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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 $1.000 \pm 0.002\,g\,l^{-1}$ in $0.5\,mol\,l^{-1}$ HNO_3, palladium nitrate modifier stock solution containing $1.000 \pm 0.002\,g\,l^{-1}$ Pd in $0.5\,mol\,l^{-1}$ HNO_3 (both produced by Merck, Darmstadt, Germany), and ammonium dihydrogen phosphate modifier solution ($10.0\,g\,l^{-1}$ $NH_4H_2PO_4$, Analytika, Prague, Czech Republic) were used. Cadmium standard solutions containing from 0.1 to $5\,\mu g\,l^{-1}$ Cd and $0.2\,mol\,1^{-1}$ 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 $0.2\,mol\,1^{-1}$ 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 $50\,mg\,l^{-1}$ 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,