

Catalytic current polarographic determination of traces of titanium in water after preconcentration by coflotation

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A new method is reported for the determination of trace levels of Ti(IV) in water by coflotation and polarography. Ti(IV) is preconcentrated and separated by coflotation using aluminium hydroxide as coprecipitant and sodium oleate as surfactant. Polarographic determination of titanium content in the froth is based on the catalytic wave of Ti(IV) in the presence of chlorate and oxalate. The effect of various cations and anions on the flotation and determination of titanium has been investigated. The method has been applied to estimation of titanium in natural fresh water samples.

This paper describes a method for the estimation of trace amounts of titanium(IV) by catalytic current polarography after preconcentration by coflotation. Coprecipitation with ferric hydroxide¹ has been used earlier for the preconcentration of traces of titanium. However, the bulky amorphous precipitates are difficult to filter and centrifugation is cumbersome for large volumes. Flotation technique for the separation of trace elements is free from these disadvantages and has been widely used to preconcentrate several trace elements from aqueous systems²⁻⁷. But flotation separation of traces of titanium has rarely been reported⁴. We have exploited the high concentration factor involved in separation by coflotation to improve the detection limits for the determination of titanium(IV) by catalytic current polarography.

Experimental

The polarography as well as the flotation apparatus used have been described in our earlier publication⁸. All the polarograms were recorded at 25°C.

All reagents, except the surfactants, were of AR grade. Sodium oleate (SO) was obtained from Loba Chemie and sodium lauryl sulphate (SLS) from

Fluka. Stock solution of Ti(IV) (1.0 mg/ml) was prepared by dissolving pure titanium dioxide in sulphuric acid and standardised gravimetrically⁹. Working solutions were prepared daily by diluting the stock solution. Stock solutions of aluminium nitrate (10 mg/ml Al), zirconium nitrate (10 mg/ml Zr), SLS (2 mg/ml), SO (2 mg/ml), sodium chlorate (1 M) and oxalic acid (0.8 M) were also prepared.

Procedure

To an aqueous solution (1000 ml) of the sample containing traces of Ti(IV), was added Al(III) solution (5 ml). The pH was adjusted to 8.0 by adding aqueous ammonia solution with stirring. Stirring was continued for 5 min, after which SO solution (5 ml) was added and the solution was transferred to the flotation cell. Nitrogen was bubbled through the solution for 2 min, and the mother liquor was drained through the side arm. The froth was collected, dissolved in 5 ml of hot 2 M sulphuric acid and the volume was made up to 10 ml.

Polarographic measurements—An aliquot of this solution was pipetted into a polarographic cell. Oxalic acid (12.5 ml, 0.8 M), sulphuric acid (2 ml, 2.5 M) and sodium chlorate (2 ml, 1 M) were added. The contents were diluted to 20 ml and deaerated for 5 min. The polarogram was recorded between 0 and -0.40 V. The titanium concentration in the solution was determined by the standard addition method.

Results and discussion

It has been reported earlier that SLS and SO are able to float aluminium hydroxide in the pH ranges 5-7.5 and 7.0-9.5 respectively⁸. In this study, we found that the colloidal precipitate of zirconium hydroxide could be floated by SLS and SO in the pH ranges 3-7.5 and 7.0-9.5 respectively.

The effect of pH on the recovery of Ti(IV) from synthetic solutions of low ionic strength ($\mu < 0.10$) by coflotation with aluminium hydroxide and zirconium hydroxide was studied. SLS and SO were used as surfactants in the pH ranges 4.0-7.0 and 7.0-9.5 respectively. The flotation behaviour was almost similar on both collectors. The recovery of Ti(IV) increased with increase in pH and 100% recovery was obtained in the pH range 7.0-9.0 on both the collectors. This indicates that the mechanism of collection of Ti(IV) is coprecipitation. Titanium(IV) hydroxide is coprecipitated on aluminium hydroxide or zirconium hydroxide which

is then floated by the surfactant. The high solubility product of titanium hydroxide is favourable for complete recovery even at very low concentrations of Ti(IV). In this study, aluminium hydroxide and SO were chosen as the coprecipitant and the surfactant respectively for the coflotation separation of Ti(IV) at an optimum pH of 8.0 due to easier dissolution of froth.

The optimum concentrations of coprecipitant and surfactant required to obtain maximum recovery at pH 8.0 were found to be 50-100 ppm and 10-15 ppm respectively. A short stirring time of 5 min was sufficient to bring about the complete recovery of titanium.

Determination of Ti(IV) by catalytic current polarography

The composition of the supporting electrolyte has to be carefully controlled to obtain a linear relationship between the catalytic current and the concentration of Ti(IV). Sodium chlorate (0.10 M), oxalic acid (0.50 M) and sulphuric acid (0.25 M) as the supporting electrolyte gave a linear calibration for Ti(IV) in the concentration range 0.01-1.0 ppm.

A comparison of the sensitivities of the catalytic current of Ti(IV) by DPP and charging current compensated dc polarography (CCDCP) showed that the dc catalytic current was 2.8 times more sensitive than the DPP catalytic current. This value agrees well with the theoretical ratio of $i(\text{CCDCP})$ to $i(\text{DPP})$ calculated for $n = 1$ under the polarographic conditions, $t = 0.5$ s and $\Delta E = 50$ mV (ref. 10). Even though CCDCP was more sensitive than DPP, the latter gave better resolution. Hence, DPP was preferred at titanium concentrations less than 0.1 ppm where it is necessary to resolve the titanium catalytic current from the large current due to the irreversible reduction of excess of chlorate (The two peaks were separated by about 200 mV). It was also seen that the interference from the chlorate peak decreased as the drop time was increased¹¹. This is because catalytic current is a function of $t^{2/3}$, whereas the irreversible current due to the reduction of chlorate does not increase much with increase in drop time. A higher drop time was preferred also because it gave a linear curve.

The effect of surfactants (SLS and SO) on the catalytic current of Ti(IV) was studied. The Ti(IV) concentration in the supporting electrolyte was 1.0 ppm. The catalytic current was suppressed by the presence of both surfactants, but the effect was less severe in the case of SO. It was observed that the reduction of DPP catalytic current by 40 ppm of surfactant was 18% and 70% in the case of SO and

Table 1—Determination of Ti(IV) in natural fresh water samples

Ti(IV) added (µg)	Ti(IV) found [†] (µg)	Ti(IV) in the sample (µg/l)
<i>Laboratory tap water</i>		
0	0.65	0.65
0.5	1.18	0.68
1.0	1.70	0.70
<i>Bore-well water</i>		
0	0.81	0.81
0.5	1.34	0.84
0.1	1.80	0.80

[†] Average of 6 replicate measurements.

SLS respectively. But at surfactant concentrations less than 10 ppm, the change in the peak current was negligibly small and within the limits of experimental error.

Effect of various cations and anions on the coflotation and determination of Ti(IV)

The influence of known amounts of added cations and anions on the coflotation of Ti(IV) in the presence of 100 ppm Al(III) and 10 ppm SO at pH 8.0 was studied. A solution containing 0.1 ppm Ti(IV) was used for this study. Fe(III), Zr(IV), Bi(III), Cu(II), Pb(II), Ni(II), Co(II), Zn(II) and Cd(II) floated along with Ti(IV), but the recovery of Ti(IV) was not affected by the presence of these ions. Except for Fe(III), Bi(III) and Cu(II), 100-fold amounts of the ions did not interfere with the polarographic determination of Ti(IV). Cu(II) and Bi(III) did not interfere when present in up to 10-fold excess. However, larger amounts of these ions were found to decrease the catalytic peak since the reduction of Cu(II) and Bi(III) occurs at more positive potentials than that of Ti(IV). There was no interference from up to 20 ppm Fe(III) in the supporting electrolyte. But if the concentration of Fe(III) was increased above this level, the catalytic current of Ti(IV) increased. Mo(VI), Cr(VI) and Sb(III) were not floated at all under the conditions used for the coflotation of Ti(IV).

The effect of anions such as chloride, nitrate, sulphate, silicate and phosphate on the coflotation of titanium was studied by adding known amounts of these ions to the solution before flotation. It was observed that flotation was incomplete above 5 ppm each of phosphate and silicate and hence recovery of Ti(IV) was about 60%. Up to 0.2 M, chloride and nitrate did not interfere with the coflotation of titanium. Sulphate was tolerated only up to 0.05 M.

Determination of Ti(IV) in synthetic solutions and real samples

Synthetic water samples were prepared by adding 0.2, 0.5, 1.0, 2.0, 4.0 and 10.0 μg of Ti(IV) to 1.0 l distilled water. Ti(IV) was determined in these sample solutions by the collocation-DPP procedure described in the experimental section. It was found that the recoveries were $> 95\%$. The relative standard deviation calculated for six replicate measurements at 1.0 $\mu\text{g/l}$ was 4%.

Samples of tap water and well water (1 l) were also analyzed and the results are shown in Table 1. The relative standard deviation for 6 replicate measurements was found to be 5%.

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