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Direct determination of cadmium in urine by electrothermal atomic absorption spectrometry after in situ electrodeposition

Eva Čurdová [a,*], Richard Koplík [b], Jaroslav P. Matoušek [c], Miloslav Suchánek [a]

[a] *Department of Analytical Chemistry, Institute of Chemical Technology, Technická 5, 166 28 Prague 6, Czech Republic*
[b] *Department of Food Chemistry and Analysis, Institute of Chemical Technology, Technická 5, 166 28 Prague 6, Czech Republic*
[c] *School of Chemistry, The University of New South Wales, UNSW, Sydney, NSW 2052, Australia*

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Abstract

Determination of cadmium in urine by ETAAS suffers from severe interferences deteriorating the precision and accuracy of the analysis. Electrodeposition step prior to ETAAS allows to avoid interferences and makes cadmium determination possible even at ultratrace levels. The proposed procedures involve electrolytic deposition of cadmium from acidified urine on previously electrolytically deposited palladium film on a graphite atomizer tube, followed by removal of residual solution, pyrolysis and atomization. Both electrodeposition processes take place in a drop of the respective solution (palladium nitrate modifier and acidified urine, respectively), when Pt/Ir dosing capillary serves as an anode and the graphite tube represents a cathode. The voltage is held at −3.0 V. Matrix removal is then accomplished by withdrawal of the depleted sample solution from the tube (procedure A) or the same but followed by rinsing of the deposit with 0.2 mol l^{-1} HNO_3 (procedure B). The accuracy of both procedures was verified by recovery test. Detection limits 0.025 and 0.030 μg Cd/l of urine were achieved for A and B procedures, respectively. Both procedures are time consuming. The measurement cycle represents 5 and 7 min for A and B procedures, respectively.

Keywords: Electrodeposition; Electrothermal atomic absorption spectrometry; Cadmium; Urine

1. Introduction

Concentration of cadmium in urine can be used as an indicator of its level in the human body [1]. Cadmium concentrations in urine or blood higher than 10 μg l^{-1} indicate a high body load resulting likely in kidney damage [2,3]. Normal values of cadmium in urine range from 0.4 to 1.3 μg l^{-1} [4].

Highly sensitive spectrometric methods, such as electrothermal atomic absorption spectrometry (ETAAS) [5–8] and inductively coupled plasma mass spectrometry (ICP-MS) [9–11] are used most frequently for cadmium determination in urine. Body fluid samples can often be analysed directly by ETAAS after appropriate dilution [12]. Owing to high concentration of inorganic salts, urine probably represents the most difficult clinical matrix. Alkali elements' salts cause severe interferences during cadmium determination by ETAAS [13] and affect the accuracy of analysis. Careful optimization and pre-treatment temperature control protocols as well as the use of modifiers [14] are therefore required. As far as the total concentration of dissolved matter in urine is concerned, the individual urine samples can differ significantly. Therefore, the matrix effects are not easily predictable. A combined chemical modifier consisting of $Pd(NO_3)_2$ and NH_4NO_3 can reduce the interferences caused by molecular alkali halides during cadmium atomization [15,16]. Even the use of transverse heated graphite atomizer (THGA) [12] does not eliminate interferences completely [8]. Moreover, the successful direct determination of volatile elements in diluted blood or urine using THGA needs the application of Zeeman background correction.

The efficient removal of inorganic matrix may be achieved by electrochemical separation of the analyte from sample solution prior to the determination by ETAAS. Various working

* Corresponding author. Tel.: +420 224 35 4262; fax: +420 224 31 0352.
E-mail address: eva.curdova@vscht.cz (E. Čurdová).

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electrodes were utilized for this purpose, such as graphite, tungsten, iridium or mercury. The electrode should have a constant area and repeatable electrochemical properties. Mechanical renewal and electrochemical activation of the electrode surface should be easily achieved [17–19]. Some procedures involved electrolytic plating of an analyte from sample solution onto the electrode, which is then transferred into the electrothermal atomizer [20]. Another approach designated as coupled in situ electrodeposition–electrothermal AAS (ED-ETAAS) [21,22] utilizes the atomizer tube as a working electrode. The electrolysis takes place inside a sample drop introduced into the graphite tube just before drying, pyrolysis and atomization. The ED-ETAAS method can be used for the determination of all elements, which are deposited on the surface of atomizer tube by electrochemical reduction or oxidation at a proper voltage [17,18]. As the analyte is deposited in a pure form, the majority of interferences are overcome [23] and better sensitivity and detection limit are achieved [24]. On the other hand, the analysis is time-consuming and less repeatable due to number of steps [25]. This technique is convenient namely for the analysis of samples with difficult matrices, such as sea water, urine, blood serum, plasma and waste water [22,23,25–28].

This work was focused on the application of electrodeposition for cadmium separation from the complex urine matrix and elaboration of standard operational procedure for cadmium determination in urine without sample decomposition. The present work was based on previous experience [20–23,25,26] and was aimed at suppressing or removing interferences so as to allow reliable cadmium determination using spectrometer equipped with deuterium lamp background corrector only.

2. Experimental

2.1. Instrumentation

All measurements were accomplished using atomic absorption spectrometer, model 932 AA (GBC, Dandenong, Australia) equipped with deuterium lamp background correction coupled with GF 3000 electrothermal atomizer and PAL 3000 auto-sampler. The atomizer was equipped with experimental software especially designed for electrodeposition by GBC. A constant voltage source STATRON type 2223 (Statron, Fürstenwalde, Germany) was used. The auto-sampler was modified by replacing the last section of the PTFE sample delivery tube with Pt/Ir tube (internal diameter of 0.25 mm, external diameter of 0.8 mm). This capillary served as an anode in an electrical circuit while a graphite tube with palladium-covered surface represented a cathode. The Pt/Ir capillary was used for delivery of a modifier, a sample and a rinsing solution as well as for removing residual solutions from the graphite tube. The outer PTFE tube was fitted tightly over the Pt/Ir capillary, leaving the last 2 mm exposed. The PTFE tube prevents elevation of the sample on the long metallic capillary. The capillary was placed in the arm of the auto-sampler and was connected by a silver wire with the positive pole of the electric circuit.

Cadmium hollow cathode lamp (Photron Pty. Ltd., Australia) was used as the radiation source. The spectrometer operated at 228.8 nm line and spectral bandwidth of 0.5 nm with the lamp current of 4 mA. Long-life thicker pyrolytic-coated graphite partition tubes (GBC, Dandenong, Australia) were used throughout all experiments. Argon was used as purge and protective gas.

2.2. Reagents and materials

Standard stock solutions of cadmium of $1.000 \pm 0.002\,\mathrm{g\,l^{-1}}$ in $0.5\,\mathrm{mol\,l^{-1}}$ HNO_3, palladium nitrate modifier stock solution containing $1.000 \pm 0.002\,\mathrm{g\,l^{-1}}$ Pd in $0.5\,\mathrm{mol\,l^{-1}}$ HNO_3 (both produced by Merck, Darmstadt, Germany), and ammonium dihydrogen phosphate modifier solution ($10.0\,\mathrm{g\,l^{-1}}$ $NH_4H_2PO_4$, Analytika, Prague, Czech Republic) were used. Cadmium standard solutions containing from 0.1 to $5\,\mu\mathrm{g\,l^{-1}}$ Cd and $0.2\,\mathrm{mol\,1^{-1}}$ HNO_3 were prepared daily from the standard stock solution. Diluted solutions of nitric acid were prepared from 65% nitric acid of Suprapur grade (Merck, Darmstadt, Germany). Inorganic salts (NaCl, KNO_3, $Mg(NO_3)_2{\cdot}6H_2O$, $Ca(NO_3)_2{\cdot}4H_2O$, $NH_4H_2PO_4$) of suprapur grade (Merck) and urea of analytical grade (Merck) were used for preparation of simulated urine matrix. Milli-Q deionised water (Millipore, Bedford, MA, USA) was used for preparation of all solutions. Reference materials (RMs) SERONORM No. 403125 and 101021 urine (SERO AS, Billingstad, Norway) were used to verify the accuracy of analyses.

2.3. Sample preparation

The reference materials were reconstituted according to the manufacturer's instructions. Practical urine samples and RMs were diluted four-fold with $0.2\,\mathrm{mol\,1^{-1}}$ HNO_3 and directly analysed by ED-ETAAS. Treated samples were immediately analysed or stored for a short term in the dark at 4 °C until analysis.

2.4. ED-ETAAS procedure

The whole procedure consists of several steps. In the first one, palladium nitrate solution (40 μl of $50\,\mathrm{mg\,l^{-1}}$ Pd) is dosed and the metallic palladium deposit is formed by electrolysis (voltage −3.0 V, time 50 s) on the wall of the graphite tube. The depleted solution is then aspirated and its residue is dried by atomizer heating. After cooling of the atomizer, the sample (20 μl) is delivered and cadmium is electrolytically deposited on the Pd-covered surface of the graphite tube (voltage −3.0 V, time 80 s). The sample matrix in remaining solution is then removed by aspiration and atomizer is dried (procedure A). A rinsing step is included into procedure B: after aspiration of depleted sample solution,

Table 1
Programme for Cd determination by ED-ETAAS without (A) and with rinsing step (B)

Step	Auto-sampler and electric circuit			Atomizer			
	Solution, volume	Voltage(V) A/B	Deposition time (s) A/B	Temperature (°C) A/B	Ramp time (s) A/B	Hold time (s) A/B	Ar flow (ml min^{-})
1. Pd deposition	$Pd(NO_3)_2$ (50 mg l^{-1} Pd in 0,1 mol l^{-1} HNO_3), 40 μl	−3.0/−3.0	50/30	20/20	–	–	0
2. Withdrawal		−3.0/−3.0	–	20/20	–	–	0
3. Drying	-	d/d	–	160/160	15/15	15/15	300
4. Cooling down	-	d/d	–	20/20	10/10	10/10	0
5. Analyte deposition	Sample, 20 μl	−3.0/−3.0	80/80	20/20	–	–	0
6. Withdrawal		−3.0/−3.0	–	20/20	–	–	0
7. Drying	-	d/d	–	120/120	15/15	15/15	300
8. Drying	-	d/d	–	140/140	5/5	5/5	300
9. Cooling down	-	d/d	–	–/20	–/10	–/10	0
10. Rinsing	0.2 mol l^{-1} HNO_3, 40 μl	–/−3.0	−/80	–/20	–	–	0
11. Withdrawal		–/−3.0	–	–/20	–	–	0
12. Drying	-	–/d	–	–/120	–/15	–/15	300
13. Drying	-	–/d	–	–/140	–/5	–/5	300
14. Pyrolysis	-	d/d	–	500/550	10/10	5/5	300
15. Cooling down	-	d/d	–	400/400	4/4, 0/0	1/1, 2/2	300, 0
16. Atomization	-	d/d	–	1800/1800	1/1	3/3	0
17. Atomizer cleaning	-	d/d	–	2200/2200	1/1	1.5/1.5	300

d, electric circuit disconnected; procedure A does not include steps 9–13.

40 μl of 0.2 mol 1^{-1} HNO_3 is delivered into the tube and the electric circuit is switched on again for 80 s under the voltage of −3.0 V. The negative potential of the tube during rinsing prevents dissolution of deposited cadmium by nitric acid solution. Subsequently, the rinsing solution is aspirated and the atomizer is dried. Pyrolysis, cooling down, atomization and atomizer cleaning steps then follow in both procedures. The whole programme is outlined in Table 1. The calibration was performed using acidified (0.15 mol l^{-1} HNO_3) aqueous standard solutions containing up to 2 μg l^{-1} of cadmium.

3. Results and discussion

Successful application of ED-ETAAS method requires a proper choice of several instrumental conditions. To achieve a good effectiveness of cadmium deposition and extend the life time of tubes [29], pre-deposition of palladium was utilized.

3.1. Optimization of temperature programme for ED-ETAAS

The optimization of the temperature programme was performed using the Seronorm 403125 urine reference material with certified cadmium concentration of 5.0 μg l^{-1}. The reconstituted sample was diluted four-fold with 0.2 mol 1^{-1} HNO_3. Both peak height and peak area were evaluated. Fig. 1 shows the dependence of net absorbance and the background signal on pyrolysis and atomization temperature for the procedure A. The optimum pyrolysis and atomization temperatures are 500 and 1800 °C, respectively. Background signal decreases with increasing pyrolysis temperature up to 600 °C, but sudden rise of background signal occurs above 600 °C. This unexpected behaviour of background was observed repeatedly. Too fast increase of pyrolysis temperature (650 or 700 °C) probably causes decrepitation of residual matrix components resulting in mass spreading along the tube to its colder ends. Thus, the matrix components remain in the tube and lead to high background of the measured signal during atomization.

The optimum times and temperatures of drying, pyrolysis and atomization are summarized in Table 1. The pyrolysis temperature is the most critical factor influencing the results. When procedure B is applied, the pyrolysis temperature can be raised to 550 °C. The effect of starting temperature for heating up to the atomization temperature was also examined. A cool-down step to 400 °C was inserted between pyrolysis and atomization steps to achieve higher gradient of the temperature increase during atomization.

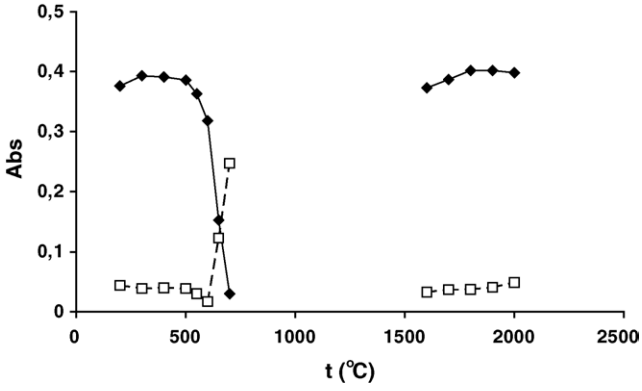

Fig. 1. Pyrolysis and atomization temperature plot for ED-ETAAS determination of cadmium. Solid line, analyte signal; dotted line, background.

3.2. Optimization of electrodeposition parameters: modifier deposition

The optimization was accomplished by following the effect of various combinations of pre-deposition parameters (volume and concentration of palladium modifier, deposition time and voltage) on the net absorbance and background signal, when diluted Seronorm 403125 urine was analysed.

Extensive evolution of hydrogen gas taking place during pre-deposition (namely under higher voltages) can cause non-uniform palladium plating on the graphite tube surface. This unwanted effect occurred when more than 60 μl of modifier were introduced. However, the dosed solution volume must be large enough so that the area on which palladium is deposited exceeds the area on which the sample solution is subsequently introduced and where electrodeposition of the analyte itself occurs. If this condition is not fulfilled, the analyte is deposited outside palladium-covered area and it could volatilise from the atomizer before the atomization step. The volume of 40 μl was therefore selected as optimum for both measurement procedures.

Even a short pre-deposition time (10 s) was adequate for depositing the required amount of palladium from the modifier solution containing 50 mg l^{-1} of Pd on the atomizer surface. However, the background signal decreased with prolonged pre-deposition time. The pre-deposition time of 50 s was found as the optimum time for analyte measurement without rinsing (procedure A). This is the time period adequate for effective reduction of the background. For the B procedure, which includes the rinsing step, the pre-deposition time of 30 s was found to be adequate. The effect of deposition time and applied constant voltage for palladium pre-deposition are mutually dependent. If a lower voltage is used, a longer pre-deposition time is necessary to achieve adequate palladium deposition and vice versa. Palladium concentration of 50 mg l^{-1} in modifier solution was chosen as a convenient level. High background signals were observed when lower Pd concentrations of modifier were applied. All above-mentioned optimum conditions are related to voltage −3.0 V maintained during deposition.

3.3. Optimization of electrodeposition parameters: analyte deposition

The duration of cadmium deposition on palladium-covered surface of the graphite atomizer under given constant voltage directly influences the sensitivity of measurements. Similar to palladium pre-deposition, the effect of the time period of cadmium deposition and the magnitude of applied voltage are mutually dependent. If a low-constant voltage is applied, it is necessary to perform electrodeposition for a longer time to achieve complete cadmium plating. Conversely, a higher voltage has to be applied for shorter time of electrodeposition. If the graphite surface is not adequately covered by palladium, the matrix residues staying in the graphite micropores may destroy the pyrolytic carbon layer during atomization. With respect to the fact that ejection of sample and/or vapour from the dosing opening occurred under higher values of applied voltage (approximately −5 V), a lower voltage (−3 V) and a longer time of electrodeposition were selected. Duration of 80 s was verified as the optimum for both procedures (see Figs. 2 and 3).

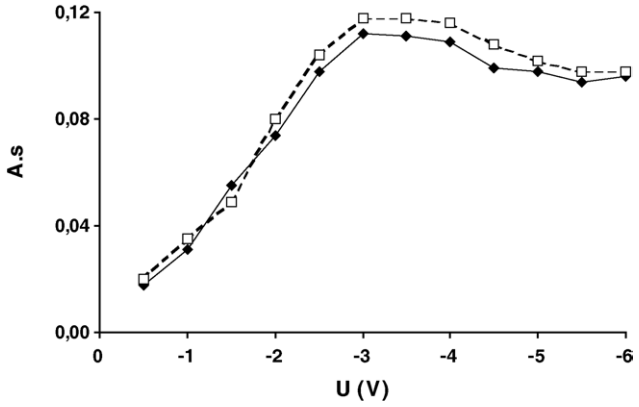

Fig. 2. Dependence of Cd signal on applied constant voltage; RM Seronorm No. 403125 diluted four-fold with 0.2 mol l^{-1} HNO_3, t_d = 70 s (Pd), t_d = 90 s (Cd). Solid line, procedure A; dotted line, procedure B.

3.4. The rinsing step

Matrix removal achieved by electrodeposition can be made more effective by introduction of rinsing/co-deposition step [21,26] into the procedure. It was observed that even when Pt capillary is positioned very carefully in the tube, several microlitres of sample remain there after sample withdrawal. The effectiveness of matrix removal by rinsing with water, 0.1 and 0.2 mol l^{-1} HNO_3 was tested. The simple rinsing of deposits using deionised water had negligible effect on the background signal even when large volumes (50 μl) were repeatedly applied and withdrawn. Re-deposition consisting of rinsing of deposit by diluted HNO_3 under voltage followed by withdrawal was proved to be useful for removal of NaCl retained in the graphite tube, especially for co-deposition of Pd and analyte [21]. Dosing 40 μl of 0.2 mol l^{-1} HNO_3, as rins-

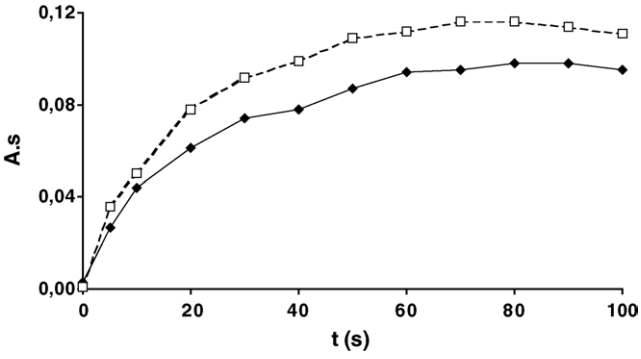

Fig. 3. Dependence of Cd signal on deposition time for sample; RM Seronorm No. 403125 diluted four-fold with 0.2 mol l^{-1} HNO_3, U = −3.0 V. Solid line, procedure A; dotted line, procedure B.

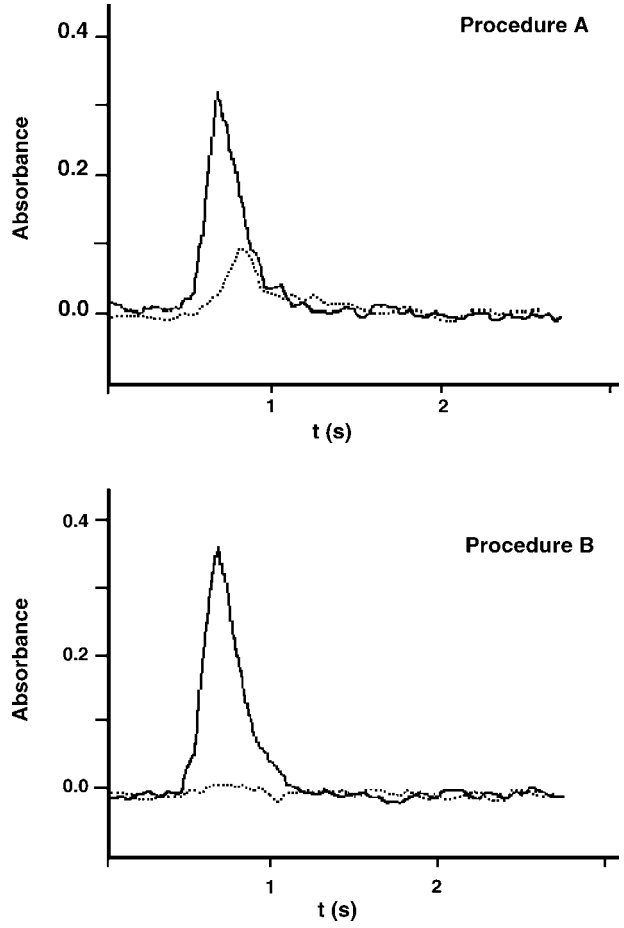

Fig. 4. Cadmium determination in urine by ED-ETAAS, procedure A and B; RM Seronorm No. 403125 diluted four fold-with 0.2 mol l^{-1} HNO_3. Solid line, analyte signal; dashed line, background.

ing solution under −3.0 V successfully eliminates the background signal originating from residual urine matrix (compare procedures A and B in Fig. 4). The negative potential of tube surface avoids losses of deposited analyte via chemical dissolution in nitric acid solution.

3.5. Optimization of constant applied voltage

The magnitude of applied constant voltage significantly influenced the cadmium amount deposited over the palladium-covered atomizer surface after a given time interval. The dependence of cadmium signal on the applied voltage was examined using four-fold diluted reconstituted RM urine No. 403125. After exceeding the value of the electrolyte decomposition voltage, the electric current and also the analyte signal increased proportionally with the voltage. Up to the value of −3.0 V, the signal grew rapidly and then it reached a stabile value up to −4.0 V (Fig. 2). However, the background signal grew more rapidly exceeding several times the analyte signal at voltages above −5.0 V. The background increase was not so pronounced for the procedure B but tailed absorbance peaks were observed at higher voltages. The value of −3.0 V of constant applied voltage was selected as the optimum for both procedures. For higher voltage values, violent gas expansion in the solution occurred resulting in sample ejection through the atomizer dosing opening. These effects cause analyte losses or at least deterioration of the atomization peaks (see downtrend of signal for voltage above −4.0 V shown in Fig. 2). Moreover violent gas evolution sprays the solution out of the palladium-covered area. Microscopic drops of sample solution spread over the tube lead to an increased background during atomisation.

3.6. Interference test

Great deal of interference caused by major components of urine is eliminated by the use of electrodeposition step. The background is effectively depressed namely using the procedure B. On the other hand, the electrochemically active trace elements can be deposited on Pd-covered tube together with cadmium. Thus, the effectiveness of cadmium deposition may be influenced via modification of electrode surface by co-deposited metals. Therefore, the effects of zinc, copper and lead on cadmium electrodeposition process were tested. Artificial samples were prepared to contain in 1 l: 750 mg Na, 650 mg K, 30 mg Ca, 20 mg Mg, 1160 mg Cl, 150 mg P and 450 mg urea. This solution represents an average matrix of four-fold diluted urine. The composition was derived from [30]. The solution was spiked with cadmium to 1 μg l^{-1} and with varying concentrations of zinc (up to 1000 μg l^{-1}), copper (up to 50 μg l^{-1}) and lead (up to 20 μg l^{-1}). These levels of metallic elements in simulated diluted urine correspond to much higher values than the normal concentrations in urine samples. These extreme values can occur only in case of intoxicated people and they are markers of metabolic abnormalities [4]. The experiments proved that the above-mentioned levels of trace metals did affect neither the net absorbance nor the residual background. Table 2 summarizes the data and gives results of statistical test comparing metal-spiked and unspiked artificial samples. The shape of absorbance peaks was not affected, too.

Table 2
Results of interference test

Composition of tested solution	Mean absorbance (peak area)	S.D. ($n = 5$)	t value ($t_{(8,0.05)} = 2.306$)
1 μg l^{-1} of Cd	0.114	0.009	
1 μg l^{-1} of Cd + 1000 μg l^{-1} of Zn	0.120	0.010	0.892
1 μg l^{-1} of Cd + 50 μg l^{-1} of Cu	0.115	0.003	0.211
1 μg l^{-1} of Cd + 20 μg l^{-1} of Pb	0.113	0.008	0.166

Table 3
Cadmium contents ($\mu g\,l^{-1}$) in practical urine and in RMs determined by ED-ETAAS

Material	ED-ETAAS procedure A ($n = 10$)	ED-ETAAS procedure B ($n = 20$)	Reference value
SERONORM No. 403125	4.790 (0.835)	5.040 (0.629)	5.0 ± 0.5
SERONORM No. 101021	0.338 (0.065)	0.401 (0.055)	0.35 ± 0.16
Urine (adult)	0.120 (0.045)	0.139 (0.040)	–
Urine (adult) with spike 1 $\mu g\,l^{-1}$	1.192 (0.055)	1.156 (0.050)	–
Recovery (%)	107	102	

The values in parentheses are standard deviations.

3.7. Analytical figures of merit and accuracy

The method can be applied for cadmium determination in urine with linear range of 0.1–2.0 $\mu g\,l^{-1}$. Based on repeated analyses of blanks (0.15 $mol\,l^{-1}$ HNO_3) limits of detection (LOD) and quantification (LOQ) were calculated using 3σ and 10σ criteria, respectively. Considering four-fold dilution of urine sample, the LOD and the LOQ for procedure B were 0.03 and 0.09 $\mu g\,l^{-1}$ Cd, respectively. The procedure A showed slightly better LOD and LOQ values.

Both procedures are time-consuming. Duration of one measurement represents approximately 5 and 7 min for A and B procedures, respectively. Therefore, the full calibration (four standard solutions, two measurement per solution) takes 40 and 56 min, respectively.

Repeatability of measurements of practical urine samples taken immediately before analysis is satisfactory. Relative standard deviation values range from 3 to 5% at approximately 1 $\mu g\,l^{-1}$ level (equivalent to 4 $\mu g\,l^{-1}$ of urine) and from 4 to 8% at approximately 0.2 $\mu g\,l^{-1}$ level (equivalent to 1 $\mu g\,l^{-1}$ of urine). R.S.D. values dramatically raise up to approximately 30% when cadmium concentration in urine approaches to LOQ. Worse repeatability is also encountered when reconstituted reference urine samples are analysed. The reconstitution of freeze-dried urine introduces substantial variability to the whole analytical process even when cadmium concentration is rather high (see Table 3).

Accuracy of the optimized procedures A and B was tested using reference urine samples. The results obtained by both procedures correspond with the reference values. Moreover, full recovery of cadmium was found for a spiked sample of practical urine (Table 3).

The ruggedness of the method was tested relating to small deviations of seven parameters (volume of modifier solution, concentration of Pd in modifier solution, Pd pre-deposition time, analyte deposition time, applied voltage, pyrolysis temperature, atomization temperature). Pyrolysis temperature (550 °C versus 600 °C) was the only parameter affecting the results significantly.

4. Conclusion

In spite of the fact that coupling of the sample electrodeposition with the ETAAS method generates many problems, the proposed and verified standard operational procedure can be recommended for the direct determination of cadmium in urine. The procedure is more laborious compared with conventional ETAAS method but provides much more reliable results.

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