CARBON PASTE ELECTRODE MODIFIED WITH THIOUREA-FUNCTIONALIZED RESIN FOR DETERMINATION OF LEAD

Tomáš MIKYSEK[a], Ivan ŠVANCARA[1a], Ana BANIÇA[b], Florinel G. BANIÇA[b]
and Karel VYTŘAS[a]
[a]Department of Analytical Chemistry,
The University of Pardubice, CZ–532 10 Pardubice,
[b]Department of Chemistry, Norwegian University of Science and Technology,
N–7491 Trondheim

In this contribution, a carbon paste electrode modified with thiourea-functionalised resin is described in terms of its electroanalytical characterisation and applicability to the determination of Pb^{2+} ions. Commercially marketed macroporous resin, QuadraPure™TU, added to the carbon paste mixture in an amount of 30% (v/v), contains thiourea residual groups being able of effectively complexing the Pb^{2+} ions. Within the method development, a special attention was paid to the pre-concentration step, modification process, proper measuring regime, as well as the optimisation of important experimental parameters. When using the square-wave voltammetric mode in combination with open-circuit accumulation, intermediate electrolytic reduction at a constant potential, and

---

[1] To whom correspondence should be addressed.

subsequent anodic stripping step, the resultant signal for lead could be calibrated within a very wide concentration range of 5-25 000 µg l^{-1} Pb^{2+}, with a limit of detection (3σ) of about 1 µg l^{-1}, and without serious interferences from other heavy metal ions as confirmed in special studies. Practical usefulness of the method has been tested on selected water samples and the respective results verified by means of recovery rates, certified reference material, and ICP-MS reference determinations.

Introduction

In modern electroanalysis, chemically modified carbon paste electrodes (CMCPEs) play an important role and their practical applications to the determination of numerous metal ions are of continuing interest for lengthy decades [1], including a certain renaissance that characterises the latest years [2]. Within a myriad of various modifiers, one of the most widely used groups is represented by sulphur-containing compounds, natural or synthetic thio-derivatives, as well as some other related materials, coming to the fore *via* the dynamic progress in new technologies. An instant popularity of such modifiers can be explained by high chemical reactivity of various sulphides, disulphides, thiols, and other related compounds [3,4], enhanced yet by thiophilicity of many inorganic analytes, which is the particular case of heavy metal ions [1]. This is illustrated in Table I, surveying more than 40 different methods [5-47] that have hitherto been proposed in inorganic analysis with CMCPEs and employed various sulphur-containing modifiers. Among them, one can find classical chemical reagents like dithizone [8,33,34], dithiocarbamate [12], rubeanic acid (dithiooxalate diimide [21]), *Bismuthiol I* [39] and *Bismuthiol II* [40], or thiooxin [43]; purposely selected sulpho- and thio-compounds (see e.g. [5,6,22,38,46]), or some special materials prepared with the aid of the above-mentioned new technologies [13,35-37].

Novel materials tested in the configurations of CMCPEs are also commercially available chelating agents belonging to macroporous chemically-functionalised resins [11] and a substance from this family is also the key-topic of this article. Namely, it is a thiourea-functionalised resin, QuadraPure™TU ("QPu" [48]) that is used for fine industrial purification of various pharmaceutical and chemical products from undesirable metal contaminants occurring in the processed raw material.

The applicability of this resin as a modifier for carbon paste has already been demonstrated in our preliminary reports [49,50], showing its activity *via* the thiourea residue (TUR) for complexing the target analytes — selected heavy metal ions.

Table I Electroanalysis with carbon paste electrodes modified with sulphur-containing compounds: Survey of methods

Ion(s) (species)	Type of CPE (modifier)	Technique (mode)	Measuring principles; (method sequences)	Linearity range (det. limit, t_{acc})	Sample(s)	Other specification (remarks)	Ref(s)
Ag^+	C/MO (thiacrown comp.)	DCV	- compl. via chelating - redn. and anodic reoxidn.	0.5-2.5 mM (0.5 mM; 5 min)	model solns.	- open circuit + MEx; no interfs from Cu^{2+}, Cd^{2+}, Ni^{2+}, and Co^{2+}	5
Ag^+	C/Nj (2,2'-dithiopy.)	CV, LSV, DPV	- compl. by -S- groups - cathodic redn.	—	model solns.	- comp. with other subst. pys - incl. interf. studies	6
Ag^+	C/PO (Ag^I-TMS)	CV, FIA-EC, POT (titr.)	- compl. with modifier - electrolytic redn.; chem. equilibria indication	$5×10^{-7}$-$1×10^{-6}$ M ($1×10^{-8}$ M; --)	radiological films, pharmaceuticals (e.g. thiopental)	- TMS: thimerosal ($C_2H_5Hg^{2+}$-thio-salicylate; in POT, Nerstian slope: 59.3 mV/decade; titr. with $AgNO_3$	7
Au^{3+} ($AuCl_4^-$)	C/Uv (dithizone)	AdSV, DPV	- accum. via adsorption - cathodic redn.	0.1-1.0 mg ml^{-1} (2 min)	model solns.	- accum. in open circuit	8
Au^{3+} ($AuCl_4^-$)	C/Uv (thiobenzanilide)	DPCSV	- accum. via -N- and -SH funct. groups; redn.	0.05-0.6 mg ml^{-1} (2 min.)	model solns.	- acc. under open circuit conds. - interfs from Hg^{2+} and Pt-metals	9
Hg^{2+}	C/MO (TQZ)	DPASV	- o.c.-accum. via compl. - MEx; redn.; reoxidn.	5-6000 mg l^{-1} (0.1 mg l^{-1}; 15 min.)	sewage sludge, plant	- TQZ: 2-thio-4(3H)-quinazoline	10
Hg^{2+}, $HgCH_3^+$	C/Nj (thiolic resin)	CV, CSV	- accum. by compl. - cathodic redn.	4 mg l^{-1} for Hg^{2+}; 2 mg l^{-1} for $HgCH_3^+$	aquatic samples	- applicable to speciation of inorg. mercury and organomercury	11
Hg^{2+}	C/MO (Zn^{II}-DDC)	DPASV	- accum. by compl.+ MEx - redn. + anodic reoxidn.	$5×10^{-8}$-$1×10^{-7}$ M ($8×10^{-10}$ M; 15 min.)	natural water, [human urine]	- DDC: diethyldithiocarbamate - samples prepared by MWD	12
Hg^{2+}	C/MO [DTTPSG]	CV, DPCSV	- accum. via modif., redn. during cathodic scanning	(RSD = ±2-3 %)	natural waters (polluted)	- DTTPSG: 2,5-dimercapto-1,3,4-thiadiazole functional. silica gel; 0.02 M KNO_3; E_a(Hg) = +0.3V.	13
Hg^{2+}, $Hg^{2+}X_n$	C/Nj [BbTSC]	CV, SWSV	- open circuit acc. via modif - cathodic redn.	— (8 ppb; 15 min.)	river water	- BbTSC: benzyl-bis-thiosemicar-bazone; studies on dissociation kinetics of Hg^{2+}-complexes	14
Hg^{2+}	C/MO [MPTNS]	CV, DPASV	- open-circuit accum. via modif., cathodic redn.	$1×10^{-7}$-$7×10^{-6}$ M ($7×10^{-8}$ M; 300 s)	model solns.	- MPTNS: 3-mercaptopropyl tri-methoxysilane (functionalised natural phyllosilicate clay (2:1)	15
Hg^{2+}	C/Nj [TZT-HDA-clay]	ASV	- adsorp. accum. by modif. + elc. redn.; anodic reoxidn.	— (0.1 mg l^{-1})	model solns.	- TZT-HDA: 2-thiazoline-2-thiol-hexadecyltrimethylammonium; study on adsorp. izoterms of Me^{2+}	16

Table I – continued

Ion(s) (species)	Type of CPE (modifier)	Technique (mode)	Measuring principles; (method sequences)	Linearity range (det. limit, t_{ACC})	Sample(s)	Other specification (remarks)	Ref (s)
Hg^{2+}	C/MO [SI-, MM-AMT]	CV, DPASV, HPLC-EC	- accum. by modif. + electrolytic redn.; anodic reoxidn.	0.002-2 mg l⁻¹ (0.1-5 mg l⁻¹)	model solns., natural water	- SI-, MM-AMT: 2-aminothiazole functionalized silica gel or montmorillonite clay; interfs. studies	17-19
Cu^{+}	C/Nj (DIDD)	CV, DPV	- accum. via compl. after chem. redn. Cu^{II} ~ Cu^{I}	$(5 \times 10^{-11}$ M, 30 min.)	CRM (urine)	- DIDD: diiminocyclopentylidine-thiomethyl disulphide; CPE regnt.	20
Cu^{+}	C/Nj (rubeanic acid)	CV, DPV	- accum. via compl. after chem. redn. Cu^{II} ~ Cu^{I}	1×10^{-7} - $5'10^{-6}$ M $(5 \times 10^{-8}$ M, 15 min.)	CRM (urine)	- CMCPE regnt. by anodic cycling in 0.1 M HNO_3	21
Cu^{+}	C/Nj [Sal-TSC]	FIA-EC	- accum. via compl. under FIA conds; volt. detection	$(1 \times 10^{-10}$ M)	tap water, sea water (CRM)	- Sal-TSC: salicylaldehyde thiosemicarbazone; effect of Cu^{2+}	22
Cu^{+}, Cu^{2+}	C/MO (4 diff. modifs.)	DCV, ASV	- accum. by compl. in situ - anodic reoxidn.	(ca 1 ppb, 3 min.)	drinking water	- modifs.: dithiooxamide, biquinoline, Cuproin, Bathocuproin - high selectivity (c_{Cu}:c_{Me} = 1 : 10⁵)	23
Cu^{+}, Cu^{2+}	CP-SPE (Cu_2S, CuS)	POT (direct)	- ion-exch. equilibrium in Cu-doped thick layer	1×10^{-5}-0.01 M $(1 \times 10^{-6}$ M)	model solns.	- disposable sensor made by screen-printed techn. ("thick film-CP")	24
Cu^{2+}	C/Nj (DQDS)	DPCSV	- accum. by chelating effect - cathodic redn.	3×10^{-9}-2×10^{-6} M	soils, minerals	- DQDS: diquinolyl-8,8'-disulphide - s.e.: 0.1 M acetate buffer	25
Cu^{2+}	C/Nj (SATP)	DPCSV	- o.c.-accum. via compl. - cathodic redn.	2×10^{-9}-1×10^{-7} M	CRMs (pepper bush, hair)	- SATP: salicylideneamino-2-thiophenol; s.e.: 0.01 M acetate buffer	26
Cu^{2+}	C/MO (ADE)	EC-FIA	- accum. via compl. under FIA conds; elchem. det.	2×10^{-6}-2×10^{-4} M $(1 \times 10^{-6}$ M, 4 min.)	model solns.	- ADE: 1,2-bismethyl(2-aminocyclo pentenecarbodithiolate) ethane	27
Cu^{2+}	C/Nj (Sal-TSC)	EC-FIA	- accum. via compl. under FIA conds; volt. detection	$(1 \times 10^{-10}$ M)	CRM (sea water), tap water	- Sal-TSC: salicylaldehyde thiosemicarbazone	28
Cu^{2+}	C/MO (L_1, L_2)	POT (direct)	- chelating effect - equilibrium potential	1×10^{-5}-0.01 M (pCu = 4.8-5.6)	solns. with humic acids	- L_1,L_2: macrocyclic thiohydrazone and thiosemicarbazone ligands	29
Cu^{2+}	C/PO (PA-DTC)	CSV	- accum. via chelating - redn.; simult. reoxidn.	(0.2 nM; 20 min.)	natural waters	- PA-DTC: pyruvaldehyde bis(N,N'-dibutyl thiosemicarbazone; solely little interfs. from Se^{IV}, S^{2-}, Ga^{3+}	30
Cu^{2+}	C/MO (MTH)	CV	- o.c.-accum. via compl. - volt. detection	(0.5 mg l⁻¹, 10 min.)	river water	- MTH: macrocyclic thiohydrazone - incl. studies on interfs.	31

8

Table I – continued

Ion(s) (species)	Type of CPE (modifier)	Technique (mode)	Measuring principles; (method sequences)	Linearity range (det. limit, t_{ACC})	Sample(s)	Other specification (remarks)	Ref(s)
Cu^{2+}	C/MO (DTPT)	PO	- chelating effect - equilibrium potential	1×10^{-6}–0.08 M (7×10^{-7}M)	electronics (waste solns.)	- DTPT: (3,4-dihydro-4,4,6-tri-methyl-2(1H) pyrimidine thione	32
Pb^{2+}	C/MO (dithizone)	DPCSV	- o.c.-accum. + MEx - cathodic redn.	20–520 mg l⁻¹ (17 mg l⁻¹, 6 min.)	natural waters	- interfs. from some ions elim. by masking except sulphide, S^{2-}	33
Pb^{2+}	C/MO (dithizone)	DPASV, FIA-EC	- open circuit accum. + MEx + elc. redn. - anodic reoxidn.	1×10^{-7}–1×10^{-5} M (8×10^{-8} M; 120 s)	contaminated soils (industrial source)	- no interfs. from Zn^{2+}, Cd^{2+}, Cu^{2+}, and Hg^{2+}; ref. detns with AAS.	34
Pb^{2+}	C/PO (PA-DTC)	CSV	- accum. via chelating - redn.; anodic reoxidn.	(2 nM Pb, 0.2 nM Cu, 20 min.)	natural waters	- PA-DTC: pyruvaldehyde bis(N,N-dibutylthiosemicarbazone; - little interfs. from Se^{4+}, Sr^{2+}, Ga^{3+}	30
Pb^{2+}	C/PO (SH-ms-SiO₂)	SWV	- accum. via compl. - redn.; anodic reoxidn.	10–1500 ppb Pb 20–1600 ppb Hg	model solns.	- SH-ms-SiO₂: thiol-based mesoporous silica; simult. detn. of Hg^{2+}	35
Cd^{2+}	C/MO (BTT+ am-SiO₂)	DPASV	- adsor. accum. via compl. - redn.; anodic reoxidn.	6×10^{-7}–4×10^{-5} M (1×10^{-7} M, 2 min.)	natural water (spiked)	- BTT: benzothiazole-thiol, am.: amorphous; s.e.: PhB (pH 7.5)	36
Cd^{2+}	C/MO [nSBA-15 + BTT]	ASV, DPV	- complexation via modif. anchored in nano-substr.; - oxidation of complex	1×10^{-6}–1×10^{-5} M (5×10^{-7} M; 120 s)	natural water (spiked)	- nSBA-15: nanostructured silica, BTT: 2-benzothiazolethiol; s.e.: PhB (pH 3), interference studies	37
Bi^{3+}	C/Nj (decan-1-thiol)	DPASV	- o.c.-accum. + redn. - anodic reoxidn.	0.02–4 ppm	model solns.	- eld. regent. in 0.01 M HCl; s.e.: 0.2 M HCl; oxidn. agents interf.	38
Bi^{3+}	C/Nj (Bismuthiol I)	DPCSV	- o.c.-accum. - cathodic redn.	0.01–4 mg l⁻¹ (5 mg l⁻¹, 2 min.)	model solns.	- incl. study on accum. mechanism and interfs from various ions	39
Bi^{3+}	C/MO (Bismuthiol II)	LSV	- o.c.-compl. accum. - cathodic redn.	3×10^{-8}–6×10^{-6} M (2×10^{-8} M, 5 min.)	actual samples (–)	- modif.: 5-thio-3-(p-carboxyphenyl -1,3,4-thiadiazoline-2-thione	40
Co^{2+}	C/MO (+ phen.) (HTTA, in situ)	DPV	- accum. via ternary	8×10^{-9}–7×10^{-7} M (1×10^{-9} M, 7 min.)	natural water	- HTTA: thiophen-carboxylic trifluoroacetate); phen.: phenanthroline	41
Mo^{VI} (MoO_4^{2-})	C/Nj (DEDC, in situ)	ASV	- accum. via redox compl. - anodic reoxidn.	5–50 ng ml⁻¹	NaWO₄ (s)	- DEDC: diethyldithio-carbamide - s.e.: acetate buffer (pH 4.8)	42
W^{VI} (WO_4^{2-})	C/PO (SH-oxin + DMSO)	CSV	- accum. via compl. - cathodic irrev. redn.	5×10^{-4}–0.001 M	complex mixtures (–)	- SH-oxin: 8-thioquinoline - s.e.: HCl-based solns.	43

Table I – continued

Ion(s) (species)	Type of CPE (modifier)	Technique (mode)	Measuring principles; (method sequences)	Linearity range (det. limit, t_{ACC})	Sample(s)	Other specification (remarks)	Ref(s)
Pd^{2+}	C/Uv (TR, *in situ*)	DPASV	- adsorp. accum. by compl. - anodic reoxidn.	1-450 mg l⁻¹ (1 mg l⁻¹, 120 s)	fresh water, catalysts	- TR: thioridazine; CPE regnt.; - interfs. studies on other Pt-metals	44
Ir^{3+}	C/DCB (Ir^{III}-PTQ)	ASV	- accum. *via* compl. - anodic reoxidn.	(3×10⁻¹⁰ M)	model solns.	- PTQ: 4-phenyl-8-thioquinolinate; - DCB: dodecyl butyrate; no interfs. from Pt-metals, Ni, and Au.	45
Mg^{2+}	C/Nj + MF (Na^+-TP, *in situ*)	SWV	- adsorp. accum. by compl. - cathodic redn.	6×10⁻⁹-9×10⁻⁸ M (5×10⁻¹⁰ M, 60 s)	tap water, urine	- TP: thiopentone; s.e.: PhB (pH11) - interference study with various Me^{n+} + some biol. materials.	46
NO_2^-; NO_3^-	C/MO [Cu^{2+}-MPS]	CV, CE-EC	- electrocatalytic reduction of both anions; - amperometric detection	0.25-120 mM (NO_2^-: 0.09 mM, NO_3^-: 0.08 mM)	water sample [urine]	- MPS: -(3-mercaptopropyl) trimethoxysilane; s.e.: 0.002 M AcB + 0.003 M CTAB (pH 5.0)	47

Abbreviations and symbols used (in alphabetical order)

– ... unspecified, not found; acc., accum. ... accumulation, accumulated; AcB ... acetate buffer; adsorp. ... adsorption, adsorbed; AdSV ... adsorptive stripping voltammetry; AmB ... ammonia buffer; ASV ... anodic stripping voltammetry; biol. ... biological; CE-EC ... capillary electrophoresis with electrochemical detection; chem. ... chemical; compl(s) ... complexation(s), complexed with; C/MO ... mineral oil-made carbon paste; CMCPE ... chemically modified carbon paste electrode; comp. ... compounds; conds. ... conditons; CP ... carbon paste; CP-SPE ... carbon paste based screen printed electrode; CPE ... carbon paste electrode; C/Nj ... carbon paste made of Nujol® oil; C/PO ... paraffin oil-made carbon paste; C/SO ... carbon paste made of silicone oil; CRM(s) ... certified reference material(s); CSV ... cathodic stripping voltammetry; CTAB ... cetyltrimethylammonium bromide; C/Uv ... carbon paste made of Uvasol®; CV ... cyclic voltammetry; det. ... detection; DCV ... direct current voltammetry; dep. ... deposition, deposited; detn(s) ... determination(s); DPA(C)SV ... differential pulse anodic (cathodic) stripping voltammetry; el. ... electrode; elc. ... electrolytic, electrolysis; elchem. ... electrochemical; elim. ... eliminated by; FIA ... flow injection analysis; FIA-EC ... FIA with electrochemical detection; functional. ... functionalised; HPLC-EC ... HPLC with electrochemical detection; incl. ... including; inorg. ... inorganic; interf(s) ... interference(s), interfering species; irrev. ... irreversible; LSV ... linear sweep voltammetry; M ... molar concentration, mol l⁻¹; MEx ... medium exchange; MF ... mercury film; min. ... minute(s); MO ... mineral oil; modif(s). ... modifier(s), modification, modified with; MWD ... microwave-assisted digestion; org. ... organic; oxidn. ... oxidation; o.c. ... open circuit; PhB ... phosphate buffer; ppm, ppb ... concentration units; POT ... potentiometry; redn. ... reduction; regnt. ... regeneration, regenerated; ref. ... reference; reoxidn. ... reoxidation; s ... second(s); volt. ... voltammetry, voltammetric; s.e. ... supporting electrolyte; simult. ... simultaneous; soln(s) ... solution(s); substr. ... substrate; SWV ... square-wave voltammetry; t_{ACC} ... accumulation time; tech. ... technology; titr(s). ... titration(s), titrated.

10

Mikysek T. *et al./*Sci. Pap. Univ. Pardubice Ser. A **15** (2009) 5–27

Experimental

Chemicals and Reagents, Stock and Standard Solutions

All the chemicals used were of analytical reagent grade and purchased from Merck or Sigma Aldrich. A stock solution of acetate buffer prepared as equimolar mixture of 1 M CH_3COOH + 1 M CH_3COONa was used as the supporting electrolyte and appropriately diluted before use. In some comparative measurements, other supporting media were also tested (their specification is given below). Standard solutions of Pb^{2+} and Cd^{2+} as the analytes of interest, as well as for other metal ions were made as 0.01 mol l^{-1} and their diluted solutions stabilised by acidifying with a few droplets of conc. HNO_3 to pH 2.

Throughout the experimental work, the solutions were prepared or diluted using doubly deionised water (18 MΩ cm^{-1}) obtained by passing through a Milli-Q$^®$ Millipore laboratory purification system (Millipore, USA) and purged with nitrogen (purity: 99.99 %; Linde Technoplyn, Prague, the Czech Republic) prior to analysis.

Apparatus and Accessories

All the measurements were performed with an AUTOLAB$^®$ electrochemical analyser (model PGSTAT 30; Ecochemie, Utrecht, The Netherlands) operated *via* the GPES 4.9 software (ibid). A three-electrode cell used comprised the working electrode, Ag|AgCl|3 M KCl as the reference, and a Pt-plate (3×5 mm) as the counter electrode. Where applicable, stirring was performed using a Teflon$^®$-coated magnetic bar rotated at ca 300 rpm.

The pH values were measured by means of a portable pH-meter (model CPH 52; Elteca, Turnov, the Czech Republic) equipped with a combined glass sensor (OP-0808P; Radelkis, Budapest, Hungary) and calibrated using commercial standard buffers.

Preparation of Modifier

Originally granulated macroporous resin (QuadraPure^{TM}TU,Sigma Aldrich, cat. N^{o}: 655 422; was divided into two fractions. The first one was used as such (with size of resin beads between 400-600 μm), the second was ground using a pestle and porcelain mortar into a fine powder (with particles of ca 50 μm as ascertained by optical microscopy).

Working Electrodes

Modified Carbon Pastes. Both fractions of granulated and pulverised QPu resin were taken in 0.2 g amounts and intimately homogenised with the same quantity of graphite powder ("RW-B" type; Ringsdorff-Werke, Germany).

Two portions of carbon powders (modified in this way) were then soaked with 0.2 g silicone oil ("MV 8000"; Lučební závody Kolín, the Czech Republic) and the mixtures obtained homogenised again according to the previously recommended procedure [51].

Chemically Modified Carbon Paste Electrodes (CMCPEs). Both carbon pastes prepared were packed into two identical cylindrical piston-driven electrode holders [52]; the whole assembly forming the resultant carbon paste electrodes, both with the same active surface ($d = 2$ mm). The renewal of the carbon paste surface was accomplished by smoothing against a filter paper.

Electrochemical Technique and Procedure

Square-wave anodic stripping voltammetry (SWASV). With this technique of choice, typical measurements consisted of four consecutive steps: (1) open-circuit accumulation made for a period, $t_{ACC} = 5\text{-}15$ min.; (2) electrolytic reduction of pre-concentrated complex at $E_{RED} = -1.0$ V *vs.* Ag/AgCl for a constant period, t_{RED}, typically for 3 min.; (3) equilibrium period, $t_{EQ} = 5$ s; and (4) the anodic stripping scan from initial potential, $E_{INIT} = -0.8$ V to the final potential, $E_{FIN} = -0.4$ V vs. ref. All four sequences were performed in 0.1 mol l^{-1} acetate buffer (pH 4.5) if not stated otherwise. The remaining instrumental conditions specifying the SWV modulation ramp were: frequency, $f_{SW} = 25$ Hz; the pulse height, $\Delta E_{SW} = 50$ mV and the potential increment (step), $i_{SW} = 5$ mV, giving the resultant scan rate, $v_{SW} = 125$ mV s^{-1}.

Model Solutions, Samples, and the Respective Analyses

Samples. Model solutions were prepared as mixtures of 18 ml deionised water + 2 ml 1 mol l^{-1} acetate buffer spiked with 25 µg l^{-1} Pb^{2+} and served for recovery rate measurements. As real samples, two water specimens were used: natural water collected from a small pond in the Southern Moravia region and tap water sampled from a laboratory pipe-line, being additionally spiked with 30 µg l^{-1} Pb^{2+}.

Finally, the third specimen was a certified reference material (CRM) of sewage sludge (category "WT-H 12-3-14"; Pb-Anal, Košice, Slovakia), representing heavily polluted industrial waste.

Sample Preparation. Both natural and tap waters were acidified with HNO$_3$ and,

prior to analysis, placed into an ultrasonic bath (Bandelin, France) for about 2 min. CRM of sewage sludge was solubilised in the presence of 65 % HNO_3 when using a microwave digestion system (Berghoff, Germany) with PC-controlled and standardised decomposition procedure. The resultant solution was then appropriately diluted for both voltammetric measurements and reference analysis with ICP-MS.
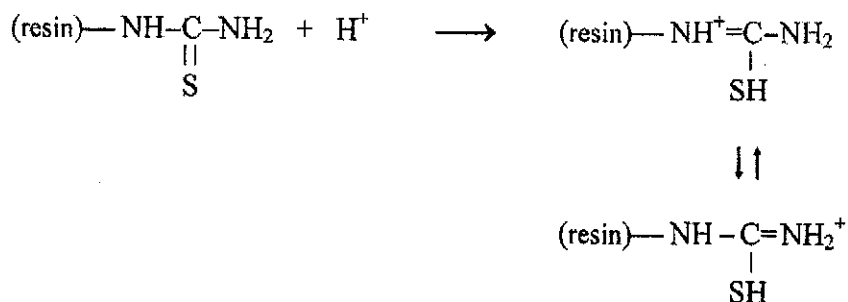
Quantitative Analysis, Evaluation of Signals, and Data Processing. The determination with SWASV was performed by multiple standard-addition method with three aliquots. The resultant analytical signals recorded as voltammetric peaks were evaluated as the respective current intensities (corrected to base-line) and computed by the instrument software.

Results and Discussion

Principles of the Method with Accumulation *via* the QuadraPure™TU Resin

Based on the already reported complexing capabilities of the resin [48] and in analogy with behaviour of similar sulphur-containing compounds, the accumulation mechanism apparently involves two consecutive steps.

At first, the thiourea residue is protonated, which leads to its tautomeric transformation into a highly reactive immino-thiolic constitution [3,4] that may exist — in the case of thiourea functional group — in two alternate structures

$$(resin)-NH-\underset{\underset{S}{\|}}{C}-NH_2 + H^+ \longrightarrow (resin)-NH^+=\underset{\underset{SH}{|}}{C}-NH_2$$

$$\updownarrow$$

$$(resin)-NH-\underset{\underset{SH}{|}}{C}=NH_2^+$$

Scheme 1a

Subsequently, the thiourea residue with the active immino-thiolic group reacts with the target ion to form the respective complex, e.g.

$$2 \ \text{(resin)} - \overset{+}{\text{NH}} = \underset{\underset{\text{SH}}{|}}{\text{C}} - \text{NH}_2 \ + \ \text{Pb}^{2+} \ \longrightarrow \ \overset{\text{(resin)} - \overset{+}{\text{NH}} = \underset{\underset{\text{S}}{|}}{\text{C}} - \text{NH}_2}{\underset{\underset{\underset{\text{(resin)} - \overset{+}{\text{NH}} = \text{C} - \text{NH}_2}{|}}{\text{S}}}{\underset{|}{\text{Pb}}}} \ + \ 2 \ \text{H}^+$$
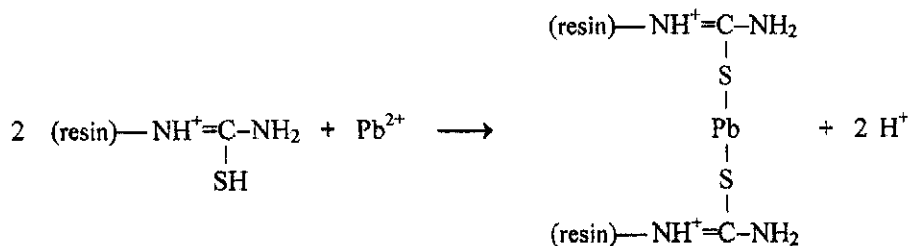
Scheme 1b

An alternative hypothesis [49,50] does not assume a complex-forming process, but the reaction where the thiourea fragment directly converts the Pb^{2+} ions into insoluble lead sulphide

$$-\text{NH}-\text{CS}-\text{NH}_2 + \text{Pb}^{2+} \longrightarrow \text{PbS} \downarrow + \text{other reactions products} \qquad (1c)$$
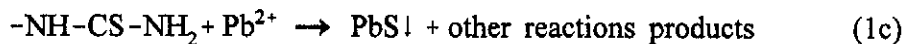
The precipitate formed can then be adsorbed onto the electrode surface, undergoing afterwards a similar pathway as the above complex structure.

In the second phase of the method, the central atom in the pre-concentrated complex (or sulphide, respectively) is electrolytically reduced to the elemental form according to the scheme: $Pb^{2+} + 2e^- \rightarrow Pb^0$. Finally, the elemental lead deposited at the electrode surface is re-oxidised by imposition of voltammetric scan in the anodic direction: $Pb^0 \rightarrow Pb^{2+} + 2e^-$.

Herein, it should be noted that such an approach, involving the intermediate reduction at a constant potential followed by the anodic stripping is quite popular within the electrochemistry with CMCPEs (see, e.g., [1,2]) because of the fact that one can avoid rather problematic cathodic detections, where parasitic signals of oxygen may seriously interfere. (Normally, molecular dioxygen is being brought into the paste during its preparation and cannot be removed, its two-step reduction giving then rise to undesirable responses that significantly affect the signal of interest [51].) This was confirmed already during initial experiments with TUR-CPE [49,50] and since there was no improvement after applying otherwise beneficial SWV ramp [55], the incorporation of the intermediate reduction into the procedure was inevitable.

The whole pre-concentration mechanism (1a,b) admits that the thiourea-residue might interact with such metal ions that exhibit thiophilicity similar to those of Pb^{2+} and Cd^{2+} ions; the former being chosen as the primary analyte. Such species could include Zn^{2+}, $Cu^{2+/+}$, Bi^{3+}, Ag^+, Hg^{2+}, Co^{2+}, and Ni^{2+} [3,4] and, therefore, all these ions were considered as potentially interfering with the determination of Pb^{2+} and/or Cd^{2+} and examined within a special study (see below).
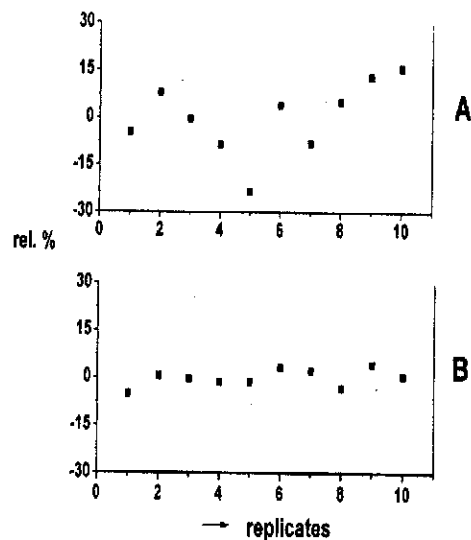
Fig. 1   Reproducibility of the response for Pb at CPEs containing QuadraPure™TU resin in its granular form (A) and after pulverisation (B). SWASV, $t_{ACC} = 10$ min, $t_{EQ} = 5$ s; $E_{RED} = -1.0$ V vs. Ag/AgCl, $t_{RED} = 180$ s; E_{INIT}: -1.0 V, $E_{FIN} = 0$ V; $c(Pb) = 100$ µg l^{-1}. For other conditions, see Experimental

QuadraPure™TU Resin as Modifier in the Carbon Paste Bulk

For modification of carbon paste, the QPu resin was initially tested in its original granular form. This rough texture, however, was found unsuitable with respect to difficult homogenisation with the native carbon paste and, mainly, because of poor electroanalytical performance of the resultant electrode. Thus, the commercial product had to be ground into a fine powder, which could be accomplished in an ordinary laboratory mortar. The effect of pulverisation is illustrated in Fig. 1, making comparison between the responses for model concentration of Pb^{2+} replicated at CPE with original granules (plot A; with the relative standard deviation, RSD > ±20%, for $n = 10$) and using carbon paste with the same amount of powdered modifier (plot B; RSD < ±5%, $n = 10$).

Regarding the content of QPu resin in the carbon paste bulk, the percentages of 10 %, 20 %, and 30 % (w/w) were examined; the last being found as optimum. This seemingly high content corresponded to those in some previous reports on CMCPEs for the determination of Pb^{2+} and one of such carbon pastes with 30 % modifier [56] has also been used as a model mixture during optimisation of the ultimate composition for TUR-CPE.

Development of Method

Next experiments were focused on searching for suitable experimental and instrumental conditions. Due to technical reasons, the initial stage of optimisation was carried out in the DPASV mode [49], whereas the proper electroanalytical characterisation of the method and the final procedure for the determination of Pb^{2+} were performed in the SWASV regime [50].

Choice of Supporting Electrolyte. Table II summarises the data evaluated from the respective measurements and used for selection of the supporting medium proper. As seen, the highest peaks for a model concentration of Pb^{2+} ions were obtained in both decimolar acetate-based solutions and thus, these media were used in further experiments chosen due to their buffering capabilities in the final procedure for quantitative determination.

Table II   Optimization of supporting electrolyte composition *via* peak characteristics of signal for Pb in model solutions

Supporting electrolyte (actual pH)	Peak potential V	Peak intensity µA	Notes
0.01 mol l⁻¹ acetate buffer (4.8)	−0.59	0.23	
0.1 mol l⁻¹ acetate buffer (4.5)	−0.60	1.64	
1.0 mol l⁻¹ acetate buffer (4.4)	−0.67	0.98	a
0.1 mol l⁻¹ ammonium acetate (5.0)	−0.61	1.44	
0.1 mol l⁻¹ HClO₄ (0.8)	−0.52	0.28	b
0.1 mol l⁻¹ HCl (0.9)	−0.56	0.35	b
0.1 mol l⁻¹ KCl (6.7)	−0.54	0.77	a

[a] Higher background current. [b] Deformed base-line near the peak of interest. Experimental conditions: SWV, t_{ACC} = 5 min.; t_{RED} = 120 s; t_{EQ} = 15 s; $c(Pb)$ = 30 µg l⁻¹. For other conditions, see Experimental

Accumulation (pre-concentration) regime. The "I_P-vs-t_{ACC}" plot in Fig. 2 reveals a curve which follows the pattern of typical adsorption isotherm. This allowed us to prolong the pre-concentration time up to 15 min for the detection of very low concentrations, achieving thus a sufficient effectiveness of the whole deposition process.

Intermediate reduction step. Similarly to the previous study, the time period appropriate for the reduction of complex was also investigated. The resultant "I_P-vs-t_{RED}" graph is illustrated in Fig. 3, demonstrating the already expected limit (within an interval of 250-300 s).

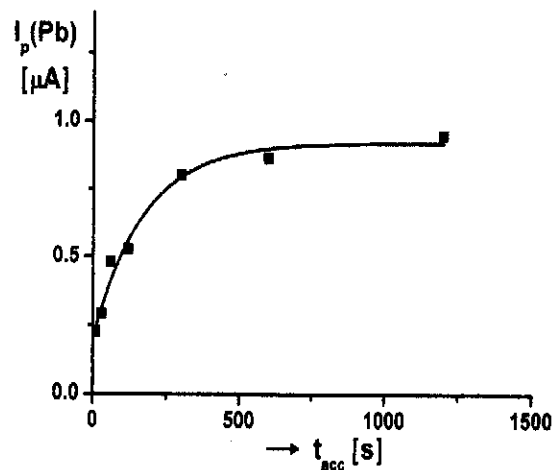In order to avoid complications with saturation effects, the optimum reduction ti-

Fig. 2 Optimization of accumulation time for determination of Pb^{2+} at lower concentration level. $c(Pb) = 30$ µg l^{-1}. For other conditions, see legend in Fig. 1
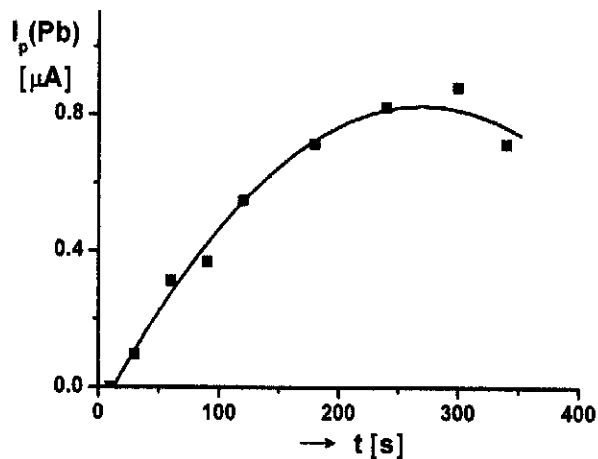

Fig. 3 Optimization of time period for intermediate reduction step at lower microgram concentration level. $t_{AAC} = 300$ s. For other conditions, see Fig. 1

me was chosen to be 120 s; i.e., a value lying still within the linear region of the curve. The performance of the reduction step was also checked with respect to the potential applied during the electrolysis. (Note that the prior accumulation step is to be performed under open-circuit conditions.)

The resulting plot is shown in Fig. 4, indicating clearly that the reduction $Pb^{2+} + 2e^- \rightarrow Pb^0$ is the most effective at potentials close to -1.0 V vs. Ag/AgCl, which was also the value of choice used in all further measurements, including examination of the method in quantitative analysis of both model and real samples. *The Stripping Step and Voltammetric Detection.* As mentioned above, voltamme-
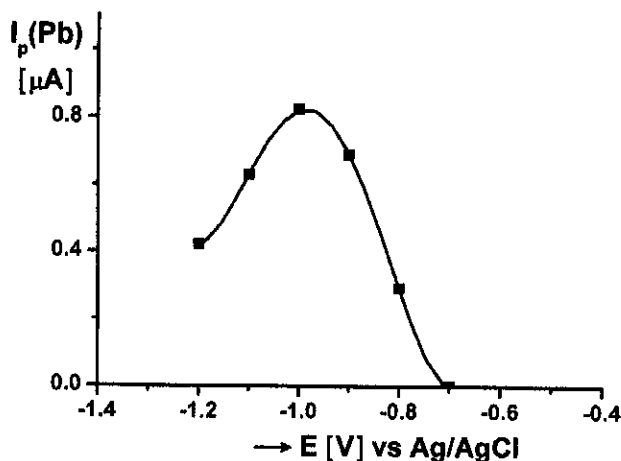
Mikysek T. *et al.*/Sci. Pap. Univ. Pardubice Ser. A 15 (2009) 5–27

17

Fig. 4 Optimization of potential applied during intermediate reduction step. t_{ACC} = 300 s, t_{RED} = 120 s. For other conditions, see Fig. 1

tric technique selected for the final characterisation was that with the square-wave modulation (SWV). The reason for its preferential use instead of originally employed differential pulse mode (DPV) was the fact that the former — in combination with modern computerised instrumentation — enables a more effective suppression of the background and, in addition, the resultant SWV curves are less deformed when using faster polarisation during the stripping step [55].

This was also experimentally proved here, and the SWV detection at a scan rate of 125 mV s^{-1} was found the most effective and applicable in all the remaining measurements.

Other Considerations. A certain drawback of the method is the necessity to perform the total regeneration of the carbon paste surface after each scan. In the case of carbon paste-based electrodes, this mechanical operation is very simple and quick [1,2]; nevertheless, it may contribute to a lower precision of the respective method if the carbon paste renewal is not reproducible. This aspect was of interest in a special study whose results did not reveal any negative effect of such mechanical regeneration (see Fig. 1). On the contrary, the resultant reproducibility beneath ±5 % rel. implies an excellent homogeneity of the electrode material used, including the distribution of modifier across the active electrode surface.

Electroanalytical Performance of the TUR-CPE

Calibration Characteristics. In this study, the TUR-CPE underwent a thorough examination with respect to determination of the Pb^{2+} ions; nevertheless, important

characteristics were also obtained for Cd^{2+}. Regarding the former, it could be detected over a very wide concentration range and hence examined in four different ranges, (i)-(iv). The respective dependences have illustrated a unique performance of the TUR-CPE, which is able to respond proportionally to the target analyte within an extremely wide concentration range of 5-25 000 $\mu g\ l^{-1}\ Pb^{2+}$. Two calibrations at the microgram concentration level are illustrated in Fig. 5; namely, for the low (plot "A") and the middle ("B") level; both given with the correspon-

$I_p = 0.0493c - 0.0029$

$R^2 = 0.996$

$I_p = 0.0267c$

$R^2 = 0.999$
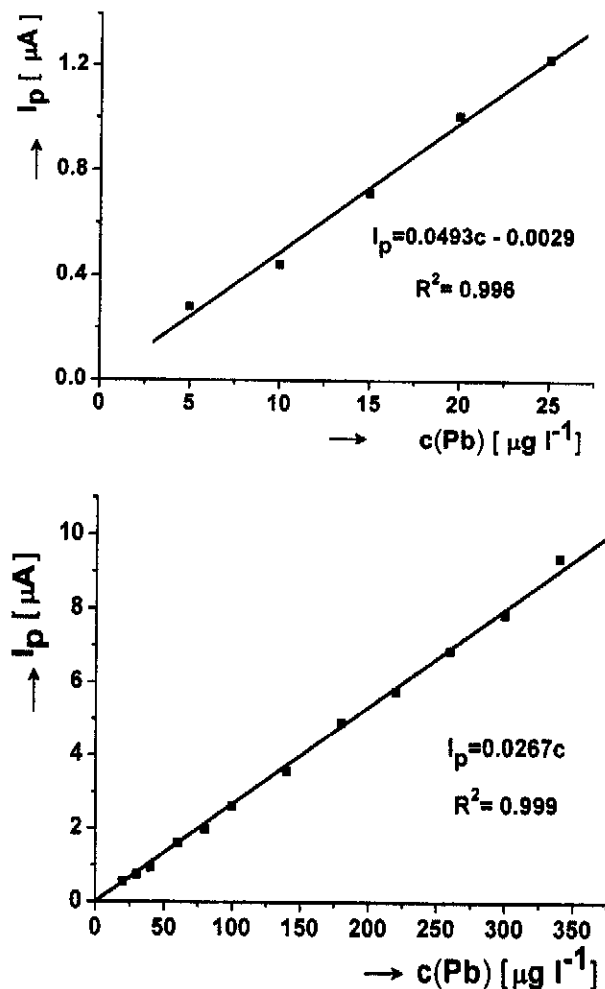
Fig. 5   Calibration plots for Pb2+ obtained by analysing model solutions with TUR-CPE within two different concentration ranges. A) 5-25 $\mu g\ l^{-1}$, B) 25-350 $\mu g\ l^{-1}\ Pb^{2+}$. Experimental conditions: SWASV; 0.1 M acetate buffer (pH = 4.5); t_{ACC} = 15 min (A) and 10 min (B); E_{RED} = -1.0 V vs. Ag/AgCl and t_{RED} = 3 min; E_{INIT} = -1.0 V, E_{FIN} = 0 V; v_{sw} = 125 mV s^{-1}. For other conditions, see Fig. 1

ding regression data. The remaining two calibrations also resulted in linear dependences characterised by the following data: (iii) concentration range: 1-5 mg l^{-1}; regression equation: $I_P(Pb) = 12.55c(Pb)$, correlation coefficient: $R^2 = 0.997$; (iv) 5-25 mg l^{-1}; $I_P(Pb) = 6.19c(Pb) + 35.89$, $R^2 = 0.997$.

Moreover, in a new calibration of the sensor, the higher milligram concentration level could be still extended up to 50 mg l^{-1} Pb without noticeable deviation from linearity. All the calibrations were constructed / calculated from the results of repeated measurements, when the individual points in each dependence were the average values from three replicates.

Extraordinarily wide dynamic range of the TUR-CPE inspired us to perform a special literature search focused on calibration characteristics of the already existing methods for the determination of Pb^{2+} on carbon paste-based and related heterogeneous carbon electrodes [1,2]. As found out, there is no comparable equivalent attaining such a broad linear range like CPE modified with QuadraPure™TU resin. Perhaps, a CMCPE described by Yantasee *et al.* [35] and employing also a SH-functionalised modifier can be mentioned herein, as its signal was proportional to the Pb^{2+} concentration in an interval of 10-1500 μg l^{-1}. Still wider linearity was reported by Majid's [57] and Mousavi's [58] groups who used CPEs modified with polyaromatic derivatives; both being able to respond up to ca 2000 μg l^{-1} Pb^{2+}. Nevertheless, even this value is still far from the upper limit of the TUR-CPE and, therefore, calibration characteristics may represent another valuable contribution to the extraordinary achievements with CPEs and CMCPEs, reviewed recently — at the dawn of the 50-years anniversary of carbon paste [2] in electrochemical and electroanalytical measurements.

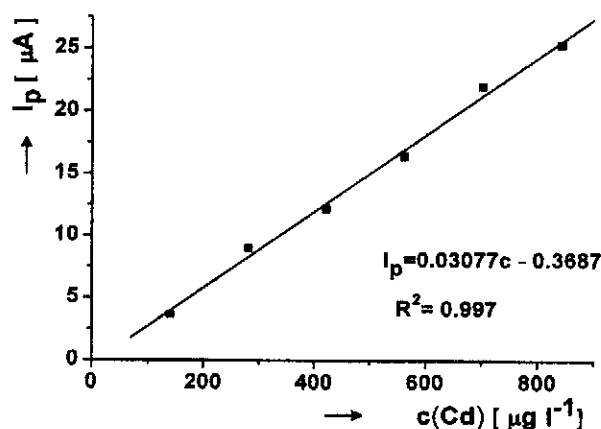In contrast to the determination of Pb^{2+}, detection characteristics for Cd^{2+}

Fig. 6 Calibration plot for Cd^{2+} obtained with TUR-CPE at concentration range 100-800 μg l^{-1} Cd^{2+}. Experimental conditions: SWASV; 0.1 M acetate buffer (pH = 4.5); $t_{ACC} = 10$ min; $E_{RED} = -1.0$ V vs. Ag/AgCl and $t_{RED} = 3$ min; $E_{INIT} = -1.0$ V; $E_{FIN} = 0$ V; $v_{sw} = 125$ mV s^{-1}. For other conditions, see Fig. 1

were less impressive, covering the calibration interval of 50-1000 μg l^{-1} with the lower value as the estimate for detection limit. The optimum operability of the TUR-CPE for cadmium was over the sub-milligram level (see Fig. 6, with the respective regression data inscribed).

Limit of Detection (LOD). The data obtained from calibration measurements with the lowest concentration range of Pb^{2+} were also exploited to characterise the method with TUR-CPE with respect to its detection capabilities. By means of the 3σ criterion, the resultant LOD was estimated to be about 1 μg l^{-1} Pb^{2+}. Although this value could scarcely compete with some LODs achieved at traditional mercury electrodes (down to 1 ng l^{-1}; see, e.g., [59]), it was fairly low in order to examine the TUR-CPE in trace analysis of two various water samples, which is described in the last section.

Interference Studies. The respective experiments were carried out with a series of model solutions containing always 30 μg l^{-1} Pb^{2+} and either the same concentration or a 10-fold excess of the interfering ion under test. Important results are gathered in Table III.

Table III Interference from selected metal ions in determination of Pb^{2+}. Survey of results

Metal ion[a,b] (Me)	Concentration Pb^{2+}; change in signal intensity[c]		Notes
Zn^{2+}	1 : 1 ... +2 %	10 : 1 ... +1 %	
Cd^{2+}	1 : 1 ... +5 %	10 : 1 ... –5 %	
Cu^{2+}	1 : 1 ... +2 %	10 : 1 ... +2 %	
Hg^{2+}	1 : 1 ... –5 %	10 : 1 ... 0 %	
Ag^{+}	1 : 1 ... –3 %	10 : 1 ... –4 %	[c] approximative values due to base-line deformations
Bi^{3+}	1 : 1 ... +15 %	10 : 1 ... +30 % [c]	
Sb^{3+}	1 : 1 ... +8 %	10 : 1 ... +5 %	
Co^{2+}	1 : 1 ... - [d]	10 : 1 ... 0 %	[d] not studied
Ni^{2+}	1 : 1 ... - [d]	10 : 1 ... 0 %	

[a] $c(Me)$ = 30 or 300 μg l^{-1}, $c(Pb)$ = 30 μg l^{-1}; b) All the ions were added as standard solutions prepared from respective nitrates or chlorides and evaluated as peak height, $I_p(Pb)$, in corresponding experiment. For other conditions, see Experimental

As it can be seen, the only serious interfering species was Bi^{3+}, whereas common metal ions like Zn^{2+} and Cu^{2+} or even Hg^{2+} and Ag^{+} practically did not affect the response of interest. These results were rather surprising and did not indicate any special affinity of the QPu resin towards the thiophilic ions investigated, except for the Pb^{2+} ions themselves. Also, such observations did not

correspond to our former hypothesis about the formation of metal sulphides [see scheme (1c)], if the respective equilibrium constants — solubility products, pK_S — are assumed as the driving force for reaction with thiourea residue. According to a bibliographical source summarising such data [60], the individual sulphides are specified by the following pKs (given in parenthesis): PbS (27.5), ZnS (24.5), CdS (27.0), CuS (24.5), Bi_2S_3 (100.0), Sb_2S_3 (93.0), Ag_2S (50.1), HgS (52.7), CoS (24.7), and NiS (18.5) [where all these values were published for $t = 25$ °C and almost all for ionic strength, $J = 0$]. As seen from this list, practically each metal ion investigated among the interfering species might readily form sulphide, and the experimentally proved selectivity towards the Pb^{2+} ions suggests that their accumulation at the TUR-CPE was apparently caused by another specific interaction like the above-postulated complex formation [scheme (1a,b)]. This assumption is also supported by the finding that solely Bi^{3+} ions interfered to more extent, which could be a certain analogy to a well-known reaction with the native thiourea used for long time in classical qualitative analysis for identification of bismuth(III) species [3,4].

Regarding the determination of cadmium and, eventually, simultaneous detection of both cadmium and lead, a special interference study was not performed due to the above- commented worse electroanalytical characteristics of this metal. Thus, some attention was paid solely to the mutual effect of both cadmium and lead during parallel detection. As found, the current intensity of cadmium ions was much smaller compared to that for the same amount of lead and, therefore, whereas lead could be determined even at a 10-fold excess in concentration, the reliable detection of cadmium could not be accomplished without having the second metal at significantly lower concentrations. All these observations have indicated actually insufficient performance of the TUR-CPE for the determination of cadmium in real samples, including common natural waters.

Analyses of Model Water Samples and Sewage Sludge

In order to assess practical applicability of the TUR-CPE, three samples with different concentration levels of Pb^{2+} were selected. The first specimen was natural water with the content of lead expected at the low microgram level, the second was a tap water additionally contaminated in order to exceed the concentration limit tolerated by local hygienic standards (in our case: 25 ± 0.01 µg l^{-1} Pb, being permitted in a Czech State Standard [61]). The third sample was a certified reference material (CRM) of sewage sludge with extremely high contents of metal pollutants, including lead.

Electrochemical determinations of Pb^{2+} in water samples were performed as single analyses ($n = 1$), when the results obtained could be compared either with those obtained by ICP-MS (for details, see [62]) or directly confronted with the
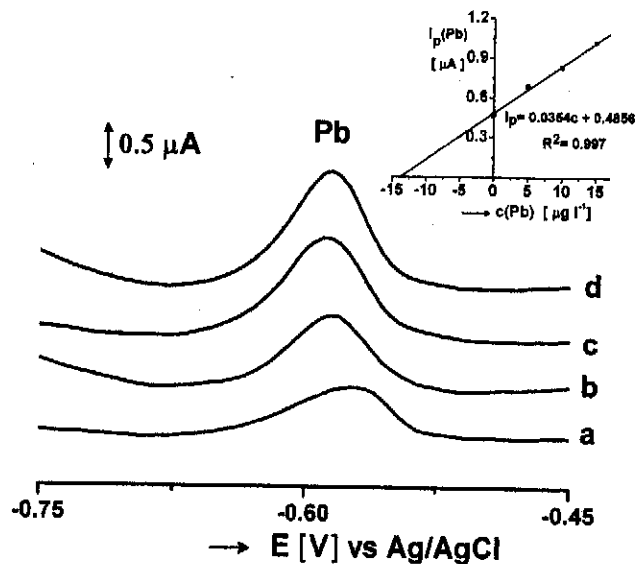
Fig. 7 Typical voltammograms obtained by analysing model sample (spiked tap water) and the graphical evaluation of multiple standard addition method used (given as insert in the upper corner). Legend: a) sample (spiked with 30 µg l^{-1} Pb^{2+}), b-d) three standard additions (as aliquots of 5 µg l^{-1} Pb^{2+}). Experimental conditions as those in Fig. 5A

spike — i.e., the content known in model solutions. SWASV analysis of natural water (illustrated by the corresponding voltammograms and graphical evaluation in our previous report [50]) revealed the trace concentration of 2.36 µg l^{-1} Pb compared to 1.47 µg l^{-1} Pb, determined by the reference spectral technique. Analysis of artificially contaminated water, shown here in Fig. 7, yielded a recovery rate of 114.3 % (spiked: 30 mg l^{-1}, found: 34.3 mg l^{-1}).

With respect to very low concentration levels analysed, the results from both analyses were considered as satisfactory. Moreover, thanks to a wide dynamic range of the TUR-CPE, the standard additions could be applied as the same aliquots although these water samples contained rather dissimilar levels of the analyte (in fact, differing in one concentration order). This has proved the robustness of the method and its prospects for routine measurements with advanced electrochemical analysers equipped with automated pre-adjusted burettes which cannot be reset *extra* for each sample [54,63].

Finally, the functioning of TUR-CPE in the upper concentration range was tested by the analysis of digested sewage sludge. The respective determinations were performed in three replicates ($n = 3$), yielding a result of 2.2 ± 0.2 mg g^{-1} Pb (expressed as the mean and the RSD). This value agreed with the content certified in the documentation, 2.3 ± 0.1 mg g^{-1}, as well as with the result of reference ICP-MS whic found 2.3 ± 0.2 mg g^{-1} Pb.

Conclusion

In this contribution, recently developed thiourea residue bulk-modified carbon paste electrode, TUR-CPE, has been further characterised and shown to offer a very attractive electroanalytical performance for the determination of Pb^{2+}. A particularly valuable feature is its capability of operating within an extremely wide concentration range of 5-25000 µg l^{-1} Pb^{2+} when the individual calibrations performed have exhibited only minimal tendencies toward saturation, which indicates an excellent functioning of the modifier used. Such a linearity represents a unique achievement among all hitherto reported chemically modified CPEs or related carbon ink-based electrodes [1,2], including sensors utilising the latest technologies and materials [64,65], and pre-determines the TUR-CPE for various practical applications.

Within the study, the thiourea residue-modified electrode was also, for the first time, examined for the determination of cadmium; however, in this case, the resultant electroanalytical performance was only average and — e.g., for trace analysis — major improvements are yet necessary.

Acknowledgements

References

[1] Kalcher K., Švancara I., Metelka R., Vytřas K., Walcarius A., in: *The Encyclopedia of Sensors*, Vol. 4 (Grimes C.A., Dickey E.C., Pishko M.V., eds.), pp. 283-430, American Scientific Publishers, Stevenson Ranch (USA), 2006.

[2] Švancara I., Vytřas K., Kalcher K., Walcarius A., Wang J.: Electroanalysis **21**, 7 (2009).

[3] Okáč A.: *Qualitative Inorganic Analysis* (in Czech), pp. 81-82, 348, and 458. The Publishing House of Czechoslovak Academy of Sciences, Prague, 1963.

[4] Svehla Gy.: *Vogel's Qualitative Inorganic Analysis*, 7th Ed. pp. 174-176 and 269-270, Longman Publ., Singapore, 1996.

[5] Tanaka S., Yoshida H.: Talanta **36**, 1044 (1989).

[6] Sugawara K., Tanaka S., Taga M.: J. Electroanal. Chem. **304**, 249 (1991).

[7] Ibrahim H.: Anal. Chim. Acta **545**, 158 (2005).

[8] Kalcher K.: Fresenius Z. Anal. Chem. **325**, 181 (1986).

[9] Cai X.-H., Kalcher K., Neuhold C. G., Diewald W., Magee R. J.: Analyst **118**, 53 (1993).

[10] Cai X.-H., Kalcher K., Lintschinger J., Neuhold C. G.: Microchim. Acta **112**, 135 (1993).

[11] Agraz R., Teresa Sevilla M., Hernandez L.: J. Electroanal. Chem. **390**, 47 (1995).

[12] Khoo S.-B., Cai Q.-T.: Electroanalysis **8**, 549 (1996).

[13] Dias N. L., do Carmo D. R.: Electroanalysis **17**, 1540 (2005).

[14] Colilla M., Mendiola M. A., Procopio J. R., Teresa Sevilla M.: Electroanalysis **17**, 933 (2005).

[15] Tonle I. K., Ngameni E., Walcarius A.: Sensors Actuators B **110**, 195 (2005).

[16] Dias N. L., do Carmo D. R., Gessner F., H. Rosa A.: Anal. Sci. (Japan) **21**, 1309 (2005).

[17] Dias F., Newton L., do Carmo D. R., Rosa A. H.: Electrochim. Acta **52**, 965 (2006).

[18] Dias N. L., do Carmo D. R., Rosa A. H.: Sep. Sci. Technol. **41**, 733 (2006).

[19] Dias N. L., Caetano L., do Carmo D. R., Rosa A. H.: J. Brazil. Chem. Soc. **17**, 473 (2006).

[20] Won M.-S., Park J.-M., Shim Y.-B.: Electroanalysis **5**, 421 (1993).

[21] Won M.-S., Kim H.-J., Shim Y.-B.: Bull. Korean Chem. Soc. **17**, 1142 (1996).

[22] Chang C.-H., Liu C.-Y.: Fenxi Kexue Xuebao **44**, 231 (1997).

[23] Monien H.: Fresenius Z. Anal. Chem. **237**, 409 (1968).

[24] Tymecki L., Jakubovska M., Achamatowicz S., Koncki R., Glab S.: Anal. Lett. **34**, 71 (2001).

[25] Sugawara K., Tanaka S., Taga M.: Analyst **116**, 131 (1991).

[26] Sugawara K., Tanaka S., Taga M.: Fresenius J. Anal. Chem. **342**, 65 (1992).

[27] Safavi A., Pakniat M., Maleki N.: Anal. Chim. Acta **335**, 275 (1996).

[28] Chang C.-H., Li C.-Y.: Kexue Xuebao **44**, 231 (1997).

[29] Jesus Gismera M., Mendiola M.A, Rodriguez Procopio J., Teresa Sevilla M.: Anal. Chim. Acta **385**, 143 (1999).

[30] Qu J.-Y., Liu M., Liu K.-Z.: Anal. Lett. **32**, 1991 (1999).

[31] Rui Perez J., Mendiola M.A., Teresa Sevilla M., Saidman S.B.: Electroanalysis **14**, 449 (2002).

[32] Abbaspour A., Moosavi S. S. M.: Talanta **56**, 91 (2002).

[33] Molina Holgado T., Pinilla Macias J. M., Hernandez L. H.: Anal. Chim. Acta **309**, 117 (1995).

[34] Vázquez M. D., Tascón M. L., Deban L.: J. Enviroment. Sci. **41**, 2735 (2006).

[35] Yantasee W., Lin Y.-H., Zemanian T. S., Fryxell G. E.: Analyst **128**, 467 (2003).

Mikysek T. *et al.*/Sci. Pap. Univ. Pardubice Ser. A **15** (2009) 5–27

25

[36] Marino G.,.Bergamini M. F, Teixeira M. F. S., Cavalheiro E. T. G.: Talanta **59**, 1021 (2003).

[37] Cesarino I., Marino G., Matos J. D. R., Cavalheiro E. T. G.: J. Brazil. Chem. Soc. **18**, 810 (2007).

[38] Kalcher K.: Fresenius Z. Anal. Chem. **325**, 186 (1986).

[39] Cai X.-H., Kalcher K., Magee R. J.: Electroanalysis **5**, 413 (1993).

[40] Ferri T., Paci S., Morabito R.: Ann. Chim. (Rome) **86**, 245 (1996).

[41] Huang S.-S., Chen Y., Li X.-F., Li F.-M.: Guangdong Gongye Daxue Xuebao **14**, 128 (1997).

[42] Monien H., Jacob P., Jaenisch B.: Fresenius Z. Anal. Chem. **267**, 108 (1973).

[43] Shumilova M. A., Trubachev A. V., Kurbatov D. I.: Zh. Anal. Khim. **52**, 753 (1997).

[44] Raber G., Kalcher K., Neuhold C. G., Talaber C., Kölbl G.: Electroanalysis **7**, 137 (1995).

[45] Ulakhovich N. A., Medyantseva E. P., Mashkina S. V.: Zh. Anal. Khim. **52**, 331 (1997).

[46] Farghaly O. A.: Talanta **63**, 497 (2004).

[47] Shiddiky M. J. A., Won M.-S., Shim Y.-B.: Electrophoresis **27**, 4545 (2006).

[48] Hinchcliffe A., Hughes C., Pears D. A., Pitts M. R.: Org. Process Res. Dev. **11**, 477 (2007).

[49] Mikysek T., Ion A., Švancara I., Vytřas K., Banica F. G., in: *YISAC 2006, 13th Youth Investigators' Seminar on Analytical Chemistry*, Book of Abstracts, p. P-2. University of Zagreb, 2006.

[50] Mikysek T., Švancara I., Vytřas K., Banica F. G.: Electrochem. Commun. **10**, 242 (2008).

[51] Švancara I., Schachl K.: Chem. Listy **93**, 490 (1999).

[52] Švancara I., Metelka R., Vytřas K., in: *Sensing in Electroanalysis* (Vytřas K., Kalcher K., eds.), pp. 7-18. University of Pardubice, Pardubice, 2005.

[53] Wang J.: *Stripping Analysis: Principles, Instrumentation, and Applications*, VCH, Deerfield Beach (Florida, USA), 1985.

[54] Ostapczuk P., Froning M., in: *Specimen Banking - Environmental Monitoring and Modern Analytical Approaches* (Rossbach M., Schladot J. D., Ostapczuk P., eds.), pp. 153-165. Springer, Berlin, 1992.

[55] Economou A., Voulgaropoulos A.: Sci. Pap. Univ. Pardubice, Ser. A **10**, 33 (2004).

[56] Sevilla Escribano M. T., Rodríguez Procopio J., Pinilla Macías J. M., Hernández Hernández L.: Intern. J. Environ. Anal. Chem. **37**, 107 (1989).

[57] Majid S., El Rhazi M., Amine A., Curulli A., Palleschi G.: Microchim. Acta **143**, 195 (2003).

[58] Mousavi M. F., Rahmani A., Golabi S. M., Shamsipur M., Sharghi H.: Talanta **55**, 305 (2001).

[59] Ostapczuk P.: Anal. Chim. Acta **273**, 35 (1993).

[60] Kotrlý S., Šůcha L.: *Handbook of Chemical Equilibria in Analytical Chemistry*, pp. 206-216, Ellis Horwood, Chichester (UK), 1985.

[61] Czech Hygienic Standard, §252, Collection of Laws of the Czech Republic, The Ministry of Agriculture, Prague, 2004.

[62] Husáková L., Černohorský T., Šrámková J., Vavrušková L.: Food Chem. **105**, 286 (2007).

[63] Graabæk A. M., Jeberg B.: Inter. Labor. **22**, 33 (1992).

[64] Hart J. P., Crew A., Crouch E., Honeychurch K. C., Pemberton R. M.: Anal. Lett. **37**, 789 (2004).

[65] Jones S. E. W., Compton R.G.: Curr. Anal. Chem. **4**, 177 (2008).