

USE OF ELECTROANALYTICAL TECHNIQUES FOR DETERMINATION OF TRACE METALS IN CASSITERITE ORE

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ABSTRACT

Simultaneous determination of trace metals in a cassiterite sample has been performed using electroanalytical techniques, viz. DCP, DPP and DPASV. The analysis of trace metals was carried out using 0.1M $(\text{NH}_4)_2$ tartrate, 0.005M EDTA and 11M HCl as supporting electrolytes, separately, and 0.001% gelatin as a maximum suppressor. Eight elements, Ti, Pb, Sn, Fe, Mn, Sb, Cd and W, have been analysed in a cassiterite sample. The method of standard addition was used for quantitative analysis. The percentage recovery and statistical data reveal the reliability of the observed results. The accuracy of the methods was verified by comparing the observed voltammetric results with those obtained using the atomic absorption spectroscopic method. The tried detection limits of the electroanalytical techniques used for the said metals are also reported. The proposed methods are precise, accurate and fast.

INTRODUCTION

Cassiterite is the chief ore of tin and is found in many localities with other economically important mineral deposits /1,2/. In cassiterite, tin is associated with a large number of elements, such as Pb, Fe, Mn, In, Cd, Ti, Tl, Sb, Be, Bi, Nb, Ta and W /3,4/. Trace analysis of a cassiterite sample has been carried out mainly using the atomic absorption spectroscopic method /5,6/. In addition, various other analytical methods have been developed in the past for the determination of trace metals in geological samples /7-11/. Currently,

electroanalytical techniques have established themselves as versatile analytical tools for quick and precise determination of trace metals in geological samples /12-14/. In fact, these techniques are more sensitive than any other conventional methods for trace metals analysis of environmental, biological, industrial and particularly of geological samples /15-19/.

The present paper deals with the trace analysis of metals in a cassiterite sample using direct current polarography (DCP), differential pulse polarography (DPP) and differential pulse anodic stripping voltammetry (DPASV). The voltammetric results were compared with those obtained using the atomic absorption spectroscopic method (AAS).

EXPERIMENTAL

Sample:

The cassiterite sample was collected from the Govindpal Nerli area, which is located 70 km south of Jagdalpur, Bastar District, M.P., India.

Instrumentation:

Polarographic and voltammetric measurements were made on an Elico (India) Model CL-90 pulse polarograph coupled with an X-Y polarocard Model LR-108. The electrode system consisted of a dropping mercury electrode (DME) as a working electrode, a coiled platinum wire electrode as an auxiliary electrode and a saturated calomel electrode (SCE) as a reference electrode. The electrochemical cell used had the provision for inserting a bubbler for de-aerating the solution and for passing nitrogen gas. A glassy carbon fibre electrode (NF 12, Sigtii Eletitogitit, UK) was used for DPASV.

The pH measurements were made on a Systronics digital pH-meter Model 335.

Chemical and Reagents:

AnalaR grade chemicals were used. Stock solutions of ammonium tartrate (1M), EDTA disodium salt (0.1M), Ti^{+4} , Pb^{+2} , Sn^{+2} , Fe^{+2} , Sb^{+3} , Cd^{+2} and W^{+6} (0.01M) were prepared by dissolving the required amounts of their soluble salts in doubly distilled water. Gelatin (0.1%) solution was prepared in hot

distilled water. The solutions were standardized by known methods and diluted as required.

Preparation of Sample Solution:

The cassiterite sample solution was prepared by the fusion method /20/. One gram of finely pulverized cassiterite sample was taken into a platinum crucible along with 8 g of anhydrous sodium carbonate and 16 g of sodium peroxide. The crucible was first heated slowly and then more vigorously to a red hot state for about one hour. It was then allowed to cool and distilled water was added to dissolve the melt. The solution was then transferred to a beaker and acidified with hydrochloric acid. Due to acidification some brownish precipitate was obtained. The solution was filtered and the precipitate and insoluble residue was transferred to a crucible, ignited and fused with fusion mixture and treated as above. Both the solutions were mixed and diluted with doubly distilled water up to 100 ml and subjected to polarographic/voltammetric analysis.

Preparation of Analyte and Recording of Polarograms/Voltammograms

The analysis of trace metals in cassiterite sample was carried out by preparing the analyte in three different supporting electrolytes separately, as described below.

(1) In 0.1M (NH₄)₂ tartrate:

To 10ml of the sample solution, 10 ml of 1M (NH₄)₂ tartrate as a supporting electrolyte and 1ml of 0.1% gelatin solution as a maximum suppressor were added. The final volume of the analyte was made up to 100ml by doubly distilled water. The pH of the test solution was first adjusted to 1.0 ± 0.1 and then to 7.0 ± 0.1 , as the analysis of the sample was carried out at two different pH values.

(2) In 0.005M EDTA disodium salt:

To 10ml of the sample solution, 5ml of 0.1M EDTA (disodium salt) solution as supporting electrolyte and 1ml of 0.1% gelatin as a maximum suppressor were added. The final volume of the analyte was made up to 100ml by doubly distilled water. The pH of the test solution was adjusted to 1.1 ± 0.1 .

(3) In 11M HCl

To 5ml of the sample solution, 94ml of 11.6M HCl as supporting electrolyte, and 1ml of 0.1% gelatin solution as a maximum suppressor, were added. The pH of the test solution was adjusted to 1.1 ± 0.1 .

Each analyte was placed in the polarographic cell, equipped with the electrode assembly specified above. Pure nitrogen gas was passed through the test solution and subjected to polarographic and voltammetric analysis. The polarograms and voltammograms were recorded with instrumental parameters indicated in Table 1. For DPASV the deposition potential was fixed at $-1.0V$ and $-1.60V$ in the case of $0.1M (NH_4)_2$ tartrate, $-1.50V$ in the case of $0.005M$ EDTA and $-1.0V$ in the case of $11M$ HCl as supporting electrolytes. The deposition time was 60 sec. and 10 sec. resting period.

Table 1
Instrumental Parameters

Parameters	Value
Initial applied voltage	0.0 V _{vs} SCE
Sensitivity	1 μ A/V
C C Compensation	5
I R Compensation	4
Height of Hg	140.0 cm
Time Constant	10 ms
Pulse amplitude	50 mV
Drop time	0.5 sec.
Aquisition	Fast
Scan rate	12 mV.s ⁻¹
O/P zero	0
Temperature	25 \pm 2°C
On Polarocard	
X-Axis	100 mV.cm. ⁻¹ /200 mV. cm. ⁻¹
Y-Axis	200 mV.cm. ⁻¹ /500 mV. cm. ⁻¹

RESULTS AND DISCUSSION

The direct current polarogram [Fig. 1(A)] of the sample solution in 0.1M $(\text{NH}_4)_2$ tartrate at $\text{pH} = 1.0 \pm 0.1$, produced two well-defined waves with $E_{1/2}$ values = -0.31V and -0.52V vs SCE, indicating the presence of two metal ions in the sample. However, the differential pulse polarogram [Fig. 1(B)] of the sample in 0.1M $(\text{NH}_4)_2$ tartrate ($\text{pH} = 1.0 \pm 0.1$) produced three distinct peaks with E_p values = -0.38V , -0.52V and -0.56V vs SCE, indicating the presence of Ti^{+4} , Pb^{+2} and Sn^{+2} in the sample. To investigate for the presence

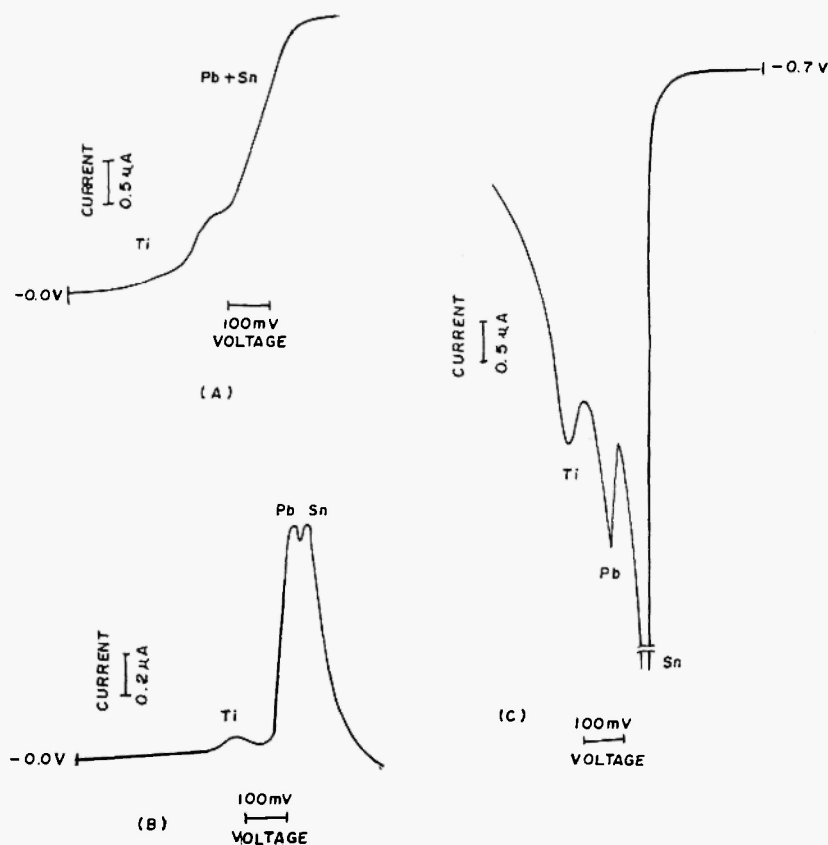


Fig. 1: (A) Direct current polarogram; (B) Differential pulse polarogram; (C) Differential pulse anodic stripping voltammogram of cassiterite sample in 0.1M ammonium tartrate + 0.001% gelatin. $\text{pH} = 1.0 \pm 0.1$.

of other trace metals in the sample its direct current polarogram and differential pulse polarogram were recorded at $\text{pH} = 7.0 \pm 0.1$ [Fig. 2(A) and 2(B)]. The figure clearly shows two distinct waves/peaks with $E_{1/2}/E_p$ values = $-1.41\text{V}/-1.45\text{V}$ and $-1.60\text{V}/-1.61\text{V}$ vs SCE, indicating the presence of Fe^{+2} and Mn^{+2} , respectively. The differential pulse anodic stripping voltammograms were also recorded for the sample solution in 0.1M $(\text{NH}_4)_2$ tartrate at both $\text{pHs} = 1.0 \pm 0.1$ and 7.0 ± 0.1 . The DPAS voltammograms [Fig. 1(C) and 2(C)] showed well-defined peaks with $E_p = -0.21\text{V}$, -0.31V , -0.39V , -0.80V and -1.48V vs SCE, respectively, indicating the presence of Ti^{+4} , Pb^{+2} , Sn^{+2} , Fe^{+2} , and Mn^{+2} in the sample.

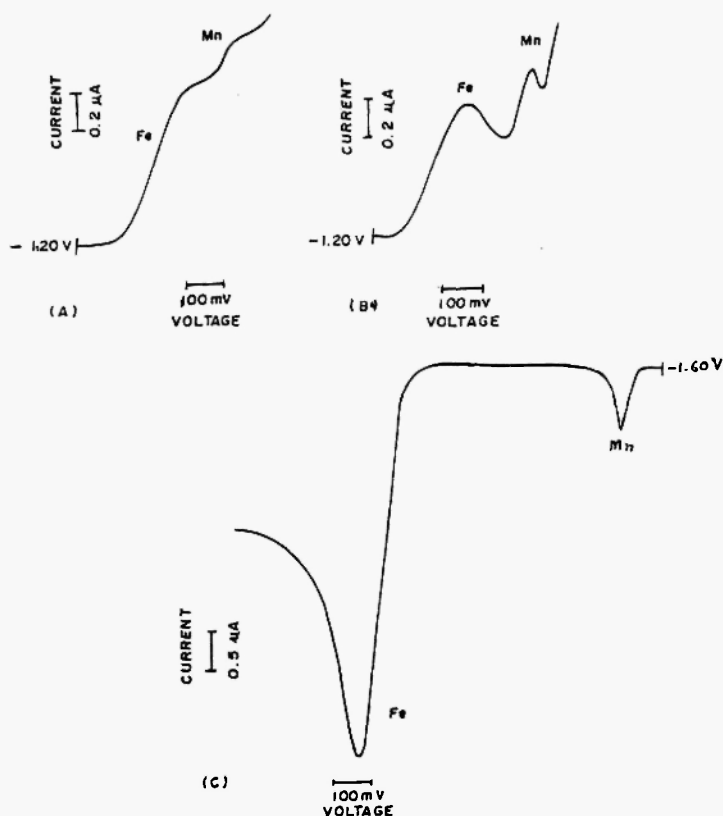


Fig. 2: (A) Direct current polarogram; (B) Differential pulse polarogram; (C) Differential pulse anodic stripping voltammogram of cassiterite sample in 0.1M ammonium tartrate + 0.001% gelatin. $\text{pH} = 7.0 \pm 0.1$.

The direct current polarogram and differential pulse polarogram [Fig. 3(A,B)] of the sample solution in 0.005M EDTA disodium salt ($\text{pH} = 1.2 \pm 0.1$) gave two well-defined waves/peaks with $E_{1/2}/E_p = -0.57\text{V}/-0.56\text{V}$ and $-0.74\text{V}/-0.76\text{V}$ vs SCE, indicating the presence of Sb^{+3} and Cd^{+2} in the sample. The DPAS voltammogram [Fig. 3(C)] of the sample solution in 0.005M EDTA (disodium salt) also produced two well defined peaks with E_p

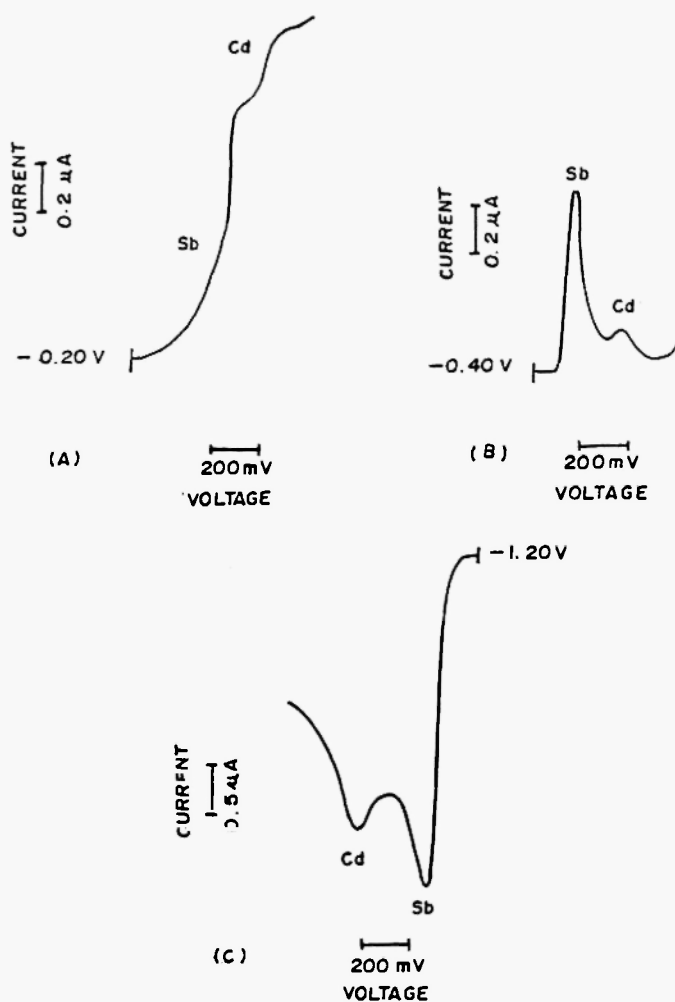


Fig. 3: (A) Direct current polarogram; (B) Differential pulse polarogram; (C) Differential pulse anodic stripping voltammogram of cassiterite sample in 0.05M EDTA + 0.001% gelatin. $\text{pH} = 1.2 \pm 0.1$.

= -0.98V and -0.72V vs SCE, indicating the presence of Sb^{+3} and Cd^{+2} in the sample.

Analysis of Tungsten

To investigate for the presence of tungsten in the sample, 11M HCl was used as a supporting electrolyte. The d.c. polarogram and d.p. polarogram [Fig. 4(A,B)] in 11M HCl ($\text{pH} = 1.1 \pm 0.1$) produced a well-defined wave and peak with $E_{1/2}/E_p = -0.74\text{V}/-0.75\text{V}$ vs SCE, indicating the presence of W^{+6} in the sample. The differential pulse anodic stripping voltammogram [Fig. 4(C)] also produced a well defined peak with $E_p = -0.78\text{V}$ vs SCE, confirming the presence of W^{+6} in the sample.

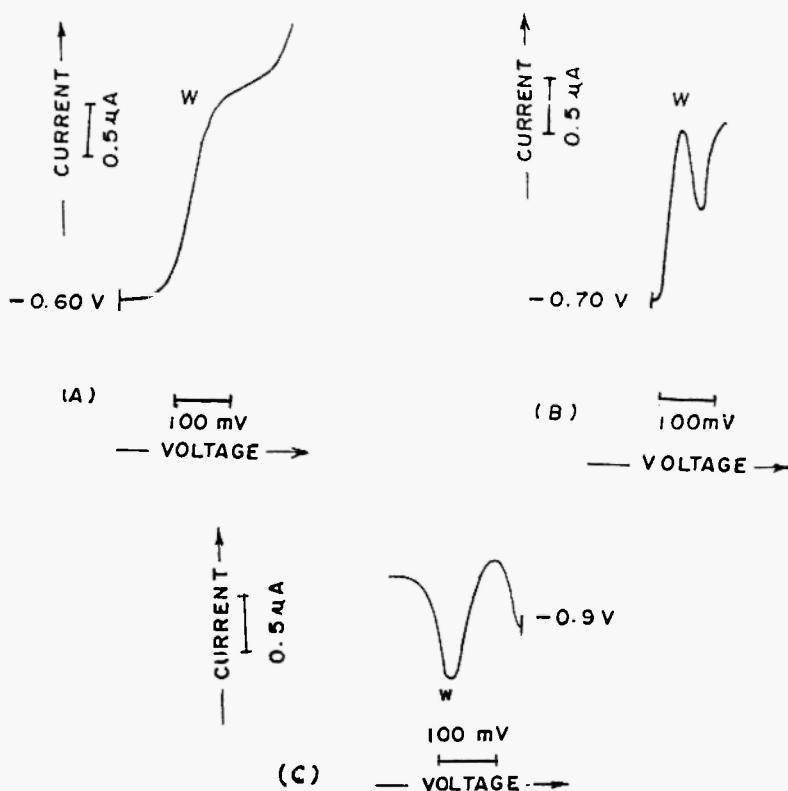


Fig. 4: (A) Direct current polarogram; (B) Differential pulse polarogram; (C) Differential pulse anodic stripping voltammogram of cassiterite sample in 11M HCl. $\text{pH} = 1.1 \pm 0.1$.

To ascertain for the presence of the said metal ions in the sample, a known quantity of standard solution of each metal ion was added to the analyte and the polarograms and voltammograms were recorded under the identical experimental conditions. An increase in the wave and peak height of each metal ion signal was observed without any change in $E_{1/2}$ and E_p values.

Based on the presence of the above-mentioned metal ions in the sample, some synthetic samples with varying concentrations of the said metal ions were prepared and their polarograms and voltammograms were recorded under identical experimental conditions as indicated earlier. The results indicated no change in $E_{1/2}$ and E_p values of the above-mentioned metal ions, thus confirming the possibility of an accurate simultaneous multi-element qualitative and quantitative determination of the reported metal ions in the sample. The concentration of each metal ion (taken/found) in the synthetic samples by using DPP is given in Table 2. It is clear from the above dis-

Table 2
Analysis of synthetic samples (mg/100ml analyte)[#]

Composition of synthetic samples				
Ti	0.38 (0.35)*	0.47 (0.47)	0.57 (0.56)	0.62 (0.60)
Pb	3.32 (3.30)	3.74 (3.71)	3.74 (3.69)	3.93 (3.90)
Sn	11.87 (11.80)	13.05 (13.04)	14.25 (14.19)	14.24 (14.20)
Fe	1.67 (1.63)	1.95 (1.93)	2.23 (2.20)	2.51 (2.46)
Mn	0.05 (0.04)	0.11 (0.09)	0.16 (0.16)	0.27 (0.26)
Sb	3.40 (3.34)	3.89 (3.86)	3.89 (3.84)	4.14 (4.12)
Cd	0.28 (0.26)	0.28 (0.24)	0.33 (0.33)	0.39 (0.38)
W	0.55 (0.52)	0.73 (0.71)	0.92 (0.88)	1.01 (0.96)

[#] Average of four determinations.

* () Amount found using DPP (mg/100ml analyte)

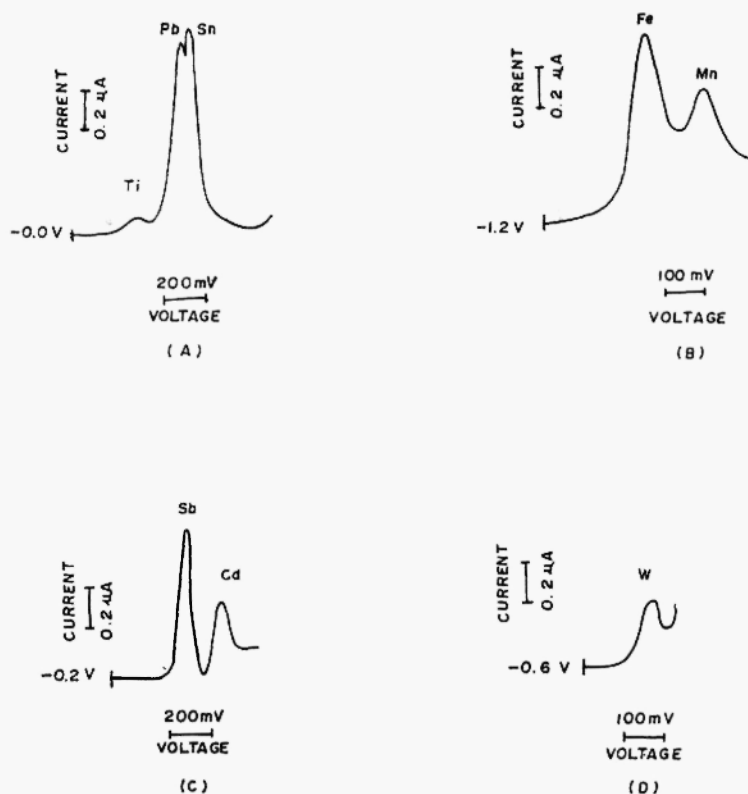


Fig. 5: Differential pulse polarogram of a synthetic sample containing Ti^{+4} (0.38), Pb^{+2} (3.32), Sn^{+2} (11.87), Fe^{+2} (1.67), Mn^{+2} (0.05), Sb^{+3} (3.40), Cd^{+2} (0.28) and W^{+6} (0.55) mg per 100 ml analyte.

(A) In 0.1M ammonium tartrate + 0.001% gelatin, $\text{pH} = 1.0 \pm 0.1$.

(B) In 0.1M ammonium tartrate + 0.001% gelatin, $\text{pH} = 7.0 \pm 0.1$.

(C) In 0.005M EDTA + 0.001% gelatin, $\text{pH} = 1.2 \pm 0.1$.

(D) In 11M HCl + 0.001% gelatin, $\text{pH} = 1.1 \pm 0.1$.

cussion that the nature of the supporting electrolyte plays a significant role in polarographic and voltammetric analysis. After detailed study it was found that 0.1M $(\text{NH}_4)_2$ tartrate, 0.005M EDTA (disodium salt) and 11M HCl are ideal media for the trace metals analysis in cassiterite sample.

Minimum Tried Detection Limits

The minimum tried detection limits of the DCP, DPP and DPASV techniques for the measurements of individual and combined metal ions in a mixture were examined by preparing synthetic samples. The detection limits are given in Table 3. It shows that the DPASV method using glassy carbon fibre electrode is highly sensitive in determining the reported metal ions down to nanogram level.

Table 3
Minimum tried detection limits

Metal Ion	DCP $\mu\text{g.l}^{-1}$	DPP $\mu\text{g.l}^{-1}$	DPASV ng.l^{-1}
Ti^{+4} <i>Individual</i>	4.8	0.048	4.8
<i>Combined</i>	4.8	0.096	9.6
Pb^{+2} <i>Individual</i>	20.72	0.207	20.72
<i>Combined</i>	20.72	0.207	20.72
Sn^{+2} <i>Individual</i>	11.8	0.118	11.8
<i>Combined</i>	11.8	0.118	11.8
Fe^{+2} <i>Individual</i>	5.6	0.56	2.8
<i>Combined</i>	5.6	0.56	2.8
Mn^{+2} <i>Individual</i>	5.4	0.54	2.7
<i>Combined</i>	5.4	0.54	2.7
Sb^{+3} <i>Individual</i>	12.2	0.122	12.2
<i>Combined</i>	12.2	0.122	12.2
Cd^{+2} <i>Individual</i>	6.0	0.06	6.0
<i>Combined</i>	6.0	0.06	6.0
W^{+6} <i>Individual</i>	9.5	0.95	9.5
<i>Combined</i>	9.5	0.95	19.5

Table 4
Results on cassiterite sample analysis for metal ions (mg/g⁻¹)

Metal ions	Parameter	DCP		DPP		DPASV	
		Added	found	Added	found	Added	found
Ti ⁴⁺	Amount	-	4.15	-	4.15	-	4.15
		4.31	8.32	4.31	8.26	4.31	8.40
	R%		98.22%		97.63%		99.29%
	S.D.		0.04		0.02		0.04
Pb ²⁺	Amount	-	34.80	-	34.80	-	34.79
		35.22	69.92	35.22	69.91	35.22	69.93
	R%		99.85%		99.84%		99.88%
	S.D.		0.09		0.02		0.02
Sn ²⁺	Amount	-	124.64	-	124.63	-	124.64
		125.82	249.62	125.82	249.78	125.82	249.76
	R%		99.66%		99.73%		99.72%
	S.D.		0.04		0.04		0.07
Fe ²⁺	Amount	-	18.44	-	18.44	-	18.44
		18.97	37.10	18.97	37.05	18.97	37.10
	R%		99.03%		99.17%		99.17%
	S.D.		0.2		0.07		0.20
Mn ²⁺	Amount	-	0.24	-	0.24	-	0.24
		0.27	0.49	0.27	0.50	0.27	0.50
	R%		96.07%		98.07%		98.07%
	S.D.		0.02		0.02		0.03
Sb ³⁺	Amount	-	33.6	-	33.6	-	33.6
		34.09	66.54	34.09	66.54	34.09	66.98
	R%		98.30%		98.30%		98.95%
	S.D.		0.48		0.18		0.48
Cd ²⁺	Amount	-	0.89	-	0.89	-	0.89
		0.78	1.62	0.78	1.64	0.78	1.66
	R%		97.00%		98.20%		99.40%
	S.D.		0.02		0.05		0.05
W ⁶⁺	Amount	-	9.66	-	9.66	-	9.66
		9.19	18.70	9.19	18.74	9.19	18.78
	R%		99.20%		99.41%		99.78%
	S.D.		0.09		0.07		0.04
	C.V.		0.93%		0.72%		0.41%

Results are average of four determinations

R% = Recovery (%)

S.D. = Standard Deviation

C.V. = Coefficient of Variance

Quantitative Analysis of Metal Ions

After ascertaining the presence of the said metals, the method of standard addition was employed in order to evaluate the concentrations of the metal ions present in the sample solution. The results are given in Table 4. The results indicate that the percentage recovery is over 99% for most of the metal ions, with high accuracy and precision of determination.

The final analysis results for cassiterite sample are reported in Table 5. The voltammetric results were compared with those obtained on cassiterite sample using the atomic absorption spectroscopic method (AAS), which are in good agreement. The electroanalytical techniques are versatile, specific and selective for the qualitative and quantitative oligo-analysis of trace metals in cassiterite sample. These techniques are less time consuming and more economical. As such, it may be stated that they may prove to be a great asset for geochemical laboratories undertaking the analysis of metals at minor and trace levels.

Table 5
Final analysis results: Comparison of AAS and voltammetric trace analysis data for cassiterite sample

Metal Ion	Amount found in mg.g ⁻¹	
	Voltammetry	AAS
Ti ⁺⁴	4.15	4.09
Pb ⁺²	34.80	34.62
Sn ⁺²	124.64	124.60
Fe ⁺²	18.44	18.39
Mn ⁺²	0.24	0.25
Sb ⁺³	33.6	33.5
Cd ⁺²	0.89	0.84
W ⁺⁶	9.66	9.56

ACKNOWLEDGEMENT

The authors are highly grateful to Prof. S.P. Banerjee, Head, Department of Chemistry, Dr. H.S. Gour University, Sagar, for providing the necessary laboratory facilities.

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