

Short communication

Ion chromatographic determination of trace level phosphorus in purified quartz

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Abstract

Trace levels of phosphorus in purified quartz are determined by ion chromatography. In situ reagent purification, matrix digestion and oxidation of phosphorus to orthophosphate ion are carried out simultaneously in a vapour phase digestion (VPD) assembly using a mixture of HF, HNO₃ and H₂O₂. A drastic reduction (475 times) in phosphate blank from reagents (HF/H₂O₂) was achieved in the VPD through in situ purification of the reagent. The residues remaining after volatilisation (solvent/matrix), mostly consisting of insoluble phosphate/fluoride salts of divalent and trivalent cations, were solubilised by ion-exchange dissolution. Phosphate was analysed on the IonPac AS17 column with suppressed conductivity detection. The results of the ion chromatography (IC) method were compared with a spectrophotometric method. Accuracy was evaluated by analysing a certified reference material (silicon, NIST 57a). The method detection limit was 0.05 µg g⁻¹.

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1. Introduction

High-purity quartz is the basic material for the manufacture of semiconductor-grade silicon, photovoltaic materials and is also used in various frequency control applications [1]. The electro-physical properties of these silica-based materials essentially depend on trace quantities of impurities, especially those of Group III/V elements (boron and phosphorus).

For the analysis of quartz for trace metals, various spectroscopic techniques [2] and also ion chromatography (IC) [3] have been used. Determination of a non-metal like phosphorus by quadrupole ICP-MS [4] is prone to severe interferences. Spectrophotometric methods based on ion associates with basic dyes [5] offer adequate sensitivity, but are tedious and time consuming. IC with conductivity detection has been utilised for the determination of phosphorus (as phosphate) in a broad range of samples [6,7]. However, no report concerning the IC analysis of trace levels of phosphorus in quartz has been made until now, although it provides sensitive and accurate analysis of this element after its con-

version to orthophosphate ion. This is mainly due to the difficulty of extracting phosphorus from a ceramic matrix like quartz. Nevertheless, extraction and oxidation of phosphorus from solid materials (river sediment SRM) have been carried out using hydrogen peroxide–formic acid [8] after microwave-assisted digestion. Buldini et al. [9] reported UV oxidation photolysis for the determination of trace levels of phosphorus in high-purity cadmium telluride.

Advances in sample treatment techniques [10] enhance the capabilities of IC to handle complex matrices. Generally sample digestion using concentrated acids leads to the overloading of low-capacity IC columns and the low pH of the digest can cause disruption of the ion-exchange equilibrium. Nevertheless, Kaiser et al. [11] described the determination of anions in concentrated weak acids (HF, etc.) by coupling an ion exclusion column (ICE) to an anion-exchange column. Quartz matrix is usually dissolved with the aid of HF in the presence of oxidising agents, mainly nitric acid and hydrogen peroxide. GR/AR grade HF are often contaminated with traces of phosphate and the dissolution procedure requires quantities of acids in excess of 10 times the sample weight [12], which results in unacceptable reagent blank values. Phosphates and pyrophosphates are also added as stabilisers [13] to various grades of hydrogen peroxide,

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which further contributes to the process blank. By exploiting vapour phase digestion one can circumvent the reagent blank problem, because isopeistic distillation of the reagents during digestion leads to in situ purification. Recently, Eiolla and Peramaki [14] described a vapour phase digestion (VPD) approach to reduce process blank of phosphorus and other analytes [15] from a nitric acid–hydrogen peroxide mixture.

This paper reports the simultaneous purification of reagents, matrix dissolution ($\text{SiO}_2 \rightarrow \text{H}_2\text{SiF}_6$), and oxidation of phosphorus to orthophosphate in a VPD system using a mixture of $\text{HF-HNO}_3\text{-H}_2\text{O}_2$. After SiF_4/HF evaporation, the residual insoluble precipitate, mostly consisting of phosphates/fluorides of Ca, Mg, Fe, Al, Cu, etc. is solubilised by ion-exchange dissolution.

2. Experimental

2.1. Reagents and standards

De-ionised water used to prepare blanks, standards, samples and eluents, was produced in-house from a reverse osmosis de-ionised water system (RO/DI). Before use, the de-ionised water was further purified ($18\text{ M}\Omega\text{ cm}^{-1}$) with a Milli-Q system (Milipore, Bedford, USA). Hydrofluoric acid (AR grade, 48%), nitric acid (AR grade, 70%), hydrogen peroxide (AR grade, 30%) were obtained from SD Fine Chemicals, Mumbai, India. Sodium hydroxide (suprapur grade, Merck, India) was used for the preparation of eluent. Dilute working standards of Al, Fe, Mg, Ca and Cu were prepared from 1000 mg l^{-1} stock solutions (Merck). Standard stock solution (1000 mg l^{-1}) of phosphate and pyrophosphate were prepared by dissolving their respective GR grade salt (Merck) in de-ionised water.

2.2. Preparation of resin

A swollen water slurry (15 g) of a strongly acidic cation-exchanger (Dowex-50W, 50–100 mesh), after cleaning thoroughly in a column was decanted into a syringe (30 ml capacity, Dispovan, India). Excess water from the resin was removed under pressure exerted by pressing the piston of the syringe. Resin thus obtained after removal of excess water is suitable for batch mode operation, as the sample volume change due to uptake or release of solvent from the resin is negligible.

2.3. VPD apparatus

The quartz samples were digested using a multi-channel vapour phase digestion (MCVPD) assembly, similar to that described previously [3]. The sample rack in that design was modified so that 10 samples (including three blanks) could be digested within a reasonable time (6 h) when a mixture of HF, HNO_3 and H_2O_2 was used instead of HF alone. The modified VPD assembly is shown in Fig. 1. The polypropyl-

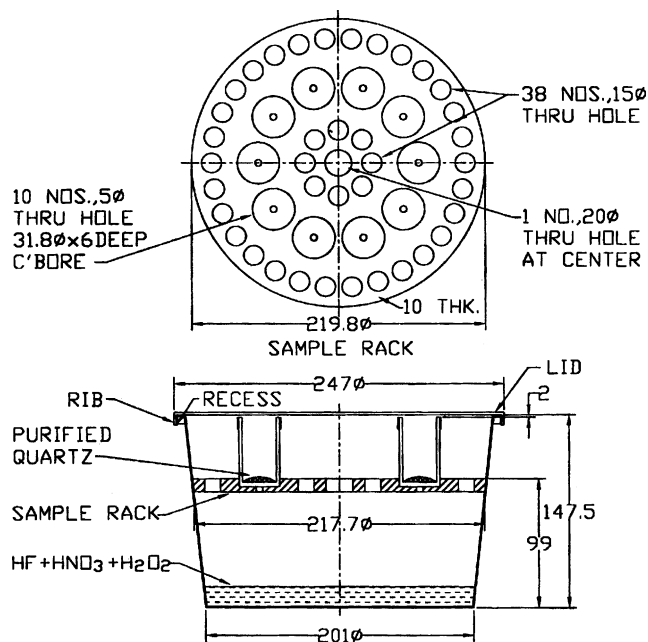


Fig. 1. VPD assembly.

ene vessel is divided into a reagent (lower portion) and a sample (upper portion) compartment by placing the sample rack. The polypropylene vessel and lid have an air-locking arrangement through a rib in the lid and corresponding recess in the vessel. To prevent reagent droplets from falling into the PFA sample vial and splashing the contents out of it, the sample vials were kept in the sample rack, which held the top of the PFA vial just 2 mm from the bottom surface of the lid.

2.4. Instrumentation and IC conditions

Analyses were carried out on a Dionex (Sunnyvale, CA, USA) DX-300 IC system, which consisted of an advanced gradient pump (AGP-1), a liquid chromatographic module (LCM-3) and a conductivity detector (CDM-3). Separation was carried out on an IonPac AS 17 (250 mm \times 4 mm) column (Dionex) with an IonPac AG 17 (50 mm \times 4 mm) guard column. Anion self-regenerating suppressor (ASRS, 4 mm) from Dionex was used in the recycle mode to reduce the conductivity due to the eluent, which was 20 mM sodium hydroxide at a flow of 1 ml min^{-1} . For sample loading, a Rheodyne injection valve (model 9126) with a $50\text{ }\mu\text{l}$ sample loop (PEEK) was used. Data acquisition and processing was performed with chromatography software (Aimil Winacds 6.2) through an advanced computer interface.

2.5. Sample preparation

Purified quartz samples obtained after magnetic separation ($1\text{ g} \times 7$, –50 to 100 mesh) were weighed into the PFA vials and were placed in the grooves (31 mm dia) of the sample rack. HNO_3 (25 ml), HF (120 ml) and H_2O_2 (10 ml) were

poured into the reagent reservoir through a polypropylene funnel. The vessel was capped and kept on IR hot plate (surface temperature $\approx 90^\circ\text{C}$) for 6 h. When the dissolution was complete, the VPD assembly was allowed to cool to room temperature. The PFA vials were taken out with a plastic forceps, capped and dried externally in a fume hood. PFA vials containing around 3 ml of residual liquid were evaporated to dryness on IR hot plate under sub boiling condition ($<85^\circ\text{C}$) in an exhausted clean hood. After complete dryness, the insoluble residues were shaken with cation-exchanger (1 g) in the presence of 3 ml of DI water for 10 min in a mechanical shaker. Then the resins were filtered in a filtration device made from a syringe. A 3 mm plug of wet Pyrex glass wool was inserted into the lower end of the syringe and rinsed well with DI water. The resin slurry was slowly decanted in to the syringe and the filtrate was collected into a pre weighed PFA vial (7 ml capacity). The piston was pressed to remove remaining filtrate from the resin bed. The filtrate, which was acidic after cation-exchange equilibration, was adjusted to pH (≈ 8) by incremental addition of 40–50 μl of 1 M NaOH by an Eppendorf micropipette. The PFA vials were weighed gravimetrically (to avoid further dilution and for better precision) to find out the dilution factor. Generally dilution factor between 3.3 and 3.5 was used.

2.5.1. Digestion and processing (silicon, NIST SRM 57a)

A silicon (NIST 57a) reference material with a certified concentration of phosphorus was analysed to check the accuracy of the IC method. The metal powder in triplicate (0.1 g \times 3) was taken for dissolution in the VPD assembly. The complete procedure described above was carried out. As the silicon metal SRM contains high amounts of metal cations (Ca-1700 ppm, Al-4700 ppm, Fe-5000 ppm, etc.) the insoluble residues were treated with 2 g of cation-exchange resin in 6 ml of DI water. The pH was adjusted by adding 700 μl of 1 M sodium hydroxide. Thus, a dilution factor of around 67 was utilised.

3. Results and discussion

3.1. Vapour phase digestion

Purified quartz can be digested by HF vapour [3] to determine trace metals. This approach requires modification to prevent loss of phosphorus. If phosphorus is present in an oxidation state lower than +5, it may be lost as phosphine [16], unless oxidising agents are present during dissolution. Nitric acid [17], hydrogen peroxide [8,9] or a mixture of these [18] is normally recommended for the oxidation of phosphorus species to orthophosphate ion. A mixture of HF, HNO₃ and H₂O₂ was, therefore, used in the VPD. Experimental work indicated that 6 h is sufficient for complete dissolution of seven quartz samples (1 g \times 7 and three blanks).

3.2. Minimisation of reagent blank

The required amounts of HF (10 ml for 1 g sample), HNO₃ (1 ml) and H₂O₂ (three drops) were evaporated to dryness at sub boiling temperature (85 $^\circ\text{C}$) on an IR hot plate and the residue was leached into 2 ml DI water and analysed by IC to find out phosphate blank levels. The reagent blank for the processing of 1 g of quartz was found to be 19 μg . In order to determine traces of phosphorus (0.2–10 $\mu\text{g g}^{-1}$ levels) in quartz and to fully exploit the sensitivity of suppressed IC, the reagent blank should be minimised. Although acid vapour phase digestion has been widely used to reduce reagent blanks for cations, not many papers describe the use of the VPD approach to reduce anionic blanks like phosphate. To study this aspect, several blanks were prepared by subjecting them to the same procedure as the sample and the mean blank values were calculated. Fig. 2a depicts the chromatogram of the process blank, when AR/GR grade reagents HF (10 ml), HNO₃ (1 ml) and H₂O₂ (three drops) were used for the direct dissolution of quartz (1 g). Fig. 2b is the chromatogram of a process blank for phosphate obtained by VPD using the same grade reagents. A comparison of the chromatograms demonstrates the in situ purification efficiency of the described VPD system with respect to phosphate. The absolute process blank ($n = 5$) of phosphate in the VPD was around 40 ng, which is an about 500-fold improvement compared with direct dissolution.

3.3. Release of phosphate through ion-exchange dissolution

Purified quartz is a suitable matrix for the IC determination of trace metals [3], because the resulting silica matrix

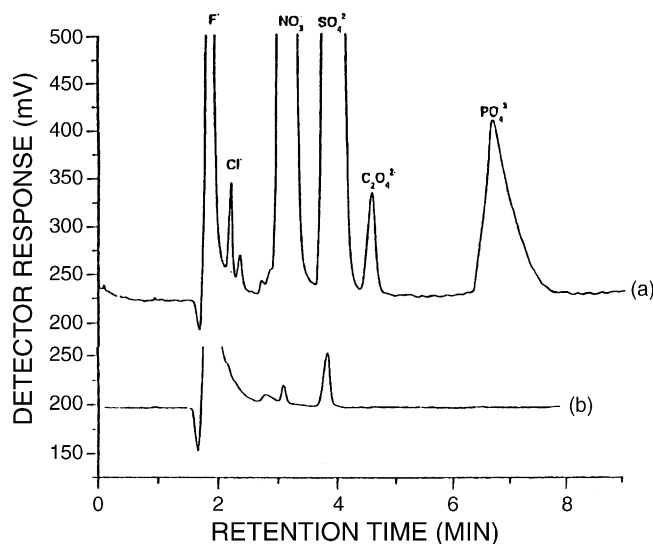
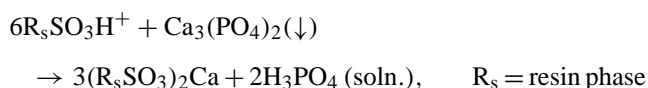


Fig. 2. (a) Chromatogram of phosphate obtained as reagent blank, when AR grade of HF (10 ml), HNO₃ (1 ml) and H₂O₂ (three drops) were used in the direct dissolution of quartz. (b) Chromatogram showing phosphate reagent blank when the same AR grade reagents were used in the vapour phase digestion. For details, see text.

along with unreacted HF can be completely volatilised. So, initially it looked possible, that by using a mixture of oxidising agents along with HF, followed by matrix volatilisation, phosphorus can be determined by IC after its conversion to orthophosphate ion. To evaluate the merits of this approach, a quartz sample (phosphorus value determined by spectrophotometric method [5]) was digested in the VPD. The residues remaining after evaporation to dryness were leached into 3 ml DI water and analysed by IC after filtration (0.2 μm filter unit connected to a syringe). However, no signal for phosphate was observed. A known amount of pyrophosphate standard (10 μg) was now spiked into both blank ($n = 3$) and sample ($n = 5$), and the whole sequence of VPD, matrix (SiF_4 , HF, HNO_3) evaporation was carried out. It was observed that, for the blank, both hydrolysis (pyrophosphate to phosphate) and recovery of phosphate were quantitative, whereas for the quartz sample, the recovery was zero. These purified quartz samples [19] contain Li, Na, K, Ca, Mg, Al and Fe, etc. at 50–600 $\mu\text{g g}^{-1}$ (all impurities combined). Cations like Ca, Mg, Al, Fe, etc. are known to form insoluble phosphates of very low solubility product. Various authors [20] have reported the conversion of insoluble salts into a soluble form with a cation-exchanger. Recently, Slingsby and Pohl [21] described a sample preparation approach prior to IC which utilises the reverse of the last process, i.e. conversion of soluble substances into an insoluble form. With quartz samples after matrix evaporation, the insoluble phosphates were released by shaking the water leachate of the residues with a cation-exchanger (H^+ form), which can be represented by:



Release of the phosphates of other cations like Al and Fe can be explained in a similar fashion. The cation-exchange resin was equilibrated in the batch method. Particularly in this instance, the batch method is more suitable than a column, because the aqueous suspension of finely dispersed insoluble precipitates then comes into better contact with the resin. Both Na^+ and H^+ form cation-exchangers were found suitable for dissolution, but the equilibration time with the former was around 40 min while the H^+ form could dissolve the precipitates within 10 min. This can be attributed to the fact, that all these water-insoluble phosphate precipitates are soluble in acidic solution. As the metal cations are exchanged with the H^+ ion of the resin, the latter are released into the solution and decrease the pH, which facilitates the dissolution of the precipitates. After cation-exchange equilibration the trace metals left in the filtrate were analysed by ICP-AES/ICP-MS; more than 99% of Fe^{3+} , Al^{3+} , Ca^{2+} , Mg^{2+} , etc. were found to be removed due to the greater affinity of the strongly acidic cation-exchanger for multi-valent ions.

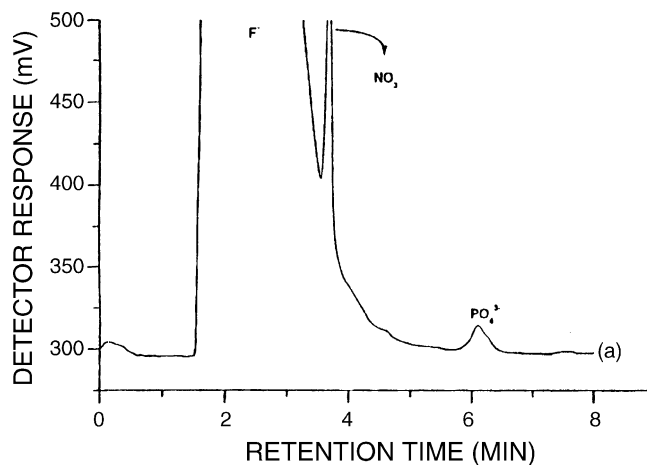


Fig. 3. Chromatogram of trace level of phosphorus as phosphate in purified quartz 2. For details, see text.

3.4. Recovery study and detection limits

It was, of course, also necessary to study the recovery of trace-level phosphate. Quartz samples spiked with 5–10 μg of phosphate were digested through VPD and analysed by IC. The recovery of the spikes was 96–100%. The method limit of detection (LOD), defined as the concentration of analyte that gives a peak area of three times the standard deviation (3σ) of the process blank ($n = 3$) including VPD, was 0.05 $\mu\text{g g}^{-1}$. This is adequate for many end applications of quartz. Further improvement of the LOD will require large-volume injection [22] or taking a larger sample size.

3.5. Sample analysis—accuracy and precision

The IC method was used to determine trace-level phosphorus in three quartz samples with different levels of purity. A typical chromatogram is presented in Fig. 3, corresponding results are summarised in Table 1. Quantification was carried out using a calibration plot, which was linear ($r^2 > 0.996$) in the concentration range of 0.01–10 mg l^{-1} . Precision, expressed as R.S.D. (%), was 3–7%. The results obtained by the present method were compared with those of an in-house spectrophotometry method [5]. They were in close agreement. Applying the *t*-test with multiple samples showed that the results of two analytical procedures did not differ significantly at the 95% confidence level. Analysis of the silicon SRM (NIST 57a) by the IC method provided a value of $25 \pm 0.8 \mu\text{g g}^{-1}$ as against the certified

Table 1
Phosphorus concentration in purified quartz (QTZ) ($\mu\text{g g}^{-1} \pm \sigma$) found using IC method ($n = 3$) and independent method ($n = 2$)

Sample	IC method	Spectrophotometric method
QTZ-1	7.72 ± 0.31	7.5
QTZ-2	0.73 ± 0.05	0.76
QTZ-3	0.86 ± 0.04	0.84

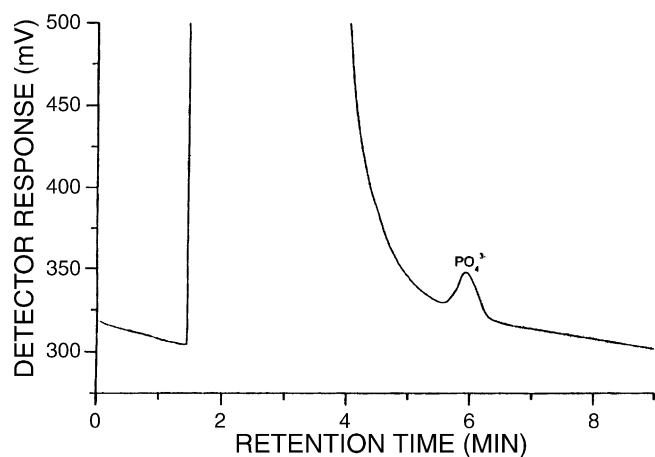


Fig. 4. Chromatogram showing phosphorus (as phosphate) in silicon SRM (NIST 57a). For details, see text.

value of $30 \pm 10 \mu\text{g g}^{-1}$ of phosphorus. As this SRM contains 1700 ppm of Ca, 4700 ppm of Al and 5000 ppm of Fe, only 100 mg of sample was taken for analysis. It is remarkable that by applying the proposed method it was possible to determine phosphorus in this particular SRM, containing such high level of trace metals, all of which form insoluble phosphates. The chromatogram of this silicon SRM (Fig. 4) shows that the residual amount of fluoride, nitrate ions (salts of trace metals), left after evaporation did not interfere with the separation and detection of phosphate.

4. Conclusion

The sample preparation approach described in this paper (VPD-matrix volatilisation-ion-exchange dissolution) provides a novel method for the determination of trace-level phosphorus in purified quartz by IC. In situ reagent purification by VPD controls the analytical blank, which is often the limiting factor for the trace-level phosphate determination by suppressed IC.

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