ELSEVIER

Available online at www.sciencedirect.com

SCIENCE DIRECT®

Food Chemistry 87 (2004) 639–645

Food Chemistry

www.elsevier.com/locate/foodchem

Analytical, Nutritional and Clinical Methods

Determination of Cd(II), Cu(II), Pb(II), and Zn(II) content in commercial vegetable oils using derivative potentiometric stripping analysis

Giacomo Dugo *, Lara La Pera, Giovanna Loredana La Torre, Daniele Giuffrida

Department of Organic and Biological Chemistry, University of Messina, Salita Sperone 31, 98166 Messina, Italy

Received 18 July 2003; received in revised form 18 December 2003; accepted 18 December 2003

Abstract

The purpose of this paper was to determine the content of Cd(II), Pb(II), Cu(II), and Zn(II) in commercial peanuts, sunflower, soy, maize, rice, grape-seed and hazelnut oils, using derivative potentiometric stripping analysis (dPSA). Previous reports provided evidence that hydrochloric acid extraction followed by dPSA was well suited for trace metals determination in oils: precision lower than 2.1% (expressed as relative standard deviation of the measurements) and detection limits ranging from 0.4 to 0.9 μg kg^{-1} were obtained for Cd(II), Cu(II), Pb(II), and Zn(II) in the studied vegetable oils. The optimised method was verified with analysing certified reference materials and the obtained accuracy ranged from 93.5% to 97.0%. The results obtained from analysis of commercial vegetable oils showed that the mean levels of cadmium were lower than 4.90 μg kg^{-1}, the average content of lead ranged from 8.60 to 55.61 μg kg^{-1}, the mean content of copper from 53.80 to 674.45 μg kg^{-1}, and zinc from 51.45 to 555.61 μg kg^{-1}.

Keywords: Cadmium; Copper; Derivative potentiometric stripping analysis; Lead; Vegetable oils; Zinc

---

1. Introduction

Vegetable oils are widely used in cooking and alimentary, cosmetic, pharmaceutical and chemical industries. Seed oils are characterized by a high content of poliunsatured fatty acids (PUFAs), particularly linoleic and linolenic acids, and α tocopherol, whereas hazelnut oil is high both in PUFAs and MUFAs as well as in fitosterols and α tocopherol (Cappelli & Vannucchi, 2000). The presence of essential fatty acids, fitosterols and α tocopherol, enhances the nutritional value of vegetable oils, since several authors have shown that MUFAs and PUFAs contribute to lowering serum cholesterol level, preventing against cardiovascular pathologies (Nestel, Noakes, Belling, Mc Arthur, Clifton, & Abbey, 1992). The presence of metals in vegetable oils depend on many factors: they might originate from the soil, fertilizers, and presence of industry or highways near the plantations, and be incorporated in the oil (La Pera, Lo Coco, Mavrogeni, Giuffrida, & Dugo, 2002a, 2002b). The metals may also be introduced during the production process (by processing steps as bleaching, hardening, refining, and deodorization) or by contamination from the metal processing equipment and thus be suspended in the oil (Carlosena, Andrade, Tomas, Fernandez, & Prada, 1999; Martín-Polvillo, Albi, & Guinda, 1994). Of all the trace element, lead and cadmium are important to consider in terms of food chain contamination because of their toxicity. Lead and cadmium cause both acute and chronic poisoning, adverse effects on the kidney, liver, heart, vascular and immune system. Moreover lead and cadmium exposure cause chromosome aberration, cancer and birth defects (Heyes, 1997); the main sources of these elements are the combustion of fuel, industrial emissions, varnishes and chemical colorants (Rojas, Herrera, Poirier, & Ostrosky-Wegman, 1999). Some micronutrients as copper and zinc, are essential for plant growth and human nutrition at low doses but may also be toxic for humans, animals and plant at high doses. Copper and zinc are re-

---

* Corresponding author.
E-mail address: dugogia@isengard.unime.it (G. Dugo).

0308-8146/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.foodchem.2003.12.035

quired in our diet because they exhibit a wide range of biological functions such as components of enzymatic and redox systems (McLaughlin, Parker, & Clarke, 1999). An excess of Cu(II) induces both lipid peroxidation of lipid membrane and the peroxidation of fatty acid in oils, leading to a rapid formation of undesirable products that negatively influence the quality of oil, particularly its organoleptic properties (Calapaj, Chiricosta, Saija, & Bruno, 1988). Taking into account the metabolic role of some metals and the large use of vegetable oils, it is of great concern to evaluate the presence of Cd(II), Cu(II), Pb(II), and Zn(II) in a large number of commercial vegetable oils. La Pera et al. (2002a, 2002b) studied the trace element composition of a large number of Italian olive oil samples, the concentration ranges found were 0–2.1 μg kg^{-1} for Cd, 9.1–50.0 μg kg^{-1} for Cu, 15.4–70 μg kg^{-1} for Pb and 68.0–576.0 μg kg^{-1} for Zn, whereas few data were found about the presence of these elements in seed oils (Nash, Mounts, & Kwolek, 1983; Martín-Polvillo et al., 1994); the values reported were 1.0–5.5 μg kg^{-1} for Cd, 3.1–129.0 μg kg^{-1} for Cu, and 3.6–152.0 μg kg^{-1} for Pb, any information was found about zinc. The European Community fixed at 100 μg kg^{-1} (rule CE 466/2001, 2001) the legal limits for lead concentration in vegetable oils, for cadmium, copper and zinc any legislation actually exist. The analytical techniques conventionally used for heavy metals determination in edible oils are both emission and absorption spectrophotometry (Calapaj et al., 1988; Martín-Polvillo et al., 1994; Karadjova, Zachariadis, Boskou, & Stratis, 1998). These analytical methods request a time consuming sample pre-treatments involving the complete destruction of the organic matrix as wet digestion, and dry ashing. La Pera et al. (2002a, 2002b, 2003) demonstrated that that hydrochloric acid extraction followed by derivative potentiometric stripping analysis (dPSA) was a rapid, sensitive and precise method to determine simultaneously trace concentrations of Cd(II), Cu(II), Pb(II), and Zn(II) in oily matrices and the glassy carbon mercury coated working electrode was well suited for this purpose. Stripping techniques, particularly in the voltammetric mode, have been extensively applied to the analysis of heavy metals ions in environmental, biological and food matrices (Sanna, Pilo, Piu, Tapparo, & Seeber, 2000); this is especially due to their excellent sensitivity which allow to assess the low metal concentrations frequently encountered. Derivative stripping potentiometry, also named derivative stripping chronopotentiometry, as stripping voltammetry is a two phase technique: a deposition step during which metal ions are reduced at constant potential (accumulation), followed by the stripping step (quantification) involving re-oxidation by a chemical oxidant. The analytical signal is the time taken for re-oxidation (transition or stripping time, τ); reliable determination of τ is achieved by measuring the area under the peak in the $\mathrm{d}t/\mathrm{d}E$ vs E plot, where $\mathrm{d}t/\mathrm{d}E$ represent the inverse of the time derivative of the recorded E (Town & Van Leewen, 2001). The stripping time is proportional to the concentration of the metal and to the electrolysis time, nevertheless by lengthening the electro-deposition time the sensitivity of the method should be increased (Jagner, 1978; La Pera et al., 2002a, 2002b). It was empirically proved that stripping voltammetry (SV) is more susceptible than stripping chronopotentiometry to interferences by electro-active organic molecules and by capacitive currents, that caused a sensitivity decrease. The transformation of SCP E/t data into $\mathrm{d}t/\mathrm{d}E$ format allows the elimination of capacitive current and reduces the impact of induced adsorption of organic molecules onto the working electrode surface (Town & Van Leewen, 2001, 2002). Nevertheless SCP is more suitable than SV for analysis of samples containing significant amounts of organic matter (Dugo, La Pera, Lo Turco, Mavrogeni, & Alfa, 2003a, 2003b; La Pera et al., 2002a, 2002b).

The goal of this study is to use derivative potentiometric stripping analysis as an attractive alternative to both spectroscopic and voltammetric methods, to determine simultaneously trace concentrations of Cd(II), Cu(II), Pb(II), and Zn(II) in commercial vegetable oil samples. Fixing the deposition potential at −1200 mV for 120 s, detection limits ranging from 0.4 to 0.9 μg kg^{-1} were obtained; moreover the optimised method was verified with analysing certified reference materials and the obtained accuracy ranged from 93.5% to 97.0%.

2. Materials and methods

2.1. Materials

A potentiometric stripping analyzer PSA ION 3 (Steroglass, S. Martino in Campo, Perugia, Italy), equipped with a conventional three-electrode cell was used for the analysis of Cd(II), Cu(II), Pb(II), and Zn(II) in vegetable oil samples. The working electrode was a glassy carbon electrode coated with a thin mercury film; the reference electrode was an Ag/AgCl electrode (3M KCl), and a platinum wire auxiliary electrode was used (La Pera et al., 2002a, 2002b).

Ultra pure hydrochloric acid (34–37%), Hg(II) (1000 mg kg^{-1}, 1 M in hydrochloric acid) and Cd(II), Cu(II), Pb(II), Zn(II) (1000 mg kg^{-1}, 0.5 N in nitric acid) standard solutions were purchased by Panreac (Barcelona, Spain); $\mathrm{Ga(NO_3)_3 \cdot 3H_2O}$ (5 g, 99.9%) and absolute methanol (99.9%) used to clean the electrodes were purchased from Aldrich Chem. Co. (Milwaukee, WI, USA). A certified reference oily matrix CertiPUR, containing 100 mg kg^{-1} of Cd(II), Cu(II), Pb(II), Zn(II), was purchased from Merk (Damstadt, Germany). To carry out the recovery text, oily solutions containing 10.0, 50.0 and 200.0 μg kg^{-1} of each metal were prepared for dilution with *n*-exane (Carlo Erba, Milano) of the certified reference oily matrix. 35% H_2O_2, used in the extraction procedure, was purchased from Carlo Erba Reagenti (Milan, Italy). A centrifuge ALC 4217 (ALC International s.r.l., Milan, Italy) was employed in the extraction procedure. Ultra pure water (18.2 M Ω cm^{-1}) was used.

All the studied samples were commercial refined vegetable oils. Seed oils were produced in Italy, nut oils in Turkey. Particularly peanut oils ($n = 6$), sunflower oils ($n = 6$), soy oils ($n = 6$) maize oils ($n = 6$), rice oils ($n = 5$), grape seed oils ($n = 3$) and hazelnut oil ($n = 3$) were analyzed. Peanut, sunflower, soy, maize and rice oils were stored in can, grape-seeds and hazelnut oils were stored in dark glass bottles.

2.2. Methods

2.2.1. Sample preparation

Dugo et al. (2003a, 2003b) described the hydrogen peroxide and hydrochloric acid extraction procedure in a previous paper concerning the determination of selenium in vegetable oils. A 3.0 g aliquot of oil, 2.0 ml of 35% H_2O_2 and 10.0 ml of 36% ultrapure-hydrochloric acid were placed in a teflon beaker. The extraction was carried out for about 30 min under magnetic stirring at 90 °C. The mixture was cooled and then centrifuged at 4800 rpm for 5 min: the acid phase was taken apart in a 20.0 ml volumetric flask, while the organic layer was extracted again for 10 min with 8.0 ml of boiling water under the same conditions described earlier; after the centrifugation, the second extract was added to the volumetric flask and brought to the mark with ultrapure water.

2.2.2. Derivative potentiometric stripping analysis

The electrodes were stored in ultra-pure water; before starting each analysis, they were well cleaned with absolute methanol and filter paper. Before each analysis, the plating of the working electrode was executed by electrolysing a 20.0 ml volume of 1000.0 μg ml^{-1} Hg(II) standard solution, at −950 mV for 1 min. The concentrations of Cd(II), Cu(II), Pb(II), and Zn(II) were simultaneously determined: 1.00 ml of acid extract, 10.0 ml of ultra-pure water, 1.00 ml of 1000 μg ml^{-1} Hg(II) as oxidant agent and 0.50 ml of 10 μg ml^{-1} Ga(III) – in order to prevent Cu–Zn complex formation on the mercury film – were placed in the electrochemical cell. For an accurate simultaneous determination of the four elements, the pH of the sample had to be included in the range 1.8–2.2 (La Pera et al., 2002a, 2002b; La Pera, Saitta, Di Bella, & Dugo, 2003). The deposition potential was fixed at −1200 mV for a time ranging from 60 to 180 s; the final acquisition potential was 0 mV. The quantitative analysis was executed by the multiple points standard additions method: optimum precision and accuracy was obtained by executing two standard additions of Cd(II), Cu(II), Pb(II), and Zn(II) standard solutions in order to double and triplicate the signal area of the sample; each measurement was performed four times (Renman & Jagner, 1997). The correlation coefficients of the obtained calibration curves were always >99.5% and the range of linearity was 0–1000 μg kg^{-1} for all the studied metals. Each analysis lasted 25 min.

3. Results and discussion

3.1. Electrochemical parameters: effect of electrolysis time on sensitivity

The optimized electrochemical parameters that ensure the maximum analytical sensitivity for Cd(II), Cu(II), Pb(II), and Zn(II) analysis in vegetable oils are given in Table 1. In this conditions the potential peaks of Zn(II), Cd(II), Pb(II) and Cu(II), were, respectively, observed at −950, −640, −430 and −260 mV (Fig. 1). The sensitivity expressed as the slope of the calibration curve ($R^2 \geqslant 0.995$), is proportional to the electrolysis time: Fig. 2 shows the liner correlation up to 120 s and Table 2 reports the detection limits calculated at different times of electrolysis. The detection limits were evaluated using the expression $3\sigma/S$ (Pharmeauropa, 1999) where σ indicated the standard deviation of the

Table 1
Optimised analytical conditions for the simultaneous determination of Cu(II), Pb(II), Cd(II), and Zn(II) in vegetable oils

	Cu	Pb	Cd	Zn
Potential range (mV)	−1200, −90	−1200, −90	−1200, −90	−1200, −90
Electrolysis potential (mV)	−1200	−1200	−1200	−1200
Electrolysis time (s)	120	120	120	120
Stripping time (s)	10	10	10	10
Acquisition final potential (mV)	0	0	0	0
Peak potential (mV)	−260	−430	−640	−950

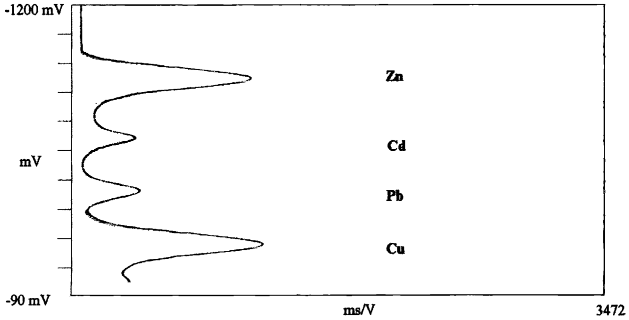

Fig. 1. Simultaneous determination of Zn(II), Cd(II), Pb(II), and Cu (II) in hydrochloric acid extracts of vegetable oils using dPSA. The electrochemical conditions are given in Table 1.

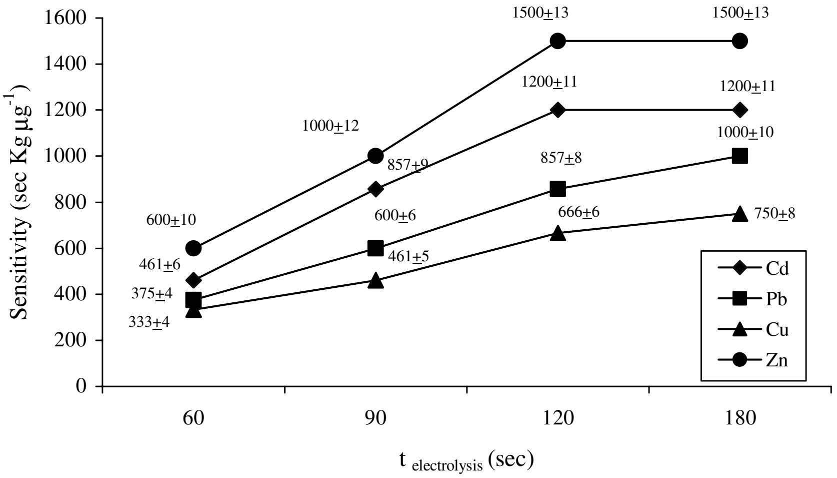

Fig. 2. Effect of varying the electrolysis time on the sensitivity (ms kg µg^{-1}) for Cd(II), Pb(II), Cu(II), and Zn(II) analysis in commercial vegetable oils. Each value was the mean of three measurements.

Table 2
Limits of detection (LOD) found for Cu(II), Pb(II), Cd(II), and Zn(II) determination by dPSA in an oily matrix at different electrolysis times

Electrolysis time (s)	Cu (µg kg^{-1})	Pb (µg kg^{-1})	Cd (µg kg^{-1})	Zn (µg kg^{-1})
60	1.8	1.6	1.3	1.0
90	1.3	1.0	0.7	0.6
120	0.9	0.7	0.5	0.4
180	0.8	0.6	0.5	0.4

response (set at 200 ms) obtained by ten measurements on the oily reference matrix, S (ms/ppb) was the sensitivity. An electrolysis time of 120 s was used for the analysis of the vegetable oils.

3.2. Precision and reproducibility

Instrumental precision and method reproducibility were tested on a sunflower oil by extracting three times the same oil sample and quantifying four times each metal in the same extract. The instrument precision is indicated as mean r.s.d.%, while the reproducibility is represented by the total r.s.d.%. The obtained results are given in Table 3.

3.3. Recovery test

In order to asses the accuracy of the method described, ensuring that analytes loss or sample contamination did not occur during both the extraction procedure and the chronopotentiometric analysis, recovery tests from the certified reference oil, were performed. The certified oil which contained 100 mg kg^{-1} of each metal, was diluted with *n*-exane to obtain three standard oily matrices, respectively, containing 10.0, 50.0 and 200.0 µg kg^{-1} of Cd(II), Cu(II), Pb(II), and Zn(II). The dilution was performed in order to obtain concentrations similar to those really found in oils. The certified reference oil and the standard oily solutions

Table 3
Instrument precision and method and reproducibility, for the determination of Cu(II), Pb(II), Cd(II), and Zn(II) in seed oils by dPSA[a]

	Cu (µg kg^{-1})	Pb (µg kg^{-1})	Cd (µg kg^{-1})	Zn (µg kg^{-1})
First extraction				
Mean ± SD (µg kg^{-1})	101.40 ± 0.78	16.80 ± 0.36	0.49 ± 0.01	299.45 ± 2.96
r.s.d.%	0.80	2.14	2.0	1.00
Second extraction				
Mean ± SD (µg kg^{-1})	100.54 ± 0.61	15.78 ± 0.21	0.46 ± 0.01	289.15 ± 2.14
r.s.d.%	0.60	1.33	2.1	0.74
Third extraction				
Mean ± SD (µg kg^{-1})	104.35 ± 0.99	17.44 ± 0.53	0.52 ± 0.01	303.11 ± 2.83
r.s.d.%	0.95	2.95	1.92	0.93
Precision (mean r.s.d. %)	0.78	2.14	2.00	0.90
Total mean ± SD (µg kg^{-1})	102.10 ± 2.00	16.67 ± 0.84	0.52 ± 0.02	297.24 ± 7.24
Reproducibility (total r.s.d.%)	1.96	5.04	3.85	2.43

[a] Instrument precision and method reproducibility were tested on a sunflower oil sample subjected to hydrochloric acid extraction treatment.

were subjected to the extraction procedure described above; each extract was analyzed three times. The mean obtained recoveries were 96.5 ± 2.1% for cadmium, 97.0 ± 2.7% for copper, 95.0 ± 1.8% for lead, and 93.5 ± 1.7% for zinc. In a previous paper, concerning the determination of heavy metals in olive oils by dPSA, La Pera et al. (2002a, 2002b) performed confirmation analysis by graphite furnace atomic absorption spectroscopy and the results of the two methods agreed within the 5% for Cd(II), Cu(II), Pb(II), and Zn (II).

3.4. Concentration of Cd(II), Cu(II), Pb(II), and Zn(II) in commercial vegetable oils

Various samples of commercial seed were analyzed, Table 4 shows the range of Cd(II), Cu(II), Pb(II), and Zn(II) concentrations determined by dPSA in the studied vegetable oils. Fig. 3 provides evidence that cadmium is present in very low amounts, maize oils presented the highest mean concentration of Cd (4.90 ± 1.0 μg kg^{-1}; $n = 6$), rice oils the lowest (0.71 ± 0.25 μg kg^{-1}; $n = 5$). Lead was also present in low concentrations, nuts oils showed the highest mean value (55.61 ± 9.05 μg kg^{-1}; $n = 3$), rice oil the lowest (8.60 ± 2.25 μg kg^{-1}; $n = 5$). Refined nuts oils also presented the highest average amounts of zinc (555.61 ± 59.18 μg kg^{-1}) and maize oils the lowest (51.45 ± 10.55 μg kg^{-1}; $n = 6$) that had also the lowest mean content of copper (53.80 ± 10.02 μg kg^{-1}; $n = 6$); whereas soy oils showed the highest levels of this element (674.45 ± 97.15 μg kg^{-1}; $n = 6$). These data evidenced that heavy metals amount, particularly cadmium and lead, in commercial vegetable oils are very low and close to ones found in literature for seeds and olive oils. Moreover lead content is lower than the legal limit (100 μg kg^{-1}) in all the studied sample. Copper concentrations found in this work were higher to those

Table 4
Concentrations (mean × standard deviation) of Cu(II), Pb(II), Cd(II), and Zn(II) found in commercial vegetable oils by dPSA

Oil	*n*	Cu (μg kg^{-1})	Pb (μg kg^{-1})	Cd (μg kg^{-1})	Zn (μg kg^{-1})
Peanuts	1	65.1 ± 0.5	5.1 ± 0.1	3.51 ± 0.07	300.1 ± 2.7
	2	122.4 ± 1.0	15.6 ± 0.4	nd[a]	53.0 ± 0.5
	3	100.0 ± 0.9	10.2 ± 0.2	1.36 ± 0.02	389.0 ± 3.3
	4	79.8 ± 0.7	9.5 ± 0.2	2.54 ± 0.03	463.3 ± 4.0
	5	110.1 ± 0.9	5.6 ± 0.1	3.12 ± 0.03	498.1 ± 4.3
	6	95.0 ± 0.8	14.0 ± 0.3	2.9 ± 0.03	330.0 ± 2.5
Sunflower	1	55.0 ± 0.4	5.0 ± 0.1	0.51 ± 0.00	175.1 ± 1.8
	2	153.0 ± 1.2	15.5 ± 0.5	4.15 ± 0.04	310.0 ± 2.7
	3	100.2 ± 0.9	7.0 ± 0.2	2.12 ± 0.03	280.0 ± 2.6
	4	80.7 ± 0.7	12.3 ± 0.4	1.01 ± 0.01	200.5 ± 1.9
	5	145.1 ± 1.2	10.1 ± 0.2	0.8 ± 0.00	198.2 ± 1.6
Soy	1	440.1 ± 3.9	10.7 ± 0.2	2.53 ± 0.04	29.7 ± 0.3
	2	854.0 ± 8.1	43.3 ± 0.9	5.03 ± 0.07	41.0 ± 0.4
	3	790.3 ± 7.7	15.6 ± 0.4	4.55 ± 0.07	41.5 ± 0.4
	4	688.3 ± 7.0	22.2 ± 0.5	4.06 ± 0.06	35.6 ± 0.3
	5	600.2 ± 6.8	35.6 ± 0.8	2.56 ± 0.04	41.0 ± 0.4
Maize	1	27.0 ± 0.2	5.7 ± 0.1	2.58 ± 0.06	25.5 ± 0.25
	2	79.1 ± 0.7	10.9 ± 0.2	6.72 ± 0.13	76.3 ± 0.75
	3	35.2 ± 0.4	10.1 ± 0.2	6.05 ± 0.13	50.1 ± 0.50
	4	68.0 ± 0.6	6.0 ± 0.1	3.51 ± 0.07	35.6 ± 0.31
	5	60.4 ± 0.6	8.9 ± 0.2	5.75 ± 0.12	70.2 ± 0.76
Rice	1	43.0 ± 0.4	5.7 ± 0.1	nd	131.0 ± 1.2
	2	100.1 ± 1.1	10.9 ± 0.3	nd	260.1 ± 2.4
	3	55.5 ± 0.6	10.0 ± 0.2	1.54 ± 0.03	200.5 ± 2.1
	4	98.2 ± 1.0	6.9 ± 0.1	0.83 ± 0.01	150.1 ± 1.3
	5	49.3 ± 0.6	9.5 ± 0.2	1.44 ± 0.03	220.3 ± 2.2
Grape seeds	1	80.2 ± 0.6	7.5 ± 0.2	2.12 ± 0.05	150.0 ± 1.4
	2	94.3 ± 0.8	15.6 ± 0.5	4.62 ± 0.10	390.1 ± 4.3
	3	90.1 ± 0.7	11.1 ± 0.4	3.95 ± 0.09	240.2 ± 2.6
Nuts	1	200.1 ± 2.3	40.1 ± 0.8	1.13 ± 0.02	495.1 ± 4.2
	2	274.2 ± 2.6	61.9 ± 1.3	2.65 ± 0.06	661.7 ± 6.5
	3	251.0 ± 2.5	55.9 ± 1.0	2.17 ± 0.05	510.1 ± 4.3

Each value was the mean of three determinations.

[a] *nd = not detectable (<0.50 μg kg^{-1}, $E_{\mathrm{dep}} = -1200$ mV, $t_{\mathrm{electrolysis}} = 120$ s).

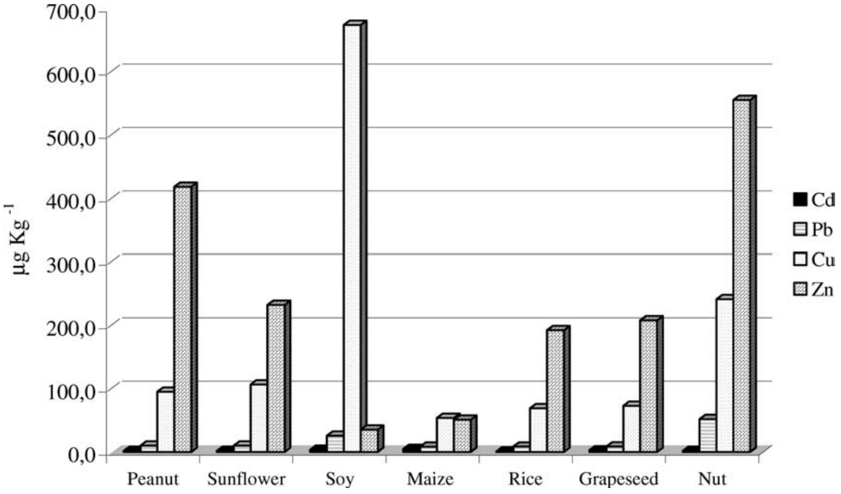

Fig. 3. Mean content of Cd(II), Pb(II), Cu(II), and Zn(II) in commercial vegetable oils.

published for seed and olive oils, whereas the levels of zinc are similar to those determined in olive oils. Particularly the obtained results provide evidence that soy oil is a good source of copper (>500 μg kg^{-1}), whereas peanuts and nuts oils are a good source of zinc (>300 μg kg^{-1}). The proposed method based on derivative potentiometric stripping analysis provides a rapid, sensitive and reliable procedure to detect simultaneously trace levels of Cd, Pb, Cu and Zn in vegetable oils. Moreover this technique do not request a sample preparation based on a pre-concentration step or the complete destruction of the organic matrix, that often cause a severe loss of trace metals. Nevertheless the proposed method could represent an attractive alternative to spectroscopic and voltammetric techniques for trace metal analysis in food matrices.

References

Calapaj, R., Chiricosta, S., Saija, G., & Bruno, E. (1988). Method for the determination of heavy metals in vegetable oils by graphite furnace atomic absorption. *Atomic Spectroscopy, 9*, 107–109.

Cappelli, P., & Vannucchi, V. (2000). *Chimica degli alimenti. Conservazione e trasformazione*. Bologna: Zanichelli, pp. 498–506.

Carlosena, A., Andrade, J. M., Tomas, X., Fernandez, E., & Prada, D. (1999). Classification of edible vegetables affected by different traffic intensities using potential curves. *Talanta, 48*, 795–802.

Dugo, G., La Pera, L., Lo Turco, V., Mavrogeni, E., & Alfa, M. (2003a). Determination of selenium in nuts by cathodic stripping potentiometry. *Journal of Agricultural and Food Chemistry, 51*, 3722–3725.

Dugo, G., La Pera, L., Pollicino, D., & Saitta, M. (2003b). Determination of selenium content in different types of seed oils by cathodic stripping potentiometry (CSP). *Journal of Agricultural and Food Chemistry, 51*, 5598–5601.

European Community, rule n.466/2001. European Official Gazette, 16th March 2001.

Heyes, R. B. (1997). The carcinogenicity of metals in humans. *Cancer Causes and Control, 8*, 371–385.

Jagner, D. (1978). Instrumental approach to potentiometric stripping analysis of some heavy metals. *Analytical Chemistry, 50*, 1924–1929.

Karadjova, I., Zachariadis, G., Boskou, G., & Stratis, J. (1998). Electrothermal atomic adsorption spectrometric determination of aluminium, cadmium, chromium, copper, iron, manganese, nickel and lead in olive oil. *Journal of Analytical Atomic Spectrometry, 13*, 201–204.

La Pera, L., Lo Coco, F., Mavrogeni, E., Giuffrida, D., & Dugo, G. (2002a). Determination of copper(II), lead(II), cadmium(II) and zinc(II) in virgin olive oils produced in sicily and apulia by derivative potentiometric stripping analysis. *Italian Journal of Food Science, 14*, 389–399.

La Pera, L., Lo Curto, S., Visco, A., La Torre, L., & Dugo, G. (2002b). Derivative potentiometric stripping analysis (dPSA) used for determination of cadmium, copper, lead and zinc in in sicilian olive oils. *Journal of Agricultural and Food Chemistry, 50*, 3090–3094.

La Pera, L., Saitta, M., Di Bella, G., & Dugo, G. (2003). Simultaneous determination of Cd(II), Cu(II), Pb(II) and Zn(II) in citrus essential oils by derivative potentiometric stripping analysis. *Journal of Agricultural and Food Chemistry, 52*, 1125–1129.

Martín-Polvillo, M., Albi, T., & Guinda, A. (1994). Determination of trace elements in edible vegetable oils by atomic absorption spectrophotometry. *Journal of American Oil Chemicals Society, 71*, 347–351.

McLaughlin, M. J., Parker, D. R., & Clarke, J. M. (1999). Metals and micronutrients – food safety issues. *Field Crop Research, 60*, 143–163.

Nash, A. M., Mounts, T. L, & Kwolek, W. F. (1983). Determination of ultratrace metals in hydrogenated vegetable oils and fats. *Journal of American Oil Chemical Society, 60*, 811–814.

Nestel, P. J., Noakes, M., Belling, G. B., Mc Arthur, M., Clifton, P. M., & Abbey, J. M. (1992). Plasma cholesterol lowering potential of edible oils blends suitable for commercial use. *American Journal of Clinical Nutrition, 55*, 46–50.

Pharmeuropa (1999). *The European Pharmacopoeia Forum. Technical guide for the elaboration of monograph* (3rd ed.), p. 66.

Renman, R., & Jagner, D. (1997). Asymmetric distribution of results in calibration curve and standard addition evaluation. *Analytica Chimica Acta, 357*, 157–166.

Rojas, E., Herrera, L. A., Poirier, L. A., & Ostrosky-Wegman, P. (1999). Are metals dietary carcinogens. *Mutation Research, 443*, 157–181.

Sanna, G., Pilo, M. I., Piu, P. C., Tapparo, A., & Seeber, R. (2000). Determination of heavy metals in honey by anodic stripping voltammetry at microelectrodes. *Analytica Chimica Acta, 415*, 165–173.

Town, R. M., & Van Leewen, H. P. (2001). Fundamental features of metal ion determination by stripping chronopotentiometry. *Journal of Electroanalytical Chemistry, 509*, 58–65.

Town, R. M., & Van Leewen, H. P. (2002). Effects of adsorption in stripping chronopotentiometric metal speciation analysis. *Journal of Electroanalytical Chemistry, 523*, 1–15.