ELSEVIER

On-line dissolution of borate melt for simultaneous matrix isolation, concentration and flame atomic absorption determination of lead in phosphate rock

Jamal A. Sweileh*

Department of Chemistry, University of Qatar, P.O. Box 2713, Doha, Qatar

Abstract

A previously developed on-line flow injection system for solid sample dissolution is described for matrix isolation, concentration and determination of lead in phosphate rock borate melt with flame atomic absorption spectroscopy (FAAS) detection. The flow system can handle slurries and allow solid sample digestion, simultaneous matrix isolation and analyte concentration. Various flow parameters were optimized including, sample size, flow rate, pH and buffer composition. Compared with direct determination by FAAS, the proposed method resulted in almost total elimination of matrix effect and a 15-fold increase in detectability. Ten samples per hour can be processed and analyzed for lead with a detection limit of $0.13\,\mu g\,g^{-1}$ using simple equipment and a flame atomic absorption spectrometer. The analytical results obtained by the proposed method compared favorably with those obtained by mixed-acid digestion of the phosphate rock and graphite furnace atomic absorption spectroscopy (GFAAS). © 2001 Elsevier Science B.V. All rights reserved.

Keywords: On-line digestion; Flow injection; Solid sample insertion; Cation exchange; Lead; Atomic absorption; Phosphate rock; Borate glass

1. Introduction

Strong acid dissolution of rock is a popular technique in many laboratories despite several shortcomings such as slowness, and high reagent and energy consumption [1–3]. Furthermore, acid digestion does not bring about total dissolution of the siliceous part of the sample, unless hydrofluoric acid is used in platinum containers.

Borate fusion is an alternative method for total rock dissolution prior to instrumental analysis by X-ray fluorescence (XRF) of the solid melt [4] or by atomic spectroscopy of the dissolved melt [5–7]. Two main drawbacks are usually encountered in sample dissolution by fusion; the first is contamination of the sample with the flux, which is critical for trace element analysis. Fortunately, pure fluxes are available commercially. The second drawback is the high salt content of the dissolved melt with the resulting high background emission or absorption when atomic spectroscopy is employed for quantification [7].

In atomic absorption, matrix effects (due to molecular absorption of incompletely atomized species in the cell or light scattering) can be eliminated by background correction using a deuterium lamp or other

---

* Tel.: +974-485-2196; fax: +974-485-2795.
E-mail address: sweilehj@qu.edu.qa (J.A. Sweileh).

techniques. However, such techniques may lead to over- or under-correction with subsequent erroneous results especially when dealing with trace elements. In such cases, matrix removal and analyte concentration is necessary [8–18].

The lead concentration in Jordanian phosphate rock is generally less than $5 \mu g \, g^{-1}$. This is well below the limit of quantification ($6.5 \mu g \, g^{-1}$) by flame atomic absorption assuming a dilution factor of 50 (2 g of rock per 100 ml). Using a larger phosphate rock sample would lead to a higher background absorption signal and consequent deterioration of analytical precision [7]. Therefore, a more sensitive and expensive analytical technique is required or else matrix removal is performed. This is the main reason of focusing on the determination of lead in phosphate rock.

In this work, a previously developed system [19] is used for matrix isolation and chelation concentration of lead from a phosphate rock borate melt prior to flame atomic absorption determination.

2. Experimental

2.1. Reagents, chemicals and samples

All chemicals are of analytical reagent quality or better, and spectroscopically pure sodium tetraborate and sodium carbonate were used. Distilled de-ionized water was used for preparation of stock solutions in acid washed polyethylene bottles. Working standards were prepared by dilution of the above stocks prior to use. Buffer solutions were cleaned by several passages through a glass column of Chelex-100 resin (15 cm × 1.2 cm diameter).

A set of Jordanian phosphate rock samples was selected to represent the various grades. Samples labeled QS1 through QS9 were from Ruseifa area near Amman with calcium oxide content range of 16.5–52.5%. Their phosphate content expressed as P_2O_5 ranges between 20 and 33%. These are in-house made reference materials with lead content in the range of $0–5 \mu g \, g^{-1}$. A certified reference phosphate rock material of Moroccan origin (BCR no. 32) was also included. Although it is not certified for lead, the 'indicated' value is $5 \mu g \, g^{-1}$. All samples are in powdered form with grain size of less than 100 mesh.

2.2. Fusion

In a 25 ml platinum crucible $1.000 \pm 0.001 \, g$ of the dried phosphate rock powder was mixed with $4.000 \pm 0.001 \, g$ of flux (a powdered homogenized mixture of 100 g Na_2CO_3, 100 g K_2CO_3, 50 g $Na_2B_4O_7$ and 1 g $NaNO_3$ [7]) using a nickel plated spatula. The crucible was held with a platinum tipped tongue and heated on a regular Bunsen burner for about 6 min with gentle swirling. The cherry-red melt was cooled immediately after the addition of few crystals of KI anti-wetting agent and the solidified melt fragments were collected and pulverized in a clean agate mortar.

2.3. Mixed-acid digestion

Five grams ($\pm 0.001 \, g$) of phosphate rock was digested with 80 ml of HCl (37% w/w), HNO_3 (70% w/w), H_2O mixture (1:2:2 by volume), on a hot plate to near dryness. Next, 2 ml HNO_3 was added to dissolve the soluble salts followed by 10 ml of water and the solution in the covered beaker was boiled for 10 min, cooled and filtered into a 100 ml volumetric flask. The insoluble residue was thoroughly washed with hot water before cooling and completing the filtrate in the flask to the mark.

2.4. Instruments

Graphite furnace analyses were performed on a Perkin-Elmer model Analyzer 700 atomic absorption spectrometer equipped with a deuterium lamp background corrector using a Perkin-Elmer model HGA graphite furnace unit with a AS 800 auto-sampler. The instrument is controlled by a microcomputer-based data acquisition system consisting of a Perkin-Elmer Analyzer software, a Dell GX1 microcomputer and a Hewlett-Packard model 895 CXI printer. Flame atomic absorption work was performed using an ATI Unicam double beam spectrometer model 929. Associated hardware and software components have been described earlier [7]. Instrumental parameters for the determination of lead by both instruments are summarized in Table 1.

A schematic diagram of the flow system used in this work is shown in Fig. 1. It is similar to that reported earlier for the solid sample insertion, digestion, matrix isolation and analyte determination. Details of

Table 1
Instrumental parameters for the determination of lead in phosphate rock by GFAAS and by FAAS

Parameter	Instrument		
	GFAAS	FAAS	
Wavelength (nm)	283.3	217.0	
Lamp current (mA)	7	7	
Slit width (nm)	0.7	0.5	
Background correction	On	On	
Flame type	–	Air/C_2H_2	
Heating cycle	Temperature (°C)	Ramp time (s)	Hold time (s)
Drying	90	1	10
	130	50	20
Ashing	1100	20	10
Atomization	1800	0	4
Cooling	20	5	4
Cleaning	2600	1	5

material, fabrication and dimensions are reported elsewhere [19].

2.5. Procedure

The powdered melt is manually inserted in the sample chamber, S, and dissolved on-line with 2 M HNO_3 carrier solution. The sample insertion chamber shown in detail at the top right corner of Fig. 1 is a modified PVC unit originally designed for use in drip irrigation systems. Details of the modifications made is published elsewhere [19]. The sample chamber volume is nominally 250 µl. After passage in the digestion coil, DU, the digest is neutralized and buffered by merging with ammonia and buffer streams at T_1 and T_2, respectively. Next, lead ions are retained on a coarse-particle chelating mini column, C (Chelex-100, +50 mesh, Sigma, Poole, Dorset, UK), while the
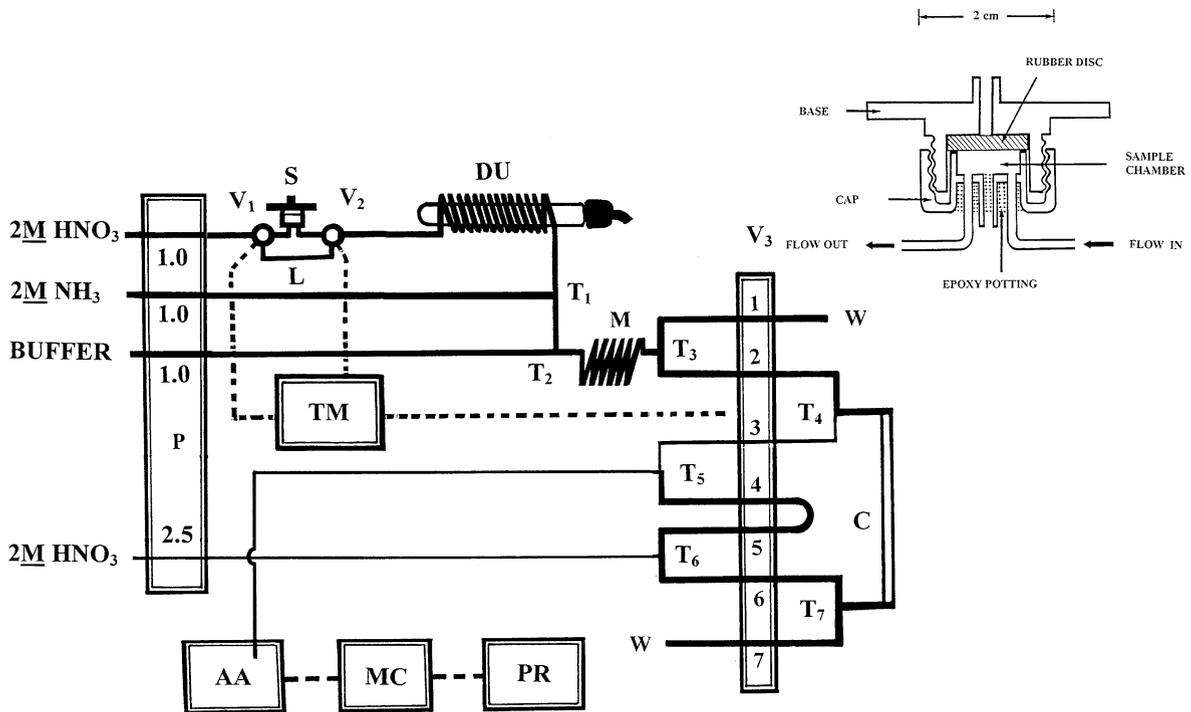
Fig. 1. Schematic diagram for on-line solid melt digestion matrix isolation, concentration and flame atomic absorption analysis of lead in phosphate rock. P, peristaltic pump; S, sample insertion unit; V_1 and V_2, three-way solenoid valves; L, bypass; DU, digestion unit; M, mixing coil; TM, programmable timer; V_3, multi-channel pinch valve; AA, flame atomic absorption spectrometer; MC, micro-computer; PR, printer; W, waste. The figures on the pump are the flow rates in ml min^{-1}. Line thickness indicates relative internal diameter of tubing, and dashed lines are electrical wires. The insert at the top right corner shows details of the sample insertion device.

precipitated sample matrix (mainly calcium phosphate and borate) is driven to waste via T_7. Finally, the multi-channel pinch valve, V_3, is switched to the elution mode and the 2 M HNO_3 eluant stream elutes the retained lead into the nebulizer of the flame atomic absorption detector. The programmable timer, TM, controls the sequential operation of all valves.

3. Results and discussion

3.1. Melt digestion

Although on-line digestion of a single chunk of melt is possible, a powdered sample is digested in a shorter time. Melt weights as high as 0.50 g can be accommodated in the insertion chamber. Initial experiments showed that accelerated digestion of powdered melt employing the heating source was not necessary because the heat of solution is enough for the complete digestion. With the heating source set to "low" (42°C) there is less pressure build-up in the system and more precise analytical results. Powdering the sample is advantageous in terms of sample homogeneity and speed of dissolution.

Increasing the digestion acid flow rate from 0.5 to 1.5 ml per min gave no effect on the lead signal. Flow rates higher than 1.5 ml min^{-1} resulted in gradual drop in lead signal height, a lowering of 19% for a flow rate of 2.5 ml min^{-1}. This could be due to slow kinetics of lead chelation or to the incomplete dissolution of the melt during the progressively shorter digestion time with increasing flow rate.

Although higher concentration than 2 M HNO_3 is more efficient in melt dissolution, it was not incorporated because it causes visible deterioration (yellowness) of the PVC or Tygon tubes and other components of the system. Furthermore, a high level of digesting acid requires an equally high level of neutralizing base with subsequently higher levels of salts that impair lead concentration and detection.

3.2. Matrix isolation and concentration

Upon merging the acidic digest with neutralizing 2 M ammonia and 0.5 M ammonium acetate buffer streams [20], the pH of the combined stream is raised to about 7.8 which results in precipitation of a colloidal

suspension of mainly calcium phosphate and borate. This suspension is passed through the column end screens unimpeded while lead ions are partially sorbed on the Chelex-100 resin beads. Although lead recovery under the optimized conditions is slightly less than 60% (for a 0.5 μg g^{-1} lead in the melt), this recovery is fairly reproducible for analytical application. The low recovery of lead may be attributed to the presence of solid matrix salts which tends to adsorb some of the lead ions at slightly basic pH values. Over 90% of the major matrix elements of the rock and the flux were isolated from the analyte. The 75% of the iron was also removed probably as the hydrated oxide.

Direct aspiration of the mixed-acid digested rock sample (5 g per 100 ml) into the flame atomic absorption spectrometer resulted in a very small signal which is below the liquid of quantification [7]. The Chelex-100 concentration system described here resulted in a 15-fold improvement in detectability and easy quantification for lead.

Increasing the mass of powdered melt from 0.05 to 0.50 g resulted in a linear increase in lead signal. Larger sample sizes were not tried, as this requires modification of the sample insertion unit by increasing the volume of the chamber. However, the output signal is high enough for a reasonably accurate determination of lead in phosphate rock.

3.3. Effect of pH of loading solution

The effect of pH on retention of lead was conducted by injecting 480 μl of 1.0 μg ml^{-1} of lead in 2 M HNO_3 carrier digestion solution. The 480 μl loop volume rotary manual sample injection valve was placed in the by-pass line (L) of the sample insertion unit. The pH of the buffer solution stream was varied between 4.0 and 9.0 by proper change of composition (sodium acetate–acetic acid or ammonia–ammonium chloride). Maximum retention of lead is achieved between pH 7.2 and 8.5. A middle pH value of 7.8 was used for subsequent tests using 0.5 M ammonia–ammonium acetate [20].

3.4. Effect of eluant

Other parameters being constant as described in Section 3.3, increasing eluant strength from 0.2 to 4 M affects the sharpness of the lead signal with the effect

Table 2
Analytical results for the determination of lead in phosphate rock by on-line digestion of the borate melt with FAAS detection and by mixed-acid digestion of the rock with GFAAS detection

Sample no.	Concentration of lead[a] (μg g^{-1})		95% *t*-test of significance $t(0.05, 4) = 2.78$
	On-line digestion FAAS	Mixed-acid digestion GFAAS	
QS1	1.6 ± 0.3	1.8 ± 0.1	1.09
QS2	2.1 ± 0.2	2.3 ± 0.2	1.22
QS3	0.6 ± 0.3	0.7 ± 0.2	0.48
QS4	1.1 ± 0.3	1.4 ± 0.1	1.64
QS5	2.1 ± 0.2	2.2 ± 0.1	0.77
QS8	3.8 ± 0.3	4.1 ± 0.2	1.44
QS9	5.3 ± 0.2	5.1 ± 0.1	1.55
BCR no. 32	4.6 ± 0.3	4.8 ± 0.1	1.09

[a] Uncertainty is the standard deviation for triplicate results.

being minimal above 2.5 M HNO$_3$. Therefore, a 2 M HNO$_3$ eluant was adopted to avoid the destructive effect of more concentrated HNO$_3$ on non-Teflon parts and tubing in the system.

Hydrochloric acid is a good eluant and causes less damage to PVC and Tygon parts. However, chloride ions cause more spectral interference than nitrate ions in the determination of lead by flame or electro-thermal atomic absorption [21,22].

3.5. Analysis of phosphate rock samples

The proposed on-line system can analyze for lead in the solid ore sample in 20 min (14 min for fusion and 6 min for on-line dissolution, processing and analysis). This is much faster, easier and less expensive than the alternative mixed-acid digestion and GFAAS analysis that could take up to 40 min.

Due to the lack of a lead certified phosphate rock samples, a set of in-house prepared standard phosphate rock samples and an international phosphate rock reference material (BCR no. 32) were used to test the developed method. The borate glass discs of the selected rock samples were pulverized in an agate mortar and analyzed in triplicate by the optimized method. The same rock samples were also digested by the conventional mixed-acid method outlined in Section 2.3, and determined in triplicate by the more sensitive GFAAS.

The calibration standards were 4 g of flux mixture and 1 g of pure calcium phosphate, which has been spiked with 0–20 μg of lead and processed as for the samples. The calibration curve was linear with a slope of 0.031 ± 0.002 AU g μg^{-1} and an intercept of 0.004 ± 0.001 absorbance unit. The correlation coefficient was 0.997. The comparative results by both methods are presented in Table 2. These results confirm the applicability of the proposed on-line method for the determination of traces of lead in phosphate rock, which was not possible by FAAS without concentration and matrix isolation [7]. Six replicates of QS1 and QS8 showed a relative standard deviation of 5.6 and 4.5%, respectively, indicating reasonable precision for this low level of lead in the rock.

Analytical data by the proposed flow method is generally lower than those obtained by GFAAS (Table 2). However, *t*-testing of significance at 95% confidence level, $t(0.05, 4) = 2.78$, shows that the differences in the results between the two techniques are not significant.

4. Conclusions

The proposed method is capable of complete dissolution of the powdered melt, separation of over 85% of the matrix components of the sample-flux solution, and 15-fold concentration of the lead prior to on-line FAAS detection. The unique column design, which does not include filtering elements, allows low pressure simultaneous concentration of the analyte and removal of the precipitated matrix components. The automated closed system avoids contamination from outside sources. Combined with the fast fusion technique for phosphate rock which was developed

earlier [7], the proposed simple and inexpensive method offers a new alternative to the lengthy classical mixed-acid digestion and filtration of the insoluble residue prior to graphite furnace atomic absorption determination of lead.

References

[1] R. Bock, A Handbook for Decomposition Methods in Analytical Chemistry (translated by I.L. Marr), International Textbook Co., Glasgow, UK, 1979.

[2] P.G. Jeffery, D. Hutchinson, Chemical Methods of Rock Analysis, 3rd Edition, Pergamon Press, Oxford, 1981.

[3] Methods Used and Adopted by Association of Florida Phosphate Chemists, 7th Edition, Bartow, FL, 1991.

[4] J.A. Sweileh, J.K. Van Peteghem, Can. J. Appl. Spectrosc. 40 (1995) 8.

[5] J. Bozic, D. Maskery, S. Maggs, H. Susil, F.E. Smith, Analyst 114 (1988) 1401.

[6] A.A. Wittmann, G.M.H. Willay, Spectrochim. Acta Part B 40 (1985) 253.

[7] J.A. Sweileh, Al-Manarah 4 (1999) 173.

[8] J. Minczewski, J. Chewastowska, R. Dybczynski, Separation and Preconcentration Methods in Inonganic Trace Analysis, Ellis Horwood, Chichester, UK, 1982.

[9] S.R. Bysouth, J.F. Tyson, Anal. Chim. Acta 214 (1988) 329.

[10] E. Debrah, C.E. Adeeyinwo, S.R. Bysouth, J.F. Tyson, Analyst 115 (1990) 1543.

[11] R. Purohit, S. Devi, Anal. Chim. Acta 259 (1992) 53.

[12] Z. Liu, S. Huang, Anal. Chim. Acta 281 (1993) 185.

[13] D. Rodriguez, P. Fernandez, C. Perez-Conde, A. Gutierrez, C. Camara, Fr. J. Anal. Chem. 349 (1994) 442.

[14] S. Rio-Segade, B. Perez-Cid, C. Bendicho, Fr. J. Anal. Chem. 351 (1995) 798.

[15] O. Elshole, G. Schulze, Fr. J. Anal. Chem. 353 (1995) 119.

[16] V.K. Jain, S.S. Sait, P. Shrivastav, Y.K. Agrawal, Talanta 45 (1997) 397.

[17] C. Ke, K. Lin, Anal. Chem. 71 (1999) 1561.

[18] B. Noresson, P. Hashemi, A. Olin, Talanta 46 (1998) 1051–1063.

[19] J.A. Sweileh, Microchem. J. 65 (2000) 87.

[20] R.A. Nickson, S.J. Hill, P.J. Worsfold, Anal. Chim. Acta 351 (1997) 311.

[21] G.F.R. Gilchrist, C.L. Chakrabarti, J. Cheng, D.M. Huges, J. Anal. Atom. Spectrom. 8 (1993) 623.

[22] A.A. Ashy, A.A. Samarkandy, K.M. Emara, Int. J. Chem. 6 (1995) 11.