

## Simultaneous Determination of Cd(II), Cu(II), Pb(II), and Zn(II) in Citrus Essential Oils by Derivative Potentiometric Stripping Analysis

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Citrus essential oils are widely used in the food, cosmetics, and pharmaceutical industries, so the determination of heavy metals content is of great importance to guarantee their quality. The present work deals with the quantification of Cd(II), Cu(II), Pb(II), and Zn(II) in different varieties of citrus essential oils, using derivative potentiometric stripping analysis. Two different metals extraction procedures, involving concentrated hydrochloric acid treatment and acid–alcoholic dissolution, are tested on lemon, mandarin, sweet orange, and bergamot essential oils, and they give very similar results. Cd(II), Cu(II), Pb(II), and Zn(II) recovery tests spanned from 95 to 100.50%, providing evidence that metals quantification remained unaffected by the cleanup steps of the two procedures. The repeatability of the hydrochloric acid extraction method, applied on different varieties of essential oils, is >95.00% for Cd(II), Cu(II), Pb(II), and Zn(II), whereas the repeatability of the acid–alcoholic dissolution method is >93.00% for Cu and Cd only in lemon oil. Detection limits obtained for the four analytes, using both procedures, ranged from 0.10 to 0.98 ng g<sup>-1</sup> in lemon, mandarin, sweet orange, and bergamot essential oils.

**KEYWORDS:** Cadmium; citrus essential oils; copper; derivative potentiometric stripping analysis; lead; zinc

### INTRODUCTION

Citrus essential oils are complex mixtures of many classes of volatile (85–98%) and nonvolatile (2–15%) compounds, such as terpenes, hydrocarbons, esters, aldehydes, and ketones; the main difference between essential oils of different varieties is in the composition of the volatile fraction (1). Citrus essential oils are mainly used as aromatizing agents for food, beverages, and cosmetics and as additives in some pharmaceuticals (2). Their wide use implies a strict control of the presence of organic and inorganic contaminants. The determination of pesticide residues (3, 4) and plasticizers (5–8) in essential oils is well documented; however, there is a lack of available data regarding the presence of heavy metals. Some reports concerning the microelements composition of citrus peel extracts were found (9, 10). Some metals, such as iron, copper, zinc, and cobalt, are nontoxic at moderate concentrations, while cadmium, lead, mercury, and arsenic are toxic even in very low amounts and constitute a significant health hazard (11). Metals levels in citrus essential oils mostly depend on the type of soil, but they are also affected by the extraction procedures, such as scraping or pressing, since the fruits inevitably come in contact with metallic surfaces (12). In the work described in this paper, derivative potentiometric stripping analysis (dPSA) (13) is used to determine the concentrations of Cd(II), Cu(II), Pb(II), and Zn-

(II) in different types of citrus essential oils. Potentiometric and voltmetric stripping techniques represent a viable alternative to atomic absorption spectroscopic (AAS) methods to determine trace metals concentrations in a variety of matrices, such as alloys, food, biological materials, and environmental samples (14–16). Moreover, one of the future possibilities for dPSA is multielement analysis. For the simultaneous determination of Cd(II), Cu(II), Pb(II), and Zn(II), a conventional three-cell electrode is used. The working electrode is a mercury-coated electrode that is widely employed for the electroanalytical stripping determinations of mercury-soluble elements, chosen for the ability to renew the electrode surface prior to each analysis (17). Metals quantification in oily matrices has always been very problematic, because these elements are present in very small quantities in a complex organic substrate; therefore, sample preparation is a critical step in the whole analytical procedure. In a previous work, dPSA was used to determine heavy metals content in a fatty matrix, olive oil, and concentrated hydrochloric acid sample treatment was found to be well suited for metals extraction (18). In the present work, two different procedures for metals extraction from citrus essential oils are employed: concentrated hydrochloric acid treatment and acid–alcoholic dissolution, after the evaporation of the volatile fraction. The last method exploits the volatility of the greatest part of the organic matter of the sample. Acidification to pH < 2, which characterizes both of the procedures, may dissociate some organic complexes or release metals adsorbed

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**Table 1.** Analytical Conditions for Determination of Pb, Cu, Cd, and Zn

	Pb	Cu	Cd	Zn
integration range, mV	-580 to -380	-380 to -140	-760 to -590	-1100 to -750
potential range, mV	-1200 to -100	-1200 to -100	-1200 to -100	-1200 to -100
conditioning potential, mV	50 × 5 s	50 × 5 s	50 × 5 s	50 × 5 s
accumulation potential, mV	-1200	-1200	-1200	-1200
accumulation time, min	2	2	2	2
stripping time, s	10	10	10	10
acquisition final potential, mV	0	0	0	0
sampling time, $\mu$ s	300	300	300	300
discharge potential, mV	-430	-260	-640	-950
agitation speed, turns/s	2	2	2	2
no. of cycles	4	4	4	4
no. of standard additions	2	2	2	2

**Table 2.** Method and Instrument Repeatability Calculated for dPSA Determination of Cd, Cu, Pb, and Zn in Lemon Essential Oil<sup>a</sup>

	metals concentration (ng g <sup>-1</sup> )							
	hydrochloric acid treatment				acid-alcoholic dissolution			
	Cd	Cu	Pb	Zn	Cd	Cu	Pb	Zn
first extraction	1.53	17.56	105.00	804.89	1.52	22.47	109.53	811.93
	1.50	17.56	104.72	807.66	1.65	21.52	109.29	813.30
	1.50	17.90	104.07	804.68	1.60	23.52	109.51	806.92
mean	1.51	17.67	104.60	805.74	1.59	22.50	109.44	810.72
SD	0.02	0.20	0.48	1.66	0.07	1.00	0.13	3.36
rsd	1.32	1.13	0.46	0.21	4.40	4.44	0.12	0.41
second extraction	1.57	17.07	110.50	800.02	1.63	20.33	112.76	807.73
	1.54	17.05	111.11	802.66	1.65	23.41	112.89	812.12
	1.59	16.70	112.10	804.98	1.60	21.21	114.06	809.00
mean	1.57	16.94	111.24	802.55	1.63	21.65	113.24	809.62
SD	0.03	0.21	0.81	2.48	0.03	1.59	0.72	2.26
rsd	1.91	1.24	0.73	0.31	1.84	7.3	0.64	0.28
third extraction	1.50	17.10	107.33	806.60	1.45	19.15	104.44	808.20
	1.46	16.89	108.01	804.44	1.49	18.66	106.63	805.00
	1.51	16.77	107.99	805.00	1.50	18.03	107.00	807.15
mean	1.49	16.92	107.78	805.35	1.48	18.61	106.02	806.78
SD	0.03	0.17	0.39	1.12	0.03	0.56	1.38	1.63
rsd	2.01	1.00	0.36	0.14	1.84	3.00	1.30	0.20
mean rsd %	1.75	1.12	0.52	0.22	2.72	4.91	0.69	0.30
total mean	1.50	17.18	107.87	804.55	1.57	21.37	109.49	809.04
total SD	0.07	0.43	3.32	1.74	0.08	1.30	3.73	2.03
total rsd %	4.67	2.50	3.10	0.22	5.1	6.08	3.41	0.25
repeatability, %	95.33	97.50	96.90	99.78	94.99	93.92	96.59	99.75

<sup>a</sup> Hydrochloric acid treatment and acid-alcoholic dissolution as metals extraction procedures were tested. Each sample was extracted three times, and each extract was analyzed in triplicate.

on colloidal species. Measurements at such extreme pH values have already been done in speciation studies (19).

## MATERIALS AND METHODS

**Reagents.** Three Sicilian citrus essential oil samples, respectively extracted from lemon, sweet orange, and mandarin, and one Calabrian bergamot essential oil sample, produced in the crop year 1999–2000, were analyzed. All oils were sampled in dark glass bottles, with blind nipples, and stored at 4 °C until the analyses. Ultrapure hydrochloric acid (34–37%), Hg(II) (1000  $\mu$ g mL<sup>-1</sup>, 1 M in hydrochloric acid), and Cd(II), Cu(II), Pd(II), Pb(II), and Zn(II) (1000  $\mu$ g mL<sup>-1</sup>, 0.5 N in HNO<sub>3</sub>) standard solutions were purchased from Panreac (Barcelona, Spain); Ga(NO<sub>3</sub>)<sub>3</sub>·3H<sub>2</sub>O (5 g, 99.9%) was purchased from Aldrich Chemical Co. (Milwaukee, WI). By dilution with ultrapure water, solutions containing 1  $\mu$ g mL<sup>-1</sup> of Cu(II), 1  $\mu$ g mL<sup>-1</sup> of Cd(II), 1  $\mu$ g mL<sup>-1</sup> of Pb(II), 5  $\mu$ g mL<sup>-1</sup> of Zn(II), 10  $\mu$ g mL<sup>-1</sup> of Ga(III), and 100  $\mu$ g mL<sup>-1</sup> of Pd(II) were prepared. Moreover, by dilution with HPLC-grade methanol (Carlo Erba Reagenti, Milan, Italy), 1  $\mu$ g mL<sup>-1</sup> solutions of Cu(II), Cd(II), Pb(II), and Zn(II) were prepared. The extracts were filtrated on a carbon column (Supelclean ENVI-Carb SPE, 0.5 g,

6 mL), purchased from Supelco (Bellefonte, PA). The methanol used to activate the column and to dissolve the oily nonvolatile residue was HPLC-grade purchased from Carlo Erba Reagenti. Ultrapure water (18.2 M $\Omega$  cm<sup>-1</sup>) was prepared at the Department of Organic and Biological Chemistry, University of Messina.

**Apparatus.** Metals analyses were carried out by using a PSA ION 3 potentiometric stripping analyzer (Steroglass, S. Martino in Campo, Perugia, Italy), connected to an IBM-compatible personal computer. The analyzer operates under the control of the NEOTES 2.0.1 software package (Steroglass). The analytical procedure can be completely controlled by this program, which makes it possible to elaborate potentiometric data relative to the four metals analyzed simultaneously. The determination was carried out in a conventional three-electrode cell. The working electrode was a glassy carbon one coated with a thin mercury film; the reference electrode was an Ag/AgCl electrode (3 M KCl), and a platinum wire auxiliary electrode was used. Samples pH values were controlled by a pH meter (MI229 BDH) equipped with glass + combination pH electrodes (BDH, Milan, Italy). To confirm the analytical results of the potentiometric method, the oily extracts were subjected to AAS using a Shimadzu 800 series graphite furnace atomic absorption spectrometer, equipped with auto sampler ASC-6100.

**Table 3.** Recoveries Obtained for Hydrochloric Acid Treatment and Acid-Alcoholic Dissolution

	hydrochloric acid treatment					acid-alcoholic dissolution				
	metal concn (ng g <sup>-1</sup> )	metal added (ng g <sup>-1</sup> )	metal found (ng g <sup>-1</sup> )	theor (ng g <sup>-1</sup> )	recovery (%)	metal concn (ng g <sup>-1</sup> )	metal added (ng g <sup>-1</sup> )	metal found (ng g <sup>-1</sup> )	theor (ng g <sup>-1</sup> )	recovery (%)
Cd	1.50	2.00	3.31 ± 0.05	3.50	94.57	1.60	2.00	2.40 ± 0.04	2.60	92.30
	1.50	5.00	6.30 ± 0.29	6.50	97.11	1.60	5.00	6.45 ± 0.05	6.60	97.72
	1.50	10.00	11.16 ± 0.30	11.50	96.49	1.60	10.00	11.09 ± 0.05	11.60	95.60
					96.06 ± 1.32					95.21 ± 2.73
Cu	18.00	10.00	26.99 ± 1.67	28.00	96.41	21.00	10.00	30.76 ± 1.09	31.00	99.21
	18.00	20.00	36.74 ± 1.28	38.00	96.68	21.00	50.00	71.89 ± 1.90	71.00	101.25
	18.00	100.00	117.77 ± 1.39	118.00	99.81	21.00	100.00	120.54 ± 1.41	121.00	99.62
					97.63 ± 1.89					100.03 ± 1.08
Pb	111.10	50.00	162.81 ± 3.31	161.10	101.07	109.00	50.00	154.31 ± 0.56	159.00	97.05
	111.10	100.00	207.34 ± 2.01	211.10	98.07	109.00	100.00	203.20 ± 2.06	209.00	97.22
	111.10	200.00	307.85 ± 2.27	311.10	98.96	109.00	200.00	307.13 ± 2.91	309.00	99.40
					99.37 ± 1.54					97.89 ± 1.31
Zn	808.00	50.00	871.91 ± 6.26	858.00	101.62	813.00	50.00	861.67 ± 4.44	863.00	99.85
	808.00	100.00	913.93 ± 11.17	908.00	100.67	813.00	100.00	911.44 ± 4.80	913.00	99.09
	808.00	1000.00	1789.17 ± 12.89	1808.00	98.96	813.00	1000.00	1801.60 ± 4.49	1813.00	99.37
					100.42 ± 1.35					99.44 ± 0.38

**Table 4.** Metal Mean Concentrations<sup>a</sup> and Standard Deviations (ng g<sup>-1</sup>) Determined by dPSA and AAS on Both Acid and Methanolic Extracts

sample	Cd		Cu		Pb		Zn	
	dPSA	AAS	dPSA	AAS	dPSA	AAS	dPSA	AAS
	Acid Extracts							
lemon	1.57 ± 0.03	1.43 ± 0.03	16.94 ± 0.21	16.00 ± 0.20	111.24 ± 0.81	103.60 ± 1.10	802.55 ± 2.48	799.60 ± 3.00
mandarin	1.81 ± 0.05	1.60 ± 0.05	277.71 ± 3.00	265.60 ± 3.98	174.80 ± 5.23	168.20 ± 6.70	1275.75 ± 10.00	1255.16 ± 12.30
sweet orange	8.96 ± 0.50	7.80 ± 0.95	83.06 ± 1.40	78.05 ± 1.96	76.53 ± 2.00	70.40 ± 2.98	1640.30 ± 13.16	1605.30 ± 17.52
bergamot	22.22 ± 1.90	20.12 ± 2.55	379.60 ± 5.90	365.80 ± 4.50	75.56 ± 1.40	69.40 ± 1.99	821.21 ± 4.02	821.21 ± 8.15
	Methanol Extracts							
lemon	1.63 ± 0.03	1.55 ± 0.05	21.65 ± 1.59	18.10 ± 2.65	113.24 ± 0.72	103.30 ± 7.15	809.62 ± 2.26	788.99 ± 9.10
mandarin	1.80 ± 0.05	1.65 ± 0.08	277.05 ± 3.64	269.56 ± 5.10	177.60 ± 5.85	169.40 ± 7.41	1266.30 ± 11.00	1240.90 ± 13.50
sweet orange	8.10 ± 0.20	7.90 ± 0.50	85.45 ± 2.00	79.89 ± 3.63	77.64 ± 2.33	70.15 ± 3.39	1650.50 ± 12.99	1599.80 ± 18.96
bergamot	22.50 ± 1.96	18.16 ± 2.58	375.75 ± 6.00	360.56 ± 7.12	75.55 ± 2.01	70.00 ± 4.16	785.12 ± 5.50	771.01 ± 9.98

<sup>a</sup> Each value is the mean of three determinations.

**Table 5.** Detection Limits (ng g<sup>-1</sup>) of Cd(II), Cu(II), Pb(II), and Zn(II) As Determined for the Hydrochloric Acid Extraction Method and Acid-Alcoholic Dissolution

sample	hydrochloric acid extraction				acid-alcoholic dissolution			
	Cd	Cu	Pb	Zn	Cd	Cu	Pb	Zn
lemon	0.55 ± 0.03	0.12 ± 0.03	0.50 ± 0.02	0.48 ± 0.01	0.43 ± 0.04	0.11 ± 0.05	0.32 ± 0.02	0.34 ± 0.01
mandarin	0.30 ± 0.02	0.12 ± 0.02	0.50 ± 0.03	0.48 ± 0.01	0.45 ± 0.03	0.15 ± 0.02	0.50 ± 0.03	0.60 ± 0.04
sweet orange	0.30 ± 0.01	0.10 ± 0.01	0.31 ± 0.02	0.80 ± 0.06	0.50 ± 0.02	0.60 ± 0.03	0.90 ± 0.07	0.60 ± 0.04
bergamot	0.61 ± 0.03	0.20 ± 0.02	0.31 ± 0.03	0.81 ± 0.06	0.15 ± 0.02	0.10 ± 0.01	0.21 ± 0.03	1.00 ± 0.07

**Procedures.** *Hydrochloric Acid Extraction.* A 8.60/g (10.00 mL) sample aliquot and a 10/mL volume of 36% ultrapure hydrochloric acid (Panreac, Barcelona, Spain) were introduced into a Teflon beaker. The extraction was carried out for about 30 min under magnetic stirring at 90 °C. The acidified sample, that formed an emulsion, was transferred in a separating funnel and left to cool for about 5 min. To favor the separation of the two phases, the mixture was spiked with 1.00 mL of ultrapure methanol, and then the acid layer was collected in a 20.00-mL flask. The organic layer was extracted again with 4.50 mL of concentrated hydrochloric acid for 5 min under the same conditions described earlier and then washed with 4.50 mL of boiling water; washings were added to the acid extracts and made up to the mark with water. The obtained solution was passed through a carbon column (Supelclean ENVI-Carb SPE tubes, 0.50 g, 6.00 mL), previously activated by 2.00 mL of methanol followed by 2.00 mL of ultrapure water;

the first drops of the eluate were discarded. The filtered solution was used for the simultaneous determination of Cd(II), Cu(II), Pb(II), and Zn(II).

*Acid-Alcoholic Dissolution.* A 2.60/g (3.00 mL) aliquot of essential oil was weighted in a porcelain capsule and introduced into a stove maintained at 160 °C for 2 h, to remove the volatile organic compounds that represent the greatest fraction of the oil. After evaporation, the oily residue was spiked with 1.00 mL of concentrated hydrochloric acid, followed by 8.00 mL of pure methanol. The mixture was filtered on a carbon column as previously described and used for the analysis.

*Potentiometric Determination.* All analyses were done in a conventional three-electrode cell: working electrode was a glassy carbon electrode coated with a Hg film, the reference electrode was an Ag/AgCl electrode, and the counter was a Pt electrode. The electrodes were stored in ultrapure water; before starting each analysis, they were well cleaned with pure absolute methanol and filter paper. The

plating of the working electrode was done as reported previously (18). The concentrations of Cd(II), Cu(II), Pb(II), and Zn(II) were determined simultaneously: 1.00 mL of acid or methanolic extract, 17.50 mL of ultrapure water, 1.00 mL of 1000  $\mu\text{g mL}^{-1}$  Hg(II) as oxidant agent, and 0.50 mL of 10  $\mu\text{g mL}^{-1}$  Ga(III)—in order to prevent Cu–Zn complexes formation on the mercury film—were put into the electrochemical cell. For an accurate simultaneous determination of the four analytes, the pH of the sample must always be in the range 1.8–2.2 (13, 18). The quantitative analysis was done by the multiple points standard additions method (20). Optimum precision and accuracy were obtained by making two 0.10-mL standard additions respectively of 1.00  $\mu\text{g mL}^{-1}$  of Cd(II), Cu(II), and Pb(II) and 0.10 mL of 5.00  $\mu\text{g mL}^{-1}$  Zn(II) and performing four measurements on these. The potentiometric parameters are reported in Table 1.

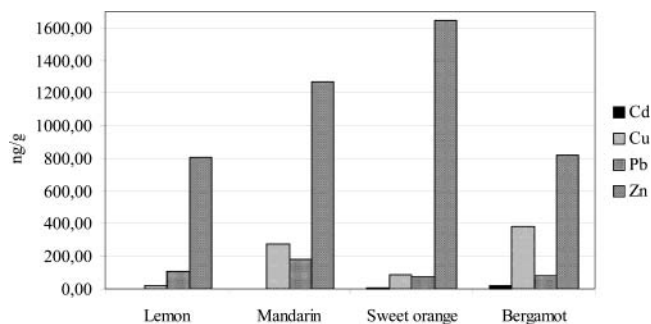
**Precision and Repeatability Evaluation.** Methods and instrument repeatability were evaluated by extracting the same oil sample three times by the two different procedures described above and quantifying in triplicate each metal in the same extract. The instrument precision is indicated as mean *rsd* %, while the precision of the two methods is represented by the total *rsd* %. Methods repeatability for each metal was calculated by subtracting from 100, as the theoretical value, the total percent standard deviation. Repeatability tests were conducted on each sample; Table 2 reports the results obtained for the lemon essential oil.

**Recovery Tests.** For a greater accuracy in quantification of metallic ions, the possibility of decreases or increments of their amounts, due to the cleanup steps of the two different extraction procedures, was considered. Recovery tests were managed by spiking the citrus essential oil samples with different amounts of 1  $\mu\text{g mL}^{-1}$  methanolic standard solutions of each of the four analytes. Due to the solubility of methanol in the citrus essential oil, the spiked moisture was left under magnetic stirring only for 30 min to obtain a completely homogeneous mixture. Both the spiked and unspiked samples were then processed by the two different procedures described. Each sample was subjected to a recovery test; Table 3 reports the results obtained for the lemon essential oil.

**Graphite Furnace Atomic Absorption Spectroscopy Analysis (GFAAS).** Both acid and alcoholic extracts of lemon, mandarin, sweet orange, and bergamot oils were analyzed in triplicate by GFAAS for Cd, Cu, Pb, and Zn determination. The analyses of Pb and Cd were carried out by adding, for each injection, 5  $\mu\text{L}$  of a  $\text{Pd}(\text{NO}_3)_2$  solution (Pd concentration 100  $\mu\text{g mL}^{-1}$ ) as a matrix modifier. The working wavelengths were 228.8 nm for Cd, 324.8 nm for Cu, 283.3 nm for Pb, and 213.9 nm for Zn. The obtained results are reported in Table 4.

## RESULTS AND DISCUSSIONS

**Method.** Comparison between GFAAS and dPSA analysis shows no statistically significant differences for all samples examined. Detection limits were evaluated using the expression  $3\sigma/S$  (18, 21) applied on nine determinations, where  $\sigma$  is the peak threshold (set at 200) and  $S$  is the sensibility obtained from the calibration curve of each analyte, with correlation coefficients  $>99.90\%$ . The calculated detection limits for an essential oil hydrochloric acid extract span from 0.30 to 0.61  $\text{ng g}^{-1}$  for Cd, 0.10 to 0.20 for Cu, 0.31 to 0.50  $\text{ng g}^{-1}$  for Pb, and 0.48 to 0.81  $\text{ng g}^{-1}$  for Zn. The calculated detection limits for an essential oil alcoholic extract range from 0.15 to 0.50  $\text{ng g}^{-1}$  for Cd, 0.10 to 0.60 for Cu, 0.32 to 0.90  $\text{ng g}^{-1}$  for Pb, and 0.34 to 0.98  $\text{ng g}^{-1}$  for Zn (Table 5). This provides evidence that both of the proposed sample pretreatments are highly suitable for dPSA determination of very low amounts of Cd(II), Cu(II), Pb(II), and Zn(II) in citrus essential oils. Both of the employed extraction procedures give repeatability values  $>95.00\%$  for the four metals in all types of studied essential oils, with the exception of the acid–alcoholic dissolution method repeatability which is  $>93.00\%$  for Cu and Cd analysis in lemon essential oil only. Recovery tests of Cd(II), Cu(II), Pb(II), and Zn(II), executed on lemon, mandarin, orange, and bergamot essential oils, yielded results in the range 95.00–100.50%. This



**Figure 1.** Outline of Cd, Cu, Pb, and Zn concentrations in lemon, mandarin, sweet orange, and bergamot essential oils as determined by dPSA on their hydrochloric acid extracts.

provided evidence that the two extraction procedures described do not cause significant losses or increases of metals concentrations in the sample, and thus they are suitable for different types of citrus essential oils; moreover, they give very similar results of metals amounts in different types of essential oils.

**Application.** Due to the great similarity between results obtained by both of the studied extraction procedures applied on lemon, mandarin, sweet orange, and bergamot essential oils, Figure 1 is elaborated utilizing data obtained by dPSA analysis of their hydrochloric acid extracts. It is evident that Cd is the metal present in the lowest amount and Zn the highest in all types of essential oils. Cd concentrations smaller than 2.00  $\text{ng g}^{-1}$  are present in lemon and mandarin oil samples; the Cd concentrations in sweet orange and bergamot oils are respectively  $8.25 \pm 0.21$  and  $23.31 \pm 1.00$   $\text{ng g}^{-1}$ . Cu concentrations show a significant variability in the studied citrus essential oils. The lowest Cu level is found in the lemon essential oil sample,  $17.18 \pm 0.20$   $\text{ng g}^{-1}$ , followed by sweet orange,  $85.18 \pm 1.45$   $\text{ng g}^{-1}$ ; mandarin and bergamot samples show higher Cu values, respectively  $278.30 \pm 3.20$  and  $380.00 \pm 5.45$   $\text{ng g}^{-1}$ . Sweet orange and bergamot oils show very similar Pb concentrations, respectively  $75.94 \pm 2.06$  and  $77.92 \pm 1.02$   $\text{ng g}^{-1}$ ; higher amounts are obtained from lemon and mandarin oils,  $107.87 \pm 3.32$  and  $180.28 \pm 6.15$   $\text{ng g}^{-1}$ . Sweet orange and mandarin oils present very high levels of Zn, respectively  $1647.49 \pm 12.27$  and  $1267.37 \pm 10.14$   $\text{ng g}^{-1}$ ; moreover, very similar Zn concentrations, respectively  $820.45 \pm 3.99$  and  $804.55 \pm 1.66$   $\text{ng g}^{-1}$ , are present in bergamot and lemon essential oil samples.

**Conclusions.** Derivative potentiometric stripping analysis, besides being a precise and inexpensive technique for the simultaneous analysis of trace metals in citrus essential oils, has excellent sensitivity due to preconcentration of the analytes on the mercury film. Both of the extraction procedures employed are well suited to dPSA metals quantification; hydrochloric acid extraction requires more passages than acid–alcoholic dissolution but is less time-consuming, so it is more suited for routine analysis.

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