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Trace Determination of Titanium by Differential Pulse Polarography

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VARIOUS polarographic techniques such as cathode ray polarography¹, a c. polarography², oscillopolarography³ and DPP^{4,5} have been reported for trace analysis of titanium(IV). Present work describes DPP procedure for trace determination of titanium(IV).

Experimental

The investigations were carried out on a Metrohm-E-506 Polarecord instrument. Electrodes employed were DME as working electrode, Ag/AgCl (satd. KCl) as reference electrode and Pt-metal as auxiliary electrode. The recording parameters maintained during the studies were as follows: initial potential, 0.0 V; potential range, -2.0 V; drop-time 1 s^{-1} ; paper speed, 60 mm min^{-1} ; scan rate, 8 mV s^{-1} ; and pulse amplitude, 16 mV. Total volume of the solution was 25 ml and deaeration was carried out by bubbling nitrogen for 15 min.

All chemicals used were of A R. grade. Stock solutions were prepared in double-distilled water and working solutions were prepared by suitable dilutions. Titanium solution (0. M) was prepared by dissolving TiO_2 in concentrated H_2SO_4 and volume made up with DDW.

Procedure: To a cell, 25 ml of solution containing EDTA (0.015 mol), KBrO_3 (0.004 mol) and NaOAc (0.1 mol) (pH 5.2) and 0.1% gelatin (25 μl) were added and a blank recording was made followed by addition of 75 μl of Ti^{IV} solution (3 ppm) and the polarogram was recorded.

A variety of electrolytes namely malonic acid, 5-sulphosalicylic acid, tartaric acid, citric acid, acetic acid, HCl, H_2SO_4 , HNO_3 , H_3PO_4 , HClO_4 , each at concentrations 0.01, 0.05, 0.1 and 0.2 M and a solution (I) containing EDTA (0.015 mol), KBrO_3 (0.004 mol) buffered with 0.1 M NaOAc and acetic acid at pH 4.8, 5.2, 5.6 and 6.0 were used for choice of base electrolyte.

Ti^{IV} exhibited well-defined peak in organic acids ($\geq 0.05 \text{ M}$) and solution (I). Solution (I) at pH 5.2 was selected as a supporting electrolyte as it showed high peak symmetry, good reproducibility and maximum peak current value.

Gelatin, triton-x-100 and bromophenol blue in the range 1×10^{-6} – $1 \times 10^{-3}\%$ were used as maximum suppressors. A $1 \times 10^{-4}\%$ gelatin solution was also used as it gave symmetric peak with evenly rising steps and improved baseline. Linear calibration plots were obtained in the range 1–10 ppm, 0.1–1 ppm, 10–100 ppb and 2–10 ppb of Ti^{IV} . The lowest determinable limit was found to be 2 ppb. The RMD, SD and CV values for 1 ppm and 2 ppb were 0.14%, 4.6, 0.18% and 1.6%, 0.05, 2.0% respectively. Thus the method is highly sensitive and precise. The method was found to be fairly selective except for Co^{II} , Sn^{IV} and Sb^{III} which interfered. Ni^{II} could be tolerated upto 1 : 50 ratio, Bi^{III} and As^{III} upto 1 : 20, Pb^{II} and W^{VI} upto 1 : 10, Zn^{II} and Cd^{II} upto 1 : 5, and Cr^{III} and Cu^{II} upto 1 : 2 ratio.

Determination of Ti in corn and barley: A known weight of dried and powdered plant material was dry-ashed in a muffle furnace at $600 \pm 25^\circ$. The ash was dissolved in concentrated HNO_3 and the solution boiled to dryness. The residue was taken up in double-distilled water and volume was made upto 100 ml. In case of barley, the ash was boiled with dilute HCl for 5 min. Undissolved silica was filtered off and the volume made upto 100 ml. A 10 ml aliquot was used for analysis. The results are presented in Table I and Fig. 1 (curves a and b; B=blank).

TABLE I – TITANIUM CONTENT IN PLANT MATERIALS AND COAL

| Sample | Ti mg/100 g sample | |
|--------|-------------------------|--------------------------|
| | Calibration plot method | Standard addition method |
| Corn | 0.0214 | 0.0214 |
| Barley | 0.0248 | 0.0274 |
| Coal | 5.0180 | 4.8700 |

Determination of Ti in coal: An accurately weighed sample of coal from Rawanwara (Madhya Pradesh) was processed as described for barley. Quantitation of titanium in above samples was made with calibration plot method and standard

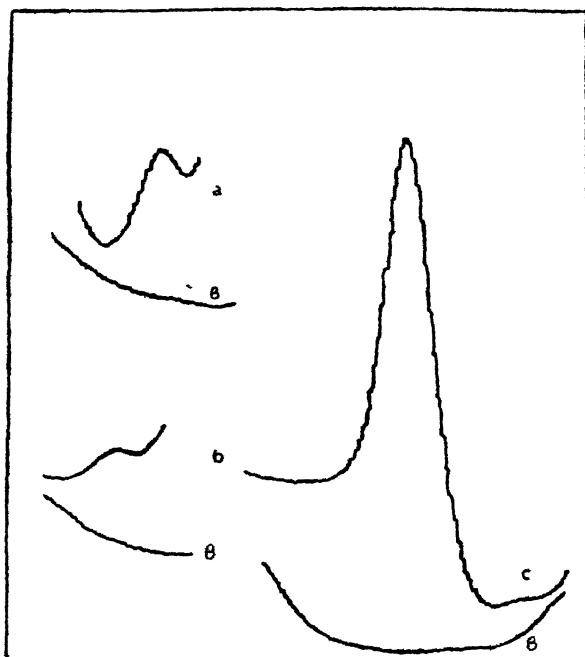


Fig. 1

addition method. The results are presented in Table 1 and Fig. 1 (curve c ; B=blank).

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Spectrophotometric Determination of Nitrite (Nitrogen Dioxide)

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WE report here a spectrophotometric method for the determination of nitrite/nitrogen dioxide by azo dye formation. Acidified *p*-rosaniline hydrochloride diazotised with nitrite/nitrogen dioxide and coupled with *N*-1-naphthylethylenediamine

dihydrochloride yields a red-violet dye which absorbs at 560 nm. Taking advantage of this reaction a sensitive spectrophotometric method has been developed for the determination of nitrite/nitrogen dioxide.

Experimental

All the chemicals used were of A. R. grade. Double-distilled water was used for making the following solutions unless otherwise specified: sodium nitrite, 6 $\mu\text{g ml}^{-1}$ in 0.001 *M* NaOH; *N*-1-naphthylethylenediamine dihydrochloride, 0.1% solution in water; *p*-rosaniline hydrochloride, 0.04% solution in 0.72 *M* HCl; alkaline sodium arsenite, 1 g of arsenous oxide dissolved in water and 100 ml of 1.2 *M* NaOH and the volume made up 2 dm^3 .

A Hilger and Watts H 700 spectrophotometer with 1 cm cell was used for absorbance measurement.

Procedure: 0.5, 1, 2, 3, 4 and 5 ml of the sodium nitrite solutions were placed in a series of 50 ml volumetric flasks. The *p*-rosaniline hydrochloride solution (2 ml) was added, shaken well and then the *N*-1-naphthylethylenediamine dihydrochloride solution (0.5 ml) was added to each flask. The full colour developed within 30 min and the absorbance for 560 nm was measured against a reagent blank. A linear absorbance concentration profile was obtained (Beer's law) in the concentration range of 0.04 – 0.40 $\mu\text{g ml}^{-1}$ of nitrite.

In another experiment 0.5, 1, 2, 3 and 4 ml of the sodium nitrite solutions were placed in the sodium arsenite solution (10 ml) and the experiment was repeated as before. Absorbances were little affected by the presence of sodium arsenite for lower nitrite concentrations.

Results and Discussion

p-Rosaniline hydrochloride when acidified with hydrochloric acid reacts with nitrite to yield a diazo compound which when coupled with *N*-1-naphthylethylenediamine dihydrochloride produces a red-violet dye having an absorption maximum at 560 nm.

The effect of varying the quantities of the diazotising agent and coupling agent was studied. 2 ml of 0.04% acidified dye and 0.5 ml of 0.1% *N*-1-naphthylethylenediamine hydrochloride were found to be best for full colour development. Reproducibility of the method was checked by taking several samples of same concentration of nitrite and the standard deviation was found to be ± 0.009 . Sensitivity determined from the slope of the calibration graph was found to be 0.833 absorbance unit per $\mu\text{g ml}^{-1}$ and Sandell's sensitivity 0.0012 $\mu\text{g cm}^{-2}$.