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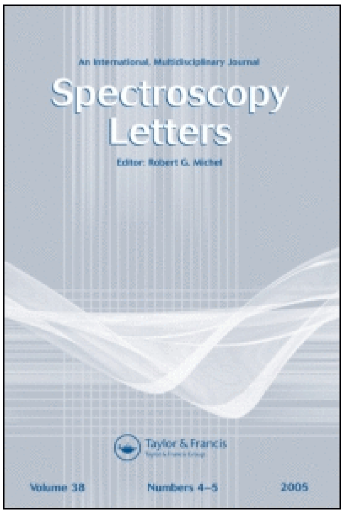

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K. Fujiwara[a,b]; M. A. Mignardi[a]; G. Petrucci[a]; B. W. Smith[a]; J. D. Winefordner[a]
[a] Department of Chemistry, University of Florida, Gainesville, FL [b] Faculty of Integrated Arts and Sciences, Hiroshima University, Hiroshima, Japan

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DETERMINATION OF PHOSPHOROUS BY ICP-AES USING SOLID-PHASE HYDRIDE GENERATION[*]

Key Words: Atomic Emission Spectroscopy, Solid-Phase Hydride Generation, Inductively-Coupled Plasma, Phosphorous

K. Fujiwara[†], M. A. Mignardi, G. Petrucci, B. W. Smith,
and J. D. Winefordner[‡]

Department of Chemistry, University of Florida,
Gainesville, FL 32611.

ABSTRACT

A reliable and sensitive analytical optical method for the determination of phosphorous in oceanographic and environmental materials does not exist. In this work, a novel hydride generation method was used to form phosphine from a sample containing phosphate mixed with 7 % sodium borohydride. By heating the mixture to 500 °C, phosphine was reproducibly generated and collected in a cold trap. Phosphine was then introduced into an ICP where several atomic emission lines for phosphorous were observed. Copper emission did not spectrally interfere with phosphorous atomic emission with this hydride generation-ICP-AES method. This hydride generation method allows the use of small sample volumes (< 5 μL).

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[†] On leave from the Faculty of Integrated Arts and Sciences, Hiroshima University, Higashisenda-machi, Hiroshima 730, Japan.

[‡] To whom correspondence should be sent.

Analytical figures of merit are given for determination of phosphorous in synthetic mixtures.

INTRODUCTION

Phosphorous is an important environmental, biological, and geochemical element. For example, the determination of P in seawater as well as river and lake water is of vital importance as the assay of organophosphorus compounds in gasolines.[1,2] Colorimetry is the most common analytical technique for detecting P as a phosphomolybdenum heteropoly blue using the molybdenum blue method.[2] Some authors have also used the molybdenum blue method with the long capillary cell atomic absorption spectrometry (AAS) and thermal lensing colorimetry.[3,4] Detection limits for P utilizing thermal lensing can be in the pg range.[3] The molybdenum blue method, however, has several drawbacks; a complex is also formed with silicate which can interfere with phosphorous determination, the process is time consuming (analysis time is ca. 20 min), and only phosphorous in the orthophosphate form and not total phosphorous can be measured.[1,5] The direct measurement of P has also been performed by AAS and atomic emission spectrometry (AES), but these techniques have exhibited poor analytical figures of merit.[2]

Direct solution nebulization is the most common sample introduction method of choice for optical emission spectrometry (OES). However, for elements such as As, B, Ge, P, Pb, Sb, Si, Sn, and Te, direct solution nebulization results in poor detection limits and spectral interferences due to incomplete salt dissociation.[5-7] The conversion of these elements into volatile hydrides has proven useful in these measurements.[6] Important characteristics of generating volatile hydrides include good preconcentration, chemical separation of the analyte from the sample matrix, and more efficient sample introduction as compared to direct solution nebulization.[6] In OES, the volatile analyte hydride species is stripped from the analytical sample and carried by a gas to the atomizer.[8] Until recently, the low reduction potentials of B, Si, and P has limited their quantitative conversion to the corresponding hydrides (borane, silane, and phosphine, respectively). The reduction of the phosphate ion (PO_4^{-3}) is difficult because its reduction potential is higher than water, and so its reduction must be done under dry conditions. Hashimoto, et al., describe a hydride generation method for P which takes place in a non-aqueous environment - a heated quartz reaction cell.[2] Drying the sample with a borohydride (e.g., $NaBH_4$) solution at 45 °C and then rapid heating of this mixture to ca. 500 °C resulted in total conversion of P to phosphine. Unlike the molybdenum blue method, the hydride generation technique is applicable to the determination of total phosphorous and total dissolved phosphorous in water.[5]

The detection of hydrides has most commonly involved AAS since the instrumentation is readily available in most laboratories.[7] Several authors have reported the detection of phosphine with a gas chromatograph coupled to a flame photometric detector (GC/FPD).[2,5] Phosphine has been detected by AES using an ICP, MIP, or DCP as the atomization-excitation cell.[7,9-13] The work presented here involves the use of an ICP-AES for detection of phosphine generated by a batch method (as opposed to a continuous method).[14] The P emission was detected with a multichannel spectral observation technique using an image intensified photodiode array coupled to a 1-m spectrometer. A novel sample introduction system is described to prevent ICP torch shutdown (as experienced by other workers),[9,12] and phosphorous could be detected without spectral interference from a high concentration of Cu.

EXPERIMENTAL

Instrumentation

Figure 1 is a schematic diagram of the optical and sample introduction system used in this work. A fused silica lens, L_1, (23 cm focal length) collected radiation emission from the ICP and collimated it to a second fused silica lens, L_2, (5 cm focal length). L_2 focused the collimated radiation at the entrance slit of a J-Y H10 0.1 m focal length monochromator (Instruments SA, Inc.,

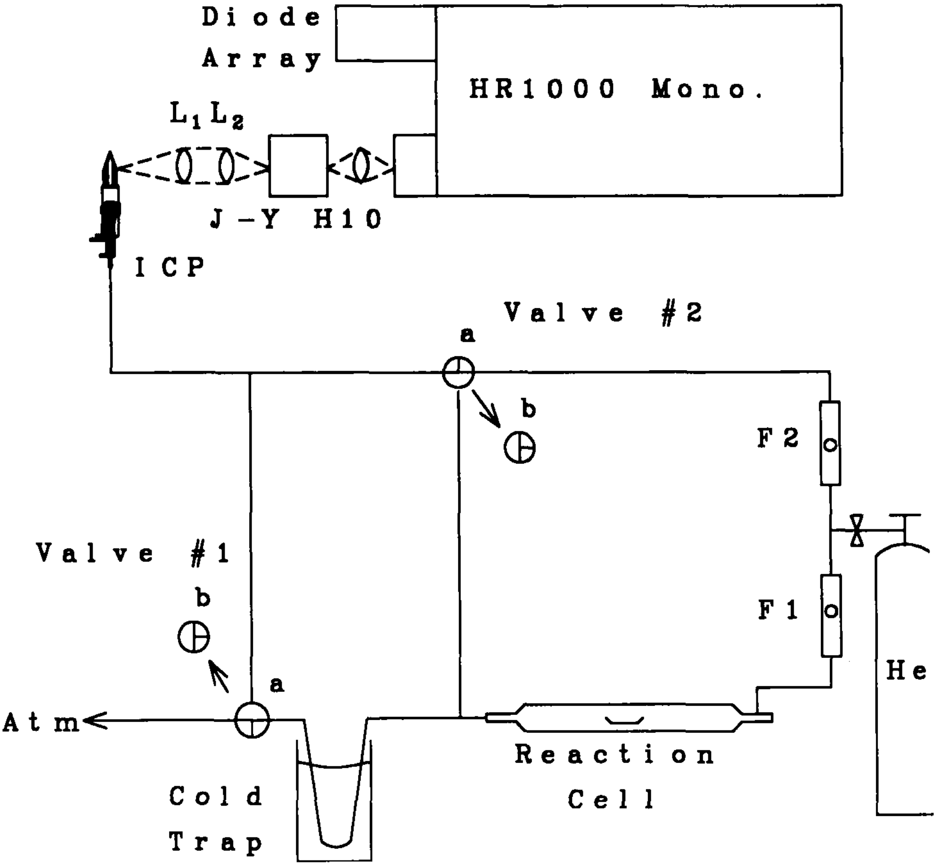

Figure 1. Schematic diagram of optical system and hydride generation sample introduction system.

Metuchen, NJ) acting as a pre-disperser. The pre-disperser filtered out lower order plasma emission. The exit-plane image of the pre-disperser was focused as a 1:1 image on the entrance slit of a 1-m focal length spectrometer (model HR1000, ISA).[15] The resolution of the 1-m spectrometer in first order was not sufficient to fully resolve the many atomic emission lines of P. Therefore, it was used in the fifth order. With 0.22 mm slits, the spectral bandpass in fifth order was 0.022 nm. Apertures were used to prevent overfilling of the monochromators. The sample introduction system

Table 1. Experimental Operating Conditions

I. ICP	
Operating frequency	27.12 MHz
Forward power	1.2 kW
Reflected power	20 W
Ar coolant flow rate	16 L min^{-1}
Ar auxiliary flow rate	1.7 L min^{-1}
He carrier flow rate	0.6 L min^{-1}
Observation height	8 mm
II. Ultrasonic Nebulizer	
Operating frequency	1.35 MHz
Forward power	37 W
Reflected power	3 W
Sample uptake rate	3.3 mL/min
III. Hydride Generation System	
Furnace temperature	460-500 °C
Reaction time	2 min
He carrier flow rate	0.6 L min^{-1}

of the ultrasonic nebulizer is described elsewhere.[16] Table 1 is a list of the experimental conditions.

The sample introduction system for the generation of phosphine consisted of two sections - the reactor and ICP section. The reactor section consisted of a quartz reaction cell, a U-shaped tube in liquid N_2, and a tube leading to atmosphere. The ICP section by-passed the entire reactor section. Two 3-mm three-way valves coupled the reactor to the ICP. The three-way valves allowed He to pass either directly into the ICP or through the liquid N_2 cold trap and then into the ICP. The quartz reaction tube and sample boat were described in detail elsewhere.[2,5,17] As described previously, a "b-type" quartz sample boat was used.[2] Nalgene plastic tubing (0.25 in i.d., 0.0625 in wall) was used throughout the sample introduction system.

Sample preparation

A stock solution of phosphate was prepared from analytical grade potassium hydrogen phosphate (K_2HPO_4) (Fisher Scientific Co., Fair Lawn, NJ). A stock solution of Cu (1000 mg L^{-1} in 2 % HNO_3) was obtained from Inorganic Ventures, Inc. (Brock, NJ). Working solutions of phosphate and copper were made by serial dilutions of the stock solutions. A synthetic mixture of phosphate and copper was also prepared. A 7 % solution of sodium borohydride ($NaBH_4$) (Eastman Kodak Co., Rochester, NY) in 4 % NaOH (Fisher Scientific) was prepared daily as described by Hashimoto.[2] All solutions were prepared with distilled, demineralized water (Barnstead Sybron Corporation, Boston, MA).

Procedure

The detailed procedure for the hydride generation of phosphine has been described in detail elsewhere;[2,5,17] however, several modifications to the existing phosphine generation procedure were made. In this study, 50 - 100 μL aliquots of aqueous solutions of phosphate were introduced to clean dry quartz sample boats. The samples were then dried for several hours at 60-70 °C within a dry nitrogen gas stream. Once dry, a 300-500 μL aliquot of the $NaBH_4$ solution was introduced on top of the dried phosphate samples. The samples were again dried in a dry nitrogen gas stream but at 40-45 °C for at least 3 hours.

Before a prepared quartz sample boat was placed into the quartz reaction cell, the three-way valves were turned as indicated by valve position "a" in Fig. 1. With the valves in this position, the reactor and ICP sections of the sample introduction system were isolated from one another. Therefore, the He flow rate through each section was independent and set at 600 mL min^{-1} for each section with flowmeters F1 and F2. The U-shaped tube was placed into a liquid N_2 dewar and the quartz reaction cell was placed in a cylindrical electrothermal furnace and heated to 460-500 °C. The sample boat containing the dried mixture of phosphate and $NaBH_4$ was inserted and sealed within the heated portion of the quartz reaction cell. The reaction was allowed to proceed for 2 min with He continuously flowing independently through both sections. The reaction temperature and time used were as previously optimized.[2] The reaction section of the sample introduction system was isolated from the ICP such that the torch would not shut down due to exposure to the atmosphere or to the generation of reaction by-products (i.e., H_2, H_2O, and CO_2). These reaction by-products were thus ventilated to the atmosphere. Upon completion of the reaction, the reaction section He flow was then turned off with flowmeter F1, and the three-way valves were turned to valve position "b" to flush He through the cold trap and into the ICP. We were successful in maintaining the plasma torch if the He flows were changed in the following manner: (i) the reaction section He flows were turned off first with flowmeter F1 so as not to introduce too much He flow into the ICP; (ii) three-way valve no. 1 was turned to valve position "b" to allow the collected phosphine in the cold trap to be flushed into the ICP; and then (iii) three-way valve no. 2 was also turned to valve position "b" to direct He from flowmeter F2 through the cold trap. By-passing the reaction cell at this step in the procedure prevented the ICP from receiving any residual reaction by-products. In our system, the operation of valve no. 2 was critical since the ICP received no carrier flow for about 1 s. Once both valves were in position "b", the U-shaped tube was removed from liquid N_2 and immersed into a room temperature water bath (25 °C). The collected phosphine passed into the ICP as a well-defined plug. After about 5 s, three-way valve no. 2 was turned back to valve position "a" - to redirect He through the ICP section, thus, by-passing the reaction section. Three-way valve no. 1 was then turned back to valve position "a" so the quartz sample boat could be removed and replaced with a new sample. Before inserting the U-shaped tube back into liquid N_2, it was heated with a heat gun to drive off any possible trapped contaminants and water. The determination of P was also compared to a direct solution nebulization of a phosphate solution.

The pre-dispersing monochromator was set for the first order P emission lines at ca. 214 nm (spectral bandpass, 16 nm) while the HR1000 monochromator was set to pass the P spectral lines in fifth order at 10729 Å. The emission spectra obtained for several lines of phosphorous was simultaneously detected by the photodiode array.

One complete scan of the photodiode array required 33 ms. For the determination of P utilizing direct solution nebulization of phosphate, 300 data acquisition spectra were averaged to achieve a total acquisition time of 10 s. For the determination of P utilizing the hydride generation of phosphine, only 10 data acquisition spectra were averaged; however, 20 averaged spectra were collected sequentially during the introduction of phosphine so to record the entire temporal evolution of P. Analytical calibration curves were plotted as P emission peak height versus the concentration or amount of P. The computer software supplied with the photodiode array allowed for automatic baseline subtraction from the emission peak height.

RESULTS AND DISCUSSION

Figure 2 shows 5 prominent P emission lines (213.547, 213.620, 214.911, 215.295, and 215.408 nm) within the window of the photodiode array. This spectrum was generated by aspirating a 1 μg mL^{-1} solution of phosphorous (as phosphate) into the ICP with the ultrasonic nebulizer. Direct nebulization of phosphate into the ICP allowed optimization of the experimental system for detection of P: plasma r.f. power, observation height, spectral peak positions on the photodiode array, and Ar and He flow rates. Ar was the plasma coolant and auxiliary gas and He was the carrier gas for both the direct nebulization and hydride generation sample introduction systems. Figure 3 is a three dimensional spectrum showing the temporal appearance of P emission by introducing phosphine (1 μg P) into the ICP by the new hydride generation system. Each sequential spectrum in Fig. 3 was averaged for 330 ms (i.e., 10 data acquisition spectra were averaged) before collecting the next sequential emission spectrum. The complete plug of generated phosphine lasted only 1-2 s. If more than 10 data acquisition spectra were averaged for one sequential spectrum, the possibility of missing the maximum P emission signal existed.

As mentioned previously, Cu is a common interferent with P in ICP-AES. Figure 4 shows two spectra of synthetic mixtures of P and

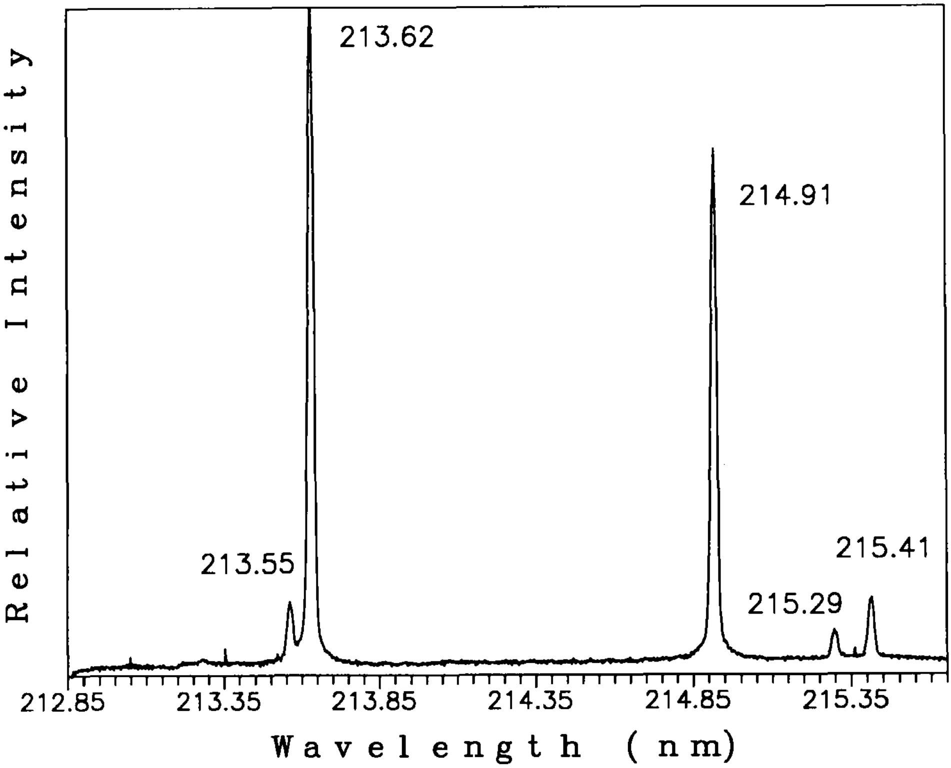

Figure 2. Direct solution nebulization of phosphorous (1 μg mL^{-1}).

Cu in a 1:10 ratio, respectively. Fig. 4a was obtained by direct solution nebulization and only the two ion emission peaks of Cu (213.598 and 214.897 nm) were observed. Fig. 4b was obtained by the hydride generation of phosphine. In Fig. 4b, the 5 P emission peaks are clearly resolved despite the high concentration of Cu within the mixture. The new hydride generation system physically separates P from Cu from the sample matrix.

Figure 5 is a log-log calibration curve for P using the hydride generation system. The log-log slope of this curve is 1.01 indicating good linearity. The linear dynamic range (LDR) is about two orders of magnitude. However, the LDR can be extended by using one of the less intense P emission lines (e.g., the 215.408 nm

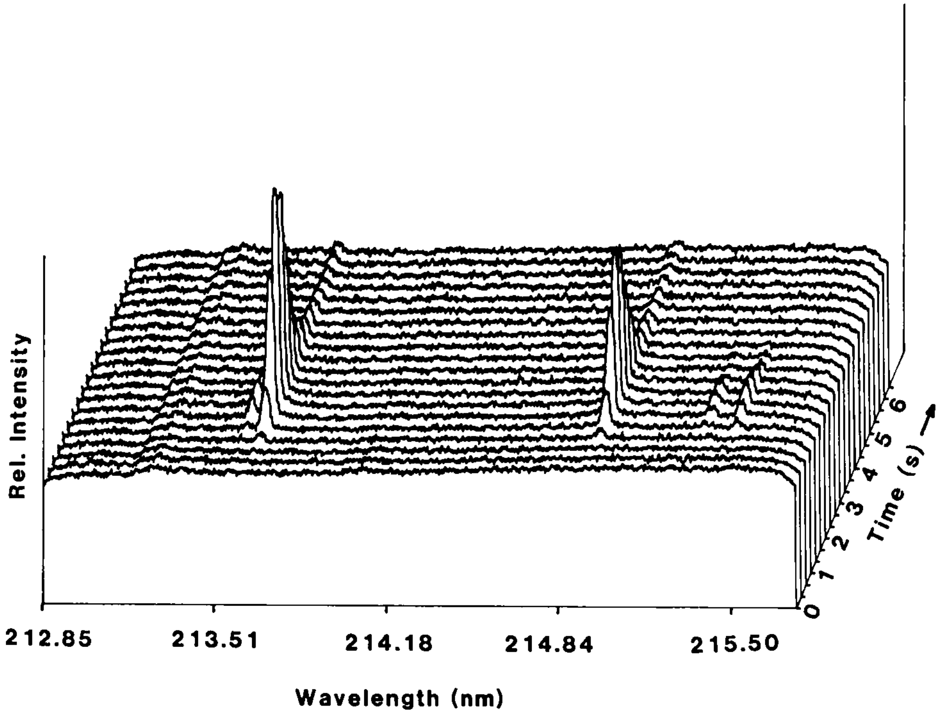

Figure 3. Three dimensional spectrum showing P (1 µg) emission intensity versus time of elution of phosphine from cold trap.

line). The precision (> 10 %) of the hydride generation-ICP-AES technique is poor. The poor precision is possibly a result of leaks within the hydride generation system. Table 2 lists the limits of detection (LODs) for P obtained in this work. The LODs by other methods of analysis are also given for comparison. The LODs for direct solution nebulization of phosphate and hydride generation of phosphine in this work were 5 ng mL^{-1} and 10 ng, respectively. The low detection limit achieved in this work with ultrasonic nebulization-ICP-AES makes this an attractive technique for detection of total P; however, Cu is a potential spectral and chemical interferent in this case. Although the colorimetry methods for P achieve good limits of detection, they can not measure total

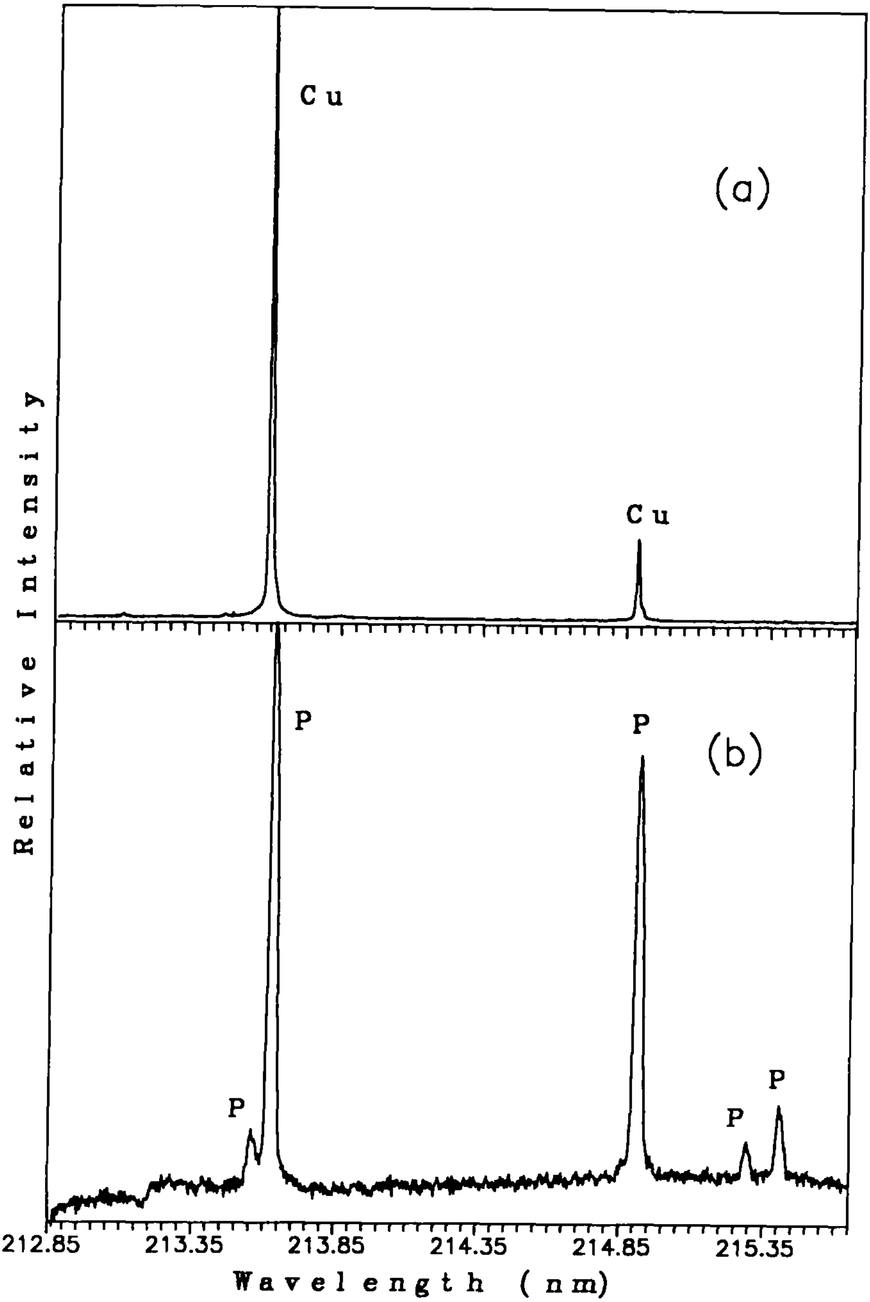

Figure 4. Spectra of the effect of Cu interference on P: a) direct solution nebulization (100 μg mL^{-1} Cu: 10 μg mL^{-1} P); b) hydride generation method (10 μg Cu: 1 μg P).

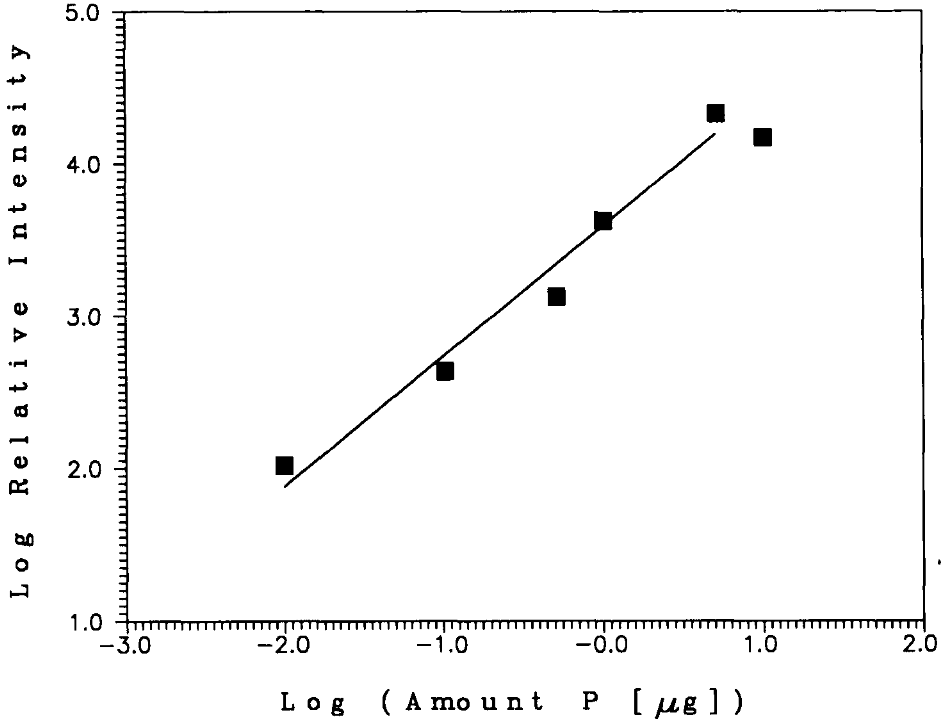

Figure 5. Log-log calibration curve using the hydride generation method for phosphorous determination.

P in solution and suffer from interferences due to silica and arsenic. The determination of total P in solution as well as its separation from the sample matrix makes the hydride generation of phosphine an attractive alternative to other optical methods. Previous work with a GC/FPD achieved an LOD two orders a magnitude better than obtained in this work using ICP-AES for detection of the hydride generated phosphine. The poorer LOD by ICP-AES is a result of several reasons: (i) the atomic emission transitions of phosphorous have rather poor oscillator strengths; (ii) the excitation energy of phosphorous is transferred to many atomic lines that are not ground state transitions; and (iii) many of the ground

Table 2. Detection Limits of Phosphorous

I. Direct Solution Nebulization or Injection of Phosphate	
ICP-AES[18]	100 ng mL^{-1}
Flame-AAS[19]	30 ng mL^{-1}
Furnace-AAS[19]	20 ng mL^{-1}
ICP-AES[19]	50 ng mL^{-1}
ICP-AES[a]	5 ng mL^{-1}
II Hydride Generation of Phosphine	
GC/FPD[5]	0.1 ng
ICP-AES[a]	10 ng
III Colorimetry of Phosphate	
Molybdenum-Blue[5]	1 ng mL^{-1}
Thermal Lensing[4]	5 pg mL^{-1}

[a] This Work

state transitions of phosphorous occur in the low UV (i.e., < 180 nm) where the transmission and detection efficiencies of spectroscopic instrumentation is poor. On the contrary, the FPD is based on a single emission band of molecular HPO at 528 nm. The efficiency of detecting this single molecular emission band in the FPD accounts for the much better LODs than in ICP-AES. Also, the FPD, a hydrogen-air flame, has much lower background emission than that of an ICP. Better solid angle collection and a more sophisticated valve switching system (i.e., leak proof and fast switching) in the previous work may also account for the better LODs achieved with the GC/FPD than with the system used in this work.

The chemical reaction by-products in hydride generation, H_2, H_2O, and CO_2, result in the instability of ICP emission.[6,7] Even so, much work has been done using an ICP with hydride generation because of the improved detection limits (by an order of magnitude) compared to direct solution nebulization.[6,9,12,18,19] In order to minimize torch shutdown, many workers have used low carrier gas flow (60 mL min^{-1}), high r.f. powers (> 2 kW), and low $NaBH_4$ concentrations (< 1.5 %). With our sample introduction system, we were able to maintain the plasma at high carrier gas flow rates (600 mL min^{-1}), relatively low power (1.2 kW), and high $NaBH_4$ concentrations (7 %). One problem we did encounter was collection of H_2O within the U-shaped tube after generation of phosphine. Water, unless removed by heating the U-shaped tube between samples, caused poor recoveries of P.

CONCLUSION

The gas phase introduction of P as phosphine from hydride generation into an ICP makes this technique attractive because of the low detection limits compared to direct solution nebulization of phosphate. This hydride generation system is easily detachable (in less than 2 min) from the ICP; therefore, the ICP is not dedicated only to hydride generation. The LOD achieved with direct nebulization of phosphorous was better than the hydride generation method (see Table 2). This can be explained by a poor conversion efficiency (approximately 45%) of phosphate to phosphine by the latter method, whereas the ultrasonic nebulization of phosphate is totally sufficient. However, a major advantage of the hydride generation method is its freedom from the spectral interferences of copper (see Figure 4). Although the possibility of a copper spectral interference in flame AAS is low, flames are poor atomization cells for aqueous phosphorous. Disadvantages of our method include the need for a collection device such a the liquid N_2 cold trap, and the potential for interferences from concomitants within the sample mixture in the formation of phosphine. The sample preparation time is rather long because of the drying time involved; however, many samples can be prepared simultaneously. Also, once prepared, the samples are stable indefinitely to atmospheric conditions. The time of analysis utilizing the described ICP-AES hydride generation system should be faster than using a GC/FPD. Further improvements in the sample introduction system (i.e., leak proofing, more sophisticated valves, and teflon tubing) should allow better precision and detection limits for P utilizing ICP-AES. Also, the ability to detect more than one P emission line improves the informing power of this technique.

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