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1971 VOLUME 18, NO. 7 JULY

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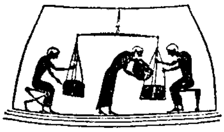

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L. Erdey Memorial Issue of Talanta

Mrs. ANNA SCHNEER-ERDEY receives from Prof. R. BELCHER (on left), Chairman of the Editorial Board of *Talanta*, a specially bound copy of the L. Erdey Memorial Issue (*Talanta*, 1970, **17**, 1141–1228). This Issue perpetuates the memory of her late husband, who was a Member of the Advisory Board of the journal from its inception. The presentation took place in April 1971 in the Institute for General and Analytical Chemistry of the Technical University of Budapest. A second bound copy was presented to Prof. E. PUNGOR (on right) who has succeeded Prof. Erdey as Head of the Institute.

Members of Staff of the Institute of General and Analytical Chemistry and Guests specially invited to the presentation.

Talanta, 1971, Vol. 18, pp. 655 to 664. Pergamon Press. Printed in Northern Ireland

DETERMINATION OF FLUORIDE IN OXIDES WITH THE FLUORIDE-ION ACTIVITY ELECTRODE

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(*Received* 22 *July* 1970. *Accepted* 21 *November* 1970)

Summary—The application of the fluoride-ion activity electrode to the determination of fluoride in various samples has been studied. Samples are decomposed by fusion and the fluoride concentration is determined by a standard-addition or a direct method. The standard-addition method is unsuitable, owing to a positive bias. The direct method, however, is rapid, accurate and precise. The fluoride content of exploration ores, fluorspar, opal glass, phosphate rock and various production samples, has been successfully determined. The success of the direct method depends on the effectiveness of the system used to buffer pH and ionic strength and complex possible interferences (Al^{3+}, Ca^{2+}, Fe^{3+}). The effect of interferences has been studied and found to be minimal. The procedures are rapid and accurate and may be substituted for the traditional Willard and Winter or pyro hydrolysis methods, with considerable saving of time.

THE USE of fluoride-specific electrodes is now well known and has been reviewed by Pungor and Tóth[1] in their general survey of ion-specific electrodes. Our laboratory requires analysis of diverse ore and production samples for fluoride content. Fluoride in inorganic samples is normally determined by the Willard and Winter method[2] and more recently by a pyrohydrolysis[3] method. The Willard and Winter method is relatively slow and is accurate only in the hands of a competent analyst. The pyrohydrolysis method is more rapid but is not applicable to all samples. The availability of the fluoride-ion activity electrode, therefore, prompted a search for a method which is faster, more accurate, and simpler than the other techniques. A method has been developed which permits the direct determination of fluoride in various ore samples in the concentration range from 100 ppm to over 45% fluoride. The proposed method is faster than and as accurate as the distillation or pyrohydrolysis methods.

EXPERIMENTAL

Apparatus

All readings were taken with an Orion Model 801 digital pH meter. Fluoride activity was determined with an Orion fluoride-ion activity electrode (Model 94-09) and a conventional fibre-type saturated calomel electrode. All solutions were stirred with a magnetic stirrer earthed through the pH meter. All readings were taken while the solutions were stirred at room temperature (23°). Because dilute fluoride solutions ($10^{-5}M$) may require up to an hour for equilibrium to be reached, an asbestos pad was placed under the plastic beaker to minimize heating effects. The fluoride electrode was coated with silicone oil (Orion 94-00-03) before use each day. The computer program was written in Basic for a G.E. time-sharing system.

Reagents

All chemicals were of reagent grade quality.

Complexing buffer solution (*CBS*). A 35·3-g portion of DCTA (diaminocyclohexanetetra-acetic acid) was added to 1 litre of water and then 40% sodium hydroxide solution was added dropwise until the salt dissolved. After addition of 600 g of sodium citrate dihydrate and 120 g of sodium chloride the solution was diluted to 2 litres, and the pH adjusted to 6·0 with hydrochloric acid. This solution was approximately $1M$ in citrate, $1M$ in sodium chloride and $0{\cdot}06M$ in DCTA.

Total ionic strength adjustment buffer (TISAB). Glacial acetic acid (57 ml), sodium chloride (58 g) and sodium citrate (0·3 g) were dissolved in 500 ml of water. The pH was adjusted to 5·5 with sodium hydroxide and the solution was diluted to 1 litre.

Flux solutions. (*a*) A 10-g portion of a 6:4 Na_2O_2–Na_2CO_3 mixture was fused in an iron crucible over a hot Méker burner flame. The cooled melt was knocked into a plastic beaker, 50 ml of water were added, and the solution was heated slightly. The slurry was transferred to a 200-ml volumetric flask, diluted to the mark, mixed, and transferred to large centrifuge tubes. After centrifuging, the supernatant liquid was filtered through dry filter paper into a polyethylene bottle. (*b*) Same procedure as for (*a*), except that the flux was fused in a zirconium crucible and the slurry was diluted to 250 ml.

Fluoride standards. A $0{\cdot}1M$ sodium fluoride solution was prepared from reagent grade NaF (dried at 120° for 2 hr) and was stored in polyethylene. This stock solution was standardized with the fluoride electrode by comparison with the Orion 100-ppm standard fluoride solution, or by titration with thorium to a visual sodium alizarin sulphonate end-point. Stock $0{\cdot}01M$ and $0{\cdot}001M$ solutions were prepared by dilution and were stored in polyethylene bottles.

Fluoride standards to be used for samples containing less than 0·25% fluoride were prepared as follows. A 50-ml portion of flux solution (*a*) was added to each of five 200-ml volumetric flasks. Then 1·4, 4·0, 10·0, and 20·0 ml of $10^{-3}M$ sodium fluoride and 6·0 ml of $10^{-2}M$ sodium fluoride were added to individual flasks. One drop of Bromocresol Purple indicator solution was added to each flask and concentrated hydrochloric acid added dropwise until the colour changed. After addition of 100 ml of CBS, the solutions were diluted to the mark. These fluoride standards were 7×10^{-6}, 2×10^{-5}, 5×10^{-5}, 1×10^{-4} and $3 \times 10^{-4}M$ in fluoride.

Standards to be used for samples containing more than 0.25% fluoride were prepared as follows. A 20-ml portion of flux solution (*b*) was transferred to each of five 200-ml volumetric flasks. Then 2·0, 10·0, and 20·0 ml of $10^{-3}M$ and 6·0 and 20·0 ml of $10^{-2}M$ sodium fluoride were added to individual flasks. The acidity was adjusted as above, 100 ml of CBS were added and each solution was diluted to the mark. These standards were 1×10^{-5}, 5×10^{-5}, 1×10^{-4}, 3×10^{-4}, and $1 \times 10^{-3}M$ in fluoride.

The standards were stored in polyethylene bottles and were stable for at least four weeks.

Procedures

Fluoride-ion activity electrode. The concentration of fluoride in the samples was determined with the fluoride-ion activity electrode by either the method of standard additions or a direct method.

(1) *Method of standard additions.* Between 0·2 and 1·0 g of sample (−100 mesh) was fused with 10 g of sodium peroxide in an iron crucible over a hot Méker burner flame. The cooled melt was knocked into a plastic beaker and 50 ml of water were added. Any melt remaining in the crucible was dissolved with a few drops of hydrochloric acid and washed into the beaker. The slurry was gently heated, cooled, transferred to a 200 ml volumetric flask and diluted to the mark. A portion of this solution was centrifuged and filtered. Then 20 ml of the filtrate were transferred by pipette into a 100-ml volumetric flask and 30 ml of 80% orthophosphoric acid were added. The solution was cooled and diluted to the mark. This solution was transferred to a plastic beaker and three 0·3-ml increments of $0{\cdot}1M$ sodium fluoride were added successively to the rapidly stirred solution, the fluoride activity (potential) being recorded before and after each fluoride addition. The samples required 5–10 min to reach a steady potential reading before the addition of any fluoride. After the addition(s), equilibration was rapid and most readings were recorded in less than 2 min. A blank was run which required almost an hour to reach a steady initial potential. The fluoride concentration in the solution was then determined by means of the equation

$$C_F = \left(\frac{X_i}{\text{antilog}\,\dfrac{\Delta E_i}{A}} \right)$$

where C_F = concentration of fluoride in sample (mmole), X_i = concentration of added fluoride (mmole), ΔE_i = change in potential on addition of X_i, and A = Nernst slope, 59·2 mV at 25°.

In order to increase the accuracy of the technique, three different concentrations of fluoride were added to the sample and three C_F values were determined. A plot of the log of total fluoride in the sample ($C_F + X_i$) *vs.* ΔE_i resulted in a straight line with a slope (A) close to the Nernst value of 59·2 mV at 25°. Substitution of this experimentally determined slope (A) in the original equation resulted in an improved value for the fluoride concentration. A computer program was written to speed calculations and print out the amount of fluorine in the samples. A reagent blank was determined and subtracted.

(2) *Direct method.*

Procedure A (100 ppm–0·25% fluoride). A 1·000-g sample (−100 mesh) was fused with 10 g of 6:4 Na_2O_2–Na_2CO_3 mixture in an iron crucible over a hot Méker burner flame. The cooled melt was knocked into a plastic beaker and the transfer of any melt remaining in the crucible aided with a few drops of hydrochloric acid. Then 100 ml of water were added and the solution was heated gently, cooled, transferred to a 200-ml volumetric flask and diluted to the mark. A portion of this solution was centrifuged and the supernatant liquid filtered through dry filter paper (Whatman No. 40). A 25.0-ml aliquot of the clear filtrate was transferred to a 100-ml volumetric flask and 1 drop of Bromocresol Purple indicator solution was added. Hydrochloric acid was added dropwise until the colour changed to yellow. If a precipitate was present when the colour changed, more acid was added dropwise until the precipitate disappeared. Then 50 ml of CBS were added and the solution was diluted to the mark.

The potentials of three or four fluoride standards and up to four samples were determined. The solutions were stirred for 5 min before readings were recorded. The fluoride concentration of the sample was then read from a semilog plot of the potentials of the fluoride standards.

It was noted that the electrode has a slight memory. If a solution of lower fluoride molarity ($\sim 10^{-5}M$) was read after one of higher molarity ($\sim 10^{-4}$), the time required to reach a steady potential for the lower fluoride solution was much greater than if the two solutions were of similar molarity. Therefore, whenever possible, in order to speed the determinations, the samples were divided into groups of similar molarity and each group was read (along with its standards) separately, starting with the most dilute. This method allowed one analyst to complete 12 samples daily.

Procedure B (0·25% to >50% fluoride). A 0·2-g sample was fused in a zirconium crucible with 10 g of 6:4 Na_2O_2–Na_2CO_3 flux. The melt was knocked into a plastic beaker and traces of melt were removed from the crucible with a few drops of hydrochloric acid. The slurry was heated in a water-bath, cooled, and diluted to 250 ml in a volumetric flask. A portion of the solution was centrifuged and the supernatant liquid was filtered through dry filter paper (Whatman No. 40). A 10·0-ml aliquot of the filtrate was transferred to a 100-ml volumetric flask and treated as in Procedure A.

The potentials of up to six samples were recorded. Next the potential of three of four fluoride standards were determined and the samples were read again. The average potential of the sample was then used to determine the fluoride concentration from a semilog plot of the potentials of the fluoride standards. The potential of a solution was read at 2-min intervals until a steady potential (equilibrium) was reached. Except for the first sample, which required up to 1 hr, equilibrium was normally reached in 5–15 min.

Determination of fluoride by Willard and Winter method[2,4]

A 0·5-g sample (−100 mesh) was fused with 10 g of 1:1 Na_2O_2–Na_2CO_3 mixture in an iron crucible. The cold melt was transferred to a 250-ml distillation flask and the crucible was rinsed with perchloric acid. Approximately 75–150 mg of finely ground quartz sand (−400 mesh) was added and the flask was connected to the apparatus. Then 40 ml of 70% perchloric acid and 5 ml of 85% orthophosphoric acid were added to the flask and the end of the condenser was positioned in 20 ml of water. The flask was heated with a flame until the temperature reached 130°, then steam was introduced and heating continued. The temperature was held at 140–150°, until 300 ml of distillate had been collected. The distillate was diluted to 500 ml and 250 ml of this solution were adjusted to pH 3·00–3·05. After the addition of 2 ml of 0·05% sodium alizarin sulphonate solution the solution was titrated with standard thorium solution to the maximum pink colour. Lower concentrations of fluoride were determined by the Eriochirome Cyanine R–zirconyl chloride method as described by Megregian.[5]

RESULTS AND DISCUSSION

Because of the diverse composition of the samples, the method of standard additions as described by Baumann[6] was first used. Initial standard-addition experiments indicated a high bias and therefore a fluoride reagent blank was determined. The blank value was $1{\cdot}9 \times 10^{-3}$ mmole of fluoride per 100 ml of final solution and this value was subtracted from all results (C_F). The use of steam-stripped phosphoric acid did not significantly reduce the blank value. In addition to a blank correction, most results required a slope correction. The slope of the standard additions line was normally between 57 and 61 mV, and thus the slope correction was slight.

The blank and slope-corrected results, presented in Table I, show that the method of standard additions still has a slight positive bias. This bias was also noted for

TABLE I.—DETERMINATION OF FLUORIDE BY STANDARD ADDITIONS METHOD

Sample	F, %	
	Willard and Winter	Fluoride-ion activity electrode*
NBS 91—Opal Glass (SiO_2, 67%)(Al_2O_3, 6)(CaO, 10) (K_2O, 3)(Na_2O, 8)	5·72†	5·82 ± 0·11 (4)§
Unionmelt—20 Grade (SiO_2, 53%)(Al_2O_3, 4)(CaO, 28)(MgO, 10)	1·68	1·68 ± 0·10 (6)
Unionmelt—50 Grade (SiO_2, 39%)(MnO, 42)(Fe_2O_3, 2)($(Al_2O)_3$, 4) (CaO, 5)(MgO, 1)	1·69	1·65 ± 0·06 (4)
Unionmelt—80 Grade (SiO_2, 36%)(MnO, 7·5)(TiO_2, 1)(Fe_2O_3, 1) (Al_2O_3, 16)(CaO, 22)(MgO, 12)	2·32	2·44 ± 0·07 (4)
Unionmelt—85 Grade (SiO_2, 39%)(MnO, 12)(TiO_2, 19) (Al_2O_3, 5)(Fe_2O_3, 2)(CaO, 18)	1·87	1·98

* Slope and blank corrected.
† NBS value.
§ Numbers in parentheses are the number of determinations.

recoveries (106%) of known concentrations of fluoride. These findings are similar to those of Baumann.[6] Because of the bias and relatively high blanks, the method of standard additions is not recommended.

In the direct method the potential of the sample solution is compared with the potentials of a group of standard fluoride solutions. The fluoride concentration of the sample is then read directly from the graph of standard fluoride solution potentials if the standard and sample solutions have the same pH and ionic strength. In addition, any interfering ions in the sample which precipitate or complex fluoride must either be removed in the sample preparation procedure or must be complexed with a suitable chelating agent.

The pH of sample and standard is maintained constant by addition of a suitable buffer. A constant ionic strength is achieved by addition of a high concentration of sodium chloride to both sample and standard solutions. A suitable chelating agent was selected by studying its ability to complex aluminium, which is considered a major interference because it forms a strong complex with fluoride and is difficult to remove conveniently in the sample preparation steps. The chelating agent's effectiveness was determined by studying the change in potential of a buffered fluoride solution on addition of aluminium (Fig. 1). The mixture TISAB (total ionic strength adjustment buffer), an effective pH and ionic strength buffering system, was ineffective in removing the aluminium interference. A mixture of phosphate and TISAB or of DCTA and TISAB had a higher aluminium tolerance. The most effective system was a mixture of citrate, DCTA and sodium chloride (CBS). The complexing buffer solution (CBS) effectively buffered the pH and ionic strengths of the solutions and complexed large amounts of aluminium. This buffering system was therefore used in all subsequent direct procedures.

The fluoride concentrations of tungsten exploration samples were determined by the direct method. The samples were also analysed by the Willard and Winter and

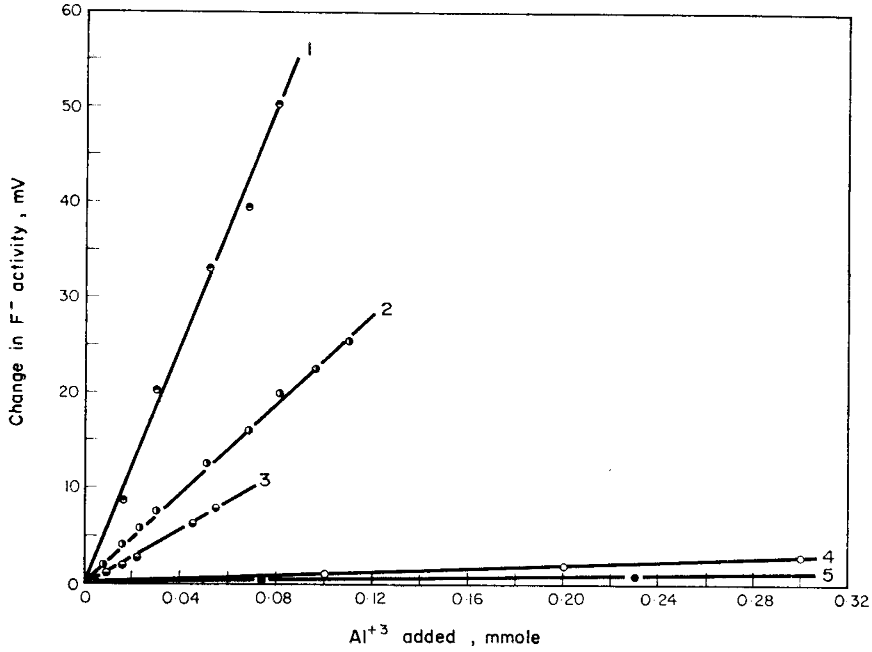

FIG. 1.—Effect of Al^{3+} on fluoride activity in various buffer systems.
1. 0·14 mmole of F^-, 50 ml of TISAB.
2. 0·14 mmole of F^-, 25 mmole of PO_4^{-3}, 50 ml of TISAB.
3. 0·05 mmole of F^-, 50 ml of TISAB, 3 mmole of DCTA.
4. 0·005 mmole of F^-, 50 ml of CBS.
5. 0·05 mmole of F^-, 50 ml of CBS.
All solutions were diluted to 100 ml; pH = 6·0

pyrohydrolysis methods. The results are presented in Table II. The excellent agreement between the Willard and Winter and the fluoride electrode results attests to the accuracy of the proposed method. A stream sediment sample, analysed 7 times by the fluoride electrode method, had a standard deviation of 18 ppm and a 50-ppm range for the 7 results. The pyrohydrolysis results demonstrate the unsuitability of this method for many of these samples.

During the exploration ore study, the recovery of fluoride in some samples containing higher (>0·25%) amounts of fluoride was low (by ~5 % relative) by the direct fluoride electrode method (Procedure A). Thus, the various sample preparation steps were checked for possible fluoride loss.

Samples are normally decomposed by fusion with a hot (900°) flux, and fluoride loss at this temperature might be possible. To minimize this possibility, the samples were decomposed at 520° according to the method of Chu.[7] However, the results were the same, whichever method of fusion was used. Fluoride loss due to volatilization is, therefore, not the source of error.

Occlusion or co-precipitation of fluoride by the metal hydroxides was shown to be minimal. A known concentration of fluoride was added to a slurry of the melt and the analysis was completed by the direct method (Procedure A). The results showed no fluoride was lost.

TABLE II.—DETERMINATION OF FLUORIDE IN TUNGSTEN EXPLORATION SAMPLES

Sample	Fluoride, *ppm*		
	Willard and Winter	Pyrohydrolysis	Fluoride-ion activity electrode (direct method–Procedure A)
QTZ-Monzonite	90	65	110
Marble	630	290	600
Granite	910	810	960
Tactite-Garnet	2300	190	2400(2)*
Marble	1600	1200	1700
Tactite	200	25	190
Tactite	70	<15	130
Hornfels	700	125	790
Stream sediment #1	470	290	520
Stream sediment #2	760(2)*	620	760(2)
Stream sediment #3	650(2)	535	600(2)
Limestone	15200	290	14200
Wollastonite and Hornfels	200	25	220(2)
Tactite	110	10	210
Stream sediment #4	490	110	460 ± 16(3)
Stream sediment #5	740(2)	550	800(2)
Tactite	620(2)	290	670(2)
Stream sediment #6	480 ± 19(3)	—	460 ± 18(7)

* Numbers in parentheses are the number of determinations.

The cause of the low fluoride recoveries was traced to aluminium. Fluoride recoveries in samples containing 15–20% Al_2O_3 were 83%, while samples containing 5–10% Al_2O_3 gave 94% recovery by the direct method (Procedure A). Figure 1 shows that although CBS is more effective in removing the aluminium interference than are the other systems studied, the interference is not removed completely. Figure 1 also shows that the aluminium interference is a function of the concentration of aluminium in the final solution (ratio of Al^{3+}/CBS) and not a function of the Al^{3+}/F^- ratio. Therefore, by starting with a smaller sample and by using higher dilution factors, the aluminium concentration in the final solution can be decreased. The fluoride concentration will also decrease but because the fluoride electrode functions satisfactorily down to $1 \times 10^{-5}M$ fluoride, no loss in accuracy will occur.

When the changes discussed above were incorporated into the procedure, the accuracy of the determinations improved. Results for a number of production, research and NBS samples are presented in Table III. These results show the agreement between the Willard and Winter and the direct electrode method. In addition, the precision study made on the NBS 91 (Opal Glass) standard demonstrates the excellent repeatability (and accuracy) of the proposed method.

Some of these samples were analysed by a double Willard and Winter procedure. The residue (SiO_2) left in the distillation flask after the Willard and Winter distillation was fused again with Na_2O_2–Na_2CO_3 mixture and this melt was then treated by the Willard and Winter technique. This second distillate contained 1–3% (relative) additional fluoride, which was added to the amount found in the first distillate.

The determination of fluoride in the fluorspar samples (Table III) required a slight modification of the fluoride electrode procedure used for the other samples. A sample weight of 0·1 g and a larger dilution were used.

TABLE III.—DETERMINATION OF FLUORIDE IN ORE, PRODUCTION AND NBS SAMPLES

Sample	F, %		
	Willard and Winter	Fluoride-ion activity electrode direct method (Procedure B)	Other results
Unionmelt—20	1·68	1·66(2)*	
Unionmelt—50	1·69	1·72	
Unionmelt—80	2·32	2·30	
Unionmelt—85	1·87	1·90(2)	
Unionmelt—50—Std.	—	2·06 ± 0·06(3)	1·95†
Unionmelt—60—Std.	—	1·84 ± 0·03(3)	1·80†
Unionmelt—90 (SiO_2, 32%; MnO, 17; Al_2O_3, 18; CaO, 8)	2·14‡	2·11	
Unionmelt—90	2·48	2·57	
Unionmelt—709 (SiO_2, 37%; MnO, 5; Al_2O_3, 1; CaO, 49; Na_3AlF_6, 7)	4·74	4·77	
Unionmelt—709	4·48‡	4·23	
Ore	6·86‡	7·32	
Ore	4·71‡	4·82 ± 0·03(3)	
NBS 91, Opal Glass	—	5·75 ± 0·003(8)	5·72§
Fluorspar, Mexican	42·0	41·8	
Fluorspar, 79A	47·4	47·0	

* Numbers in parentheses are the number of determinations.
† Recommended value from 7 laboratories.
‡ Willard and Winter, double distillation.
§ NBS recommended value.

The determination of fluoride in phosphate rock was attempted by the direct method (Procedure B). The fluoride recoveries for both NBS 120a and 56b were low. The high concentration of CaO in these samples makes them resistant to Na_2O_2–Na_2CO_3 fusion. If these samples are first attacked with hydrochloric acid and the residue then fused, the accuracy of the results improves. In fact, if the samples are attacked with hydrochloric acid only, similar to the method of Edmond,[8] accurate results are also achieved. The results appear in Table IV. Even though acid decomposition is sufficient, the samples were decomposed by acid followed by fusion of

TABLE IV.—DETERMINATION OF FLUORIDE IN PHOSPHATE ROCK

Sample	Method of decomposition	F, %	
		NBS	Fluoride-ion activity electrode (modified procedure B)
NBS 120a, Phosphate Rock (P_2O_5, 34%)(Al_2O_3, 0·9) (Fe_2O_3, 1)(CaO, 50)	HCl only	3·92	3·87 3·99
NBS 120a, Phosphate Rock	HCl + fusion	3·92	4·01
NBS 56b (P_2O_5, 32%)(CaO, 44) (SiO_2, 10)	HCl only	3·4	3·43 3·33
NBS 56b	HCl + fusion	3·4	3·25

the residue to show that the fusion step does not affect the technique's accuracy. Samples high in alkaline earth oxides, and of unknown response to acid or alkaline-fusion attack, would require both acid and fusion decomposition for the most accurate results to be obtained.

Some of the samples discussed in Table III were decomposed with hydrochloric acid to determine whether the fluoride could be leached from the sample as in the phosphate rock procedure. The amount of fluoride recovered was between 63 and 86% for some of the Unionmelts and was 16% for the opal glass.

Interferences

The effect of possible interferences on the accuracy of the direct fluoride activity method was studied. The elements of interest are found in many of the ore and production samples. A mixture of 6 g of sodium peroxide and 4 g of sodium carbonate was fused in a zirconium or iron crucible and the melt slurried with water. A known concentration of fluoride and the element of interest was then added to the slurry. The analysis was completed by a direct method (Procedure A or B). The effect of the added elements on the fluoride recovery is presented in Table V.

None of the elements studied interfered with Procedure B, except aluminium at its highest concentration. We assumed any deviation greater than ±0·07% was

TABLE V.—EFFECT OF INTERFERENCES ON THE DIRECT FLUORIDE-ION ACTIVITY ELECTRODE METHODS

Metal (salt added)	Metal in "sample", %		Wt. ratio Metal/F^-	F, %		Deviation, %
	Procedure A (1·0-g sample)	Procedure B (0·2-g sample)		Added	Found	
Al	1	—	5·3	0·19	0·19	0
($AlCl_3·6H_2O$)	6	—	32	0·19	0·18	−0·01
	10	—	53	0·19	0·16	−0·03
	8	—	85	0·094	0·088	−0·006
	16	—	170	0·094	0·085	−0·009
	—	5·5	2·3	2·38	2·32	−0·06
	—	14	5·9	2·38	2·36	−0·02
	—	28	12	2·38	2·32	−0·06
	—	45	19	2·38	2·31	−0·07
	—	96	40	2·38	2·21	−0·17
Ca	5	—	26	0·19	0·18	−0·01
($CaCl_2$)	10	—	53	0·19	0·18	−0·01
	16	—	170	0·094	0·092	−0·002
	—	50	21	2·38	2·31	−0·07
Si	5	—	26	0·19	0·18	−0·01
($Na_3SiO_3·9H_2O$)	10	—	53	0·19	0·19	0
	—	50	21·0	2·38	2·43	+0·05
Cr	2	—	11·0	0·19	0·18	−0·01
(Na_2CrO_4)	5	—	21	0·19	0·19	−0·01
	—	50	21	2·38	2·37	−0·01
W	—	8	8·4	0·95	0·95	0
($Na_2WO_4·2H_2O$)	—	24	25	0·95	0·95	0
	—	47	49	0·95	0·95	0
	—	71	75	0·95	0·95	0

significant because the results in Table III indicate the precision of the method is ~±0·07% at the 95% confidence level.

None of the elements interfered with Procedure A, except the aluminium at the highest concentrations used. This evaluation is arbitrary because of the lack of any statistical data at this fluoride level.

Iron crucibles were used for Procedure A and zirconium crucibles for Procedure B. Zirconium crucibles were used because it was felt the bulky iron precipitate from the crucible (5–10 ml) changed the available volume of the volumetric flask and could produce high results. Later studies indicated that iron crucibles did not produce high results and the crucible material did not affect the results. These results also demonstrated that iron or zirconium does not interfere with the fluoride determination.

The effect of changing the flux weight and/or ratio was examined and the results are presented in Table VI. Various flux compositions were fused in a zirconium crucible, cooled, and slurried in water, then 0·25 mmole of sodium fluoride were added, and the experiments were completed by Procedure A. Potentials for all test solutions were compared with that of a solution prepared from a flux composition of 6:4 Na_2O_2–Na_2CO_3 and the fluoride molarities were calculated from any potential differences. Rather large changes in both flux ratio and amount had no effect on fluoride recovery. Therefore, for routine application, the flux can be measured by volume rather than weighed.

TABLE VI.—EFFECT OF FLUX CHANGE ON FLUORIDE RECOVERY

Flux composition		Fluoride found, *M*
Na_2O_2, *g*	Na_2CO_3, *g*	
6	4	$1·0 \times 10^{-4}$
8	2	$0·97 \times 10^{-4}$
4	6	$0·99 \times 10^{-4}$
9	6	$0·98 \times 10^{-4}$
4	3	$1·0 \times 10^{-4}$

Acknowledgment—All the Willard and Winter and pyrohydrolysis results were contributed by P. S. Bechtel. We wish to recognize his efforts. The advice of P. Greenberg, H. J. O'Hear, and H. F. Wendt is greatly appreciated.

Zusammenfassung—Die Anwendung der auf die Fluoridaktivität ansprechenden Elektrode auf die Bestimmung von Fluorid in verschiedenen Proben wurde untersucht. Die Proben werden durch Schmelzen aufgeschlossen und die Fluoridkonzentration entweder durch Zugabe eines Standards oder direkt bestimmt. Die Methode mit Standardzugabe ist ungeeignet, da sie einen systematischen positiven Fehler aufweist. Die direkte Methode ist jedoch schnell, genau und richtig. Der Fluoridgehalt von Erzen aus Versuchsbohrungen, Flußspat, Opalglas, Phosphatgestein und verschiedenen Proben aus der Produktion wurde mit Erfolg bestimmt. Der Erfolg der direkten Methode hängt von der Wirksamkeit des Systems ab, das pH und Ionenstärke puffert und mögliche Störelemente (Al^{3+}, Ca^{2+}, Fe^{3+}) komplex bindet. Der Einfluß von Störungen wurde untersucht und als sehr gering befunden. Die Verfahren sind rasch und genau und können unter erheblicher Einsparung von Zeit an Stelle der herkömmlichen Verfahren nach Willard und Winter oder der Pyrohydrolyse eingesetzt werden.

Résumé—On a étudié l'application de l'électrode d'activité à ion fluorure pour le dosage du fluorure dans divers échantillons. Les échantillons sont décomposés par fusion et la concentration en fluorure est déterminée par une addition d'étalon ou par une méthode directe. La méthode d'addition d'étalon ne convient pas, à cause d'une polarisation positive. La méthode directe, toutefois, est rapide, précise et fidèle. On a déterminé avec succès la teneur en fluorure de minerais d'exploration, de fluorspar, de verre opale, de roche au phosphate et de divers échantillons de production. Le succès de la méthode directe dépend de l'efficacité du système utilisé pour tamponner le pH et la force ionique et des interférences possibles de complexes (Al^{3+}, Ca^{2+}, Fe^{3+}). On a étudié l'influence des interférences et les a trouvé être minimes. Les techniques sont rapides et précises et peuvent être substituées aux méthodes traditionnelles de Willard et Winter ou à la pyrohydrolyse, avec une économie considérable de temps.

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DETERMINATION OF RARE EARTHS IN SELECTED RARE EARTH MATRICES BY SPARK SOURCE MASS SPECTROMETRY*

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(*Received* 21 *September* 1970. *Accepted* 16 *October* 1970)

Summary—Three methods of preparing rare earth samples for mass spectrographic analysis are presented. Techniques for adding appropriate internal standards are described and relative sensitivity factors for rare earth impurities in rare earths, lanthanum, yttrium and scandium matrices are presented. Although indium has some value as an internal standard in rare earth samples, best analytical results are obtained when selected rare earths are used as internal standards.

THE SPARK SOURCE mass spectrograph has been shown to be useful in survey analyses of rare earth metals and rate earth oxides.[1] This paper describes three methods of introducing internal standards into rare earth samples for the purpose of providing quick and reliable procedures, which do not introduce contaminants, for quantitative determination of trace rare earths in rare earth matrices (including the elements scandium, yttrium and lanthanum).

Internal standardization

Desirable chemical and physical properties for spark source mass spectrographic reference standards have been outlined by Taylor.[2] An optimum mass (m/e) range for an internal standard in rare earth matrices is between 90 and 123. This mass range is free of interference by singly and multiply charged rare earth ions as well as molecular ion clusters of rare earths. Lines for both singly and doubly charged rare earth ions are close enough to this mass range to minimize errors due to variation in photoplate emulsions. The element indium, which has isotopes at mass numbers 113 and 115, fits most of the other criteria listed by Taylor and can be used as an internal standard. However, certain of its chemical and physical properties are dissimilar to rare earths, making it sometimes difficult to incorporate indium into certain samples. For this reason selected other rare earths can also be used as internal standards for particular rare earth matrices.

Methods employed

Each of the three methods described below is effective within its own inherent limitations. Low blank levels for rare earths can be maintained in all three methods but the procedures vary considerably in the possible introduction of contaminants that are not themselves rare earths. Although results were obtained in a straightforward manner which permits valid evaluation of each technique, the reader must refer to the overall procedure for a general comparison of the three methods.

Method I. Dry blending. A procedure identical to that described by Taylor[2] was used. Weighed quantities of rare earth oxides were dry-blended with indium oxide.

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* Work was performed in the Ames Laboratory of the U.S. Atomic Energy Commission. Contribution No. 2838.

The resulting oxide mixtures were pelleted with graphite powder. Two examples are given here to show how homogeneous such mixtures can be made. Figure 1 is a picture of an electron microprobe readout indicating the homogeneity of yttrium in an yttrium oxide–graphite pellet. Variations in the yttrium concentration are clearly discernible. Figure 2 represents the results of a microprobe investigation of another mixture in which the trace level constituents, (doped) Gd_2O_3 and In_2O_3, as well as the matrix material, Tm_2O_3, are shown. Each reading corresponds to a 2-μm diameter sampling of the three components. The points were obtained by using linear scan of a pellet surface, with samplings taken every 5 μm. The erratic variations in the ordinate values for the various components are attributed to changes in the graphite concentration in the pellet, which is verified by pictures of graphite intensity maxima which occur in the same regions as the minima of Fig. 2. However, the results shown in the figure indicate good mixing of In_2O_3 and Gd_2O_3 with the matrix, Tm_2O_3.

For mass spectrographic studies, four rare earth oxide matrices (Y_2O_3, La_2O_3, Er_2O_3, and Tm_2O_3) were doped with other rare earth oxides at three impurity levels (nominally 500, 200 and 50 ppma*). Each mixture was sampled in duplicate and sparked on separate photoplates. A determination was obtained from each plate by comparing the average intensity of the individual rare earths (3–5 values) with the average indium intensity (also 3–5 values) for that plate.

Method II. Oxalate precipitation. Rare earths can be quantitatively precipitated in a pure form from a dilute hydrochloric acid solution by adding an excess of oxalic acid. The oxide is obtained by firing the precipitated oxalate at 800° for 1 hr. However, since the internal standard indium could not be quantitatively precipitated with the rare earths in this manner, it was introduced by first blending indium oxide into the graphite which was subsequently mixed with the doped rare earth oxides to form a pellet. This method of entry for indium is convenient but does not provide as homogeneous a mixture of indium with the rare earths as did Method I above. This fact is demonstrated by irregular darkening of photoplates by the indium lines, in comparison with that from the rare earth lines, and also by the comparison of the precision of electrical detection measurements of indium and rare earth line intensities. Indium is thus not a satisfactory internal standard when this method of preparing samples is used.

Five different matrices (Y_2O_3, Sc_2O_3, Ho_2O_3, Tm_2O_3, and Er_2O_3) were doped with rare earths at three concentration levels (200, 50 and 10 ppma). Each preparation was sampled three times and each sample was sparked on two separate photoplates. Each plate was used as a determination (6 determinations) by comparing the average intensity of each rare earth with an average intensity of either Pr or Lu as the internal reference. For most of the determinations, only one or two values were obtained on a plate.

Method III. Nitrate calcination. Indium can be quantitatively converted into its oxide by dissolving the metal in nitric acid and subsequently evaporating slowly to dryness and firing to the oxide at 800°. Rare earth oxides can be produced in the same manner. This method permits accurate and versatile handling of solutions containing known quantities of indium and rare earths. (The standard solutions must be

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* ppma = parts per million atoms.

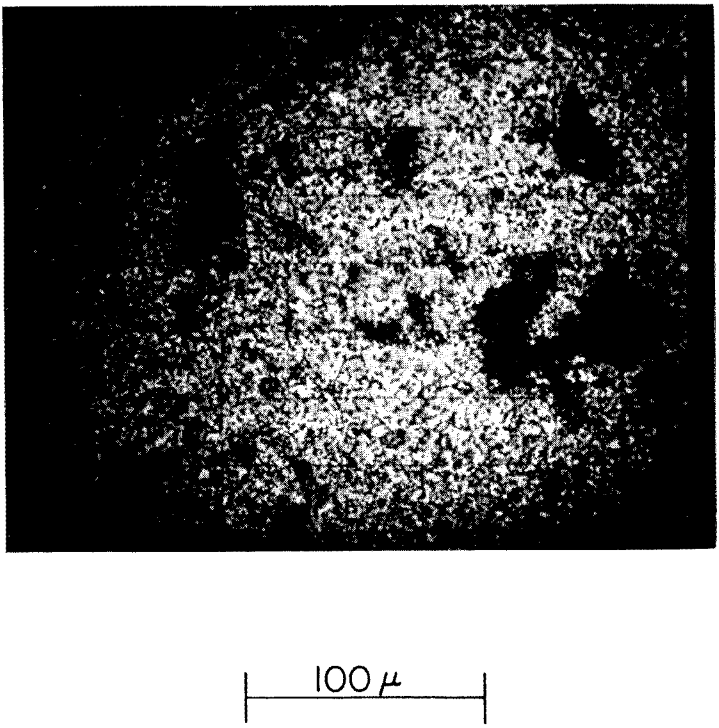

FIG. 1.—Distribution of yttrium in Y_2O_3-graphite pellet; light areas are yttrium.

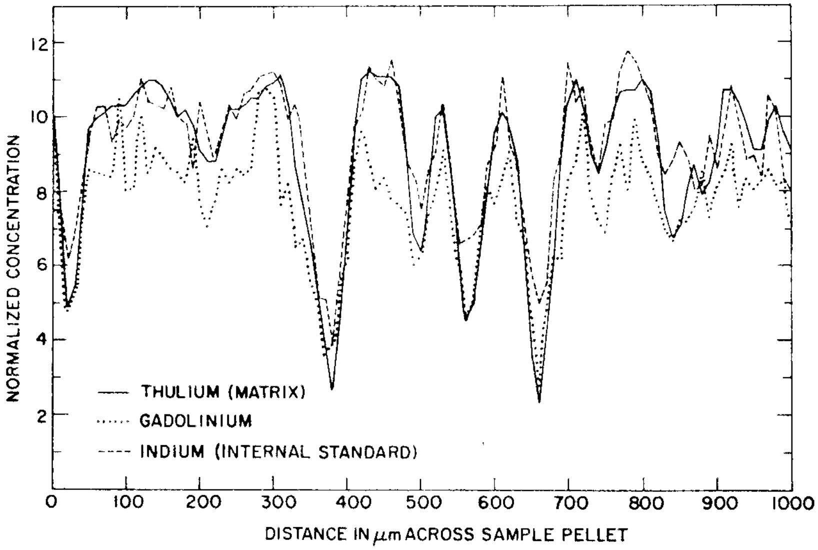

FIG. 2.—Spacial distribution of Gd, In and Tm in a Tm_2O_3-graphite pellet.

maintained at a pH of 3 or less to assure that no precipitation occurs, especially for very low concentrations.)

Four rare earth oxide matrices (Sc_2O_3, Tm_2O_3, Ho_2O_3 and Y_2O_3) were doped with four rare earths (La, Nd, Eu and Dy) and indium at 50 ppma. (Sc_2O_3 requires addition of hydrochloric acid for dissolution in nitric acid; this solution is diluted with nitric acid during evaporation to eliminate volatilization of chlorides.) Two photoplates were prepared for each preparation. Determinations were made from single exposures by comparing the rare earth intensities with the indium and the lanthanum intensities.

EXPERIMENTAL

Reagents and materials

Reagent grade nitric, hydrochloric, and oxalic acid were used. National Carbon Company's SP1 graphite was used as a pelleting medium.

Mixing and pelleting

Spex Industry (Metuchen, N.J.) mixer mills Models No. 5000 and 8000 (with agate and alundum vials, respectively) were used for blending the weighed oxides in Method I and for blending the indium oxide with graphite in Method II. Final mixing of the oxides with graphite was performed manually with a boron carbide mortar and pestle. The mixture contained a ratio of 2·5–3 mole of graphite per mole of rare earth. This mixture was pressed under 280 MN/m^2 (40000 psi) into a disc 12·7 mm in diameter and ~0·8 mm thick. The electrical resistance of the pellets was found to be less than 0·2 ohm/mm. A 12 μm Teflon or 50 μm polyethylene film was used as an interface between the die, plug, and pellet to prevent contamination from the die.

Apparatus

The spark source mass spectrograph used for this work was Model Graf II-2 of Nuclide Corporation, State College, Pa. Source chamber pressure while sparking was between 6×10^{-6} and 3×10^{-5} mbar. Analyser pressure was in the low 10^{-8} mbar region. Samples were presparked for approximately 20 min before analytical results were collected. The duty cycle of the spark involved a ratio of repetition rate (pulse/sec) to pulse width (μsec) of 100/10 or 32/32 for Method III. For Methods I and II this duty cycle ratio was varied between 32/10 and 100/32.

Photoplate handling

Ilford Q-2 plates were used for ion detection. The plates were developed in half-strength ID-19 developer for 4 min, fixed in IF-2 acid hypo fixing solution for 1 min, and dried in air. The plates were read with a Model 23-100 Jarrell-Ash microphotometer, using a slit-width of 5 μm and a slit-height of 0·5 mm. The transmittance scale was set at 100% for a clear glass plate and at 0% for an opaque plate.

RESULTS

Line intensities were computed according to the method outlined by Owens and Giardino[3] which includes the line-width correction, the inverse square root of mass effect on emulsion response, and calibration of the emulsion response curve according to the Churchill two-line method. For each determination a relative sensitivity factor (RSF) was computed from the photoplate line intensities according to equation (1).

$$\mathrm{RSF}_{(\mathrm{unk},\mathrm{ref})} = \frac{(\mathrm{Intensity}_{\mathrm{unk}})(\text{Doped level of element}_{\mathrm{ref}})}{(\mathrm{Intensity}_{\mathrm{ref}})(\text{Doped level of element}_{\mathrm{unk}})} \qquad (1)$$

The subscripts unk and ref refer to the individual element and to the internal reference element respectively. Averaged RSF values for each matrix and method are given in Table I. All values in this table have been normalized with lanthanum taken as unity, for ease of comparison. An overall average RSF is given in column 14 and the average deviation of this value is given in column 15.

Reproducibilities of the RSF are illustrated by relative standard deviations which were calculated according to equation (2)

$$S_{\mathrm{rel}} = \frac{100}{\bar{C}_j}\left(\frac{\sum_{i}^{n}(C_i - \bar{C}_j)^2}{n-1}\right)^{1/2} \qquad (2)$$

where S_{rel} is the estimate of the relative standard deviation; $\bar{C}_j$ is the average; C_i is the ith value of the population; n is the total number of determinations in the population. Student's t-test was used to reject values significantly divergent at the 95% confidence level. Values for S_{rel} are given for the three methods in Tables II, III and IV. Data are presented in this manner because plots of the working curves showed no concentration effect. The median, maximum, and minimum of S_{rel} for each of the three methods are given in Table V.

Error evaluation

Variations in the results may be attributed to photoplate reading, emulsion variation and data evaluation, sample inhomogeneity and matrix effects, and fluctuations in physical characteristics of the discharge plasma. Several statistical evaluations of these errors have been made (for metal samples)[4,5] and these evaluations have been used as guides in interpreting the errors in this work.

Examination of the isotopic abundance ratio offers a convenient method for measuring the overall precision of the photoplate reading, emulsion variation and data evaluation procedure. This is because isotopic ratios should be unaffected by inhomogeneities (for a single exposure) and should be affected in a similar manner by variations in the plasma. Results obtained for selected isotopic ratios are given in

TABLE I.—AVERAGE RELATIVE SENSITIVITY FACTORS FOR EACH MATRIX AND ELEMENT

Matrix	Y_2O_3			Tm_2O_3			Er_2O_3		Sc_2O_3		Ho_2O_3		Overall average*	Average deviation %
method element	I	II	III	I	II	III	I	II	II	III	II	III		
Y	—	—	—	—	0·83	—	1·20	1·38	1·06	—	—	—	1·12	15
La	1·00	1·00	1·00	1·00	1·00	1·00	1·00	1·00	1·00	1·00	1·00	1·00	—	—
Ce	—	0·68	—	—	0·71	—	—	0·66	0·81	—	0·69	—	0·71	5·6
Pr	1·36	1·31	—	(1·00)†	1·42	—	1·29	1·41	1.42	—	1·32	—	1·32 (1·36)	6·6 (3·5)
Nd	1·40	1·43	1·43	(0·84)†	1·37	1·26	1·36	1·08	1·25	1·10	1·34	1·31	1·26 (1·30)	10 (7·3)
Sm	1·78	1·99	—	1·73	1·94	—	1·48	1·65	1·63	—	2·18	—	1·80	10
Eu	2·16	2·05	2·20	—	2·88	2·24	1·74	2·30	1·81	1·92	2·38	2·66	2·21	12
Gd	1·05	1·18	—	0·82	1·31	—	1·14	0·97	1·49	—	1·43	—	1·17	15
Tb	—	1·09	—	—	1·17	—	—	0·92	0·98	—	1·17	—	1·07	8·7
Dy	1·36	1·70	1·30	1·30	1·12	0·83	0·93	1·00	1·19	1·06	(1·81)	—	1·24 (1·18)	19 (16)
Ho	1·11	1·34	—	(0·82)	(0·97)	—	(0·46)	(0·66)	1·33	—	—	—	0·96 (1·26)	28 (7·9)
Er	1·20	1·43	—	(0·91)	(0·84)	—	—	—	1·09	—	—	—	1·09 (1·24)	16 (10)
Tm	1·36	1·48	—	—	—	—	(0·43)	(0·93)	1·47	—	(2·13)	—	1·30 (1·44)	32 (3·6)
Yb	2·13	2·58	—	(3·00)	(2·95)	—	(1·12)	—	1·78	—	—	—	2·26 (2·16)	26 (13)
Lu	—	1·05	—	—	0·87	—	—	0·65	0·75	—	1·15	—	0·89	18

* Values in parenthesis obtained by recalculation after deleting values enclosed in parentheses in the body of the table.

† Values deleted owing to falling outside limits set by Student's t-test at 95% confidence level.

TABLE II.—RELATIVE STANDARD DEVIATION (S_{rel}, %) OF RARE EARTH SENSITIVITIES RELATIVE TO INDIUM FOR METHOD I—DRY BLENDING*

Element	Y_2O_3	La_2O_3	Er_2O_3	Tm_2O_3
Y	—	13·5	25	21
La	13	—	15·5	19
Pr	20	27	24	29
Nd	20	19	31	24
Sm	21	25	27	19
Eu	15	23	21	—
Gd	18	24	27	17
Dy	18	35	23	18
Ho	13	—	—	22
Er	25	45	—	22
Tm	16	14	—	—
Yb	15	30	28	16

* Each S_{rel} value was computed from six determinations on six different photoplates (i.e. two determinations at each of three concentration levels-500, 200, and 50 ppma).

Table VI. Pooled estimates of the standard deviation were computed according to equation (3).

$$S_{\mathrm{rel,p}} = \left(\frac{\sum_{i}^{n} (n_j - 1) S_i^2}{(n_i - 1)} \right)^{1/2} \tag{3}$$

Data used in this computation were obtained from the eight photoplates used with Method III. The precision varies from 5·4 to 7·4%. This is larger than errors normally associated with the microphotometer reading alone (estimated[4] to be about 1–2%) which implies that plate emulsion inhomogeneity and data evaluation are at fault. Four factors which are considered to be contributing to the photoplate error in this work are: more than a third of the results reported here were taken outside the minimum-error transmittance range of the calibration curve,[6] the densitometer reading error was consistently greater than that reported by others, the Churchill two-line method for obtaining the calibration curve and for subsequently evaluating transmission data was not working ideally and the lines on the plates obtained from our mass spectrograph do not have the ideal intensity profile recommended[5] for minimizing errors. In any event the variation shown by S_{rel} in Table VI represents the entire error due to photoplate reading, emulsion variations and data evaluation under the experimental conditions.

The median relative standard deviation for Method I is 21%. Sample inhomogeneity and variations in the spark plasma might be suspected to be a major problem in this method. The homogeneity of the simultaneously precipitated rare earths used in Method II should be very good. However, the median deviation for this method is 17%, only a slight improvement over Method I.

A major source of error for Methods I and II may be due to an error in measuring relative exposure levels by the ion-beam monitoring system. This ion-beam monitoring error would become larger for samples pelleted in graphite (as compared to homogeneous metal samples) where inhomogeneities in the oxide–graphite ratio, as shown in Figs. 1 and 2, cause variations in the relative levels of oxide and carbon ion-currents. Thus, the total ion-beam monitor would not accurately indicate exposure levels due to oxide lines alone unless the exposures were long enough to average out all of the variations in the pellet.

TABLE III.—RELATIVE STANDARD DEVIATION (S_{rel}) OF RARE EARTH SENSITIVITIES (METHOD II—OXALATE PRECIPITATION)*

Element	Y_2O_3 concentration (ppma)			Combined†	Sc_2O_3 concentration (ppma)			Combined†	Ho_2O_3 concentration (ppma)			Combined†	Element	Tm_2O_3 concentration (ppma)			Combined†	Er_2O_3 concentration (ppma)			Combined†
	10	50	200		10	50	200		10	50	200			10	50	200		10	50	200	
—	—	—	—	—	—	28	29	35	—	—	—	—	Y	8	5	8	7	22	17	18	22
La	11	6	13	13	6	12	14	15	11	14	23	16	La	8	10	5	11	5	6	5	7
Ce	34	19	11	22	11	17	14	22	14	15	14	15	Ce	13	6	16	13	25	16	24	26
Pr	16	7	28	20	16	4	16	18	11	15	28	18	Nd	9	9	6	10	17	4	15	15
Nd	20	18	24	20	16	12	11	15	27	20	11	23	Sm	16	19	17	17	14	17	14	15
Sm	28	18	11	22	24	17	18	20	34	20	17	27	Eu	11	18	14	14	18	21	23	20
Eu	20	4	14	13	9	6	13	12	10	13	28	18	Gd	22	19	14	18	16	14	9	13
Gd	12	10	17	13	18	11	15	22	35	14	26	25	Tb	36	11	10	26	10	13	9	11
Tb	9	6	7	12	21	7	7	17	16	15	10	13	Dy	15	11	10	13	21	10	5	13
Dy	15	20	16	18	19	18	13	17	10	9	12	14	Ho	17	8	12	15	2	27	10	24
Ho	4	6	4	7	6	8	10	28	—	—	—	—	Er	—	11	18	14	—	—	—	—
Er	17	22	25	20	10	14	10	14	—	—	—	—	Tm	—	—	—	—	8	19	7	15
Tm	18	14	37	24	9	7	10	20	33	14	27	33	Yb	33	20	22	26	—	—	—	—
Yb	22	10	18	20	12	13	14	14	—	—	—	—	Lu	13	6	12	16	29	20	12	20
Lu = internal reference					Lu = internal reference				Lu = internal reference				Pr = internal reference					Pr = internal reference			

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* The S_{rel} at each concentration level was computed from six determinations on six different plates (i.e. three samplings of each preparation—each sampling was determined twice on separate plates).

† Data at all concentration levels treated as a single population.

TABLE IV.—RELATIVE STANDARD DEVIATION ($S_{\rm rel}$) OF RARE EARTH SENSITIVITIES RELATIVE TO INDIUM*

IV-A Method III with In as reference

Element	Sc_2O_3 plates 844	845	Tm_2O_3 plates 846	847	Ho_2O_3 plates 848	849	Y_2O_3 plates 851	852
La	13	14	20	14	21	18	17	19
Nd	12	13	21	15	20	22	14	19
Eu	11	11	16	15	14	19	8	15
Dy	14	13	28	30	—	—	18	19

IV-B Method III with La as reference

Element	Sc_2O_3 plates 844	845	Combined†	Tm_2O_3 plates 846	847	Combined†	Ho_2O_3 plates 848	849	Combined†	Y_2O_3 plates 851	852	Combined†
Nd	5·6	3·7	4·9	5·4	4·5	5·2	4·4	5·3	5·3	7·8	7·4	7·5
Eu	7·1	9·6	10·8	13·0	9·2	12·6	7·9	12·0	11·5	9·1	8·9	8·9
Dy	6·6	5·3	7·2	5·2	12·0	9·3	—	—	—	4·8	6·5	6·0

* Each $S_{\rm rel}$ value computed from between 18 to 25 determinations on each plate.

† Data from both photoplates treated as a single population.

TABLE V.—MEDIAN AND EXTREME $S_{\rm rel}$ VALUES FOR EACH OF THE METHODS

Method	Median	Minimum	Maximum
I	21	13	45
II	17	7	35
IIIA	15	8	30
IIIB	7	3·7	13

TABLE VI.—$S_{\rm rel}$ (POOLED) OF ISOTOPIC RATIOS

Element	Nd	Nd	Nd	Eu	Dy
Nuclides	142/143	142/146	146/143	153/151	162/161
Actual ratio	2·23	1·57	1·41	1·09	1·35
Calculated ratio	2·20	1·58	1·38	1·09	1·36
$S_{\rm rel}$, %	6·2	7·4	7·0	5·4	6·5
Number of values	167	168	169	168	131

This possible monitoring difficulty led to the data-handling procedure used in Method III, *i.e.* the use of each individual exposure as a determination. This procedure requires the internal reference to have an isotope line of appropriate intensity within the dynamic range of the emulsion on each exposure. Even so, this does not eliminate errors due to plasma variations, which affect elements differently and cause variations in relative elemental sensitivities in spite of simultaneous detection.

The reproducibility is improved with Method III, especially when lanthanum is used as the internal reference, as shown in Table IV-B. The median $S_{\rm rel}$ value is 7% which is as good as the photoplate detection scheme will allow (see Table VI). The fact that lanthanum as internal reference yields better results than indium is attributed to the fact that lanthanum is considerably closer in mass to the other rare earths, which would minimize variant mass effects, and that lanthanum has physical and chemical properties more similar to the rare earths than has indium (the physical properties of indium are similar to those of europium and the S_{rel} values are lower for europium in Table IV-A).

DISCUSSION

The overall average RSF shown in Table I indicates that, within the error limit for this experiment, the relative elemental sensitivities are essentially independent of the matrix and of the three methods. Overall averages for Dy, Ho, Er, Tm, and Yb were recomputed after the values in parentheses had been deleted because of a tendency for elements to have unusually high or low sensitivities when their masses are within approximately 5 mass units of the matrix nuclidic masses. The overall average RSF shown after recomputation is considered to be more indicative of an element's relative sensitivity when the matrix nuclidic masses are not within 5 mass units. Reasons for the unusual elemental sensitivities caused by this effect have not been identified, but space-charge effects both in the ion optical system and on the photographic plate are suspected. Rather large matrix effects have been observed when the ratio of graphite to rare earth in the makeup of the pellet is altered (*i.e.* the sensitivities tended to become similar as the amount of graphite increased).

A convenient method for analysing rare earth samples is to use a two-step process. The first step is a general survey analysis (by sparking metals as self-electrodes or pelleting oxide samples in graphite which has been predoped with indium oxide) prior to any chemical alteration of the sample. The second step involves dissolving the sample in nitric acid, adding an appropriate aliquot of the internal standard (such that reference intensities can be compared with impurity intensities for the same exposure), converting into the oxide, pelleting in pure graphite, and finally sparking two halves of the pellet against each other with subsequent analysis according to Method III. This allows setting of absolute limits on the rare earth determinations and subsequent use of the rare earths determined, as reference elements in the spectra obtained in the first step.

Since a concentration effect has not been observed between 10 and 500 ppm, it is not expected below 10 ppm or in the ppb region, for which many routine rare earth determinations are made in these laboratories.

CONCLUSION

Trace rare earths in rare earth oxide matrices can be determined by spark source mass spectrography. Accuracy approaches that of the inherent photoplate evaluation scheme if the sample is doped with a known level of a reference element of similar chemical and physical properties and within a reasonable mass range. Rare earths themselves best suit these requirements although indium has some value.

Instrumental improvements which give greater control over operating parameters and photoplate evaluation schemes with more valid handling of data are expected to improve significantly the reproducibility for this type of analysis.

Electrical methods[7] for detecting ions are particularly convenient for rare earth determinations, and this new development is also being used at this laboratory to permit improvements in speed and accuracy of these analyses.

Acknowledgements—The authors wish to acknowledge the efforts and assistance of Jennings Capellen in helping to collect the analytical results.

Zusammenfassung—Drei Methoden zur Aufbereitung seltener Erdproben zur massenspektrographischen Analyse werden angegeben. Verfahren zur Zugabe geeigneter innerer Standards werden beschrieben und relative Empfindlichkeitsfaktoren für seltene Erden als Verunreinigungen in den Grundmaterialien Lanthan, Yttrium und Scandium angegeben. Zwar besitzt Indium als innerer Standard in seltenen Erdproben einigen Wert; die besten Analysenergebnisse erzielt man jedoch mit ausgewählten seltenen Erden als inneren Standards.

Résumé—On présente trois méthodes de préparation d'échantillons de terres rares pour l'analyse spectrographique de masse. On décrit des techniques pour l'addition d'étalons internes appropriés et l'on présente les facteurs de sensibilité relative pour les impuretés de terres rares dans les matrices de terres rares lanthane, yttrium et scandium. Quoique l'indium ait quelque valeur comme étalon interne dans les échantillons de terres rares, les meilleurs résultats analytiques sont obtenus lorsqu'on utilise comme étalons internes des terres rares sélectionnées.

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POSSIBILITIES FOR SEPARATION AND SIMULTANEOUS DETERMINATION OF *N*-UNSUBSTITUTED- AND *N*-SUBSTITUTED NITROIMIDAZOLES AND CRITERIA FOR THEIR IDENTIFICATION

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(*Received* 23 *June* 1970. *Accepted* 15 *November* 1970)

Summary—The *N*-unsubstituted nitroimidazoles have an imino hydrogen atom in contrast to the *N*-substituted derivatives, and react with hydroxide to give the yellow nitroimidazole anions. The difficulty of reducing the nitro-group in these anions, together with the shift of the absorption maximum to longer wavelengths makes it possible to analyse polarographically or spectrophotometrically a mixture of *N*-unsubstituted nitroimidazole with *N*-substituted derivatives. The presence of the *N*-unsubstituted nitroimidazole and the *N*-substituted derivatives is first established by chromatography. Other criteria are also proposed for distinguishing between these substances.

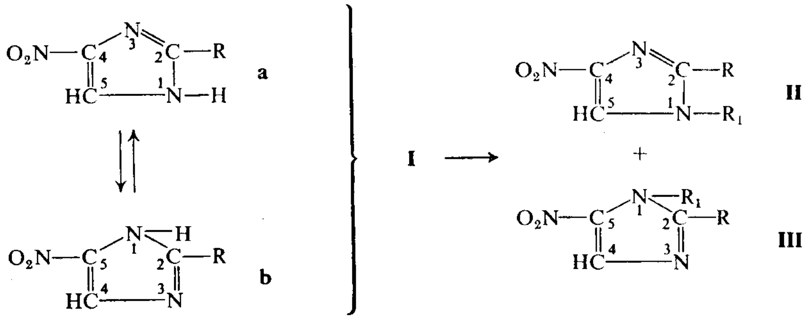
THE NITROIMIDAZOLES in which the nitro-group is in the 4 or 5 position, exist in two tautomeric structures because the hydrogen atom may be bound to either nitrogen atom. Such a compound is designated as 4(5)-nitroimidazole.[1] The 4(5)-nitroimidazole behaves as a mixture of the two tautomers in substitution of the imino hydrogen atom, giving two *N*-substituted derivatives corresponding to 4- and 5-nitroimidazole, respectively (Scheme 1). In contrast, when the nitro group is in the 2 position and positions 4 and 5 are unsubstituted, the compound is not tautomeric and gives only one derivative in substitution of the imino hydrogen atom (Scheme 2).

During substitution according to scheme 1 all three compounds of general formulae **I**, **II** and **III** are usually present, but when substitution proceeds according to scheme 2, only two compounds (**IV** and **V**) are present. These general types of compound differ in properties.

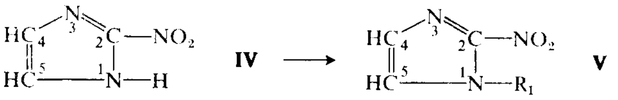
4(5)-Nitroimidazole (**I**) exists in solution as an equilibrium mixture of **Ia** and **Ib**, with **Ia** predominating. Both forms can be protonated, or dissociated to give the yellow nitroimidazole anion.[2–5]

The behaviour of *N*-substituted 4- and 5-nitroimidazoles is often identical with that of the 4(5)-nitroimidazoles. The ultraviolet spectra are very similar in acidic and neutral media,[6,7] but an important difference is that the *N*-substituted compounds do not form anions in alkaline media. The *N*-substituted compounds differ in their pK_{BH^+} values.[1,8] The $E_{1/2}$ values of 4-nitroimidazoles and 4(5)-nitroimidazoles are almost identical in acid, in neutral and in weakly alkaline media. Similar considerations apply to 2-nitroimidazoles (**IV**) and (**V**).

Several methods for thin-layer chromatographic separation[9,10] and for polarographic[11–21] and spectrophotometric[22,23] determination of nitroimidazoles have been



Scheme 1



Scheme 2

suggested. However, a separation and simultaneous analysis of a mixture of nitroimidazoles during the process of substitution of the imino hydrogen atom has not yet been proposed.

This paper presents analytical methods for identification and simultaneous determination of *N*-unsubstituted nitroimidazole and *N*-substituted derivatives.

EXPERIMENTAL

Chromatography

Thin-layer chromatography (TLC) was done on unactivated 0·25-mm layers of silica gel G, in an atmosphere saturated with solvent by evaporation from a smooth filter paper folded in a U-shape and placed in the solvent reservoir. Development was at room temperature for 20–30 min (solvent front travel $\sim$0·15 m). Tin(II) chloride and *p*-dimethylaminobenzaldehyde mixture[24] was used as detecting reagent. *N*-Unsubstituted nitroimidazoles and 5-nitroimidazoles give two different red colours, and the 4-nitroimidazoles give a yellow colour. The developers used are listed in Table I.

Polarography

The cell used had a separated calomel electrode.

RESULTS AND DISCUSSION

Chromatographic separations

Table I lists the conditions and R_f values for the 2- methyl-4(5)-nitroimidazole(**VI**), 1-(2-hydroxyethyl)-2-methyl-4-nitroimidazole(**VII**), 1-(2-hydroxyethyl)-2-methyl-5-nitroimidazole(**VIII**) (Metronidazole), 1,2-dimethyl-4-nitroimidazole(**IX**), 1,2-dimethyl-5-nitroimidazole(**X**) (Dimetridazole), 1-(carboxymethyl)-2-methyl-4-nitroimidazole(**XI**), 1-(carboxymethyl)-2-methyl-5-nitroimidazole(**XII**), 1-(carbomethoxymethyl)-2-methyl-4-nitroimidazole(**XIII**), 1-(carbomethoxymethyl)-2-methyl-5-nitroimidazole(**XIV**), 1-(carbethoxymethyl)-2-methyl-4-nitroimidazole(**XV**), 1-(carbethoxymethyl)-2-methyl-5-nitroimidazole(**XVI**), 4(5)-nitroimidazole(**XVII**), 2-ethyl-4(5)-nitroimidazole(**XVIII**), 1-methyl-2-nitroimidazole(**XIX**) and 2-nitroimidazole(**IV**). For separation of **VI**, **VII** and **VIII** or **VI**, **IX** and **X**, or of **IV** and **XIX**, we recommend developer 1; for separation of **VI**, **XI** and **XII**, developer 2; for separation of **VI**, **XIII** and **XIV** or **VI**, **XV** and **XVI**, developer 3.

TABLE I.—CHROMOATOGRAPHIC SEPARATIONS

Compound	R_f values		
	Developer 1	2	3
IV	~0		
VI	0·06	0·83	0·37
VII	0·35		
VIII	0·65		
IX	0·25		
X	0·65		
XI	~0	0·56	
XII	~0	0·46	
XIII	~0		0·38
XIV	~0		0·49
XV	~0		0·39
XVI	~0		0·55
XVII	0·06		
XVIII	0·06		
XIX	0·45		

Developer 1—diethylamine.
Developer 2—n-butanol–acetone–acetic acid (75:75:1).
Developer 3—benzene–diethylether–acetic acid–methanol (30:30: 9:5).

Simultaneous polarographic determinations

Sodium hydroxide has been used as supporting electrolyte for simultaneous determination of **VI**, **VII** and **VIII**[25] and of **VI**, **IX** and **X**.

In aqueous Britton-Robinson universal buffers over the range pH 2–10, and in sodium hydroxide solutions of various concentrations, **VII** and **IX** yield reduction waves with more negative half-wave potentials than those for **VIII** and **X**. It seems logical that the compounds in which the nitro-group is located near the electron-donor system (tertiary nitrogen) should reduce at a more negative potential. Therefore, at pH 2–10, $E_{1/2}$ for **VI** is almost the same as that for **VII** and **IX**, but in strongly alkaline medium is considerably more negative than that for **VII** and **IX** because of the difficulty of reducing a nitro-group in a nitroimidazole anion (which is not produced in the case of the *N*-substituted nitroimidazoles). So in $0{\cdot}1M$ sodium hydroxide it is possible to determine simultaneously **VI**, **VII** and **VIII** ($E_{1/2}$ values −0·90, −0·68 and −0·57 V respectively) or **VI**, **IX** and **X** ($E_{1/2}$ values −0·90, −0·70 and −0·58 V respectively); see Fig. 1. These compounds appear together in the reaction mixtures during the synthesis of Metronidazole(**VIII**) and Dimetridazole(**X**), respectively.

All 4(5)-nitroimidazoles, being compounds with an imino hydrogen atom, show the same behaviour in a strongly alkaline medium. Thus the three *N*-unsubstituted 4(5)-nitroimidazoles **VI**, **XVII** and **XVIII** have similar $E_{1/2}$ values, −0·90, −0·92 and −0·91 V *vs*. S.C.E.

Because of the tautomeric nature of 4(5)-nitroimidazoles, two *N*-substituted nitroimidazole isomers are obtained after substitution of the imino hydrogen atom. The simultaneous polarographic determination of isomeric pairs is possible only if their $E_{1/2}$ values differ by at least 100 mV. Such is the case with **VII** and **VIII**, and **IX** and **X**, although the differences are rather small ($\Delta E_{1/2}$ is about 110 mV). The $\Delta E_{1/2}$ values for the pairs **XI** and **XII**, **XIII** and **XIV**, and **XV** and **XVI** are not sufficient, however, for simultaneous determination. The difference in $E_{1/2}$ between two

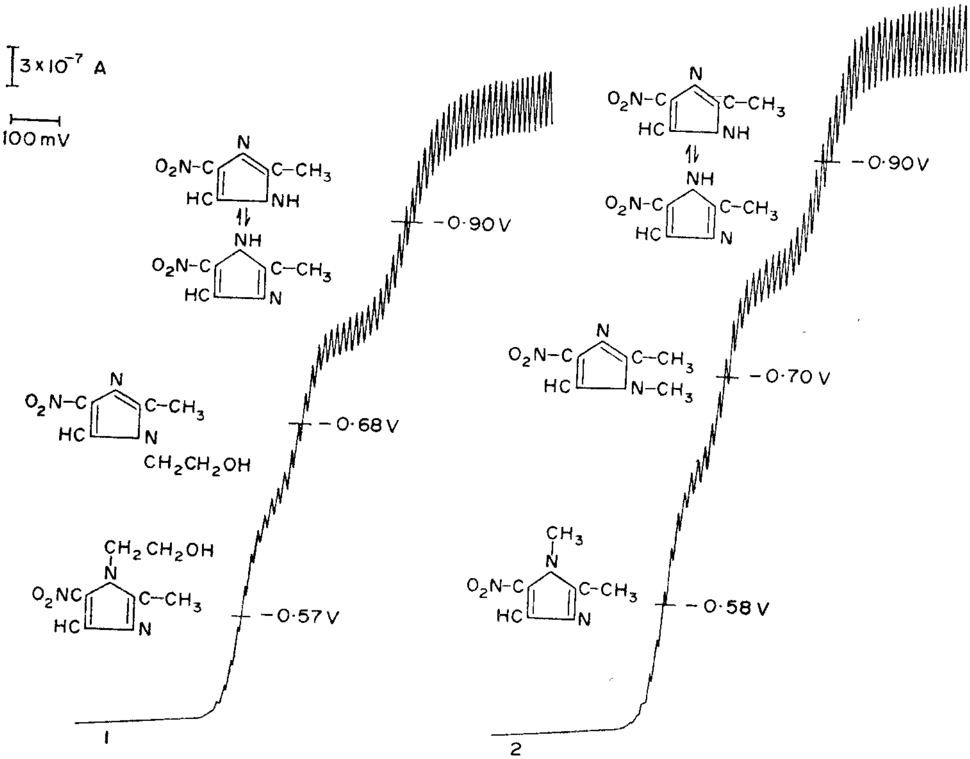


FIG. 1.—Curve 1, equimolar mixture of 2-methyl-4(5)-nitroimidazole(VI), 1-(2-hydroxyethyl)-2-methyl-4-nitroimidazole (VII) and 1-(2-hydroxyethyl)-2-methyl-5-nitroimidazole (VIII) (Metronidazole). Curve 2, equimolar mixture of 2-methyl-4(5)-nitroimidazole (VI), 1,2-dimethyl-4-nitroimidazole (IX) and 1,2-dimethyl-5-nitroimidazole (X) (Dimetridazole).

0·1*M* sodium hydroxide as supporting electrolyte. Concentration of each compound is $10^{-4}M$. The curves start at −0·2 V *vs.* S.C.E.

isomeric pairs is influenced by the nature of other substituents in the molecule, especially by the substituent in position 1.

As expected, compounds **IV** and **XIX** have almost identical $E_{1/2}$ values in acid and neutral media, but in strongly alkaline medium $E_{1/2}$ for **IV** is shifted considerably, which makes it possible to determine the compounds simultaneously ($E_{1/2}$ in 0·1*M* sodium hydroxide for **IV** is −0·84 V; for **XIX** −0·51 V; Fig. 2).

Simultaneous spectrophotometric determination

All the nitroimidazoles examined absorb in the ultraviolet when in neutral and acid media. In 0·1*M* sodium hydroxide the spectra of the *N*-unsubstituted nitroimidazoles (but not those of the *N*-substituted derivatives) are shifted to the near visible region of the spectrum.[2,7,8,26–29] This may be utilized to determine the content of any *N*-unsubstituted derivative occurring together with *N*-substituted derivatives. When it has been chromatographically established that the reaction mixture contains only one *N*-substituted derivative together with the *N*-unsubstituted one, it is possible to determine both compounds simultaneously in 0·1*M* sodium hydroxide.

The polarographic or spectrophotometric method, using 0·1*M* sodium hydroxide

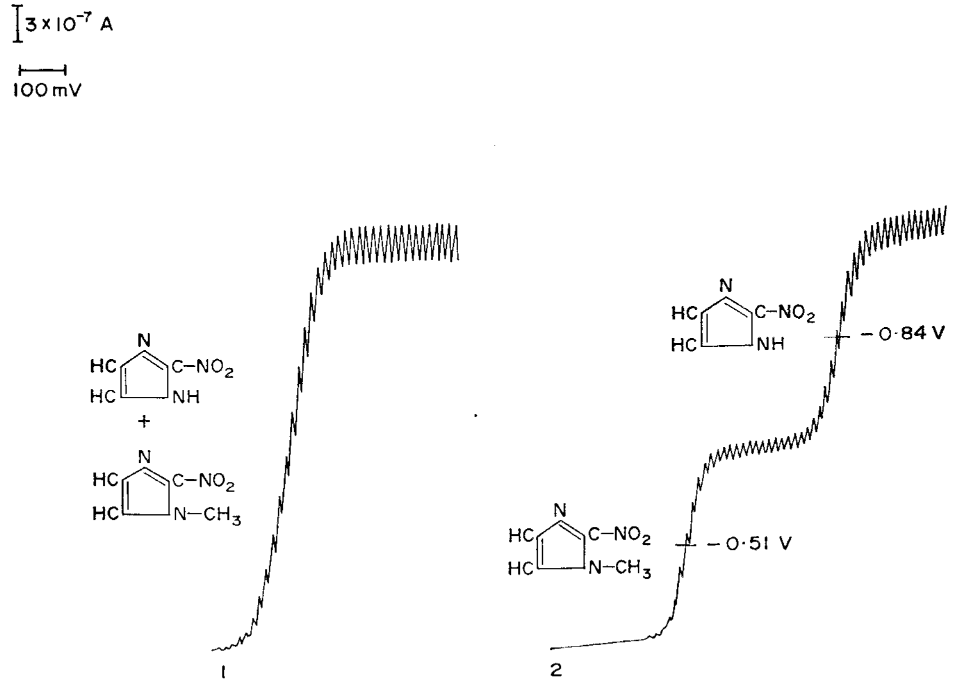


FIG. 2.—Curves 1, 2, equimolar mixture of 2-nitroimidazole (IV) and 1-methyl-2-nitroimidazole (XIX).

Curve 1, Britton-Robinson buffer pH 4·3; curve 2, 0·1*M* sodium hydroxide. Concentration of each compound is $10^{-4}M$. Curve 1 starts at 0 V *vs.* S.C.E. Curve 2 starts at −0·2 V *vs.* S.C.E.

as a medium, should be generally applicable to mixtures of this type and to mixtures of the heterocyclics with properties similar to those of these compounds.

Some criteria for distinguishing N-unsubstituted nitroimidazoles and their N-*substituted derivatives*

The following criteria are indicative of N-unsubstituted nitroimidazoles.

1. Red colour with tin(II) chloride in *p*-dimethylaminobenzaldehyde reagent on silica gel thin layers.
2. Absorption in the ultraviolet in acid and neutral media, but in the near visible in strongly alkaline media.
3. A strongly negative shift of $E_{1/2}$ of *N*-unsubstituted nitroimidazoles in strongly alkaline media, from that at pH 2–8, where 4(5)- and 2-nitroimidazoles have nearly the same $E_{1/2}$ values as 4- and *N*-substituted 2-nitroimidazoles, respectively.
4. An *N*-unsubstituted nitroimidazole does not decompose on standing for 24 hr at room temperature in 0·5*M* sodium hydroxide, in contradistinction to *N*-substituted derivatives.

To differentiate between 4- and 5-nitroimidazole isomers NMR has been proposed.[30,31] The following criteria may also be used.

1. In the developers 1 and 3 a 4-nitroimidazole exhibits a lower R_f value than does the corresponding 5-nitroimidazole.
2. On thin layers of silica gel, with tin(II) chloride in *p*-dimethylaminobenzaldehyde

reagent, the 4-nitroimidazoles give a yellow colour and 5-nitroimidazoles a red.

3. $E_{1/2}$ values of the 4-nitroimidazoles are more negative than those of the corresponding 5-nitroimidazoles in buffers at pH 2–10, or in 0·1*M* sodium hydroxide. In the latter, at a potential that reduces 4-nitroimidazole, a 4(5)-nitroimidazole will not be reduced, which permits, besides simultaneous determination of the compounds, conclusions to be drawn about the structure of the compounds.
4. If a 4-nitroimidazole and the corresponding 5-nitroimidazole are to be differentiated, the 4-compound shows the least degradation after standing in 0·5*M* sodium hydroxide for 24 hr (if the degradation is so rapid that this treatment destroys the compounds, 0·1*M* alkali can be used, or the reaction time shortened).

EXAMPLE—DETERMINATION OF DIMETRIDAZOLE IN REACTION MIXTURES

Dimetridazole (1,2-dimethyl-5-nitroimidazole, **X**) is a new drug for the prevention and treatment of blackhead in turkeys and chickens, canker in pigeons[10] and vibrionic dysentery in swine,[32] and is obtainable as a pure preparation. It can be identified by TLC[10] and determined polarographically[11,17,19,20] or spectrophotometrically.[23] To optimize conditions for its synthesis, however, it must be determined together with the starting material **VI** and the reaction product 4-isomer **IX**.

Simultaneous polarographic determination of **VI**, **IX** *and* **X**

In acid media **X** gives a diffusion-controlled 4-electron wave deformed by a sharp maximum; a small addition of gelatin (0·005%) suppresses the maximum completely. The half-wave potentials of the 4-electron wave shift to more negative values by −0·063 V per pH unit ($E_{1/2}$ = −0·19 V at pH 3·4 and −0·62 V at pH 10·2). A second, 2-electron, wave appears at a more negative potential. In alkaline media a 6-electron reduction takes place.

In acid media **IX** behaves similarly, but the first wave is at a more negative potential ($E_{1/2}$ = −0·16 V at pH 2·3 and −0·66 V at pH 10·2). With increasing pH values the height of the second, 2-electron, wave decreases and the wave vanishes completely at pH > 9.

In acid, neutral and weakly alkaline media the half-wave potentials of **VI** and **IX** are almost identical. In a strongly alkaline medium $E_{1/2}$ of **VI** is shifted to a considerably more negative potential. So, in 0·1*M* sodium hydroxide it is possible to determine simultaneously **VI**, **IX** and **X** at −0·90, −0·70 and −0·58 V respectively. The wave-heights are a linear function of concentration from 5×10^{-5} to $2 \times 10^{-3}M$ for each compound. There is, however, a drawback in the use of the strongly alkaline solution, as only **VI** is stable under these conditions. An alkaline solution is necessary for complete conversion into the nitroimidazole anion,[2] and the loss by decomposition must be compensated for by working to a strict time schedule, with measurement of polarograms at a fixed time after the solution has been made alkaline. The method of standard addition is used.

Procedure. Weigh a sample from the reaction mixture, dissolve it in distilled water and make up to 100 ml, so that the concentration of nitroimidazoles is about $10^{-3}M$. Transfer a 2-ml portion to a polarographic cell, and add water (3 ml) and 0·2*M* sodium hydroxide (5 ml). Deaerate the solution with pure nitrogen for exactly 5 min and then record the polarogram over the range from −0·2 to −1·2 V *vs.* S.C.E.

Transfer another 2-ml portion of the sample solution to a polarographic cell, and add 1 ml each of $1 \times 10^{-3}M$ standard solutions of **VI**, **IX** and **X** and 5 ml of 0·2*M* sodium hydroxide, and proceed

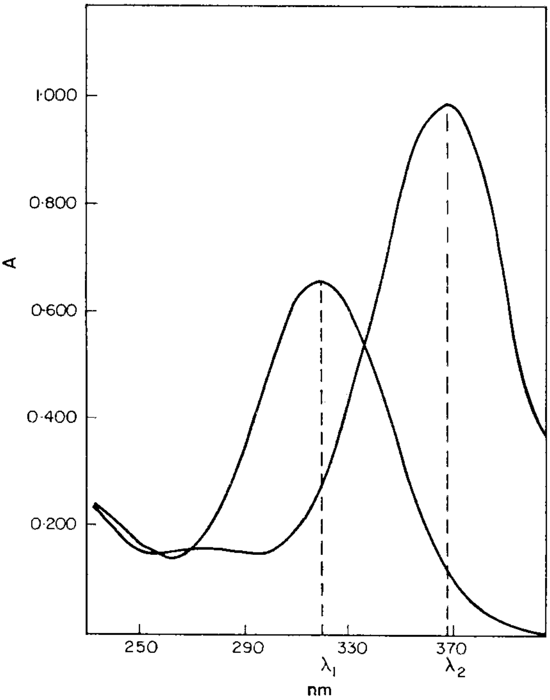


FIG. 3.—Ultraviolet spectra of 2-methyl-4(5)-nitroimidazole (VI) and 1,2-dimethyl-5-nitroimidazole (X) (Dimetridazole) in 0·1*M* sodium hydroxide. Concentration of the compounds is 10 μg/ml.

as before. If it has been chromatographically established that **IX** is absent, then add 1 ml of standard solution of **VI** and 2 ml of standard solution of **X**. Evaluate the polarograms by

$$\% = \frac{h \cdot c \cdot 100}{h' \cdot w}$$

where % = amount of compound present in the reaction mixture, h = wave-height for the sample, c = weight of standard added (g), w = weight of the sample in the cell (g), h' = wave-height for the standard (*i.e.* increase in wave-height when standard is added).

Simultaneous spectrophotometric determination of VI *and* X

In 0·1*M* sodium hydroxide **VI** gives a maximum at 368 nm and **X** at 320 nm (Fig. 3). Grimison[22] has used these conditions for the determination of compounds present in reaction mixtures after the alkaline methylation of 4(5)-nitroimidazoles.

Procedure. Weigh a sample from the reaction mixture and dissolve it in 0·1*M* sodium hydroxide to give a standard volume (*e.g.* 100 ml) of nitroimidazole concentrations of about 10 μg/ml. Measure the absorbance at 368 and 320 nm in 10-mm silica cells against the alkali as reference.

Determine the composition by application of similtaneous equations. The absorptivities have been determined, and can be used to give the empirical equations $c_1 = 10{\cdot}67A_2 - 1{\cdot}71A_1$; $c_2 = 0{\cdot}81A_1 - 5{\cdot}02A_2$, where A_1 = absorbance at 320 nm, A_2 = absorbance at 368 nm, c_1 = μg of VI/ml and c_2 = μg of X/ml.

Acknowledgements—We wish to express our gratitude to Dr. P. Viaud, Directeur des Recherches Pharmaceutiques Rhone-Poulenc, Paris; to Dr. M. Kochergin, Ordzhonikidze, S., All-Union Scientific-Research Chemical-Pharmaceutical Institute, Moscow; and to Mr. R. Maksimović and Mr. S. Mikalački, Research Laboratory "Galenika" Zemun, for preparing the substances we used in our investigations.

Zusammenfassung—Die nicht N-substituierten Nitroimidazole haben im Gegensatz zu den N-substituierten Derivaten ein Imino-Wasserstoffatom und regieren mit Hydroxid zu den gelben Nitroimidazol-Anionen. Die schwierige Reduzierbarkeit der Nitrogruppe in diesen Anionen sowie die langwellige Verschiebung des Absorptionsmaximums ermöglicht die polarographische oder spektrophotometrische Analyse eines Gemisches aus nicht N-substituiertem Nitroimidazol und N-substituierten Abkömmlingen. Die Anwesenheit des nicht N-substituierten Nitroimidazols und der N-substituierten Derivate wird zuerst durch Chromatographie festgestellt. Auch andere Kriterien zur Unterscheidung dieser Substanzen werden vorgeschlagen.

Résumé—Les nitroimidazoles N-non substitués ont un atome d'hydrogène imino, à l'opposé des dérivés N-substitués, et réagissent avec l'hydroxyde pour donner les anions nitroimidazole jaunes. La difficulté de réduction du groupe nitro dans ces anions, jointe au déplacement du maximum d'absorption vers les plus grandes longueurs d'onde rend possible d'analyser polarographiquement ou spectrophotométriquement un mélange de nitroimidazole N-non substitué avec des dérivés N-substitués. La présence de nitroimidazole N-non substitué et des dérivés N-substitués est d'abord établie par chromatographie. On propose aussi d'autres critères pour distinguer entre ces substances.

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Talanta, 1971, Vol. 18, pp. 683 to 689. Pergamon Press. Printed in Northern Ireland

SENSITIVITY AND DETECTABILITY FOR MANGANESE(II) DETERMINATION IN SOLUTION BY KINETIC METHODS OF ANALYSIS

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(*Received* 21 *September* 1970. *Accepted* 21 *October* 1970)

Summary—The use of nitrilotriacetic acid to enhance the catalytic effect of manganese ions on the oxidation of Malachite Green cations is reported. This effect permits a noticeable increase in sensitivity for the determination of micro and submicro amounts of manganese ions in aqueous solution. The detectability, however, is not so dramatically altered. Comparison is made with other kinetic methods for the determination of manganese in solution.

THE IMPORTANCE of manganese determinations in solution at the microgram level is widely recognized. Such determinations can be accomplished by oxidation of manganese(II) to permanganate with periodate or persulphate as oxidizing agents.[1] Kinetic methods of analysis based on the catalytic role of manganese(II) seem, however, to offer a more sensitive and reliable approach at the microgram and submicrogram levels.[2]

In connection with an investigation into the use of manganese(II) as a catalytic titrant, a considerable increase was observed in the rate of oxidation of the Malachite Green cation (MG^+) by periodate in acetate-phosphate buffers of pH 3·50 and 5·50 in the presence of certain aminopolycarboxylic acids.[3] The shape of the catalytic titration curves[3] made it explicit that either nitrilotriacetic acid (NTA) promoted the catalytic effect of manganese ions or the NTA–Mn complex(es) formed exerted a more pronounced catalytic effect than the hydrated manganese ions alone. This provided a basis for increasing the sensitivity of determinations of manganese(II) in aqueous solution. The results reported here were collected to evaluate the effect of NTA on the sensitivity, detectability, and reliability of the kinetic determination of micro and submicro amounts of manganese in solution.

EXPERIMENTAL

Reagents and solutions

All chemicals used, except the Malachite Green perchlorate, were of analytical grade. Water was purified by distilling demineralized distilled water in a borosilicate glass still equipped with a quartz immersion heater.

The possible metal content of NTA and other aminopolycarboxylic acids used was reduced as described earlier.[3] The Malachite Green perchlorate was prepared by Therold E. Bailey, of our department, from Malachite Green oxalate by precipitation with excess of sodium perchlorate in aqueous solution. The product, filtered off, washed with cold water and dried over concentrated sulphuric acid in a vacuum desiccator, gave an elemental analysis corresponding to the formula $C_{23}H_{25}N_2ClO_4$. The use of an ultrasonic cleaner (disintegrator) ensures quick and complete dissolution of Malachite Green perchlorate in water. Buffers and other solutions were prepared and handled as reported earlier.[3]

Apparatus

A Cary 14 spectrophotometer and 10-mm glass cells that were kept at 25·0 ± 0·2° by circulating water through a jacketed cell-holder.

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Experimental procedure for kinetic measurements

The change in absorbance of the reacting mixture was followed during the 15 min after starting time. The reactants, solution *1* (Malachite Green and catalyst), and solution *2* (buffer, aminopolycarboxylic acid and periodate) were brought to 25° in a water-bath, then mixed, and the timer was started. Overall pseudo first-order constants, k^*, were calculated as slopes of first-order plots.

RESULTS AND DISCUSSION

Some values of k^* are given in Table I. Values obtained by using ethylenediamine-*N*,*N*,*N*′,*N*′-tetra-acetic acid (EDTA) and ethyleneglycol bis(2-aminoethyl ether)tetra-acetic acid (EGTA) are included for comparison. Both EDTA and EGTA have been observed to increase the rate of the catalysed reaction at $\text{pH} > 5$. EGTA also increases the catalytic effect of manganese at the lower pH of 3·40, but EDTA acts as an inhibitor at this pH.

The kinetics and mechanism(s) of the catalysed and/or promoted reactions offer quite a variety of interesting points and though a detailed report is outside the scope of this note, a few trends are presented below since they are significant for the analytical application.

The effect of the aminopolycarboxylic acid is in general preceded by an "induction period" similar to the one observed with manganese alone at the 10^{-5}–$10^{-6}M$ level. This induction period, as would be expected, decreases as the concentration of aminopolycarboxylic acid or manganese increases. Such a trend is shown in Figs. 1 and 2. This short induction period is very probably associated with either the accumulation

TABLE I.—EFFECT OF SOME AMINOPOLYCARBOXYLIC ACIDS ON THE OVERALL PSEUDO FIRST-ORDER CONSTANT FOR THE OXIDATION OF MALACHITE GREEN CATION BY PERIODATE IONS, CATALYSED BY MANGANESE(II)

Ligand concentration, *M*	Mn(II) concentration *M*	$k^* \times 10^2$, *min*$^{-1}$ pH = 3·40	pH = 5·40
None	None	0·505	0·295
None	$1\cdot02 \times 10^{-7}$	0·570	0·631
	$5\cdot10 \times 10^{-7}$	1·42 (*a*)	
	$1\cdot02 \times 10^{-6}$	0·553 (*b*)	1·72
		3·05 (*c*)	
NTA, $1\cdot02 \times 10^{-6}$	$1\cdot02 \times 10^{-7}$	0·701	0·802
	$5\cdot10 \times 10^{-7}$	3·21 (*b*)	1·43 (*c*)
	$1\cdot02 \times 10^{-6}$	7·05	2·19
$1\cdot02 \times 10^{-5}$	$1\cdot02 \times 10^{-7}$	2·07 (*c*)	1·70
	$5\cdot10 \times 10^{-7}$	13·7	7·74
	$1\cdot02 \times 10^{-6}$	34·9	17·0
$1\cdot02 \times 10^{-4}$	$5\cdot10 \times 10^{-8}$		5·15
	$1\cdot02 \times 10^{-7}$	3·71	9·65 (*a*)
EDTA, $1\cdot07 \times 10^{-5}$	$1\cdot02 \times 10^{-7}$		0·17 (*a*)
			0·28 (*b*)
	$5\cdot10 \times 10^{-7}$		0·74 (*d*)
			5·53 (*c*)
EGTA, $1\cdot09 \times 10^{-5}$	$5\cdot10 \times 10^{-7}$	0·32 (*d*)	
		6·23 (*b*)	

Initial concentration of MG^+: $1\cdot00$–$1\cdot33 \times 10^{-5}M$.
Initial periodate concentration: $3\cdot10 \times 10^{-3}M$.
Temperature: 25 ± 0·2°. Time interval: 15 min, except: (*a*) 1–6 min, (*b*) 7–15 min, (*c*) 3–15 min, (*d*) 1–3 min.
$k^* = [\log (A_1/A_2)]/(t_2 - t_1)$, where A_1 and A_2 are the absorbances at times t_1 and t_2 respectively.

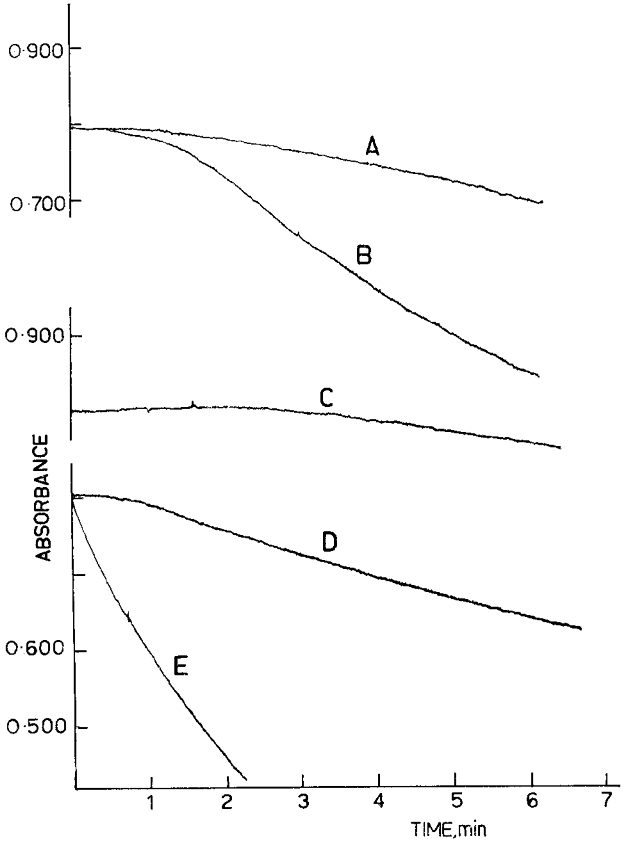

FIG. 1.—Effect of NTA concentration on "induction period."
Initial concentrations: MG^+ $1{\cdot}33 \times 10^{-5}M$; Mn(II) $1{\cdot}02 \times 10^{-7}M$; periodate $3{\cdot}10 \times 10^{-3}M$; phosphate–acetate buffers.
A: pH = 3·40, NTA = $1{\cdot}02 \times 10^{-5}M$
B: pH = 3·40, NTA = $1{\cdot}02 \times 10^{-4}M$
C: pH = 5·40, NTA = $1{\cdot}02 \times 10^{-6}M$
D: pH = 5·40, NTA = $1{\cdot}02 \times 10^{-5}M$
E: pH = 5·40, NTA = $1{\cdot}02 \times 10^{-4}M$

of catalyst in the required form [manganese(III) or (IV)] or combination with a reactive intermediate as in a free radical mechanism. If the concentration of the ligand is increased at the lower pH, the induction period is eliminated as can be seen in Fig. 3, curves *A* and *C*. At the higher pH of 5·40, however, the course of the reaction seems quite different and the rate is faster during the first 3–5 min, slowing down somewhat after this time (curves *B* and *D*, Fig. 3). Even though good first-order plots can be constructed from the experimental results, computer calculations have shown in some cases a continuous decrease in the instantaneous slopes for the first-order treatment, as shown in Table II. A plot of $1/[MG^+]$ *vs.* time, for instance, for the reaction at pH 5·40 with $1{\cdot}02 \times 10^{-4}M$ NTA and $1{\cdot}02 \times 10^{-7}M$ manganese, comes closer to a straight line after 5 min of reaction than does the first-order plot.

From a practical analytical viewpoint the use of NTA to improve the sensitivity and detectability for traces of manganese in solution by use of the basic method

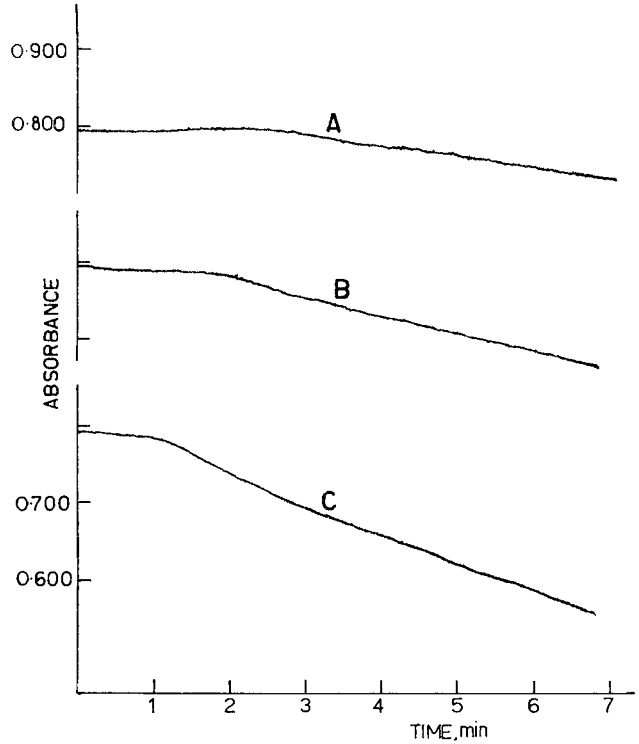

FIG. 2.—Effect of manganese concentration on the "induction period". MG+ at zero time, $1 \cdot 33 \times 10^{-5}M$; periodate $3 \cdot 10 \times 10^{-3}M$; NTA $1 \cdot 02 \times 10^{-6}$; pH 5·40 (phosphate–acetate buffer). Manganese(II): *A*: $1 \cdot 02 \times 10^{-7}M$, *B*: $5 \cdot 10 \times 10^{-7}M$, *C*: $1 \cdot 02 \times 10^{-6}M$.

TABLE II.—CHANGE IN INSTANTANEOUS SLOPE WITH TIME FOR THE FIRST ORDER TREATMENT OF DATA

Time, *min*	k^* *min*$^{-1}$	Time, *min*	k^* *min*$^{-1}$
1	$10 \cdot 6 \times 10^{-2}$	8	$5 \cdot 91 \times 10^{-2}$
2	$10 \cdot 3 \times 10^{-2}$	9	$4 \cdot 74 \times 10^{-2}$
3	$9 \cdot 60 \times 10^{-2}$	10	$4 \cdot 39 \times 10^{-2}$
4	$9 \cdot 01 \times 10^{-2}$	11	$3 \cdot 86 \times 10^{-2}$
5	$8 \cdot 53 \times 10^{-2}$	12	$4 \cdot 08 \times 10^{-2}$
6	$7 \cdot 51 \times 10^{-2}$	13	$3 \cdot 38 \times 10^{-2}$
7	$6 \cdot 79 \times 10^{-2}$	14	$3 \cdot 17 \times 10^{-2}$

MG+ $1 \cdot 30 \times 10^{-5}M$; periodate $3 \cdot 10 \times 10^{-3}M$; pH 5·40 (acetate–phosphate); temperature 25 ± 0·2°; Mn(II) $1 \cdot 02 \times 10^{-7}M$; NTA: $1 \cdot 02 \times 10^{-4}M$.

developed by Fernandez *et al.*[4] was the main point under consideration in this study. This method operates at a relatively low pH, offering some selectivity over those at higher pH values. The term "detectability" will be used here to indicate the "smallest quantity of material that can be detected with certainty."[5] Sensitivity, on the other hand, will be defined as "the ratio of change in the output signal (or physical parameter) produced by an increment of the material to be determined to

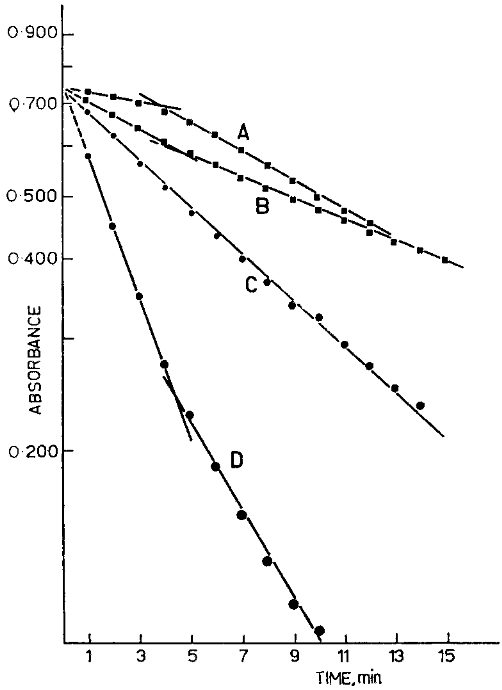

FIG. 3.—Typical first-order plots in presence of NTA.
MG$^+$ and periodate concentrations as in Figs. 1 and 2. Phosphate-acetate buffers.
Manganese(II) 1·02 × $10^{-7}M$.
A: pH = 3·40, NTA = 1·02 × $10^{-5}M$.
B: pH = 5·40, NTA = 1·02 × $10^{-5}M$.
C: pH = 3·40, NTA = 1·02 × $10^{-4}M$.
D: pH = 5·40, NTA = 1·02 × $10^{-4}M$.

that increment."[5] Figure 4 shows a plot of k^* values *vs.* manganese concentration for reactions in the presence of NTA. An increase in NTA concentration from 1·02 × 10^{-6} to 1·02 × $10^{-5}M$ increases the sensitivity considerably but the gain in detectability is insignificant. An NTA concentration of 1·02 × $10^{-4}M$ allows detection of smaller amounts of manganese, but the sensitivity is smaller for lower than for higher concentrations of manganese (curve *A*, Fig. 4). A similar situation has recently been reported[3] in the comparison of two kinetic methods for determination of microgram amounts of EDTA. Lower values for the detectability can be obtained, of course, if the absorbance is measured after a longer time (*cf.* Ref. 4, where to reach a detectability of ~0·4 ng/ml measurements were made 3 hr or more after mixing). The incorporation of NTA at the $10^{-4}M$ concentration level shortens this time considerably. NTA at the $10^{-3}M$ level did not increase the sensitivity or improve the detectability. Taking into account speed and simplicity, the method by Janjic *et al.*[2] offers probably the lowest value reported for the detectability of manganese in aqueous solution by kinetic methods. They report that the "differential" method[6] allows determinations at the 0·30 ng/ml level with very good accuracy, in 5 min. If their method of determination is extrapolated to the 5 × $10^{-8}M$ manganese level, the change in absorbance for the same period is 0·109; for the method using NTA ($10^{-4}M$) the corresponding value is 0·202. If the comparison is made at the $10^{-7}M$ manganese level with 10^{-4} or

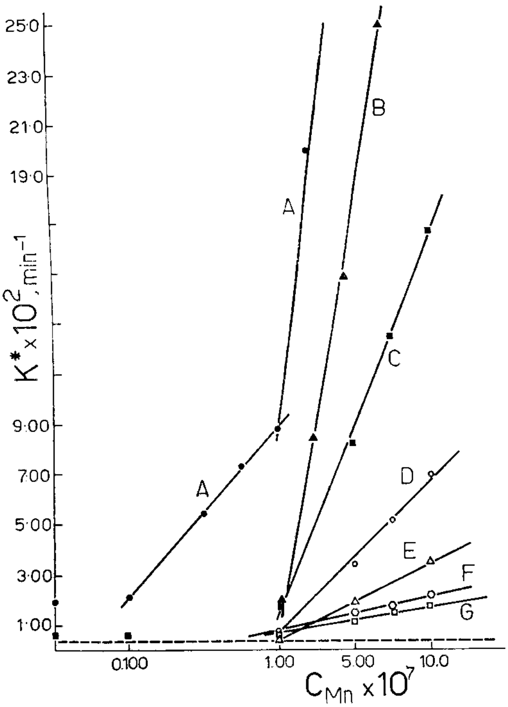

FIG. 4.—Plots of k^* *vs.* manganese concentration.
Malachite Green and periodate concentration, and buffer composition as in previous figures.
A: pH = 5·40, NTA = $1\cdot02 \times 10^{-4}M$
B: pH = 3·40, NTA = $1\cdot02 \times 10^{-5}M$
C: pH = 5·40, NTA = $1\cdot02 \times 10^{-5}M$
D: pH = 3·40, NTA = $1\cdot02 \times 10^{-6}M$
E: pH = 3·40, NTA = none
F: pH = 5·40, NTA: $1\cdot02 \times 10^{-6}M$
G: pH = 5·40, NTA: none.

$10^{-5}M$ NTA, the approach reported here is still more sensitive. The relative standard deviation for 10 determinations of $5\cdot08 \times 10^{-8}M$ manganese was 0·8%.

CONCLUSION

A distinction between sensitivity and detectability is shown to be necessary in certain methods of analysis using kinetics. The incorporation of NTA ($\sim 10^{-5}M$) in the reaction mixture of Malachite Green and periodate in acetate–phosphate buffers (pH = 3·40)[4] results in a considerable increase in sensitivity for the determination of manganese in solution at concentrations of $10^{-7}M$ or larger. With NTA concentrations of the order of $10^{-4}M$ it is possible to improve the detectability and obtain a sensitivity that compares well with that reported for other kinetic methods of analysis for manganese in solution.

Acknowledgements—The National Science Foundation is gratefully acknowledged for financial aid (Grant No. GP-8284) in acquiring the Cary 13 spectrophotometer. The authors are indebted to Steve A. Rigney and Benny E. Simpson for obtaining and checking certain experimental results. This work was supported by the Research Foundation (Oklahoma State University) and the National Science Foundation (Grant No. GP-13472).

Zusammenfassung—Es wird über die Verwendung von Nitrilotriessigsäure zur Verstärkung des katalytischen Effekts von Manganionen auf die Oxidation von Malachitgrün-Kationen berichtet. Dieser Effekt erlaubt eine merkliche Steigerung der Empfindlichkeit bei der Bestimmung von Mikro- und Submikromengen Manganionen in wäßriger Lösung. Die Nachweisgrenze jedoch wird nicht so stark geändert. Vergleiche mit anderen kinetischen Methoden zur Bestimmung von Mangan in Lösung werden angestellt.

Résumé—On rapporte l'emploi d'acide nitrilotriacétique pour exalter l'influence catalytique d'ions manganèse sur l'oxydation de cations Vert Malachite. Cette influence permet un accroissement notable en sensibilité pour la détermination de micro- et submicroquantités d'ions manganèse en solution aqueuse. La possibilité de détection, toutefois, n'est pas si sérieusement modifiée. On effectue une comparaison avec d'autres méthodes cinétiques pour la détermination du manganèse en solution.

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Talanta, 1971, Vol. 18, pp. 691 to 696. Pergamon Press. Printed in Northern Ireland

PROPERTIES AND ANALYTICAL APPLICATIONS OF THE HETEROPOLYMOLYBDATES OF PHOSPHORUS, ARSENIC, SILICON AND GERMANIUM—IV*

DETERMINATION OF PHOSPHOMOLYBDIC AND SILICOMOLYBDIC ACIDS *VIA* THE MOLYBDENUM CONTENT, WITH PHENYLFLUORONE

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(*Received* 3 *March* 1970. *Accepted* 15 *November* 1970)

Summary—Procedures are proposed for the determination of phosphorus and silicon in the ppM range, by extraction of phosphomolybdic and silicomolybdic acids with organic solvent, decomposition of the complex and spectrophotometric determination of its molybdenum content.

THE DETERMINATION OF small amounts of phosphorus and silicon is gaining in practical importance. The molar absorptivity of phosphomolybdic and silicomolybdic acids, even in organic solvents, is 2·0–2·4 × 10^3 l.mole^{-1}.mm^{-1}, and that of molybdenum blue is somewhat lower. Boltz and co-workers[1,2] have proposed new methods based on the determination of the molybdenum content of the heteropoly acids, in which case the 1:12 molar ratio gives an amplification effect. The heteropoly acids were extracted with an organic solvent, and the extract was scrubbed with hydrochloric acid to remove traces of molybdate reagent. The heteropoly acid was decomposed with ammonia–ammonium chloride buffer and the stripped molybdenum measured at 230 nm. The method is more cumbersome than the direct determinations and the sensitivity improved by only a factor of 2. Absorption in the far ultraviolet range arises from the small amount of organic solvent carried over into the aqueous solution.

We thought the method could be improved by forming a molybdate complex with a considerably higher absorptivity at a wavelength in the visible range. For this purpose we selected the phenylfluorone[3] and the methylfluorone[4] methods, but prefer the former.

For phosphomolybdic acid it is sufficient to shake the organic phase with water in order to decompose the complex and strip the molybdenum. For silicomolybdic acid, however, a buffer solution at pH 8–9 is needed to decompose the complex, and the electrolyte tends to interfere by precipitating colloidal molybdenum-phenylfluorone complex. In order to prevent this, a medium containing at least 60% of alcohol is needed.

The red complex formed by molybdenum(VI) with either fluorone is soluble in alcohol and remains in aqueous solution in presence of acids and gum arabic. The absorption maximum is at 526 nm (Fig. 1), where the absorption of the reagent is negligible. A solution containing 0·1 mg of molybdenum, mixed with 1 ml of 0·5% gum arabic solution and 0·75 ml of 5*M* sulphuric acid, requires for maximum colour

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* Part III—Talanta, 1971, **18**, 577.

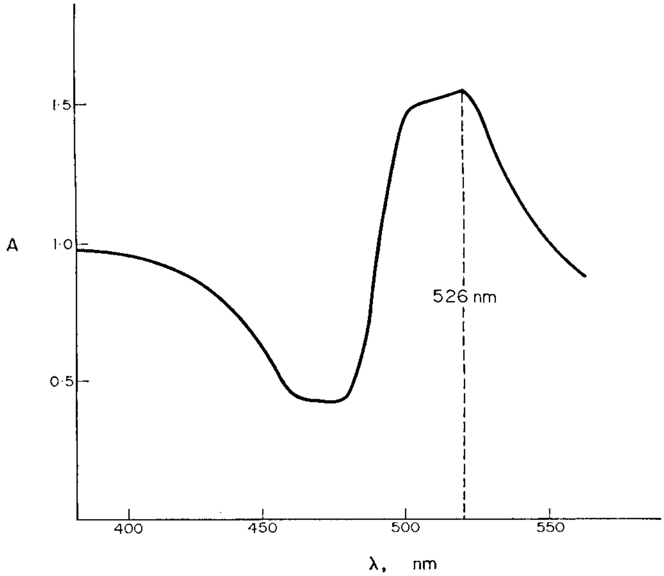

FIG. 1.—Absorption spectrum of molybdenum–phenylfluorone complex (reagent solution as blank).
$C_{Mo} = 100\ \mu g/25$ ml.

development at least 4·4 ml of 0·03% phenylfluorone solution in a total volume of 25 ml. The optimum final sulphuric acid concentration in presence of 5 ml of phenylfluorone solution is 0·30–0·35*N*. Colour development is complete in 5–10 min and the colour is stable for about 30 min, but fades after 60 min and a precipitate appears on further standing. The absorbance is lowered considerably if perchloric or hydrochloric acid is used instead of sulphuric acid. There is no colour in phosphoric acid medium.

Beer's law is obeyed at 526 nm up to 4·8 μg of molybdenum per ml; the molar absorptivity is $4{\cdot}38 \times 10^3$ $\text{l.mole}^{-1}.\text{mm}^{-1}$. The sensitivity for molybdenum is somewhat higher than that of other methods. The drawback is that iron(III), tin(II), tungsten, chromium, antimony and germanium also give coloured compounds.

Job's method shows that the complex has a molybdenum: fluorone ratio of 1:2. The 60% alcohol medium shifts the absorption maximum to 523 nm and three times as much reagent is needed for complete reaction. The Lambert–Beer law holds up to a molybdenum concentration of 1·4 μg/ml; the molar absorptivity is $1{\cdot}10 \times 10^4$ $\text{l.mole}^{-1}.\text{mm}^{-1}$. Reaction is immediate, and results are reproducible if measurements are made within 5 min. A precipitate appears within 60 min. No protective colloid is needed.

EXPERIMENTAL

Extraction of phosphomolybdic acid

The best and most selective solvent for phosphomolybdic acid is, according to Wadelin and Mellon,[5] n-butyl acetate, and experiment confirms this opinion.

It is absolutely essential to separate the phosphomolybdic acid, dissolved in the organic phase, completely from the excess of molybdate in the aqueous phase; that is, the organic solvent must be freed from the last traces of water. This can be done by filtration of the butyl acetate layer through anhydrous sodium sulphate. The efficiency of extraction was determined by taking 0·5, 1·0 and 2·0 μg of phosphorus, as potassium dihydrogen phosphate, acidifying with perchloric acid to various degrees, adding molybdate to give a final concentration of $10^{-2}M$, diluting to 10 ml, extracting with 10 ml of n-butyl acetate, drying the organic phase, stripping the molybdenum with two 5-ml portions of water and determining the molybdenum with phenylfluorone. The results are summarized in Table I and show that the optimum acid concentration is 0·5–0·7*M*.

TABLE I.—THE EFFECT OF ACID CONCENTRATION ON THE EXTRACTION OF PHOSPHOMOLYBDIC ACID

	P 0·5 μg			P 1·0 μg			P 2·0 μg			P absent
$HClO_4$, *M*	Mo found, μg	P found,* μg	%	Mo found, μg	P found,* μg	%	Mo found, μg	P found,* μg	%	Mo found,† μg
0·01	0·0	0·00	0	0·0	0·00	0	0·0	0·00	0	0·0
0·06	2·2	0·07	14	11·4	0·32	32	39·6	1·08	51	1·2
0·11	11·6	0·32	68	24·8	0·68	68	55·2	1·50	75	1·2
0·34	12·6	0·35	70	30·0	0·82	82	58·6	1·58	79	1·2
0·45	14·4	0·40	80	31·8	0·86	86	64·2	1·74	87	1·2
0·57	14·6	0·41	82	30·8	0·84	84	65·8	1·76	89	1·2
0·69	14·6	0·41	82	31·2	0·85	85	63·8	1·75	87	1·2
0·80	14·8	0·41	82	26·4	0·74	74	55·2	1·50	75	1·2
1·03	2·6	0·08	16	5·8	0·16	16	12·6	0·36	18	1·2

* Measured against a blank extraction.

† Molybdate extraction measured against a phenylfluorone reagent blank.

TABLE II.—EFFECT OF MOLYBDENUM CONCENTRATION ON THE EXTRACTION OF PHOSPHOMOLYBDIC ACID

		P 0·5 μg			P 1·0 μg			P 2·0 μg			P absent
Mo, *M*	Optimum acid concentration, *N*	Mo found, μg	P found,* μg	%	Mo found, μg	P found,* μg	%	Mo found, μg	P found,* μg	%	Mo found,† μg
0·005	0·3–0·5	13·2	0·36	72	27·6	0·75	75	57·2	1·54	77	0·5
0·01	0·5–0·7	14·6	0·41	82	31·8	0·86	86	65·8	1·76	88	1·2
0·02	0·6–0·8	16·2	0·44	88	31·6	0·86	86	69·0	1·86	93	2·0
0·06	1·2–1·7	16·0	0·44	88	32·0	0·87	87	66·4	1·80	90	6·0
0·1	1·7–2·6	16·8	0·46	92	32·2	0·88	88	66·0	1·78	89	8·8

* Measured against a blank extraction.

† Molybdate extraction measured against a phenylfluorone reagent blank.

As expected, the optimum acid concentration increases with increasing molybdenum concentration (Table II). Increasing the molybdenum concentration above 0·01*M* does not much improve the efficiency of extraction, but it increases the amount of molybdenum extracted in the blank run. Accordingly a molybdenum concentration of 0·01*M* was chosen and about 90% of the heteropoly acid was extracted with two portions of butyl acetate. Some typical results are shown in Table III; each result is the mean of three measurements, with a spread of 2–3%. For quantities of phosphorus >3 μg the Lambert–Beer law is not obeyed and a suitable sample aliquot should be taken. For quantities <0·5 μg the results are uncertain and it is then preferable to use a final volume of 10 ml for the determination of molybdenum; the results of such measurements are also given in Table III. The extraction yields acceptable results even at higher dilutions; when the initial volume for extraction was 50 ml and contained 0·1–0·5 μg of phosphorus, *i.e.*, 2–10 ppM, the error ranged from ±10% at the lower end of the range to ±6% at the upper.

The method is relatively rapid and simple, though separation of the phases needs a certain amount of practice. The molar absorptivity calculated for phosphorus is $5{\cdot}2 \times 10^4$ l.mole^{-1}.mm^{-1} and this method has one of the highest known spectrophotometric sensitivities. Silicon does not interfere, because silicomolybdic acid is not extracted. These results furnish an unequivocal proof that the composition corresponds to the ratio P:Mo = 1:12, even at such high dilution.

TABLE III.—PHOSPHORUS DETERMINATION

Initial volume,* *ml*	Final volume,† *ml*	P taken, *μg*	Mo found *μg*	P found *μg*	Error %
10	25	0·5	18·2	0·49	−2
		1·0	37·3	1·01	+1
		1·5	54·0	1·47	−2
		2·0	72·6	1·95	−3
		2·5	87·0	2·35	−6
		3·0	107·2	2·85	−5
10	10	0·10	3·7	0·10	0
		0·20	7·0	0·19	−5
		0·30	10·8	0·29	−3
		0·40	14·4	0·40	0
		0·50	18·0	0·49	−2

* Volume of phosphomolybdic acid solution before extraction.
† Volume of phenylfluorone solution in spectrophotometric measurement.

Extraction of silicomolybdic acid

It was verified that the solvent proposed by Lueck and Boltz,[1] a 1:5 mixture of n-pentanol and diethyl ether, is suitable for the extraction of silicomolybdic acid. As for phosphorus the molybdenum concentration used was 0·01*M* and the final acid concentration 0·4*N*. As suggested, it is best to add the acid in two portions: first enough to form the heteropoly acid, and then more to reach the concentration necessary for the extraction. This is because the heteropoly acid is not formed instantaneously, and a high excess of acid decreases the reaction rate, probably because of the formation of polysilicic acids.

A few changes had to be made from the method used for phosphomolybdic acid. First, the extract could not be freed from free molybdate by drying with sodium sulphate, but repeated washing with acid had to be used. Consequently, the heteropoly acid could not be decomposed with water, because of the remaining acid. Accordingly, 1*M* ammonia solution was used. For the molybdenum determination the solution then had to be neutralized, and the large amount of electrolyte present caused a colloidal precipitate to separate from the solution. On account of this, the determination in alcohol medium was used.

With a starting volume of 10 ml and two extractions, the efficiency of extraction was 86–87%, whereas with a starting volume of 50 ml it was 75%. Further extraction caused but a slight improvement in efficiency. The results are, however, reproducible, and the method is suitable for analytical purposes, but a calibration curve must be constructed for known amounts of silicon; it is not possible simply to construct a calibration curve for molybdenum and to calculate the result as was the case for phosphomolybdic acid.

Results are summarized in Table IV.

Although the extraction efficiency was not 100%, the experiments prove that the silicon–molybdenum ratio of 1:8 quoted by some authors[6,7] is impossible, because more molybdenum than would correspond to this was recovered in every case. If the solutions were left to stand for two days before

TABLE IV.—RESULTS OF SILICON DETERMINATION

Cell, *mm*	Si taken, *μg*	Si found, *μg*	Error %
10	0·10	0·11	+10
	0·20	0·21	+5
	0·30	0·29	−3
	0·50	0·51	+2
5	0·25	0·25	0
	0·50	0·49	−2
	0·75	0·74	−1
	1·00	1·04	+4
	1·25	1·25	0
	1·50	1·48	−1

extractions, to allow the α-modification to form, the results were the same, *i.e.* both forms are equally well extracted. The theoretical value of the molar absorptivity for silicon is $1{\cdot}32 \times 10^4$ l.mole^{-1}.mm^{-1} but in practice the value is lower by 10–25%, depending on the initial volume, because of the extraction lower efficiency. Phosphorus and arsenic interfere with the determination, because their heteropoly acids are also extracted. Iron(III) interferes by forming an ether-extractable complex, and giving a colour reaction with phenylfluorone.

Determination of Phosphorus and Silicon

Reagents

Molybdate solution, 0·1*M* (*calculated for* MoO_4^{2-}). Prepared from analytical grade sodium or ammonium molybdate. Stored in a polythene bottle.

Perchloric acid. Analytical grade 70% perchloric acid diluted 1 + 1 and 1 + 10, and stored in polythene bottles.

Sulphuric acid. Analytical grade, 2·5 and 5*M.*

Hydrochloric acid. Analytical grade, diluted 1 + 1.

Ammonia solution, 1*M.*

Gum arabic solution. Analytical-grade gum arabic (1 g) dissolved in hot water (200 ml) and the solution filtered.

Sodium sulphate. Analytical grade, anhydrous.

n-Butyl acetate. Commercial solvent purified by distillation.

n-Pentanol–diethyl ether. A 1:5 mixture of the solvents, previously purified by distillation.

Phenylfluorone solution. Analytical grade phenylfluorone (0·30 g) dissolved in 600–700 ml of 96% alcohol and 50 ml of 2·5*M* sulphuric acid, with cautious heating and stirring, and after cooling diluted to 1 litre with alcohol.

Phosphorus stock solution, 100 *mg/l.* Prepared from potassium dihydrogen phosphate, stored in a polythene bottle and diluted as required.

Silicon stock solution 100 *mg/l.* Prepared from sodium silicate enneahydrate, standardized gravimetrically, stored in a polythene bottle, and diluted as required use.

Molybdenum stock solution 100 *mg/l.* Prepared from sodium molybdate and diluted as required.

Determination of phosphorus

Measure a portion of approximately neutral sample solution containing 0·1–3 μg of phosphorus into a 100-ml separating funnel which has a short stem with a carefully greased and precisely fitting stop-cock. Add perchloric acid and molybdate reagent in such amounts that their final concentrations will be 0·5 and 0·01*M* respectively. Dilute to 10, 25 or 50 ml, shake thoroughly and let stand for 5 min, then shake vigorously with 5 ml of n-butyl acetate. Transfer the aqueous phase to another separating funnel and repeat the extraction with another 5 ml of solvent. Discard the aqueous solution and combine the organic phases in the first funnel, washing the second with 2 ml of solvent.

Leave the organic phase until all the remaining aqueous phase has collected in the bottom of the funnel, then separate it with utmost care so that the bore of the stop-cock is finally filled with organic solvent. Rinse the stem and stopper thoroughly with distilled water, inside and outside. The error caused by thus stripping some molybdenum is much lower than that caused if some aqueous phase is left.

To remove the last traces of aqueous phase prepare a tube fitted with a coarse fritted-glass disc with a 5–6-mm thick layer of anhydrous sodium sulphate on it. Wet this layer with a few drops of the solvent. Pass the butyl acetate solution through the filter, without suction, into another separating funnel, rinsing the original funnel and the filter twice with 2 ml of solvent and combining the filtrate and washings. If the expected amount of phosphorus is more than 0·5 μg, shake the organic phases with 10 ml of water for 1 min, transfer the aqueous phase to a 25-ml standard flask, repeat the extraction with 5 ml of water, and combine the aqueous phases. Utmost care must be taken to avoid droplets of organic solvent getting into the flask. Add 1 ml of gum arabic solution, 0·75 ml of 5*M* sulphuric acid and 5·00 ml of phenylfluorone reagent, mix, and measure the absorbance in a 10-mm cell *vs.* a reagent blank at 526 after 10–30 min.

If only 0·1–0·5 μg of phosphorus is expected, extract with 5 + 2 ml of water and use a 10-ml flask, 0·5 ml of gum arabic solution, 0·30 ml of sulphuric acid and 2·00 ml of phenylfluorone reagent.

Prepare calibration curves by taking molybdate standards through the phenylfluorone procedure, to cover the ranges 0–120 μg of Mo (25-ml flasks) and 0–20 μg (10-ml flasks). Calculate the phosphorus content from the molybdenum determination, assuming a molar ratio P:Mo = 1:12. If the amount of phosphorus is less than 1 μg, it is advisable to determine the amount of molybdenum extracted in the absence of phosphorus and to apply a correction accordingly. Alternatively prepare phosphorus calibration curves by applying the whole procedure to phosphorus standards covering the ranges 0–0·5 and 0–3 μg of P. The absorbance of a blank run should again be taken into consideration for <1 μg of phosphorus.

Determination of silicon

Measure a portion of neutral sample solution containing 0·1–1·5 μg of silicon into the 100-ml separating funnel. Add hydrochloric acid and molybdate reagent to obtain final concentrations of 0·05 and 0·01*M* respectively. Dilute to 10, 25 or 50 ml, wait for 10 min, raise the hydrochloric acid concentration to 0·4*M*, and shake vigorously with 5 ml of 1 : 5 mixture of n-pentanol and diethyl ether for 1 min. Transfer the aqueous phase into a second, similar, separating funnel and extract again with 5 ml of solvent. Wash the united organic phases with three 2·5-ml portions of diluted (1 + 10) perchloric acid. In each case, the stem and the stopper of the separating funnel are carefully washed with distilled water, inside and outside. Shake the organic phase with 6 ml of ammonia solution for 1 min, and transfer the aqueous solution into a 25-ml volumetric flask, taking utmost care to keep droplets of organic solvent out of the flask. Neutralize the solution with 2·5*M* sulphuric acid, using a drop of phenolphthalein solution as indicator. Make basic by addition of drop of ammonia solution. Immediately before measurement, add 15 ml of phenylfluorone reagent, dilute to volume, shake, and measure the absorbance in a 5- or 10-mm cell at 523 nm *vs.* a reagent blank. Prepare a calibration curve to cover the range 0–1·5 μg of Si, by use of sodium silicate standards, taking care always to use the same initial volume. The absorbance of a blank solution containing no silicon must be taken into consideration, just as in the phosphorus determination.

Zusammenfassung—Es werden Verfahren zur Bestimmung von Phosphor und Silicium im ppM-Bereich vorgeschlagen: Phospho- und Silicomolybdänsäure werden mit einem organischen Lösungsmittel extrahiert, der Komplex zersetzt und der Molybdängehalt spektrophotometrisch bestimmt.

Résumé—On propose des techniques pour la détermination du phosphore et du silicium dans le domaine du p.p.M., par extraction des acides phosphomolybdique et silicomolybdique avec un solvant organique, décomposition du complexe et dosage spectrophotométrique de sa teneur en molybdène.

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ULTRAVIOLET ABSORPTION AND LUMINESCENCE PROPERTIES OF SOME CANNABIS CONSTITUENTS

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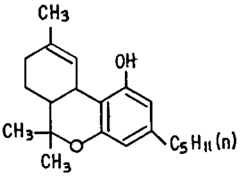
(*Received* 14 *August* 1970. *Accepted* 21 *November* 1970)

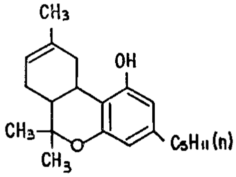
Summary—The characteristics of the absorption, fluorescence and phosphorescence spectra of the cannabinols have been determined. The data provide a basis for the detection of these compounds at concentrations down to 10 ng/ml.

The detection, characterization and determination of the cannabinols and their metabolic and photochemical products present an urgent problem in the forensic field. There is a particular requirement for sensitive and specific methods of analysis for the examination of crude plant extracts, cannabis resin, and body fluid specimens after the active constituents have been isolated.[1]

This paper describes the application of luminescence spectrophotometry to this problem. We have studied the absorption, fluorescence and phosphorescence spectra of Δ^9- and Δ^8-tetrahydrocannabinols (THC) (**I** and **II**), cannabidiol (CBD) (**III**) and cannabinol (CBN) (**IV**). In addition we have determined the phosphorescence lifetimes of these substances at 77° K. Certain characteristic spectroscopic changes, due to photochemical effects induced by exciting light, were observed during prolonged excitation.



I Δ^9-TETRAHYDROCANNABINOL (Δ^9-THC)



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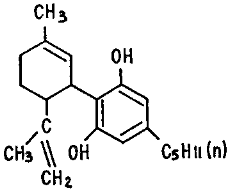
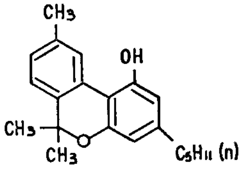


III CANNABIDIOL (CBD)



IV CANNABINOL (CBN)

EXPERIMENTAL

Instrumentation

The luminescence spectrophotometer used in this work has been described previously.[2] The system comprises a 2-kW high-pressure discharge lamp (Mazda XE/D), two 500-mm grating monochromators (Bausch and Lomb 33-86-45) and an EMI 9558 B photomultiplier tube with associated power supply (Brandenberg 470) and picoammeter (Keithley 414 S). Spectra were recorded on a Beckman model 93502 potentiometric chart recorder. The photomultiplier was equipped with a cooling device[3] to minimize dark current when very low photomultiplier anode currents were measured. For fluorescence measurements at 25° the quartz cell was mounted in a machined brass block which was bored to allow passage of water from a constant-temperature bath. Phosphorescence measurements were made at 77°K, by using a cylindrical quartz sample tube mounted in a quartz Dewar flask containing liquid nitrogen. A rotating-can phosphoroscope attachment[4] inserted around the Dewar flask was used to eliminate fluorescence when phosphorescence emission was studied. Phosphorescence lifetimes were determined by photographing the cathode ray oscillograph trace of the phosphorescence decay after extinction of the excitation beam (Tektronix 502 A oscilloscope with Polaroid camera). All absorption measurements were made with a Uvispek H 700 spectrophotometer (Hilger and Watts).

Reagents

Samples of Δ^8-THC, Δ^9-THC, CBN and CBD (approximately 95% pure) were provided by the Home Office Central Research Establishment, Aldermaston. Further samples of Δ^8-THC and Δ^9-THC (98–99% pure) were found to give spectroscopic characteristics identical to those previously determined. It would appear therefore that the impurities present in the original samples did not qualitatively affect the luminescence properties of the cannabinols. Ethanol was purified by distillation through a Widmer fractionating column until all fluorescent impurities had been removed. Water used as a solvent was freshly distilled and passed through an ion-exchange column (Elgastat B102). All other reagents were of analytical grade.

Procedure

All solutions were prepared and handled in a darkroom equipped with photographic safelights (Ilford 900 BR). The acidic and alkaline ethanolic solutions were prepared by adding 2·5 ml of 2*M* hydrochloric acid or sodium hydroxide to 47·5 ml of the solution in 100% ethanol. The solutions were therefore 0·1*M* with respect to acid or alkali. The concentrations of the cannabinols in solution were calculated from their molar absorptivities at 280 nm.[5,6] It was found that the presence of oxygen in solution did not affect the luminescence characteristics of the cannabinols and therefore no attempts were made to remove air from the solutions, although specimens for study at 77° K were de-aerated on the vacuum line to avoid cracking of the solvent glass.

All absorption and fluorescence measurements were carried out at 25 ± 0·5°. The excitation wavelength for the luminescence spectra was 280 nm (bandwidth 8 nm). The spectra are not corrected for instrumental response.

RESULTS

Ultraviolet absorption spectra. The ultraviolet absorption spectra of the cannabinols, measured in 100% ethanol (Figs. 1–4), show a marked absorption band over the range 275–285 nm characteristic of the phenolic structures assigned to these compounds.[7–10] Δ^9-THC and Δ^8-THC both show absorption maxima at 278 and 283 nm. CBD possesses a very similar absorption spectrum with a single absorption maximum at 278 nm. The absorption spectrum of CBN shows a small shift to longer wavelengths with an intense maximum at 285 nm, consistent with the results of Jacob and Todd.[11] All these spectra were unchanged in acidic ethanol.

In alkaline solutions in ethanol, typical bathochromic shifts were observed, indicating ionization of the phenolic groups present. In each case acidification of the solution regenerated the spectrum of the undissociated phenol. (A typical example is shown in Fig. 5.)

Significant photochemical changes take place when the cannabinols are exposed to ultraviolet light for several hours. These give rise to changes in absorption spectra (Figs. 1–4). In the case of Δ^8-THC and CBD only small changes are observed (Figs. 2 and 3). Δ^9-THC and CBN undergo more marked changes (Figs. 1 and 4).

Fluorescence spectra

The fluorescence spectra of the cannabinols were measured in 100% ethanol at 25°. The spectra obtained showed significant changes which depended on the duration of

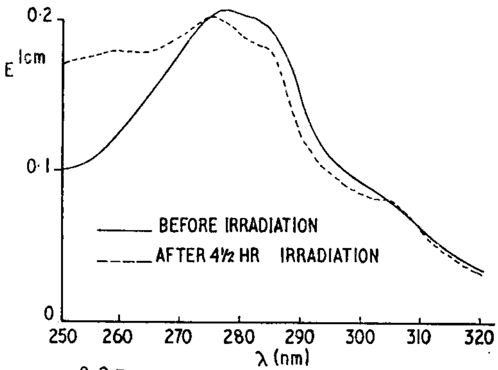


FIG. 1.—Absorption spectra of 1·3 × $10^{-4}M$ Δ^9-THC in 100% EtOH.

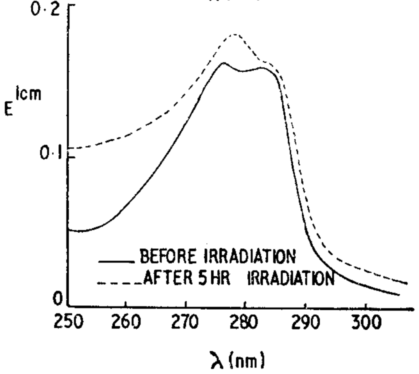


FIG. 2.—Absorption spectra of 1·0 × $10^{-4}M$ Δ^8-THC in 100% EtOH.

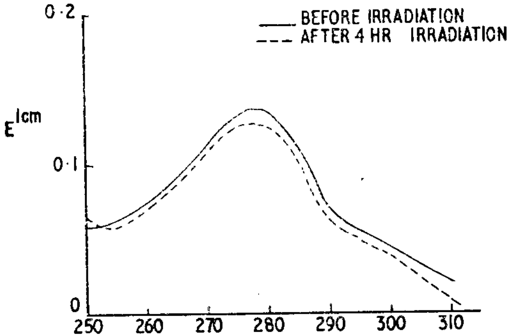


FIG. 3.—Absorption spectra of 8·4 × $10^{-5}M$ CBD in 100% EtOH.

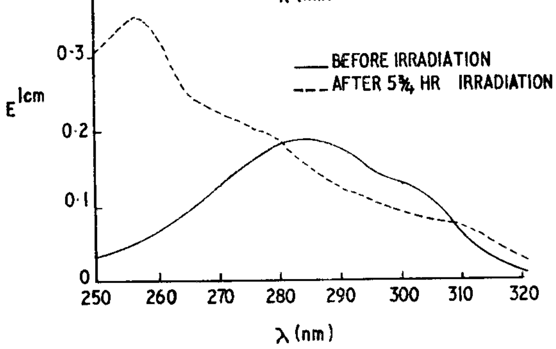


FIG. 4.—Absorption spectra of 1·1 × $10^{-5}M$ CBN in 100% EtOH.

irradiation. All the cannabinols show closely similar behaviour, possessing an intrinsic fluorescence with a single prominent peak at 318 nm (Figs. 6–9). The spectra change radically on prolonged irradiation, yielding new peaks at 366 and 383 nm, with a shoulder at 405 nm. Similar results were obtained in acidified ethanol.

Use of a quartz-windowed photomultiplier (EMI 9558 QB) shifts the intrinsic fluorescence peak at 318 nm to 307 nm.

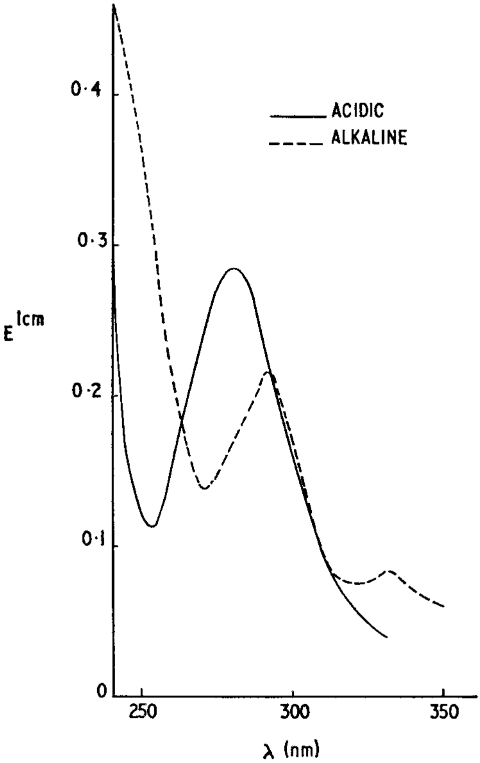


FIG. 5.—Absorption spectra of 1·2 × $10^{-4}M$ Δ^9-THC in 95% EtOH.

Phosphorescence spectra and phosphorescence lifetimes

Phosphorescence spectra of the four cannabinols were measured in 100% ethanol, at 77° K. Well-defined spectra were obtained (Figs. 10–13). The emission maxima appeared at about the same wavelengths for each compound. It is evident however that Δ^9-THC and CBN can be distinguished from Δ^8-THC and CBD by the general shape of their spectra.

The phosphorescence lifetimes of the four compounds (Table I) lie close together within the range 1–2 sec. It is of interest to note that CBD possesses a significantly longer lifetime than the remainder of the group.

DISCUSSION

The spectroscopic data which we have presented provide a reliable means of detecting and identifying the cannabinols. The combined measurements of absorption,

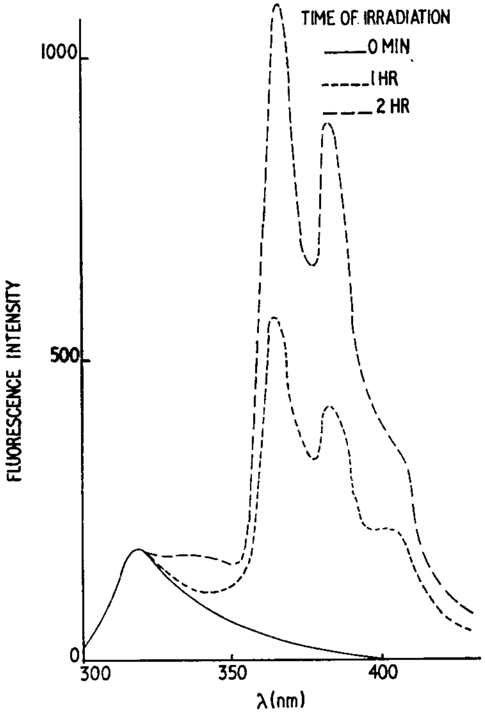


Fig. 6.—Fluorescence spectra of $1{\cdot}3 \times 10^{-4}M$ Δ^9-THC in 100% EtOH after various periods of irradiation.

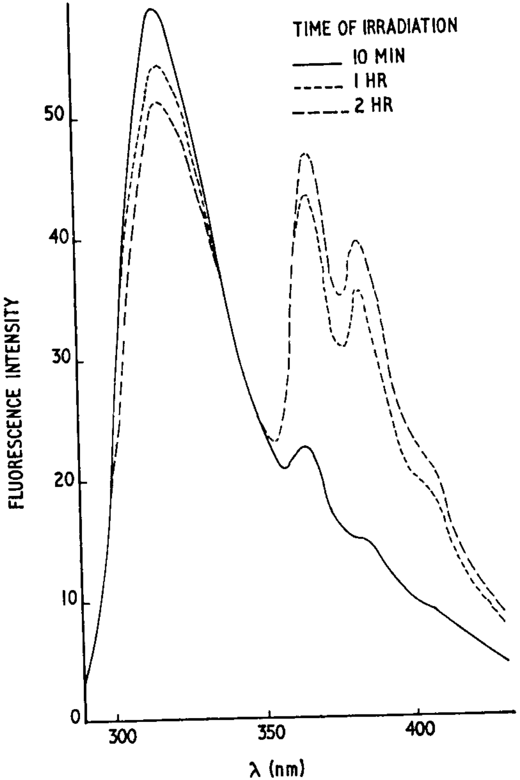


Fig. 7.—Fluorescence spectra of $1{\cdot}0 \times 10^{-4}M$ Δ^8-THC in 100% EtOH after various periods of irradiation.

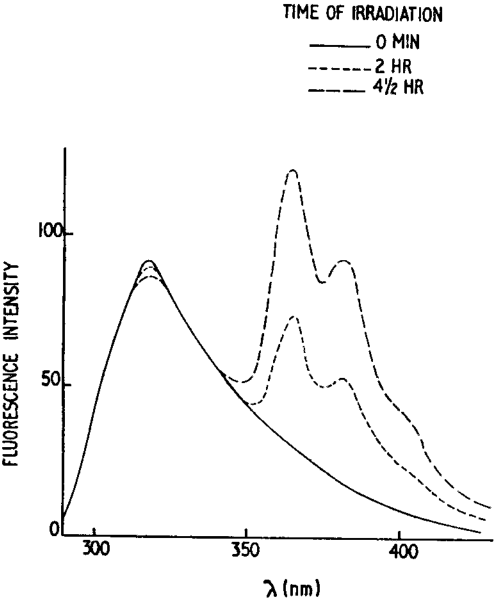


Fig. 8.—Fluorescence spectra of 8·4 × $10^{-5}M$ CBD in 100% EtOH after various periods of irradiation.

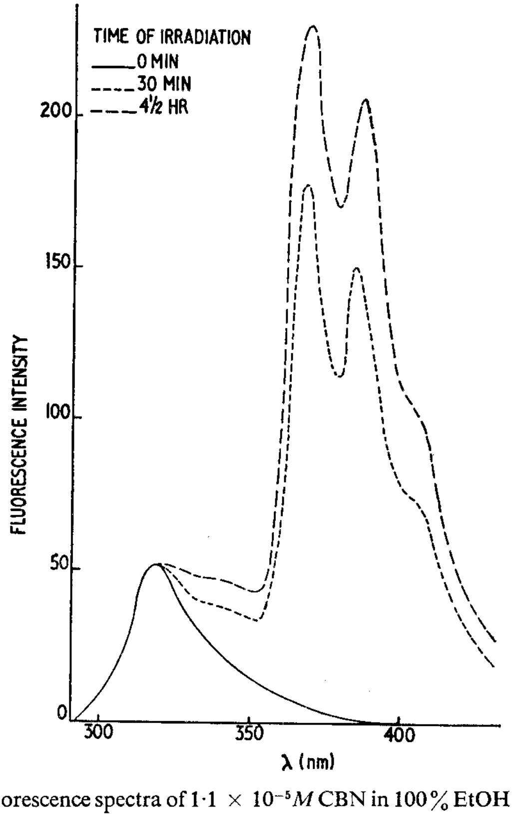


Fig. 9.—Fluorescence spectra of 1·1 × $10^{-5}M$ CBN in 100% EtOH after various periods of irradiation.

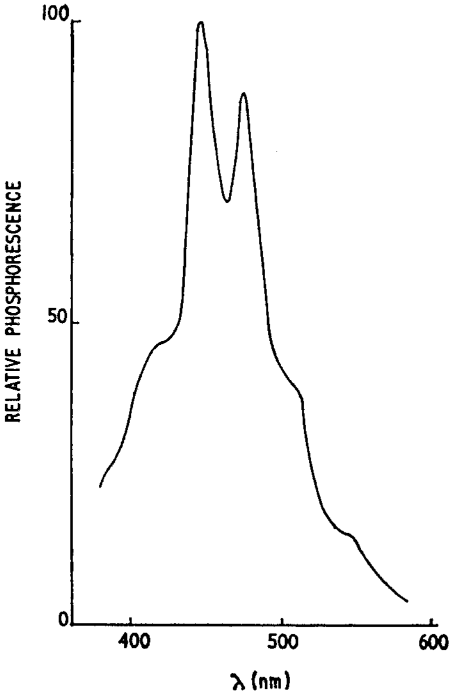


FIG. 10.—Phosphorescence spectrum of $1{\cdot}3 \times 10^{-4}M$ Δ^9-THC in 100% EtOH at 77°K.

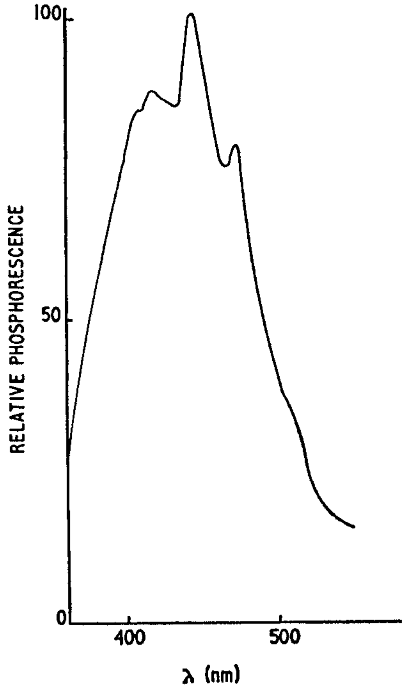


FIG. 11.—Phosphorescence spectrum of $1{\cdot}0 \times 10^{-4}M$ Δ^8-THC in 100% EtOHat 77°K.

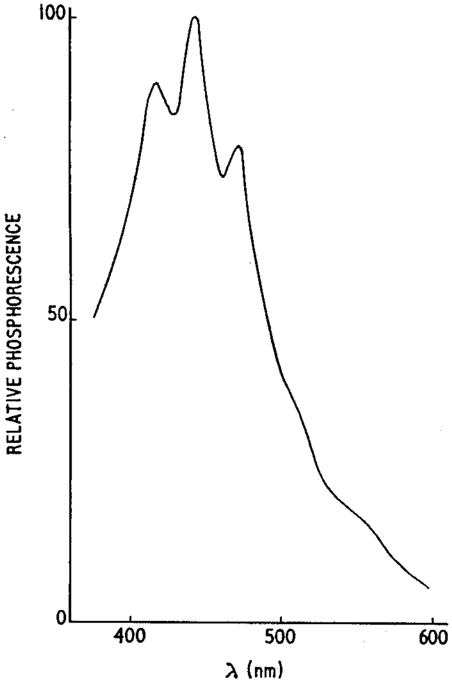


Fig. 12.—Phosphorescence spectrum of 8·4 × $10^{-5}M$ CBD in 100% EtOH at 77° K.

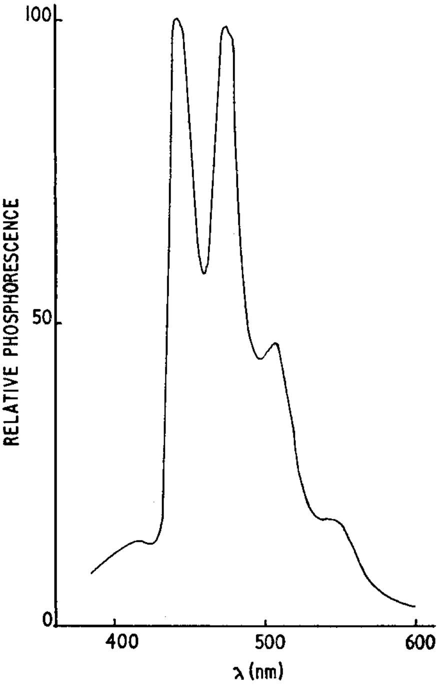


Fig. 13.—Phosphorescence spectrum of 1·1 × $10^{-5}M$ CBN in 100% EtOH at 77° K.

TABLE I.—PHOSPHORESCENCE LIFETIMES OF THE CANNABINOLS AT 443 nm

Compound	Lifetime, *sec*
Δ^9-Tetrahydrocannabinol	1·66 ± 0·02
Δ^8-Tetrahydrocannabinol	1·64 ± 0·08
Cannabidiol	2·00 ± 0·04
Cannabinol	1·54 ± 0·02

fluorescence and phosphorescence spectra afford several parameters for the characterization of these compounds.

Trace amounts of the cannabinols can be detected by means of the intense fluorescence emission peaks at 366 and 382 nm which develop on irradiation. In order to identify these peaks at low concentrations in solution, it is necessary to correct for the reflected light from the sample tube and Dewar flask and for the intrinsic fluorescence of the solvent. We have been able to detect the cannabinols in amounts as low as 10 ng/ml ($\sim 3 \times 10^{-8} M$).

It is evident that the spectroscopic estimation of the cannabinols is complicated by photochemical changes. A further understanding of this photochemistry is desirable before complete quantitative analysis of these compounds can be achieved.

Acknowledgements—The authors would like to thank Drs. A. S. Curry and A. Patterson of the Home Office (Central Research Establishment) for making available the compounds used in this study and for their valuable discussions.

Zusammenfassung—Die charakteristischen Absorptions-, Fluoreszenz- und Phosphoreszenzspektren der Cannabinole wurden bestimmt. Mit Hilfe der Ergebnisse können diese Verbindungen bei Konzentrationen bis herunter zu 10 ng/ml bestimmt werden.

Résumé—On a déterminé les caractéristiques des spectres d'absorption, de fluorescence et de phosphorescence des cannabinols. Les données fournissent une base pour la détection de ces composés à des concentrations descendant jusqu'à 10 ng/ml.

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Talanta, 1971, Vol. 18, pp. 707 to 716. Pergamon Press. Printed in Northern Ireland

DETERMINATION OF NANOGRAM AMOUNTS OF NICKEL BY FLAMELESS ATOMIC-ABSORPTION SPECTROSCOPY

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(*Received* 2 *September* 1970. *Accepted* 20 *November* 1970)

Summary—A simple flameless atomizer, made from a heated graphite resistor, was investigated for the determination of nickel in various salts. The parameters characterizing its behaviour were optimized, to yield an absolute detection limit of 0·1 ng of nickel.

IN SPITE of the high degree of reliability and development reached by the different techniques of atomic spectroscopy (A.S.), the ultimate limit in sensitivity is far from being reached.

This sensitivity depends first on the efficiency of the nebulizer–burner system in converting the analyte into free gaseous atoms. If we consider the premix burner, which is on the whole the most efficient,[1] only 15% of the solution is at best transferred into the flame.[2] For the subsequent steps the efficiencies are much higher because, as de Galan and Winefordner[3] and Koirtyohann and Pickett[4] have shown, by a suitable choice of the experimental conditions an overall efficiency of 50–100% for all the processes in the flame can be obtained for the majority of the elements usually detected by A.S. This means that no drastic improvement in the overall atomization efficiency, and hence in sensitivity, may be expected, and in seeking a substantial increase of the signal-to-noise (S/N) ratio, efforts must be channelled in other directions.

An interesting approach to this problem exploits the possibility of modulating the amplitude of the optical output by the cyclic injection of atoms of analyte in the measuring spectrometer. This technique was pioneered by Herrmann,[5–8] and reached a high degree of development in the apparatus of Malmstadt.[9,10] This approach is based on the well-known fact that usually a better S/N ratio can be obtained with pulsed rather than continuous excitation of the same average intensity. In the case considered, the input power (optical, thermal) remains constant and it is the injection of atoms that is pulsed and acts as a control element in the measuring device, like a grid in a triode.

As a limiting case of this method we may consider the "single shot" technique where a "burst" of atoms from a known volume of sample solution is produced for each measurement. When this process is realized in such a system that the atoms can remain in the optical path or are slowly swept through by an inert gas, an important shortcoming of the flame is avoided. In fact as Pickett and Koirtyohann have pointed out,[11] the concentration of atoms along the optical path in the conventional flame system is low, owing to the high propagation rate[12] of the flame itself (the atoms "reside" in the optical path for some fraction of a millisecond). On the same basis Hieftje and Malmstadt[9,10] emphasize that in order to increase considerably the S/N ratio, it is necessary to make observations only in the region with the highest concentration of atoms of analyte.

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The desolvation, vaporization and dissociation of the sample into atoms with the flameless atomizer is usually accomplished by electrical heating even if other sources such as a flash of light,[13] a "laser shot"[14,–16] or a sputtering technique[17–21] are used.

Following L'Vov,[22–24] this technique of producing atoms is usually associated with atomic-absorption spectroscopy (AAS) or sometimes with atomic-fluorescence spectroscopy (AFS), but the joint use of some other energy source[25–27] (for instance microwave or radiofrequency sources) permits excitation of the gaseous atoms and the analytical information is obtained from atomic-emission spectroscopy.

Recently Brandenberger and Bader[28–30] proposed as atomic source a platinum wire plated with the element of interest, the latter then being vaporized by electrical heating, whereas Massmann,[31] and West and Williams,[32] used graphite in the form of a crucible[31] or a filament,[32] with vaporization by electrical heating. Few elements were investigated and the reported results appear interesting, taking into account the simplicity of these flameless atomizers.

Following this approach we have investigated the behaviour of this source of atoms in the case of nickel, for which rapid and sensitive methods of determination are important, owing to its wide industrial use as a catalyst.

EXPERIMENTAL

Reagents

All the chemicals used were of analytical-grade purity. Stock solutions were prepared with demineralized water and stored in polyethylene bottles. The nickel solutions were standardized by EDTA titration. The most dilute solutions were freshly prepared before use.

The argon used was certified to contain $<0\cdot1$ ppm v/v of oxygen and <5 ppm v/v of water and was used without further purification. The hydrogen supply was used after a preliminary purification with a copper-based catalyst to remove oxygen.

Apparatus

A Densatomic Spectrometer (Optica, Milan) was used after substitution of a flameless atomizer (Fig. 1), very similar to the type described by West *et al.*,[32] for the nebulizer-burner system.

An Ni–Cr hollow-cathode lamp was operated at 30 mA (max. permissible current 40 mA).

Owing to the impulse character of the signals the overall time-response of the detector–amplifier–recording system was measured ($\sim$0·5 sec) and found consistent with the time-rise of the signal ($\sim$1–1·2 sec).

As heating element, Pt, W and Mo ribbons (0·03 mm thick) were tried in some preliminary tests; since the results were poor we eventually resorted to graphite (spectrographic grade—Ultra Carbon Corp., U.S.A.) using test bars 2·5 mm^2 in cross-sectional area and 15 mm in length.

Temperatures up to 1600° were determined with a Pt/(Pt,Rd 10%) thermocouple. To evaluate higher temperatures, the spectral emission of the graphite at 500 nm was measured, under different heating conditions, the spectrometer being used in the emission mode. A temperature scale as a function of input power was thus defined, taking 1500° as reference temperature and assuming the spectral emissivity of the carbon to be constant.

Two optically polished quartz windows were sealed with RTV-102 adhesive (General Electric, U.S.A.) to the ends of the tube.

For heating, a home-made transformer with maximum output 16 V and 100 Å, fed through a Variac (Type 40 C, General Radio, U.S.A.) was used.

The flow-meters were calibrated according to the gas used.

The sample (usually 2·5 or 5 μl) was injected with a micrometer syringe; with some corrosive solutions, spurious signals were detected, originating from the nickel of the stainless steel of the syringe needle. This difficulty was overcome by putting a polyethylene capillary inside the needle.

RESULTS AND DISCUSSION

Heating materials

Platinum, molybdenum and tungsten resistance wires were found unsuitable, since in the case of the platinum the maximum permissible temperature was too low to

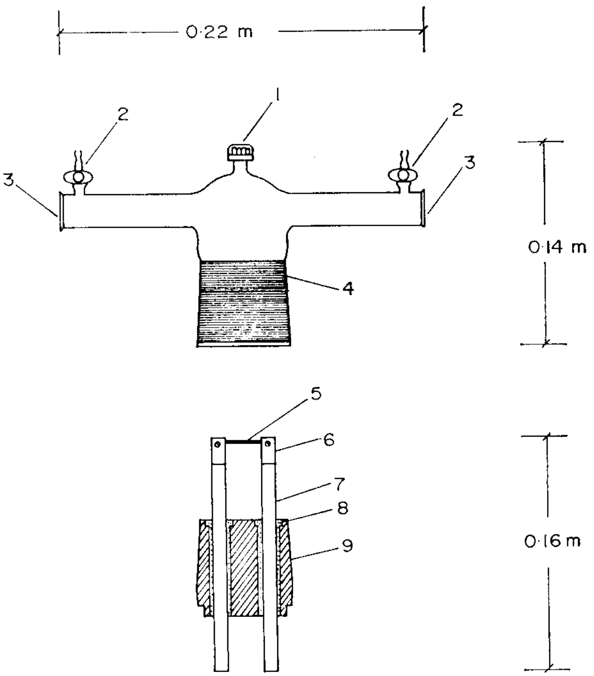

FIG. 1.—Flameless atomizer.
(1) injection port; (2) inlet and outlet for the inert gas; (3) quartz windows; (4) Pyrex cell; (5) heating element; (6) stainless-steel electrode; (7) copper rod; (8) Teflon insulator; (9) stainless-steel cone.

yield a useful atomic population, and the other two materials reacted with traces of oxygen, giving an interfering signal.

When we resorted to a graphite element an absorption signal was present at the most important analytical lines of nickel, even in the absence of nickel. This signal increased with the temperature of the graphite; it could be ascribed to the molecular bands of C_2,[33] which, as Clarke and Fox have shown,[34] is the most important species vaporized from carbon in the range 2200–3100°. An alternative explanation of this absorption signal involves the scattering of light by soot formed[35] all around the graphite. This spurious signal could be at least partially suppressed by addition of hydrogen, in agreement with the literature.[34,35]

The maximum temperature used was about 2500°.

Slit-width

Because of the continuous character of this interfering signal, the width of the band-pass is important as far as the S/N ratio is concerned: a slit-width of 0·05 mm, corresponding to a band-pass of 0·25 nm, was found convenient.

Flow-rate of sweeper gas

The concomitant effects of carbon absorption and slit-width are shown in Fig. 2 as a function of the flow-rate of the inert gas. In these curves the ordinates are proportional to the absorption signals measured at time $t = 2$ sec (temperature $\sim$ 2500°).

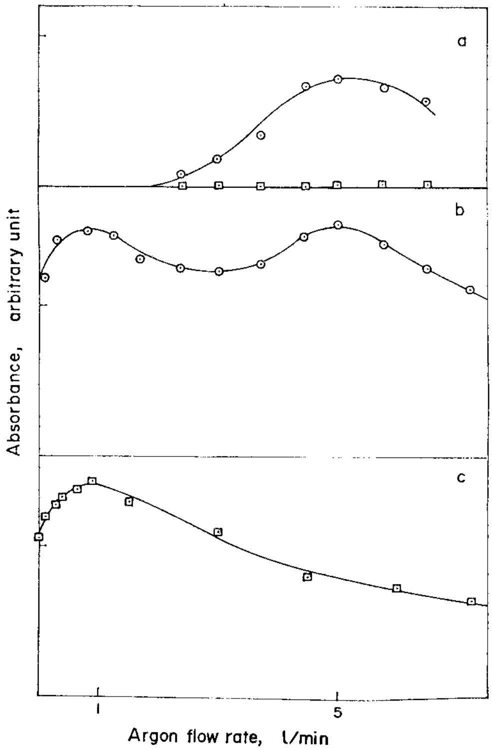

Fig. 2.—Optical response at 232·0 nm as a function of the flow-rate of argon gas: (*a*) graphite alone; (*b*) and (*c*) 2·5 ng of Ni.
The response was measured 2 sec after the switching on of the electric power, corresponding in curves *b* and *c* to the peak of the response. Slit-width: ○ = 0·3 mm; ⊡ = 0·05 mm.

This time represents the time lag, when nickel is present between the switching on* of the electric power and the peak of the response.

The maximum in curve *a* could be the resultant of two opposite effects. With increasing flow-rate, the sweeper gas is better able to collect along the optical path the carbon species emitted from the heated graphite, and this enhances the absorption signal; on the other hand, a depressive effect, possibly due to cooling of the emitting surface, is building up at the highest flow-rates. From comparison of curves *a* and *b* it seems safe to assume that the second maximum of curve *b* cannot be attributed to the nickel absorption, but is due to the vaporization of the graphite.

The general trend of curve *c* has been replicated for different nickel compounds, and appears to be independent of the anion used.

Important parameters in the description of this curve are the length of vaporization, the flow-rate of the sweeper gas, and the life-time of the gaseous nickel atoms. These parameters are not mutually independent; for instance, the life-time of the atoms depends in a complicated way on the flow-rate since this parameter affects the thermal gradient near the emitting surface, increasing flow favouring the molecular recombination encounters in this region. On the other hand the same parameter has

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* Actually the time-scale starts at the beginning of the last step of the thermal cycle.

an opposite effect, also with increasing flow, on the atomic population, because of the dilution of the vaporized species.

Undoubtedly the problem is very involved and we should not attempt an analytical interpretation, being satisfied with a qualitative description.

In a very crude approximation, disregarding the effects due to the thermal gradient, we should expect that the absorption signals would remain constant up to the point at which the "transit" time of the atoms becomes equal to the vaporization time. At flow-rates higher than this the signal starts to decrease because not all the gaseous atoms can be contemporaneously present in the optical path. As can be seen from curve *c* this pattern is roughly followed. The increase in the signal in the first part of the curve could be the result of the increasing dilution of the evaporated species, which makes recombination encounters less probable. Unless otherwise stated, an inert gas flow-rate of 1 l./min was used.

Length of vaporization

At the flow-rate of 1 l./min, corresponding to the maximum in curve *c*, the free atoms are swept from the thermal source through the whole tube in about 1 sec, as calculated from the geometrical data of the cell. This time roughly sets the length of vaporization, which can also be estimated from the rise-time (1–1·2 sec) of the impulse response of the absorption curves *vs.* time.

Effect of water

A preliminary survey showed that the evaporation of the water, when very fast, gives an apparent absorption signal at each wavelength investigated. Since no fogging of the quartz windows was detected, this signal could be explained as being caused by light-scattering by the minute water droplets which, owing to the much lower temperature, are condensing away from the heated graphite surface. For this reason we have first separated the water from the rest of the solution; to avoid loss of part of the solute because of the boiling off of the water, gentle heating at 50–70° for about 2 min was found convenient.

Choice of analytical lines

With the apparatus and conditions described, of the several lines examined, the most sensitive, at 232·0 and 341·4 nm, were practically equivalent in terms of S/N ratio.

Analytical curves

The nickel salts investigated can be grouped in three classes. Nickel chloride is representative of the first, consisting of salts which vaporize at relatively low temperature without decomposition.

The common oxyanion salts such as the nitrate, sulphate and acetate, belong to a second class, having in common the decomposition to NiO as intermediate stage.[36–38]

Nickel oxalate is different again, producing metallic nickel directly by thermal decomposition.[39]

Undoubtedly this last compound should offer the most straightforward path for getting a free atom population, but unfortunately is of limited analytical use because of its low solubility. Since oxalic acid decomposes at lower temperature than nickel oxalate, we have tried to by-pass this difficulty by producing this salt directly on the graphite element, by injection of nickel solutions of different salts into a drop of 0·1M oxalic acid previously deposited. Disappointingly, the recovery of free atoms, as indicated by the absorption signal, was very low, possibly owing to formation of the volatile $Ni(CO)_4$, which would be favoured by the large excess of the decomposition products from oxalic acid. A lower excess of acid did not improve the results and these experiments were discontinued.

A convex calibration curve, as in Fig. 3, is a common feature for nickel oxy-salts and should be related to an equilibrium in the gas phase. The bond between Ni and O is of medium strength, the dissociation energy being 363 kJ/mole. Recent findings,[40] disproving earlier observations,[41] claim that the vaporization of NiO occurs primarily by dissociation to the elements. Our observations, without questioning this conclusion, suggest, because of the thermal gradient mentioned above, the possibility of recombination of the evaporating species. In these conditions the partial pressure of NiO in the gas phase can reach a much higher value than the equilibrium one.

The curve in Fig. 2 is obtained provided that the sample undergoes a proper thermal cycle. This means that it is necessary to keep the sample at the decomposition temperature for a time sufficient (usually 1 min) to yield nickel oxide as a dissociation product of the starting nickel oxy-salt and then to "flash heat" this deposit at 2500°. Without this "thermal stop" a signal is reduced by as much as 50%.

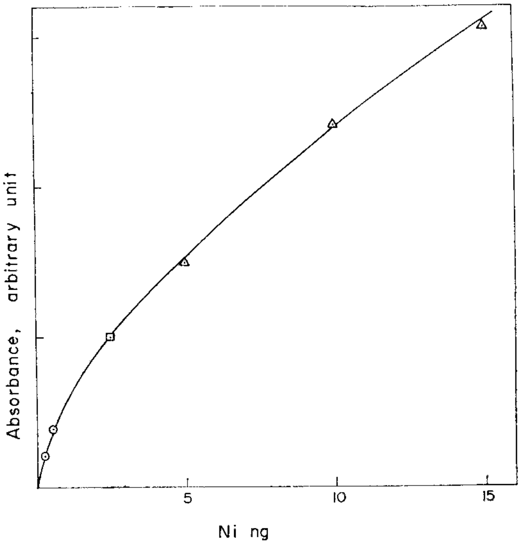

FIG. 3.—Analytical curve for Ni from $Ni(NO_3)_2$.
○ = 0·1 ppm, □ = 1 ppm, △ = 2 ppm solutions; argon flow-rate = 1 l./min; slit-width = 0·05 mm; λ = 341·4 nm.

It is difficult to assess the importance of a reduction of NiO during the "thermal stop". According to the literature,[42–46] reduction by CO is favoured over the direct reduction by carbon, at least for temperatures lower than 700–800°. A possible source of CO is the reaction with carbon of the traces of oxygen present in the sweeper gas. However, this reduction cannot go to completion, since the addition of hydrogen to the argon gas (see Fig. 5) increases the signal.

In the case of nickel sulphate the absorption signal is more critically dependent on the thermal cycle. This could be related to the high temperature of decomposition (600°) of this salt. As has been reported for NiO derived from other salts,[47] it is possible that at this temperature NiO is sintered, with consequent greater difficulty of vaporization.

The shape of the analytical curve for nickel chloride (Fig. 4) follows the same pattern. As expected from the equilibrium laws, a large constant excess of chloride would make the curve straighter. We did not attempt to use an excess of chloride larger than 150 ng, because of the severe lowering of the signal strength.

Dilution effect

As shown in Figs. 3 and 4 different concentrations of nickel were used. This was necessary because an unhappy shortcoming of the device we used was the dependence of the strength of the signal on the concentration of sample for equal weights of nickel. This dilution effect causes a 30% loss in the response when 10 μl of 1 ppm nickel-solution were diluted to 20 μl.

Since for smaller volumes, up to 7·5 μl, this effect was negligible, we took this as the maximum permissible volume, without further investigation.

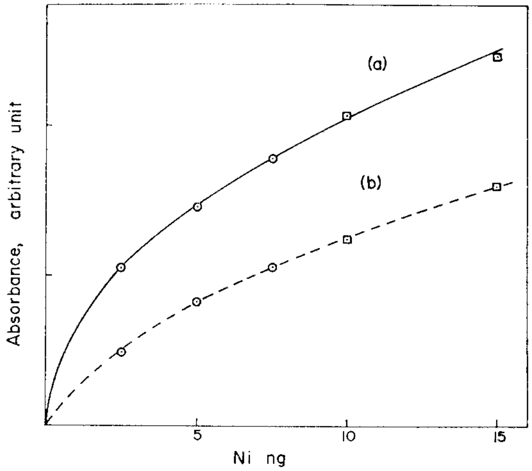

FIG. 4.—Analytical curve for Ni from $NiCl_2$.
○ = 1 ppm, □ = 2 ppm solutions; argon flow-rate = 1 l./min; slit-width = 0·05 mm; λ = 341·4 nm. Curve *a*: $NiCl_2$ alone; curve *b*: $NiCl_2$ with 150 ng of Cl from NaCl.

Hydrogen effect

The reduction of $NiCl_2$ and NiO by hydrogen gas[48] could, possibly, be a simple route for producing gaseous nickel atoms. Some preliminary results are reported in Fig. 5. No interference originating from hydrogen has been detected at the wavelength investigated and similar trends are obtained with chloride and acetate. A low level of hydrogen has a beneficial effect on the signal, because the partial reduction of NiO gives fewer chances for recombination of vaporized nickel and oxygen atoms. A higher level of oxygen impurity in the hydrogen than in the argon could explain the trend in the following part of the curve, in terms of capture of nickel atoms by the oxygen of the sweeper gas.

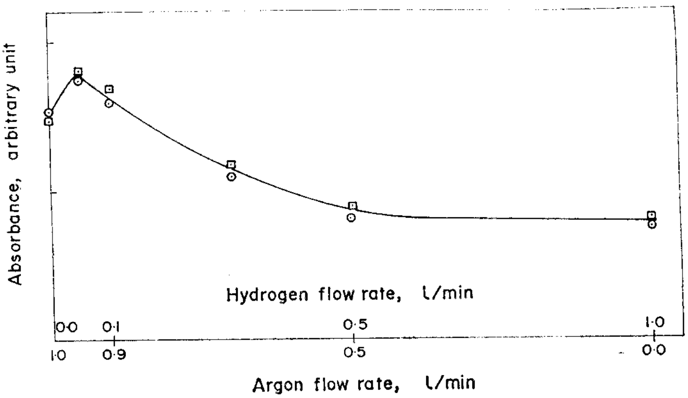

FIG. 5.—Optical response for 2·5 ng of Ni, measured at the peak, *vs.* the concentration of hydrogen.
The total flow is kept constant at 1 l./min; slit-width = 0·05 mm; λ = 341·4 nm.
□ = from 1-ppm $NiSO_4$ solution; ○ = from 1-ppm $Ni(NO_3)_2$ solution.

TABLE I

Ni, *ng*	No. of samples	Relative standard deviation, %
0·25	15	10
0·5	15	12
2·5	20	13
5	20	7
7·5	10	7
10	10	5

Detection limit

Since this technique makes use of discrete samples the response depends on the amount of sample, and the detection limit will accordingly be expressed as an absolute detection limit.

In Table I relative standard deviations are reported as a function of the quantity of nickel. The trend appears surprising, since we should expect a decrease of the relative standard deviation with increasing amount of nickel, but because of the complexity of this system we would not speculate too much on this trend. We only tentatively suggest that in the overall process of transformation of nickel compound into gaseous free atoms, some intermediate step could be by-passed or, at least, lose its importance at low nickel levels. In that case the fluctuations of the variables controlling such an intermediate step would no longer influence the overall response. From the relative standard deviation of 10% for 0·25 ng of nickel it is estimated that the absolute detection limit is approximately 0·1 ng. The use of a high-intensity hollow-cathode lamp and a better purification of the sweeper gas should permit a considerable improvement in sensitivity.

Acknowledgement—We thank Prof. P. Papoff for his encouragement and helpful criticism during the course of this work. Financial support from Consiglio Nazionale delle Ricerche is fully acknowledged.

Zusammenfassung—Zur Bestimmung von Nickel in verschiedenen Salzen wurde eine einfache Einrichtung zur Erzeugung von Atomen untersucht, die aus einem erhitzten Graphitwiderstand besteht. Die für sein Verhalten wesentlichen Parameter wurden optimiert; so wurde eine absolute Nachweisgrenze von 0,1 ng Nickel erreicht.

Résumé—On a étudié un atomiseur sans flamme simple, fait d'une résistance en graphite chauffée, pour le dosage du nickel dans divers sels. Les paramètres caractérisant son comportement ont été rendus optimaux, pour donner une limite de détection absolue de 0,1 ng de nickel.

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Talanta, 1971, Vol. 18, pp. 717 to 732. Pergamon Press. Printed in Northern Ireland

SPECTROPHOTOMETRIC DETERMINATION OF THE PROTOLYTIC DISSOCIATION CONSTANTS OF THE NEW CHROMOGENIC REAGENT "PALLADIAZO"—II*

STUDY OF THE PROTONATION PROCESSES UNDERGONE BY THE AZO-GROUPS OF THE REAGENT IN SULPHURIC ACID MEDIA

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(*Received* 24 *March* 1970. *Accepted* 30 *June* 1970)

Summary—The protonation of the reagent 1,8-dihydroxynaphthalene-3,6-disulphonic-2,7-bis(azophenyl-*p*-arsonic) acid ("palladiazo") has been investigated by a spectrophotometric method in 0·25–18*M* sulphuric acid media. Graphical assessment of the experimental results points to the protonation of only one azo-group, although a two-stage protonation process cannot be conclusively ruled out at very high acidity. The first protonation instability constant is $pK_9 = -(2{\cdot}4 \pm 0{\cdot}1)$ and the second is tentatively estimated as $-7{\cdot}4$. Most of the current views on the complexation and protonation reactions of bis(azophenyl)chromotropic acid derivatives with metal cations and protons are reviewed and critically discussed in some detail in order to interpret the experimental findings. It is concluded that the fully protonated palladiazo molecule exists in very concentrated acid media predominantly in the form of a symmetrical positively charged tautomeric quinonehydrazone proton complex species which is responsible for the appearance of a very strong single absorption band with a maximum at 665 nm which gives the protonated reagent solutions a characteristic deep-emerald-green colour.

THE SPECIAL nature of the protonation processes undergone by the azo-groups of the reagents derived from the azophenyl- and bis(azophenyl)chromotropic acids have made it advisable to study this aspect of the protolytic behaviour of palladiazo in addition to the other protolytic equilibria described in Part I.[1]

The protonation of azo and bisazobenzene derivatives in acid media is of wide general interest and has received the attention of several authors.[2–9] The main conclusion is that stepwise protonation of the two azo-groups of bisazobenzene derivatives takes place as the acidity of the medium increases, with accompanying bathochromic shifts and hyperchromic effects. The nature of the hydrogen–nitrogen bonds formed as a result of the protonation processes is still the subject of discussion. Jaffé *et al.*[4–8] postulate the formation of non-localized H—N bonds, assuming that every proton belongs simultaneously to both N-atoms of each —N=N— group instead of giving rise to the formation of a tautomeric mixture of $—NH^+=N—$ and $—N=NH^+—$ species. According to Gerson *et al.*[2] this mechanism cannot be

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* Communication presented at the International Symposium on Analytical Chemistry, Birmingham, July, 1969

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considered as definitely well-established. On the other hand Cilento[9] considers that the strong bathochromic shifts observed with this type of compound as the acidity of the medium increases derive from the possibility of combination of the proton with the azo groups to form π-complexes,[10] in which d orbitals participate.

The basic problem posed by the protonation of the azo-groups is still more complicated in the case of the bisazo chromotropic acid derivatives since the *peri*-OH phenolic groups in these reagents can be expected to form intramolecular hydrogen-bonds with the α and δ N-atoms of the azo-groups, thereby giving rise to the establishment of the characteristic azo-quinonehydrazone tautomeric equilibria.[11] Special attention has been paid to the mechanism of protonation of the azo-groups in azo- and bisazo derivatives of chromotropic acid, and different hypotheses have been made concerning the mode of formation of six-membered cyclic structures of great stability between the azo and the *peri*-OH phenolic groups.[12]

The protonation of reagents exhibiting the general bis(azophenyl)chromotropic acid structure is a well-known phenomenon, but it is uncertain whether there is protonation of only one[13–16] or of both[17–18] azo-groups.

REVIEW OF THE PROTONATION OF BIS (AZOPHENYL)CHROMOTROPIC ACID DERIVATIVES

Protonation is a special case of the general reaction of bis(azophenyl)chromotropic acid derivatives with cations. Most Russian authors[19–22] assume that the behaviour of these reagents in concentrated acid media implies essentially the same reaction mechanism as that of the reaction with different highly-polarizing cations; it is postulated that the proton replaces the central atom in the cyclic structures formed during complexation.

However, a few authors[23,24] have postulated the possibility of complete protonation of the molecule through its two azo-groups. The one-step protonation theory is, in our opinion, an oversimplified picture since the characteristic formation of conjugated acids by the azo-groups of these reagents in very strong acid media can hardly be supposed to be identical in nature with the normal complexation process exhibited by even highly charged cations.

An argument against this theory can be based on the correlation of the spectral features exhibited by this type of reagent when undergoing reaction with highly charged cations [Th(IV), Pu(IV), U(IV), *etc.*] and when examined in very strong acid media (*viz.* concentrated perchloric or sulphuric acid). In the case of metal reactions, two absorption bands with maxima at about 610 and 670 nm can be observed, whereas for the acidic media only one absorption maximum can usually be observed (at 660–670 nm) although there is a bulge in the 630 nm region which clearly corresponds to a submerged secondary absorption band. If we accept the current views of most Russian authors[19,21–25] and assume that in the first case the two absorption bands are related to the presence of two rather independent chromophoric centres due to distortion of the symmetry of the reagent molecule by electronic rearrangements caused by complexation by only one of the two salt-forming substituents that are *o*,*o*′- to the azo-groups, it is obvious that in the second case we may assume establishment of a more symmetric molecular structure, presumably derived from a greater conjugation of the two chromophoric centres, and that a much weaker secondary absorption band (630–640 nm) might be expected to arise from the attainment of a greater molecular coplanarity. These experimentally well-established facts are difficult to reconcile with the theory of protonation of only one azo-group, since if this were the case the corresponding spectra of these reagents in concentrated acid media would have to resemble much more closely those exhibited by the strong metal complexes. On the other hand, if we expect the two azo-groups to undergo protonation under such high-acidity conditions—whereby they would saturate their potential co-ordinating capacity—the resulting symmetric fully protonated molecular structure would qualitatively explain more satisfactorily the appearance of a unique strong absorption band in the 670 nm region. The main objections raised by the Russian authors against the two-stage protonation mechanism derive both from theoretical considerations of the electronic processes expected to occur under the conditions considered, and from the correlation of experimental facts with the predictions of the MO–LCAO method.[26–28] According to the results obtained by the application of this method the fully protonated molecule of these reagents would show its maximum absorption at ~570 nm as compared with the ~670 nm value found experimentally. An argument in favour of the predictions of the MO–LCAO method has been put forward by Petrova *et al.*[85] who have found that in some special cases (substitution of the phenyl groups in 3,3′ and/or 4,4′ positions by some electron-releasing substituents[86]) allows the complete stepwise protonation of the two azo groups, because of the increased nucleophilic character induced in the azo-groups. As a result of the two-step protonation process, important spectral hypsochromic effects are observed—as predicted[26–28]—accompanied by the appearance of "uncommon" absorption bands characteristic of the "third type" of reactions exhibited by some bis(azophenyl)-chromotropic acid derivatives[16,27,33]. A very interesting feature common to this type of reagent is the disappearance of the two-step protonation mechanism referred to by the authors as a "transition form"[85] when aqueous-organic media are used, whereby the reaction begins to be affected by small amounts of the organic solvent ($\geq 5\%$ ethanol) added to increase the reagent solubility. Another curious fact derives from the statement that the trend to give rise to the appearance of the" transition forms" (exhibited by reagents that give reactions of the "third type") is especially accentuated for some electron-withdrawing substituents[86] in the 3,3′ and/or 4,4′ positions (*viz.* –COOH, $-NO_2$) on the phenyl groups, but a possible two-step protonation mechanism is postulated only for reagents of this kind which contain –OH and/or $-OCH_3$ groups in positions other than 2,2′ on the phenyl groups, as shown by the considerably higher basicity exhibited by the resulting reagents.

A qualitative argument in favour of our views concerning the essentially different nature of the reaction mechanism implied by the complexation and protonation reactions undergone by these reagents when reacting with some metal cations or with protons in concentrated acid media, can be inferred from the experimental results reported by Klygin *et al.*[87] of the differently substituted reagents (nitrochromazo, arsenazo III) which are protonated in concentrated perchloric acid medium, only arsenazo III was shown to undergo reaction with Th(IV), Zr(IV), U(VI) in such a medium, giving rise to the appearance of a characteristic strong secondary absorption band (~610 nm) which is not shown by the pure reagents. As a result the authors conclude that while the protonation reaction exhibits similar and common characteristics for most of the reagents of this type the possible formation of metal complexes in strong acid media depends essentially on the nature of the particular substituents of the two phenyl groups (–SO_3H and –AsO_3H_2 groups in 2,2′ positions are very suitable complex-forming groups for the purpose). Furthermore, the investigation of the protonation process of arsenazo III by trial and error chemical and mathematical methods has led Klygin *et al.*[87] to postulate a rather convincing mechanism for the protonation of these reagents which differs essentially from the current views of most authors, since they arrive at the conclusion that complete protonation of the azo groups of these reagents in concentrated perchloric acid involves the formation of adducts of the general type $[H_nR(HClO_4)_4]$ (co-ordination of two undissociated perchloric acid molecules by each of the azo-groups) while the corresponding monoazophenyl derivatives undergo protonation to yield $[H_nR(HClO_4)_2]$ addition compounds by the same reaction mechanism. When the protonation of the azo-groups takes place in concentrated nitric acid the formation of undissociated $[H_nR(HNO_3)_m]$ adducts has been shown to involve half as many nitric acid molecules as do the perchloric acid adducts (only one molecule of nitric acid is bound to each of the azo-groups). In a preceding communication[1] we have briefly considered the possibility of the reagent palladiazo forming rather unstable addition compounds with concentrated perchloric acid.

Although the MO–LCAO method has an undeniable utility and has often partially elucidated the reagent structures arising as a result of complexation and protonation, Buděšínský[17,18] disagrees essentially with the one-stage protonation theory. He considers that the numerous electronic side-effects and the wrong hypotheses made about the stereochemistry of these reagents and upon which the MO–LCAO theoretical treatment is based, invalidate the method. On the other hand, Buděšínský's arguments in favour of the two-stage protonation theory are of a rather qualitative and intuitive nature, based on logical assumptions about the symmetry and stereochemistry which can explain more satisfactorily the high stability of the metal or proton complex species built by these reagents.[17,18,29]

To explain the symmetrically observed appearance of only a single break in the absorbance *vs.* acidity (H_0) function for a two-stage protonation scheme this author assumes that because of the high symmetry of the molecule and the comparatively long distance between the azo-groups the difference in basicity between the two azo-groups is too small to allow the two-stage protonation process to be detected by means of this function, the criterion being that ΔpK must be more than $\sim 0{\cdot}6$ for two breaks to appear.[30] However, this statement conflicts sharply with the values reported earlier by this author for the two protonation constants ($pK_9 = -2{\cdot}4$; $pK_{10} = -5{\cdot}5$ according to our notation) of the arsenazo III reagent.[31] Buděšínský's arguments are based on the assumption that the two halves of the molecule of this class of reagent behave as two practically independent entities. This overlooks to a major extent the possible electronic perturbations induced in the second chromophoric —N=N— group as a result of the complexation process undergone by the first azo-group, which can be expected to be associated with very strong electronic rearrangements relative to the original state of the non-complexed reagent molecule. On the other hand, in our opinion, the presence of two nearly independent chromophoric centres (which can be assumed to occur to some extent only when the reagents contain bulky substituents on the phenyl groups, at sites *o,o′*- to the azo-groups) would give rise to the appearance of a unique absorption band with a maximum at considerably below 540 nm (pH 2–7; aqueous solutions) by analogy with arsenazo I and the sterically hindered arsenazo II reagents. Arsenazo II has exactly a doubled molecular structure of arsenazo I and both it and its metal complexes have spectral properties nearly identical with those of arsenazo I and its corresponding metal complexes. Were it not for the strong steric hindrance, arsenazo II should have a bathochromically shifted arsenazo I absorption band, forming as well metal complexes considerably stronger than those of arsenazo I, because of the longer electronic resonance system which would arise if the possibility of coplanarity and strong conjugation of its molecule were not strongly blocked by steric hindrance.[21] Buděšínský's arguments about the assumed independence of both chromophoric centres can also be objected to on the grounds that regardless of the nature, number and position of substituents on the phenyl groups, reagents derived from the fundamental bis(azophenyl)chromotropic acid structure generally exhibit a typical strong absorption band at about 540 nm.

In addition to the main absorption band at about 540 nm, almost all these reagents have a characteristic rather strong secondary absorption band at 625–640 nm. The true origin of this secondary absorption band, which has been ignored by most authors, is not yet clear although it seems to be related mainly to the isomeric composition of a given reagent in a given medium. This question will be dealt with in more detail elsewhere[32] since, in addition to the important influence of displacement of the characteristic azo–quinonehydrazone equilibria, we postulate that the stereoisomeric composition of the reagent might determine the ratio of the molar absorptivities at 540 nm and 630 nm. Whatever the true origin of this secondary absorption band, we feel justified in ruling out its attribution to the presence of two partially independent chromophoric centres, since even *p,p′*- *p,m′*- or *m,m′*- bisphenyl-substituted reagents[27,33–35] of this kind (which can be expected to exhibit a high degree of conjugation between their two chromophoric centres by virtue of their high symmetry and coplanarity and lack of possible steric hindrance) show the two absorption bands very distinctly. Palladiazo is not expected to prove an exception.

The experimental facts resulting from study of protonation of palladiazo in concentrated sulphuric acid media have induced us to attempt to clarify current views on these points.

EXPERIMENTAL

Reagents and apparatus

The reagents and apparatus have been described in Part I.[1] Measurements were made 2–4 days after preparation of the solutions (in 10-ml volumetric flasks) for the reasons outlined elsewhere.[1]

Procedure and results

The protonation study of palladiazo has been carried out in sulphuric acid media of acidity between 0·25 and 18*M*. The H_0 acidity values have been taken from the data of Brand[37] and Högfeldt.[38] We used the spectrophotometric method of Muk *et al.*[39] to determine the protonation constants and the number of protons involved in the protonation process. This simple method has been widely used in studies of similar compounds.[39–43]

The protonation of the palladiazo $[H_8L]$ neutral molecule can be written as

$$B + nH^+ \rightleftharpoons H_nB^{n+} \tag{1}$$

with stability constant

$$K_{8+n} = \frac{[H_nB]^{n+}}{[B][H^+]^n}\,. \tag{2}$$

Taking logarithms and using the Hammett acidity function, we obtain

$$H_0 = -\log\,(a_{H_3O^+} + f_B/f_{BH^+}) = -\log h_0 \tag{3}$$

$$\log\frac{[H_nB]^{n+}}{[B]} = -nH_0 + \log K_{8+n} \tag{4}$$

if we assume that only one proton is involved in the first protonation stage of palladiazo ($n = 1$) and that the activity coefficient term in (3) can be taken as unity as a first approach.

A plot of the left-hand side of equation (4) *vs.* H_0 results in a straight line, the slope of which gives the average number of protons involved in the protonation process and the intercept on the axis gives $\log K_{8+n}$. To calculate the value of the left-hand side of (4) we have to determine experimentally $\bar{E} = f(\lambda, H_0)$ for at least two different wavelengths corresponding to the absorption maxima of the base ([B]) and protonated acid ($[H_nB]^{n+}$); the optimum wavelengths to use are 540 and 665 nm.

These functions are shown in Fig. 1 where the limiting ε_{H_nB} and ε_B values needed to calculate $[H_nB]^{n+}$ and [B] for each H_0 value are indicated as calculated from the limiting flat portions of the curves, assuming that at low and high acidity only the pure species, [B] and $[H_nB]$ respectively, exist.

The analysis of Fig. 1 confirms a number of facts[1,36] connected with the behaviour of palladiazo in perchloric acid media, since in sulphuric acid media the following phenomena also occur.

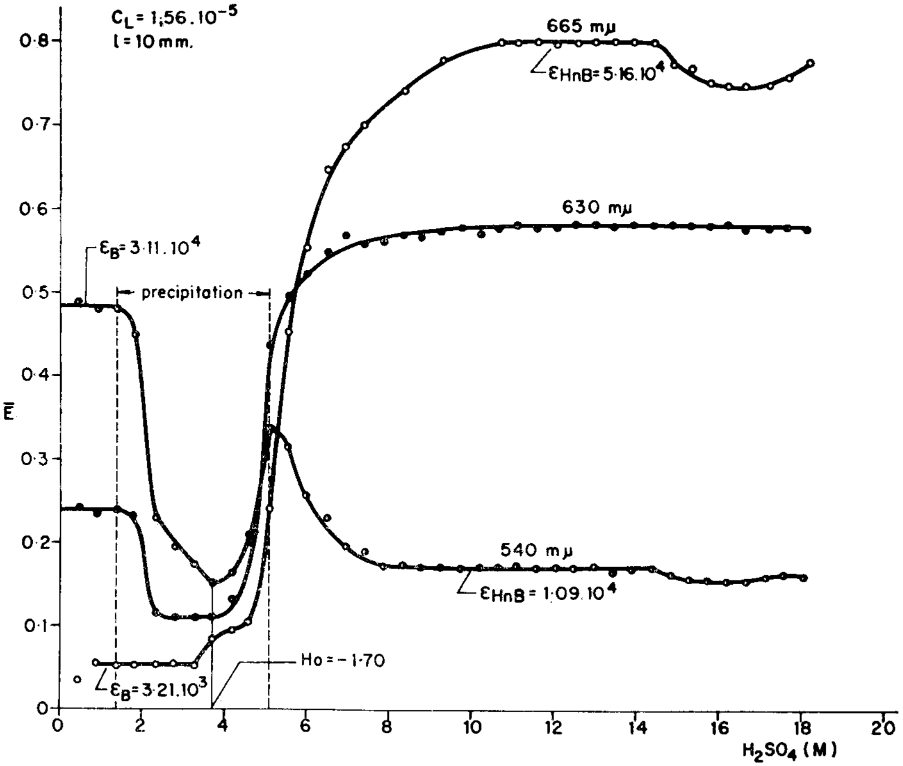


FIG. 1.—Spectrophotometric investigation of the $\bar{E} = f(H_0, \lambda)$ protonation function of palladiazo in sulphuric acid.

(*i*) The existence of a pronounced instability interval within the acidity region $-0{\cdot}5 \leq H_0 \leq -2{\cdot}6$ where the reagent exhibits very low solubility.

(*ii*) The existence of a point of minimum solubility at an acidity value close to $H_0 = -1{\cdot}7$.

(*iii*) The appearance of a discontinuity in the functions shown in Fig. 1, at high acidity values ($H_2SO_4 \geqslant 14{\cdot}5M$; $H_0 \geqslant -7{\cdot}2$) which gives rise to a decrease of the corresponding limiting ε_{H_nB} values.

In contrast to solutions of palladiazo in perchloric acid, the reagent seems very stable with time in sulphuric acid media.

From these results (Fig. 1) we have calculated [B] and $[H_nB]$ by solving for each H_0 value the simultaneous equations

$$\left.\begin{aligned} \varepsilon^{540}_{H_nB} \,.\, [H_nB] \,.\, l + \varepsilon^{540}_{B} \,.\, [B] \,.\, l &= \bar{E}^{540} \\ \varepsilon^{665}_{H_nB} \,.\, [H_nB] \,.\, l + \varepsilon^{665}_{B} \,.\, [B] \,.\, l &= \bar{E}^{665} \end{aligned}\right\} \quad (5)$$

where l is the path length, and made a plot of equation (4).

Figure 2 reproduces the plot and shows that in the protonation of palladiazo in concentrated acid media there is one proton taken up by one azo-group, and log K_9 is $-2{\cdot}4 \pm 0{\cdot}1$ as compared with $-1{\cdot}88$ and $-2{\cdot}07$ obtained by means of the trial and error graphical method used for the palladiazo perchloric acid system.[1] Muk[42] reported independently a value of $-1{\cdot}45$ for the protonation constant of a palladiazo preparation which was not submitted to any special purification process.[45]

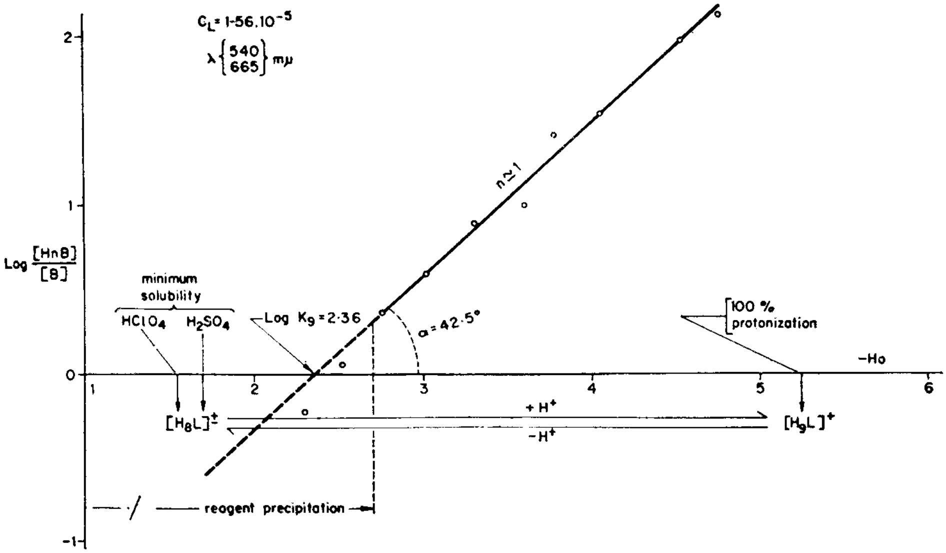


FIG. 2.—Graphical determination of the instability constant and number of protons involved in the protonation of palladiazo.

Very recently Petrova *et al.*[85] have reported a value log $K_9 = -3{\cdot}35$ for the protonation constant of a reagent named "arsanilic S" by Savvin *et al.*[28] which is identical with "palladiazo". The reasons underlying this apparent disagreement between Petrova's findings and ours can be traced very easily, since both values have been obtained by using different acidity functions and acid media. Savvin *et al.*[88] have found that Hammett's H_0 acidity function as established for aqueous perchloric or sulphuric acid solutions,[89,90] cannot be applied directly to account for the protonation process undergone by bis(azophenyl) chromotropic acid derivatives in such media. This fact has led them to establish a new acidity scale[88] based on the use of suitable reagents of this type as indicators. The resulting H_0' function has been shown to differ considerably from the original H_0 scale based on the use of aniline derivatives as indicators.[89,90] However, since many of the reagents investigated by these authors were not sufficiently soluble in aqueous perchloric acid systems, they have resorted to the use of a different acidity scale established for an organic (20% ethanol)–sulphuric acid (80%)–water mixed system,[91] based on the use of different monoazobenzene derivatives as indicators, whereby these authors have assumed the validity of certain *a priori* simplifications.

After suitable correction of our value (log $K_9 = -2{\cdot}2 \pm 0{\cdot}2$)—as obtained by using the common H_0 acidity function—according to the above-mentioned implications we have found a value for the protonation (stability) constant log $K_9 = -(2{\cdot}7 \pm 0{\cdot}3)$ based on the use of the H_0' aqueous–organic acidity function,[91] while a value of $-(3{\cdot}3 \pm 0{\cdot}3)$ has been obtained using Savvin's[88] H_0' acidity function, which agrees very closely with that reported by Petrova *et al.*[85] for the reagent "arsanilic S". It might prove relevant that after carrying out the pertinent correlation of the values reported for the different acidity scales we have found that the acidity values furnished by Savvin's[88] H_0' function for aqueous perchloric acid solutions are still appreciably greater than those obtained by means of the aqueous ethanolic sulphuric acid function.[91]

DISCUSSION

Our conclusion that a proton is taken up by only one of the azo-groups is in agreement with most Russian authors but in disagreement with Budĕšínský's assumptions.

Since the protonation of bis(azophenyl)chromotropic acid derivatives is of relevance to the question of the general complexation mechanism for their reaction with metal ions, the main mechanisms postulated will be briefly and critically reviewed.

Current views on the reaction mechanisms of bis(azophenyl)chromotropic acid derivatives

According to most Russian authors[19,21–25,46] only half of the fundamental symmetric bis(azophenyl)chromotropic acid structure participates in complex formation. Bonding of the cation simultaneously brings about a pronounced deactivation of the other half of the molecule. Consequently, two absorption bands, with maxima at *ca.* 610 and 660 nm, appear as a result of the distortion of the initial molecular and electronic symmetry of a given reagent. Most of the earlier arguments are based on studies of arsenazo III, which shows a single absorption band with a maximum at 540 nm. Consideration of the extent of conjugation of the two chromophoric centres of this reagent and its coplanarity and symmetry has led to the generalization that the appearance of a single absorption band with a maximum at ~540 nm proves the validity of the basic hypotheses adduced to account for the appearance of a new absorption band when the reagent undergoes complexation with cations.

In our opinion, this argument is too simple and inaccurate since almost all the symmetric reagents derived from the fundamental structure give rise to two absorption bands with maxima at 540–550 and 625–640 nm. It cannot be assumed that these two characteristic absorption bands originate from the presence of two more or less independent chromophoric centres, for the reasons outlined above. Therefore the case of the single absorption band shown by arsenazo III must be considered rather as a curious exception to the general rule. Some of the exceptional differences in physicochemical behaviour exhibited by arsenazo III can be related to the particular properties of the arsonic groups (very bulky non-planar substitutents; strong negative induction effect) placed in the 2,2′ positions on the phenyl groups of the structure, as disclosed unambiguously by Muk and Savvin.[42] Petrova *et al.*[85] explain the extremely highly acidic properties disclosed for this reagent (log $K_9 = -5{\cdot}07$ in sulphuric acid media[40])—which depart sharply from the predictions based on the application of Hammett's equation[44,92–94] to the 2,2′ arsono substitution considered, as established by different authors[42,85]—as a consequence of the resulting steric hindrance which gives rise to a considerable distortion of the planarity of the molecule (in contrast with most of the remaining reagents of this kind, the molecule of which seems to be essentially planar, regardless of the nature, number and position of substituents other than $\text{-AsO}_3\text{H}_2$ in the 2,2′ positions) which results in the establishment of an electronic structure resembling more closely that of mono(azophenyl)chromotropic acid derivatives (*e.g.*, arsenazo I) which exhibit a unique hypsochromically shifted absorption band, a much lower basicity (more difficult protonation of the neutral H_nR molecules in strong acid media) and correspondingly higher molar absorptivities with increasing acidity of the resulting molecules.[42]

We conclude that the appearance of the two absorption bands (at 540–550 and 625–640 nm) does not necessarily imply the reaction postulated by the Russian authors, but rather implies changes in the characteristic azo–quinonehydrazone equilibria established originally *both* for the pure reagents and for their metal complexes. This conclusion can account satisfactorily for the appearance of the two absorption bands without excluding the possibility that both symmetrical halves of the reagent molecule might undergo independent reaction with a given cation to give rise to the formation of M_2L or M_2L_2 complexes. Generally speaking, the bathochromic shifts exhibited by the two characteristic absorption maxima of any reagent on complexation can be accounted for easily by the current theories, whereby Savvin[24] for instance assumes that the metal cation behaves as a very characteristic positive strongly auxochromic substituent which brings about important electronic rearrangements during the formation of very stable six-membered rings involving the cation and the *peri*-OH phenolic groups (or any salt-forming substituents on the phenyl groups and *o*,*o*′- to the azo-groups). As a result of this extension to Savvin's original views the important bathochromic shifts (from ~540 to ~610 and from ~630 to ~660 nm) related to the complexation reaction can be easily explained in terms of the resulting increased overall length of the resulting conjugated electronic resonance systems as well as being due to the corresponding increase in the dipole moment of the complex molecule.[24] This view is also essentially held by Armeanu[95] who considers that after the complexation of cations with this type of reagent the appearance of the first maximum (~610 nm) can be ascribed to the complex itself while the second maximum (~670 nm) derives from the establishment of the tautomeric quinone–hydrazone form in the non-reactive second half of the molecule (deactivated according to the cation-auxochromic reaction mechanism proposed by Savvin[24]).

Although most current views seem to agree that the azo tautometric form of the oxyazoaromatic derivatives is responsible for the complexation reactions—as inferred by analogy with the reactions of simple diphenols which cannot undergo tautomerization,[96,97] as well as from the application of the MO–LCAO method[26–28] to a number of reactions of cations with different mono- and bis(azophenyl)chromotropic acid derivatives—some questions still remain to be elucidated concerning the final structural state of the complex. According to Nazarenko *et al.*[20,98–100] on the basis of spectrophotometric measurements and the determination of the number of protons liberated as a result of the complexation reaction, the tautomeric quinone–hydrazone form is responsible for the characteristic colour showed by the metal complexes. This reaction mechanism is accepted by Savvin *et al.*[88] in the special case of bis(azophenyl)-chromotropic acid derivatives which contain an unsubstituted phenyl group, as they have been shown to fail to conform to the regularities implied by the applicability of Hammett's equation relating the variation of the protonation constants of the reagents in concentrated acid media to the particular substituents placed on the fundamental reagent molecular structure. A final argument about the correctness of the proposed azo–quinonehydrazone rearrangement has been supplied recently by Nazarenko *et al.*[101] as a result of the interpretation of the infrared spectra obtained for some solid complexes of this kind as compared with those of the corresponding pure reagents, whereby it is concluded that in the complexes investigated the cation is co-ordinated in partially hydrolysed form with the quinone-hydrazone form of the reagent (no protons are liberated from the *peri*-OH phenolic groups as a result of the complexation reaction since the proton is transferred to the —N=N— group to build the —NH—N= group).

Doubts about the complete validity of the original hypotheses of most Russian authors concerning the general reaction mechanism of these reagents are encountered occasionally.[47,48] Buděšínský has concluded that both halves of the molecule may undergo reaction with cations to build M_2L, ML, ML_2 and even very strong M_2L_2 complexes.[48–51] The formation of M_2L type complexes by arsenazo III with palladium(II) has been demonstrated by us[52] and the probable reaction mechanism implied by the stepwise formation of M_2L, ML and ML_2 complexes has been pointed out[52,53] as a result of comprehensive investigations on the arsenazo III–Pd(II) and palladiazo–Pd(II) systems.[54]

A very interesting question arises from the possibility of formation of very strong dimeric M_2L_2 species formed by analytically bifunctional reagents of this kind with some cations. The existence of such polynuclear compounds with arsenazo III has been postulated,[48–50,55] after the application of suitable chemical and mathematical methods.[56,57] Unfortunately, these conclusions have not found further confirmation when these methods have been applied to the interpretation of the complexation processes undergone by other differently substituted symmetric reagents of this type (i.e., sulphonazo III, phosphonazo III) which are known to form very strong complexes with some cations.[57–60] According to Savvin[21,61] the formation of M_2L_2 complexes would imply that both symmetric halves of the reagent molecule could simultaneously undergo reaction with a given cation; if this reaction mechanism were true the same reaction carried out with the corresponding analytically monofunctional reagent should give rise to the formation of an ML_2 complex[61]. In almost all cases investigated, Savvin has not been able to confirm the existence of M_2L_2 complexes, based on these assumptions. Of course these implications might be qualitatively extended to the interpretation of the one-step or two-stage protonation processes dealt with at the beginning of this article. For the reasons just outlined the correlation of the true reaction mechanisms of this type of reagent with the spectral characteristics (appearance of one or two absorption bands) must be treated with great reserve because of the important role played by tautomeric equilibria, the characteristics of which vary greatly with the nature of the medium. Once again we must express our fundamental doubts about the theories which assume a direct correlation between the complexation (*viz.* involving highly-charged cations in media of comparatively low acidity) and the reagent protonation processes which generally take place in very strongly acidic media.

The criteria of Savvin and most of the Russian authors have very recently been extended by the discovery of new types of very stable ML_2 sandwich-type complex compounds formed by the alkaline earth elements with certain bis(azophenyl)chromotropic acid derivatives.[27,33–35] This new type of reaction gives rise to some of the strongest bathochromic shifts (~180 nm) and greatest molar absorptivities ($\sim 2 \times 10^4$ l.mole. mm^{-1}) so far reported and presupposes again the systematic monofunctional reactivity of potentially bifunctional reagents, with one or more salt-forming planar substituents bound to the phenyl groups of both symmetrical molecular halves of the reagent in positions other than *o,o'*- to the azo-groups.

The bifunctional reactivity of differently substituted bis(azophenyl)chromotropic acid derivatives has been found[62,64] only when cations of the transition elements are involved. Then stepwise complex formation giving rise to M_2L and ML (and possibly to ML_2) complex species has been reported to occur as a rule, thus confirming our conclusions.[52–54] Even in the particular case of palladium(II) the possibility of the exceptional formation of ML_2 and ML-type complexes with analytical monofunctional reagents of these types is postulated.[62] As a rule, with the exception of the transition elements—which are capable of forming fairly stable bonds with both azo-groups, in which the *s,p,d* orbitals participate and permit formation of M_2L-type complexes—the Russian authors still adhere to the hypothesis of monofunctional reactivity of these reagents with most cations, regardless of their potential analytical bifunctionality.

Experimental evidence against the validity of the currently accepted theories on reaction mechanisms

The polarographic investigation of the uranium(VI)–arsenazo III system[64] seems to indicate that both $-AsO_3H_2$ groups *o*- and *o'*- to the azo-groups in this reagent participate to form a 1:1 complex species. This conclusion conflicts very clearly with some of the fundamental implications of the foregoing statements. The important role played by the second arsonic group in the arsenazo III molecule has been clearly brought into evidence by Buděšínský[65] who related the general stability increase shown by the metal complexes to the formation of very stable M_2L_2-type complexes, in the special case of most rare earth(III) ions. The bifunctionality of the arsenazo III molecule has thus been inferred from the application of suitable chemical and mathematical methods.[48,49,57] Unfortunately, as stated before, the formation of M_2L_2 complexes, if their existence can be admitted at all, has not found experimental confirmation in a number of cases where it could analogously be expected to occur.[57–60]

The important role played by the introduction of second azo and arsonic acid groups into the fundamental chromotropic acid structure is discussed by Klygin *et al.*[87] from a direct correlation of the main characteristics exhibited by the complexes built by arsenazo I and arsenazo III with some cations [Zr(IV), Th(IV), Hf(IV)] in concentrated perchloric acid media.

From considerations of stability and structure, Buděšínský[18,29] concludes that both symmetrical halves of the reagent molecule must undergo reaction with cations to build very stable octahedral or cubic structures accounting respectively for the ML and ML_2 stoichiometries. On the other hand, fractional stoichiometries have been reported occasionally for some related complexes[53,66,67] and pose many additional basic questions. Some deviations may occur in these systems because of semicolloidal or colloidal behaviour of the reagents,[36,68] self-association of the reagent molecules,[54,69] criteria of purity upon which the establishment of the reagent titre is based,[54,70,71] the possible existence of undetermined mixtures of structural and geometrical isomers[32],[72] and other complicating factors. As a rule it is best to work with overall reagent concentrations as low as possible. Very often, however, the highest sensitivity of a number of analytical reactions of great practical interest can be achieved only when working with nearly saturated reagent solutions.[24,73,74]

According to Savvin,[24] the possibility of formation of complex species richer in ligand than ML_2 can be ruled out because of the saturation of the co-ordination number of the cations and of the reagents. However, this general prediction has not often been confirmed experimentally.

Further evidence about the complexity of these reactions is provided by the reported compounds with stoichiometry ML_3 and even ML_4. Examples of these are aminomethylazo III with Cu(II),[75] arsenazo III with Th(IV),[76] U(IV),[77] Pu(IV),[78] Zr(IV),[81] U(VI)[82] and palladiazo–Pd(II) (pH = 2·5).[79,80] Our latest findings[54] seem to point to the initial formation of a highly coloured ML_2 complex ($\varepsilon^{655}_{ML_2} \sim 7 \times 10^3$ l.mole^{-1}.mm^{-1}) which decomposes totally after 2–3 days to yield a stable less-intensely coloured ML palladiazo–Pd(II) species ($\varepsilon^{650}_{ML} \sim 2{\cdot}7 \times 10^3$). We have also found that the palladiazo preparations which have been obtained in the free H_8L acid form[69] and submitted to prolonged drying (100–110°) undergo much less sensitive reactions with palladium(II) to form M_2L_3[66] or ML[54] complexes than do the corresponding sodium or calcium salts of palladiazo preparations. This may be due to the initial formation of an unstable ML_2 species (probably a sandwich-type labile complex compound) the existence of which could not be shown originally.[65] Research is currently being done to disclose the reasons underlying these striking differences in behaviour exhibited by the two types of palladiazo preparations, which otherwise are practically identical. Similar observations referring to the thermal lability of this type of reagent have been made by Spitsyn and Shvarev[102] for arsenazo III. Depending on the conditions used for drying (room temperature or 105°) following the synthesis of the reagent it has been shown to exhibit rather different absorption spectra when protonated in concentrated sulphuric acid.

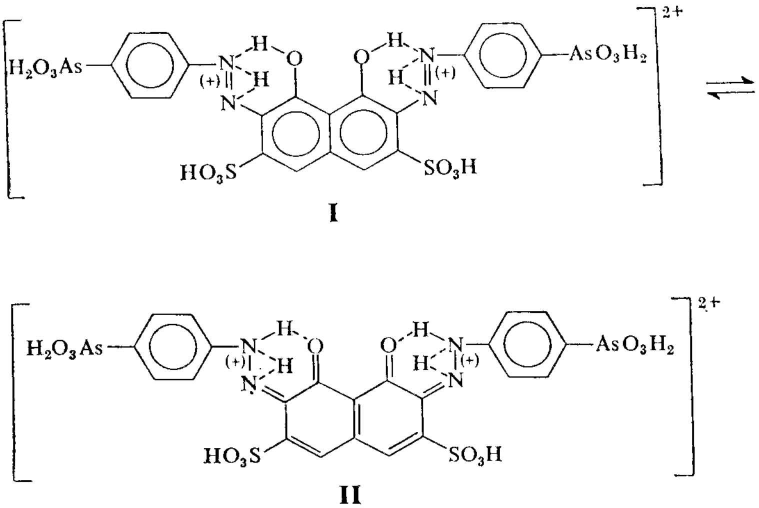
To mention a last puzzling question we may briefly refer to the arsenazo III–uranium(VI) system for which the existence of an M_2L complex has been systematically ruled out by many authors. The physical existence of this compound has been recently disclosed by one of us[83] by anion-exchange experiments. On the other hand the existence of two different ML complexes of molar absorptivities (655 nm) $5{\cdot}3 \times 10^3$ (weakly acidic media) and $8{\cdot}8 \times 10^3$ (strong acid media) l.mole^{-1}.mm^{-1} has been recently reported.[84] In this connection the results reported recently by Klygin *et al.*[103] seem to indicate further that the 1:1 U(VI)- and La(III)-arsenazo III complexes formed in concentrated perchloric acid media are ternary compounds resulting from the substitution of some of the undissociated perchloric acid molecules present in the $[H_8R(HClO_4)_4]$ adduct[87]—formed in the protonation of the reagent—by the particular cation. This striking conclusion emphasizes the clear differentiation existing between the reaction mechanisms implied by the protonation and complexation processes in strongly acidic media, as stressed repeatedly in the foregoing lines. A few interesting observations of this kind have been made recently as a result of our own researches which may lead to the discovery of extremely selective reactions of great analytical value.[104]

The formation of ML_3 and ML_4 complex species, especially in the cases when the reagents are substituted *o,o'*- to the azo-groups by bulky non-planar substituents (*viz.* $-AsO_3H_2$ groups in the case of arsenazo III) is most difficult to explain in terms of current theories on account of co-ordination and spatial requirements. All these facts, which apply in essentially the same way to *o,o'*-, *m,m'*- and *p,p'*- bis(azophenyl)-chromotropic acid derivatives, show that much remains to be done, both from the point of view of experiment and theory.

Interpretation of the protonation process undergone by palladiazo

Returning to the special case of protonation of palladiazo, we seem justified in considering that the discontinuities shown by the $\bar{E} = f(H_0, \lambda)$ functions at very high acidity values ($H_0 > -6$), as depicted by Fig. 1, might be related to protonation of the second azo group. If this hypothesis is valid, the pK_9 and pK_{10} values would differ by a factor as great as $\Delta pK \sim 5$, as calculated directly from Fig. 1 by means of a simple graphical method.[57] The fulfilment of this hypothesis would to some extent qualitatively support Savvin's views[24] that the second half of the molecule is deactivated as a result of the complexation undergone by the first half, because of a concomitant decrease of the electron density around the second azo group. If these arguments apply in practice the experimentally found strong differences in the palladiazo reagent would be satisfactorily explained.

The full protonated palladiazo molecule is best described in terms of the following tautomerization equilibrium:



I

II

From considerations similar to those in the discussion of the structure of the palladiazo molecule in concentrated sodium hydroxide media,[1] we assume the following hypotheses to apply in this case.

(*i*) The reagent is present mainly in the *trans-trans* isomeric form, as derived from the stabilizing effect brought about by the establishment of intramolecular hydrogen-bonds between the phenolic *peri*-OH and the azo-groups.

(*ii*) The formal positive charges are randomly located on the azo-groups as a result of the formation of non-localized hydrogen–azo bonds.[4–8]

(*iii*) Structure II is considered to be the predominant tautomeric palladiazo species in concentrated perchloric or sulphuric acid media, being responsible for the single strong absorption band with maximum at 665 nm since at high acidities the tautomeric equilibrium can be expected to be greatly displaced towards the formation of the more basic quinonehydrazone structure **II**. As a rule, the displacement of the tautomeric equilibria of hydroxyazo compounds towards formation of quinonehydrazone structures, as the polarity of the medium increases, is accompanied by strong bathochromic shifts and important hyperchromic effects.[11]

Acknowledgment—The authors express their warmest thanks to Dr. R. A. Chalmers who has carefully revised and commented Parts I and II of this contribution and has carried out a thorough stylistic improvement of the English text of the original manuscripts.

Zusammenfassung—Die Protonierung des Reagens 1,8-Dihydroxynaphthalin-3,6-disulfon-2,7-bis(azophenyl-p-arson) säure ("Palladiazo") wurde in 0.25 – 18 M schwefelsauren Medien spektrophotometrisch untersucht. Die graphische Auswertung der Versuchsergebnisse deutet darauf hin, daß nur eine Azogruppe protoniert wird, obwohl bei sehr hoher Säurekonzentration eine zweistufige Protonierung nicht ausgeschlossen werden kann. Die erste Dissoziationskonstante entspricht $pK_9 = -(2.4 \pm 0.1)$ und die zweite wird vorläufig zu -7.4 abgeschätzt. Zur Interpretation der Versuchsergebnisse wird eine Übersicht über die meisten gängigen Ansichten über Komplexbildungen und Protonierungen von Bis(azophenyl)chromotropsäurederivaten gegeben und diese Gesichtspunkte im einzelnen kritisch diskutiert. Es wird der Schluß gezogen, daß in sehr konzentrierter Säure das voll protonierte Palladiazo-Molekül vorwiegend in der Form eines symmetrischen positiv geladenen tautomeren Chinonhydrazons vorliegt. Diese Form ist für eine sehr starke, allein auftretende Absorptionsbande mit Maximum bei 665 nm verantwortlich; diese verleiht den protonierten Reagenslösungen eine charakteristische tief smaragdgrüne Farbe.

Résumé—On a étudié la protonation du réactif acide 1,8-dihydroxynaphtalène 3,6-disulfonique 2,7-bis (azophényl *p*-arsonique) ("palladiazo") par une méthode spectrophotométrique en milieux acide sulfurique 0,25–18*M*. L'appréciation graphique des résultats expérimentaux montre la protonation de seulement un groupe azo, quoique un processus de protonation en deux stades ne être nettement éliminé à très forte acidité. La constante d'instabilité de première protonation est $pK_9 = -(2{,}4 \pm 0{,}1)$ et la seconde est expérimentalement estimée à $-7{,}4$. La plupart des conceptions courantes sur les réactions de complexation et de protonation de dérivés de l'acide bis (azophényl) chromotropique avec les cations métalliques et les protons sont passées en revue et discutées de manière critique avec quelques détails afin d'interpréter les découvertes expérimentales. On conclut que la molécule de palladiazo totalement protonée existe en milieux acides très concentrés de manière prédominante sous la forme d'une espèce complexe protonée quinone hydrazone tautomère symétrique chargée positivement, qui est responsable de l'apparition d'une seule bande d'absorption très forte avec un maximum à 665 nm qui donne aux solutions de réactif protoné une coloration vert-émeraude foncé caracteristique.

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Talanta, 1971, Vol. 18, pp. 733 to 737. Pergamon Press. Printed in Northern Ireland

SHORT COMMUNICATIONS

Extraction with long-chain amines—V
Colorimetric determination of cobalt with nitroso-R salt

(*Received* 21 *October* 1970. *Accepted* 13 *November* 1970)

NITROSO-R salt (NRS; sodium-1-nitroso-2-naphthol-3,6-disulphonate) as an analytical reagent for the detection of cobalt was first proposed by van Klooster[1] in 1921. Since then, there have been numerous papers dealing with the basic conditions for colorimetric determination of cobalt. There has also been considerable difference in opinion as to the best wavelength for the measurement of the absorbance of the Co–NRS chelate, the influence of the amount of reagent, elimination of interferences and so on. Willard and Kaufman[2] concluded that 420 nm was the optimum wavelength for the measurement despite the fact that the reagent itself has an absorption maximum in this region. The wavelengths chosen by various authors cover the range 460–600 nm.[3–7] Confusing reports have appeared on the interference of other metals such as iron, nickel, copper, chromium and vanadium. The most serious is interference of iron, which can be masked to some extent with ammonium fluoride. On the other hand many authors prefer its previous separation by extraction or the zinc oxide method. Guerin[7] described another modification based on the construction of special calibration curves for cobalt in the presence of known amounts of iron. Duffield[8] recommends previous extraction of copper, nickel and cobalt with oxine, then separation of these three elements by paper chromatography, and cutting off of the cobalt zone. After extraction from the paper, the cobalt is determined with NRS.

All procedures described so far have used aqueous solutions and no attempts have been made to extract the NRS–cobalt chelate selectively. It has been found that this chelate is smoothly extracted with a chloroform solution of trioctylmethylammonium chloride (TOMA) which makes the reaction more sensitive and, under simple conditions, free from interferences by metals commonly present in the sample, even in large concentration. By this method it is possible to determine cobalt when iron, copper and nickel are present in the ratios (to cobalt) 6000, 1800, and 2000 respectively.

EXPERIMENTAL

Reagents

Cobalt chloride solution, 0·05*M*. Dissolve 11·9 g of reagent-grade quality in 1 litre of redistilled water and check complexometrically. Prepare a $5 \times 10^{-4}M$ solution by appropriate dilution.

Nitroso-R salt solution, $5 \times 10^{-4}M$. Prepared by dissolution of 0·047 g of the compound in 250 ml of redistilled water.

Trioctylmethylammonium chloride solution in chloroform, 5% *w/v*. Dissolve 50 g of Aliquat (General Mills Inc., Kankakee, Illinois) in 1 litre of chloroform. Shake the solution with 200 ml of 20% sodium hydroxide solution for 10 min, then with 200 ml of hydrochloric acid (1 + 1) for 10 min, and then for 10 min with 200 ml of 20% sodium chloride solution. Wash the equilibrated solution with a small amount of water and filter it through a dry filter.

Ammonium acetate solution, 0·5*M*. Dissolve 68·0 g of the reagent-grade trihydrate in 1 litre of redistilled water.

Absorption spectra of Co–NRS *chelate in aqueous solution*

The optimum measurement wavelengths reported by others, *e.g.*, 420 nm,[1] 525 nm,[2] 578 nm[7] seemed to us a little confusing. A high concentration of the reagent is necessary, especially in the presence of interfering elements that also form chelates with the reagent, which are destroyed by the addition of acid and heating for a length of time which is critical and usually recommended to be 30 sec in a boiling water-bath. After this treatment the excess of the reagent (included that liberated from the decomposed complexes) remains in the solution, giving a very high background absorbance. Attempts have been made to reduce this background. Marston and Dewey[9] discharged the yellow colour of excess of the reagent by bromination. Other authors proposed chlorine,[10] potassium bromate[11] or sodium perborate with hydrochloric acid.[12]

We therefore carried out a series of experiments to compare the conventional method with our proposed extraction method, as follows. We mixed 2·5 ml of $5 \times 10^{-4}M$ cobalt with 2·5 ml of $5 \times 10^{-3}M$ reagent, then added 0·5 ml of 10% sodium chloride solution, 2 ml of acetate buffer (pH 6) and diluted to 25 ml with water. After 15 min the spectrum was recorded against water and against a reagent blank prepared in the same way. Part of the solution was treated with 1 ml of conc. nitric acid and heated for 30 sec in a boiling water-bath and the spectrum was recorded again. Then 5 ml of the untreated solution were diluted to 25 ml and extracted with 5 ml of the chloroform/TOMA solution. After phase separation the spectrum was recorded against a blank prepared in the same way. Figure 1 shows the absorption spectra. We can see that in the presence of a 10-fold excess of reagent the curve is deformed even if the measurement is made against a reagent blank. The heating with nitric acid has an unfavourable effect on the height of the absorption maximum at 480–500 nm.

Influence of pH

It has been found that cobalt reacts quantitatively with the reagent in 15 min at normal temperature in acetate-buffered solution (pH 5·5–6). The colour is stable in acidic medium at room temperature and can be extracted very easily with chloroform/TOMA if sodium chloride is present as salting-out reagent. The colour of the extract is stable for at least 24 hr. The influence of the acidity on extraction is very small between pH 0·75 and 5·40. The extracted complex has maximum absorbance at 500 nm with an isosbestic point at 480 nm (Fig. 2). The Co:NRS ratio is 1:3. Excess of reagent has no effect on the absorbance at the maximum.

Recommended procedure for calibration curve

To *x* ml of $5 \times 10^{-4}M$ cobalt in a 150-ml separating funnel add 2 ml of $5 \times 10^{-3}M$ nitroso-R salt, 2 ml of saturated sodium chloride solution, 0·5 ml of 0·5*M* sodium acetate and dilute to 25 ml with water. Then add 5 ml of 5% TOMA-chloroform solution and shake for 2 min. After phase separation, filter the organic layer into a 10-mm cell and measure at 500 nm against a blank. Beer's law is obeyed up to 20 μg of cobalt in 5 ml of the chloroform extract.

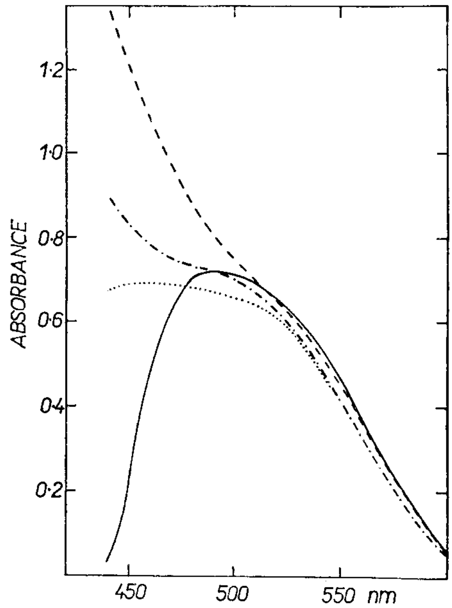

FIG. 1.—2·5 ml of $5 \times 10^{-4}M$ Co + 0·5 ml of $5 \times 10^{-3}M$ NRS + 0·5 ml of 5% NaCl solution + 2 ml of acetate buffer, pH 6, diluted to 25 ml with water; measured in 10-mm cells.

-·-·-·-·-·-·-·- in the cold against a blank;
- - - - - - - - - - - in the cold against water;
· · · · · · · · · · · after the addition of 1 ml of conc. HNO_3 and heating;
———————— in the cold, after extraction with 5 ml of TOMA-chloroform; measured against a blank.

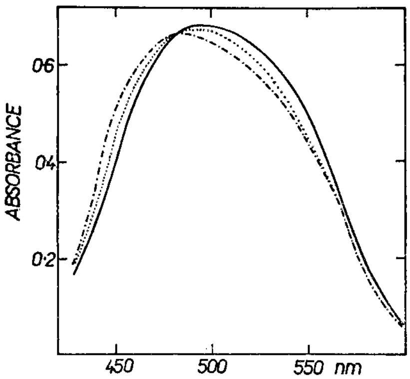

FIG. 2.—0·5 ml of $5 \times 10^{-4}M$ Co + 0·5 ml of $5 \times 10^{-3}M$ NRS + 2 ml of 5% NaCl solution, pH adjusted with HCl or NaOH and solution made up to 25 ml with water; extracted with 5 ml of 5% TOMA-chloroform; measured in 10-mm cell against a blank.

–·–·–·–·–·–·– pH 0·75
· · · · · · · · · · · · pH 1·42; 2·53; 3·28
———————— pH 4·48; 5·35.

Influence of anions and dilution

The reaction and extraction of the complex are not influenced by the presence of acetate, chloride, sulphate, fluoride and citrate (4 g of the sodium salt in 100 ml). Nitrate seriously interferes in the extraction—0·2 g of potassium nitrate per 100 ml of the solution lowers the absorbance by about 30%.

EDTA added before the reagent, prevents the reaction of cobalt, but if added after the colour development is without effect even at boiling temperature. This effect can be used for masking of various elements or impurities in the blank.

The extractions have been performed from 25–200 ml of aqueous solution and no difference in the measured absorbance have been observed.

TABLE I.—DETERMINATION OF COBALT IN THE PRESENCE OF IRON, NICKEL, COPPER, CALCIUM AND MANGANESE

Co taken, *μg*	Metal taken, *mg*	Ratio M:Co	Co found, *μg*	Procedure
14·7	5·6 Fe	380	13·8	A
8·8	14·0 Fe	1580	8·9	B
17·7	29·0 Fe	1630	17·3	D
14·7	56·0 Fe	3800	13·2	D
8·8	56·0 Fe	6300	8·8	D
14·7	14·0 Fe	950	14·5	C
14·7	0·08 Ni	60	13·8	A
14·7	29·0 Ni	1970	14·3	B
14·7	29·0 Ni	1970	14·1	D
14·7	15·0 Cu	1050	14·0	B
8·8	15·0 Cu	1970	8·8	B
8·8	0·1 Mn	12	8·7	A
8·8	29·0 Mn	3100	8·8	D
14·7	10·0 Ca	68	14·2	A
8·8	200·0 Ca	22600	9·0	D
14·7	400·0 Ca	27200	14·7	D

Interferences and masking

We have studied mainly the elements considered to give serious interference, such as iron, nickel and copper. Iron(III) and iron(II) give rise to a brown and green colour respectively after addition of the reagent. Nickel and copper react similarly, forming coloured complexes with the reagent. All these complexes can be destroyed by addition of acid and heating. The main disadvantage is that all react almost at the same time as the cobalt and therefore a large amount of reagent must be used to ensure quantitative reaction of cobalt. After the treatment with acid a large amount of free reagent remains in the solution and has a considerable absorbance. In addition, the coloured cations liberated might influence the final absorbance. For masking of iron, fluoride has been recommended. Sodium phosphate reduces the interference of these metals by forming insoluble phosphates which do not react with the reagent. Sodium citrate is also a powerful masking agent, and is useful despite the fact that the colour of the cobalt complex develops only slowly in its presence. The Co–NRS complex can be extracted and measured 1 hr after the addition of all reagents.

Four procedures were developed for determination of cobalt in the presence of common interfering elements.

Procedure A. To the slightly acid solution containing up to 20 μg of cobalt and smaller concentrations of iron, nickel, copper (manganese, calcium *etc*) add 2–5 ml of the reagent and 0·5 ml of 0·5*M* sodium acetate. After 15 min add 2 ml of 0·1*M* hydrochloric acid and extract with 5 ml of TOMA–chloroform solution, filter the organic layer through dry filter paper, and measure in a 10-mm cell at 500 nm.

Procedure B. To the solution add 0·5 g of diammonium hydrogen phosphate, then all reagents as above. After 5–10 min add 2–3 ml of 0·1*M* hydrochloric acid (to dissolve the light precipitate) and proceed as above with extraction.

Procedure C. Add to the solution 5 ml of saturated sodium fluoride solution and the other reagents, and after 15 min extract as usual.

Procedure D. Add to the solution 10 ml of sodium citrate solution (pH 6) reagent, and sodium acetate. After 1 hr extract the complex and measure as above.

All these procedures have been used for artificial mixtures of small amounts of cobalt and large amounts of nickel, copper and iron (manganese, calcium). Chromium(VI) can be extracted previously from acidic medium with TOMA–chloroform solution.[13] Some results are summarized in Table I.

Acknowledgement—The authors wish to thank Mr. J. E. House (General Mills Inc., Minneapolis, U.S.A.) for providing samples of Aliquat.

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Summary—The colorimetric determination of cobalt with nitroso-R salt (NRS) has been modified and improved by the introduction of extraction of the Co–NRS chelate into a chloroform solution of trioctylmethylammonium chloride. Ammonium phosphate, fluoride and mainly citrate were used for masking iron, nickel, copper and calcium, which under the described conditions do not interfere even in 2000-fold excess. The method is very sensitive and permits determination of about 1 μg of cobalt per ml of the extractant.

Zusammenfassung—Die kolorimetrische Bestimmung von Kobalt mit Nitroso-R-Salz (NRS) wurde durch Extraktion des Co-NRS-Chelats in eine Chloroformlösung von Trioktylmethylammoniumchlorid abgeändert und verbessert. Ammoniumphosphat, Fluorid und hauptsächlich Citrat wurden zur Maskierung von Eisen, Nickel, Kupfer und Calcium verwendet; diese Metalle stören unter den angegebenen Bedingungen selbst in 2000-fachem Überschuss nicht. Die Methode ist sehr empfindlich und erlaubt die Bestimmung von etwa 1 μg Kobalt pro ml Extraktionsmittel.

Résumé—Le dosage colorimétrique du cobalt au moyen du sel nitroso-R (NRS) a été modifié et amélioré par l'introduction d'une extraction du chélate Co–NRS dans une solution chloroformique de chlorure de trioctylméthylammonium. Le phosphate d'ammonium, le fluorure et principalement le citrate ont été utilisés pour dissimuler les fer, nickel, cuivre et calcium, qui dans les conditions décrites ne gênent pas, même quand ils sont 2000 fois en excès. La méthode est très sensible et permet le dosage d'environ 1 μg de cobalt par ml d'agent d'extraction.

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La réaction des nitrilotriacétates métalliques avec la cycloleucine

(*Reçu le* 10 *septembre* 1970. *Accepté le* 16 *novembre* 1970)

IRVING et Pettit ont étudié les complexes métalliques simples derivant de la cycloleucine.[1] Aucun complexe mixte contenant la cycloleucine n'a été decrit jusqu'à présent. Dans ce travail, nous avons étudié les complexes mixtes qui résultent de la reaction des nitrilotriacétates métalliques avec la cycloleucine, qui est un amino acide connu aussi sous le nom d'acide 1-aminocyclopentane-carboxylique.

PARTIE EXPÉRIMENTALE

Les titrages pH-métriques (a une force ionique de $0,1M$ KNO_3) ont été effectués dans une cellule thermostatée, et pour chaque température, on a étalonné le pH mètre avec des solutions tampons ayant un pH bien connu aux températures utilisées. La concentration des protons a été calculée par les formules données dans la monographie de Butler.[2]

Les solutions de nitrates métalliques utilisées ont été etalonnées préalablement par des méthodes complexométriques.[3,4]

RÉSULTATS

Sur la Fig. 1, on montre le titrage par la soude des mélanges contenant des quantités équimoléculaires de nitrate metallique (Me^{2+}), de nitrilotriacétate disodique (XH^{2-}) et de cycloleucine (LH). Si "*a*" représente le nombre de moles de base ajouté par mole de métal, on voit clairement qu'il y a deux points d'inflexion situés respectivement à $a = 1$ et $a = 2$. Pour expliquer ces résultats, on suppose que le complexe simple MeX^- et le complexe mixte $MeLX^{2-}$ se forment respectivement dans deux étapes distinctes.

En effet, jusqu'à $a = 1$ on forme le complexe simple par la réaction:

$$Me^{2+} + XH^{2-} \rightarrow MeX^- + H^+. \qquad (1)$$

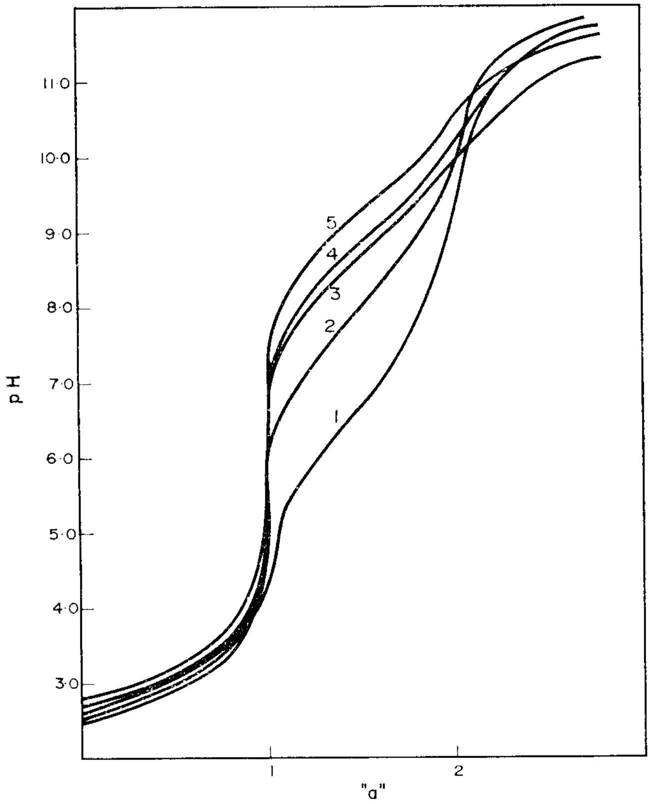
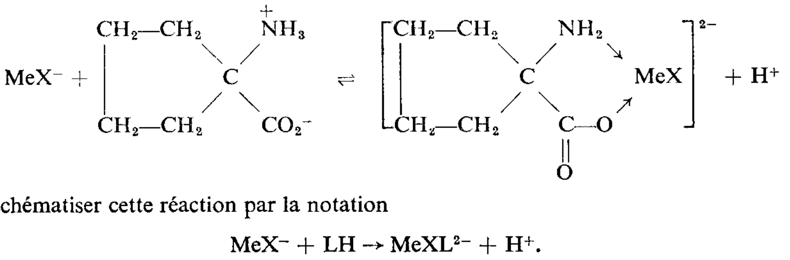


FIG. 1.—Titrage à l'aide de soude d'un mélange équimoléculaire de nitrate de métal 0,02*M* en présence de nitrilotriacétate disodique 0,02*M* et de cycloleucine 0,02*M* à une force ionique $I = 0{,}1M$ KNO_3 et à une température de 25°C. Le nombre de moles de soude ajouté par mole de métal est representé par "*a*".
1—Cu; *2*—Ni; *3*—Zn; *4*—Co; *5*—Cd.

Le complexe mixte se forme seulement entre $a = 1$ et $a = 2$ par la réaction



On peut schématiser cette réaction par la notation

$$MeX^- + LH \rightarrow MeXL^{2-} + H^+. \tag{2}$$

Dans la région située entre $a = 1$ et $a = 2$ il n'existe pas dans la solution la forme LH_2^+ du ligand, car a 25° on a pour LH_2^+ un $pK_a = 2{,}39 \pm 0{,}01$. Les seules espèces à considérer dans cette région sont: MeX^-, $MeXOH^{2-}$, $MeXL^{2-}$, LH, L^-.

On a calculé la constante de formation du complexe mixte, K_f, par la méthode de Schwarzenbach et Martell[5,6] en utilisant les points expérimentaux situés entre $a = 1$ et $a = 2$. Par rapport aux travaux antérieurs[7,8,9] nous avons amélioré la méthode de calcul de K_f en considérant l'hydrolyse des nitrilotriacétates metalliques qui s'effectue par la réaction:

$$MeX^- + H_2O \rightarrow MeXOH^{2-} + H^+. \tag{3}$$

Si C_{Me}, C_{X} et C_{L} sont respectivement les concentrations totales de métal, de nitrilotriacétate et de cycloleucine, on peut écrire les équations suivantes:

$$C_{\mathrm{Me}} = C_{\mathrm{X}} = C_{\mathrm{L}} \tag{4}$$

$$C_{\mathrm{Me}} = [\mathrm{MeX}^-] + [\mathrm{MeXOH}^{2-}] + [\mathrm{MeXL}^{2-}] \tag{5}$$

$$C_{\mathrm{L}} = [\mathrm{HL}] + [\mathrm{L}^-] + [\mathrm{MeXL}^{2-}] \tag{6}$$

$$(a - 1)C_{\mathrm{Me}} = [\mathrm{MeXL}^{2-}] + [\mathrm{MeXOH}^{2-}] + [\mathrm{L}^-] + [\mathrm{OH}^-] - [\mathrm{H}^+] \tag{7}$$

$$K_f = \frac{[\mathrm{MeXL}^{2-}]}{[\mathrm{MeX}^-][\mathrm{X}^-]} \tag{8}$$

$$K_{\mathrm{h}} = \frac{[\mathrm{MeXOH}^{2-}][\mathrm{H}^+]}{[\mathrm{MeX}^-]}\,. \tag{9}$$

A partir des équations (4)–(9), on obtient par algèbre simple les formules suivantes:

$$[\mathrm{L}^-] = \frac{\{(2 - a)C_{\mathrm{Me}} + [\mathrm{OH}^-] - [\mathrm{H}^+]\}\cdot\{1 + K_{\mathrm{h}}/[\mathrm{H}^+]\}}{\{[\mathrm{H}^+]/K_1 - K_{\mathrm{h}}/[\mathrm{H}^+]\}}\,. \tag{10}$$

$$\frac{K_f[\mathrm{L}^-]}{[1 + K_{\mathrm{h}}/[\mathrm{H}^+]]} + 1 = \frac{C_{\mathrm{Me}}}{[\mathrm{L}^-]\{1 + [\mathrm{H}^+]/K_1\}} = y\,. \tag{11}$$

Les valeurs de pK_1, qui est la constante de dissociation de LH, sont 10,12 (15°); 9,82 (25°); 9,14 (50°); 8,70 (70°). On calcule d'abord $[\mathrm{L}^-]$ par la formule (10) puis on calcule y et l'on trace le graphique de y en fonction de $[\mathrm{L}^-]/\{1 + K_{\mathrm{h}}/[\mathrm{H}^+]\}$ la droite résultante ayant une pente égale à K_f.

On a calculé auparavant dans ce laboratoire[8] les valeurs de log K_{h} a 25°. Dans ce travail, nous avons redéterminé K_{h} par la même méthode qu'auparavant[8] à d'autres températures que 25° et les valeurs de log K_{h} sont données dans le Tableau I avec l'enthalpie ($\Delta H_{\mathrm{h}}°$) et l'entropie ($\Delta S_{\mathrm{h}}°$) de la réaction d'hydrolyse.

Les constantes de formation des complexes mixtes sont données dans le Tableau II qui contient également l'enthalpie ($\Delta H_f°$) et l'entropie ($\Delta S_f°$) de la réaction de formation de complexes mixtes. Pour calculer l'enthalpie, on a trace le graphique de ln K en fonction de $1/T$ et l'on a multiplié par R la pente de la droite résultante. A chaque température, on a calculé l'entropie en utilisant les formules suivantes:

$$\Delta G° = \Delta H° - T\Delta S° \tag{12}$$

$$\Delta G° = -RT \ln K. \tag{13}$$

Les valeurs de $\Delta S°$ données dans les Tableaux I et II sont des valeurs moyennes.

TABLEAU I.—CONSTANTES D'HYDROLYSE DES NITRILOTRIACÉTATES MÉTALLIQUES À DIFFÉRENTES TEMPÉRATURES ET À $I = 0{,}1M$ KNO$_3$

Métal	15°C	$-\log K_{\mathrm{h}}$ ($\pm 0{,}02$) 25°C	50°C	70°C	$\Delta H_{\mathrm{h}}°$ *kJ/mole*	$\Delta S_{\mathrm{h}}°$ *J.K^{-1}.mole^{-1}*
Cu(II)	9,43	9,14	8,67	8,42	33 ± 0,5	−66 ± 2
Zn	10,47	10,06	9,43	9,02	48,5 ± 0,5	−40 ± 1
Co(II)	11,35	10,80	10,26	9,80	46 ± 1	−47 ± 2
Ni	11,00	10,86	10,49	10,32	23 ± 0,5	−127 ± 2
Cd	11,77	11,25	10,52	10,23	47 ± 1	−57 ± 2

TABLEAU II.—CONSTANTES DE FORMATION DES COMPLEXES MIXTES Á DIFFÉRENTES TEMPÉRATURES ET À $I = 0{,}1M$ KNO$_3$

Métal	15°C	$\log K_f$ ($\pm 0{,}02$) 25°C	50°C	70°C	$\Delta H_f°$ *kJ/mole*	$\Delta S_f°$ *J.K^{-1}.mole^{-1}*
Cu(II)	5,62	5,29	4,82	4,42	−39 ± 0,5	−29 ± 1
Ni	4,12	4,03	3,77	3,56	−17 ± 1	+20 ± 0,5
Zn	3,33	3,28	2,99	2,80	−15 ± 0,5	+12 ± 0,5
Co(II)	3,15	3,10	2,85	2,68	−17 ± 1	3 ± 0,5
Cd	3,55	2,50	2,38	2,30	−8,5 ± 0,5	23 ± 0,5

DISCUSSION

On voit que la réaction d'hydrolyse des nitriolotriacétates métalliques est une réaction endothermique et l'on obtient pour cette réaction une entrop e négative car le proton libéré est solvaté et par consequent il y a une augmentation de l'ordre dans le système.

Les constantes de formation des complexes mixtes suivent la série de Irving-Williams[10] et l'on peut les ranger dans l'ordre Cu > Ni > Zn > Co > Cd. On remarque également que la réaction de formation des complexes est une réaction exothermique.

Concernant la réaction de formation des complexes mixtes, on doit noter qu'on a obtenu un $\Delta S_f°$ negatif seulement pour le cuivre,[11] tandis que pour les autres métaux on obtient des valeurs plus petites de $\Delta S_f°$ qui d'ailleurs sont positives. Pour expliquer les $\Delta S_f°$ positifs observés dans le cas de Ni, Zn, Co, Cd, on suppose que le métal reste hexacoordonné dans le complexe mixte et que la réaction de formation des complexes est accompagnée par le remplacement de deux molécules d'eau par le ligand bicoordinant. On a obtenu un $\Delta S_f°$ negatif pour cuivre car en ce cas, du fait de l'effet Jahn-Teller, dans le complexe mixte, deux groupements carboxylés axiaux provenant du nitrilotriacetate s'éloignent et sont simultanement solvatés. On note également que la réaction de formation du complexe mixte de cuivre est plus exothermique que la réaction similaire avec le nickel. D'après Yatsimirskii,[11] c'est une preuve thermochimique de l'existence de l'effet Jahn-Teller dans le complexe mixte de cuivre. Des effets similaires ont été observés récemment par Nancollas.[12]

Il y a une relation linéaire entre K_f (cycloleucine) et K_f (glycine), qui sont respectivement les constantes de formation des complexes mixtes.

Remerciements—Nous remercions le CNR de Canada pour nous avoir subventionné ce travail.

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Summary—The formation constants of the mixed complexes which result by the reaction of metallic nitrilotriacetates with cycloleucine have been calculated for different temperatures. For the reaction of formation of mixed complexes $\Delta H_f°$ and $\Delta S_f°$ have also been calculated. The hydrolysis of metallic nitrilotriacetates has been studied at different temperatures and K_h, $\Delta H_h°$, $\Delta S_h°$ calculated.

Zusammenfassung—Die Bildungskonstanten der gemischten Komplexe, die bei der Reaktion von Metall-Nitrilotriacetaten mit Cycloleucin entstehen, wurden bei verschiedenen Temperaturen berechnet. Auch $\Delta H_f°$ und $\Delta S_f°$ für die Bildungsreaktion der gemischten Komplexe wurden berechnet. Die Hydrolyse von Metall-Nitrilotriacetaten wurde bei verschiedenen Temperaturen untersucht und K_h, $\Delta H_h°$, $\Delta S_h°$ berechnet.

Résumé—On a calculé à différentes températures les constantes de formation des complexes mixtes qui se forment par réaction des nitrilotriacétates métalliques avec la cycloleucine. On a calculé aussi les $\Delta H_f°$ et $\Delta S_f°$ pour la réaction de formation des complexes mixtes. L'hydrolyse des nitrilotriacétates métalliques a été étudée à différentes températures et on a calculé pour cette réaction K_h, $\Delta H_h°$ et $\Delta S_h°$.

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Talanta, 1971, Vol. 18, pp. 741 to 744. Pergamon Press. Printed in Northern Ireland

Identification of some polyatomic inorganic anions as their diphenyliodonium salts by infrared spectroscopy and interpretation of the spectra

(*Received* 20 *July* 1970. *Accepted* 19 *November* 1970)

ANIONS can be identified by infrared examination of their salts, and Miller and Wilkins have produced an excellent infrared atlas of 159 compounds, mostly simple salts of polyatomic anions.[1] Al-Kayssi and Magee[2] used tetraphenylarsonium chloride as a precipitant for some anions, and obtained the infrared spectra of the precipitates; the reagent is good but expensive. Haba and Wilson[3] suggested the infrared examination of potassium salts since it ensures constant cation symmetry, but the necessary ion-exchange is time-consuming and occasionally difficult.

It is now shown that diphenyliodonium precipitates[4] of various anions can be used for qualitative infrared investigation. The reagent is easily prepared, at high purity, and precipitates most of the anions similarly to the arsonium compound. The compounds formed have comparatively high molecular weights and give relatively simple spectra.

EXPERIMENTAL

Spectra were recorded with a Grubb-Parsons Spectromaster II. Potassium bromide discs were prepared in the usual manner.

Diphenyliodonium chloride (DPIC) was prepared by Beringer's[5] method.

Procedure

Evaporate a solution containing 10–30 mg of anion until crystals just appear. Add the minimum amount of water needed to redissolve the crystals. Add enough 5*M* sodium chloride to make the final chloride concentration approximately 1*M*. Add a slight excess of saturated diphenyliodonium chloride solution, cool to 0°, collect the precipitate and dry it *in vacuo* at 60°. Weigh 4–6 mg of precipitate and 1 g of potassium bromide, and grind the mixture in an agate mill. Place 0·3 g of the mixture in a die and press in the usual manner. Record the spectra over the appropriate range, against a potassium bromide compensation disc. To differentiate between chromate and molybdate, if present, add about 0·2 g of sodium citrate addition to the test solution to prevent precipitation of molybdate. If hexacyanoferrate(II) or (III) are present, add a few drops of dilute hydrochloric acid to the test solution to ensure precipitation of both.

RESULTS AND DISCUSSION

The infrared spectra indicate that the procedure may be used for detecting the anions without the necessity of separation, and for confirmation of other findings. In addition to their qualitative use they yield information on the structure of the products.

The advantages of using DPIC to obtain salts of anions that will be suitable for infrared examination are similar to those for tetraphenylarsonium chloride (TPAC), and in addition, DPIC is very easily prepared at a fraction of the cost of TPAC.

Table I gives the characteristic bands and indicates their relative intensities.

The frequencies of the characteristic bands examined are attributable to metal-oxygen bonds, to non-metal–oxygen bonds and to the C—N stretching frequencies in simple and complex cyanides.

Perchlorate, periodate and permanganate

Perchlorate can be identified by bands in the regions 620–634 and 1080–1140 cm^{-1}. These show characteristic splitting of the ClO_4 group in symmetry lower than T_d. The metaperiodate is sparingly soluble and shows a strong and characteristic split band at 826–847 cm^{-1}.

Permanganate shows a strong split band at about 900 cm^{-1}. A difficulty in the detection of the

TABLE I

No.	Anion	Characteristic bands, *cm*$^{-1}$
1	Perchlorate	623(s, sp); 628(s, sp); 634(s, sp); 938(w); 1081(vs); 1113(vs); 1141(vs)
2	Metaperiodate	550(w, b); 750(m, sh); 780(w); 826(s); 847(vs)
3	Permanganate	500–625(w, vb); 880(m); 896(s); 911(s); 919(sh)
4	Molybdate	708(s); 840(m); 900(s); 938(s)
5	Dichromate	735(s); 769(s); 862(m, sp); 922(s); 942(s)
6	Peroxodisulphate	558(s, sp); 593(m); 699(s); 745(s); 754(s); 1060(s, sp); 1110(m); 1133(m); 1271(s); 1296(s); 1306(s)
7	Hexacyanoferrate(II)	2020(m); 2070(vs)
8	Hexacyanoferrate(III)	2020(m); 2095(w); 2120(vs)
9	Thiocyanate	460(m) 729(s); 2070(vs)

b = broad; m = moderate; s = strong; sh = shoulder; sp = sharp; v = very; w = weak.

permanganate is the thermal instability of the precipitate, which decomposes explosively at 100°. It is thus sensitive to grinding and pressing. The decomposition product is manganese(IV) oxide. It is difficult, therefore, always to prepare satisfactory discs. A feature of spectra of diphenyliodonium perchlorate, metaperiodate and permanganate is the marked splitting of the major absorption bands. Such splitting is barely discernible in the corresponding tetraphenylarsonium salt spectra.[2]

Only two of the four normal vibrations of a tetrahedral XO_4 molecule or ion are infrared active; the asymmetric stretch of X—O (ν_3 band) and the deformation band (ν_4). The lowering of symmetry to C_{3v} or $C_{2\gamma}$ splits the degenerate vibration and activates the otherwise inactive vibrations. The observed splitting of the bands of the salts studied indicates a lowering of symmetry resulting from a covalent bond between the oxo-group and the diphenyliodonium ion.

Molybdate, tungstate and dichromate

Molybdate forms a precipitate with the reagent, whereas the tungstate has moderate solubility and is not precipitated. A difficulty in the infrared identification of molybdate is the fact that the ion readily polymerizes and the observed vibration modes vary with the extent of polymerization.[6] In the case of the DPIC precipite, characteristic bands occur at about 700, 840, 900 and 940 cm^{-1}. Addition of citrate to the original solution prevents the precipitation of molybdate, which further confirms its presence. Tungstate cannot be identified, since it does not precipitate.

Diphenyliodonium dichromate shows very similar absorption bands to those of ammonium and alkali metal dichromates.[1] The characteristic features are a strong and fairly broad band at 920–940 cm^{-1} and a strong broad band at about 750 cm^{-1}.

If molybdate and dichromate are both present, it is not possible to identify either unequivocally unless precipitation is made in the presence of citrate, and then only the dichromate is precipitated and can be identified.

Hexacyanoferrate(II) *and hexacyanoferrate*(III)

Under slightly acidic conditions, DPIC precipitates hexacyanoferrate(II). The infrared spectrum shows two strong bands, a sharp one at 2020 cm^{-1} and a much broader one at 2064 cm^{-1}. Hexacyanoferrate(III) precipitates under similar conditions and from neutral solution, and shows a strong band at 2120 cm^{-1} and two weaker bands at 2020 and 2090 cm^{-1}.

If both ions are present in about equal amounts, it is possible to detect both, since the main features of each spectrum are clearly observed.

Thiocyanate

The thiocyanate anion exhibits three fundamental frequencies, namely C—N stretch, C—S stretch and a doubly degenerate deformation band. In general, the bands shown by ionic thiocyanates occur at about 2050, 750 and 480 cm^{-1}. It is difficult to differentiate between ionic and covalent thiocyanates from infrared spectra. If the group is covalently bonded, either sulphur or nitrogen can be co-ordinated; the positions of the bands vary accordingly.[7] For nitrogen-bonded thiocyanates, the bands occur at 2040–2080 cm^{-1}, 780–860 cm^{-1} and 465–480 cm^{-1} whilst for sulphur-bonded thiocyanates the bands are at 2080–2120, 690–720 and 410–470 cm^{-1}, although overtones of the last mentioned may occur between 820 and 940 cm^{-1}. For sulphur-bonded thiocyanates the possibility of overlap in the higher wavenumber region must be borne in mind.

For the precipitate with DPIC, the C—N stretching, C—S stretching and CNS bending bands

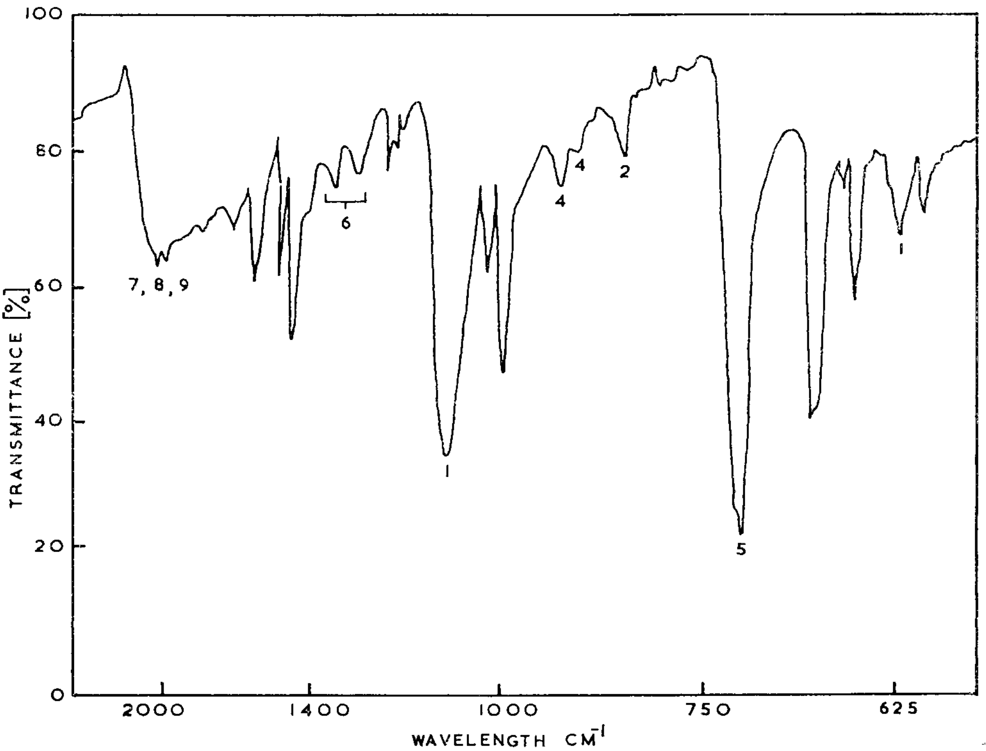

FIG. 1.—Spectrum of anion mixture, neutral conditions of precipitation. For meaning of the numbers, see Table I.

occur at 2070, 729 and 460 cm^{-1} respectively, indicating that the thiocyanate group is probably bonded *via* sulphur.

The very strong band at 2070 cm^{-1} and the strong band at 729 cm^{-1} identify thiocyanate.

Anion mixtures

The spectrum shown in Fig. 1 was obtained from the precipitate produced under neutral conditions when a mixture of the eight anions (those in Table I except permanganate) in approximately equal amounts was treated by the recommended procedure. Characteristic bands are observed for all the anions, although peroxodisulphate gives only weak bands, owing to the too high solubility.

Interferences

DPIC precipitates bromide, iodide, and halide-complexes of certain metals, *e.g.*, BiI_4^-. The spectra of these compounds are similar to those of the reagent over the range investigated and do not interfere. Several other anionic metal complexes, *e.g.*, $[Co(NCS)_4]^{2-}$, are precipitated by the reagent and these cause interference if the ligands have absorption bands in the region investigated.

Acknowledgements—A. J. B. wishes to thank the Greater London Council for financial support. We wish to record our appreciation of encouragement by the late Dr. A. I. Vogel.

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Summary—The main features of infrared spectra of the diphenyliodonium salts of some polyatomic anions are reported and interpreted, and their application in qualitative analysis discussed.

Zusammenfassung—Die wichtigsten Banden in den Infrarotspektren der Diphenyljodoniumsalze einiger vielatomiger Anionen werden mitgeteilt und gedeutet sowie ihre Anwendung in der qualitativen Analyse diskutiert.

Résumé—On rapporte et interprète les principaux caractères des spectres infra-rouges des sels de diphényliodonium de quelques anions polyatomiques, et discute de leur application en analyse qualitative.

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Talanta, 1971, Vol. 18, pp. 744 to 747. Pergamon Press. Printed in Northern Ireland

Determination of methylmercuric ions by photometric titration with dithizone

(*Received* 18 *September* 1970. *Accepted* 29 *October* 1970)

DURING the course of a study of the complexing properties of the methylmercuric ion, need arose for a rapid and accurate method for determining total CH_3Hg^+. For the determination of mercury(II), some very good methods employing dithizone (1,5-diphenyl-3-mercaptoformazan; H_2Dz) have been devised.[5,6] Some of these methods have also been applied to the determination of CH_3Hg^+, after it has been converted into mercury(II) ions.[1] According to Irving and Cox,[2] CH_3Hg^+ reacts with dithizone in acid medium, so the time-consuming preliminary step would thus seem superfluous. Experiments to test this hypothesis were, however, discouraging. The extractive titration technique yielded consistently low results, obviously because more than the equivalent amount of CH_3Hg^+ was extracted by the titrant solution of dithizone in chloroform. Moreover, the results depended upon the volume of the successive portions of dithizone solution that were used in the titration. The best results were obtained when almost the stoichiometric amount of dithizone was added in one portion and the titration was continued from that point.

It was also noted that new and old (about 3 months) dithizone solutions behaved quite differently when used to titrate, on the one hand, an acid solution of silver nitrate and, on the other, an acid solution of methylmercuric formate. In the first case, a fixed amount of the silver nitrate solution consumed more of the old than of the newly prepared dithizone solution, indicating partial decomposition of the dithizone in the old solution. When the two dithizone solutions were used to titrate equal amounts of the methylmercuric formate solution, however, the difference in consumption was within the limits of the experimental error. A possible explanation would be that methylmercuric formate forms an extractable compound with the oxidation product of dithizone. Qualitative experiments seem to verify this explanation.

Since all commercial preparations of dithizone contain appreciable amounts of the oxidation product, the observations related in the foregoing paragraphs stress the importance of purification of the dithizone solutions before their use, especially if they are to be standardized against a solution of silver(I) or mercury(II) before being used to titrate methylmercuric ions. The purification procedure described by Irving and Cox[3] has proved satisfactory.

It would be possible to avoid co-extraction phenomena if the titrations could be performed in a single phase. This could be effected by the addition of a solvent capable of dissolving both the aqueous and the organic phase used in the extractive technique. Since both the reaction product and

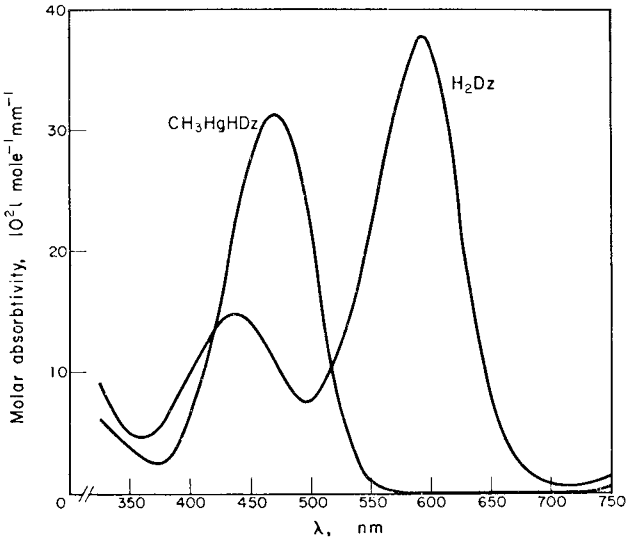

FIG. 1.—Absorption spectra for methylmercuric dithizonate, CH_3HgHDz and dithizone, H_2Dz, dissolved in a mixture of 65% ethanol, 20% chloroform and 15% water at pH 2·8.

the reagent are coloured, good possibilities exist for devising a method based upon a direct photometric titration of methylmercuric ions with dithizone. Addition of enough ethanol to make its concentration at the start of the titration 80% v/v was found sufficient to bring about the dissolution.

The theory of photometric titrations without indicators has been treated in detail by various authors, *e.g.* Ringbom,[7] and will not be repeated here. The spectra of dithizone and methylmercuric dithizonate are shown in Fig. 1. It is clear from these that a suitable wavelength for the titration is 590 nm. It should even be possible to use a simple titrator with ordinary coloured glass filters for the titration since the absorption peak of dithizone is wide and not disturbed by nearby peaks of the complex CH_3HgHDz.

Irving and Cox[2] and Irving and Kiwan[4] studied the extractability of various organomercurials with dithizone in carbon tetrachloride solution as a function of pH in the aqueous phase. They found that methylmercuric ions are completely extracted in the pH range 2–4. At $pH > 4$ there is risk of oxidation of dithizone. At $pH < 2$ the reaction between methylmercuric ions and dithizone is incomplete. It is worth noting, however, that this includes a certain margin of safety, since Irving and co-workers used methylmercuric iodide in their experiments and the iodide complexes of CH_3Hg^+ are rather strong.

It is not to be expected that the optimum acidity range for the reaction between methylmercuric ions and dithizone would be appreciably changed by the addition of ethanol. For this reason, no systematic study of pH effects has been made in this work. A buffer system consisting of sodium formate and formic acid (1:10 mole ratio) was used to establish a "pH" value between 2·5 and 3·0.

EXPERIMENTAL

Reagents

When possible, reagent grade chemicals were used throughout the work.

Methylmercuric bromide. Commercial samples of methylmercuric bromide were recrystallized twice from absolute ethanol before use.

Dithizone. A stock solution of dithizone was prepared according to the purification procedure given by Irving and Cox[3] and stored, under a layer of dilute sulphuric acid, in a refrigerator.[4]

Titrator

A somewhat modified version of the EEL phototitrator Model LF 103 equipped with a No. 106 filter was used for the titrations. In order to increase sensitivity, the barrier-layer cell was replaced by a photoresistor coupled to a simple Zener-diode controlled d.c. supply.

Procedure

As a result of the preliminary experiments and considerations, the following procedure was chosen for the photometric titrations. Place 10 ml of sample solution, containing up to 1 μmole of methylmercuric ions, in a titration cuvette and add 1 ml of buffer solution and about 40 ml of absolute ethanol. When the air bubbles have escaped, titrate the solution with successive portions of a 50 μM solution of dithizone in chloroform; read the absorbance after each addition. After the equivalence point, the absorbance will increase rather steeply. Plot the absorbance as a function of the volume of titrant. Extrapolate the straight branches of the plot and take their intersection as the equivalence point. It would be convenient to carry out the titration in a titration apparatus equipped with a logarithmic amplifier and a recorder, facilitating direct recording of the absorbance curve.

RESULTS AND DISCUSSION

Interferences

The main interfering cations are mercury(II), silver(I) and copper(II). Anions that form strong complexes with methylmercuric ions, and substances capable of oxidizing dithizone, also interfere with the titration. Most of these interferences can be avoided by separation of CH_3Hg^+ by addition of a large excess of chloride ions and extraction of the resulting methylmercuric chloride into benzene or some other suitable organic solvent. It is not necessary to strip the CH_3Hg^+ into water before its determination, since the benzene layer dissolves in the titration medium, 80% aqueous ethanol.

Results

Results of some titrations obtained by the procedure given have been collected in Table I. In general, the "taken" and "found" values agree within 0·2% which shows the accuracy of the method. When the method was used to determine total methylmercury in the organic and aqueous phases after equilibration of methylmercuric perchlorate with varying concentrations of chloride ions at pH 2, the sums generally agreed within 0·5% with the total amount of methylmercuric ions taken before the equilibration. The sensitivity of the method can be increased to about 15 μg of CH_3Hg^+, since the photometric titration technique permits the use of a 10 μM dithizone solution as titrant. However, the precision will decrease accordingly.

TABLE I.—RESULTS OF SOME TITRATIONS OF METHYLMERCURIC IONS WITH DITHIZONE

CH_3Hg^+, *nmole*			Error,
Taken	Found		%
5·50	5·52		+0·4
8.30	8.28		−0·2$_5$
10·40	10·38		−0·2
53·00	52·9		−0·1
90·00	90·0		0·0
90·00	89·7		−0·3
96·10	96·2		+0·1
96·10*	24·2 72·0	96·2	+0·1
96·10*	34·4 61·2	95·6	−0·5
96·10*	80·1 16·0	96·1	0·0

* In the lower part of the Table, the sums of the determined amounts of CH_3Hg^+ in the organic and aqueous phases after addition of varying amounts of Cl^- and equilibration with xylene are compared with the initially taken amounts of CH_3Hg^+.

Acknowledgements—The author is much indebted to Dr. Djiet Hay Liem for many valuable discussions during the course of this work. The work has been financially supported by the National (Swedish) Environment Protection Board.

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Summary—A rapid photometric titration titration technique, which makes it possible to determine methylmercuric ions with a sensitivity of 15 μg, is described. The titration takes place in 80% aqueous ethanol, which is capable of dissolving the titrant, a chloroform solution of dithizone. It has thus been possible to avoid the difficulties arising from co-extraction phenomena that occur when the extractive titration procedures developed for mercury(II) are applied to the determination of methylmercuric ions. A formate buffer is used to keep the pH in the range 2.5–3.0. The attainable precision is considerably better than 1%.

Zusammenfassung—Ein schnelles photometrisches Titrationsverfahren wird beschrieben, das die Bestimmung von Methylquecksilber-(II)-Ionen mit einer Empfindlichkeit von 15 μg ermöglicht. Die Titration wird in 80% wäßrigem Äthanol ausgeführt; darin löst sich der Titrant, eine Chloroformlösung von Dithizon. Auf diese Weise konnten die Schwierigkeiten überwunden werden, die sich bei der Bestimmung von Methylquecksilber(II)-Ionen mit den für Quecksilber(II) entwickelten extraktiven Titrationsverfahren durch Mitextraktions-Erscheinungen ergaben. Ein Formiatpuffer dient dazu, den pH im Bereich 2,5–3,0 zu halten. Man kann erhebl ich bessere Genauigkeiten als 1% erhalten.

Résumé—On décrit une technique de titrage photométrique rapide, qui rend possible le dosage des ions méthylmercuriques avec une sensibilité de 15 μg. Le titrage se fait en éthanol aqueux à 80%, qui est capable de dissoudre l'agent de titrage, une solution chloroformique de dithizone. Il a été ainsi possible d'éviter les difficultés provenant des phénomènes de co-extraction qui se produisent lorsque les techniques de titrage par extraction élaborées pour le mercure(II) sont appliquées au dosage des ions méthylmercuriques. On utilise un tampon formiate pour maintenir le pH dans le domaine 2,5–3,0. La précision que l'on peut atteindre est de beaucoup meilleure que 1%.

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Talanta, 1971, Vol. 18, pp. 747 to 751. Pergamon Press. Printed in Northern Ireland

Extractive spectrophotometric determination of micro and sub-micro amounts of fluoride

(*Received* 2 *June* 1970. *Accepted* 16 *November* 1970)

SPECTROPHOTOMETRIC fluoride determinations, based on the direct reaction between fluoride and the cerium(III) or lanthanum(III) chelate of alizarin complexan (3-[di(carboxymethyl)aminomethyl]-1,2-dihydroxyanthraquinone) are often used. The first was introduced by Leonard and West.[1] Other workers proved that the addition of an organic solvent enhanced the sensitivity and the stability of the complexes. In this manner Yamamura *et ai.*[2] and Greenhalgh and Riley,[3] used acetone or acetonitrile, while Hanocq and Molle[4] advised dimethylsulphoxide. All these determinations were described only for the range of 5–25 μg of fluoride in a sample volume of 10–75 ml. For lower amounts, such as 0·1–1 μg of fluoride in a sample volume of 2 ml, procedures involving solvent extraction and subsequent colorometric measurement were developed by Hall,[5] and Cox and Backer Dirks.[6] A method for concentrations of 0·25–7 μg of fluoride in 150 ml of water was published by Johnson and Leonard.[7] Procedures of a similar nature are described by Hirano *et al.*[8] and by Daries and Foreman.[9]

In the present paper, a simple, sensitive extractive determination with a low blank is investigated, which can be used for concentrations of 0·1–1 μg of fluoride in 4 ml of water and 5–25 μg of fluoride in 90 ml of water.

EXPERIMENTAL

Reagents

Alizarin complexan ($1{\cdot}25 \times 10^{-3}M$)-pH 4·3 *buffer mixture.* Dissolve 263·3 mg of alizarin complexan dihydrate and 10·5 g of hydrated sodium acetate in 350 ml of water. Adjust the pH with glacial acetic acid potentiometrically. Transfer the solution to a 500-ml standard flask and make up to the mark with water. The solution is stable for a considerable length of time.

Cerium(III) *nitrate*, $1{\cdot}375 \times 10^{-3}M$. Dissolve 303·1 mg of cerium(III) nitrate [$Ce(NO_3)_3.6H_2O$, purity 98·5%] in water to make 500 ml of solution.

Stock fluoride solution, 100 μg/ml. Dissolve 221·1 mg of pure sodium fluoride in water and dilute to 1 litre. Store in a polythene container.

Standard fluoride solutions, 1 μg/ml *and* 0·5 μg/ml. Dilute 10-ml portions of the stock fluoride solution to 1 or 2 l. Store in polythene containers. The standard fluoride solutions should be freshly prepared every week.

Buffer solution pH 9. Dissolve 77·1 g of ammonium acetate in 350 ml of water and add 10 ml of $8M$ ammonia solution. Adjust the pH with ammonia potentiometrically and dilute to 500 ml with water.

Extracting solvent, 5% *v/v triethylamine in n-pentanol.* Dilute 25 ml of triethylamine with n-pentanol to 500 ml.

Preparation of the standard curves

Procedure I *for* 0·1–1 μg *of fluoride* (*sample volume* 4 *ml*). In 100-ml standard flasks take 0, 5, 10, 20, 30, 40 and 50 ml of 0·5 μg/ml standard fluoride solution and make up to the mark with water. These solutions contain respectively 0, 0·1, 0·2, 0·4, 0·6, 0·8 and 1·0 μg of fluoride per 4 ml. In stoppered 10-ml tubes take 4 ml of fluoride solution, 0·5 ml of the alizarin complexan–buffer mixture and 0·5 ml of cerium(III) nitrate solution and mix well. After 1 hr add 0·5 ml of extraction solvent and 0·5 ml of pH 9 buffer and immediately shake for 2 min. Allow to stand for 10 min. Transfer the organic layer to a microcentrifuge tube and centrifuge for 2 min (4000 rpm). Transfer the extract to a 10-mm cell (narrow enough to be filled by 0·2 ml of solution) and measure the absorbance at 570 nm against water as reference.

Procedure II *for* 5–25 μg *of fluoride* (*sample volume* 90 ml). In 100-ml calibrated flasks take 0, 5, 10, 15, 20 and 25 ml of 1 μg/ml standard fluoride solution. Dilute to approximately 80 ml and add 5 ml of alizarin complexan-buffer mixture and 5 ml of cerium(III) nitrate solution. Dilute to volume and mix. After 1 hr pour the solution into a 250-ml separating funnel, add 10 ml of extracting solvent and 10 ml of pH 9 buffer and immediately shake for 2 min. Allow to stand for 10 min. Transfer the organic layer into a centrifuge tube, and centrifuge for 2 min (4000 rpm). Transfer the extract into a 10-mm cell and measure the absorbance at 570 nm against water as reference.

RESULTS AND DISCUSSION

Calibration curves

The calibration curves are linear up to 1·5 and 40 μg of fluoride for Procedures I and II respectively except for a slight curvature at the lowest concentrations (0–0·2 μg of fluoride for Procedure I and 0–5 μg for Procedure II) but in practice this presents no problem. For Procedure II the reproducibility for the blank and a 25-μg fluoride sample was checked by repeating the experiment 10 times during a period of a fortnight. The mean absorbances were 0·024 with standard deviation $s = 0{\cdot}002$ for the blank and 0·416 with $s = 0{\cdot}0035$ (corresponding to 0·2 μg of fluoride) for the sample. The absorbance is stable (within ±0·003) for at least 24 hr.

Extraction with different volumes of solvent

Procedure II was used but there were some differences during development of the method. Initially, 10 ml each of the alizarin complexan–buffer mixture and the cerium(III) nitrate solution were used and no pH 9 buffer was used during the extraction. Before and after extraction the pH of the aqueous phase was measured, and the pH after extraction was taken as the pH during extraction. The results are shown in Fig. 1. The dotted line refers to the absorbance, without extraction, of the aqueous phase at 610 nm, in a 10-mm cell against water as reference. Extraction with solvent volume ratio of 1:1 gives a sharp reduction in the blank value, while the sensitivity is about equal. This procedure provides a means of nearly completely separating the fluoride complex from the cerium(III)–alizarin complexan chelate. At other volume ratios, the blank value and sensitivity increase, a ratio of 1:10 being the optimum.

Further experiments showed that at constant volume-ratio absorbance was strongly dependent on the pH. As a consequence, the pH during extraction must be kept constant. It was also found that slight variations (even ±0·1) of the pH before the extraction gave rise to large variations of the pH during extraction. For these reasons a pH 9 buffer was added before extraction. Other experiments showed that with extraction with a volume ratio 1:10 the final concentrations of alizarin complexan and cerium(III) nitrate could be reduced to $6{\cdot}25 \times 10^{-5}M$ and $6{\cdot}875 \times 10^{-5}M$ respectively as in Procedure II. The result was that the blank was halved without loss of sensitivity.

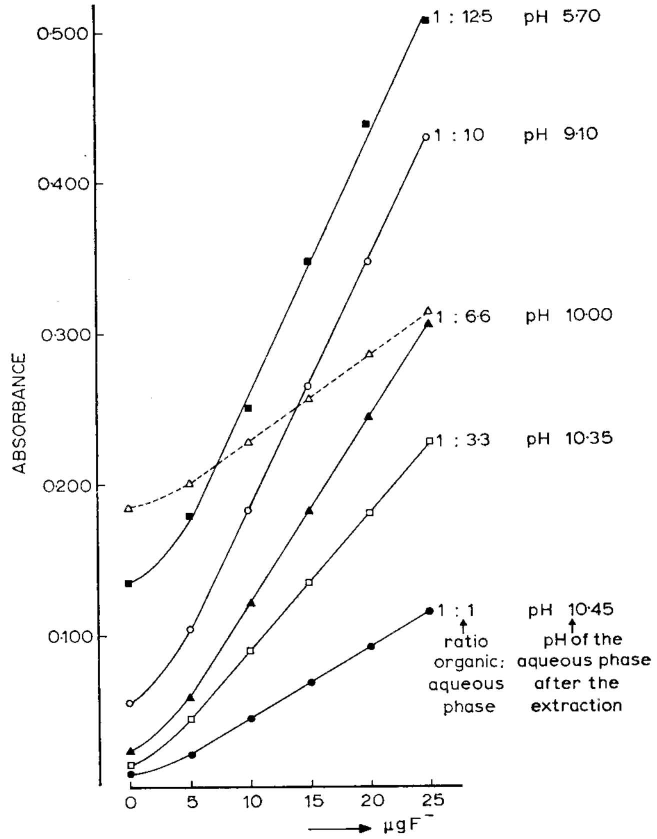

FIG. 1. Extraction with different volumes of extractant.
Dotted line: Absorbance of the aqueous phase before extraction, measured at 610 nm in a 10-mm cell against water as reference.

Effect of temperature

It is found that between 15 and 25° the absorbance increases with temperature at the rate of 0·001/deg for the blank and 0·002/deg for 25 μg of fluoride.

Interferences

Some results are shown in Table I and are in agreement with those of other workers. Presumably certain interferences are inevitable.

TABLE I.—INTERFERENCE OF IONS IN THE DETERMINATION OF 25 μg OF FLUORIDE

Ion	Added as	[Ion]/[F^-]	Absorbance	Difference caused %
none			0·416*	
SO_4^{2-}	Na_2SO_4	25	0·422	+1·4
		100	0·400	−3·8
Cl^-	NaCl	250	0·416	0·0
		1000	0·413	−0·7
HCO_3^-	$NaHCO_3$	25	0·428	+2·9
		250	0·457	+9·9
		1000	0·474	+13·9
		1000†	0·399	−4·1
NO_3^-	$NaNO_3$	500	0·405	−2·6
		2000	0·360	−13·6
PO_4^{3-}	KH_2PO_4	1	0·394	−5·3
Al^{3+}	$Al_2(SO_4)_3$	1	0·370	−11·1
Fe^{3+}	$Fe(NO_3)_3$	1	0·428	+2·9

* The mean of 10 separate determinations, accumulated over a period of a fortnight, standard deviation 0·0035.

† Before colour development glacial acetic acid was first added to make the pH of the solution approximately 5, and then the solution was boiled.

CONCLUSION

The results obtained compare favourably with others reported for microgram and submicrogram determinations of fluoride. For determination of 5–25 μg of fluoride the extraction procedure involves more work than the non-extractive procedures do, but the low blank, greater sensitivity and good accuracy cancel this disadvantage. The method described here is less sensitive than the method of Johnson and Leonard,[7] but the latter has a much higher value for the absorbance of the blank (0·339, $s = 0·007$). The great feature of this work is the low blank value (0·024, $s = 0·002$), obtained with a simple procedure, albeit at the expense of sensitivity. The determination of 0·1–1 μg of fluoride proposed here is simpler than those published by Hall[5] and by Cox and Backer Dirks,[6] and has about twice the sensitivity.

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Summary—A simple and sensitive extractive spectrophotometric determination of fluoride with the cerium(III)–alizarin complexan chelate has been investigated. The fluoro chelate formed is extracted into n-pentanol containing triethylamine. It is possible to achieve under selected conditions a selective extraction of the cerium(III)–alizarin complexan–fluoride chelate. The stability of the chelate, the effect of temperature and the low absorbance of the blank are discussed. It is found that it is necessary to add a pH 9 buffer before the extraction. Procedures are given for the determination of 0.1–1 μg of fluoride in a 4-ml sample and 5–25 μg of fluoride in a 90-ml sample.

Zusammenfassung—Ein einfaches und empfindliches extraktivspektrophotometrisches Verfahren zur Bestimmung von Fluorid mit dem Chelat aus Cer(III) und Alizarincomplexan wurde untersucht. Das gebildete Fluorochelat wird in Triäthylamin enthaltendes *n*-Pentanol extrahiert. Unter geeigneten Bedingungen ist eine selektive Extraktion des Chelats aus Cer(III), Alizarincomplexan und Fluorid zu erreichen. Die Stabilität des Chelats, der Einfluß der Temperatur und die geringe Extinktion der Blindlösung werden diskutiert. Vor der Extraktion muß ein pH 9-Puffer zugesetzt werden. Vorschriften zur Bestimmung von 0,1–1 μg Fluorid in einer 4 ml-Probe und von 5–25 μg Fluorid in einer 90 ml-Probe werden angegeben.

Résumé—On a étudié une méthode de dosage spectrophotométrique par extraction, simple et sensible, du fluor avec le chélate cérium(III)-alizarine complexan. Le fluorochélate formé est extrait en *n*-pentanol contenant de la triéthylamine. Il est possible de réaliser dans des conditions choisies une extraction sélective du chélate cérium(III)-alizarine complexan-fluorure. On discute de la stabilité du chélate, de l'influence de la température et de la faible absorption du témoin. On a trouvé qu'il est nécessaire d'ajouter un tampon pH 9 avant l'extraction. On donne des techniques pour le dosage de 0,1–1 μg de fluorure dans un échantillon de 4 ml et de 5–25 μg de fluorure dans un échantillon de 90 ml.

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Talanta, 1971, Vol. 18, p. 753. Pergamon Press. Printed in Northern Ireland

PRELIMINARY COMMUNICATION

Iodobenzene dichloride as a new oxidimetric titrant in non-aqueous media

(*Received* 16 *November* 1970. *Accepted* 20 *November* 1970)

IN THE COURSE of a search for new redox titrants for use in non-aqueous media (a topic on which the literature is rather scarce[1] and which has been receiving increasing attention in recent years[2]) we found that iodobenzene dichloride, $C_6H_5ICl_2$, is ideally suited for this purpose. This compound is easily prepared by passing chlorine through a solution of iodobenzene in chloroform,[3] when it separates out as shining yellow needle-shaped crystals. It has sufficient solubility in glacial acetic acid to provide a $0{\cdot}05M$ solution. Such solutions have satisfactory keeping qualities when kept in amber bottles out of contact with moisture.

Preliminary experiments show that such diverse reductants as I^-, ascorbic acid, Sn(II), Fe(II) and As(III) may be conveniently determined by titrating with iodobenzene dichloride in glacial acetic acid medium, with electrometric and visual end-point detection. The reduction product appears to be iodobenzene and the formal potential (as defined by Lingane[4]) is about $+1{\cdot}2$ V. A systematic study is under way and the detailed results will be published later. Solvents other than glacial acetic acid, such as acetonitrile, are also being examined.

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Summary—Iodobenzene dichloride in anhydrous acetic acid is proposed as a new oxidimetric titrant in non-aqueous media.

Zusammenfassung—Jodbenzoldichlorid in wasserfreier Essigsäure wird als neues nichtwäßriges oxidimetrisches Titrationsmittel vorgeschlagen.

Résumé—On propose le dichlorure d'iodobenzène en acide acétique anhydre comme nouvel agent de titrage oxydimétrique en milieux non aqueux.

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PUBLICATIONS RECEIVED

Ultramicro Elemental Analysis: GÜNTHER TÖLG. Wiley-Interscience, New York, 1970. Pp. 200. £5.15.

On every analyst's bookshelf are a number of well-thumbed hand-books relating to his art, written by the expert for the exponent: to these will certainly be added this compilation of methods and techniques, many of them developed by the author himself, for ultramicro (organic) elemental analysis. The many drawings and photographs, along with the detailed procedures, will ensure as far as is possible in print alone a reasonable chance of success for the novice. This volume is a very readable and welcome translation of the 1967 German edition. The first 50 pages discuss apparatus and general procedures, then follow sections on the determination of C & H, O, N, S, F, Cl, Br, I, P, and As, at levels typically in the 1–5 μg range.

PAPERS RECEIVED

Rapid separation and determination of mercury: IVAN KRESSIN. (4 *March* 1971)

Dosage quantitatif des substances tensioactives par électroadsorption: E. VERDIER, F. G. MONTELONGO and J. PIRO. (2 *April* 1971)

Dosage du glycérol dans les glycérines techniques—III. Collaboration internationale au sein de l'I.S.O. et analyse statistique des résultats des essais circulaires effectués: R. MORMONT. (26 *April* 1971)

Colorimetric determination of bismuth(III) via a new spot reaction: G. S. DESHMUKH and S. S. CHATTOPADHYAY. (27 *April* 1971)

Détermination gravimétrique de l'iode sous forme de $NtIJCl_2$: N. GANTCHEV, V. KANAZIRSKA and DR. ATHANASSOVA. (28 *April* 1971)

Resin beads as indicators in redox and precipitation titrations: MOHSIN QURESHI, SAIDULZAFAR QURESHI and MIGHAT ZEHRA. (30 *April* 1971)

Potentiometric titration of copper with sodium tetraphenylboron using a permselective membrane: SUDARSHAN LAL and GARY D. CHRISTIAN. (3 *May* 1971)

Determination of traces of ferrous ion in the presence of ferric ion using the bathophenanthroline method: TAKAYUKI MIZUNO. (4 *May* 1971)

Extreme Spurenanalyse der Elemente—I. Methoden und Probleme der Probenvorbehandlung, Trennung und Anreicherung: G. TÖLG. (5 *May* 1971)

Le microdosage colorimétrique des phosphates dans des milieux diverses produits biologiques, pharmaceutiques et alimentaires: GH. GHIMICESCU and VASILE DORNEANU. (7 *May* 1971)

Fluorimetric and phosphorimetric characteristics of several vitamins: JEAN-JACQUES AARON and J. D. WINEFORDNER. (10 *May* 1971)

Interaction of cobalt(II) chloride with 2-nitroso-1-naphthol in a 96:4 benzene–ethanol solution: VINCENZO CARUNCHIO, ALESSANDRO BONDOLI and MARIA ANTONIA FOGAROLI. (11 *May* 1971)

Determination of nitrite in the presence of nitrate: M. H. HASHMI, A. U. AFZAL, N. A. CHUGHTAI, F. R. MALIK and IFTIKHAR AHMAD. (12 *May* 1971)

A new method for the estimation of dibutyl phosphate (DBP): RAMENDRA SHANKER and K. S. VENKATESWARLU. (12 *May* 1971)

Simple modifications of Bödeker's reaction of sulphites: G. S. JOHAR, J. P. SINGH, G. MAJUMDAR and UMESH AGARWALA. (12 *May* 1971)

Characterization of ion-selective membrane electrodes—I. The electrode function: CANDIN LITEANU and IONEL C. POPESCU. (17 *May* 1971)

Catalytic reactions—II. Activation: P. R. BONTCHEV. (19 *May* 1971)

Simultaneous determination of oxygen and nitrogen in iron and steel by spark-source mass spectrography: SHOHEI ODA, ZENJI OHASHI, KEIICHI FURUYA and HITOSHI KAMADA. (19 *May* 1971)

Determination of thoria from thorium ores by emission spectrography: N. C. KOTHARI. (19 *May* 1971)

The use of liquid–liquid interface-membranes as ion-sensitive electrodes—I. The n-butanol–water interface as indicating electrode for the potentiometric titration of some acids and bases: C. LITEANU and MARIA MOISCU. (20 *May* 1971)

NOTICE

107th EVENT OF THE EUROPEAN FEDERATION OF CHEMICAL ENGINEERING

THIRD EUROPEAN SYMPOSIUM ON SIZE REDUCTION

This meeting will be held at the Palais des Festivals, 50, La Croisette, 06-Cannes, France, on 5–8 October 1971. Details may be obtained from the Secrétariat du Symposium sur la Fragmentation, Syndicat National des Industries D'Équipement M.T.P.S., 10, avenue Hoche, 75-Paris-08, France.

SUMMARIES FOR CARD INDEXES

Determination of fluoride in oxides with the fluoride-ion activity electrode: M. A. PETERS and D. M. LADD, *Talanta*, 1971, **18**, 655. (Union Carbide Corporation, Mining and Metals Division, Niagara Falls, New York 14302, U.S.A.)

Summary—The application of the fluoride-ion activity electrode to the determination of fluoride in various samples has been studied. Samples are decomposed by fusion and the fluoride concentration is determined by a standard-addition or a direct method. The standard-addition method is unsuitable, owing to a positive bias. The direct method, however, is rapid, accurate and precise. The fluoride content of exploration ores, fluorspar, opal glass, phosphate rock and various production samples, has been successfully determined. The success of the direct method depends on the effectiveness of the system used to buffer pH and ionic strength and complex possible interferences (Al^{3+}, Ca^{2+}, Fe^{3+}). The effect of interferences has been studied and found to be minimal. The procedures are rapid and accurate and may be substituted for the traditional Willard and Winter or pyrohydrolysis methods, with considerable saving of time.

Determination of rare earths in selected rare earth matrices by spark source mass spectrometry: D. A. GRIFFITH, R. J. CONZEMIUS and H. J. SVEC, *Talanta*, 1971, **18**, 665. (Institute for Atomic Research and Department of Chemistry, Iowa State University, Ames, Iowa 50010, U.S.A.)

Summary—Three methods of preparing rare earth samples for mass spectrographic analysis are presented. Techniques for adding appropriate internal standards are described and relative sensitivity factors for rare earth impurities in rare earths, lanthanum, yttrium and scandium matrices are presented. Although indium has some value as an internal standard in rare earth samples, best analytical results are obtained when selected rare earths are used as internal standards.

Possibilities for separation and simultaneous determination of *N*-unsubstituted- and *N*-substituted nitroimidazoles and criteria for their identification: DRAGICA DUMANOVIĆ, SMILJKA PERKUČIN and JIŘI VOLKE, *Talanta*, 1971, **18**, 675. (Research Laboratory "Galenika", Zemun, Yugoslavia and J. Heyrovský Institute of Polarography, Czechoslovak Academy of Sciences, Prague, Czechoslovakia.)

Summary—The *N*-unsubstituted nitroimidazoles have an imino hydrogen atom in contrast to the *N*-substituted derivatives, and react with hydroxide to give the yellow nitroimidazole anions. The difficulty of reducing the nitro-group in these anions, together with the shift of the absorption maximum to longer wavelengths makes it possible to analyse polarographically or spectrophotometrically a mixture of *N*-unsubstituted nitroimidazole with *N*-substituted derivatives. The presence of the *N*-unsubstituted nitroimidazole and the *N*-substituted derivatives is first established by chromatography. Other criteria are also proposed for distinguishing between these substances.

ОПРЕДЕЛЕНИЕ ФТОРИДА В ОКИСЯХ С ИСПОЛЬЗОВАНИЕМ ЭЛЕКТРОДА НА ОСНОВЕ АКТИВНОСТИ ФТОРИДИОНА:

M. A. Peters and D. M. Ladd, *Talanta*, 1971, **18**, 655.

Резюме—Изучено применение электрода на основе активности фторидиона в определении фторида в разных образцах. Образци разлагают плавлением а концентрацию фторида определяют методом стандартной добавки или непосредстевенным методом. Метод стандартной добавки неподходящий вследствие позитивной методической ошибки. В отличии от этого, непосредственный метод является быстрым, точным и воспроизводимым. Успешно определена концентрация фторида в рудах исследования, флюорите, опаловом стекле, фосфоритной руде и разных образцах производства. Успех непосредственного метода зависит от эффективности системы использованой для буфферирования pH и ионной силы и для маскирования мешающих ионов (Al^{3+}, Ca^{2+}, Fe^{3+}). Влияние мешающих веществ незначительно. Предложенные методы являются быстрым и точным и ими можно пользоваться вместо обыкновенных методов Вилларда и Винтера или пирогидролиза, с значительной экономией времени.

ОПРЕДЕЛЕНИЕ РЕДКОЗЕМЕЛЬНЫХ ЭЛЕМЕНТОВ В ИЗБРАННЫХ РЕДКОЗЕМЕЛЬНЫХ МАТРИЦАХ МЕТОДОМ МАСС-СПЕКТРОМЕТРИИ С ИСКРОВЫМ ИСТОЧНИКОМ:

D. A. Griffith, R. J. Conzemius and H. J. Svec, *Talanta*, 1971, **18**, 665.

Резюме—Предложены три метода подготовки образцев редких земель к анализе методом масс-спектрометрии. Описана методика добавления подходящих внутренных стандартов и приведены относительные факторы чувствительности для редкоземельных примесей в матрицах лантана, иттрия и скандия. Хотя индий в известной мере полезен в качестве внутренного стандарта для образцев редких земель, самые лучшие результаты получены использованием избранных редкоземельных элементов в качестве внутренных стандартов.

ВОЗМОЖНОСТЬ РАЗДЕЛЕНИЯ И ОДНОВРЕМЕННОГО ОПРЕДЕЛЕНИЯ И-НЕЗАМЕЩЕННЫХ И И-ЗАМЕЩЕННЫХ НИТРОИМИДАЗОЛОВ И КРИТЕРИИ ИХ ОТОЖДЕСТВЛЕНИЯ:

Dragica Dumanovic, Smiljka Perkucin and Jiri Volke, *Talanta*, 1971, **18**, 675.

Резюме—В отличии от N-замещенных нитроимидазолов N-незамещенные производные имеют атом иминоводорода и реагируют с гидроокисью с образованием жёлтых нитроимидазоланионов. Трудное восстановление нитрогруппы в этих анионах, вместе с смещением максимума светопоглощения к большим длинам волн позволяет анализировать смеси N-незамещенных и N-замещенных производных нитроимидазола полярографическим или спектрофотометрическим методом. Прежде всего присутствие N-незамещенного нитроимидазола и N-замещенных производных определяют хроматографическим методом. Также предложены другие критерии для распознавания этих веществ.

Sensitivity and detectability for manganese(II) determination in solution by kinetic methods of analysis: HORACIO A. MOTTOLA and CARL R. HARRISON, *Talanta*, 1971, **18**, 683. (Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74074, U.S.A.)

Summary—The use of nitrilotriacetic acid to enhance the catalytic effect of manganese ions on the oxidation of Malachite Green cations is reported. This effect permits a noticeable increase in sensitivity for the determination of micro and submicro amounts of manganese ions in aqueous solution. The detectability, however, is not so dramatically altered. Comparison is made with other kinetic methods for the determination of manganese in solution.

Properties and analytical applications of the heteropolymolybdates of phosphorus, arsenic, silicon and germanium—IV. Determination of phosphomolybdic and silicomolybdic acids *via* the molybdenum content, with phenylfluorone: A. HALÁSZ, K. POLYÁK and E. PUNGOR, *Talanta*, 1971, **18**, 691. (Institute for Analytical Chemistry, University for Chemical Engineering, Veszprém, Hungary.)

Summary—Procedures are proposed for the determination of phosphorus and silicon in the ppM range, by extraction of phosphomolybdic and silicomolybdic acids with organic solvent, decomposition of the complex and spectrophotometric determination of its molybdenum content.

Ultraviolet absorption and luminescence properties of some cannabis constituents: A. BOWD, P. BYROM, J. B. HUDSON and J. H. TURNBULL, *Talanta*, 1971, **18**, 697. (Applied Chemistry Branch, Royal Military College of Science, Shrivenham, Wiltshire, England.)

Summary—The characteristics of the absorption, fluorescence and phosphorescence spectra of the cannabinols have been determined. The data provide a basis for the detection of these compounds at concentrations down to 10 ng/ml.

Determination of nanogram amounts of nickel by flameless atomic-absorption spectroscopy: S. DIPIERRO and G. TESSARI, *Talanta*, 1971, **18**, 707. (Istituto di Chimica Analitica, Universita' di Bari, Via G. Amendola 173, Bari 70126, Italy.)

Summary—A simple flameless atomizer, made from a heated graphite resistor, was investigated for the determination of nickel in various salts. The parameters characterizing its behaviour were optimized, to yield an absolute detection limit of 0·1 ng of nickel.

ЧУВСТВИТЕЛЬНОСТЬ И ОБНАРУЖИМОСТЬ ОПРЕДЕЛЕНИЯ МАРГАНЦА(II) В РАСТВОРЕ ПРИМЕНЕНИЕМ КИНЕТИЧЕСКИХ МЕТОДОВ АНАЛИЗА:

HORACIO A. MOTTOLA and CARL R. HARRISON, *Talanta*, 1971, **18**, 683.

Резюме—Сообщено использование нитрилотриуксусной кислоты для усиления каталитического эффекта ионов марганца на окисление катионов малахитового зеленого. Этот эффект вызывает значительное повышение чувствительности определения микро- и субмикроколичеств ионов марганца в водном растворе, но не влияет в значительной мере на обнаружимость. Метод сравнен с другими кинетическими методами определения марганца в растворе.

ХАРАКТЕРИСТИКА И ПРИМЕНЕНИЕ В АНАЛИЗЕ ГЕТЕРОПОЛИМОЛИБДАТОВ ФОСФОРА, МЫШЬЯКА, КРЕМНИЯ И ГЕРМАНИЯ—IV. ОПРЕДЕЛЕНИЕ ФОСФОРНОМОЛИБДЕНОВОЙ И КРЕМНЕМОЛИБДЕНОВОЙ КИСЛОТ ПУТЕМ ОПРЕДЕЛЕНИЯ СОДЕРЖАНИЯ МОЛИБДЕНА ФЕНИЛФЛУОРОНОМ:

A. HALÁSZ, K. POLYÁK and E. PUNGOR, *Talanta*, 1971, **18**, 691.

Резюме—Предложены методы определения фосфора и кремния в небольших концентрациях (частей на миллион), основывающиеся на извлечении фосфорномолибденовой и кремнемолибденовой кислот органическим растворителем, разложении комплекса и спектрофотометрическом определении его содержания молибдена.

ХАРАКТЕРИСТИКИ УЛЬТРАФИОЛЕТОВОГО ПОГЛОЩЕНИЯ И ЛЮМИНЕСЦЕНЦИИ НЕКОТОРЫХ СОСТАВЛЯЮЩИХ ВЕЩЕСТВ КАННАБИСА:

A. BOWD, P. BYROM, J. B. HUDSON and J. H. TURNBULL, *Talanta*, 1971, **18**, 697.

Резюме—Определены характеристики спектров поглощения, флуоресценции и фосфоресценции каннабинолов. Полученные данные представляют собой основу для определения этих соединений при концентрациях до 10 нг/мл.

ОПРЕДЕЛЕНИЕ НАНОГРАММОВЫХ КОЛИЧЕСТВ НИКЕЛЯ МЕТОДОМ БЕЗПЛАМЕННОЙ АТОМНО-АБСОРБЦИОННОЙ СПЕКТРОСКОПИИ:

S. DIPIERRO and G. TESSARI, *Talanta*, 1971, **18**, 707.

Резюме—Исследован несложный безпламенный атомизатор, сконструированный из графитового резистора, для определения никеля в разных солях. Определены оптимальные условия для получения чувствительности 0,1 нг никеля.

Spectrophotometric determination of the protolytic dissociation constants of the new chromogenic reagent "Palladiazo"—II. Study of the protonation processes undergone by the azo-groups of the reagent in sulphuric acid media: J. A. PÉREZ-BUSTAMANTE and F. BURRIEL-MARTÍ, *Talanta*, 1971, **18**, 717. (Consejo Superior de Investigaciones Científicas, Departamento de Química Analítica, Universidad de Madrid, Facultad de Ciencias, Ciudad Universitaria, Madrid-3, Spain.)

Summary—The protonation of the reagent 1,8-dihydroxynaphthalene-3,6-disulphonic-2,7-bis(azophenyl-*p*-arsonic) acid ("palladiazo") has been investigated by a spectrophotometric method in 0·25–18*M* sulphuric acid media. Graphical assessment of the experimental results points to the protonation of only one azo-group, although a two-stage protonation process cannot be conclusively ruled out at very high acidity. The first protonation instability constant is $pK_9 = -(2{\cdot}4 \pm 0{\cdot}1)$ and the second is tentatively estimated as $-7{\cdot}4$. Most of the current views on the complexation and protonation reactions of bis(azophenyl)chromotropic acid derivatives with metal cations and protons are reviewed and critically discussed in some detail in order to interpret the experimental findings. It is concluded that the fully protonated palladiazo molecule exists in very concentrated acid media predominantly in the form of a symmetrical positively charged tautomeric quinonehydrazone proton complex species which is responsible for the appearance of a very strong single absorption band with a maximum at 665 nm which gives the protonated reagent solutions a characteristic deep-emerald-green colour.

Extraction with long-chain amines—V. Colorimetric determination of cobalt with nitroso-R salt: JIŘÍ ADAM and RUDOLF PŘIBIL, *Talanta*, 1971, **18**, 733. (Analytical Laboratory, Institute of Geological Sciences, Charles University, Prague 2, Albertov 6, and Analytical Laboratory, J. Heyrovský Polarographic Institute, Czechoslovak Academy of Sciences, Prague 1, Jilská 16, Czechoslovakia.)

Summary—The colorimetric determination of cobalt with nitroso-R salt (NRS) has been modified and improved by the introduction of extraction of the Co–NRS chelate into a chloroform solution of trioctylmethylammonium chloride. Ammonium phosphate, fluoride and mainly citrate were used for masking iron, nickel, copper and calcium, which under the described conditions do not interfere even in 2000-fold excess. The method is very sensitive and permits determination of about 1 μg of cobalt per ml of the extractant.

La réaction des nitrilotriacétates métalliques avec la cycloleucine: J. ISRAELI, J. R. CAYOUETTE and R. VOLPE, *Talanta*, 1971, **18**, 737. (Departement de Chimie, Université de Moncton, Moncton, N.B., Canada.)

Summary—The formation constants of the mixed complexes which result by the reaction of metallic nitrilotriacetates with cycloleucine have been calculated for different temperatures. For the reaction of formation of mixed complexes $\Delta H_f°$ and $\Delta S_f°$ have also been calculated. The hydrolysis of metallic nitrilotriacetates has been studied at different temperatures and K_h, $\Delta H_h°$, $\Delta S_h°$ calculated.

СПЕКТРОФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ ПРОТОЛИТИЧЕСКИХ КОНСТАНТ ДИССОЦИАЦИИ НОВОГО ХРОМОГЕННОГО АГЕНТА «ПАЛЛАДИАЗО» —II. ИЗУЧЕНИЕ ПРОЦЕССОВ ПРОТОНИРОВАНИЯ АЗОГРУПП РЕАГЕНТА В СЕРНОКИСЛЫХ СРЕДАХ:

J. A. PÉREZ-BUSTAMANTE and F. BURRIEL-MARTI, *Talanta*, 1971, **18**, 717.

Резюме—Изучено спектрофотометрическим методом протонирование реагента 1,8-диоксинафталин-3,6-дисульфо-2,7-бис (азофенил-*п*-арсоновой) кислоты («палладиазо») в 0,25–18*M* сернокислых средах. Наглядная оценка опытных данных указывает на протонирование только одной из азогрупп хотя дана возможность двухэтапного протонирования при очень высоких кислотностях. Первая константа неустойчивости протонирования равна $pK_9 = -(2,4 \pm 0,1)$, а вторая, оцененная приблизительно, равна $-7,4$. Обсуждены настоящие взгляды на реакции комплексообразования и протонирования производных бис (азофенил) хромотроповой кислоты с катионами металлов и протонами и детально критически дискутированы с целью истолковать опытные данные. Сделан вывод что вполне протонированная молекула палладиазо существует в очень концентрированных кислых средах преимущественно в форме симметрического, положительно заряженного таутомерного протонного комплекса хинонгидразона, который вызывает сильный единственный максимум светопоглощения при 665 нм, а который дает растворам протонированного реагента характеристичный изумруднозеленый цвет.

ЭКСТРАКЦИЯ АМИНАМИ С ДЛИННОЙ ЦЕПЬЮ—V. КОЛОРИМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ КОБАЛЬТА С ИСПОЛЬЗОВАНИЕМ НИТРОЗО-R СОЛИ:

JIŘÍ ADAM and RUDOLF PŘIBIL, *Talanta*, 1971, **18**, 733.

Резюме—Изменен и улучшен метод колориметрического определения кобальта нитрозо-R солью (NRS) включением в метод экстракции хелата Co-NRS раствором хлорида триоктилметиламмония в хлороформе. Фосфат и фторид аммония, а в первую очеред цитрат аммония использованы для маскирования железа, никеля, меди и кальция, которые элементы не мешают определению, даже если присутствуют в 2000-кратном избытке. Метод является весма чувствительным и позволяет определять около 1 мкг кобальта на каждий мл экстракта.

РЕАКЦИЯ НИТРИЛОТРИАЦЕТАТОВ МЕТАЛЛОВ С ЦИКЛОЛЕУЦИНОМ:

J. ISRAEILI, J. R. CAYOUTTE and R. VOLPE, *Talanta*, 1971, **18**, 737.

Резюме—Рассчитаны для разных температур константы образования смешанных комплексов образующихся в реакции нитрилотриацетатов металлов с циклолеуцином. Также рассчитаны $\Delta H_f°$ и $\Delta S_f°$ для реакции образования смешанных комплексов. Изучен гидролиз нитрилотриацетатов металлов при разных температурах и рассчитаны K_h, $\Delta H_h°$, и $\Delta S_h°$.

Identification of some polyatomic inorganic anions as their diphenyliodonium salts by infrared spectroscopy and interpretation of the spectra: A. J. Bowd, D. Thorburn Burns and R. Grzeskowiak, *Talanta*, 1971, **18**, 741. (Department of Chemistry, University of Loughborough Loughborough, U.K., and Department of Chemistry, Woolwich Polytechnic, London, S.E.18.)

Summary—The main features of infrared spectra of the diphenyliodonium salts of some polyatomic anions are reported and interpreted, and their application in qualitative analysis discussed.

Determination of methylmercuric ions by photometric titration with dithizone: Folke Ingman, *Talanta*, 1971, **18**, 744. (Department of Inorganic Chemistry, Royal Institute of Technology, Stockholm, Sweden.)

Summary—A rapid photometric titration titration technique, which makes it possible to determine methylmercuric ions with a sensitivity of 15 μg, is described. The titration takes place in 80% aqueous ethanol, which is capable of dissolving the titrant, a chloroform solution of dithizone. It has thus been possible to avoid the difficulties arising from co-extraction phenomena that occur when the extractive titration procedures developed for mercury(II) are applied to the determination of methylmercuric ions. A formate buffer is used to keep the pH in the range 2.5–3.0. The attainable precision is considerably better than 1%.

Extractive spectrophotometric determination of micro and sub-micro amounts of fluoride: J. P. S. Haarsma and J. Agterdenbos, *Talanta*, 1971, **18**, 747. (Analytisch Chemisch Laboratorium of the State University, Croesestraat 77A, Utrecht, The Netherlands.)

Summary—A simple and sensitive extractive spectrophotometric determination of fluoride with the cerium(III)–alizarin complexan chelate has been investigated. The fluoro chelate formed is extracted into n-pentanol containing triethylamine. It is possible to achieve under selected conditions a selective extraction of the cerium(III)–alizarin complexan–fluoride chelate. The stability of the chelate, the effect of temperature and the low absorbance of the blank are discussed. It is found that it is necessary to add a pH 9 buffer before the extraction. Procedures are given for the determination of 0.1–1 μg of fluoride in a 4-ml sample and 5–25 μg of fluoride in a 90-ml sample.

Iodobenzene dichloride as a new oxidimetric titrant in non-aqueous media: P. N. Krishnan Nambisan and C. G. Ramachandran Nair, *Talanta*, 1971, **18**, 753. (Department of Chemistry, Kerala University, Trivandrum-1, Kerala State, India.)

Summary—Iodobenzene dichloride in anhydrous acetic acid is proposed as a new oxidimetric titrant in non-aqueous media.

ОТОЖДЕСТВЛЕНИЕ НЕКОТОРЫХ ПОЛИАТОМНЫХ НЕОРГАНИЧЕСКИХ АНИОНОВ В ФОРМЕ ИХ СОЛЕЙ ДИФЕНИЛИОДОНИЯ МЕТОДОМ ИНФРАКРАСНОЙ СПЕКРОСКОПИИ И ИСТОЛКОВАНИЕ СПЕКТРОВ:

A. J. Bowd, D. Thorburn Burns and R. Grzeskowiak, *Talanta*, 1971, **18**, 741.

Резюме—Приведены и истолкованы главные характеристики инфракрасных спектров солей дифенилиодония некоторых полиатомных анионов и рассмотрено их применение в качественном анализе.

ОПРЕДЕЛЕНИЕ ИОНОВ МЕТИЛРТУТИ ФОТОМЕТРИЧЕСКИМ ТИТРОВАНИЕМ С ДИТИЗОНОМ:

Folke Ingman, *Talanta*, 1971, **18**, 744.

Резюме—Описан быстрый метод фотометрического титрования позволяющий определять ионы метилртути с чувствительностью 15 мкг. Титрование проводят в 80 % водном растворе этилового спирта, который растворяет титрованный раствор—раствор дитизона в хлороформе. Этим образом удалось избегнуть проблемы вызванные коэкстракцией появляющейся в случае применения разработанных для ртути(II) экстрактивных методов титрования в определении ионов метилртути. Муравьинокислый буффер использован для поддерживания pH в области 2,5–3,0. Получимая воспроизводимость значительно лучше чем 1 %.

ЭКСТРАКТИВНО-СПЕКТРОФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ МИКРОИ СУБМИКРОКОЛИЧЕСТВ ФТОРИДА:

J. P. S. Haarsma and J. Agterdenbos, *Talanta*, 1971, **18**, 747.

Резюме—Изучен несложный и чувствительный экстрактивно-спектрофотометрический метод определения фторида основывающийся на хелате ализарин-комплексана с церием(III). Образующийся хелат фторида экстрагируют раствором триэтиламина в н-пентаноле. При избранных условиях можно получить селективную экстракцию хелата ализарин-комплексан-фторида с церием(III). Рассмотрены устойчивость хелата, влияние температуры и низкое светопоглощение слепой пробы. Нужно добавить перед экстракцией буфферный раствор имеющий pH 9. Приведена методика определения 0,1–1 мкг фторида в 4 мл пробы и 5–25 мкг фторида в 90 мл пробы.

ИОДОБЕНЗОЛДИХЛОРИД В КАЧЕСТВЕ НОВОГО ОКСИДИМЕТРИЧЕСКОГО ТИТРАНТА В НЕВОДНЫХ СРЕДАХ:

P. N. Kirshnan Nambisan and C. G. Ramachandran Nair, *Talanta*, 1971, **18**, 753.

Резюме—Раствор иодобензолдихлорида в безводной уксусной кислоте предложен в качестве нового оксидиметрического титранта в неводных средах.

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Volume 18, No. 7 July 1971

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Printed in Northern Ireland at The Universities Press, Belfast