

# Anodic Stripping Voltammetric Determination of Some Trace Elements in Portland Cement and the Electrostatic Precipitator Dust

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Voltammetric methods have been successfully used for the simultaneous determination of minor and trace elements in cement industry. This is based on the analysis of water leach of the cement and the electrostatic precipitator dust samples using the mercury drop electrode in the anodic direction. This analytical procedure has both good selectivity and very high sensitivity. The ions detected and determined in Portland cement and electrostatic precipitator dust using these techniques are Pb(II), Zn(II), Tl(I), and Sn(II). It is mainly observed that the concentrations of these ions under investigation differ greatly in Portland cement from the electrostatic precipitator dust.

The main component in clinker structure is the impure tricalcium silicate ( $C_3S$ , alite) which is responsible mainly for the strength of the cement after hardening. The impure dicalcium silicate ( $B-C_2S$ , belite) is established with respect to other phases by foreign ions in solid solution.

The effect of large intakes of Cd, Pb, Cr, Zn to cement raw meal on the mineralogical composition of the clinker was studied [1]. Portland cement behaves as a matrix to trap ZnO while calcium aluminates preferentially trap Cd, Pb, and Cl as calcium chloroaluminate. Chromium is trapped with a good retention efficiency in both matrixes. The effect of ZnO on the hydration reaction and physical properties of cement was studied [2]. It is found that for specimens containing ZnO > 0.6 mass %, the compressive strength of cement cured for 28 days could not be determined because setting had not occurred.

Influence of some minor trace elements in raw material on the composition and structure of clinker was investigated [3]. Raw meal of cement contains hundreds to thousands ppm of P, Cl, Cr, Cu, and Pb under various temperatures and atmospheres. All of these elements act as a flux and/or mineralizer. They made alite crystals larger and idiomorphic, increased the amount of belite, preventing it from lumping and influenced the shape and structure of clinker pores.

The effect of the minor and heavy metals on the health of the cement workers was studied [4]. Cr and

Co were the most important factors in producing sensitivity to cement among 600 workers suffering from cement dermatitis.

The heavy metals in cement dust in Helwan industrial area, Cairo, Egypt, were studied and it was found that the contents of Cr, Cu, Mn, Pb, and Zn in dust fall, however, greatly exceeded the corresponding values in cement [5].

For pollution prevention, some trace elements in cement manufacture in Germany were determined by absorption spectrometry [6].

The analysis of some of the trace elements, namely BaO,  $Cr_2O_3$ , and  $Mn_2O_3$  has been done by atomic absorption spectroscopy (AAS) method [7]. Thallium in cement kiln dust is determined photometrically by complexing with brilliant green [8].

Voltammetric techniques are also employed in the determination of the minor and trace elements in cement and cement raw materials. Minor levels of titanium in real cement samples were determined by Alternating Current (A.C.) voltammetry [9]. Also the content of Hg in cement raw material samples was determined by voltammetric measurements with a graphite electrode [10].

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Differential pulse polarography (DPP) was used to study the Fe(III) and Ti(IV) complexes which exhibit reduction peaks at  $-0.09$  V and  $-0.32$  V *vs.* Ag/AgCl/3 M-KCl, respectively at pH 4.5 [11]. Simultaneous determination of Mo(VI), Ni(II), and V(V) in cement by DPP is described [12]. A rapid and selective differential pulse polarographic method is proposed for the microdetermination of Cr(VI) in cements [13]. Small amounts of Zn in cement were determined by thiazone—benzene extraction followed by stripping in phosphoric acid solution and A.C. polarographic determination [14]. The determination of trace amounts of Cd(II) in cement by A.C. polarography was studied [15]. Trace level voltammetric determination of Mn, Fe, and Cr in cement samples in the presence of each other was performed by differential pulse voltammetry [16]. Also Cr(VI) and Cu(II) were determined by cathodic differential pulse polarography [17].

In this work, the differential pulse stripping voltammetry has been used for the determination of Pb(II), Tl(I), Zn(II), and Sn(II) in cement and electrostatic precipitator dust samples.

## EXPERIMENTAL

All solutions were prepared with doubly distilled water.  $1.0 \text{ mmol dm}^{-3}$  stock standard solutions of metal ion (Cu, Pb, Tl) were prepared by dissolving the desirable amount of the appropriate salts in bidistilled water. Also  $\text{SnCl}_2$  ( $1.0 \text{ mmol}$ ) was dissolved in HCl ( $1 \text{ dm}^3$ ) to obtain a clear solution. A  $0.1 \text{ mmol dm}^{-3}$  solution of ammonium tartrate was prepared by dissolving the suitable amount of tartaric acid (Merck) in bidistilled water followed by addition of ammonium hydroxide to adjust the pH value at  $\approx 9.0$ . An NaOH (BDH analar) solution was prepared and well stored in a polypropylene container for some days to obtain a carbonate-free solution [18]. The required molarity was achieved by dilution from such solution then standardized against oxalic acid.

An EG and G (PAR) Model 264A voltammetric analyzer, PAR 303 static mercury drop electrode (SMDE), and a PAR 0089 X-Y recorder were used for the collection of experimental data and to obtain the voltammograms. A medium-size hanging mercury drop electrode was employed in connection with  $10 \text{ cm}^3$  volume. The polarographic cell PAR model K 0060 was fitted with an Ag/AgCl (saturated KCl) reference electrode, a platinum wire was used as an auxiliary electrode. A 305 magnetic stirrer was used and it was automatically controlled by the instrument. The following parameters were used in linear stripping technique: drop size (medium), scan rate  $100 \text{ mV s}^{-1}$ . The parameters selected to perform differential pulse stripping voltammetry (DPSV) techniques are the following: pulse amplitude ( $\Delta E$ )  $25 \text{ mV}$ , scan rate  $5 \text{ mV s}^{-1}$ , pulse duration  $1 \text{ s}$ . pH Measurements were carried out using Orion 601A precision research ionalyzer dig-

ital pH-meter, fitted with combined calomel and glass electrode.

## Procedure

The cement sample or electrostatic precipitator dust ( $10 \text{ g}$ ) was given in a  $100 \text{ cm}^3$  beaker.  $50 \text{ cm}^3$  of bidistilled water was added and then stirred for 2 h (water leach). The solution was filtered through a filter paper. The precipitate was washed two or three times by small portions of bidistilled water. The pH of the filtrate was adjusted to  $3.5\text{--}4.0$  by  $\text{HNO}_3$ . The filtrate was transferred to a  $100 \text{ cm}^3$  measuring flask and then diluted with bidistilled water to the mark.

Prior to getting reliable results during the analysis of cement and dust samples, experiments were done to optimize the volume needed for each metal ion. The amount of the sample solution taken in each run was varied from one element to another using trials and errors. This was due to the degree of the solubility of the different metal species in the water during the leaching process.

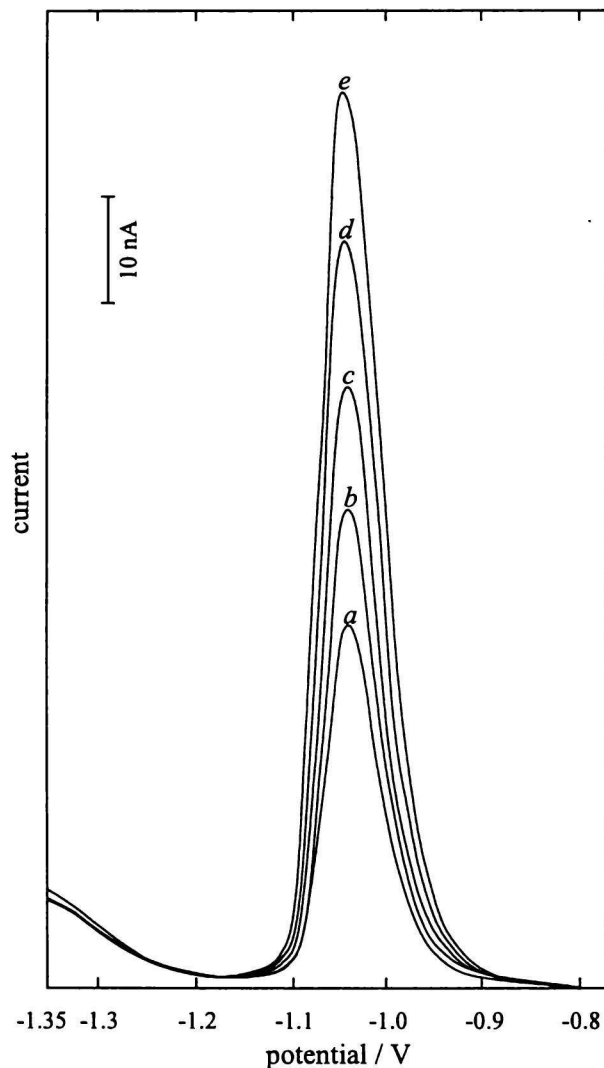
The sample solution and the supporting electrolyte were transferred into the cell and deaerated by passing nitrogen through for 16 min. The preconcentration potential was adjusted depending upon the experimental data obtained, and it was applied to the electrode for the selected time, while the solution was stirred with a magnet. The stirring was then stopped automatically depending on the deposition time and then 15 s as rest period (equilibrium time) was applied and then the voltammogram for a positive-going potential scan was recorded. Throughout this operation nitrogen was passed over the solution surface, all data were obtained at room temperature (air-conditioning ( $25 \pm 1$ ) $^\circ\text{C}$ ).

At the determination of Zn(II)  $5 \text{ cm}^3$  of the Portland cement sample solution was diluted with bidistilled water to  $10 \text{ cm}^3$ . The voltammogram was scanned in a rate of  $5 \text{ mV s}^{-1}$ ,  $\Delta E$   $25 \text{ mV}$  and pulse duration  $1 \text{ s}$  for initial potential  $-1.35 \text{ V}$  and the deposition time was fixed at  $30 \text{ s}$ .

At the determination of Pb(II) in a polarographic cell,  $0.8 \text{ cm}^3$  of Portland cement sample solution,  $0.01 \text{ M-NaOH}$ , and  $4 \times 10^{-3} \text{ M}$  ammonium tartrate were mixed in a  $10 \text{ cm}^3$  volume (pH  $\approx 11$ ). After a deposition time of  $180 \text{ s}$ , the voltammogram was scanned from  $-0.85 \text{ V}$  as initial potential.

At the determination of Zn(II) in a  $10 \text{ cm}^3$  volume cell,  $0.1 \text{ cm}^3$  of the filter dust sample solution was pipetted and the solution was diluted to  $10 \text{ cm}^3$  with bidistilled water. The voltammogram was scanned at the optimal conditions: initial potential  $-1.35 \text{ V}$ , final potential  $-0.75 \text{ V}$ , scan rate  $5 \text{ mV s}^{-1}$ ,  $\Delta E$   $25 \text{ mV}$ , pulse duration  $1 \text{ s}$ , pH  $\approx 4$ , deposition time  $10 \text{ s}$ .

At the determination of Sn(II)  $0.5 \text{ cm}^3$  volume of the dust solution was taken in a polarographic cell, then diluted to  $10 \text{ cm}^3$  with bidistilled water. The op-

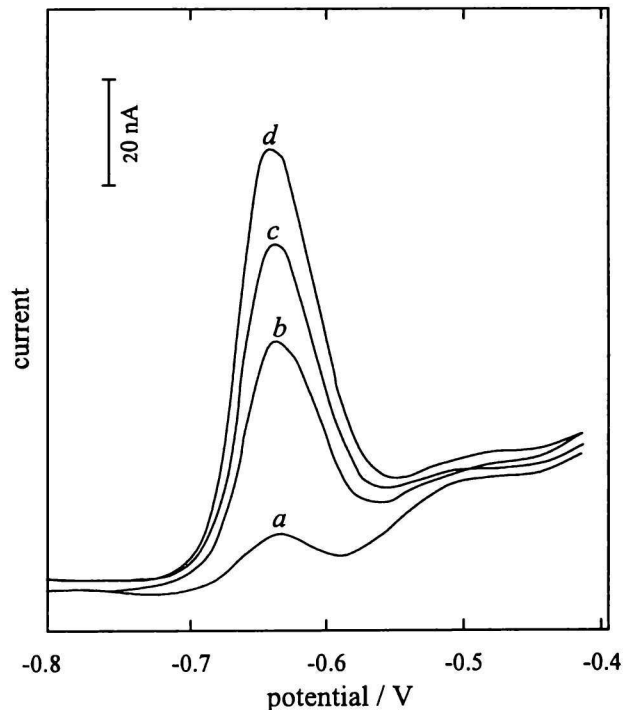


**Fig. 1.** DPASV for cement sample and different concentration of Zn(II) ions (pH 4) at accumulation time 30 s. a) Sample S; b) S +  $1 \times 10^{-7}$  M-Zn(II); c) S +  $2 \times 10^{-7}$  M-Zn(II); d) S +  $3 \times 10^{-7}$  M-Zn(II); e) S +  $4 \times 10^{-7}$  M-Zn(II).

timum conditions for the cathodic determination were: accumulation potential +0.05 V, accumulation time 15 s, pH  $\approx$  5.2, scan rate  $5 \text{ mV s}^{-1}$ , pulse duration 1 s.

## RESULTS AND DISCUSSION

At the determination of some trace elements in Portland cement by anodic differential pulse stripping voltammetry the Zn(II) peak was observed at  $-1.03 \text{ V}$ . The standard addition method was used and the voltammogram was shown in Fig. 1. A linear plot was constructed with a slope of  $150 \text{ nA}/10^{-7} \text{ M-Zn(II)}$ , standard deviation of 1.235, and correlation coefficient 0.995. The average content of the three replicates for Zn(II) ions in Portland cement was  $0.35 \text{ mg kg}^{-1}$ .



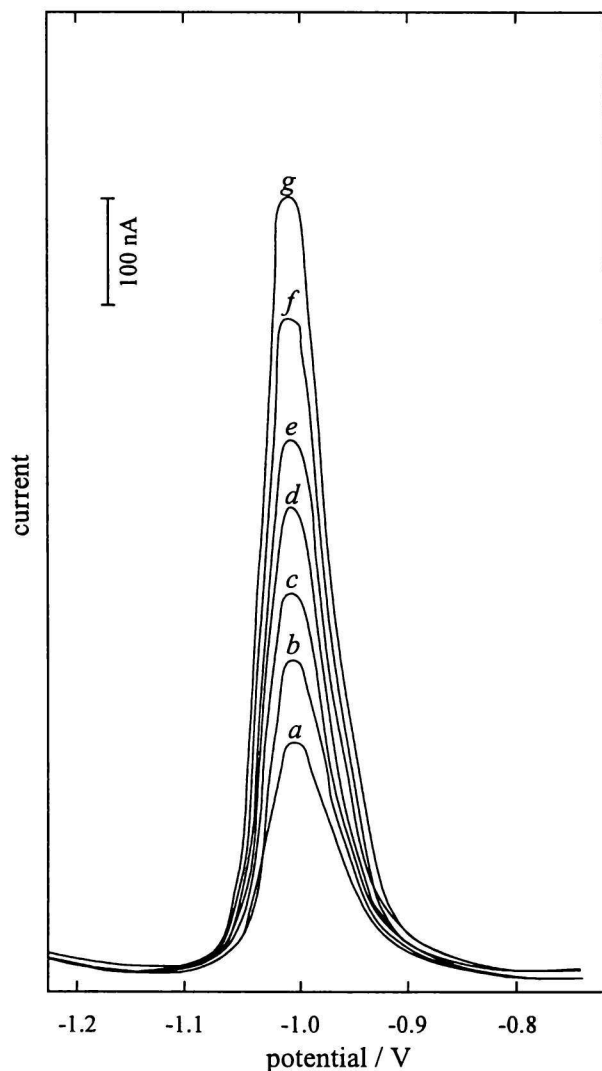
**Fig. 2.** DPASV for cement sample solution and different concentration of Pb(II) ions in  $0.01 \text{ M-NaOH}$  and  $4 \times 10^{-3} \text{ M ammonium tartrate}$  (pH 11) at accumulation time 120 s. a) Sample S; b) S +  $1 \times 10^{-8} \text{ M-Pb(II)}$ ; c) S +  $2 \times 10^{-8} \text{ M-Pb(II)}$ ; d) S +  $3 \times 10^{-8} \text{ M-Pb(II)}$ .

The peak of Pb(II) is observed at  $-0.63 \text{ V}$  using differential pulse anodic stripping voltammetry as shown in Fig. 2. The standard addition method was used giving a linear plot with a slope of  $7.5 \text{ nA}/10^{-8} \text{ M-Pb(II)}$ , standard deviation of 1.145, and correlation coefficient 0.997. The content of Pb(II) ion in Portland cement was  $0.2 \text{ mg kg}^{-1}$ .

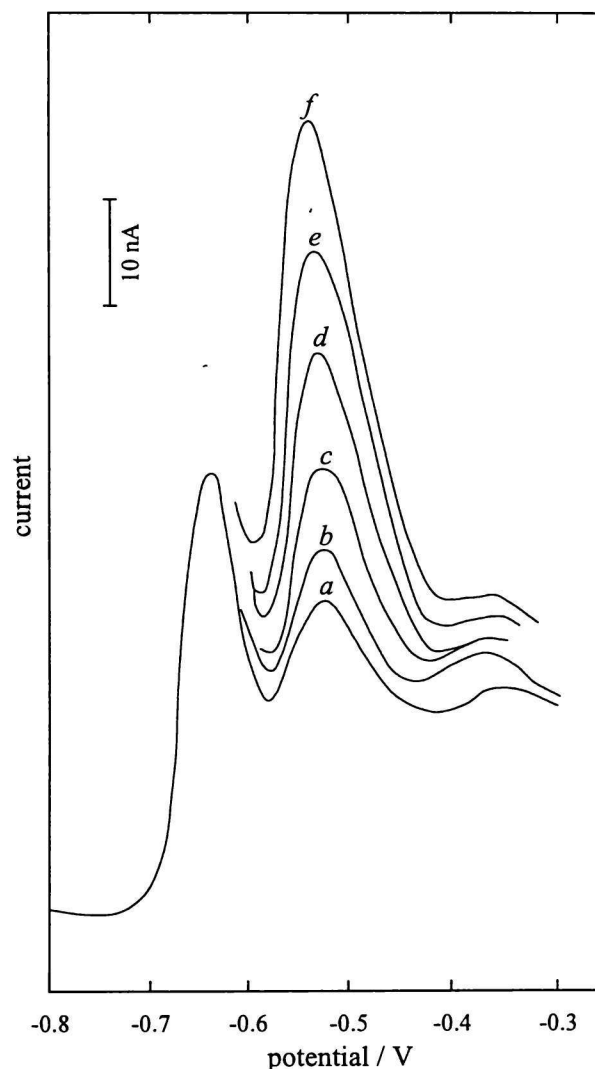
The electrostatic precipitated filter dust is one of the most important environmental problems in the cement industry. It has a harmful effect to workers health and to health of population near the industrial sites, and so many trials have been made to recycle this dust in cement-manufacturing process trying to overcome its hazardous effect. Thus it is important to know the heavy metals, which it may contain and which are the main cause of the problem.

From the anodic stripping voltammogram in the electrostatic precipitated dust the peak of the Zn(II) ion was observed at  $E_p = -1.0 \text{ V}$  (Fig. 3). The standard addition method was used for the Zn(II) determination where the content of the Zn(II) ion in the filtered dust was  $6.5 \text{ mg kg}^{-1}$ . The linear standard addition plot exhibits a slope of  $91 \text{ nA}/10^{-7} \text{ M-Zn(II)}$ , standard deviation of 1.46, and correlation coefficient 0.989.

In the previous studies it was mentioned that usually Tl(I) interferes with Pb(II) in the polarographic



**Fig. 3.** DPASV for dust sample and different concentration of Zn(II) ions (pH 4) at accumulation time 10 s and accumulation potential  $-1.35$  V. *a*) Sample S; *b*) S +  $1 \times 10^{-7}$  M-Zn(II); *c*) S +  $2 \times 10^{-7}$  M-Zn(II); *d*) S +  $3 \times 10^{-7}$  M-Zn(II); *e*) S +  $4 \times 10^{-7}$  M-Zn(II); *f*) S +  $5 \times 10^{-7}$  M-Zn(II); *g*) S +  $6 \times 10^{-7}$  M-Zn(II).



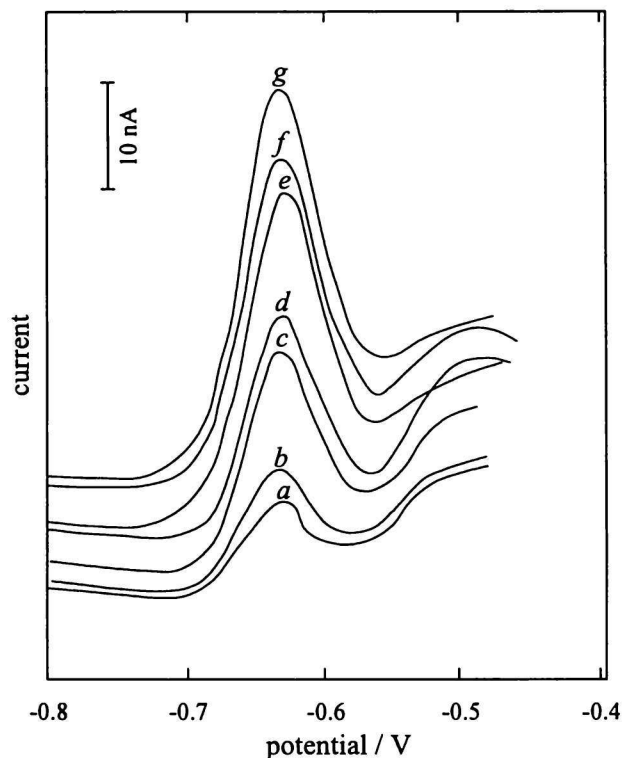
**Fig. 4.** DPASV for dust sample and different concentration of Tl(I) ions in 0.01 M-NaOH and  $4 \times 10^{-3}$  M ammonium tartrate (pH 11) at accumulation time 90 s. *a*) Sample S in the presence of  $3 \times 10^{-8}$  M-Pb(II); *b*) S +  $1 \times 10^{-8}$  M-Tl(I); *c*) S +  $2 \times 10^{-8}$  M-Tl(I); *d*) S +  $3 \times 10^{-8}$  M-Tl(I); *e*) S +  $4 \times 10^{-8}$  M-Tl(I); *f*) S +  $5 \times 10^{-8}$  M-Tl(I).

determination [19]. In supporting electrolytes which do not complex lead ion the thallium and lead waves coincide, but by employing a sodium or potassium hydroxide supporting electrolyte to shift the half-wave potential of lead, thallium can easily be determined in the presence of lead [20]. In the case of the electrostatic precipitator dust, the separation of the reduction peaks of both metal ions and simultaneous determination of Pb(II) and Tl(I) was studied.  $0.8 \text{ cm}^3$  of the dust sample solution was transferred in  $4 \times 10^{-3}$  M ammonium tartrate and 0.01 M-NaOH (pH  $\approx 11$ ) and then the solution was transferred in a  $10 \text{ cm}^3$  volume polarographic cell. The cell was degassed, then the voltammogram was recorded. The Tl(I) peak was

observed at  $-0.53$  V (Fig. 4) while the Pb(II) peak at  $-0.63$  V. The optimum conditions: initial potential  $-0.8$  V,  $\Delta E = 25$  mV, scan rate  $5 \text{ mV s}^{-1}$ . The lead was determined using deposition time 60 s, while that of Tl(I) was 90 s (Fig. 5). The content of Pb(II) in the filter dust was  $0.2 \text{ mg kg}^{-1}$ , while the content of Tl(I) in the filter dust was  $0.2 \text{ mg kg}^{-1}$ .

Tin in the electrostatic precipitator dust was determined by cathodic and anodic differential pulse stripping voltammetry (Fig. 6). The standard addition method was used. The content of Sn(II) was  $15.4 \text{ mg kg}^{-1}$ .

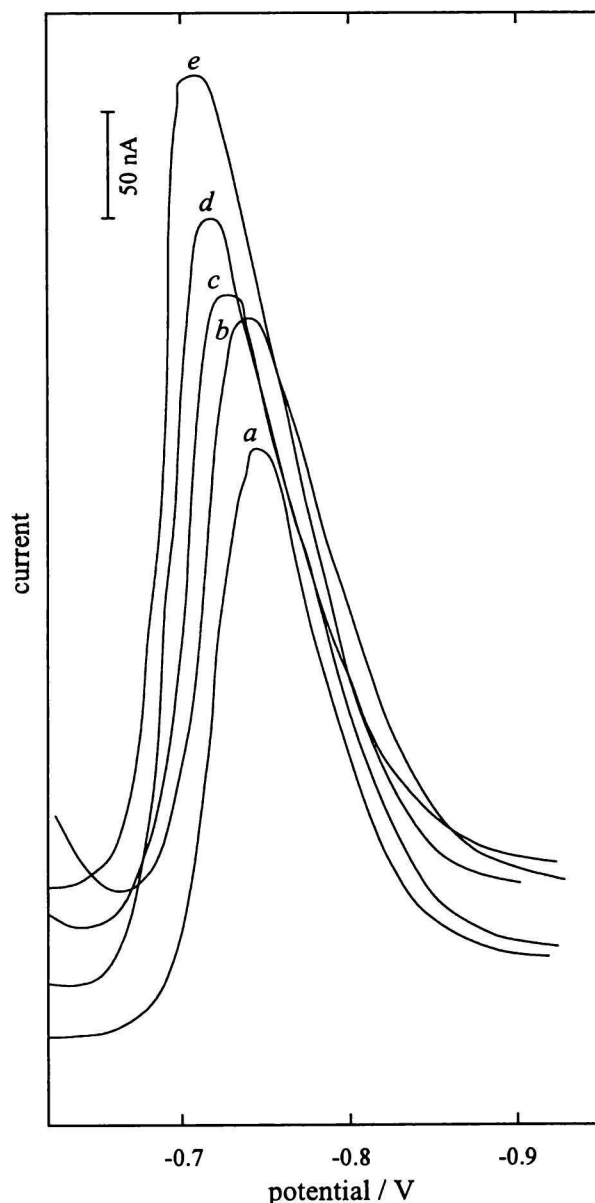
On scanning in the positive direction (anodic stripping voltammetry), Sn(II) was also determined using



**Fig. 5.** DPASV for dust sample and different concentration of Pb(II) ions in 0.01 M-NaOH and  $4 \times 10^{-3}$  M ammonium tartrate (pH 11) at accumulation time 60 s. a) Sample S; b) S +  $0.5 \times 10^{-8}$  M-Pb(II); c) S +  $1 \times 10^{-8}$  M-Pb(II); d) S +  $1.5 \times 10^{-8}$  M-Pb(II); e) S +  $2 \times 10^{-8}$  M-Pb(II); f) S +  $2.5 \times 10^{-8}$  M-Pb(II); g) S +  $3 \times 10^{-8}$  M-Pb(II).

initial potential  $-1.35$  V and accumulation time 15 s. The standard addition method was used for the determination of Sn(II) in the dust sample. The linear plot was constructed giving a straight line with a slope of  $13.3 \text{ nA}/10^{-7} \text{ M-Sn(II)}$ , standard deviation of 1.46, and correlation coefficient 0.911. The content of Sn(II) was  $15.5 \text{ mg kg}^{-1}$ . However, it was observed that spikes of Sn(II) bring shifts in the peak potential toward more positive value (Fig. 7), either cathodically or anodically, this is due to lowering in pH of the solution since Sn(II) standard solution is containing acid.

It is worthy to mention that some trials were done to detect either Sn(II) or Tl(I) in the cement samples using different supporting electrolytes but no promising results were obtained. This may be due to the insufficient solubility of Tl(I) compounds (if any are present) in water leach samples. The same is true for Sn(II). However, most Tl(I) compounds have high volatility, so this element is not incorporated in the clinker during the clinkerization process in the cement industry [21].



**Fig. 6.** DPASV for dust sample and different concentration of Sn(II) ions (pH 2.5) at accumulation time 15 s, accumulation potential  $+0.05$  V. a) Sample S; b) S +  $1 \times 10^{-7}$  M-Sn(II); c) S +  $2 \times 10^{-7}$  M-Sn(II); d) S +  $3 \times 10^{-7}$  M-Sn(II); e) S +  $4 \times 10^{-7}$  M-Sn(II).

## CONCLUSION

Building materials such as Portland cement and its by-products when treated with water erode slowly and release their components into the environment. Consequently the levels of toxic metals in cement should be known to assess the risk of pollution. There is a critical need for cement reference materials with accurately characterized analyte levels, especially for trace elements. This will allow analysts to verify the accuracy of their methods.

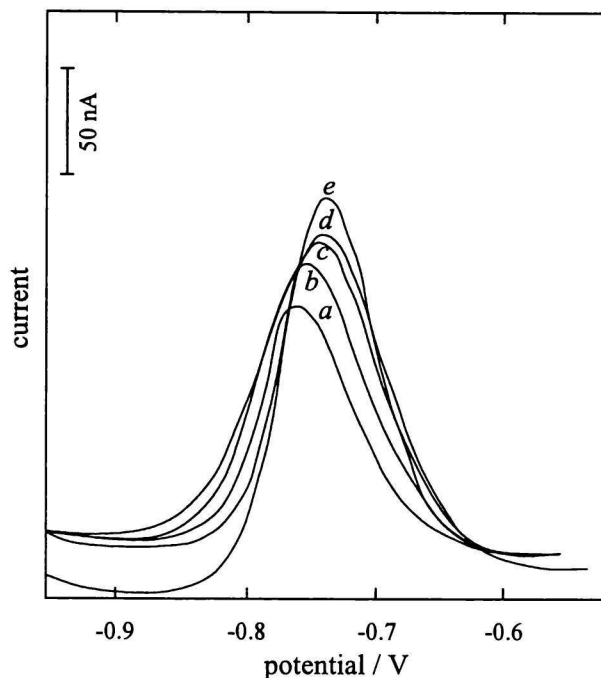


Fig. 7. DPASV for dust sample and different concentration of Sn(II) ions (pH 2.5) at accumulation time 15 s, accumulation potential  $-1.35$  V. a) Sample S; b) S +  $1 \times 10^{-7}$  M-Sn(II); c) S +  $3 \times 10^{-7}$  M-Sn(II); d) S +  $4 \times 10^{-7}$  M-Sn(II); e) S +  $5 \times 10^{-7}$  M-Sn(II).

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