Chinese Chemical Letters Vol. 11, No. 5, pp. 425–426, 2000

Determination of Phosphorus by Inductively Coupled Plasma Atomic Emission Spectroscopy after Hydride Generation

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Abstract: A continuous phosphine (PH_3) generation was developed and applied to the sensitive detection of phosphorus by ICP-AES. Phosphate ion in aqueous solution was converted to phosphine by passing the sample solution through an incandescent copper silica-tube. Detection limit is 2 ng/mL. The relative standard deviation is 4.2% for 20 ng/mL. The method is rapid and simple with low contamination and high sensitivity.

Keywords: Hydride generation, phosphate, ICP-AES.

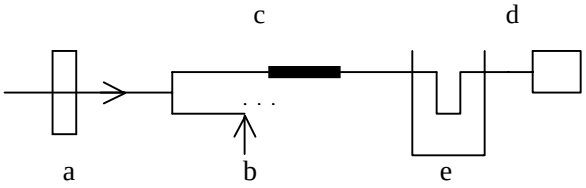
The hydride generation technique has contributed much to the improvement of the sensitivity in atomic absorption, emission and fluorescence spectroscopy of As、Sb、Bi、Se、Te、Ge、Sn and Pb[1,2]. Many workers have successfully applied this technique to determination of Cu、Zn、Cd[3,4,5]. Kazuko Matsumoto studied phosphine generation coupled with ICP atomic emission spectrometry, where phosphate in aqueous solution was first precipitated by adding $CaCl_2$ as calcium phosphate, which was then reduced to Ca_3P_2 by heating (*ca*,1100℃)together with aluminum powder[6]. The detection limit of the method was 20 ng/mL. We have contrived a completely innovative hydride generation system, where phosphate solution is continuously introduced into a flow-through copper furnace, phosphate is reduced by the heated copper to phosphine. The detection limit of phosphorus is 2 ng/mL and the method was successfully applied to the determination of phosphorus in actual samples.

Experimental

Apparatus and reagents

Atomic scan 25 inductively coupled plasma emission spectroscopy, (Thermo,Jarrell Ash Corporation), RF power 1350 W, observation height 14 mm, coolant gas flow rate 15 L/min, plasma gas flow rate 0.7 L/min, analytical line 178.287 nm. A schematic illustration of the system is depicted in **Figure 1.** The copper silica-tube is 6 mm o.d,3.5 mm i.d, and 50 mm long. The voltage regulating direct current power supply for the furnace is 300 A, 30 V, and was custom-made. Standard phosphorus solution (1 mg/mL). Active copper (+99.99%, purchased from Italy)

Figure 1 A schematic diagram of phosphine generation with the ICP-AES detection system



(a. pump, b. protect gas, c. copper silica-tube, d. gas-liquid separator, e. ice-cooling)

Results and discussion

Optimization of experimental conditions

The dependence of the intensity on protect gas flow rate (Ar) was examined from 10-40 mL/min. It was fixed at 20 mL/min in the following experiments. The effect of the carrier gas flow rate was studied while varying it from 100-300 mL/min. The intensity increases with the increase of the flow rate, however, above 300 mL/min. The intensity of phosphorus slightly decreases. Also the effect of the sample flow rate was studied while varying it from 0.5-1.5 mL/min. However, above 1.5 mL/min, silica-tube is severely damaged. Accordingly, the carrier gas and sample flow rate was fixed at 250 and 0.8 mL/min.

Although the effect of the furnace temperature must be studied, it was impossible to measure it, since the copper tube is totally covered with a brass jacket. Therefore, we express the intensity as a function of the furnace current or voltage. The intensity is low when the current is less 100 A, but at current higher than that, it increases rapidly with increasing current. Although the intensity still continues increasing, the silica tube is severely damaged when the current is higher than 200 A and can not be used in analytical work. Accordingly, the following experiments were carried out at 150 A.

Detection limit and analytical calibration curve

The calibration curve is linear from 10 ng/mL-100 μg/mL. In the lower concentration region, the curve is still linear but the slope is slightly decreased. The detection limit expressed as a concentration corresponding to three times the standard deviation in ten repetitive measurements of blank solution is 2 ng/mL. The reproducibility obtained from ten measurements of 20 ng/mL solution is 4.2%.

Application

The present method was applied to the determination of phosphorus in sodium *p*-nitrophenylphosphate, the result is as follows: calculated 8.35%, found $8.31 \pm 0.23\%$.

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Received 31 December 1999