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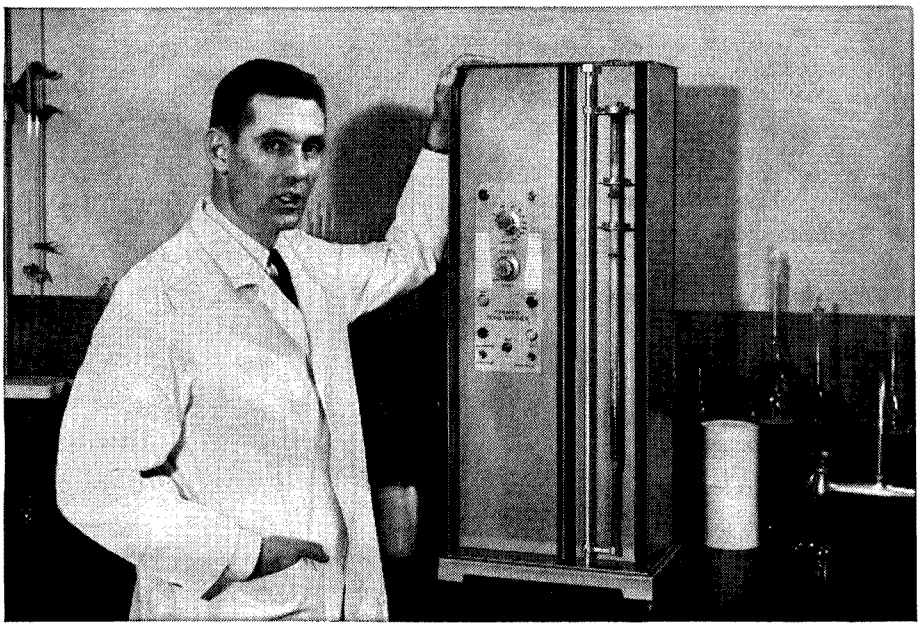

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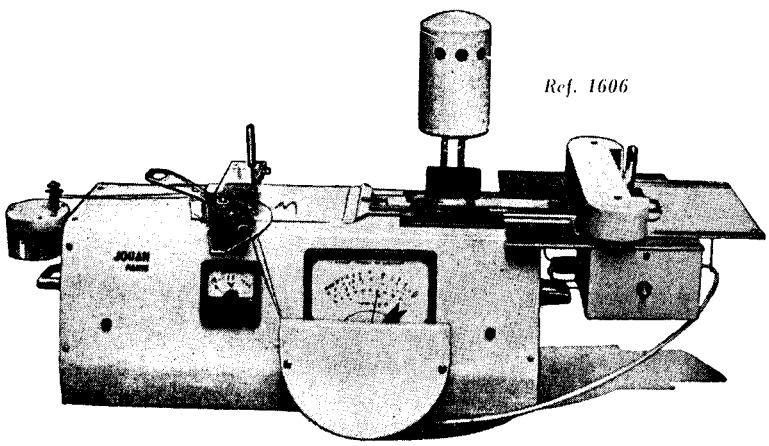

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NEW SPECIFIC ANALYTICAL PROCEDURES FOR THE DETECTION AND CHARACTERIZATION OF 1,4-NAPHTHOQUINONES

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(Received February 1st, 1960)

INTRODUCTION

Evidence for the presence of quinones in the air has been presented in a paper introducing a thermochromic test for inner ring *p*-quinones and fluorenones[1]. Further, to assist in the detection and characterization of the various families of quinones, specific tests for terminal ring *o*- and *p*-quinones[2] and for inner ring *o*-quinones[3] have also recently been described.

Quinaldinium salts and many other active hydrogen compounds can be used to detect 1,4-naphtoquinones, but other terminal ring quinones also react[2]. Phenylhydrazines have been used for the detection of 1,4-naphthoquinones[4,5], but many other types of quinones, aromatic aldehydes and ketones give just as brilliant color reactions.

It has been reported that derivatives of 1,4-naphthoquinone give a red fluorescence when a dry spot containing this material is examined under ultraviolet light[6]. In confirmation of this, 1,4-naphthoquinone and its 2,3-dichloro-, 2-hydroxy-, 2-methyl-, 2-amino-, 2-hydroxy-4-phenylimino-, 2-anilino-3-chloro-, 2-anilino-, and 2,3-dibromo-

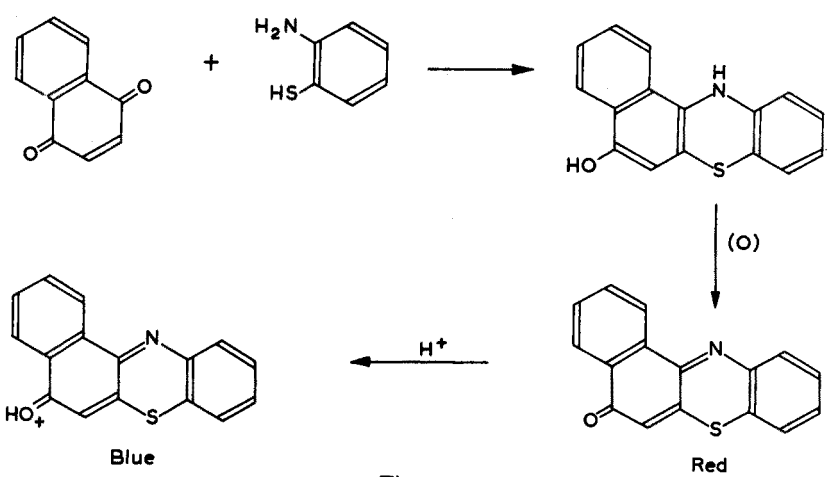

Fig. 1.

derivatives and benz[e]acephenanthrylene-9,12-dione were all found to give a dull red spot under ultraviolet light.

In this paper we would like to introduce some specific and much more sensitive methods for the detection of 2 types of 1,4-naphthoquinones.

In the first type the colorations formed in the color test probably involve the mechanism as shown in Fig. 1.

For this sequence of reactions the presence of air and acid is necessary.

As 2-hydroxy-1,4-naphthoquinone gave negative results in the terminal ring quinone tests[2] and in the present *o*-aminothiophenol test, a new method for the analysis of this compound was developed. The mechanism for the reaction is postulated as follows (see Fig. 2).

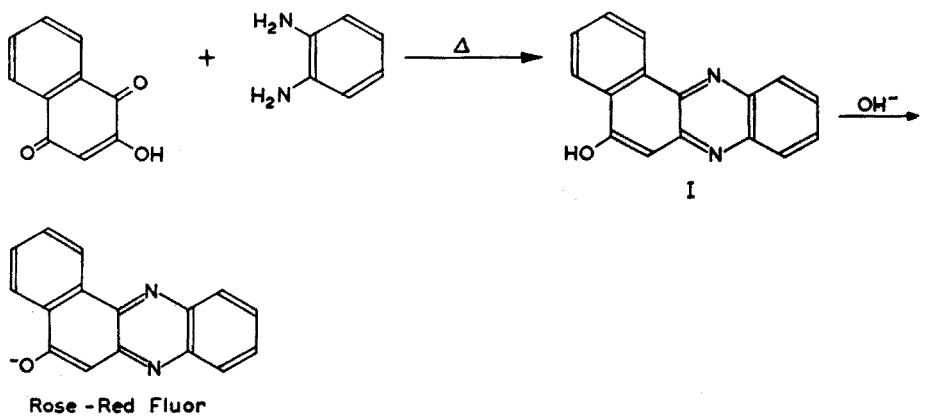

Fig. 2.

The compound, 1, was prepared by literature procedure[7] and was found to give the same striking rose-red fluorescence on paper in alkaline solution.

Color reagent

A mixture of 0.5 ml of *o*-aminothiophenol (American Cyanamid Co.) and 4 ml of concentrated hydrochloric acid was diluted to 50 ml with water. This reagent was stable for at least several days.

TABLE I

SPOT TEST FOR 1,4-NAPHTHOQUINONES

Compound	*Color*		*Ident. limit, μg*
	Base	*Cation*	
NQ[a]	Red	Blue	0.1
2-Methyl-NQ	Red	Blue[b]	0.05
2-Chloro-NQ	Red	Blue	0.01
2,3-Dichloro-NQ	Red	Blue	0.005
2,3-Dibromo-NQ	Red	Blue[c]	0.5

[a] NQ is 1,4-naphthoquinone.
[b] Steam heating the stain causes the color to change to red. However, a drop of hydrochloric acid will bring the blue color back.
[c] Unlike the other compounds, this one gave a blue ring surrounding a yellow-brown stain.

Procedure

A drop (0.03 ml) of the reagent is placed on filter paper followed by 1 μg of methanolic test solution placed in the middle of the drop. At this stage the paper can be waved in the air so as to hasten the oxidation to the red benzophenothiazone. After a 1- to 2-min waiting period, the color is noted and then a drop of concentrated hydrochloric acid is added. The color is again noted. The colors and identification limits obtained for some 1,4-naphthoquinones are presented in Table I.

Reagent for 2-hydroxy-1,4-naphthoquinone

One-half gram of *o*-phenylenediamine was dissolved in 4 ml of concentrated hydrochloric acid and 20 ml of water and then diluted to 50 ml with water. This reagent is stable for at least 1 day.

Procedure

One drop of the reagent is placed on filter paper followed by 1 μg of acetic acid test solution. The wet spot is heated with a jet of steam for 2 min. Then a drop of 10% aqueous potassium hydroxide solution is added. The paper is examined under ultraviolet light. A brilliant rose-red fluorescence denotes the presence of 2-hydroxy-1,4-naphthoquinone. The identification limit for this compound is 0.3 μg.

Remarks: In both new tests the following quinones gave negative results: benzoquinone, 2,5-dichloro-*p*-benzoquinone, 1,2-naphthoquinone, 1,2-naphthoquinone-4-sulfonic acid, phenanthraquinone, anthraquinone, and acenaphthenequinone. In addition, the following compounds also gave negative results: formaldehyde, acetaldehyde, benzaldehyde, phthalaldehyde, terephthalaldehyde, cinnamaldehyde, acrolein, acetone, benzalacetone, dibenzalacetone, anisalacetophenone, 2,4-pentanedione, benzanthrone, pyruvaldehyde, biacetyl, benzil, nitromethane, 1-octene, and 2,4-pentadiene.

In the *o*-aminothiophenol test negative results were obtained with 2-hydroxy-, 2-amino-, 2-anilino-, 2-anilino-3-chloro-, 2-hydroxy-4-phenylimino-1,4-naphthoquinones. Apparently the substitution of a fairly strong electron-donor group in the 2-position causes a negative reaction in the test. Benz[e]acephenanthrylene-9,12-dione also gave a negative result in the test.

Of the 1,4-naphthoquinones that gave positive response in the *o*-aminothiophenol test, 2-methyl-1,4-naphthoquinone was the only one which gave a blue color that faded to red on being heated with steam. Treatment with a drop of concentrated hydrochloric acid brought back the blue color. Apparently the dye formed from this quinone has a weaker basicity.

The quinones giving a positive test in the *o*-aminothiophenol procedure can be further characterized by the absorption spectra of the dyes in acid solution. For example, when 2 ml of concentrated hydrochloric acid is added to 1 ml of a methanolic solution of 1,4-naphthoquinone and 1 ml of the *o*-aminothiophenol reagent, shaken gently for 2 min and then diluted to 25 with trifluoroacetic acid, a brilliant blue solution results with wave length maxima (in the order of decreasing intensity) at 595, 772, 548, 512 (shoulder) and 700 (shoulder) mμ. The 2-methyl derivative also gave a blue color with a somewhat similar spectrum except that its long wave length band was at approximately 800 mμ. On the other hand the 2,3-dichloro- derivative

gave a purple-brown color with the long wave length band at 740 mμ while the 2,3-dibromo analogue gave a band near 775 mμ.

In the *o*-phenylenediamine test all 1,4-naphthoquinones gave the dull dark red color under ultraviolet light except 2-hydroxy-1,4-naphthoquinone which gave a gleaming rose-red fluorescence. The difference between the two types of fluorescent color is striking. The brilliant rose-red fluorescence can be easily differentiated.

The dull dark red fluorescence discovered by Green may be more easily obtained by evaporating 1 μg of an acetic acid solution of a 1,4-naphthoquinone on paper and then examining the paper. Identification limits of 1 to 10 μg are thus obtained on Whatman No. 1 filter paper in a daylit room. The dull red fluorescent spots obtained for 1,4-naphthoquinone, 2-methyl-1,4-naphthoquinone, 2,3-dichloro-1,4-naphthoquinone and benz[e]acephenanthrylene-9,12-dione faded under ultraviolet light. However, if a drop of 10% aqueous potassium hydroxide solution was added to the dry spot, the red color obtained under excitation by ultraviolet light was much more stable.

SUMMARY

A new sensitive and specific color test for 1,4-naphthoquinones is introduced. With the reagent, *o*-aminothiophenol, a red color is obtained in neutral solution and a blue color in acid solution on paper. 1,4-Naphthoquinones containing electron-donor groups in the 2-position give a negative reaction. With additional spectrophotometric studies the quinones giving a positive test can be differentiated. A new specific fluorescence test for 2-hydroxy-1,4-naphthoquinone has also been developed. Reaction with *o*-phenylenediamine on paper and then treatment with alkali gives a brilliant rose-red fluorescence.

RÉSUMÉ

De nouvelles réactions sont proposées pour l'identification des naphtoquinones-1,4. Avec l'*o*-aminothiophénol, on obtient une coloration rouge, en solution neutre, et bleue, en solution acide. L'hydroxy-2-naphtoquinone-1,4 réagit avec l'*o*-phénylènediamine en donnant une fluorescence rouge rose, en milieu alcalin.

ZUSAMMENFASSUNG

1,4-Naphtochinone reagieren mit *o*-Aminothiophenol unter Bildung einer roten Färbung in neutraler Lösung und einer blauen Färbung in saurer Lösung. Hydroxy-2-naphtochinone-1,4 reagieren mit *o*-Phenylendiamin in alkalischem Milieu unter Bildung eines Reaktionsproduktes, das eine starke rosarote Fluoreszenz zeigt.

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A METHOD FOR IDENTIFYING PARTICULATE FLUORIDE COMPOUNDS*

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(Received February 18th, 1960)

INTRODUCTION

The problems arising from fluorides in the atmosphere have been discussed by those interested in air pollution and agriculture[1,2]. The fact has been established that soluble fluoride compounds in the atmosphere can cause injury to plants, and through the plants, injury to animals[3]. It seems probable that the speed of sorption of the fluorides by the plant, and thus the extent of damage, might depend not only on the solubility of the compound but the particle size, the smaller sizes being more quickly available.

These considerations made it appear desirable to devise a test which would also indicate particle size for fluoride as an atmospheric contaminant. The general method of identifying individual species among airborne particulates has already been described by LODGE[4]. The sample is collected on a membrane filter, which is floated on a reagent designed to be a precipitant for the ion of interest. The precipitant is made as selective as possible to prevent interference. When the reaction has occurred, the filter is washed by floating on distilled water, dried, made transparent with immersion oil, and examined in the optical microscope. The reactions are seen as small circular clusters of crystals at the site of each particle containing the ion in question.

EXPERIMENTAL

The reagent used was lead chloride according to the method of SCHWARZKOPF AND HEINLEIN[5]. The test depends on adjustment of lead and chloride concentrations to give a solution which is 0.057 *M* in lead. This may be achieved by mixing one part of 10% (w/v) sodium chloride with 3.2 parts of 10% lead nitrate. Lead chloride is precipitated and removed by centrifugation. The supernate is the reagent. In the presence of fluoride ions lead chlorofluoride is precipitated, which is sufficiently insoluble to be well suited to quantitative studies. As prepared, the solution has a pH of about 5.0. This may vary, but should not be below 4.0.

A few ml are placed in a small petri dish and the sample filter with salts of soluble fluorides is placed on the surface until the filter has been thoroughly wetted for 5 min.

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It is then placed on the surface of a few ml of distilled water for 2 min, removed to a desiccator, dried and mounted. When more insoluble salts, such as fluosilicates, constitute the sample, the pH is lowered to 2.5 with acetic acid. A piece of blotting paper is soaked with the acidified reagent and the filter placed on it. The use of the blotter prevents motion of the filter and allows the reactions to form in a more compact fashion. When fluosilicates are suspected to be present, it is advisable to use a membrane filter without grid marks, as the acid reagent does not yield complete reactions around the marked lines. The fluosilicate samples react more quantitatively if the filter is first placed in a closed dish with a few drops of water and warmed very gently for half an hour. All other reaction times and procedures are the same as for soluble salts.

Insoluble fluoride-containing minerals such as cryolite and aluminum fluoride may be reacted by placing the filter on the blotter soaked with acid reagent for 1/2–1 hour. The wash on distilled water is for 3 min; the sample is dried and mounted as before. Laboratory tests show that when gaseous HF is drawn through the filter, a generalized reaction over the entire surface may be seen. After about 50 h, all the HF has diffused from the filter and the reaction no longer occurs. Therefore, samples containing HF cannot be shipped or stored but must be reacted immediately after collection. If soluble carbonates are suspected to be present, the filter must be placed in a closed dish with a few drops of HCl for one hour before reaction. This removes the carbonate but has no effect on the fluoride. Insoluble and mineral carbonates, and halides do not interfere. Sulfates and phosphates precipitate. Calcium fluoride does not react at all.

The fluoride precipitates are best seen as anisotropic white crystals in the optical microscope with crossed polars. They show polarization colors, which are especially distinctive in precipitates greater than 10 μ in diameter. The precipitates with sulfates are isotropic and extinguish completely under crossed polaroids. They may be ignored. The interference from phosphate is more serious, as it is frequently found in relation with fluorides. The precipitates are also anisotropic and visible under crossed polaroids. The distinguishing feature is their lack of polarization colors in contrast to the brilliance of the fluoride precipitate which appears to scintillate, even under reduced light, while the phosphate compound becomes fainter. Some skill with an optical microscope is required to make the identification, and practice with known compounds is advisable before heterogeneous samples are examined. Fluoride and phosphate precipitates cannot be distinguished in photographs.

Calibration

The diameters of the precipitates can be related to the diameters of the original particles[6]. This allows the sizes and mass of the original particles to be calculated. Two laboratory calibrations were made, one for soluble fluoride and one for fluosilicate. As an example of a soluble fluoride, sodium fluoride was collected on membrane filters. Similar collections of potassium fluosilicate were made for the second example. One section of the filter was examined immediately, the particles counted, and their diameters measured. A second section was reacted and the reaction sites in an equal area of the filter counted and measured. This was repeated several times to check for reproducibility. The statistical procedures involved in relating the reaction site diameter to the particle diameter, and the calculation of the geometric standard deviation have been described[6,7]. In both of these cases the reaction–particle relation was

linear, though the growth was considerably greater for the sodium fluoride. This equation is $d_r = 6.8\, d_p$ with a geometric standard deviation of $\pm$ 1%, where d_r and d_p stand for diameter of reaction and diameter of particle, respectively. The equation for the calibration using potassium fluosilicate is $d_r = 1.55\, d_p + 1.25$ with a geometric standard deviation of $\pm$ 2% (Fig. 1).

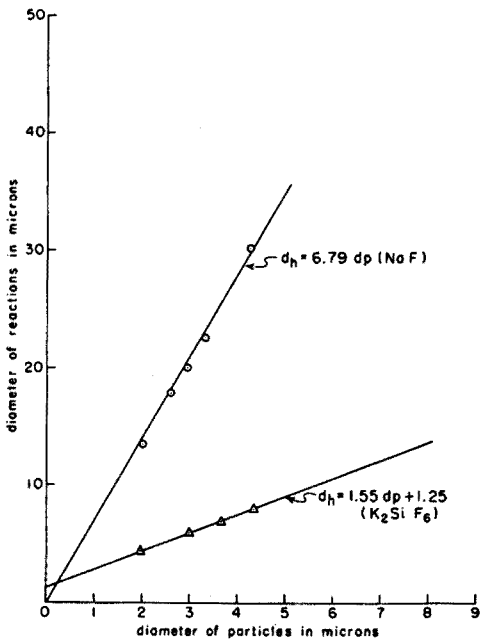

Fig. 1. Calibration curves for two typical fluoride-containing salts.

In order to find the lower limit of the test for soluble fluorides, the method was extended to the electron microscope. The sample of NaF as a test substance was collected on an electron microscope grid and reacted on a drop of reagent according to the method of TUFTS AND LODGE[8]. The grid is reacted with the sample side in contact with the reagent for 2 min and washed with the particle side away from the reagent for 1 min. Calibration was done both by measuring a series of particles and reactions from the same collection but different grids, and by measuring particles, reacting, and measuring the same reactions on the same grid. Both methods showed the calibration curve to be $d_r = 2.6\, d_p$ for NaF, with a standard deviation estimated at less than 5%.

The method is quantitative for particles having diameters at least as small as 1000 Ångstrom units.

Enlarged electron micrographs were prepared of the precipitates with fluoride, sulfate, and phosphate for close examination. The three can be distinguished by slight differences in structure. The fluoride salt is composed of tight clusters of rosettes, the sulfate precipitate has individual crystals either cubic or tetragonal in form and the phosphate has such fine structure as to appear amorphous even at high magnifications. The electron microscope method is somewhat tedious and is recommended only for special conditions where data on submicron particle sizes are desired.

Field tests

In order to test the efficiency of the method, efforts were made to take samples in the field. Simultaneous samples on membrane filters and by other standard collection methods were planned, in order to compare results. The first collections proved to be nearly totally of gaseous HF and did not survive shipment from the field site to the laboratory, suggesting that in such areas, arrangements be made for immediate reaction. The second set was obtained in an area where high particulate fluoride levels were known to occur. At the same time that the membrane filter samples were collected, samples were taken with a one cfm impinger in a Whitsell Auto-Imp sequential sampler[9]. The analysis was conducted using a perchloric acid distillation of the slightly alkaline absorption solution[10] and the distillate was titrated by the WILLIAMS method[11] as modified by ADAMS AND KOPPE[12].

The membrane filter samples were treated as described and the numbers of reactions seen counted and measured. To calculate the mass of fluoride present, the reactions were assumed to be spheres and the following formula used:

$$M = \frac{\pi}{6}\frac{R}{v}(10^{-12})\sum_i \left(\frac{D_{ri}}{6.8}\right)^3 N_i$$

where: D_{ri} = the reaction site diameter of the ith class, (μ), N_i = number of reactions in the ith class on the filter, R = density of NaF, V = volume of air sampled, (m^3) and the result is in grams per cubic meter. As many size classes may be chosen as is convenient; in the data given about ten classes were used. Another possible source of error in these data is the assumption that the fluoride is present as the sodium salt. This enters the calculation both in regard to the density and also, as TUFTS AND LODGE[8] have noted, in the particle–reaction ratio. Rough calculations for the case least conducive to a large particle–reaction ratio suggests that, if all the fluoride were actually ammonium fluoride, the mass value would be too high by a factor of about 3.5. Since in general atmospheric fluorides tend to be mixed, the choice of the sodium salt as representative is not unreasonable. Considerations of appearance may also influence the choice of the salt.

The comparison of the results of the particulate analyses and analyses of the impinger samples are shown in Table I. Although as stated above HF can be detected on

TABLE I

COMPARISON OF FLUORIDE SAMPLES COLLECTED ON MEMBRANE FILTERS AND IMPINGER

Sample date 1959	*Total air cu. ft.*[b]	*Total sample, MF. $\mu g/m^3$, as NaF*	*Average sample impinger $\mu g/m^3$, as HF*
7/10 – 7/14	3.09	0.012	2.8
7/14 – 7/16	3.09	0.019	8.1
7/16 – 7/17	11.58	0.0063	18.5
7/17 – 7/21	5.85	0.0033	9.2
8/11 – 8/12	220.99	0.14	[a]

[a] No data available, due to equipment failure.
[b] Samples were actually collected only during winds from northerly directions.

the membrane filters, other work has shown[13] that placing a filter in front of an impinger does not markedly change the results found when no filter is present. Therefore, these data are interpreted to mean that the largest amount of fluoride is present as the gas and the particulate comprises about 0.1% of the total. The presence of HF can only be deduced qualitatively on the filter. Due to a breakdown of the equipment, no impinger data are available for the last sample. The much higher mass is confirmed qualitatively, however, by the fact that during the period of this sample a severe fluoride pollution episode occurred.

In general, regardless of total numbers, the particle sizes were evenly distributed, showing a slight maximum in the one micron diameter range and few particles larger than 5-μ diameter, dry size.

Conclusions

The method is useful as a supplementary procedure for determining the ratio of particulate to gaseous fluoride in conditions of contamination or air pollution. Once the necessary skills with the optical microscope are acquired, the technique provides a rapid method for estimating the amounts of particulate fluoride in any given sample and distinguishing it from phosphates and sulfates present in the same sample. Because of the increase in reaction time for compounds of decreasing solubility, the procedure is readily applicable to the determination of soluble fluoride compounds most readily available physiologically.

ACKNOWLEDGEMENTS

Field samples were received through the courtesy of Polk County Air Pollution Control District, Florida, and the Air Pollution Research Laboratory, State College of Washington. Additional analyses of samples were provided by Kem-Tech Laboratories, Inc., Baton Rouge, La. Arrangements for obtaining the samples were made through Air Pollution Engineering Research, USPHS, Cincinnati, Ohio. Particle-reaction calibrations were made by U. NERI, laboratory assistant. This assistance is gratefully acknowledged.

SUMMARY

A method is described for identifying particulates containing fluorides and other complex fluorine compounds such as fluosilicate in samples collected on membrane filters. The filter is treated with lead chloride to precipitate lead chlorofluoride at each fluoride-containing spot. This microspot is identified by examination in a light microscope. Sulfate and phosphate, which also precipitate if present, can be distinguished and do not interfere. Calibrations are given for the fluorides and the more insoluble salts, relating the original particle size to the reaction site size. Thus the mass of the particles can be calculated. Results of some field tests in an area of fluoride pollution are given, and compared with standard testing procedures.

RÉSUMÉ

Une méthode est décrite pour l'identification des fluorures et des complexes fluorés dans les poussières atmosphériques, qu'on recueille sur un filtre à membrane et qu'on traite par le chlorure de plomb; le chlorofluorure de plomb formé est examiné au microscope.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Identifizierung von Fluoriden und komplexen Fluoriden in Staubteilchen. Die auf einem Membranfilter gesammelten Staubteilchen werden mit Bleichlorid behandelt und die entstandenen Flecken von Bleichlorofluorid unter dem Mikroskop untersucht.

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NEW COLORIMETRIC APPLICATIONS OF THE CHROMATE–*o*-DIANISIDINE SYSTEM

I. INDIRECT COLORIMETRIC DETERMINATION OF ANTIMONY(III), HYPOSULFITE, HYDRAZINE, HYDROXYLAMINE AND HYDROGEN PEROXIDE

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In a previous paper[1], we have described the reaction of chromate with *o*-dianisidine to give a deep red colour; this allows the identification of chromate up to a dilution of 1 : 2,000,000 ($D = 10^{-6.3}$) and its colorimetric determination up to a dilution of 1 : 1,700,000 (0.6 μg Cr/ml).

The methods described in the present paper are based on this colour reaction, and involve the attempted indirect colorimetric determination of some inorganic reducing agents (As^{+3}, Sb^{+3}, $S_2O_3^{-2}$, $S_2O_4^{-2}$, NH_2-NH_2, NH_2OH, and H_2O_2). The general method consists of oxidizing the ion or compound with a known excess of potassium chromate; then the excess is determined by measuring the extinction of the red colour developed when the chromate reacts with *o*-dianisidine in an acidic medium. In preliminary tests, it was shown that the compounds obtained by the chromate oxidation of each of the above reducing substances had no action on *o*-dianisidine.

At the low concentrations used in the colorimetric method, the behaviour of some of these reducing substances did not always agree with the literature data. For in-

stance, arsenic(III)[2] and sulfite[3] were not reduced by chromate at very dilute concentrations, hence their determination was not possible.

Good results were obtained for the nitrogen-containing compounds studied; hydrazine was completely oxidized to nitrogen[4,5] while hydroxylamine, whose oxidation according to the literature is not stoichiometric, several compounds, chiefly N_2O[6], being found, was also readily determined.

The method permits a simple, rapid colorimetric determination of very small amounts of the ions and compounds mentioned except for arsenic(III) and sulfite. Obviously, any other substances which are oxidized by chromate interfere in the determination.

Details of the absorption spectra between 200 and 1000 mμ of the red colour obtained at pH 1.5 and the bluish green colour at pH 3.5 are given below; the variation of the extinction and the validity of Beer's law is described in each case.

EXPERIMENTAL

The absorption spectra of the red and blue colours are shown in Fig. 1. The spectra coincide exactly with the spectra previously obtained over the range 420 to 780 mμ.

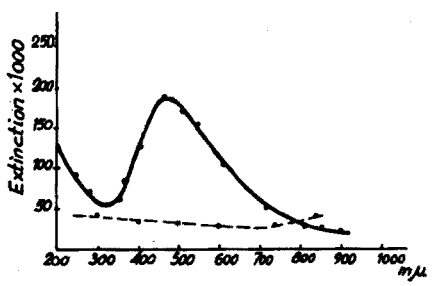

Fig. 1. Absorption spectra in the presence of substances resulting from the oxidation with chromate. •——• at pH 1.5; – – – – at pH 3.

The interval has now been extended to cover the range between 200 and 1000 mμ as a Beckman DU spectrophotometer was available for the present work. It was found

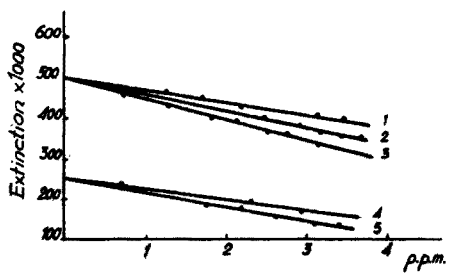

Fig. 2. Variation of the extinction with the concentration at pH 1.5 and 470 mμ. Initial chromate concentration 2 μg/ml, (1) NH_2-NH_2; (2) NH_2OH; (3) Sb^{+3}. Initial chromate concentration 1 μg/ml; (4) H_2O_2; (5) $S_2O_4^{-2}$.

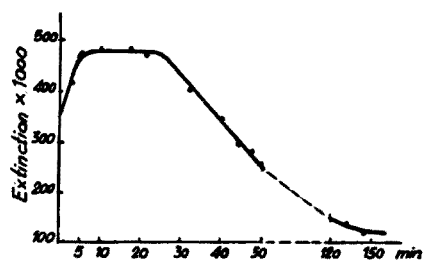

Fig. 3. Variation of the extinction with time at pH 1.5 and 470 mμ.

that the optimum wavelength was 470 mμ and the optimum pH value 1–2. The general procedure for the indirect colorimetric determinations is similar to that described previously for the determination of chromate with *o*-dianisidine[1]. The limits of validity of Beer's law for each of the compounds analysed are shown in Fig. 2. In Fig. 3 the variation of the colour extinction with time is shown; it can be seen that the values of the extinction remain constant for 25 min which is sufficient for normal usage.

PROCEDURE

2 ml of a potassium chromate solution containing 200 μg/ml are placed in a 100-ml volumetric flask. The solution containing the compound to be determined is added followed by 3 ml of 5 *N* sulfuric acid. The mixture is left for 5–10 min to ensure complete reaction, and then 0.5 ml of an *o*-dianisidine solution (0.5 g of *o*-anisidine dissolved in 50 ml of acetone and diluted to 100 ml with water) is added. The extinction is measured between 5 and 30 min after the reagent addition at a wave length of 470 mμ and with the slit suitably adjusted to attain the highest sensitivity of the spectrophotometer.

SUMMARY

New methods for the indirect colorimetric determination of antimony(III), hyposulfite, hydrazine, hydroxylamine and hydrogen peroxide, based on the colour reaction between chromate and *o*-dianisidine are described. The substance is oxidized with a known excess of chromate and the excess is determined by measuring at 470 mμ the extinction of the red complex with *o*-dianisidine at pH 1.5. The methods are simple, rapid and applicable at very low concentrations (0.1–4 μg/ml).

RÉSUMÉ

Une nouvelle méthode est décrite pour le dosage colorimétrique indirect d'antimone(III), hyposulphite, hydrazine, hydroxylamine et peroxyde d'hydrogène. Cette méthode consiste à oxyder les substances à analyser par un excès de chromate de potassium, que l'on détermine ensuite colorimétriquement par l'*o*-dianisidine.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur indirekten kolorimetrischen Bestimmung von Antimon(III), Hyposulfit, Hydrazin, Hydroxylamin und Wasserstoffperoxyd. Die zu untersuchende Substanz wird mit einem Überschuss von Kaliumchromat behandelt und dieser anschliessend mit *o*-Dianisidin kolorimetrisch bestimmt.

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NEW COLORIMETRIC APPLICATIONS OF THE CHROMATE–*o*-DIANISIDINE SYSTEM

II. INDIRECT COLORIMETRIC DETERMINATION OF SOME MERCAPTO COMPOUNDS: THIOGLYCOLIC ACID, THIOLACTIC ACID AND THIOMALIC ACID

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(Received March 11th, 1960)

An indirect colorimetric method for the determination of some inorganic reducing agents by means of the chromate–*o*-dianisidine system has already been described[1]. The compound to be determined is oxidized with a known excess of potassium chromate and the excess chromate is determined colorimetrically by measuring the extinction of the red colour developed on reaction with *o*-dianisidine in an acid medium[2].

The present work is based on the same principle; the method is extended to the determination of some organic compounds that are easily oxidized by chromate; we selected some mercapto derivatives of technical value, *i.e.* thioglycolic, thiolactic and thiomalic acids and thioglycerin.

The absorption spectra of the red (at pH 1.5) and the blue (at pH 3) colors formed by the chromate–*o*-dianisidine system were studied in the presence of the substances produced by the oxidation of the mercapto compounds. The spectra are similar to those found in the determination of pure chromate with *o*-dianisidine[2]. The variation of the extinction with time is also the same as in the previous work[1].

Figs. 1 and 2 show the lower limits of validity of Beer's law (0.1–5 μg/ml); Fig. 2 gives more detail for the dilution limit area for thioglycolic acid.

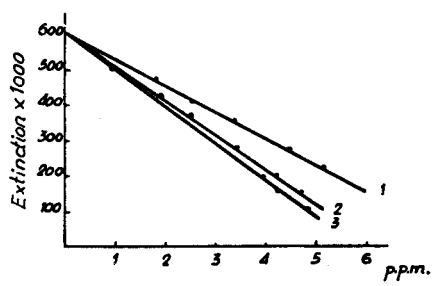

Fig. 1. Variation of the extinction with mercapto compound concentration in p.p.m. at 470 mμ and pH 1.5. (1) thiomalic acid; (2) thiolactic acid; (3) thioglycolic acid.

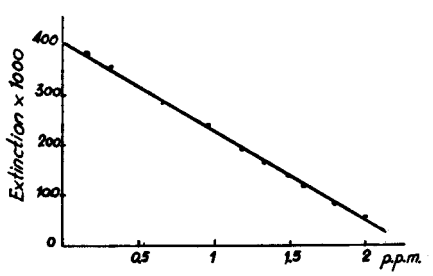

Fig. 2. Variation of the extinction in the dilution limit area; thioglycolic acid in p.p.m. at 470 mμ and pH 1.5.

This process gave good results in the determination of thioglycolic, thiolactic and thiomalic acids, but failed for thioglycerin. The procedure used is similar to that already reported[1]; the reduction of chromate by the mercapto compound also proceeds quantitatively in basic medium. One special interest of these methods is that they are the only colorimetric procedures available for the determination of thiomalic and thiolactic acids.

EXPERIMENTAL

Reagents

Potassium chromate (Analytical reagent, dried at 120°) was used to prepare a solution containing 200 mg CrO_4^{-2}/l. Mercapto compounds: all the mercapto compounds used were purified by vacuum-distillation to remove thioglycolides and other products formed by air oxidation or by intermolecular esterification: the —SH contents were titrated with iodate by the usual procedures. *o*-Dianisidine solution: 0.5 g *o*-dianisidine was dissolved in 50 ml of acetone and the volume made up to 100 ml with distilled water. Sulfuric acid and acetone: analytical grade.

Procedure

2 ml of the potassium chromate solution were placed in a 100-ml volumetric flask; the solution containing the mercapto compound is added from a microburette; an inert atmosphere should be used, in order to avoid the air oxidation of mercapto compound. This was followed by 2–3 ml of 5 *N* H_2SO_4 and the mixture was left for 5–10 min; 0.5 ml of the *o*-dianisidine solution was then added.

The readings were made at 470 mμ between 5 and 25 min after the colour had developed. The slit of the spectrophotometer was adjusted to obtain the highest sensitivity of the spectrophotometer.

SUMMARY

New indirect colorimetric methods for the determination of thioglycolic, thiolactic and thiomalic acids are described. The mercapto compound to be determinated is oxidised by a known excess of K_2CrO_4, this excess determinated by measuring the extinction at 470 mμ of the red colour developed when the CrO_4^{-2} reacts with *o*-dianisidine in acid medium. The method permits a very simple colorimetric determination of the mercapto compounds above mentioned, at a very low concentration (0.1–5 μg/ml).

RÉSUMÉ

De nouvelles méthodes sont décrites pour le dosage colorimétrique indirect des acides thioglycolique, thiolactique et thiomalique. La substance à analyser est oxydée par le chromate de potassium en excès, que l'on détermine au moyen de l'*o*-dianisidine.

ZUSAMMENFASSUNG

Beschreibung einer indirekten Methode zur Bestimmung von Thioglycol-, Thiomilch-, und Thioäpfelsäure. Sie beruht auf der Oxydation der Merkaptoverbindungen mit Kaliumchromat, dessen Überschuss mit *o*-Dianisidin kolorimetrisch bestimmt wird.

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THE SIMULTANEOUS DETERMINATION OF TRACES OF SELENIUM AND MERCURY IN ORGANIC COMPOUNDS BY X-RAY FLUORESCENCE

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(Received February 18th, 1960)

INTRODUCTION

Many of the most efficient procedures for the introduction of unsaturation into organic compounds involve catalytic dehydrogenation with selenium dioxide[1] or selenium dioxide in the presence of mercury[2]. Since both selenium and mercury are capable of forming organo-metallic compounds, they may be carried through the subsequent reactions into the final product. The toxicity of these metals requires that they be shown to be substantially absent in products intended for oral consumption by humans and animals. Thus an accurate procedure for their quantitative determination in the p.p.m. range was necessary.

The present chemical methods for the quantitative determination of microgram quantities of selenium[3,4] and mercury[5], while extremely sensitive, are difficult to apply. An X-ray absorption method[6] gives excellent results but lacks the sensitivity required. To circumvent the necessity for destruction of the sample and conversion of the elements to a known valence state and to overcome the large sample required by the chemical methods an X-ray fluorescence procedure for the quantitative determination of selenium and mercury in the solid state has been developed. The procedure is non-destructive of the sample, rapid, and accurate.

EXPERIMENTAL

Preparation of solid samples

The samples are ground in a mortar to give a fine powder. Six hundred mg of material are weighed ($\pm$ 1–2 mg) and placed in a 1.4 $\times$ 2.0 cm opening milled into a 1/8 $\times$ 1-1/4 $\times$ 1-1/2 in aluminum plate which is resting on a polished steel surface. The sample is tamped with a spatula until tightly compressed. Three thicknesses of 0.5 mm lead are placed on top of the sample which is then compressed at 8,000 lbs/sq. in. pressure in any suitable hydraulic press. The lead is removed from the back of the sample to give a brick of compound held in an aluminum sample holder. Removal of the lead was found necessary since it contributes a large amount of scatter to the background readings.

Very finely powdered samples and/or samples with a high static charge may be tamped into the holder by the addition of small droplets of Skelly B or some other

low boiling liquid in which the material is not soluble. The solvent is allowed to evaporate from the compacted sample before compression. Samples submitted as large crystals must be ground to assure the formation of a brick which will not crumble during the analysis. When properly prepared the bricks require considerable pressure to remove them from the sample holder.

Liquid samples

Materials whose selenium content and solubility permit a determination in solution are dissolved in known concentration in any suitable solvent, provided the solvent contains no heavy element (*i.e.*, halogens). The solution is added to a specially designed cell by use of a hypodermic syringe. The sample solution volume is not critical to the analysis provided the cell is full (about 2.5 ml of solution). The cell, shown in Fig. 1, is made of aluminum. The Mylar window (one mil thick) is held between the front plate and cavity block by the ten screws; no gasket is necessary to prevent leakage.

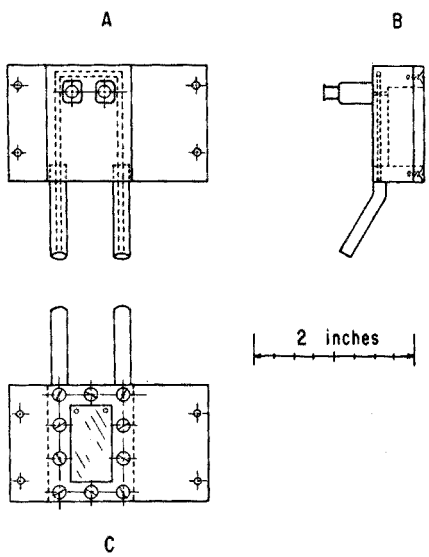

Fig. 1. Liquid sample cell. A and B: bottom and end views, respectively, showing cooling tube and hypodermic filling adapters. C: top view, showing mylar window.

Two 13-gauge hypodermic needles are used in the construction, which permits the filling and washing of the cell with a standard syringe. After the cell is filled, Teflon plugs are inserted in the needles. The cell may be temperature-controlled by the passage of water through a channel around the cell cavity.

Preparation of standard samples

The solid standard samples were prepared in the following manner: (Se): 3.149 mg of a seleno-steroid of known structure and purity (mol. wt. = 936.86) were dissolved in alcohol to give a solution containing 10.64 μg/ml of Se. Measured portions of this standard (or an appropriate dilution of it) were added to 3.000 $\pm$ 0.001 g of testosterone. The sample was dissolved in alcohol–acetone on a steam bath and, after the

initiation of crystallization, evaporated to dryness. The dried crystals were ground in a mortar to give a finely divided powder. (Hg): Samples were prepared in an identical manner except that a solution containing 3.706 μg/ml of Hg was prepared from mercuric acetate. The liquid samples were prepared by serial dilution of a standard solution of diphenylselenium containing 235 μg/ml of Se.

Instrumental settings

A General Electric XRD-5 unit was used for the analyses. The primary radiation was from a tungsten target X-ray tube operated at 50 kV and 45 mA. A lithium fluoride analyzing crystal ($2d = 4.0269$ Å) and sodium iodide (thallium activated) scintillation counter were employed.

For the determination of mercury the $L\alpha$-line at 36.00° 2θ was used, and for selenium the $K\alpha$-line at 31.88° 2θ was used. For purposes of standardization, the intensities of these lines were related to the measured intensity of the tungsten $L\beta$-line at 37.40° 2θ.

The scaler circuit was set to record the time required for the accumulation of one million counts.

Procedure

Following a 30-minute instrumental warm-up period the sample is placed in the X-ray beam, and the time required for the accumulation of one million counts is measured when the goniometer setting is 31.88° (for selenium), 36.00° (for mercury), and 37.40° (for tungsten). The sample is then reversed in the holder 180 degrees and the procedure repeated. The two countings are averaged at each of the three 2θ settings. The actual variation between the values for the two positions of the sample nearly always falls within the limits of experimental error. The two time values thus determined for a particular goniometer setting will not be exactly equal due to inhomogeneity of the X-ray beam unless there is complete dispersion of the unknown element in the sample.

RESULTS AND DISCUSSION

The statistical accuracy of radiation counting is a function of the total number of counts, rather than the time required to accumulate them. For a more valid comparison of counting rates (intensity) then, the pre-set count, rather than the pre-set time method is used, and readings are taken from a timer which is synchronized with the scaler, and which stops automatically when the pre-set count is accumulated.

Ideally, the concentration of selenium is proportional to the intensity of the $K\alpha$-line at 3.88° 2θ, determined by

$$M/t_{(31.88°)}, \text{ where } M = \text{one million counts and } t_{(31.88°)} = \text{time elapsed at } 2\theta = 31.88°$$

Two sources of error invalidate this: The primary radiation used to excite the sample varies somewhat from day to day, so samples run one day cannot be referred to a standard curve prepared previously, and sample surface inconsistencies cause wide variations in loss of X-ray energy due to scattering.

It was found, however, that the ratio of the intensity M/t of selenium to that of tungsten (from the X-ray tube) was a value independent of the above variables. For this reason, the concentration of selenium is found by taking the ratio of intensities:

$$\frac{I_{Se}}{I_w} = \frac{M/t_{(31.88°)}}{M/t_{(37.4°)}} = \frac{t_{(37.4°)}}{t_{(31.88°)}}$$

and the concentration of mercury from the ratio of intensities:

$$\frac{I_{Hg}}{I_w} = \frac{t_{(37.4°)}}{t_{(36.0°)}}$$

These intensity ratios are shown as functions of concentration of selenium and mercury, respectively, in Figs. 2 and 3.

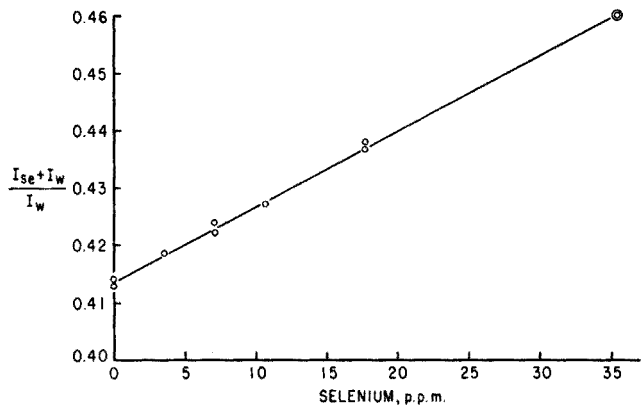

Fig. 2. Selenium, intensity ratio *vs.* concentration.

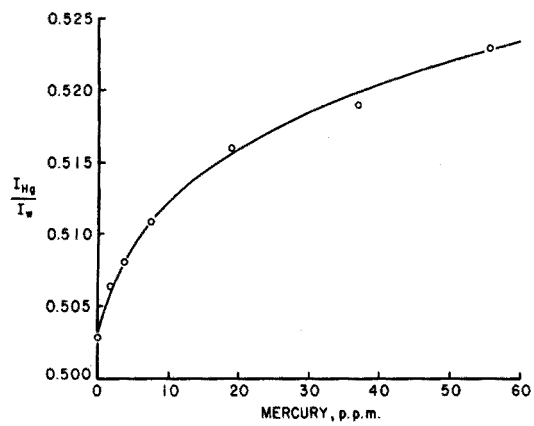

Fig. 3. Mercury, intensity ratio *vs.* concentration.

Fig. 4 shows a standard curve for the determination of selenium in solution.

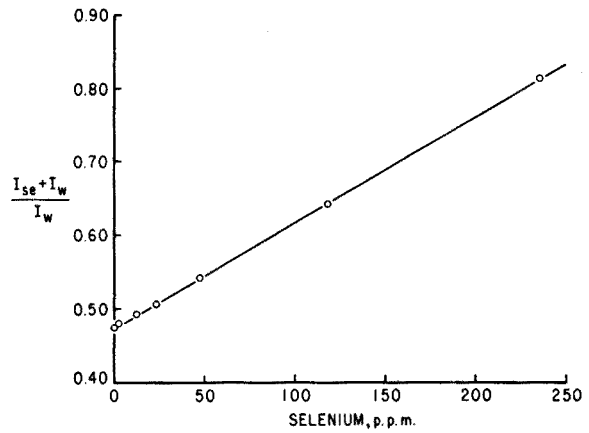

Fig. 4. Selenium in solution; intensity ratio *vs.* concentration.

Application of the method of least squares to the data from which the selenium calibration curves were drawn gives the following equations for the straight lines ($y = mx + b$) at the 95% confidence level:

Solid state (Fig. 2), $y = (0.001314 \pm 0.000036)x + (0.4134 \pm 0.0067)$;
Solution (Fig. 4), $y = (0.001442 \pm 0.000019)x + (0.4748 \pm 0.0197)$.

The curvature of the mercury plot, Fig. 3, is marked. This is expected for a heavy element in a light matrix[7]. The appearance of a straight line for selenium in Figs. 1 and 3 is explained on the basis of the occurrence of a secondary tungsten line coin-

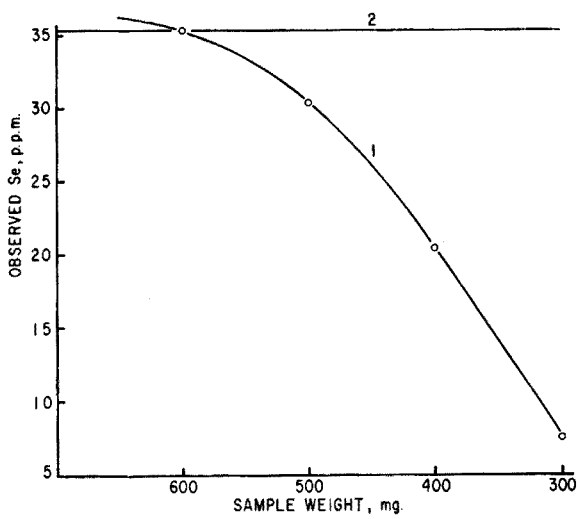

Fig. 5. Observed Se (p.p.m.) *vs.* total sample weight (mg). All samples 35.47 p.p.m. Se (theory). 1. Observed selenium, p.p.m., 2. Theoretical selenium, p.p.m.

cident with the selenium line at 31.88° 2θ. Hence, the plot is actually one of concentration *vs.* the ratio of intensities:

$$\frac{I_{Se} + I_{w1}}{I_{w2}}$$

where I_{w1} and I_{w2} are both larger than I_{Se}. In addition selenium should be considered as a lighter element in the same matrix. This consideration alone will cause the line to straighten considerably when compared with that of mercury[7].

The effect of sample size on the analysis is shown in Fig. 5 and it is seen that in the 600-mg range the variation of $\pm$ 10 mg in the sample size introduces only a small error. By means of the curve in Fig. 5 it is possible to correct for sample size when a 600-mg sample is not available. The error introduced by this correction increases rapidly below 500 mg. Above 600 mg the curve would presumably level off as essentially infinite sample thickness was approached. No samples larger than 600 mg were prepared due to the difficulty encountered in packing them into the 1/8-inch thick sample holders.

The average time requirement for each analysis, including sample preparation, is forty-five minutes.

SUMMARY

A procedure for the simultaneous determination of selenium and mercury in organic compounds has been developed. The method, which is based upon X-ray fluorescence, gives results which are accurate to $\pm$ 1 p.p.m. in the range of 2 to 40 p.p.m. for both selenium and mercury. The procedure is rapid and is non-destructive of the sample. A 600-mg sample is required.

RÉSUMÉ

Une méthode d'analyse par rayons X proposée pour le dosage simultané du sélénium et du mercure dans des substances organiques.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur gleichzeitigen Bestimmung von Selen und Quecksilber in organischen Verbindungen. Sie beruht auf der Anwendung der Röntgenfluoreszenz Analyse.

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A SPECIFIC SPOT TEST FOR IRON

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Color reactions by phenyl-α-pyridyl ketoxime with a number of cations including ferrous iron was reported by SEN[1]. Since its first introduction, phenyl-α-pyridyl ketoximes has been employed for spectrophotometric determination of palladium and gold[2,3]. Recently TRUSSEL AND DIEHL used this reagent for the spectrophotometric determination of iron(II)[4]. In this paper a highly selective method for the detection of iron by a spot test based upon the formation of an intensely colored violet chelate of iron(II) with phenyl-α-pyridyl ketoxime is being reported.

EXPERIMENTAL

Reagent solution

A 1% solution of phenyl-α-pyridyl ketoxime*[2] in a 95% ethanol was used as reagent solution.

Procedure for the test

The test may be carried out in either of the following ways: (*a*) Place one drop of the test solution (50 μg) in the depression of a white spot plate. Add a few crystals of ascorbic acid, or hydroxylamine hydrochloride or sodium hydrosulfite followed by the addition of two drops of the reagent solution. The mixture is then made basic by the addition of two drops of 0.5 *M* sodium carbonate solution or by the addition of two drops of 6 *N* ammonia. A violet color confirms iron. (*b*) Place a drop of the test solution on a Whatman 40 filter paper. Add a drop of 10% solution of ascorbic acid and two drops of the reagent solution. Hold the wet spot over a bottle of ammonia. A violet coloration confirms iron.

Interfering ions

The following ions do not interfere with the test: Li^+, Na^+, K^+, Rb^+, Ag^+, Cs^+, Be^{+2}, Mg^{+2}, Ca^{+2}, Zn^{+2}, Sr^{+2}, Cd^{+2}, Ba^{+2}, BO_2^-, Al^{+3}, Ga^{+3}, Ce^{+3}, Tl^{+3}, CO_3^{-2}, SiO_3^{-2}, Ti^{+4}, GeO_3^{-2}, Zr^{+4}, Pb^{+2}, Th^{+4}, NH_4^+, NO_3^-, PO_4^{-3}, VO^{+2}, As^{+3}, Sb^{+3}, Bi^{+3}, $S_2O_3^{-2}$, SO_3^{-2}, SO_4^{-2}, Ca^{+2}, MoO_4^{-2}, TeO_3^{-2}, TeO_4^{-2}, WO_4^{-2}, UO_2^{+2}, VO_4^{-2}, Cl^-, Mn^{+2}, Br^-, I^-, Ni^{+2}, Ru^{+3}, Rh^{+3}, Pd^{+2}, Ir^{+4}, Pt^{+4}, acetate, oxalate, succinate, tartrate, citrate.

* Available from G. F. Smith Chemical Co., Columbus, Ohio.

Color of the copper chelate and the color of cobalt (when the amount is more than ten times the amount of iron) chelate tend to mask the iron test. Cyanide inhibits the test.

Sensitivity

Limit of identification = 0.05 μg; dilution limit = 1 : 1,000,000.

Detection of iron in presence of copper

Detection of iron in the presence of copper can be accomplished in a number of ways. Copper may be precipitated as cuprous iodide or cuprous thiocyanate and the iron test is then performed in the usual way. Copper may also be reduced to the metallic state with sodium hydrosulfite prior to the iron test.

The test may be seen on a filter paper or a spot plate. Place a drop of the test solution on a filter paper (or in the depression of a spot plate) followed by a drop of a 10% solution of ammonium thiocyanate (or potassium iodide) and two drops of a 10% solution ascorbic acid. Add two drops of the reagent solution and hold the paper over a bottle of concentrated ammonia (or add two drops of 0.5 M Na_2CO_3 when spot plate is used). A violet coloration confirms the presence of iron.

The test is thus virtually free from any interference. The test may be applied for the detection of ferrous iron in the presence of ferric iron in which case no reducing agent should be used.

ACKNOWLEDGEMENT

Grateful thanks are expressed to Prof. PHILIP W. WEST for research facilities.

SUMMARY

A highly selective and sensitive spot test for iron is based on the formation of a violet colored chelate with phenyl-α-pyridyl ketoxime. The limit of identification = 0.05 μg.

RÉSUMÉ

La phényl-α-pyridylcétoxime réagit avec le fer(II) pour former un chélate violet. Cette réaction permet une identification très sélective et sensible du fer (limite d'identification 0.05 μg).

ZUSAMMENFASSUNG

Eine sehr empfindliche Tüpfelprobe auf Eisen beruht auf der Bildung eines violett gefärbten Chelates mit Phenyl-α-pyridylketoxim. Nachweisgrenze = 0.05 μg.

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A NEW METHOD FOR THE DETERMINATION OF NITRATES

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Nitrates serve as an index of pollution in water, and oxides of nitrogen have now been recognized as one of the more important pollutants in air. The determination of nitrates up to the present has depended upon methods which are either nonspecific or nonsensitive. The present study was undertaken to investigate possible methods for the determination of nitrates that would meet the requirements common to water and air pollution studies.

The nitrate ion does not ordinarily form anionic complexes. Because of this fact and the fact that nitrate salts are so highly soluble, the determination of this ion is quite difficult. The usual reactions of nitrate are of the redox type, which makes its determination subject to a large number of interferences from other oxidants. Specific determinations involving a redox reaction with nitrate are unlikely, because the ion cannot be conveniently separated from its interferences. The method most widely used at present is the phenoldisulfonic acid method[1] which is based on the formation of a specific nitro compound. This procedure is subject to a number of interferences, the most serious being chloride ion. The method is time-consuming and difficult to perform. Also, it requires a large volume of sample, which is a distinct disadvantage. Other methods such as the nitration of 1,2,4-xylenol[2], the determination of nitrates as nitrites with the Griess reaction[3], and the reduction of nitrates to ammonia and subsequent Nesslerization of the latter[4], are subject to interferences and are all quite involved, requiring large samples and relatively lengthy preparation times.

WEST AND SARMA[5] developed a spot test for nitrate using a solution of 4,5-dihydroxy-2,7-naphthylene disulfonic acid (chromotropic acid) in concentrated sulfuric acid. The test is very sensitive and is free of common interferences. The fact that this reagent gives a yellow color which appears to vary with the nitrate concentration, and because the reaction is both sensitive and highly selective indicated that it might well be a suitable reagent for the quantitative determination of nitrates.

REAGENTS AND APPARATUS

A purified form of 4,5-dihydroxy-2,7-naphthylene disulfonic acid (disodium salt) was obtained by the addition of solid sodium sulfate to a saturated solution of Eastman practical grade salt of chromotropic acid. The salting out procedure was carried out

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twice to insure high purity. The purified product was then dissolved into A.R. grade concentrated sulfuric acid to give a 0.1% stock solution. The nitrate reagent was prepared by adding 1 ml of concentrated HCl to 10 ml of the stock solution and diluting to 100 ml with concentrated H_2SO_4. The solutions of the ions listed for the interference study were prepared from reagent grade salts and were free of nitrates. The interference solutions used for the study of phenoldisulfonic acid reagent were free of chlorides as well as nitrates, because the former constitute serious interferences with this particular reagent. All standard nitrate solutions were prepared by diluting proper amounts of a stock solution prepared by dissolving pure sodium nitrate in distilled water.

A Beckman Model DK recording spectrophotometer was used to determine the wavelength at which maximum absorbance occurs. All measurements of absorbances were made with a Beckman Model B spectrophotometer which was equipped with matched quartz cells. All volumes were measured with Exax grade 10-ml volumetric flasks and volumetric pipets of 1-, 2-, and 3-ml capacities respectively.

EXPERIMENTAL

Two samples containing 5 and 30 p.p.m. respectively of nitrate ion were used to study the effect of varying acid concentrations. 2 ml of the samples were treated with varying amounts of concentrated sulfuric acid containing chromotropic acid. The mixtures were each diluted to 10 ml with distilled water, the color allowed to develop for five minutes and the absorbances then measured at 415 mμ as suggested by SARMA[5]. All absorbance values were corrected for back-ground due to the reagent. The results indicated that an initial acid concentration of 60% to 70% is sufficient for maximum color development.

A study was made of the effects of reagent concentration on absorbance measurements by investigating several concentrations of chromotropic acid in concentrated sulfuric acid. Reagent concentrations above 0.1% (w/v) gave extremely high blank backgrounds which interfered with the determination. A reagent of 0.01% gave a much lower background, high absorbance with nitrate, and results which complied with Beer's Law over concentrations of 5 to 55 p.p.m.

The wavelength at which maximum absorbance occurs is generally very critical for quantitative work. The wavelength (415 mμ) suggested earlier[5] is suitable for visual estimations for a concentration range of 5 to 50 p.p.m.; however, it was felt that this was not necessarily the optimum for trace analysis studies and an investigation was made to establish the optimum wavelength to be used to obtain maximum sensitivity.

3-ml portions of standard nitrate samples (1 through 5 p.p.m.) were treated with 7 ml of 0.01% reagent in concentrated sulfuric acid, respectively, and their absorbances run on the Beckman DK recording spectrophotometer. The results, shown in Fig. 1, indicate that maximum absorbance is obtained at 357 mμ.

The reagent-sample contact time studies indicated that two minutes contact would be sufficient for a maximum color development, and that once formed, the color remains stable for at least 96 hours.

The experiments revealed no effect of temperature on color development. The temperature studies were carried out by treating known samples of nitrate all in

exactly the same way and then immersing them in a bath of boiling water for measured periods of time, diluting the sample to 10 ml, and measuring the absorbances.

A preliminary investigation of interferences indicated that the chloride ion might cause high results. A blank containing no nitrate but high chloride concentrations gave no reading, but a sample containing 1500 μg per ml of chloride and 15 μg of nitrate ion gave such a high reading that it was thought possible that increased sensitivity might be obtained by including chloride ion in the reagent and taking advantage of this effect.

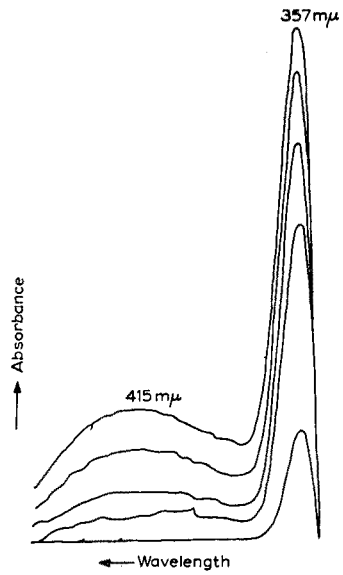

Fig. 1. The determination of the wavelength at which maximum absorbance occurs.

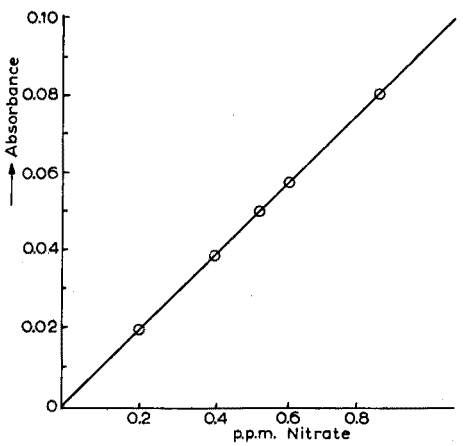

Fig. 2. Microdetermination of nitrate.

1 ml of concentrated hydrochloric acid was added to 100 ml of the 0.01% reagent. A sample containing 5 p.p.m. of nitrate ion was treated with this modified reagent (3 ml of sample diluted to 10 ml with reagent) and the resulting solution was used to determine the wavelength at which maximum absorbance would occur. The resulting plot from the Beckman DK recording spectrophotometer indicated that there was no shift in wavelength due to the addition of the chloride ion. The new reagent containing the chloride ion was then used to test a series of standard nitrate samples ranging from 1 to 5 μg per ml of nitrate ion and was found to give excellent sensitivity.

The results shown in Table I, even though not strictly linear, are quite suitable for quantitative work. It was realized immediately from these results that it should be possible to determine much smaller quantities of nitrate ion using a reagent solution containing chloride. Standard nitrate solutions were prepared for the range of 0.2 to 1.0 p.p.m. nitrate ion. 3 ml of these samples were placed in 10-ml volumetric flasks and treated by diluting up to the mark with the modified reagent. A contact time of 30 min was used so as to allow the mixture to cool to room temperature prior to measurement. The results of the absorbance measurements are plotted in Fig. 2.

TABLE I

Nitrate concentration (p.p.m.)	*Absorbance (357 mμ)*	
	With added chloride	*Without chloride*
1.0	0.208	0.065
2.0	0.438	0.133
3.0	0.618	0.214
4.0	0.710	0.325
5.0	0.760	0.400

It is of interest to note that a discontinuity exists in the working curve. At low concentrations (up to approximately 1 p.p.m. of nitrate) a linear response is obtained, but above this a distinct displacement of the curve occurs so that a separate working graph must be prepared for the range of 1 to 10 p.p.m.

TABLE II

INTERFERENCE STUDIES

Ions investigated	*Chromotropic acid method*	*Phenoldisulfonic acid method*	*Ions investigated*	*Chromotropic acid method*	*Phenoldisulfonic acid method*
aluminum	none	slight	lead	none	none
ammonium	none	none	magnesium	none	none
antimony(III)	none	none	manganese(II)	none	slight
antimony(V)	none	none	mercury(II)	none	none
arsenic(III)	none	none	molybdate	10 : 1	none
arsenic(V)	none	none	nickel	none	none
barium	none	none	palladium(II)	none	none
beryllium	50 : 1	none	perchlorate	none	none
bismuth(III)	50 : 1	none	*m*-phosphate	none	none
borate	none	none	*o*-phosphate	none	none
bromate	great	great	platinum(IV)	none	none
bromide	great	great	ruthenium(III)	slight	slight
cadmium	none	none	selenate	none	none
calcium	none	none	selenite	none	none
cerium(III)	none	slight	sodium	none	none
cerium(IV)	none	none	sulfate	none	none
chromium(III)	none	great	sulfite	none	none
chromium(VI)	none	great	tellurium	none	none
chlorate	great	great	tin(II)	none	none
chloride	none	great	tin(IV)	none	none
cobalt(VI)	none	none	titanium(III)	great	none
copper(II)	none	great	titanium(IV)	great	none
fluoride	none	none	tungstate	none	none
iodate	30 : 1	none	vanadium(II)	none	none
iodide	slight	great	vanadium(V)	none	none
iron(II)	50 : 1	none	uranate	none	none
iron(III)	10 : 1	10 : 1	uranyl	none	none
gold(III)	none	great	zinc	none	none
			zirconium	none	none

Interference studies

A ratio of 1 : 100 nitrate ion to interference ion was used as a standard in an attempt to determine which ions would cause interference with determination of nitrates. A control sample and the sample containing the ion under investigation for interference were compared with an interference blank. Absorbances were measured at 357 mμ, and the results obtained on the control and interference samples were compared. If the two readings differed by more than 10%, the ion was listed as an interference. The results are listed in Table II.

RECOMMENDED PROCEDURES

Water analysis

Pipet 3 ml of the sample into a 10-ml volumetric flask. Fill the flask to the mark with 0.01% purified chromotropic acid in concentrated sulfuric acid with chloride ion added as described above. Allow the mixture to cool to room temperature, dilute to the mark, and measure the absorbance at 357 mμ. The concentrations may then be determined from a standard calibration curve, constructed by plotting known concentrations *versus* their absorbances.

Air analysis

Collect the air sample (20 l minimum) directly into 7 ml of 0.01% purified chromotropic acid in concentrated sulfuric acid with chloride ion added. Transfer the reagent-sample mixture to a 10-ml volumetric flask and fill to the mark with distilled water. Allow the mixture to cool to room temperature and measure the absorbance at 357 mμ. The concentrations may then be determined from a standard calibration curve.

Separate curves should be used for concentration ranges of 0.0 to 0.8 p.p.m. and from 1.0 to 5.0 p.p.m. nitrate ion. If the sample contains more than 5 p.p.m. nitrate, it should be diluted.

CONCLUSIONS

Prior to this work, the quantitative determination of nitrates depended on a method which is not sensitive to trace quantities of nitrate ion. The method, employing phenoldisulfonic acid, required 100 μg or more of nitrates present in the sample in order to produce sufficient color to be measured with reasonable accuracy. Samples containing one p.p.m. nitrate ion, or less, required the use of large volumes of sample with consequent tedious evaporation and associated errors. Using the phenoldisulfonic acid method, the extent of evaporation is extremely critical, the temperature of the evaporated sample prior to treatment is highly important, and the amount of mixing of the sample with the reagent is very critical. Perhaps the most serious disadvantage of the phenoldisulfonic method for the determination of nitrates is the fact that chlorides are a very significant interference. If the test is not preceded by a precipitation of chloride ion with silver ion, the color may fail to develop when even small amounts of chloride are present. Since chloride ions are probably commonly present in the majority of the samples, this is an extremely serious drawback. Even after the silver sulfate treatment, care must be exercised in order to be completely sure that all of the chlorides have been precipitated and that the silver chloride has been removed from suspension. This of course requires the tedium of filtration. All of these

factors contribute to error in measurements and impose delays in the completion of a determination.

Nitrates, as a result of this study, may now be rapidly and accurately determined on samples as small as 3 ml. The procedure does not involve time-consuming evaporations which might produce losses of sample; instead it is rapid, straightforward, and simple to perform. It is truly a microdetermination involving the use of a very small portion of an often precious sample. The method has no serious interferences, especially when applied to water analysis, and it should be readily adapted to the determination of nitrogen dioxide in air, where it would be virtually free from all interfering substances. Chlorides, rather than interfering with the method, actually enhance the determination and are included in the nitrate reagent. Nitrites interfere quantitatively; however, this interference can be overcome by the addition of sulfanilic acid[5].

Phenoldisulfonic acid, which is similar to chromotropic acid, is known to react with nitrates producing a yellow tripotassium salt of nitrophenoldisulfonic acid. The high concentration of sulfuric acid involved in the new methods produces suitable conditions for nitration. Because of this and the similarity to phenoldisulfonic acid, a nitro derivative of the chromotropic acid is believed to be formed. This belief is also supported by the fact that few of the oxidizing agents interfere with this method.

SUMMARY

A new method for the spectrophotometric determination of nitrate is proposed based on the use of chromotropic acid. The method is highly selective, very sensitive, and can be quickly and easily applied. Of special significance is the lack of chloride interference (a serious restriction to the classic phenoldisulfonic acid method) and the freedom from the tedium of evaporation of samples.

RÉSUMÉ

Une nouvelle méthode sensible, sélective, simple et rapide est proposée pour le dosage spectrophotométrique des nitrates. Elle est basée sur la réaction obtenue avec l'acide chromotropique

ZUSAMMENFASSUNG

Beschreibung einer einfachen und genauen spektrophotometrischen Schnellmethode zur Bestimmung von Nitraten mit Hilfe von Chromotropsäure.

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DETERMINATION OF MAGNESIUM AND ALUMINIUM IN ZINC-BASED DIE CASTING ALLOYS

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INTRODUCTION

For the estimation of calcium and magnesium in milk JENNESS[1] used the titration with disodium ethylenediaminetetraacetate (EDTA), eliminating the interference of phosphate by removing it with the aid of anion-exchange technique. HAHN, BACKER AND BACKER[2] also applied an ion-exchange resin for the removal of phosphoric acid from cations. While JENNESS used Duolite A-4, and HAHN, BACKER AND BACKER used Amberlite IRA-400, the anion-exchange resin Dowex 1 × 8 was used in the present work. The interference of phosphate ions in the determination of magnesium may be attributed to the precipitation of magnesium ammonium phosphate when the pH of the solution is raised to 8–10, the range recommended for the titration with EDTA. FLASCHKA AND HOLASEK[3] titrated magnesium without removing phosphoric acid as did HOLTZ[4].

Recently, REILLEY AND SCHMID[5] proposed a theory of end-point detection in complexometry, with particular reference to the estimation of magnesium; they proved that the pH is an important variable in end-point detection and that the pH should indeed be between 8 and 10 for the magnesium–EDTA reaction. To obtain this pH, JENNESS used a buffer containing sodium hydroxide. The ammonia–ammonium chloride buffer of SCHWARZENBACH[6] gives better pH control. The indicator solution of JENNESS, suggested by BETZ AND NOLL[7], proved to be satisfactory and stable on storage, in contrast to most other Eriochrome indicator solutions. Another satisfactory indicator is methyl thymol blue[8]; it was confirmed that this solution was stable for about a fortnight.

The separation of magnesium ions by Dowex 1 × 8 is accomplished by simple percolation. The following points must be noted: (1) the resin should be well regenerated and washed, and free from air bubbles, (2) the solution of $MgNH_4PO_4 \cdot 6\,H_2O$ in hydrochloric acid should be prepared with a minimum of acid.

In the usual method of precipitating aluminium as aluminium hydroxide from a solution which contains mainly zinc, even after four reprecipitations the precipitate contains too much zinc to be weighed as aluminium oxide. With the particular method of precipitation described below, two successive precipitations suffice, if they are carried out in the cold by adding the solution which contains zinc to the ammonia-containing solution; this procedure may be called an inverse cold precipitation. The

cold, slightly acidic zinc solution mixed with ammonium nitrate is poured into a cold solution of ammonia containing ammonium nitrate; the latter solution contains a small excess of ammonia, so that the final pH does not appreciably exceed 8 (it is usually 8.4). When the zinc solution is poured into the ammonia solution with stirring, the zinc ions present are always surrounded by an excess of ammonium ions. The following reactions may occur:

$$Zn^{+2} + 2\ NH_3 + 2\ H_2O \rightleftharpoons Zn(OH)_2 + 2\ NH_4^+$$
$$Zn(OH)_2 + 6\ NH_3 \rightleftharpoons [Zn(NH_3)_6](OH)_2$$

The quantity of ammonia used agrees approximately with the stoichiometrically calculated amount[9,11]. It is interesting to observe that the zinc which was occluded in the precipitated aluminium hydroxide as an ammine hydroxide, was partly volatilised on ignition in a platinum crucible. A grey colour appeared on the inside of the crucible which increased in weight, as is seen after removal of the aluminium oxide with molten potassium bisulfate ($K_2S_2O_7$). As zinc oxide is not volatile, we consider that the zinc volatilised as metal, formed by reduction of the zinc-containing compound with ammonia.

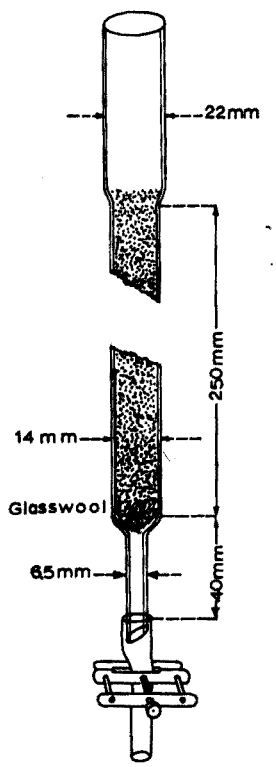

Fig. 1. Ion-exchange column.

Apparatus and reagents

A tube with approximately 20 ml of the anion-exchange resin Dowex 1 X 8, 50–100 mesh (*cf.* Fig. 1). All reagents were of analytical grade. Hydrochloric acid, $d = 1.19$, idem 0.5 *N*. Nitric acid,

d = 1.4. Tartaric acid, ammonium nitrate, diammonium hydrogen phosphate, sodium acetate. Ammonia, d = 0.91. EDTA, Eriochrome Black T indicator: 1 g dissolved in 30 ml of water and 1 ml of 1 N sodium carbonate and diluted to 100 ml with isopropanol. Methyl thymol blue indicator: 0.1% solution in water. Buffer of SCHWARZENBACH: 70 g of ammonium chloride is dissolved in 640 ml of ammonia (d = 0.91).

PROCEDURES

(*A*) *Determination of aluminium*

5 g of turnings or drillings of the alloy, from which iron was removed by a magnet, were dissolved in a mixture of 20 ml of nitric acid and 80 ml of water. Nitrous fumes were boiled out. About 5 g of ammonium nitrate and 2 ml of sulfuric acid (1 : 1) were added and the solution was electrolysed to remove copper and lead, which were determined separately. The electrolysate was poured into a 500-ml volumetric flask and diluted to the mark. Of this solution 100 ml (1 g of sample) were used for the gravimetric determination of aluminium and another 100 ml for the colorimetric determination of iron.

For the determination of aluminium, 20 ml of a 50% ammonium nitrate solution were added, and the solution was neutralized to pH 3 with ammonia using congo indicator paper (to a violet colour). If the solution did not remain clear, some drops of nitric acid were added. The solution in beaker (1) was then cooled and poured, with stirring, into another beaker (2) containing 75 ml of water, 20 ml of 50% ammonium nitrate solution and 10 ml of ammonia. Beaker (1) was washed with a dilute (*ca.* 10%) solution of ammonium nitrate, acidified with 3–4 drops of nitric acid per 100 ml. The mixture in beaker (2) was then heated to about 80°. If the temperature is much higher, ammonia evaporates and zinc may contaminate the aluminium precipitate. The precipitate was then filtered through an S. & S. White (or Whatman No. 40) paper, which had been moistened with wash liquid (20 ml of 50% ammonium nitrate solution and 3–4 drops of ammonia per 100 ml), and washed with this wash liquid. It was then dissolved in warm acid (100 ml of 2 : 3 hydrochloric acid or 105 ml of 1 : 2 nitric acid). The washed filter paper was ignited and weighed to check whether the precipitate had been properly removed.

The second precipitation was performed by the addition of about 35 ml of ammonia to neutralize the acid to pH 3. Precipitation was then carried out as before after cooling but this time 8 instead of 10 ml of ammonia were added to beaker (2). In this case, the precipitate was quantitatively transferred (with pieces of filter paper) to the filter. The filter with the precipitate was then dried, ignited in a quartz crucible and weighed.

Note: By fusing the aluminium oxide with 100 times its weight of potassium bisulfate and dissolving the melt in water and 10 ml of hydrochloric acid, any occluded zinc could be determined. After addition of 4 g of tartaric acid, the solution was heated to about 80° and an excess of 5–10 ml of ammonia was added; silica originating from the quartz crucible was filtered off and 10 ml of a 7.5% solution of thioacetamide were added. The solution was heated to about 100° and allowed to cool for 2 hours. The FeS + ZnS could then be filtered and weighed as oxides. When the quantity of iron oxide (Fe_2O_3) present was obtained from the colorimetrically determined iron, any zinc oxide present in the aluminium oxide could be calculated; the percentage of zinc in the aluminium oxide after two precipitations was never more than 0.1%.

(B) Determination of magnesium

10 g of turnings or drillings of the alloy, from which iron was removed by a magnet, were dissolved in a covered 600-ml beaker in 40 ml of hydrochloric acid and 60 ml of water. Any copper present was dissolved by adding nitric acid dropwise (about 20 to 30 drops) and heating. The nitrous fumes were boiled out. After cooling 4 g of tartaric acid were added and dissolved by stirring. The solution was then diluted to 250 ml and neutralized with about 15 ml of ammonia; another 90 ml of ammonia was then added to obtain a clear solution. After cooling to about 10° (or 20°), 4 g of diammonium phosphate were added (if desired as a filtered solution). The solution was stirred until crystals of $MgNH_4PO_4 \cdot 6\ H_2O$ appeared and then left for 4 h with occasional stirring, or left overnight. The crystals were filtered off on a porcelain filter crucible (Berlin 3A2) and washed with dilute ammonia (8 ml of ammonia in 92 ml of water), and the suction funnel was cleared of some condensed copper-ammine salts. The precipitate in the beaker was then dissolved in 8–9 ml of warm 0.5 *N* hydrochloric acid and about 10 ml of warm water; this solution was passed through the crucible containing the $MgNH_4PO_4 \cdot 6\ H_2O$ and collected in a clean beaker. The 600-ml beaker and the crucible were washed with water.

Note: Stoichiometrically 12 mg of magnesium as $MgNH_4PO_4$ require 6 ml of 0.5 *N* HCl.

The capacity of the ion-exchange resin Dowex 1 × 8 for phosphate ions is about twice as great as that given by the supplier* for chloride.

The slightly acid solution of magnesium ammonium phosphate (*i.e.* $MgCl_2$, NH_4Cl, H_3PO_4 and HCl partially as ions) was then cooled and passed through the ion-exchange column, which was washed with water. The effluent was evaporated (in an Erlenmeyer flask with a boiling tube to prevent bumping) to about 25 ml and cooled. Then 3 ml of Schwarzenbach buffer, 3 ml of ammonia (2 drops per ml of the solution) and 3 drops of indicator solution were added and the solution was titrated with 0.02 *N* EDTA which had been standardised against magnesium metal or ignited magnesium oxide. With Eriochrome Black T the colour change was from violet to blue and with the methyl thymol blue from blue to grey; with the latter indicator a grey background was advisable so that the colour change was from blue to colourless.

Regeneration of Dowex 1 × 8

For regeneration of Duolite A-4 see[1], for Amberlite IRA-400 see[2]. Regeneration was necessary for each determination. Following JENNESS, we used the resin in the acetate form and regenerated with 1 *N* sodium acetate. The pH of this solution was 7.8 as measured with Lyphan-paper L 671 with a range of 7.5–8.7. Percolation of 1 *N* sodium acetate was continued until the pH of the effluent was 7.8; 70–80 ml of solution per 20 ml of resin was required. The resin was then washed with water until the pH of the effluent and the wash water were equal, *i.e.* approx. 5. Usually about 50 ml of water were required.

Maintenance of the ion-exchange column

When the column became clogged, the running time (normally 4 ml/min) increased. The contents of the column were then transferred to a beaker with water and the resin–water mixture was shaken and decanted to remove fine particles and

* ± 0.1 mequiv./g dry resin.

waste; the resin was then returned to the column, not allowing the water to fall below the top of the resin.

RESULTS AND DISCUSSION

The suggested procedure was checked in different ways: (*A*) By analysing synthetic samples, which were prepared by suitable dissolution of pure zinc, aluminium, copper and magnesium metals and by mixing these solutions. (*B*) By comparison of the results with those obtained by reprecipitation of the magnesium as $MgNH_4PO_4 \cdot 6\,H_2O$, followed by ignition and weighing as $Mg_2P_2O_7$. (*C*) By analysis of samples of known composition. The error caused by the coprecipitation of iron as hydrated ferric oxide with the aluminium hydroxide can be allowed for; the precentage of iron amounts to 0.015% at the most. The error caused by occlusion of zinc which is weighed as zinc oxide with the aluminium oxide does not vary much and is unimportant, as

TABLE I

SYNTHETIC SAMPLES ANALYSED FOR MAGNESIUM

Added mg Mg	*Added % Mg*	*Found after one precipitation*		*Found after reprecipitation*	
		mg Mg	*% Mg*	*mg Mg*	*% Mg*
3.57	0.036	4.02	0.040	3.70	0.037
5.00	0.050	6.00	0.060	—	—
7.15	0.072	7.90	0.079	7.24	0.072
10.00	0.100	10.87	0.109	—	—
15.00	0.150	15.25	0.153	—	—
0.00	0.000	0.15	0.015	—	—
0.00	0.000	0.11	0.011	—	—

Obviously a trace of zinc was precipitated in the last two cases; this coprecipitation was more obvious when the $MgNH_4PO_4 \cdot 6\,H_2O$ was examined after one precipitation.

TABLE II

SYNTHETIC SAMPLE ANALYSED FOR ALUMINIUM

Added mg Al	*Added % Al*	*Found after inverse, cold reprecipitation as described*		*Surplus Al_2O_3 ($ZnO + Fe_2O_3$ + ash of filters) mg Al*	*Found after correction % Al*
		mg Al	*% Al*		
41.86	4.18	42.97	4.29	1.11	4.18

TABLE III

DETERMINATION OF MAGNESIUM IN ZINC-BASED DIE CASTING ALLOYS BY THE PROPOSED METHOD

Sample No.	*Found after one precipitation*		*Found after reprecipitation*		*Surplus, found after one precipitation*	
	mg Mg	*% Mg*	*mg Mg*	*% Mg*	*mg Mg*	*% Mg*
1	4.2	0.042	3.5	0.035	0.7	0.007
2	4.0	0.040	3.3	0.033	0.7	0.007
3	3.7	0.037	3.3	0.033	0.5	0.005
4	7.6	0.076	6.8	0.068	0.8	0.008
4	7.4	0.074	—	—	—	—
4*	—	—	6.9	0.069	—	—

* Gravimetric determination as $Mg_2P_2O_7$.

TABLE IV

SURPLUS FOUND IN THE ESTIMATION OF Al VIA Al_2O_3, CONTAINING OCCLUDED ZnO AND Fe_2O_3, BY DETERMINATION OF THESE IMPURITIES

Sample No.	*Al_2O_3 + Fe_2O_3 + ZnO mg*	*Fe_2O_3 + ZnO (Surplus) mg*	*% Al calculated from impure Al_2O_3*	*% Al calculated from pure Al_2O_3*
1	72.9	2.3	3.85	3.73
2	75.0	2.4	3.97	3.84
3	68.7	1.8	3.63	3.51
4	80.5	2.1	4.25	4.13
5	75.2	1.6	3.98	3.89
6	77.0	2.1	4.07	3.96
7	75.0	3.3	3.97	3.79
8	76.8	2.3	4.06	3.94
9	71.4	1.0	3.78	3.72
10	77.8	1.5	4.10	4.02
11	77.9	1.4	4.11	4.04
12	77.0	2.1	4.05	3.94

can be seen in Table IV. The amount of impurity in the aluminium oxide has a mean deviation of 0.44 and a standard deviation of 0.58.

The results for magnesium (see Tables I and III) showed that it is advisable to subtract 0.5 mg of magnesium from the amount found with one precipitation of $MgNH_4PO_4 \cdot 6 H_2O$ to obtain the correct magnesium content. This means that on the average 0.5 mg of zinc are coprecipitated in the first precipitation of magnesium ammonium phosphate hexahydrate. The correct value of magnesium would be obtained by reprecipitation. The method described above has proved to be satisfactory in production control. It is a reliable substitute for the spectrographic method of magnesium determination.

Two types of methyl thymol blue are obtainable; that sold by B.D.H. is an acid–base indicator and is not suitable for this application. The recommended metallochromic indicator is obtainable from Chemapol, Prague, Czechoslovakia (as was kindly indicated by Prof. PŘIBIL to the writer).

Specific properties of the indicators

With the Eriochrome Black T indicator solution, it is advisable to clean the flask after each titration with boiling 1 : 1 hydrochloric acid. The proper course of the titration is affected by residues of the indicator which adhere to the glass. When the titration flask is only rinsed with water, the change of colour with excess of EDTA occurs prematurely, but rapidly disappears; this happens with each addition of EDTA, so that it is very difficult to find the true end-point. With MTB, the colour change becomes indistinct when the indicator solution is kept for more than a fortnight; the solution must be stored in a dark flask in a cool place.

The determinations of magnesium and aluminium described above are simple and reproducible. When magnesium ammonium phosphate is precipitated, lead should be eliminated beforehand, but copper does not interfere. Manganese and calcium also interfere.

When ammonia solution not produced from gaseous ammonia is used, the precipitate of magnesium ammonium phosphate contains some organic matter, which when ignited forms carbon in the magnesium pyrophosphate; the carbon remains occluded in the pyrophosphate as it is very refractory in this form. The original organic matter in the $MgNH_4PO_4 \cdot 6\ H_2O$ causes trouble in subsequent filtrations, hence it is advisable to clean the porcelain filter crucible in warm aqua regia and to anneal it in an electric furnace to red heat.

The method described is also advantageous for determining magnesium in aluminium alloys. SERGEANT[10] determined magnesium in aluminium alloys after either removing or complexing all the impurities which interfere in the titration of magnesium with EDTA. We modified and shortened this method; the main constituent (aluminium) was eliminated by dissolving the alloy in sodium hydroxide, and the remaining Al + Fe + Mn was removed with ammonia and ammonium persulfate before the determination was completed as described above. All glassware must be thoroughly rinsed and in special cases boiled with hydrochloric acid, to avoid the introduction of elements which consume EDTA.

SUMMARY

A titrimetric determination of magnesium in die casting alloys is described; it is unaffected by impurities commonly present in such alloys. The visual titration with EDTA is carried out after removal of phosphoric acid with an anion-exchange resin. The aluminium present in the alloy is determined gravimetrically by a special precipitation method.

RÉSUMÉ

Une méthode est proposée pour le dosage titrimétrique du magnésium dans des alliages de zinc. Le titrage est effectué au moyen de l'éthylènediaminotétracétate disodique. Un dosage gravimétrique de l'aluminium est également décrit.

ZUSAMMENFASSUNG

Beschreibung einer komplexometrischen Bestimmung von Magnesium in Zinklegierungen. Die Titration erfolgt mit Äethylendiaminotetraessigsäure (EDTA) nach Entfernung des Phosphates mit einem Ionen-Austauscherharz. Vorhandenes Aluminium wird gravimetrisch bestimmt.

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DETERMINATION OF METAL IONS BY MEANS OF TAA AND EDTA

III. DETERMINATION OF IRON

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INTRODUCTION

We have already shown[1,2] that thioacetamide (TAA) as precipitating agent and ethylenediaminetetraacetic acid (EDTA) as masking agent considerably improve sulfide and hydroxide separations of metal ions in solution. Methods for the determination of a metal of the second group (copper)[2] and a metal precipitating as the sulfide in the third group (zinc)[1] have been described. In the present paper the determination of iron is described as representative of metals precipitating in the third group as hydroxides.

As can be seen in Tables I and II of the Part I of this series[1], it should be possible to separate iron from the group II elements by precipitation of the latter as sulfides in acid medium. After neutralisation of the centrifugate with hydroxide, EDTA is added and the solution is buffered at a pH of 10 or 11. The hydroxides of aluminium, iron and manganese can then be precipitated by adding calcium chloride (demasking agent), while cobalt, nickel and zinc remain in solution. The hydroxides can be dissolved in hydrochloric acid and the iron content measured by the spectrophotometric method described by SCHNEIDER AND JANKO[3]. Aluminium and manganese do not interfere. Obviously it should therefore be possible to determine iron by this procedure, in presence of all the other elements under consideration.

The spectrophotometric method

SCHNEIDER AND JANKO added an excess of EDTA to an iron(III) solution to form a yellow complex which is oxidised with an excess of hydrogen peroxide in ammoniacal solution. A violet solution of a Fe(III)–EDTA–H_2O_2 complex, having a maximum absorption at 525 mμ, is formed. We obtained a molecular extinction of 520 at this wavelength and confirmed that Beer's law is valid within the usual concentration limits (in a Unicam SP 500 spectrophotometer). The final colour develops rapidly and is not affected by an excess of the reagents within certain limits. The following precautions have to be taken.

1. A large excess of hydrogen peroxide often causes the formation of tiny gas bubbles, which interfere with the spectrophotometric determination; 3 ml of 30% peroxide is sufficient and does not interfere.

2. The colour is photosensitive. SCHNEIDER AND JANKO do not mention this effect.

When the colours are not measured immediately it is necessary, especially on sunny days, to place the flasks in the dark directly after dilution.

3. The colour intensity depends on the temperature, but ordinary changes in room temperature have a negligible effect.

The value of 520 for the molecular extinction of the coloured complex at 525 mμ is very suitable for the present purpose. When the colour is developed in 50- or 100-ml volumetric flasks and 1- or 4-cm cells are used for the extinction measurements, 0.15–5 mg iron can be determined.

EXPERIMENTAL

*Procedure**

The determinations are carried out in 15-ml centrifuge tubes. Add to 5 ml of the solution, containing 0.15–5 mg iron, 2 to 4 drops of 36% hydrochloric acid and 4 drops of 6% TAA solution. Heat the tubes by hanging them in a water bath for 15–30 minutes, until the precipitate coagulates. Filter the precipitate (of the group II sulfides) through a G4-glass filter stick into another centrifuge tube, as shown in Fig. 1 of Part I[1]. Wash three times with 1 ml of water and remove the wash water in the same way. Replace the centrifuge tube with the solution in the water bath and heat to decompose the excess of TAA and to drive out hydrogen sulfide. Cool and add 0.5 ml of saturated bromine water to oxidize all the iron present to iron(III). Reheat in the bath to remove the excess of bromine.

Cool and neutralize the solution with 20% potassium hydroxide solution (if a precipitate appears, dissolve in a minimum of hydrochloric acid).

Add 1 ml of 0.1 *M* EDTA. If nickel and especially cobalt is present in quantities of more than about 2.5 mg, add an extra ml of EDTA for every 0.1 mmole of these metals (see Table III). If chromium is present, the solution must be heated for 30 min in a water bath at 90° to form the extremely stable Cr(III)–EDTA complex. Cool and add 1 ml of ammonia–ammonium chloride buffer solution (pH 10 or 11). Add 1 ml of 0.3 *M* calcium chloride solution to precipitate the hydroxides of iron, manganese and aluminium. Heat the centrifuge tube for 30 min in a water bath at 95° (the solution must not boil) and finally for 10 min at 100°. Centrifuge and wash twice with a slightly ammoniacal ammonium chloride solution. The supernatant liquid can be discarded, because it contains no precipitated iron hydroxide; the precipitate remains quantitatively on the bottom of the centrifuge tube.

Dissolve the iron hydroxide in a few drops of 10 *N* HCl. If manganese and aluminium are present, the tube must be heated in a glycerol bath (105°) for complete dissolution.

Transfer the solution quantitatively to a 100-ml volumetric flask (in the case of 0.15 and 0.30 mg iron, a 50-ml flask was used) and develop the colour in the following way. Add 8–10 ml of 0.1 *M* EDTA and 3 ml of 25% ammonia. Shake the solution and add 3 ml of 30% H_2O_2. Dilute to the mark with water and measure the extinction at 525 mμ.

RESULTS

Determinations in presence of other group III elements

Two series of results were obtained, one with the buffer pH 10 and the other with the buffer pH 11 solution.

* All reagents used were of analytical grade.

(a) Results with buffer pH 10

When iron was the only group III element present, the results of the determination were usually 2–3% low. Obviously not all the iron was demasked by the addition of calcium chloride solution. This was proved by the addition of hydrogen peroxide to the supernatant liquid, when the characteristic purple colour of the Fe(III)–EDTA–H_2O_2 complex appeared. When, however, other group III elements were present, the results were usually much better; the results of some of these determinations are given in Table I.

TABLE I

DETERMINATION OF 1.50 mg OF IRON IN PRESENCE OF OTHER GROUP III ELEMENTS (PH 10)

Other group III elements present in mg						*Fe present in mg*	*Fe found in mg*	*Error in %*
Zn	*Mn*	*Ni*	*Co*	*Cr*	*Al*			
1.5						1.50	1.48	— 1.3
3							1.50	0
15							1.48	— 1.3
	2.5						1.48	— 1.3
	2.5						1.47	— 2
		2.5					1.50	0
		6					1.50	0
			2.5				1.53	+ 2
			6				1.52	+ 1.3
3			2.5				1.51	+ 0.7
3	2.5						1.50	0
3		2.5	2.5				1.50	0
	2.5	2.5					1.50	0
	2.5		2.5				1.49	— 0.7
				2.5		1.50	1.50	0
				2.5			1.50	0
				5			1.51	+ 0.7
				5			1.56	+ 4
				8			[a]	
3				2.5			1.50	0
	2.5			2.5			1.50	0
		2.5		2.5			1.53	+ 2
			2.5	2.5			1.59	+ 6
					0.5		1.44	— 4
					1.5		1.44	— 4
					1.5		1.33	—11

[a] In this experiment $Cr(OH)_3$ precipitated with iron.

The following conclusions can be drawn from Table I.

1. Aluminium interfered under these conditions. Obviously part of the iron remained in solution.

2. With only one other of the group III elements present, the results for the iron determination increased slightly in the order Zn-Mn-Ni-Co. This can be explained as follows:

a. When only zinc was present the results were low for the same reason as when no other group III elements were present;

b. for manganese the same reason as for aluminium could be valid;

c. when cobalt and nickel were present, the precipitation of iron was still not complete, but a small amount of cobalt or nickel was coprecipitated. These two elements both gave complexes with EDTA and peroxide which absorbed light at 525 mμ. For nickel the absorption was small, hence approximately correct results were obtained for the iron determinations. Cobalt absorbed strongly at 525 mμ and the results for iron were high. It was therefore necessary to add extra EDTA when nickel and cobalt were present, approximately in equivalence with the interfering element, in order to keep these metals completely in solution. A larger excess of EDTA should be avoided, because it could keep part of the iron in solution.

3. Chromium did not interfere provided that not more than 5 mg was present. Above this concentration chromium precipitated with iron as hydroxide and interfered with the spectrophotometric determination. However, addition of extra EDTA was not effective, because the large excess required to keep chromium in solution inevitably dissolved part of the iron. If iron had to be determined in presence of much chromium, this could be done by decreasing the amount of iron (see Table III).

4. If chromium was present together with nickel and cobalt high results were obtained. This can be accounted for in the same way as under *2c*.

All these difficulties vanished completely when the experiments were carried out at pH 11 because of the slow decomposition of the complex $Fe(OH)_2Y^{-3}$ (H_4Y being the symbol for EDTA) which begins at pH 10.5.

TABLE II

DETERMINATION OF 1.500 mg OF IRON IN PRESENCE OF OTHER GROUP III ELEMENTS (pH 11)

Other group III elements present in mg						*Fe present mg*	*Fe found mg*	*Error %*
Zn	*Mn*	*Ni*	*Co*	*Cr*	*Al*			
					1.5	1.500	1.478	—1.5
					1.5		1.490	—0.7
					1.5		1.490	—0.7
3		2.5	2.5				1.500	0
3	2.5		2.5				1.494	—0.4
	2.5			2.5	2.5		1.484	—1.0
				2.5	2.5		1.503	+0.2
				2.5	2.5		1.491	—0.6
			2.5	2.5			1.473	—1.8
			2.5	2.5	2.5		1.495	—0.3
		2.5		2.5			1.477	—1.5
		2.5		2.5			1.500	0

(b) Results with buffer pH 11

In Table II some results of determinations at pH 11 are given. To avoid bumping of these solutions buffered at pH 11, the centrifuge tubes should not be placed in a water bath at 100°. The best temperature in this case was 95°.

As can be seen in Table II, the results were much better than those at pH 10. At pH 11 the results were quite consistent and independent of the other elements present. Even aluminium no longer interfered. When iron was the only group III element present good results were also obtained (see Table IV).

Determinations of very small amounts of iron were also carried out at pH 11. Some of the results are given in Table III.

TABLE III

DETERMINATION OF 0.300 AND 0.150 mg OF IRON IN PRESENCE OF OTHER GROUP III ELEMENTS (pH 11)

Other group III elements present in mg						*Fe present mg*	*Fe found mg*	*Error %*
Zn	*Mn*	*Ni*	*Co*	*Cr*	*Al*			
0.6	0.6	0.6	0.6			0.300	0.310	+3
1.2		1.2					0.300	0
	2.5		2.5				0.303	+1
	2.5	2.5					0.300	0
	5						0.297	—1
	7.5						0.300	0
		7.5					0.300	0
	2.5		5.0				0.318	+6[a]
			7.5				0.318	+6[a]
			7.5				0.300	0[b]
					2.5	0.300	0.303	+1
					2.5		0.300	0
					7.5		0.290	—3
				2.5			0.296	—1
0.15	0.15	0.15	0.15	0.15	0.15		0.297	—1
0.1	0.1	0.1	0.1	0.1	0.1	0.150	0.149	—0.5
0.1	0.1	0.1	0.1	0.1	0.1	0.150	0.150	0
0.1	0.1	0.1	0.1	0.1	0.1	0.150	0.145	—3
				4		0.150	0.147	—2

[a] No extra EDTA was added in this experiment.
[b] Extra EDTA, equivalent to the quantity of cobalt present, was added.

The following remarks should be noted with regard to Table III.

1. If more than 2.5 mg of cobalt was present, extra EDTA was added to prevent coprecipitation of traces of cobalt.

2. Iron could be determined in presence of a large amount of chromium, provided that not more than 5 mg of chromium was present (see the last experiment of Table III).

3. If the amount of aluminium present was more than fifteen times the amount of iron, the results of the determinations were low.

Determination of iron in presence of copper

Copper was the only element of the second group which interfered with the spectrophotometric determination of iron, hence some determinations of iron were carried out in presence of this element by the given procedure. The results are given in Table IV.

TABLE IV

DETERMINATION OF 1.5 mg OF IRON IN PRESENCE OF COPPER (pH 11)

Cu present in mg	*Fe present in mg*	*Fe found in mg*	*Error in %*
1.5	1.500	1.494	—0.4
1.5	1.500	1.509	+0.6
3	1.500	1.497	—0.2
3	1.500	1.475	—1.5

Determination of iron in some alloys

The procedure was applied to two alloys.

a. Alloy containing about 80% Cu, 10% Al, 5% Ni, 4.5% Fe and 1% Mn. By the present method, the mean of 6 determinations was 4.52% with a corresponding standard deviation of the mean of 0.015%.

Analysis of the same alloy according to an ASTM procedure[4] gave 4.53%. This volumetric procedure, however, required more time and much more sample.

b. Chromium–nickel steel of the National Bureau of Standards (101 d), containing 18.67% Cr, 9.05% Ni, a few traces of other elements and 71.0% Fe.

The mean of 5 determinations was 70.7% with a corresponding standard deviation of 0.18%.

DISCUSSION

The method described for the determination of iron is quite generally applicable. Some anions that give precipitates with calcium ions in ammoniacal solution and that interfere with the complex formation of iron and EDTA, *e.g.* phosphate, oxalate and fluoride, should not be present.

In the absence of group II elements, the reduction of reducible anions, *e.g.* chromate, should not be omitted. This is done by carrying out the TAA part of the procedure, or perhaps in some simpler way.

This procedure of determining iron is simple and, as all the work is carried out in centrifuge tubes, little time is required for the total analysis. If only group III elements are present, a determination takes between one and two hours if chromium is absent and two hours if it is present. If group II elements are also present an additional hour is required. It is obvious that six or more determinations can be carried out simultaneously.

SUMMARY

Iron (0.15–5 mg) is determined in presence of group II and group III elements by precipitating group II elements as sulfides with TAA in hydrochloric acid medium, adding EDTA to the filtrate, buffering at pH 11, and precipitating ferric hydroxide by addition of calcium chloride. Iron is finally determined spectrophotometrically as the Fe(III)–EDTA–H_2O_2 complex.

RÉSUMÉ

Une méthode est proposée pour le dosage du fer, en présence des éléments des groupes II et III. Les éléments du deuxième groupe sont précipités à l'état de sulfures par addition de TAA. Au filtrat, on ajoute EDTA et on tamponne à pH 11; le fer est précipité ensuite comme hydroxyde, par addition d'une solution de chlorure de calcium. Le précipité obtenu est dissous et le fer est finalement dosé par spectrophotométrie, sous forme de Fe(III)–EDTA–H_2O_2.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung von Eisen in Gegenwart der Elemente der II. und III. Gruppe. Die Elemente der II. Gruppe werden als Sulfide abgetrennt und im Filtrat das Eisen als Hydroxyd gefällt. Zum Schluss wird das Eisen als Fe(III)–EDTA–H_2O_2 Komplex spektrophotometrisch bestimmt.

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SEPARATION OF NIOBIUM, TANTALUM, TITANIUM AND ZIRCONIUM FROM EACH OTHER

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The separation of niobium, tantalum, titanium and zirconium from each other is difficult because their analytical behaviour is very similar owing to their atomic volumes, ionic and covalent radii. The reactions of zirconium are somewhat different, but when associated with the other three metals, its chemical character prevents an easy separation. SCHOELLER's[1] procedure is time-consuming, the selenious acid method[2] permits the separation of niobium and tantalum together from titanium but not from zirconium, while oxine[3] distributes titanium in the fractions of both niobium and tantalum. Pyrogallol[4], however, precipitates both niobium and tantalum and leaves titanium and zirconium in solution.

The three reagents, N-benzoyl-N-phenyl hydroxylamine[5], cinnamyl hydroxamic acid and N-cinnamoyl-N-phenyl hydroxylamine[6], which have been utilised by the authors for the determination of niobium and tantalum, also precipitate titanium and zirconium. Even rigorous pH control and the use sequestering agents such as hydrogen peroxide, oxalic, tartaric and citric acids, EDTA, salicylic acid and ascorbic acid fail to prevent precipitation. The problem can be solved as follows: both niobium and tantalum are precipitated by the pyrogallol method[4], leaving titanium and zirconium in solution as pyrogallol complexes. From the residue, niobium and tantalum are recovered by the N-benzoyl-N-phenyl hydroxylamine method[5]. From the solution, pyrogallol is first removed by digestion with perchloric acid and then zirconium and titanium are determined by the salicylhydroxamic acid[7] and the cupferron[8] methods respectively.

EXPERIMENTAL

The chemicals, reagents and standard solutions used were the same as described earlier[5-8]. B.D.H. indicator papers were used for all pH measurements.

Procedure

Aliquots of standard solutions of niobium, tantalum, titanium and zirconium were mixed and diluted to about 300 ml. Sufficient strong sulphuric acid to make its concentration between 5 and 10% (v/v) was added. All four elements were then precipitated at room temperature by the addition with stirring of an excess of N-benzoyl-N-phenyl hydroxylamine solution; the precipitate was filtered, washed with warm water and ignited in a silica crucible. The ignited mass was then fused with potassium bisulphate and extracted with about 200 ml of 5% pyrogallol solution. The solution

was just neutralised with aqueous ammonia, treated with 15 ml of concentrated hydrochloric acid, digested on a boiling water bath for about 15 min and then left to stand overnight; niobium and tantalum separated as a flaky sediment. The precipitate was filtered, washed with 1% pyrogallol solution, dried and ignited. The ignited residue was again fused with potassium bisulphate and the whole procedure was repeated to free niobium and tantalum from titanium and zirconium. The mixed oxides of niobium and tantalum were then separated by the N-benzoyl-N-phenyl hydroxylamine method[5].

The filtrates and washings containing titanium and zirconium were mixed, evaporated nearly to dryness, and digested first with fuming nitric acid and then with a mixture of perchloric and sulphuric acids, in order to decompose the organic matter completely. After fuming, the solution was cooled, and diluted with water to give an acid strength of 5%. Sufficient hydrogen peroxide (20 vol.) was then added and zirconium was precipitated and determined by the salicylhydroxamic acid procedure[7]. From the zirconium filtrate, titanium was recovered by precipitation with cupferron[8] after hydrogen peroxide had been decomposed by boiling. Typical results are shown in Table I.

TABLE I

Taken, mg				*Found, mg*			
TiO_2	ZrO_2	Nb_2O_5	Ta_2O_5	TiO_2	ZrO_2	Nb_2O_5	Ta_2O_5
10.6	11.2	12.5	11.7	10.5	11.0	12.6	11.7
21.2	22.4	25.0	23.4	21.0	22.3	25.2	23.3
42.4	44.8	50.0	46.8	86.9[a]		97.2[b]	
31.8	33.6	50.0	46.8	65.2[a]		97.0[b]	
42.4	44.8	12.5	11.7	87.0[a]		24.5[b]	

[a] mixed oxides of titanium and zirconium.
[b] mixed oxides of niobium and tantalum.

SUMMARY

A method for the separation and determination of titanium, zirconium, niobium and tantalum is described. Niobium and tantalum are separated with pyrogallol from titanium and zirconium and determined by the N-benzoyl-N-phenyl hydroxylamine method. Pyrogallol is decomposed, and zirconium and titanium are determined by the salicylhydroxamic acid and cupferron methods respectively.

RÉSUMÉ

Une méthode est décrite pour la séparation et le dosage du titane, du zirconium, du niobium et du tantale, les uns en présence des autres. Le pyrogallol permet la séparation du niobium et du tantale d'avec le titane et le zirconium.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Trennung und Bestimmung von Titan, Zirkonium, Niob und Tantal. Niob und Tantal werden von Titan und Zirkonium mit Hilfe von Pyrogallol getrennt. Die weiteren Trennungen erfolgen mit N-benzoyl-N-phenylhydroxylamin, Salicylhydroxamsäure und Kupferron.

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THORIUM DETERMINATIONS WITH 8-HYDROXYQUINALDINE

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The list of organic reagents for the precipitation of thorium was thought "too lengthy" in 1954[1], and since then it has become more so. Some of these reagents have been studied only sparingly. Many yield precipitates that are either variable in composition or unstable at drying temperatures, and for weighing must be ignited to thorium dioxide. In such instances, the favourable gravimetric factor inherent in most organic precipitants is lost, although the reagents may remain useful for effecting separations.

Studies with a thermobalance have proven helpful in comparing and evaluating precipitants for thorium and, in fact, have provided evidence[2] that the possibility of weighing some of the precipitates may have been too hastily rejected. A compound that has good thermal stability[3] is that which thorium forms with 8-hydroxyquinaldine, by the reaction of one mole of thorium with four of the organic reagent[4]. No substantial study of 8-hydroxyquinaldine as an analytical reagent for thorium appears, however, to have been made, although in one context or another this compound has been given considerable attention[5] since the discovery[6] that, unlike the parent compound 8-hydroxyquinoline, it does not precipitate aluminium, a property that is attributed[7,8] to a steric effect of the methyl group in the 2 position in 8-hydroxyquinaldine.

This paper is concerned with the conditions that permit the quantitative precipitation of thorium by 8-hydroxyquinaldine as the 1 : 4 chelate, with gravimetric and bromometric determinations of thorium using this reagent, and with the merits of these.

EXPERIMENTAL

Apparatus

Measurements of pH were made with a Beckman Model G pH meter (Beckman Instruments Inc., South Pasadena, U.S.A.) using a 1190–80 glass electrode for pH values below 10 and a 11–505–75 electrode for values above that, each in association with a saturated calomel reference electrode. Measurements of pH plotted in Fig. 2 were made on the filtrates, after they had cooled to room temperature.

The thermobalance was a Chevenard-type photographically recording instrument (TBP Nr. 27, S.A.D.A.M.E.L., La Chaux de Fonds, Switzerland). The rate of heating was 2.5°/min, and the sensitivity was 0.85 mm/mg.

Reagents

The 8-hydroxyquinaldine was obtained both by synthesis[6] and by the purification (steam distillation, followed by crystallization from 70% ethanol) of a commercial product (Aldrich Chemical Co., Milwaukee, U.S.A.). In each instance, the material was a white crystalline solid, m.p. 71.5–72°.

The thorium nitrate (tetrahydrate) was a highly purified product (Code 103, Lindsay Chemical Co., West Chicago, U.S.A.). Stock solutions of thorium, kept at a pH below 2 with hydrochloric acid, were standardized gravimetrically by precipitation with ammonia and ignition to thorium dioxide[9].

All other chemicals were analyzed grade.

Precipitation of thorium as the 1:4 8-hydroxyquinaldine chelate

We found that the sparse directions available[4] for the precipitation of thorium with 8-hydroxyquinaldine led to a precipitate that, though it contained all the thorium sought (as shown by ignition to thorium dioxide), had only 95%, at most, of the thorium as the 1 : 4 8-hydroxyquinaldine chelate. It appeared that a significant amount of the thorium was being precipitated as hydrous thoria or other hydroxo complexes. A study was therefore made of variables that affect the precipitation of thorium by 8-hydroxyquinaldine, with the objective of developing a simple and reliable procedure for the determination of thorium.

Concentration of reagent

Precipitations were done as set forth in Procedure I, except that the amount of excess 8-hydroxyquinaldine was varied; the precipitates were subsequently treated as in Procedure II, except for the use of low-porosity Selas crucibles instead of fritted-glass ones. The results are in the first two columns of Table I.

TABLE I

EFFECT OF EXCESS 8-HYDROXYQUINALDINE ON THE PRECIPITATION OF THORIUM AS $Th(C_{10}H_8ON)_4$

Concentration of thorium: 0.7 mg/ml. pH of precipitation: 8.1 ± 0.1. Thorium taken was equivalent to 128.6 mg of $Th(C_{10}H_8ON)_4$ and to 39.3 mg of ThO_2.

Excess reagent (%)	*Weight of ppt. (mg)*	*Weight of ThO_2 (mg)*
90	128.5	
65	128.4[a]	39.3
60	128.4	
50	124.2	39.2
35	120.5	39.4
20	108.5	39.0
10	98.4	

[a] This value is an average of 10 determinations (average deviation: 0.2); the other values represent, for the most part, a single determination.

Even though the pH of the solution is appropriate (*vide infra*) for the quantitative precipitation of thorium (from solutions of concentration 0.7 mg Th/ml) the precipitation is not quantitative as the 1 : 4 chelate unless there is a 60% or greater excess of 8-hydroxyquinaldine. The addition of the precipitant "in slight excess"[4] is not a sufficient direction. Ignition to thorium dioxide of the precipitates obtained with an excess of reagent less than 60% showed that the thorium was quantitatively precipitated (Table I), indicating that some of the thorium had precipitated in a form other than the 1 : 4 chelate. With an excess of 60% or greater, however, the precipitation of thorium as the 1 : 4 chelate is not less than 99.8% complete from solutions of concentration 0.7 mg Th/ml. For subsequent precipitations from such solutions, a nearly 70% excess of reagent was used.

A 70% excess is insufficient, however, to precipitate thorium quantitatively as the chelate from solutions with less than about 0.7 mg Th/ml*. From solutions only one-fiftieth as concentrated as this, thorium can nevertheless be precipitated quantitatively if the concentration of 8-hydroxyquinaldine corresponds to 65–70% excess for a solution containing 0.7 mg Th/ml.

Adjustment of pH

The concentration of the aqueous ammonia used to raise the pH to within the desired range, and the way in which the ammonia is added, are important factors in obtaining a precipitate of the pure thorium chelate. If the ammonia is concentrated, the results can be low by as much as 7%, even when the base is added drop by drop, with rapid stirring (Fig. 1, Curve A). In fact, with the ammonia as dilute as 0.5 *M* the results are low (by as much as 1%) if it is added rapidly without stirring. On the other hand, base as concentrated as 1 *M* may be used if added drop by drop, with efficient stirring. Under these conditions, and with a 70% excess of precipitant and the pH adjusted to 8.0–8.5, thorium is quantitatively precipitated solely as the chelate. The average

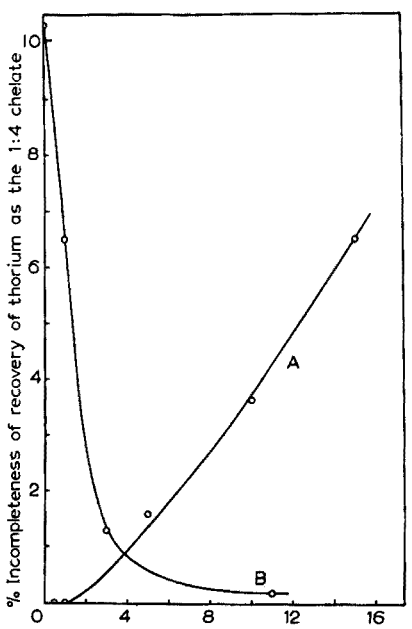

Fig. 1. Effect on recovery of thorium, as $Th(C_{10}H_8ON)_4$, of: (*A*) Molarity of ammonia used to adjust the pH; (*B*) Time of digestion (at 70°C) after pH adjustment by rapid addition of 15 *M* ammonia. In the experiments of Curve A, the ammonia was added drop by drop, with stirring, and the precipitates were digested for one hour at 70°. In the experiments of Curve B, the formation of hydroxo complexes of thorium was encouraged by rapid addition of ammonia, with little regard for stirring. In all experiments, the concentration of thorium in the original solution was 0.7 mg/ml, the pH of precipitation was 8.0–8.5, the excess of precipitant was 70%, and the precipitates were analyzed bromometrically. Each point is the average of at least two determinations; the two lowest points on Curve A summarize 15 determinations.

* When the pH after precipitation is 8.0–8.5.

of 15 determinations on a solution that contained 33.6 ± 0.1 mg of thorium (concentration 0.7 mg/ml) was 33.7_6 mg, with an average deviation of 0.0_5 mg.

The low results — that is, low as the chelate — induced by adjusting the pH with concentrated ammonia, or even with relatively dilute ammonia added rapidly, are likely due to the precipitation of some of the thorium as hydroxo complexes, occasioned by local excesses of hydroxyl-ion. When local excesses were encouraged by using 5 *M* and 15 *M* ammonia without care in stirring, and when (by eliminating the digestion) the metathesis of any hydroxo complexes to the chelate was hindered, the error rose to over 10%. The error — here calculated as the % thorium not precipitated as the chelate* — was greater the higher the concentration of the added ammonia. Ignition, to thorium dioxide, of precipitates formed under the same conditions showed that the thorium was being precipitated quantitatively: concentration of ammonia, stirring, and digestion affect the nature of the precipitate that is first formed, but not (provided the pH is appropriate) the completeness of precipitation.

If local excesses of hydroxyl-ion initially induce precipitation of some hydroxo complexes when the chelate is the stable form for the precipitate under the conditions existing in the solution, then the hydroxo compounds should in time metathesize to the chelate. The data of Curve B of Fig. 1 show that this occurs. This metathesis was also observed in thermogravimetric experiments. A thermogram for a precipitate digested for only two minutes indicated that the precipitate was not all thorium chelate, whereas the thermogram for a similarly induced precipitate that had been digested for 11 hours was identical with the thermogram of pure chelate.

Provided, then, that the pH be chosen properly (*vide infra*), the thorium will finally be solely (and quantitatively) as the chelate, even though initially some of it precipitates in another form. Under other precipitation conditions (*i.e.*, careful addition of 0.5 or 1 *M* aqueous ammonia) the thorium can be obtained initially (or at least after short digestion) quantitatively as the chelate.

pH control

The data of Fig. 2 show that thorium can be precipitated quantitatively as the chelate in the pH range 6.1 to 11.5, at least with the concentrations of thorium and reagent used. Beginning at a pH of 11.5, precipitation (though complete) is partly as, say, hydrous thoria; by a pH of 13.0, the precipitate is almost entirely hydrous thoria**.

For the experiments summarized in Fig. 2, Procedures I and III were used except that the pH of precipitation was varied over a wide range, with consequent variation in the buffering medium. The solutions were buffered in the acid range by ammonium acetate and acetic acid, and in the alkaline range (to pH 9) by ammonium acetate and ammonia. For pH values above 9, appropriate volumes of 1 *M* and 2 *M* sodium hydroxide were added after the solution had been brought to pH 9 with ammonium acetate

* The per cent of the thorium precipitated as the 1 : 4 chelate was determined bromometrically.
** With increasing pH, the concentration of hydroxyl-ion of course increases, but (for a given stoichiometric concentration of 8-hydroxyquinaldine) the concentration of the chelating anion approaches a maximum (corresponding to complete dissociation of the reagent). This leads to the eventual dominance of hydroxyl-ion in controlling the concentration of metal-ion in solution, through the precipitation of hydroxo complexes of thorium ("hydrous thoria") rather than the chelate. The pK_{OH} of 8-hydroxyquinaldine is such that it is largely dissociated by a pH of 11.

and ammonia. Accordingly, the portion of the curve in Fig. 2 for pH values above 9 was not established in properly buffered solutions and the "break-point", shown at pH 11.5, may be a bit in error*.

The foregoing and related experiments established conditions for the quantitative precipitation of thorium as the 1 : 4 chelate and showed that the precipitate can be dried at 110° to the anhydrous compound, $Th(C_{10}H_8ON)_4$. Other experiments abundantly confirmed earlier observations[4,10] that 8-hydroxyquinaldine can be dibrominated quantitatively. These results led to gravimetric and bromometric procedures for thorium, the details of which follow.

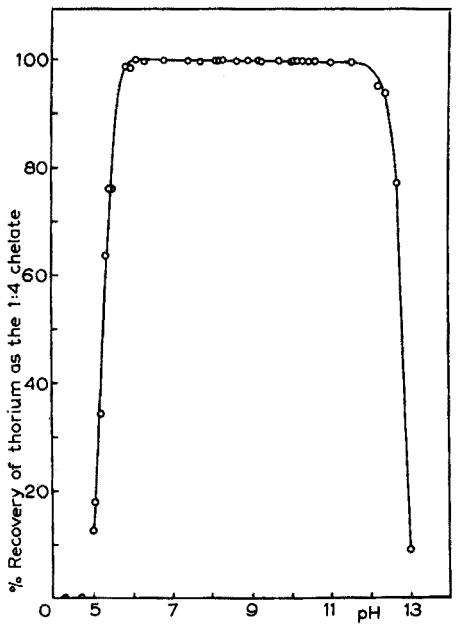

Fig. 2. pH Range for precipitation of thorium as $Th(C_{10}H_8ON)_4$; the concentration of thorium in the original solution was 0.7 mg/ml.

PROCEDURES

1. *Precipitation of thorium*

Pipet a 50-ml portion of the solution containing thorium at a concentration not higher than 0.7 mg/ml ($3 \cdot 10^{-3}$ *M*) into a beaker. Heat the solution to about 70° and slowly add 8.0 ml of a solution of 8-hydroxyquinaldine (prepared by dissolving 2.0 g of the reagent in 6.3 ml of glacial acetic acid and diluting the solution with water to 100 ml). Then add, slowly with stirring, 2.0 g of ammonium acetate dissolved in 10 ml of hot (70°) water. Adjust the pH to within the range 8–9 (making use of narrow-range pH paper) with 1.0 *M* aqueous ammonia, adding it drop by drop with vigorous stirring. (This should bring the volume to about 90 ml). Finally, allow the precipitate to digest for one hour at about 70°. (Some of the excess 8-hydroxyquinaldine may volatilize

* Since the flat portion of the "pH curve" is broad, a small uncertainty at the "breakpoint" is of little practical significance.

during the digestion and condense on the underside of the covering watch glass; this should not be washed down).

2. Gravimetric determination of thorium

After the precipitation and digestion of the precipitate as directed above, allow the solution to cool somewhat and then filter through a medium-porosity fritted-glass crucible and wash the precipitate, using for the transferring and washing about 75 ml of hot 0.15 *M* aqueous ammonia. Dry the precipitate for one hour at 110° ± 5° and weigh as $Th(C_{10}H_8ON)_4$. (The gravimetric factor is 0.2683).

3. Bromometric determination of thorium

After the precipitation and digestion of the precipitate as directed in Procedure I, allow the solution to cool somewhat and then filter through No. 40 Whatman paper and wash the precipitate carefully, using for the transferring and washing about 100 ml of hot 0.15 *M* aqueous ammonia. Dissolve the precipitate through the paper, using 50 ml of warm 4 *N* hydrochloric acid, and catch the solution in an iodine flask. Follow the acid with 50 ml of water. To the 8-hydroxyquinaldine solution, now 2 *M* in hydrochloric acid, add 2.0 g of potassium bromide (dissolved in 10 ml of water) and 3 drops of a 0.1% aqueous solution of the sodium salt of methyl red. Titrate, carefully, with standard potassium bromate solution (about 0.02 *M*) until the solution becomes yellow and then add, rapidly, 1.0 to 1.5 ml of the bromate solution. Quickly stopper the flask, and then pour a few ml of a solution of potassium iodide (1.0 g per 10 ml of water) around the lip of the flask. After 5 min, allow the iodide solution to run into the flask and add more, to bring the total added to 10 ml. Immediately titrate the liberated iodine with a standard thiosulfate solution (about 0.1 *M*, standardized against potassium bromate). Calculate the content of 8-hydroxyquinaldine, and hence of thorium, from the titers involved, allowing for the indicator blank.

When less than about 5 mg of thorium is present, the washed precipitate should be dried, while still on the paper, for one hour at 110°, to volatilize coprecipitated 8-hydroxyquinaldine. Then put the precipitate and paper into an iodine flask, treat with 50 ml of warm 4 *N* hydrochloric acid and 50 ml of water, and do the bromination and titration as indicated above.

RESULTS

Gravimetric determination

The very good accuracy and precision of the gravimetric method are shown in Table II. The method is sensitive, too: the precipitation of the thorium chelate can be quantitative from solutions that contained the metal at concentrations as low as 0.012 mg/ml. This value, about $5 \cdot 10^{-5}$ *M*, is the lowest concentration at which experiments were done.

For quantitative precipitation from solutions with less than about 0.7 mg Th/ml an excess of reagent greater than 70% is required, as mentioned earlier. This is provided for in Procedure I, above.

The wash liquid is alkaline to aid in the removal of any coprecipitated 8-hydroxyquinaldine. Even so, when less than about 5 mg of thorium is precipitated (in which event the excess of precipitant is large) the precipitate may retain a significant amount of 8-hydroxyquinaldine. This is of no consequence, for any that remains is volatilized

during the drying at 110° (as several experiments proved). Experiments using the thermobalance showed that the thorium chelate can withstand 110°, without detectable volatilization, for at least three hours.

The thermolysis curve found[3] for this thorium chelate was essentially confirmed. The compound has no water of crystallization, and is stable to about 180°.

TABLE II

DETERMINATIONS OF THORIUM AS $Th(C_{10}H_8ON)_4$

Approx. concn. of thorium (mg/l or p.p.m.)	*Thorium taken (mg)*	*Thorium recovered (mg)*[a]	
		Gravimetrically[b]	*Bromometrically*
690	34.51	34.45 ± 0.05	34.55 ± 0.02
680	34.1	34.10 ± 0.06	34.14 ± 0.04
410	20.4	20.47 ± 0.02	20.43 ± 0.05
140	6.81	6.79 ± 0.03	6.80 ± 0.03
27	1.36	1.34 ± 0.04	
12	0.68	0.67 ± 0.03	0.65 ± 0.02[c]

[a] Each value is an average of 7–13 determinations; the precision measure is the average deviation.
[b] Weighed as $Th(C_{10}H_8ON)_4$, after drying the precipitate for one hour at 110°.
[c] Precipitates were dried for one hour at 110°, before dissolution in acid, to avoid interference from coprecipitated reagent.

Bromometric determination

Procedure III yields precise determinations of 8-hydroxyquinaldine (and, therefore, of thorium). Some 22 bromometric determinations of thorium (at a concentration of 0.7 mg/ml) gave 33.21 mg with an average deviation of 0.03 mg and a standard deviation of 0.05 mg. The bromometric procedure is fully as accurate as the gravimetric procedure, as results over a wide range of concentrations show (Table II).

We observed, as did BERGES[10], that a very finely divided brown precipitate sometimes forms when the iodide is added. Although the cloudiness due to this precipitate diminishes as the thiosulfate is added, the end-point is obscured with resultant decrease in both precision and accuracy. (Obscure end-points from a similar cause have been encountered[11] in the bromometric determination of 8-hydroxyquinoline.) The amount of the precipitate depends on the amount of excess potassium bromate. In the bromination procedure recommended above, it is entirely avoided by restricting the excess bromate to not more than 1.5 ml.

DISCUSSION

This investigation gave no evidence for any compound of thorium and 8-hydroxyquinaldine (2-methyl-8-hydroxyquinoline) other than that represented by $Th(C_{10}H_8ON)_4$. It is well established, however, that there are two thorium compounds of 8-hydroxyquinoline, of 1 : 4 and 1 : 5 stoichiometry, although there has been disagreement[12] about the temperature ranges over which these are stable. Almost certainly, however, the 1 : 5 compound is not stable above about 80°[13,14]. As consequences of this limitation on the drying temperature, the determination of thorium by weighing this compound not only is lengthy but also is exposed to error from the coprecipitation of the reagent (8-hydroxyquinoline not being appreciably volatile below 85°[14]). In contrast, the 8-hydroxyquinaldine precipitate can be safely dried to the anhydrous 1:4

chelate at 110°, at which temperature 8-hydroxyquinaldine is readily volatilized. The ease with which this chelate may be freed of excess 8-hydroxyquinaldine likewise permits accurate bromometric determinations of thorium by means of this reagent.

The recommended gravimetric and bromometric procedures using 8-hydroxyquinaldine have advantages over commonly used methods for the standardization of thorium solutions. The usefulness of 8-hydroxyquinaldine for determinations of thorium in the presence of other metals is, of course, restricted by the unselective character of this reagent (though its inability to precipitate aluminium gives it a further advantage over 8-hydroxyquinoline).

Under easily achieved conditions, thorium is precipitated by 8-hydroxyquinaldine, quantitatively as the chelate, over fully 5 pH units — a broader pH range for quantitative precipitation than that reported for any other organic precipitant for thorium, insofar as we know.

Under the conditions of our work, the pH of incipient, and of quantitative, precipitation of thorium by 8-hydroxyquinaldine are each substantially higher than the corresponding values found[15], under not greatly different conditions, for the precipitation of thorium by 8-hydroxyquinoline. This is in accord with what has been found[4,7,16] for the precipitation of other metals by these two related reagents. Such comparisons are not really proper, however, unless among other conditions of the experiments the concentrations (both of metal and reagent) are the same, for these influence the pH of precipitation. With all conditions comparable, the difference in the pH of precipitation for the chelates of a given metal with two related reagents should reflect differences in the intrinsic solubility[17] and stability of the chelates, and in the acidity of the reagents. The latter two of these are ordinarily related, in that a given metal commonly forms the more stable chelate with the weaker acid[18]. When this is so, two opposing effects[7,17] bear on the pH of precipitation of the chelate: the more stable of the two chelates does not require as high a concentration of the chelating anion to bring about its precipitation (which argues for a lower pH of precipitation) but, on the other hand, the weaker of the two acids holds protons more firmly and so, to compare with the stronger acid as a provider of the chelating anion, requires a higher pH. A given metal would be expected to form a more stable chelate with 8-hydroxyquinaldine than with 8-hydroxyquinoline, for the former is the weaker acid (both its pK_{NH} and pK_{OH} are higher). In point of fact, however, the 8-hydroxyquinaldine chelates are somewhat less stable, at least in 50% aqueous dioxane[19,20], than the corresponding 8-hydroxyquinoline chelates. (The lesser stability of the 8-hydroxyquinaldine chelates is attributed[19,20] to a steric hindrance to their formation, occasioned by the methyl group in the 2 position in 8-hydroxyquinaldine). Thus, with respect to the precipitation of the chelates of a given metal with these particular reagents, the two factors — chelate stability and reagent anion concentration — should operate, not in opposition but in concert, to favour the precipitation of the 8-hydroxyquinoline chelate at a lower pH than the 8-hydroxyquinaldine chelate.

A reversal of these relative positions for pH of precipitation would be expected only if an 8-hydroxyquinoline chelate had a much higher intrinsic solubility, or was much more prone to supersaturation, than the corresponding 8-hydroxyquinaldine chelate. Neither of these is probable, nor does either appear to be so, for the available experimental data indicate that the chelates of 8-hydroxyquinoline do precipitate at a lower pH than the corresponding chelates of 8-hydroxyquinaldine.

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SUMMARY

Conditions under which thorium can be quantitatively precipitated as a 1 : 4 chelate with 8-hydroxyquinaldine have been established. This precipitate can be dried and weighed as the anhydrous compound, $Th(C_{10}H_8ON)_4$, or dissolved in acid and the thorium determined by the dibromination of the released 8-hydroxyquinaldine. Both methods are sensitive, precise and accurate, and have favourable analytical factors; the methods are well suited to the standardization of thorium solutions. 8-Hydroxyquinaldine has distinct advantages over the parent compound, 8-hydroxyquinoline, for the determination of thorium.

RÉSUMÉ

Une étude a été effectuée sur la précipitation du thorium par l'hydroxy-8-quinaldine. Deux méthodes de dosage sont ensuite proposées: 1. Par pesée du précipité $Th(C_{10}H_8ON)_4$; 2. Par titrage iodométrique, après bromuration de l'hydroxy-8-quinaldine en excès. L'hydroxy-8-quinaldine présente des avantages sur l'hydroxy-8-quinoléine.

ZUSAMMENFASSUNG

Zur gravimetrischen Bestimmung von Thorium eignet sich 8-Hydroxychinaldin besser als 8-Hydroxychinolin. Der erhaltene Niederschlag kann als $Th(C_{10}H_8ON)_4$ gewogen oder, nach Auflösen des Niederschlags in Säure, das Thorium bromometrisch bestimmt werden.

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SUR LA STABILITÉ THERMIQUE DES ÉTALONS ANALYTIQUES. VIII*

CLÉMENT DUVAL

avec la collaboration technique de

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(Reçu le 2 mars 1960)

Dans cette huitième série, nous présentons une étude thermogravimétrique et spectrophotométrique relative aux douze corps suivants: acétate de baryum, acétate de plomb, nitrate de plomb, nitrate de potassium, chlorure de magnésium, nitrate d'ammonium, citrate d'ammonium, nitrate de cobalt, nitrate d'uranium, téréphtalate de sodium, sulfure de sodium, palmitate de potassium.

Toutes ces substances ont été chauffées sur la thermobalance à enregistrement photographique, avec échauffement linéaire de 300° par heure et avec des poids de substance de l'ordre de 200 mg. Les spectres infrarouges ont été realisés sur poudre, avec vaseline comme agglomérant, entre 6 et 15 μ, sur le spectromètre Perkin-Elmer 12C, avec optique de chlorure de sodium.

Acétate de baryum

Le produit commercial utilisé, pris dans un flacon déjà ouvert, correspond au monohydrate; il n'est pas hygroscopique et on peut le peser tel quel. Si l'on voulait prendre le sel anhydre, il conviendrait de porter cet hydrate en thermostat vers 105°. La déshydratation s'effectue normalement entre 72 et 96°; le sel anhydre reste à peu près stable jusqu'à 240°; il perd lentement du poids jusqu'à 480° et le départ d'acétone s'effectue jusqu'à 542°. Le résidu, à poids constant, est constitué par le carbonate de baryum suivant une réaction très classique qui semble remonter à Chenevix (Fig. 1).

Le spectre infrarouge nous permet de mesurer les fréquences suivantes: 931 (F), 1021 (F), 1053 (aF), 1347 (f), 1419 (F), 1542 (TF) cm^{-1}.

Acétate de plomb

Ce sel signalé avec 3 molécules d'eau pour les usages analytiques, nous en a accusé un peu moins si l'on tient compte du poids du résidu (environ 2.3 H_2O). De toute façon, on ne peut guère l'utiliser pour faire une pesée directe car il se déshydrate dès la température ordinaire (Fig. 2) et la perte d'eau est déjà sensible à 44°. Sa déshydratation se poursuit jusque vers 100° mais le produit anhydre ne fournit pas de palier horizontal. Sa dissociation est achevée à 448°; au-delà nous réalisons le palier sensiblement horizontal de l'oxyde de plomb PbO.

* Pour le septième mémoire de cette série, voir *Anal. Chim. Acta*, 20 (1959) 263.

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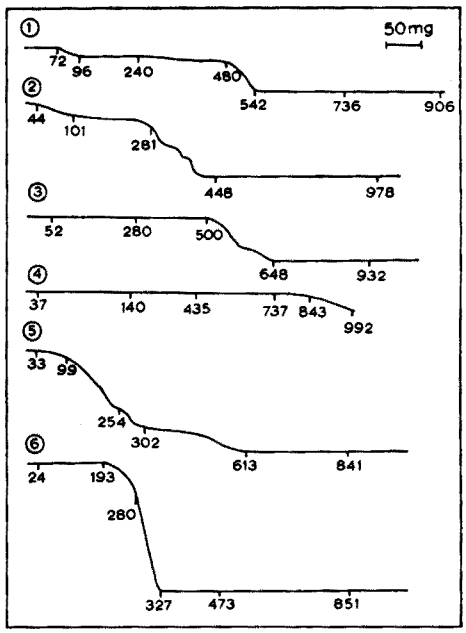
Le spectre infrarouge nous a permis d'enregistrer et de mesurer les fréquences suivantes: 933.5 (aF), 1020 (aF), 1051 (f), 1337 (aF), 1405 (F), 1550 (TF) cm^{-1}.



Figs. 1–6.

Nitrate de plomb

Le nitrate de plomb cristallise anhydre. Sa courbe de thermolyse indique qu'il est stable jusqu'à 280°, puis la dissociation s'amorce lentement jusqu'à 500°; elle s'accélère ensuite et à 648°, on obtient le palier horizontal de l'oxyde PbO (Fig. 3). Pour faire une liqueur titrée il est donc possible de peser le nitrate de plomb tel quel, en le prélevant du flacon.

Le spectre infrarouge, réalisé sur poudre, est tout à fait en accord avec celui de MILLER ET WILKINS[1] et présente dans la région étudiée les quatre bandes suivantes: 725.5 (F), 806.5 (aF), 838 (aF), 1369 (F), plus un épaulement au voisinage de 1306 cm^{-1}.

Nitrate de potassium

Ce sel est anhydre et stable depuis la température ordinaire jusqu'à 737° au moins. Toutefois, un examen minutieux de la courbe (Fig. 4) semble indiquer une légère dissociation portant sur 1/200 du poids soumis à l'expérience dès 140°. La décomposition ne devient appréciable que vers 843°. Rappelons, en accord avec divers auteurs, qu'il se forme du nitrite de potassium et des vapeurs nitreuses et que le passage par le point de fusion situé vers 339° ne se signale par aucune dissociation nette.

Le spectre infrarouge, déjà mesuré par de nombreux auteurs, en particulier par MILLER ET WILKINS[1], nous a présenté, dans la région précitée, les deux bandes fortes fondamentales à 825 et 1394 cm^{-1}.

Chlorure de magnésium

Ce corps déliquescent, soumis à une recristallisation, contient 5.6 molécules d'eau qu'il commence à perdre dès la température ordinaire. Il est donc impossible de confectionner une liqueur titrée par pesée directe et, de plus, la déshydratation ne conduit pas à un palier du sel anhydre (Fig. 5) parce qu'avec nos conditions opératoires, la vapeur d'eau libérée produit la décomposition et on arrive au palier de l'oxyde de magnésium MgO à partir de 613°.

Le chlorure de magnésium hydraté ne donne pas et ne doit pas donner de spectre infrarouge dans le région du chlorure de sodium, à l'exclusion de la bande caractéristique de l'eau.

Nitrate d'ammonium

Ce sel, vendu anhydre, a été séché préalablement dans le dessiccateur avec anhydride phosphorique car on sait que l'eau intervient dans la vitesse et la température de décomposition. Lorsque le flacon a été ouvert plusieurs fois, il est bon de porter le sel à une température inférieure à 193° car il se montre hygroscopique. C'est à cette dernière température que la sublimation et la décomposition en vapeur d'eau et oxyde azoteux commencent à se faire sentir et cette dernière s'accélère brusquement vers 280° en accord avec d'autres auteurs, pour s'achever, d'une manière nette, vers 327° (Fig. 6). Le palier qui suit est relatif au poids du creuset vide.

On sait que ce sel peut exister sous cinq modifications cristallines dont les spectres infrarouges sont différents. Le produit pur pour analyses, que nous avons utilisé, présentait deux bandes fortes relatives à NO_3 pour 837 et 1370 cm^{-1} et une bande relative à NH_4 pour 1405 cm^{-1}.

Citrate d'ammonium

Le citrate diammonique que nous avons utilisé $(NH_4)_2HC_6H_5O_7$ était anhydre et bien sec. Il s'est montré stable jusqu'à 161°; après quoi, la décomposition et la combustion se produisent sans accident; le creuset est vide vers 630°; les dernières traces de carbone sont longues à brûler (Fig. 7).

Le spectre d'absorption infrarouge accuse les bandes suivantes, bien marquées et assez fortes: 833, 892, 922, 1090, 1110, 1210, 1240, 1297, 1365 et 1435 cm^{-1}.

Nitrate de cobalt(II)

Ce sel est très déliquescent et contient ordinairement plus de 6 molécules d'eau. Il est à peu près impossible d'en faire une liqueur titrée par pesée directe car il se déshydrate d'une façon continue et perceptible dès 34°. La dissociation ne se distingue pas de la déshydratation avec notre vitesse de chauffe et se ralentit beaucoup aux approches de 290° (Fig. 8). Un palier légèrement oblique s'étend jusque vers 700°, température au-dessus de laquelle, on obtient l'oxyde Co_3O_4.

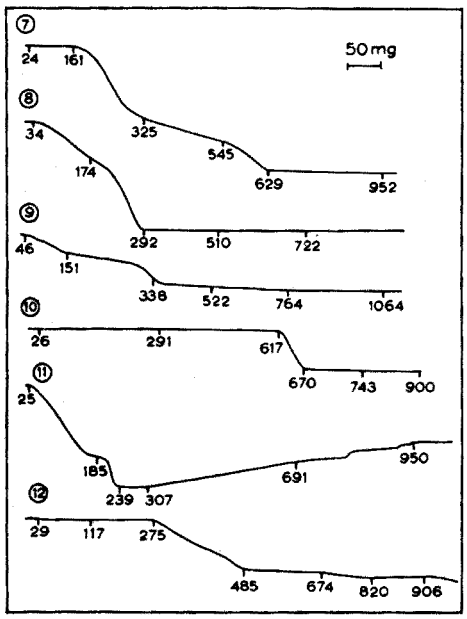
Le spectre infrarouge, réalisé sur un produit beaucoup plus sec, nous a donné les bandes: 837.2 (F), 1380 (F) cm^{-1}.

Nitrate d'uranyle

Le nitrate d'uranyle est un sel hexahydraté bien sec, mais il se montre à peine plus stable que le nitrate de cobalt(II). En effet, il commence à se déshydrater dès 46°;

on ne peut pas faire la distinction entre la perte d'eau et la décomposition (Fig. 9). Toutefois, vers 350°, la vitesse diminue quand on approche du résidu UO_3, lequel perd à son tour de l'oxygène et dès 760°, on aboutit à l'oxyde U_3O_8. Il est permis de faire une liqueur titrée avec le sel extrait d'un flacon neuf.

A côté des bandes fortes de 943 et 1034 cm^{-1} relatives à UO_3, nous avons enregistré dans le spectre infrarouge, deux autres bandes fortes, l'une à 839, l'autre à 1350 cm^{-1}.



Figs. 7–12.

Téréphtalate de sodium

Ce sel est stable au moins jusqu'à 300° et se montre anhydre. La perte de poids qu'il éprouve ensuite jusqu'à 617° est vraiment minime mais la décomposition se produit brusquement entre 617 et 670°. Le carbone résiduel brûle extrêmement lentement et vers 840° le creuset est vide (Fig. 10).

Le spectre infrarouge permet d'enregistrer les maxima suivants: 746 (F), 760 (f), 826 (F), 895 (f), 1023 (f), 1397 (TF), 1566 (TF) cm^{-1}.

Sulfure de sodium

Le sulfure de sodium incolore utilisé, contient à peu près 9 molécules d'eau lorsqu'on le sort du flacon pour la première fois, mais il est très hygroscopique. Il est difficile d'en faire directement une liqueur titrée car sa déshydratation commence vers 30°. La courbe tracée (Fig. 11) indique que le produit anhydre donne un palier à peu près horizontal entre 240 et 307°; après quoi, la courbe remonte à peu près linéairement et vers 950°, on arrive au sulfite de sodium qui n'est pas rigoureusement pur. Ce sel ne donne pas de spectre infrarouge dans la région du chlorure de sodium.

Palmitate de potassium

Le palmitate de potassium, légèrement humide tel que nous l'avons utilisé, devient

sec et montre un poids constant de 40 à 275°. À cette température la décomposition s'amorce et s'effectue progressivement jusqu'à 485°; alors le carbone brûle lentement et le creuset est vide à 820° (Fig. 12). Il faudra donc sécher ce corps, d'aspect savonneux, avant sa pesée.

Le spectre infrarouge permet d'enregistrer les bandes suivantes: 913 (aF), 1010 (f), 1095 (f), 1379 (aF) et 1437 (F) cm^{-1}.

RÉSUMÉ

Nous avons tracé la courbe de thermolyse et donné le spectre d'absorption infrarouge sur solide, de douze substances pouvant servir comme étalons. L'acétate de plomb, le chlorure de magnésium, le nitrate de cobalt(II) et le sulfure de sodium ne peuvent être pesés directement pour confectionner une liqueur titrée.

SUMMARY

Description of the thermolysis curves of 12 substances; determination of their i.r. absorption spectra in order to examine whether or not they are suitable as standards. It was found that lead acetate, magnesium chloride, cobalt(II) nitrate, and sodium sulphide cannot be weighed directly for the preparation of a standard solution.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung von Standardsubstanzen auf deren Eignung als solche auf Grund von IR Spektren und thermolytischem Verhalten. Bleiacetat, Magnesiumchlorid, Kobaltnitrat und Natriumsulfid können nicht direkt gewogen werden zur Herstellung von Normallösungen.

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ACID ALIZARIN BLACK SN METALLOCHROMIC INDICATOR FOR CALCIUM

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The development which made ethylenediaminetetraacetic acid (EDTA) a reagent of practical significance was undoubtedly the evolution by SCHWARZENBACH, BIEDERMANN AND BANGERTER of the complexometric water-hardness determination based on the use of Eriochrome Black T and Murexide as visual indicators[1]. However, many newer indicators have been proposed for this determination and a recent examination has shown that with these, results may vary markedly[2]. Unquestionably, in dilute calcium solution, one of the most clear-cut end-points is obtained with the tris-hydroxy bis-azo dyestuff Acid Alizarin Black SN (C. I. Mordant Black 25). One of the peculiar features of this indicator, however, is that it gives a much sharper

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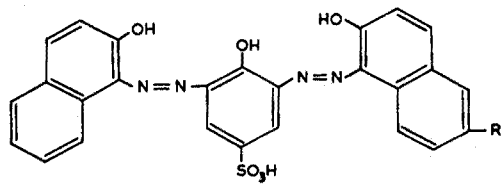
end-point in dilute (0.01 *M*) calcium solution than it does in strong (0.1 *M*) solution. This paper reports an examination of this phenomenon and discusses the suitability of Acid Alizarin Black SN and the closely related dyestuff Acid Alizarin Black SE as metallochromic indicators for cations other than calcium.

Metallochromic properties of Acid Alizarin Black SN and SE



R = —SO_3H: Acid Alizarin Black SN (C.I. Mordant Black 25),
R = —H: Acid Alizarin Black SE (C.I. Mordant Black 10).

In common with all other metallochromic reagents of the hydroxy-azo or hydroxy aminomethyl (dicarboxymethyl) variety, both molecules function as acid–base indicators. Thus AABSN is red-coloured below pH 5.4, turquoise blue between pH 6.5–12.4 and gradually assumes a purple shade at pH > 12.8. AABSE behaves similarly.

Both dyestuffs were tested as metallochromic reagents and for this purpose were used as a 0.1% aqueous solution (AABSN) or as a 2% dispersion on pulverised sodium chloride (AABSE). Particular attention was paid to reactions with the alkaline earths and towards metals of the alkali-sulphide group. In all cases the colour changes produced on chelation of the dyestuff with a metal ion were found to be hypsochromic.

AABSN gave a red-purple to blue end-point in the titration of 0.02 *M barium* with EDTA in an ammonium hydroxide solution at pH 11.5; the colour change was gradual over a few drops of titrant. The use of a diethylamine buffer at pH 12.5 did not improve matters. With *calcium* the same indicator gave a very sharp (1 drop) red to turquoise end-point between pH 11.5–12.5 using ammonia, diethylamine or sodium hydroxide buffers. *Strontium* behaved similarly, giving sharp red to turquoise end-points in the same media; *magnesium* afforded only unsatisfactory vague end-points from red-purple to blue over the range pH 8.5–10 in all media examined. With *cadmium*, AABSN yielded a sharp red to blue end-point at pH 8.5 in a borax buffer; an indistinct purple to turquoise end-point was obtained in ammonia at pH 11.5 and none whatsoever in ammonia–ammonium chloride at pH 10. Optimum conditions for *manganese* were obtained with a very sharp purple to turquoise end-point at pH 10 in ammonia–ammonium chloride buffer. Less well defined end-points were obtained at pH 8.5 and 11.5. *Nickel* gave a sharp purple to turquoise-blue end-point in hot solution at pH 11.5 (ammonia) and *zinc* behaved similarly. Of the other ions examined only *thorium* deserves special mention. It was observed to give a very sharp crimson to orange end-point at pH 4 in a sodium acetate–acetic acid buffer.

AABSE was found, rather surprisingly, to be very much inferior as an indicator for all the above ions (only with calcium was a reasonable red to blue end-point obtained, but even this was inferior to the AABSN end-point). In addition, AABSE

was observed to give a purple to blue end-point with copper(II) over the entire pH range 4–11.5, but the response was rather too sluggish for indicator purposes.

Although the two molecules differ only in that AABSN contains an extra sulphonic acid group, which is not involved directly in the chelating action, there is a marked difference in their metallochromic properties; it is perhaps most noticeable with thorium, copper and calcium. Since the reaction of these indicators with calcium was judged to be of most analytical significance, further examination was confined to the calcium chelates.

Reaction of AABSN with calcium

It was observed that whereas AABSN gave a sharp, but poorly defined purple to turquoise end-point in the titration of calcium at the 0.1 *M* dilution level a much more clear-cut end-point was obtained in $\leqslant$ 0.02 *M* solutions. In the latter instance the colour of the solution was purple over 90% of the titration, but near the end, the colour changed to red and passed sharply through to turquoise at the equivalence point. This performance suggested the possibility of the calcium and indicator ions reacting to form more than one complex. Accordingly, it was decided to investigate the spectrophotometry of chelate formation to obtain evidence in support of this theory.

Since the sample of dyestuff available to us was of commercial origin, it was first of all assayed and found to be only 88% pure. A pure product was obtained from the commercial material by extracting its aqueous solution with benzene, ether and finally chloroform. The aqueous solution was evaporated to dryness, dissolved in methanol and saturated with gaseous hydrochloric acid. The solution was then filtered and evaporated to crystallisation point. The dark red crystals thus obtained were removed and dried under vacuum over caustic soda. It should perhaps be stressed at this point that the commercially available material is entirely adequate for normal indicator purposes and the above purification procedure was only necessary to obtain a sample for quantitative studies on the pure dye itself.

The spectrophotometric examination was made with $5 \cdot 10^{-4}$ *M* aqueous calcium and indicator solutions in a diethylamine buffer system. Fig. 1 shows the absorption spectra of the free dyestuff at pH 12.5 (A), the dyestuff in the presence of a $\frac{1}{2}$ molar ratio of calcium ions (B), and the dyestuff in the presence of a large excess of calcium

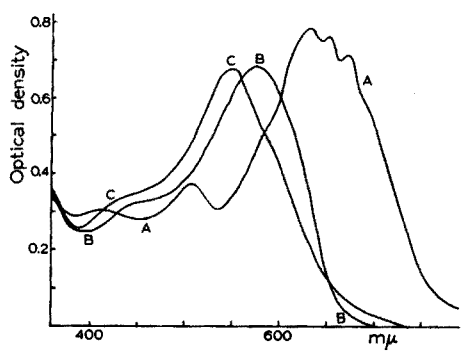


Fig. 1. Acid Alizarin Black SN. A, free indicator, pH 12.5; B, indicator + excess Ca^{+2}; C, indicator + 1/2 mole Ca^{+2}.

ions (C). The three spectra therefore represent the forms of the chromogenic species beyond the end-point immediately before it and as it would be during the bulk of a titration in dilute solution. This experiment reveals the presence of a bright red complex between the indicator and calcium, λ_{max} 548 mμ, when low concentrations of calcium are present and of a purple complex, λ_{max} 573 mμ, when there are preponderant amounts of calcium. The main absorption band of the metal-free indicator at this pH is broader and shows triplet peaks in order of decreasing intensity at 632, 652 and 673 mμ. In addition the free dyestuff shows a distinct absorption band of low intensity at 507 mμ.

Thus the existence of more than one indicator complex between calcium and the dyestuff is suggested.

Fig. 2 shows the spectra obtained in a repeat experiment with AABSE in place of AABSN. In this instance the purity of the commercial material was found to be *ca.* 83%, but since this dyestuff was much less soluble in water it was not found entirely practicable to take it through the same purification procedure as AABSN. Consequently we contented ourselves by removing the bulk of impurities, which were inorganic in nature, by recrystallising from methanol. Whilst this may not have removed traces of organic impurities, the expected close similarity in overall structure of the absorption spectrum of the metal-free dyestuff to that of AABSN substantiates the purity of the sample. In this instance it will be seen that in the presence of a small amount of calcium a complex is formed with λ_{max} = 550 mμ. The presence of a large excess of calcium yields an absorption band of much higher intensity (*cf.* AABSN) with only a 10 mμ increase in the wavelength of maximum absorption. The shape of the two spectra are very similar. The metal-free dyestuff shows a main absorption band, λ_{max} = 636 mμ, with a sharp band of low intensity at 509 mμ. This experiment

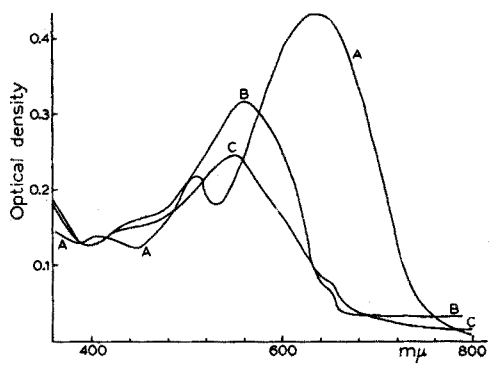


Fig. 2. Acid Alizarin Black SE. A, free indicator pH, 12.5; B, indicator + excess Ca^{+2}; C, indicator + mole ratio Ca^{+2}.

clearly shows that the separation between the various absorbing species with AABSE is somewhat less and that whilst there is a suggestion that two complexes may exist there is a much smaller separation between the two bands and also a considerable difference in extinction.

The structure of the chelate formed between calcium and AABSN were then determined by a procedure of continuous variations. For the red complex, measurements

were made at 545 mμ, *i.e.* following the formation of the red complex and at 630 mμ following the disappearance of the blue dyestuff. The corrected plot of the former is shown in Fig. 3 (A). Both experiments give clear-cut evidence of the existence of a fairly well defined complex in what the AABSN–calcium ratio is 2 : 1.

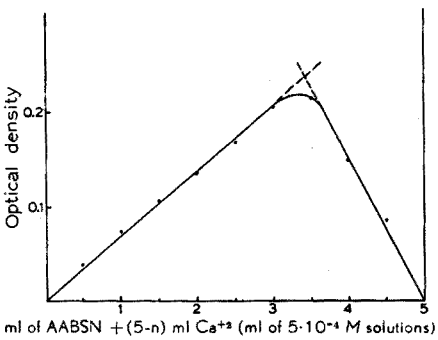


Fig. 3. (A) Acid Alizarin Black SN, 2 : 1 chelate, corrected continuous variations plot, $\lambda = 545$ mμ.

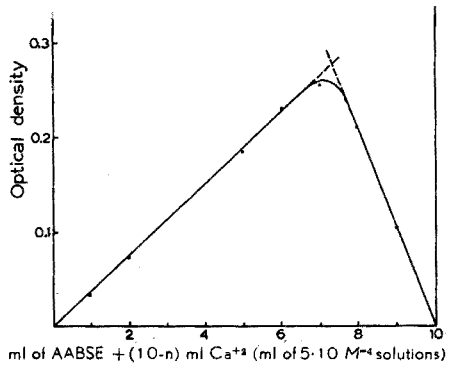


Fig. 3. (B) Acid Alizarin Black SE, calcium complex, corrected continuous variations plot, $\lambda = 560$ mμ.

Similar experiments conducted at 570 mμ suggested evidence of a rather weak complex in which there is AABSN–calcium ratio of 1 : 1. Best results were obtained in this instance by studying the variations procedure between calcium and a solution containing the 2 : 1 AABSN–calcium formulation.

With AABSE evidence could only be obtained of a 2 : 1 chelate of Fig. 3 (B). Variation procedures were made at 560 mμ and at 635 mμ again following the formation of the purple complex and the consumption of the metal-free dyestuff. Both experiments give evidence of a strong well defined 2 : 1 reagent–calcium complex.

DISCUSSION

As a result of the above examination it is evident that AABSN forms a stable 2 : 1 chelate with calcium ion in dilute solution. When large amounts of calcium are present a 1 : 1 chelate is formed, but this is a considerably weaker complex. It is of interest to note that the extinction value of the 2 : 1 and 1 : 1 chelates are almost equal. The maximum absorption of the red-form (end-point species) is separated from that of the metal free dyestuff at the same pH by *ca.* 100 mμ. The wavelength separation for the 1 : 1 chelate and the free dye is *ca* 80 mμ and there is considerably more overlap of the absorption spectra of the two forms (*cf.* Fig. 1). Normally in a titration only a few drops of indicator are added. Consequently in using 0.1 *M* Ca^{+2} solutions, the chance of the 2 : 1 indicator–calcium chelate appearing in solution is very slight. Thus though the end-point is sharp (80-mμ shift) there is not a great colour contrast. In dilute solution ($\leqslant$0.02 *M* Ca^{+2}) there is a distinct possibility of the 2 : 1 chelate being formed before the titration has proceeded to the end-point. Consequently a much more distinct end-point is obtained.

With AABSE it is debatable whether the 10-mμ shift observed in λ_{max} for the metal-indicator complex is due to the existence of more than one complex and the

marked increase in the extinction value tends to suggest that there may in fact only be one. We could find no definite evidence of the existence of anything other than a 2 : 1 indicator–calcium chelate in this instance from spectrophotometric studies of continuous variation and conclude that with AABSE the poorer end-point is entirely due to the inferior separation (86 mμ between the λ_{max} values for the metal-free indicator and the 2 : 1 chelate). The overlap between the spectra is also very considerable, *cf.* Fig. 2.

AABSN gives a very sharp well defined end-point in the titration of calcium in dilute solution and in our experience it is the sharpest and most clear cut of all those we have examined. We have also found[2] that it is particularly useful in that it is applicable for the determination of calcium in the presence of magnesium over the range where Calcon (CI Mordant Black 17) is not applicable. In this range it is the only indicator to give 100% recovery of calcium.

Finally it may be said that the indicator AABSN has considerable potentialities for the titration of strontium, thorium, manganese, nickel, zinc and cadmium.

EXPERIMENTAL

Reagents for titration of calcium

0.01 M EDTA: Prepared from disodium ethylenediaminetetraacetic acid, dihydrate dissolved in glass-distilled or de-ionised water and standardised against pure magnesium metal using Solochrome Black 6 B as indicator[3] at pH 10; *0.01 M $CaCl_2$:* Prepared from oven-dried AR grade calcium carbonate dissolved in a slight excess of 0.1 *N* HCl and diluted to volume; *Diethylamine; Acid Alizarin Black SN;* 0.1% aqueous solution.

Procedure

25.00 ml of 0.01 *M* calcium chloride were pipetted into a 250-ml conical flask and the solution was diluted to 50–70 ml with distilled water. 2 ml of diethylamine buffer were added and 5–6 drops of indicator solution. The solution was then titrated rapidly with 0.01 *M* EDTA till the warning red shade of the 2 : 1 indicator–calcium chelate appeared a few drops from the end-point. The titration was then completed dropwise till the red colour changed sharply to turquoise-blue.

ACKNOWLEDGEMENT

We wish to thank the Clayton Aniline Company for the award of a research studentship to one of us (R.A.C.) and we are indebted to the same organisation for the provision of the original sample of both dyes used in the examination.

SUMMARY

The metallochromic properties of the closely related tris-hydroxy bis-azo dyestuffs Acid Alizarin Black-SN and -SE are examined. The former is shown to be a particularly excellent complexometric indicator for calcium in dilute solution and is also recommended for strontium, manganese, nickel, zinc, cadmium and thorium. Both indicators are shown to form 2: 1 indicator–calcium chelates, on the basis of spectrophotometric evidence, and the unusual behaviour of the former indicator in strong calcium solutions is explained.

RÉSUMÉ

Le noir acide d'alizarine SN est proposé comme indicateur pour le titrage complexométrique du calcium, au moyen de l'éthylènediaminotétracétate disodique. Il peut être recommandé également pour le strontium, le manganèse, le nickel, le zinc, le cadmium et le thorium.

ZUSAMMENFASSUNG

Als Indikatoren bei der komplexometrischen Titration von Calcium, Strontium, Mangan, Nickel, Zink, Cadmium und Thorium mit Äthylendiaminotetraessigsäure (Natriumsalz) eignen sich die Säuren von Alizarinschwarz SN und SE.

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RADIOCHEMICAL SEPARATION OF ^{95}Zr AND ^{95}Nb WITH TRI-*n*-BUTYL PHOSPHINE OXIDE

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INTRODUCTION

Tri-*n*-octyl phosphine oxide is an excellent extractant for zirconium, the extraction of which from acidic solutions has been studied[1]. In the course of a study on the extraction of zirconium with organophosphorus compounds, it was observed that the extraction behaviors of ^{95}Zr and ^{95}Nb with tri-*n*-butyl phosphine oxide (TBPO) are quite different so that their mutual separation should be possible. Several methods including anion-exchange resins[2–5], cation-exchange resins[6,7] and TTA extraction[8], have been used for the separation of ^{95}Zr and its daughter ^{95}Nb. Extraction by tri-*n*-butyl phosphine oxide from nitric acid solution provides a rapid and efficient separation method for these isotopes, and the present article describes the details of the procedure.

EXPERIMENTAL

Chemicals

Tracer ^{95}Zr and its daughter ^{95}Nb: The tracer ^{95}Zr was supplied by Oak Ridge National Laboratory in the form of oxalate. The ^{95}Zr oxalate was converted to nitrate by repeated boiling and evaporation with concentrated nitric acid, and finally dissolved in 6 *N* nitric acid. Tri-*n*-butyl phosphine oxide: The tri-*n*-butyl phosphine oxide was obtained from Tama Chemicals, Tokyo, Japan, and was dissolved in carbon tetrachloride at concentrations of 0.001, 0.002, 0.005, 0.01, 0.02, 0.05 and 0.1 *M*. Other chemicals such as nitric acid and carbon tetrachloride were of reagent grade, and the carbon tetrachloride was purified by the distillation before use.

Preliminary test

Nitric acid (2 *N*) solutions containing ^{95}Zr and ^{95}Nb in radio-chemical equilibrium were shaken with equal volumes of 0.01 *M* TBPO, and the organic and the aqueous

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phases were then separated. The organic phase was repeatedly washed with 2 N HNO_3 pre-equilibrated with 0.01 M TBPO, and the aqueous phase was washed with 0.01 M TBPO pre-equilibrated with 2 N HNO_3. In the organic phase, the species with the Kd value of $\sim$ 100 was collected, whereas the species with the Kd value of $\sim$ 0.1 was found in the aqueous phase. The measurement of both absorption curves and half lives identified these species as ^{95}Zr in the organic phase and ^{95}Nb in the aqueous phase.

RESULTS

Distribution coefficients of ^{95}Zr and ^{95}Nb

The species obtained by the preliminary test were identified as pure ^{95}Zr and ^{95}Nb, and the distribution coefficients of these species were determined over the nitric acid concentration range of 1–13 N. The results are shown in the Fig. 1. The effect of solvent concentrations on the distribution coefficients was then studied at a fixed nitric acid concentration of 2 N; the results are shown in the Fig. 2.

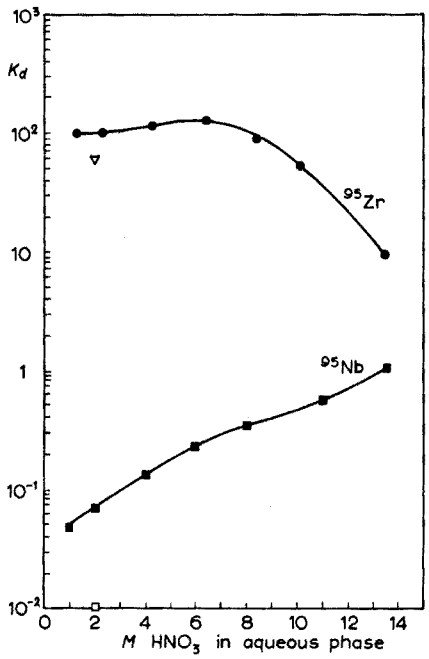

Fig. 1. Distribution coefficients of ^{95}Zr and ^{95}Nb with 0.01 M TBPO. ▽ and □ indicates the Kd values with 0.005 M TBPO.

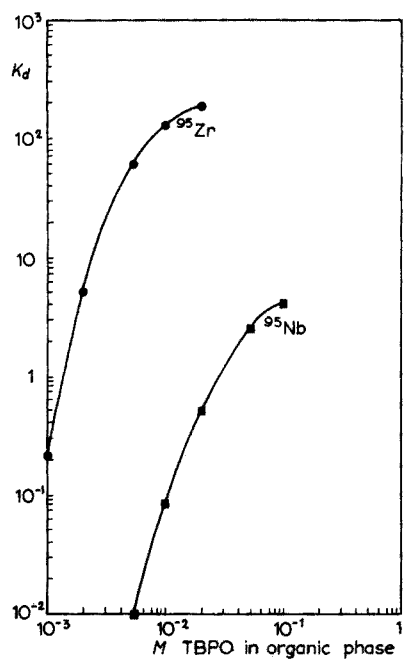

Fig. 2. Distribution coefficients of ^{95}Zr and ^{95}Nb with various TBPO concentrations and a 2 M HNO_3 aqueous phase.

Proposed procedure for the separation

If ^{95}Zr and ^{95}Nb in radiochemical equilibrium are separated completely, the activity ratio should be about 1 : 2 which gives a measure of the optimum TBPO concentration; on extraction with 0.005 M TBPO, the activity ratio of two phases was determined to be 1 : 2. As regards the nitric acid concentration, the lower the concentration, the better the separation, but the choice of nitric acid concentration is re-

stricted because of the possible hydrolysis of the species in aqueous phase below 2 *N* HNO_3; a 2 *N* nitric acid solution was therefore selected.

Equal volumes of the 2 *N* nitric acid stock solution of ^{95}Zr and ^{95}Nb and of 0.005 *M* TBPO in carbon tetrachloride were shaken, and the aqueous and the organic phases were separated. ^{95}Zr was extracted into the organic phase, whereas ^{95}Nb remained in the aqueous phase. The organic phase was washed with an equal volume of 2 *N* nitric acid pre-equilibrated with 0.005 *M* TBPO, and then diluted with an equal volume of carbon tetrachloride. The back-extraction of ^{95}Zr was made with concentrated nitric acid; the repetition of the back-extraction with concentrated nitric acid gave a 95% yield of ^{95}Zr. The back-extract was washed with carbon tetrachloride to remove the remaining TBPO. The aqueous phase which contained ^{95}Nb was washed with 0.005 *M*

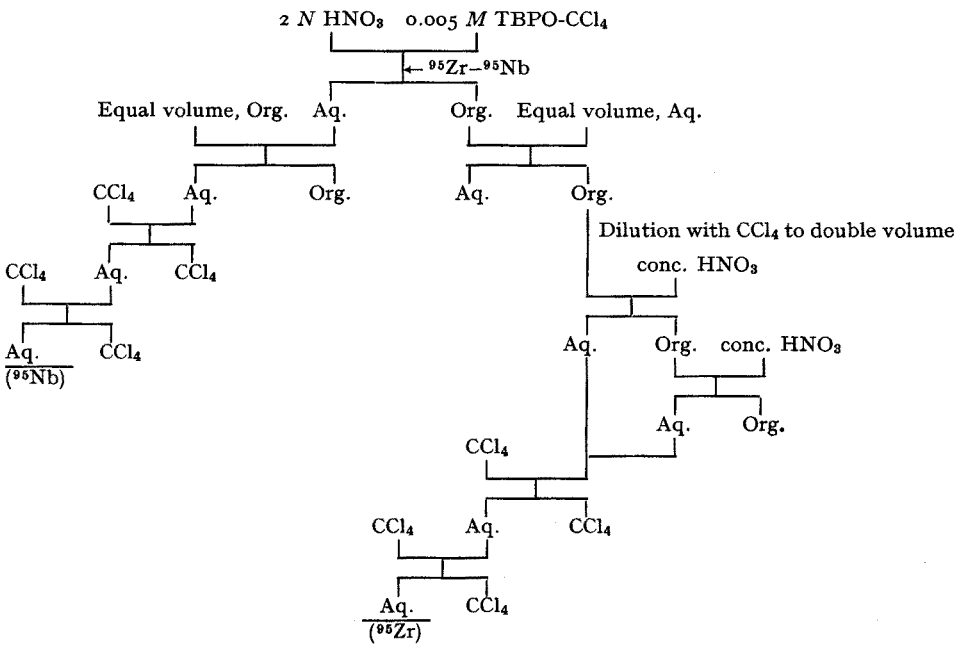

Fig. 3. Separation scheme.

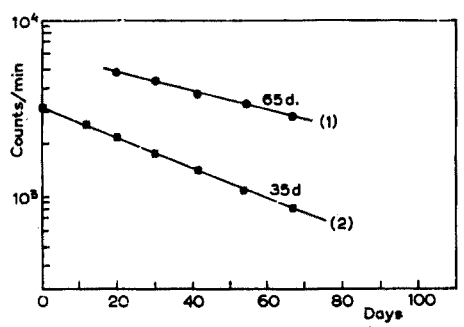

Fig. 4. Half-lives of the separation products. (1) Species collected in the organic phase (^{95}Zr). (2) Species collected in the aqueous phase (^{95}Nb).

TBPO pre-equilibrated with 2 *N* HNO_3 and then with carbon tetrachloride to remove any remaining TBPO. The entire separation scheme is illustrated in the Fig. 3.

The *Kd* values of ^{95}Zr and ^{95}Nb thus separated were compared to these listed[1], and good agreement was observed. The absorption curves and half lives confirmed that the ^{95}Zr and ^{95}Nb obtained were in a pure form. The half lives of the separated species are shown in the Fig. 4.

The scrubbing solution must be pre-equilibrated with the solvent because of the appreciable solubility of TBPO in water. The extraction of ^{95}Zr and ^{95}Nb from hydrochloric acid solution was examined, but the distribution coefficients were too close, and the separation was not possible.

ACKNOWLEDGEMENT

The authors wish to express their appreciation to Drs. KENJIRO KIMURA, TAKASHI MUKAIBO, KEIICHI OSHIMA and KEIJI NAITO for their suggestions and encouragement.

SUMMARY

^{95}Zr and ^{95}Nb behave differently on extraction from nitric acid solutions with tri-*n*-butyl phosphine oxide (TBPO). These isotopes can be separated efficiently by extraction with 0.005 *M* TBPO from 2 *N* nitric acid solution. ^{95}Zr was extracted into the organic phase and ^{95}Nb remained in aqueous phase. Separation from hydrochloric acid solution was not possible.

RÉSUMÉ

Une méthode est proposée pour la séparation de ^{95}Zr d'avec ^{95}Nb. On procède par extraction, en solution HNO_3 2 *N*, au moyen d'oxyde de tri-*n*-butyl-phosphine (0.005 *M* dans le tétrachlorure de carbone). ^{95}Zr passe dans la phase organique, alors que ^{95}Nb reste dans a phase aqueuse.

ZUSAMMENFASSUNG

Die Trennung des ^{95}Zr von ^{95}Nb kann durch Extraktion der salpetersauren Lösung mit tri-*n*-Butylphosphinoxyd–Tetrachlorkohlenstoff erfolgen, wobei unter den angegebenen Bedingungen nur das ^{95}Zr von der organischen Phase aufgenommen wird.

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ANALYSIS OF MCPA/TBA HERBICIDE FORMULATIONS

I. A LIQUID–LIQUID CHROMATOGRAPHIC METHOD FOR DETERMINATION OF 2,3,6-TRICHLOROBENZOIC ACID

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During the last two years, a new selective herbicide has been in extensive commercial use, in cereal crops, for the control of certain weeds which are not susceptible to the long-established "hormone" weedkillers such as MCPA and 2,4D. This herbicide* is composed essentially of an aqueous solution of the alkali metal salts of trichlorobenzoic (TBA) and methylchlorophenoxyacetic (MCP) acids together with formulants added to assure satisfactory field performance. The principal physiologically active constituents of the mixture are 2,3,6-trichlorobenzoic acid and 4-chloro-2-methyl phenoxyacetic acid (4C2M) and methods were therefore required for the specific determination of these acids.

The acidic impurities in the mixture result from the manufacturing processes used for its constituent technical MCPA and technical TBA. Technical MCPA normally contains 85–100% 4C2M, the principal acidic impurities being 6-chloro-2-methyl phenoxyacetic acid (6C2M) 4,6-dichloro-2-methylphenoxyacetic acid (46C2M), 2-methylphenoxyacetic acid (2M) and the corresponding chlorinated cresols. Glycollic acid may also be present. Technical TBA usually contains a minimum of 40% 2,3,6-TBA, possible impurities (depending on the manufacturing process employed) including the 3 monochloro-acids, 6 dichloro-acids, 5 isomeric trichloro-acids, 3 tetrachloro-acids and pentachlorobenzoic acid.

The determination of 236 TBA in MCPA–TBA mixtures will be described in this part of the series. Part II describes the determination of 4C2M.

INTRODUCTION

Although the phytotoxicity of 236 TBA has been known for some time, it is only recently that commercial use has been made of its weedkilling properties. Because of this and the fact that other trichlorobenzoic acids have little commercial application, little work has apparently been carried out on the analytical chemistry, and particularly the quantitative separation, of chlorinated benzoic acids.

VELDSTRA[1] described an investigation of the U.V. spectra of some of the chlorobenzoic acids but his paper was mainly concerned with the determination of the effect of physical structure on physiological activity. It is clear from this paper that the

* Commercial name "Fisons 18–15".

direct determination of 236* by spectrophotometric methods will be extremely difficult, bearing in mind the complexity of technical TBA and the comparative similarity of spectra of the acids present.

It is probable that infra-red spectrophotometric methods could be used for the determination of 236, but in the absence of a suitable instrument at the time, it was decided to investigate partition chromatography.

The paper chromatography of chlorobenzoic acids has been described[2] and a liquid–liquid chromatographic method for separation of mono-chlorobenzoic acids is given by BHARGAVA AND HEIDELBERGER[3].

From theoretical considerations, it was expected that the di-*ortho* substituted acids would be stronger acids than their corresponding isomers. It should therefore be possible, for example, to separate 236 from 245 easily by partition between an organic solvent and a buffer solution. However, separation of, for example, 236 from 246, might be more difficult. It was thought that chromatographic separation of the MCP acids from 236 would present no difficulty.

Consequently an attempt was made to apply the experience, gained in this laboratory with liquid–liquid chromatographic methods, to the problem.

EXPERIMENTAL

Some preliminary U.V. spectrophotometric measurements were carried out on all the chlorobenzoic acids which were possible impurities. This work confirmed VELDSTRA's observations that "*ortho* substitution" appreciably reduced the molar extinction coefficient. Quantitative U.V. measurements on solutions of the chlorobenzoic acids in organic solvents enabled us to determine partition coefficients at low concentrations, between these solvents and aqueous solutions.

The first aim was to find a pair of solvents between which the partition coefficient** of 236 was about 1 : 3 to 1 : 15. To determine the effect of "polarity" of the moving phase, iso-octane, chloroform and ether were tried in separating funnel experiments involving a solvent and either a mineral acid or phosphate buffer solution.

The solubility of the acids is very low in iso-octane (236 *ca.* 2 g/l; 245 *ca.* 0.2 g/l) and the only work ever carried out with this solvent was separating funnel experiments with varying concentrations of hydrochloric acid as aqueous phase. Iso-octane and *N* hydrochloric acid gave suitable partition coefficients but the system was extremely sensitive to small changes in the acid concentration.

It was found that a suitable partition coefficient with 236 in chloroform could be obtained only by using 0.25 *M* sodium dihydrogen phosphate–phosphoric acid buffers containing a very small proportion of phosphoric acid. At this pH the buffer is not very efficient, and would probably result in asymmetric elution peaks if applied to liquid–liquid chromatography.

Ether was a slight improvement from the point of view of obtaining a suitable partition coefficient with a stable buffer, (A 12 : 1 mixture of 0.25 *M* NaH_2PO_4 and 0.25 *M* Na_2HPO_4 gave a figure of 1 : 5 for 236) and work was continued with this solvent system. In order to assess whether chromatographic separations were likely

* Throughout this paper these acids will be referred to by the position of their chlorine atoms (*e.g.* "236" = 2,3,6-trichlorobenzoic acid).

** All partition coefficients are expressed organic solvent: aqueous solution.

to be achieved, 245, 2356, and 26 were also examined and the approximate partition coefficients (at 0.25 mg/ml original concentration in ether and at room temperature) were 2.5 : 1, 1 : 3.3 and 1 : 11 respectively.

Chromatography using ether as solvent

Preliminary experiments with column chromatography were accomplished using columns 10 cm long by 9 mm diameter and prepared from 3.25 g of Celite 535* mixed with 1.6 ml of the chosen buffer. Using rather coarse kieselguhr these columns were easy to pack by MARTIN's method and gave an indication of the retention factor to be expected. The flow rate (2 ml/min) was the fastest which could be practically used with the method of detection employed (U.V. spectroscopy). Using the "12 : 1 buffer" column, 245, 2356, 236, and 26 were eluted in the predicted order, the elution volumes being, respectively, 4 ml, 6 ml, 10 ml and 14 ml.

These results showed that slightly more alkaline conditions would give better separations and exploratory columns were therefore prepared from 8 : 1 and 4 : 1 buffer solutions which indicated that 8 : 1 buffer would probably give the most satisfactory results.

Consequently, "full size" columns were prepared using a glass column 35 cm long by 1.4 cm diameter packed with 25 g of Hyflo Super-Cel containing 12.5 ml of phosphate buffer prepared from 8 vol. 0.25 *M* solution of sodium dihydrogen phosphate and 1 vol disodium hydrogen phosphate. The positions of the acids on the chromatogram derived from this column were determined spectrophotometrically in the effluent at 270 mμ. Table I shows partition coefficients of a number of acids, expected to be

TABLE I

APPROXIMATE PARTITION COEFFICIENTS OF CHLOROBENZOIC ACIDS

(Original concentration *ca.* 0.25 mg/ml ether, ether: 8 : 1 buffer solution)

Acid	*Coefficient calculated from chromatography*	*Coefficient from separating funnel experiments*
23	1 : 4.4	—
24	1 : 1.6	—
25	1 : 1.6	—
26	1 : 15	1 : 19
34	1 : 0.8	—
35	1 : 0.8	—
345	1 : 0.8	—
235	1 : 1.4	—
245	1 : 0.8	1 : 0.5
234	1 : 1.4	—
246	1 : 7.9	—
236	1 : 8.2	1 : 8.7
2346	1 : 4.7	—
2356	1 : 4.8	1 : 5.0
2345	1 : 1.5	—

* Supplied by Johns Manville Ltd., Artillery Row, London.

present, determined by separating funnel experiments. The first column of the table shows partition-coefficients derived from chromatography. These figures are necessarily inaccurate because of the asymmetry displayed by the eluted peaks.

It was evident that 236 + 246 could be separated from the other acids. The chromatographic method was therefore applied to synthetic mixtures of chlorobenzoic acids and to technical TBA samples. The acids in the effluent fraction from the column were determined by non-aqueous titrimetry using FRITZ AND LISICKI's[3] method with 0.01 *N* sodium methylate in 6 : 1 benzene: methanol and thymol blue indicator. Analytical results were satisfactory and the method was used for some time in the routine determination of 236 + 246 in Technical TBA.

It was clear however, from asymmetry of the eluted peaks, that overloading of the columns was probably occurring resulting in occasional imperfect separation. Some improvement was achieved by increasing the pH of the buffer by reducing the ratio to 6 : 1, but a far greater improvement was found by increasing the concentration of buffer used as static phase. Buffer solutions made from 4 *M* sodium phosphate solutions were found to be impracticable because of the relatively low solubility of the sodium salts of some of the acids (*e.g.* 245 and 2356) observed in the course of separating funnel experiments. This difficulty did not arise with "2 *M*" buffers but the preparation of solutions of this concentration presented solubility problems. The potassium salt was therefore substituted for disodium hydrogen phosphate.

Table II, which shows partition ratios obtained by equilibrating 10-ml quantities of the two components of the system, illustrates the improvement achieved by a change of concentration of buffer and shows a dependence of partition ratio on concentration likely to cause trailing peaks with "0.25 *M*" buffer, whereas, although a slight concentration effect is observed with "2 *M*" buffer, the sense is reversed resulting in practically symmetrical peaks.

TABLE II

EFFECT OF CONCENTRATION ON PARTITION COEFFICIENT OF 236 BETWEEN DIETHYL ETHER AND BUFFER SOLUTIONS

Original weight of acid in mg/10 ml ether	*Partition coefficients*	
	6 : 1 "0.25 M" buffer	*1 : 1 "2 M" buffer*
0.90	1 : 30	1 : 5.0
2.25	1 : 26	1 : 6.0
4.5	1 : 21	1 : 6.2
6.75	1 : 19	1 : 7.0
9.0	1 : 17	1 : 7.5
11.25	1 : 16	1 : 7.4
13.5	1 : 15	1 : 7.2
15.75	1 : 14	1 : 8.0
18.0	1 : 13	1 : 8.4

A different ratio of phosphate solutions is required when using 2 *M* phosphate solution since concentration in the aqueous phase profoundly affects the partition coefficient and also the pH of mixture. A 1 : 1 ratio of the two 2 *M* phosphate solutions was found to be satisfactory, and has high buffer stability. Although the retention factor is lower than that with 0.25 *M* buffer, the symmetry of the eluted fraction enables satisfactory separations to be obtained.

A series of synthetic mixtures of chlorobenzoic acids was analysed using "full-size" columns (ether: "2 *M*" phosphate buffer) and typical results are given in Table III which shows that the method was reasonably accurate.

TABLE III

RECOVERIES OF CHLOROBENZOIC ACIDS USING ETHER/"2 *M*" BUFFER CHROMATOGRAPHIC COLUMNS

Acid	*Theory %*	*Percentage*		
		1	*2*	*3*
245	44.5	45.6	44.6	44.5
2356	23.7	23.1	23.9	24.2
236	31.8	31.2	31.0	31.4

Total weight of sample = 10 mg.

Chromatography using isopropyl ether as solvent

The use of ethyl ether was satisfactory under normal conditions but, during very hot weather, the high evaporation rate resulted in a number of columns giving inadequate separations. It was therefore decided to investigate an alternative solvent, and isopropyl ether was chosen. Commercially available isopropyl ether was found to be satisfactory after an initial chemical purification (distillation was avoided owing to its known hazard).

As expected, it was necessary to reduce the pH of the static phase to achieve suitable partition ratios when operating on the isopropyl ether column. A ratio of 7.5 ml of 2 *M* sodium dihydrogen phosphate to 5.0 ml of 2 *M* dipotassium hydrogen phosphate gave satisfactory results (including separation of 236 from 246) and details of the method finally adopted are given later. Fig. 1. shows the type of separation obtained.

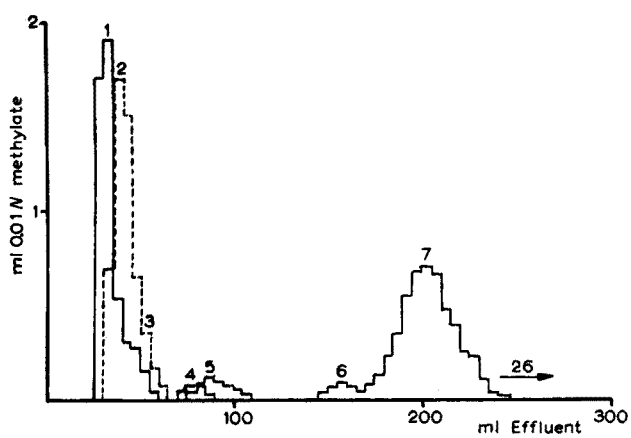

Fig. 1. Types of separation obtained: – – – – MCPA; ———— TBA; (1) Mixed chlorobenzoic acids; (2) 4C2M + 46C2M; (3) 6C2M; (4) 2 *M*; (5) 23, 2346, 2356; (6) 246; (7) 236.

The first eluted acid fraction contains monochlorinated acids, 24, 25, 34, 35, 234, 235, 245, 345, 2345, and a partial separation of these constituents into two "peaks" occurs in this fraction. The second eluted acid fraction contains 23, 2346, 2356, with

a slight separation of the dichloro-acid from the two tetrachloro-acids. The third eluted acid fraction contains 246 (which is usually present in very small and only just detectable quantities) and is immediately followed by the fourth acid fraction containing 236. Finally 26 is eluted.

Experiments have shown that pentachlorobenzoic acid would be eluted between 245 and 2356. This would "blur" the first separation, but since sharp separations have always been obtained with commercial TBA samples it is assumed that pentachlorobenzoic acid is not normally present. This assumption is confirmed by synthetic work which proved that pentachlorobenzoic acid was extremely difficult to prepare.

At this stage, the constituents from the technical MCPA present in the formulation were checked for elution characteristics. It was found, as predicted, that all were eluted before 236 and the position of the phenoxyacetic acids are also shown superimposed on Fig. 1. Chlorocresols precede the first chlorobenzoic acids, and glycollic acid is removed during the preliminary ether extraction of acids described in "Method".

As a final check on the qualitative validity of the proposed method, a sample of commercial formulation was chromatogrammed. The 236 fraction was compared with a solution of pure 236 by ultraviolet spectrophotometry. There was no detectable difference between the two spectra.

Titrimetry of eluted fractions

Quantitative chromatographic work, involving non-aqueous titrimetry of the eluted isopropyl ether fractions with 0.01 *N* sodium methylate in 6 : 1 benzene–methanol and thymol blue indicator showed that recoveries of up to 105% were obtained. The modified titration stage was therefore carefully reinvestigated using a potentiometric method of comparison.

The apparatus used was a U-shaped cell with a sintered glass disc in one of the limbs. The longer arm was half filled with a saturated solution of lithium chloride in methanol and contained a saturated calomel electrode. The other limb was two-thirds filled with a solution of the acid under examination in isopropyl ether and contained a glass electrode and a fine stainless steel needle reaching to a point just above the sintered glass disc. Nitrogen was led in through this needle and the glass electrode was placed as close as was practicable to the sintered glass disc. The pH meter used was checked for grid current on the input valve and although the whole apparatus was shielded electrically it was necessary to avoid external electrical interference.

Experiments were carried out using four typical acids present in commercial TBA (26, 245, 236, 2356). The potentiometric titration of these acids immediately showed that the colour change of the indicator used in previous work was not coincident with the inflection point. Examination of numerous indicators showed that bromothymol blue gave better results on the 5-ml scale used. It did, however, demonstrate that some shift of colour change with this indicator occurred with increasing concentration of titrant. A change to a similar titrant with dried isopropyl ether substituted for benzene was found to diminish but not eliminate the effect and the poor solubility of bromothymol blue in isopropyl ether, rendered some fractions untitratable. An immediate benefit was found by adding sufficient methanol to the eluent to match the composition of the titrant solvent and the colour changes were then found to be coincident with inflection points at concentrations of the four acids ranging from 1–6 mg/5 ml of eluent solution.

It was proposed to use benzoic acid as a primary standard for sodium methylate titrant, so this acid was also tested in a similar way. It was found to give an inflection point at the colour change of bromothymol blue within the same range of concentration as the acids investigated above. It suffers from the slight defect of low solubility of the sodium salt in the titrant but this did not influence the accuracy of standardisation.

Diethyl ether was used as a convenient solvent for the prepared sample (for chromatography or determination of "total acidity") and for benzoic acid for standardisation. The small quantity of diethyl ether used was shown not to affect the accuracy of the end-point and this solvent had the advantage of higher solvent power for the acids. The blank in all cases was negligible.

The use of bromothymol blue is, as noted above, complicated by the low solubility of the indicator in isopropyl ether and, in the case of the fractions of large volume, the original indicator, thymol blue, was retained because, although the results were slightly in error, the quantities of 26 (the only acid titrated in large volumes) present in commercial formulations are usually small enough to render this error negligible.

METHOD

Apparatus

The chromatograph tube consists of 35 cm of glass tube of 14 mm i.d., the lower end reduced to 5 mm i.d., and with a B.19 socket at the upper end fitted with ears for retaining springs below the joint. The solvent is contained in a tap funnel provided with B.19 joints at top and bottom and with ears to mate up with the corresponding ears on the tube. A 5- or 10-ml microburette calibrated in 0.01-ml divisions is used for the titrant: 1-ml pipette graduated between two marks.

Reagents

All reagents of analytical reagent grade unless otherwise stated.

Benzoic acid; dilute hydrochloric acid (1 : 1); diethyl ether (laboratory reagent grade); sodium sulphate (anhydrous); nitrogen.

Prepared kieselguhr

Allow Hyflo Super-Cel* to stand overnight under concentrated hydrochloric acid, wash with water until the washings are neutral to litmus and dry at 100–110° in an oven.

Equilibrated isopropyl ether (moving phase)

Wash technical isopropyl ether (Shell Chemical Co.) twice with 1 *N* sodium hydroxide solution and successively with water until the washings are neutral to litmus.

Buffer solution

(*A*) potassium hydrogen phosphate 2 *M*; (*B*) sodium dihydrogen phosphate 2 *M*.

Mix in proportions 1 volume of *A* and 1.5 volume of *B* and shake with an equal volume of equilibrated isopropyl ether before use.

Preparation of the column

Weigh 25 g of prepared Hyflo Super-Cel into a mortar. Add dropwise from a graduated pipette with stirring, 12.5 ml of buffer solution. Triturate gently but thoroughly to homogenize the Hyflo Super-Cel buffer mixture. Add sufficient equilibrated isopropyl ether to form a thin slurry and mix well. Having plugged the bottom of the column with a small wad of ether-extracted cotton wool, pack the slurry into the column, with a perforated disc plunger using MARTIN's[4] method. The length of a

* Supplied by Johns Manville Ltd., Artillery Row, London.

normal column is about 30 cm. Wash through with about 50 ml of equilibrated isopropyl ether using an applied pressure, at 2.5–3 ml/min.

Titrant (0.01 N sodium methylate in isopropyl ether)

Dissolve 2.5 g of metallic sodium in 100 ml of methanol (purified by distillation from potassium hydroxide), cool and add to 800 ml of dried isopropyl ether (washed with sodium hydroxide and dried over sodium sulphate followed by sodium). Add a further 100 ml of purified methanol. This produces an approximately 0.1 *N* "stock titrant" which should be allowed to stand 2–3 days before use. It should be kept in a bottle and protected from carbon dioxide.

To prepare the 0.01 *N* sodium methylate, mix 400 ml of purified and dried isopropyl ether with 100 ml of purified methanol. Pass nitrogen through for 15 min. Add 50 ml of 0.1 *N* "stock titrant" (carefully pipette to avoid any deposit and to avoid absorption of carbon dioxide) and continue passing nitrogen in order to mix thoroughly. The 0.01 *N* solution should be protected from atmospheric carbon dioxide. The method of standardisation is given below.

Indicator (1)

Dissolve 0.1 g of bromothymol blue in 50 ml of purified methanol. Pass nitrogen through this solution and add sufficient "stock titrant" to convert the indicator to the green form. Add this solution to 1 l of purified methanol which has had carbon dioxide removed by bubbling purified nitrogen through it for 15 min. This solution should be stored in a bottle equipped with suitable dispensing devices incorporating means for the exclusion of atmospheric carbon dioxide.

Indicator (2)

Dissolve 0.4 g of thymol blue in 100 ml of purified methanol and add sufficient "stock titrant" to give the neutral colour.

Standardisation of titrant

Weigh out accurately about 0.5 g of benzoic acid. Dissolve in diethyl ether and make up to 100 ml in a volumetric flask after adjusting the temperature to 20°. Pipette, at 20°, a 1-ml aliquot into a clean dry test tube (*Note 1*, p. 279), pass nitrogen for 1 minute and titrate with 0.01 *N* methylate using 1 ml of indicator (1) to the green colour of the indicator. Repeat the standardisation at least twice. If W_s is weight of benzoic acid used and t_s is the titre:

$$\text{Normality} = 8.19 \frac{W_s}{t_s} \times 0.01\ N$$

PROCEDURE

(1) Preparation of sample

Weigh accurately sufficient sample to contain 1.8–2.2 g (*Wg*) of acids. Dilute to 60–80 ml with distilled water and add, with good agitation, sufficient 1 : 1 hydrochloric acid to make the solution definitely acid. Extract with 3 × 30-ml of diethyl ether, combine the solvent extracts and wash with 2 × 10-ml portions of distilled

water. Combine the water washings and shake them with 10 ml of ether. Combine all the ether extracts, dry with sodium sulphate and make up accurately to 200 ml with diethyl ether after adjusting the temperature to 20°. This is the stock solution. It should be used at 20° and evaporation losses should be avoided.

(2) Determination of "total acids" content of stock solution

Pipette 1 ml of stock solution at 20° into a test tube (*Note 1*). Pass nitrogen through for 1 min and titrate with 0.01 *N* titrant using 1 ml of indicator (1) to the green colour. If t = ml of 0.0100 *N* methylate consumed, f = factor of titrant, then the "total acids" content (expressed as TBA):

$$= \frac{45.1t}{W} \% \text{ w/w.}$$

(3) Determination of 2,3,6-trichlorobenzoic acid

Apply nitrogen pressure to the top of the column until the moving phase just falls to the level of the kieselguhr packing. Release the pressure and pipette (*Note 1*, p. 279) 1 ml of stock solution at 20° on to the top of the column and force the ether layer down to the top of the packing. Wash down the sides of the column with 2 ml of moving phase and again apply pressure to the top of the column until the solvent has fallen to the level of the kieselguhr. Repeat this operation. Fill the reservoir, fit to the top of the column and apply sufficient pressure to produce a flow rate of 2 ml/min. Collect 60 × 5-ml fractions followed by 2 × 100-ml fractions. Pass nitrogen for 1 min through each 5-ml fraction and titrate to the green colour with 0.01 *N* methylate titrant using indicator (1). Pass nitrogen for 2 min through each 100-ml fraction and titrate to the grey colour with 0.01 *N* methylate using indicator (2). The resultant titres will fall into five groups (*Notes 2* and *4*).

Fractions 1–4: These contain no significant titratable acids since they represent the dead volume of the column.

Fractions 5–12: These fractions contain the chlorobenzoic acids except 23 and the di-*ortho* substituted acids together with all the MCP acids.

Fractions 13–27: These fractions contain 2356, 2346, and 23.

Fractions 28–60: These fractions contain 246 and 236 which are usually separated (*Note 3*).

Fractions 61–62 (100 ml): These fractions contain 26.

Calculation of "active" (236 content)

The titres in group 4 fall into two distinct fractions resolved or resolvable by inspection. The second and major fraction is 236. If titre of 236 fraction in ml 0.01000 *N* methylate = t ml, then

$$\% \text{ 236 in sample} = \frac{45.1t}{W} \% \text{ w/w}$$

Notes

1. It is important that the same pipette is used for standardisation, determination of "total acids" and chromatography. Considerable care should be taken during

pipetting operations, to avoid loss of isopropyl ether by "creeping" or evaporation. Care should also be taken to avoid errors due to temperature changes (isopropyl ether has a relatively high coefficient of expansion).

2. The distribution of the acids on the column is slightly dependent on packing technique. The numbers of fractions shown should be taken as a guide, as slight variations in position may occur from column to column. It is preferable to run a synthetic sample or known commercial sample to check the column before analysing an unknown.

3. The efficiency of column varies somewhat with the skill of the operator packing the column. In our experience all columns achieve satisfactory separations into the five "groups" indicated, but columns sometimes fail to separate 236 and 246 completely in "group 4". 246 is usually present in small quantities (up to 5% of the 236 content) and even when a complete separation is not achieved, an approximation can usually be made which is accurate enough for most practical purposes.

4. With some commercial samples, it has been found that the sum of the fraction titres does not equal the amount predicted from the "total acid" content of the stock solution. This is due to the presence of small quantities of unidentified acids which are not eluted from the column until after the 26 and in some cases are retained on the column. For this reason it is inadvisable to use columns for more than two determinations on certain commercial samples.

DISCUSSION

The partition coefficients of the acids, using the isopropyl ether/"2 *M*" buffer system finally adopted, have not been determined directly by separating funnel experiments, but practical column experiments show that there is little difference in the relative positions of acids when compared with the ether/"0.25 *M*" buffer system which was investigated earlier. The partition data of typical acids calculated from column performance using the adopted method is given in Table IV.

TABLE IV

PARTITION COEFFICIENT OF TYPICAL CHLOROBENZOIC ACIDS CALCULATED FROM COLUMN MEASUREMENTS

Acid	*Partition coefficient*
245	1 : 0.8
2356	1 : 4.8
236	1 : 14.0

The partition isotherms of the acids were still virtually linear so that symmetrical peaks were obtained.

Chromatographic analyses of standard solution of pure acids have been carried out and the results obtained confirm the accuracy expected from the potentiometric study. Since the "p*K* values" of other possible acidic impurities are unlikely to differ appreciably from those tested it was assumed that the titration technique was valid for commercial formulations. Results obtained on a mixture of pure TBA acids are given in Tables V and VI.

TABLE V

RECOVERIES OF CHLOROBENZOIC ACIDS USING ISOPROPYL ETHER/"2 *M*" BUFFER CHROMATOGRAPHIC COLUMNS

Acid	*Added*	*Found*					
		1	*2*	*3*	*4*	*5*	*6*
245	41.5	41.4	41.4	41.6	41.2	42.8	42.4
2356	17.5	18.0	18.0	18.4	18.1	17.4	17.1
236	41.0[a]	40.4	40.4	40.1	40.6	39.8	40.5

[a] Total weight of sample is 10 mg. The 236 acid was shown chromatographically to contain *ca.* 1% of 2356.

TABLE VI

DETERMINATION OF 236 IN PRESENCE OF TECHNICAL MCPA

MCPA present (4C2M)	*236 present g/l*	*236 found g/l*	
100	48	48.5	48.8
100	24	23.7	24.3
50	48	49.2	48.5
50	96	97.0	96.6

ACKNOWLEDGEMENTS

The authors would like to thank G. F. LAWS and H. G. HAYNES for synthesising most of the chlorobenzoic acids used in checking the method, and the directors of Fisons Pest Control Limited for permission to publish this paper.

SUMMARY

A liquid–liquid partition chromatographic method has been developed for the determination of 2,3,6-trichlorobenzoic acid in MCPA/TBA herbicides. The system used is isopropyl ether–phosphate buffer and eluted acid fractions are titrated in non-aqueous solution with sodium methylate solution. The effect of all possible chlorobenzoic acid and methyl chlorophenoxyacetic acid impurities has been investigated. A precision of about $\pm 2\%$ is applicable to the method.

RÉSUMÉ

Une méthode chromatographique a été mise au point pour le dosage de l'acide trichloro-2,3,6-benzoïque dans des herbicides. On effectue un titrage de l'éluat, en solution non aqueuse, au moyen de méthylate de sodium.

ZUSAMMENFASSUNG

Beschreibung einer chromatographischen Methode zur Bestimmung von 2,3,6-Trichlorbenzoesäure in Herbiciden durch Titration mit Natriummethylat in nicht-wässrigem Medium.

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THE DIRECT DETERMINATION OF URANIUM IN CONCENTRATES BY SPECTROPHOTOMETRIC TITRATION WITH FERRIC SULPHATE

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INTRODUCTION

Methods most widely used at present for the determination of large amounts of uranium involve reduction of uranium to the +4 state with metallic reductors such as lead, zinc or cadmium, followed by titration with ceric sulphate, potassium dichromate or sodium vanadate[1]. These methods, however, may not be directly applied to uranium concentrates, since several elements, particularly iron, interfere seriously. For this reason a preliminary separation of uranium is usually carried out. The determination may be made much more selective by the use of a milder agent, such as bismuth metal or amalgam for reduction of uranium, and a milder oxidant, such as ferric sulphate, for titration of the reduced solution. Under these conditions the only common interfering elements are those which induce the atmospheric oxidation of uranium(IV)[2]. This may be controlled to some extent by carrying out the reduction and titration under nitrogen.

The titration of uranium(IV) with iron(III) is usually carried out at 90°, and the end-point detected potentiometrically[3,4]. Titration at this high temperature is inconvenient, and the danger of atmospheric oxidation is greatly increased. It is shown in this paper that high temperatures are necessary only for the rapid establishment of equilibrium potentials at the indicator electrode, since in dilute sulphuric acid solution at room temperature the oxidation of uranous ions by ferric ions is very rapid. This reaction has previously been investigated spectrophotometrically[5,6], and amperometrically at the dropping mercury electrode[5].

A procedure for the determination of uranium in concentrates is described in this paper, in which reduction is carried out under nitrogen with bismuth amalgam, and the reduced solution is titrated spectrophotometrically with ferric sulphate in a nitrogen atmosphere. Copper, molybdenum and vanadium interfere to some extent, but are not usually present in Australian uranium concentrates in sufficient amounts to cause serious error. A complete determination may be carried out in about 70 min, with a precision of 2 to 3 parts per thousand.

Apparatus

Spectrophotometer: A Hilger "Uvispek" was used without modification. A carriage for the titration cell was constructed from perspex, and shaped to fit in the position of the normal cell carriage. A raised cover for the cell compartment was also made of perspex. Three holes were drilled in the cover, two for nitrogen tubes, and one for the burette tip. Both the cover and the cell carriage were painted matt black.

Titration cell: This is shown in Fig. 1. The T-shaped titration cell had two flat, circular windows cemented to the body of the vessel, and a light path of about 3 cm. The nitrogen inlet and outlet connecting tubes were Nylex, painted matt black, and closed at the ends by stopcocks. Nitrogen was used both to stir the solution and to exclude oxygen. The burette port of the titration cell was closed by a small serum cap.

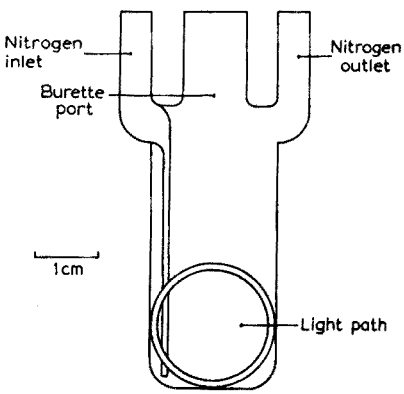

Fig. 1. Titration cell.

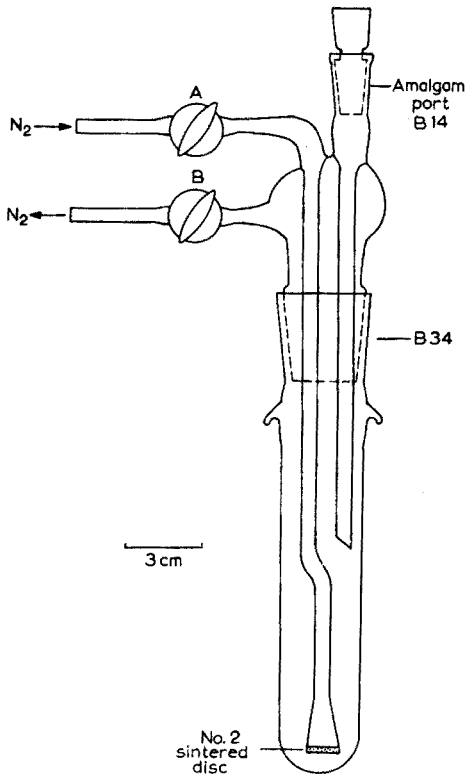

Fig. 2. Reduction vessel.

Reduction vessel: This vessel, shown in Fig. 2, is a modification of that described by SCRIBNER AND REILLEY[7]. By diluting the sample solution to volume before reduction, and taking an aliquot of the reduced solution, the greatest difficulty in the use of liquid amalgams, viz. quantitative separation of the two phases, is obviated.

Burette: An A-grade 5-ml burette, graduated in 0.01-ml divisions was used. A short piece of heavy-walled rubber tubing was fitted to the tip to act as a light seal. The burette is positioned so that its tip is just immersed in the solution in the titration cell.

Cathode ray polarograph: A linear-sweep cathode ray polarograph from Southern Instruments Computer Division, England, was used for the oxidation-rate studies.

The uranous–ferric reaction

There is some confusion in the literature regarding the rate of oxidation of uranous ion by ferric ion. Several authors[3,8,9] have reported the reaction,

$$U(IV) + 2\ Fe(III) \rightarrow U(VI) + 2\ Fe(II)$$

to be very slow at room temperature. Others[5] have suggested that the reaction is rapid if carried out in a suitable medium.

In order to determine the optimum conditions for the titration of uranium(IV) with iron(III) at room temperature, the reaction was studied in sulphuric, hydrochloric and perchloric acid solutions, using spectrophotometry and cathode ray polarography. The uranium(IV) concentration may be followed on a spectrophotometer by utilizing the sharp absorption peak of U(IV) at 650.0 mμ, and both the uranium(VI) and iron(III) concentrations at any instant may be determined by cathode ray polarography. These two separate techniques showed that:

1. In sulphuric acid solutions less than 1 *N* acid, the reaction at 20° is very rapid, equilibrium being established in less than 10 sec even when the titration is 80% complete. The rate decreases with increasing acid concentration, but the titration is still practicable up to 5 *N* H_2SO_4.

2. In perchloric acid solutions the reaction is slower than in sulphuric acid, and the rate decreases with increasing acid concentration.

3. In hydrochloric acid solutions at room temperature the oxidation of uranous ion by ferric ion is extremely slow, even at low acid concentrations. This is probably due to the formation of an iron(III)-chloro complex, which lowers the standard potential of the Fe^{+2}/Fe^{+3} system.

These results show that dilute sulphuric acid is the most suitable medium for the proposed titration. The end-point may be detected spectrophotometrically or amperometrically at the dropping mercury electrode.

The titration may also be carried out in 0.5 *N* H_2SO_4 at room temperature using amperometry with two polarised platinum electrodes ("dead-stop" end-point), and an applied potential of 10 mV. The titration is rather slow before the end-point, but the first trace of excess ferric ion causes an immediate steady galvanometer reading. Oxygen should be excluded during the titration by bubbling nitrogen. The detection of the end-point is not as precise as by spectrophotometric titration.

The following potentiometric indicator systems did not give a satisfactory end-point at room temperature in 0.5 *N* H_2SO_4: S.C.E. – Pt, S.C.E. – Hg, W – Pt and Pt – Pt (polarized 1.5 μA). The failure of these potentiometric systems to detect the end-point is apparently due to sluggishness in the setting up of an equilibrium potential at the indicator electrode.

Spectrophotometric detection of end-point

The spectrophotometric titration of uranium(IV) with ferric ammonium sulphate may be followed either by utilizing the sharp absorption peak of U(IV) at 650 mμ[5], or the Fe(III) wave at 350 mμ[6]. Uranium(IV) in sulphuric acid solution obeys Beers' law over the concentration range studied, and has a molar absorptivity of 42 at 650 mμ. This is a convenient sensitivity for the conditions of the determination, and, moreover, the molar absorptivity remains constant over a sulphuric acid concentration range of at least 1–7 *N*. It is also advantageous to work in the visible region if the spectrophotometer is to be used for other routine estimations. Uranyl, ferrous and ferric ions in sulphuric acid solution have molar absorptivities of less than one at 650 mμ.

In order to minimize induced oxidation of uranium during the titration, a relatively high acidity, 3.5 *N*, was used. At this concentration of sulphuric acid the reaction is rather slow in the vicinity of the end-point, and readings are not taken in this region.

A typical titration plot is shown in Fig. 3. A titration may be carried out in 15 min.

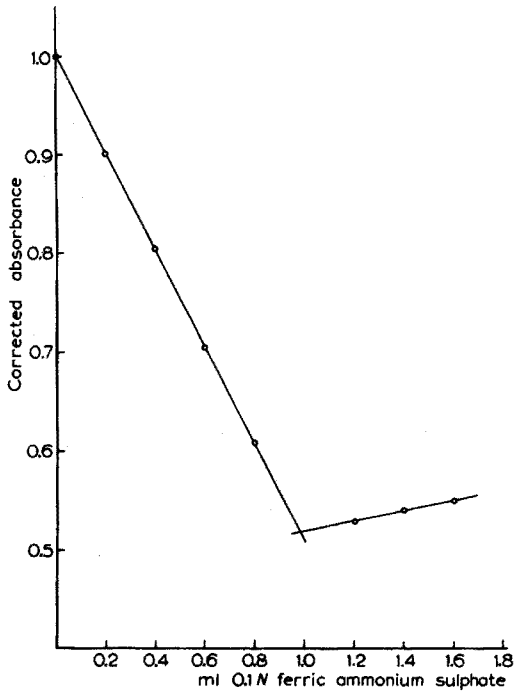

Fig. 3. Spectrophotometric titration of uranium(IV) with ferric sulphate.

Reduction of uranium with bismuth amalgam

The reduction of uranyl ion by bismuth amalgam may be represented by:

$$3\ UO_2^{+2} + 2\ Bi + 8\ H^+ \rightleftharpoons 3\ U^{+4} + 2\ BiO^+ + 4\ H_2O$$

Conditions for the reduction are therefore favoured by high sulphuric acid concentrations[10,11]. A shaking time of over an hour is required for complete reduction in 3 *N* H_2SO_4, 20 min in 5 *N* H_2SO_4 and 5 min in 7 *N* H_2SO_4. Reduction proceeds only to the +4 state in 7 *N* sulphuric acid. Very little reaction occurs in perchloric acid solutions of any concentration.

If large amounts of oxidizing agents are present in the sample solution, they should be removed by a preliminary reduction with hydroxylamine sulphate.

EXPERIMENTAL

Reagents

Bismuth amalgam: Add 20 g of reagent grade granular bismuth to 900 g of pure mercury. Cover the mixture with 1 *N* sulphuric acid and warm and stir until dissolved. Cool to room temperature, then wash the amalgam well with water. Transfer to a separatory funnel, and allow the liquid portion of the amalgam to drain into a second funnel containing 1 *N* sulphuric acid. Store the amalgam in this funnel and run off as needed.

0.1 N ferric ammonium sulphate: Dissolve 12 g of reagent-grade material in 3.5 *N* sulphuric acid.

Dilute to 250 ml with 3.5 N H_2SO_4. Standardize against pure, dry U_3O_8, using the procedure outlined.

Nitrogen: Commercial nitrogen containing less than 5 v.p.m. of oxygen was used without further purification.

Procedure

Weigh a dried sample of the concentrate containing 50–100 mg U_3O_8 into a small flask. Dissolve by heating with 10 ml of 2.5 N $HClO_4$. Evaporate to fumes of $HClO_4$ to dehydrate silica, and continue heating until the silica is colorless. Dilute with water, filter, and wash with hot 0.1 N H_2SO_4. Add 5 ml of conc. H_2SO_4 to the filtrate, cool, and dilute to 25 ml in a volumetric flask.

Transfer about 15 ml of the solution to the dry reductor tube. Insert head of vessel and connect nitrogen source. Open cock A and pass nitrogen at a moderate rate for 1 min. Close cock A and simultaneously remove stopper from amalgam port. Add 2 ml bismuth amalgam with nitrogen still flowing. Replace stopper and open cock A. Close cocks A and B simultaneously. Remove the nitrogen tube, and clamp the reductor in the arm of a wrist-action shaker. Shake vigorously for 5–10 min. Pipette 5 ml of water into the titration cell and fit the serum cap. Place the cell in position in the spectrophotometer and pass nitrogen at a convenient rate. Set the wave length at 650 mμ.

Remove the head of the reduction vessel and, with a dry pipette, immediately transfer a 5-ml aliquot of the reduced uranium solution into the titration cell, through the serum cap. Insert the 5-ml burette containing 0.1 N ferric ammonium sulphate. Zero the instrument and set the absorbance scale reading at a convenient value, say 1.000. Close the nitrogen inlet and outlet taps, and with the selector switch on "measure", open the slit and adjust the "check" position to balance. Close the slit and pass nitrogen. Add the first increment of the titrant. Interrupt nitrogen flow, open slit and measure absorbance. Close slit, start nitrogen and add second increment of titrant. Repeat this procedure until a full titration curve is obtained. Correct each absorbance reading for the dilution effect, and plot corrected absorbance *versus* titre.

Study of interferences

Using the procedure described above, the following elements, when present in equal concentration to uranium (wt. %), did not interfere in the spectrophotometric titration:

Ce, Co, Cr, Fe, Ni, P, Sb, Sn, Ti and W.

Copper, molybdenum and vanadium interfered to varying degrees, and were studied in more detail.

Copper: Copper is notorious for its ability to induce the air-oxidation of uranium(IV)[2]. Slightly low results were obtained in the spectrophotometric titration even when extreme measures were taken to exclude oxygen from the titration cell. The error is approximately proportional to the copper concentration. The maximum permissible copper content, for an error of less than 2 parts per thousand, is 3% of the uranium concentration. Since uranium concentrates processed in this country usually contain less than 0.2% copper, this limit is not likely to be exceeded.

Molybdenum: In the presence of oxygen, molybdenum causes low results in the titration of uranium with ferric sulphate. If oxygen is excluded, however, slightly high

results are obtained. This is possibly due to the formation of traces of molybdenum (III) in the bismuth reductor. Molybdenum may be tolerated up to 2% of the uranium concentration.

Vanadium: Vanadium, like copper and molybdenum, induces the air-oxidation of uranium(IV). Vanadium is reduced only to the +4 state by bismuth amalgam in 7 *N* sulphuric acid. The maximum permissible vanadium content is 5% of the uranium concentration.

The presence of large amounts of ferrous iron, while not affecting the final result, causes the spectrophotometric titration in 3.5 *N* H_2SO_4 to be inconveniently slow. When analysing ores, where the iron content usually exceeds the uranium content, the sulphuric acid should not be more than 0.5 *N* during the titration.

Analysis of concentrates and high-grade ores

Table I shows the results obtained by the direct spectrophotometric titration on five standard uranium concentrates, and two standard high-grade ores. The concentrates were analysed by an independent laboratory using the classical method consisting of a cellulose column separation of uranium from nitric acid–ether solution, followed by precipitation with ammonia and ignition to U_3O_8. The uranium content of the ores was determined by cathode ray polarography after a mercury cathode separation[12].

TABLE I

DETERMINATION OF URANIUM IN CONCENTRATES AND ORES BY SPECTROPHOTOMETRIC TITRATION WITH FERRIC SULPHATE

Sample No.	*Direct spectrophotometric titration* % U_3O_8	*Number of determinations*	*Relative standard deviation(n–1)* %	*Reference method* % U_3O_8
C1	64.8	6	0.35	64.55
C2	63.1	6	0.19	63.35
C3	71.9	6	0.20	72.00
C4	23.90	4	0.33	23.90
C5	24.48	4	0.28	24.55
ore 1	8.33	3	0.54	8.3
ore 2	7.52	3	0.67	7.6

SUMMARY

A direct method is presented for the determination of uranium in concentrates by spectrophotometric titration with ferric sulphate, after a bismuth amalgam reduction. The oxidation of U(IV) by Fe(III) was found to be rapid and complete at room temperature, under suitable conditions. Copper, molybdenum and vanadium interfere to some extent, and their maximum permissible concentrations are discussed. A complete determination may be carried out in little over an hour with a precision of 2–3 parts per thousand. An Uvispek spectrophotometer was adapted for spectrophotometric titrations without modification of the instrument.

RÉSUMÉ

Une méthode est proposée pour le dosage de l'uranium. On procède par titrage spectrophotométrique de l'uranium(IV) au moyen de sulfate ferrique. L'uranium(IV) est obtenu par réduction au moyen d'un amalgame de bismuth.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung von Uran in Konzentraten durch spektrophotometrische Titration mit Eisen(III)-sulfat nach Reduktion mit Wismutamalgam.

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AUTOMATIC DERIVATIVE SPECTROPHOTOMETRIC TITRATION OF EXCESS EDTA IN THE DETERMINATION OF COBALT, COPPER OR IRON

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EDTA has been used for the determination of copper, iron and cobalt, and metal indicators have been applied to the end-point detection, in both direct titration or back-titration procedures[1]. However, the intense colors of EDTA complexes formed by these metals limit their determination to only a few milligrams. Lately WILKINS[2] introduced a class of metal indicators, "the metalfluorechromic indicators," which can be applied to the chelometric titration of macro amounts of metals yielding highly colored EDTA complexes. WILKINS used Calcein W as a visual fluorescence indicator in the determination of cobalt, iron, copper, chromium, and nickel in a back-titration procedure. The titrations were carried out in a dark enclosure under ultraviolet illumination, and the end-point for titration of excess EDTA was observed as a quenching of the green fluorescence of the free indicator.

Recently the authors described an automatic titration method for the determination of calcium and magnesium[3], which uses the automatic derivative spectrophotometric end-point detection system provided in the "Spectro-Electro" titrator[4]. The same method is well suited for both macro and micro automatic titration methods for copper, iron, and cobalt. Calcein W is used as an absorption indicator for the automatic end-point and as a fluorescence indicator to signal the presence of excess EDTA prior to back titration.

CHARACTERISTICS OF THE METHOD

A beaker of sample solution is inserted into the "Spectro" titrator, Calcein W indicator is added, and standard EDTA added until in excess, as indicated by a definite appearance of a green fluorescence. The fluorescence is easily observed visually from the illumination by the incident beam from the tungsten source in the "Spectro" unit. The small excess of EDTA is then automatically titrated in a few seconds with a standard copper solution using the same Calcein W as an absorption indicator. At the end-point a rapid increase in absorbance occurs at about 500 mμ when the last traces of free indicator are tied up with the copper. This absorbance change produces an end-point signal for automatic termination of the titration. The properties of Calcein W to both fluoresce and absorb in the visible and not to be blocked by copper, iron or cobalt make it advantageous over other metal indicators.

The absorption curves of the species present in the titration of copper, at the beginning of the back-titration, and of those present at the automatic end-point, at pH

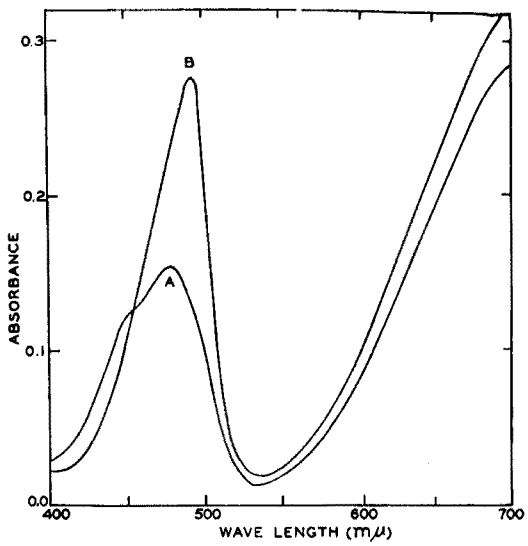

Fig. 1. Absorption spectra of copper complexes and free Calcein W. A. Cu-EDTA + Cu-Calcein W + excess EDTA + free Calcein W curve, $3.3 \cdot 10^{-3}$ *M* Cu-EDTA, $0.7 \cdot 10^{-3}$ *M* EDTA, 0.00015% Calcein W, buffered at pH 4.4, at the beginning of the back-titration. B. Cu-EDTA + Cu-Calcein W curve, $4 \cdot 10^{-3}$ *M* Cu-EDTA, buffered at pH 4.4, at the automatic end-point.

4.4, are given in Fig. 1. Similar curves are given for iron in Fig. 2 and for cobalt in Fig. 3. The absorption curves of free Calcein W and those of EDTA complexes of copper, iron, and cobalt are given in Fig. 4.

It can be seen from Figs. 1, 2 and 3, that at 500 mμ, the difference in absorbance between the absorbing species present at the beginning of the back-titration and those present at the automatic end-point is about the same, 0.14 of an absorbance unit for about 13 mg of copper, iron or cobalt in a volume of 60 ml. The relative change in absorbance becomes smaller as the concentration of metal increases, because the

EDTA complexes of copper, iron, and cobalt also absorb somewhat at 500 mμ (see Fig. 4).

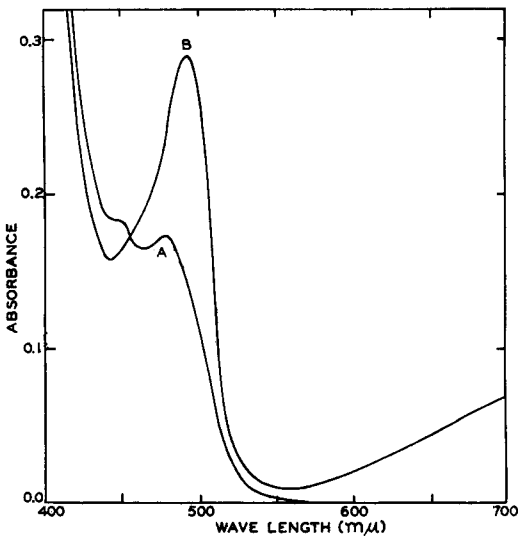

Fig. 2. Absorption spectra of iron complexes and free Calcein W. A. Fe-EDTA + Fe-Calcein W + excess EDTA + free Calcein W curve, $3.3 \cdot 10^{-3}$ *M* Fe-EDTA, $0.7 \cdot 10^{-3}$ *M* EDTA, 0.00015% Calcein W, buffered at pH 4.4, at the beginning of the back-titration. B. Fe-EDTA + Cu-EDTA + Cu-Calcein W curve, $3.3 \cdot 10^{-3}$ *M* Fe-EDTA, $0.7 \cdot 10^{-3}$ *M* Cu-EDTA, buffered at pH 4.4, at the automatic end-point.

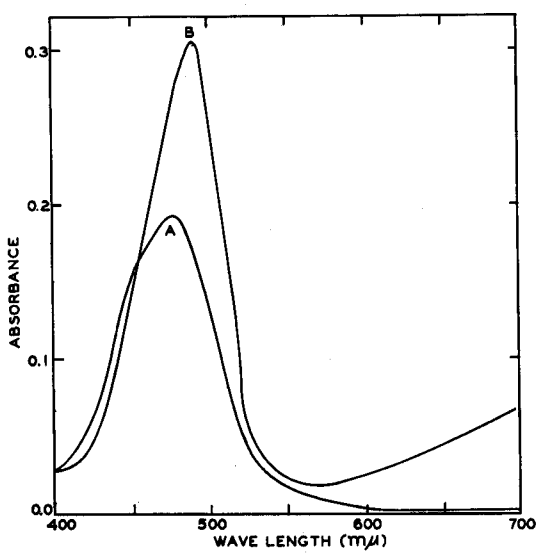

Fig. 3. Absorption spectra of cobalt complexes and free Calcein W. A. Co-EDTA + Co-Calcein W + excess EDTA + free Calcein W curve, $3.3 \cdot 10^{-3}$ *M* Co-EDTA, $0.7 \cdot 10^{-3}$ *M* EDTA, 0.00015% Calcein W, buffered at pH 4.4, at the beginning of the back-titration. B. Co-EDTA + Cu-EDTA + Cu-Calcein W curve, $3.3 \cdot 10^{-3}$ *M* Co-EDTA, $0.7 \cdot 10^{-3}$ *M* Cu-EDTA, buffered at pH 4.4, at the automatic end-point.

Recorded titration curves for copper, iron, and cobalt are shown in Fig. 5. It is seen that the change in voltage output for iron and cobalt decreases as the amount of metal titrated increases. However the rate of change in output voltage during a titration is a maximum at the equivalence point and sufficient to ensure an automatic end-point.

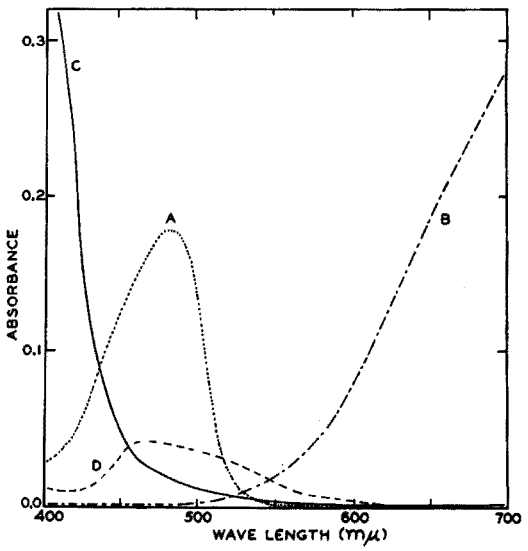

Fig. 4. Absorption spectra of free Calcein W, Cu-EDTA, Fe-EDTA, and Co-EDTA complexes. A. Calcein W curve, 0.00015% Calcein W buffered at pH 4.4. B. Cu-EDTA curve, $3.3 \cdot 10^{-3}$ *M* Cu-EDTA, buffered at pH 4.4. C. Fe-EDTA curve, $3.3 \cdot 10^{-3}$ *M* Fe-EDTA, buffered at pH 4.4. D. Co-EDTA curve, $3.3 \cdot 10^{-3}$ *M* Co-EDTA, buffered at pH 4.4.

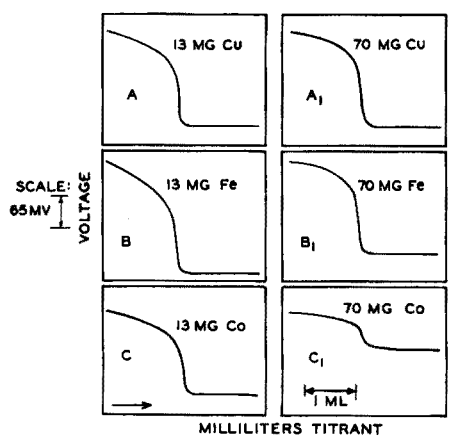

Fig. 5. Recorded curves from output of detector circuit for the EDTA back-titration of copper, iron and cobalt with Calcein W as indicator and copper as titrant. A and A_1. Copper + Calcein W at pH 4.4. B and B_1. Iron + Calcein W at pH 4.4. C and C_1. Cobalt + Calcein W at pH 4.4.

In curves A and B of Figs. 1, 2, and 3 the absorbance difference between about 600 and 700 mμ is due to the Cu–EDTA complex formed in the back-titration. This

results in a small continuous increase of absorbance up to the equivalence point. This could be used for detection of the end-point graphically, but it is not desirable for automatic termination.

The automatic end-points are reproducible and accurate within 0.01 ml of 0.04 *M* copper solution, or better, so that relative errors are within about ±0.1%.

Apparatus

The Sargent-Malmstadt "Spectro-Electro" titrator was used[4]. A 5-ml buret, graduated in 0.01-ml divisions and equipped with delivery and refill stopcocks and titrant reservoir was used for the standard copper solution and a 10-ml self-zeroing buret equipped with delivery and refill stopcocks for the EDTA solution.

Reagents

Standard 0.04 M copper solution: Dissolve 2.542 g reagent grade copper sheet in slight excess of concentrated nitric acid, heat to boiling to expel oxides of nitrogen and dilute to the mark in a 1-liter volumetric flask with deionized water.

EDTA solution: To prepare a 0.04 *M* EDTA solution, dissolve 14.89 g of disodium ethylenediaminetetraacetate dihydrate in deionized water and dilute to 1 liter. Standardize this solution against the standard copper solution and store it in polyethylene bottles.

Buffer solution: Mix 638 ml of 2 *N* acetic acid with 362 ml of 2 *N* sodium acetate.

Calcein W indicator: 0.1% in 0.001 *N* sodium hydroxide.

PROCEDURE

Preparation of automatic titrator

The "Spectro-Electro" titrator is switched to the "Spectro" position; the polarity switch thrown to position 2; the filter wheel turned to the 500 mμ position; the pegs in the base set to properly position the 100-ml beaker; stirrer No. A, delivery tips and burets for standard EDTA reagent and copper titrant connected; and the titrant delivery set at about 3 ml/min.

Standardization of EDTA solution

Pipet a 4-ml aliquot of EDTA solution into a 100-ml beaker, dilute to about 45 ml with deionized water and add 10 ml of the buffer and 4 drops of the indicator solution. Insert beaker in titrator, push the start button to start the delivery of titrant and read the buret after automatic termination at the end-point.

Titration of copper

Dilute the slightly acid sample solution of copper to about 40 ml with deionized water in a 100-ml beaker, buffer strongly, add 4 drops of indicator solution and insert the beaker into the titrator. Start the stirrer and add EDTA solution until the appearance of the green fluorescence of the free indicator. Push the start button to start the delivery of copper titrant and read the buret after automatic termination at the end-point.

Titration of iron or cobalt

The same procedure as for the titration of copper is applied.

RESULTS AND DISCUSSION

Analysis of solutions containing relatively large amounts of copper, iron, and cobalt gave the results shown in Table I. It is seen that the relative errors are about ±0.1%

TABLE I

AUTOMATIC TITRATION RESULTS FOR SAMPLES CONTAINING KNOWN AMOUNTS OF COPPER, IRON, AND COBALT

Sample No.	Copper		Sample No.	Iron		Sample No.	Cobalt	
	Taken, mg	Found, mg		Taken, mg	Found, mg		Taken, mg	Found, mg
1	5.08	5.08	9	4.47	4.48	17	4.71	4.72
2	5.08	5.09	10	4.47	4.47	18	4.71	4.71
3	10.17	10.18	11	11.17	11.19	19	18.82	18.81
4	10.17	10.18	12	11.17	11.15	20	18.82	18.84
5	25.42	25.43	13	22.34	22.33	21	28.23	28.23
6	25.42	25.42	14	22.34	22.34	22	28.23	28.20
7	50.83	50.86	15	44.68	44.66	23	47.38	47.41
8	50.83	50.85	16	44.68	44.69	24	47.38	47.41

or less. When small amounts ($<$ 10 mg) of metals are determined, either a more dilute (0.01 M) EDTA solution or a 5-ml microburet, can be used in order to decrease the effect of buret reading errors; a 0.01 M standard copper solution is used as titrant.

At a delivery rate of 3 ml/min a blank of 0.03 ml of 0.04 M copper solution is applied; a blank of 0.05 ml is applied when 0.01 M copper solution is used as titrant. The excess of EDTA solution should be at least 1 ml so there will be enough time (at least 10 seconds) for the titrator to be activated before the end-point is reached. A large excess of EDTA solution increases the titration time unnecessarily.

ACKNOWLEDGEMENT

This research was supported in part by the United States Air Force under contract No. AF 18(603)-137, monitored by the Air Force Office of Scientific Research and Development Command.

SUMMARY

The metalfluorechromic indicator Calcein W is used as an absorption indicator at 500 mμ for the automatic titration of excess EDTA with copper titrant in the "Spectro-Electro" derivative titrator. Copper, iron or cobalt are determined by adding a small excess of standard EDTA, as visually indicated in the titrator by the fluorescence of Calcein W, with the subsequent automatic titration of excess EDTA. The intense colors of the EDTA complexes of these cations do not cause any difficulty by the automatic spectrophotometric method, and macro as well as micro quantities of the metals can be determined with relative errors of 0.1% or less.

RÉSUMÉ

Une méthode automatique de titrage spectrophotométrique est proposée pour le dosage du cobalt, du cuivre et du fer; on traite la solution à analyser par un excès d'EDTA que l'on titre au moyen d'une solution étalon de cuivre, en présence de calcéine W, comme indicateur.

ZUSAMMENFASSUNG

Es wird eine automatische spektrophotometrische Titrationsmethode zur Bestimmung von Kobalt, Kupfer und Eisen beschrieben. Die zu analysierende Lösung wird mit einem Überschuss von EDTA versetzt und mit Kupferlösung in Gegenwart von Calcein W automatisch zurücktitriert.

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Short Communications

Modification of Beckman DK-2 spectrophotometer circuitry and operation

The spectrophotometric determination or detection of ions having low molar absorptivities (such as the rare earths) can be enhanced on the Beckman DK-2 automatic recording spectrophotometer by modifying procedure and circuitry. Procedure A involves a modified nulling operation which will provide more than 1½ times the normal pen excursion on absorbance peaks without materially influencing the noise level. Procedure B involves a modification of the circuitry which, in combination with A, yields about 2½ times the normal pen excursion with a slight increase in the noise level. Relative graphs of erbium absorbance peaks are shown in Fig. 1.

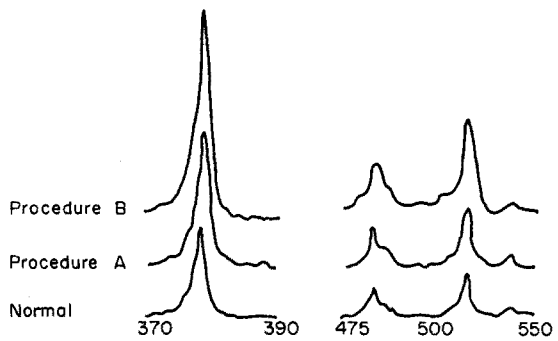

Fig. 1. Erbium absorbance peaks.

Procedure A

With the sample and reference solutions in place, zero the DK-2 in the normal manner. Then turn the zero adjust dial all the way to the left (applying maximum negative bias). Bring the needle back to the zero position with the 100 adjust dial. (For convenience in this operation, the —0.3 to +0.7 scale setting to locate the zero pen position can be used). These settings will now give greater pen excursion. For maximum resolution, a relatively slow speed with a short period should be used.

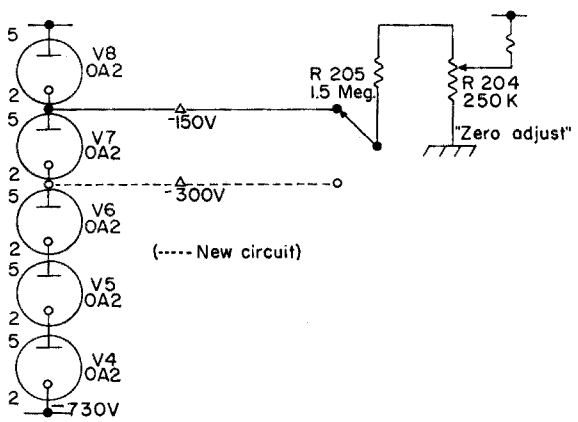

Fig. 2. Wiring diagram.

Procedure B

When the amplifier is operated with increased gain, additional negative bias is required to set the recorder zero coincident with zero transmission. This additional voltage is obtained by changing connections at the photomultiplier voltage-supply regulator tubes so that minus 300 V is supplied to the bias control and series regulator rather then —150 V. For convenience, a switch is installed so the operator can change from one voltage to the other. With the switch in the —300 V position, the steps in procedure A are followed. A pen excursion of about 2½ times normal operation is obtained. The wiring diagram for the new circuit is shown in Fig. 2.

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Received May 21st, 1960

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Notes on the preparation and construction of silver reductor columns*

Silver for use in silver reductor columns is prepared by a number of methods. The reductor originally described by WALDEN, HAMMETT AND EDMONDS[5] used silver precipitated from an acidified silver nitrate solution by a copper sheet. Columns filled with this silver have a high reducing capacity but a very slow flow rate. The silver is very finely divided and packs down so tightly that liquid flow through the column is impeded; it is usually necessary to operate the column under reduced pressure. Silver prepared by reduction with sulfurous acid or formaldehyde is also finely divided and behaves similarly.

Silver deposited electrolytically as low density "trees" was introduced by SMITH AND CAGLE[4]. It is now commercially available and is in common use. Electro-deposited silver forms a porous column and permits a rapid flow rate. Its major disadvantage is that it requires frequent regeneration. Although this is simply performed by treatment with dilute ammonia it would be advantageous to have a column which did not require frequent regeneration.

A column combining the advantages of both types of silver and eliminating their disadvantages can be prepared by mixing the two types. By selection of various ratios of electro-deposited to copper-reduced silver, a column can be tailored to have various flow rates and capacities. For many applications a 1 : 1 ratio (v/v) is satisfactory. The use of pulverized silver metal (2) and metal platelets (1) should provide still greater flexibility in the preparation of a column.

In using a reductor column the operator must pay close attention to the height of the liquid and not allow the liquid to drain below the level of the silver. If air enters

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

the column, entrapment ensues, and the solution may channel around much of the silver.

The danger of air entrapment can be overcome by use of the column shown in Fig. 1. The design is similar to that of self-leveling ion-exchange columns[3]. With the delivery tube opening above the level of the top of the silver bed, the liquid level will always

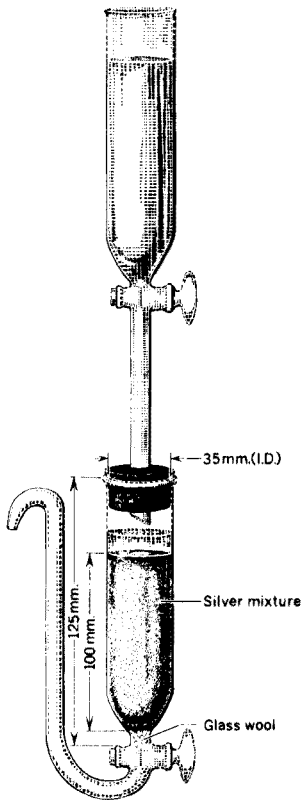

Fig. 1. Self-leveling reductor column.

remain above the silver. A tall form funnel is used for the feed solution in order to take advantage of the increased hydrostatic head of the liquid. The flow rate can be controlled by adjustment of the stopcocks and the column can be used without attention by the operator.

The column used in this laboratory was constructed from two 125-ml cylindrical separatory funnels. To reduce breakage the exit tube was fabricated from polyethylene tubing. Commercially available self-leveling ion-exchange columns would be more convenient.

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Techniques of a. c. polarography

The purpose of this communication is to acquaint those contemplating the use of a.c. polarography with some phenomena observed by us which were not readily apparent. A Sargent Model XXI polarograph was modified according to Miller for use as an a.c. recording unit[1]. It was found to be necessary to ground the negative side of the recorder slidewire to obtain a referenced or non-floating a.c. response. This ground in no way interferes with the d.c. operation. Additional changes from the original work were the construction of the a.c. circuitry in an external unit (Fig. 1) and connecting the d.c. DME lead and the a.c. signal secondary connection at the series capacitor by means of an on-off switch. This allows the a.c. unit to be completely removed during d.c. operation. A master a.c.–d.c. switch was located on the polarograph panel. The 110-V a.c. for the transformer primary could not be placed on this switch since it resulted in a very high base line. It was necessary to place a 110-V a.c. on-off switch on the external unit. A 1,000 Ohm precision resistor was connected (on-off switch) across the cell leads in the a.c. unit so that calibration could be effected conveniently.

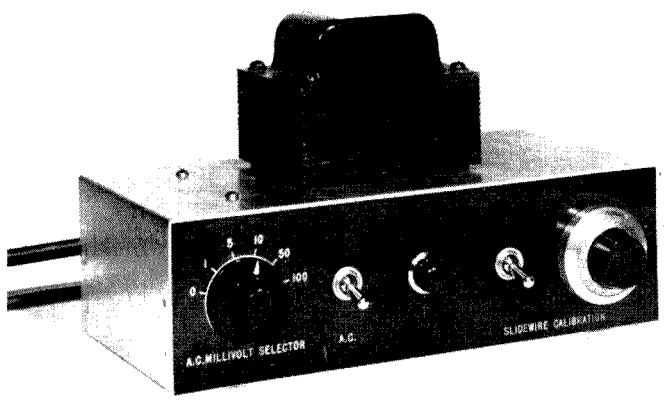

Fig. 1. a.c. control unit.

One advantage of a.c. polarography is the ability to obtain polarograms without first removing oxygen from the solution. On examination of Zn it was found that a large increase in peak height resulted if the solution was deaerated. Purging the cell with air caused the peak height to decrease. If the solution was made alkaline (pH 10) or if the solution was buffered (pH 6.5), a peak was obtained which was not sensitive to the presence of oxygen. The peak heights in alkaline media were much smaller, for identical concentrations, than those obtained in either deaerated unbuffered solutions or slightly acidic buffered solutions. The same effects were noted, differing only in magnitude, when Pb(II), Cd(II), Fe(II), Cr(III), and Ni(II) were examined. This sensitivity to oxygen was not seen with K, Ba, or BrO_3^-. These results can be explained

by the interaction of hydroxyl, produced by the reduction of oxygen, with the former ions to form their insoluble hydroxides or hydrous oxides in the diffusion layer thus restricting the normal diffusion processes[2]. Hydroxyl ion does not form insoluble compounds with the latter ions. In buffered systems, hydroxyl is taken up and exerts no effect and in very alkaline solutions, the amount of hydroxyl generated is negligible compared to the concentration already present. BREYER, GUTMANN AND HACOBIAN[3] have reported these same effects for Zn, Pb(II), and Cd(II), offering a slightly different explanation for the Zn case based on the irreversibility of zincate ion reduction. However, we found basic zinc solutions were detected as well as Fe(II) and Ni(II), both of which, in the absence of complexing agents, are also irreversible reductions. RAMAIAH *et al.*[4], have also noted the decrease of Cd peak height with increasing pH.

Organic compounds whose reduction waves are due to proton reduction also exhibit a large increase in peak height if oxygen is removed. This was found to be true for gibberellic[5], malic, and oxalic acids. If the reduction is due to some other organic function, *e.g.*, aldehyde, double bond, nitro group, the effect of oxygen is not as pronounced. In unbuffered solutions, benzaldehyde and diethyl maleate waves show very slight decreases after removing oxygen. No change is observed if the solutions are buffered. Nitrobenzene and *p*-nitrophenol in unbuffered solutions exhibit slight increases of peak height after oxygen removal. These results may be caused by a pH effect in the diffusion layer (increasing in the presence of oxygen). Both benzaldehyde and diethyl maleate exhibit increased i_d/C ratios as pH increases in this region (pH 7)[6]. The i_d/C ratios of nitrobenzene and *p*-nitrophenol decrease when pH is increased[6]. No significant changes were observed in peak height for unbuffered solutions of iodoform or gibberellic acid (non-proton reduction peak).

Using a mercury pool anode, it was noted that accurate placement of the DME was important. The distance between the tip of the electrode to the mercury pool can vary considerably in d.c. polarography; however, using the a.c. system, a difference of 10 mm between runs would cause a peak height differential of 15%–20%.

Frequently, at low concentrations, sensitivity had to be increased, resulting in an increase in mercury drop oscillation signal. The most effective means found for damping was a 10 μf to 30 μf condenser inserted in series with the recorder input (terminal 4), negative side toward the recorder. This condenser decreased the signal 10% to 30% but sensitivity could be increased without as much oscillation being detected.

The author wishes to express his appreciation to Mr. HAROLD PLUMMER for the construction and wiring of the a.c. control unit.

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Über eine indirekte volumetrische Bestimmung von Anionen mit Redoxindikatoren

ERDEY UND BODOR[1] beschrieben die Verwendung von Variaminblauhydrochlorid (4-Amino-4'-methoxy-diphenylaminhydrochlorid) als neuen reversiblen Redoxindikator in der Massanalyse. In Lösungen mit reduzierenden Eigenschaften ist dieser Indikator farblos, in schwach oxydierend wirkenden dagegen entstehen blaue, violette oder rote Färbungen. Das Variaminblau fand breite Anwendung für Reaktionen, welche in schwach saurem Medium (pH = 2–6) verlaufen. In den vor Kurzem publizierten Arbeiten über argentometrische[2,3] und mercurimetrische[4,5] Bestimmungen der Chlorid-, Bromid-, Jodid-, Rhodanid-, Cyanid- und Salpetersäure-Ionen wurde auch dieser Indikator zur Anzeige des Titrationsendpunktes angewandt. Am Äquivalenzpunkt bei Fällungsreaktionen oder bei Reaktionen, in deren Verlauf schwach dissozierte Verbindungen entstehen, reagiert der Überschuss der Titrierlösung mit dem Indikator unter Blaufärbung der Lösung.

Variaminblau als Indikator wurde schon früher bei der volumetrischen Bestimmung von Zink und Blei mit Kaliumhexacyanoferrat(II)-lösung verwendet[6]. Die guten Ergebnisse, welche mit dieser Methode bei Bleibestimmungen erhalten wurden, veranlassten uns zur Ausarbeitung einer indirekten massanalytischen Bestimmungsmethode für Anionen, die mit Bleinitrat schwerlösliche Salze bilden. Wir fällten in essigsauren Lösungen, die mit Natriumacetat gepuffert waren, Sulfat-, Chromat- und Phosphat-Ionen mit überschüssiger 0.1 *N* Bleinitratlösung. Die Niederschläge wurden abfiltriert und mit 20%-igem Methanol–Wasser Gemisch ausgewaschen. Der Überschuss an Blei(II)-ionen wurde in Gegenwart von 1 Tropfen 0.1 *N* Kaliumhexacyanoferrat(III)-lösung und 3 Tropfen 1%-iger Variaminblauacetatlösung mit 0.1 *N* Kaliumhexacyanoferrat(II)-lösung titriert. Die Titrationen wurden bei etwa 60° durchgeführt. Am Äquivalenzpunkt verursacht der Kaliumhexacyanoferrat(II)-Überschuss einen Farbumschlag der Lösung von Violett nach milchgelb. Zwei- und dreiwertige Kationen stören und müssen vorher entfernt werden z.B. durch Fällung mit Natrium- oder Kaliumcarbonatlösung. Grosser Überschuss an Natrium-, Kalium- oder Ammonium-ionen stört ebenfalls. Die Ergebnisse sind gut reproduzierbar und stimmen mit den, nach anderen Verfahren erhaltenen Werten überein. Eine ausführliche Beschreibung der Methode wird demnächst erscheinen.

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Eingegangen den 12. Mai 1960

BOOK REVIEWS

Separation and Identification of Food Colours Permitted by the Colouring Matters in Food Regulations, 1957, The Association of Public Analysts, London, 1960, 31 p. Price: 21s. net.

A committee appointed by the Association of Public Analysts has published its results on its investigation of the identification of 30 dyes which are permitted in Great Britain for use in foodstuffs. The results appear in a small book comprising 31 pages of which half are taken up with absorption curves. The methods for isolation and paper chromatographic separation of the dyes and their final identification by means of paper chromatography, absorption curves, and chemical tests, are described clearly and concisely. A dyestuff which does not belong to the list of those which are permitted is demonstrated by its failure to be identified as one of these. A continuation of these investigations is promised with the object of finding methods for the direct identification of dyestuffs which occur frequently and which are not in the list of those permitted by law.

F. REIMERS (Copenhagen)

Anal. Chim. Acta, 23 (1960) 300

Les cahiers techniques du Centre National de Coordination des Études et Recherches sur la Nutrition et l'Alimentation, IV. Le dosage microbiologique des vitamines du groupe B, Centre National de la Recherche Scientifique, Paris, 1959, 183 p.

Bien que l'analyse chimique soit en général plus sûre et plus rapide, elle ne permet pas encore de doser facilement toutes les vitamines du groupe B, surtout dans les milieux complexes. Dans ce cas, il faut avoir recours aux dosages microbiologiques qui présentent parfois l'avantage d'une grande sensibilité.

Dans un premier chapitre, l'auteur expose les principes des méthodes microbiologiques avec concision et clarté. Il en montre les difficultés, il met en évidence les sources d'erreurs. Il décrit les souches utilisées, les milieux de base des dosages, la technique en tube et sur gélose, la validité des résultats et des calculs, les méthodes d'extraction, la spécificité, problème si délicat et souvent difficile à résoudre et il termine cette première partie par un exposé fort bien venu sur les avantages et inconvénients des méthodes microbiologiques.

La suite de cet ouvrage comprend le dosage des vitamines du groupe B, soit: la thiamine, la riboflavine, les vitamines PP, B_6, l'acide pantothénique et le coenzyme A, la bioline, l'acide folique et la vitamine B_{12}. Chaque méthode y est décrite avec beaucoup de soins et de détails. Regrettons seulement que l'auteur n'ait pas donné à propos de chaque dosage, la sensibilité, la précision et l'exactitude.

Une bibliographie fort complète accompagne chaque chapitre de cet ouvrage.

D. MONNIER (Genève)

Anal. Chim. Acta, 23 (1960) 300

Trace Technique using the K 1000 Cathode Ray Polarograph, Vol. 1, par J. HETMAN, F.R.I.C., Southern Instruments, Camberley, Surrey, 1959, Prix 25s.

L'auteur a réuni, dans ce premier volume, diverses méthodes de dosage, effectuées au moyen du polarographe à rayons cathodiques K 1000. On y trouve, par exemple, le dosage du *m*-dinitrobenzène dans le benzène, du nitrobenzène dans l'aniline, le dosage simultané de l'acide fumarique et de l'acide maléique, le dosage simultané du cuivre, du plomb, du fer dans l'acide phosphorique, le dosage du fer dans le foie animal, etc. Trente méthodes sont ainsi proposées. Pour chacune d'elles, l'auteur indique en quelques mots le mode de préparation de l'échantillon, l'électrolyte de base utilisé, ainsi que l'électrode de référence. On trouve en outre une photographie du polarogramme, sur laquelle on peut relever les potentiels et estimer la sensibilité de la méthode. L'exposé se termine par l'interprétation des résultats et des remarques s'il y a lieu. Une bibliographie sur ces méthodes, dont l'auteur a fait une synthèse, termine ce volume.

Ouvrage intéressant, d'un emploi facile et qui permet d'un coup d'oeil de se rendre compte de la valeur d'une méthode et de ses possibilités.

D. MONNIER (Genève)

Anal. Chim. Acta, 23 (1960) 300

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