

Simultaneous Determination of Trace Amounts of Vanadium and Cobalt in Steel and Environmental Materials with 2-(5-nitro-2-pyridylazo)-5-[*N*-*n*-propyl-*N*-(3-sulfopropyl)amino]phenol by Reversed-Phase High-Performance Liquid Chromatography

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Abstract

2-(5-Nitro-2-pyridylazo)-5-[*N*-*n*-propyl-*N*-(3-sulfopropyl)amino]phenol (Nitro-PAPS) is used as a precolumn chelating reagent for the reversed-phase high-performance liquid chromatographic separation and simultaneous determination of vanadium and cobalt. The metal-Nitro-PAPS chelates are separated on an ODS column with acetonitrile–water (55:45) containing 0.01 mol dm⁻³ acetic acid, 0.01 mol dm⁻³ tetrabutylammonium bromide (TBA⁺Br⁻), and 10⁻⁴ mol dm⁻³ EDTA as an eluent. In this method, the vanadium and cobalt can be determined selectively at the sub-parts-per-billion level without any preliminary concentration and separation. The detection limits, defined as the concentrations equivalent to 3 times the standard deviation of the blank signal, are 17 ppt for vanadium and 55 ppt for cobalt at 0.002 absorbance unit full scale (593 nm). These results suggest that vanadium and cobalt in steel and environmental materials can be successfully determined without preseparation and preconcentration of these metal ions.

Introduction

In recent years, rare metals have been increasingly used in the development of frontal materials. For example, vanadium and cobalt have been used as raw materials for electronic and magnetic materials, catalytic agents, and various steels (1), and they are also known to be essential elements for organisms. However,

it has been pointed out that a high intake of these metals in animals results in toxicosis (2,3). As a result, a highly sensitive analytical technique for detecting trace amounts of cobalt and vanadium is required in the development of new materials and the analysis of vital functions, as well as for environmental analysis. The most commonly used analytical techniques for cobalt and vanadium have been graphite furnace atomic absorption spectrometry (GF-AAS) and inductively coupled plasma atomic emission spectrometry (ICP-AES). However, direct determination of these metal ions is often lacking in sensitivity and is limited due to interferences from the matrix. Therefore, some form of pretreatment, such as preconcentration or preseparation of the analytes from the matrix, is required (4–6).

Many azo dyes such as 2-(3,5-dibromopyridylazo)-5-[*N*-ethyl-*N*-(3-sulphopropyl)amino]phenol (7) and its related compounds (8–13) containing 2-(5-nitro-2-pyridylazo)-5-[*N*-*n*-propyl-*N*-(3-sulfopropyl)-amino]phenol (Nitro-PAPS, HR⁻) (14) and 2,2'-dihydroxyazobenzene (15–17) are known to be useful for high-performance liquid chromatography (HPLC) because they react nonspecifically with various metal ions to form chelates having high molar absorptivity on the order of 10⁵ dm³ mol⁻¹ cm⁻¹. For example, vanadium- and cobalt-Nitro-PAPS chelates ($\epsilon_{\nu}^{593\text{nm}} = 8.1 \times 10^4$, $\epsilon_{\text{Co}}^{590\text{nm}} = 1.1 \times 10^5$) have a higher molar absorptivity than 4-(2-pyridylazo)resorcinol (PAR) chelates ($\epsilon_{\nu}^{545\text{nm}} = 3.5 \times 10^4$, $\epsilon_{\text{Co}}^{510\text{nm}} = 5.6 \times 10^4$) (18,19) and 2-(5-bromo-2-pyridylazo)-5-[*N*-*n*-propyl-*N*-(3-sulfopropyl)amino]phenol (5-Br-PAPS) ($\epsilon_{\nu}^{589\text{nm}} = 5.47 \times 10^4$, $\epsilon_{\text{Co}}^{589\text{nm}} = 9.8 \times 10^4$) (20,21), and these chelates often exhibit their absorption maxima in a similar wavelength region. The nature of these

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chelates therefore seems to be very favorable for high-performance liquid chromatography (HPLC) determination.

In the present study, a highly sensitive, selective, and rapid method for the simultaneous determination of trace amounts of vanadium and cobalt by ion-pair reversed-phase partition HPLC based on preliminary complexation of the metal ions with Nitro-PAPS, one of the most sensitive reagents in many azo dyes, was investigated. The proposed method was successfully applied to the determination of trace amounts of vanadium and cobalt in steel and environmental substances containing many kinds of matrix elements.

Experimental

Reagents and apparatus

Nitro-PAPS, disodium salt, and dihydrate were purchased from Dojindo Laboratories (Kumamoto, Japan), and a stock solution was prepared by dissolving 0.0906 g of Nitro-PAPS in 200 cm³ of water (9×10^{-4} mol dm⁻³). Standard metal ion solutions were 1.00 mg cm⁻³ solutions for atomic absorption spectrophotometry purchased from Wako Pure Chemical Industries (Tokyo, Japan) and were accurately diluted to a fixed concentration with diluted nitric acid. A 0.1 mol dm⁻³ acetate buffer solution was prepared by mixing 0.1 mol dm⁻³ acetic acid with 0.1 mol dm⁻³ sodium hydroxide solution prepared with pH-meter control using suprapur sodium hydroxide monohydrate (Merck, Tokyo, Japan). A 5×10^{-3} mol dm⁻³ disodium hydrogenphosphate solution was dissolved in 1.774 g of disodium hydrogenphosphate in 250 cm³ of water. The mobile phase was 55% (v/v) acetonitrile–water containing 0.01 mol dm⁻³ acetic acid, 0.01 mol dm⁻³ tetrabutylammonium bromide (TBA⁺Br⁻), and 10^{-4} mol dm⁻³ ethylenediaminetetraacetic acid (EDTA). The acid, ammonia water, and other chemicals used were high-purity reagents obtained from Wako Pure Chemical Industries, and water purified by a Millipore Milli-Q system was used.

The chromatographic system consisted of a Hitachi (Toyko, Japan) model L-7100 pump, a Rheodyne (Rohnert Park, CA) model 7125 injector with a 100- μ L sample loop, a Hitachi model L-7420 variable-wavelength spectrophotometric detector with a 10-mm flow-through cell, and a Hitachi model D-7500 integrator. A 5- μ m particle size ERC-ODS-1282 column (Erma Cr., 250 mm \times 6-mm i.d.) was used for all experiments. A Hitachi model U-3210 spectrophotometer was used to measure the absorption spectra and the absorbance. A Horiba (Toyko, Japan) model F-22 pH meter, calibrated daily at pH 4.01 and 6.86 using buffer solutions provided by Toa Denpa was used for all pH measurements. In order to minimize contamination, the labware made of glass, Teflon, and polyethylene (e.g., beakers, volumetric flasks, etc.) was soaked in 4 mol dm⁻³ hydrochloric acid and then soaked overnight in 3 mol dm⁻³ nitric acid. The labware was then thoroughly rinsed first with deionized water and then with high-purity water. It was then dried on a clean drying shelf.

Recommended procedure

A sample solution containing less than 10 ng cobalt and 20 ng vanadium was placed in a 10-cm³ volumetric flask. To this solu-

tion, 1–3 cm³ of 5×10^{-3} mol dm⁻³ disodium hydrogenphosphate solution and 1 cm³ of 1 mol dm⁻³ acetate buffer solution (pH 4.0) were added successively. If necessary, 1 mol dm⁻³ sodium hydroxide solution was added to neutralize the solution and to keep the pH of the final solution at 4.0, followed by the addition of 1–3 cm³ of 9×10^{-4} mol dm⁻³ Nitro-PAPS solution. Under these experimental conditions, the Nitro-PAPS reacted immediately with the metal ions to form stable water-soluble complexes. The mixture was then diluted to volume with water. The derivatization solution could be prepared within 20 min. A 100-mm³ portion of the solution was loaded into a 100- μ L loop for HPLC with an eluent consisting of 0.01 mol dm⁻³ tetrabutylammonium bromide (TBA⁺Br⁻), 1×10^{-4} mol dm⁻³ EDTA, and 0.01 mol dm⁻³ acetic acid in acetonitrile–water (55:45, v/v) at a flow rate of 1.0 cm³/min. The apparent pH of the eluent was approximately 4.6. The detector setting of 0.002 absorbance unit full-scale (AUFS) at 593 nm was used for recording the chromatograms. If a sample solution containing more than 10 ng of cobalt and 20 ng of vanadium is to be analyzed, the appropriate AUFS setting is between 0.016 and 0.032. The interference encountered at higher concentrations can be circumvented by the addition of Nitro-PAPS in sufficient excess (the addition of 3 cm³ of 9×10^{-4} mol dm⁻³ Nitro-PAPS solution). Iron(III) in large quantity caused a leading of the iron(III) peak on the chromatogram, and the determination of vanadium was influenced; however, this type of effect can be masked by the addition of 1–3 cm³ of 5×10^{-3} mol dm⁻³ disodium hydrogenphosphate solution.

Acid digestion of the pond sediment

The National Institute for Environmental Studies (Ibaraki, Japan) Certified Reference Material number 2 (pond sediment) was used as a sample for the determination of vanadium and cobalt. The certified values (in % for Al, Fe, Ca, K, Si, Ti, and P, and in μ g/g for others) in NIES number 2 are as follows (reference values in parentheses): V (250); Co, 27 ± 3 ; Al, 10.6 ± 0.5 ; Fe, 6.53 ± 0.35 ; Ca, 0.81 ± 0.06 ; K, 0.68 ± 0.06 ; Na, 0.57 ± 0.04 ; Zn, 343 ± 17 ; Cu, 210 ± 12 ; Pb, 105 ± 6 ; Cr, 75 ± 5 ; Ni, 40 ± 3 ; As, 12 ± 2 ; Cd, 0.82 ± 0.06 ; Si (21); Ti (0.64); P(0.14); and Mn (770). Portions of 0.1–0.3 g of pond sediment (accurately weighed) were placed into a 50-cm³ PTFE beaker and treated with 10 cm³ of HF–HNO₃ (1:1) at 150°C on a hot plate. After heating to dryness, 20 cm³ of HNO₃–HClO₄ (1:1) was added. The mixture was left in a beaker covered by a poly(tetrafluoroethylene) (PTFE) lid until a pale yellow solution was obtained, and the solution was then evaporated to dryness. The total time required for digestion was approximately 2 days. After cooling, the residual solid was dissolved in 10 cm³ of concentrated nitric acid, and the solution was diluted to 50 cm³ with water. A 1-cm³ portion of this solution was further diluted to 10 cm³ with water in a volumetric flask. A 2-cm³ portion of this solution was subjected to analysis by the recommended procedure.

Acid dissolution of the steel

The certified values (%) in steel (JSS 174-7) from The Japan Iron and Steel Federation (Toyko, Japan) are as follows: V, 0.065; Co, 0.011; C, 0.042; Si, 0.21; Mn, 0.40; Al, 0.034; B, 0.0076; Zr, 0.014; Sb, 0.0102; and Nb, 0.020. Steel samples of 0.1–0.15 g

(accurately weighed) were placed into a 50-cm³ PTFE beaker and dissolved in 2 cm³ of concentrated nitric acid with gentle heating on a hot plate until completely dissolved. After cooling, the samples were diluted to 25 cm³ with water in a volumetric flask. The time required for the acid dissolution of the steel was less than 1 h. A 1-cm³ portion of this solution was further diluted to 25 cm³ with water in a volumetric flask. A 1-cm³ portion of this solution was subjected to analysis by the recommended procedure.

Sampling and processing of the sea water

Coastal sea water collected from Abashiri, Hokkaido, Japan was filtered through a 0.45- μ m membrane filter, acidified to pH 1.6 with nitric acid, and stored in a polypropylene bottle that was cleaned as previously described. A 5-cm³ portion of sea water was subjected to analysis by the recommended procedure.

Results and Discussion

Precolumn complexation reactions and absorption spectra

The effect of pH on the formation of the V(V)- and Co(III)-Nitro-PAPS complexes was investigated. The Co(II) chelate with Nitro-PAPS and its analogues are known to immediately oxidize to the Co(III) chelate in an acidic medium (22). The maximum absorbance values were obtained in the pH ranges of 3.1–7.4 for Co(III) and 3.4–4.2 for V(V). The optimum pH of 4.0 with acetate buffer was chosen for the simultaneous determination. The absorption maxima of these complexes are near 590 nm in aqueous media. The molar absorptivity (ϵ) values are 1.1×10^5 dm³ mol⁻¹ cm⁻¹ at 590 nm for Co(III) chelate and 8.1×10^4 dm³ mol⁻¹ cm⁻¹ at 593 nm for V(V) chelate. The best wavelength for the detection of the complexes in the mobile phase solution is 593 nm. The composition of the metal complexes was found by the molar ratio method (metal, Nitro-PAPS) to be 1:1 for the V(V) complex and 1:2 for the Co(III) complex; these complexes formed the anionic chelates VO₂R⁻ and CoR₂⁻, respectively.

HPLC studies

In order to establish the optimum mobile phase conditions, the effects of some variables on the HPLC behavior of the complexes were examined. The effects of the eluent mixture of acetonitrile, methanol, and tetrahydrofuran with water on the separation were investigated. It was found that an acetonitrile–water system is the most suitable for use as an eluent. The capacity factor (k') of each complex decreases with increases in the acetonitrile content of the acetonitrile–water eluent; the greater the acetonitrile composition in the mobile phase, the sharper the peak of both chelates. Well-resolved peaks were obtained at a 55% acetonitrile content. The apparent pH of the mobile phase was maintained at 4.6 with acetic acid. The retention behavior of the complexes was also investigated in the concentration range of 2.5×10^{-3} to 2.0×10^{-2} mol dm⁻³ using tetrabutylammonium bromide (TBA⁺Br⁻) as an ion-pairing reagent. The capacity factor of both complexes increased gradually with increases in the TBA⁺ concentration, and when the TBA⁺ concentration was in the range of 1.0×10^{-2} to $2.0 \times$

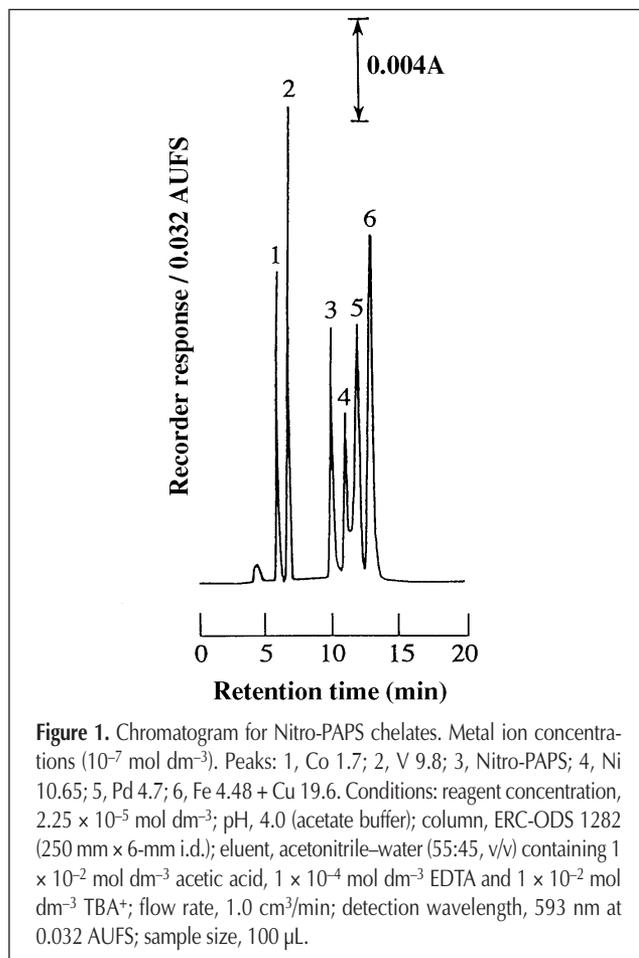


Figure 1. Chromatogram for Nitro-PAPS chelates. Metal ion concentrations (10^{-7} mol dm⁻³). Peaks: 1, Co 1.7; 2, V 9.8; 3, Nitro-PAPS; 4, Ni 10.65; 5, Pd 4.7; 6, Fe 4.48 + Cu 19.6. Conditions: reagent concentration, 2.25×10^{-5} mol dm⁻³; pH, 4.0 (acetate buffer); column, ERC-ODS 1282 (250 mm \times 6-mm i.d.); eluent, acetonitrile–water (55:45, v/v) containing 1×10^{-2} mol dm⁻³ acetic acid, 1×10^{-4} mol dm⁻³ EDTA and 1×10^{-2} mol dm⁻³ TBA⁺; flow rate, 1.0 cm³/min; detection wavelength, 593 nm at 0.032 AUFS; sample size, 100 μ L.

10^{-2} mol dm⁻³ for both chelates, there was almost no change in k' . The peak shape of each chelate was good, and a baseline separation was obtained. Therefore, a TBA⁺ concentration of 1.0×10^{-2} mol dm⁻³ was available in the mobile phase. In order to mask the metal ion contaminants from the walls of the HPLC system, 1×10^{-4} mol dm⁻³ of Na₂EDTA was also added to the mobile phase.

A typical chromatogram for the separation of the V(V)- and Co(III)-Nitro-PAPS complexes is shown in Figure 1. The Nitro-PAPS chelates were eluted in the order of cobalt and then vanadium, and the retention times were 5.7 and 6.6 min, respectively, at a flow rate of 1.0 cm³/min. The 2 peaks for the metal ions were resolved and well-separated from the Nitro-PAPS peak.

The effect of diverse metal ions was investigated. Among the Zn(II), Cu(II), Ni(II), Cd(II), Mn(II), Fe(III), Pb(II), Hg(II), and Pd(II) ions studied, only Cu(II), Ni(II), Fe(III), and Pd(II) showed peaks that were well-resolved in relation to V(V) and Co(III), and the other ions showed no peaks under the conditions employed. The retention times of Cu(II), Ni(II), Fe(III), and Pd(II) are more than 10 min, but the 10^{-5} mol dm⁻³ order concentrations of those metal ions appear to have little effect on the determinations of vanadium and cobalt, as shown in Figure 1. In addition, Zn(II), Pb(II), and Hg(II) chelates were probably decomposed on the column during the elution process, and Cd(II) and Mn(II) do not react with Nitro-PAPS at pH 4. The peak height calibration curves are linear over the metal concentration range of 0.25–1.0 ppb for cobalt and 0.5–2.0 ppb for vanadium at 0.002 AUFS and

over the range of 1.0–3.0 ppb for cobalt and 5.0–15.0 ppb for vanadium at 0.016 AUFS. The detection limits, defined as 3 times the standard deviation of the blank signal, are 55 ppt for cobalt

and 17 ppt for vanadium at 0.002 AUFS. The relative standard deviations of the determinations ($n = 5$) are 5.3% for cobalt (0.5 ppb) and 5.4% for vanadium (1 ppb) at the intermediate concentration of the calibration curve at 0.002 AUFS.

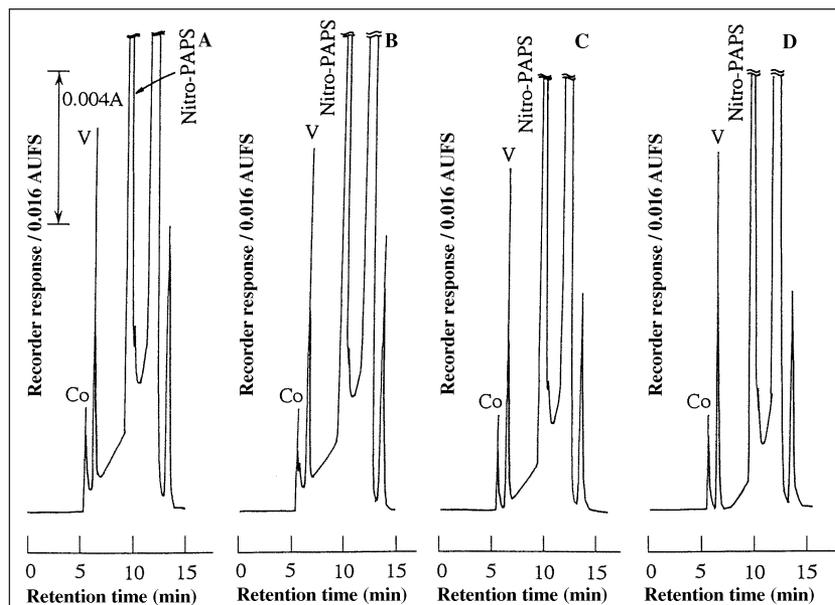


Figure 2. Chromatograms for the steel sample solution after the addition of various concentrations of disodium hydrogenphosphate; $[\text{Na}_2\text{HPO}_4]$ in the precolumn derivatization solution ($\times 10^{-3} \text{ mol dm}^{-3}$) was 1.0 (A), 2.5 (B), 5.0 (C), and 15 (D). Conditions: same as those described in Figure 1 except the reagent concentration was $1.8 \times 10^{-4} \text{ mol dm}^{-3}$. The precolumn derivatization solution was prepared by the acid dissolution of steel followed by the recommended procedure.

Practical application

The proposed method has been successfully applied to the determination of vanadium and cobalt in steel (JSS 174-7), pond sediment (NIES number 2), and sea water. The iron content in steel is approximately 99.2%, and thus the iron content in steel is roughly 1400 times that of vanadium and 9500 times that of cobalt at a molar ratio. It was found that such a large amount of iron interferes with the determination of vanadium and cobalt in steel. Therefore, the masking of iron by the addition of disodium hydrogenphosphate was examined. The effect of disodium hydrogenphosphate concentration is shown in Figure 2; these results are based on the precolumn derivatization solution being injected into the HPLC at a standing time of about 24 min after preparation of the solution according to the previously described recommended procedure by using an acid-dissolved steel solution. In Figure 2A–2C, the leading of the peak arises from an iron chelate, preventing a baseline analysis of vanadium and cobalt. It became apparent that the baseline analysis of vanadium and cobalt in steel can be

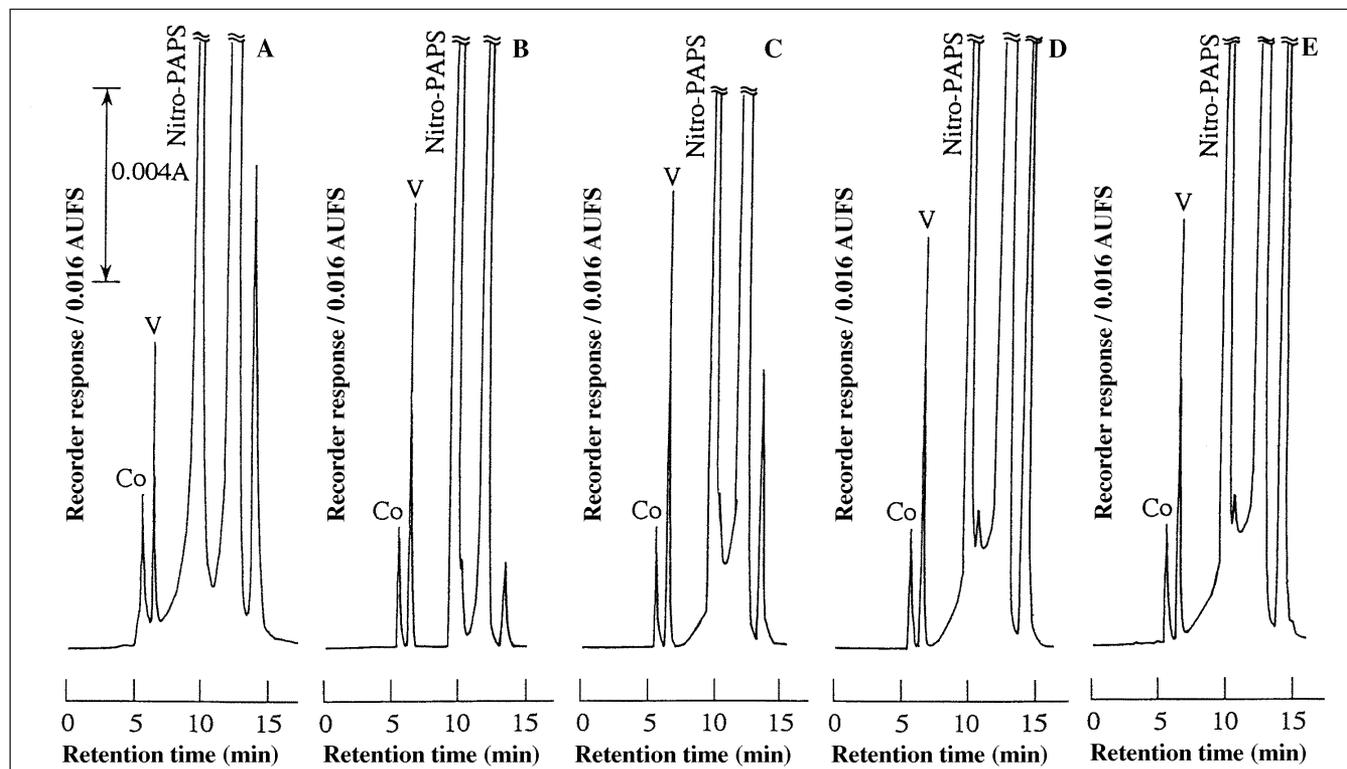


Figure 3. Chromatograms for the steel sample solution when the derivatization solution was injected into the HPLC at various standing times after preparation of the solution; standing time (min) was 1 (A,B), 24 (C), 90 (D), 120 (E). Conditions: same as those described in Figure 2, except $[\text{Na}_2\text{HPO}_4]$ in the precolumn derivatization solution was not added (A) or $1.5 \times 10^{-2} \text{ mol dm}^{-3}$ (B–E).

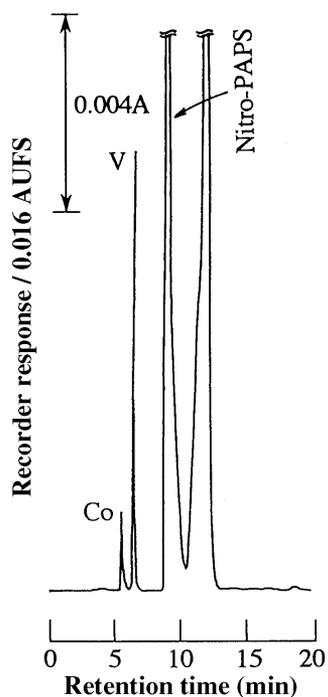


Figure 4. Typical chromatogram for the determination of cobalt and vanadium in pond sediment. The column and eluent are the same as those described in Figure 3. The precolumn derivatization solution was prepared by the acid dissolution of the pond sediment followed by the recommended procedure.

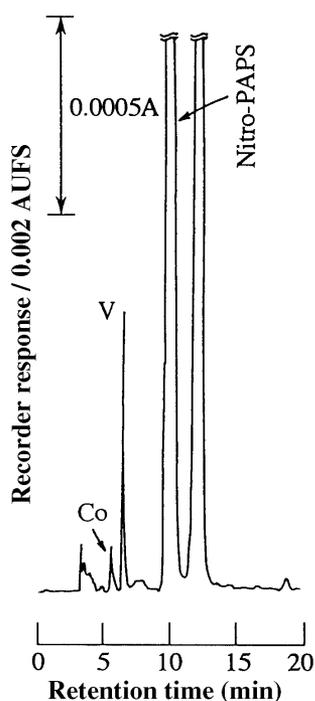


Figure 5. Typical chromatogram for the determination of cobalt and vanadium in sea water collected on July 16, 1997. The column and eluent are the same as those described in Figure 3. The precolumn derivatization solution was prepared by the sampling and processing of the sea water followed by the recommended procedure.

Table I. Determination of Vanadium and Cobalt in Steel, Pond Sediment, and Sea Water

Sample	Found*	Certified, reference or reported value
Steel		
V	0.061 ± 0.002% (n = 4)	0.065% [†]
Co	0.0118 ± 0.0001% (n = 4)	0.011% [†]
Pond sediment		
V	247 ± 8 µg/g (n = 3)	250 µg/g [‡]
Co	25 ± 3 µg/g (n = 3)	27 ± 3 µg/g [‡]
Sea water (April 23)		
V	1.3 ± 0.1 ng/cm ³ (n = 5)	1.5–2.0 ng/cm ^{3§}
Co	not detected	0.032 ng/cm ^{3§}
Sea water (July 16)		
V	2.0 ± 0.1 ng/cm ³ (n = 4)	—
Co	not detected	—

* 95% confidence level.
[†] Certified value.
[‡] Reference value.
[§] Reported in reference 23.

achieved by the addition of 1.5×10^{-2} mol dm⁻³ of disodium hydrogenphosphate, as shown in Figure 2D. Subsequently, the effect of standing time (the time from the preparation of the precolumn derivatization solution containing 1.5×10^{-2} mol dm⁻³ of disodium hydrogenphosphate until the solution is injected into the HPLC) was investigated. In Figure 3B, the leading of the iron peak could not be observed as clearly after a standing time of 1 min. However, the leading of the iron peak became progressively larger with an elapsed time from 24 min to 2 h, as shown in Figure 3C–3E because of the formation of iron–Nitro-PAPS chelate by the following ligand exchange reaction: $\text{Fe–HnPO}_4^{(n-3)} + \text{Nitro-PAPS} \rightleftharpoons \text{Fe–Nitro-PAPS} + \text{HnPO}_4^{(n-3)}$. From these results, it became clear that the precolumn derivatization solution should be injected into the HPLC within 90 min after preparation of the solution for baseline analysis.

The 3 kinds of practical samples were analyzed at 0.016 AUFS for the analysis of steel and pond sediment and at 0.002 AUFS for the analysis of sea water using the techniques of an absolute calibration curve and standard addition, respectively. Typical chromatograms for the pond sediment and sea water are shown in Figures 4 and 5, respectively, and the analytical results are shown in Table I. The cobalt and vanadium contents obtained for steel and pond sediment are in good agreement with certified or reference values. The analytical values for vanadium in sea water are approximately the same as the literature values (23). In the analysis of sea water, a cobalt peak arising from the reagent blank was observed (Figure 5). The cobalt content in sea water could not be determined because the cobalt content in sea water is reported to be 0.03 ppb (23), which is less than the detection limit. The vanadium content in sea water collected on April 23, 1997, was less than that in sea water collected on July 16, 1997. The effect of floating ice, which leaves the Abashiri coast along

the Sea of Okhotsk in April, seems to be the reason for the different vanadium content in the collected sea water samples (23).

Conclusion

The proposed method is simple, selective, and sensitive for the routine analysis of vanadium and cobalt in environmental and steel materials. Trace amounts of vanadium and cobalt in environmental and steel materials can be determined simultaneously without any preconcentration or preseparation in the presence of various matrices, although AAS, GF-AAS, ICP-AES, and inductively coupled plasma mass spectrometry (ICP-MS) are frequently affected by the matrix in equivalent samples. Consequently, these metal ions can be determined with a shorter analysis time than by these conventional methods and at the same time remain free from contamination arising from preconcentration and preseparation procedures. The sensitivity of the proposed method (detection limit $0.017 \mu\text{g dm}^{-3}$ for V and $0.055 \mu\text{g dm}^{-3}$ for Co) is higher than that of AAS (40 for V and 6 for Co) and ICP-AES (2 for V and 2 for Co) (24), and it is comparable with that of GF-AAS (0.2 for V and 0.01 for Co) and ICP-MS (0.1 for V and 0.03 for Co) (24). Another advantage of the method is that the required apparatus is common in chemical laboratories, and the chelating agent (Nitro-PAPS) is commercially available for analytical use at a reasonable cost. This technique could provide a new and simple means by which many laboratories could perform trace vanadium and cobalt analyses of environmental and industrial materials such as pond sediment, sea water, electronic high-purity grade materials, etc.

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