·4	5·5
8×10^{-2}	54·4	54·4	7·5	4·8
10^{-1}	49·4	49·4	7·5	4·7
2×10^{-1}	34·1	33·4	6·8	4·5
3×10^{-1}	25·3	24·3	6·5	4·5
5×10^{-1}	14·4	13·1	6·2	4·6
1	−0·5	−2·0	6·0	4·9
2	−16·7	−17·9	6·3	5·3
3	−26·6	−28·2	5·9	5·5
4	−34·7	−36·2	6·0	5·6
5	−41·9	−43·7	5·7	5·6
6	−49·1	−50·8	5·8	5·6

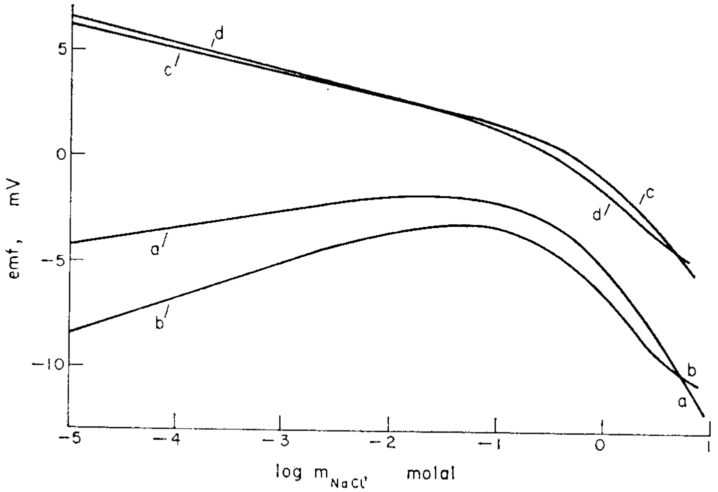

FIG. 1.—Liquid junction potentials calculated with the Henderson equation. *a–b:* for 1*M* KNO_3 bridge; *c–d:* for saturated KCl bridge; *a* and *c* using limiting conductivities; *b* and *d* using conductivities calculated for the respective concentrations.

The values of E_j plotted in Fig. 1 allow the calculation of the e.m.f. between the chloride bridge and the nitrate bridge (ΔE_j) for a junction obeying the Henderson equation. It is of interest to compare such calculated ΔE_j values with the experimentally available ΔE_j. For the reference solution of 0·1m sodium chloride, ΔE_j has been determined in 47 experiments as 7·5 ± 0·3 mV. Employing this value and the difference between the e.m.f.'s of columns *b* and *c* in Table I, the values listed in column *d* are obtained. Comparison with the Henderson equation values (column *e*) shows that the agreement is only fair, so that at least one of the bridges, and probably both, will contribute E_j's not following exactly the Henderson equation. It should be noted that the use of limiting conductivities reduces the agreement considerably.

When a saturated potassium chloride bridge is employed against a chloride-sensitive electrode, the leakage of potassium chloride into the test solution has to be considered. For test solutions containing a high chloride concentration such a leakage can be insignificant. For dilute chloride solutions it is necessary to allow for the contamination. Actually two effects of the contamination have to be considered: the first is simply the increase of the concentration of chloride; the second is the increase of the ionic strength of the solution, which affects the activity coefficient of the ions. The two effects can differ not only in magnitude but also in sense: in dilute solutions the two effects will in general oppose each other.

The contamination can be studied by observing the change of e.m.f. with time. After a period in which the e.m.f. changes due to the step-change in the activity of the test solution,[2] the e.m.f. assumes a steady final value when no appreciable contamination occurs, while an approximately linear decrease (or increase) of e.m.f. with time is found when contamination does occur. Two such examples of contamination are presented in Fig. 2.

The corrected e.m.f. (E_{corr}) can be easily evaluated from the experimental e.m.f. (E_{exp}) by using equation (1), which follows from the geometry of Fig. 2:

$$E_{corr} = E_{exp} - t(\mathrm{d}E_{exp}/\mathrm{d}t)_{lin} \tag{1}$$

where the subscript "lin" denotes the linear part of the curve. The E_{corr} so obtained is plotted as open circles in Fig. 2.

The slope of e.m.f. against time in the linear part of the curve is controlled mainly by three factors: the rate of leak of the bridge solution into the test solution; the volume of the test solution; and the initial concentrations of the bridge solution and the test solution. In the case illustrated in Fig. 2 (where the bridge is a saturated potassium chloride solution) the rate of leak is about 5×10^{-7} mole of potassium chloride per hour, and the volume of the test solution is about 30 ml. Under these conditions no extrapolation is necessary for test solutions above 10^{-1} m; extrapolation can yield results within our experimental precision for solutions down to 10^{-3} m; between 10^{-3} and 10^{-4} m the intercept is accurate only within ±1 mV; below 10^{-4} m the extrapolation can give only qualitative estimates. These considerations apply to the results for the chloride bridge listed in column *b* of Table I.

The next point of interest is how the leakage of a concentrated electrolyte affects the activity coefficients in the test solution, through the change in the ionic strength. Under the conditions described above, the molality of the sample has been found to increase by about $1{\cdot}5 \times 10^{-5}$ m/hr. Thus for a 10^{-4} m sample of sodium chloride

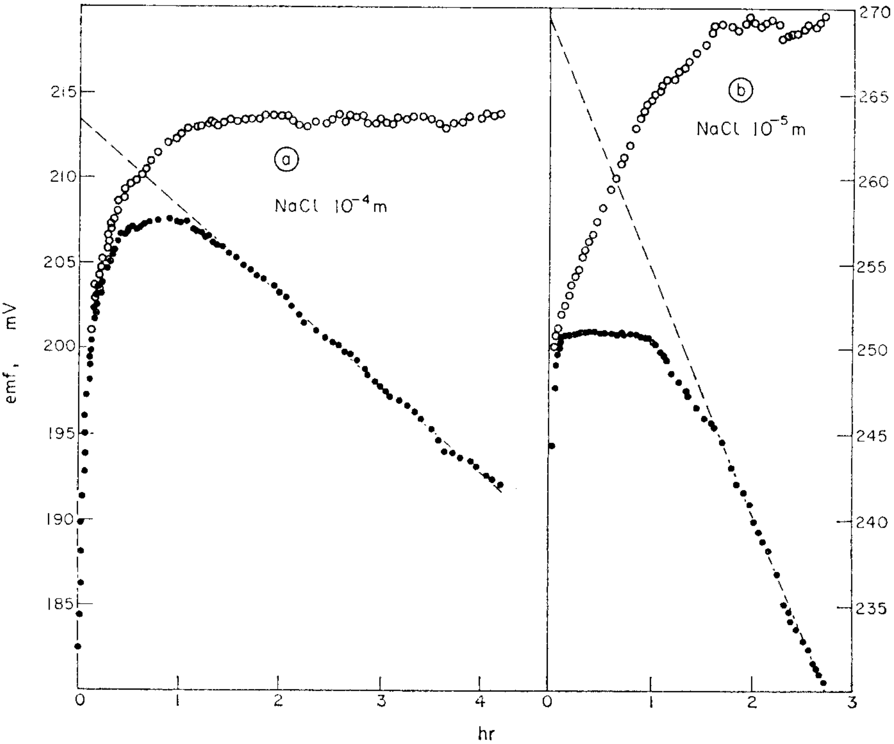

FIG. 2.—Change of e.m.f. with time for a chloride electrode soaked in 0·1 m NaCl. Filled circles: experimental results; open circles: corrected by use of equation (1); *a*— in 10^{-4} m NaCl; *b*— in 10^{-5} m NaCl.

the $\gamma_{\pm}$ would change after 1 hr of measurements from 0·995 to 0·994—an insignificant effect. For more concentrated test solutions the effect would be even smaller, as the relative change in ionic strength would be smaller. For more dilute test solutions the relative change in ionic strength will become more significant, but the actual effect on $\gamma_{\pm}$ will be negligible, as in one hour $\gamma_{\pm}$ can change only from 1·000 (for an infinitely dilute solution with no leakage) to 0·995 (due to the leakage). These considerations support our assumption that the change in $\gamma_{\pm}$ due to the change in ionic strength caused by the liquid junction may be safely neglected.

Choice of the reference solution

In order to obtain reproducible results with electrodes which have a standard potential $E°$ that is not constant, it is necessary to choose a reference solution and to assign to it a reference e.m.f. This has been stated briefly previously.[1] However there is a difference between the choice of a reference solution for a reference e.m.f., and the choice of a reference solution for a reference γ. As a new approach will now be suggested, this point requires some elucidation. Theoretically the best reference solution would be a very dilute one, so that its activity coefficient would be close enough to unity, and the various conventions for the single-ion activities would yield the same activity coefficients within the experimental accuracy. For example, in the aqueous solutions of sodium chloride, $\gamma_{\pm \text{NaCl}}$ is 0·965 at 10^{-3} m, while $\gamma_{\pm \text{KCl}}$ has the same value at the same concentration of potassium chloride. Thus at this concentration $\gamma_{\mathrm{Cl^-(McInnes)}} = \gamma_{\mathrm{Cl^-(Guggenheim)}}$ even though both coefficients still differ significantly from unity, since an error of $\pm 0{\cdot}5$ mV corresponds approximately to 0·02 in γ. For a sodium chloride solution of 10^{-4} m, $\gamma_{\pm} = 0{\cdot}995$, so that this solution would be dilute enough for γ to be assumed to be unity even within the experimental precision of $\pm 0{\cdot}1$ mV. Unfortunately the e.m.f.'s obtained with the best available chloride and sodium electrodes are not Nernstian at 10^{-4} m, as can be seen on plotting the results tabulated in Table I: at 10^{-4} m the e.m.f.'s (corrected for E_j) fall about 3 mV below the Nernst slope. Furthermore, measurements in such dilute solutions suffer from various experimental difficulties, especially the risk of contamination on preparation and during the measurement. From practical considerations the 0·1 m sodium chloride solution has been chosen as the reference solution. Such choice suffices for compiling a reproducible and unambiguous table of experimental e.m.f.'s for a set of electrodes even with a reasonably unstable E°, but still leaves open the choice of a reference γ for the comparison of the various conventions for $\gamma_{\mathrm{Cl^-}}$ and $\gamma_{\mathrm{Na^+}}$. The objections to the choice of the 10^{-4} m sodium chloride solutions have been stated above in connection with the reference solution for the e.m.f. One alternative approach is to use again the e.m.f. of the 0·1 m reference solution as the starting point for the calculation of γ. The great advantage of such an approach is that the e.m.f.'s of the reference solution are completely reproducible since they are chosen arbitrarily, while the e.m.f.'s of any other solution will in general be subject to some experimental error. However, this approach has at least one considerable disadvantage which did not apply to the choice of the 0·1 m solution as reference for the e.m.f. By assignment of the "correct" γ to the 0·1 m concentration according to some assumption, the coefficients calculated for the vicinity of the 0·1 m concentration will appear also to be nearly "correct", and the inconsistency of the assumption will become apparent (if at all) only at some distance from the 0·1 m concentration. On the other hand, when the very dilute solution is used as reference, the various γ's will all start near unity, and their divergence from the curve calculated with a wrong assumption will be marked in the interesting range of concentrations between 10^{-2} and 6 m (compare Figs. 3 and 4 with Fig. 5). Thus the method using the 0·1 m solution as reference is less sensitive than that using the very dilute solution.

A compromise was attempted in our previous work,[1] the 10^{-3} m solution of sodium chloride being used as basis for calculations. At this concentration the behaviour of the electrodes appears still to be Nernstian, the experimental results are fairly reproducible, and the various conventions yield the same γ, even though it is not unity. The results on the whole justified this approach, but the deviation of the γ's obtained for low concentrations was considerable, as was pointed out in the discussion of the results.

It appears worthwhile to compare the results obtained by the two approaches. For brevity we shall refer to the choice of the 10^{-3} m solution for reference as "approach I", while the choice of the 10^{-1} m solution will be referred to as "approach II". In practice, the difference between the two approaches is equivalent to a choice of two different standard potentials (E°) for the electrode, as can be seen from the following quantitative considerations. We employ an asterisk to mark the values corresponding to the reference solution of our choice. In the Nernstian range the relation between the e.m.f. (corrected for E_j) of the first reference solution (E_{I}^*), the standard potential

($E_I°$), the molality (m_I*), and the activity coefficient taken from the literature using one of the single-ion conventions discussed (γ_I*), is:

$$E_I{}^* = E_I{}^\circ - \frac{RT}{F}\ln m_I{}^* - \frac{RT}{F}\ln \gamma_I{}^*. \tag{2}$$

So $E_I°$ is determined by the experimental E_I*, the known m_I* and the chosen γ_I*. When approach II is tried, $E_{II}°$ is obtained similarly from well defined values. Obviously $E_I°$ should equal $E_{II}°$ had all our assumptions been correct. The fact is that $E_I° \neq E_{II}°$, so that the interchange of the two approaches is not trivial.

The following relations are easily deduced from equation (2):

$$E_I{}^\circ - E_{II}{}^\circ = E_I{}^* - E_{II}{}^* + \frac{RT}{F}\ln\frac{m_I{}^*\,\gamma_I{}^*}{m_{II}{}^*\,\gamma_{II}{}^*} \tag{3}$$

and for *any* concentration

$$\ln\frac{\gamma_I}{\gamma_{II}} = \frac{F}{RT}(E_I{}^\circ - E_{II}{}^\circ) = \text{constant} \tag{4}$$

It is thus evident that the γ's of one approach can be obtained from the γ's of the other approach merely by multiplication by the constant factor of $\exp[(E_I{}^\circ - E_{II}{}^\circ)F/RT]$.

In our case the activity coefficients γ_{Cl^-} have first been calculated by approach II and the equation

$$E = E^\circ - E_j - \frac{RT}{F}(\ln m_{Cl^-} + \ln \gamma_{Cl^-}) \tag{5}$$

where E is the experimental value of e.m.f. appearing in Table I, E_j is taken from Fig. 1, and $E°$ is calculated from the reference solution of 0·1 m sodium chloride with E = 49·4 mV and the corresponding γ's taken from the literature; for the test of the MacInnes convention γ_{Cl^-} was taken as 0·770, while for the Guggenheim convention it was taken as 0·778.[3,4] These reference γ's are shown by asterisks in Figs. 3 and 4.

It should be noted that when approach II is adopted it is necessary to present the results in two separate figures, as $\gamma^*_{II(\text{Guggenheim})} \neq \gamma^*_{II(\text{MacInnes})}$, so that the calculated γ's appearing in one figure differ from the corresponding γ's appearing in the second figure. On the contrary, when approach I is adopted, a single figure suffices (*cf.* Fig. 5), as $\gamma^*_{I(\text{Guggenhiem})} = \gamma^*_{I(\text{MacInnes})}$.

In the results dealt with in this paper the scatter of e.m.f.'s at 10^{-3} m is small. The average value of 157·5 mV for the chloride bridge given in Table I compares well with the average of 157·6 mV obtained previously with the Ag/AgCl electrode.[1] The average value of 161·4 mV for the nitrate bridge is taken from 3 readings: 161·5, 161·3 and 161·4, taken at intervals of one month. It appears therefore that the use of approach I is justified in this case. The γ's calculated by using this approach are presented in Fig. 5.

The consistency of the results

The γ's corresponding to the two conventions discussed are drawn in Figs. 3–5 as continuous curves, while the γ's calculated with the aid of equation (5) are shown as points. The 24 sets of points plotted are based on the 24 values tabulated in Table I; these are average values, representing over 100 experimental measurements. The scatter of the points is slight between the concentrations 10^{-3} and 6 m, thus supporting

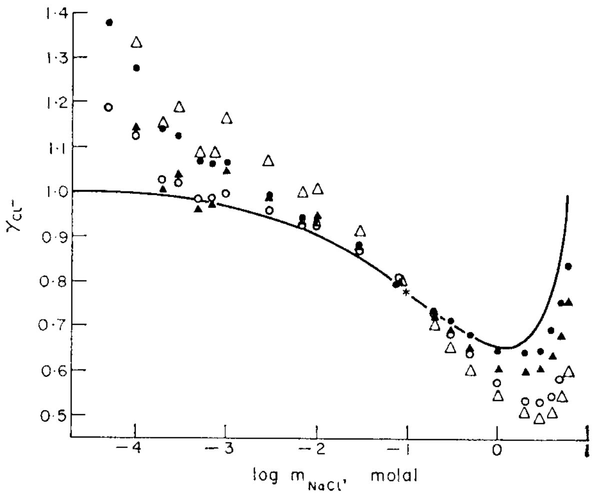

FIG. 3.—Single-ion activity coefficients calculated assuming the Guggenheim convention and using 0·1 m NaCl as standard.
Curve—interpolated from literature values. Circles—for KNO_3 bridge. Triangles—for KCl bridge. Open figures—without correction for E_j. Filled figures—corrected for E_j.

the precision of the results. Below 10^{-3} m the results obtained with the chloride bridge are considerably more scattered than those obtained with the nitrate bridge, as explained above.

It can be seen that in all cases the inconsistency between the theoretical curve and the experimental results grows rapidly below 5×10^{-4} m; this appears to be the concentration at which the chloride electrode ceases to behave as an ideal ion-specific electrode. Thus a valid comparison between the fit of the points to the theoretical curves can be made only for concentrations above 10^{-3} m. In this range the MacInnes

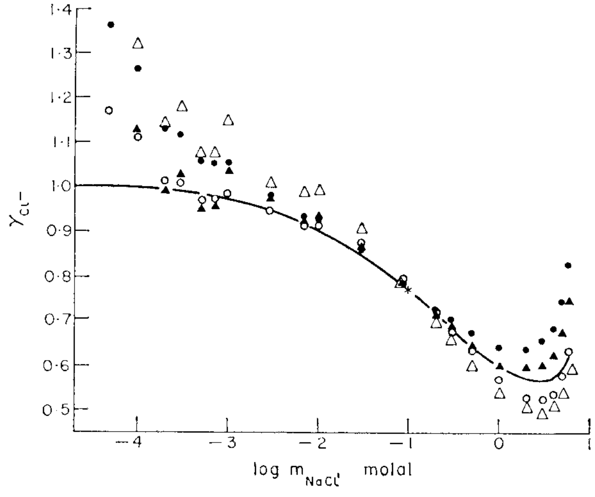

FIG. 4.—Single-ion activity coefficients calculated assuming the MacInnes convention and using 0·1 m NaCl as standard.
Symbols as in Fig. 3.

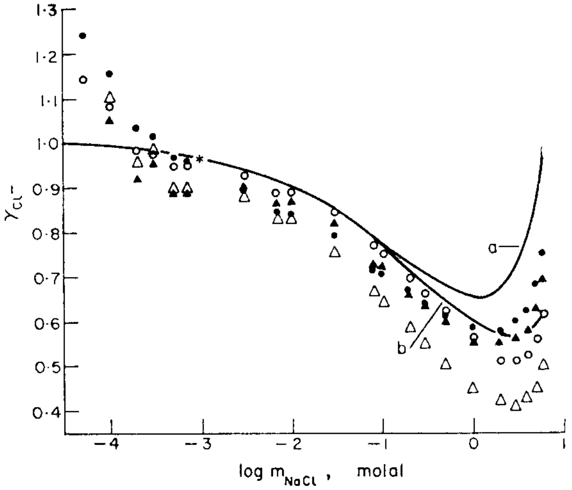

FIG. 5.—Single-ion activity coefficients 10^{-3} m NaCl as standard. *a*—Guggenheim convention; *b*—MacInnes convention. Symbols as in Fig. 3.

convention appears to give a better fit than the Guggenheim convention. To obtain a quantitative comparison the root mean square deviation from the theoretical curves has been calculated for the 16 concentrations between 10^{-3} and 6 m. The results are summarized in Table II.

Since our experimental precision yields γ's accurate within $\pm 0{\cdot}01$, it can be seen from Table II that approach I favours significantly the MacInnes convention. When approach II is used the experiments with the chloride bridge favour the MacInnes convention, while those with the nitrate bridge slightly favour the Guggenheim convention, but the difference in RMS deviation is still within the experimental error, so that it is not significant.

Similar calculations were carried out for the results without correction for E_j. The RMS deviations are well over 0·1 (all favouring the MacInnes convention). The only exception is the RMS deviation for the nitrate bridge without correction for E_j: for the Guggenheim convention it is 0·16, in line with the results quoted above, but for the MacInnes convention it is only 0·03—a better fit than that of any previous results, as can also be seen in Figs. 3–5. Thus the conclusion could be reached, if not all the evidence was considered, that the neglect of E_j gives more consistent results than allowance for E_j. The consistency in this case is probably due to the discrepancy

TABLE II.—ROOT MEAN SQUARE DEVIATION FROM THE THEORETICAL γ_{Cl^-} OF THE COEFFICIENTS CALCULATED FROM THE EXPERIMENTAL e.m.f.'s CORRECTED FOR E_j

		RMS deviation for	
		Guggenheim convention	MacInnes convention
Approach I	KCl bridge	0·13	0·04
	KNO_3 bridge	0·11	0·06
Approach II	KCl bridge	0·10	0·05
	KNO_3 bridge	0·06	0·08

between the real E_j's and those obtained with the Henderson equation, as remarked in the section dealing with the effects of E_j.

The following conclusions appear justified. When approach II produces a significantly better fit for one of the single-ion conventions, it is to be expected that approach I, had it been experimentally justified, would produce an even better fit for this convention. On the other hand the absence of significant fit on the use of approach II does not necessarily indicate that approach I would also fail to yield a significant difference of fit between the conventions. Approach I appears thus to be preferable whenever the experimental conditions allow it. Only if the electrode is suspected of non-Nernstian behaviour or if the readings are not reproducible at the low concentration reference solution is it advisable to employ approach II.

Finally, the effect of the use of different electrodes may be considered. The possibility of getting different results when using different makes of electrodes has already been pointed out.[5] As a concrete example the recent paper of Hansen *et al.*[6] illustrates how the use of 3 different chloride electrodes yields 3 different sets of results. According to the measurements reported, there is a considerable difference between the results obtained with an Ag/AgCl electrode of the second kind, and a solid membrane electrode, even though the final results are equivalent. This may be due to the fact that the method of measurement was different for each electrode. In our case comparison of column *b* in Table I of the present paper with Table I of reference[1] shows that the results obtained with the solid membrane chloride electrode agree within the experimental error with those obtained with the Ag/AgCl electrode. In fact, the range of agreement extends from 10^{-5} to 6 m sodium chloride, while the claim of the manufacturers[7] is only up to 1 m. The response time of the solid membrane electrode is also comparable with that of the Ag/AgCl electrode, so that in all respects the two electrodes appear to be equivalent in pure aqueous sodium chloride solutions.

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Zusammenfassung—Die EMK-Werte zwischen einer Chloridelektrode und einer Bezugselektrode wurden in wäßrigen NaCl-Losungen zwischen 10^{-5} und 6 m gemessen, wobei Brücken mit gesättigtem KCl und mit 1 M KNO_3 verwendet wurden. Der Effekt der verschiedenen Brückenlösungen wird berechnet und diskutiert. Die Konsistenz der Ergebnisse wird untersucht, wenn man die Annahmen nach MacInnes oder nach Guggenheim verwendet. Die Wahl verschiedener Bezugspunkte für die Standardisierung der EMK-Werte und Aktivitätskoeffizienten wird diskutiert. Die Ergebnisse mit einer Ag/AgCl-Elektrode zweiter Art und mit einer Chloridelektrode mit fester Membran werden verglichen.

Résumé—On a mesuré les valeurs de f.é.m. entre une électrode au chlorure et une électrode de référence en solutions aqueuses de NaCl entre 10^{-5} et $6M$, en utilisant des ponts de KCl saturé et de KNO_3 $1M$. On calcule l'influence des diverses jonctions liquides et en discute. On examine la consistance des résultats en admettant, soit la convention de Mac Innes, soit celle de Guggenheim. On discute du choix de différents points de référence pour l'étalonnage des f.é.m. et pour les coefficients d'activité. On effectue une comparaison entre les résultats obtenus avec une électrode Ag/AgCl de deuxième espèce et une électrode au chlorure à membrane solide.

REFERENCES

1. A. Shatkay and A. Lerman, *Anal. Chem.*, 1969, **41**, 514.
2. G. Johansson and K. Norberg, *J. Electroanal. Chem.*, 1968, **18**, 239.
3. H. S. Harned and B. B. Owen, *The Physical Chemistry of Electrolytic Solutions*, Reinhold, New York, 1964.
4. R. Parsons, *Handbook of Electrochemical Constants*, Butterworths, Bethesda, 1959.
5. A. Shatkay, *Biophys. J.*, 1968, **8**, 912.
6. L. Hansen, M. Buechele, J. Koroshek and W. Warren, *Am. J. Clin. Path.*, 1968, **49**, 834.
7. *Instruction Manual, Halide Electrodes*, 2nd Ed. Orion Research Inc., Cambridge, Mass., 1967.

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PREPARATION OF D-(—)-*trans*-1,2-DIAMINOCYCLOHEXANE-*N*,*N*,*N*′,*N*′-TETRA-ACETIC ACID AND ITS USE AS A SPECTROPOLARIMETRIC REAGENT FOR LEAD

P. E. REINBOLD and K. H. PEARSON
Department of Chemistry, Texas A & M University, College Station, Texas 77843, U.S.A.

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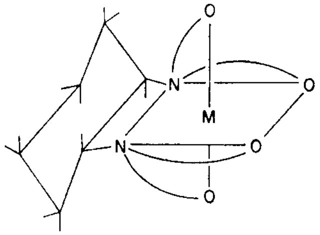
Summary—D-(—)-*trans*-1,2-diaminocyclohexane-*N*, *N*, *N*′, *N*′-tetra-acetic acid [D(—)DCTA] was prepared stereospecifically in good yield by the condensation of the resolved diamine, D-(—)-*trans*-1,2-diaminocyclohexane, with sodium chloroacetate at 16°, followed by use of a strong cation-exchanger to obtain the free acid. Distinct differences were noted in the infrared spectra of the optically active acid and the racemate. The molecular rotation of D(—)DCTA showed strong dependence on the pH of the solution. D(—)DCTA was used as a stereospecific chelometric reagent in the spectropolarimetrically monitored determination of lead.

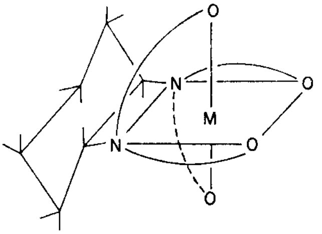
THE REAGENT *trans*-1,2-diaminocyclohexane-*N*,*N*,*N*′,*N*′-tetra-acetic acid (DCTA) was first prepared by Schwarzenbach and Ackermann[1] in their study on the effect of the positions of the nitrogen atoms on the thermodynamic stability of metal–ligand complexes for a series of diaminocyclohexanetetra-acetic acids. The complexes of DCTA with most metal ions are more stable than those of EDTA or 1,2-propylenediaminetetra-acetic acid (PDTA).[2] This greater stability (generally 1–2 units in log K for most of the metal complexes) can be attributed to the fact that during chelation, the carbon chain between the nitrogen atoms in both EDTA and PDTA has to be rotated to bring the nitrogen atoms into the same plane for chelation between the nitrogen atoms and the metal ion to occur. The thermodynamically preferred chair configuration of *trans*-DCTA, with the nitrogen atoms in equatorial positions, demands that very little reorientation of the nitrogen atoms is necessary for chelation to occur.

Commercially available *trans*-DCTA is a racemic mixture of the two possible optical isomers, D(—) and L(+). Ferrone attempted the resolution of DCTA into its optical isomes, using (+)-phenylethylamine, (+)-camphor sulphonate, and (—)-quinine, but none of these attempts gave a crystalline diastereoisomer. He also tried to prepare the L-(+)-isomer of the acid by direct synthesis from L-(+)-*trans*-1,2-diaminocyclohexane [L(+)chxn] and sodium chloroacetate, following the general method used in the preparation of ethylenediaminetetra-acetic acid, but obtained only a viscous syrup which would not crystallize upon acidification.[3] Dwyer and Garvan also failed in their attempt to resolve the racemic acid with (+)-cinchonine, but were successful in the resolution by using the (—)-*cis*-dinitrobis(ethylenediamine)cobalt(III) ion.[4] This procedure is very long and tedious and the yield is extremely low.

The work by Dwyer and Garvan showed that only two of the four possible isomers of the metal chelate were obtained,[4] the $(+)_{546}[\text{Co}(-)\text{DCTA}]^-$ and $(-)_{546}[\text{Co}(+)\text{-DCTA}]^-$ isomers, proving that both optical isomers of *trans*-DCTA are completely stereospecific in their reaction with the cobalt(III) ion. Models show that it is impossible to obtain the isomers $(+)_{546}[Co(+)DCTA]^-$ and $(-)_{546}[Co(-)DCTA]^-$ because of the fixed stereochemistry of the cyclohexane ring and its inability to accompany certain chirality, because of steric hindrances of the methylene groups of the ring and the acetato groups (see Fig. 1). Failure to racemize solutions of these optically active complexes at 100° with activated charcoal confirmed this conclusion experimentally. This conforms with Jaeger's theory that one configuration of the complex is incompatible with one optical isomer of the ligand.[5]



L*- $[M(D(-)DCTA)]^{n-}$



D*- $[M(D(-)DCTA)]^{n-}$

FIG. 1.—Stereospecificity of D(−)DCTA in forming L*-$[M\text{-}(D(-)DCTA)]^{n-}$ complexes.

D-(−)-*trans*-1,2-diaminocyclohexane-*N*,*N*,*N′*,*N′*-tetra-acetic acid [D(−)DCTA] was prepared by stereospecific condensation of the resolved diamine with concentrated sodium chloroacetate solution in a strongly basic medium, followed by the use of a strong cation-exchange resin to obtain the free acid.

Spectropolarimetric titrimetry is a relatively new analytical technique first described by Kirschner and Bhatnagar.[6] The optical rotation of the system is constantly monitored while the titration proceeds. An inflection in the change of the optical rotation indicates the end-point of the titration. Spectropolarimetric titrimetry has been applied to acid-base titrations, as well as to different metal systems.[7] Recent work by Pearson *et al.*[8,9,10] has shown the use of D-(−)-1,2-propylenediaminetetra-acetic acid as titrant for transition, heavy and lanthanide metals. The spectropolarimetric method offers several advantages over other chelometric methods, especially in choice of pH range for quantitative titration, because the pH range is not limited by the need to ensure a sharp indicator colour transition; the optically active ligand and stereospecifically formed complex serve as self-indicators. Since the observed rotation is essentially linear over large concentration ranges, the end-point is located by graphical extrapolation. The large molecular rotation values of many of the complexes make the method very sensitive.

In this work the synthesis and some properties of D-(−)-*trans*-1,2-diaminocyclohexane-*N,N,N′,N′*-tetra-acetic acid are described, together with its use as titrant for lead.

EXPERIMENTAL

Resolution of racemic trans-1,2,*-diaminocyclohexane and isolation of* D-(−)-trans-1,2- *diaminocyclohexane*

Technical grade racemic *trans*-1,2-diaminocyclohexane was distilled under reduced pressure, b.p. 75–80°/16 mbar. Then 200 g of racemic diamine were added dropwise with mechanical stirring to a solution of L-(+)-tartaric acid (350 g in 400 ml of water), the temperature being maintained below 55°. This mixture was allowed to cool to about 5° and kept cold for an hour, after which it was filtered (sintered-glass Büchner filter). The white crystals of the diastereoisomer, D-(−)-*trans*-1,2-diaminocyclohexane L-(+)-tartrate, were washed with 120 ml of ice water and sucked dry. The filtrate was set aside for later use in an attempt to isolate the L(+) isomer of the diamine. The crystals of the diastereoisomer were dissolved in the least amount of boiling water necessary (~325 ml), by adding the crystals in small portions to a beaker of hot water, with mechanical stirring to prevent burning of the product. A litre of absolute ethanol was added to the solution, which was then allowed to cool (with stirring) to about 5° during one hour, and then filtered. The specific rotation of a 1% solution of the diastereoisomer in water was determined to be +12·1° at 589 nm and this value was compared with the literature value[4] of +12·0°. This measurement served as the criterion of purity. The yield was 90%.

The diastereoisomer was suspended in water by stirring, and solid sodium hydroxide was added. The colour turned darker and the mixture separated into two layers. The upper layer was decanted off and distilled from solid potassium hydroxide under reduced pressure, b.p. 75–80°/16 mbar.

Preparation of D-(−)-trans-1,2-*diaminocyclohexane*-N,N,N′,N′-*tetra-acetic acid*

A solution of 280 g (3 mole) of monochloroacetic acid in 150 ml of water was cooled to 10° and a cold solution of sodium hydroxide, 240 g (6 mole) in 500 ml of water, was added dropwise with mechanical stirring, the temperature being kept below 16°. Then 58 g (0·5 mole) of the previously resolved D-(−)1,2-diaminocyclohexane were slowly added through a dropping funnel, the temperature being kept below 16° during the addition and for six days more and then being raised to and kept at 19° for an additional six days, the solution being stirred throughout. The pH was adjusted to 3·5 with concentrated hydrochloric acid and the solution evaporated on a steam-bath in a current of air to a volume of 600 ml. The solid sodium chloride was removed by filtration (sintered-glass Büchner funnel). The filtrate was poured into 2 l. of vigorously stirred absolute ethanol and stirred overnight to allow crystallization. The crystals were suspended in 600 ml of glacial acetic acid and heated, with stirring, to 40° in order to dissolve the disodium salt of D(−)DCTA. The undissolved sodium chloride was filtered off and washed with 30 ml of warm glacial acetic acid. The washings and filtrate were combined and added slowly to 3 l. of benzene and the mixture was stirred overnight. The viscous syrup deposited was crystallized by decanting off the benzene and pouring the viscous syrup into 2 l. of rapidly stirred acetone. This mixture was stirred for 1 hr and the crystals formed were allowed to settle out. The acetone was decanted off, 2 l. of fresh acetone were added, and the mixture was stirred overnight to dissolve traces of acetic acid. It was then filtered and the white solid was allowed to dry in air. The solid was dissolved in 1·5 l. of demineralized water and evaporated on a steam-bath to approximately 1 l., much of the acetic acid and acetone being thereby removed. The pale yellow solution was pumped onto a large heated ion-exchange column packed with Dowex 50W-X8, a strong cation-exchange resin which had been previously washed with 8 l. of hot 6*M* hydrochloric acid, followed by 12 l. of demineralized water, to remove traces of the iron(III) generally present in the material and to convert the resin into the acid form. The column was washed with 2 l. of cold demineralized water and these first 2 l. of pale yellow eluate were discarded, as they contained traces of acetic acid and only negligible amounts of the optically active material. The column was then heated to 95–100° and the active acid was eluted with ~44 l. of boiling demineralized water at a flow-rate of 10 l./hr until the eluate no longer showed optical activity. The eluate was reduced to about 400 ml by vacuum stripping and 600 ml of reagent grade acetone were added. After cooling of the solution overnight in an ice-bath, white crystals formed. They were collected on a medium porosity sintered-glass Büchner funnel and dried first in air and then overnight in a vacuum oven at 115°/4 mbar. The yield was 33%.

The specific rotation at 589 was −53·4° for a 0·5% aqueous solution (literature value[4] for the anhydrous acid −53·0°). M.p. 236–238° (decomp.), literature value[4] 237°. Calculated for $C_{14}H_{22}N_2O_8$: C 48·55%; H 6·40%; N 8·09%; O 36·96%; found C 48·8%; H 6·3%; N 8·2%; O 36·7%.

Visual chelometric titrations with standard lead solution (Xylenol Orange as indicator) showed 100·0 ± 0·15% purity.

Apparatus

A Perkin–Elmer Model 141 Photoelectric Polarimeter with a 0·1-m flow-through cell was used to monitor the titration. The titration vessel was constructed from a 125-ml Erlenmeyer flask with one glass tube attached at the bottom centre and another about one-fifth up the side, and was connected to the flow-through cell with Tygon tubing. A magnetic stirrer both mixed the solution and pumped it through the polarimeter cell. A 5-ml microburette with the tip immersed below the surface of the liquid was used to deliver the titrant.

Reagents

With the exception of the solution of D(−)DCTA, all solutions were prepared from reagent grade chemicals. D(−)DCTA, prepared as above, and reagent grade potassium hydroxide were dissolved in demineralized water and this solution was standardized by visual titration against standard lead solution at pH = 4·7, with Xylenol Orange as indicator. All solutions were stored in polyethylene bottles.

Effect of pH on the molecular rotation of D(−)*DCTA*

Dwyer and Garvan[11] reported that the molecular rotation of D-(−)-1,2-propylenediaminetetraacetic acid varied as the pH was changed. Pearson *et al.*[8] also studied this pH dependence and attributed it to the degree of protonation of the ligand. A similar investigation was made with D(−)DCTA at the 5 wavelengths available on the instrument and the results are shown in Figs. 2 and 3.

Spectropolarimetric titration of lead

An aliquot of lead solution was buffered to pH 4·7 with sodium acetate–acetic acid buffer and diluted with demineralized water to 100 ml in the titration vessel. The flow-through polarimeter cell was inserted in the instrument, and the digital read-out set at zero. The titrant was relatively concentrated in order to minimize dilution effects. After each incremental addition of titrant, the rotation was read when it had stabilized, and the titration graph was plotted, a dilution correction

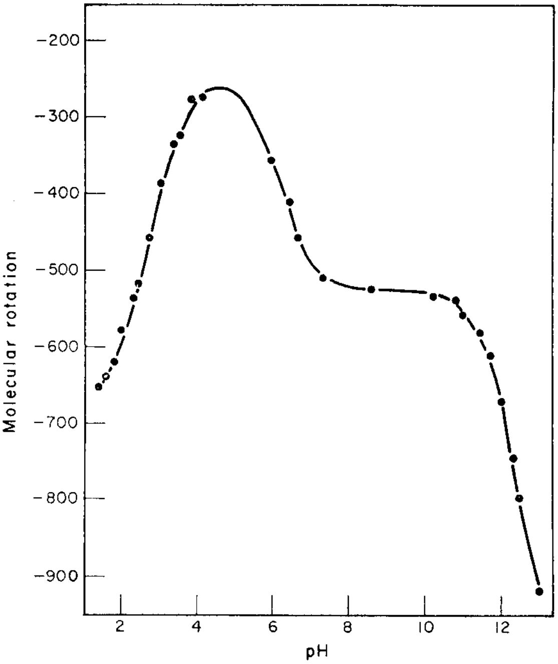


FIG. 2.—The molecular rotation of D(−)DCTA *vs.* pH at 365 nm, $\mu = 0{\cdot}50$ (KNO_3).

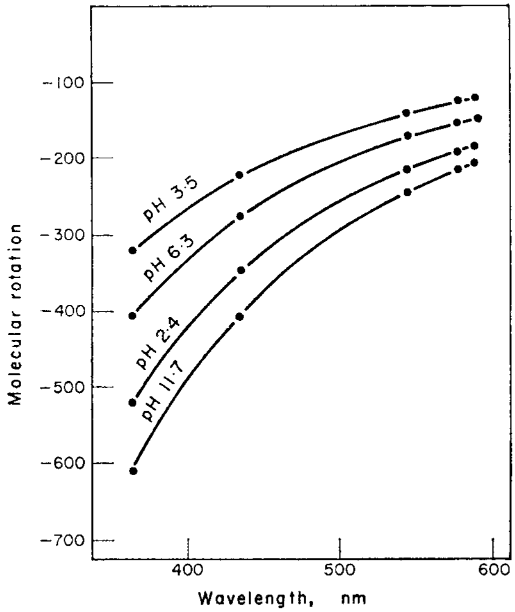


FIG. 3.—Optical rotatory dispersion spectra of D(−)DCTA at various pH values, $\mu = 0{\cdot}50$ (KNO_3).

being applied, and extrapolated to give the end-point. Generally only five points before and five after the end-point are needed.

RESULTS AND DISCUSSION

The change in the molecular rotation of D-(−)-DCTA with pH is due to successive dissociations of the ligand. The points of inflection of the curve occur at pH values near p*K* values for the racemic acid.

The infrared spectra of both the racemic and the D-(−)-isomer of *trans*-DCTA in Nujol mull were recorded on a Beckmann IR-12 instrument and showed distinct differences, Figs. 4 and 5. The weak broad band at 2550 cm^{-1} has been assigned to

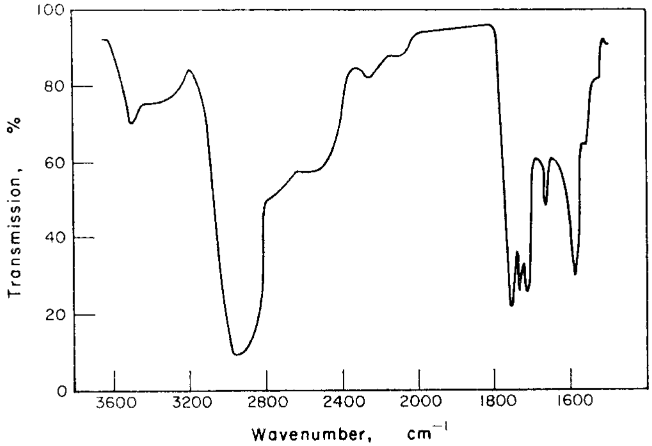


FIG. 4.—Infrared spectrum of racemic *trans*-1,2-diaminocyclohexane-*N*,*N*,*N*′,*N*′-tetra-acetic acid.

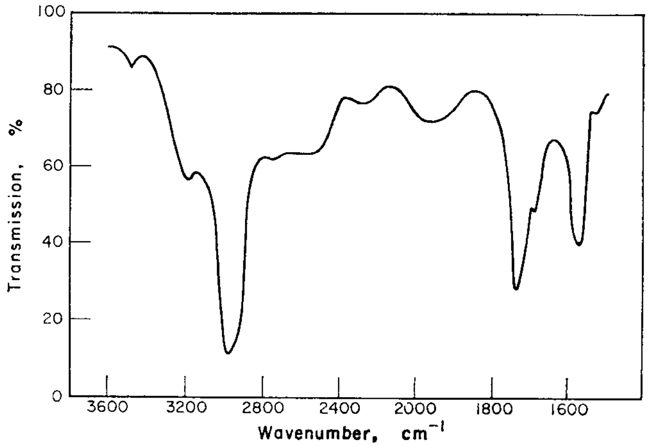


FIG. 5.—Infrared spectrum of D-(−)-*trans*-1,2-diaminocyclohexane-*N*,*N*,*N*′,*N*′-tetra-acetic acid.

the protonated nitrogen; this would suggest that the structure of the optical isomer could allow a higher degree of protonation of one of the nitrogen atoms. The carbonyl stretching bands in the neighbourhood of 1585–1735 cm^{-1} are not as sharp for the optically active DCTA as for the racemate; this suggests a greater degree of intramolecular hydrogen bonding in the case of the optically active isomer. These conclusions appear to be consistent with the solubility differences: the racemate is very insoluble in water, whereas the optically active isomer is very difficult to crystallize from an aqueous solution. Similar results have been reported by Dwyer and Garvan in their studies of the infrared spectra of racemic and optically active 1,2-propylenediaminetetra-acetic acid.[11]

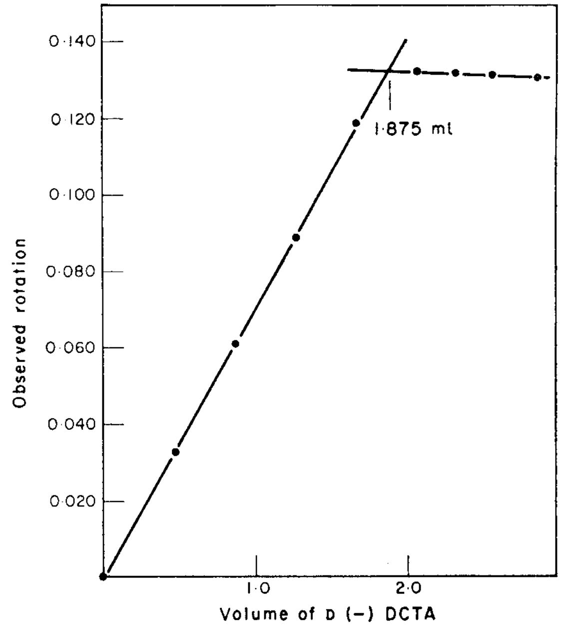


FIG. 6.—Spectropolarimetric titration of 2·0 mg of lead with D(−)DCTA at pH = 4·7 and 365 nm.

A typical titration plot for lead is shown in Fig. 6, and the results are shown in Table I. They agreed within experimental error with those obtained spectropolarimetrically with D-(−)-1,2-propylenediaminetetra-acetic acid and visually with EDTA. Although the molecular rotation of the lead–D(−)DCTA complex is somewhat greater than that of the lead–D-(−)PDTA complex at 365 nm, the sensitivity at this wavelength is not significantly greater. The wavelength of 365 nm was selected because it gave the greatest difference between the molecular rotations of the lead complex and the ligand.

TABLE I.—CONDITIONS AND RESULTS FOR THE SPECTROPOLARIMETRIC TITRATION OF LEAD WITH D-(−)-*trans*-1,2-DIAMINOCYCLOHEXANE-*N*,*N*,*N*′,*N*′-TETRA-ACETIC ACID

[D(−)DCTA], *M*	pH 4·7 buffer, *ml*	Lead Taken, *mg*	Found, *mg**
0·08395	25·00	20·20	20·25 ± 0·03
0·05110	25·00	20·20	20·23 ± 0·01
0·005230	10·00†	2·020	2·036 ± 0·007

* Average of at least 3 determinations.

† Total volume of the solution was 50 ml, and a smaller titration cell was employed.

Acknowledgement—This study was supported by The Robert A. Welch Foundation Fellowship Grant A-262. It is taken in part from the Ph.D. dissertation of P.E.R.

Zusammenfassung—D-(−)-*trans*-1,2-Diaminocyclohexan-N,N,N′,N′-tetraessigsäure (D(−)DCTA) wurde in guter Ausbeute stereospezifisch durch Kondensation von optisch aktiven D-(−)-*trans*-1,2-Diaminocyclohexan mit Natriumchloracetat bei 16° und Freisetzung der Säure mit Hilfe eines Kationenaustauschers erhalten. Zwischen den Infrarotspektren der optisch aktiven Säure und denen des Racemats wurden deutliche Unterschiede gefunden. Die molare Rotation von D(−)-DCTA ist stark vom pH der Lösung abhängig. D(−)DCTA wurde als stereospezifisches chelometrisches Reagens bei der spektropolarimetrisch verfolgten Bestimmung von Blei verwendet.

Résumé—On a préparé stéréospécifiquement l'acide D-(—)-*trans*-1,2-diaminocyclohexane N,N,N′,N′-tétracétique (D(—)DCTA) avec un bon rendement par condensation de la diamine dédoublée, D-(—)-*trans*-1,2-diaminocyclohexane, avec le chloracétate de sodium à 16°, suivie de l'emploi d'un échangeur cationique fort pour obtenir l'acide libre. On a noté des différences marquées dans les spectres infra-rouges de l'acide optiquement actif et du racémate. Le pouvoir rotatoire moléculaire du D(—)DCTA s'est révélé être fortement dépendant du pH de la solution. On a utilisé D(—)DCTA comme réactif chélatométrique stéréospécifique dans la détermination contrôlée spectropolarimétriquement du plomb.

REFERENCES

1. G. Schwarzenbach and H. Ackermann, *Helv. Chim. Acta*, 1949, **32**, 1682.
2. A. E. Martell and L. G. Sillén, *Stability Constants of Metal-Ion Complexes*, 2nd Ed., Chem. Soc. Spec. Publn. No. 17, London, 1964.
3. B. A. Ferrone, *Ph.D. Thesis*, University of Illinois, 1957.
4. F. P. Dwyer and F. L. Garvan, *J. Am. Chem. Soc.*, 1961, **83**, 2610.
5. F. P. Dwyer and D. P. Mellor, *Chelating Agents and Metal Chelates*, p. 209. Academic Press, New York, 1964.
6. S. Kirschner and D. C. Bhatnagar, *Anal. Chem.*, 1963, **35**, 1069.
7. K. H. Pearson and S. Kirschner, *Anal. Chim. Acta*, 1969, **48**, 339.
8. R. J. Palma, Sr., P. E. Reinbold and K. H. Pearson, *Anal. Chem.*, 1970, **42**, 47.
9. R. J. Palma, Sr. and K. H. Pearson, *Anal. Chim. Acta*, 1970 **42**, 416.
10. D. L. Caldwell, P. E. Reinbold and K. H. Pearson, *Anal. Chem.*, 1970, **42**, 416.
11. F. P. Dwyer and F. L. Garvan, *J. Am. Chem. Soc.*, 1959, **81**, 2955.

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EDTA TITRATION OF CALCIUM AND MAGNESIUM WITH A CALCIUM-SELECTIVE ELECTRODE

T. P. HADJIIOANNOU and D. S. PAPASTATHOPOULOS
Laboratory of Analytical Chemistry, University of Athens, Athens, Greece

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Summary—Direct semi-automatic and automatic derivative potentiometric EDTA procedures for the determination of calcium and/or magnesium with a calcium-selective electrode are described. Calcium is titrated in the presence of magnesium at pH 12·0 and the total calcium and magnesium is determined at pH 9·7. Calcium in the range 1–8 mg and magnesium in the range 0·7–5 mg are determined semi-automatically with average errors of about 0·2 and 0·3% respectively and automatically with average errors of 0·4 and 0·7%. Titration times vary from a few seconds to a few minutes.

THE RECENT development of a large number of ion-selective electrodes has resulted in a renewal of interest in analytical potentiometry. During the past three years, a considerable amount of work has been published which deals with the use of such electrodes, and in particular of a calcium-selective electrode.[1–21] Liquid–liquid membrane as well as solid-membrane calcium-selective electrodes are now commercially available,[4,17] the former being more widely used. The electrode responds to the activity of the ionized calcium in the sample, which depends on the ionic strength of the sample. Therefore, the working curve, *E vs.* [Ca^{2+}], should be prepared with standards which have practically the same composition as the samples. Even with such precautions, direct potentiometric techniques are unlikely to give an accuracy better than ±1·2%, because the accuracy of measurements is seldom better than ±0·15 mV and the maximum slope of the working curve is 29·6 mV per activity decade at 25°. Titration techniques yield more accurate results than those obtained by the direct method, because the titration curve is reproducible and the equivalence point can be easily located. In practice, some easily distinguishable point on the titration curve (*e.g.*, a point of inflection or the mid-point of the section of maximum slope) is chosen as the "end-point" and it is assumed that the consumption of the titrant in going from this point to the equivalence point is small.[19] However, such titrations are time-consuming, requiring at least 20 min,[21] because many points are required for each titration curve and each potential measurement is made 30–60 sec after the addition of titrant.[5,16]

It is shown in the following presentation that the control unit of an automatic differential potentiometric titrator coupled with a recording electrometer and a constant-rate burette can be used for the automatic EDTA titration of calcium and/or magnesium with a calcium-selective electrode. It is not necessary to know the end-point potential, because the electronic circuit computes the second derivative voltage of the ordinary potentiometric curve, and this voltage is ideally suited to trigger a relay system which turns the burette off at the inflection point (end-point) of the titration.[22–25] It is also possible to determine calcium and/or magnesium semi-automatically by recording the potentiometric titration curve. The end-point is read from the plot after the titration is completed. Samples containing only calcium or magnesium are titrated at pH 9·7. In samples containing calcium and magnesium, calcium is automatically titrated at pH 12·0 in the presence of magnesium as magnesium hydroxide; total calcium and magnesium is determined at pH 9·7 and magnesium is calculated by difference. Titration times range from a few seconds to a few minutes.

EXPERIMENTAL

Apparatus

A block diagram of the automatic titration system is shown in Fig. 1. The automatic titration controller (S-29691, E. H. Sargent Co.) of the Sargent-Malmstadt titrator was used. The control unit is coupled with a direct-reading, constant rate, motor-driven, automatic burette (Model C, S-11120-10, E. H. Sargent Co.), which provides a titrant delivery rate of 1 ml/min (in the present work the delivery rate was $\frac{5}{6}$ of the nominal because the available line voltage frequency was 50 Hz). The burette is plugged into the valve outlet on the back of the control unit. A special cell unit, shown in Fig. 2, was constructed. The unit consists of a beaker platform, a propeller-driven stirring system, an indicator electrode (Orion calcium-activity electrode, Model 92-20), a reference electrode (Coleman saturated calomel electrode, No. 3-512) and a delivery tip. Bakelite rings of different diameters can be inserted in the platform to hold beakers of various sizes. Most of the titrations were performed at room temperature, in a 50-ml beaker.

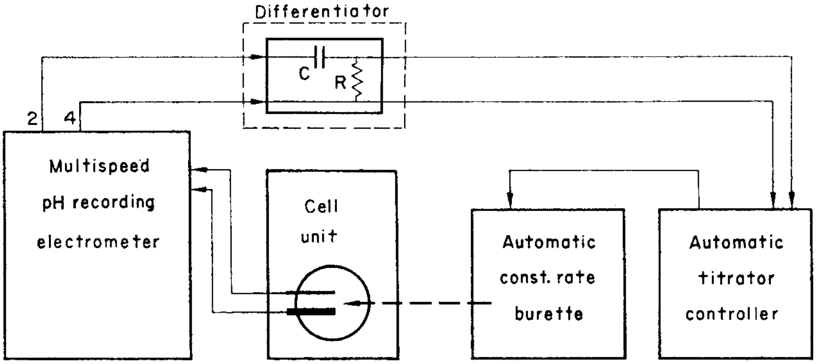

FIG. 1.—Block diagram of automatic titration system.

For automatic titrations the voltage between the electrode pair is fed to the input of a multispeed pH-recording electrometer (Model EUW-301 M, Heath Co.) and the output signal from points 2 and 4 of the chassis plug "U" is fed to the control unit. After the initial assembly and connection of the burette and the electrometer to the control unit, the usual operations consist of placement of sample vessel, pushing the automatic button on the control unit and reading the burette after the automatic termination of the titration. For semi-automatic titrations the control unit is not used and the burette is connected for actuation to the 110-V socket (second from bottom on side of recorder) of the recording electrometer.

Reagents

All solutions were prepared in demineralized water from reagent-grade materials.

Buffer solution. Glycine (37·5 g) dissolved in about 700 ml of water, adjusted to pH 9·7 with 2*M* sodium hydroxide, and diluted to 1 litre. The solution is kept refrigerated when not in use.

EDTA solution, 0·0600*M*. Standardized against standard zinc solution, which is prepared by dissolving reagent grade zinc (>99·9% Zn) in hydrochloric acid, Eriochrome Black T being used as indicator; stored in polyethylene bottles.

Magnesium solution, 0·01000*M*. Prepared from $MgSO_4.7H_2O$ and standardized against the EDTA solution.

Standard calcium solution, 0·01000*M*. Primary standard calcium carbonate is dried in an oven for 3–4 hr at 110° and 1·0009 g are dissolved in the least necessary amount of hydrochloric acid and diluted with water to 1 litre. When this solution was analysed gravimetrically or by titrating against the standard EDTA solution, after the addition of a known amount of standard zinc solution, with Eriochrome Black T as indicator, the results obtained agreed within 0·2% with the theoretical value.

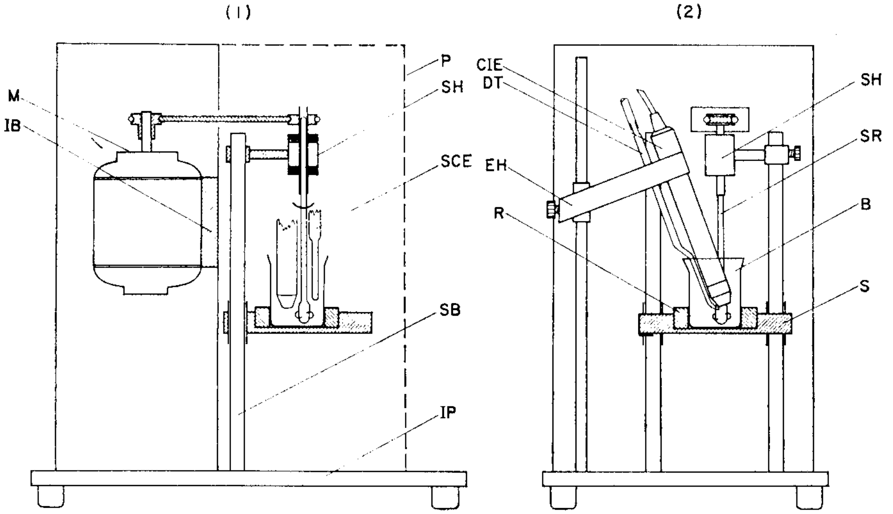

FIG. 2.—Left side-view (1) and front view (2) of the cell unit (scale 1:6). MC—Motor chamber, M—motor (Citenco, type 7 FA/47 200-230-volt a.c., 50 Hz, 1300 rpm), IB—insulation base plate of motor, P—protecting wire net, SH—stirring-rod holder with 2 ball-bearings, SCE—saturated calomel electrode, SB—slide bar, IP—iron plate, CIE—calcium ion electrode, DT—delivery tip (Sargent S-29704), EH—electrode holder (Orion Model 92-00-01), R—Bakelite ring, SR—stirring rod (Sargent S-76669-A), B—50-ml squat beaker, S—sliding platform.

Procedure

Preparation of cell unit and multispeed pH-recording electrometer. Place the stirrer slightly offset from centre and approximately 3 mm from the bottom of the beaker. Place the right-angled delivery tip immediately above the propeller and about 1 mm from the shaft of the stirrer, so that the delivery flow is directed at the shaft. Place the electrodes about 15 mm from the bottom and close to but not touching the sides of the titration beaker. Use small-diameter gum-rubber tubing to connect the tip of the burette to the delivery tip. Mount the complete assembly so that the beaker can be replaced without disturbing the electrode, burette and stirrer assembly. Adjust the scale of the electrometer to read from +50 mV to −150 mV, left to right. Set the chart speed at the desired value (usually 0·15 M/min) and turn the function switch to "Standby".

Semi-automatic titration of calcium and/or magnesium. Take a 25-ml aliquot of the sample in a 50-ml beaker and add 2 ml of buffer solution. Lock the burette "ON" by pressing its delivery push button and turning it by a one-fourth turn. Start the stirrer and after a few seconds turn the function switch to the "Record" position to obtain the titration curve for calcium plus magnesium. For the greatest accuracy calibrate the recorder for each titration, using the burette reading. Use this procedure when the sample contains only calcium or magnesium. Titrate calcium in another 25-ml aliquot of the sample without buffer but with 0·25*M* sodium hydroxide added to bring the pH to 12·0. Calculate the magnesium content by difference from the volumes of EDTA used, subtract also the difference in the blanks.

Automatic determination of calcium and/or magnesium. The procedure is the same as for the semi-automatic method except that at the beginning the function switch is turned to the "Measure" position and the titration is started by pushing the "automatic" button and is automatically terminated at the end-point.

When not in use the calcium electrode is stored in a $10^{-3}M$ calcium chloride solution.

RESULTS AND DISCUSSION

The calcium electrode responds rapidly to changes in calcium activity and with efficient stirring it can be used to follow the course of a complexometric titration of calcium and/or magnesium with continuous addition of titrant. The point of maximal rate of potential change is very close to the equivalence point. Thus at a delivery rate of 0·05 mmole of EDTA/min the end-point (mid-point of the section of maximum slope of the curve) is located beyond the equivalence point by about 0·02 ml of 0·06*M* EDTA. The electrode response to changes in magnesium activity is slower than for calcium and the equivalence point is overshot by 0·05 ml of 0·06*M* EDTA. The blank becomes larger, 0·07–0·10 ml, in automatic titrations. However, the precise definition of the end-point that the calcium electrode provides makes possible the accurate automatic titration of calcium and magnesium even with a blank of 0·10 ml.

The slope of the titration curve, the overall voltage change, and the blank, all depend on sample composition, buffer used, and on experimental conditions, *e.g.*, titrant delivery rate and concentration, stirring rate, size of beaker, position of delivery tip and depth of electrode immersion. The slope and the overall voltage change decrease whereas the blank increases slightly with increasing ionic strength of the test solution. Thus for the titration of 4 mg of calcium the rate of potential change near the equivalence point decreased from about 9 to 3 mV/sec, when the ionic strength of the test solution was increased from 0·03 (pure calcium chloride solution) to 0·4 (calcium chloride sample with added sodium chloride). The blank remained about the same for the semi-automatic method, but it increased for the automatic method by about 0·02 ml of 0·06*M* EDTA. Therefore, if the ionic strength of the test solution is high, for better accuracy with the automatic method the blank should be determined with standards closely approximating to the sample ionic composition. If the preparation of such standards is not easily feasible, the blank can be determined by analysing two portions of the sample differing slightly in magnitude, so that the ionic strength is about the same in both test solutions. For samples containing only calcium or magnesium the blank was determined by titrating standard calcium or magnesium solutions.

When the ionic strength was increased by addition of sodium chloride, the voltage between the electrode pair shifted to more positive potentials, because of sodium interference.[15] Therefore for high ionic strength the scale was adjusted to read from +100 mV to −100 mV. A span of 100 mV, with full scale from 0 to −100 mV, was used in the semi-automatic method for magnesium.

Ammonia/ammonium chloride, tris, ethylenediamine, and glycine buffers were tried. Partial complexing of calcium and/or magnesium, which results in errors in direct potentiometry, has no other effect except the shift of the titration curve. Such shifts were observed during precision studies, even for the same buffer and sample, but had no appreciable effect on the accuracy. Thus, while semi-automatic and automatic end-point potentials for replicates differed by up to 10 mV, the corresponding titrant volumes differed by less than 2%. The glycine buffer was chosen because it gave the greatest rate of potential change in the region of the equivalence point. The amount of buffer added should be such that the pH of the solution at the end-point is greater than 8. In the titration of calcium in presence of magnesium the amount of sodium hydroxide added is such that the pH of the solution at the end-point is greater than 11·2.

The differentiation shows up the signal noise. To minimize noise and the number of false signals, the following precautions were taken: (1) the upper three-quarters of the electrode body were wrapped in aluminium foil, which then was grounded to a common outlet with the electrometer, the burette, the cell unit base and the control unit; (2) the motor was shielded from the rest of the unit and grounded to a separate outlet; (3) a wire net was set in front of the cell unit; (4) the signal was overdamped by turning the damping control on the electrometer clockwise by at least a quarter-turn beyond the point where the pen stopped "jittering"; (5) a special electrode holder was used to avoid trapping of air bubbles on the porous disc; (6) efficient clockwise stirring at 1300 rpm was provided to accelerate the change of sample liquid in immediate contact with the electrode membrane, without drawing air into the solution.

Occasionally during the titration of total calcium and magnesium the addition of titrant was stopped automatically before the equivalence point was reached, usually near a point corresponding to the calcium content of the sample. False early end-points can be easily detected from the potential value shown on the electrometer. If one should occur near the end-point, the titration must be finished semi-automatically by depressing the manual button on the control unit. This is necessary because the control unit has a built-in 10-sec time delay circuit in the automatic control that overrides the end-point signal. If desired, the 10-sec delay interval may be over-ridden for titrations less than 0·25 ml by releasing the delivery push button on the burette, actuating the automatic button, delaying for 10 sec, then engaging the delivery push button.

TABLE I.—TITRATION RESULTS FOR SAMPLES CONTAINING KNOWN AMOUNTS OF CALCIUM OR MAGNESIUM

Taken, *mg*		Found, *mg*		Error %	
Calcium	Magnesium	Semi-automatic	Automatic	Semi-automatic	Automatic
1·202		1·207	1·185	+0·4	−1·4
2·004		2·004	2·012	—	+0·4
4·008		4·016	4·004	+0·2	−0·1
6·012		6·012	6·012	—	—
8·016		8·008	8·040	−0·1	+0·3
		Av.		0·14	0·44
		Std. devn., for 4 mg Ca ($n = 6$)		0·38	0·60
	0·729	0·733	0·723	+0·5	−0·8
	1·216	1·221	1·199	+0·4	−1·4
	2·431	2·424	2·455	−0·3	+1·0
	3·647	3·647	3·651	—	+0·1
	4·86	4·84	4·88	−0·4	+0·4
		Av.		0·32	0·72
		Std. devn., for 2·4 mg Mg ($n = 8$)		0·34	1·10

Hundreds of samples containing known concentrations of calcium and/or magnesium in different amounts and in different ratios, were titrated to check the proposed method. Some representative data are shown in Tables I–III. The average errors in semi-automatic and automatic titrations were about 0·2 and 0·4% respectively for samples containing only calcium, 0·3 and 0·7% for samples containing only magnesium (Table I) and 0·3 (Table II) and 1·7% (Table III) for total hardness of synthetic samples containing only calcium and magnesium. The error for calcium and magnesium was larger in samples containing both these elements. The large error for magnesium in sample 6, Table III, actually amounts to less than 0·02 ml of titrant. The relative standard deviations for the semi-automatic and automatic titration of

Table II.—Semi-automatic titration results for samples containing known amounts of calcium and magnesium

Taken, *ppm*			Found, *ppm*			Error %		
Calcium	Magnesium	Total hardness as $CaCO_3$	Calcium	Magnesium	Total hardness as $CaCO_3$	Calcium	Magnesium	Total hardness
198·8	61·1	748	197·7	62·0	749	−0·5	+1·5	+0·1
158·5	49·1	598	159·2	48·5	597	+0·4	−1·2	−0·2
99·4	30·5	374	99·3	30·6	374	−0·1	+0·3	—
39·7	49·1	301	39·4	48·9	300	−0·8	−0·4	−0·3
59·5	36·8	300	59·1	36·3	297	−0·7	−1·4	−1·0
18·9	10·4	90	19·5	10·0	90	+3·2	−3·8	—
					Av.	1·0	1·4	0·3

Table III.—Automatic titration results for samples containing known amounts of calcium and magnesium

Taken, *ppm*			Found, *ppm*			Error %		
Calcium	Magnesium	Total hardness as $CaCO_3$	Calcium	Magnesium	Total hardness as $CaCO_3$	Calcium	Magnesium	Total hardness
198·8	61·1	748	199·0	61·7	751	+0·1	+1·0	+0·4
158·5	49·1	598	157·2	48·4	592	−0·8	−1·4	−1·0
99·4	30·5	374	99·9	31·2	378	+0·5	+2·3	+1·1
39·7	49·1	301	39·7	48·8	300	—	−0·6	−0·3
59·5	36·8	300	59·2	35·5	294	−0·5	−3·5	−2·0
18·9	10·4	90	19·1	11·5	95	+1·1	+10·6	+5·5
					Av.	0·5	3·2	1·7

4 mg of calcium were 0·38 and 0·6% respectively, whereas for 2·4 mg of magnesium they were 0·34 and 1·1%.

The first and third derivative curves were also used for the semi-automatic and automatic titrations respectively. They were obtained by differentiating the output signal from points 2 and 4 of the chassis plug "U" by a simple resistance-capacitance differentiator (Fig. 1. $R = 0{\cdot}5\,\mathrm{M\Omega}$, $C = 0{\cdot}47\,\mu\mathrm{F}$). Results obtained were less accurate and precise than those obtained by using the titration curve or its second derivative curve.

The semi-automatic method provides the best accuracy but it requires longer times than the automatic method. For greater accuracy, samples containing less than 0·02 mmole of titrated ions or more than 0·2 mmole per 25 ml of solution should be titrated with more dilute or more concentrated solutions respectively.

The regular voltage *vs.* volume curve for the titration of calcium, together with its recorded first derivative curve, are shown in Fig. 3. It can be seen that the first derivative end-point (Fig. 3B) occurs slightly later than the ordinary titration curve end-point (Fig. 3A).

To check the possibility of back-titration with the proposed method, calcium solutions were analysed indirectly, semi-automatically and automatically, by titrating

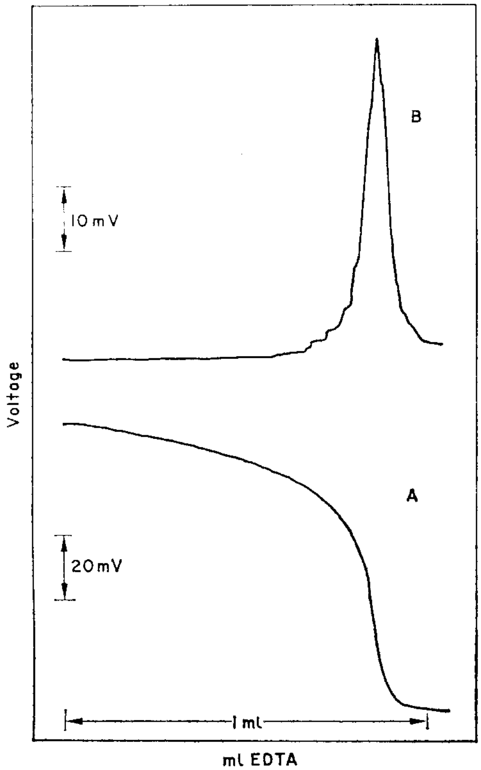

FIG. 3.—Recorded curves for the semi-automatic titration of calcium with EDTA. A—Ordinary titration curve. B—First derivative curve.

excess of EDTA with standard calcium solution. Results obtained were as accurate but less precise than those obtained for the direct titration of calcium with EDTA.

An attempt was made to improve the magnesium titration by substituting a $10^{-3}M$ magnesium chloride solution for the internal calcium chloride reference solution. The blank was slightly decreased, 0·03 ml compared with 0·05 ml, but the accuracy and precision remained the same, for both semi-automatic and automatic titrations.

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Zusammenfassung—Direkte halb- und vollautomatische derivativ-potentiometrische Verfahren zur Bestimmung von Calcium und/oder Magnesium mit EDTA und einer Calcium-selektiven Elektrode werden beschrieben. Calcium wird in Gegenwart von Magnesium bei pH 12,0 titriert und die Summe von Calcium und Magnesium bei pH 9,7. Calcium im Bereich 1–8 mg und Magnesium im Bereich 0,7–5 mg lassen sich halbautomatisch mit durchschnittlichen Fehlern von 0,2 bzw. 0,3%, vollautomatisch mit durchschnittlichen Fehlern von 0,4 bzw. 0,7% bestimmen. Die Titrationszeiten liegen bei einigen Sekunden bis einigen Minuten.

Résumé—On décrit des techniques EDTA potentiométriques dérivées directes, semi-automatiques et automatiques, pour le dosage du calcium et/ou du magnésium avec une électrode sélective du calcium. On titre

le calcium en la présence de magnésium à pH 12,0 et le total calcium et magnésium est déterminé à pH 9,7. Le calcium dans le domaine 1–8 mg et le magnésium dans le domaine 0,7–5 mg sont déterminés semi-automatiquement avec des erreurs moyennes d'environ 0,2 et 0,3% respectivement et automatiquement avec des erreurs moyennes de 0,4 et 0,7%. Les temps de titrage varient de quelques secondes à quelques minutes.

REFERENCES

1. M. E. Thompson, *Science*, 1966, **153,** 866.
2. M. E. Thompson and J. W. Ross, *ibid.*, 1966, **154,** 1643.
3. J. W. Ross, *ibid.*, 1967, **156,** 1378.
4. *Instruction Manual, Calcium Ion Electrode*, Model 92–20, Orion Research Inc., Cambridge, Mass., 1966.
5. J. A. King and A. K. Mukherji, *Naturwissenschaften*, 1966, **53,** 702.
6. S. C. Glauser, E. Ifkovits, E. M. Glauser and R. W. Sevy, *Proc. Soc. Exp. Biol. Med.*, 1967, **124,** 131.
7. F. S. Nakayama and B. A. Rasnick, *Anal. Chem.*, 1967, **39,** 1022.
8. A. Shatkay, *ibid.*, 1967, **39,** 1056.
9. A. Shatkay, *J. Phys. Chem.*, 1967, **71,** 3858.
10. G. A. Rechnitz, *Chem. Eng. News*, June 1967, 146.
11. G. A. Rechnitz, A. Shatkay and M. S. Frant, *Anal. Chem.*, 1968, **40,** 456.
12. A. Shatkay, *Biophys. J.*, 1968, **8,** 912.
13. W. G. Roberston and M. Peacock, *Clin. Chim. Acta*, 1968, **20,** 315.
14. I. Oreskes, C. Hirsch, K. Douglas and S. Kupfer, *ibid.*, 1968, **21,** 303.
15. G. A. Rechnitz and Z. F. Lin, *Anal. Chem.*, 1968, **40,** 696.
16. A. K. Mukherji, *Anal. Chim. Acta*, 1968, **40,** 354.
17. G. A. Rechnitz and T. M. Hseu, *Anal. Chem.*, 1969, **41,** 111.
18. R. Huston and J. N. Butler, *ibid.*, 1969, **41,** 200.
19. M. Whitfield and J. V. Leyendekkers, *Anal. Chim. Acta*, 1969, **45,** 383.
20. M. Whitfield, J. V. Leyendekkers and J. D. Kerr, *ibid.*, 1969, **45,** 399.
21. M. Whitfield and J. V. Leyendekkers, *ibid.*, 1969, **46,** 63.
22. H. V. Malmstadt and E. R. Fett, *Anal. Chem.*, 1954, **26,** 1348.
23. H. V. Malmstadt and T. P. Hadjiioannou, *Anal. Chim. Acta*, 1958, **19,** 563.
24. E. H. Sargent Co., *Scientific Apparatus and Methods*, 1958, No. 2.
25. *Instruction Manual, pH Recording Electrometer*, Model EUW-301, Heath Co., Benton Harbor, Mich., 1966.

Talanta, 1970, Vol. 17, pp. 407 to 414. Pergamon Press. Printed in Northern Ireland

DETERMINATION OF Co, Cu, Fe, Ga, W, AND Zn IN ROCKS BY NEUTRON ACTIVATION AND ANION-EXCHANGE SEPARATION

O. Johansen and E. Steinnes
Institutt for Atomenergi, Isotope Laboratories, Kjeller, Norway

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Summary—A neutron-activation method for the simultaneous determination of cobalt, copper, gallium, iron, tungsten and zinc in rocks is described. The method is based on anion-exchange separation in hydrochloric acid media. Chemical yield is higher than 97% for all elements, except for tungsten, where the recovery of the carrier is established by re-activation. The precision is about 1·3% for the iron determination and about 3% for cobalt, copper, gallium and zinc.

Since the pioneer work of Kraus and Nelson,[1] anion-exchange separation of metals in relatively concentrated hydrochloric acid media has been extensively used in analytical chemistry. In activation analysis, a large number of investigators have used this technique for radiochemical separations of a number of elements in various matrices. Applications to activation analysis of geological material, however, have been rather scarce.[2–5]

The only previously published neutron-activation method for rocks based on anion-exchange in hydrochloric acid media as a single separation step, seems to be a work on the simultaneous determination of copper, gallium and zinc, carried out in the authors' laboratory.[4] The present investigation is an extension of this work, including the determination of cobalt, iron and tungsten in addition to the three elements mentioned above. Instead of alkaline fusion, as used in the previous paper, hydrofluoric acid is used for decomposition of the samples. In this way a somewhat simpler method is obtained, giving results of higher precision and accuracy.

Although lengthy, the decomposition of the irradiated rock samples with hydrofluoric acid was found to possess several advantages compared to decomposition with sodium hydroxide as previously used.[4] First the disadvantage of introducing a solution of high salt concentration onto the anion-exchange column is avoided. Secondly, as silicon is removed during the dissolution step, there is no risk of obtaining reduced flow-rates through the columns because of precipitation of silica on the resin.

After dissolution of the evaporated sample in $9M$ hydrochloric acid, with boric acid as a complexing agent for the remaining fluorides, the resulting solution is added to the anion-exchange column. The individual elements are then eluted, after appropriate washing steps, with solutions of hydrochloric acid of gradually decreasing molarity (Co with $4M$, Cu with $3M$, Fe and Ga with $0{\cdot}5M$ hydrochloric acid, and finally Zn with $1M$ ammonia). The recovery of each element has been studied by means of separate radioactive tracer experiments, six for each element. The results, which are given in Table I, show that the recoveries are better than 97% for the five elements studied, and that a reproducibility of the order of 1% can be obtained. If samples and standards are treated the same, a separate step for chemical yield determination should be unneccessary.

In the course of the experiments, activity from ^{187}W was observed in the elution fractions containing copper. Tracer experiments showed that 30–40% of the tungsten was eluted together with copper, while the remaining activity was found on the column after the elution, probably because of hydrolysis. After the introduction of a re-activation step for chemical yield determination, this element was determined in the same fraction as copper.

In most of the zinc fractions, the 0·56-MeV γ-ray of ^{122}Sb was observed. It was shown by tracer experiments that antimony is quantitatively retained on the column until the elution step with $1M$ ammonia. In some samples, however, the fraction of antimony eluted even in this fraction was rather low. Furthermore, the complete exchange of radioactive and carrier atoms during the dissolution step is doubtful. The determination of this element was therefore omitted.

EXPERIMENTAL

Apparatus

Counting equipment. A 400-channel gamma-spectrometer with a well-type 75 × 75 mm NaI (Tl) crystal.

Anion-exchange columns. Columns of 12 mm internal diameter filled with Dowex 1-X8 (100–200 mesh, chloride form) to 85 ± 5 mm height of resin bed. Before use, the columns are equilibrated with $9M$ hydrochloric acid.

Reagents

Standards. The standards used for cobalt, copper and zinc are solutions of the respective metals in dilute nitric acid. For gallium, a solution of the metal in dilute sulphuric acid is used. The tungsten standard used is a solution of tungstic oxide in dilute ammonia. The following concentrations have been found suitable: Co, 0·5 mg/ml; Cu, 1·0 mg/ml; Ga, 0·2 mg/ml; W, 0·02 mg/ml; Zn, 2·0 mg/ml. About 100 mg of high purity iron metal is used as the iron standard.

Carrier solutions. The following concentrations are used: Co, 10 mg/ml; Cu, 4 mg/ml; Fe, 10 mg/ml; Ga, 1 mg/ml; W, 2 mg/ml; Zn, 10 mg/ml.

Treatment of samples and standards for irradiation

Accurately weighed standard rock samples (about 100 mg) are wrapped in sheets of aluminium foil. A composite standard of Cu, Co, Ga and Zn is prepared by sealing 100 μl of each standard solution in a silica ampoule. In a second ampoule 100 μl of the W standard are sealed. The Fe standard is wrapped in aluminium foil. The irradiations are carried out for 20 hr at a thermal neutron flux of about 3×10^{10} n . mm^{-2} . sec^{-1}, ten samples in each irradiation. The samples are allowed to stand for 30 hr, for the decay of ^{56}Mn and ^{24}Na activity.

Radiochemical separation procedure

The irradiated rock powder is transferred to a 250-ml polypropylene beaker containing 5 ml of concentrated hydrofluoric acid, 5 ml of concentrated nitric acid and 500 μl of each of the carrier solutions. After evaporation of the solution to dryness on a water-bath, an additional 5 ml of concentrated hydrofluoric acid are added, and the mixture is evaporated to dryness again. This step is repeated. The residue is dissolved in 10 ml of $9M$ hydrochloric acid + 1 ml of 2% boric acid solution. The solution is allowed to stand for at least 2 hr.

The irradiated standard solutions, after centrifugation of the ampoules at moderate speed, are transferred to a 50-ml volumetric flask. The iron metal standard is dissolved in a few ml of $9M$ hydrochloric acid and transferred to the same flask. The solution is diluted to the mark with $9M$ hydrochloric acid. Three aliquots of 5 ml each are transferred to separate 250-ml polypropylene beakers and treated as described above.

The sample solutions and the corresponding standard solutions are passed through the columns at a flow-rate of approximately 0·5 ml/min. When the solution has reached the top of the resin bed, washing is performed with three 5-ml portions of $9M$ hydrochloric acid. Cobalt is eluted with three 5-ml portions of $4M$ hydrochloric acid, copper and tungsten with four 5-ml portions of hydrochloric acid, iron and gallium with four 5-ml portions of $0{\cdot}5M$ hydrochloric acid and zinc (and some antimony) with four 5-ml portions of $1M$ ammonia.

All the eluates are collected in 100-ml polyethylene screwcap bottles for gamma-activity measurements.

Activity measurements

The gamma-ray measurements of 12·8-hr ^{64}Cu (0·51 MeV), 13·8-hr ^{69m}Zn (0·44 MeV) and 14·0-hr ^{72}Ga (0·83 MeV) are started as soon as possible after the elution. In some samples, a minor correction for the contribution of the 0·48-MeV γ-ray of ^{187}W to the 0·51-MeV peak of ^{64}Cu has to be applied. The measurement of 24-hr ^{187}W (0·068 MeV) is postponed until 2 days after the elution, to reduce the ^{64}Cu activity of this fraction to a suitable level. Measurements of 5·3-y ^{60}Co (1·33 MeV), 45-d ^{59}Fe (1·29 MeV) and 245-d ^{65}Zn (1·11 MeV) in the respective fractions are accomplished after one week. Peak area calculations are performed after the method of Covell.[6]

The eluted fractions are essentially free of activities other than those already mentioned. In the cobalt fraction, activity of ^{233}Pa (from thorium) is observed in most samples. This activity, however, does not affect the measurement of the 1·33-MeV peak of ^{60}Co. Traces of the major activities ^{24}Na or ^{140}La due to incomplete washing could interfere in the measurements. The presence of these nuclides, as revealed by presence of the 2·75 MeV or 1·60 MeV γ-rays respectively, has not been confirmed in any sample.

In samples containing appreciable amounts of gold, difficulties might be encountered with interference from the 0·41-MeV γ-ray of ^{198}Au in the measurement of ^{69m}Zn. No such interference is indicated, however, in the present samples. In the zinc fractions, in addition to ^{122}Sb–^{124}Sb, trace activities of ^{59}Fe have been observed in a few samples. This interference is easily removed by spectrum stripping.

The results presented for zinc have been obtained from the measurement of ^{69m}Zn. Results calculated from the ^{65}Zn measurements, however, are in good agreement with those from ^{69m}Zn.

TABLE I.—CHEMICAL YIELD (%) OBTAINED FOR Co, Cu, Fe, Ga AND Zn

Experiment no.	Cu	Co	Fe	Ga	Zn
1	98·0	99·5	96·8	100·7	100·2
2	99·3	99·4	97·4	95·9	100·6
3	99·4	96·5	97·5	99·2	100·3
4	99·7	98·4	97·3	100·6	97·6
5	95·9	98·0	96·6	98·4	101·0
6	98·8	96·6	98·2	97·7	99·9
Average	98·5 ± 1·3	98·1 ± 1·3	97·3 ± 0·6	98·8 ± 1·3	99·9 ± 1·2

Chemical yield determination for tungsten

After measurement, the fractions containing tungsten are transferred to volumetric flasks and diluted to 100 ml with water after addition of 0·5 ml of concentrated hydrofluoric acid. After thorough mixing and shaking, 1·00 ml of each fraction is sealed in a polyethylene ampoule. After 30 min irradiation at a neutron flux of about $1{\cdot}5 \times 10^{11}$ n . mm^{-2} . sec^{-1} and 2 days delay, the relative recovery of tungsten carrier in samples and standards is established by means of γ-spectrometry, and corrections are applied to the calculated results.

RESULTS AND DISCUSSION

The results obtained for the elements in question in five different U.S. Geological Survey standard rocks are shown in Table II. Five replicate determinations of each element are reported in all cases except for tungsten. The precision is indicated for each element by the calculated relative standard deviation of a single value.

In Table III, the mean values of the present work are compared with literature values obtained by neutron activation. For sample W-1, the "recommended values" from the recent compilation by Fleischer[7] are included in the Table. Correspondingly, the mean values from the compilation of Flanagan[8] for the other four standard rocks have been included. In several cases, however, these mean values are not especially useful for the discussion of accuracy, because they have been calculated from all

TABLE II.—CONTENT OF Fe, Cu, Ga, Zn, Co AND W IN FIVE U.S.G.S. STANDARD ROCKS

Standard rock	Total Fe as % Fe_2O_3		Cu, *ppm*		Ga, *ppm*		Zn, *ppm*		Co, *ppm*		W, *ppm*	
	6·78		59·5		21·4		81·8		14·9			
	6·66		57·6		19·9		84·1		14·9		0·42	
Andesite AGV-1	6·69	6·75 ± 0·07	56·2	57·9 ± 1·5	20·8	21·0 ± 0·7	85·8	81·1 ± 4·3	14·8	14·8 ± 0·2	0·42	0·45
	6·81		59·2		21·7		74·9		14·7		0·52	
	6·82		57·1		21·0		78·9		14·5			
	13·50		16·3		22·6		127·1		34·7			
	13·58		15·4		21·6		124·3		38·1		0·20	
Basalt BCR-1	13·27	13·40 ± 0·15	15·6	15·7 ± 0·4	21·7	22·2 ± 0·4	130·2	127·4 ± 2·2	36·0	36·2 ± 1·4	0·21	0·24
	13·24		15·6		22·6		127·2		36·8		0·31	
	13·40		15·4		22·4		128·4		35·2			
	2·74		9·01		22·4		80·1		4·44			
	2·70		9·22		22·6		81·3		4·05		0·03	
Granite G-2	2·57	2·65 ± 0·04	9·27	9·14 ± 0·16	22·4	22·5 ± 0·1	80·8	80·6 ± 1·1	4·54	4·35 ± 0·18	0·04	0·04
	2·60		8·93		22·4		80·6		4·39		0·05	
	2·64		9·29		22·6		80·4		4·35			
	4·28		35·3		22·7		97·1		6·37			
	4·29		33·4		21·9		96·6		6·11		0·11	
Granodiorite GSP-1	4·30	4·31 ± 0·09	31·3	32·7± 1·7	20·8	21·7 ± 0·8	93·8	96·7 ± 2·1	6·87	6·40 ± 0·30	0·13	0·12
	4·35		31·2		22·0		99·6		6·57			
	4·41		32·2		21·0		96·5		6·09			
	11·20		114·8		19·0		85·2		43·2			
	11·12		117·2		19·1		80·4		45·5		0·40	
Diabase W-1	11·06	11·12 ± 0·08	108·7	113·6 ± 3·7	16·7	18·4 ± 1·0	86·5	84·9 ± 2·4	43·2	44·5 ± 1·2	0·35	0·38
	11·03		116·4		18·5		86·5		45·7		0·39	
	11·21		110·7		18·7		85·6		45·1			
Mean relative standard deviation, %		1·25		3·0		2·9		2·7		3·3		

TABLE III.—COMPARISON OF PRESENT MEAN VALUES WITH PREVIOUS NEUTRON-ACTIVATION RESULTS AND AVERAGE VALUES FROM RECENT COMPILATIONS.[7,8]

	Standard rock	Total Fe % Fe_2O_3	Cu *ppm*	Ga *ppm*	Zn *ppm*	Co *ppm*	W *ppm*
AGV-1	Present work	6·75	57·9	21·0	81·1	14·8	0·45
	Previous neutron-activation values	6·1[10]	52[4]	21[4]	87[4]	13·2[9]	
						14·7[10]	
						17[12]	
	Flanagan,[8] average	6·80	63·7	18·4	112	15·5	1·1
BCR-1	Present work	13·40	15·7	22·2	127·4	36·2	0·24
	Previous neutron-activation values	12·9[10]	13[4]	24[4]	115[4]	36[9]	
						36·3[10]	
						36[12]	
	Flanagan,[8] average	13·51	22·4	21·6	132	35·5	0·7
G-2	Present work	2·65	9·14	22·5	80·6	4·35	0·04
	Previous neutron-activation values	2·46[10]	6·7[4]	24[4]	77[4]	4·3[9]	
		2·76[11]				4·3[10]	
						5·0[12]	
	Flanagan,[8] average	2·77	10·7	20·7	74·9	4·9	0·4
GSP-1	Present work	4·31	32·7	21·7	96·7	6·40	0·12
	Previous neutron-activation values	4·0[10]	33[4]	24[4]	108[4]	5·2[9]	
						7·0[10]	
						8·5[12]	
	Flanagan,[8] average	4·33	35·2	18·8	143	7·5	0·5
W-1	Present work	11·12	113·6	18·4	84·9	44·5	0·38
	Previous neutron-activation values	10·71[10]	116[4]	20[4]	83[4]	41·6[9]	0·40[27]
		10·17[18]	112[14]	18[20]	85[25]	52[13]	0·46[28]
		12·20[19]	120[15]	18·3[22]	82·8[26]	49[14]	0·49, 0·27[29]
			110[16]	16·5[23]	76[18]	53·7[18]	0·58[31]
			116[17]	15·5[24]			
	Fleischer,[7] recommended value	11·09	110	16	82	50	—

data available, including those obtained by analytical techniques not especially suited for precision work in the trace concentration region. For a major element such as iron, however, these mean values should probably be good estimates of the "true" values.

The results obtained for each element are discussed in detail below.

Iron

Neutron-activation analysis has not been extensively used for iron determination in rocks so far. This is mainly due to the fact that good conventional chemical methods are available, which differentiate between the oxidation states of iron. The few neutron-activation data available so far for the standard rocks do not appear to be very promising. By the present method, however, iron can be determined with a precision that can be considered as satisfactory for most purposes. The fact that the mean values, with the exception of G-2, are in agreement with the average values of Flanagan[8] or the recommended value by Fleischer[7] within 1% or less, indicates that the accuracy of the results is good. The present method for determining total iron, although too detailed for routine determination of this element alone, should still be very useful for obtaining iron data simultaneously with the determination of other elements included in the scheme.

Copper, gallium and zinc

By the present method, the precision for the determination of these elements has been improved to about 3% from approximately 5% obtained in the previous work.[4] The copper results from this work are slightly higher than the previous values, especially at low copper content. The present results are believed to be more accurate, because the ^{64}Cu activity in the present case has been measured in a fraction essentially free from other activities, while in the previous work, ^{64}Cu was eluted in the same fraction as ^{72}Ga and ^{59}Fe. Interference from the $^{64}Zn(n, p)^{64}Cu$ reaction has been estimated to be negligible.

The gallium results from this work are about 5% lower on average. This is consistent with the fact that the gallium content of the standard solution used in the previous work, made from Ga_2O_3 which is very difficult to dissolve completely, was found to be 6% lower than that used in the present work, made from metallic gallium. The present results are also in better agreement with other literature data.

The mean values for zinc in the two sets of data are in reasonable agreement, although the difference is as high as 10% in the cases of BCR-1 and GSP-1.

Cobalt

This element can be determined by purely instrumental activation analysis, using an NaI detector,[9] a Ge(Li) detector,[10] or two NaI detectors coupled in coincidence.[12] The radiochemical values from this work, however, show higher precision than those obtained by the instrumental methods. The agreement of the present set of data with the previous values is reasonably good, especially with the work of Gordon *et al.*[10]

Tungsten

The results obtained for tungsten in this work are not as precise, mainly because of the low content of tungsten in the samples. The result for W-1, although slightly lower than previous literature data, is still in reasonable agreement with most of them.[27,28] The values cited by Flanagan[8] for the other standard rocks are from a work by Chan and Riley,[31] using a spectrophotometric method. These values are in considerable disagreement with those from the present work. Although a considerable number of elements can now be determined by some variant of instrumental activation analysis, it seems that the use of methods employing radiochemical separations is still justified, even for those elements which can be estimated instrumentally, if precise and accurate results are required. The main objection to such methods is that a large amount of time and work is often necessary. The present method, however, as well as similar methods based entirely on ion-exchange separations, should not be considered too unfavourable in this respect. A considerable number of samples can be handled simultaneously, and the column operations are well suited for automation.

Zusammenfassung—Ein Neutronenaktivierungsverfahren zur gleichzeitigen Bestimmung von Kobalt, Kupfer, Gallium, Eisen, Wolfram und Zink in Gesteinen wird beschrieben. Das Verfahren beruht auf Trennung durch Anionenaustausch in salzsauren Medien. Die chemische Ausbeute ist bei allen Elementen höher als 97%, außer bei Wolfram; hier wird die Ausbeute an Träger durch erneute Aktivierung ermittelt. Die Genauigkeit beträgt etwa 1,3% bei der Eisenbestimmung und etwa 3% bei Kobalt, Kupfer, Gallium und Zink.

Résumé—On décrit une méthode par activation de neutrons pour la détermination simultanée des cobalt, cuivre, gallium, fer, tungstène et zinc dans les roches. La méthode est basée sur une séparation par échange anionique en milieux acide chlorhydrique. Le rendement chimique est supérieur à 97% pour tous les éléments, à l'exception du tungstène, où la récupération de l'entraîneur est établie par réactivation. La précision est d'environ 1,3% pour la détermination du fer et d'environ 3% pour les cobalt, cuivre, gallium et zinc.

REFERENCES

1. K. A. Kraus and F. Nelson, *Proc. Intern. Conf. Peaceful Uses At. Energy*, Geneva, 1956, **7**, 113.
2. H. Arino, H. H. Kramer, V. J. Molinski, R. S. Tilbury and W. H. Wahl, *U.S. at Energy Comm. Rept. NYO-10175*, 1964.
3. L. Greenland and G. G. Goles, *Geochim. Cosmochim. Acta*, 1965, **29**, 1285.
4. A. O. Brunfelt, O. Johansen and E. Steinnes, *Anal. Chim. Acta*, 1967, **37**, 172.
5. O. Landström, K. Samsahl and C. G. Wenner, *Rept. AE-296*, aktiebolaget atomenergi Stodcholing 1967.
6. D. F. Covell, *Anal. Chem.*, 1959, **31**, 1785.
7. M. Fleischer, *Geochim. Cosmochim. Acta*, 1969, **33**, 65.
8. F. J. Flanagan, *ibid.*, 1969, **33**, 81.
9. A. O. Brunfelt and E. Steinnes, *ibid.*, 1966, **30**, 921.
10. G. E. Gordon, K. Randle, G. G. Goles, J. B. Corliss, M. H. Beeson and S. S. Oxley, *ibid.*, 1968, **32**, 369.
11. W. S. Sijperda, *unpublished work*, 1968, cited in Ref. 8.
12. L. P. Greenland, *U.S. Geol. Surv. Prof. Paper 600-B*, 1968.
13. M. H. Carr and K. K. Turekian, *ibid.*, 1961, **23**, 9.
14. A. A. Smales, D. Mapper and A. J. Wood, *Analyst*, 1957, **82**, 75.
15. H. Hamaguchi, R. Kuroda, K. Tomura, M. Osawa, K. Watanabe, N. Onuma, T. Yasunaga, K. Hosohava and T. Endo, *Geochim. Cosmochim. Acta*, 1961, **23**, 296.
16. O. Högdahl, *Progress Report II*, University of Michigan, 1962, pp. 62–67.
17. L. Greenland and J. F. Lovering, *Geochim. Cosmochim. Acta*, 1965, **29**, 821.
18. A. Alian and R. Shabana, *Microchem. J.*, 1967, **12**, 427.
19. J. C. Norman and L. A. Haskin, *unpublished work*, 1967, cited in Ref. 8.
20. D. F. C. Morris and M. E. Chambers, *Talanta*, 1960, **5**, 147.
21. M. Fleischer, *Geochim. Cosmochim. Acta*, 1965, **29**, 1263.

22. E. A. Vincent and G. Nightingale, *unpublished work*, 1963, cited in Ref. 21.
23. M. S. Das and H. B. Desai, *unpublished work*, 1963, cited in Ref. 21.
24. K. F. Fouché and A. A. Smales, *Chem. Geol.*, 1967, **2**, 5.
25. T. B. Pierce and P. F. Peck, *Analyst*, 1962, **87**, 369.
26. R. H. Filby, *Anal. Chim. Acta*, 1964, **31**, 557.
27. D. H. F. Atkins and A. A. Smales, *ibid.* 1960, **22**, 462.
28. A. Amiruddin and W. D. Ehmann, *unpublished work*, 1961, cited in Ref. 30.
29. M. Fleischer and R. E. Stevens, *Geochim. Cosmochim. Acta*, 1962, **26**, 525.
30. H. Hamaguchi, R. Kuroda, T. Shimizu, I. Tsukahan and R. Yamamoto, *ibid.*, 1962, **26**, 503.
31. K. M. Chan and J. P. Riley, *Chem. Geol.*, 1967, **2**, 171.

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CATALYTIC THERMOMETRIC TITRATIONS IN NON-AQUEOUS SOLVENTS BY COULOMETRICALLY GENERATED TITRANT

VILIM J. VAJGAND
Institute of Chemistry, Faculty of Science
University of Belgrade, Studentski trg 16, Yugoslavia

and

FERENC F. GAÁL and SMILJANA S. BRUSIN
Institute of Chemistry, University of Novi Sad, Yugoslavia

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Summary—Catalytic thermometric titrations have been developed for tertiary amines and salts of organic acids in acetic and propionic anhydride with titrant coulometrically generated at a mercury and/or platinum anode, hydroquinone being added to the solution titrated if the platinum anode is used. The results obtained are compared with those obtained by coulometric titration with the end-point detected either photometrically or potentiometrically.

IN A PREVIOUS communication we announced the principles of catalytic thermometric titration of bases by the coulometric generation of hydrogen ions in a mixture of acetic anhydride and acetic acid.[1] Mather and Anson[2] determined small amounts of bases and were the first to give a coulometric method for the titration of bases in a mixture of acetic acid and acetic anhydride, for the generating hydrogen ions by processes at a mercury anode. The end-point was detected potentiometrically, a slow and complicated procedure.

In the present paper we describe the catalytic thermometric titration of bases with coulometric generation of the titrant and compare the results obtained with mercury and platinum generator anodes. When the platinum anode is used, hydroquinone is added as anode depolarizer and source of hydrogen ions[2,3] in order to give a current efficiency of 100%. For the indicator reaction, use is made of the exothermic reaction between acetic or propionic anhydride and the water present, as well as of the addition reaction of acetic anhydride with the quinoid system, catalysed by hydrogen ions. The amount of water in this indicator reaction is of decisive importance for the shape of the titration curve in catalytic thermometric titration. Figure 1 shows the titration curve for pyridine in a supporting electrolyte consisting of a mixture of acetic acid and acetic anhydride (1:7) that was 0·1*M* in sodium perchlorate. For observation of the effect of water alone, hydrogen ions were generated (in the absence of hydroquinone) on a platinum anode with a current of 2·7 mA. The curves obtained show that with a lower water content in the sample there is a lower increment in temperature after the equivalence point, and that the sharpest slope of the curve is achieved if the water content is under 0·4%.

Another possible indicator reaction is the addition of acetic anhydride to the quinoid system, also an exothermal process, which permits the determination of very weak bases as well, since it is possible to avoid even traces of water in the system.

Other organic solvents can also be used for anodic titrant generation. Thus we extended our studies to the system of mixtures of propionic anhydride and propionic

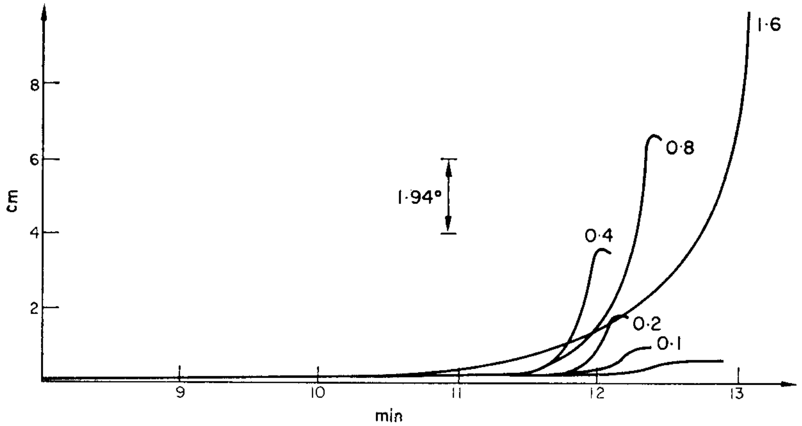

FIG. 1.—The effect of water in the indicator reaction on the shape of curves in catalytic thermometric titrations. The numbers on the curves represent the percentage of water added in the analysis.

acid, which also gave us satisfactory results. Coulometric generation of base in the catholyte permits the determination of acids, if the titration is carried out in acetone. Vaughan and Swithenbank[4] determined the titration end-point from the temperature increase when titrating different acids in acetone with butyltrimethylammonium hydroxide or by potassium hydroxide in methanol or isopropanol. Coulometric titration makes it possible to simplify this excellent method for the determination of acids by eliminating the addition of the titrant. We detected the titration end-point also on the basis of the endothermic effect appearing if the titration is done in a mixture of acetone and diacetone alcohol.

Coulometric titration simplifies the procedure and avoids errors due to volume change, difference in temperature between solutions, *etc.*

EXPERIMENTAL

Solvents and reagents

All chemicals used were either of *pro analysi* purity, or pharmaceuticals. Preparation and standardization of solutions have been described earlier.[1,5]

For the preparation of solutions free of water and of acetic anhydride, use was made of acetic acid (C. Erba, s.g. 1·051, RP grade) and propionic acid (C. Erba, s.g. 0·993, min. 99%, RP grade). Acetic anhydride and propionic anhydride were used without special purification.

Sodium perchlorate was prepared from sodium hydroxide and perchloric acid and recrystallized several times.

The indicators were 0·25% solution of Crystal Violet in acetic acid, 0·25% solution of Methyl Violet in acetic acid, and 0·1% solution of Malachite Green in acetic anhydride.

Apparatus

Hydrogen ions were generated at a mercury anode (*ca.* 300 mm^2) at a constant current density of 3 or 9 μA/mm^2, or at a platinum electrode at a current of 0·9 or 2·7 mA. The platinum anode consisted of a platinum wire (16 mm long, diameter 0·5 mm) sealed into the bottom of the titration vessel. The cells were isolated during the determination in order to prevent the influence of outside temperature changes. The solution to be analysed was separated from the catholyte by a sintered glass disc, porosity 4.

The recorder of a Radiometer polarograph Po 3h was used to register the temperature indicated by the thermistor, or the change in photocurrent (in a large colorimeter[3]) resulting from the change in absorbance of the titrated solution. The thermistor was connected according to the diagram in Fig. 2, which also shows the generator circuit.

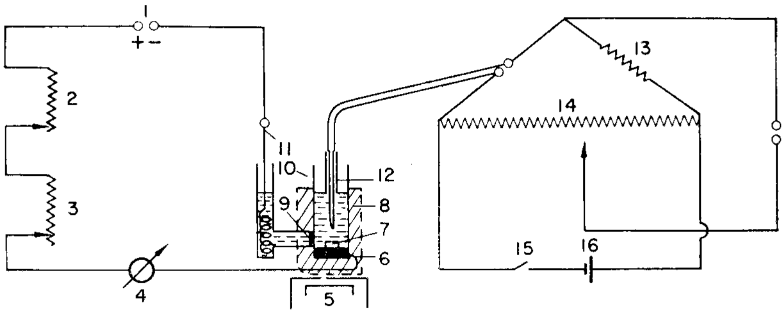

FIG. 2.—Schematic diagram of coulometric catalytic thermometric titration. 1—Source of d.c. (voltage stabilizer ST-12, RR Zavodi Niš). 2—10 kΩ semi-variable resistor. 3—100 kΩ semi-variable resistor. 4—Milliammeter BL 2 with scale in 0·01-mA divisions. 5—Magnetic stirrer. 6—Mercury anode. 7—Magnet. 8—Insulator. 9—Sintered-glass disc, porosity 4. 10—Coulometric titration cell. 11—Platinum cathode. 12—Thermistor (5 kΩ). 13—5 kΩ resistor. 14—10 kΩ rheostat. 15—Switch. 16—2·6-V battery. 17—Recorder.

Procedure

A supporting electrolyte was prepared, consisting of 0·1M sodium perchlorate in 1:7 acetic acid–acetic anhydride mixture. For end-point detection by the catalytic thermometric method, a definite volume of a 10% solution of water in acetic acid was added, so that the water content in the indicator reaction system amounted to below 0·2%. A solution of the substance to be analysed was prepared in the supporting electrolyte, and 7-ml samples were taken. In photometric titrations 14 ml of sample solution were used. The electrolysis was made at a constant current of 0·9 or 2·7 mA, and the sample weights were such that the time of electrolysis was about 10 min (with a precision of 0·1 sec.). When hydrogen ions were generated at a platinum electrode, about 2 mg of hydroquinone per ml was also added.

The left-hand cuvette of the adapted colorimeter was filled with pure solvent and illuminated with a yellow light-bulb; the right-hand cuvette was filled with the solution to be analysed, plus one drop of 0·25% Crystal Violet solution. For caffeine, Malachite Green was used as indicator, and since caffeine is a very weak base, the titration was done in acetic anhydride which was 0·1M in sodium perchlorate.

RESULTS AND DISCUSSION

The titration end-point was determined in three ways: potentiometrically,[2] photometrically,[3] and by catalytic thermometry. The end-point in catalytic thermometric titrations was determined from the graph of temperature against time, as illustrated in Fig. 3, curve A. If the amount of water in the indicator reaction is reduced from 2% to below 0·2% and the titration done in acetic anhydride, the detection of the end-point in catalytic thermometric titrations of bases is greatly simplified because the indicator reaction becomes instantaneous. The reproducibility is improved by a factor of almost 2. In addition, by reducing the amount of water or completely eliminating it in the indicator reaction, it is possible to determine even very weak bases. In determination of the weak base caffeine the changes in temperature at the end-point are fairly small. For example, after about 0·04 cb has passed, after the equivalence point, the change in temperature amounts to only 0·06–0·19°, yet it is possible to detect the end-point satisfactorily. The differential thermometric technique[6] is especially useful in this case.

As can be seen from Table I, bases have successfully been determined in amounts of 1–3 mg. For any particular substance the maximum deviation of results from the mean for the three methods amounts to ±1%. The average deviation of individual measurements is ±0·4%. The weak bases antipyrine (pK_b = 12·40 in water) and caffeine (pK_b = 13·39) have successfully been determined. We have not been able to

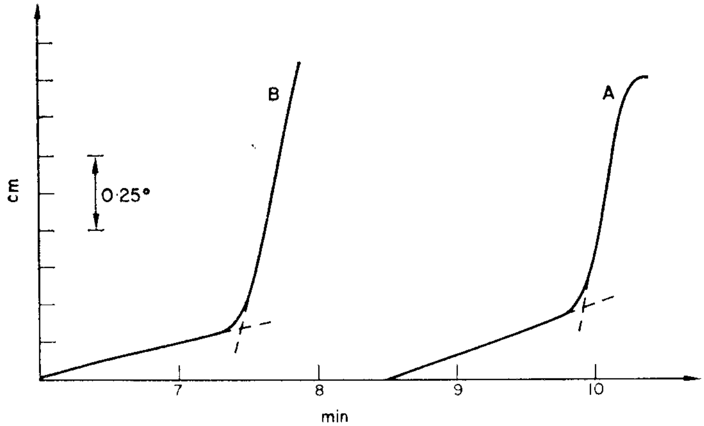

FIG. 3.—Catalytic thermometric titration curves for (*A*) 16 μmole of potassium acetate in acetic anhydride at constant current of 2·7 mA, (*B*) 6·7 μmole of benzoic acid in acetone at constant current of 1·5 mA.

determine caffeine by catalytic thermometric titration when using a mercury generator electrode, since during the titration, or rather at the equivalence point, there is no jump in the temperature rise. This confirms that in catalytic thermometric titration of very weak bases the equivalence point can be determined only by the acetic anhydride-hydroquinone indicator reaction, owing to the hindrance of water in the system titrated. The advantages of the platinum generator electrode are obvious.

The photometric titration curve is given in Fig. 4. Its shape depends on the indicator, photocell and source of light used. At the titration end-point, with Crystal Violet as indicator, there will be a maximum in the absorbance, because as hydrogen ions are generated and neutralize the base, the violet colour changes first to pure blue, and then to green and yellow. This maximum indicates the end-point (Fig. 4, curve 1). If Malachite Green is used as indicator, the titration end-point is determined from the inflexion point (Fig. 4, curve 2) since the colour change is from green to yellow.

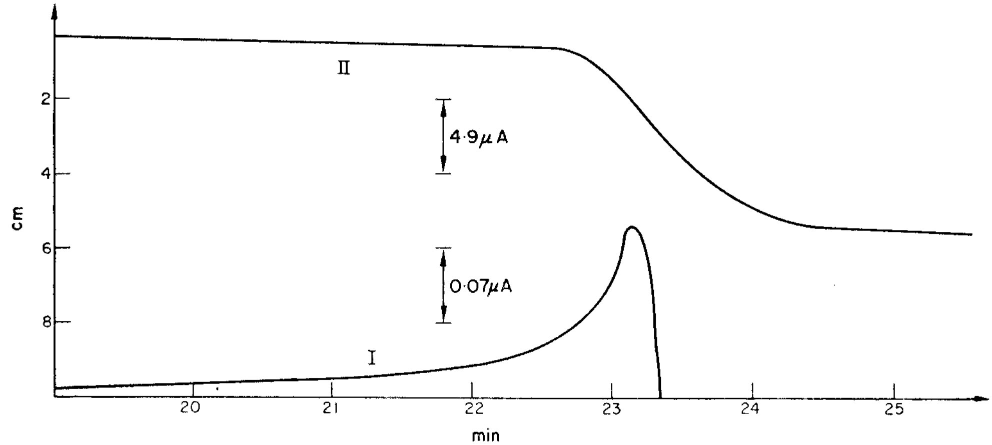

FIG. 4.—Photometric titration curve for 38·7 μmole of pyridine in acetic anhydride in the presence of: I—Crystal Violet as indicator; II—Malachite Green as indicator.

Table I.—Comparison of results obtained by potentiometric, catalytic thermometric and photometric titration by coulometric generation of titrant, for some bases in acetic anhydride (current 2·7 mA)

Substance titrated	Potentiometric titration						Catalytic thermometric titration						Photometric titration					
	Hg electrode			Pt electrode			Hg electrode			Pt electrode			Hg electrode			Pt electrode		
	n	Found, *mg*	m.d. %	*n*	Found, *mg*	m.d. %	*n*	Found, *mg*	m.d. %	*n*	Found, *mg*	m.d. %	*n*	Found, *mg*	m.d. %	*n*	Found, *mg*	m.d. %
K acetate	4	1·63	0·6	4	1·63	0·1	4	1·63	0·4	6	1·64	0·2	6	1·64	0·7	4	1·64	0·4
Na benzoate	4	1·90	0·3	4	1·91	0·2	6	1·93	0·5	6	1·92	0·4	4	1·94	0·5	4	1·93	0·2
Antipyrine	4	2·18	0·3	5	2·18	0·7	6	2·21	0·3	6	2·20	0·2	4	2·20	0·1	4	2·21	0·6
Quinoline	4	1·35	0·2	4	1·35	0·1	5	1·35	0·7	6	1·36	0·5	4	1·35	0·5	5	1·35	0·8
4-Picoline	5	1·31	0·8	5	1·31	0·5	5	1·32	0·5	7	1·32	0·6	4	1·30	0·5	4	1·30	0·3
Caffeine	3	2·41	0·2	5	2·42	0·6	—	—	—	9	2·44	0·5	3	2·42	0·3	4	2·44	0·4

n = number of titrations.
m.d. = Mean deviation, %.

TABLE II.—COMPARISON OF RESULTS IN THE DETERMINATION OF PYRIDINE BY DIFFERENT METHODS (CURRENT 2·7 mA)

		Coulometric method, Pt anode				
				Photometric, in the presence of		
	Potentiometric titration with 0·005*M* $HClO_4$ in acetic acid	Potentiometric	Catalytic thermometric	Crystal Violet	Methyl Violet	Malachite Green
No. of determinations	3	3	7	6	5	4
Found, *mg*	1·55	1·56	1·56	1·54	1·54	1·56
Average deviation, %	0·2	0·9	0·4	0·3	0·4	0·3

TABLE III.—COMPARISON OF RESULTS OBTAINED BY POTENTIOMETRIC, CATALYTIC THERMOMETRIC AND PHOTOMETRIC TITRATION BY COULOMETRIC GENERATION OF TITRANT FOR SOME BASES IN PROPIONIC ANHYDRIDE (CURRENT 0·9 mA)

Substance titrated	Potentiometric titration						Catalytic thermometric titration						Photometric titration					
	Hg electrode			Pt electrode			Hg electrode			Pt electrode			Hg electrode			Pt electrode		
	n	Found, *mg*	m.d.	*n*	Found, *mg*	m.d.	*n*	Found, *mg*	m.d.	*n*	Found, *mg*	m.d.	*n*	Found, *mg*	m.d.	*n*	Found *mg*	m.d.
Cinchonine	4	1·20	0·4	5	1·28	0·4	6	1·21	0·5	6	1·23	0·3	4	1·22	0·8	4	1·22	0·7
Pyridine	3	1·16	1·1	4	1·16	1·3	5	1·15	0·4	5	1·15	0·4	3	1·15	1·8	3	1·16	0·9
Triethyl-amine	4	0·81	0·3	5	0·83	0·7	6	0·82	0·4	9	0·83	0·8	4	0·84	1·0	3	0·84	1·1

n = number of determinations.
m.d. = mean deviation, %.

Methyl Violet behaves similarly to Crystal Violet, except that the maximum is less pronounced. Taking as example the determination of pyridine by different methods, it can be concluded that the results are in good agreement (Table II). The maxima when Crystal Violet is used as indicator are sharper if the platinum generator electrode is used.

Potentiometric titrations of bases with the coulometric generation of hydrogen ions were carried out according to Mather and Anson,[2] and took a very long time (30–40 min) because of discontinuous titration around the equivalence point.

In Table III comparative results are given of catalytic thermometric, potentiometric and photometric titrations of some bases in a mixture of propionic anhydride and propionic acid (7:1), which is $0{\cdot}1M$ in sodium perchlorate.

Coulometric determinations of acids in acetone or mixtures of acetone and diacetone alcohol as catholyte, with catalytic thermometric detection of the end-point by an exothermal or endothermal indicator reaction were carried out in a supporting electrolyte consisting of $0{\cdot}5M$ sodium perchlorate solution in acetone.

The acetone used as solvent should be dry. At higher water content in the acetone the temperature changes after the equivalence point are poor whereas at a low water content good titration curves are obtained, as illustrated in Fig. 3, curve B. The results are in good agreement with those obtained by other instrumental methods. Thus, for example, in six successive determinations of 0·8-mg samples of benzoic acid the average deviation amounted to 1·5%.

Acknowledgement—This work was supported partly by the Research Fund of the Autonomous Province of Vojvodina.

Zusammenfassung—Katalytische thermometrische Titrationen für tertiäre Amine und Salze organischer Säuren wurden entwickelt. Sie werden in Essigsäure- und Propionsäureanhydrid ausgeführt; der Titrant wird an einer Quecksilber- und/oder an einer Platinanode coulometrische erzeugt. Bei Verwendung der Platinanode wird der zu titrierenden Lösung Hydrochinon zugesetzt. Die Ergebnisse wurden mit solchen verglichen, die durch coulometrische Titration mit photometrischer oder potentiometrischer Endpunktsanzeige erhalten wurden.

Résumé—On a élaboré des titrages thermométriques catalytiques pour les amines tertiaires et les sels d'acides organiques en anhydrides acétique et propionique avec l'agent de titrage engendré coulométriquement sur une anode de mercure et/ou platine, de l'hydroquinone étant ajoutée à la solution titrée si l'on emploie l'anode de platine. Les résultats obtenus sont comparés avec ceux obtenus par titrage coulométrique avec le point de fin de réaction détecté soit photométriquement soit potentiométriquement.

REFERENCES

1. V. J. Vajgand, T. A. Kiss, F. F. Gaál and I. J. Zsigrai, *Talanta*, 1968, **15**, 699.
2. W. B. Mather, Jr., and F. C. Anson, *Anal. Chim. Acta*, 1959, **21**, 468.
3. V. J. Vajgand and R. P. Mihajlović, *Talanta*, 1969, **16**, 1312.
4. G. A. Vaughan and J. J. Swithenbank, *Analyst*, 1965, **90**, 594.
5. V. J. Vajgand and F. F. Gaál, *Talanta*, 1967, **14**, 345.
6. *Idem*, *Bull. Soc. Chim. Beograd*, in the press.

Talanta, 1970, Vol. 17, pp. 423 to 430 Pergamon Press. Printed in Northern Ireland

DOSAGE PROTOMETRIQUE DES HYDROGENES MOBILES A L'AIDE DE L'AMIDURE DE SODIUM

MARCEL MIOCQUE, JEAN-MICHEL VIERFOND et ANNICK REYNET
Laboratoire de la Pharmacie, Hôpital Claude Bernard, Paris XIXème, et Laboratoire de Chimie Organique de la Faculté de Pharmacie de Paris

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Résumé—L'amidure de sodium est décomposé par les composés à hydrogène mobile avec dégagement stoechiométrique d'ammoniac qui est dosé par un acide titré. La technique proposée a été appliquée à des représentants de diverses familles; les résultats observés sont interprétés et l'intérêt pratique de la méthode discuté.

ON DÉSIGNE sous le nom de composés à hydrogène mobile des molécules dans lesquelles un ou plusieurs hydrogènes, peu ionisés ou non ionisés à l'état statique, sont cependant liés à l'atome porteur (C, O, N, S) par une liaison suffisamment polarisée pour permettre la formation d'une combinaison de type salin, par action des bases fortes:

$$A - H + B^- \rightleftarrows BH + A^-$$

Les méthodes de détermination des hydrogènes mobiles font donc appel le plus souvent à l'utilisation de réactifs basiques. Ainsi, les hydroxydes d'ammoniums quaternaires[1,2] ou les alcoolates[3,4,5] ($B^- = OH^-$ et $B^- = RO^-$) permettent-ils le dosage protométrique des acides carboxyliques, des phénols et des thiols. Ces procédés ne sont en réalité qu'une extension de la protométrie classique dont ils accroissent le domaine d'application.

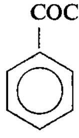
Les acidités plus discrètes, correspondant par exemple au remplacement de l'hydrogène dans l'acétylène ou le diphénylméthane, requièrent pour leur mise en évidence d'autres procédés qui empruntent le plus souvent leurs réactifs à la chimie organique préparative. La méthode la plus anciennement connue, due aux travaux de Tschugaeff et Zerevitinoff, utilise les organomagnésiens[6–9] et notamment l'iodure de méthylmagnésium dont l'attaque par un composé AH s'accompagne d'un dégagement de méthane aisément mesurable:

$$AH + CH_3MgI \rightarrow CH_4 + AMgI.$$

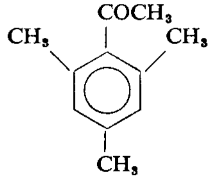
Plus récemment les hydrures complexes, et particulièrement $AlLiH_4$, ont été proposés comme réactifs titrants: ils sont décomposés par les composés de type AH avec libération stoechiométrique d'une molécule d'hydrogène:

$$4AH + AlLiH_4 \rightarrow 4H_2 + AlLiA_4.$$

Un des inconvénients fondamentaux de ces méthodes réside dans le caractère nucléophile du réactif alcalin qui se manifeste parfois préférentiellement au caractère basique; ainsi CH_3MgI révèle seulement 0,12 hydrogène mobile dans l'acétophénone, le réactif magnésien attaquant le carbonyle au niveau du carbone fonctionnel plutôt que d'éliminer un proton du CH_3. Cet inconvénient disparaît d'ailleurs dans le cas de la triméthyl-2,4,6 acétophénone dont l'attaque nucléophile est empêchée par encombrement stérique et pour laquelle 1H est régulièrement substitué dans le CH_3.



(0,12 H mobile[15])



(1 H mobile[15]).

Semblablement, $AlLiH_4$ a tendance à s'additionner sur les cétones plutôt qu'à attaquer les hydrogènes des carbones α. On pouvait donc penser que des agents plus fortement basiques réaliseraient avec plus d'efficacité la substitution au niveau des hydrogènes mobiles.

C'est pourquoi nous avons repris l'étude de l'utilisation de l'amidure de sodium. Ce réactif, essayé dès 1899 par Shryver[10] pour le dosage des phénols, fut repris en 1943 par Palfray et Sabetay[11] et appliqué au dosage des alcools; les auteurs ne poussèrent pas l'étude de ce procédé qui ne pouvait selon eux être utilisé "comme méthode de dosage que dans quelques cas particuliers". Plus récemment, Heilmann et Glenat ont vérifié, par la mesure de l'ammoniac évolué, la sodation d'alcools tertiaires acétyléniques à l'aide de l'amidure de sodium.[12]

La réaction de l'amidure de sodium avec les composés AH peut être schématisée comme il suit:

$$AH + NaNH_2 \rightarrow ANa + NH_3.$$

Les principaux problèmes techniques se situent, sur le plan pratique, au niveau du solvant, du réactif basique et de l'appréciation quantitative de l'ammoniac libéré.

(*a*) Le *solvant* choisi fut d'abord l'éther éthylique desséché sur sodium: les résultats qu'il donne paraissent plus réguliers que ceux observés par Palfray avec le benzène. Toutefois, on peut reprocher à l'éther une polarité insuffisante et un point d'ébullition trop bas. Après avoir essayé divers solvants (T.H.F., dioxanne, pyridine, D.M.F., diméthylaniline, diéthylaniline), nous avons retenu la diéthylaniline en raison de sa purification facile, de sa polarité basique et de son point d'ébullition élevé (Eb = 215°).

(*b*) *L'amidure de sodium* commercial conservé à sec s'altère rapidement avec dégagement d'ammoniac. Sa conservation sous huile de vaseline minimise cet inconvénient: le réactif renferme toujours de l'ammoniac mais il est facile de l'éliminer par un balayage d'azote et la décomposition spontanée en cours de dosage peut être tenue pour négligeable.

Signalons à titre indicatif que nous pratiquons actuellement des dosages avec un amidure commercial conservé en vase clos sous huile de vaseline depuis 1962, date de nos premiers essais.

(*c*) *Le dosage de l'ammoniac* dégagé peut être réalisé très simplement à l'aide du montage décrit plus bas et qui comprend une enceinte à dégagement sous agitation, balayée par un courant d'azote. L'ammoniac est entraîné à travers un réfrigérant ascendant et vient barboter dans une solution d'acide borique où il est neutralisé au fur et à mesure de son dégagement par un acide titré (indicateur rouge de méthyle + bleu de méthylène). Cette modalité de dosage est simple, elle a fait ses preuves dans l'évaluation de l'azote total en analyse biochimique,[13,14] et elle permet de suivre directement le dégagement d'ammoniac et d'apprécier facilement son terme.

On peut illustrer l'évolution de la réaction par deux types de courbes représentés ci-dessous. La courbe 1 mentionne les quantités d'acide titrant ajoutées en fonction du temps: après la période préliminaire de dégagement de l'ammoniac qui souille le réactif, l'évolution spontanée d'ammoniac devient pratiquement nulle, et la prise d'essai peut être introduite après 15 minutes environ.

On observe alors, après un temps variable, le dégagement gazeux dû à l'hydrogène mobile, la fin de la réaction étant marquée par le retour à un dégagement négligeable.

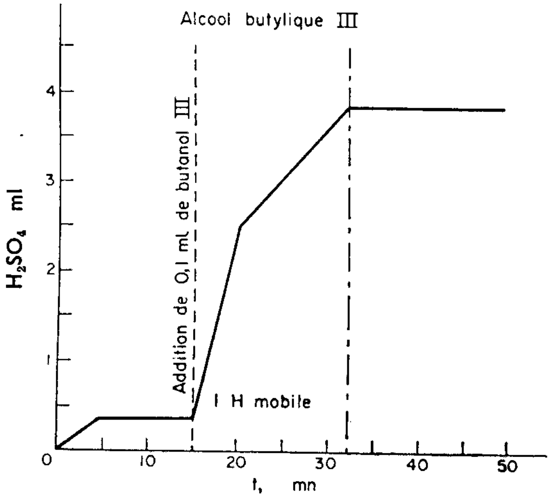
La courbe 2 traduit les mêmes résultats en exprimant l'intensité du dégagement gazeux par périodes de 5 minutes.

PARTIE EXPERIMENTALE

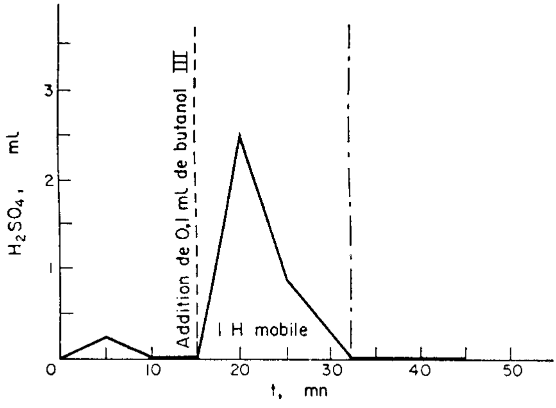
Réactifs

Solution d'acide sulfurique environ 0,5N étalonnée sur carbonate acide de potassium.

Solution tampon d'acide borique à 3 %, de pH 5,5.



Courbe 1.



Courbe 2.

Solution de rouge de méthyle à 0,1 % dans l'alcool à 95°.
Solution de bleu de méthylène à 0,1 % dans l'alcool à 95°.
Amidure de sodium conservé sous huile de vaseline.
Diéthylaniline fraîchement redistillée après dessiccation sur baryte durant plusieurs jours.

Appareillage (*Fig. 1*)

Une fiole à trois tubulures (3) est munie d'une adduction d'azote gazeux qui traverse au préalable une fiole de Durand renfermant de l'acide sulfurique concentré (1).

Elle est surmontée par un réfrigérant vertical (4) relié à un bécher (5) contenant 50 cm^3 de la solution d'acide borique, 8 gouttes de solution de rouge de méthyle, et 4 gouttes de la solution de bleu de méthylène.

La burette renfermant l'acide sulfurique titrant est disposée au-dessus du bécher.

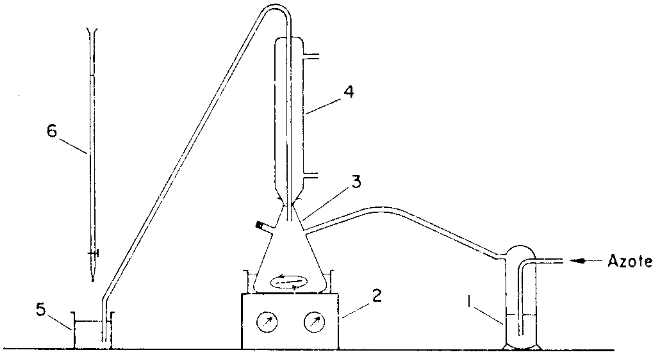


Fig. 1.—Appareillage.

Mode opératoire

Après passage d'un courant d'azote dans l'appareil, on introduit, au temps 0, environ 1 g d'amidure de sodium sous 10 cm^3 de diéthylaniline. On met en route l'agitateur magnétique et on neutralise l'ammoniac au fur et à mesure de son dégagement en maintenant, par affusions ménagées de l'acide titrant, l'indicateur à sa teinte rose initiale. Après 10 minutes environ, cette coloration se stabilise et, vers la minute 15, on introduit rapidement la prise d'essai évaluée par double pesée ou par mesure à la pipette de précision pour les liquides de densité connue.

Le dégagement d'ammoniac se traduit par un virage de l'indicateur du rose au vert: l'addition immédiate d'acide sulfurique (retour à la teinte initiale) est poursuivie goutte à goutte jusqu'à stabilité de la coloration. Lorsque le dégagement est achevé, nous élevons la température du bain d'eau à 70°: ce changement des conditions provoque fréquemment un nouveau dégagement d'ammoniac évalué comme précédemment.

La courbe 3 illustre ce phénomène dans le cas de l'acétylacétone qui présente un hydrogène mobile à froid et deux à chaud (solvant = diéthylaniline).

La quantité théorique (n cm^3) d'acide sulfurique correspondant à un hydrogène mobile est calculée en fonction de la prise d'essai p et du poids moléculaire M du composé analysé et du titre t de l'acide sulfurique titrant:

$$n = \frac{p}{tM}.$$

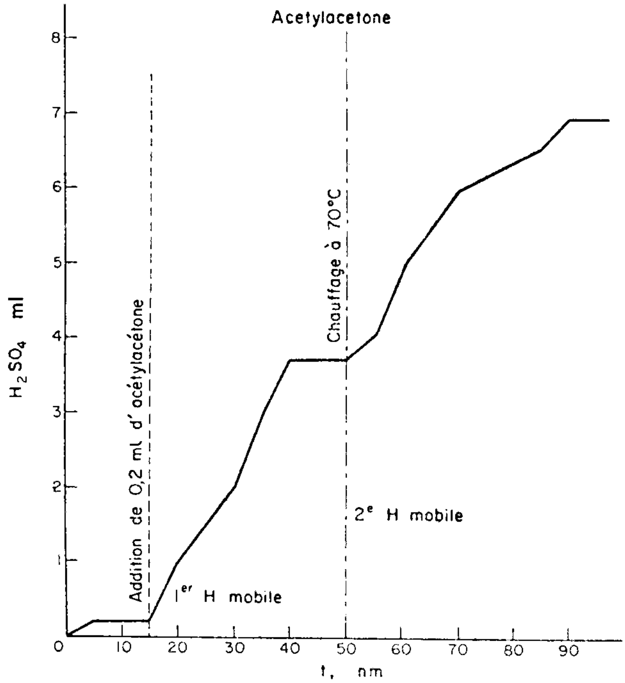
Le rapport entre la quantité d'acide réellement utilisée n et la quantité théorique correspond au nombre d'hydrogènes mobiles par mole.

Les essais effectués avec l'acide benzoïque et divers alcools montrent qu'on peut attendre de la méthode une précision de l'ordre de 3 %.

APPLICATION DE LA MÉTHODE DANS DIVERSES FAMILLES CHIMIQUES

Les résultats de cette étude sont regroupés dans le tableau I.

On y remarque certaines anomalies: ainsi, l'absence de réaction de l'acide benzoïque dans l'éther et la mauvaise réactivité du résorcinol et de l'hydroquinone dans ce solvant.



Courbe 3.

D'une façon générale, la révélation des hydrogènes mobiles se fait mieux dans la diéthylaniline:

—l'acide benzoïque, la pipéridine, le benzamide, l'urée, le phtalimide, le fluorène, inactifs dans l'éther, manifestent dans la diéthylaniline une ou plusieurs acidités vis-à-vis de l'amidure;

—avec l'acétylacétone, les alcools acétyléniques, l'acide salicylique, le malonate d'éthyle, on met en évidence dans l'éther un hydrogène mobile tandis que la détermination à chaud dans la diéthylaniline en révèle deux.

L'un des avantages de la méthode à l'amidure réside dans la possibilité de mettre en évidence les hydrogènes mobiles des cétones, l'amidure agissant plutôt par sa basicité que par son caractère nucléophile, à l'inverse des magnésiens[15,16] et de l'hydrure double d'aluminium lithium.[17]

Intérêt de la technique proposée

La technique décrite est susceptible de rendre des services dans plusieurs domaines distincts:

(1) En tant que méthode de dosage d'un individu chimique connu: il paraît possible d'adapter le mode opératoire décrit en vue notamment du contrôle des médicaments.

(2) Dans l'élaboration des structures, l'utilisation des méthodes physiques demeure dans la plupart des cas la modalité de travail la plus efficace. Il peut néanmoins être utile de disposer en outre de méthodes chimiques simples. Citons, à titre d'exemple, la mise en évidence de la fonction alcool dans les alcools **I, II, III, IV** issus de la réduction alcoylante des diarylcétones.[18] Les composés de ce type dans lesquels R est

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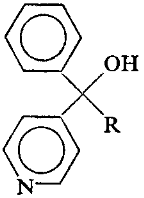

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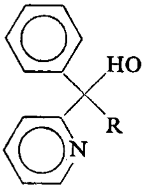

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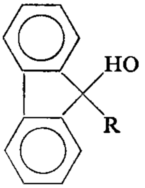

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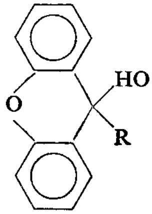
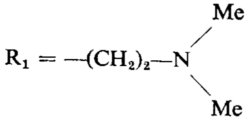


TABLEAU 1.

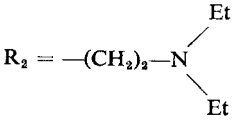
Composés essayés	Solvant		Composés essayés	Solvant	
	Ether éthylique	Diéthylaniline		Ether éthylique	Diéthylaniline
Acides			Amides		
Benzoïque	0	1,00	Acétamide	0,67	1,00*
Salicylique	0,85	1,97*	Benzamide	#0	0,98
Phénols			Acétanilide		0,93
α-Naphtol	1	0,99	Urée	0,20	2,07*
Résorcinol	0,05	1,14*	Thiourée		3,92
Hydroquinone	0,10	1,40*	Uréthanne		1,40*
Alcools			Salicylamide		0,98*
Ethylique	0,98		Benzène sulfonamide		1,99*
n Butylique	1,01	1,01	Imides		
Butylique III	0.97	1,00	Succinimide	#0,00	2,00
Cyclohexanol		1,00	Phtalimide	#0,00	0,99*
Thiols			Dérivés nitrés		
Thiophénol		1,04*	Nitrométhane		0,98*
Butylmercaptan		1,00	Acétyléniques		
Carbonylés			Hexyne	0,91	0,89
Acétophénone	1,01	1,03	Méthyl pentynol	0,96	1,00; 2,00*
Acétone	0,83	1,14	Ethynylcyclohexanol		1,00; 1,93*
Acétylacétone	1,07	1,00; 1,90*	Nitriles		
Esters			Cyanure de benzyle	1,28	2,01*
Acétylacétate d'éthyle	1,01	1,36*	Acétonitrile	0,10	0,44
Malonate d'éthyle	0,96	1,00; 1,82*	Propionitrile		0,40
Cyanacétate d'éthyle	1,01	1,01*	Hétérocycles		
Amines			Carbazole	0,92	1,00*
Aniline	1,33	0,50*	Carbures		
Diphénylamine		1,00	Fluorène	#0,00	0,94*
Pipéridine	#0,00	0,97*	Diphénylméthane	#0,00	0,16*
Morpholine		0,90*	Amidine		
			N-Phénylbenzamidine		1,95*

* Détermination effectuée à la température de 70°.

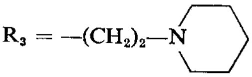
une chaîne azotée ne présentent pas en infra-rouge de bande OH visible, en raison de la liaison hydrogène alcoolique-azote basique; de plus, le proton de l'oxhydryle y est souvent peu visible en RMN. Or, l'analyse chimique a montré pour tous ces composés la présence attendue d'hydrogène mobile, confirmant ainsi la structure proposée (résultats rassemblés dans le tableau II).

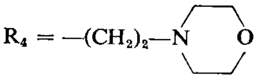


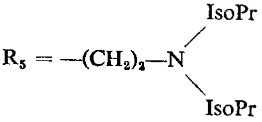
$R_1 = -(CH_2)_2-N(Me)_2$



$R_2 = -(CH_2)_2-N(Et)_2$



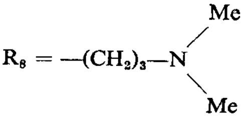




$R_5 = -(CH_2)_2-N(IsoPr)_2$

$R_6 = -Bu$

$R_7 = -CH_2-C\equiv CH$



$R_8 = -(CH_2)_3-N(Me)_2$

TABLEAU II.

Composé essayé		H mobile	Composé essayé		H mobile
I	R_2	0,97	III	R_1	0,95
	R_8	1,02		R_2	1,05
				R_4	1,05
II	R_1	0,98		R_5	1,01
	R_2	1,04		R_6	0,94
	R_3	1,01		R_8	0,98
	R_4	1,00			
	R_5	0,99	IV	R_1	0,99
	R_6	1,02		R_3	0,95
	R_7	0,99		R_4	0,98

(3) Cette méthode peut enfin donner des indications sur la réactivité de diverses molécules organiques vis-à-vis des amidures alcalins. C'est un des domaines dont nous développons actuellement l'étude.

Summary—Sodium amide is decomposed by compounds containing active hydrogen, with stoichiometric release of ammonia, which can be determined by titration with acid. The proposed technique has been applied to representatives of various types of compound.

Zusammenfassung—Natriumamid wird durch Verbindungen, die aktiven Wasserstoff enthalten, unter stochiometrischer Freisetzung von Ammoniak zersetzt. Der Ammoniak kann durch Titration mit Säure bestimmt werden. Das vorgeschlagene Verfahren wurde auf Repräsentanten verschiedener Verbindungsklassen angewandt.

BIBLIOGRAPHIE

1. R. H. Cundiff et P. C. Markunas, *Anal. Chem.*, 1956, **28**, 792.
2. G. A. Harlow, C. M. Noble et G. E. A. Wyld, *ibid.*, 1956, **28**, 787.
3. J. S. Fritz et N. M. Lisicki, *ibid.*, 1951, **23**, 589.
4. H. E. Zaugg et F. C. Garven, *ibid.*, 1958, **30**, 1444.
5. D. B. Bruss et G. A. Harlow, *ibid.*, 1958, **30**, 1836.
6. L. Tschugaeff, *Ber.*, 1902, **35**, 3912.
7. T. Zerevitinoff, *ibid.*, 1907, **40**, 2023.

8. *Idem*, *ibid.*, 1908, **41,** 2233.
9. *Idem*, *ibid.*, 1914, **47,** 2417.
10. S. B. Schryver, *J. Soc. Chem. Ind.*, 1899, **18,** 553.
11. L. Palfray, S. Sabetay et M. Garry, *Bull. Soc. Chim. France*, 1943, **10,** 131.
12. P. Heilmann et R. Glenat, *ibid.*, 1961, 1178.
13. E. J. King et I. D. P. Wooton, *Micro-analysis in Medical Biochemistry*, 3ème édition, p. 54. Churchill, Londres, 1956.
14. P. Fleury, *Fiches techniques de chimie biologique*, (fiche Urine; 4 bis). Librairie Vega, Paris, 1949.
15. E. P. Kohler, J. F. Stone, et R. C. Fuson, *J. Am. Chem. Soc.*, 1927, **49,** 3181.
16. F. A. Hochstein, *ibid.*, 1949, **71,** 305.
17. B. Buděšínský, *Chem. Listy*, 1963, **57,** 26.
18. J. A. Gautier, M. Miocque, C. Fauran et M. Duchon d'Engeniéres, *Bull. Soc. Chim. France* 1965, 3162.

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SHORT COMMUNICATIONS

Estimation of thiosemicarbazide with chloramine-T

(*Received* 23 *April* 1969. *Revised* 29 *October* 1969. *Accepted* 23 *November* 1969)

THIOSEMICARBAZIDE is of importance in the characterization of aldehydes, ketones and polysaccharides and as a metal-complexing agent. The methods for its estimation reported so far are based on its oxidation by alkali metal hypohalites,[1,2] lead tetra-acetate,[3] and by chloramine-T at 60°,[4] are limited to the estimation of small quantities,[3] and are slow.

In the present investigations we examined the behaviour of certain oxidizing titrants towards thiosemicarbazide under various conditions. With dichromate, hexacyanoferrate(III), vanadate(V) and cerium(IV) oxidation occurred to a very limited extent even at high temperatures and in the presence of catalysts such as silver sulphate. However, the reaction between chloramine-T (CAT) and thiosemicarbazide (TSC) was found to proceed under certain experimental conditions with a mole ratio of 1:6, with a probable stoichiometric equation:

$$NH_2NHCSNH_2 + 6[CH_3C_6H_4SO_2NCl]^- + 6H_2O \rightarrow 6CH_3C_6H_4SO_2NH_2 + 6Cl^- + CO_2 + N_2 + NH_4^+ + H^+ + SO_4^{2-} \quad (1)$$

A direct titration of TSC at room temperature with chloramine-T with a visual or potentiometric end-point was not practicable, because the oxidation, though rapid, was not instantaneous, and a back-titration procedure was developed. The present method is rapid, with the added advantage that amounts of TSC up to 150 mg can be estimated.

EXPERIMENTAL

Reagents

Thiosemicarbazide was purified by recrystallization. About 2·0 g of the purified material were accurately weighed and dissolved in a litre of solvent to give an approximately 0·025*M* solution. Chloramine-T solution (~0·1*N*) was standardized by the iodometric method. All other reagents were of accepted grades of purity. Standard buffer systems[5] were used.

Preliminary studies

Known amounts of TSC solution were added to a known excessive volume of CAT in an iodine-flask. The reaction mixture was set aside for various intervals of time at room temperature, with occasional shaking. Then the excess of CAT left unconsumed was determined by back-titration. TSC and its oxidation products were found to have no action on the iodide used.

A typical set of results for the extent of oxidation of TSC in 30 min by an excess of CAT is given in Table I. It is seen that oxidation is slow at pH <1, faster in the pH range 1–3 and slower again at pH >5. Oxidation is fastest at pH 4, and TSC is quantitatively oxidized even with only a 40% excess of CAT. With a 10–20% excess, however, the reaction is complete only after 2 hr.

Detailed investigation of the TSC system has brought out the following facts.

(*i*) At any pH up to 10, TSC forms a complex with CAT, which rapidly decomposes in acidic solutions with a quick change of colour from orange-red to pale yellow and evolution of gaseous products. Thus the disappearance of the yellow colour and appearance of a white precipitate may be taken as a rough guide to the completion of oxidation of TSC with the required stoichiometry. The complex has a broad absorption band around 350 mμ, but attempts to establish its structure were not successful, owing to its instability and the rapid evolution of gaseous products.

(*ii*) At high pH (in presence of 2*M* sodium hydroxide) one mole of TSC consumes only about 10 equivalents of the oxidant. This is attributed to the decrease in the potential of the CAT-sulphonamide system with increase in pH.[6] However, the procedure could not be standardized for the estimation of TSC.

(*iii*) At low pH, presence of chloride (other than the very low concentration resulting from progressive consumption of CAT) in higher concentrations, was found to affect the oxidation, a lower

TABLE I.—EXTENT OF OXIDATION OF THIOSEMICARBAZIDE WITH CHLORAMINE-T

Medium	$\frac{\text{mmole CAT used}}{\text{mmole TSC taken}}$
0·502*N* H_2SO_4	5·54
0·100*N* H_2SO_4	5·70
pH 1	5·96
pH 2	5·96
pH 3	5·96
pH 4	6·00
pH 5	5·96
pH 6	5·90
pH 8	5·80
pH 10	5·75
pH 11–12	5·05
pH $>$12	4·90

TSC taken 0·3289 mmole: CAT taken 3·711 mmoles: time 30 min.

amount of oxidant being used than expected from equation (1). In the pH range 3–5 the presence of chloride up to 0·02*M* did not affect the oxidation.

(*iv*) The 1:6 stoichiometry holds only if the TSC is added to the CAT.

Recommended procedure

Prepare a solution of TSC (~0·025*M*) or of a TSC complex in sodium acetate–acetic acid buffer of pH 4. Add an aliquot containing 0·02–1·5 mmole to a measured excessive (~50–60%) volume of 0·1*N* chloramine-T solution in an iodine-flask and set aside for about 30 min, shaking occasionally. Rinse down with 20 ml of water, add 10 ml of 20% potassium iodide solution and 10 ml of 6*M* hydrochloric acid and titrate with 0·2*M* sodium thiosulphate. Run a blank with CAT solution alone. The

Table II.—ESTIMATION OF THIOSEMICARBAZIDE AND ITS COMPLEXES WITH CHLORAMINE-T

TSC taken, *mg*	TSC recovered, *mg*	TSC taken, *mg*	TSC recovered, *mg*
4·01	4·02	50·1	50·2
10·14	10·09	60·1	60·0
30·25	30·1	90·1	89·9
40·1	39·9	110·2	110·1
$Zn(TSC)_2SO_4$*		$Ni(TSC)_2(NO_3)_2$†	
Taken, *mg*	Found, *mg*	Complex taken, *mg*	Complex found, *mg*
2·33	2·34	2·22	2·23
5·83	5·84	4·88	4·86
11·66	11·68	5·56	5·58
13·45	13·42	9·78	9·82
23·32	23·36	11·11	11·16
37·6	37·7	16·65	16·73
48·4	48·4	24·45	24·51

* Prepared by mixing TSC and $ZnSO_4$ solutions in the stoichiometric proportions, scratching the beaker with a glass rod to induce precipitation, filtering off, washing with water, and drying at 40–50°. The composition was checked by standard methods of analysis.

† Prepared according to ref. 7.

number of g of TSC (x) in the experimental solution is given by

$$x = 7{\cdot}593y(V_1 - V_2)$$

where y is the normality of the thiosulphate, V_1 is the blank titration and V_2 the volume of thiosulphate used to titrate the excess of CAT left over after oxidation of TSC.

RESULTS AND DISCUSSION

There will, of course, be interference by any other species present that are oxidizable by CAT or which can oxidize iodide. In particular, thiocyanate and hydrazine (from which TSC is made) will interfere by reducing CAT. The method is useful, however, for analysis of TSC complexes of metals. Zinc and nickel appear to catalyse the oxidation, which was complete within 5 min when zinc and nickel TSC complexes were analysed.

Some typical results are given in Table II and include analyses of some TSC complexes. The values obtained are accurate within 0·5%.

Department of Postgraduate Studies
and Research in Chemistry
Manasa Gangotri
Mysore-6, India

D. S. Mahadevappa
A. S. Ananda Murthy

Summary—A rapid and accurate method for the estimation of thiosemicarbazide in aqueous solution has been developed based on its oxidation with chloramine-T at room temperature and pH 4. The effect of such variables as pH, mode of addition of reagents and concentration of chloride ion on the extent of oxidation has been studied.

Zusammenfassung—Eine schnelle und genaue Methode zur Bestimmung von Thiosemicarbazid in wäßriger Lösung wurde entwickelt. Sie beruht auf Oxidation mit Chloramin T bei Raumtemperatur und pH 4. Der Einfluß des pH, des Verfahrens bei der Zugabe der Reagentien und der Konzentration von Chlorid auf den Oxidationsgrad wurde untersucht.

Résumé—On a élaboré une méthode rapide et précise pour l'estimation du thiosemicarbazide en solution aqueuse, basée sur son oxydation par la chloramine-T à température ordinaire et pH 4. On a étudié l'influence de variables telles que le pH, le mode d'addition des réactifs et la concentration de l'ion chlorure sur le degré d'oxydation.

REFERENCES

1. A. Gaffre, in *Volumetric Analysis*, Vol. III, ed. I. M. Kolthoff and R. Belcher, p. 386. Interscience, New York, 1957.
2. J. Pijck, A. Campe and A. Claeys, *Bull. Soc. Chim. Belges*, 1964, **73**, 898.
3. L. Suchomelová and J. Zýka, *J. Electroanal. Chem.*, 1963, **5**, 57.
4. A. Berka and J. Zýka, *J. Ceskoslov. Farm.*, 1956, **5**, 335.
5. A. Findlay, *Practical Physical Chemistry*, p. 268. Longmans, London, 1954.
6. A. R. V. Murthy and B. S. Rao, *Proc. Indian Acad. Sci.*, 1952, **35**, 69.
7. K. A. Jensen and E. Rancke-Madsen, *Z. Anorg. Allgem. Chem.*, 1934, **219**, 243.

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Kinetochromic spectrophotometry—III.

Determination of fluoride by catalysis of the zirconium–Methylthymol Blue reaction

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The majority of spectrophotometric methods for the determination of trace amounts of fluoride are indirect, and involve the bleaching action of the fluoride ion on soluble coloured complexes of zirconium with organic reagents such as Alizarin Red S[1] or Eriochrome Cyanine R.[2] Few direct colorimetric procedures for the determination of fluoride exist, but that based on the formation of a ternary complex between alizarin complexan, cerium and fluoride has been widely accepted and is highly selective and quite sensitive.[3] In the first paper of this series a kinetochromic procedure was described for determining fluoride ion, based on the reaction between zirconium and Xylenol Orange, which yielded an effective molar absorptivity of 2·00 × 10⁴ l.mole⁻¹ . mm⁻¹ for the fluoride ion.[4] The application of the catalysis, by several anions, of the reaction between zirconium and Methylthymol Blue (MTB) to the determination of small amounts of sulphate has also been reported.[5] The fluoride ion also accelerates this reaction to produce a similar kinetochromic effect. The reaction is much more sensitive for fluoride, however, and by the procedure described in this paper an effective molar absorptivity for fluoride of 3·23 × 10^4 l.mole^{-1}.mm^{-1} at 586 nm may be obtained with a development time of 60 min. Sulphate does not interfere when present in less than equimolar quantities with fluoride, but arsenate and phosphate interfere seriously and must be removed by sample pretreatment.

EXPERIMENTAL

Reagents

The Methylthymol Blue (MTB) reagent solution (5 × $10^{-4}M$) and zirconium stock solution ($10^{-2}M$) were prepared and kept as previously described.[5] A stock solution ($10^{-2}M$) of analytical grade sodium fluoride was prepared, stored in a polythene container, and diluted to 5 × $10^{-5}M$ as required.

Preparation of calibration graph for fluoride

Transfer 0, 1·0, 2·0, 3·0, 4·0 and 5.0-ml portions of 5 × $10^{-5}M$ sodium fluoride solution to a series of six 50-ml volumetric flasks containing 10 ml of 5 × $10^{-4}M$ MTB solution and 7 ml of 5*M* hydrochloric acid. At reference time zero add by pipette 10 ml of $10^{-3}M$ zirconium solution to the first flask. After 30 sec dilute the solution to 50 ml with distilled water, mix and leave to stand. Repeat for the other flasks at 2-min intervals. Allow the solution to stand for 60 min. Measure the absorbance of each solution at 586 nm against a water blank, using 2-mm silica cells, and permit 2 min to elapse between measurement of successive solutions. Develop a blank and standards (containing 3·0 and 5·0 ml of 5 × $10^{-5}M$ fluoride solution) with each group of samples. The calibration graph extends over the range 0·01–0·095 ppm of fluoride (0·50–4·75 μg). The calibration graph must be established each day, owing to a slight but progressive decrease in sensitivity over the 5-day period during which the $10^{-3}M$ zirconium solution may be used.

RESULTS AND DISCUSSION

Reaction conditions

The measurements of the absorbance produced by fluoride samples are made at 586 nm, the wavelength of maximal absorption of the zirconium–MTB complex.[5] As in the previous reactions,[4,5] the age of the zirconium solution employed for the determination of fluoride has a pronounced effect on the reaction rate and sensitivity attainable. A $10^{-2}M$ zirconium stock solution in 0·0125*M* hydrochloric acid which was allowed to age for 2–7 days was found to be most satisfactory. An aliquot of this solution was diluted to $10^{-3}M$ and made 0·05*M* in hydrochloric acid. This solution could be used for up to five days. The MTB, hydrochloric acid and fluoride (or sample) solutions can be mixed in any order in the recommended procedure, but the zirconium solution must be added last and the solution should then be diluted to volume *immediately*. Provided that temperature variations are less than ±3°, reproducible reaction rates and sensitivities are obtained with day-to-day operation of the method.

Effect of hydrochloric acid, MTB and zirconium concentrations. Figure 1 shows the variation in net absorbance for 0·095 ppm fluoride with variation in hydrochloric acid concentration between 0·3 and 1·1*M*, for different development times. The highest sensitivity compatible with a uniform calibration curve is obtained after a development time of 60 min using a solution 0·7*M* in hydrochloric acid.

The effect of MTB concentration and the ratio of MTB:Zr concentration on the net absorbance for fluoride was investigated for 0·7*M* hydrochloric acid solutions. As shown in Fig. 2*a*, for a 60-min development period, a concentration ratio of 1:2 produces the highest sensitivity. As shown in Fig. 2*b*, the highest sensitivity after 60 min is obtained by using an MTB concentration of $10^{-4}M$.

Calibration graph and sensitivity

Unlike the linear calibration graph obtained for the determination of sulphate, the catalytic action of fluoride on the zirconium–MTB system consistently produced a smooth curve. The effect of development time upon the shape of the calibration curve measured against a water blank at 586 nm, is shown in Fig. 3. After 60 min the smoothest calibration curve is obtained for the range

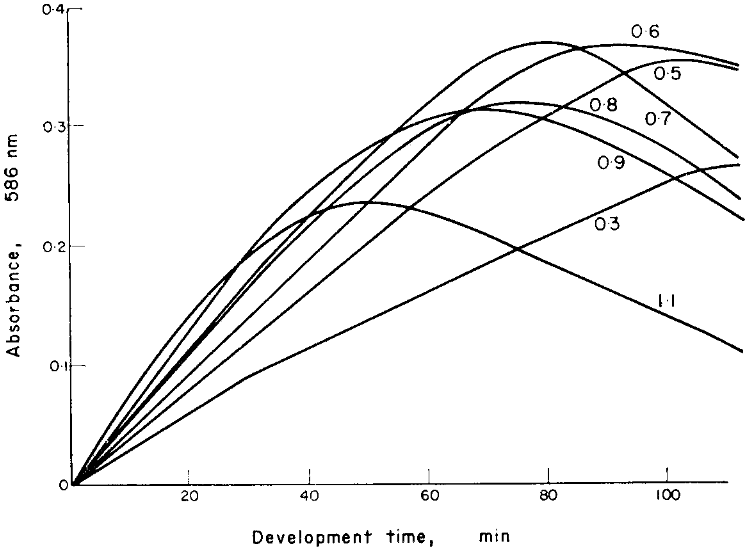
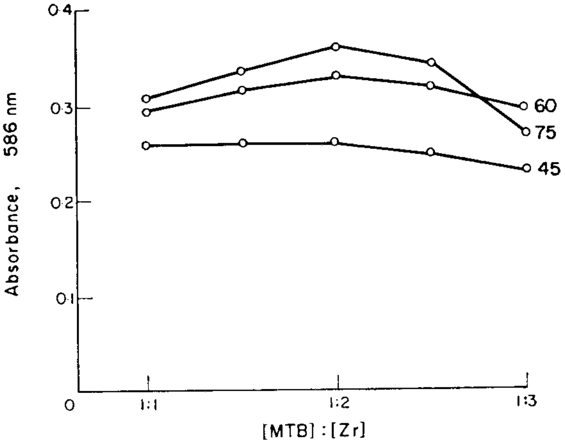


FIG. 1.—Effect of acidity on rate of development.
Net difference in absorbance of catalysed and uncatalysed reactions with varying concentration of HCl in final solution. $2 \times 10^{-4}M$ MTB; 0·3, 0·5, 0·6, 0·7, 0·8, 0·9, 1·1M HCl; 4·75 μg F^-; 2-mm cells, 586 nm.



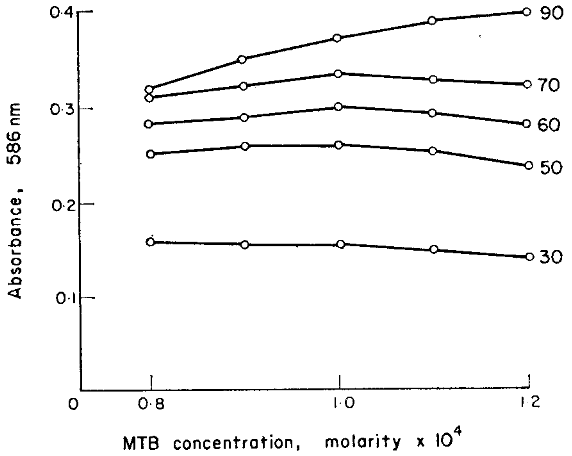
(a)

FIG. 2a.—Effect of MTB:Zr ratio at various development times.
Variation in net absorbance of catalysed and uncatalysed reactions for various MTB:Zr ratios, with development time. 0·7M HCl; $10^{-4}M$ MTB; 4·75 μg F^-. 2-mm cells, 586 nm. 1×10^{-4}, $1{\cdot}5 \times 10^{-4}$, $2{\cdot}0 \times 10^{-4}$, $2{\cdot}5 \times 10^{-4}$, $3{\cdot}0 \times 10^{-4}M$ $ZrOCl_2$. Development times in min.

0·25–4·75 μg of fluoride, with an effective molar absorptivity (4·75 μg of fluoride) of $3{\cdot}23 \times 10^4$ l.mole^{-1}.mm^{-1}. Owing to the curvature of the calibration graph, an effective molar absorptivity of $4{\cdot}00 \times 10^4$ l.mole^{-1}.mm^{-1} is obtained over the range 2·5–4·75 μg of fluoride.

Precision. The recommended procedure was used to determine 4·75 μg of fluoride repeatedly over a period of three months. The average net absorbance for 10 determinations after 60 min, in 2-mm cells, was 0·323 and the standard deviation 0·007.

Interference. The effect of diverse ions upon the kinetochromic action of fluoride on the zirconium–Xylenol Orange reaction, and of sulphate on the reaction between zirconium and MTB has



(b)

FIG. 2b.—Effect of MTB concentration.
Net difference in absorbance of catalysed and uncatalysed reactions for varying MTB concentrations at constant Zr:MTB ratio of 2:1. 4·75 μg F^-, 2-mm cells, 586 nm. 0·7M HCl; 8·0 × 10^{-5}, 1·0 × 10^{-4}, 1·1 × 10^{-4}, 1·2 × $10^{-4}M$ MTB; 1·6 × 10^{-4}, 1·8 × 10^{-4}, 2 × 10^{-4}, 2·2 × 10^{-4}, 2·4 × $10^{-4}M$ $ZrOCl_2$ respectively. Development times in min.

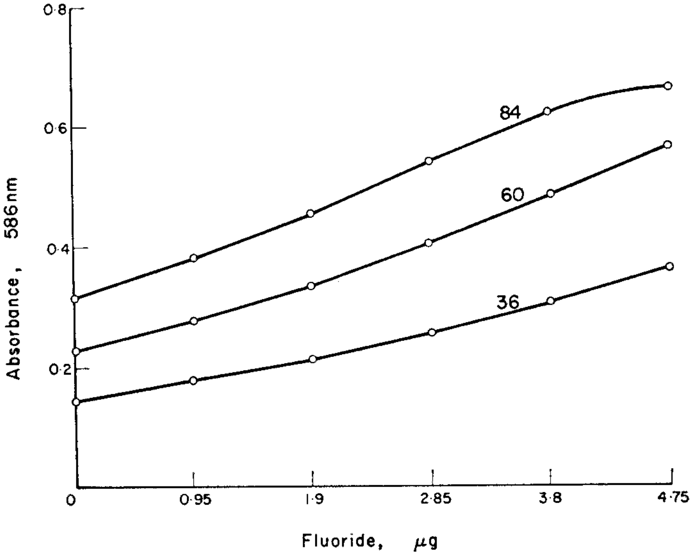


FIG. 3.—Effect of development time on calibration curve.
Variation in net absorbance of catalysed and uncatalysed reactions with fluoride concentration at different development times. 0·7M HCl; $10^{-4}M$ MTB; 2 × $10^{-4}M$ $ZrOCl_2$; 4·75 μg F^-, 2-mm cells, 586 nm, development times in min.

already been investigated.[4,5] Those ions which interfered in these procedures again showed similar effects. It was established that the presence of less than equimolar quantities of arsenate and phosphate ions, relative to the fluoride, caused serious additive interferences, but that sulphate could be tolerated when present in up to equimolar proportions with fluoride.

Removal of interference. Pretreatment of the sample solution, containing fluoride and interfering cations, with a strongly acidic cation-exchange resin such as Amberlite R-120[7] is effective in removing cationic interference from iron, manganese, thorium, vanadium, *etc.*

Procedures for the prior removal from solution of phosphate as the insoluble silver salt have been given by Fennell[8] and Colson,[9] while removal of sulphate interference has recently been described by Oliver[10].

CONCLUSION

The procedure described in this paper can be used to determine 0·25–4·75 μg of fluoride ion in aqueous solution, after a development time of 60 min, with an effective molar absorptivity of $3{\cdot}23 \times 10^4$ l.mole^{-1}.mm^{-1}. The method is more sensitive and also more rapid than the comparable method based on the catalytic action of fluoride on the zirconium–Xylenol Orange system.[4] It suffers from the same serious interference from phosphate, arsenate, and to a lesser extent, sulphate as that procedure, but is much freer from cationic interference than the cerium(III) or lanthanum alizarin complexan procedure, and has far greater sensitivity.

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Department of Chemistry
Imperial College of Science and Technology
London S.W.7, England

R. V. Hems
G. F. Kirkbright
T. S. West

Summary—The determination of 0·5–4·75 μg of fluoride ion by its catalytic action upon the slow reaction between Methylthymol Blue and zirconium(IV) in aqueous solution is described. Calibration curves obtained after 60 min under optimal conditions are smooth, and yield an effective molar absorptivity of $3{\cdot}23 \times 10^4$ l.mole^{-1}mm^{-1} at 586 nm. There is considerably less cationic interference than in the alizarin complexan–cerium(III) or lanthanum procedure, but more serious anionic interference is encountered when phosphate, arsenate and, to a lesser extent, sulphate ions are present in the sample solution.

Zusammenfassung—Die Bestimmung von 0,5–4,75 μg Fluorid durch seine katalytische Wirkung auf die langsame Reaktion zwischen Methylthymolblau und Zirkonium(IV) in wäßriger Lösung wird beschrieben. Nach 60 min unter optimalen Bedingungen erhaltene Eichkurven sind stetig und entsprechen einem effektiven molaren Extinktionskoeffizienten von $3{,}23 \cdot 10^4$ l mol^{-1} mm^{-1} bei 586 nm. Es gibt viel weniger Störungen durch Kationen als bei den Verfahren mit Alizarin-Complexan und Cer(III) oder Lanthan. Dagegen gibt es Störungen, wenn Phosphat, Arsenat, und in geringerem Maße, wenn Sulfat zugegen sind.

Résumé—On décrit la détermination de 0,5–4,5 μg d'ion fluorure par son action catalytique sur la réaction lente entre le Bleu de Méthylthymol et le zirconium (IV) en solution aqueuse. Les courbes d'étalonnage obtenues après 60 mn dans les conditions optimales sont régulières et donnent un coefficient d'absorption moléculaire réel de $3{,}23 \times 10^4$ l.mole^{-1}.mm^{-1}, à 586 nm. Il y a considérablement moins d'interférences cationiques que dans la technique Alizarine Complexan-cérium (III) ou lanthane, mais des interférences anioniques plus sérieuses sont rencontrées lorsque des ions phosphate, arséniate et, à un degré moindre, sulfate, sont présents dans la solution échantillon.

REFERENCES

1. H. E. Zittel and T. M. Florence, *Anal. Chim. Acta*, 1968, **40**, 27.
2. S. Megregian, *Anal. Chem.*, 1954, **26**, 1161.
3. R. Belcher, M. A. Leonard and T. S. West, *J. Chem. Soc.*, 1959, 3577.
4. M. Cabello-Tomas and T. S. West, *Talanta*, 1969, **16**, 781.
5. R. V. Hems, G. F. Kirkbright and T. S. West, *ibid.*, 1969, **16**, 789.
6. T. S. West, *Chem. Ind. (London)*, 1966, 1005.
7. R. McGillivray and S. C. Woodger, *Analyst*, 1966, **91**, 611.
8. T. R. F. W. Fennell, *Chem. Ind. (London)*, 1955, 1404.
9. A. F. Colson, *Analyst*, 1963, **88**, 26.
10. F. H. Oliver, *ibid.*, 1966, **91**, 771.

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ANNOTATION

Composition of the thorium(IV)–8–hydroxyquinoline adduct compound

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THE orange adduct, $Th(C_9H_6NO)_4 \cdot C_9H_7NO$, formed between thorium(IV) and 8-hydroxyquinoline (HQ) has been used as the basis of gravimetric and bromometric determinations of thorium for several years.[1,2] Surprisingly, however, the nature of this compound is not well understood, and there have been several conflicting studies regarding both its structure and composition.

Recent carbon-14 and infrared evidence[3] has strongly indicated that the additional HQ molecule is co-ordinated, as a zwitterion, to the central thorium ion, and is not merely an unco-ordinated crystal-lattice component as thought earlier. Similarly, in contrast to earlier work,[4,5] more recent work has suggested that the stoichiometry of the orange adduct prepared by conventional precipitation is not strictly 5:1.[6,7] Much of the analytical data supporting this recent claim, however, is not conclusive since the purported HQ:Th ratio (~4·8:1) was established solely by the bromometric determination of HQ in the precipitate; a determination of thorium was not made. In view of the difficulty in drying the adduct without partial loss of the thermally volatile molecule of HQ, it is possible that the results reflect the presence of water and/or the loss of some HQ. In a further report,[8] an HQ:Th ratio of 4·8:1 was also reported for the adduct prepared by precipitation from homogeneous solution.

In the present report, conclusive evidence is provided to show that the compound prepared by conventional precipitation is not the pure 5:1 adduct; two independent analytical procedures, each unambiguous, were used. The results show that the composition of the adduct is very difficult to reproduce from one preparation to the next.

The thermal reaction by which the tetrakis compound, $Th(C_9H_6NO)_4$, is prepared from the orange adduct has been reported many times, but there is considerable disagreement on the conditions required for the preparation.[1,9] A simple procedure for the preparation of the pure tetrakis compound is described in the present work.

EXPERIMENTAL

Stock solutions containing 1·4 mg of Th/ml were prepared from thorium nitrate hexahydrate (analytical-reagent grade) and adjusted to about pH 1·5 with freshly boiled nitric acid. The purity of all other chemicals was as previously described.[10]

The orange adduct was prepared as follows. A 25-ml portion of the thorium stock solution was diluted to 50 ml and the solution heated to 70°. A solution of HQ (0·143 g dissolved in 0·5 ml of glacial acetic acid and diluted to 7 ml with water) was slowly added, followed by a solution of ammonium acetate (2·0 g in 15 ml of water) added with stirring at a rate of 5 ml/min. Dilute aqueous ammonia (1·0*M*) was then added (5 ml/min) until the pH was 6–7. The final volume was adjusted to about 90 ml with water and the mixture allowed to digest for 1 hr at 70°. After filtration and washing with about 100 ml of hot water, the compound was dried in a stream of air for 3 hr and stored over phosphorus pentoxide. The compound was freshly prepared as required.

The molar ratio was established in two ways. (*i*) The thorium was determined by ignition[11] to ThO_2 at 900° and the HQ by bromometric titration,[10] and the molar ratio calculated (Table I). In one preparation, the compound was dried at 50° *in vacuo* for 72 hr before analysis. (*ii*) The ratio of the sublimed HQ to the residual tetrakis compound obtained on thermal conversion was determined. The conversion was effected quantitatively by heating (oil-bath) *in vacuo* (0·13 mbar) 150–200 mg of the adduct at 165–170° for 1½ hr. The sublimed HQ was collected in the initial portion of a U-tube immersed in a bath of solid carbon dioxide. A tiny droplet of moisture was observed below the HQ deposit in the U-tube. The sublimed HQ and residual tetrakis compound were separately dissolved in 4*M* hydrochloric acid and determined bromometrically, and the ratio $HQ:ThO_4$ was calculated (Table II). For the sample sizes taken, the deficiency of HQ (relative to $ThO_4 . HQ$) amounted to 2–4 mg, which is considerably more than the error expected in the bromometric titration.[10]

The same thermal procedure was used to prepare the pure tetrakis compound. The HQ and thorium contents were determined as described above. Analysis gave the following results: Th, 28·54 ± 0·04% (4 results; theoretical, 28·69%); HQ as Q^-, 71·37 ± 0·05% (10 results; theoretical, 71·31%); molar ratio Q^-: Th, 4·02 ± 0·01. The precision quoted is the standard error.

TABLE I.—ANALYSIS OF THE ORANGE Th(IV)-HQ ADDUCT

Th, %	HQ,* % (as Q^-)	Molar ratio HQ:Th
24·13†	72·62	4·84
±0·05	±0·04	±0·01
24·35†	73·54	4·86
±0·05	±0·05	±0·01
24·25†	74·28	4·94
±0·05	±0·06	±0·01
24·45¶	73·73	4·88

* HQ = 8-hydroxyquinoline.

† For the first three preparations, each result is the average of two determinations. The precision measure is the overall deviation.

¶ Compound dried *in vacuo* at 50° for 72 hr. For $Th(Q)_4 \cdot HQ$, Th = 24·33% and HQ, expressed as Q^- = 75·57%.

TABLE II.—MOLAR RATIO $HQ:ThQ_4$ IN THE ORANGE ADDUCT

HQ sublimed, *mg*	ThQ_4 residue, *mg*	Molar ratio $HQ:ThQ_4$
36·6	213·9	0·953
29·6 *	184·4	0·913
24·8	155·3	0·889
23·7 *	136·8	0·963
21·3	123·2	0·962

* Two determinations of the molar ratio were made on the material of a single preparation.

DISCUSSION

The data of Tables I and II, obtained by different analytical methods, show that the orange compound is deficient in HQ. Furthermore, the composition of the adduct varies (4·84:1 to 4·96:1) from one preparation to the next, even though the experimental conditions were not intentionally altered.

Since thermal loss of the additional HQ molecule is reported to begin at about 80°,[12,13] the samples were dried without heating to avoid any loss of the volatile species. Because of the mild drying conditions, the samples probably retained a small amount of moisture. The presence of moisture, however, would not affect the molar ratio of HQ:Th and $HQ:ThQ_4$.

The presence of water in the adduct was confirmed by the observation of moisture in the U-tube after the thermal reaction, and by infrared analysis. Under increasingly rigorous drying conditions, the integrated intensity of the broad absorption band centred at 3350 cm^{-1} (*e.g.*, spectrum B in reference 3) decreased, and became zero when the orange compound was dried *in vacuo* at 50° for 72 hr (spectrum A, reference 3). To minimize the effect of differences in sample size, a ratio of the integrated intensity of the 3350 cm^{-1} and 1100 cm^{-1} bands was made. Analysis of the anhydrous compound also yielded a value of HQ:Th significantly lower than 5:1 (Table I), although in this instance, there was the possibility of partial volatilization of the additional HQ molecule.

The variation in the results suggests that the composition is very sensitive to slight changes in the experimental conditions. This variation was obtained even though the amounts of thorium, HQ, ammonium acetate, aqueous ammonia, the rates of addition of each reagent, and the total volume of the final solution were kept reasonably constant in each preparation. In this regard, it is interesting that Cardwell *et al.*[14] observed that the composition of the compound is dependent on the rate at which the pH of the solution is adjusted. The results of the present study suggest that the sensitivity of the composition to such an experimental variable is even greater than previously thought, and that very carefully controlled experiments are required to attain reproducibility and perhaps, even a strict 5:1 stoichiometry. Variables such as the percent excess of HQ, method of pH adjustment, and temperature and time of digestion should be investigated. For example, in the present study, a 33% excess of HQ was used; this amount may not be sufficient to suppress thorium hydrolysis entirely as the pH is raised to its final value.

If it is assumed that the extent of hydrolysis is negligible and that the extra HQ molecule is coordinated to the central thorium ion and is monodentate,[3] it is reasonable to suggest that the deficient

HQ is replaced by co-ordinated water. The average composition can then be written as $Th(C_9H_6NO)_4 \cdot 0{\cdot}9C_9H_7NO \cdot 0{\cdot}1H_2O$. Simple calculation shows that the amount of bound water in the adduct would be about 0·2 mg/100 mg. This concentration is too small for detection by infrared analysis and could not lead to the droplet size observed in the U-tube. Therefore, the bulk of the water present in the orange adduct taken for analysis must have been unbound moisture.

In the past, erratic results have sometimes been reported in the bromometric determination of thorium by means of 8-hydroxyquinoline. In gravimetric work, some workers have ignited the precipitated adduct to ThO_2, or have thermally converted it to the tetrakis compound in order to obtain reproducible results. Clearly, the non-stoichiometry of the adduct and the thermal volatility of the additional HQ molecule detract greatly from the usefulness of the adduct as an analytical compound. A superior analytical compound is tetrakis(2-methyl-8-hydroxyquinolinato)thorium(IV).[15] This easily prepared compound is stoichiometric and thermally stable.

Tetrakis(8-hydroxyquinolinato)thorium(IV) can be easily prepared in reasonably pure form by heating the orange adduct according to the procedure described earlier. The effect of varying the temperature, time and sample size was not investigated further. The main advantage in preparing the tetrakis compound *in vacuo* is that its oxidative decomposition cannot occur as readily as in air.

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Department of Chemistry
McMaster University
Hamilton, Ontario, Canada

A. CORSINI
J. ABRAHAM

Summary—The orange compound formed between thorium(IV) and 8-hydroxyquinoline by conventional precipitation is non-stoichiometric. The composition is very sensitive to experimental conditions; the average ratio of bound 8-hydroxyquinoline to thorium was found to be 4·9 : 1. The deficiency of 8-hydroxyquinoline is due either to partial hydrolysis of thorium, or to the presence of co-ordinated water. A simple procedure for the preparation of the pure tetrakis compound is described.

Zusammenfassung—Die orange Verbindung, die man durch konventionelle Fällung aus Thorium(IV) und 8-Hydroxychinolin erhält, ist nicht stöchiometrisch zusammengesetzt. Die Zusammensetzung hängt sehr empfindlich von den Versuchsbedingungen ab; das mittlere Verhältnis von gebundenem 8-Hydroxychinolin zu Thorium wurde als 4,9 : 1 gefunden. Der Abmangel an 8-Hydroxychinolin ist entweder durch teilweise Hydrolyse von Thorium oder durch Vorhandensein koordinierten Wassers begründet. Ein einfaches Verfahren zur Darstellung der reinen Tetrakis-Verbindung wird beschrieben.

Résumé—Le composé orange formé entre le thorium(IV) et la 8-hydroxyquinoléine par précipitation classique n'est pas stoechiométrique. La composition est très sensible aux conditions expérimentales; on a trouvé que le rapport moyen de la 8-hydroxyquinoléine liée au thorium est de 4,9 : 1. Le déficit en 8-hydroxyquinoléine est dù soit à une hydrolyse partielle du thorium, soit à la présence d'eau de coordination. On décrit une technique simple pour la préparation du composé tétrakis pur.

REFERENCES

1. R. G. W. Hollingshead, *Oxine and Its Derivatives*, Vol. II, Chap. 25, Butterworths, London, 1954.
2. C. J. Rodden and J. C. Warf, in *Analytical Chemistry of the Manhattan Project, National Nuclear Energy Series*, Division VIII, Vol. 1, pp. 184, 187–88. McGraw-Hill, New York, 1950.
3. A. Corsini and J. Abraham, *Chem. Commun.*, 1968, 856.
4. F. Frere, *J. Am. Chem. Soc.*, 1933, **55**, 4362.
5. F. Hecht and W. Ehrmann, *Z. anal. Chem.*, 1935, **100**, 98.
6. R. Bock and F. Umland, *Angew. Chem.*, 1955, **67**, 420.
7. K. Takiyama, E. D. Salesin and L. Gordon, *Talanta*, 1960, **5**, 231.
8. C. E. Crouthamel and C. E. Johnson, *ibid.*, 1961, **8**, 377.
9. A. Corsini, *On Thorium Oxinates and Their Analytical Properties*, Ph.D. Thesis, McMaster University, Hamilton, Ontario, 1961.

10. A. Corsini and J. Abraham, *Talanta*, 1968, **15**, 562.
11. T. Moeller and M. V. Ramaniah, *J. Am. Chem. Soc.*, 1953, **75**, 3946.
12. W. W. Wendlandt, *Anal. Chem.*, 1956, **28**, 499.
13. J. H. Van Tassel and W. W. Wendlandt, *J. Am. Chem. Soc.*, 1959, **81**, 813.
14. T. J. Cardwell, R. W. Cattral, J. V. Kingston and R. J. Magee, *Inorg. Nucl. Chem. Letters*, 1967, **3**, 491.
15. A. Corsini and R. P. Graham, *Anal. Chim. Acta*, 1960, **23**, 248.

Talanta, 1970, Vol. 17, pp. i to ii. Pergamon Press. Printed in Northern Ireland

PAPERS RECEIVED

Separation and determination of mixtures containing *p*-aminosalicylic acid and *m*-aminophenol: Martin I. Blake and James Hunt. (13 *January* 1970)

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A microwave excited emissive detector for gas chromatography. Further studies with sulphur compounds: R. M. DAGNALL, S. J. PRATT, T. S. WEST and D. R. DEANS. (19 *March* 1970)

Talanta, 1970, Vol. 17, p. iii. Pergamon Press. Printed in Northern Ireland

PUBLICATIONS RECEIVED

Acids and Bases—Their Quantitative Behaviour: R. P. BELL, 2nd Ed. Methuen, London, and Barnes & Noble, New York, 1969. Pp. 111. £1·30.

The first edition of this book appeared in 1952, since which time the use of several new techniques has increased our knowledge of some aspects of the field, and created a considerable amount of renewed interest. This second edition is as brief and readable as its predecessor, but contains useful additions on the rates of very fast reactions such as proton exchange, and the uses of hydrogen isotopes for helping in the elucidation of some acid–base reactions. Other chapters cover the nature of acids and bases, acid–base equilibria in water, acids and bases in non-aqueous solvents, interionic attraction in acid–base equilibria, acid–base strength and molecular structure, and alternative uses of the terms acid and base. This book should have a very wide readership, and ought to be read by all final-year students of chemistry.

Advances in Chromatography, Vol. 8: Ed. J. CALVIN GIDDINGS and ROY A. KELLER, Marcel Dekker, New York, 1969. Pp. xvi + 400. 198s.

This invaluable series continues to compress the vast literature in a highly heterogeneous field into a readable volume. The topics are diverse. They include chapters on the principles of gel filtration, the thermodynamics of liquid–liquid chromatography, the selection of optimum solvents for countercurrent distribution, the separation of chloroplast pigments and a series of sections on gas chromatography relating to the performance of various types of columns, flow programming, analysis of vehicular exhaust emissions, and the study of reaction kinetics. The articles are up to date and the standard of book production high.

Characterisation and Analysis of Polymers by Gas Chromatography, Vol. 3: MALCOLM P. STEVENS, Marcel Dekker, New York and London, 1969. Pp. xii + 198. 122s.

This book is the third volume in a series devoted to Techniques and Methods of Polymer Evaluation; the earlier two were concerned with thermal analysis. Particular emphasis is placed in the current volume on applications of gas–liquid chromatography to the identification of volatile components either in polymers as such or in chemically or thermally degraded polymers. Useful assistance is given in applying pyrolysis to the identification of polymers by "fingerprint" type comparisons with known polymers. Topics covered include—the analysis of volatile materials in polymers, the characterisation of polymers by thermal and chemical degradation, and the study of monomeric purity. The bibliography is comprehensive and up to date.

SUMMARIES FOR CARD INDEXES

Atomic-fluorescence spectroscopy of lead: VÁCLAV SYCHRA and JAROSLAV MATOUŠEK, *Talanta*, 1970, **17**, 363. (Department of Analytical Chemistry, Technical University, Prague 6, Czechoslovakia.)

Summary—The fluorescence spectrum of lead excited with a high-intensity hollow-cathode lamp has been investigated and the probable mechanism of fluorescence transitions is suggested. It is confirmed experimentally that the most intense fluorescence line at 405·78 nm is mostly due to direct-line fluorescence. The premixed air–hydrogen flame, the separated air–acetylene flame, and the oxy-hydrogen flame diluted with argon have been used, the last mentioned giving a detection limit of 0·02 ppm with the line at 405·78 nm.

Substoichiometric determination of traces of palladium by neutron-activation analysis: G. B. BRISCOE and S. HUMPHRIES, *Talanta*, 1970, **17**, 371. (Department of Chemistry, The University of Aston in Birmingham, Gosta Green, Birmimgham, 4, England.)

Summary—A highly selective, rapid, one-step radiochemical separation procedure for palladium has been developed. It is based on the solvent extraction of palladium diethyldithiocarbamate from a $5M$ hydrochloric acid solution with a substoichiometric amount of copper diethyldithiocarbamate in chloroform. The separation has been applied to the determination of traces of palladium by neutron-activation analysis, in platinum, the rocks W-1 and PCC-1 and a biological material (kale). Amounts of palladium down to 10^{-8} g have been determined.

Further study of individual ion activities in pure aqueous sodium chloride: ADAM SHATKAY, *Talanta*, 1970, 381. (Isotope Department, Weizmann Institute of Science, Rehovot, Israel.)

Summary—The e.m.f. values between a chloride electrode and a reference electrode were measured in aqueous NaCl solutions between 10^{-5} and 6 m, saturated KCl and $1M$ KNO_3 bridges being used. The effect of the various liquid junctions is calculated and discussed. The consistency of the results is inspected, assuming either the MacInnes or the Guggenheim convention. The choice of different reference points for the standardization of the e.m.f.'s and for the activity coefficients is discussed. A comparison is made between the results obtained with an Ag/AgCl electrode of the second kind and a solid membrane chloride electrode.

ОПРЕДЕЛЕНИЕ СВИНЦА МЕТОДОМ АТОМНО-ФЛУОРЕСЦЕНТНОЙ СПЕКТРОСКОПИИ:

VACLAV SYCHRA and JAROSLAV MATOUSEK, *Talanta* 1970 **17**, 363.

Резюме—Изучен спектр флуоресценции свинца, возбужден высокоинтенсивной лампой с полым катодом и предложен вероятный механизм флуоресцентных переходов. Подтверждено опытом что наиболее интенсивная флуоресцентная линия при 405,78 нм является главным образом в результате флуоресценции непосредственной линии. Использованы предварительно смешанное пламя воздуха и водорода, отделенное пламя воздуха и ацетилена и разбавленное аргоном пламя кислорода-водорода. Последнее позволяет получить чувствительность 0,02 мг/л с использованием линии при 405,78 нм.

СУБСТЕХИОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ СЛЕДОВ ПАЛЛАДИЯ МЕТОДОМ НЕЙТРОННОАКТИВАЦИОННОГО АНАЛИЗА:

G. B. BRISCOE and S. HUMPHRIES, *Talanta*, 1970, **17**, 371.

Резюме—Разработан высокоизбирательный, быстрый, одноэтапный радиохимический метод выделения палладия. Метод основан на извлечении диэтилдитиокарбамината палладия из раствора 5 *M* соляной кислоты с субстехиометрическим количеством диэтилдитиокарбамината меди в хлороформе. Метод применен в определении следов палладия методом нейтронноактивационного анализа в платины, горных породах W-1 и PCC-1 и в биологическом материале (кудрявой капусте). Определены следы палладия до 10^{-8} г.

ДАЛЬНЕЙШЕЕ ИЗУЧЕНИЕ ИНДИВИДУАЛЬНЫХ АКТИВНОСТЕЙ ИОНОВ В ЧИСТОМ ХЛОРИДЕ НАТРИЯ:

ADAM SHATKAY, *Talanta*, 1970, **17**, 381.

Резюме—Измерены величины э.д.с. между хлоридным электродом и электродом сравнения в водных растворах хлорида натрия в области концентрации 10^{-5} до 6 *M*, с использованием мостов из насыщенного KCl и 1 *M* KNO_3. Вычислен и обсужден эффект разных жидкостных мостов. Осмотрено постоянство результатов, предполагая конвенцию Макиннеса или Гуггенгейма. Обсужден выбор различных точек сравнения для стандартизации э.д.с. и коэффициентов активности. Сравнены результаты полученные с использованием электрода Ag/AgCl второго типа и хлоридого электрода с твердой мембраной.

Preparation of D-(−)-*trans*-1,2-diaminocyclohexane-*N*,*N*,*N*′,*N*′-tetra acetic acid and its use as a spectropolarimetric reagent for lead: P. E. REINBOLD and K. H. PEARSON, *Talanta*, 1970, **17**, 391. (Department of Chemistry, Texas A & M University, College Station, Texas 77843, U.S.A.)

Summary—D-(−)-*trans*-1,2-diaminocyclohexane-*N*, *N*, *N*′, *N*′-tetra-acetic acid [D(−)DCTA] was prepared stereospecifically in good yield by the condensation of the resolved diamine, D-(−)-*trans*-1,2-diaminocyclohexane, with sodium chloroacetate at 16°, followed by use of a strong cation-exchanger to obtain the free acid. Distinct differences were noted in the infrared spectra of the optically active acid and the racemate. The molecular rotation of D(−)DCTA showed strong dependence on the pH of the soluton. D(−)DCTA was used as a stereospecific chelometric reagent in the spectropolarimetrically monitored determination of lead.

EDTA titration of calcium and magnesium with a calcium-selective electrode: T. P. HADJIIOANNOU and D. S. PAPASTATHOPOULOS, *Talanta*, 1970, **17**, 399. (Laboratory of Analytical Chemistry, University of Athens, Athens, Greece.)

Summary—Direct semi-automatic and automatic derivative potentiometric EDTA procedures for the determination of calcium and/or magnesium with a calcium-selective electrode are described. Calcium is titrated in the presence of magnesium at pH 12·0 and the total calcium and magnesium is determined at pH 9·7. Calcium in the range 1–8 mg and magnesium in the range 0·7–5 mg are determined semi-automatically with average errors of about 0·2 and 0·3% respectively and automatically with average errors of 0·4 and 0·7%. Titration times vary from a few seconds to a few minutes.

Determination of Co, Cu, Fe, Ga, W and Zn in rocks by neutron activation and anion-exchange separation: O. JOHANSEN and E. STEINNES, *Talanta*, 1970, **17**, 407. (Institutt for Atomenergi, Isotope Laboratories, Kjeller, Norway.)

Summary—A neutron-activation method for the simultaneous determination of cobalt, copper, gallium, iron, tungsten and zinc in rocks is described. The method is based on anion-exchange separation in hydrochloric acid media. Chemical yield is higher than 97% for all elements, except for tungsten, where the recovery of the carrier is established by re-activation. The precision is about 1·3% for the iron determination and about 3% for cobalt, copper, gallium and zinc.

ПРИГОТОВЛЕНИЕ *D*-(-)-*транс*-1,2-ДИАМИНОЦИКЛОГЕКСАН-*N,N,N′,N′*-ТЕТРАУКСУСНОЙ КИСЛОТЫ И ЕЕ ИСПОЛЬЗОВАНИЕ В КАЧЕСТВЕ СПЕКТРОПОЛАРИМЕТРИЧЕСКОГО РЕАГЕНТА ДЛЯ СВИНЦА:

P. E. Reinbold and K. H. Pearson, *Talanta*, 1970, **17**, 391.

Резюме—*D*-(-)-*транс*-1,2-диаминоциклогексан-*N,N,N′,N′*-тетрауксусная кислота (*D*)-(ДЦТА) приготовлена стереоспецифически с хорошим выходом конденсацией разрешенного диамина-*D*-(-)-*транс*-1,2-диаминоциклогексана-с хлороацетатом натрия при 16°, с последующим выделением чистой кислоты на сильном катионообменнике. Обнаружены характеристичные разници в инфракрасных спектрах оптически активной кислоты и рацемата. Молекулярная ротация *D*(-)ДЦТА оказалась сильно зависимой от pH раствора. *D*(-)ДЦТА использована в качестве стереоспецифического хелатометрического реагента в спектрополариметрическом определении свинца.

ТИТРАЦИЯ КАЛЬЦИЯ И МАГНИЯ С ЭДТА С ИСПОЛЬЗОВАНИЕМ СЕЛЕКТИВНОГО ДЛЯ КАЛЬЦЯ ЭЛЕКТРОДА:

T. P. Hadjiioannou and D. S. Papastathopolous, *Talanta*, 1970, **17**, 399.

Резюме—Описаны методы непосредственного полуавтоматического и автоматического деривативного потенциометрического титрования кальция и/или магния с ЭДТА, с использованием селективного для кальция электрода. Кальций титруют в присутствии магния при pH 12,0, а сумму кальция и магния определяют при pH 9,7. Кальций определяют полуавтоматическим способом в пределах 1–8 мг а магний в пределах 0,7–5 мг с средной ошибкой 0,2 и 0,3 %, соответственно, а автоматическим способом с средной ошибкой 0,4 0,7 %, соответственно. Продолжительность титрования колебается от несколько секунд до несколько минут.

ОПРЕДЕЛЕНИЕ Co, Cu, Fe, Ga, W И Zn В ГОРНЫХ ПОРОДАХ МЕТОДАМИ НЕЙТРОННОЙ АКТИВАЦИИ И ИОНООБМЕННОГО РАЗДЕЛЕНИЯ:

O. Johansen and E. Steinnes, *Talanta*, 1970, **17**, 407.

Резюме—Описан метод одновременного нейтронно-активационного определения кобальта, меди, галлия, железа, вольфрама и цинка в горных породах. Метод основан на анионообменном разделении металлов в солянокислых средах. Химический выход больше чем 97 % для всех элементов за исключением вольфрама. В этом случае восстановление носителя определяют реактивированием. Воспроизводимость определения около 1,3 % в случае железа и около 3 % в случае кобальта, меди, галлия и цинка.

Catalytic thermometric titrations in non-aqueous solvents by coulometrically generated titrant: VILIM J. VAJGAND, FERENC F. GAÁL and SMILJANA S. BRUSIN, *Talanta*, 1970, **17**, 415. (Institute of Chemistry, Faculty of Science, University of Belgrade, Studentski trg 16, Yugoslavia.)

Summary—Catalytic thermometric titrations have been developed for tertiary amines and salts of organic acids in acetic and propionic anhydride with titrant coulometrically generated at a mercury and/or platinum anode, hydroquinone being added to the solution titrated if the platinum anode is used. The results obtained are compared with those obtained by coulometric titration with the end-point detected either photometrically or potentiometrically.

Dosage protométrique des hydrogènes mobiles à l'aide de l'amidure de sodium: MARCEL MIOCQUE, JEAN-MICHEL VIERFOND and ANNICK REYNET: *Talanta*, 1970, **17**, 423. (Laboratoire de la Pharmacie, Hôpital Claude Bernard, Paris XIXème, and Laboratoire de Chimie Organique de la Faculté de Pharmacie de Paris.)

Summary—Sodium amide is decomposed by compounds containing active hydrogen, with stoichiometric release of ammonia, which can be determined by titration with acid. The proposed technique has been applied to representatives of various types of compound.

Estimation of thiosemicarbazide with chloramine-T: D. S. MAHADEVAPPA and A. S. ANANDA MURTHY; *Talanta*, 1970, **17**, 431. (Department of Postgraduate Studies and Research in Chemistry, Manasa Gangotri, Mysore-6, India.)

Summary—A rapid and accurate method for the estimation of thiosemicarbazide in aqueous solution has been developed based on its oxidation with chloramine-T at room temperature and pH 4. The effect of such variables as pH, mode of addition of reagents and concentration of chloride ion on the extent of oxidation has been studied.

КАТАЛИТИЧЕСКИЕ ТЕРМОМЕТРИЧЕСКИЕ ТИТРАЦИИ В НЕВОДНЫХ РАСТВОРИТЕЛЯХ С ИСПОЛЬЗОВАНИЕМ КУЛОНОМЕТРИЧЕСКОЙ ГЕНЕРАЦИИ ТИТРАНТА:

VILIM J. VAJGAND, FERENC F. GAÁL and SMILJANA S. BRUSIN, *Talanta*, 1970, **17**, 415.

Резюме—Разработаны методы термометрического титрования третичных аминов и солей органических кислот в ангидриде уксусной и пропионовой кислот, с использованием кулонометрической генерации титранта на ртутном и/или платиновом электроде, с добавлением раствору гидрохинона в случае использования платинового анода. Полученные результаты сравнены с результатами кулонометрического титрования с применением фотометрического или потенциометрического обнаружения конца титрования.

ПРОТОНОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ АКТИВНОГО ВОДОРОДА АМИДОМ НАТРИЯ:

MARCEL MIOCQUE, JEAN-MICHEL VIERFOND and ANNICK REYNET, *Talanta*, 1970, **17**, 423.

Резюме—Амид натрия разлагается действием соединений содержащих активный водород с стехиометрическим выделением аммиака, который может быть определен титрованием с кислотой. Предложенный метод применен на представители разных классов соединений.

ОПРЕДЕЛЕНИЕ ТИОСЕМИКАРБАЗИДА ХЛОРАМИНОМ Т:

D. S. MAHADEVAPPA and A. S. ANANDA MURTHY, *Talanta*, 1970, **17**, 431.

Резюме—Разработан быстрый и точный метод определения тиосемикарбазида в водном растворе, основан на его окислении хлорамином Т при комнатной температуре и pH 4. Изучено влияние на степень окисления разных факторов-pH, способа добавления реагентов и концентрации хлоридиона.

Kinetochromic spectrophotometry—III. Determination of fluoride by catalysis of the zirconium–Methylthymol Blue reaction: R. V. Hems, G. F. Kirkbright and T. S. West, *Talanta*, 1970, **17**, 433. (Chemistry Department, Imperial College, London, S.W.7, England.)

Summary—The determination of 0·5–4·75 μg of fluoride ion by its catalytic action upon the slow reaction between Methylthymol Blue and zirconium(IV) in aqueous solution is described. Calibration curves obtained after 60 min under optimal conditions are smooth, and yield an effective molar absorptivity of $3 \cdot 23 \times 10^4$ $\text{l.mole}^{-1}.\ \text{min}^{-1}$ at 586 nm. There is considerably less cationic interference than in the alizarin complexan–cerium(III) or lanthanum procedure, but more serious anionic interference is encountered when phosphate, arsenate and, to a lesser extent, sulphate ions are present in the sample solution.

Composition of the thorium(IV)–8-hydroxyquinoline adduct compound: A. Corsini and J. Abraham, *Talanta*, 1970, **17**, 439. (Department of Chemistry, McMaster University, Hamilton, Ontario, Canada.)

Summary—The orange compound formed between thorium(IV) and 8-hydroxyquinoline by conventional precipitation is non-stoichiometric. The composition is very sensitive to experimental conditions; the average ratio of bound 8-hydroxyquinoline to thorium was found to be 4·9 : 1. The deficiency of 8-hydroxyquinoline is due either to partial hydrolysis of thorium, or to the presence of co-ordinated water. A simple procedure for the preparation of the pure tetrakis compound is described.

КИНЕТОХРОМНАЯ СПЕКТРОФОТОМЕТРИЯ—III. ОПРЕДЕЛЕНИЕ ФТОРИДИОНА НА ОСНОВЕ КАТАЛИЗА РЕАКЦИИ ЦИРКОНИЯ С МЕТИЛТИМОЛОВЫМ ГОЛУБИМ:

R. V. Hems, G. F. Kirkbright and T. S. West, *Talanta*, 1970, **17**, 433.

Резюме—Описано определение 0,5–4,75 мкг фторидиона на основе его каталитического действия на медленную реакцию циркония(IV) с метилтимоловым голубим в водном растворе. В оптимальных условиях после 60 мин получаются ровные калибрационные крывые, давая эффективное молярное светопоглощение $3{,}23 \times 10^4$ л. моль$^{-1}$. мм$^{-1}$ при 586 нм. В этом методе встречается значительно меньше влияние катионов чем в методах основанных на реакции ализарин-комплексана с церием(III) или лантаном, но более серьезное влияние если в растворе пробы присутствуют фосфат-, арсенат- и—в меньшей мере—сульфатионы.

СОСТАВ АДДУКТА ТОРИЯ(IV) С 8-ОКСИХИНОЛИНОМ:

A. Corsini and J. Abraham, *Talanta*, 1970, **17**, 439.

Резюме—Оранжевый аддукт образующийся из тория(IV) и 8-оксихинолина конвенциональным осаждением является нестехиометрическим. Состав аддукта сильно зависим от опытных условий; определено средное отношение связанного тория и 8-оксихинолина 4,9:1. Недостаток 8-оксихинолина вызван либо частичным гидролизом тория, либо присутствием координированной воды. Описан несложный метод приготовления чистого тетракис-аддукта.

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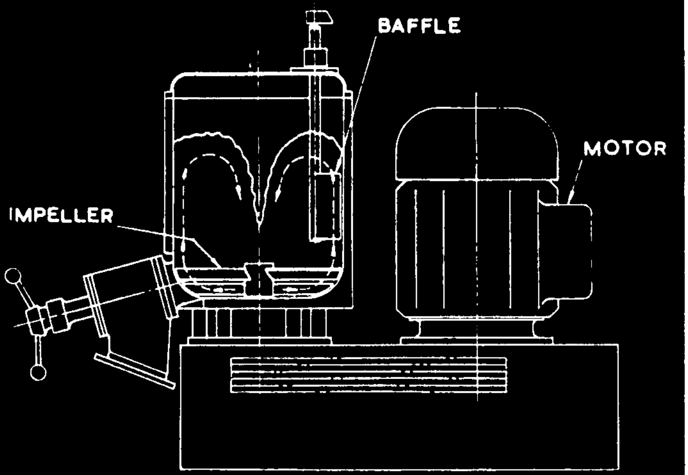

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