

SELECTED ELECTROANALYTICAL DETERMINATION METHODS OF ZINC IN MATERIALS OF DIFFERENT ORIGINS

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Abstract

Zinc is a naturally wide spread element, which generally finds its use in industry but also in numerous pharmaceutical, cosmetic and stomatology materials. Taking into consideration its frequent occurrence (in almost all biological materials) and its low quantities, a good choice of analytical method for zinc assay is a necessity. Apart from spectrophotometric methods – especially AAS (Atomic Absorption Spectrometry) which is a method of choice for zinc determination, also electroanalytical methods are used. Most frequently ASV (Anodic Stripping Voltammetry) or Polarography is applied. Despite the need of samples digestion electrochemical methods offer a price convenient method for determination of zinc, even in trace amounts (ppt – parts per trillion). Currently there is also new information about ion selective electrodes suitable for zinc assay.

Keywords: zinc assay, electroanalytical methods, anodic stripping voltammetry, polarography

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Introduction

Beginning of electrochemistry can be dated back to 1783 when an Italian physics Alessandro Volta constructed first galvanic cell consisting of zinc and silver platelets divided by paper soaked with salt solution [1].

Over for hundred years have passed since this first experiments and now in XXI century many complicated analytical methods has its roots in first observations made by pioneers of electrochemistry. Jaroslav Heyrovský can be called as a one of father of polarography. During the time when he was an assistant at the Department of Inorganic and Analytical Chemistry of Charles University, he started experiments with mercury drops. He began to measure the exact weights of the collected amounts started from the 100 and later 80 drops of mercury falling into different types of solutions from the dropping mercury electrode. Using a potentiometer, he applies different values of potential to these drops with respect to the layer of mercury at the bottom of the measuring cell.

Today we have many techniques more or less selective, basing on physical or physicochemical phenomena. Increasing computing power of computers allows better more complex data analysis in a short time. Table 1 shows examples of instrumental methods based on physical and chemical phenomena.

Tab.1. Examples of instrumental methods based on physical and chemical phenomena [5]

Phenomenon	Analytical method
Electrochemical deposition	Electrogravimetry Coulometry
Current flow between the electrodes	Polarography, Voltammetry
Change in electrode potential	Potentiometry

Zinc functions and occurrence

In human organism there is 2-4 g of zinc. Located in all tissues, but mainly in muscles (55%), bones (30%), skin, liver, kidneys and spleen [3,4]. Zinc has many functions in human organism: it is an activator of many enzymes ex. histidine desaminase (catalysing deamination reaction), arginase (which takes part

in ornithine cycle), lecithinase – braking down lecithin, and dipeptidases: gliciloglicinase, glicinoleucinase or thripeptidases (braking down numerous tripepthides). It occurs in many enzymes as a central ion: carbonic anhydrase (catalysing reversive reaction of HCO_3^- creation from water and carbon dioxide), lactate dehydrogenase (catalysing last part of glycolytic chain), malate dehydrogenase taking part in Krebs cycle, glutathione dehydrogenase (catalysing change of L glutamate in α ketoglutarate and NH_4^+ , alcohol dehydrogenase (catalysing transition of ethanol in acetic aldehyde), alcalic phosphatase (catalysing phosphate ester dephosphorylation), carboxyptepidases decomposing peptide bond and RNA polymerase taking part in transcription. Zinc also has an important role in free radical sweeping – it is the central ion in superoxide dismutase. Zinc is also present in aminoacyl-tRNA synthases – enzymes taking part in amino acid activation [6,15]. Furthermore zinc is an element necessary for keeping good state and growth of skin and mucosa [6]. Zinc is also known as an immunomodulation agent [12,14].

Analytical Methods

Zinc ions despite their wide distribution, in terms of analysis lay a complex problem. With concentration ranges from 30 ppb (see water) to 5000 ppm (soil) in various biological and inorganic materials, zinc most frequently found with other ions (mostly heavy metals – copper and lead) can produce difficulties in precise and accurate assay [13].

Polarography

Historically the oldest of chosen electrochemical analysis methods – the polarography allowed a reliable and easy method for simple analysis of solutions containing zinc. Polarographic measurements are

done using DME (Dropping Mercury Electrode) – consisting of glass capillary connected to mercury reservoir. A differentiating potential is applied to the electrode and the current measured. Plotting a curve of current as a function of applied voltage creates a polarographic curve. Taking into consideration that oxygen also depolarizes the DME all samples has to by deoxygenated (usually by saturation of the sample with inert gas). Today Polarographic measurements are performed on polarographic – voltammetric devices connected to computer equipped with specialized software capable of making both polarographic and voltammetric measurements [Fig. 1].



Fig. 1 Typical Polarographic/Voltammetric analyzer – MTM Anko; (M161 Analyser), (M164 CGMDE – Controlled Growth Mercury Electrode – Stand)

Polarography in its initial form could not assay depolarizers concentrations below approximately 6 ppm (parts per million), due to large capacitive current of the DME. After introduction of more complex analysers and new polarographic techniques, DPP (Differential Pulse Polarography) now allows zinc assay in concentrations as low as 0.1 ppm [18].

Since the introduction of HMDE (Hanging Mercury Drop Electrode) and solid state electrodes according to IUPAC the method of recording curves of the current as a function of potential should be called “voltammetry” instead “polarography” [19].

Voltammetry

The base of using this method is to determine the intensity depending on the current flowing through the stationary electrode indicative of the voltage applied to the electrode (but working electrode polarography is stationary electrode what means that surface is not changing).

The test is conducted in the DC polarograph system consisting of: linear voltage generator, potentiostat, the current measurement and recorder.

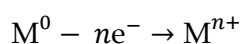
From electrochemical point of view, determination using anodic stripping voltammetry can be divided into two main stages:

Deposition of substance on the electrode – analyte is reduction at constant potential. The solution is continuously mixed – changes of current are not recorded. Collection of the substance is described by the reaction:



On the surface of the electrode is produced film or amalgam, what depends on the nature of the metal and secreted electrode material. This is the stage which is usually not recorded.

Anodic oxidation stage - the polarization of the anode electrode direction, separated metal goes into solution according to the reaction:



At this stage, the current flowing by the analyte is registered. Anodic oxidation causes the diffusion of the analyte ions, which changes appearing current.

To make the measurement, it is necessary to bring the bias voltage changing electrode according to the program characteristic measurement technique which was used. At the same time the current flowing through the working electrode is measured. A voltammetric curve illustrating current to bias voltage is recorded as a result of analysis. Line voltage

generator produces a voltage changing linearly with the required speed between the initial and final potential. Line connection involving a potentiostat is applied to the electrodes; also current of the working electrode is measured. The signal obtained from the measurement is recorded as a function of bias voltage by the DVR [6].

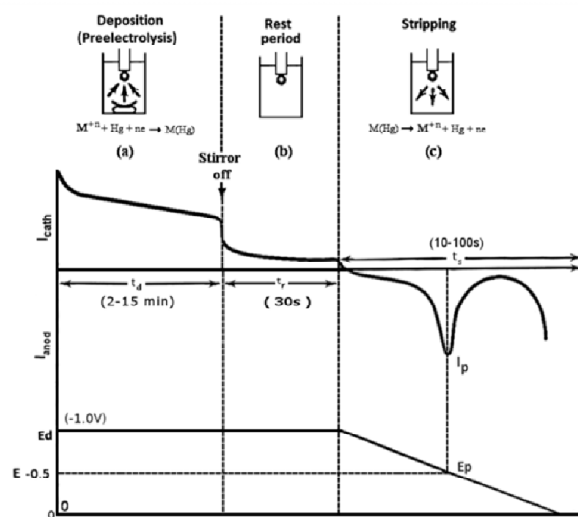


Fig. 2 The principle of detection the substance by anodic stripping voltammetry. (a) deposition of a substance on the hanging mercury drop (b) mixing the solution (c) discharge the drop [6]

Except to these basic features and functions, systems may also have additional functions to control the lifetime drops or concentration time control techniques used as stripping techniques.

All of these methods are important in determining not only zinc but also a many of other ions, what can be used in the analysis of a wider range of pharmaceutical preparations, cosmetics and dental preparations.

Ion Selective Electrodes – ISE

Recently there was new information about the possibility of zinc assay with the application of ISE. Measurement consists of the creation of an electrode with a selective response to determined analyte (most frequently metal cations), and building a cell with ISE and reference electrode (single junction SCE – saturated calomel electrode or silver – chloride

electrode) and recording potential changes in sample solution. Plotting a calibration curve $E_{\text{cell}}=f(\log C_{\text{analyte}})$ (or using a standard addition method etc.) allows precise determination of the analyte. This kind of electrodes give a Nernstian potential response in a wide range of analyte concentrations (zinc ISE in concentration range 32 ppb – 6500 ppm with medium slope of 29.4 mV per decade and a detection limit of 17 ppb [7]).

Conclusion

Electrochemistry is one of the most dynamically developing fields of science. The wide range of available methods allows to individual selection of the type of analysis. In the case of zinc, a metal with a very wide range of applications, adequate is to use methods such as atomic absorption spectrometry (AAS), Atomic Emission Spectrometry (AES) and anodic stripping voltammetry (ASV). Among them, anodic stripping voltammetry is a method with great potential, a low cost of analysis, process automation, and low detection limit.

Resumo

Zinko estas natura spurelemento, kiu estas uzata por teknikaj celoj kaj ankaŭ estas aplikata en multaj materialoj uzataj por farmacia, kosmetika kaj stomatologia celoj. Ofte estas bezonata ekzakta metodo por determini malgrandan koncentritecon de zinko en biologiaj provaĵoj kaj samtempe malmultekosta. Krom metodo AAS, kiu estas ofte uzata por determini zinkon ankaŭ elektrokemiaj metodoj estas rekomendataj. Ofte estas uzataj voltamperometriaj metodoj, precipe metodo ASV, kiu ebligas determini zinkon en koncentriteco ppb, eĉ ppt. Lastempe oni mencias pri jonselektiva elektrodo por zinko, kiu ebligas determini koncentritecon de zinkjonoj.

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