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ESTIMATION OF FLUORIDE USING ALIZARIN COMPLEXAN

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Summary

The proposed method was developed for the estimation of fluoride in rock phosphate and has also been used in analysis of stock foods containing rock phosphate. The Ce^{III}-alizarin complexan colour method is used to measure the amount of fluoride ion. The sensitivity of the colour reaction is enhanced by developing the colour in 20% w/v acetone. Cations are removed from the sample by ion exchange. Phosphate is removed with silver nitrate and the excess silver is precipitated as the chloride. The optical densities of the test solutions are read by differential spectrophotometry.

Introduction

The Ce^{III}-alizarin complexan colour for the estimation of fluoride ion, unlike the classical colour bleaching methods, is specific for fluoride and shows a very high tolerance to interfering ions. Yamamura, Wade, and Sikes (1962) showed that Al(III), Fe(III), and phosphate are capable of interfering with this method when the ion to fluoride molar ratio is low. Moderately high concentrations of sulphate do interfere but this is not a problem in the analysis of rock phosphate.

From an acidic solution of the sample, the cations are removed by an ion exchange resin which is in the H form. Phosphate is then removed from the neutralized column effluent, using silver nitrate. Any silver ions left in solution are precipitated as the chloride just before colour development.

A plastics chromatography column is used to hold the ion exchange resin and where possible plasticsware is used instead of glassware to avoid loss of fluoride.

Full colour development takes about 45 min when fluoride is present. When no fluoride is present, as in a blank, full colour development takes about 2 hr. Since it is more accurate and convenient to have all solutions taking the same time to reach full colour development, both the fluoride standards and the test solutions were read against an arbitrarily chosen blank which contained 4 μgF^- per 100 ml solution.

Materials and Methods

Reagents.—

1. Bio-Rad Cationic resin AG 5OW-X8H (100-200 mesh) or equivalent.
2. AR nitric acid (3N solution).
3. AR sodium hydroxide (1·5N solution).
4. Phenolphthalein indicator solution (0·2% solution).
5. AR silver nitrate (0·1N solution).
6. Buffer solution (pH 4·3). Dissolve 60 g sodium acetate ($CH_3COONa.\ 3H_2O$) (AR) in 500 ml water. Add 115 ml glacial acetic acid. Dilute to 1 litre.
7. Alizarin complexan or Alizarin Fluorine Blue (Hopkins and Williams) (5 x 10^{-4}M solution). Suspend 96·2 mg complexan in freshly distilled water. Stir the solution while adding just sufficient 1·5N sodium hydroxide solution to dissolve all the solid. Add dilute hydrochloric acid until the purple colour of the solution just changes to red (pH 5-6). Dilute to 500 ml. Store the solution in a polythene container in diffuse light.
8. Cerous nitrate hexahydrate solutions. (*a*) *Bulk solution* (10^{-2}M).—Prepare a 10^{-2}M Ce^{III} solution and standardize it against EDTA at pH 5·2, using an acetate buffer and xylenol orange as indicator. (*b*) *Working* Ce^{III} *solution* (5 x 10^{-4}M).—Dilute 25 ml bulk Ce^{III} solution to 500 ml. Store in a polythene container.
9. AR sodium chloride (0·1N solution).
10. Acetone (freshly distilled).
11. AR sodium fluoride solutions. (*a*) *Bulk solution* (40) μgF^-ml).—Dissolve 442·1 mg NaF in water and dilute to 1 litre. Dilute 50 ml of this solution to 250 ml. This solution contains 40 μgF^-/ml. (*b*) *Working fluoride standard* (0·8 μgF^-/ml).—Dilute 20 ml bulk fluoride solution to 1 litre. Store all fluoride solutions in polythene containers.

Apparatus.—Plasticsware, where possible, was used instead of glassware. All measurements were made in 4-cm cuvettes at 610 mμ, using a Unicam SP 600 spectrophotometer.

Preparation of ion exchange column.—Make a water slurry with the resin and allow it to become fully swollen. Fill a plastics chromatography column or plastics tube (18 mm diam.) with the resin so that the resin bed occupies a volume of 50 ml. Pass 50 ml 6N HCl through the column to convert the resin to the H form. Wash the column with water until the effluent is chloride-free. The flow rate should be about 1–2 drops per sec. The column is now ready for use.

Standard curve.—The order and detail of reagent addition in developing the colour should be closely adhered to, otherwise erratic colour development may result.

Into a series of 100-ml volumetric flasks pipette 5, 10, 15 . . . . . 50 ml of working fluoride standard solution. These solutions contain 4, 8, 12, ... 40 μgF^-. Dilute each solution to about 50 ml with water. To each flask add in order, *with vigorous swirling of the contents during each addition,* 10 ml alizarin complexan, 2 ml buffer solution and 10 ml Ce^{III} working standard solution. From a dip pipette add 20 ml acetone, again swirling the contents during the addition. The volume of acetone need not be exactly 20 ml but it must be constant. Dilute the solutions almost to volume. Stopper the flasks and mix the contents well. Cool quickly to room temperature. Store the solutions in diffuse light for 60 min. Then make the solutions to the mark and mix. Read the optical densities of the solutions at 610 mμ, using the 4 μgF^-/100 ml solution set at 100% transmission. Use 4-cm cuvettes. Plot the optical density *v.* μgF^- per 100 ml solution.

Beers' Law holds from 4 to 30 μgF/100 ml, with only a slight deviation detectable at about 35 μgF^- per 100 ml.

The colour development procedure is that of Belcher and West (1961*a*, 1961*b*).

Procedure.—For rock phosphate, transfer 50 mg of the finely powdered sample to a plastics beaker. For stockfoods, ash 1 g sample in a platinum dish at 550°C.

To the sample in the beaker or platinum dish add 10 ml 3N nitric acid and place the container in a constant-temperature bath (55°C) for 20 min. Swirl the solution frequently. Transfer the solution to a 100-ml volumetric flask and dilute to volume with water. To avoid loss of fluoride by attack on the glassware, quickly pour the solution into a plastics beaker. Filter the solution through a 15-cm Whatman No. 40 paper supported on a plastics funnel. Collect the filtrate in a plastics beaker.

Pass a 50 ml aliquot of the filtered solution through the resin column at a rate of 1–2 drops per sec. Three 5-ml portions of water followed by 60 ml water are used to wash the aliquot onto and through the resin bed. Collect the effluent in a plastics beaker containing 10 ml 1·5N sodium hydroxide. (After each sample, run a 30-ml water wash through the resin column before treating the next sample. After four sample runs, reconvert the resin to the H form.)

Add 1 drop phenolphthalein to the contents of the beaker. Add dropwise either dilute sodium hydroxide or nitric acid as required until the solution has just a faint permanent pink colour. Add enough 0·1N silver nitrate solution (0·9 ml $\equiv$ 1 mgP) to just combine with the phosphate present in solution. Transfer the solution to a 200-ml volumetric flask and quickly adjust to volume. Filter the solution through a 15-cm Whatman No. 42 paper, collecting the filtrate in a plastics beaker.

Transfer a suitable aliquot (50-150 ml) of the clear solution to a 200-ml volumetric flask containing 2 ml 0·1N sodium chloride. Add 1 drop dilute nitric acid and then dilute the contents of the flask to volume. Transfer the solution to a plastics beaker. Cover the beaker and store in the dark for 10 min.

Filter the solution through a 15-cm Whatman No. 42 paper, using plasticsware as before.

Transfer a suitable aliquot (25-50 ml) of the filtered solution to a 100-ml volumetric flask and, if necessary, dilute the contents to 50 ml with water. Develop the colours of the test solutions in the same way as the colours for the standard curve. At the same time, develop the colour for 5 ml (4 μgF) working fluoride standard which is to be set at 100% transmission.

Read the optical densities of the test solutions, in 4-cm cuvettes, against the 4 μgF/100 ml solution at a wave length of 610 mμ. Using the optical densities and the standard curve, calculate the fluoride percentage in the sample.

Results and Discussion

Recovery tests were carried out using known weights of sodium fluoride and lead fluorochloride. Table 1 shows the calculated amounts of fluoride present in the solutions together with the amounts found by analysis. The recoveries of fluoride were better than 99% of the calculated amounts.

TABLE 1

RECOVERY OF FLUORIDE

Sample	Run No.	μg F^-		Recovery (%)
		Calculated	Found	
PbFCl	1	32·7	32·7	100·0
PbFCl	2	32·7	32·5	99·4
PbFCl	3	30·2	30·4	100·7
NaF	1	25·0	24·8	99·2
NaF	2	25·0	25·1	100·4
NaF	3	7·9	8·0	101·3

Four rock phosphate samples and one stockfood (a poultry laying all-mash) sample were analysed for fluoride, using two different weights of each sample. The results of the replicate determinations of fluoride and the phosphorus percentage in each sample are shown in Table 2.

TABLE 2

REPLICATE ANALYSES OF SAMPLES

Sample	Ref. No.	P %	F^- % found	
Chris-Phos	634	15·8	1·10	1·10
Chris-Phos	635	16·0	1·84	1·86
Tricaphos	636	18·0	0·11	0·12
Chris-Phos	6,722	15·8	1·72	1·74
Stockfood .. .. (Laying All-Mash)	6,723	1·5	0·04	0·04

After the precipitation of phosphate as silver phosphate, there are still sufficient silver ions left in solution to interfere in the development of the colour. An experiment was conducted with solutions containing the same amounts of fluoride but various amounts of silver ions added as silver nitrate. The colour was developed in the usual way. A positive bias was recorded in the optical densities of the solutions containing added silver (Table 3). This experiment was repeated, but just before colour development the added silver ions were removed as silver chloride. All solutions in this test had the same optical density (Table 3). Depending on the aliquots used in the procedure for analysing a sample, after the phosphate present has been precipitated with added silver ions an error of 0·75 to 1·0% can be introduced into the estimated amount of fluoride present in solution if the silver ions remaining in solution are not removed as silver chloride.

TABLE 3

INTERFERENCE OF SILVER IONS

Molar Ratio Ag/F*	Optical Density	
	Ag Present	Ag Removed
220	·190	·129
73	·157	·128
50	·138	·128
No Ag added	·128	·129

*All solutions contained 5μgF/100 ml as sodium fluoride.

To avoid small losses of fluoride by attack on the glassware, especially from acid solutions, it is recommended that when glassware has to be used the solution should be transferred as quickly as possible from the glass container to a plastics one.

However, the greatest single error which can be introduced into the method is in the colour development step. Meticulous attention must be paid to the details and conditions set out in the colour development procedure. Reproducible results will be obtained only when these conditions are satisfied.

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