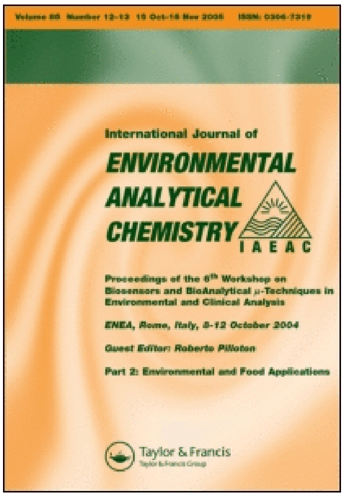

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Extraction-Spectrophotometric or -Atomic Absorption Spectrophotometric Determination of Titanium Using Caffeic Acid and a Liquid Ion Exchanger

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EXTRACTION–SPECTROPHOTOMETRIC OR -ATOMIC ABSORPTION SPECTROPHOTOMETRIC DETERMINATION OF TITANIUM USING CAFFEIC ACID AND A LIQUID ION EXCHANGER

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A selective and sensitive method for the extraction followed by a spectrophotometric or atomic absorption spectrophotometric determination of titanium(IV) in trace amounts is described. The molar absorptivity of the caffeic acid-Aliquat 336 complex is $5.7 \times 10^4 \mathrm{l\,mol^{-1}\,cm^{-1}}$ at 380 nm; the yellow coloured complex obeys Beer's law in the range 0.05–1.2 mg/l of titanium in the final extract. The method is applied to the preconcentration, separation and determination of titanium(IV) in steel, industrial effluents and environmental samples.

KEY WORDS: Caffeic acid, titanium, extraction and AAS determination.

INTRODUCTION

Liquid ion exchangers are useful for the separation of metal ions.[1–6] Several attempts have been made to develop colour in the liquid ion exchanger phase after extraction from the aqueous phase,[7] but the extraction of coloured species into the liquid ion exchanger phase has received much less attention.

The present investigation describes the formation of a yellow coloured titanium-caffeic acid-Aliquat 336 complex and direct absorption measurement of the complex in the ion exchanger phase. The method is applied to the determination of microgram amounts of titanium(IV) in metal alloys and in environmental samples and to its separation from closely associated metals such as vanadium and molybdenum by selective elution.

EXPERIMENTAL

Chemicals and Reagents All chemicals were of analytical reagent or generalpurpose reagent grade from BDH Chemicals and E. Merk unless otherwise specified.

Caffeic acid 0.1% solution was prepared in methanol.

Standard titanium solution A stock solution of titanium was prepared by heating 0.2 g of pure titanium(IV) oxide in a Pyrex flask with 8.0 g of ammonium sulphate and 25 ml of concentrated sulphuric acid. After cooling, the resulting solution was transferred to a 250 ml calibrated flask. The Pyrex flask was washed with 10 × 5 ml of 5% sulphuric acid. Finally the titanium solution was adjusted to 250 ml with water. The solution was standardised spectrophotometrically with N-phenylbenzohydroxamic acid (PBHA)[8] and the titanium content was found to be 400 mg/l. The solution was further diluted to obtain a level of 5 mg/l of titanium.

Buffer solutions Buffer solutions in the range of pH 2.0–5.5 were prepared from mixtures of sodium citrate and hydrochloric acid and sodium acetate and acetic acid.[9]

Ion exchangers Amberlite LA-1 (N-dodecyltrialkylmethyl) amine (Rohm & Hass, Philadelphia, PA, USA), Aliquat 336 (tricaprylmethyl ammonium chloride) (Fluka) and trioctylamine (Fluka) dissolved in suitable solvents in varying concentrations were used.

Apparatus

A VSU 2P (Carl Zeiss, Jena) spectrophotometer with matched quartz cells was used for spectral measurements.

A GBC 901 atomic absorption spectrophotometer (AAS) equipped with a Ti hollow-cathode lamp was used. The measurements were made at 304.3 nm with a 20 mA current; nitrous oxide-acetylene was used. For details of the procedure, see ref. 10.

Procedure

A sample solution (0.25–6.0 ml) containing 1.25–30.0 mg/l of the metal was taken in a 60 ml separatory funnel. Adjustment of the aqueous phase to pH 3.0 and to a total volume of 15 ml using buffer solution was carried out after adding 5 ml of a 0.1% solution of caffeic acid. The mixture was shaken gently with 5 ml of a 1% solution of Aliquat 336 in toluene for about 1 min. The two layers were allowed to settle. After drying over anhydrous sodium sulphate, the organic layer was transferred carefully to a 25 ml calibrated flask. The anhydrous sodium sulphate was washed with toluene and the washings were collected. Finally, the combined extract was adjusted to 25 ml with the toluene and the absorbance was measured at 380 nm against a reagent blank.

To calculate the distribution ratio, D, and the percentage extraction, E, the titanium concentration in the aqueous phase was determined[11] using a calibration graph. The metal content in the organic phase was determined by the procedure given below.

Titanium was eluted from the ion exchanger phase with 2 N sulphuric acid and determined spectrophotometrically.[11]

For the elution of titanium, the layer obtained after extracting the complex from the aqueous phase was shaken with 5 ml of 2 N sulphuric acid for 5 min. The two phases were allowed to settle and the aqueous layer was separated carefully. The organic layer was again shaken with 2 ml of 2 N sulphuric acid and the aqueous layer was collected. The combined aqueous extracts were mixed with 2 ml of hydrogen peroxide (20 vol. %) and diluted to 10 ml with 2 N sulphuric acid. The absorbance was measured at 410 nm. The amount of titanium was calculated using a calibration graph.

Determination of Titanium in Sample Solutions

A titanium sample solution was prepared by dissolving a high steel sample (British standard) in hydrofluoric acid and, after evaporation nearly to dryness, fuming the residue with 10 ml of concentrated sulphuric acid and then diluting to 500 ml with 4 % sodium oxalate solution. An aliquot of the solution was taken and 10 ml of 0.1 % tin(II) chloride solution were added to reduce iron(III), chromium, zirconium vanadate, etc. The titanium content was determined according to the procedure.

Determination of Titanium in Industrial Effluents

A 100 ml volume of effluent was acidified with hydrochloric acid and about 1 g of sodium sulphide was added to precipitate any molybdenum present. The contents were filtered and hydrogen sulphide was boiled off from the filtrate by adding concentrated nitric acid. A 20 ml volume of a 0.1 % tin(II) chloride solution was added and the titanium was determined according to the procedure.

Determination of Titanium in Plant and Soil Samples

1 g of the soil or plant (ash) sample was digested with a mixture of perchloric and nitric acids and centrifuged to remove the siliceous material. The mother liquor was concentrated by heating and diluted to 100 ml with 0.05 M hydrochloric acid. An aliquot of the solution was taken and about 1 g of sodium sulphide was added to precipitate molybdenum. After centrifugation the mother liquor was heated with a few drops of concentrated nitric acid to boil off hydrogen sulphide, diluted and, then, 10 ml of 0.1 % tin (II) chloride solution were added. The titanium content was determined according to the procedure.

RESULTS AND DISCUSSION

The extractability of the titanium(IV)-caffeic acid complex with a liquid anion

Table 1 Effect of pH on extraction of titanium with caffeic acid and Aliquat 336[a]

pH	*Absorbance*	*Extraction (%)*
2.0	0.200	33.3
2.5	0.232	38.7
2.8	0.599	99.9
3.0	0.601	100
3.2	0.600	100
3.5	0.250	41.7
4.0	0.160	26.7
4.5	0.100	44.5
5.5	0.050	9.3

[a]Conditions: titanium: 0.500 mg/l λ_{max}: 380 nm
caffeic acid: 5 ml (0.1 %)
Aliquat 336: 5 ml (1.0 %)

exchanger shows the anionic nature of the complex. The yellow complex is extracted with a 1 % solution of Aliquat 336 at pH 3.0. The extracted species has maximum absorbance at 380 nm.

Optimization of the Extraction

Effect of pH The titanium complex was extracted at various pH values. Extraction was very poor at low (<2.5) and at high (>4.0) pH. The extraction at pH 2.8–3.2 was quantitative (Table 1).

Reagent concentration The absorbance of titanium was constant when using an excess of the reagent. Extraction with various concentrations of the reagent showed that 1–2 ml of 0.1 % caffeic acid was adequate for quantitative extraction of the sample, whereas extraction was incomplete at lower concentrations.

Electrolytes The extraction was carried out under the optimum conditions with various amounts of sodium chloride and potassium chloride. The electrolytes had no effect on the extraction of the titanium complex.

Aliquat 336 concentration The optimum concentration of Aliquat 336 was studied by varying the concentration from 0.5 to 15 % in toluene. The extraction was quantitative for 1 % and over, and remained constant up to 6 %. A tendency to form an emulsion was observed at higher concentrations. A 1 % solution of Aliquat 336 in toluene was adopted for extraction.

Diluents Titanium was extracted with 1–3 % Aliquat 336 solutions in various solvents. Equilibration was affected by maintaining the ratio of organic to aqueous phase at 1:1.

The extraction was very poor with chloroform; carbon tetrachloride and xylene showed incomplete extraction. The extraction was quantitative with toluene and

Table 2 Effect of various diluents on extraction of titanium with caffeic acid and Aliquat 336[a]

Diluent	*Extraction(%) at Aliquat 336 concn. (%)*		
	1	*3*	*5*
Toluene	99.9	99.9	99.9
Benzene	99.8	99.8	99.8
Xylene	88.0	88.0	88.0
Carbon tetrachloride	40.0	41.0	41.0
Hexane	64.0	64.0	64.0
Chloroform	43.0	43.0	45.0
Isobutylmethylketone	60.0	60.0	60.0

[a]Conditions: titanium: 0.500 mg/l λ_{max}: 380 nm
caffeic acid: 5 ml (0.1 %) pH: 3.0

Table 3 Effect of liquid anion exchanger on extraction of titanium[a]

Liquid anion exchanger	*Diluent*	*Extraction (%)*
Aliquat 336 (1 %)	toluene	99.9
	xylene	92.5
Amberlite LA-1(1 %)	toluene	96.0
	xylene	73.0
Trioctylamine (1 %)	toluene	90.0
	xylene	65.0

[a]Conditions: titanium: 0.500 mg/l λ_{max}: 380 nm
caffeic acid: 5 ml (0.1 %) pH: 3.0

benzene and a clear separation was obtained. Hence toluene was used as solvent in subsequent work (Table 2). The recovery of titanium is $99.9 \pm 0.05\,\%$.

Type of liquid anion exchanger Titanium was extracted with three extractants in various diluents (Table 3). Aliquat 336 in toluene was found to be the best choice.

Equilibrium time and stability For extraction, the time of shaking was varied from 15 sec to 5 min. The extraction was quantitative within 30 sec. The complex extracted under optimum conditions was stable for several days.

Optical properties. The coloured complex obeys Beer's law from 0.05 to 1.2 mg/l of titanium (in the final extract of 25 ml) at 300 nm and the optimum range (Ringbom plot)[12] was 0.1–1.0 mg/l. The molar absorptivity is $5.7 \times 10^4\,\mathrm{l\,mol^{-1}\,cm^{-1}}$.

Stripping

After extraction of titanium into the organic phase, it was stripped with 15 ml of

Table 4 Effect of diverse ions on titanium extraction (Ti taken, 0.8 mg/l)

Foreign ion	*Added as*	*Tolerance limit (mg)*
Ag^+	$AgNO_3$	25
Be^{2+}	$BeSO_4$	30
Mg^{2+}	$MgSO_4$	30
Ca^{2+}	$Ca(NO_3)_2$	30
Ba^{2+}	$BaCl_2$	30
Sn^{2+}	$Sn(NO_3)_2$	40
Pb^{2+}	$Pb(NO_3)_2$	40
Cd^{2+}	$CdSO_4$	40
As^{3+}	$As_2>O_3$	30
Co^{3+}	$CoCl_2$	30
Cu^{2+}	$CuSO_4$	40
Hg^{2+}	$HgCl_2$	30
Ni^{2+}	$NiCl_2$	25
Zn^{2+}	$ZnSO_4$	35
Mn^{2+}	$MnCl_2$	20
Cr^{3+}	$CrCl_3$	25[a]
Al^{3+}	$AlCl_3$	40
V^{5+}	NH_3VO_3	40[b]
MoO_4^{2-}	$(NH_4)_6Mo_7O_{24}$	8[c]
Zr^{4+}	$Zr(NO_3)_4$	10[a]
U^{6+}	$UO_2(CH_3COO)_2$	5[a]
Cl^-	NaCl	50
Br^-	NaBr	20
I^-	NaI	30
CH_3COO^-	CH_3COONa	50
Cit^-	Citric acid	50
SO_4^{2-}	Na_2SO_4	50
PO_4^{3-}	Na_3PO_4	30

[a] Stripped with 0.5 M hydrochloric acid.
[b] Stripped with 0.2 M sodium acetate solution.
[c] Washed with 0.2 M sodium chloride solution.

varying concentrations (0.05–5 M) of sulphuric acid, hydrochloric acid, nitric acid, sodium sulphate, sodium chloride, sodium carbonate and sodium hydroxide solutions. Stripping was complete with 0.2 N sulphuric acid. The volume of sulphuric acid required was found to be low and elution was complete even with 5–8 ml of 0.2 N sulphuric acid. The metal content was determined photometrically by the hydrogen peroxide method,[11] as the stripping agent will not interfere with the method.

Effect of Diverse Ions

Titanium was extracted in the presence of a large number of different ions (Table 4). The recovery experiments showed a $99.9 \pm 0.5\%$ recovery of titanium. Interference studies were carried out by measuring the absorbance of the extracted liquid ion exchanger phase and conditions were established for the removal of interfering

Table 5 Determination of titanium in standard samples[a]

Material	*Certified value (%)*	*Found (%)*	*CV*
Titanium	0.15	0.15	6.7
Titanium	0.60	0.61	1.6
Titanium oxide	0.015	0.014	14.3
Mild steel	0.130	0.131 0.133	2.7
Burnt refractory	2.93	2.92 2.93 2.95	0.68
Mild steel	0.034	0.034	2.9
Silicon aluminium	0.180	0.178 0.180	2.8

[a] British standard samples; average of 10 determinations.

ions from the organic phase by eluting with suitable solvents. The tolerance limit was set as the amount of foreign ion causing a change of ±0.02 absorbance unit or ±2% error in the recovery of titanium.

Moderate amounts of various metal ions commonly associated with titanium can be tolerated and also most of the common anions. Fluoride interfered seriously. Low concentrations of vanadium (40 ppm) did not interfere. The vanadium extracted together with titanium can be stripped by shaking the organic phase with 10 ml of 0.2 M sodium acetate solution for 5 min. Titanium was subsequently stripped with 10 ml of 2 N sulphuric acid. Interfering molybdenum (IV) was removed either by precipitation with sulphide prior to the extraction or the extracted molybdenum(IV) was eluted from the organic phase by washing this phase with 5 ml of 0.2 M sodium chloride solution. Moderate amounts of chromium, iron and zirconium were tolerated in the presence tin(II) chloride and any metal extracted into the organic phase can be removed by shaking with 5 ml 0.5 M hydrochloric acid for 5 min before the separation of titanium. Uranium also can be separated from titanium by stripping with 5 ml of 0.5 M hydrochloric acid; titanium can then be recovered with 10 ml of 2 N sulphuric acid.

To test the recovery and reliability of the method, titanium was determined in British standard samples (Table 5). The samples were analysed either directly or by the standard addition technique. The results are in good agreement with the certified values.

The present method has been applied for the determination of titanium in various environmental samples. The data are given in Table 6. The chromium industrial waste and chromium samples were collected from the industrial area of Ankleshwar Gujarat (India). The soil and plant samples were collected in around 50 m^2 area of Nandesari, Baroda; each sample was analysed in triplicate. The concentration range is given in Table 6. The analyses were also done by atomic absorption spectrophotometer; the values are in good agreement with those obtained by the present method.

Comparing the performance of reagents such as gallic acid and sodium

Table 6 Determination of titanium in environmental samples

Material	*AAS (ppm)*	*Present method (ppm)*
Nàndesari soil sample[a]	8–190	10–200
Pulp and paper unit[b]	62.3	61.5
Paint and pigment unit[c]	68.0	70.0
Chromium sample	13.0 mg	13.1 mg
Chromium industrial waste	10.3 mg	10.2 mg
Monazite sand[d]	25.0 mg	24.9 mg
Nandesari plants sample (Dhatoora)[a]	5–390	5–400

[a] About 70 samples were determined for titanium and each sample was analysed thrice. The concentration range is reported.

[b] Samples from Nepa Nagar paper mill ($n = 6$).

[c] Samples from G.I.D.C. area of Vapi ($n = 6$).

[d] From Trirandam (India).

acetate,[13] and chromotropic acid and iron[15] with that of caffeic acid shows that caffeic acid is a sensitive and selective reagent for titanium determination.

References

1. I. S. El Yamani, M. Y. Farah and F. A. El Alaim, *Abd. Talanta* **25**, 523 (1978).
2. S. G. Piracva, I. V. Pyatinitakii and L. N. Demutakaya, *Ukr. Khim., Zh.* **44**, 978 (1978).
3. F. L. Moore, *Anal. Chem.* **29**, 1660 (1957).
4. E. Cerrai and C. Testa, *Anal. Chim. Acta.* **26**, 204 (1962).
5. H. Onashi and Y. Toite, *Bunseki Kagaku* **14**, 1141 (1965).
6. S.k. Menon, Y. K. Agrawal and M. N. Desai, *Talanta* **36**, 678 (1989).
7. J. P. Shukla and M. S. Subramanium, *J. Radioanal. Chem.* **50**, 159 (1979).
8. B. K. Afghan, R. G. Maryati and D. E. Ryan, *Anal. Chem. Acta.* **41**, 131 (1968).
9. J. A. Dean, (ed), *Lange's Handbook of Chemistry*, 12th ed. (McGraw Hill, New York, 1979).
10. Methods for Chemical Analysis of Water and Wastes. EPA-600-4-79-020, US Environmental Protection Agency, Ohio, 1979.
11. E. B. Sandell, *Colorimetric Determination of Traces of Metals* (Interscience, New York, 1965.)
12. A. Ringbom, *Z. Anal. Chem.* **21**, 332 (1949).
13. V. I. Ptukh, G. I. Chadova, A. S. Aksel'rod and K. N. Manrina, *Zavod. Lab.* **47**, 30 (1977).
14. M. T. Dorado and A. Gomez Coedo, *Sel. Fuddicion* **129** (1979).
15. D. Aromaityte, S. Ramonaite and L. Kruopaite, *Liet. TSR Ankst. Mokyklu Moks. Darb. Chem. Technol.* **16** (1974).