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

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

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

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

SPECTROPHOTOMETRIC fluoride determinations, based on the direct reaction between fluoride and the cerium(III) or lanthanum(III) chelate of alizarin complexan (3-[di(carboxymethyl)aminomethyl]-1,2-dihydroxyanthraquinone) are often used. The first was introduced by Leonard and West.[1] Other workers proved that the addition of an organic solvent enhanced the sensitivity and the

stability of the complexes. In this manner Yamamura *et ai.*[2] and Greenhalgh and Riley,[3] used acetone or acetonitrile, while Hanocq and Molle[4] advised dimethylsulphoxide. All these determinations were described only for the range of 5–25 μg of fluoride in a sample volume of 10–75 ml. For lower amounts, such as 0·1–1 μg of fluoride in a sample volume of 2 ml, procedures involving solvent extraction and subsequent colorometric measurement were developed by Hall,[5] and Cox and Backer Dirks.[6] A method for concentrations of 0·25–7 μg of fluoride in 150 ml of water was published by Johnson and Leonard.[7] Procedures of a similar nature are described by Hirano *et al.*[8] and by Daries and Foreman.[9]

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

EXPERIMENTAL

Reagents

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

Cerium(III) nitrate, 1·375 × 10⁻³M. Dissolve 303·1 mg of cerium(III) nitrate [Ce(NO$_3$)$_3$.6H$_2$O, purity 98·5%] in water to make 500 ml of solution.

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

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

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

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

Preparation of the standard curves

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

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

RESULTS AND DISCUSSION

Calibration curves

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

Extraction with different volumes of solvent

Procedure II was used but there were some differences during development of the method. Initially, 10 ml each of the alizarin complexan–buffer mixture and the cerium(III) nitrate solution

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

Further experiments showed that at constant volume-ratio absorbance was strongly dependent on the pH. As a consequence, the pH during extraction must be kept constant. It was also found that slight variations (even ± 0.1) of the pH before the extraction gave rise to large variations of the pH during extraction. For these reasons a pH 9 buffer was added before extraction. Other experiments showed that with extraction with a volume ratio 1:10 the final concentrations of alizarin complexan and cerium(III) nitrate could be reduced to $6.25 \times 10^{-5}M$ and $6.875 \times 10^{-5}M$ respectively as in Procedure II. The result was that the blank was halved without loss of sensitivity.
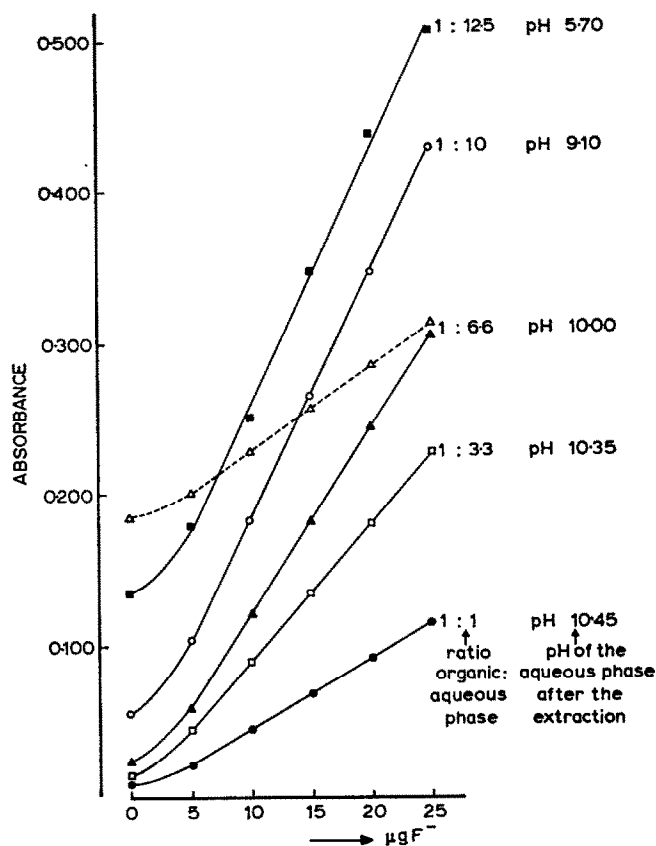

FIG. 1. Extraction with different volumes of extractant.
Dotted line: Absorbance of the aqueous phase before extraction, measured at 610 nm
in a 10-mm cell against water as reference.

Effect of temperature

It is found that between 15 and 25° the absorbance increases with temperature at the rate of 0.001/deg for the blank and 0.002/deg for 25 μg of fluoride.

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Interferences

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

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

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

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

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

CONCLUSION

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

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

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

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

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