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A sensitive method for determination of phosphorous by continuum source graphite furnace atomic absorption spectrometry after a novel ionic liquid assisted cloud point extraction†

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Wall and platform atomisation have been investigated for the determination of phosphorus using palladium modifier in continuum source graphite furnace atomic absorption spectrometry (CS-GFAAS). Wall is found to have a better sensitivity compared to platform. This could be due to increase in population of non resonance line used in determination of phosphorus, since wall is heated directly. However, wall has inherent matrix interference problems, hence a matrix separation and pre-concentration procedure using ionic liquid assisted cloud point extraction is described. The method is based on the formation of hydrophobic ion-associate between anionic phosphomolybdate and 1-butyl-3-methylimidazolium chloride in the presence of H_2SO_4. The non-ionic Triton X-114 micelles have been used for pre-concentration of this ion-associate from a bulk aqueous phase into a small surfactant-rich phase. The main parameters affecting the extraction process are optimized. The characteristic mass of 0.4 ng is achieved after cloud point extraction. Under the optimized conditions, the pre-concentration factor is 50. The limit of detection is 0.06 μg g^{-1}, for solid samples and 0.6 ng mL^{-1} for water. The recoveries are in the range of 95–98% with 2–4% relative standard deviation. The accuracy of the procedure is validated by analyzing NIST 8435 whole milk powder, 1549 non-fat milk powder, 1548 total diet and 1568a rice flour, and BCR 063R skim milk powder certified reference materials.

1 Introduction

Phosphorous is an element which is not typically determined by AAS because of the reasons like non availability of atomic resonance lines in the UV region, difficulty in atomization due to the formation of volatile species, its interaction with graphite surface when GFAAS is used, and spectral interference due to overlap of PO molecular absorbance band. For determination of P by atomic spectroscopy the non-resonance line doublet at 213.5–213.6 nm has been recommended and used, since the two resonance lines of this element lie in the vacuum UV (167.16 nm and 178.77 nm) region.[1] A non-resonance line involves the transition from an excited state which is generally less populated, hence leading to poor intensity and consequently, poor limit of detection (LOD). The introduction of HR-CS-AAS (high-resolution continuum source atomic absorption spectrometer) with xenon short arc lamp in recent years has helped access to all wavelengths in the region 190–900 nm with sufficiently high intensity. Therefore, this technique has been very useful in understanding the problems related to determination of phosphorous by AAS.

Selection of suitable chemical modifier is very important for the determination of phosphorous using GFAAS to prevent pre-atomization losses.[2] Therefore, in the past many modifiers have been suggested but no definite conclusion could be made.[3] HR-CS-AAS with its ability to see both phosphorous atomic lines and PO molecular bands simultaneously have helped to find suitable chemical modifiers for its determination. From among the different modifiers, like La, NaF, Pd, Pd + Ca, Pd + ascorbic acid, it has been found that the Pd based modifiers are most suitable because they predominantly form atoms and inhibit the formation of PO molecules observed in other cases.[4,5] Atomization of phosphorous has been investigated using a HR-CS-AAS from a graphite platform as well as from a tantalum boat inserted in a graphite tube, where a two step atomization is proposed.[6] With HR-CS-AAS, artifacts during measurement of phosphorous using the line source at 213.6 nm non-resonance line by D_2 background correction in GFAAS has been studied.[7] It has been found later that Zeeman background can successfully correct such structured background due to PO molecule.[8] Both GFAAS and HR-CS-GFAAS has been used to determine phosphorous directly using solid sampling technique without dissolution in food, plastics and in biological materials, and more recently in biodiesel.[9–13]

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The limits of detection of phosphorous reported in these methods are poor, when compared to other elements usually determined by GFAAS. One of the main reasons for this is the use of a non-resonance line which is thinly populated. This population has been increased by using a higher and fast atomization temperature in the range of 2600–2700 °C used with platform GFAAS.[10] However, use of wall atomization can populate the upper non resonance levels faster since the wall is directly heated while the platform is heated indirectly through radiations from the wall surface. This can improve the limit of detection of phosphorous, but needs a matrix separation procedure to reduce the inherent matrix interference problems associated with wall atomization because analyte after atomization from the wall recombines in the central part of the tube which is at a lower temperature than wall. Hence, it is envisioned that the concepts of combining an efficient matrix separation and analyte pre-concentration with wall atomization in CS-GFAAS can improve the sensitivity and limit of detection of phosphorus.

For demonstrating the analytical applicability of the above concept, we have selected an environmentally friendly cloud point extraction (CPE) procedure. Over the three decades, only two CPE procedures have been reported for the determination of phosphorus in various water samples. Afkhami and Norooz-Asl[14] and Katsaounos *et al.*[15] have extracted the blue and yellow heteropoly acids, respectively, using micelles and mixed-micelles CPE and determined spectrophotometrically.

In this work, for the first time, we describe an ionic liquid assisted cloud point extraction procedure for the separation and pre-concentration of phosphorus from microwave digested food CRMs and water samples. Determination has been carried out using CS-GFAAS with wall atomization. The method is based on the formation of extractable hydrophobic ion-associations between anionic phosphomolybdate in acidic condition with an ionic liquid 1-butyl-3-methylimidazolium chloride (BMIC). This ion associate is then extracted from the bulk aqueous phase into a small volume of Triton X-114 surfactant-rich phase. Accuracy of the procedure is verified by analyzing NIST 8435 whole milk powder, 1549 non-fat milk powder, 1548 total diet and 1568a rice flour and BCR 063R skim milk powder certified reference materials. The method has been then applied to water samples.

2 Experimental

2.1 Instrumentation

The phosphorous concentrations in the dissolved surfactant-rich phases were determined by using continuum source graphite furnace atomic absorption spectrometry (Contra AA 700, Analytik Jena AG, Jena, Germany). A transversely heated graphite tube with and without a platform, an MPE 60 auto sampler and a xenon short arc lamp in hot-spot mode operated at 300 W as a continuum radiation source were used. A high resolution double monochromator consisting of a prism and an echelle grating, providing a spectral bandwidth per pixel of *ca.* 2 pm at 200 nm, was used. A linear charge coupled device (CCD) array detector with total 588 pixels, out of which 200 pixels were used for the determination of dispersed radiation. The phosphorous absorption was measured using the central pixel ±1. Argon with a purity of 99.99% was used as the purge gas in all stages, except during atomization step. An analytical line at 213.6175 nm was used to measure the absorbance of the phosphorous signal. The optimized temperature program used for the determination of phosphorous in the final surfactant-rich phase is given in Table 1. All the matrices were digested using a MARS (CEM, Matthews, NC, USA) microwave digester and high pressure PTFE vessels.

2.2 Reagents and standard solutions

Ultra pure water (18.3 MΩ cm) obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA) was used to prepare all the solutions. Sub-boiled HNO_3 was prepared in our laboratory using the quartz stills. Suprapur H_2SO_4 (Merck, Darmstadt, Germany), Triton X-114 (Sigma-Aldrich, Steinheim, Germany) and tetra butyl ammonium bromide (TBAB) (Sigma-Aldrich, Steinheim, Germany) and ionic liquid, 1-butyl-3-methylimidazolium chloride (Chemsworth, Surat, India) solutions of 10% m/v in water were prepared by dissolving 1 g in 10 mL Milli-Q water. A 10% m/v solution of Aliquat-336 (Sigma-Aldrich, Steinheim, Germany) was prepared by dissolving 3 g of Aliquat-336 in 30 mL methanol. A 2% m/v solution of ammonium molybdate tetrahydrate (Merck, Darmstadt, Germany) was prepared in 10% v/v H_2SO_4. The phosphorus stock (1 mg mL^{-1}) solution was used to prepare the working standards in 2% v/v HNO_3. The 1 mg mL^{-1} palladium modifier prepared in 2% v/v HNO_3 from the 10 mg mL^{-1} stock solution in 15% v/v HNO_3 (Sigma-Aldrich, Steinheim, Germany) was used as a modifier. Methanol from (Merck, Darmstadt, Germany) was used for dissolving the surfactant-rich phase. Stock standard solutions of (1 mg mL^{-1}) analytes such as Ca^{2+}, Mg^{2+}, Cu^{2+}, Cd^{2+}, Pb^{2+}, Ni^{2+}, Ge^{4+}, Cr^{6+}, Hg^{2+}, Si^{4+} and As^{5+} used for interference study were prepared using their respective salts. All the polypropylene containers were cleaned with a mixture of 10% v/v nitric and hydrochloric acids and then with Milli-Q water.

2.3 Microwave digestion procedure

Accurately weighted 200–300 mg of certified reference materials were transferred into the pre-cleaned high pressure vessels. To this 2 mL HNO_3 was added and kept for pre-digestion at room temperature for 30 minutes. The vessels were then closed and

Table 1 Optimized temperature program used for the determination of phosphorous in the surfactant-rich phase after cloud point extraction using CS-GFAAS

Step	Temperature/ °C	Ramp/ °C s^{-1}	Hold/ s	Ar flow/ mL min^{-1}
Drying-1	80	6	20	250
Drying-2	90	3	20	250
Drying-3	110	5	10	250
Pyrolysis	1700	300	10	250
Gas adoption	1700	0	5	250
Atomization	2700	2700	4	0 (read)
Cleaning	2750	1500	3	250

digested using an optimized microwave program: 100 °C for 3 min, 150 °C for 3 min and 200 °C for 5 min using maximum power of 600 W and pressure of 500 psi. After cooling, the vessels were opened and 1 mL H_2O_2 was added to the digest and the same temperature program was repeated. The digests were made up to 20 mL using ultrapure water. Process blanks were also prepared in a similar manner.

2.4 Cloud point extraction procedure

Aliquots of 0.1–0.2 mL digests were taken in pre-cleaned polypropylene centrifuge tubes and acidified with 2.5 mL of 10% v/v H_2SO_4. To this 1 mL of 2% m/v ammonium molybdate, 0.1 mL of 10% m/v 1-butyl-3-methylimidazolium chloride and 1 mL of 10% m/v Triton X-114 were added and made up to 25 mL using Milli-Q water. These solutions were mixed well for 2 min and then heated to 90 °C. After 20 min heating gravitational phase separation was obtained. The 0.2 mL surfactant-rich phase was easily separated by decanting the bulk aqueous phases after cooling the solutions in a refrigerator for 10 min. The viscosity of the surfactant-rich phase was reduced by dissolving it in 0.3 mL acetonitrile containing 0.05 mL HNO_3, so that total volume is 0.5 mL. It was then analyzed for phosphorus using CS-GFAAS by using an aliquot of 10 μL with 5 μL palladium modifier using wall atomization in peak heights. Process blanks were also prepared and analysed in a similar manner.

3 Results and discussion

3.1 Optimization of temperature programme for wall/platform

Fig. 1a shows pyrolysis and atomization temperature curves obtained by injecting 10 μL of the 5 μg mL^{-1} phosphorus (50 ng absolute) along with palladium modifier using wall as well as platform. Peak heights of the absorbance spectra were measured in both cases. It is observed that nearly 4–5 times higher signal is obtained from wall than platform atomization. Besides this, when the pyrolysis and atomization temperatures were increased between 1100 to 1800 °C and 2000 to 2800 °C, respectively, in the case of wall atomization there is gradual increase in signal until pyrolysis temperature of 1700 °C, and atomization temperature of 2700 °C was reached, beyond which losses were observed. In the case of platform atomization no such increase in the absorbance signal was observed with the same increase in pyrolysis and atomization temperatures, but was constant throughout and losses were seen at 1800 and 2800 °C.

The mechanism of atomization of phosphorus in the presence of palladium modifier has been described by Lepri *et al.*,[4] where palladium was the active compound, which was bound to phosphorus strongly. It stabilizes species like PO by acting as an electron donor due to elevated electron density though π electron interaction of the graphite system. The sharp peak obtained suggests that the species does not penetrate deeply into the graphite structure and remains on the surface. Stabilization temperature of 1700 °C was also reported by other authors,[3] however, the difference between the wall and platform

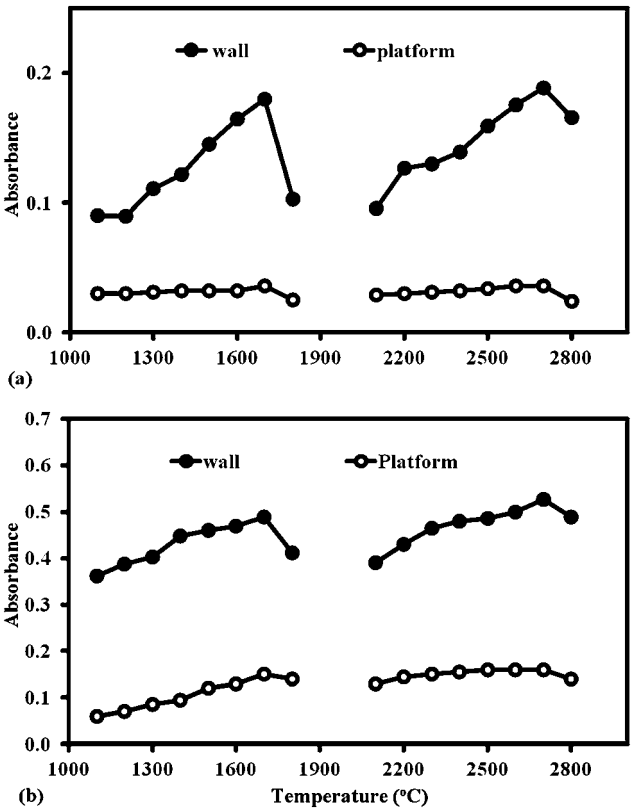

Fig. 1 Effect of pyrolysis and atomization temperatures on the absorbance of 50 ng P (absolute), inside the furnace; wall *vs.* platform atomization with palladium modifier (a) P aqueous standard, 5 μg mL^{-1}, and (b) P in surfactant rich phase 0.1 μg mL^{-1} aqueous standard subjected to cloud point extraction.

was that much sharper peaks are formed with wall than with platform and when peak height was measured, a higher absorbance signal was obtained for wall. Since the atomization mechanism is common for both wall and platform, the only difference is that the wall was heated directly and this will increase the population density of the non-resonance lines of phosphorus compared to the platform which was heated through radiations from wall. The fact that there is an increase in absorbance signal with increase in atomization temperature in the case of wall atomization supports this assumption.

Since the phosphorus was determined in CS-GFAAS after its cloud point extraction as a phosphomolybdate complex, the effect of pyrolysis and atomization temperatures on phosphomolybdate complex after CPE was studied using wall and platform atomization in the presence of palladium modifier, and the results are shown in Fig. 1b. The loss in phosphorus signal was observed at the same pyrolysis and atomization temperatures as observed for aqueous standards that is beyond 1700 and 2700 °C, respectively. An absorbance signal of 0.5265 for 50 ng phosphorus was obtained after pre-concentration of low levels of phosphorus. However additional stabilization is observed in surfactant-rich phase, where phosphorus is present as phosphomolybdic complex along with ionic liquid and non-ionic micelles after CPE. The absorption profile of aqueous phosphorus in three (abs *vs.* wl *vs.* time) and two (abs *vs.* time)

dimensions using wall and platform atomization are shown in Fig. 2 and 3 (after CPE). With platform atomization additional stabilisation in signal was also seen, but the increase in absorbance was not to the same extent as obtained with wall atomization. It is also observed from the three dimensional spectra that no additional species were observed in wall atomization after cloud point extraction. Therefore, a wall atomization was used for determination of phosphorus.

3.2 Direct determination of phosphorus from digested CRMs

At first microwave digested CRMs were analysed directly by using wall atomization and peak height with Pd modifier. The results are given in Table 2. From this table it is seen that the recovery of around 31–37% was obtained for all CRMs analysed. By using Pd and ascorbic acid (W coated tube)[10] there was not much improvement in the recovery. The absorbance signal obtained was severely suppressed in the presence of these matrixes, and therefore a separation procedure was necessary.

3.3 Optimization of cloud point extraction parameters

Since the phosphorous exists as an anionic species in the acidic solution, its direct CPE is impossible due to high hydrophilicity. Its hydrophilicity is reduced by converting it into phosphomolybdate yellow that is used very well in the spectrophotometric determination. Hence, in the present procedure the cloud point extraction efficiency of phosphomolybdate has been studied by forming its ion-associate with ionic liquid. Therefore, the parameters affecting the ionic liquid assisted cloud point extraction procedure were optimized for maximum signal using 20 ng mL^{-1} phosphorous standards along with BCR 065R skim milk powder digest. In all these experiments the maximum absorbance signal obtained was normalised to 100% and then the subsequent signals were shown as % recovery based on this signal.

3.3.1 Selection of non ionic surfactants and phase transfer reagent. The success of cloud point extraction depends mainly on the hydrophobicity of the extracting surfactant and their efficient interaction and kinetic transfer of hydrophobic metal chelates and ion-associates into the micellar aggregates during their phase separation. Hence, the selection of surfactant depends on its hydrophobicity. It will vary with structures of head and tail groups of surfactants. In this study, Triton X-114 and Nonidet P-40 non-ionic surfactants were selected to study the extraction efficiency of phosphorus, which differ in their number of ethylene oxide groups. Therefore, the effect of these surfactants on the recovery of phosphorus were studied in the range of 0.1–1% m/v in the presence of 1% v/v H_2SO_4, 0.08% m/v ammonium molybdate and 0.04% m/v ionic liquid. The results are shown in Fig. S1.† The results show that the recoveries (maximum signal normalised to 100%) increased with an increase in the concentration of Triton X-114 and Nonidet P-40 from 0.1% to 0.3%, and then reached a plateau with recoveries between 96–100% and 68–70%, respectively, up to a concentration of 0.6%. Further increase in the concentration of Triton X-114 and Nonidet P-40 above 0.6% causes the decrease in the recovery up to a studied concentration of 1%. These results indicate that Nonidet P-40 is unable to extract phosphorus quantitatively. The hydrophobicity of the surfactants depends on the hydrophilic–lipophilic balance (HLB values) lower its value, the more hydrophobic is the surfactant. The values of HBL for Nonidet P-40 and Triton X-114 are 13.5 and 12.3, respectively. It indicates the Triton X-114 is more hydrophobic

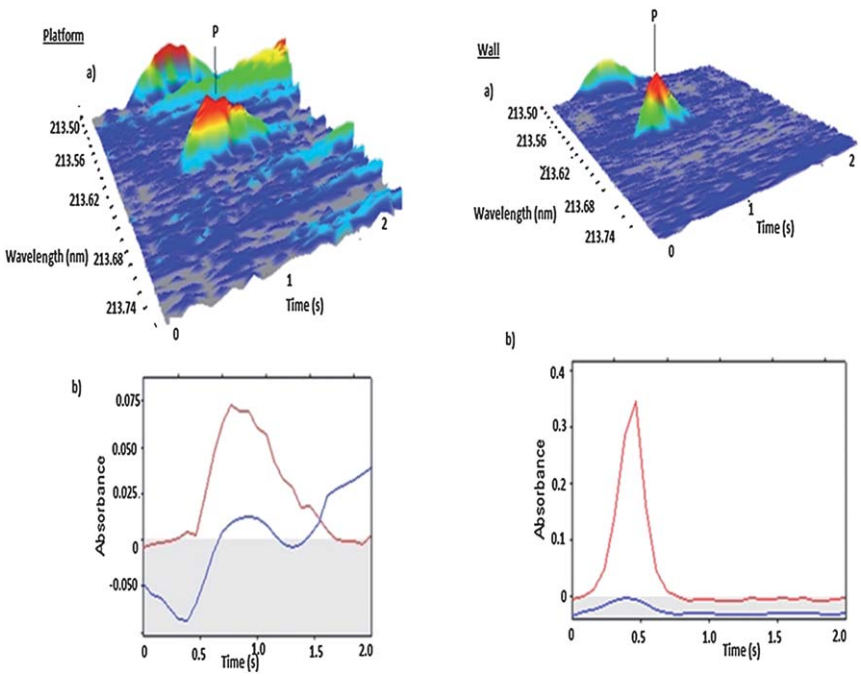

Fig. 2 Absorption profile of aqueous phosphorus (100 ng absolute) in (a) three and (b) two dimensions using wall and platform atomization of CS-GFAAS before CPE.

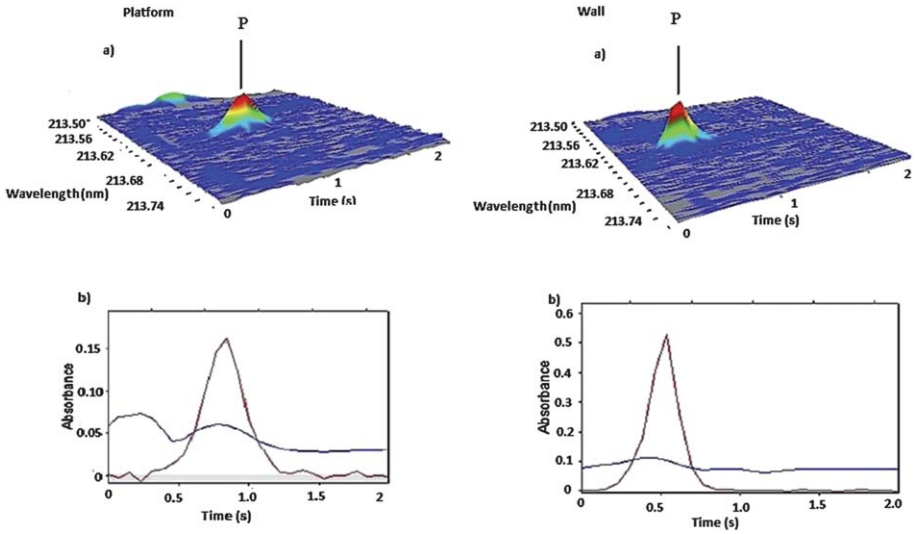

Fig. 3 Absorption profile of aqueous phosphorus (50 ng absolute) in (a) three and (b) two dimensions using wall and platform atomization of CS-GFAAS after CPE.

than Nonidet P-40, hence its extraction efficiency is better than Nonidet P-40 from aqueous phase and therefore selected for this work.

The success of the cloud point extraction also depends on the hydrophobicity of the extracting species, which interact through van der Waals forces with extracting micellar aggregates. Hence, the recovery (maximum signal normalised to 100%) of phosphorus was studied by using various phase transfer reagents such as aliquat-336, TBAB and BMIC ionic liquid in the range of 0–0.2% m/v in presence of 1% v/v H_2SO_4, 0.08% m/v ammonium molybdate, and 0.4% m/v Triton X-114. The results are shown in Fig. 4. It shows that in the case of BMIC ionic liquid, the recoveries in the range of 96–100% were obtained in the concentration range of 0.4% to 0.12% m/v, beyond this range lower recovery between 85 and 90% was observed. With TBAB and aliquat-336, the recoveries were found to give a maximum extraction of around 70% and decreased gradually and reached a minimum of 55% and 20%, respectively, beyond concentration of 0.12%. The poor recovery for aliquat-336 and TBAB may be due to steric hindrance of tri octyl and tetra butyl group around the quaternary nitrogen which prevents the close approach of the anionic phosphomolybdate.

These experiments indicate that overall extraction mechanism of phosphomolybdate complex could be due the combined synergic effects of surfactant micelles as well as ionic liquid molecules, because in the absence of ionic liquid at least 40% recovery has been obtained by Triton X-114 micelles and ionic liquid assists in further enhancement of the recovery.

3.3.2 Optimization of acid and ammonium molybdate concentration. The phosphomolybdic acid is formed in sulphuric acid medium; therefore, it was optimized along with nitric acid for its maximum signal (normalised to 100%) in the range of 0.1 to 4% v/v. Fig. S2† shows that nearly 95–100% and 92–98% recoveries were obtained between 0.5 and 2% v/v sulphuric and nitric acids, and the presence of nitric acid up to 2% did not have any effect on extraction efficiency. Therefore, the digests used in the present CPE procedure contains only 0.1% v/v HNO_3 after dilution, which does not affect these recoveries.

Amount of ammonium molybdate was optimized, in the range of 0.01–0.15% m/v to convert water soluble phosphate into hydrophobic phosphomolybdate for efficient cloud point extraction. The study was performed using phosphorus standard and BCR 065R digest and results are shown in Fig. S3.† A recovery between 95 and 100% was obtained when ammonium molybdate concentration was in the range 0.07 to 0.15% in standard and digest. Hence, a concentration of 0.08% m/v ammonium molybdate was selected.

3.3.3 Effect of extraction temperature and time. The effect of extraction temperature on recovery (maximum signal normalised to 100%) and pre-concentration factor (PCF), defined as the ratio of concentration of analyte in the surfactant rich phase (SRP) to the concentration of analyte aqueous phase of phosphorus were studied in the range of 30–90 °C using a 20 minute extraction time. The results are shown in Fig. S4.† From this figure it is observed that the maximum recovery of 97–100% was obtained between temperatures of 70 and 90 °C. It indicates

Table 2 Direct determination of phosphorus in various digested certified reference materials using CS-GFAAS ($n = 3$)

Matrices	Certified value/%	Measured value/%	Recovery/%
BCR-063R skim milk powder	1.110 ± 0.130	0.381 ± 0.09	34 ± 2
NIST 1549 non fat milk powder	1.062 ± 0.022	0.393 ± 0.102	37 ± 3
NIST1568a rice flour	0.153 ± 0.008	0.050 ± 0.012	32 ± 2
NIST 1548 total diet	0.324 ± 0.004	0.112 ± 0.085	35 ± 4
NBS 8415 whole egg powder	1.001 ± 0.032	0.309 ± 0.055	31 ± 3

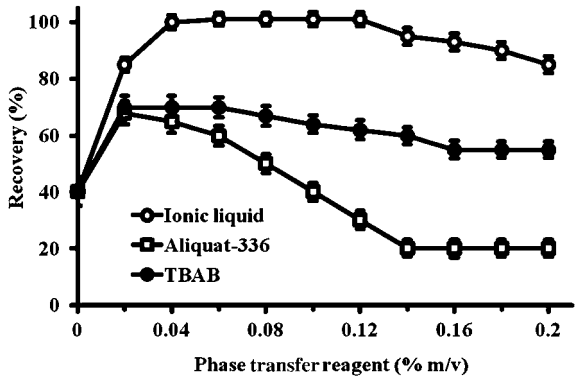

Fig. 4 Effect of phase transfer reagents such as ionic liquid, aliquat-336 and TBAB concentrations on the recovery (%) of phosphorus in the presence of 1% v/v H_2SO_4, 0.07% m/v ammonium molybdate and 0.5% m/v Triton X-114. The error bars indicate the relative standard deviation at each measurement ($n = 4$).

that at high extraction temperatures (>70 °C) hydrophobicity of extracting Triton X-114 micelles is enhanced due to increases in the efficiency of dehydration process.

The PCF, was also found to increase with an increase in the extraction temperature and reached the highest value of 50 at 90 °C temperature. This is because of reduction in volume of the surfactant rich phase due to dehydration, a process, where the water molecules surrounded by the extracting micellar aggregates, and ion-associate in SRP are removed with increasing temperature. Hence, a 90 °C extraction temperature was selected.

Optimization of extraction time was carried out between 20 and 60 min. The extraction of phosphorus is efficient in all studied time intervals possibly due to the fast reactivity of hydrophobic ion-associates formed between phosphomolybdate and ionic liquid with enhanced hydrophobic Triton X-114 micelles aggregates. Therefore, 20 min extraction time was selected. Under the optimized conditions, the pre-concentration factor and phase volume ratio were found to be 50 and 0.02, respectively.

3.4 Interference and recovery

In order to evaluate the performance of this procedure to various environmental matrices, the highest tolerability of various common interfering ions were studied. These include metallic oxy-anionic species that may interact with molybdate and thus impair the recovery of phosphorus. With a relative error of less than ±5%, the highest tolerable limits of the various interfering ions on the recovery of 50 ng mL^{-1} phosphorus were found to be 400 mg L^{-1} of Ca^{2+} and Mg^{2+}; 100 mg L^{-1} of Cu^{2+}, Cd^{2+}, Pb^{2+} and Ni^{2+}; 80 mg L^{-1} of Ge^{4+}; 40 mg L^{-1} of Cr^{6+} and Hg^{2+}; 30 mg L^{-1} of Si^{4+} and 10 mg L^{-1} of As^{5+}. These results demonstrate the selectivity of the proposed procedure for the extraction of phosphorus.

The CPE recovery of P was studied by spiking the phosphorus in the range of 40–100 ng mL^{-1} to tap water, ground water and digests of skim milk powder and total diet compared to the same aqueous standard subjected to CPE. The results obtained are given in Table 3. The recoveries were in between 95 and 98%, which indicated that the studied matrices have no significant effect on the recoveries of phosphorus during CPE. The relative standard deviations of the measurements were in between 2.5 and 4%.

3.5 Analytical figures of merit

Under the optimized conditions, the calibration curve was obtained using phosphorus standards in the range of 20–200 ng mL^{-1} after CPE. The correlation coefficient (R^2) was 0.9991. Quantifications of phosphorus in samples have been performed by using aqueous calibration. The characteristic mass (m_0) and limit of detection (LOD) for wall and platform atomization in peak height and area are given in Table 4 along with the values reported in the literature using CS/LS-GFAAS. The LOD of the method calculated based on three times the standard deviation of ten measurements of procedural blanks was 0.6 ng mL^{-1} for water and 0.06 μg g^{-1} for digested solids like milk powder and rice flour, *etc*. A characteristic mass of 0.4 ng was obtained using wall atomization. These values are best reported so far for P in literature to the best of our knowledge. The relative standard deviation (RSD, $n = 3$) of the measurements was between 2 and 4%. Sample throughput after CPE was about 20 measurements per hour.

3.6 Validation of the procedure by analysis of reference materials

The accuracy of the results obtained by the proposed procedure was validated by analyzing the NIST (8435 whole milk powder, 1549 non-fat milk powder, 1548 total diet and 1568a rice flour) and BCR (063R skim milk powder) certified reference materials after microwave digestion. The results are given in Table 5. The values obtained are in good agreement with certified values. The Student's *t*-test was applied at the 95% confidence level, which

Table 3 Recovery of phosphorus from various matrices after separation and pre-concentration using an ionic liquid assisted cloud point extraction and determined by CS-GFAAS ($n = 10$)

Matrices	Spiked/ng mL^{-1}	Found/ng mL^{-1} (mean ± SD)[a]	Recovery/%
Tap water	40	39 ± 1	98 ± 2.5
Ground water	60	58 ± 2	97 ± 3.4
Skim milk powder BCR 065R	100	95 ± 4	95 ± 4.0
Total diet NIST 1548	100	97 ± 3	97 ± 3.0

[a] Mean of ten determinations ± standard deviations.

Table 4 Comparison of characteristic mass, m_o, and limit of detection (LOD) of phosphorus using CS/LS-GFAAS

	Characteristic mass, m_o/ng				LOD/μg g^{-1}
	Wall		Platform		Wall
Modifiers/Matrices	Peak height	Peak area	Peak height	Peak area	Peak height
Pd modifier, water[a]	1.2	3.1	7.0	11.0	200 ng mL^{-1}
Phosphomolybdate-ion associate, after CPE, water[a]	0.4	1.4	1.4	2.8	0.6 ng mL^{-1}
Rice flour, whole egg, milk powder[a]	0.4	1.4	1.4	2.8	0.06
Pd and $Mg(NO_3)_2$, slurry sampling, honey and milk powder[b]	—	—	—	15	2
Pd modifier[c]	—	—	—	13	—
Pd and $Mg(NO_3)_2$ in bio diesel[d]	—	—	—	5	0.5
Pd, ascorbic acid (W coated) solid sampling biological[e]	—	—	—	5	5

[a] Present work. [b] Ref.11. [c] Ref.4. [d] Ref.10. [e] Ref. 9.

Table 5 Analytical results for the determination of phosphorus in certified reference materials and typical water samples using CS-GFAAS after using the proposed extraction procedure

	Measured values/% (mean ± $ts(n)^{-1/2}$)[a]	
Matrices	Proposed CPE	Certified values
BCR-063R, skim milk powder	1.082 ± 0.065	1.023 ± 0.128
NIST-1549 non fat milk powder	1.062 ± 0.032	1.114 ± 0.056
NIST1568a rice flour	0.159 ± 0.008	0.165 ± 0.010
NIST 1548 total diet	0.324 ± 0.009	0.313 ± 0.020
NBS-8415 whole egg powder	1.000 ± 0.032	1.015 ± 0.058
Samples		
Tap water[b]	30 ± 2	—
Ground water[b]	75 ± 3	—

[a] $t_{0.95} = 3.18$, $n = 4$ and s = standard deviation. [b] Values are in ng mL^{-1}.

showed that the measured values of phosphorus in these matrices provided better confidence limits compared with the certified values. These results show no adverse effects of these studied matrixes on cloud point extraction of phosphorus even in completely digested samples. The procedure was applied to real water samples and values obtained were in the expected range.[16]

4 Conclusions

Sensitivity of phosphorous can be greatly improved by using a wall atomization that provides the best limit of detection so far reported, in combination with an efficient separation and preconcentration CPE procedure. It involves extraction of ion-associate between phosphomolybdate and ionic liquid from bulk aqueous phase into small volume of surfactant-rich phase. It provides interference free determination of phosphorous in digested matrices. The micelles and molybdate act as extracting agent and also as a modifier in the furnace in combination with Pd. This procedure can be applied to monitoring of phosphorous in various water bodies where a higher level (100 μg mL^{-1}) of P can cause accelerated plant growth and consequent eutrophication problems leading to deficiency of oxygen in the water.[16] This procedure uses eco-friendly reagents and precedes the green chemistry pathway.

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