CHEMISTRY LETTERS, pp. 1367-1370, 1987.

Simultaneous Determination of Phosphate, Silicate, and Arsenate by On-line Column Flow Injection Analysis

Yoshio NARUSAWA* and Takahiro HASHIMOTO
Department of Chemistry, College of Science, Rikkyo(St. Paul's) University,
3-34-1, Nishi-Ikebukuro, Toshima-ku, Tokyo 171

The simultaneous determination of phosphate, silicate and arsenate has been examined by adapting an anion-exchange column to the flow injection analyzer. Determination is based on the absorption at 810 nm of the heteropoly blue formed with ascorbic acid as reducing agent. Detection limits(S/N = 3) are 3.1 ng, 0.55 ng and 3.0 ng for phosphorus, silicon and arsenic, respectively.

Ruzicka and Hansen1) first determined phosphate by a flow injection analysis based on formation of 12-molybdophosphoric acid. Thereafter, many reports have been presented by many authors2-7) on the determination of phosphate and silicate by flow injection techniques. Kuroda et al.3) determined phosphate in silicate rocks based on phosphomolybdenum blue formation, by adding tartaric acid into the molybdenum(VI) solution to prevent formation of 12-molybdosilicic acid. Yoza et al.4,5) studied separation and determination of inorganic phosphates by installing an anion-exchange column to the FIA manifold. Hirai et al.6) and Yokoyama and Tarutani7) determined silicate by FIA based on formation of 12-molybdosilicic acid, whereas Ramachandran and Gupta8) determined silicate spectrophotometrically based on formation of silicomolybdenum blue. The latter authors examined the effect of the reducing agents for 12-molybdosilicic acid, and pointed out that the mixture of ascorbic acid and antimony(III) was most effective for the reduction of 12-molybdosilicic acid and that the molybdenum blue formed was most stable. As for arsenic, arsenite or arsenate was determined electrochemically or arsine was determined by atomic absorption spectrometry using the flow injection manifold for generation of active hydrogen.2) Arsenic has never been determined so far by FIA based on the molybdenum blue method. In the present work, we performed preliminary experiments for the simultaneous determination of phosphate, silicate and arsenate using an anion-exchange column installed in FIA manifold.

Twice-distilled water was used for all solution preparations. All chemicals used were of reagent grade and used without further purification. All solutions were stored in polyethylene or teflon bottles. Stock solutions(10.0 mmol/dm^3) of phosphate, silicate and arsenate were prepared by dissolving anhydrous potassium dihydrogenphosphate KH_2PO_4, sodium metasilicate nonahydrate $Na_2SiO_3 \cdot 9H_2O$ and disodium hydrogenarsenate heptahydrate $Na_2HAsO_4 \cdot 7H_2O$, respectively. With respect to silicate, a solution of sodium metasilicate Na_2SiO_3(Si 1000 ppm in 0.2 mol/dm^3 Na_2CO_3, commercially available) was also used as the standard. Ammonium molybdate solution was prepared by dissolving 5.30 g $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ and 16.7 cm^3 H_2SO_4 in water and diluted to 1.0 dm^3. Ascorbic acid solution was prepared by dissolving 1.75 g ascorbic acid and 2.5 cm^3 glycerin in water and diluted to 250 cm^3. This solution was prepared every time just before use. Volumetric flasks were filled with the mixture of $HNO_3:H_2O_2:H_2O=2:1:2$, left overnight and washed with water.

The flow injection analyzer used was a JASCO FIU-300 equipped with a JASCO UVIDEC-340 double beam spectrophotometer with an 8-µl flow cell. As separation column, an anion-exchange column (15 cm x 4.6 mm i.d., TSK-gel SAX, 5 µm) was employed. The diagram of the flow injection manifold for the spectrophotometric determination of phosphate, silicate and arsenate is given in Fig. 1. It is based on the separation using an anion-exchange column and the post-column reaction to

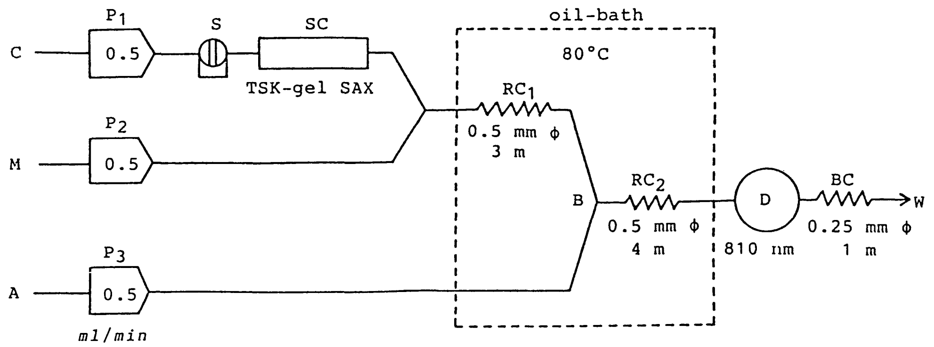

Fig. 1. Flow injection system.

C = carrier(eluent); M = ammonium molybdate(VI) solution; A = ascorbic acid solution; S = sample injector(20 µl); P_1, P_2, and P_3 = pumps; SC = separation column(TSK-gel SAX); RC_1 = reaction coil(0.5 mm i.d., 3 m); RC_2 = reaction coil (0.5 mm i.d., 4 m); BC = back-pressure coil(0.25 mm i.d., 1 m); D = detector; W = waste. Eluent = 0.10 M KCl + 0.010 M NH_3 + 0.0010 M Na_2EDTA. The manifold was made of 1.0 mm i.d. teflon tubing except for RC_1, RC_2, and BC.

form the heteropoly blue.

Phosphate reacted with the molybdenum(V)-molybdenum(VI) reagent,[4,5] whereas silicate did not. Therefore, ascorbic acid should be added at point B after phosphate, silicate and arsenate formed heteropoly acids. Because the formation of the heteropoly blue for silicate was rather slow at room temperature, reaction coil RC_2 in Fig. 1, as well as RC_1, were immersed in an oil-bath at 80 °C. A sample solution was injected into the carrier stream(C) via a loop-valve injector(S)(20 µl). The composition of eluent was examined, and it was found that the chloride ion concentration affected significantly the elution of these anions. When the chloride ion concentration was low, it was advantageous for the separation of these ions, but it took much time for analysis. For the appropriate separation, the chloride ion concentration was set at 0.10 mol/dm^3. Ammonia was necessary in order to hold these anions as PO_4^{3-}, SiO_3^{2-}, and AsO_4^{3-}; and 10 mmol/dm^3 ammonia was sufficient. A negative solvent peak was observed without Na_2EDTA, but a small positive solvent peak was observed by adding 1.0 mmol/dm^3 Na_2EDTA, although the reason for it was not clear. Thus the eluent used for the carrier in Fig. 1 was 0.10 M KCl + 0.010 M NH_3 + 0.0010 M Na_2EDTA. For the reducing agent, Ramachandran and Gupta[8] used ascorbic acid/antimony tartrate. They also examined tin(II) chloride, but it was not adequate, because tin itself formed the heteropoly blue.[9] As a result, we used only ascorbic acid as the reducing agent.

Absorbance of heteropoly blue formed was monitored at 810 nm against water reference. A typical result is shown in Fig. 2. The order of elution was metasilicate, orthophosphate, and arsenate. This is interpreted as being due to the ionic charge of these anions. However, the order of orthophosphate and arsenate cannot be elucidated at present, because the data are too few.

Working curves for these species did not show linear relationships between peak height(absorbance) and concentration. However, each species showed a good correlation between logarithm of absorbance and logarithm of concentration over two or three dynamic ranges. Calibration curves for these ions are shown in Fig. 3. Measurements were repeated at least three times for each point and the coefficients of variation were less than 3% except for lower concentration ranges. Detection limits(S/N = 3) were 1 µM for SiO_3^{2-}(0.55 ng as Si), 5 µM for PO_4^{3-}(3.1 ng as P) and 2 µM for AsO_4^{3-}(3.0 ng as As). Upper limits were 2 mM for SiO_3^{2-}, 0.5 mM for PO_4^{3-} and 0.2 mM for AsO_4^{3-}. The linear portion of the calibration curve seems to be larger for bivalent anions than for tervalent anions.

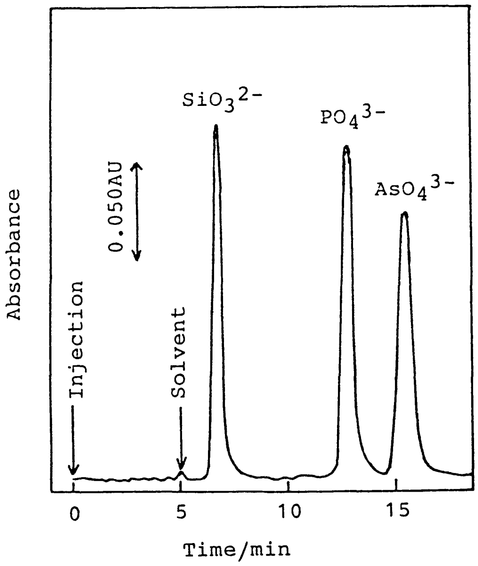

Fig. 2. FIA profiles of silicate, phosphate, and arsenate. $[SiO_3^{2-}]$ = 0.20 mM, $[PO_4^{3-}]$ = 0.50 mM, $[AsO_4^{3-}]$ = 0.20 mM. Eluent = 0.1 M KCl + 10 mM NH_3 + 1 mM Na_2EDTA. Retention time(min): SiO_3^{2-} = 6.67, PO_4^{3-} = 12.83, AsO_4^{3-} = 15.50.

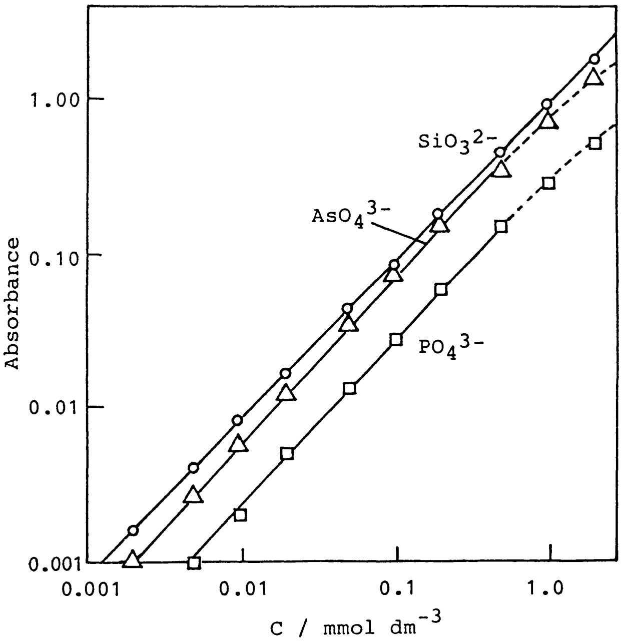

Fig. 3. Calibration curves for silicate, phosphate, and arsenate. Coefficients of correlation (r): SiO_3^{2-} = 0.99997; PO_4^{3-} = 0.99966; AsO_4^{3-} = 0.99994.

The authors wish to thank Professor Koji Ishida, Nippon Medical School, for his helpful discussions.

References

1) J. Ruzicka and E. H. Hansen, Anal. Chim. Acta, 78, 145 (1975).
2) See e.g., "Flow Injection Analysis Bibliography 1974-February 1985," Tecator AB, 1985; N. Yoza, J. Flow Injection Anal., 1, 32, 49 (1984); Y. Baba and N. Yoza, ibid., 2, 61, 168 (1985); Y. Baba and N. Yoza, ibid., 3, 49 (1986); T. Imato and M. Watanabe, ibid., 3, 121 (1986).
3) R. Kuroda, I. Ida, and K. Oguma, Mikrochim. Acta, 1, 377 (1984).
4) N. Yoza, H. Hirano, Y. Baba, and S. Ohashi, J. Chromatogr., 325, 385 (1985).
5) N. Yoza, Y. Sagara, H. Morioka, T. Handa, H. Hirano, Y. Baba, and S. Ohashi, J. Flow Injection Anal., 3, 37 (1986).
6) Y. Hirai, T. Yokoyama, N. Yoza, T. Tarutani, and S. Ohashi, Bunseki Kagaku, 30, 350 (1981).
7) T. Yokoyama and T. Tarutani, J. Flow Injection Anal., 2, 30 (1985).
8) R. Ramachandran and P. K. Gupta, Anal. Chim. Acta, 172, 307 (1985).
9) T. Yamase, Yuki Gosei Kagaku Kyokai Shi, 43, 249 (1985).

(Received April 21, 1987)