Provided for non-commercial research and educational use only.
Not for reproduction or distribution or commercial use.

Volume 581, issue 1, 2 January 2007 ISSN 0003-2670

ELSEVIER

ANALYTICA CHIMICA ACTA

An international journal devoted to all branches of analytical chemistry

Editors: Alan Townshend (Hull, Great Britain)
Paul J. Worsfold (Plymouth, Great Britain)
Lutgarde Buydens (Nijmegen, Netherlands)
Ulrich J. Krull (Toronto, Canada)
Richard P. Baldwin (Louisville, KY, USA)
Purnendu K. Dasgupta (Lubbock, TX, USA)
Liang Li (Edmonton, Canada)
Hian Kee Lee (Singapore)

Editorial Advisers:

Available online at www.sciencedirect.com ScienceDirect

This article was originally published in a journal published by Elsevier, and the attached copy is provided by Elsevier for the author's benefit and for the benefit of the author's institution, for non-commercial research and educational use including without limitation use in instruction at your institution, sending it to specific colleagues that you know, and providing a copy to your institution's administrator.

All other uses, reproduction and distribution, including without limitation commercial reprints, selling or licensing copies or access, or posting on open internet sites, your personal or institution's website or repository, are prohibited. For exceptions, permission may be sought for such use through Elsevier's permissions site at:

http://www.elsevier.com/locate/permissionusematerial

Available online at www.sciencedirect.com
ScienceDirect
Analytica Chimica Acta 581 (2007) 168–173
ANALYTICA CHIMICA ACTA
www.elsevier.com/locate/aca

On-line flow injection solid sample introduction, leaching and potentiometric determination of fluoride in phosphate rock

Jamal A. Sweileh*

Department of Chemistry, The Hashemite University, P.O. Box 150459, Postal Code 13115, Zarka, Jordan

Received 24 May 2006; received in revised form 31 July 2006; accepted 31 July 2006
Available online 7 August 2006

Abstract

A flow injection method with on-line solid sample dissolution was developed for the determination of fluoride in phosphate rock. The fluoride was selectively leached (98–102.4 % recovery) from a 50-mg powdered phosphate rock sample with 0.50 M citric acid. Using the zone sampling technique the fluoride in the buffered leachate was determined by injecting 87 μL into the carrier stream using a fluoride ion-selective electrode detector. The sensing element of the electrode was housed in a home-made sleeve-type flow-through cell. On-line solid sample digestion with 0.50 M citric acid at 55 °C resulted in minimum dissolution of interfering iron and aluminum ions with improved accuracy and calibration linearity. The incorporation of relatively high level of fluoride in the carrier stream (40 $\mu g\,mL^{-1}$) facilitated the determination of high levels of fluoride in phosphate rock (up to 4.1%) with out the need for excessive on-line dilution.

The optimized flow system was applied for the determination of fluoride in phosphate rocks samples and a reference material at a rate of nine samples per hour with a relative standard deviation ($n = 5$) of 2.95–4.0 %. Comparison of the proposed flow injection method with the standard method, which involves steam distillation from sulfuric acid solution and manual titration with thorium nitrate, showed no evidence of bias at the 95% confidence level.

Keywords: On-line leaching; Flow injection; Solid sample introduction; Fluoride; Potentiometry; Phosphate rock

1. Introduction

Several techniques are available for the determination of fluoride such as titration with thorium nitrate [1–3], spectrophotometry with different chromogenic reagents [1,4–9] and potentiometry using the fluoride ion-selective electrode either manually [1,10–12] or in the flow injection analysis (FIA) mode [13–15].

Despite the widespread popularity of fluoride ion-selective electrode methods of analysis, this technique is prone to various interferences mainly due to matrix effects such as complexation of fluoride ion by iron, aluminum and calcium ions [4,14,16,17]. This interference was overcome by addition of various masking agents that complex the interfering cations [11,12,16,17,19] or by prior separation of fluoride from the sample matrix [1,20,21,22].

Automation of potentiometric fluoride determination by FIA gained a wide popularity because of controlled contamination, reduced labor cost and high sample throughput. With FIA systems there is no need to reach a steady state or stable potential reading that could require few minutes. The transient peak-shaped signal is reproducible enough for quantitative analysis. However, the nature of this FIA signal imposes new challenges to the analytical chemist because it may lead, in certain cases, to non-Nernstian response function [13] and non-linear calibration curves [23,24]. Despite the above mentioned challenges, FIA technique of fluoride determination found many applications in liquid samples [14,16,21,25].

There is a limited number of reports on the determination of fluoride in phosphate rock, all of which involved the manual batch mode of analysis [2,17,26–28]. Several chemical interferences plague the determination of fluoride in phosphate rock. The success of the ion-selective electrode determination of fluoride in phosphate rock is affected by the matrix composition and the method of sample treatment [17,27,28]. Ideally sample treatment should affect complete recovery of fluoride and removal

---

* Tel.: +962 5 390 3333x5084; fax: +962 5 382 6613.
E-mail address: jsweileh@hotmail.com.

0003-2670/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.aca.2006.07.086

or masking of potentially interfering metal cations such as iron, aluminum and silicon. The fluoride electrode response is also affected by ionic strength, pH and temperature of the measured solution [18,23,26,29].

In this work, we report the application of FIA with on-line solid sample dissolution and potentiometric detection for the determination of fluoride in phosphate rock. Sample treatment involves digestion with citric acid which was developed earlier in this laboratory [28]. This leaching method with citric acid, a weak acid, resulted in quantitative recovery of fluoride but minimal dissolution of interfering metal ions. Such ions were masked effectively by the digestion solution.

2. Experimental

2.1. Reagents

All solutions were prepared from reagent or analytical grade chemicals using singly distilled water. Potassium fluoride (Fluka, dried for 2 h at 110 °C) was used for the preparation of 12500 $\mu g\ mL^{-1}$ fluoride stock in polypropylene bottle. Solutions of lower fluoride concentrations were prepared daily by serial dilution of the above stock. Fluoride-containing citrate buffer solution (1 M, pH 6.0) was also prepared in polypropylene bottle using tri sodium citrate (BDH) and pH adjustment with hydrochloric acid (Lab Scan). Other chemicals and solutions have been described elsewhere [28].

2.2. Sample selection

A set of Jordanian phosphate rock samples were selected to represent a wide range of fluoride content (1.2–4.1%), aluminum oxide content (0.15–4.9%) and iron(III) oxide content (0.06–3.3%). Samples labeled QS5, QS6 and QS8 are in-house prepared phosphate rock standards used for quality control in Jordan Phosphate Mines Company. The sample labeled E is a high-grade phosphate rock shipment sample (%F = 3.5) while the sample labeled S is a low grade phosphate rock ore sample (%F = 1.3) from Shidiyya Mine in southern Jordan. Finally, a certified reference material phosphate rock sample (BCR no. 32) of Moroccan origin was included (certificate value 4.04% F).

2.3. Equipment and instruments

The flow injection system used is shown schematically in Fig. 1. It is based on the design developed earlier for on-line processing of solid samples. Details of sample chamber, S, fabrication and dimensions are reported elsewhere [30,31]. All reagents are propelled by a 4-channel variable speed peristaltic pump (Gilson, model Minipulse II) in 1.2 mm i.d. PVC or silicone tubes. The three-way solenoid valves (V1 and V2) are pinch-type which facilitate smooth slurry pumping (P/N 075 PWMP 12–32, Biochem Valve Corp. Boonton, NJ, USA). The leaching solution, D, is pumped through the common port of the pinch valve, V1 (the tube preceding the tee in Fig. 1). In the ON-position (solenoid activated) the valve pinches the upper tube while the lower tube is not pinched thus allowing the solution to flow through the lower (bypass) tube. In the OFF-position (solenoid is not activated) the lower tube is pinched while the upper tube is not thus the solution flow through the upper tube.

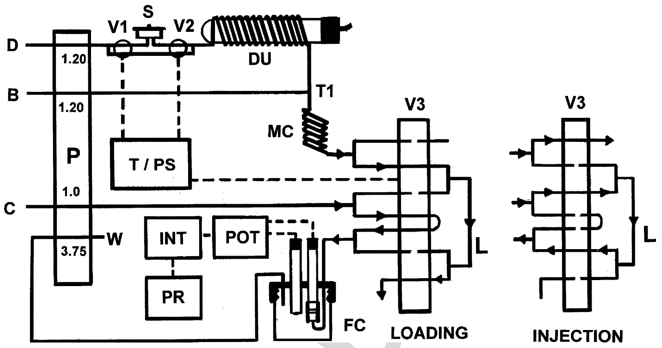

Fig. 1. A flow injection diagram for the determination of fluoride in phosphate rock; D, leaching solution: B, buffer solution C, carrier solution; P, peristaltic pump (numbers indicate flow rates in mL min^{-1}); S, sample injection valve; V1 V2, three-way solenoid valves; DU leaching unit; M, mixing coil; V3, multi-tube pinch valve L, sample loop; W, waste; FC, flow cell; POT, potentiometer; INT, integrator; PR, printer; PS/T; power supply & timer. Solid lines indicate tubes, dashed lines are electrical connections and arrows indicate fluid flow direction.

The sample leaching unit, DU, is a 320-cm long Tygon tube (1.2 mm i.d. 0.4 mm wall thickness) wrapped around the cylindrical glass envelope of a 100-W tungsten lamp (Philips). Leaching temperature is controlled by incorporating a household light dimmer in the power circuit of the lamp. The dimmer changes the brightness of the lamp which in turn changes the amount of dissipated heat reaching the glass envelope which serves as the heating source for the solution flowing inside the coil. This arrangement is capable of temperature control (±2 °C) between room temperature and 65 °C. The sampling valve, V3, is a multiple (up to 10 channels) pinch-type solenoid valve (P/N 0136/-99) which was purchased from Cole-Parmer Co., Vernon Hill Ill. USA. All valves are powered by a 12 V dc power supply and their sequential operation is controlled by a programmable timer (Mitsubishi Electric Corp. Tokyo, Japan [31]). Connectors and tees are 1.2 mm i.d. polypropylene barbed fittings from Cole-Parmer. The flow cell of the fluoride ion-selective electrode is constructed as follows: the sensing element of the fluoride electrode is snuggly fitted at one end of Tygon tube sleeve, T (Fig. 2). At the other end of the Tygon sleeve a rigid 3 mm thick plastic disc, D, was tightly fitted. The diameter of the disc is similar to that of the fluoride ion-selective electrode body (Metrohm). The flow stream is pumped into the flow cell though a hole in the centre of the disc and exits from any of six holes (about 2.0 mm diameter) cut in the wall of the Tygon sleeve. To eliminate potential entrapment of insoluble residue in the cell the holes were cut such that the lower edge of each hole is flush with the upper surface of the disc. The nominal volume of the flow cell is 300 μL but could be varied by pushing the disc closer or farther away from the fluoride-sensing crystal.

Both the fluoride electrode and the saturated calomel reference electrode (Metrohm) are submerged in a 50-mL plastic bottle filled with the carrier solution through holes cut in the cap. The depth of each electrode is controlled by rubber O-rings

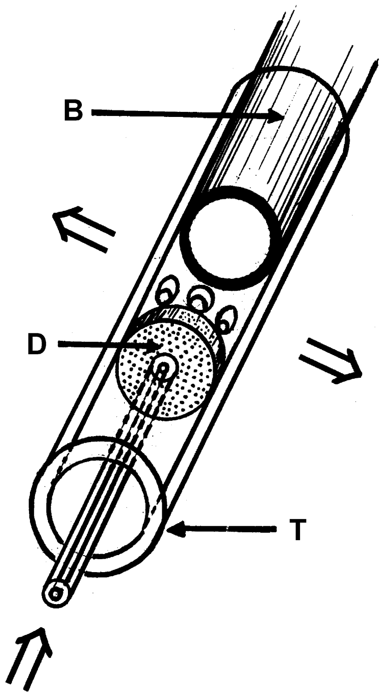

Fig. 2. A three-dimensional drawing depicting details of the flow cell (not exactly to scale): B, body of fluoride electrode; T, Tygon sleeve tube; D, rigid plastic disc. Arrows indicate direction of fluid flow.

slipped on the electrode body. The solution level in the beaker is kept constant by drawing the excess effluent in the waste stream, W. The generated fluoride signal is processed by a potentiometer (Metrohm, model 629), stored and displayed by a single channel integrator with video display (P-E Nelson, model 1022) and a Hewlett-Packard printer.

2.4. Analytical procedure

In typical operation, V1 and V2 are activated for 30 s. This allows the leaching solution, D (0.50 M citric acid) to bypass the sample chamber, S, and flow through the bypass line. The base section of the sample chamber is opened and approximately 50 ± 0.1 mg of the powdered sample (weighed by difference) is inserted in the chamber and the base screwed close. When V1 and V2 are turned off the leaching solution sweeps the sample to the leaching unit, DU, set at 55 °C at a rate of 1.2 mL min^{-1}. At the end of the leaching coil the leachate stream is buffered by merging with buffer stream, B (1.00 M sodium citrate of pH 6.00 with 40 μg F$^-$ mL^{-1}) at T1. The combined stream is mixed in the 50-cm mixing coil, MC, and fed to the sampling valve, V3 which was set in the loading cycle. Any discontinued line in V3 indicates that the channel is pinched close. After 310 s V3 is activated for 120 s and the selected sample in the loop, L, is injected in to the carrier stream, C (1.00 M sodium citrate buffer of pH 6.00 with 40 μg F$^-$ mL^{-1}) which transports the sample to the flow cell, FC (Fig. 1, INJECTION). One minute after the injection cycle starts V1 and V2 are activated to set the system ready for the next sample. Quantification is based on peak height (mV) measurement of the transient signal.

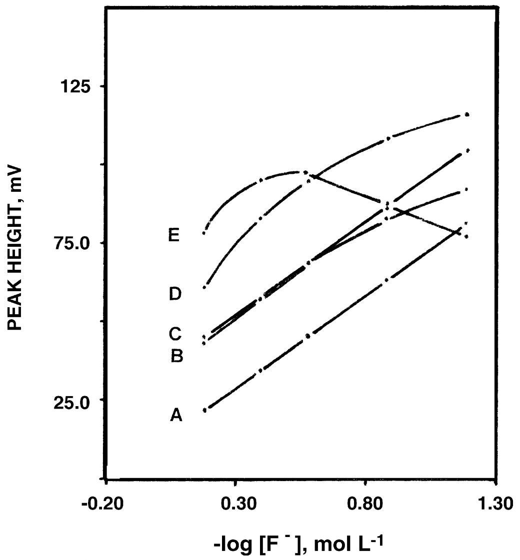

Fig. 3. The effect of fluoride concentration in the carrier stream on the fluoride calibration curve by flow injection analysis: (A) 30 μg mL^{-1}; (B) 40 μg mL^{-1}; (C) 60 μg mL^{-1}; (D) 100 μg mL^{-1}; (E) 200 μg mL^{-1}.

3. Results and discussion

3.1. Effect of buffer and carrier composition

Initial tests using potassium fluoride solution in the sample chamber showed a slow baseline recovery when using fluoride-free buffer and carrier streams. This problem was observed by other workers [13,14,24,32]. Therefore, the buffer was fortified with a fixed concentration of fluoride that is close to the fluoride level in the sample. The slow attainment of baseline potential (due to dissolution of electrode sensing element, contamination or adsorption) results in baseline drift, wide peaks and loss of linear analytical range [14,24]. The larger the difference in fluoride concentration between the sample and the carrier (and buffer) stream the more pronounced is this “memory effect”. In order to select the optimum concentration of fluoride in the buffer and carrier streams a family of calibration curves were generated by inserting 200 μL of 1.25, 2.50, 7.50, 10.0 and 12.5 mg mL^{-1} standard fluoride solution but variable concentration of fluoride in the buffer and carrier streams ranging from 30 to 200 μg mL^{-1}. In these tests the leaching solution was 0.50 M citric acid pumped at 1.0 mL min^{-1} in a 500-cm (1.2 mm i.d.) leaching coil heated to 60° C. Fig. 3 is a plot of the obtained calibration curves. It is evident from Fig. 3 that a linear calibration curve is possible only if the fluoride concentration in the carrier is slightly higher than that of the most concentrated calibration standard. High levels of fluoride in the carrier lead to non-linear calibration curves (Fig. 3C and D) and even double-valued calibration curve at the highest tested fluoride level (Fig. 3E).

For fluoride standard solutions up to 12.5 mg mL^{-1} the buffer and carrier fluoride concentration should not exceed 40 μg mL^{-1}. Furthermore, excessively higher fluoride levels in the carrier solution lead to more scattered data. The closeness of the fluoride level in the carrier and the analyzed sample is necessary to allow faster re-establishment of equilibrium conditions between samples with consequent baseline stability [13,24]. Although 30 or 40 μg mL^{-1} fluoride levels in the buffer or carrier solution performed equally well, the higher level of the two was selected because it gave better precision.

Using lower fluoride concentration (in the carrier and buffer solutions) than those of the sample range is possible and gives more sensitive positive peaks [14]. However, this is not followed here in order to desensitize the method and thus avoid excessive on-line dilution of the samples. Furthermore, it was observed that using a low concentration of fluoride in the buffer and carried have some drifting effect on the baseline. This drift is probably due to the gradual dilution of fluoride in the flow cell reservoir with continued injection of samples with lower fluoride level.

The citrate buffer concentration was optimized under the same conditions by injecting 200 μL of 10 mg mL^{-1} fluoride but varying the buffer and carrier concentration of sodium citrate between 0.10 and 2.50 M (pH 6.00). As the citrate concentration was increased there was a corresponding increase in fluoride peak by approximately 7% (data not shown). Citrate buffer concentrations in excess of 1.00 M lead to higher R.S.D. values, therefore, a 1.00 M buffer and carrier concentration was chosen for farther optimization.

3.2. Effect of sample mass and particle size

Preliminary tests in the batch mode showed that 50 mL of 0.50 M citric acid is optimum for complete recovery of fluoride from 50-mg sample of phosphate rock by agitation for 15 min at 55 °C. Starting with 0.50 M citric acid digestion solution pumped at 1.0 mL min^{-1} and setting the leaching temperature to 55 °C the rock sample size (sample E) was increased from 15 to 320 mg. Other parameters are as indicated in Section 3.1. Results showed that as the phosphate rock sample mass increased fluoride recovery remained essentially constant (92%) up to 50 mg mass but decreases steadily at higher masses. The decrease of recovery at higher masses is generally due to low concentration of leaching reagent. Percent fluoride recovery was determined from a calibration curve similar to that in Fig. 3B.

The effect of rock particle size on fluoride recovery was studied by gringing portions of sample E to pass 100, 170, 200, 270, 325 and 400 mesh and subjecting 50 mg masses of these portions to fluoride analysis using the above conditions. Results showed that as rock particle size was decreased there was a corresponding increase in recovery. Full recovery (98–102.4%) was achieved for mesh sizes of 325 and 400. Therefore, grinding the samples to pass 325 mesh was used for further optimization.

3.3. Effect of leaching coil dimensions

For a 50-mg of 325-mesh rock sample E leached under the optimized conditions above, the length of the 1.2-mm i.d. digestion coil was varied between 50 and 500 cm. This resulted in an initial steep rise in fluoride recovery with quantitative recovery for coil lengths of 300 cm or more. Analytical precision is best for short tubes and R.S.D. increased from 0.75 to 1.40%, furthermore, peak width increased form 84 to 118 s. With other parameters as above, and for a 300 cm long coil, increasing the coil internal diameter from 0.53 to 2.2 mm resulted in an increase in fluoride recovery with full recovery in a 1.2 mm i.d. tube. Larger diameter tubes showed progressively shorter and wider fluoride peak response. Furthermore, there is a dramatic loss of precision with R.S.D. increasing from 1.1 to 4.8%. For subsequent tests a 300 cm with 1.2 mm i.d. tube was selected because of full recovery and reasonable R.S.D. of 1.36%. With continued service for 3 months it was noticed that the leaching Tygon tube lost some elasticity, however, fluoride leaching efficiency was not affected.

3.4. Effect of flow rates

Using the optimized parameters above the flow rate of the leaching solution was increase from 0.29 to 3.75 mL min^{-1} by varying the pump tube diameter. The waste stream flow rate was also increased accordingly to maintain the liquid level in the bottle of the flow cell. Results indicated a steady fluoride recovery for flow rates up to 1.24 mL but gradual loss of recovery (down to 54%) for higher flow rates. A leaching solution flow rate of 1.20 mL min^{-1} was adopted as optimum value to maintain full recovery of fluoride.

Changing the carrier flow rate, between 0.29 and 3.75 mL min^{-1}, resulted in sharper but shorter peaks response functions; peak height dropped from 28.0 to 11.1 mV while peak width was decreased from 226 to 42 s. A carrier flow rate of 1.0 mL min^{-1} was selected because of good precision of 2.16% R.S.D. compared with 2.67 % R.S.D. for the highest flow rate ($n = 5$).

3.5. Effect of zone sampling loop volume

Direct pumping of the leachate solution into the flow cell resulted in high baseline noise and lengthy injection cycle. Zone sampling using V3 was introduced to cool down the digest, reduce baseline noise and to shorten the injection cycle. By proper timer programming the selected sampling zone was that of maximum fluoride concentration because it gave the best analytical precision.

Under the above optimized conditions varying the loop volume (by varying the length of the loop L in Fig. 1) from 44 to 350 μL resulted in a linear loss of peak height from 33 to 5 mV and a modest increase of peak width from 76 to 97 s. Replicate analysis ($n = 5$) showed an improvement of precision from 3.20% R.S.D. for a 44 μL volume to 1.88% R.S.D. for 350 μL. In order to achieve room temperature stability, maintain a wide working range and obtain reasonable precision (2.82% R.S.D.) a small loop volume of 87 μL was selected. Fig. 4 shows typical peaks obtained.

3.6. Application to real samples

The optimized flow injection system was applied to the determination of fluoride in the selected number of phosphate rock samples and a phosphate rock certified reference material. The same rock samples were also analyzed by the standard ASTM wet chemical method which involves steam distilla-

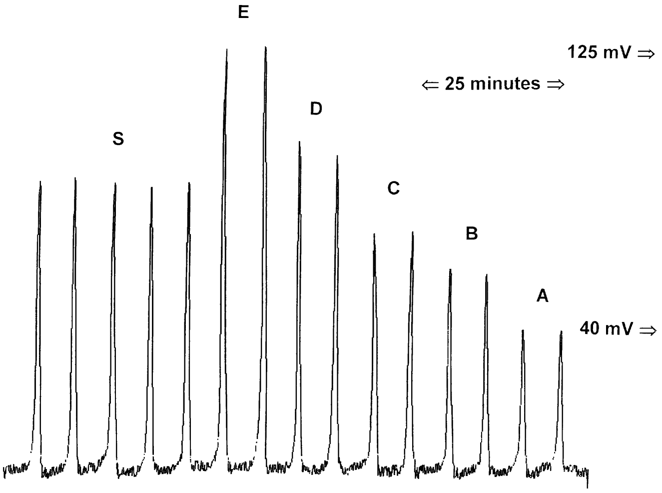

Fig. 4. Typical peaks obtained using $40\,\mu g\,F^{-1}\,mL^{-1}$ in buffer and carrier streams. Fluoride standards used: (A) $12.5\,\mu g\,mL^{-1}$; (B) $10.0\,\mu g\,mL^{-1}$; (C) $7.50\,\mu g\,mL^{-1}$; (D) $2.50\,\mu g\,mL^{-1}$; (E) $1.25\,\mu g\,mL^{-1}$. S shows replicate analyses of 50-mg phosphate rock of sample S.

Table 1
Comparative determination of fluoride in phosphate rock by on-line digestion with citric acid and flow injection potentiometry, and by the standard ASTM method

Sample ID	% Fluoride leaching-FIA	% Fluoride ASTM method	t_{exp}	F_{exp}
QS5	2.49 ± 0.09	2.51 ± 0.06	0.475	1.26
QS6	1.97 ± 0.07	1.99 ± 0.06	0.55	1.36
QS8	1.01 ± 0.04	0.98 ± 0.04	1.36	1.00
E	3.46 ± 0.10	3.52 ± 0.08	1.26	1.56
S	1.28 ± 0.05	1.28 ± 0.04	0.00	1.56
BCR no. 32	4.12 ± 0.11	4.07 ± 0.07	0.99	2.47

The uncertainty next to each result is the 95% confidence limit for five replicates, $t(0.05, 8) = 2.31$ and $F(0.05, 4, 4) = 6.388$.

tion separation of fluoride from strong sulfuric acid solution at 160 °C, followed by titration with thorium nitrate solution [1]. Table 1 summarizes the analytical data obtained by both methods.

T-testing of significance for each pair of mean fluoride values showed no evidence of bias between the developed method and the manual ASTM method at the 95% confidence level ($n = 5$) (Table 2). The slight differences in % fluoride for each data pair can be attributed to random errors. Furthermore, F-test of significance showed that the two methods are of statistically identical analytical precision with 95% confidence (refer to Table 1).

Table 2
Analytical features of the proposed leaching-FIA method as compared with the ASTM method for the determination of fluoride in phosphate rock

Parameter	Leaching-FIA method	ASTM method
Sample treatment time (min)	5	75
Sample analysis time (min)	2	15
Precision (R.S.D., %)	2.6–3.9	1.7–4.0
Analytical range ($\mu g\,F\,g^{-1}$ sample)	500–42000	50–10000

4. Conclusions

Coupled with on-line leaching of fluoride with citric acid solution, the developed flow injection potentiometric method offers a simple and fast technique for the determination of fluoride in phosphate rock. This could serve as a viable substitute to the labor-intensive ASTM method of steam distillation separation of fluoride from strong sulfuric acid solution of the rock and thorium nitrate titration. The demonstrated success of the proposed method is due to elimination of matrix interference of multi-valent metal ions by a combination of selective dissolution of fluoride and the effective complexation of the slight amount of co-dissolved metal ions by citric acid. This method precludes the need for exotic complexing reagents usually recommended in the potentiometric determination of fluoride in real samples.

Acknowledgement

The generous donation of phosphate rock samples and reference material by Jordan Phosphate Mines Company is highly appreciated.

References

[1] Annual Book of ASTM Standards, Vol. 11.03, Philadelphia, PA, 1992, p. 125.
[2] R. Fabian, I. Kotsis, P. Zimany, P. Halmos, Talanta 46 (1998) 1273.
[3] P.E.A. Asea, Analyst 109 (1984) 395.
[4] W.J. Williams, Handbook of Anion Determination, Butterworths & Co., London, 1979, p. 335.
[5] J.V.G. Adelantado, V.P. Martinez, A.C. Moreno, F.B. Reig, Talanta 32 (1985) 224.
[6] J. Tusl, Anal. Chem. 41 (1969) 352.
[7] A. Yuchi, N. Hokari, H. Wada, G. Nakagawa, Analyst 118 (1993) 219.
[8] M.E.L. Gonzalez, M.J.S. Delgado, L.M.P. Diez, Anal. Chim. Acta 178 (1985) 331.
[9] T.J. Cardwell, R.W. Catteral, M. Mitri, Anal. Chim. Acta 214 (1988) 433.
[10] Standard Methods for the Examination of Water and Wastewater, 19th ed., American Public Health Association, 1995, p. 4–59.
[11] A. Yuchi, N. Yanai, H. Wada, G. Nakagawa, Analyst 113 (1988) 1405.
[12] M.S. Corbillon, M.P. Carril, J.M. Madariaga, I. Uriarte, Analyst 120 (1995) 2227.
[13] J. Slanina, W.A. Lingerak, F. Bakker, Anal. Chim. Acta 117 (1980) 91.
[14] D.E. Davey, D.E. Mulcahy, G.R. O'Connell, Anal. Lett. 19 (1986) 1387.
[15] M. Trojanowicz, P.W. Alexander, D.B. Hibbert, Anal. Chim. Acta 366 (1998) 23.
[16] D.E. Davey, D.E. Mulcahy, T.J. Muggleton, G.R. O'Connell, Anal. Lett. 25 (1992) 607.
[17] L. Evans, R.D. Hoyle, J.B. Macaskill, NZ. J. Sci. 13 (1970) 143.
[18] M.S. Frant, J.M. Ross, Anal. Chem. 40 (1968) 1169.
[19] B. Vickery, M.L. Vickery, Analyst 101 (1976) 445.
[20] J.A. Maxwell, Rock and Mineral Analysis, Chemical Analysis Series, vol. 27, 2nd ed., Inter-Science, 1968, p. 211.
[21] T.J. Cardwell, R.W. Cattrall, M. Mitri, Talanta 41 (1994) 115.
[22] I. Papaefstathiou, M.D. Luque de Castro, Anal. Chem. 67 (1995) 3916.

[23] W. Frenzel, P. Bratter, Anal. Chim. Acta 187 (1986) 1.
[24] M. Trojanowicz, W. Matuszewski, Anal. Chim. Acta 138 (1982) 71.
[25] K. Itai, H. Tsunoda, Clin. Chim. Acta 308 (2001) 163.
[26] H. Hara, C. Huang, Anal. Chim. Acta 338 (1997) 141.
[27] C.R. Edmond, Anal. Chem. 41 (1969) 1327.
[28] A.O. Al-Othman, J.A. Sweileh, Talanta 51 (2000) 993.
[29] M. Fouskaki, S. Sotiropoulou, M. Kodi, N.A. Chaniotakis, Anal. Chim. Acta 478 (2003) 77.
[30] J.A. Sweileh, Microchem. J. 65 (2000) 87.
[31] J.A. Sweileh, Anal. Chim. Acta 448 (2001) 151.
[32] M.G. Glaister, G.J. Moody, J.D.R. Thomas, Analyst 110 (1985) 113.