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Differential Pulse Polarography Method for the Determination of Trace Fe, Ni, Pb, Zn, Se and Cu in Black Tea Leaves

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Authors' contributions

This work was carried out in collaboration between both authors. Author SK designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Authors SK and GS managed the analyses of the study. Authors SK and GS managed the literature searches. Both authors read and approved the final manuscript.

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ABSTRACT

In this work a new and simple polarographic method has been established for the determination of trace elements present in tea. After digestion with acids, tea samples were analyzed using various electrolytes such as acetate and ammonia at different pH values in the presence or absence of EDTA. Thus, it was possible tochoosethe best medium for the determination of6 trace elements in one tea sample. Polarographic peaks of copper and iron could be separated in HAc at about pH =7 in the presence of EDTA and their quantities were determined. Ni and Zn peaks could be separated and determined in ammonia buffer at about pH= 10. Lead could be determined at pH= 2HAc electrolyte. Selenite, was determined from its hydrogen catalytic peak in KCl, pH= 2 medium in the presence of Mo (VI). The LOD was found as 2.4×10^{-7} for instead of (S/N=3).The trace element ranges in black tea were found as, Fe 35 µg/g, Cu 45 µg/g, Ni 19 µg/g, Zn 22 µg/g, Pb 28 µg/g and Se 77 µg/g.

Keywords: Dried black tea; element determination; trace elements; DP polarography.

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1. INTRODUCTION

Trace elements have an important role in biological functions of hormones, vitamins, enzymes and some proteins. The plants used in human nutrition are the most important source for the required elements. They partially supply human nutritional requirements for essential elements such as K, Ca, Mg, Cr, Co, Fe, F, I, Cu, Mn, Mo, Ni, Se, and Zn. Several metals, such as Pb, As, and Cd are known to be potentially toxic. With the possibility of accumulating in bones, lead may act as a metabolic poison, replacing calcium. Cadmium, on the other hand, may accumulatein the liver and kidney. Sometimes, the daily intake of these heavy metals may increase above the permissible levels. Thus, in case of excessive intake, the analysis for certain elements in various foods including tea leaves is of special interest.

Several methods are being used for the determination of trace elements in biological materials.

For the determination of Se in garliccathodic stripping voltammeter was used [1] and it was shown that 370–485 ng g^{-1} was present in three different garlic samples. A fluorimetric method has shown that [2] selenium content in cabbage, onion, bean and pumpkin was very low. In one work [3] using electrothermal atomic absorption spectrometry (ETAAS) Se in fruits, meat and in fish were determined. Lead and cadmium in cauliflower in the Finnish market have been determined by ETAAS [4]. Cow liver was investigated for its trace elements using DP polarography [5] and Se, Cu, Cd, Pb and Zn contents could be determined. Lead and selenium content of cow milk was determined using DP Polarography [6]. 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 [7]. It was found that the element contents of all samples had larger quantities of elements in summer. Dried red grapes were analyzed with DPPolarography for their trace element quantities such as Fe, Cu, Pb, Zn, Bi Cr, Mo, Se and Ni [8]. Cabbage is a leafy vegetable and is part of the human diet all over the world. There are several varieties of it and a cole known as *Brassica oleraceae*var *acephale*is one of them. This type of cole grows in the Black Sea region, Mediterranean coast and Southern Europe. It is analyzed for its trace element content using DPPolarography and it was possible to determine nine very important elements [9].

Tea samples are mostly studied for their fluoride content and for the effect of brewing on fluoride content. In our former work we used fluoride selective electrode and determined fluoride contents of three different brands of Turkish teas. The teas are brewed and drunk. In this study, we worked on the factors that would increase the fluoride in brewing. The most appropriate brewing time and water temperature were determined. These conditions were tested in three different tea samples and the fluoride was measured the most [10].

In one work Fluoride contents of Chinese black tea in Hong Kong was analyzed Fluoride [11]. In one other work fluoride contents in tea and in soil from tea plantations are determined. Fluoride release into tea liquor during infusion has been studied [12].

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 pre-concentration procedures which are time-consuming and with risk of contamination. The results obtained with DPPolarography are very reproducible, since with the use of a dropping mercury electrode, the behavior of the electrode is independent of its past history.

Tea is consumed in Turkey and also in the world as a soft drink in large quantities. It is an important drink because of its minerals and vitamin contents.

Since there is no work found in the literature for the determination of trace elements in tea leaves, using polarography, we decided to establish a simple and fast polar graphic method for this purpose.

2. EXPERIMENTAL

2.1 Material Preparation

A polarographic analyzer “Entek Electronics Model 2016” equipped with a mercury drop timer was used. The natural drop time of the electrode was in the range 2-3 s (drop size: 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 10^{-3} M and more dilute ones were prepared 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 buffer, and HAc–NaAc buffer with or without0.1 M EDTA were used over a wide pH range.

1.0 M HAc–NaAc buffer: It was prepared by adding 6 g of solid NaOH, washed with distilled water in order to remove the carbon-ate 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 de-sired value using a pH meter.

0.1 M Se (IV) solution: 0.28 g of SeO_2 is dissolved in distilled water by heating 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 black tea sample

Black tea samples were used from Turkish blend teas Çaykur- Kamelya. For this purpose first black tea leaves were dried until constant weight at 110°C.About 1 g of dried tea sample was taken and was left wait with 15 mL of HNO_3 for about one week for digestion. Then it was evaporateduntil about 1 mL was left. After digestion it is diluted into 10 mL in a volumetric flask with distilled water. The digested and diluted sample was kept in refrigerator at 4°C.

For the determination of selenite on the other hand, after evaporation of the HNO_3 acid, about 2 mL of HClhad to be added and it was once more evaporated in order to reduce selenate into selenite since selenateformed during digestion is not electroactive [6]. 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 [13].

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 reactions. The peak potential values of elements which are possible to exist in tea samples were determined in several electrolytes such as HAc (pH=4.0) and NH_3 (pH=9.8) with or without EDTA (pH=7) in the presence of digested tea sample. The results obtained are summarized in Table 1. For each element, the best medium for its determination and separation from other elements have been selected dusing these results.

As can be seen from Table 1 for selenium the peak potentials in HAc, pH=4.0medium was given, we applied here a specific and more sensitive method developed by us.

From these results the peak potentials were used for the qualitative and quantitative analysis of the tea sample. The overlapping peaks could also be separated according to these results. The procedures are given below in detail for each element and the results obtained are summarized in Table 2.

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

	Acetate buffer pH=4.0	**Acetate buffer electrolyte in presence of EDTA pH=4.0**	**Acetate buffer electrolyte in presence of EDTA pH=7.0**	**Ammonium buffer pH=9.8**
Cu (II)	-0.14	-0.20	-0.30	-0.40
Fe (III)	-0.07	-0.13	-0.17	-0.35
Pb (II)	-0.4	-0.40	-0.96	-0.70
Mo (VI)	---	-0.4, -0.6	-0.82	-1.70
Ni (II)	---	----	-0.90	-0.80
Zn (II)	-0.97	-1.10	-1.15	-1.0
Cd (II)	-0.59	-1.00	-1.23	----
Se (IV)	-0.55	-0.67	----	----

Table 2. Traceelementsquantities in in the presence of digested black tea (V vs. SCE)

Elements	**$\bar{x}$(μg / g)**	**$\bar{x}\pm$ ts / $\sqrt{N}$(μg / g)**
Fe (III)	35	35 ± 3
Cu (II)	45	45 ± 3
Pb (II)	28	28 ± 2
Ni (II)	8	8 ± 1
Zn (II)	22	22 ± 3
Se (IV)	77	77 ± 6

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

3.2 Determination of Fe (III) and Cu (II)

In polarographic methods it is not so easy to separate the peaks of Fe (III), Cu(II) and mercury. These peaks are usually overlapped at about zero volts. However, their reduction peaks can shift to more negative potentials in the presence of complexing agents and they can be separated. It was found that copper and iron peaks can be separated in the presence of EDTA, at higher pH values. Thus, we decided to use complexing agents.

The determination of Cu (II) was made at pH= 6.3 acetate bufferelectrolyte in the presence of EDTA and digested tea sample. As can be seen from Fig. 1, the peak of Cu(II) appeared at about – 0.3 V and it responded well to standard additions. Copper content was found as 45±3 µg/g for 90 % confidence interval N=4.

The determination of Fe (III) in tea was made in acetate buffer electrolyte at pH about 7.0 in the presence of EDTA and digested tea sample. As can be seen from Fig. 2, Fe (III) peak was at about -0.20 V at pH =7 and thus Cu(II) and Fe(III) peaks could be separated in this medium. Fe(III) content was determined using the peak at -0.20 with standard additions and the result found was, 35±3 µg/g for 90% confidence interval, N=3.

3.3 Determination of Pb (II)

Lead determination was made in 15 mL acetic acid (pH=2.0) electrolyte without the addition of EDTA. Pb (II) peak was at much higher negative potential at higher pH values in the presence of EDTA and it was also small. Since Pb (II) peak was largest in1 M acetic acid (pH=2) conditions, this medium was used for its determination.

However, here we have to mention that, according to our former studies [14], Pb (II) may form intermetallic compound in the presence of selenite, Se(IV).It is thus, very important not to use HCl for the digestion, since during wet digestion without using HCl, Se (VI) will be formed which will not form intermetallic compound with Pb (II). But in the presence of HCl Se(VI) will be reduced into Se(IV) and will form intermetallic compound with Pb.

Because of this interference between Se (IV) and Pb (II), correct results cannot be obtained.

Under the above given conditions, where HCl was not added for digestion (HAc, pH=2) lead content could be determined from the peak at about -0.35 V Fig. 3 by standard additions, and the result found was 28±2 µg/g for 90% (CI) and N=4.

3.4 Determination of Ni (II) and Zn (II)

In HAc buffer, Ni and Zn cannot be well separated even at higher pH values, but in ammonia buffer at about pH 10, their peaks are well separated. In 1M NH_3/ NH_4^+ medium at pH = 9.8, in the presence of digested tea sample, Ni(II) peak was at -0.8V and Zn(II) peak was at -1.1V. Ni (II) quantity was determined from this peak at -0.8V, Fig. 4, by standard additions and the result found was 19±1 µg/g for 90 % (CI) and N=4.As can be seen from Fig. 4 there is another peak at about -0.4V which must belong to Cu(II) as can be seen in this medium from Table 1.

For the determination of Zn, ammonia buffer pH=10 was used andzinc was observed at about -1.1 V (Fig. 5). The content of Zn could be determined from this peak precisely and the result found was 22±3 µg/g for 90% (CI) and N=4.

3.5 Determination of Selenite, Se(Iv)

For the determination of selenite, the digestion of black tea had to be made in the presence of HCl as given above in section of “Preparation of the black tea sample”. Thus, it was possible to reduce selenate into selenite, which was formed during digestion with HNO_3. This step is important since for selenite determination we can use the hydrogen catalytic peak formation, developed by us, [15]. With this method it is possible to determine very low selenite concentrations. This kind of catalytic hydrogen peak can be obtained by the addition of high concentration of Mo (VI) in the presence of selenite. As can be seen from Fig. 6, this peak was formed at about -1.2 V after the addition of Mo (VI) to form heteropoly acid. The selenite concentration could be determined from this peak after the addition of standard 10^{-5}M selenite. The result found was 77 ±6µg/g for 90 % (CI) and N=4.

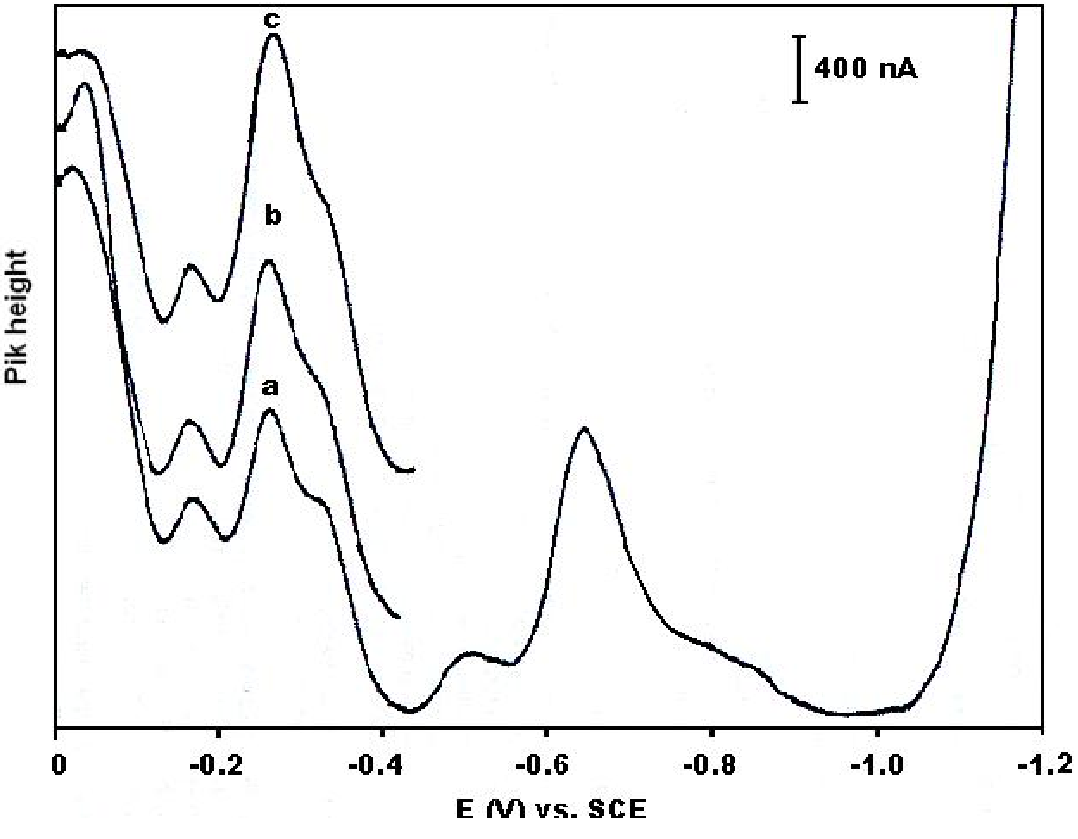

Fig. 1. Determination of Cu (II)

a) 12 mL Acetate buffer electrolyte in presence of 3 mL 0.1M EDTA+ 0.4mL sample (pH =6.24), b) a+ 0.1 mL 10^{-3} M Cu(II), c) b+ 0.1 mL10^{-3} M Cu(II), Sample: Digested 1 g of dry tea sample in 10 mL distilled water

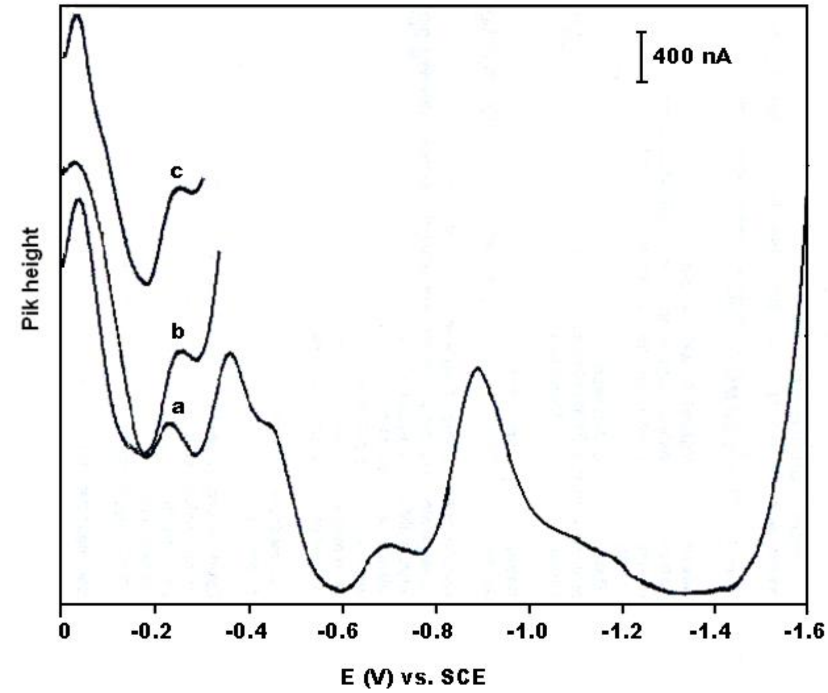

Fig. 2. Determination of Fe (III)

a)15 mL Acetate buffer electrolyte in presence of 3 mL 0.1M EDTA + 0.4 mL sample(pH= 7.02), b) 0.1 mL 10^{-3} M Fe(III), c) 0.1 mL 10^{-3} M Fe(III)

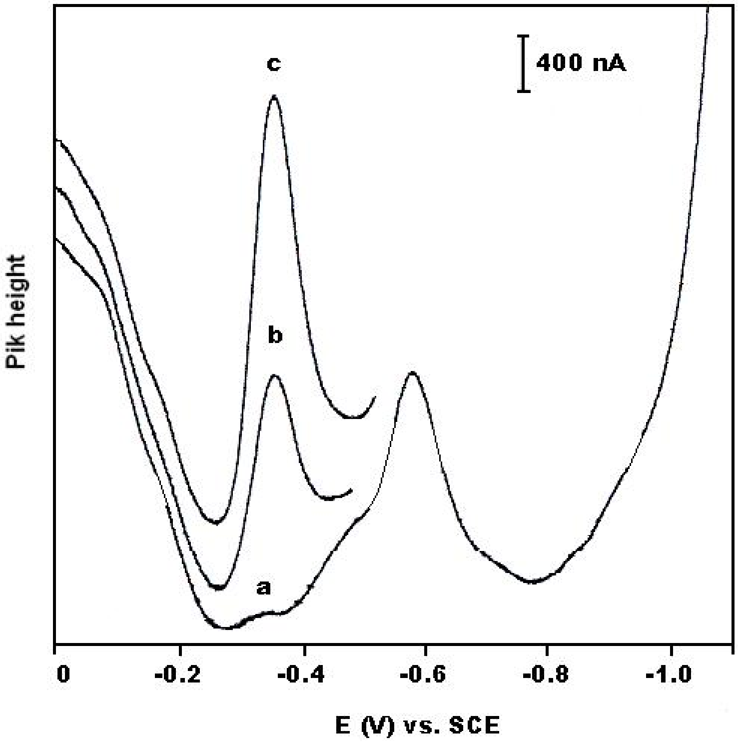

Fig. 3. Determination of Pb (II)

a) 15 mL 1 M HAc + 0.4 mL sample(pH= 2.1), b) a + 0.1 mL 10^{-3} M Pb(II), c) b + 0.1 mL 10^{-3} M Pb(II)

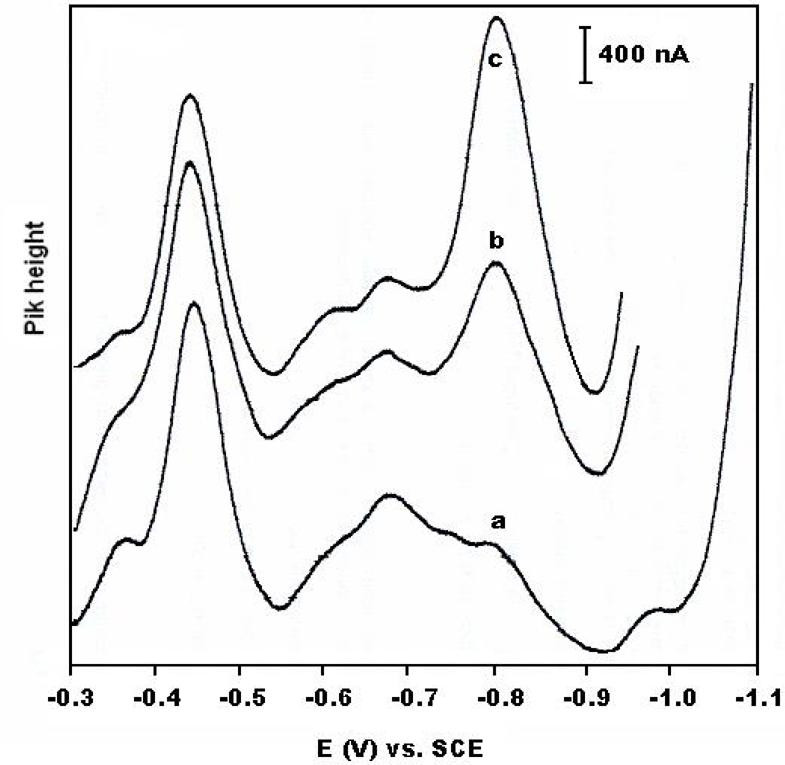

Fig. 4. Determination of Ni (II)
a)15 mL NH_3/NH_4^+ + 0.4 mL sample (pH = 9.8), b) a + 0.1 mL 10^{-3} M Ni(II), c) b + 0.1 mL 10^{-3} M Ni(II)

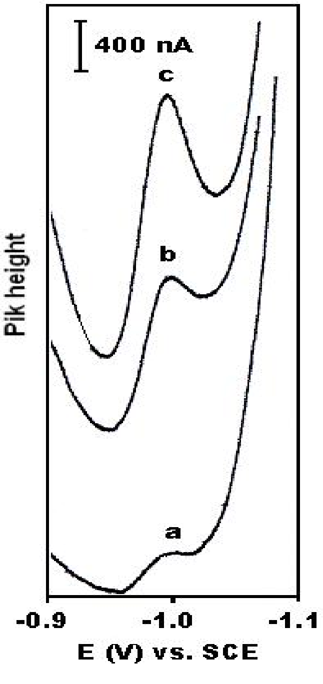

Fig. 5. Determination of Zn (II)
a) 15 mL NH_3/NH_4^+ + 0.4 mL sample (pH = 9.8), b) a + 0.1 mL10^{-3} M Zn(II), c) b + 0.1 mL10^{-3} M Zn(II)

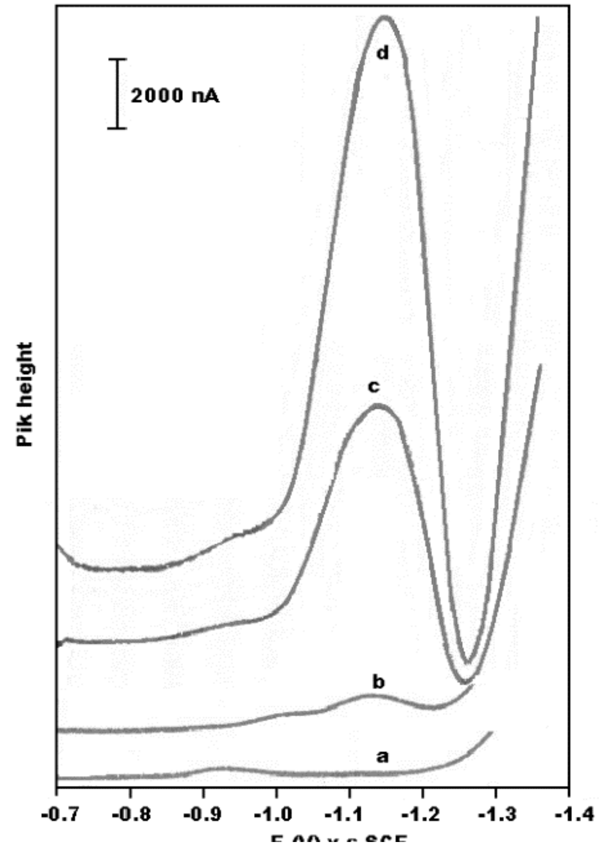

Fig. 6. Determination of Se (IV)

a) 10 mL KCl/ HCl (pH=2), b) + 0.2 mL sample, c) + 0. 5 mL 10^{-3} M Mo(VI), d) + 1.6 mL 10^{-5} M Se(IV)

4. CONCLUSIONS

Plants used in human nutrition are the most important source for the required elements. Among these plants, the most common and most consumed are various teas, vegetables and dried grapes. Tea is used in Turkey as a soft drink in large quantity, it is also used in the world as a soft drink in high quantities. It is an important drink because of its minerals and vitamin contents.

It is not simple to determine the elements and their quantities in a natural sample since the composition is not known at the beginning. The problems can be solved easily using DP polarography. For this, first the polarograms of digested samples have to be taken in various electrolytes and pH. The peaks in polarograms for each element can be identified by standard additions. The possible peak overlaps and interferences can be eliminated by changing the electrolyte and pH. After these steps an idea will be obtained for the determination of each element in the sample.

In this investigation a DP polarographic method is established for the determination of trace elements in tea leaves. Care has been taken during digestion procedure so that the losses and interferences are minimized.

After digestion it was possible to determination of Cu, Fe, Ni, Zn, Pb and Se with high sensitivity. This proposed method can be applied safely for many biological samples.

This method seems to enable determination of at least six trace elements in tea by using an inexpensive instrument and without any time-consuming separation and preconcentration procedures.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. İnam R, Somer G. Determination of selenium in garlic by cathodic stripping voltammetry. Food Chem. 1999;66:381-385.
2. Herrero CL, Mejuto MM, Rodriguez B, Martinez FB. Fluorimetric determination of selenium in foods, Ann. Bromatol. 1987;39: 133-138.
3. Eurola HM, Ekholm IP, Ylinen EM, Koivistoninen EP, Pekka E, Varo TP. Fluorimetric determination of selenium in foods, J. Sci. Food Agric. 1991;56:57-62.
4. Tahvonen R, Kumpulainen J. Lead and cadmium in berries and vegetables on the Finnish market, Fresenius J. Anal. Chem. 1991;340:242-245.
5. Somer G, Guliyeva G, Ekmekci G, Şendil O. Simultaneous determination of copper, lead, cadmium, zinc, and selenium in cow liver by DPP. Can. J. Chem. 2003; 81:31-36.
6. İnam R, Somer G. A direct method for the determination of selenium and lead in cow's milk by differential pulse stripping voltammetry, Food Chem. 2000;69:345-349.
7. Somer G, Ünal Ü. A new and direct method for the trace element determination in cauliflower by differential pulse polarography. Talanta. 2004;62:323-327.
8. Somer G, Kalaycı Ş. A new and simple method for the simultaneous determination of Fe, Cu, Pb, Zn, Bi Cr, Mo, Se and Ni in dried red grapes using differential pulse polarography. Food Anal. Met. 2015;8:604-608.
9. Somer G, Nakışçı A, Kalaycı Ş, Şahin F. Trace element determination in brassica oleraceae var. acephale by Differential Pulse Polarography. Turk J. Chem. 2006; 30:419-423.
10. Kalaycı Ş, Somer G. Factors affecting the extraction of fluoride from tea, application to tea samples, Fluoride. 2003;36(4):267-271.
11. King NM, Tsang MCK. Fluoride content of Chinese and black teas available in Hong Kong, Fluoride. 1987;20:18-21.
12. Fung KF, Zhang ZQ, Wong JWC, Wong MH. Assessment of trace metal distribution and contamination in surface soils of Hong Kong, Environmental Pollut. 1999;104:197-205.
13. Somer G, Özyörük G, Green ME. Determination of trace heavy elements in air particulates by differential-pulse polarography. Analyst. 1985;110:151-156.
14. İnam R, Somer G. An unusual polarographic behavior of Selenite in the Presence of Some Cations, Analytical Sciences. 1998;14:399-402.
15. İnam R, Somer G. Differential pulse polarographic determination of trace selenium (IV) and molybdenum(VI) using catalytic hydrogen wave, Talanta. 1999; 50:609-616.

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