

Application of potentiometric stripping analysis with constant inverse current in the analytic step for determining lead in glassware

BILJANA M. KALIČANIN^{1#}, NIKOLA J. MARJANOVIĆ^{2#} and ZVONIMIR J. SUTUROVIĆ^{2#}

¹*University of Niš, Faculty of Technology, Bulevar Oslobođenja 124, YU-16000 Leskovac and*

²*University of Novi Sad, Faculty of Technology, Bulevar Cara Lazara 1, YU-21000 Novi Sad, Yugoslavia*

(Received 7 June, revised 5 November 2001)

The trace amounts of lead in extraction glassware products were determined by potentiometric stripping analysis with constant inverse current in the analytic step (PSA-_{iR}), an electrochemical technique of high sensitivity and selectivity. This paper deals with an investigation which was directed to the effect of a great number of factors on the results of PSA-_{iR}, of lead in glassware, such as the mercury time electro-deposition, the electrolysis potential, the solution stirring rate and the constant inverse current. Linearity of the lead analytical signal was achieved within the range of mass concentrations from 2.5 µg/dm³ to 4.5 µg/dm³. A detection limit of 0.64 µg/dm³ was obtained, with a reproducibility of 4.14 % expressed as the coefficient of variation. The analyses were carried out using a computerized stripping analyzer of domestic design and manufacture (Faculty of Technology, Novi Sad and "Elektrouniverzal", Leskovac). The accuracy of the method was confirmed by parallel analyses using flameless atomic absorption spectrophotometry as the reference method.

Keywords: potentiometric stripping analysis, constant inverse current, lead, glassware.

INTRODUCTION

Lead can cause a variety of adverse health effects in humans.¹ At relatively low levels of exposure, these effects may include interference with the red blood cell chemistry, delays in the normal physical and mental development in babies and young children, slight deficits in the attention span, hearing and learning abilities of children, and a slight increase in the blood pressure of some adults. It appears that some of these effects, particularly the changes in the levels of certain blood enzymes and in the aspects of the neurobehavioral development of children, may occur at blood lead levels so low as to be essentially without a threshold. Chronic exposure to lead has been linked to cerebrovascular and kidney disease in humans. Lead has the potential to cause cancer from a lifetime exposure at levels above the action level.

Serbian Chemical Society active member.

The follow-up of the content of lead belonging to the first group of toxic elements is of special importance due to its cumulative-toxic effect.

Regarding the fact that the toxic and catalytic effect of some metals also becomes manifested at the contents lower than 1 mg/kg,² only a few instrumental techniques provide for their determination, namely, neutron-activation analysis, atomic absorption spectrophotometry, plasma-emission spectrometry and electrochemical stripping analysis. The detection limit, selectivity and reproducibility, rapidity and simplicity of electrochemical stripping analysis (ESA), as well as the price of the device give it some priority.^{7,9}

In this work potentiometric stripping analysis was modified to include constant inverse current in the analytic step (PSA-_{iR}).

The superimposition of constant inverse current in the analytic step has a double effect: it leads to the re-reduction of the already oxidized deposit, as well as to the reduction of the oxygen contents in the vicinity of the working electrode.^{3,8} Application of this technique considerably increases the sensitivity of the determination of lead, as the rate of oxidation of the deposit is reduced along with the concentration of oxygen. The value of the reduction current must be selected to ensure that the rate of oxidation is great than the rate of re-reduction.^{4,5}

The aim this study was to define a method for determining the soluble lead in glassware by applying potentiometric stripping analysis with constant inverse current in the analytic step (PSA-_{iR}).³⁻⁷ In order to carry out the assigned task, a great number of sample preparation procedures were examined and the corresponding conditions for the lead PSA-_{iR} analysis defined.

EXPERIMENTAL

Apparatus

The stripping analyzer M1, produced by Elektrouniverzal, Leskovac and the Faculty of Technology, Novi Sad, is a highly automated instrument for potentiometric and chronopotentiometric stripping analysis, with microprocessor control of the complete process.⁸ The analyzer has a program for automatic qualitative and quantitative determination, involving the calculation of the content of elements. The instrument can be programmed to employ deposition potentials between -2 and 2 V and constant currents for the electrolysis or stripping step between -50 and 50 μ A, with parameter setting accuracies of $\Delta E < 2$ mV and $\Delta I < 0.2$ μ A.

The electrochemical cell consists of a Teflon mechanical stirrer (1000-6000 rpm.), an electromagnetic valve, electrodes and the process vessel.

A glassy carbon (SIGRADUR-G) working electrode of 7.07 mm² total surface area was pressed into a Teflon tube (outer diameter 8 mm) at an elevated temperature. An Ag/AgCl, KCl (3.5 mol/dm³) electrode was used as the reference and a platinum wire as counter electrode. The reference electrode was connected with the solution to be analyzed by a salt bridge (0.2 mol/dm³ KNO₃).⁸

A matrix printer RGB 105G was used for recording.

Comparative sample analyses were carried out on a flameless spectrophotometer Perkin Elmer 1100.

Chemicals and solutions

Acetic acid, glacial (p.a., Merck); hydrochloric acid (supra pure, Merck); acetone (p. a., Kemika); standard lead solution, 1 g/dm³ (Titrisol, Merck); standard mercury solution, 1 g/dm³

(Titrisol, Merck). The working standard solutions of lead and mercury were prepared by diluting the respective standard stock solution with bidistilled water.

Preparation of the samples

The samples in whose extracts the lead contents were to be determined comprised diverse glassware products made by "SFS"-Paraćin, as well as glass ampoules made by "FS"-Pančevo which are used by FHI "Zdravlje" Leskovac for packing its products. For the examination itself, 8 kinds of glassware samples for food and pharmaceutical products were used.

After examining a great number of sample preparation methods, the preparation procedure defined in the standard methods for this purpose¹⁰ was adopted; it has also been applied for the determination of lead in ceramics.⁷

The samples for analysis were prepared by extraction with 4 % acetic acid solution. The samples were filled with the acid to 5 mm below the upper edge of the vessels and then they were left at a temperature of 22 ± 2 °C. The extraction lasted for $24 \text{ h} \pm 10$ minutes.¹⁰ After the extraction, the extracts were immediately transferred to polyethylene bottles.

For the potentiometric stripping analysis, a 25 cm^3 aliquot of the extract was taken and analyzed without dilution.

Preparation of the working electrode

A thin-layer mercury electrode on glassy carbon as an inert support was used. Before the preparation of the electrode, the glassy carbon surface was prepared by wiping with filter paper soaked first with acetone and then with distilled water. The mercury film was formed electrolytically from a solution containing 100 mg/dm^3 mercury(II)-ions and 0.02 mol/dm^3 hydrochloric acid, at a constant current of $50 \mu\text{A}$ for 240 s.^{3,11} Once deposited, the mercury film could be used for 25–30 analyses.

RESULTS AND DISCUSSION

The PSA-_{iR} of lead

In order to determine the optimal conditions of the PSA-_{iR} of lead in the chosen supporting electrolyte, the effects of the time of the electrodeposition of mercury, of the electrolysis potential, of the solution stirring rate and of the constant inverse current were examined. After optimization of the conditions for the determinations, both the linearity of the analytical signal and the detection limit were defined.

The time of the mercury electrodeposition. The mercury film on glassy carbon as an inert support was formed electrolytically from a solution containing 100 mg/dm^3 mercury(II) and 0.02 mol/dm^3 hydrochloric acid, at a constant current of $50 \mu\text{A}$ for 60 to 300 s. The effect of the time of the electrodeposition of mercury was investigated on the basis of the reproducibility of the analytical lead PSA-_{iR} signal for mass concentrations of lead of $5 \mu\text{g/dm}^3$ and $15 \mu\text{g/dm}^3$. The oxidation time dependence (τ_{ox}) of lead PSA-_{iR} on the mercury deposition time (t_{depHg}) is shown in Fig. 1.

Regarding the results of the investigations, it can be said that the best results were obtained with a mercury deposition time of 240 s, when a reproducibility of 0.00 %, expressed as the coefficient of variation, was obtained.

The electrolysis potential. In order to define the optimal electrolysis potential, potentials from -0.80 V to -1.10 V were examined with respect to $3.5 \text{ mol/dm}^3 \text{ Ag/AgCl}$ for $c_{\text{m}} = 5 \mu\text{g/dm}^3$. For each particular potential, five repeat measurements were made.

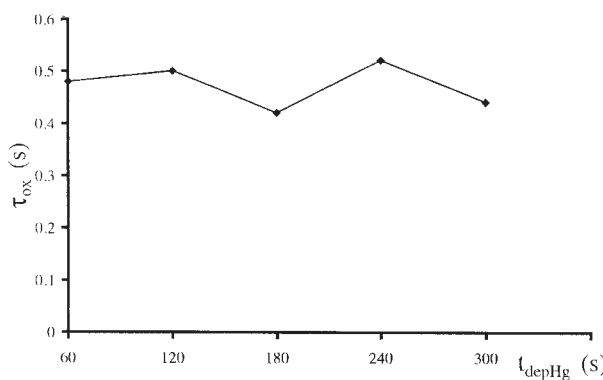


Fig. 1. Dependence of the oxidation time on the mercury deposition time $c_m = 5 \mu\text{g}/\text{dm}^3$; $i_R = 1.2 \mu\text{A}$; $E = -0.96 \text{ V}$ (Ag/AgCl, KCl $3.5 \text{ mol}/\text{dm}^3$).

The highest values of the analytical signal were obtained at a potential of -0.96 V with a reproducibility of 2.56 % expressed as the coefficient of variation.

The dependence of the oxidation time (τ_{ox}), as a quantitative characteristic of PSA- i_R , on the electrolysis potential (E) is shown in Fig. 2.

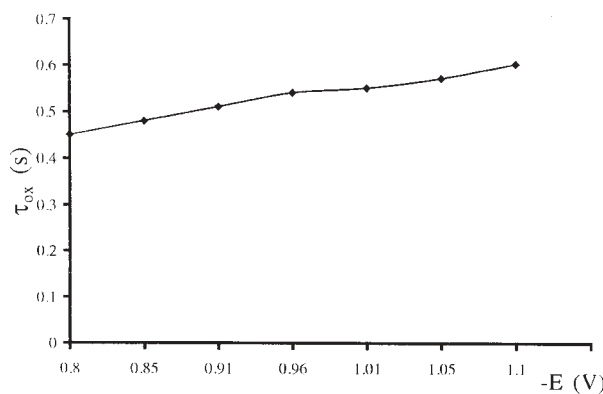


Fig. 2. Dependence of the oxidation time on the electrolysis potential $c_m = 5 \mu\text{g}/\text{dm}^3$; $i_R = 1.2 \mu\text{A}$; $t_{\text{el}} = 360 \text{ s}$.

The stirring rate of the solution. The stirring rate of the solution (that is, of a Teflon rod stirrer) was examined at the values of 1000, 2000, 4000 and 5000 rpm (Fig. 3). The investigation can not be carry out at a solution stirring rate of 6000 rpm because the mercury layer peeled from the surface of the glassy carbon electrode. The optimal stirring rate was 4000 rpm., with a variation coefficient of 3.50 % for a lead content of $5 \mu\text{g}/\text{dm}^3$, which was adopted for subsequent experiments.

The constant inverse current. The effect of the constant inverse current on the analytical signal of lead (τ_{ox}) for a lead content of $1.5 \mu\text{g}/\text{dm}^3$; $t_{\text{el}} = 420 \text{ s}$, and for a lead content of $5 \mu\text{g}/\text{dm}^3$; $t_{\text{el}} = 180 \text{ s}$ on the reproducibility of the determinations expressed through the coefficient of variation are presented in Table I.

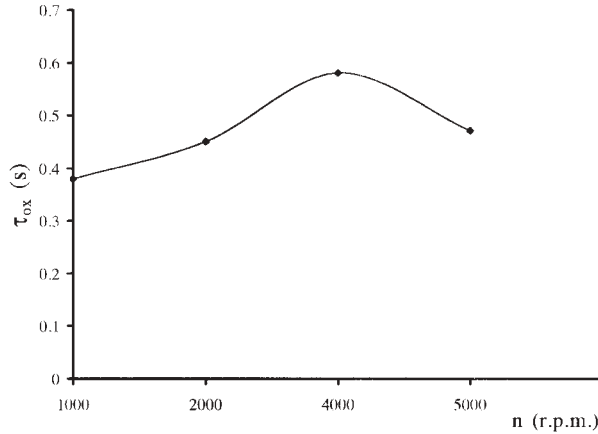


Fig. 3. Dependence of the oxidation time on the solution stirring rate $c_m = 5 \mu\text{g}/\text{dm}^3$; $i_R = 1.2 \mu\text{A}$; $E = -0.96 \text{ V}$ (Ag/AgCl, KCl $3.5 \text{ mol}/\text{dm}^3$).

TABLE I. The reproducibility of the analytical signals expressed through the oxidation time (τ_{ox}) and variation coefficient (C_v) of the constant inverse current (i_R)

$-i_R/\mu\text{A}$	Pb concentration			
	$1.5 \mu\text{g}/\text{dm}^3$		$5.0 \mu\text{g}/\text{dm}^3$	
	τ_{ox}/s	$C_v/\%$	τ_{ox}/s	$C_v/\%$
0.1	—	—	0.49	5.53
0.5	0.51	7.73	0.54	8.10
1.2	0.55	6.13	0.95	6.18
1.6	0.63	5.10	1.29	6.61
2.0	0.88	4.13	2.69	3.72

The optimal value of the inverse current for a lead content of $1.5 \mu\text{g}/\text{dm}^3$ was $1.6 \mu\text{A}$ with a reproducibility of 5.10 %, while for a lead content of $5 \mu\text{g}/\text{dm}^3$ the optimal current was $1.2 \mu\text{A}$ with a reproducibility of 6.18 %.

The linearity of the analytical signal. The effect of the linearity of the analytical signal on the lead PSA- i_R was examined for mass concentrations in the range of $2.5\text{--}4.5 \mu\text{g}/\text{dm}^3$ at an electrolysis potential of -0.96 V ; an electrolysis time of 360 s, a reduction current of $1.2 \mu\text{A}$ and a solution stirring rate of 4000 rpm.

The experiments were performed in the following way: first the analytical signal of a $2.5 \mu\text{g}/\text{dm}^3$ solution of lead was measured using a mercury layer electrode, then the electrode was rinsed with bidistilled water, and dried on filter paper, then the same procedure was repeated with lead solutions containing 3, 3.5, 4.0 and $4.5 \mu\text{g}/\text{dm}^3$. After the first series, the mercury layer was peeled off and a new mercury layer was deposited for a new series of determinations in the same concentration range. The linearity of the signal was examined for the three series. For each linear function ($\tau = a + bc_m$), the parameters a , b and the correlation coefficient (r) were calculated. The mean values for a , b and r are presented in Table II.

TABLE II. The values of the parameters of the linear functions $\tau = a + bc_m$

Number of repetitions	a/s	$b/s \text{ dm}^3 \text{ mg}^{-1}$	r
I Series	0.221	0.226	0.996
II Series	0.359	0.186	0.994
III Series	0.333	0.202	0.996

From the obtained high values of the correlation coefficient ($r > 0.990$), it can be said that there is a very good linearity of the analytical signal within the examined lead concentration range.

Considering the intercept size (a) on the oxidation axis and the values of the slope (b), it can be concluded that the standard addition method for these contents of lead is not reliable since it introduces errors into the calculation.

Detection limit. The detection limit of the PSA-_{iR} of lead is $0.64 \mu\text{g}/\text{dm}^3$, for an electrolysis time of 600 s, at an electrolysis potential of -0.96 V , with a stirring rate of 4000 rpm and an inverse current of $2 \mu\text{A}$. Good reproducibility was obtained with $C_v = 4.14 \%$.

For lower lead contents it is necessary to employ a larger inverse current. In this way an inverse current of $2 \mu\text{A}$ was applied for the least determined lead content.

The PSA-_{iR} of soluble lead in glassware

On the basis of the above examinations, a method for the determination of the soluble lead in glassware using potentiometric stripping analysis with a constant inverse current in the analytical step was defined. The defined method considers the analysis of samples (extracts of glassware with 4 % acetic acid as the extractant and supporting electrolyte) on a thin-layer mercury electrode with an electrodeposited mercury depth of 130 nm on glassy carbon as an inert support. The mercury layer had been formed at a constant current of $50 \mu\text{A}$ and a deposition time of 240 s. The electrolysis potential was -0.96 V against a Ag/AgCl, KCl ($3.5 \text{ mol}/\text{dm}^3$) electrode, during 360 s. The inverse current was $1.2 \mu\text{A}$ and the stirring speed was 4000 rpm.

TABLE III. Lead contents in the glassware extracts determined by the PSA-_{iR} and AAS method

Sample No.	Sample type dm^3	Sample color	The lead contents/ $(\mu\text{g}/\text{dm}^3)$		$C_v/\%$	$\delta_T/\%$
			PSA (calibr. curve)	AAS		
I	Jar (0.72)	Colorless	2.93	2.80	6.82	4.64
I	Jar (1.5)	Colorless	2.91	1.80	4.12	61.67
II	Bottle (0.70)	Green	2.86	2.80	5.24	2.14
IV	Bottle for pharm. products (0.06)	Brown	2.70	2.80	4.81	-3.57
V	Bottle (0.13)	Colorless	2.38	1.80	6.30	32.22
VI	Bottle (0.70)	Green	2.29	1.80	3.05	27.22
VII	Bottle (1.00)	Colorless	2.30	1.80	7.40	27.77
VIII	Jar (0.72)	Colorless	1.82	0.80	5.49	127.50

The results obtained by the PSA-_{iR} method and the results of the reference AAS method are given in Table III, together with results of the relative deviation between the two methods and the coefficients of variation.

The results of the comparative analyses show there is a very good agreement between the PSA-_{iR} and the AAS method. With the sample (VIII) there is a somewhat greater relative deviation which is the consequence of the very low lead content of that sample. On the basis of the values of the coefficient of variation, it can be concluded that it is possible by application of the calibration curve method to obtain more reproducible values than by the standard addition method where the deviations are somewhat greater. Hence, the calibration curve method is proposed as the standard method for the determination of lead in glassware samples.

CONCLUSION

The selectivity, sensitivity and reproducibility of the PSA-_{iR} method for the determination of the soluble lead in glassware were defined. The defined method considers the analysis of samples (extracts of glassware with 4 % acetic acid as the extractant and the supporting electrolyte) on a thin-layer mercury electrode; at an electrolysis potential of -0.966 V (Ag/AgCl, $3.5\text{ mol/dm}^3\text{ KCl}$), during 360 s, with a reduction current of $1.2\text{ }\mu\text{A}$ and at a stirring rate of 4000 rpm. The soluble lead contents leached from the glassware ranged from $1.82\text{ }\mu\text{g/dm}^3$ to $2.93\text{ }\mu\text{g/dm}^3$.

Regarding the fact that the maximal allowed content of released lead from glassware into acetic acid are $5.0\text{ }\mu\text{g/dm}^3$ for small glassware ($V < 1.1\text{ dm}^3$), and $2.5\text{ }\mu\text{g/dm}^3$ for large glassware ($V > 1.1\text{ dm}^3$),¹² it can be said that all the examined glass samples were within the specified limits regarding the lead contents. All the results were confirmed by parallel AAS analysis.

ИЗВОД

ПРИМЕНА ПОТЕНЦИОМЕТРИЈСКЕ СТРИПИНГ АНАЛИЗЕ СА КОНСТАНТНОМ ИНВЕРЗНОМ СТРУЈОМ У АНАЛИТИЧКОМ КОРАКУ ЗА ОДРЕЂИВАЊЕ РАСТВОРЉИВОГ ОЛОВА У СТАКЛЕНОЈ АМБАЛАЖИ

БИЉАНА М. КАЛИЧАНИН¹, НИКОЛА Ј. МАРЈАНОВИЋ² и ЗВОНИМИР Ј. СУТУРОВИЋ²

¹Универзитет у Нишу, Технолошки факултет, Булевар ослобођења 124, 16000 Лесковац и ²Технолошки факултет, 21000 Нови Сад

Трагови олова у екстрактима стаклених амбалажних производа, одређени су потенциометријском стрипинг анализом са константном инверзном струјом у аналитичком кораку (PSA-_{iR}), електрохемијском техником високе осетљивости и селективности. Испитан је утицај већег броја фактора на резултате PSA-_{iR} олова из стаклене амбалаже, као што су време депоновања живе, потенцијал електролизе, брзина мешања раствора и константна инверзна струја. Након оптимизације услова, испитана је линеарност аналитичког сигнала олова у области масених концентрација од $2,5$ до $4,5\text{ }\mu\text{g/dm}^3$. Остварена је граница детекције од $0,64\text{ }\mu\text{g/dm}^3$ уз репродуктивност од $4,14\%$, изражену као коефицијент варијације. Исправност дефинисане методе одређивања олова је потврђена паралелним ана-

лизама са беспламеном атомском апсорпционом спектрофотометријом. Анализе су изведене на систему за електрохемијску стрипинг анализу домаће конструкције и производње (Технолошки факултет, Нови Сад и Електроуниверзал, Лесковац).

(Примљено 7. јуна, ревидирано 5. новембра 2001)

REFERENCES

1. EPA 800/4-83-043 (1999) 125
2. *Službeni list SRJ* **5** (1992) 83
3. D. Jagner, A. Graneli, *Anal. Chim. Acta* **83** (1976) 19
4. Z. Suturović, *Ph. D. Thesis*, University of Novi Sad, 1992
5. D. Jagner, *Anal. Chem.* **51** (1979) 342
6. D. Jagner, *Analyst* **107** (1982) 593
7. N. Marjanović, Z. Suturović, J. Marjanović, N. Keser, *APTEFF* **31** (2000) 469
8. Z. Suturović, N. Marjanović, *Nahrung* **42** (1998) 36
9. B. M. Kaličanin, Z. B. Todorović, N. J. Marjanović, Z. J. Suturović, *Res. J. Chem. Environ.* **5** (2001) 7
10. ISO 7.086/1-1982 (E)
11. Z. Suturović, N. Marjanović, P. Dokić, *Electroanal.* **9** (1997) 111
12. ISO 7.086/2-1982 (E).