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Selenium determination in biscuits and pasta: Development of chronopotentiometric stripping determination by using a sulphide as an internal standard

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ABSTRACT

Being common in chromatographic techniques internal standard method is rarely applied in electrochemical stripping determinations. One of the reasons for such rare use of this elegant quantification method is because optimal conditions of accumulation at the electrode for individual compounds producing a reproducible signal may vary significantly. These criteria are much stricter when selenium is in question due to very complex mechanism of its accumulation at mercury electrodes which implies simultaneous cathodic mercury dissolution and chemical reaction. Elements that are in the analytical step stripped cathodically from mercury electrodes are rare, further limiting the application of the internal standard method when electrochemical selenium determination is in question.

In this work the possibility of using sulphide for selenium quantification by chronopotentiometric stripping analysis was investigated. Optimal experimental parameters were defined in two-component systems. Dimensionless factors defining the ratio of proportionality constants of the two elements were calculated for different selenium concentration ranges at different sulphide contents. Sulphide content that was chosen as adequate for selenium concentrations reasonably to be expected in food samples was 500 μg/dm^3. Determined detection limit of chronopotentiometric stripping determination of selenium by using a sulphide as an internal standard was 0.04 μg/dm^3 (RSD=7.6%; n=5). Defined quantification method was confirmed by analysing spiked standard solutions and standard reference material. The method was used for selenium determination in biscuit and pasta samples. Calculated contents were statistically compared with those obtained by using graphite furnace atomic absorption spectrometry.

1. Introduction

Selenium is an essential element that exerts its effects through selenoenzymes involved in essential functions such as redox homoeostasis and thyroid hormone metabolism. The best know selenium containing enzymes are glutathione peroxidase and iodotironine-5-deiodinase. Required daily intake of selenium for healthy adults of average weight is 0.04–0.1 mg [1]. Selenium deficiency has been associated with several diseases such as heart failure and cancer [2], whereas the element is toxic at levels little above those required for its essential functions. Biochemical and physiological effects of selenium depend mostly on its amount and chemical form. Selenide, selenomethionine, selenocysteine and other organoselenium compounds are efficient in preventing certain types of diseases, while in case of some other diseases inorganic selenite is recommended [3].

A variety of analytical methods can be applied for the determination of trace amounts of selenium in different samples. Considering that selenium can be present in −2, 0, +4, and +6 oxidation states and that different forms exhibit different effects, applied instrumental method for selenium determination must be specific to particular species or the species must be separated prior determination. Routine analytical methods for detecting selenium quantitate only total selenium. The most commonly reported instrumental methods used for the determination of total selenium are fluorimetry [4,5], neutron activation analysis [6,7], atomic absorption spectroscopy [8,9], and inductively coupled plasma emission spectrometry [10]. More recent methods utilise inductively coupled plasma atomic emission spectrometry and inductively coupled plasma mass spectrometry for total selenium determination, and in conjunction with high-performance liquid chromatography [11–13] or gas chromatography [12,14] for speciation.

Among electrochemical techniques that are selective towards Se^{4+}, differential pulse polarography [15,16] and differential pulse

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cathodic stripping voltammetry [17,18] can be used. In many applications, chronopotentiometric stripping analysis of selenium appeared to be well suited because of the inexpensive instrumentation, and the excellent sensitivity [3]. Speciation is possible since only tetravalent selenium is electrochemically active.

In stripping techniques quantitative analysis is usually performed by the calibration curve or standard addition method. Calibration approach suffers from many drawbacks, especially in respect to the accuracy of the determination and practical considerations. Dependence of the analytical signal on concentration is usually defined in matrix of blank which can never simulate adequately the behaviour of the analyte in the sample matrix due to influence of other substances accompanying the analyte in the sample. Consequently, electrode processes and baseline are different in the blank and in the sample, modulating analytical signals differently. Defined calibration curve, thus, does not represent the dependence adequately. Standard addition method minimises the influence of interfering substances from the sample matrix and partially compensates their influence. This simple method for content calculation can be applied only in the linear range and for the negligible intercept.

Since usually traces of selenium are determined in food samples, in order to achieve sufficient sensitivity relatively long electrolysis is required, usually up to 600–900 s. In stripping techniques electrolysis longer than 900 s is considered irrational and poorly justified. When defining calibration curve, analysis for each selenium concentration should be repeated several times, as well as the analysis of the sample itself. Great number of analyses compromises the stability of the mercury film electrodes leading to erroneous results, especially under long electrolysis times. The internal standard method enables simple and rapid concentration calculation avoiding multiple steps and electrode damage. The method is based on comparing and expressing through numerical factors the behaviour of the analyte and the standard. Once calculated, the factors enable calculation of the analyte concentration in the sample by performing a single analysis.

The method of internal standard is very common in chromatographic techniques where it is required for the standard to fulfil certain criteria, such as the absence from the sample and good separation from other components of the mixture. It is recommended to use the standard which would represent chromatographic behaviour of all mixture components, therefore, it should elute in retention window to approximate all components of the mixture. In another word, used internal standard should be approximately in the middle of the chromatogram or multiple internal standards must be applied. On opposite to chromatographic techniques where the method is somewhat common, the method of internal standard is rarely applied in stripping techniques for content calculation. Difficulty in finding a compound absent from the sample which would produce well defined analytical signal under experimental conditions optimal to the target analyte, make this quantification approach very challenging and rare in electroanalytical practice.

Publications describing the application of the internal standard for content calculation in stripping techniques are very few and refer mostly to lead and cadmium determination [19–21]. Difficulty of finding the substance which would fulfil criteria to be absent from the sample, producing well defined signal under same experimental conditions as the target analyte, is the main cause of method limitation in stripping techniques. Even though stripping techniques offer the possibility of performing multielement analysis, the number of potential internal standards is very limited because each analyte demands very strict experimental conditions in respect to the type of the working electrode, the medium, electrolysis potential etc. Furthermore, chosen internal standard must not interfere with the target analyte in the electrochemical concentrate nor in the dissolution step.

The aim of this work was to eliminate the errors in selenium content calculation arising when calibration curve is used and to simplify selenium determination by stripping chronopotentiometry. Literature search demonstrated that in electroanalysis selenium content previously has never been calculated via internal standard. Furthermore, sulphide has never played the role of the internal standard for the purposes of quantification of any analyte. This work represents a novel approach to quantification of quite problematic analyte, selenium, and describes successful application of sulphide for the determination of selenium in biscuits and pasta by chronopotentiometric stripping technique minimising total duration of the analysis, improving the sensitivity of the determination and simplifying the overall analytical procedure.

2. Materials and methods

2.1. Instrumentation

Chronopotentiometric stripping analysis was performed using the computerised system for electrochemical stripping analysis of our own construction (M1 analyser). The instrument has a programme for automatic calibration of the current and voltage, with the parameter setting accuracies $\Delta E < 2$ mV and $\Delta i < 0.2$ μA. Accuracy of dissolution time measurement is 50 ms, and in all other cases 0.25 ms. Quantitative characteristic of the analyte, i.e. the transition time, was measured as a time between two inflection points. Inflection points are determined by programme derivation and are indicated at the chronopotentiogram as horizontal dotted lines [22]. During analytical step, the potential is measured with the frequency of 40 Hz between two inflection points. Derivative curve is internally registered, even though only standard potential vs. time curve is displayed to the user. The M1 analyser was connected to Epson LX-850 printer.

Mercury film electrode was used as a working electrode. Films of mercury were formed on the glassy carbon surface ($d=3$ mm) by a constant current (−50 μA) electrolysis from the separate solution containing 100 μg/dm^3 of Hg^{2+} and 0.02 mol/dm^3 of HCl for 240 s. The thickness of the formed mercury film was ~130 nm. Prior each mercury film deposition glassy carbon was cleaned mechanically by a filter paper wetted, first with acetone, and then with triply distilled water. Platinum wire ($\varphi=0.7$ mm, $l=7$ mm) served as a counter electrode and the reference was Ag/AgCl, KCl (3.5 mol/dm^3) electrode.

Atomic absorption measurements were made by using spectrometer with graphite furnace (Graphite furnace atomic absorption spectrometer—GFAAS) (Thermo Electron Corporation, S series GE711344v 1.26).

Samples were prepared in automated system for microwave digestion (Milestone Srl).

2.2. Chemicals and reagents

All chemicals used in this work were of analytical reagent grade (Merck, Darmstadt, Germany, pro-analysis) except acids which were of extra purity (Merck, Darmstadt, Germany, suprapur). Used chemicals included: $Na_2SeO_3 \cdot 5H_2O$, $Na_2S \cdot 9H_2O$, HCl, HNO_3, acetone, H_2O_2, acetic acid, ascorbic acid, $MgNO_3$, $Ni(NO_3)_2 \cdot 6H_2O$, and $Pd(NO_3)_2$. For all dilutions and dissolutions triply distilled water was used.

Selenium stock solution (2 g/dm^3 of Se^{4+}) was prepared by dissolving sodium–selenite pentahydrate in 0.1 mol/dm^3 hydrochloric acid and was kept in polyethylene bottle in the dark. Working solutions of selenium were prepared by diluting selenium stock solution with triply distilled water. Stock solution of sulphide was prepared daily by dissolving appropriate weight of