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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

sediment present in the sample was homogenised by rigorous shaking or by means of an ultrasound device to reach a representative portion of the specimen.

When the CAdSV methods were applied for the determination of Co and of total Cr, the urine samples had to be decomposed using UV irradiation procedure. The UV digestion procedures were experimentally selected and optimised to ensure the total decomposition of organic matter present in the urine as well as to oxidize the Cr(III) to Cr(VI) completely.

UV-photolysis of urine samples was carried out in three subsequent steps: *In case of cobalt determination* (i) 2 ml of sample was placed in the decomposition vessel and 100 μl of H_2O_2 was added and the mixture was then irradiated for 45 min. (ii) Then, the next 100 μl of H_2O_2 was added again and irradiation process was continued for 45 min. (iii) Finally, 10 ml of H_2O was added and the irradiation process was repeated for another 120 min. After completion of the irradiation procedure the volume of the decomposed sample was set to 50 ml. *In case of chromium determination* (i) 2 ml of sample was placed into the decomposition vessel and 100 μl of H_2O_2 was added; the mixture was then irradiated for 60 min. (ii) The next 100 μl of H_2O_2 was added and irradiation was proceeded for 60 min. (iii) pH was adjusted to 8.0 and the irradiation was continued for 4 h. The volume of the decomposed sample was set to 50 ml. The third step (iii) was required to reach a decomposition of the organic matrix which was not destroyed in the first two steps and to complete the oxidation of Cr (III) to Cr (VI), which is necessary to perform the CAdSV determination of total chromium.

The reference material Lyphochek Level 1-69011 and Level 2-69012, freeze-dried urine used for method validation and quality control (BIO-RAD, Anaheim, USA), was reconstituted according to the manufacturer's instructions.

2.5. Optimisation of the analytical procedures

2.5.1. ET-AAS procedure

Urine samples were analyzed directly by the ET-AAS method using the calibration procedure. An artificial urine sample suggested by Dawson et al. [17] was used for the purpose of optimising the conditions of the determination. The stock sample of artificial urine was prepared by dissolving single components in deionised water to reach the following final concentrations: 50.8 g l^{-1} NaCl, 30.9 g l^{-1} $NH_4H_2PO_4$, 28.6 g l^{-1} KCl, 3.12 g l^{-1} $CaCO_3$, 4.18 g l^{-1} $MgCl_2{\cdot}6H_2O$, 6.7 ml l^{-1} H_2SO_4 (98%), 87 ml l^{-1} HCl (36%). An organic matrix was simulated by addition of urea (186 g l^{-1} $CO(NH_2)_2$, in accordance to SRM NYC 403125 by Nycomed). An artificial urine stock solution was 10-fold diluted to obtain "urine equivalent" concentration. The concentrations of the solutions used in the calibration and contained "urine equivalent" ranged from 0.5 to 4 μg l^{-1} of Co and from 0.5 to 5 μg l^{-1} of Cr. The calibrations were performed by means of the instrument software. A single urine calibration graph was constructed for each element, from which all calculations were made in a single analytical run. All calibration plots were linear in the investigated concentration ranges. Correlation coefficients found were 0.9992 and 0.9995 for Co and Cr, respectively. Sample volumes injected into the furnace were 20 μl. The temperature programme used for the purpose of the method optimisation is presented in Table 1.

Table 1
Temperature programme for a graphite furnace

Step	Final temperature (°C)	Ramp time (s)	Hold time (s)	Gas type
1	60	15	10	Inert
2	85	45	5	Inert
3	120	10	10	Inert
4	250	10	10	Inert
5	1100	17	15	Inert
6	1100	0	1	None
7	2500	1	0.6	None
8	2600	1	0	Inert
9	40	25	5	Inert

2.5.2. CAdSV procedure

The CAdSV methods with nioxime and nitrite for Co [13] and with DTPA and nitrate for Cr [15,16], which were elaborated earlier for measurement of Co and Cr ultra-traces in water samples, were optimised and applied for chromium and cobalt quantification in human urine. The analyzed solution consisted of 8 ml of urine sample, 0.5 ml of 2 M acetic buffer, 1 ml of 2.5 M KNO_3 and 0.5 ml of 0.2 M DTPA. The solution was deaerated with pure argon for 5 min in a voltammetric cell, and then a pre-treatment procedure was applied (new drop generation, accumulation, 15 s equilibration). Quantitative measurements were performed by the differential pulse mode (DPV). Instrumental parameters of the analysis of chromium were selected as follows: the chromium–DTPA complex was accumulated at the potential of −950 mV for 20 s with stirring, after a resting period of 15 s the potential was scanned from −950 to −1400 mV in the differential pulse mode using a pulse amplitude of 50 mV. After each standard addition the solution was deaereated for 1 min.

In the case of cobalt determination, 10 ml of the analyzed solution containing 0.1 M ammonia buffer (pH 9.2), 1×10^{-4} M nioxime, 0.5 M $NaNO_2$ and 2 ml of decomposed urine sample was introduced to the voltammetric vessel. The solution was deaerated with pure argon for 5 min and quantitative measurements were performed by the differential pulse mode (DPV). The optimal voltammetric procedure comprised the adsorptive accumulation of the Co–nioxime complex on a HMDE at −800 mV for 30 s with stirring, followed by 15 s of rest period. The potential was then scanned from −1000 to −1200 mV in the differential pulse mode using a pulse amplitude 50 mV. After each standard addition the solution was deaerated for 1 min.

3. Results and discussion

Reagent blanks containing ultra pure water or an artificial urine were also analyzed to verify the reagents' purity and determine the laboratory blank. The use of ultra pure reagents and clean-air conditions was found to be necessary in order to obtain blanks results with minimal signals for the elements of interest. For voltammetric aims it was necessary to purify some components of the supporting electrolytes (sodium nitrite, ammonia buffer) to obtain a very low blank. This was done in an additional cleaning step with Chelex ion exchanger [18].

3.1. Optimisation and characteristics of the ET-AAS method of Co and Cr determination

Pyrolysis temperature curves were recorded for aqueous and artificial urine (1:1) solutions containing 10 $\mu g\,l^{-1}$ of cobalt and 2 $\mu g\,l^{-1}$ of chromium. The experiments demonstrated that a diluted artificial urine solution simulated the real samples better and was more useful for the optimisation purpose. Interferences originating mainly from matrix alkali metal chlorides and phosphorus compounds have occurred when the pyrolysis temperature applied was below than 1000 °C. These interferences have been also observed both with the majority of undiluted urine samples and with diluted ones (1:1 and 1:2). The temperature of pyrolysis is one of the most crucial parameters for improving selectivity and reducing vapour phase interferences in ET-AAS and therefore the correct choice of time and temperature of the pyrolysis step is essential for overcoming the matrix interferences [19,20]. It was found that is necessary to use ash temperature higher than 1000 °C for removing this problem. The optimal ash temperature found for cobalt aqueous solution was 700 °C and for chromium 1000 °C. For the analysis of solutions containing the artificial urine matrix, an ash temperature of 1100 °C could be applied for both cobalt and chromium. This phenomenon is possible to clarify using observation by Tekgkul and Akman [21]. They studied the combined effects of NaCl and $MgCl_2$ on manganese determination. They observed that interference by NaCl was reduced when using high pyrolysis temperatures, since MgO produced by hydrolysis of $MgCl_2$ (in our case one of the matrix components) stabilized the analyte. A significant reduction of the background signal was observed for both elements when this temperature was applied. The selected atomisation temperature was 2500 °C. This temperature was sufficient for the determination of cobalt and chromium and it was not necessary to use any chemical modifier, which could be a source of contamination. Detection limits (DLs) for the determined elements when using an Avanta P instrument were 0.13 and 0.18 $\mu g\,l^{-1}$ for Co and Cr, respectively. The reproducibility determined by the relative standard deviations and evaluated from 10 repeated measurements of 0.5 $\mu g\,l^{-1}$ of Co and 0.3 $\mu g\,l^{-1}$ of Cr in urine solution was better than 5% for both cobalt and chromium.

3.2. Optimisation and characteristics of the CAdSV procedures of Co and Cr determination

CAdSV is very sensitive to the presence of organic matrix and therefore it was very important to elaborate the optimal procedure for the sample decomposition. UV photolysis was chosen as the most convenient for this purpose. In contrast to the traditional techniques such as thermally induced or microwave-induced digestion, only very small amounts of reagents (H_2O_2) are required for carrying out UV photolysis, leading to extremely low blank values. In case of chromium determination the UV-irradiation procedure also enables the oxidation of Cr(III) to Cr(VI), which is a necessary condition for the CAdSV determination of total chromium. The CAdSV allows to determine cobalt in form of the Co(II)–nioxime complex. Addition of $NaNO_2$ to the solution containing nioxime and ammonia buffer provides a substantial enhancement of the voltammetric signal of cobalt due to the catalytic effect occurring during the reduction of Co (II)-nioxime (Fig. 1). Fig. 1 shows the voltammogram recorded for the Co (II)-nioxime complex before and after addition of nitrite into the solution analyzed. Apparently, the addition of the oxidizing agent to the solution significantly improves the Co current response. Co quantification was performed by the standard addition procedure. Examples of Co and total Cr determination by means of the CAdSV are shown in Fig. 2.

Detection limits (DLs) calculated as the three times standard deviation of repeated measurements ($n = 10$) of the blanks were found to be 0.009 $\mu g\,l^{-1}$ for Co and 0.002 $\mu g\,l^{-1}$ for Cr. The limit of detection in UV-digested and 25-fold diluted urine sample was found to be 0.009 $\mu g\,l^{-1}$. The reproducibility of the method was evaluated from 10 repeated measurements of 0.011 $\mu g\,l^{-1}$ of cobalt and 0.018 $\mu g\,l^{-1}$ of chromium in decomposed urine solution. The relative standard deviations for 10 repeated measurements were equal to 3.2% for Co and to 6.3% for Cr.

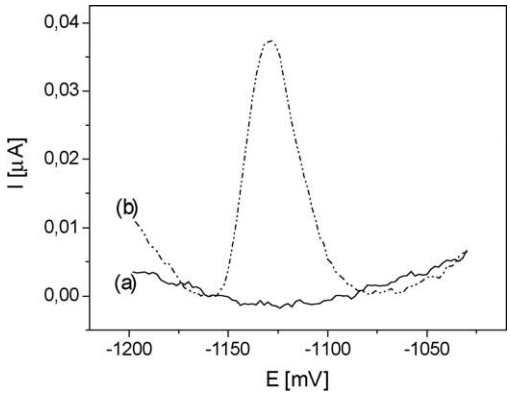

Fig. 1. Voltammograms of 0.011 $\mu g\,l^{-1}$ of Co recorded on hanging mercury-dropping electrode in the solution containing (a) 0.1 M ammonia buffer, 1×10^{-4} M nioxime, and (b) 0.1 M ammonia buffer and 0.5 M $NaNO_2$. $E_{acc} = -800$ mV, $t_{acc} = 30$ s. Instrumental parameters: $v = 10$ mV/s, $\Delta E = 50$ mV, $E_s = 2$ mV.

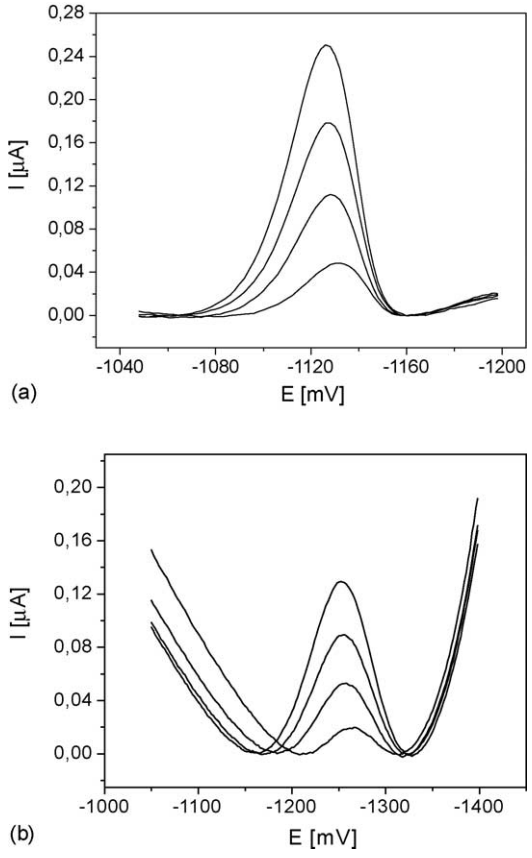

Fig. 2. The examples of the cobalt (a) and chromium (b) CAdSV determination in the urine samples by the standard addition method. (a) Curve (1): 2 ml of the sample with addition of the supporting electrolyte to final volume of 10 ml, curves (2)–(4): as (1) + 0.02, 0.04 and 0.06 μg l^{-1} Co(II), respectively. Instrumental parameters: $E_{acc} = -800$ mV, $t_{acc} = 30$ s, $v = 10$ mV/s, $\Delta E = 50$ mV, $E_s = 2$ mV. (b) Curve (1): 8 ml of the sample with addition of the supporting electrolyte to final volume of 10 ml, curves (2)–(4): as (1) + 0.1, 0.2 and 0.3 μg l^{-1} Cr(VI), respectively. Instrumental parameters: $E_{acc} = -950$ mV, $t_{acc} = 20$ s, $v = 25$ mV/s, $\Delta E = 50$ mV, $E_s = 2$ mV. The voltammetric curves of Cr(VI) were obtained after subtraction of the background curve.

Analytical recoveries from urine samples ($n = 4$) spiked with the known amounts of cobalt or chromium standard solutions were 96% for Co and 98% for Cr.

3.3. Precision and accuracy

Two lyophilised reference control urine samples of certified levels (Lyphochek Level 1 and Level 2, BIO-RAD, Anaheim, USA) were used to assess precision and accuracy (see Table 2).

Table 3
Results[a] of the inter-laboratory comparison programme for chromium and cobalt determination in urine given in μg l^{-1}

Element	CAdSV	ET-AAS
Co	0.93 ± 0.07	0.9 ± 0.2
	0.81 ± 0.09	0.6 ± 0.2
Cr	0.25 ± 0.08	0.21 ± 0.02
	0.3 ± 0.2	0.34 ± 0.01

[a] Each value is the mean ± S.D. of four analytical runs.

3.4. Application and comparison of CAdSV and ET-AAS method for urine analysis

The levels of the selected elements cobalt and chromium in urine samples obtained from 10 patients after surgical intervention were measured independently using both examined techniques. Both the real urine samples and commercially available reference material were investigated. While the determination of cobalt in human urine reference material by means of CAdSV methods was free of problems, it was not possible to determine chromium correctly in accordance with the declared value using this method. In this case CAdSV-measured total chromium content after UV-irradiation was much lower than declared value and also measured by ET-AAS. It was probably caused by the presence of very stable non-active organometallic compounds, which were not been completely destroyed during the UV-irradiation process. But not even further irradiation removed this problem. This problem was not observed in case of chromium determination in real urine samples. Therefore we can suppose that matrix constitution of SRM is much more complicated than for all real urine samples used in our study. This idea could be supported by observation of Krushevska et al. [22]. The mentioned authors found higher residual carbon content after open-focused microwave system for the urine reference material (NIST SRM 2670 Toxic Metals in Freeze-dried Urine) than that for the 24 h urine samples.

ET-AAS had insufficient sensitivity to determine Co and Cr in all real urine samples. Therefore only samples with higher Co and Cr contents could be used for a validation of the CAdSV method. The results obtained by means of ET-AAS and CAdSV methods were in good agreement with each other and are shown in Table 3.

Table 2
Determination[a] of cobalt and chromium in certified BIO-RAD Lyphochek standards by ET-AAS and CAdSV method given in μg l^{-1}

	SRM	Declared	Acceptable	ET-AAS	CAdSV
Cobalt	Level 1-69011	3.3	2.6–4.0	3.9 ± 0.2	[b]
	Level 2-69012	10.6	8.5–12.7	10.6 ± 1.0	12.2 ± 0.6
Chromium	Level 1-69011	3.9	3.1–4.6	3.4 ± 0.3	[b]

[a] Each value is the mean ± S.D. of three analytical runs.
[b] Not determined.

Although the precision of ET-AAS method is comparable with that of CAdSV and its application is even more rapid due to minimal requirements for sample preparation, only the use of CAdSV can ensure sufficient sensitivity of the determination of cobalt and chromium in all investigated urine samples.

4. Conclusions

What can be seen from the presented investigation and results is that the CAdSV method has several advantages over the ET-AAS as far as cobalt and chromium determination in human urine of non-occupationally exposed population is concerned. The voltammetric technique offers the higher sensitivity and much lower detection limits, which are also lower than those obtained using inductively coupled plasma mass spectrometry (ICP-MS) [23,24]. It should be mentioned, however, that such comparison is relatively unfair since the samples for AAS were not pre-treated and no pre-concentration was implemented for subsequent ET-AAS. But, furthermore, the relatively low cost of the voltammetric instrumentation as another advantage of this CAdSV technique should also be taken into account when compared with the ET-AAS and ICP-MS technique, which is still inaccessible for many laboratories because of its very high acquisition cost. The applicability of the CAdSV method was validated by the analysis of the reference materials and by a comparison with the results obtained using ET-AAS method for samples containing higher levels of Co and Cr.

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