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Determination of cadmium(II) and zinc(II) in olive oils by derivative potentiometric stripping analysis

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Abstract

A method for the determination of cadmium(II) and zinc(II) in olive oils by derivative potentiometric stripping analysis after dry ashing of the sample is described. The metal ions were concentrated as their amalgams on the glassy carbon working electrode that was previously coated with a thin mercury film and then stripped by a suitable oxidant. Potential and time data were digitally converted into $dt dE^{-1}$, and E was plotted vs. $dt dE^{-1}$, thus increasing sensitivity of the method and improving resolution of the analysis. Quantitative analysis was carried out by the method of standard additions; a good linearity was obtained in the range of concentrations examined. Recoveries of 92–102% for cadmium(II) and of 89–99% for zinc(II) were obtained from an olive oil spiked at different levels. The detection limits were 5.1 ng g^{-1} for cadmium(II) and 7.6 ng g^{-1} for zinc(II) and the relative standard deviations (mean of nine determinations) were 4.1% and 5.2%, respectively. Results obtained on commercial olive oils were not significantly different from those obtained by inductively coupled plasma atomic emission spectrometry (ICP-AES).

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1. Introduction

The presence of trace metals is an important factor as far as the olive oil quality is concerned. The presence of heavy metals in olive oils is due to both endogenous factors, connected with the plant metabolism, and hexogenous factors due to contamination during the agronomic techniques of production and collection of olives, during the processes of oil extraction and treatment, as well as due to systems and materials of packaging and storage (Cichelli, Oddone, & Specchiarello, 1992; De Felice, Gomes, & Catalano, 1979; Farhan, Rammati, & Ghazi-Moghaddam, 1988). Among heavy metals, cadmium(II) plays a major role. Its presence is due to the growing use of sewage sludges and other wastes in agricultural lands. Cadmium(II) is absorbed by plants and enters the food chain; in man, it is permanently retained owing to its

metabolic inertness and may cause severe problems to human health (Crosby, 1977). FAO/WHO fixed an allowable daily intake of cadmium(II) of $7 \mu\text{g kg}^{-1}$ of body weight (Crosby, 1977). Zinc(II) is an essential metal for human body in minimal amounts, whereas it is dangerous in higher quantities, and moreover its presence in soil reduces the cadmium(II) absorption by the plant (Choudhary, Bailey, Grant, & Leisle, 1995).

Sample preparation is a critical step in the whole analytical procedure for the determination of heavy metals in olive oils; classical methods usually employed are wet digestion, dry ashing, acid extraction, closed-vessel and focused open-vessel microwave dissolution, dilution (Allen, Siitonen, & Thompson, 1998; Crosby, 1977; Garrido, Frias, Diaz, & Hardisson, 1994) as well as basic alcoholic solubilization (Wahdat, Hinkel, & Neeb, 1995). The analytical techniques frequently used for the subsequent determination are both emission and absorption spectrophotometric techniques as well as electroanalytical techniques (Calapaj, Chiricosta, Saija, & Bruno, 1988; Hendrikse, Slikkerveer, Folkersma, & Dieffenbacher, 1991; Ibrahim, 1991; Wahdat et al., 1995). Potentiometric stripping analysis (PSA) is an

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electroanalytical technique that allows the determination of some trace metals of nutritional and toxicological interest in a wide range of concentrations (Jagner & Westerlund, 1980; Mannino, 1982), since the dissolved metals concentrate on the working electrode during the electrodeposition step (pre-electrolysis), thereby substantially lowering the detection limits. Therefore, PSA is similar to anodic stripping voltammetry (ASV) in the first step, but differs from ASV in the stripping step, because the reduced metal ions are chemically oxidized and the potential vs. time behaviour at the working electrode is measured. In derivative potentiometric stripping analysis (dPSA), a variant of PSA developed by Jagner and Åren (1978) in order to facilitate evaluation of the analytical signal by using its derivative, already employed by us for the determination of lead in oil products (Lo Coco, Monotti, Rizzotti, & Ceccon, 1999) and of lead and cadmium in hard and soft wheat (Lo Coco, Monotti, Rizzotti, & Ceccon, 2000), potential and time data are digitally converted into $dt dE^{-1}$ and E is plotted against $dt dE^{-1}$. This allows both the sensitivity of the method to be increased and the resolution of the analysis to be improved. The E vs. $dt dE^{-1}$ curve obtained exhibits a maximum at the point where the conventional PSA curve would show a sharp variation of the potential with time. The potential vs. $dt dE^{-1}$ curve has the form of a stripping voltammetry curve and the peak, symmetrical with respect to the abscissa, has an area normally proportional to the concentration of the analyte.

In this paper dPSA was utilized for the determination of cadmium(II) and zinc(II) in olive oils after dry ashing of the sample.

2. Experimental

2.1. Standards and reagents

All glassware was rinsed with 10% (v/v) nitric acid. Ultra-pure water obtained by the Pure Lab RO and the Pure Lab UV systems (USF, Ransbach-Baumbach, Germany), ultra-pure and certified hydrochloric acid (C. Erba, Milan, Italy), pure mercury(II) chloride and pure sodium acetate for analysis (C. Erba), a cadmium(II) standard solution containing $1000 \text{ ng } \mu\text{l}^{-1}$ of cadmium, a zinc(II) standard solution containing $1000 \text{ ng } \mu\text{l}^{-1}$ of zinc and a gallium(III) standard solution containing $1000 \text{ ng } \mu\text{l}^{-1}$ of gallium (Panreac Quimica, Barcellona, Spain) were employed. By dilution with water, a solution containing $1 \text{ ng } \mu\text{l}^{-1}$ of cadmium(II), a solution containing $1 \text{ ng } \mu\text{l}^{-1}$ of zinc(II) and a solution containing $1 \text{ ng } \mu\text{l}^{-1}$ of gallium(III) were prepared.

2.2. Instrumentation and software

Determinations were carried out by a PSA ION³ potentiometric stripping analyzer (Steroglass, S. Mar-

tino in Campo, Perugia, Italy), connected to an IBM-compatible personal computer. The analyzer operated under the control of the NEOTES software package (Steroglass). The analytical procedure can be completely controlled by this program, as already described in previous papers (Lo Coco et al., 1999; Lo Coco et al., 2000).

ICP-AES measurements were carried out with an ICP-AES 1000 instrument (Perkin Elmer, Norwalk, CT, USA).

2.3. Electrodes and electrochemical cell

The three-electrode system and the electrochemical cell utilized were already described in previous papers (Lo Coco et al., 1999; Lo Coco et al., 2000).

2.4. Analytical procedure

2.4.1. Preliminary sample processing

A 10 g sample aliquot was exactly weighed in a 50 ml platinum crucible. A proper quantity of filter paper was placed in the crucible before and after the addition of the sample. The crucible was transferred on a heating plate and the temperature slowly increased until the sample was completely carbonized. The carbonized material was then burnt in a muffle oven by slowly increasing the temperature up to $500 \text{ }^\circ\text{C}$, and maintained until white ashes were obtained. If carbon particles remained, the crucible was cooled to room temperature, the residue was moistened with a few drops of concentrated nitric acid and the crucible was kept again in a muffle oven for 30 min at $500 \text{ }^\circ\text{C}$. The crucible was then cooled to room temperature and ashes were dissolved with small volumes of 2 M hydrochloric acid, that were quantitatively transferred to a 50 ml volumetric flask. The volume was filled up to the mark with 2 M hydrochloric acid.

2.4.2. Determination of cadmium(II)

A 10 ml volume of the solution obtained as described in the preceding section was introduced into the electrochemical cell together with 10 ml of water and 1.0 ml of a mercury(II) chloride solution containing $1000 \text{ ng } \mu\text{l}^{-1}$ of mercury(II) ion in 1 M hydrochloric acid. Before analysis, the working electrode was coated with a thin mercury film by electrolyzing 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 and the potential -0.9 V ; the potential of the electrodes was monitored every $300 \text{ } \mu\text{s}$. Quantitative analysis was carried out by the method of standard additions by adding twice $20 \text{ } \mu\text{l}$ of a solution containing $1 \text{ ng } \mu\text{l}^{-1}$ of cadmium(II).

2.4.3. Determination of zinc(II)

A 10 ml volume of the solution obtained as described in the Section 2.4.1 was buffered at pH 4.8 by adding a 10 ml volume of 4 M sodium acetate solution and spiked with 100 μl of a solution containing 1 $\text{ng}\mu\text{l}^{-1}$ of gallium(III). The solution obtained was introduced into the electrochemical cell; from this point the procedure was the same as that described in the preceding section with the only differences concerning (i) the electrolysis potential, which was -1.3 V , (ii) the time of electrolysis, which was 240 s and (iii) the two standard additions, that spanned from 50 to 150 μl of a solution containing 1 $\text{ng}\mu\text{l}^{-1}$ of zinc(II).

2.4.4. Determination of recoveries

A 20–40 μl volume of a solution containing 1 $\text{ng}\mu\text{l}^{-1}$ of cadmium(II) and a 30–90 μl volume of a solution containing 1 $\text{ng}\mu\text{l}^{-1}$ of zinc(II) were added to 10 g of olive oil. The spike/oil mixture was equilibrated under stirring for 12 h, then processed as described in the Sections 2.4.2 and 2.4.3.

2.5. Statistical analysis

A Student *t*-test was used to determine whether significant differences existed between results obtained by dPSA and ICP-AES.

3. Results and discussion

In this paper the determination of cadmium(II) and zinc(II) in olive oils by dPSA is described. Preliminary sample processing was carried out with a proper quantity of filter paper in order to avoid squirts and to favour combustion and under proper ashing conditions to prevent volatilization losses (Black, 1975; Crosby, 1977; Thiers, 1957). The determination of zinc(II) was carried out with an excess of gallium(III) to prevent the formation of Cu(II)–Zn(II) intermetallic compounds by forming much more stable Cu(II)–Ga(III) intermetallics (Psaroudakis & Efsthathiou, 1987; Psaroudakis & Efsthathiou, 1989). In Fig. 1 the stripping curves for a sample of olive oil are reported. Cadmium(II) and zinc(II) were oxidized at approximately -0.72 and -1.11 V , respectively, vs. the reference electrode under the conditions described. The method of standard additions was used for quantitative determinations. Peak areas relative to both sample and two standard additions were measured. By plotting these areas vs. total cadmium(II) and zinc(II) amounts, straight lines were obtained. A good linearity was obtained in the range of concentrations examined, as is shown by both the equations of the lines $Y = 5.3 \times 10^7 X + 2.6 \times 10^5$ for cadmium(II) and $Y = 3.9 \times 10^7 X + 2.7 \times 10^5$ for zinc(II), and the determination coefficients which were 99.8% and 99.9% re-

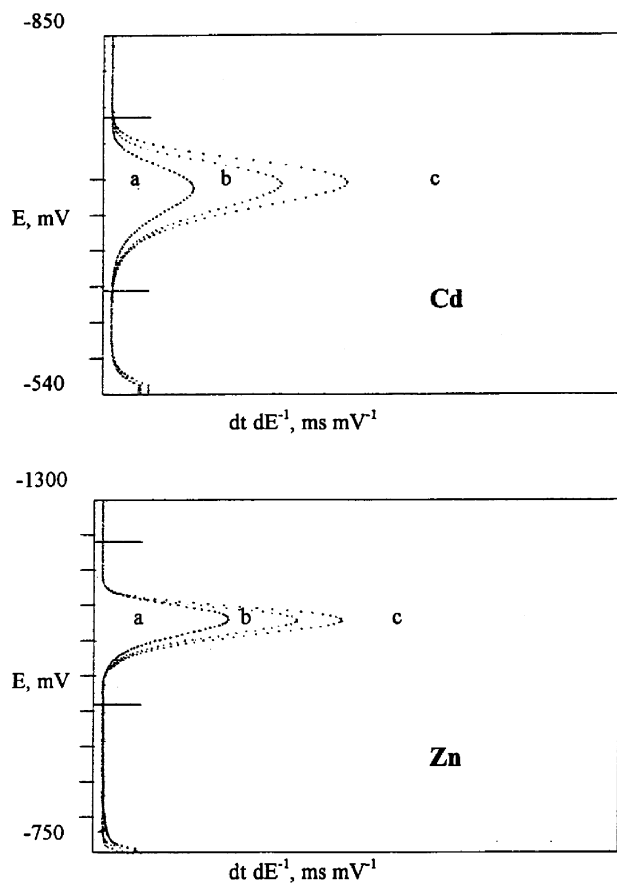


Fig. 1. Stripping curves relative to cadmium(II) and zinc(II) determination in a sample of olive oil added with a cadmium(II) amount of 10 ng g^{-1} : (a) sample; (b,c) sample added with one and two standard additions, respectively, as described in Section 2.

spectively. To determine the recoveries of cadmium(II) and zinc(II), appropriate volumes of a diluted cadmium(II) solution and a zinc(II) solution were added to a sample of olive oil. To favour the equilibration between the spike aqueous solution and the oil, the spike/oil mixture was equilibrated under stirring for 12 h. The oil components present, particularly free fatty acids and phospholipids, and the low concentrations of the metals added allowed an homogeneous dissolution of the spike in the oil to be obtained. Both spiked and unspiked samples were analyzed in triplicate by the proposed method. The results obtained are reported in Table 1; as may be seen, recoveries ranged from 92% to 102% for cadmium(II) and from 89% to 99% for zinc(II). The repeatability of the method was evaluated by carrying out the determination three times on the same sample of olive oil; each solution was analyzed three times. Since the cadmium(II) content was lower than the detection limit for all samples examined, an olive oil sample was added with a cadmium(II) amount of 10 ng g^{-1} to carry out the repeatability tests. The values obtained were subjected to statistical analysis by employing the same

Table 1
Recoveries (ng g^{-1}) of cadmium(II) and zinc(II) added to a sample of olive oil^a

Originally present	Added	Found	Recovery (%)
<i>Cadmium(II)</i>			
ND	10	9.8 ± 0.4	98 ± 4
ND	15	14.4 ± 0.5	96 ± 3
ND	20	19.0 ± 0.6	95 ± 3
<i>Zinc(II)</i>			
25.5	15	38.1 ± 0.8	94 ± 2
25.5	30	51.6 ± 2.2	93 ± 4
25.5	45	66.9 ± 2.9	95 ± 4

ND = not detectable.

^a Each figure is the mean of three determinations; each determination was repeated three times. The confidence interval of the mean value corresponds to a 95% probability.

software running all the analytical steps. The average concentrations were 9.8 ng g^{-1} for cadmium(II), with a standard deviation of 0.4 ng g^{-1} and a relative standard deviation of 4.1%, and 25.5 ng g^{-1} for zinc(II), with a standard deviation of 1.3 ng g^{-1} and a relative standard deviation of 5.2%. The confidence interval of the mean value was ± 1.3 , ± 1.8 and ± 2.4 for cadmium(II) and ± 1.2 , ± 1.7 and ± 2.7 for zinc(II), corresponding to a probability of 90%, 95% and 99% respectively. In PSA the detection limit depends on the determined element and matrix as well as on electrolysis time, and therefore it is possible to enhance the sensitivity of the method by choosing an appropriate electrodeposition time. By using the working conditions stated above, the detection limits were 5.1 ng g^{-1} for cadmium(II) and 7.6 ng g^{-1} for zinc(II) by setting 200 as the peak threshold and by utilizing the expression $3\sigma S^{-1}$, where S is the sensitivity obtained from the calibration graph and σ is the peak threshold (Massart, Dijkstra, & Kaufman, 1978). The method was applied to cadmium(II) and zinc(II) determinations in

Table 2
Cadmium(II)^a and zinc(II) concentrations (ng g^{-1}) as determined in different commercial samples of olive oils. Each figure is the mean of three determinations; each determination was repeated three times. The confidence interval of the mean value corresponds to a 95% probability

Sample	Zinc(II)	
	dPSA	ICP-AES
1	25.5 ± 1.2	26.7 ± 1.0
2	38.8 ± 1.5	40.5 ± 1.3
3	45.4 ± 2.0	47.8 ± 2.1
4	62.3 ± 3.1	64.8 ± 3.0
5	28.8 ± 1.4	28.0 ± 1.8
6	44.2 ± 1.7	44.8 ± 2.0
7	37.4 ± 1.7	38.9 ± 2.3
8	68.3 ± 2.7	65.3 ± 2.6
9	26.1 ± 1.1	27.0 ± 1.3
10	28.6 ± 1.3	28.1 ± 1.4

^a Cadmium(II) was not detected in any of the samples analyzed by both analytical methods.

different commercial samples of olive oils. The results were compared with those obtained by an ICP-AES method and are shown in Table 2. As may be seen, no statistically significant differences between the two methods were obtained for all samples examined.

4. Conclusions

The proposed method provides a sensitive and convenient procedure for the determination of cadmium(II) and zinc(II) in olive oils by dPSA. A slow dry ashing step with respect to sample pretreatment and a short time of analysis are required. In addition, the cost and size of the instrumentation are low. Furthermore, the extensive and flexible software supporting the instrumentation makes it possible not only to fully automate the analysis, but also to present the results digitally and graphically, and to store them for possible future processing and statistical treatment.

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