

Voltammetric analysis of selected toxic inorganic substances in air and water

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Abstract: - Voltammetric methods represent an independent alternative besides other procedures in use, such as, e.g., spectrophotometric or separation methods, and can be perceived as their useful supplement. The aim of this paper was suggested suitable methods of determination of selected toxic inorganic substances. The results of this research show a new approach to the problem of pollutants in environment, especially in air or water. Arsenic, mercury and thalium were studied in this paper.

Key-Words: - arsenic, thalium, mercury, voltammetry

1 Introduction

The present-day voltammetric methods are a follow-up to the invention of a Czech chemist Jaroslav Heyrovský, who as early as 1922 invented an analytical method – excellent at that time – which made it possible to determine various chemical substances on the basis of measurement of electrical current flowing through a drop of mercury. It was not until 1959, when the invention of polarographic analysis (as the method was later named) brought Nobel prize to Prof. Heyrovský, and a number of chemists dealing with this method and its modern modifications regard it as Czech national treasure. In 1960s, the significance of classic polarography decreased, because its sensitivity and selectivity ceased to satisfy the requirements of praxis, and the method was replaced with spectrophotometric and chromatographic procedures. As early as at that time, there began to appear several papers by Barker [1] in England and by Osteryoung and Parry [2] in USA; these scientists were instrumental in later revival of polarographic analysis, namely by elimination of the capacity current, which limited the sensitivity of classic polarography; developed were pulse voltammetric techniques, which made it possible to determine concentrations of substances as low as 10^{-7} mol.l⁻¹, and techniques making use of accumulation of analyzed substance on the surface of working electrode down to the concentrations of 10^{-10} or 10^{-12} mol.l⁻¹. At present, it is possible to determine all elements across the periodic table, and there also exist applications in the area of analysis

of organic compounds or inorganic anions. As compared with chromatographs and spectrophotometers, voltammetric analyzers are cheaper and can be arranged for applications as portable instruments in fieldwork.

All voltammetric techniques are based on measurements of dependence of current on inserted voltage in an electrode system composed of a polarized indication electrode, non-polarized reference electrode and, as the case may be, indifferent auxiliary electrode in the case of three-electrode connection.

The success rate of analyses depends on the selection of working electrodes, which can be classified as mercury electrodes and electrodes made from solid materials. The mercury electrodes which, in the case of voltammetric analysis, offer almost ideally homogeneous, easily renewable surface, have at present been replaced (because of the toxicity of mercury vapors) by Silver Solid Amalgam Electrode (AgSAE), which is much more gentle to environment in which analysts work, and can be used in the form of several modifications. The surface of AgSAE can be modified by means of mercury film (MF-AgSAE – Mercury Film-modified Silver Solid Amalgam Electrode) or meniscus (m-AgSAE – Meniscus Modified Silver Solid Amalgam Electrode), or it is possible to work with a polished electrode in the absence of mercury (p-AgSAE - Polished Silver Solid Amalgam Electrode). AgSAE represents (like mercury electrodes) a versatile electrode enabling determination of a number of both organic and

inorganic substances [3]. AgSAE combines advantages of mercury electrodes and solid working electrodes. Its largest advantage is the electrochemical properties that are close to those of mercury, especially the high hydrogen voltage, and they can easily be regenerated. Like the solid electrode, they also exhibit very good wear resistance thus enabling measurements in flow-type systems and field-research analyzers.

Application of solid electrodes made from such materials as carbon, platinum, gold, diamond etc. is connected with a number of problems in voltammetric analysis. The surface of these electrodes is usually non-homogeneous and, during analysis, it can adsorb both the substance from the solution and products of electrode reactions. These facts cause irreproducibility of results in repeated measurements. The abovementioned phenomena can be suppressed or completely eliminated by applying suitable potentials, both from the negative and the positive areas. These electrodes have the advantage of being applicable to monitoring of oxidation processes at considerably positive potentials; thus, they can be used, e.g., for analyses of phenols, amines, sulfur compounds, or some functionalized aromatic hydrocarbons. A detailed description of application possibilities of voltammetry is summarized, e.g., in the database POLAVOLT [4].

2 Experimental

2.1 Instrumentation

Electrochemical measurements were carried out using electrochemical analyzer EP 100 (HSC Service, Bratislava, Slovakia). A HMDE or a gold rotating disc electrode (AuRDE) with the rotating speed 1500 revolutions per minute served as the working electrode (HSC Service, Slovakia), saturated Ag/AgCl was used as the reference and the platinum wire as the auxiliary electrode (both from Monokrystaly, Turnov, Czech Republic).

3 Results and Discussion

When planning a method for solving a particular analytical problem, it is necessary to choose a suitable working electrode, technique (the most frequently used method is differential pulse voltammetry and, for lower concentrations, dissolution voltammetry), suitable parameters for preparatory treatment of sample and subsequent

analysis, and suitable method of evaluation – peak height, peak area, current magnitude, wave height, etc.

The applications of voltammetric methods suffer from the disadvantage of their low selectivity and considerable influence of the matrix, especially in the case of analyses of complicated samples. When developing the method, one has to pay great attention to accompanying compounds, choice of the basic electrolyte in which the determination is realized, and especially to elimination of interfering components.

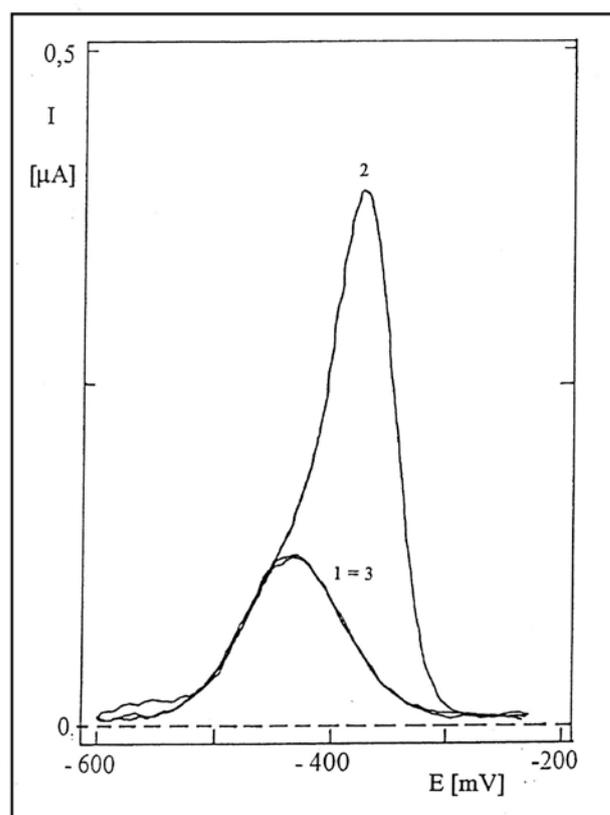


Fig. 1 Voltammograms of thallium after accumulation on HMDE before and after masking of lead. Curve 1 - $2 \times 10^{-6} \text{ mol.l}^{-1} \text{ Tl}^{+}$; Curve 2 - $2 \times 10^{-6} \text{ mol.l}^{-1} \text{ Tl}^{+}$ and $5 \times 10^{-6} \text{ mol.l}^{-1} \text{ Pb}^{2+}$; Curve 3 - $2 \times 10^{-6} \text{ mol.l}^{-1} \text{ Tl}^{+}$ and $5 \times 10^{-6} \text{ mol.l}^{-1} \text{ Pb}^{2+}$ and 0.01 mol.l^{-1} Chelaton 3.

For example, in the voltammetric determination of thallium [5], one can especially expect interfering effects of Pb^{2+} ions, which usually accompany thallium in real samples, and whose half-wave potential is found near $E_{1/2}$ of Tl^{+} ions (see Fig. 1). If Chelaton 3 is added into the basic electrolyte (acetate of citrate buffer), the interfering bivalent metal ions are masked by formation of stable

complexes, and the determination of thallium provides correct results even in very complex matrices, such as acid extracts of soot, fly ash, or fly ash from glass furnaces. An example of voltammetric curves obtained by practical analysis of soot from a local fire chamber is presented in Fig. 2.

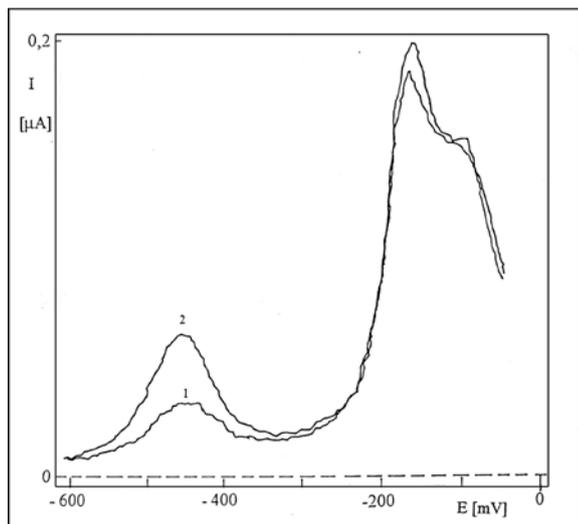


Fig. 2 Voltammograms of thallium in the leachate of soot with a time of accumulation 6 minute after masking of lead. Supporting electrolyte: $0,01 \text{ mol.l}^{-1}$ citrate buffer (pH 5.5); $0,001 \text{ mol.l}^{-1}$ Chelaton 3; potential of accumulation: -600 mV ; Curve 1 - Tl^+ in sample; Curve 2 – standard addition (204 ng Tl^+).

Voltammetry also enables speciation analysis; for example, determination of individual forms of arsenic, which significantly differ in toxicity.

In waters, arsenic is usually present as As^{5+} , but also in the instable form of As^{3+} , and it is frequently bonded to organic compounds. The determination of trivalent arsenic can make use of its electrochemical concentrating on mercury drop in the presence of cupric ions, during which copper at first forms amalgam on the surface of the electrode, and the amalgam then reacts with arsenic and forms an intermetallic compound with stoichiometry Cu_3As_2 . The voltammetric determination subsequently uses cathode reduction giving AsH_3 . However, this method as it is published by R. S. Sadana [6] does not provide reliable results. It was found that the results strongly depend upon copper concentration in the solution. Therefore, large attention must be paid to the preparatory phase of analysis, too [7].

Before the analysis proper, pentavalent arsenic has to be reduced to trivalent arsenic by action of

potassium iodide in acidic medium after elimination of oxygen by introducing argon. The method can be applied to samples of mineral waters, fly ash from power stations, or urine from workers in glass industry. Examples of measured curves of these practical samples are presented in Fig. 3.

The elaborated method provides results analogous to those obtained from spectral analysis methods (AAS, ICP, ICP-MS); however, the acquisition costs of voltammetric analyzer are incomparably lower (ca 15-times).

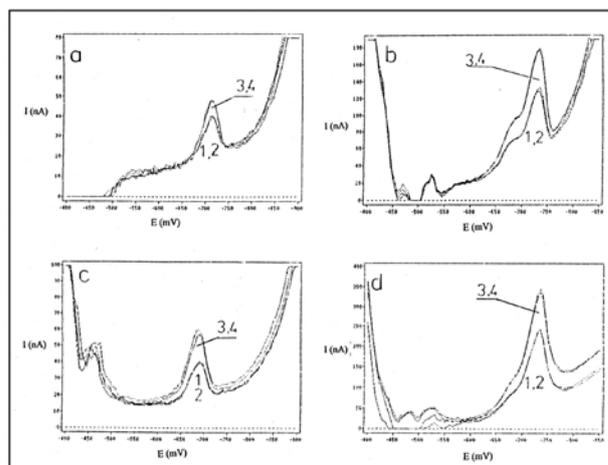


Fig. 3 Voltammograms of arsenic in different selected samples. Supporting electrolyte: $3,5 \text{ mol.l}^{-1}$ HCl, 0,25 % hydrazine hydrochloride, $1,5 \times 10^{-3}$ Cu^{2+} ; tome of accumulation: 90 or 180 s; potential of accumulation: -400 mV ; conditions of As^{5+} reduction: $5,8 \text{ mol.l}^{-1}$ HCl, 1,8 % KCl, under inert atmosphere of Ar; a – Bílinská kyselka, b – Ida, c – leachate of stabilisate, d – human urine; 1,2 – sample; 3,4 – standard addition As^{3+} .

Serious ecological problems include – inter alia – the presence of mercury in components of environment. Mercury has a strong accumulation ability. It accumulates in sediments of water reservoirs, rivers, aquatic fauna and flora, and it can pass over to food chain. Its determination can make use of voltammetric methods using solid indication electrodes. Good results were obtained with application of gold rotation disc electrode Au-RDE. In the concentrating step, mercury can be accumulated on the surface of the electrode and then determined by means of anodic oxidation in acidic medium of $0,5 \text{ mol.l}^{-1}$ HCl. Heavily polluted waste waters can contain substances that interfere with direct determination of Hg, or make it completely impossible. For handling such samples, a method of Hg separation has been suggested [8]. The

separation is based on reduction of Hg^{2+} ions to Hg^0 with an SnCl_2 solution. The elementary mercury is then stripped away with air and trapped on a gold electrode. After the separation is finished, the electrode is connected into electrochemical analyzer, and Hg is anodically dissolved in the medium of pure basic electrolyte. The obtained recording is then used for quantitative evaluation. Examples of such curves are presented in Fig. 4.

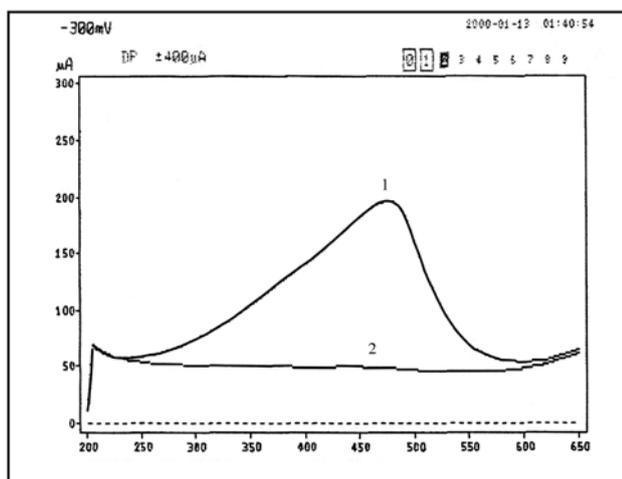


Fig. 4 Voltammograms of mercury at the gold disc electrode. Hg^{2+} concentration: $2.19 \times 10^{-7} \text{ mol.l}^{-1}$; Supporting electrolyte: $0.5 \text{ mol.l}^{-1} \text{ HCl}$; analyzed: $43.85 \text{ } \mu\text{g Hg/l}$; reducing agent: 2 % SnCl_2 (10 ml); $E_{in} +200 \text{ mV}$; $E_{fin} +650 \text{ mV}$; $v 25 \text{ mV.s}^{-1}$; pulse amplitude: 80 mV; Curve 1 – anodic oxidation of transferred mercury; Curve 2 – controlled anodic oxidation of transmission electrode.

The results of this research show a new approach to the problem of pollutants in environment in comparison with other methods.

4 Conclusion

In conclusion, it can be stated that voltammetric methods offer broad applications in the area of trace analysis of inorganic pollutants. The fact that the frequency of application of these techniques in contemporary analytical laboratories corresponding with their real possibilities is caused, in the present author's opinion, by small promotion of these methods.

These methods have the advantage of possible determination within a broad concentration range, both in organic and in inorganic matrices. Besides the total amount, it is also possible to determine the individual forms of elements. On the other hand, it has to be admitted that polarographic and

voltammetric methods will never attain the selectivity of separation methods and, therefore, they are not suitable for analysis of multi-component mixtures.

Voltammetric methods represent an independent alternative besides other procedures in use, such as, e.g., spectrophotometric or separation methods, and can be perceived as their useful supplement.

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