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A new and direct method for the determination of trace elements in spinach using differential pulse polarography

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ABSTRACT

For the trace determination of elements in spinach a new differential pulse polarographic (DPP) method is established. The polarograms were taken in various electrolytes and pH values in the presence of digested spinach sample. Trace element determinations were made in acetate and ammonia electrolytes at various pH values, with or without EDTA. Fe and Cu peaks could be separated and determined at pH 7, acetic acid electrolyte in the presence of EDTA. Ni and Zn peaks could be separated and determined in ammonia buffer at pH 10. Lead could be determined at pH 2 acetic acid and Mo (VI) was determined at pH 4 acetate buffer, EDTA medium. Selenite was determined from its hydrogen catalytic peak. The trace element in spinach was found as Fe 15 μg/g, Cu 17 μg/g, Ni 8 μg/g, Zn 27 μg/g, Pb 47 μg/g, Mo 43 μg/g, and Se 762 μg/g.

1. Introduction

Trace elements have an important role in biological functions of hormones, vitamins, enzymes and some proteins. These are being taken first from the earth to the plants then from plants to the animals. Thus, the plants used in human nutrition are the most important source for the required elements. For the determination of these kinds of samples many analytical methods are being used.

Cathodic stripping voltammetry has been used for the determination of Se in three different garlic samples [1]. A fluorimetric method has shown that selenium content in cabbage, onion, bean and pumpkin was very low [2]. In one work, Se was determined using electrothermal atomic absorption spectrometry (ETAAS) in wheat, in fruits, in meat and in fish [3].

Lead and cadmium in vegetables on the Finnish market have been determined by ETAAS [4]. Cow liver was investigated for its trace elements using DPP and Se, Cu, Cd, Pb and Zn contents were determined [5]. Arsenic and selenium levels in vegetable and herbage samples have been determined by X-ray fluorescence spectroscopy [6]. Lead and selenium content in cow milk was determined using DPP [7]. Cauliflower samples were analyzed for their trace element contents for Fe, Cu, Pb, Mo Se, Zn, Cr, Cd, Ti using DP polarography. Their seasonal change in concentration was also investigated. It was found that the quantities of elements were larger in summer [8]. Dried red grapes were analyzed with DPP for their trace elements such as Fe, Cu, Pb, Zn, Bi Cr, Mo, Se and Ni [9]. Cabbage (*Brassica oleraceae* var. *acephale*) was analyzed for its trace element content using DPP and it was possible to determine nine very important elements [10].

There are only a few references for spinach analysis. However, these are mostly for the presentation of a new method where reference spinach samples were used for validation. Spinach leaves, tomato leaves and apple leaves were employed as standard reference materials to optimize the presented new analytical procedure [11]. Uranium in spinach was determined by ICP-MS using spinach standard reference sample [12]. On the other hand selenium was determined using hydride generation atomic fluorescence spectrometry (HG-AFS) and standard spinach sample was used again as reference [13].

Electrochemical methods are mostly preferred for trace analysis and speciation analysis because of their high selectivity and very low detection limits without necessitating tedious extraction or preconcentration procedures which are time-consuming and with risk of contamination. The results obtained with DPP are very reproducible, since with the use of a dropping mercury electrode, the behavior of the electrode is independent of its past history. The aim of this work was to establish a simple polarographic method for the determination of as many as possible trace elements in spinach, being an important food in human life. Since there is no work found in the literature for the determination of trace elements in spinach, we have decided to use DP polarography for this purpose.

2. Materials and methods

2.1. Materials

A polarographic analyzer "Entek Electronics Model 2016" equipped with a mercury drop timer was used. The natural drop time of the

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electrode was in the range 2–3 s (mercury flow rate: 2.4 mg s^{-1}). A Kalousek electrolytic cell with a saturated calomel electrode (SCE), separated by a liquid junction, was used in the three-electrode configuration. The counter electrode was platinum wire. The polarograms were recorded with a Linseis (LY 1600) X-Y recorder under the conditions of a drop life of 1 s, a scan rate of 2–5 mV s^{-1}, and pulse amplitude of 50 mV.

2.2. Reagents

All chemicals used were of analytical-reagent grade (proanalysis). Triply distilled water was used in the preparation of all solutions. Solutions of ions were prepared 10^{-3} M or more dilute, before every use in order to avoid the aging process of solution.

To expel the oxygen present in polarographic cell, 99.999% pure nitrogen was passed through the solution. The mercury used in the dropping mercury electrode was obtained from Merck (Darmstadt, Germany). Contaminated mercury was cleaned by passing it successively through dilute HNO_3 (3.0 M) and water columns in the form of fine droplets by using a platinum sieve. This mercury is then washed in the same way until no acidic reaction was observed. The collected mercury was stored in a closed vessel covered with water. It was dried between sheets of filter paper when it was needed. The mercury used is not lost since it was collected quantitatively, without causing any pollution. Thus, no mercury loss is possible and it can be used continuously. Before use, a DPP polarogram of this mercury was recorded in order to confirm the absence of impurities.

2.2.1. Preparation of reagents

Various supporting electrolytes including NH_3—NH_4Cl and AcOH—AcONa with or without EDTA were used over a wide pH range.

1.0 M AcOH—AcONa electrolyte: It was prepared by adding 6 g of solid NaOH, washed with distilled water in order to remove the carbonate formed, into 57 mL of 1.0 M AcOH, and diluting into 1 L with distilled water. The pH was adjusted with the addition of acid or base to the desired value using a pH meter.

0.1 M Mo(VI) solution: 0.88 g of $(NH_4)_6\,Mo_7O_{24}\cdot 4H_2O$ is dissolved in distilled water and diluted into 50 mL.

0.1 M Se(IV) solution: 0.28 g of SeO_2 is dissolved in hot distilled water and diluted into 50 mL.

Standard 0.1 M Pb(II), Zn(II), Ni(II), and Cu(II) solutions were prepared from their standard nitrate solutions; only for Fe(III) solution, its chloride salt was used.

2.2.2. Preparation of the spinach sample

For this purpose first wet spinach leaves were dried until constant weight at 110 °C. A sample of about 1 g was taken and was left wait in 15 mL of HNO_3 for a few days for digestion. Then it was evaporated until about 1 mL was left and then it is diluted into 10 mL in a volumetric flask with distilled water. The digested and diluted sample was kept in Teflon bottle in refrigerator.

Here it has to be mentioned that H_2SO_4 was not used for digestion so that Pb could be determined without the danger of $PbSO_4$ formation [14]. For the determination of selenite on the other hand, after evaporation of the sample, about 2 mL of HCl was added and it was once more evaporated in order to reduce selenate into selenite for its determination [15].

3. Results and discussion

3.1. Preliminary experiments

The peak potentials of elements are strongly dependent on the nature of the medium. Although the peak potentials are known approximately in certain electrolytes, they may change in the presence of digested sample because of interference and complex formation [16].

Table 1
Effect of electrolytes and pH on peak potentials in the presence of digested spinach (V vs. SCE).

	pH 4 (1 M AcOH + 0.1 M EDTA)	pH 7 (1 M AcOH + 0.1 M EDTA)	pH 10 (1 M NH_3)
Cu (II)	−0.20	−0.30	−0.40
Fe (III)	−0.13	−0.17	−0.35
Pb (II)	−0.40	−0.96	−0.70
Mo (VI)	−0.4, −0.6	−0.82	−1.70
Ni (II)	–	−0.90	−0.80
Zn (II)	−1.10	−1.15	−1.0

The peak potential values of elements which are possible to exist in spinach were determined in several electrolytes with or without EDTA and pH values changing between 2, 4, 6, 9 in the presence of digested spinach sample. The results obtained are summarized in Table 1. For each element the best medium for its determination and separation from other elements has been chosen using these results. Selenite is not given in this table, since for selenite a specific and sensitive method which was developed by us was applied [17]. From these results the peak potentials were used for the qualitative and quantitative analysis of the spinach sample. The overlapping peaks could also be separated according to these results. The procedures are given below in detail and the results obtained are summarized in Table 2.

3.2. Determination of Fe(III) and Cu(II) in digested spinach sample

In polarographic methods it is not so easy to separate their peaks. Both of these peaks and mercury peaks are usually overlapped at about zero volts. Their reduction peaks can shift to more negative potentials in the presence of complexing agents and thus they can be separated. It was found that in the presence of EDTA, copper and iron peaks can be separated at higher pH values.

The determination of Fe(III) in spinach was made at pH 7 acetate buffer electrolyte in the presence of EDTA. As can be seen from Fig. 1, the peak appeared at about −0.15 V and it responded well to standard additions. The copper peak was at about −0.22 V and thus both peaks could be separated in this medium. Fe(III)content is determined using the peak at −0.15 V with standard additions and the result found was, 15 ± 3 μg/g for 90% confidence interval (CI) and N = 4. Copper quantity was determined from the peak at −0.22 V. The result found was as17 ± 2 μg/g, for 90% (CI) and N = 4.

3.3. Determination of Pb(II)

Lead determination was made in pH 2 acetic acid electrolyte without the addition of EDTA. At higher pH values in the presence of EDTA, Pb(II) peak was at much more negative potential and it was small, which made its determination difficult. Since Pb(II) peak was largest under

Table 2
Trace element quantities in dried spinach sample.

Elements	$\bar{x} \pm ts / \sqrt{N}$ (μg/g)
Cu (II)	17 ± 2
Fe (III)	15 ± 3
Mo (VI)	43 ± 4
Pb (II)	47 ± 4
Ni (II)	8 ± 1
Zn (II)	27 ± 3
Se (IV)	762 ± 64

CI 90%, N = 4.
$\bar{x}$: Arithmetic mean, s: standard deviation, t: Student's *t*-test.