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Catalytic adsorptive stripping voltammetry versus electrothermal atomic absorption spectrometry in the determination of trace cobalt and chromium in human urine

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Abstract

Two methods of the determination of cobalt and chromium in human urine of non-occupationally exposed populations—highly sensitive catalytic adsorptive stripping voltammetry (CAdSV) and electrothermal atomic absorption spectrometry (ET-AAS)—are evaluated and compared. The CAdSV methods are based on adsorptive accumulation of a cobalt–nioxime (1,2-cyclohexanedione dioxime) or a chromium–DTPA (diethylenetriammine-*N*,*N*,*N*′,*N*″,*N*″-pentaacetic acid) complexes on a hanging mercury drop electrode, followed by a stripping voltammetric measurement of the catalytic reduction current of the adsorbed complex in the presence of sodium nitrite in case of cobalt or in the presence of sodium nitrate in case of chromium determination. In the CAdSV procedure UV-photolysis was used for the sample pre-treatment; the ET-AAS determination did not require any separate preliminary decomposition of the analyte urine samples. The accuracy of the procedures was checked by the analysis of commercially available quality control urine samples. The detection limits (3σ) were 0.13 $\mu g\,l^{-1}$ for Co and 0.18 $\mu g\,l^{-1}$ for Cr in ET-AAS determination and 0.007 $\mu g\,l^{-1}$ for Co and 0.002 $\mu g\,l^{-1}$ for Cr in CAdSV measurements. Precision (R.S.D.) was less than 5% for both methods. The study has shown that the CAdSV is a more reliable and sensitive technique for the determination of very low cobalt and chromium contents in urine, the detection of which is not possible when using the AAS technique.

Keywords: Cobalt; Chromium; Urine; Nioxime; Diethylenetriammine-*N*,*N*,*N*′,*N*″,*N*″-pentaacetic acid; ET-AAS; CAdSV

1. Introduction

Difficult matrices with very low trace metal levels such as body fluids represent serious problem for reliable analysis, which is an important prerequisite for the accurate assessment of the present internal exposure of an individual, for prevention and control of pollution and diagnosis and treatment of adverse health effects. The presence of some matrix components could lead to interference effects and therefore most of the methods require a previous digestion of samples [1,2]. Cobalt and chromium are known to be essential to humans and their concentration in urine is generally considered to be near 0.5 ppb in healthy population [3,4]. Among the techniques which are commonly used for the determination of cobalt and chromium in biological materials, only neutron activation analysis [5] and mass spectrometry [6,7] have a sufficient sensitivity for direct measurement of such trace amounts. However, these expensive techniques are not still extended in a routine biochemical practice.

Electrothermal atomic absorption spectrometry is the most widely used method for the determination of trace elements

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in biological fluids due to its reliability, sensitivity and relatively low cost of instrumentation. It is not reliable enough, to determine precisely cobalt and chromium at sub-ppb levels, because such levels are near to the detection limit of the technique. Therefore, some preliminary preconcentration steps are required [8,9], but unfortunately, such procedures are time-consuming. The CAdSV is an extremely sensitive technique which offers low detection limits [10,11], sometimes much lower than those of the appropriate ET-AAS techniques. For some elements the detection limits are even lower than those obtained by means of inductively coupled mass spectrometry technique. The CAdSV methods for the determination of ultra traces of cobalt and chromium involve mainly the formation and adsorptive collection of cobalt or chromium complexes on the hanging mercury drop electrode in the accumulation step, followed by a stripping voltammetric measurement of the catalytic reduction current of the adsorbed complex in the presence of oxidation agent [11–15].

The aim of this study was to evaluate the possibility of utilizing the CAdSV for the determination of cobalt and chromium in human urine of non-occupationally exposed general population. The CAdSV technique has been compared with the ET-AAS method, the most conventional technique used for this purpose. The Co (II)–nioxime–nitrite system was chosen for cobalt determination by means of CAdSV due to its excellent sensitivity and extremely low limit of detection in comparison with other voltammetric stripping procedures [12–14]. A method based on the catalytic adsorptive accumulation of the Cr–diethylentriamine-*N*,*N*,*N*′,*N*″,*N*″-pentaacetic acid (DTPA) complex combined with the catalytic reaction in the presence of nitrate [15,16] was chosen for the determination of chromium. So far, these methods have not been applied for the determination of cobalt and chromium in urine samples.

2. Experimental

2.1. Apparatus and equipment

Atomic absorption spectrometer Avanta P (GBC, Australia) equipped with GF 3000 graphite furnace, with auto sampler PAL 3000 and deuterium arc correction in double beam arrangement was used for quantitative determination of cobalt and chromium by means of ET-AAS. The wavelengths of the hollow cathode lamps for Co and Cr were 240.7 and 357.9 nm, respectively. Pyrolytically coated graphite tubes (GBC P/N: 56GB725) were used for all experiments. The hollow cathode lamps used for the AA determination were purchased from Photron Pty. (Australia).

All electrochemical determinations were performed using the electrochemical Analyzer, Model EA9, MTM, Poland. All voltammetric curves were obtained with conventional three-electrode system consisting of the hanging mercury drop electrode, a silver–silver chloride (3 M KCl) electrode as a reference and platinum wire auxiliary electrode. Surface area of the HMDE was 1.68 mm^2.

UV-photolysis of urine samples was carried out in quartz tubes by means of Mineral 8 UV Digester with 150 W UV lamp (Mineral, Warsaw, Poland).

All dilutions and sample preparations were made using deionised water (conductivity below 0.08 $\mu S\,cm^{-1}$) produced by an ion-exchange system DEMIWA 5-ROI (WATEK, Czech Republic) or Cobrabid-Aqua (Warsaw, Poland).

2.2. Reagents and solutions

All reagents were of analytical grade. Cobalt and chromium stock solutions (1 $g\,l^{-1}$) were obtained from Analytica Co. Ltd. (Prague, Czech Republic). Standard solutions containing 10 $mg\,l^{-1}$ of cobalt and chromium were prepared by the appropriate dilution of the stocks (1 $g\,l^{-1}$) using deionised water. Matrix components used for the preparation of artificial urine solution as follows: sodium chloride, potassium chloride, magnesium chloride, calcium carbonate, hydrochloric acid (36%), sulphuric acid (98%) and urea were Suprapur® (Merck, Germany).

Ammonia buffer (1 M) was prepared by mixing of the corresponding amounts of NH_4Cl and ammonia solution (Suprapur®, Merck). Nioxime solution (0.1 M) was prepared by dissolving the appropriate amount in ethanol (96%, analytical grade). Sodium nitrite (5 M) was prepared by dissolving the corresponding amount of the salt in deionised water. DMG and sodium nitrite were of analytical grade, purified by re-crystallisation from ethanol and water, respectively. Potassium nitrate (1 M) was prepared by dissolving a corresponding amount of the salt (POCh, Poland) in deionised water. The solid reagent of AR grade was purified by coprecipitation of the impurities on $La(OH)_3$ and crystallized from water. Acetate buffer (2 M, pH 6.0) was prepared by mixing the corresponding amounts of 96% acetic acid and 25% ammonia solution (both Suprapure®, Merck). A diethylentriamine-*N*,*N*,*N*′,*N*″,*N*″-pentaacetic acid (DTPA) solution (0.2 M) was prepared by dissolving an appropriate amount of the reagent (Carl Roth, Germany) and addition of 25% ammonia (Suprapur®) till pH 6.0.

All solutions were stored at 4 °C. Prior to analysis, all glass and plastic ware was immersed in 2 M nitric acid for 24 h followed by rinsing with deionised water.

2.3. Sampling and storage

Urine samples were collected into polyethylene containers and frozen at −20 °C. All plastic ware was cleaned with 2 M nitric acid prior to use as described above.

2.4. Sample preparation

No special pre-treatment steps were performed in the case of cobalt and chromium determination by ET-AAS—urine samples were analyzed directly. Before measurements, the