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Short Communication

Separation and determination of trace amounts of vanadium(V), chromium(III) and iron(III) with 2-(2-thienylazo)-5-diethylaminophenol chelates by high-performance liquid chromatography

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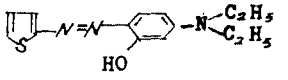
ABSTRACT

A reversed-phase high-performance liquid chromatographic method for the separation and the determination of vanadium(V), chromium(III) and iron(III) with 2-(2-thienylazo)-5-diethylaminophenol chelates on a C_{18}-bonded stationary phase by using methanol–tetrahydrofuran–water (20:15:65, v/v/v) containing 0.05 *M* lithium sulphate and 0.04 *M* acetate buffer (pH 5.5) as mobile phase and with spectrophotometric detection at 570 nm was developed. The method has high sensitivity, the detection limits being 0.5 ppb for vanadium(V), 2 ppb for chromium(III) and 1 ppb for iron(III). Under the optimum conditions, most other metal ions did not interfere, *e.g.*, up to 1000 μg of magnesium(III), cadmum(II), zinc(II), lead(II), maganese(II), calcium(II), barium(II), tin(II, IV) and tungsten (VI), 400 μg of thorium(IV), 200 μg of iron(II), bismuth(III), zirconium(IV), 150 μg of gallium(III) and 120 μg of lanthanum(III) in the determination of 2.5 μg of iron(III) and chromium(III) and 1 μg of vanadium(V). The method can be applied to the simultaneous determination of trace amounts of vanadium(V), chromium(III) and iron(III) in water, tea leaves and rice samples.

INTRODUCTION

High-performance liquid chromatography (HPLC) is extensively applied to the separation and determination of inorganic ions. Most studies involve the reversed-phase (RP) HPLC of metal ion chelates, because the methods are rapid, convenient, highly sensitive and allow the selective determination of metal ions. In these methods, the most commonly used chelating agents include sodium diethyldithiocarbamate (DDTC) [1], dithizone [2], 8-hydroxyquinoline [3], β-diketones [4], pyridylazo dyes such as PAR [5] and 5-Br-PAPS [6] and others [7], azo compounds of chromotropic acid [8,9] and porphyrins [10].



TADAP

The colour reaction of 2-(2-thienylazo)-5-diethylaminophenol (TADAP) with metal ions and their analytical application have not previously been reported. We found that it can form red or violet-red chelates of maximum absorption wavelength between 520 and 600 nm with vanadium(V), chromium(III), iron(III), cobalt(II), nickel(II), gallium(III), indium(II), titanium(IV), zirconium(IV), bismuth(III), copper(II), etc. The colour reactions have high sensitivity, but showed poor selectivity in the determination of metal ions by using spectrophotometry because of mutual interferences.

In this work it was found that the RP-HPLC determination of vanadium(V), chromium(III) and iron(III) with TADAP chelates has very good selectivity and the usual metal ions and anions do not interfere in the determination. The method can be applied to the determination of trace amounts of vanadium(V), chromium(III) and iron(III) in water, tea leaves, rice and other samples.

EXPERIMENTAL

Apparatus

The HPLC system consisted of a Model LC-6A pump (Shimadzu, Kyoto, Japan), a Rheodyne (Cotati, CA, USA) Model 7125 injection valve (20-μl sample loop), a Model C-R3A chromatographic data processor (Shimadzu), a column packed with 9–11-μm YWG-C_{18} ODS (250 × 4.0 mm I.D.) (Dalian Institute of Chemical Physics, Academia Sinica, China), a Model SPD-6AV UV-VIS spectrophotometric detector (Shimadzu) and a Model U-3400 spectrophotometer (Hitachi, Kyoto, Japan). A Model SA-720 pH meter (Orion, Cambridge, MA, USA), a Model CQ-50 ultrasonicator for degassing the mobile phase (Shanghai Ultrasonic Instrument Factory, Shanghai, China) and a Model 800 centrifuge (Shanghai Operating Apparatus Factory, Shanghai, China) were used.

A Model WF-1A atomic absorption spectrometer (Beijing Second Optical Instrument Factory, Beijing, China) was used for the determination of chromium and vanadium using a Model WF-4A graphite furnace and for the determination of iron using an air–acetylene flame.

Reagents

All solutions were prepared with analytical-reagent grade chemicals and all water used was doubly distilled.

TADAP (analytical-reagent grade, Beijing Chemical Factory, Beijing, China) was prepared as a 0.1% solution in ethanol.

Stock standard solutions of various metal ions of concentration 1 mg/ml were prepared by the usual method from highly pure metal oxides or salts. Working standard solutions of concentration 1–10 μg/ml were prepared by dilution with water.

The mobile phase was methanol–tetrahydrofuran–water (20:15:65, v/v/v) containing 0.05 *M* lithium sulphate and 0.04 *M* acetate buffer (pH 5.5). The mobile phase was filtered through a 0.45-μm membrane filter and degased using a Model CQ-50 ultrasonic bath before use.

General procedure

Amounts of 1 μg of vanadium(V), 2.5 μg of chromium(III) and 2.5 μg of iron(III) were placed in a 25-ml volumetric flask, 2.0 ml of acetic acid–sodium acetate buffer solution (pH 5.5), 4.0 ml of ethanol and 2.0 ml of 0.1% ethanolic TADAP solution were added and mixed and diluted to about 20 ml with water. After heating in a water-bath at 80–90°C for 10 min, the solution was cooled to room temperature, diluted to the mark with water and centrifuged for 3 min at 3000 rpm.

An aliquot of 20 μl of the solution was injected into the chromatograph with the 20-μl loop injector. The flow-rate of the mobile phase was 0.9 ml/min and the elutes were monitored at 570 nm with an SPD-6AV UV-VIS spectrophotometric detector. The sensitivity was set at 0.08 a.u.f.s. The amounts of metal ions eluted were determined from the peak areas.

Determination of vanadium(V), chromium(III) and iron(III) in water

A clean, filtered 15.0-ml water sample was placed in a 25.0-ml volumetric flask, then vanadium(V), iron(III) and chromium(II) were determined as described under *General procedure.*

Determination of vanadium(V), chromium(III) and iron(III) in tea leaves and rice

A 1.000-g amount of oven-dried tea leaves or rice was weighed into a crucible, covered and ashed in an electric oven at 750°C for 3 h. The ash was dissolved nitric acid (1:1) and the solution was evaporated nearly to dryness. The residue was dissolved in and diluted to 52.0 ml with water. A 15.0-ml volume of this solution was placed in a 25-ml volumetric flask for the determination of vanadium(V) and chromium(III), but 0.5 ml of the solution for the determination of iron(III). The determination was then carried out as described under *General procedure.*

RESULTS AND DISCUSSION

Absorption spectra of the chelates

The characteristics of the chelates of TADAP with vanadium(V), chromium(III) and iron(III) and their absorption spectra are shown in Table I and Fig. 1. The composition ratios of the chelates were established by Job's method and the equilibrium shift method. Under similar conditions, TADAP also forms sensitive coloured chelates with titanium(IV), zirconium(IV), bismuth(III), gallium(III), cobalt(II), nickel(II), copper(II) and some noble metals. Their maximum absorption wavelength are all between 520 and 600 nm. However, trace amounts of vanadium(V), chromium(III) and iron(III) can be satisfactorily separated and determined in the presence of the above-mentioned interfering ions by RP-HPLC with spectrophotometric detection at 570 nm.

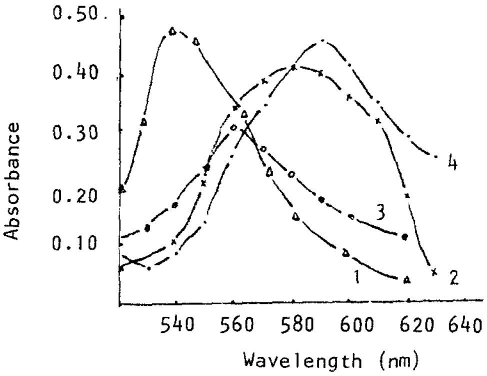


Fig. 1. Absorption spectra of TADAP and its chelates with metal ions (5 μg/25 ml). pH, 5.5. 1 = TADAP against water; 2 = V(V) against reagent blank; 3 = Cr(III) against reagent blank; 4 = Fe(III) against reagent blank.

Effect of the composition and pH of the mobile phase

A number of combinations of organic solvents and water such as methanol–water, methanol–acetonitrile, methanol–acetonitrile–water and methanol–tetrahydrofuran–water were investigated as mobile phases. The methanol–tetrahydrofuran–water mixture was found to be the best because it gives better peak shapes and a more effective separation of vanadium(V), chromium(III) and iron(III) than the other mixtures, and it was adopted in subsequent work.

The retention times of the chelates of chromium(III) and iron(III) decrease with increase in the tetrahydrofuran concentration in the mobile phase, but the effect is smaller with the vanadium(V) chelate. The best separation was obtained using methanol–tetrahydrofuran–water (20:15:65, v/v/v) as the mobile phase.

TABLE I

COLOUR REACTION CHARACTERISTICS OF TADAP CHELATES WITH VANADIUM(V), CHROMIUM(III) AND IRON(III)

Metal ion	λ_{max} (nm)	pH	Temperature (°C)	Composition ratio (M:L)
V(V)	585	4.2–6.7	25	1:1
Cr(III)	560	3.0–6.2	80–90 (10 min)	1:2
Fe(III)	590	4.2–6.8	25	1:2

Using the methanol–tetrahydrofuran–water system in the absence of any counter ions, the peaks of chromium(III) and iron(III) chelates are slow to appear and are low, flat and tailing, although that for the vanadium(V) chelate is good. When different inorganic salts such as lithium sulphate, sodium sulphate, sodium dihydrogenphosphate, sodium bromide, potassium nitrate and potassium iodide were added, it was found that lithium sulphate gave the greatest improvement in chromatographic characteristics, and led to very satisfactory separations of all three chelates, but the effect of the other compounds was not remarkable. The suitable concentration range of lithium sulphate is between 0.04 and 0.08 *M*. If the anions of the inorganic salts have complexing ability or are strongly reducing, *e.g.*, PO_4^{3-}, I^- or Br^-, they will lead to a decrease in sensitivity for the determination of iron(III). In subsequent experiments we chose 0.05 *M* lithium sulphate.

The effect of the pH of the mobile phase on the retention time was investigated. At pH >6.0 or <4.0 the peak areas decrease, but at pH >6.5 the retention time was prolonged. Therefore, the optium pH range is between 5.0 and 6.0. In subsequent experiments acetic acid–sodium acetate buffer solution (pH 5.5) was used.

TABLE II

DETERMINATION OF VANADIUM, CHROMIUM AND IRON IN WATER, TEA LEAVES AND RICE

Sample	Element	Content determined	Average content	Standard deviation	Relative standard deviation (%)	AAS[a] method
Tap water	V (ppb)	0.62, 0.65, 0.63	0.63	0.015	2.4	0.59
	Cr (ppb)	23.3, 22.8, 23.2	23.1	0.264	1.1	24.2
	Fe (ppm)	0.24, 0.238, 0.238	0.24	0.001	0.5	0.242
Spring water	V (ppb)	1.32, 1.28, 1.30	1.30	0.02	1.5	1.30
	Cr (ppb)	9.83, 9.70, 10.22	9.92	0.27	2.7	10.3
	Fe (ppm)	0.126, 0.125, 0.127	0.126	0.001	0.7	0.127
Tea leaves	V (ppb)	650, 680, 680	670	17	2.6	664
	Cr (ppb)	260, 272, 268	267	6	2.3	273
	Fe (ppm)	78.9, 176.8, 178.4	178.0	1.1	0.6	182
Rice	V (ppb)	135, 138, 138	137	1.7	1.3	134
	Cr (ppb)	84.8, 85.3, 84.4	84.5	0.6	0.7	85.6
	Fe (ppm)	23.4, 22.6, 23.4	23.1	0.46	1.9	23.3

[a] Atomic absorption spectrometric.

Effect of foreign ions

The effect of foreign ions on the determination of 2.5 μg of iron(III) and chromium(III) and 1 μg of vanadium(V) was studied under the optimum conditions. Most other ions do not interfere (relative error ≤5%), *e.g.*, to 1000 μg of magnesium(II), cadmium(II), zinc(II), lead(II), molybdenum(VI), manganese(II), calcium(II), tin(II, IV), tungsten(VI) and barium(II), 400 μg of thorium(IV), 200 μg of iron(II), bismuth(III) and zirconium(IV), 150 μg of gallium(III), 120 μg of lanthanum(III), 80 μg of indium(III), 30 μg of copper(II) and nickel(II) and 25 μg of cobalt(II). Hence the method has high selectivity.

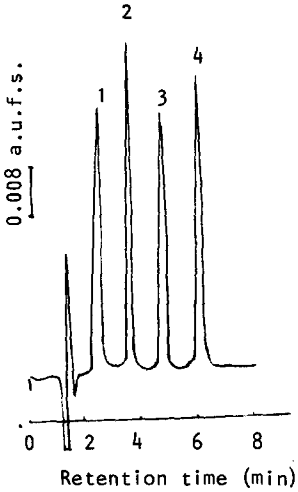


Fig. 2. Standard chromatogram. V(V), 1 μg in 25 ml; Cr(III), 2.5 μg in 25 ml; Fe(III), 2.5 μg in 25 ml. Peaks: 1 = V(V); 2 = TADAP; 3 = Cr(III); 4 = Fe(III).

Calibration graph and detection limits

Calibration graphs of peak area *versus* metal ion concentration were linear in the concentration ranges 0–200 ppb for vanadium(V), 4–400 ppb for chromium(III) and 5–400 ppb for iron(III).

The detection limits, calculated as the concentrations that gave a signal twice the background noise (signal-to-noise ratio = 2), were 0.5 ppb for vanadium(V), 2 ppb for chromium(III) and 1 ppb for iron(III). A standard chromatogram is shown in Fig. 2.

Results of analysis of samples

The results for the determination of vanadium, chromium and iron in water, tea leaves and rice are shown in Tables II and III. The relative standard deviations are between 0.7% and 2.7% ($n = 8$) and the recoveries are between 94.2% and 100.5%.

TABLE III

RECOVERY OF DETERMINATION OF V(V), Cr(III) AND Fe(III)

Sample	Element	Amount determined (ng)	Amount added (ng)	Total amount determined (ng)	Recovery (%)
Tap water	V	9.45	100.0	109.5	100.5
	Cr	364.5	100.0	437.4	97.4
	Fe	3.63×10^3	$10.0 \cdot 10^3$	$13.42 \cdot 10^3$	94.2
Tea leaves	V	670	100.0	772.0	100.3
	Cr	267	100.0	358	96.6
	Fe	178.0×10^3	$100.0 \cdot 10^3$	$276.0 \cdot 10^3$	98.9

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