

VOLTAMMETRIC DETERMINATION OF ZIRCONIUM AT LOW CONCENTRATIONS IN ENVIRONMENTAL SAMPLES

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ABSTRACT

Trace level determination of zirconium in different matrices using differential pulse polarography is reported. The optimum analytical conditions were found with a limit of determination of 0.01 µg/ml, and SD, ± 0.002.

INTRODUCTION

Zirconium is a peculiar metal from the point view of its extensive use in nuclear power plants because of its low thermal-neutron capture cross-section, and its resistance to corrosion by superheated stream /1/. Zirconium and its compounds are also used in electronic tubes, in chemical apparatus, in alloys, in colored glazes, and as refractors. In spite of wide applications the sources of zirconium are limited. It is mostly obtained from zircon, and it constitutes 162 ppm in the earth's crust and 2.6×10^{-5} ppm in sea water /2/. Zirconium is encountered in atmospheric and industrial emissions; however it has a low order of toxicity. Thus, it is imperative to have a precise and accurate method for the determination of zirconium in different matrices.

Most of the methods available for the determination of zirconium are optical methods. The spectrophotometric determination is often based upon the reaction of zirconium with an organic reagent such as alizarin red S /3,4/, xylenol orange /5-9/, 1-(2-pyridylazo)-2-naphthalenol (PAN) /10/, arsenazo /11/, thorin /12,13/, 4-(2-thiazolylazo) resorcinol (TAR) /14/, and 4-(2-pyridylazo) resorcinol (PAR) /15, 16/, although the sensitivity of these determinations is not very high. Other instrumental techniques such as

fluorophotometry /17/, X-ray fluorescence /18/, atomic emission spectrometry /19–22/ and chromatography /23, 24/, are also described in zirconium determination.

The aim of the present work was to develop an alternate method using voltammetry which possesses higher sensitivity, particularly for the oxidation state specific determinations as in the case of zirconium whose aqueous chemistry is confined exclusively to a very stable quadrivalent state. Differential pulse polarography (DPP) and stripping voltammetry have proved to be useful in such determinations /25, 26/.

The polarography of zirconium at DME was first carried out by Laubengaver and Eaton /27/ who showed that the complete reduction of zirconyl ion to the metallic state takes place at a potential of about -1.60 V vs SCE. Subsequently amperometric /28/, AC polarographic /29/ and linear sweep voltammetric /30/ studies of zirconium were reported. Many reports have shown the use of fumaric acid /31/, tartaric acid /32/ and methyl-thymol blue /33/ in indirect polarographic determination of zirconium.

These investigations on zirconium electrochemistry have led to the conclusion that the more negative reduction potential of Zr^{4+} (≈ -1.69 V) makes it difficult to obtain a true polarographic wave of zirconium due to the discharge of hydrogen at dropping electrode. To overcome this problem the authors have utilized the complexing ability of 2-(2-hydroxy-3,6-disulfo-1-naphthyl azo) benzene – arsonic acid commonly named as thoron. Basically the method is based on the shift of half-wave potential ($E_{1/2}$) of the metal ion due to the presence of complexing agent /34/. The optimal conditions for the determination of zirconium using DPP technique in different matrices at very low concentrations were devised. DPP procedures on the same lines for the determination of rhenium /35/, germanium /36/, molybdenum /37/, tungsten /38/ and indium /39/ have been reported earlier.

EXPERIMENTAL

Instrumentation

A PAR polarographic analyzer (Model 174-A) along with a drop timer (Model 174/70) and X-Y recorder (Model RE 0074), all from EG&G, U.S.A. was used for polarographic measurements. A dropping mercury electrode (DME) was employed as the working electrode. The instrumental settings for DPP were as follows: modulation amplitude, 50 mV; clock time of pulse, 1s;

pulse duration, 57 ms; and scan rate 5 mV/s. An Ag/AgCl and a platinum wire were used throughout as reference and auxiliary electrodes, respectively. Thoron ($0.34 \times 10^{-4}\text{M}$) was used in 0.1M KCl supporting electrolyte.

An inductively coupled plasma (ICP) based atomic emission spectrophotometer (Model 1M Jobin–Yuan) France, was also used for sample analysis. The instrument has a polychromator, sequential facility and axial viewing plasma frequency 48.68 MHz. It has a concentric quartz nebulizer and halographic blazed grating with 3600 grooves.

Sample Preparation

The industrial effluent samples (100 ml aliquot) were digested with 1 ml of an oxidizing mixture of nitric acid and hydrochloric acid until it fumed. Subsequently, the contents were transferred to a volumetric flask and made up to the requisite volume.

The soil samples from Jawar Mines, Udaipur were powdered and leached in an acid mixture ($\text{HCl} + \text{H}_2\text{SO}_4$). This was followed by vigorous shaking and washing. Contents were then filtered, and heated till the solution fumed to remove volatile impurities /40/.

Chemicals & Reagents

All chemicals used were of reagent grade purity. Stock solution of zirconium was prepared from zirconium oxychloride. Other reagents employed in different steps, as described in the text, include: thoron dye, potassium chloride and nitrates of cadmium, zinc and thorium. Solutions were prepared in doubly distilled water.

All the experiments were carried out at $25 \pm 1^\circ\text{C}$. The test samples were deaerated by bubbling purified nitrogen for 20 min. prior the polarographic measurements. Traces of oxygen present in nitrogen were removed by passing the gas through ammonium vanadate solution kept in contact with amalgamated zinc /41/.

RESULTS AND DISCUSSION

Polarographic Characteristics of Zirconium

Preliminary observations on electroreduction of Zr(IV) indicated the

suitability of thoron ($0.34 \times 10^{-4}\text{M}$) in 0.1M potassium chloride medium where a single polarographic wave of Zr(IV) to elemental state was obtained at 1.49 V vs Ag/AgCl. The $E_{1/2}$ of the wave was found to be pH dependent. At $\text{pH} > 5$ the wave became ill-defined and finally disappeared while at $\text{pH} 2.9$, the wave appeared to be diffusion-controlled as shown in Fig. 1. The wave height increased linearly with the concentration of zirconium in range $(0.05\text{--}1.0) \times 10^{-3}\text{M}$. The nature of the electrode reaction was evaluated by log-plot analysis, which illustrated the irreversible process under these experimental conditions.

Optimal Conditions for Zirconium Determination

Zr(IV) also showed a sharp DP peak at -1.49V . A linearity of peak current was observed between 0.01 and 0.1 ppm of zirconium concentration

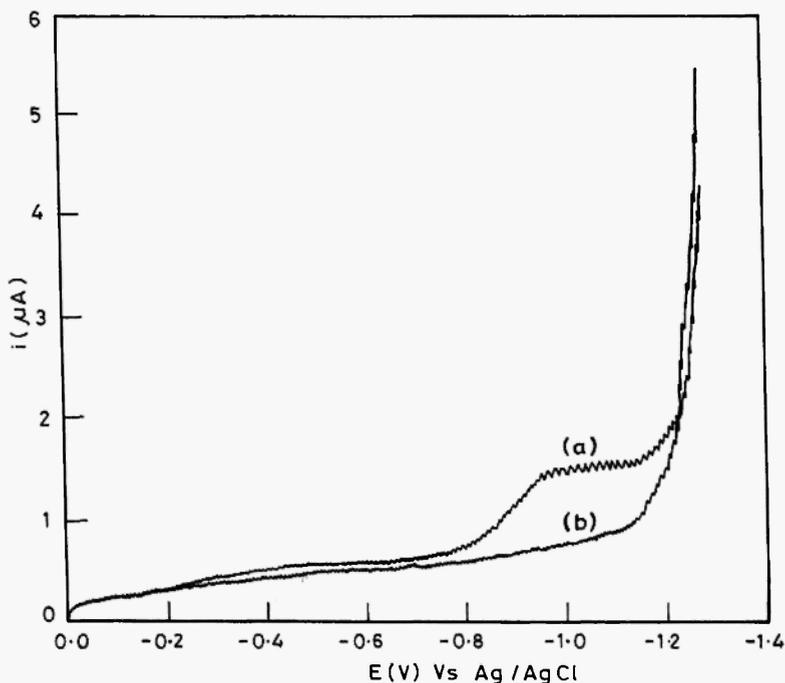


Fig. 1: DC polarogram of Zr(IV) in $0.34 \times 10^{-4}\text{M}$ thoron + 0.1M KCl
 (a) Zr (IV) = $0.1 \times 10^{-3}\text{M}$
 (b) Blank solution of thoron in potassium chloride

(Fig. 2). The characteristics of the calibration curve were as follows: slope = 9.0727; coefficient of correlation (r), = 0.9993 and standard deviation, SD = 0.336.

The DP peak was found suitable for quantitation of zirconium where a limit of determination of 0.01 $\mu\text{g/ml}$ was achieved.

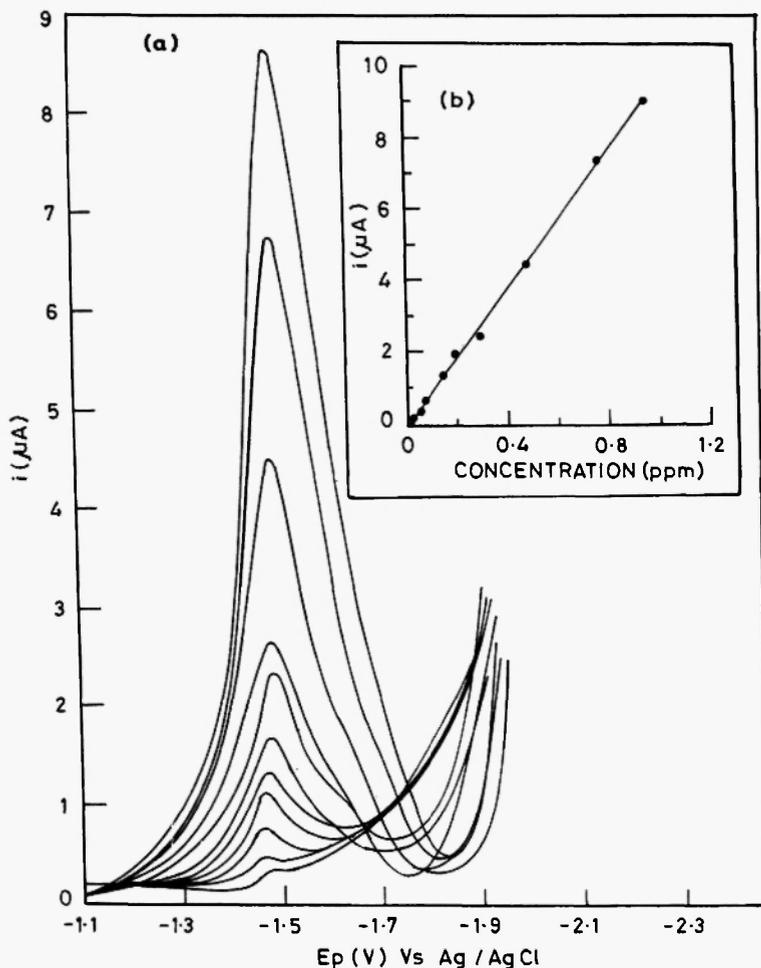


Fig. 2: (a) DP polarograms of Zr(IV) at different concentrations in $0.34 \times 10^{-1}\text{M}$ thoron + 0.1M KCl.
(b) Plot of calibration curve peak height vs concentration of zirconium.

Interference

DP polarograms of zirconium were also recorded in the presence of other common cations such as Pb^{2+} , Cd^{2+} , Zn^{2+} and Th^{4+} . The DP peaks of these metal ions were distinguishable from each other and indicated no interference in determination of zirconium as shown in Fig. 3. The Eps are listed in Table 1. Similarly, titanium did not show DP peak in thoron complexing medium, thus does not interfere.

Applications

The DPP reduction of Zr(IV) in thoron ($0.34 \times 10^{-4}\text{M}$) in 0.1M potassium chloride medium was made the basis for zirconium determination in soil and industrial effluents. The prepared samples were taken into the polarographic cell and DP polarograms were recorded in the potential range of -1.0 to -1.8

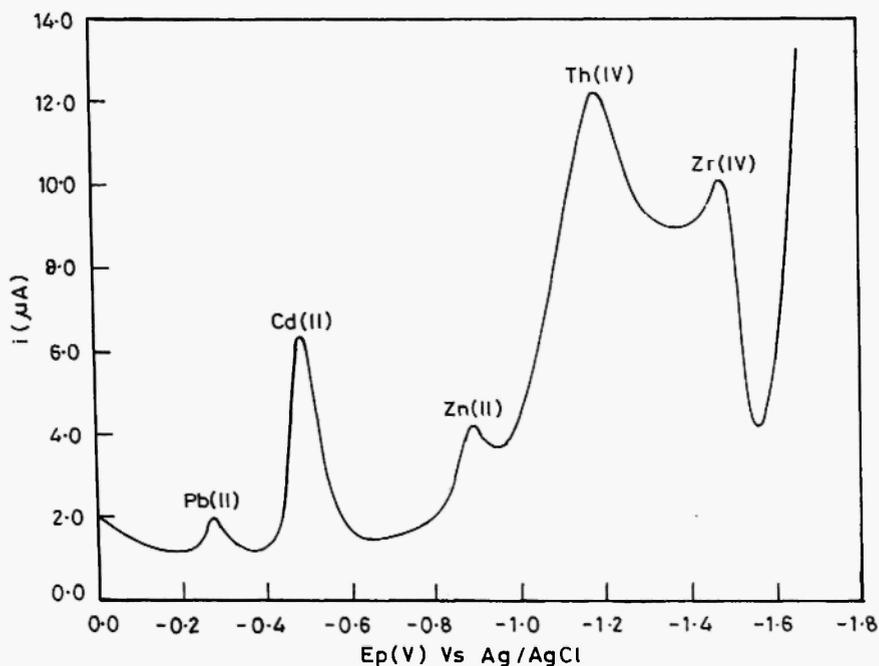


Fig. 3: DPP of a solution containing Pb(II) , Cd(II) , Zn(II) , Th(IV) and Zr(IV) in $0.34 \times 10^{-4}\text{M}$ thoron + 0.1M KCl.

Modulation amplitude = 50 mV; pulse duration = 57 ms,

Clock time of pulse = 1s and scan rate = 5 mV/s

V. The peak currents were measured at -1.49 V after making blank corrections.

Quantitation in all observations was made by standard addition method /42/. The results of zirconium determination are summarized in Table 2.

ICP-atomic emission spectrometry /43/ was used to compare the results obtained by DPP. The data are included in Table 3.

Table 1

Peak potentials of metal ions in thoron (0.34×10^{-4} M) in 0.1M KCl

S.No.	Metal ion	Peak potential - E_p (V) vs Ag/AgCl
1.	Lead (II)	0.28
2.	Cadmium (II)	0.48
3.	Zinc (II)	0.89
4.	Thorium (IV)	1.20
5.	Zirconium (IV)	1.49

Table 2

DPP determination of zirconium

Sample	N	Zirconium concn. (ppm)			S.D. (\pm)	C.V. (%)
		Min.	Max.	Avc.		
Industrial Effluent*	4	0.130	0.192	0.167	0.028	16.7
Soil [†]	5	0.034	0.078	0.060	0.016	28.0

* Marudhar Industrial Area. Jodhpur

+ Jawar Mines, Udaipur

S.D. = Standard Deviation

C.V. = Coefficient of Variation

Table 3
Comparison of DPP results by ICP–AES method in soil samples

Sample No.	Zirconium concn. (ppm)	
	DPP	AAS
1.	0.10	0.12
2.	0.28	0.35
3.	0.44	0.50
4.	0.42	0.50
5.	ND	<0.05

ND = Not detected

CONCLUSION

The complexation of thoron with zirconium has enabled its determination which is otherwise not possible in simple supporting electrolytes. The suggested DPP method is more specific, sensitive and rapid in comparison to the commonly used spectrophotometric methods of zirconium estimation since it provides a simple approach for trace level determination of zirconium in presence of commonly found metal ions, lead, cadmium and zinc. The results obtained by the present procedure are in good agreement in terms of measurement (detection limit, 0.01 $\mu\text{g/ml}$) and precision (SD, ± 0.002 at 0.02 ppm).

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