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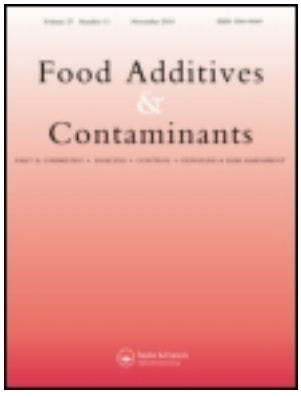

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Determination of cadmium and lead in vegetables by stripping chronopotentiometry

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A method for the determination of cadmium and lead in vegetables by stripping chronopotentiometric analysis, after digestion of the sample with concentrated sulphuric acid and dry-ashing, is described. Metal ions were concentrated as their amalgams on a glassy carbon-working electrode previously coated with a thin mercury film and then stripped by a suitable oxidant. Potential and time data were digitally derived and E *was plotted versus* dt/dE^{-1}*, thus increasing both the sensitivity of the method and the resolution of the analysis. Quantitative analysis was carried out by the method of standard addition; good linearity was obtained in the range of examined concentrations, as was shown by the determination coefficients, which were 0.998 (*$n = 4$*) for cadmium and 0.993 (*$n = 4$*) for lead. Recoveries of 85–100% for cadmium and of 84–97% for lead were obtained from a sample spiked at different levels. Accuracy was demonstrated by analysis of a matching reference sample of cabbage. The detection limits were 1.8 ng* g^{-1} *of wet mass for cadmium and 5.1 ng* g^{-1} *of wet mass for lead. The relative standard deviations (mean of nine determinations), evaluated on a real sample, were 6.7 and 6.2%, respectively. Results obtained on 10 different commercial samples of pepper (*Capsicum annuum*), and egg plant (*Solanum melongena*) were not significantly different from those obtained by graphite furnace atomic absorption spectrophotometry technique. The average content was in the range 3.1–18.6 ng* g^{-1} *for cadmium and 38.2–64.3 ng* g^{-1} *for lead.*

Keywords: stripping chronopotentiometry, cadmium, lead, vegetables

Introduction

Pollution by heavy metals in the biosphere produced by industrial and domestic activity can create serious problems in the use of soils in agriculture (Fytianos *et al.* 2001). The absorption of heavy metals in the biosphere by cultivated plants in contaminated soils has been studied by several authors (Kuboi *et al.* 1986, Xian 1989, Gigliotti *et al.* 1996, Fytianos *et al.* 2001). The amount of metals absorbed by plants is different between species; moreover, the absorption changes in different specimens (Berrow and Burridge 1991). Absorption depends on both the availability of metals and different environmental factors affecting such bioavailability (Brown and Rattigan 1979). High heavy-metal concentrations in soil influence the physiological functions of plants, cause an imbalance of nutrients and have negative effects on both the synthesis and functioning of important biological compounds such as enzymes, vitamins and hormones (Greger and Kautsky 1993).

Cadmium and lead have no essential functions and are toxic even at low concentrations for plants, animals and humans. Owing to their metabolic inertness, they assume a role of primary importance from the toxicological point of view (Coultate 1990). The Food and Agriculture Organization/World Health Organization (FAO/WHO) fixed weekly intake limits of 7 μg kg^{-1} body weight for adults for cadmium (World Health Organization 1992) and of 25 μg kg^{-1} for lead (Berg 1994). Regulation 466/2001

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of the European Committee of 8 March 2001 fixes the maximum limits in foodstuffs for some contaminants such as cadmium and lead. Maximum levels for cadmium and lead in vegetables as defined in Article 1 of Council Directive 90/642/EEC are, respectively, 50 and 100 ng g^{-1} wet weight. The Regulation is linked by Directive 2001/22/EC of the European Committee of 8 March 2001 that lays down the sampling methods and the methods of analysis for the official control of the levels of cadmium and lead and other contaminants in foodstuffs. Determination in vegetables can be carried out with atomic absorption spectrophotometry (Ohta *et al*. 1990), inductively coupled plasma atomic emission spectrometry (Zaray *et al*. 1995), inductively coupled mass spectrometry (Beary *et al*. 1997) or X-ray fluorimetric spectrometry (Aragyraki *et al*. 1997). In recent years, stripping chronopotentiometry (SCP) has been employed for trace and ultratrace metal determinations in food matrices (Mannino 1982, 1983). SCP is the actual name that substitutes the old terminology for potentiometric stripping analysis (PSA) (Fogg and Wang 1999). SCP is a versatile electro-analytical technique first proposed by Bruckenstein and Bixler (1965) and further developed by other authors (Jagner and Åren 1978, Jagner 1978, 1982). SCP is a two-step technique: the first step (preconcentration) is electrolysis of the solution containing the metal ions, which are amalgamated on a mercury-coated glassy carbon electrode; the second step (stripping) is a chemical re-oxidation of the deposited metals (Estela *et al*. 1995). Potential and time data are digitally derived and E is plotted versus dt/dE^{-1} to increase both the sensitivity and the resolution of the analysis (Jagner and Åren 1978). In the present work, SCP was used for the determination of cadmium and lead in vegetables after previous digestion with sulphuric acid and dry ashing of the sample.

Materials and methods

Standards and reagents

All glassware was rinsed with 10% (v/v) ultrapure nitric acid (Carlo Erba, Milan, Italy). Ultrapure water obtained by the Pure Lab RO and the Pure Lab UV system (USF, Ransbach-Baumbach, Germany), ultrapure and certified hydrochloric acid (Carlo Erba), pure sulphuric acid for analysis, pure mercury (II) chloride (Carlo Erba), standard solutions of cadmium and lead of 1000 mg l^{-1} (Panreac Quimica, Barcelona, Spain) were used. A 2-M hydrochloric acid solution, a solution containing 0.5 ng μl^{-1} of cadmium and a solution containing 1.0 ng μl^{-1} of lead were obtained by dilution with water.

Instrumentation and software

Determinations were carried out with a PSA ION^3 potentiometric stripping analyser (Steroglass, S. Martino in Campo, Perugia, Italy) connected to an IBM-compatible personal computer. The analyser operated under the control of a NEOTES software package (Steroglass). Atomic absorption spectrophotometric measurements were carried out by a Spectra 110 spectrophotometer equipped with a graphite furnace (Varian, Victoria, Australia). Cadmium was determined using the following instrumental parameters: drying, 30 s at 125°C; ashing, 30 s at 500°C; atomizing, 10 s at 1900°C; wavelength 228.8 nm. Lead was determined using the following instrumental parameters: drying, 30 s at 125°C; ashing, 30 s at 500°C; atomizing, 10 s at 2770°C; wavelength 283.3 nm.

Electrodes and electrochemical cell

A three-electrode system consisting of a 3-mm diameter glassy carbon working electrode, a platinum wire counter electrode and a silver/silver chloride/saturated potassium chloride reference electrode (Steroglass) was used for all measurements. The electrochemical cell consisted of a 40-ml vessel supplied with an electrical spiral stirrer. Electrochemical measurements were performed at the first step (electrolysis) under stirring conditions and at the second step (stripping) under quiescent conditions.

Preliminary sample processing

A total of 10 g of each representative sample collected as reported in annex I of Directive 2001/22/EC was exactly weighed in a 50-ml quartz crucible and dried at 120°C for approximately 12 h. A total of 1–2 ml sulphuric acid was added to the sample

to wet all the mass. The sample was completely carbonized on a hot plate, then transferred in a muffle oven and the temperature was slowly increased up to 500°C. The sample was dry-ashed for 12 h until white ashes were obtained. If carbon particles remained, the crucible was cooled at room temperature, the residue was moistened with a few drops of water and 0.5–1.0 ml concentrated nitric acid, and the crucible was kept again in a muffle oven for 30–60 min at 500°C. The crucible was then cooled at room temperature and the ashes dissolved with 10 ml 2 M hydrochloric acid gently heating on a hot plate. The solution was then cooled at room temperature and quantitatively transferred to a 50-ml volumetric flask. The volume was filled up to the mark with 2 M hydrochloric acid. The same treatment was used for the preparation of five blanks.

Determination of cadmium and lead

A 10-ml volume of the solution obtained as described above was introduced into the electrochemical cell together with 10 ml water and 1.0 ml of a mercury (II) chloride solution containing 1000 mg l^{-1} mercury (II) in 1 M hydrochloric acid. Before analysis, the working electrode was coated with a thin mercury film by electrolysing a mercury (II) chloride solution of a concentration equal to that added to the sample at −0.9 V against the reference electrode for 1 min. For the subsequent determination, the electrolysis time was 300 s at a potential of –0.9 V; the potential of the electrodes was monitored every 300 μs. Quantitative analysis was carried out by the method of standard addition by adding both 100 μl of a solution containing 0.5 ng μl^{-1} cadmium and 100 μl of a solution containing 1.0 ng μl^{-1} lead.

Results and discussion

The present paper describes the determination of cadmium and lead in vegetables by a stripping chronopotentiometric method after previous mineralization of the sample with sulphuric acid and dry ashing. The time required for sample pretreatment was necessary for a slow dry ashing to prevent volatilization losses as described by several authors and as reported by Crosby (1977). Figure 1 shows the stripping curves for cadmium and lead for a sample of egg plant. Cadmium and lead were oxidized at approximately −0.61 and −0.42 V, respectively, under the conditions described, and peak areas (ms) relative to the sample and three standard additions were measured.

These areas were plotted versus total amounts of cadmium and lead. A good linearity was obtained in the range of examined concentrations, as is shown

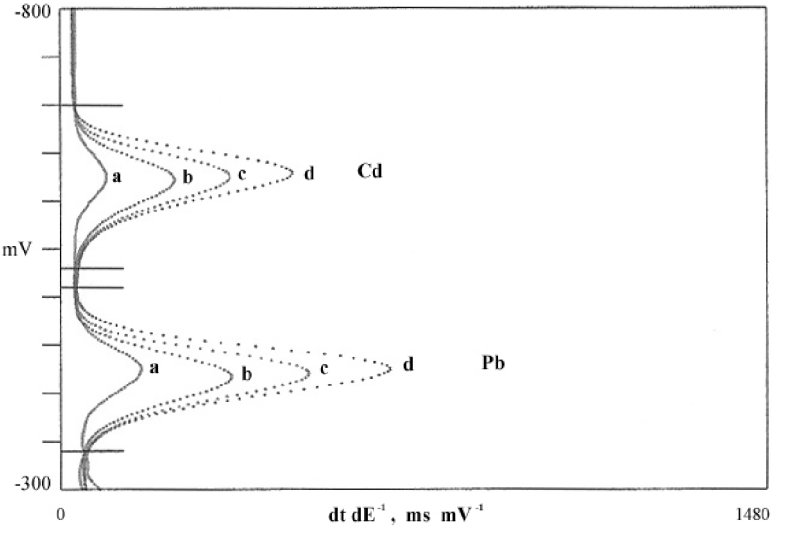

Figure 1. Stripping curves relative to cadmium and lead determination in a sample of egg plant: (a) sample and (b–d) sample added with one, two and three aliquots, respectively, of both 100 μl of a solution containing 0.5 ng μl^{-1} cadmium and 100 μl of a solution containing 1.0 ng μl^{-1} lead.

by both the equations of the lines $Y = 9.9 \times 10^7 X + 3.7 \times 10^3$ for cadmium (slope error $\pm 0.3 \times 10^7$; intercept error $\pm 0.5 \times 10^3$) and $Y = 5.1 \times 10^7 X + 7.1 \times 10^3$ for lead (slope error $\pm 0.3 \times 10^7$; intercept error $\pm 1.1 \times 10^3$), where Y is the integrated area (ms) and X is the analyte mass (mg). Determination coefficients (R^2) were 0.998 ($n = 4$) ($t_{calc} > t_{crit}$; 22.3 > 4.3) for cadmium and 0.993 ($n = 4$) ($t_{calc} > t_{crit}$; 11.9 > 4.3) for lead (Analytical Methods Committee 1988).

The accuracy for lead and cadmium was evaluated by adding at the same time of the addition of 1–2 ml sulphuric acid, appropriate volumes of a cadmium (II) and lead (II) solution to a sample of egg plant; both the spiked and unspiked samples were analysed three times (three independent treatments on the same sample) by the proposed method and each analysis was repeated three times. The results are reported in table 1. As shown, recoveries were 85–100% for cadmium and 84–97% for lead.

The accuracy was established by analysing a matching reference sample (GBW08504 cabbage approved by State Bureau of Metrology, Beijing, P. R. China). The cadmium ($29 \pm 3\,ng\,g^{-1}$ dry weight, mean ± SD) and lead ($280 \pm 35\,ng\,g^{-1}$ dry weight) values agreed well with the cadmium ($27 \pm 4\,ng\,g^{-1}$ dry weight) and lead ($271 \pm 48\,ng\,g^{-1}$ dry weight) certified values ($t_{exp} < t_{crit}$; 1.1 < 4.3, $n = 3$, $p = 0.95$; RSD 10.3% for cadmium and 0.4 < 4.3, $n = 3$, $p = 0.95$; RSD, 12.5% for lead) (Massart *et al.* 1978).

The repeatability of the method was established by carrying out three independent treatments on the same sample of egg plant and each solution was analysed three times. The values obtained were subjected to statistical analysis by employing the same software running all the analytical steps. The average concentrations were $7.9\,ng\,g^{-1}$ for cadmium, with a RSD of 6.7% and $38.2\,ng\,g^{-1}$ for lead, with a RSD of 6.2%.

Table 1. Ranges of recoveries ($ng\,g^{-1}$) of cadmium and lead added to a sample of egg plant. Values are the average of three determinations. Each determination was repeated three times.

Originally present	Added	Found (minimum–maximum)	Range (%) (minimum–maximum)
Cadmium			
7.9	5	11.3–12.9	88–100
7.9	10	15.5–17.7	87–99
7.9	15	19.6–22.6	85–99
Lead			
38.2	20	49.2–56.6	85–97
38.2	40	65.5–75.3	84–96
38.2	60	83.1–95.7	85–97

By using the working conditions stated above, the detection limits were $1.8\,ng\,g^{-1}$ for cadmium and $5.1\,ng\,g^{-1}$ for lead for a signal of three times the SD (s) of five blanks and by using the expression $3\,sS^{-1}$, where S is the slope of the linear regression of calibration curve (Long and Winefordner 1983). The analytical data presented on the quality control of the proposed method were obtained considering some of the performance criteria laid down in Annex 2 of Directive 2001/22/EC of European Committee of 8 March 2001.

The method was applied to cadmium and lead determinations in 10 different commercial samples of vegetables. The results were compared with those obtained by graphite furnace atomic absorption spectrophotometry (GFAAS) and are shown in table 2. A paired Student's t-test showed that the means ($t_{calc} < t_{crit}$; 1.5 < 2.2, for cadmium and 1.4 < 2.2 for lead) not significantly differ (Massart *et al.* 1978).

The averages found for the analysed samples showed a range of concentrations of $3.1–18.6\,ng\,g^{-1}$ for cadmium and of $38.2–64.3\,ng\,g^{-1}$ for lead.

The major points in favour of SCP are the possibility of simultaneous analysis of different species in the same solution, very low detection limits, instrumental price and maintenance costs. Electrode interferences and intermetallic compounds are the major disadvantages. SCP can be regarded as an alternative and/or complementary technique with respect to the GFAAS technique that has significant instrumental and maintenance costs. SCP can be the best choice for laboratories with a small number of analyses of different types of substances. The total analysis time required for the determination of cadmium and lead for each sample is comparable for the two techniques.

Conclusions

The proposed method provides a sensitive and inexpensive analytical procedure for the determination of cadmium and lead in vegetables by stripping chronopotentiometric analysis. A procedure of slow

Table 2. Concentrations of cadmium and lead ($ng\,g^{-1}$) determined in 10 different commercial samples of vegetables by stripping chronopotentiometry (SCP) and by graphite furnace atomic absorption spectrophotometry (GFAAS). Values are the average of three determinations. Each determination was repeated three times.

	Cadmium		Lead	
Sample	SCP	GFAAS	SCP	GFAAS
Egg plant 1	3.1	2.8	60.8	61.2
Egg plant 2	4.7	4.9	62.3	60.3
Egg plant 3	6.4	6.3	54.2	54.0
Egg plant 4	7.5	7.0	44.8	44.0
Egg plant 5	7.9	8.2	38.2	39.1
Pepper 1	8.4	8.0	41.4	40.3
Pepper 2	12.1	11.3	55.6	56.0
Pepper 3	18.6	19.0	61.5	62.0
Pepper 4	13.4	12.4	64.3	61.8
Pepper 5	7.3	7.2	39.2	38.0

dry ashing with respect to sample pretreatment was required to prevent volatilization losses. Analysis can be undertaken in a short time. SCP can be regarded as an alternative and/or complementary technique with respect to the GFAAS technique and can be considered a good choice for small- and medium-sized laboratories. In addition, the cost of instrumentation is low, and having a small size the required space is moderate. Furthermore, the extensive and flexible software supporting the instrumentation makes it possible not only to automate fully the analysis, but also to present the results digitally and graphically, and to store them for possible future processing and statistical treatment. Electrode interferences and intermetallic compounds are the major drawbacks of the SCP method.

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