

# Voltammetric Determination of Arsenic in Zinc Oxide Used as a Feed Additive

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## Abstract

Cathodic stripping voltammetry at a hanging mercury drop electrode was applied for determination of arsenic in samples of zinc oxide intended for use as a feed additive. The determinations were carried out in acidic medium in the presence of Cu(II). The As(V) was prereduced to As(III) by potassium iodide and ascorbic acid at ambient temperature. The detection limit was  $0.1 \text{ ng mL}^{-1}$ . The feasibility of simultaneous determination of arsenic and cadmium in such analysis was also shown. The electrothermal atomic absorption spectrometry was used as a reference method.

**Keywords:** Voltammetry, Arsenic

## 1. Introduction

Zinc as an enzyme constituent or an enzyme activating component participates in metabolism of proteins and carbohydrates. Zinc deficiency among animals mainly caused by its incomplete bio-availability from nutriment and feed results in: osseous system disorders, reproductivity disturbances and anomalous hair or wool growth. Besides, biochemical changes in blood composition often accompanied by leukopenia and arteriosclerosis occur. Zinc oxide is added to feed in order to meet zinc requirements in animals. Before addition, the content of toxic elements such as lead, cadmium and arsenic in the zinc oxide has to be analytically determined because these elements usually are presented in materials used in zinc and zinc oxide production.

Various analytical methods are used for arsenic determination in environmental samples and among them are also electroanalytical methods. For arsenic determination in drinking water samples DC polarography was used [1] and in alloy steels pulse polarography was used [2].

Anodic stripping voltammetry at gold electrode was applied in arsenic determination in seawater and in electrolytic copper [3–5]. The same technique but employing graphite electrode was used in seawater [6, 7]. Arsenic determination can also be carried out with use of platinum electrode [3]. Cathodic stripping voltammetry (CSV) determinations of preconcentrated arsenic on HMDE are described in literature, too. Holak developed a procedure for arsenic determination in acidic solution containing Se(IV) [8]. Determination of arsenic was also carried out by CSV on HMDE in presence of copper(II) [9–11]. Zima et al. determined arsenic by CSV preceded by a combination of electrolytic deposition as As(Hg) and reoxidation with adsorptive deposition of a complex of arsenic(III) with pyrrolidine dithiocarbamate (PDC) on the HMDE in weakly acidic conditions [12].

Various reducing agents have been investigated to reduce arsenic(V) to arsenic(III) prior to its determination by voltammetry including  $\text{Na}_2\text{SO}_3$  [3],  $\text{N}_2\text{H}_4/\text{HCl}/\text{HBr}$  [10],  $\text{NaBr}/\text{N}_2\text{H}_4/\text{H}_2\text{SO}_4$  [8], gaseous  $\text{SO}_2$  [4] and KI [11]. Although arsenic(V) is considered to be electrochemically inactive, it can be determined directly by potentiometric and constant-current stripping analysis without prior chemical reduction to arsenic(III) in strongly acidic solution on a gold electrode provided that extremely low reduction potentials are used [13]. Moreover arsenic(V) becomes electroactive when phenols, such as catechol [14, 15] and pyrogallol [15], or aliphatic polyhydroxy compounds, such as D-mannitol, are added to

perchloric acid solutions of arsenic(V) [16]. Under these conditions arsenic(V) can be determined by polarographic methods.

In this article the voltammetric method of arsenic determination in technical zinc oxide used as feed additive is described. Stripping voltammetry based on the peak of cathodic reduction of preconcentrated arsenic on HMDE in the presence of Cu(II) was applied.

To avoid heating the solution during the reduction step and to shorten the reduction process a solution of potassium iodide and ascorbic acid was used as a reducing agent. This agent is often used for arsenic(V) to arsenic(III) reduction in hydride-generation technique to improve the sensitivity of AAS determinations [17, 18].

## 2. Experimental

### 2.1. Reagents

$\text{HNO}_3$  ( $d = 1.40 \text{ g mL}^{-1}$ ),  $\text{HCl}$  ( $d = 1.15 \text{ g mL}^{-1}$ ),  $\text{H}_2\text{SO}_4$  ( $d = 1.84 \text{ g mL}^{-1}$ ) Suprapur (Merck). Standard solutions of As(III), As(V), Cd(II), Cu(II) containing  $1 \text{ mg mL}^{-1}$  were prepared from ampoules Titrisol (Merck); KI, ascorbic acid,  $\text{H}_2\text{O}_2$  were of analytical grade (POCh Gliwice, Poland). All solutions were prepared using Milli-Q water.

### 2.2. Apparatus

Voltammograms were obtained using a Princeton Applied Research 264A Polarographic Analyzer equipped with an X-Y recorder (RE 0150 PAR) and a following electrode system: HMDE as a working electrode, saturated Ag/AgCl as a reference electrode and Pt-wire as an auxiliary electrode. Determinations were carried out in a quartz voltammetric cell.

### 2.3. Procedure

For the determination of arsenic content in zinc oxide approximately 1 g of analyzed material was weighted and transferred into a beaker. Then 5 mL of  $\text{HNO}_3$  (conc.) and 2 mL of 30 %  $\text{H}_2\text{O}_2$  were added and the mixture was heated under cover for 20 min. After complete digestion, the solution cooled down to the ambient temperature was transferred into a 50 mL volumetric flask and made up to the mark. Next 200  $\mu\text{L}$  of the sample solution

was pipetted into a voltammetric cell where 200  $\mu\text{L}$  of hot  $\text{H}_2\text{SO}_4$  (conc.) were added. After cooling down, 200  $\mu\text{L}$  of  $\text{HCl}$  (conc.) and 100  $\mu\text{L}$  of 10 % solution of potassium iodide and ascorbic acid were added and the mixture was left for 10 min at ambient temperature. Then 9 mL of water, 50  $\mu\text{L}$  of 1  $\text{g mL}^{-1}$  copper(II) solution and 1 mL of  $\text{HCl}$  (conc.) were added to reach 1 M  $\text{HCl}$  concentration in the final solution.

The solution was purged with argon gas for 10 min. The preconcentration was carried out at the potential of  $-0.42\text{ V}$  in a stirred solution for 120 s. After the resting time of 15 s the voltammetric curves of cathodic reduction of arsenic were recorded in the potential range from  $-0.42$  to  $-0.90\text{ V}$  using differential pulse technique with scan rate  $10\text{ mV s}^{-1}$  and amplitude  $50\text{ mV}$ .

For quantitative determinations the double standard addition method was used.

### 3. Results and Discussion

In the first stage of experiments the use of potassium iodide and ascorbic acid for arsenic(V) reduction was investigated. It was checked whether the chemical reduction of arsenic(V) to arsenic(III) was complete and whether the presence of the reductants and the products of their oxidation influenced the analytical signal. The reduction was found to be quantitative after 10 min at ambient temperature and the examination of the recorded voltammetric curves showed no interferences on the signal of reduction of arsenic (Fig. 1).

The use of potassium iodide as a reducing agent was reported by Eguiarte et al. They applied CSV at HMDE for arsenic determination in soils in strongly acidic solution (3.8 M  $\text{HCl}$ ) with addition of  $\text{NaHCO}_3$  in presence of  $10\text{ }\mu\text{g mL}^{-1}$  of copper [11].

To avoid such aggressive conditions, based on the investigation of the influence of  $\text{HCl}$  concentration on the peak current, in this article determinations were carried out in 1 M  $\text{HCl}$  solution with good results. Yet for digestion of zinc oxide nitric acid was used and to remove nitrate ions from solution, before the reduction of arsenic(V) to arsenic(III), hot  $\text{H}_2\text{SO}_4$  (conc.) was added. Therefore

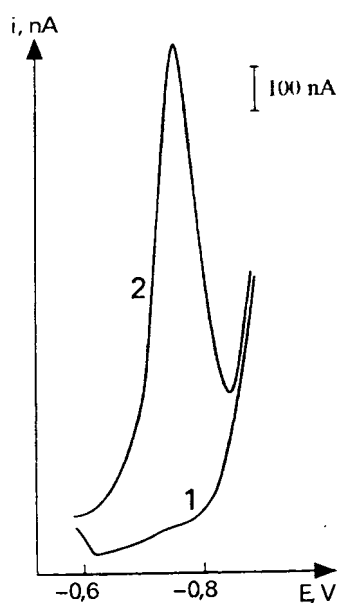


Fig. 1. DPCV curves of As at HMDE. Deposition potential  $-0.42\text{ V}$ , deposition time 120 s, scan rate  $10\text{ mV/s}$ , ampl.  $50\text{ mV}$ , clock time  $0.5\text{ s}$ . 1) supporting electrolyte: 1 M  $\text{HCl}$  and  $5\text{ }\mu\text{g mL}^{-1}$   $\text{Cu(II)}$ , 2) as 1 + 2  $\text{ng mL}^{-1}$  As.

the resulting mixture of  $\text{HCl}$  and  $\text{H}_2\text{SO}_4$  was taken as the supporting electrolyte.

As arsenic cannot be determined directly at a mercury electrode because of its low solubility in mercury to achieve good results the determination is carried out in the presence of copper(II) like in the previous work [9–11]. The preconcentration on the electrode during electroreduction process is based on formation of an intermetallic As-Cu compound. The investigation of the effect of copper concentration on the peak current shows that addition of copper causes the increase of the arsenic peak current up to  $7\text{ }\mu\text{g mL}^{-1}$  of copper. Although at higher concentration of copper the signal increases, it is split into two peaks and is shifted towards more negative potentials (Fig. 2). According Sadana this can be caused by formation of another compound of unknown stoichiometry [10]. Whereas the concentration of copper(II)  $4\text{--}6\text{ }\mu\text{g mL}^{-1}$  in the analyzed solution yields well-shaped arsenic reduction signals at  $-0.72\text{ V}$ . That is the reason why the investigations described in this article were carried out in a solution containing  $5\text{ }\mu\text{g mL}^{-1}$  of copper(II).

The influence of the preconcentration potential and preconcentration time on analytical signal was studied. Best results were reached using the preconcentration potential of  $-0.42\text{ V}$  with the preconcentration time less than 5 min. The peak current was found to increase with accumulation time up to 5 min. If preconcentration time was above 5 min. changes in the peak character were observed, as for high copper concentration.

The sample preparation step consists of digestion of analysed material in an  $\text{HNO}_3/\text{H}_2\text{O}_2$  mixture. To inspect this analysis step and to control the arsenic losses during heating several 1 g samples of zinc oxide with arsenic content below detection limit were simultaneously digested. They were spiked respectively with: 5, 10 and  $50\text{ }\mu\text{g}$  of As(V). Then they were analyzed according to the described procedure. Recovery close to 100 % of spiked amount of arsenic was found (Table 1).

From the conducted experiments it follows that the arsenic determination can be carried out in the presence of large amounts of zinc, in the presence of 100-fold excess of lead and 600-fold excess of cadmium which are also voltammetrically monitored in zinc oxide. Beside the described method allows simultaneous determination by standard addition method of arsenic and cadmium (Fig. 3). In the zinc oxide sample containing  $43 \pm 3\text{ }\mu\text{g/g}$  of arsenic the cadmium content  $650 \pm 15\text{ }\mu\text{g/g}$  was found.

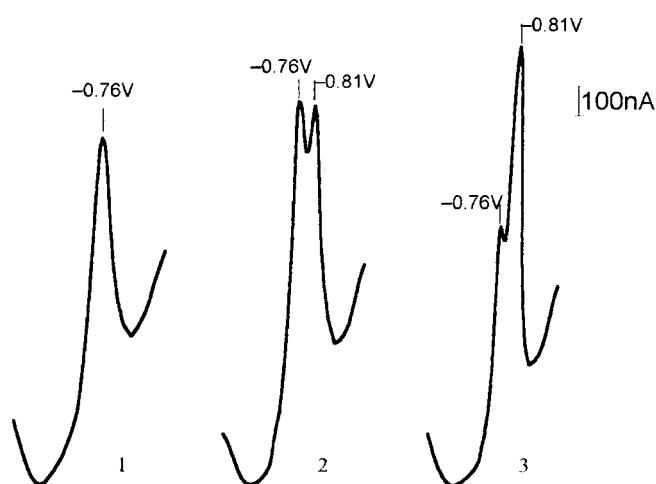
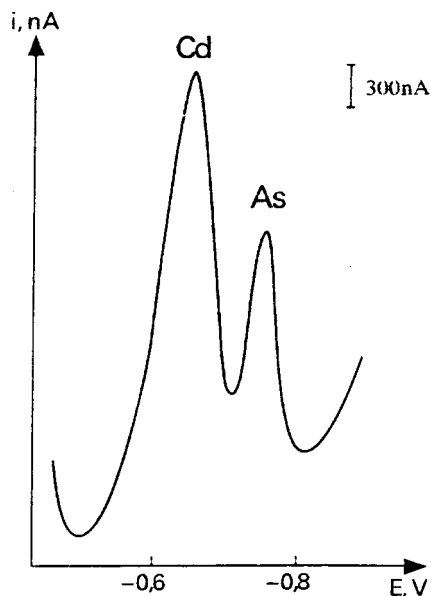


Fig. 2. The influence of Cu concentration on the peak character of As at HMDE. Conditions as in Figure 1. Concentration of  $\text{HCl}$  1 M, concentration of As  $2\text{ ng mL}^{-1}$ . 1)  $5\text{ }\mu\text{g mL}^{-1}$   $\text{Cu(II)}$ ; 2)  $7\text{ }\mu\text{g mL}^{-1}$   $\text{Cu(II)}$ ; 3)  $8\text{ }\mu\text{g mL}^{-1}$   $\text{Cu(II)}$ .

Table 1. Recovery of As for the digestion step ( $n = 3$ ).

Added amount [ $\mu\text{g}$ ]	Found amount [ $\mu\text{g}$ ]	Recovery [%]
5.0	$4.8 \pm 0.2$	96
10.0	$9.8 \pm 0.5$	98
50.0	$53 \pm 2$	105


 Fig. 3. DP voltammetric curves of As and Cd in zinc oxide sample. Voltammetric conditions as in Figure 1. As concentration  $4 \text{ ng mL}^{-1}$ , Cd concentration  $800 \text{ ng mL}^{-1}$ .

Under these conditions determination of trace amounts of arsenic at levels much lower than the limits found in regulations for feed preparations ( $40 \mu\text{g g}^{-1}$ ) is possible [19].

The RSD value at  $n = 6$  in a material with relatively high arsenic content ( $46 \mu\text{g g}^{-1}$ ) was found to be 7%.

For all determinations the arsenic content in corresponding blanks was checked. The arsenic signal could not be seen in spite of long preconcentration times. The arsenic content in the blank solution was estimated below  $0.5 \mu\text{g g}^{-1}$ .

 Table 2. Results of arsenic content determinations in technical zinc oxide used as feed additive. Results are expressed as a mean  $\pm$  SD.

Sample number	$n$	As content [ $\mu\text{g/g}$ ] (by CSV method)	As content [ $\mu\text{g/g}$ ] (by GFAAS method)
1	6	$43 \pm 3$	$46 \pm 3$ ( $n = 8$ )
2	3	$14 \pm 2$	—
3	2	6	—

Electrothermal atomic absorption spectrometry (with  $\text{NiSO}_4$  as a modifier) was used as a reference method. Double standard additions method was applied. The results of arsenic determinations in samples of zinc oxide are presented in Table 2.

## 4. Acknowledgement

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