

A SPECIFIC SOLVENT-EXTRACTION METHOD FOR THE DETERMINATION OF TRACE QUANTITIES OF FLUORIDE

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A method is described for the specific determination of trace quantities of fluoride. The procedure depends upon the solvent extraction and subsequent colorimetric measurement of the blue complex formed between fluoride and the cerous-alizarin complexan chelate. Concentrations of 0.25 to 7 $\mu\text{g.}$ of fluoride in 150 ml. of water can be determined. The method has been shown to be applicable to distillates from strong acid and has been used for solid samples of low fluoride content.

PRESENT methods for the determination of trace quantities of fluoride depend upon non-specific reactions with dyestuff-metal chelates. Examples are the thorium-alizarin S or zirconium-Eriochrome-cyanine R systems described by Snell (1959). They are capable of high sensitivity but do not distinguish between fluoride and other complex-forming ions such as phosphate, sulphate, citrate or oxalate.

The method from which we have developed the present technique makes use of a specific and positive reaction between fluoride ions and the cerous chelate of the dyestuff alizarin complexan (3-aminomethylalizarin-*NN*-diacetic acid) first described as a spot-test by Belcher, Leonard and West (1959). This has been applied to the quantitative determination of fluorine in organic compounds on the submicro (Belcher, Leonard and West, 1959) and semi micro scales (Johnson and Leonard, 1961).

Alizarin complexan, due principally to the powerful nitrogen diacetic acid chelating centre, forms a highly associated red complex with cerous ions at pH 4.0 to 4.6. In the presence of low concentrations of fluoride ions (5 to 200 $\mu\text{g./100 ml.}$) the usual non-specific bleaching effect exerted on metal-dye chelates does not occur; instead the fluoride ion itself enters the structure to form a blue colour with a different spectrum from that of both the cerous chelate (red) and the free alizarin complexan (yellow). The sensitivity of this reaction in aqueous solution is similar to that of the best bleaching systems. Leonard and West (1960), discussing theoretical aspects of the reaction, drew attention to the possibility of selective extraction of the fluoride complex into an organic solvent system. Such an extraction method should lead to an increase in sensitivity and this we have found to be the case. It is necessary to use an extractant consisting of a dilute solution of a hydrophobic amine in a higher alcohol. The presence of an amine is essential, hence the extraction must be of the ion-association type (Morrison and Freiser, 1957). Many combinations of amine and alcohol will serve, but the most satisfactory in sensitivity, preferential extraction of the fluoride complex, and clean separation is tribenzylamine in a mixture of pentyl and secondary butyl alcohols. The

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extraction procedure described below increases the sensitivity of the aqueous reaction ten-fold and allows the accurate determination of 0.25 to 7 $\mu\text{g.}$ of fluoride in 150 ml. of water, i.e., 0.002 p.p.m. to 0.05 p.p.m.

EXPERIMENTAL

Apparatus. 250 ml. separating funnels were used with a large temperature controlled water bath deep enough to allow almost complete immersion of the funnels.

A jacketed distillation apparatus was essentially as described by Huckabay, Welch and Metler (1947) but modified by the addition of a spray trap between the steam generator and the apparatus, and an efficient two-sphere spray trap between the jacket and the downward condenser.

Extinction values were measured in 4.0 cm. cells with a battery operated Unicam S.P. 600 visual range spectrophotometer.

Reagents

*Alizarin complexan** and *cerous nitrate* have the composition described by Johnson and Leonard (1961).

Acetate buffer (pH 4.3) is composed of hydrated sodium acetate (75 g.) glacial acetic acid (75.0 ml.) made up to 1 litre with water.

Standard fluoride solution (1.00 $\mu\text{g./ml.}$). Dissolve about 22 mg. (accurately weighed) of dried analytical reagent grade sodium fluoride in water and adjust the volume to 1 litre. Dilute an aliquot of this solution containing 1.00 mg. of fluoride (approx. 100 ml.) to 1 litre. Store in a polythene container.

Extraction solution. 0.06 per cent tribenzylamine in 30:70 pentanol-*s*-butanol.

Mix together 600 ml. of reagent grade pentanol and 1,400 ml. reagent grade *s*-butanol. Weigh out 1.20 g. of tribenzylamine (recrystallised from ethanol if necessary) and dissolve by gentle warming in approximately 100 ml. of the alcohol mixture. Transfer the solution of amine to the bulk of the alcohol mixture and mix well.

Procedure

Preparation of calibration graph. Into each of a series of eight 250 ml. separating funnels place 150-*n* ml. of distilled water (*n* = ml. of fluoride solution subsequently added); 0 to 7 ml. of standard fluoride solution (1.00 $\mu\text{g./ml.}$); 10.0 ml. of alizarin complexan solution and 2.0 ml. of pH 4.3 buffer solution. Mix the solutions and place the separators in a water bath, maintained at 25° ($\pm 0.2^\circ$) for 10 min., swirling the solutions periodically. Then add 10.0 ml. of cerous nitrate solution to each separator, mix thoroughly and replace in the bath for a further 10 min., again with occasional swirling. Add 40.0 ml. of the extracting solution, previously adjusted to 25°, to each of the separators in turn, shaking for 15 sec. immediately after each addition. Maintain the contents of the separators at 25° for 1 hr. shaking each for 30 sec. every 10 min. Remove

* Available from Messrs. Hopkin and Williams Ltd.

the separators and allow to stand for 15–20 min. at approximately 20–25°, run off and discard the aqueous layer, shaking the contents of the separator as little as possible. Swirl the organic layers around the interior surface of the separators and allow to stand for 5 min. with occasional slight agitation. Run off any additional aqueous layer, at the same time bringing the liquid interface to the bottom of the stopcock bore. Place small loosely packed plugs of cotton wool in the stems of the separators and pass the alcoholic solutions into 25 ml. graduated flasks. Rinse down the walls of the separators with dehydrated alcohol B.P. reagent and allow the rinsings to drain into the standard flasks until the

TABLE I
EFFECT OF FOREIGN IONS

Ion	Wt. of ion ($\mu\text{g.}$) causing 10 per cent decrease in the extinction at 580 $m\mu$ produced by 4.12 $\mu\text{g.}$ fluoride	Molar ratio interfering ion/fluoride
Citrate	67.5	1.64
Phosphate	26.6	3.96
Carbonate	4,050	311
Perchlorate	6,830	325
Sulphate	10,300	495
Nitrate	11,800	875
Chloride	21,300	2,760
Ferric*	82.2	6.77

* Ferric iron forms a red-brown chelate with alizarin complexan which is extracted into the organic layer and causes an initial increase in extinction value. As the ferric ion concentration increases, however, a progressively dense purple precipitate is formed and the density of the filtered alcohol layer decreases.

mark is reached. Shake the flasks well to dissolve any water droplets and read the extinctions of the solutions against that containing no fluoride in 4.0 cm. cells at 580 $m\mu$, the absorption maximum of the blue complex. Unknown fluoride solutions (150 ml.) are treated similarly.

When a preliminary distillation is necessary, place the sample in the inner bulb of the distillation apparatus and rinse down the walls of the entry tube with as small a volume as possible of distilled water followed by the rapid addition of 25 ml. of 60 per cent w/v sulphuric acid. Connect the steam generator, already heated to a temperature of 60–80°, to the apparatus, replace the stopper and heat the liquid in the jacket (sym. tetrachlorethane) until it refluxes in the condenser. Heat the steam generator to boiling and collect 150 ml. of distillate. Treat this solution for colour development, extraction and measurement as described above.

Significant amounts of fluoride were frequently found in new glass apparatus and several trial runs were then made before estimations began. This agrees with the findings of the Society for Analytical Chemistry Subcommittee report (1944).

Effect of Foreign Ions

The quantitative effect of some foreign ions has been evaluated. Table I shows the molar ratio of interfering ion necessary to bring about a 10 per cent reduction in the colour produced from 4.12 $\mu\text{g.}$ of fluoride.

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RESULTS AND DISCUSSION

Calibration graphs prepared as described are linear over the range 0 to 5 $\mu\text{g.}$ of fluoride but at higher concentrations a slight increase in slope is apparent. In the range 0 to 5 $\mu\text{g.}$ the sensitivity is 0.13 extinction unit per $\mu\text{g.}$ of fluoride. The blank value, prepared as described, is high but

TABLE II
RECOVERY EXPERIMENTS ON STANDARD FLUORIDE SOLUTIONS

Wt. fluoride taken ($\mu\text{g.}$)	Wt. fluoride found ($\mu\text{g.}$)	No. of determinations
<i>Without distillation</i>		
1.00	0.99 \pm 0.07	5
2.00	1.99 \pm 0.04	5
4.12	4.12 \pm 0.03	5
5.00	5.07 \pm 0.03	7
<i>With distillation</i>		
1.00	1.01 \pm 0.06	8
2.00	1.98 \pm 0.09	6
5.00	5.16 \pm 0.09	7

reasonably reproducible; fifteen separate determinations, accumulated over a period, gave a mean value of 0.399 with a standard deviation of 0.007 when measured against pure ethanol.

The precision of the method was determined by applying the procedure to known volumes of standard fluoride solution. Table II lists the results obtained.

Initially, distillation recoveries were made using the more usual 60 per cent perchloric acid rather than sulphuric acid but low values were

TABLE III
RESULTS OBTAINED ON SOME SOLID MATERIALS

Sample	Wt. taken (g.)	Wt. fluoride added ($\mu\text{g.}$)	Wt. fluoride found ($\mu\text{g.}$)	Fluoride content of sample (p.p.m.)	Fluoride recovered ($\mu\text{g.}$)
Potassium hydrogen phosphate (Analar) ..	5.00	0	1.11	0.22	—
	5.00	0	1.06	0.21	—
	5.00	2.00	3.38	—	2.29
	5.00	2.00	3.26	—	2.17
Calcium phosphate	0.1085	0	2.01	18.5	—
	0.1215	0	2.34	19.2	—
	0.0892	2.00	3.51	—	1.83
	0.0948	2.00	3.78	—	1.99
Baking powder (previously ashed with 1 ml. 10 per cent sodium carbonate before distillation)	0.6173	—	2.90	4.7	—
	1.1560	—	4.50	3.9	—
	0.8880	—	4.17	4.7	—
	0.8491	—	3.82	4.5	—
	0.8307	—	3.74	4.5	—
	0.7280	—	2.77	3.8	—

obtained. These were shown to be due to the presence of perchlorate ions in the distillate.

Table III lists results obtained on samples for which trace fluoride determinations are commonly required. The sample of calcium phosphate was a reagent grade material, as opposed to bone phosphates which usually contain much higher proportions of fluoride.

Distillations in the absence of sample gave low and fairly reproducible blanks of 0.19 ± 0.06 μg . fluoride.

Where samples of fluoride in concentrations greater than 5 μg . in 50 ml. of water and free from all interfering ions, are available, the thorium-alizarin titration procedure is applicable if a titrant as dilute as 0.00025M is used. Such a method is more rapid than the present one and is capable of similar precision: sulphate and phosphate, however, produce gross interference. The method described is of value where low concentrations of fluoride are present or where only small quantities of sample are available such as in the analysis of human blood serum. It is far less susceptible to interference than the titration method and is specific for fluoride.

In addition to the types of sample discussed, it seems probable that the method would be of value for effluent and atmospheric pollution studies.

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The paper was presented by DR. LEONARD. The following points were made in the discussion.

The blue colour was formed between 1 and 200 μg . of fluoride per 100 ml.; over 500 μg . the bleaching effect of the fluoride began to interfere. The limiting factor was mainly the variation in density readings of the spectrophotometer. Interference from cyanide was negligible. Temperature control was important. The alizarin complex had a zwitterion arrangement similar to that of the EDTA molecule.