# Selective Determination of Trace-Bismuth by Extraction-Differential Pulse Polarography in Non-aqueous Media ☆

*Pournaghi-Azar\*, Mohammad Hossein and Bahar, Solyman*

Electroanalytical Chemistry Laboratory, Faculty of Chemistry, University of Tabriz

Tabriz , I.R. Iran

**ABSTRACT:** *The voltammetric characteristics of bismuth(III)-oxinate in chloroform at the mercury electrode were investigated and a quasi-reversible behavior for Bi(III) oxinate reduction was confirmed. Preceded by the extraction of Bi(III) oxinate in chloroform, differential pulse polarography was developed in the extracts for determination of the trace-bismuth. The linear range of the calibration graph and the detection limit respectively were: $1 \times 10^{-6} - 5 \times 10^{-5}$ M and $4.7 \times 10^{-7}$ M of Bi(III). Suitability and accuracy of the proposed method for determination of trace-bismuth was established by the analysis of a metallic aluminum sample.*

**KEY WORDS:** *Voltammetry in chloroform, Bismuth(III) oxinate, Chloroform, Aluminum, Differential pulse polarography, Bismuth determination*

## INTRODUCTION

Several sensitive methods have been developed for determination of bismuth. These include: hydride generation inductively coupled plasma (HG-ICP) [1], electrothermal vaporization ICP-Mass spectrometry (ETV-ICP-MS) [2], atomic absorption spectrometry (AAS) [3,4], potentiometric stripping analysis (PSA) [5], anodic stripping voltammetry [6,7], cathodic stripping voltammetry (CSV) [8].

In order to determine bismuth in solutions at concentration levels lower than its detection limits by the methods reviewed above, a preliminary preconcentration step was considered and the combined methods were used. These include liquid-liquid extraction /spectrometry (LLE-S) [9], solid phase extraction /spectrometry (SPE-S)

[10,11], solid phase extraction / inductively-coupled plasma spectroscopy (SPE-ICPS) [12], liquid-liquid extraction / atomic absorption spectrometry (LLE-AAS) [13] and coprecipitation / potentiometric stripping analysis (CP-PSA) [14]. One of the most effective separation and preconcentration procedures to enhance the selectivity as well as sensitivity of the electroanalytical methods in trace metal analysis is liquid-liquid extraction of metal chelates. The method involves complexation of metal ions with chelating agents followed by extraction into an organic solvent of low dielectric constant.Therefore, direct application of electronalytical methods for the determination of the chelate in the extracts seems to enhance selectivity and sensitivity of the methods [19]. In previous

works, we have developed the differential pulse polaro-graphic methods for determination of uranium in minerals [20] and sea-water [19], copper in tea-leaves [21] and steel [22] and molybdenum in cereals [23]. In addition we have suggested the anodic stripping voltammetric methods for determination of lead in gasoline and gas oil [25] and copper in human hair [26]. In this work ,the use of liquid-liquid extraction for separation of Bi(III)-oxi-nate and its differential pulse polarographic determina-tion in organic phase is described.

## EXPERIMENTAL
### *Chemicals and reagents*

Chloroform, perchloric acid, nitric acid, bismuth(III) nitrate, 8-hydroxy quinoline (oxine), methanol, glacial acetic acid, sodium acetate, tributylamine, tetrabutyl-ammonium chloride (TBACl) and tetrabutylammonium perchlorate (TBAP) were of pure analytical grade. The supporting electrolyte used was 0.5M tributylammonium perchlorate (tri-BAP). Tri-BAP was prepared by gradual neutralization of a given volume of concentrated perchlo-ric acid with the required amount of tributylamine while cooling the solution in iced water. The salt formed was crystallized by step-wise evaporation of the solvent on the water bath and cooling at room temperature. The crystals were dried at 50 $^0$C.

### Standard bismuth solution

A $10^{-3}$ M aqueous solution of $Bi(NO_3)_3$ was prepared as a stock solution. The standard aqueous solutions were prepared by successive dilution of the stock solution. Doubly-distilled water was used to prepare all solutions.

### Extractant solution

A 0.1M solution of oxine in chloroform was pre-pared.

### Standard solutions of Bi(III)-oxinate

A $10^{-3}$ M stock solution of Bi(III)-oxinate was pre-pared by direct dissolution of $Bi(NO_3)_3$ in the extraction solution. The standard solutions of bismuth(III) oxinate were prepared by successive dilution of the stock solution by the extraction solution.

### *Apparatus*

All voltammograms were recorded on a three-electrode system. A polarograph model E 626 with a VA-Stand E 663 (from Metrohm) were used. A multipurpose instrument from EG & G PAR including (a) potentiostat/galvanostat model 273, (b) electrochemical analysis soft-ware 3,00 model 270 coupled with an IBM personal computer and (c) a Laser Jet 5L (Hewlet Packard) printer was used to record the cyclic voltammograms.

### *Electrodes*

The reference electrode Ag/AgCl (sat.), TBACl (sat.) and TBAP 0.5M in chloroform in a separated com-partment was directly immersed in the reaction cell. The working electrodes were dropping mercury electrode (DME) and hanging mercury drop electrode (HMDE); the auxiliary electrode was a platinum wire.

### *Procedures*
#### Extraction and voltammetry of Bi(III)-oxinate

A 5 mL portion of the aqueous standard solution of $Bi^{+3}$ was transferred into a 100 mL separatory funnel,the pH of the solution was adjusted to 2, at which the extraction of Bi(III)-oxinate is complete [27], Bi(III) was extracted with 5 mL of 0.1M chloroform solutions of oxine, four times after shaking for10 min. The organic phase was separated and collected. A 10 mL portion of extract was transferred into the voltammetric cell and the required amount of supporting electrolyte (0.2 M tri-BAP) was added. Then, the solution was deaerated for 20 min with nitrogen gas (99.999%) presaturated with chlo-roform. The voltammograms were recorded by sweeping of the electrode potential over a desired range, with sui-table scan rate depending on the technique used.

## RESULTS AND DISCUSSION
### *Voltammetric investigations of Bi(III)-oxinate at the mercury electrode*

Considering that the presence of oxine in chloroform does not restrict the potential range for mercury electrodes [25] and the Bi(III)-oxinate can be extracted quan-titatively into chloroform [27], we have first investigated the voltammetric characteristics of Bi(III)-oxinate in

chloroform at the mercury electrode in the presence of 0.25 M tri-BAP + 0.1 M oxine as supporting electrolyte, commonly used in chloroform.

Differential pulse polarography of Bi(III)-oxinate in chloroform exhibited a well-defined polarogram with a potential peak of -0.23 V (Fig.1). The $i_p$ values are linearly dependent on the Bi (ox)$_3$ concentration in the range $1 \times 10^{-6}$ - $5 \times 10^{-4}$ M. Cyclic voltammetry for potential scanning between 0.2 and -0.6 V showed one cathodic peak and one anodic peak with peak potentials of -0.46 and -0.05 V, respectively (Fig.2), the potential peak separation $\Delta E = E_p^a - E_p^c$ was 435 mV. The controlled potential coulometric measurements confirmed the exchange of three electrons at the reduction process. These findings lead us to conclude that the reduction of Bi(III) oxinate in the presence of 0.2M tri-BAP + 0.1M oxine is a three-electron quasi-reversible process.

## Analytical performances of the method

The calibration graph was constructed by means of standard solutions of Bi(III)-oxinate over concentration range $9.8 \times 10^{-7}$ - $8.3 \times 10^{-6}$ M in chloroform. The regression equation was I = 1.8 + 22.4 C ( I in nA and C in μM) and the detection limit of the method (taken as the concentration that gave a signal equal to blank plus three times of its standard deviation, calculated from the calibration graph) found to be $4.7 \times 10^{-7}$ M of Bi(III) oxinate.
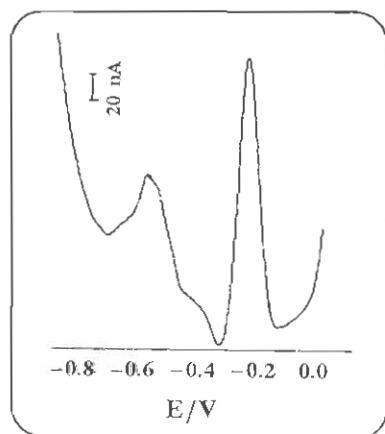


*Fig.1: Differential pulse polarogram of 10 μM Bi(III) oxinate in chloroform in the presence of 0.25M tri-BAP + 0.1M oxine as supporting electrolyte, potential sweep rate: 4 mV s$^{-1}$, pulse amplitude: 50mV*
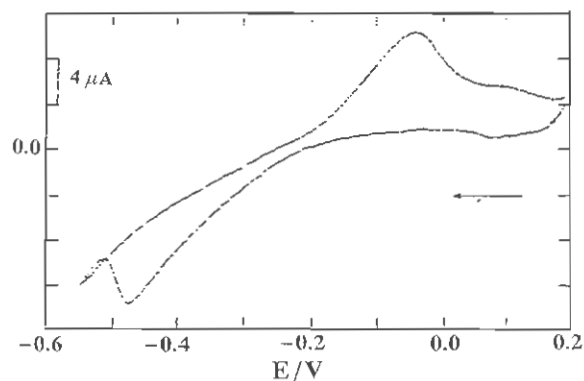


*Fig.2: Cyclic voltammogram of 0.5 mM Bi(III) oxinate in CHCl$_3$ in the presence of 0.25M tri-BAP + 0.1M oxine as supporting electrolyte, potential scan rate: 100 mV s$^{-1}$*

The DP polarograms for Bi(III) oxinate solutions over concentration rang $9.8 \times 10^{-7}$ - $8.3 \times 10^{-6}$ M and corresponding calibration graph are shown in Fig 3 .

## Extraction efficiency

We have investigated the extraction efficiency of Bi (ox)$_3$ from the aqueous solution at pH 2. For this purpose we have constructed a calibration graph by means of chloroform extracts using the aqueous solutions of bismuth(III) nitrate over concentration range $1 \times 10^{-6}$ -$10 \times 10^{-6}$ M ( concetration range in the extracts).The regression equation, I = 1.74+ 21.9 C ( I in nA and C in μM) for the calibration graph is very close to that of constructed by means of the standard Bi(III) oxinate solutions in chloroform. These findings suggested that the two calibration graphs nearly overlapped and the extraction efficiency of Bi(III) oxinate was about 100%. Thus the standard addition method in the voltammetric cell can be used for the determination of Bi(III) oxinate with the polarogragraphic measurements.

## Selectivity study

Among the concomitant metal ions, four groups are distinguished:

1- Metal ions such as Pb(II), Cd(II), Mn(II) and Co(II) the oxinats of which are not extracted in chloroform under the extraction conditions of Bi(III) oxinate ( pH between 2 and 4) [28 ].
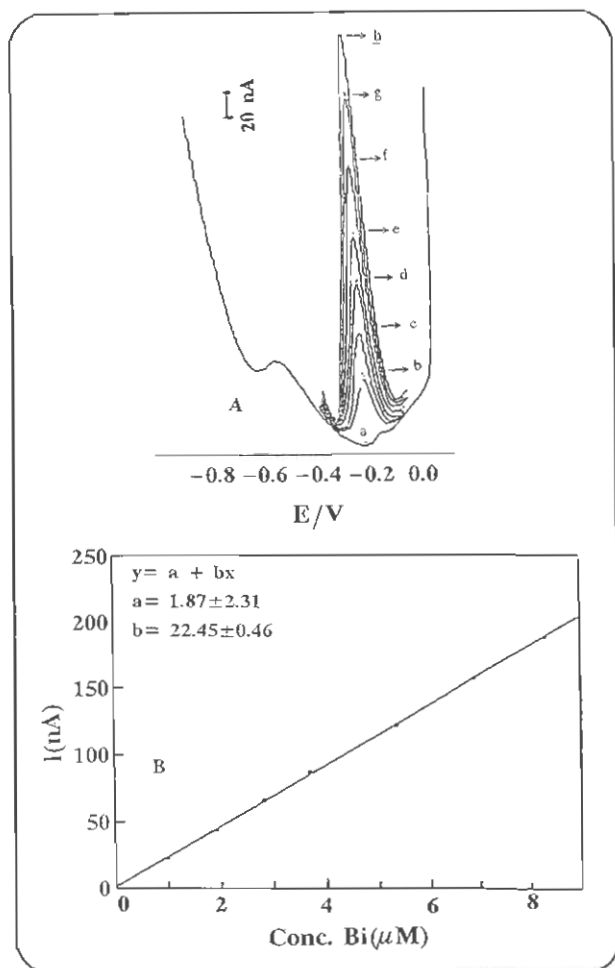
*Fig.3: (A) Differential pulse polarograms of Bi(III) oxinate in chloroform (a) 0 (b) 0.98 μM, (c) 1.92 μM, (d) 2.8 μM, (e) 3.70 μM, (f) 5.36 μM (g) 6.90 μM and (h) 8.36 μM. (B) Plot of $I_p$ versus Bi(III) oxinate concentration. Supporting electrolyte: 0.25 M tri-BAP + 0.1 M oxine, potential sweep rate: 4 mV s$^{-1}$, pulse amplitude: 50mV*

2- Metal ions such as Zn (II), Ni(II) and Pd(II), the oxinates of which are extracted in chloroform at pH 2-4, but they are electroinactive in the extracts, under the polarographic conditions of Bi(III) oxinate [28].

3- Metal ions such as Mo(VI) and U(VI) which are extracted as oxinates in chloroform under extraction conditions of Bi(III) oxinate, but their reduction peaks are sufficiently separated from that of Bi (III) oxinate [20,23].

4- Metal ions such as Fe(III) and Cu(II) which their oxinate are extractable and electroactive in chloroform;

these metal ions seriously interfere the measurement of Bi(III) oxinate peak current. Therefore, their extraction into chloroform must be prevented [24, 29] .

An extensive study was carried out to provide the aqueous solution conditions that prevent the extraction of Fe(III) and Cu(II) oxinates into chloroform. It was found that the presence of ascorbic acid and phenanthroline in aqueous phase, simultaneously, prevent the extraction of Fe(III) oxinate in chloroform. Indeed, ascorbic acid reduces Fe(III) to Fe(II); subsequent complexation of Fe(II) with phenanthroline in the solution will prevent the reoxidation of Fe(II) to Fe(III) by dissolved oxygen during the extraction process. Results obtained from this study, showed that ascorbic acid and phenanthroline at concentrations of about 100 and 10 times greater than that of Fe(III), respectively, are effective for this purpose and a selective extraction of Bi(III) from a mixture of Bi(III) + Fe(III) with any ratio is possible. The mean recovery for three replicate extractions of $4 \times 10^{-5}$ M Bi$^{3+}$ from the aqueous solutions in the presence of $2 \times 10^{-4}$ M of Fe$^{3+}$ plus $2 \times 10^{-2}$ M of ascorbic acid and $2 \times 10^{-3}$ M phenanthroline was 100.1% with a relative standard deviation of 3% . A representative example of the corresponding DP polarograms is shown in Fig.4. We also have found that the concomitant Cu(II) ion may be eliminated from the aqueous solution by its reduction to Cu(I) by HSO$_3^-$ and subsequent precipitation in the presence of SCN$^-$ as CuSCN. The CuSCN formed is separated from the solution by centrifugation and the solution is subjected for the bismuth extraction. The experimental investigation showed that when the concentration of Cu$^{2+}$ in the solution is lower than $10^{-3}$ M, a 1ml portions of HSO$_3^-$ 10% (w / v) and 0.5 mL of SCN$^-$ 1 M are sufficient. Fig.5 shows the DP polarograms of the chloroform extracts obtained from the solutions of Bi$^{3+}$ $10^{-5}$ M plus Cu$^{2+}$ $5 \times 10^{-5}$ M in the absence and presence of 1mL of HSO$_3^-$ 10% ( w / v) and 0.5 mL of SCN$^-$ 1M. On the other hand, it was confirmed that the presence of the masking agents (ascorbic acid, phenanthroline, HSO$_3^-$ and SCN$^-$) does not affect the extraction efficiency and polarographic peak currents of Bi(III) oxinate (Fig.6). After optimization of the solution conditions for the selective extration of Bi(III) oxinate from aqueous solution the effect of some

other ions on the determination of $10^{-5}$ M Bi(III) from aqueous solution was examined. Note that an ion is considered to interfer seriously if it gave a determination error of more than 5%. The results are shown in Table 1.

### Precision and accuracy of the method

Bismuth spiked doubly distilled water ($4 \times 10^{-6}$ M) was analyzed by the proposed method, using the standard addition method in a voltammetric cell. The recovery of bismuth was 99.8% and the relative standard deviation for three replicate determinations was 2%.
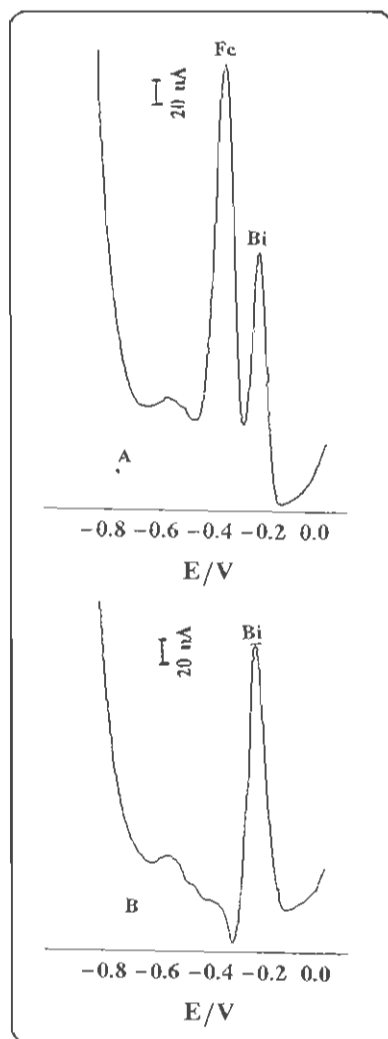
*Table 1: Effect of some cations on the determination of bismuth*

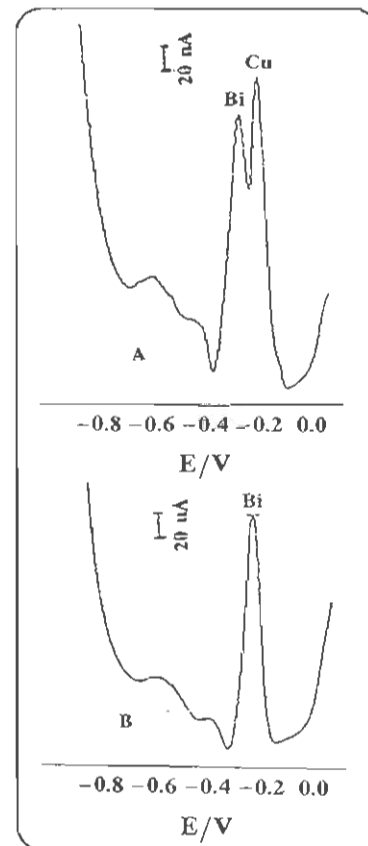| Cation | Type of error | Tolerated mole ratio |
|---|---|---|
| $Fe^{3+}$ | + | >50 |
| $Cu^{2+}$ | + | >50 |
| U(VI) | — | >100 |
| Mo(VI) | — | >200 |
| $Pb^{2+}$ | — | >200 |
| $Zn^{2+}$, $Ni^{2+}$, $Co^{2+}$, $Pd^{2+}$, $Cd^{2+}$, $Mn^{2+}$ | — | >1000 |



*Fig.5. Dp polarogrms of 10 mL chloroform extract obtained from 5 mL aqueous solution of $5 \times 10^{-5}$ M $Cu^{2+} + 10^{-5}$ M $Bi^{3+}$ (A) in the absence and (B) in the presence of 0.05 M of thiocyanate and 1% (w/v) sodium hydrogen sulfite, experimental conditions same as in Fig.3*

It was intended to investigate the suitability and accuracy of the method for determinat ion of bismuth in a real sample. For this purpose, a pure metallic aluminum sample containing a certified trace of bismuth was analyzed. The sample was dissolved by the following procedure:
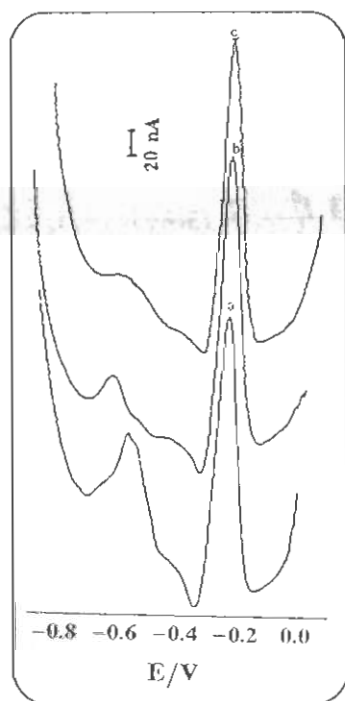


*Fig.4: Dp polarogrms of 10 mL chloroform extract obtained from 5 mL aqueous solution of $10^{-4}$ M $Fe^{3+} + 10^{-5}$ M $Bi^{3+}$ (A) in the absence and (B) in the presence of $10^{-3}$ M of phenanthroline and $10^{-2}$ M of ascorbic acid, experimental conditions same as in Fig.3*

*Fig.6: Dp polarogrms of 10 ml chloroform extract obtained from 5 ml aqueous solution of $10^{-5}$ M $Bi^{3+}$ (a) in the absence, (b) in the presence of $10^{-3}$ M of phenanthroline and $10^{-2}$ M of ascorbic acid and (c) in the presence of 0.05 M of thiocyanate and 1% (w/v) sodium hydrogen sulfite, experimental conditions same as in Fig.3*

Approximately 0.1g of the samples were dissolved in the minimum volume of 6M HCl containing a few drops of 30% (w / v) hydrogen peroxide by gently heating of the mixture and then diluting to 100 mL with 0.1M HCl in a volumetric flask. 10 ml of the solution was subjected to extraction of Bi(III) oxinate and then to a differential pulse polarographic measurement. Using a standard addition method, the average percentage of bismuth found for three replicate determinations for an aluminum sample (from local Simkat company) was 0.0012% with a relative standard deviation of 4.1% (s = 0.000042 ) which is in good agreement with the certified amount of 0.0013% ($t_{exp} = 3.3 < t_{theo} = (4.30)_{95\%}$ ).

## CONCLUSIONS

Bi(III)-oxinate can be reduced according to a three-electron quasi-reversible process to metallic bismuth at the mercury electrode in the presence of 0.2 M of tri-BAP

as supporting electrolyte in chloroform. Bi(III) oxinate is extracted into chloroform selectively and then subjected to differential pulse polarogrphy for the determination of trace-bismuth in the extracts. The detection limit of the proposed method is relatively low and is applicable for trace-bismuth determination in the alloys.

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