



Development of Sensitive Voltammetric Method for Determination of Thorium in Waste Waters

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Abstract

An indirect voltammetric determination method of thorium based on the displacement reaction between Th (IV) and Zn (II) - EDTA complex in ammonium acetate buffer medium is described. The limit of quantification of 0.005 ppm was observed using differential pulse polarography. The possibly associated metal ions did not interfere in measurements. The method has been successfully applied for the analysis of thorium in waste water samples.

Keywords: Thorium, differential Pulse polarography, waste waters analysis.

Introduction

The tremendous uses of thorium in nuclear reactors as a substitute of uranium has made it immensely important element. It can also be used in refractory materials and incandescent gas mantles. Other applications of thorium include in heat resistant ceramics, in gas tungsten arc welding electrodes, additives in alloys and as a catalyst in petroleum cracking. In regard to toxicity, the radioactivity of thorium overrides other toxicity considerations. Acute exposure can lead to cause cancer and dermatitis¹. Therefore, it is appropriate to develop a simple analytical method for the determination of thorium.

Most applications of chemical analysis to the samples of nuclear technology important elements involve trace determination at very low concentration. High sensitivity of the employed method must further be accompanied by sufficient selectivity, precision and accuracy. In this way several methods such as spectrophotometry²⁻⁴, mass spectrometry⁵, AAS^{6,7}, XRD⁸, ICP-AES⁹, NAA¹⁰ and X-ray fluorescence¹¹ are reported in determination of microgram level of various metal ions. In most cases procedures requires preliminary treatment of the sample (in addition to any concentration step) to bring thorium to the proper step for measurement by preoxidation or reduction. The voltammetric methods are considered more suitable because due to certain selectivity of the redox potential, these can identify and determine different forms of an element as in case of thorium, which shows three oxidation states of +2, +3 and +4. Differential pulse polarography (DPP) and anodic stripping voltammetry have proved useful in such determinations¹². Thus it is of interest to investigate the suitability of these methods in determination of thorium.

The electrochemical data on thorium reveals that tetravalent thorium is the only ionic species that has been characterized in aqueous solutions. Further, reduction potential of Th⁴⁺ is too

negative (-1.83V vs NHE) to permit thorium wave before reduction of hydrogen ion or other cation of supporting electrolyte¹³. It makes voltammetric determination of thorium rather difficult. Many authors have therefore employed supporting electrolytes which makes a complex with thorium so that reduction potential might sufficiently be shifted and measurable. Gritzner et al¹⁴ have shown polarographic behavior of thorium in dimethyl formamide and dimethyl sulphoxide. Mosrafa et al¹⁵ have used Th (IV) complex with alanines in these observations. Electrochemical studies of Th (IV) in dimethyl sulphoxide and propylene carbonate are reported by Duyckaerts and Deguedre¹⁶. Cassaure and coworkers¹⁷ have described electrochemical behaviour of thorium (IV) in LiCl-KCl eutectic melts. Sindhu et al¹⁸ have reported polarographic determination of thorium (IV) with 3-hydroxypyridine-2-thiol. Linear sweep oscillographic polarography and pulse polarographic determination of thorium is given by Plock and Vasquez¹⁹, and Das et al²⁰, respectively. Li and Coworkers²¹ have described adsorptive voltammetric study of thorium-alizarin complexon at a carbon paste electrode. The anodic stripping voltammetric determination of thorium has also been shown by Liu et al²². Herein we suggest an indirect differential pulse polarographic determination method of thorium. It is based on the displacement reaction between Th (IV) and Zn (II) - EDTA complex in ammonium acetate buffer medium. The DPP determination of tellurium^{23,24}, gallium²⁵, osmium²⁶ and silver²⁷ were reported earlier.

Material and Methods

Instrumentation: A microprocessor based pulse polarographic analyzer (Model CL-362) in combination with a drop-timer assembly, all from Elico Limited, Hyderabad, India, was used for polarographic measurements. Current voltage curves were recorded by an Epson printer (Epson-LX-300+II). The instrumental settings for DPP were as follows: a dropping

mercury electrode (DME) as the working electrode; pulse amplitude, 50 mV; pulse duration, 57ms; clock time of pulse, 0.5s; scan rate, 12mV/sec and charging current compensation, 20%. Potentials were measured against a saturated calomel electrode (SCE). Platinum wire was used as auxiliary electrode while ammonium acetate buffer was the supporting electrolyte.

A systronics UV-vis spectrophotometer (Model UV – 108) with a wavelength range of 190-900nm was also used for sample analysis. A tungsten – halogen deuterium lamp and wide range photomultiplier were used as the light source and detector, respectively. The spectral band width was 0.5nm.

The pH studies were made by a systronics digital pH meter (Model – 355).

Sample Preparation: Samples of industrial waste from common nala in Basni Industrial Area of Jodhpur were collected in polyethylene containers. These were filtered to separate any suspended particulate matter and acidified with HCl to pH \approx 2 for storage. 50ml aliquot of the sample was treated with 1 ml of an oxidizing mixture of acids to destroy biological materials²⁸. The treated samples were spiked with certain concentration of thorium and were taken as test solution for analysis work.

Chemicals: Chemicals used were of reagent grade purity. Standard solution of thorium was prepared from thorium nitrate of B.D.H. Other reagents employed in different steps, as described in the text, include: nitrates of lead, zinc and nickel, vanadium dioxide, EDTA disodium salt and ammonium acetate.

Test solutions were deaerated for 20 minutes by passing purified nitrogen. All of the experiments were carried out in an air-conditioned laboratory where the temperature was maintained at 25 \pm 1 $^{\circ}$ C.

Results and Discussion

The voltammetric determination of thorium was studied in complexing media of Zn-EDTA in sodium acetate buffer (pH 4.03) because of its more negative reduction potential. The method is based on the displacement of Zn²⁺ equivalent of Th⁴⁺ and indirect measurement of thorium by DPP. A sharp DP peak was obtained at -1.06V as shown in figure-1

Peak current increases linearly with the concentration of thorium up to 10ppm. DP polarograms at different concentration of thorium are recorded in figure-2. The calibration curve drawn in Fig 3 shows following characteristics: Slope, 0.0360; Intercept, 0.0208; Coefficient of correlation (r), 0.9990.

Interference: The major ions commonly present in industrial wastes such as copper and lead were tested for interference during thorium determination. The reduction of Cu²⁺ occurred at positive potential (>0.0V), and did not interfere. Similarly, the

DP peak of Pb²⁺ was noticed at -0.45V which was well-separated from that of Th⁴⁺ at -1.06V as shown in figure-3.

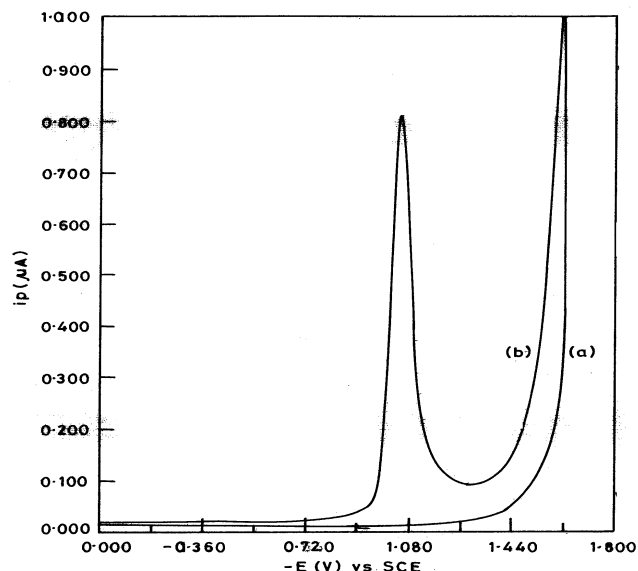


Figure-1
DP Polarogram of Zn (II) equivalent to Thorium in Acetate buffer (pH 4.03) (a) Blank solution of Acetate buffer (pH 4.03) (b) Zn (II) equivalent to Thorium (IV) in Acetate buffer (pH 4.03) Th = 7.5 ppm, Zn-EDTA = 1 x 10⁻⁴M

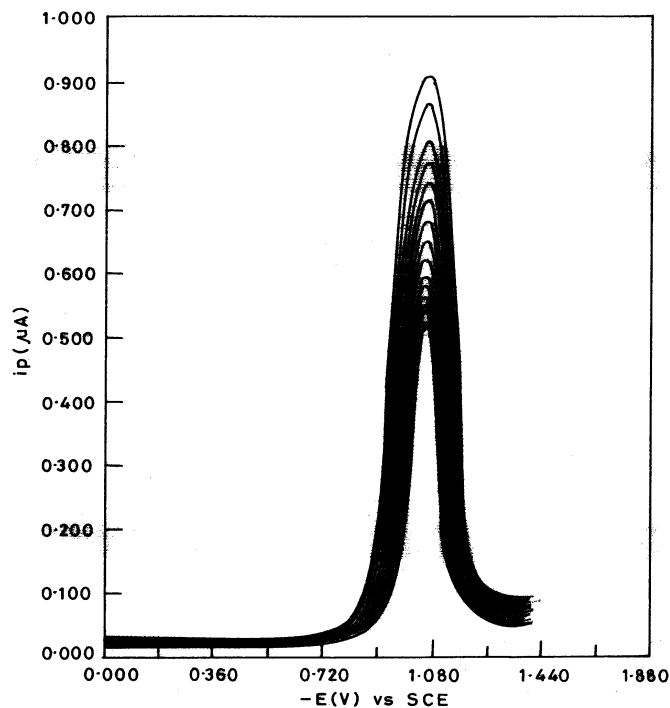


Figure-2
DP Polarograms of Thorium (IV) at different concentrations in acetate buffer (pH 4.03) Minimum concentration = 0.01 ppm, maximum concentration = 10 ppm

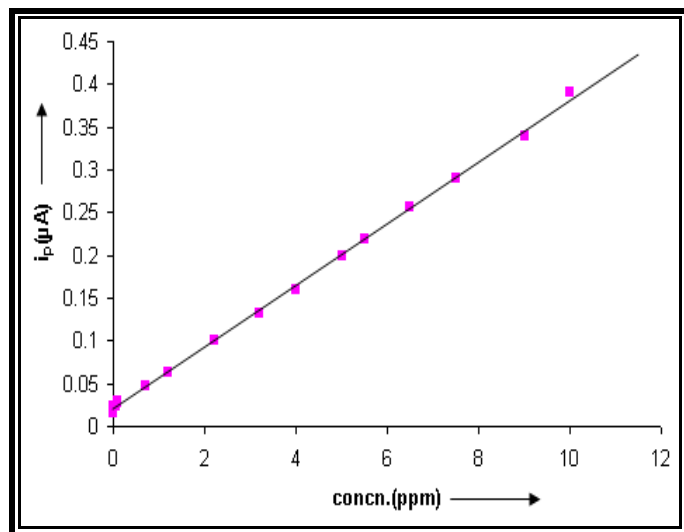


Figure-3

The plot of calibration curve, concentration in (ppm) vs peak current (μA) Minimum concentration = 0.01 ppm, maximum concentration = 10 ppm

DPP Parameters: modulation amplitude, 25 mV; pulse duration, 57 ms; drop time, 0.5s; scan rate, 12mV/s; deaeration time, 20 min; W. E = DME; h = 65 cm.

Uranium might also be present with thorium due to their wide use in nuclear reactors. U^{6+} in presence of Zn-EDTA showed distinguishable DP peak at -0.237V, illustrating no interference. Peak potential of metal ions is shown in table-1.

Table-1

Peak potentials of metal ions in presence of Zn – EDTA complex Supporting electrolyte: 0.01M ammonium acetate buffer

| S.No. | Metal ion | - Ep(V) vs SCE |
|-------|--------------|----------------|
| 1 | Copper (II) | +0.005 |
| 2 | Uranium (VI) | -0.237 |
| 3 | Lead (II) | -0.448 |
| 4 | Cadmium (II) | -0.617 |
| 5 | Thorium (IV) | -1.060 |

Limit of Determination

The minimum amount of thorium which could be determined under these experimental conditions was 0.005 ppm.

Analytical Applications: The voltammetric observations on Th^{4+} were applied to analyze thorium in industrial wastes. The prepared samples were taken into the complexing polarographic medium of Zn-EDTA in ammonium acetate buffer and DP polarograms were recorded from -0.8 to -1.2 V. The peak currents were noted at -1.06V after making blank corrections. The concentrations were determined by standard addition method²⁹. Thus results of determination of thorium are presented in table2.

Table-2

DPP determination of thorium in industrial waste samples

| Sample | Thorium(IV) concentration (ppm) | | S.D (\pm) | C.V (%) |
|--------|---------------------------------|-------|---------------|---------|
| | Present | Found | | |
| 1. | 3.6 | 3.58 | 0.026 | 0.687 |
| 2. | 3.0 | 2.94 | 0.113 | 3.826 |
| 3 | 2.8 | 2.78 | 0.026 | 0.943 |
| 4 | 2.0 | 1.90 | 0.047 | 2.480 |

Validation: The UV-Vis spectrophotometric method based on reaction of thorium with thorin in aqueous medium was used to compare the results of DPP determination of thorium. The comparative data are included in table-3. It revealed that DPP measurements were quantitative in terms of average recovery of 97.48 %.

Table-3

Comparison of results of thorium determination by DPP and UV – Vis spectrophotometry

| Sample | Thorium concentration(ppm) | | |
|------------------|----------------------------|--------------|----------|
| | DPP | Recovery (%) | UV – Vis |
| 1 (3.6) | 3.58 | 99.44 | 3.52 |
| 2 (3.0) | 2.94 | 98.00 | 2.91 |
| 3 (2.0) | 1.90 | 95.00 | 1.85 |
| Average Recovery | | 97.48 | |

n = number of determinations = 3, Values shown in parentheses are thorium concentration in ppm.

Conclusion

From the present work it was concluded that in presence of Zn-EDTA complex the limit of voltammetric determination of thorium by using DPP technique could be lowered down from 0.01 $\mu\text{g/mL}$ to 0.005 $\mu\text{g/mL}$ as reported in our earlier work³⁰.

The suggested method of thorium determination is further specific, rapid and convenient due to simple sample preparation and no interference from major ions particularly of uranium.

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