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Selective Determination of Vanadium in River Water by High-performance Liquid Chromatography

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A method for the selective determination of vanadium in river water using high-performance liquid chromatography after preconcentration with a convenient evaporator was investigated. 2-(5-Bromo-2-pyridylazo)-5-(N-propyl-N-sulfopropylamino)phenol was used as a precolumn chelating reagent for V(V) in the presence of CyDTA. The detection limit of the proposed method was 35 ng l^{-1} after the 25 fold enrichment procedure.

Vanadium is one of the most important elements in biological and environmental sciences. Recently, more sensitive and selective methods for the determination of V have become increasingly required. High-performance liquid chromatography (HPLC) is one of the available methods to reply to the requirement. Many chelating reagents such as 8-quinolinol,[1,2] Shiff bases,[3] 4-(2-pyridylazo)resocinol,[4,5] and some other azo dyes[6] have been studied for the determination of V by HPLC.

2-(5-Bromo-2-pyridylazo)-5-(N-propyl-N-sulfopropylamino)phenol (5-Br-PAPS) seems to be a suitable reagent for the determination of metal ions with HPLC because the molar absorptivities and the formation constants of the metal complexes are mostly large. Thus the reagent has been used for the sensitive spectrophotometric determination and HPLC separation of V(V).[7,8] In this paper, on the basis of the results described in the previous works,[7,8] a highly sensitive and selective HPLC method was investigated for the determination of V in river water. The selectivity of the method was improved by the addition of CyDTA to both sample and mobile phase solutions as a masking reagent. The determination of V at the µg l^{-1} level was achieved by the present method after preconcentration using a handmade evaporator which was devised to prevent contamination from the environment.

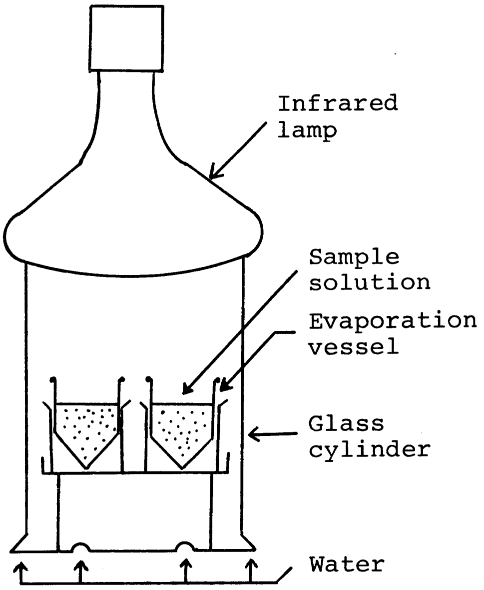

Fig. 1. Schematic diagram of handmade evaporator.

The HPLC system was consisted of a Nihon Seimitsu Kagaku NSP-800-3U pump, a Japan

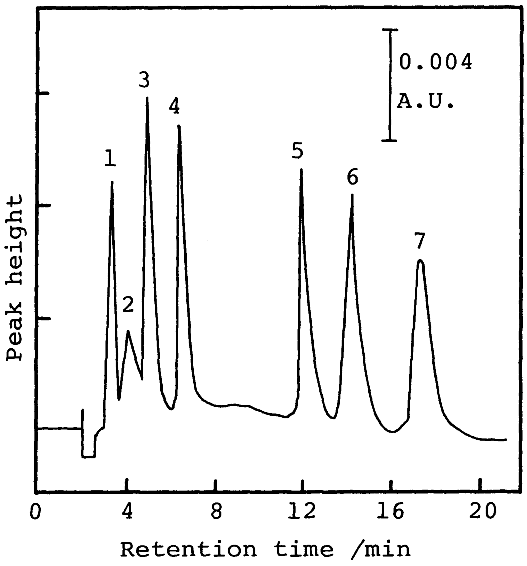

Fig. 2. Typical chromatogram of Metal-5-Br-PAPS complexes
5-Br-PAPS: 2×10^{-4} M, ammonium acetate: 1.0×10^{-2} M.
1:V(V), 2:In(III), 3:Cu(II), 4:Fe(III), 7:Ni(II).
V,Co:0.2 μg/ml, In,Fe:0.5 μg/ml
Cu,Ni:0.4 μg/ml.

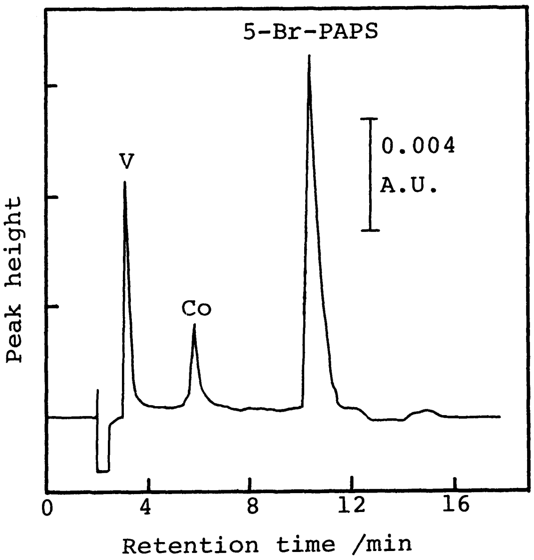

Fig. 3. Chromatogram of Metal-5-Br-PAPS system using CyDTA.
CyDTA, 5×10^{-3} M. Other conditions are the same as those in Fig. 1.

Spectroscopic hexane damper, and a Uvidec-100 II W-VIS absorption detector, a Rheodyne 7125 loop injector equipped with a 20 μl sample loop, and a Hitachi 561 recorder. A Merck Lichrosorb RP-18 column (125 mm x 4 mm I.D.) was used.

The handmade evaporator shown in Fig. 1 was used for the preconcentration. It was assembled with a heating IR lamp (500 W) placed closely on the top of a glass cylinder (188 mm x 130 mm I.D.) and evaporation vessels (10 ml) put on a dish (21 mm x 90 mm I.D.) which adhered on a glass table (200 ml beaker) in the glass cylinder. The sample solution placed in the evaporation vessel was evaporated gently by the heating lamp and the bottom of the glass cylinder was cooled with water.

Distilled and deionized water was further purified by a Milli-Q system. Analytical grade methanol was filtered with a Millipore filter (0.45 μm) after distillation. V(V) standard solution (1000 μl^{-1}) was prepared by dissolving ammonium metavanadate into 0.5 M nitric acid. 5-Br-PAPS was obtained from Dojindo Laboratories. Other reagents used were of analytical reagent grade. The mobile phase was a methanol/water (65:35) solution containing 1×10^{-4} M 5-Br-PAPS, 0.1 M lithium chloride, 1×10^{-4} M CyDTA, and acetate buffer (pH 4.0).

The recommended procedure is as follows. Ten ml of river water filtered through a Millipore filter (0.45 μm) was placed in an evaporation vessel. To the sample solution, 0.5 ml of 60% nitric acid and 1.0 ml of 0.4 w/v% potassium

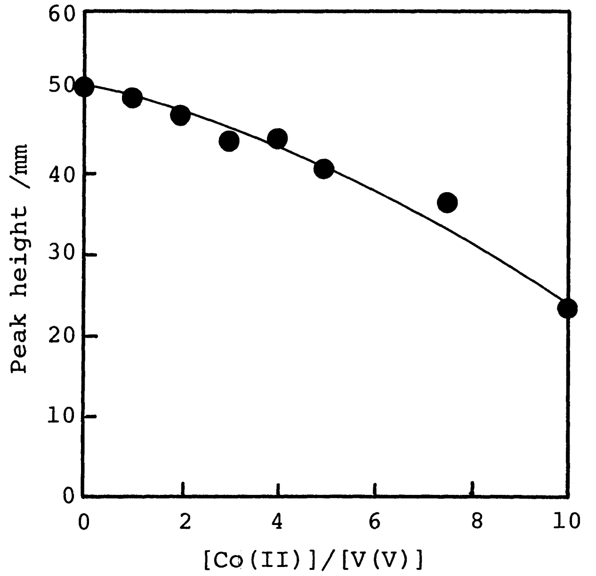

Fig. 4. Effect of Co(II) on peak height of V(V).
5-Br-PAPS:2 x 10^{-4}M, ammonium acetate:1.0 x 10^{-2}M, CyDTA: 5 x 10^{-3}M,
V:0.2 μg/ml.

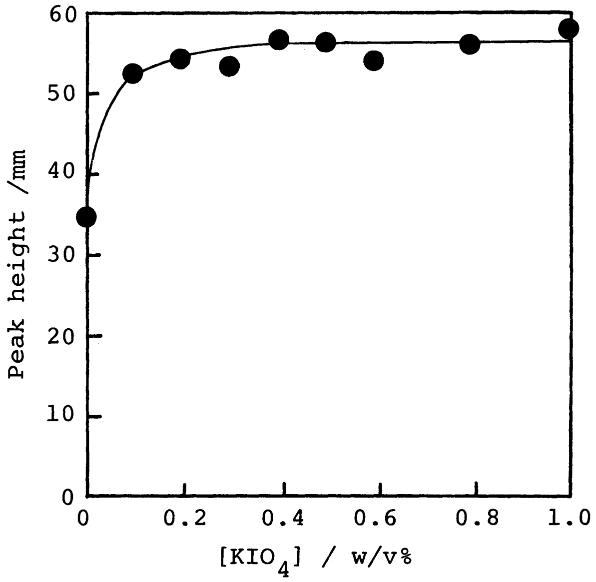

Fig. 5. Effect of KIO_4 concentration for peak height of V(V).
V(V):0.2 μg/ml, Co(II):1.0 μg/ml. Other conditions are the same as those in Fig. 4.

periodate solution were added. The solution was evaporated to dryness. The residue was dissolved in 0.4 ml of 0.2 M nitric acid by shaking for 2 min in the vessel stoppered with a screw cap, and then the solution was left 10 min. To 0.2 ml aliquots of the solution, 30 μl of 0.4 w/v% potassium periodate solution, 30 μl of 5 x 10^{-2} M CyDTA solution, 20 μl of 1.0 x 10^{-2} M 5-Br-PAPS solution, and 20 μl of 4.0 M ammonium acetate solution were added. An aliquot of the solution (20 μl) was injected into the HPLC. The flow rate of the mobile phase was 0.6 ml min^{-1} and the eluant was monitored at 580 nm.

The conditions of the V(V) complex formation with 5-Br-PAPS were discussed in the previous paper.7) V(V) reacted quantitatively with 5-Br-PAPS in the pH range 3.5 - 6.0 to form a 1:1 complex, which had an absorption maximum at 589 nm.

Figure 2 shows the typical chromatogram of several metal-5-Br-PAPS complexes. The V(V) complex was eluted first among these metal complexes, so that it was not appreciably interfered by other metals and the sharp peak of the V(V) complex was obtained. The selectivity of V determination was improved further by the addition of CyDTA into the sample solution and the mobile phase. All metal ions except Co(II) examined were masked completely with CyDTA as shown in Fig. 3. The Co(II)-5-Br-PAPS complex was formed partially even in the presence of CyDTA. Figure 4 shows that Co(II) interfered with the determination of V(V). It is thought that the valence of V(V) is reduced to the lower state by catalytic action of Co(II). Therefore potassium periodate, an oxidation agent, was examined to suppress the interference of Co(II). The interference of Co(II) was suppressed and the peak height of V(V) recovered by the addition of potassium periodate, as shown in Fig. 5.

The calibration curve for V at 0.02 aufs (absorbance unit full scale) was linear over the V concentration range of 0.01 - 0.2 mg l^{-1} and detection limit at the signal-to-noise ratio of three was 0.87 μg l^{-1}. All metal ions examined such as Al(III), Fe(III), Co(II), and Zn(II) did not interfere with the determination of V at the concentration level found in common river water. The river water samples from the Kinu river (Tochigi) were analyzed for the V contents by the present recomended procedure. The simple evaporation system was used for the preconcentration since the direct determination of V in river water with the HPLC method was not feasible because of insufficient sensitivity. The detection limit of V at the original sample solution was 35 ng l^{-1} after 25-fold enrichment. The sensitivity of the present method was higher than the graphite furnace atomic absorption spectrometry (GFAAS).9) The analytical results are summarized in Table 2. The result obtained by the proposed method (HPLC) and GFAAS were in good agreement with each other.

Table 1. Analytical results for vanadium in river water a)

Method	V content/μg l^{-1}
This work	2.10 ± 0.13 (n=7)
Micro-solvent extraction-GFAAS	1.95 ± 0.10 (n=4)
Coprecipitation-floatation-GFAAS	2.03 ± 0.08 (n=4)

a) Sample: The Kinu river (Tochigi) water taken at Dec. 11, 1985.

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