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THE DEVELOPMENT OF A HIGH SENSITIVITY METHOD FOR THE ELECTROCHEMICAL DETERMINATION OF SOLUBLE LEAD IN GLASS WARE

Trace amounts of lead extracted from glass ware products were determined by selectivity. In order to ascertain the optimum conditions for determining the effects of the time of mercury electrodeposition, electrolysis potential, solution stirring rate and electrolysis time of the lead analytical signal were examined. The accuracy of the method was confirmed by parallel analyses by flameless atomic absorption spectrophotometry as the reference method.

The analyses are carried out using a computerized stripping analyzer of domestic design and manufacture (Faculty of Technology, Novi Sad and "Elektro-univerzal", Leskovac).

In order to ascertain that glass objects, once in contact with acetic acid, do not release more lead than permissible, it is necessary to set up an efficient control as the only means of increasing protection and reducing the risk of possible poisoning with food packed in them. The follow-up of the contents of lead belonging to the first group of toxic elements is especially important due to its cumulative toxic effect. The determination, as well as the follow-up of the heavy metal residuals must be a constituent part of the control of glass ware used in the technological process of manufacturing food, pharmaceutical and chemical products [1,2]. As the content of trace heavy metals is very important in manufacturing food and pharmaceutical products, there are numerous instrumental techniques (neutron-activation analysis, plasma-emission spectrometry, atomic absorption spectrophotometry and electrochemical stripping analysis) for their determinations.

Electrochemical stripping analysis (ESA) has the greatest sensitivity (10^{-11} mol/dm³), just after neutron-activation analysis (10^{-21} mol/dm³). Besides, the cost of its application and operation is much lower than of the other above-mentioned techniques, while the procedure for carrying out the analysis is relatively simple and fast.

The aim of the paper is to define the method for determining soluble lead in glass ware by applying potentiometric stripping analysis (PSA) with oxygen as the oxidant [3-6].

EXPERIMENTAL

Instrumentation

The M1, stripping analyzer, produced by Elektro-univerzal Leskovac and the Faculty of Technology, Novi Sad, is a highly automatic instrument for potentiometric and chronopotentiometric stripping analysis, with

microprocessor control of the complete process [7]. The analyzer has a program for automatic qualitative and quantitative determination, involving the calculation of element contents. The instrument can be programmed to give deposition potentials between -2 and 2 V and a constant current for the electrolysis or stripping step between -50 and 50 μ A, with the parameter setting accuracies $\Delta E < 2$ mV and $\Delta I < 0.2$ μ A.

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

A glassy carbon (SIGRADUR-G) working electrode of a total surface area of 7.07 mm² was pressed into the 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 the counter electrode. The reference electrode was connected with the solution to be analyzed by a salt bridge (0.2 KNO₃) [8].

Here the PSA modification with oxygen as the oxidant was applied with diffusion conditions of mass transfer during the analytical step. This PSA modification is the simplest one since it uses already present diluted oxygen as the means of oxidation which reduces the contamination risk when applying other oxidation means.

After the proscribed time reserved for lead extraction, the extracts of the glass products were transferred to polyethylene bottles.

An aliquot of 25 cm³ was taken, for potentiometric stripping analysis and analyzed without dilution.

RESULTS AND DISCUSSION

The PSA of lead

In order to optimise the PSA determination of soluble lead, the effects of the electrolysis potential, the solution stirring rate and the electrolysis time of the lead analytical signal were investigated. After optimizing the

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determination conditions, both the linearity and the reproducibility of the analytical signal were defined.

The effect of electrolysis potential on lead PSA

To define the optimal electrolysis potential, the potentials from -0.80 V to -1.10 V were examined against the Ag/AgCl, KCl (3.5 mol/dm^3) reference electrode for an electrolysis time of 900 s for a solution with a concentration of $5 \text{ } \mu\text{g/dm}^3$ and at a stirring rate of 4000 min^{-1} .

These investigations were carried out in two ways:

In the first part the lead contents were determined on the formed thin-layered deposited mercury in the potential range from -0.80 V to -1.10 V, then the mercury was removed and again formed in the same solution in the same range of potentials and for the same electrolysis time. The investigations under these conditions were repeated five times.

In the second part of the investigation, five analyses were done on the mercury deposited layer at one potential value (for example -0.80 V), then the mercury layer was removed and deposited again for the next potential value.

The effect of the electrolysis potential on the lead analytical signal (τ_{OX}) for a lead content of $5 \text{ } \mu\text{g/dm}^3$; $t_{\text{el}} = 900$ s on the reproducibility of the determinations expressed by the variation coefficient (C_V) are presented in Table 1.

Table 1. The reproductibility of the analytical signals expressed by the oxidation time (τ_{OX}) and variation coefficient (C_V) of the electrolysis potential for determinations of the same thin-layered mercury and for determinations on a different thin-layered mercury

-E (V)	The same mercury layer		A different mercury layer	
	τ_{OX}^* (s)	C_V (%)	τ_{OX}^* (s)	C_V (%)
0.80	0.45 ± 0.037	8.24	0.42 ± 0.017	4.16
0.85	0.48 ± 0.022	4.60	0.50 ± 0.022	5.88
0.91	0.51 ± 0.033	6.50	0.58 ± 0.028	3.92
0.96	0.54 ± 0.020	3.76	0.52 ± 0.020	2.97
1.01	0.55 ± 0.022	3.95	0.53 ± 0.027	4.44
1.05	0.57 ± 0.021	3.60	0.49 ± 0.027	5.26
1.10	0.60 ± 0.038	6.45	0.58 ± 0.020	5.87

* The values represent the mean oxidation time of five repetitions \pm standard deviations.

It may be seen in Table 1 that on the same mercury layer the lead analytical signal has good increasing linearity of the electrolysis potential. But the same dependencies investigated on different layers were disorderly with increasing or decreasing values. From these investigations (from the shape and character of the functional dependencies) it may be concluded that

it is better to perform the analysis of the same series on the same mercury layer. It may be pointed out that at negative values of the electrolysis potentials, the reproducibility decreases because of hydrogen evolution on the working electrode, so the value -0.96 V was chosen for the optimum potential.

The comparative sample analyses were carried out on a flameless, 1100 "Perkin Elmer" spectrophotometer.

Chemicals

All the chemicals used were of analytical-reagent grade produced by Merck. Nitric, acetic and hydrochloric acids were ultra-pure grade (Suprapur, Merck). Lead stock solution (1 g/dm^3) were "Titrisol" produced by Merck. All containers and cells were washed with nitric acid (1:1) and doubly distilled water.

Pretreatment of the working electrode

Pretreatment of the glassy carbon electrode was simple. Prior to each measurement the electrode surface was cleaned mechanically by chromatographic filter paper wetted by doubly distilled water. After that the working electrode surface was cleaned by a constant current ($8 \text{ } \mu\text{A}$) for 20 cycles from -0.8 V to $+0.8$ V in 0.01 mol/dm^3 sulphuric acid solution and then washed with doubly distilled water.

A thin-layered mercury electrode on glassy carbon was used as an inert support. Before electrode formation, the glassy carbon surface was prepared by being swept with filter paper first soaked 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 $50 \text{ } \mu\text{A}$ for 240 s [3, 9]. Once deposited, the mercury film could be used for 25–30 analyses.

Preparation of the Samples

The samples in the extracts of which the lead contents were determined, comprise diverse glass ware products made by "SFS" – Paraćin, as well as glass ampoules made by the Glass Factory Pančevo, otherwise used by "Zdravilje" Leskovac for packing its products.

Seven kinds of glass ware samples for food and pharmaceutical products were used for the examination:

BK1 – small bottles for pharmaceutical products, 0.03 dm^3 volume, brown color,

BK2 – ampoules for pharmaceutical products, 0.002 dm^3 volume, colorless,

BK3 – jar, 0.37 dm^3 volume, colorless,

BK4 – bottle for strong alcoholic drinks, 1 dm^3 volume, colorless,

BK5 – ampoules for pharmaceutical products, 0.01 dm^3 volume, colorless,

BK6 – jar, 0.21 dm^3 volume, colorless,

BK7 – small bottles for pharmaceutical products, 0.015 dm³ volume, brown color.

After examining a larger number of the sample preparation methods, the preparation procedure defined in the standard methods for this purpose [1] was adopted.

The samples for the analysis were prepared by extraction with 4% acetic acid solution. The samples were filled with acid to 5 mm from the upper edge of the vessels and then they were left at 22 ± 2 °C. The extraction lasted for 24 hours ± 10 minutes [1].

The effect of electrolysis time on lead PSA

The effect of the electrolysis potential on the lead PSA results was examined within the time range from 480 s to 900 s for a lead content of 5 µg/dm³.

By examining the effect on the lead PSA results, the optimal time of 480 s was chosen for a lead content of 5 µg/dm³ with the reproductibility expressed by a variation coefficient (C_v) of 3.00%.

The effect of solution stirring rate on lead PSA

The solution stirring rate (the rate of revolution of a Teflon stick stirrer) was examined at the values of 1000, 2000, 4000 and 5000 min⁻¹. At a solution stirring rate of 6000 min⁻¹ the investigation could not be performed because the mercury layer peeled off from the surface of the glassy carbon electrode. The optimal stirring rate of 4000 min⁻¹ was adopted with a variation coefficient of 3.99% for a lead content of 5 µg/dm³.

The effect of the linearity of the analytical signal on lead PSA

The effect of the linearity of the analytical signal on lead PSA was examined for mass concentrations of 2–16 µg/dm³ at an electrolysis potential of -0.96 V; an

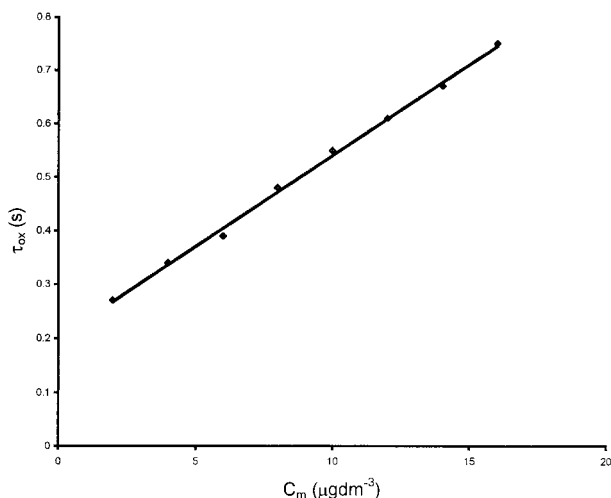


Figure 1. Linearity of the analytical signal of lead in PSA; $t_{tox} = 0.034 C_m + 0.202$; $r = 0.999$

electrolysis time of 480 s and a solution stirring rate of 4000 min⁻¹.

The analytical lead signal dependence in PSA on the mass concentration is shown in Figure 1.

Regarding the high value of the correlation coefficient ($r > 0.990$) it may be said that there is very good linearity of the analytical signal within the examined lead concentration range.

PSA of soluble lead in glass ware

On the basis of the above examinations the method for determining soluble lead in glass ware by potentiometric stripping analysis (PSA) with oxygen as the oxidizer was defined. The defined method consists of sample analysis (the extracts of the bottles, glass vessels, pharmaceutical jars and ampoules with 4% acetic acid as the extractant and supporting electrolyte) on a thin-layered mercury electrode with an electrodeposited mercury layer of 130 nm on glassy carbon as an inert support formed at a constant current of 50 µA; for an electrodeposition time of 240 s; at an electrolysis potential of -0.96 V against Ag/AgCl, KCl (3.5 mol/dm³) electrode, for 900 s and at a stirring rate of

Table 2. Lead contents in the glass ware extracts determined by applying PSA and AAS

Sample	Potentiometric stripping analysis						AAS
	Calibration curve method			Standard addition method			
	Pb (µg/dm ³)	Rel. dev.* (%)	C _v (%)	Pb (µg/dm ³)	Rel. dev.* (%)	C _v (%)	Pb (µg/dm ³)
BK 1	3.59	-5.52	4.40	2.95	-22.37	10.20	3.80
BK 2	4.23	-27.07	3.10	5.12	-11.72	0.20	5.80
BK 3	3.60	20.00	6.51	3.15	5.00	14.8	3.00
BK 4	3.88	38.57	7.45	4.33	54.64	8.30	2.80
BK 5	12.19	-4.76	9.43	15.06	17.60	8.80	12.80
BK 6	3.92	3.15	9.43	5.92	55.79	6.10	3.80
BK 7	5.80	-14.70	8.60	6.20	-8.82	11.10	6.80

* Relative deviations calculated on the basis of the AAS reference method.

$$\text{Rel. dev.} = [C_m(\text{PSA}) - C_m(\text{AAS})/C_m(\text{AAS})] \cdot 100$$

4000 min⁻¹.

The analysis was repeated three times while the soluble lead contents were determined by applying the calibration curve method and the standard addition method of PSA and the calibration curve method of flameless AAS.

The results of the comparative analyses show good agreement of the results by applying PSA and AAS used as reference method. The best result agreement was achieved in the case of samples with micro lead contents achieved by the great sensitivity of the given method in analyzing soluble lead in glass ware.

Under the optimal conditions of the PSA technique detection limit in the examined medium was $1.70 \mu\text{g}/\text{dm}^3$ of lead, which justifies the application of the developed method for analysing soluble lead in glass ware.

On the basis of the variation coefficient values it may be concluded that by applying the calibration curve method it is possible to obtain more reproducible values than with the standard addition method, where the deviations are somewhat greater. So for this reason it is proposed that the calibration curve method is suitable as the standard method for this purpose.

Regarding the fact that the maximal allowed contents of released lead from glass ware by acetic acid are $5.0 \text{ mg}/\text{dm}^3$ for small glass ware ($V < 1.1 \text{ dm}^3$), and $2.5 \text{ mg}/\text{dm}^3$ for large glass ware ($V > 1.1 \text{ dm}^3$) [2], it may be, stated that all the examined glass samples, were acceptable regarding the lead contents.

CONCLUSION

A sensitive, selective and reproducible method for determining soluble lead in glass ware by PSA with oxygen as the oxidizer been defined. The defined method involves the analysis of extracts from bottles,

pharmaceutical jars and ampoules with 4% acetic acid as the extracting agent and supporting electrolyte.

The analyses were carried out at an electrolysis potential of -0.96 V (Ag/AgCl , $3.5 \text{ mol}/\text{dm}^3 \text{ KCl}$) for 900 s and a stirring rate of 4000 min^{-1} .

The defined method enables the determination of soluble lead content in glass ware, in the range of mass concentrations from $3.59 \mu\text{g}/\text{dm}^3$ to $12.19 \mu\text{g}/\text{dm}^3$.

All the results were confirmed by parallel AAS comparative analysis.

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IZVOD

RAZVOJ VISOKOOSETLJIVE METODE ZA ELEKTROHEMIJSKO ODREĐIVANJE IZLUŽENOG OLOVA IZ STAKLENE AMBALAŽE

(Naučni rad)

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U radu su ispitani uslovi za određivanje tragova rastvorljivog olova u ambalažnom staklu potenciometrijskom stripping analizom (PSA), sa kiseonikom kao oksidansom.

U cilju optimizacije određivanja ispitani su uticaji potencijala elektrolize, brzine mešanja rastvora i vremena elektrolize na analitički signal PSA olova. Postignuta je veoma dobra linearnost analitičkog signala u širokom opsegu masenih koncentracija olova ($2-16 \mu\text{g}/\text{dm}^3$). Kao pomoćni elektrolit je korišćena 4% sirćetna kiselina koja je ujedno korišćena i za ekstrakciju olova iz staklene ambalaže.

Sva ispitivanja su izvedena uz primenu kompjuterizovanog stripping analizatora M1, konstruisanog i proizvedenog u Jugoslaviji (Tehnološki fakultet, Novi Sad i "Elektrouniverzal", Leskovac).

Definisana metoda za PSA rastvorljivog olova iz ambalažnog stakla podrazumeva analizu uzoraka (ekstrakata staklene ambalaže) na tankoslojnoj živinoj elektrodi debljine oko 130 nm, pri potencijalu elektrolize od -0.96 V (Ag/AgCl , $3.5 \text{ mol}/\text{dm}^3 \text{ KCl}$), tokom 900 s i pri brzini mešanja (obrtanja mešaća) od 4000 min^{-1} .

Ispravnost metode je potvrđena paralelnim analizama sa bezplamenom AAS, kao referentnom metodom.

Na osnovu rezultata ispitivanja uzoraka staklene ambalaže, može se reći da su svi ispitani uzorci bili veoma dobrog kvaliteta, jer je sadržaj rastvorljivog olova za oko 3000 puta manji od maksimalno dozvoljenih sadržaja propisanih međunarodnim standardom ISO 7086/2.

Ključne reči: Elektrohemija • Analiza • Olovo • Staklo • Ambalaža •

Key words: Electrochemistry • Analysis • Lead • Glass • Glass ware •

