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A new and direct method for the trace element determination in cauliflower by differential pulse polarography

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Abstract

Using the DPP polarograms of wet digested cauliflower sample in acetate buffer at pH values of 2, 4 and 6, Fe, Zn, Mo, Se, Cr, Cd, Pb, Ti and Cu quantities were determined. The best separation and determination conditions for Zn, Se and Mo was pH 2; for Cr, Zn, Mo and As was pH 4; for Pb pH 6, for Ti, Cu and Fe was pH 6–7 EDTA, for Cd pH 2 EDTA and for lead pH 6, all in acetate buffer. The trace element ranges for cauliflowers from two different seasons were (first figure for winter, the second for summer) for Se 120–250 $\mu g\,g^{-1}$, Fe 70–85 $\mu g\,g^{-1}$, Cu 320–150 $\mu g\,g^{-1}$, Ti 90–120 $\mu g\,g^{-1}$, Cr 130–630 $\mu g\,g^{-1}$, Zn 90–550 $\mu g\,g^{-1}$, Mo 170–230 $\mu g\,g^{-1}$, Cd 20 $\mu g\,g^{-1}$ (in winter) and Pb 130–300 $\mu g\,g^{-1}$ in dry sample. Cd was under the detection limit in summer. The length of digestion time had no effect on the recovery of copper, iron, molybdenum and zinc between 15 and 3 h of digestion.

Keywords: Cauliflower; Trace elements; Determination; Differential pulse polarography

1. Introduction

Trace elements take a very important place for a healthy growing and healthy life of human being. They have an important role in biological functions of vitamins, hormones, 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. Among these cauliflower is a vegetable being used mostly in winter and therefore it will be interesting to find out its element content. Different techniques and methods have usually been required for the trace element determination in biological material.

Determination of selenium in garlic, cauliflower, chive, broccoli, leek and Brussels sprout have been made by gas chromatography [1]. The highest selenium content found was in garlic, chive, and Brussels sprouts 31, 22 and 25 $\mu g\,kg^{-1}$, respectively. Cathodic stripping voltammetry has been used [2] for the determination of Se in garlic and it was shown that 370–485 $ng\,g^{-1}$ was present in three different garlic samples. A fluorimetric method has shown that [3] selenium content in cabbage, onion, bean and pumpkin was very low. In one work [4] using electrothermal atomic absorption spectrometry (ETAAS) 0.05–0.35 $mg\,kg^{-1}$ Se in wheat, 0.01–1.20 $mg\,kg^{-1}$ Se in fruits, 0.16–4.9 $mg\,kg^{-1}$ Se in meat and 0.54–3.80 $mg\,kg^{-1}$ Se in fish were determined. Lead and cadmium in vegetables on the Finnish market have been determined by ETAAS and among them it was found that 6 $\mu g\,kg^{-1}$ Pb and 5 $\mu g\,kg^{-1}$ Cd [5] was present in cauliflower. Cow liver was investigated for its trace elements using DPP [6] and Se, Cu, Cd, Pb and Zn contents were found to be 2.1, 8.1, 1.1, 0.6 and 1.2 $mg\,g^{-1}$ dry liver, respectively. Arsenic and selenium levels in 1 g of vegetable and herbage samples have been determined by X-ray fluorescence spectroscopy [7] and a detection limit of 100 ng was obtained.

The determination of trace elements in biological and food matrices is quite difficult. AAS has been used mostly for these purposes. However, the determinations of some elements such as selenium, arsenic and tin have to be made by hydride generation. Many interferences and matrix effects affect this analytical technique and also some losses may take place during volatilizations, which causes poor sensitivity and reproducibility. Electrochemical methods have the advantage that they require relatively inexpensive instrumentation, have demonstrated ability for multi-element

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determination [6,8,9] and are capable of determining elements accurately at trace and ultra trace levels [10].

The purpose of this investigation was to establish a simple polarographic method for the determination of as many as possible trace elements in cauliflower, being an important food in human life.

2. Experimental

2.1. Apparatus

A PAR Model 174 A polarographic analyzer system, equipped with a PAR mercury drop timer, was used. A Kalusek electrolytic cell with reference saturated calomel electrode (SCE), separated by liquid junction, was used in three-electrode configuration. The natural drop time of mercury electrode was in the range 2–3 s (2.4 mg s^{-1}). A platinum wire was used as a counter electrode. The polarograms were recorded with a Linseis LY 1600 X–Y recorder. DP polarograms were recorded under the conditions of a drop life of 1 s, a scan rate of 5 mV s^{-1} and a pulse amplitude of 50 mV.

2.2. Reagents

All the reagents used were of analytical grade. Triply distilled water was used in preparation of all solutions. Nitric acid (65%), perchloric acid (70%), hydrochloric acid (37%) were used in digestion procedure. The mercury (Analar) used was obtained from BDH Chemicals Ltd., Poole, England. The 0.1 M stock solutions were used for the preparation of working solutions of 10^{-3} to 10^{-5} M by daily dilution. Contaminated mercury was cleaned by passing it successively through dilute HNO_3 (3.0 M) and water columns in the form of fine droplets. The collected mercury was dried between sheets of filter paper.

2.3. Procedure

2.3.1. Digestion of samples

Cauliflowers harvested in summer and winter were chosen for sample. The body of cauliflower without the green leaves was first cut into small pieces by a blender, and then dried in an oven until constant weight. About 5 g of it was wet digested in a long-necked 100 ml flask with acid mixture HNO_3:$HClO_4$ (1:1). First 20 ml of this acid mixture was added and let wait over night with a glass funnel covering the mouth of the flask. Next day the flask was heated over flame by turning the flask until nitrogen oxide fumes were completely given off. When the digestive sample turned yellowish to deep dark brown there was a danger of explosion, so about 5 ml HNO_3 had to be added, cooling the flask for about two minutes before addition. Digestion was completed with the appearance of white fumes of perchloric acid when approximately 1.0 ml solution remained. Finally 2.0 ml of hydrochloric acid was added and heated for about 10 min to convert all selenium(VI) to selenium(IV). The digested sample was cooled to room temperature rinsed the funnel into flask with water and the contents were transferred into a 10.0 ml calibrated flask, making up to mark with triply distilled water. This sample was kept in Teflon bottle in refrigerator. The same amount of acids, after vaporization had no impurity peak when polarogram was taken under same conditions.

2.3.2. Polarographic determination

A total of 10.0 ml of acetic acid-acetate buffer (1.0 M) in the polarographic cell was de-aerated by stream of nitrogen gas (99.999%) for about 4.0 min. Polarograms were taken by scanning the potential from 0.0 to −1.5 V at a scan rate of 5 mV s^{-1}. If addition of EDTA was needed then 5.0 ml of buffer, 3.0 ml of 0.3 M EDTA and 2.0 ml of water was used as the electrolyte. The peak potentials of Se(IV), Fe(III), Cu(II), Ti(IV), Cr(III), Pb(II), Zn(II), As(III), As(V), Cd(II) and Mo(VI), which are commonly found in foodstuff were determined at different pH values, 2, 4, 6 and 7 in acetate buffer and in the presence and absence of EDTA. The polarogram of the digested sample was taken under various conditions and the trace elements in the sample were determined by standard additions.

3. Results and discussion

Cauliflowers harvested in two different seasons were prepared for analysis and their polarograms were taken under several pH and buffer conditions. At each condition the elements commonly found in food samples were added into the polarographic cell and their peak potentials were recorded in the presence of cauliflower sample. Eight different samples (A_1, A_2, A_3, B_1, B_2, C_1, C_2 and C_3) depending on the harvesting season and digestion time were prepared. A and B samples were harvested in winter from different sources and in different months, sample A in February and sample B in April. Summer sample C was prepared from four cauliflowers from different sources taken in August.

A polarogram of C_1 sample taken at pH 2 in acetate buffer is given in Fig. 1 as an example. There are peaks at −0.23, −0.50, −0.68 (broad), −0.83 and −1.03 V. According to our preliminary studies the peak at −0.23 V belongs to Mo(VI), the peak at −0.50 V to Se(IV), the peak at −0.83 V to Cr(III) and the peak at −1.03 V to Zn(II). Their presence was confirmed by standard additions. Copper and iron peaks are near zero volt at this pH and can not be obtained separately. The broad peak at about −0.68 V may belong to Cd(II), Ti(IV) or As(III) since their peak potentials overlap under this condition. Their presence has been confirmed under different conditions. The optimum conditions for the above given nine elements have been defined and it was found that the best condition for the separation and determination of Zn was pH 2 and 4, for Se pH 2, for Mo

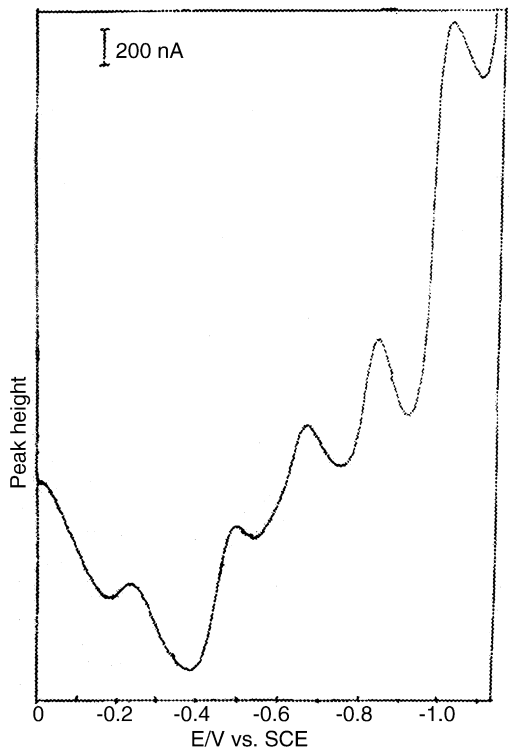

Fig. 1. DPP polarogram of digested cauliflower sample: 10 ml acetate buffer, pH 2, +0.1 ml digested sample.

pH 2, 4 and 6, for Ti pH 2 and 7 both in EDTA, for Fe and Cu pH 6–7 in EDTA, for Cr pH 4 and 7, for As pH 2 with EDTA, for Cd pH 2 with EDTA and for lead pH 6. Thus, it was possible to determine the quantities of some elements in more than one media and the results could be confirmed.

3.1. Effect of digestion time on recoveries

Samples, called A (winter) were digested first for long time, A_1 for 29, A_2 for 15 and A_3 for 11 h. It was observed that some of the element concentrations were decreasing with digestion time. Lead content in sample A after 29 h of digestion was 24 $\mu g\,g^{-1}$, but for 15 h it was 45 $\mu g\,g^{-1}$ and for 9 h it was127 $\mu g\,g^{-1}$. The same was observed with B and C samples for some other metal ions. While the digestion time for B_1 and B_2 it was 9 and 6 h, for C_1, C_2 and C_3 it was 6, 3.5 and 3 h, respectively. It was observed that with longer digestion times some elements, Ti, Se, Cr, and Pb were lost. As can be seen from Table 1 less than 3 h of digestion time prevents losses. In further analysis 3 h or less digestion time has been applied. The selenium content is also dependent on time when HCl had to be used for the reduction of selenium(VI) to selenium(IV). After digestion of the sample the addition and heating up the solution with HCl shall not take longer than 10 min according to our previous work [11].

3.2. Determination of iron and copper

A sample of 0.1 ml digested cauliflower solution was added into a solution containing 5.0 ml acetate buffer +3.0 ml 0.3 M EDTA + 2 ml water (pH 7) and the polarogram was taken. At this pH, copper and iron peaks could be separated, since the peak for iron was at −0.08 V and for copper it was at −0.32 V. While winter sample B contained 70 ± 8 $\mu g\,g^{-1}$ iron, summer sample C contained 84 ± 7 $\mu g\,g^{-1}$ iron. On the other hand, winter sample A contained 320 ± 26 $\mu g\,g^{-1}$ copper and summer sample C contained 150 ± 20 $\mu g\,g^{-1}$ copper, and which shows that there is a significant difference between seasons. The length of digestion time (15, 6 and 3 h) had no effect on both iron and copper.

3.3. Determination of selenium

Selenium was determined at pH 2 in acetate buffer from its peak at −0.50 V. As can be seen from Fig. 2 it could be well defined from other peaks in this medium. In winter cauliflower (sample B) selenium content was 120 ± 11 $\mu g\,g^{-1}$ and in summer sample it was 250 ± 21 $\mu g\,g^{-1}$, which is nearly two times higher than winter sample. The selenium content in summer sample has been determined with a method established by us [12] and a result of 269 ± 24 $\mu g\,g^{-1}$ has been obtained.

The effect of digestion time was large as expected, Table 1.

3.4. Determination of molybdenum

Molybdenum has been determined at different pH values, 2, 4 and 6, in acetate buffer (Table 2). The peak potential used for its determination at pH 2 was −0.23 V, at pH 4 −0.35 V and at pH 6 it was −1.1 V. In winter sample B, the quantity found was 166 ± 18 $\mu g\,g^{-1}$ and in summer sample C it was 223±20 $\mu g\,g^{-1}$. Similar quantities have been found from the peaks measured at different pH values. Digestion time had small effect (about 15–20%), showing that not much volatilization takes place during digestion. While the

Table 1
Effect of digestion time on element quantities in cauliflower ($\mu g\,g^{-1}$)

Digestion time (h)	Se(IV) (B)	Se(IV) (C)	Ti(IV) (B)	Ti(IV) (C)	Pb(II) (A)	Pb(II) (C)	Cr(III) (C)	Zn(II) (C)
15	35	–	–	–	45	–	–	
9	58	–	57	–	127	–	–	
6	122	156	96	87	130	162	460	239
3.5	125	252	92	115		298	630	498
3		250	–	120		310	620	530

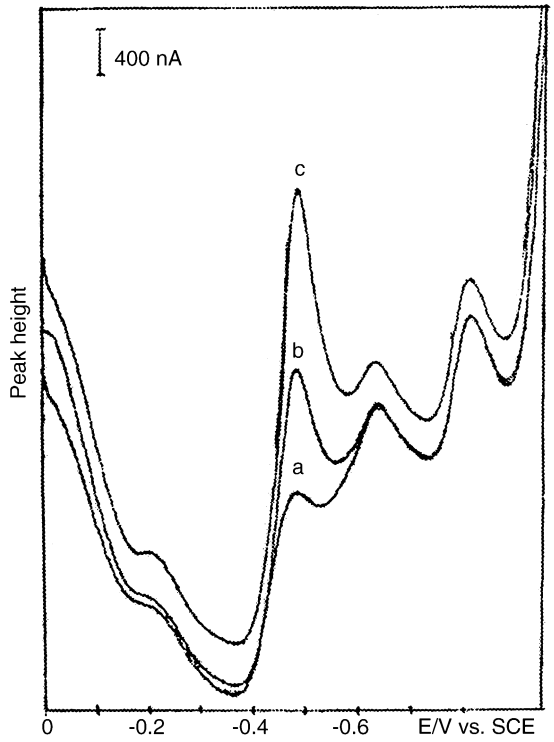

Fig. 2. Determination of selenium(IV) in cauliflower sample: (a) 10 ml buffer, pH 2.0, +0.1 ml sample, (b) (a) + 0.1 ml 1×10^{-3} M Se(IV), (c) (b) + 0.1 ml 1×10^{-3} M Se(IV).

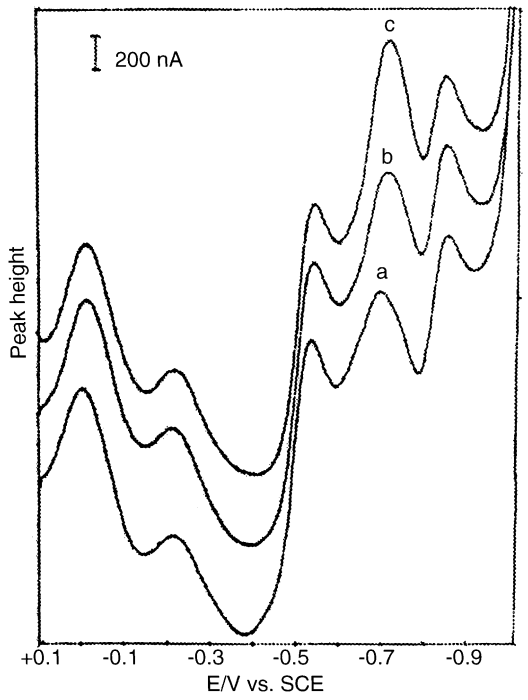

Fig. 3. Determination of cadmium in cauliflower sample: (a) 2.0 ml buffer, pH 2, +5.0 ml 0.1 M EDTA + 3 ml water + 0.2 ml sample, (b) (a) + 0.1 ml 1×10^{-3} M Cd(II), (c) (b) + 0.1 ml 1×10^{-3} M Cd(II).

content was 190 $\mu g\,g^{-1}$ after 6 h of digestion it was 230 and 215 $\mu g\,g^{-1}$ after 3.5 and 3 h of digestion.

3.5. Determination of cadmium

It could be separated best in EDTA at pH 2 from the elements present, where it had a peak at −0.71 V. As can be observed from Fig. 3 under this condition copper(II) has a peak at about −0.08 V, titanium at −0.25 V, selenium at −0.57 V and cadmium at −0.71 V. Cadmium was present only in winter samples in small quantities one being 15 ± 4 and the other $23 \pm 4\,\mu g\,g^{-1}$.

3.6. Determination of titanium

Titanium could be determined both at pH 2 and 7 in EDTA solutions. The peak for Ti(IV) could be separated from Cu and Fe peaks at these pH values. While Cu and Ti peaks were at −0.08 and −0.24 V at pH 2 (see Fig. 3), they were −0.31 and −0.44 V at pH 7, respectively. Iron peak was in both cases at about −0.02 V, which did not cause interference. The reproducibility was very good between the results obtained at different pH values. For two different winter samples A and B the Ti contents were 127 ± 6 and $96 \pm 4\,\mu g\,g^{-1}$, respectively. The summer sample C on the other hand contained $120 \pm 5\,\mu g\,g^{-1}$, which was not significantly different than winter value.

Digestion time had a profound effect, titanium quantity increased with 6, 3.5 and 3 h of digestion time from 87 to 120 and then to 125 $\mu g\,g^{-1}$, respectively.

3.7. Determination of chromium

Chromium could be separated and determined in a solution of acetate buffer, pH 4, with a peak at −0.87 V and also at pH 7 at −1.12 V. A polarogram of cauliflower sample taken at pH 4 is shown in Fig. 4. Here, the peak at −0.23 V belongs to Cu(II), the peak at −0.5 V to Mo(VI), the peak at −0.70 V to Se(IV). The peak at −0.87 V belongs to Cr(III), which was determined with standard additions.

Table 2
Trace element quantities in cauliflower samples[a]

Sample	Se(IV)	Fe(III)	Cu(II)	Ti(IV)	Cr(III)	Zn(II)	Mo(VI)	Cd(II)	Pb(II)
A			320 ± 26	127 ± 6	131 ± 25	85 ± 7		15 ± 4	127 ± 9
B	120 ± 11	70 ± 8		96 ± 4	173 ± 12	95 ± 8	166 ± 18	23 ± 4	
C	250 ± 21	84 ± 7	150 ± 20	120 ± 5	630 ± 45	550 ± 26	223 ± 20	N.D.	313 ± 11

[a] $\mu g\,g^{-1}$, $x \pm t \times s/\sqrt{n}$, t: confidence interval, 90% ($n = 4$).

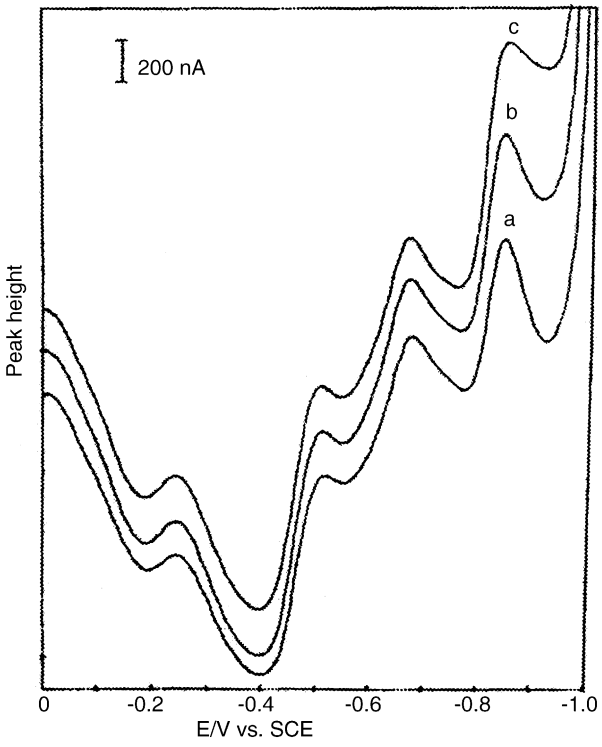

Fig. 4. Determination of chromium in cauliflower sample: (a) 10.0 ml buffer, pH 4, +0.1 ml sample: (b) (a) + 0.2 ml 1×10^{-3} M Cr(III), (c) (b) + 0.2 ml 1×10^{-3} M Cr(III).

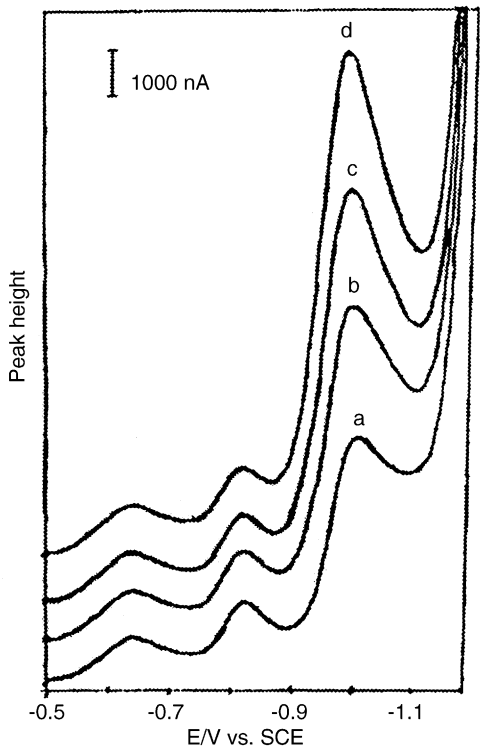

Fig. 5. Determination of zinc in cauliflower sample: (a) 10.0 ml buffer, pH 2, +0.1 ml sample, (b) (a) + 0.05 ml 1×10^{-2} M Zn(II), (c) (b) + 0.05 ml 1×10^{-2} M Zn(II), (d) (c) + 0.05 ml 1×10^{-2} M Zn(II).

Two different winter samples A and B contained 131 ± 25 and $173 \pm 12\ \mu g\ g^{-1}$, respectively. Summer samples on the other hand contained $630 \pm 45\ \mu g\ g^{-1}$ which is about three times larger.

Digestion time had also a profound effect, after 6 h of digestion $500\ \mu g\ g^{-1}$, after 3.5 h, $620\ \mu g\ g^{-1}$ and after 3 h, $630\ \mu g\ g^{-1}$ of chromium was obtained.

3.8. Determination of lead

Lead was determined at pH 6 in acetate buffer using its peak at −0.46 V. In winter sample of A the lead content was $127 \pm 9\ \mu g\ g^{-1}$, and in summer sample C it was $313 \pm 11\ \mu g\ g^{-1}$. The digestion time had a profound effect, with a digestion time of 6, 3.5 and 3 h, 162, 298 and $313\ \mu g\ g^{-1}$ of lead content was found, respectively.

3.9. Determination of zinc

Zinc was determined at two different pH values, pH 2 and 4 in acetate buffer at about −1.0 V. A polarogram taken at pH 2 is given in Fig. 5. In winter samples A and B, the quantity was 85 ± 7, and $95 \pm 8\ \mu g\ g^{-1}$, respectively and in summer sample C, it was $550 \pm 26\ \mu g\ g^{-1}$. Digestion time was also affective on zinc content. While after 6 h digestion time zinc content was $239\ \mu g\ g^{-1}$, it was 498 and $530\ \mu g\ g^{-1}$ after 3.5 and 3 h of digestion.

All of the results obtained for the element quantities in cauliflower are summarised in Table 2.

4. Conclusion

Trace elements in cauliflowers can be determined with a simple and cheap instrumental technique DPP, from one digested sample solution without any extraction or pre concentration. Wet digestion less than three hours prevents losses of some volatile species. Zinc(II), molybdenum(VI) and selenium(IV) could be separated and determined from one polarogram taken at pH 2 in acetic acid–acetate buffer, chromium(III) could be determined in the same solution after adjustment of pH to 4 and lead(II) after adjustment to 6. Titanium(IV), copper(II) and iron(III) could be separated and determined at pH 7 EDTA, and cadmium(II) at pH 2 EDTA. The accuracy of the results has been confirmed by measuring the element quantities in different conditions and with a synthetic sample containing similar quantities of ions present in cauliflower.

Acknowledgements

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