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**VOLTAMMETRIC DETERMINATION
OF HEAVY METALS IN NATURAL WATERS
AND BIOLOGICAL SAMPLES
BY USING A CHEMICALLY MODIFIED
CARBON PASTE ELECTRODE**

Efterpi N. ILIADOU^a, Stella T. GIROUSI^a, Anastasios N.
VOULGAROPOULOS^{a1} and Karel VYTRÁS^b

^aAnalytical Chemistry Laboratory, Department of Chemistry,
Aristotle University of Thessaloniki, GR-54006 Thessaloniki

^bDepartment of Analytical Chemistry,
University of Pardubice, CZ-53210 Pardubice

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The behaviour of copper, lead and cadmium was studied with a new chemically modified carbon paste electrode, with different supporting electrolytes (HCl, HClO₄, H₂SO₄, NH₃-NH₄Cl). The optimum conditions for the determination of the above mentioned metals were studied either separately or simultaneously in mixtures of 2 or 3 of them. The method for their simultaneous determination was more sensitive after deposition of a mercury film "in situ" after addition of Hg (II). Detection limits are 5.00 μg l⁻¹, 7.00 μg l⁻¹, 2.00 μg l⁻¹ for copper, cadmium and lead, respectively. The relative standard deviation at a concentration level of 6.00–7.50 ppb, varies within the range 5.00–8.00 % for

¹ To whom correspondence should be addressed.

90 sec of preconcentration time. Copper, cadmium and lead were determined in synthetic as well as in natural samples by anodic stripping voltammetry (ASV).

Introduction

Nowadays the environmental pollution problem has become very important due to the technological and industrial development. Certain efforts are demanded in order to eliminate environmental dangers. It is important to rely on accurate results in order to evaluate the sources as well as the extent of the environmental dangers. Environmental protection involves analytical methods for the analysis of different kinds of samples such as natural waters (river, lake, sea, underground, rain) soil, plants, agricultural and biological samples.

Information obtained about the concentrations of toxic metals in biological samples is very useful since their toxicity originates from the fact that they are biologically non-degradeable and have tendency to accumulate in vital organs of man, where they act with progressive toxicity over long periods of time [1]

The development of new methods as well as the optimization of the already existing methods is one of the future trends of the modern analytical chemistry. Electrochemical methods are very sensitive and allow the determination of trace and ultratrace metals.

For the determination of heavy metals the Hanging Mercury Drop Electrode (HMDE) is mainly used as a working electrode. In order to avoid the use of the toxic metallic mercury, new solid electrodes were used such as (platinum, gold, palladium, silver, carbon) [2,3,4]. The analytical characteristics of the different working electrodes usually employed in voltammetry are reviewed elsewhere [5]. Carbon Paste Electrodes (CPEs), more specifically are based on carbon paste (a mixture of a lipophilic organic liquid binder, the pasting liquid, and carbon powder or powdered graphite) which is packed in a suitable electrode body [6,7].

The first carbon paste electrode was an attempt to prepare a renewable carbon electrode that could be used in positive potential ranges, where mercury is not applicable because of oxidation of the electrode material.

It was described as a new approach for investigating the electrochemical behavior of some organic compounds by using the pasting liquid itself as a solvent for the organic substances under study [8, 9].

The method was considered as the first pioneering contribution to the forthcoming development of chemically modified carbon paste electrodes (CMCPEs) in the 1970s.

CMCPEs were used either for direct voltammetric determinations or as amperometric detectors in flow or batch systems [10].

CMCPEs were used for the determination of various inorganic and organic analytes but not much for the simultaneous element determinations. Recently, a paper appeared in the literature describing simultaneous determination of Zn,

Cu, Cd, Pb, Hg (using as the working electrode) a carbon paste electrode, chemically modified with the chelating resin Amberlite IRC 718 [11]. The major disadvantage of the method is that involves medium exchange which is not practical for routine analysis.

In this paper we present a new chemically modified carbon paste electrode, easily prepared and showing reproducible results, applied in the simultaneous determination of Cu, Cd and Pb in natural and synthetic samples.

Experimental

Standard solutions of Pb, Cd and Cu were made up from Titrisol solutions (E. Merck) and standards of lower concentrations were obtained by appropriate dilution with milli-Q water.

HCl, HClO₄, NH₃, H₂SO₄, Hg(NO₃)₂ were s.p grade purchased from E. Merck.

All the other reagents used were of Merck pro analysi grade. Milli-Q water was used throughout the experimental work.

Apparatus

The voltammetric measurements were carried out using a Metrohm Herisau E 506 Polarecord equipped with a Metrohm Herisau E 505 voltammetric stand.

As the working electrode a modified carbon paste electrode was used; the counter electrode was platinum wire and the reference electrode was Ag/AgCl with saturated KCl.

pH measurements were taken with an ORION Research Model 701 A digital ion analyzer at 25 ± 0.05 °C. Eppendorf micropipettes were used to pipette µl volumes of solutions.

Electrode Preparation

The pastes were prepared by careful hand-mixing of material "x" and pasting liquid "y" [12] using a porcelain pestle and mortar which were always thoroughly washed with acetone before the paste was homogenized. The mixture was heated until it became paste. The paste was packed into piston-like electrode bodies, made from polyethylene, whose design has been described elsewhere [7]. Filled electrodes were allowed to stand for approximately two days with their active surface immersed in distilled water. A copper wire was used as an electrical contact. 0.05 g of graphite powder was used for the electrode construction. The whole mass of the electrode did not exceed 0.01 g.

The surface of the electrode was $\leq 0.2 \text{ cm}^2$

Mercury films were prepared *in situ* according to previously described procedures [13]. The mercury film was stripped off during an anodic potential scan and, hence, generated again for the next measurement.

Sample Preparation

Benzine.

The sample (5 ml) was placed in a glass beaker, 5–10 ml of anhydrous acetic acid was added, and the mixture was boiled in order to decompose the organolead compounds [14]. After the sample was left to cool down to ambient temperature, the supporting electrolyte solution was added to render the volume 20 ml.

Beverages, Natural Juices, Wines.

Carbon dioxide was removed from carbonated samples and the wet mineralization procedure was performed as described elsewhere [15,16].

According to the given procedure 250–300 ml of the sample was transferred into 1 l erlenmyer flask, warmed to room temperature, closed with a 1-hole stopper with a tube inserted, and shaken in automatic shaker 20–30 min [15].

A 5 ml aliquot of the sample, after the removal of carbon dioxide if necessary, was filtered and placed in a quartz cup, heated at 100 °C to dryness (30 min), and cooled down to 20 °C.

Thereafter, 0.1 ml HClO_4 and 0.5 ml HNO_3 were added to the dried sample and the mixture was heated to 100 °C until NO_x evolution ceased evaporation residue. Then the temperature was gradually increased to 200 °C until a colorless liquid resulted.

Certified Reference Materials

The digestions of CRMs were performed as described in literature [17].

Voltammetric Procedure

The digest was quantitatively transferred into a 25 ml volumetric flask by adding of 5 ml 1 mol l^{-1} HCl. Aqueous solution of $10^{-3} \text{ mol l}^{-1}$ $\text{Hg}(\text{NO}_3)_2$, up to a final

concentration of $1.5 \times 10^{-5} \text{ mol l}^{-1}$ [16,17,18], was added and the volumetric flask was filled up to the mark by addition of $1 \text{ mol l}^{-1} \text{ HCl}$. The solution was transferred in the electrochemical cell and was deaerated with N_2 gas for 5 min. The nitrogen flow was stopped and after 15 s equilibration time the potential was set at -1.20 V and the voltammogram was recorded using the differential pulse modulation (DP) with a scan rate of 10 mV s^{-1} and a pulse amplitude of 50 mV .

Results and Discussion

Physicochemical Characteristics of the Chemically Modified Carbon Paste Electrode

The physicochemical characteristics of the chemically modified electrode were tested by measuring the resistance, the analytical signal for a given concentration of the analyte, the sensitivity, the residual current and the usable potential range.

The suitability of the carbon paste depends on the material resistance, the quality of the filling material and the way of filling the electrodes.

The test was made in a cadmium solution $10^{-7} \text{ mol l}^{-1}$ in $1.0 \text{ mol l}^{-1} \text{ HCl}$. The useful potential window was -1.0 V to $+0.5 \text{ V}$ in acidic solution and -1.8 V to $+1.0 \text{ V}$ in alkaline solutions (pH 9.2), the resistance was 5–10 Ohm, the peak current was $0.067 \text{ } \mu\text{A}$, while the residual current was $1 \text{ } \mu\text{A}$.

Effect of Variation of Studied Parameters. Effect of Supporting Electrolyte

Various supporting electrolytes were tested for their suitability in the simultaneous determination of the metals. The supporting electrolytes tested were the following: $1 \text{ mol l}^{-1} \text{ HCl}$, $1 \text{ mol l}^{-1} \text{ HClO}_4$, $1 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$, $1 \text{ mol l}^{-1} \text{ NH}_3\text{-NH}_4\text{Cl}$.

The most suitable supporting electrolyte for the simultaneous determination is $1 \text{ mol l}^{-1} \text{ HCl}$ because of the higher peak currents of the 3 metals observed in it. The effect of different supporting electrolytes on the peak heights is demonstrated in Fig. 1. The effect of the addition of Hg^{2+} solution was studied; the optimum Hg^{2+} concentration is observed at $15 \text{ } \mu\text{mol l}^{-1}$ and the results are demonstrated in Fig. 2.

It has been confirmed that a mercury film deposited *in situ* consists of a very thin layer of mercury droplets [13,21-24] and the distribution of the size of droplets principally determines the behavior of the mercury film electrode.

Effect of pH Variation

The pH was varied in the range from 2.5 to 10. The peak heights of copper, lead and cadmium decreased strongly. The optimum pH value was observed at 2.5. Figure 3 shows the dependence of the peak heights upon pH.

Effect of the Deposition Potential and Time Variation

The deposition potential was varied between -0.4 to -1.40 V, at potentials more negative than -1.0 V a plateau was reached. The optimum deposition potential

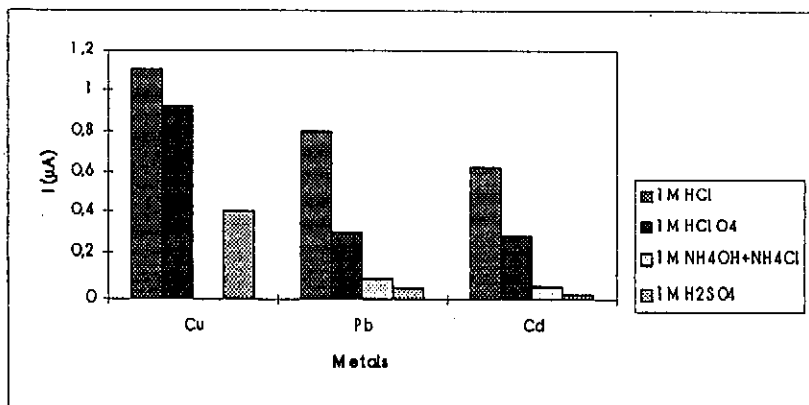


Fig. 1 Effect of variation of different supporting electrolytes on the differential pulse peak heights of Cu, Pb, Cd present at concentrations $2 \times 10^{-6} \text{ mol l}^{-1}$. Standard instrumental parameters were used

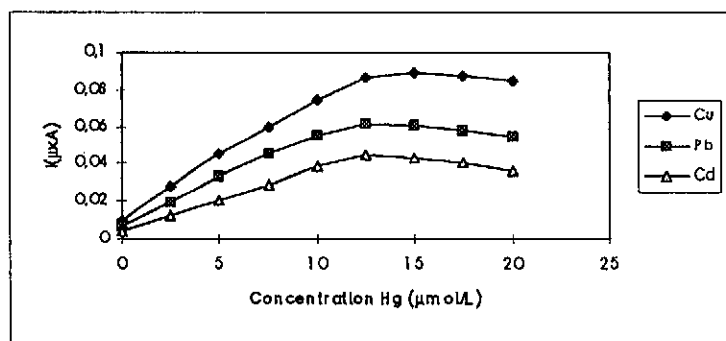


Fig. 2 Effect of variation of Hg^{2+} concentration on the differential pulse peak heights of Cu, Pb, Cd present at concentrations $2 \times 10^{-6} \text{ mol l}^{-1}$. Standard instrumental parameters were used

is observed at -1.2 V for the simultaneous determination of Cu, Pb and Cd.

Variation of deposition time from 15 to 125 sec, at a deposition potential of -1.2 V, showed that all the peak heights increased almost linearly up to 90 sec of deposition, and for longer periods of deposition time a plateau is reached.

In Figs 4 and 5 the dependence of the peak heights upon deposition potential and time are shown, respectively. The optimum conditions for the simultaneous determination are: supporting electrolyte: 1 mol l^{-1} HCl, $C_{\text{Hg}^{2+}} = 15 \text{ } \mu\text{mol l}^{-1}$, $\text{pH} = 2.5$, deposition potential: -1.2 V, deposition time: 90 s.

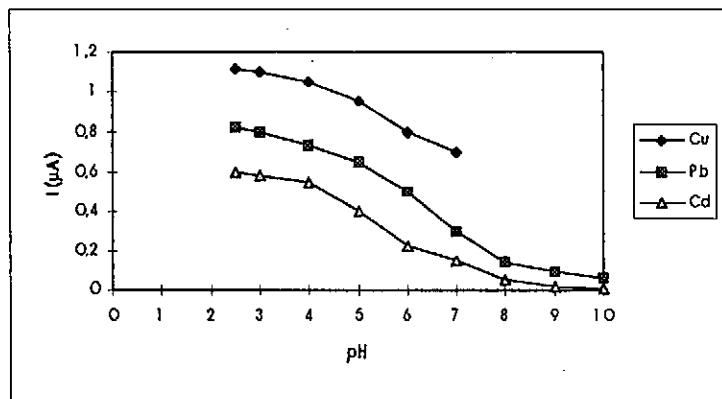


Fig. 3 Effect of variation of pH on the differential pulse peak heights of Cu, Pb, Cd, present at concentrations of $2 \times 10^{-6} \text{ mol l}^{-1}$. Standard instrumental parameters were used

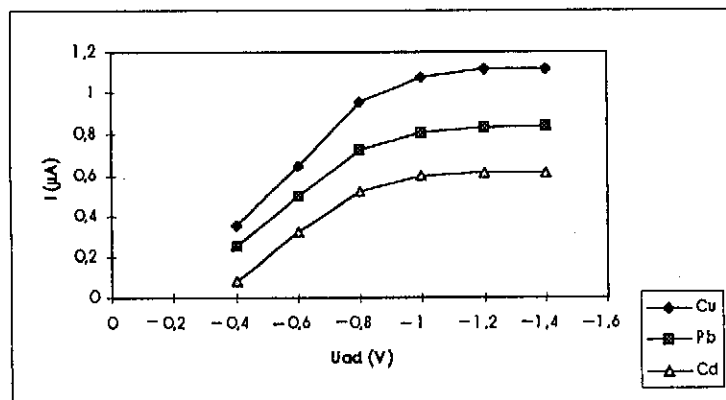


Fig. 4 Effect of variation of deposition potential on the differential pulse peak heights of Cu, Pb, Cd, present at concentrations of $2 \times 10^{-6} \text{ mol l}^{-1}$. Standard instrumental parameters were used

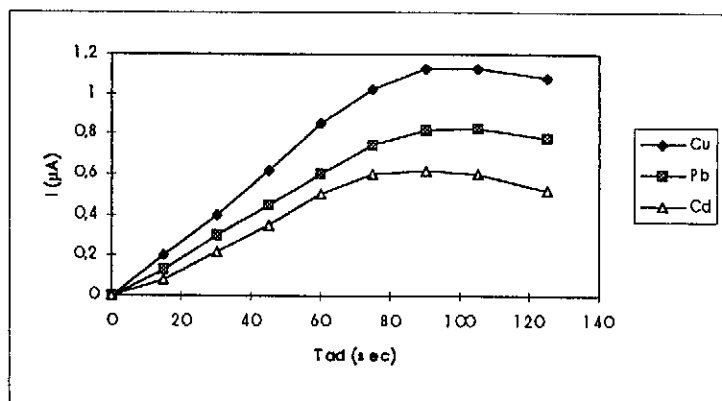


Fig. 5 Effect of variation of deposition time on the differential pulse peak heights of Cu, Pb, Cd present at concentrations of 2×10^{-6} mol l⁻¹. Standard instrumental parameters were used

In Fig 6 a differential pulse voltammogram of Cu, Pb, Cd recorded under the optimum conditions is shown before and after the addition of Hg(II).

Analytical Figures of Merit

The calibration curves of Cu, Pb and Cd are linear in the range of $0.5 - 5 \times 10^{-6}$ mol l⁻¹ and are described by the least-square equations:

for Cu

$$y = -0.191 + 0.264x$$

for Pb

$$y = -0.217 + 0.219x$$

and for Cd

$$y = -0.180 + 0.158x$$

The limit of detection (C_L) was calculated, according to IUPAC, by measuring 9 blank samples and using as criterion the equations: A) $X_L = X_b + 3S_b$ where X_L is the smallest measure of response, X_b is the mean of the lowest level measures, S_b is the standard deviation of the lowest level measures and B) $C_L = 3S_b/S$ where S is the slope of the calibration curve.

The limits of detection are $5.00 \mu\text{g l}^{-1}$, $7.00 \mu\text{g l}^{-1}$, $2.00 \mu\text{g l}^{-1}$ for copper, cadmium and lead, respectively. The selectivity of the method was tested by the recovery of the metals in synthetic aqueous mixtures. The results are shown in

Table I.

Seven replicate determinations were performed to estimate the reproducibility and accuracy of the proposed method at 2 different concentration levels, and the results are demonstrated in Table II.

Applications

The method was applied to the determination of copper, cadmium and lead in synthetic aqueous mixtures as well as in petrol/gas, beverages, natural juices, wines and certified reference materials (CRM). The results are shown in Tables III-VI.

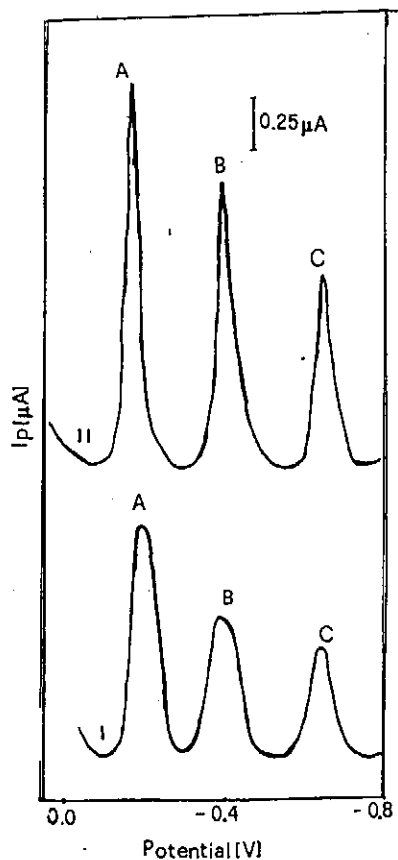


Fig. 6 Differential pulse voltammogram of Cu, Pb, Cd present at concentrations of $2 \times 10^{-6} \text{ mol l}^{-1}$ I) Before and II) after the addition of Hg^{2+} . The voltammogram was recorded at the optimum conditions. Standard instrumental parameters were used

Table I Recoveries of Cu, Cd and Pb, in synthetic samples, with the method proposed

Composition and concentrations of the synthetic mixture, $\mu\text{g l}^{-1}$	Cu			Pb			Cd			
	Added	Found	Recovery (%)	R.S.D (%)	Found	Recovery (%)	R.S.D (%)	Found	Recovery (%)	R.S.D (%)
Cu (15.1)+Ni (26.7)	14.8±0.6	98.0	3.10	-	-	-	-	-	-	-
Cu (22.5)+Mn (10.7)	21.9±1.2	97.3	4.30	-	-	-	-	-	-	-
Pb (24.5) +Co (40.5)	-	-	-	24.0±0.6	97.9	2.00	-	-	-	-
Cd(47.2) +Bi (68.2)	-	-	-	-	-	-	-	48.1±1.4	102	2.30
Cu(21.2)+Pb(12.0)+Cr(14.7)+Co (7.4)	22.1±1.2	104	5.10	12.9±0.7	108	4.40	-	-	-	-
Cd(12.5)+Cu(25.3)+Co(45.2)+Ni(29.6)	26.2±1.3	104	4.00	-	-	-	-	13.1±0.6	105	3.90
Cd(30.8)+Pb(17.7)+Zn(17.9)+Bi(41.6)	-	-	-	18.6±0.7	105	3.20	-	30.1±0.7	97.8	1.90
Cu(15.4)+Cd(24.9)+Bi(17.8)+Mn(12.5)	16.2±1.0	105	4.80	-	-	-	-	23.2±1.2	93.2	4.20
Cu(7.9)+Cd(26.3)+Pb(15.6)+Ni(31.2)+Cr(15.3)	7.10±0.4	89.9	5.30	16.1±1.0	103	4.80	-	25.0±1.5	95.1	4.70
Cu(12.6)+Pb(26.2)+Cd(18.7)+Co(14.9)+Mn(21.1)	11.9±0.7	94.4	4.60	25.4±0.9	96.9	2.80	-	18.1±1.2	96.8	5.20
Cu(17.2)+Pb(19.7)+Cd(11.5)+Zn(16.7)+Ni(56.2)	16.4±0.8	95.3	3.80	20.1±1.15	102	4.60	-	12.2±0.5	106	3.60

Table II Recoveries of Cu, Cd and Pb with the method proposed

Element	t = 30 s				t = 60 s				t = 90 s				
	Added µg l ⁻¹	Found µg l ⁻¹	Recovery %	R.S.D %	Found µg l ⁻¹	Recovery %	R.S.D %	Found µg l ⁻¹	Recovery %	R.S.D %	Found µg l ⁻¹	Recovery %	R.S.D %
Cu	7.00	7.70±1.05	110	11.0	7.30±0.80	104	9.10	7.00±0.69	100	8.00	7.00±0.69	100	8.00
	71.0	71.8±3.6	101	4.00	72.5±3.8	102	4.20	70.5±4.6	99.3	5.30	70.5±4.6	99.3	5.30
	712	718±18	101	2.00	730±20	102	2.20	734±17	103	1.90	734±17	103	1.90
	3563	3545±61.5	99.5	1.40	3538±79	99.3	1.80	3527±66	99.0	1.50	3527±66	99.0	1.50
Pb	6.00	6.40±0.99	107	12.5	5.80±0.61	96.7	8.50	6.70±0.51	111	6.10	6.70±0.51	111	6.10
	61.5	60.8±3.7	98.9	4.90	62.3±3.9	101	5.10	61.9±3.8	101	4.90	61.9±3.8	101	4.90
	616	613±19	99.6	2.50	618±30	100	3.90	620±27	101	3.50	620±27	101	3.50
	3078	3113±108	101	2.80	3012±119	97.9	3.20	3010±115	97.8	3.10	3010±115	97.8	3.10
Cd	7.5	7.80±1.31	104	13.6	6.90±0.50	92.0	6.30	7.40±0.46	98.7	5.00	7.40±0.46	98.7	5.00
	74	73.5±4.3	99.3	4.70	73.0±4.0	98.6	4.10	74.8±2.2	101	2.40	74.8±2.2	101	2.40
	741	747±46	101	5.00	751±21	101	2.30	742±16	100	1.70	742±16	100	1.70
	3555	3539±118	99.5	2.70	3561±84	100	1.90	3548±48	99.8	1.10	3548±48	99.8	1.10

Table III Determination of lead in standard and synthetic solutions

Sample	Pb ppm	Found Pb ppm	Recovery %	R.S.D %
AH93	354	357±8	-	1.96
AH95	383	378±12	-	2.59
AH98	412	410±16	-	1.95
91/115	673	667±20	-	2.80
95/130	892	889±12	-	3.40
1-A	973	967±34	99.4	6.30
2-A	1,354	1,349±3	99.6	3.70
3-A	1,091	1,085±28	99.4	4.30
4-A	1,123	1,127±26	100	5.10

n = 5, P = 0.95

Composition (v/v%) of the mixtures:

1-A toluene (25) + isooctane (45) + n-heptane (30)

2-A toluene (25) + isooctane (58) + n-heptane (17)

3-A toluene (25) + isooctane (56) + n-heptane (15)

4-A toluene (25) + isooctane (48) + n-heptane (27)

Table IV Determination of lead in petrol/gas

Type of petrol/gas	Pb mg l ⁻¹ ASTMD	R.S.D %	Pb mg l ⁻¹	R.S.D
SUPER	110±5	3.80	130±6	4.30
REGULAR	320±91	2.50	300±12	3.40
UNLEADED	3.10±0.11	3.20	2.80±0.10	4.00

P = 0.95, n = 5

Conclusion

In this work a new optimized chemically modified carbon paste electrode was applied to the simultaneous determination of Cu, Cd and Pb in natural and synthetic samples, with a minor sample preparation. The sensitivity of the method was optimized by addition of Hg (II) solution.

Measurements were mostly carried out using a PA-3 polarographic

analyser (Laboratorní přístroje, Praha); some analytical parameters were evaluated also using a PAR 174A device (Princeton Applied Research). A three-electrode cell was used for measurements, consisting of a CPE as the working electrode, silver-silver chloride and a platinum wire as reference, or counter electrodes, resp.

Table V Determination of copper, cadmium and lead in beverages, natural juices and wines

Sample	Cu ppb		Pb ppb		Cd ppb	
	CMCPE	HMDE	CMCPE	HMDE	CMCPE	HMDE
Pepsi-cola	28.1±2.0	30.2±1.5	10.5±0.6	9.80±0.70	<17.5	0.350±0.030
Coca Cola	32.5±1.8	34.0±1.7	12.7±0.7	11.7±0.8	<17.5	0.280±0.040
Fanta	38.6±2.0	37.5±1.8	15.6±0.5	13.8±0.6	<17.5	0.520±0.030
Banana nectar	141±5	131±4	9.30±0.27	9.90±0.37	<17.5	3.40±0.06
Lemonade	67.0±4.0	69.0±5.0	39.9±1.3	35.7±1.1	<17.5	2.70±0.05
Peach nectar	164±6	154±5	28.4±1.1	26.7±1.1	<17.5	1.34±0.21
Mantari- nade	117±3	113±3	11.2±0.4	13.2±0.6	<17.5	2.21±0.03
Red wine (1993)	82.4±0.60	83.5±0.5	26.4±0.70	25.6±0.6	<17.5	2.60±0.03
Red wine (1994)	112±1	110±1	43.7±0.6	42.4±0.5	<17.5	3.20±0.03
Red wine (1993)	83.2±0.7	81.3±0.5	23.5±0.5	24.8±0.5	<17.5	1.70±0.04
White wine (1994)	91.7±0.4	93.8±0.4	39.4±0.5	40.5±0.4	<17.5	1.31±0.04
White wine (1993)	77.2±0.4	75.6±0.3	22.3±0.6	21.4±0.7	<17.5	1.5±0.05
White wine (1993)	80.9±0.5	82.8±0.4	36.8±0.5	35.6±0.5	<17.5	0.90±0.06

CMCPE - Chemically Modified Carbon Paste Electrode

HMDE - Hanging Mercury Drop Electrode

Table VI Determination of copper, cadmium and lead in certified reference materials

Sample	Cu ppm	Pb ppm	Cd ppm
CRM 278 mussel tissue	9.27±0.15	1.93±0.12	0.36±0.02
	9.60±0.16*	1.91±0.40*	0.34±0.02*
CRM 281 rye grass	9.44±0.40	2.45±0.15	1.32±0.05
	9.65±0.38*	2.38±0.11*	1.20±0.03*

* Certified values

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