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Determination of Cobalt and Nickel in Biological Materials Using Catalytic Adsorptive Stripping Voltammetry

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Abstract: The paper discusses the utilisation of the catalytic adsorptive stripping voltammetric method for the simultaneous determination of Co and Ni in biological materials such as hair, oyster tissue, bovine liver and oriental tobacco leaves. For this purpose the most sensitive and selective catalytic-adsorptive system with nioxime and nitrite has been selected. The optimal parameters, including concentration of the supporting electrolyte, pH and accumulation time and potential, have been established. To decompose the sample material microwave digestion with nitric acid has been applied, providing a blank-free approach for the accurate determination of Co and Ni. The elaborated method has been tested on certified reference materials and good agreement between the voltammetric results and the certified values has been obtained.

Keywords: Catalytic adsorptive stripping voltammetry; nioxime; nitrite.

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Introduction

Measurement of cobalt and nickel in biological samples is very important, since at low concentrations these trace elements are essential for humans and other living organisms, whereas at higher concentrations toxic effects have been shown to occur. The role of cobalt as a component of vitamin B12 is well established. Both an excess and a deficiency of Co can cause serious health issues such as the inability to synthesize the DNA constituent thymidine, anaemia, degeneration of nerve cells and abnormality of metabolic processes.

Thus, the distribution and behavior of Co and Ni in ecosystems requires special attention and environmental surveillance as well as quality control in food, medicine and toxicology. The most common optical methods like spectrophotometry, AAS and ICP AES often do not offer the necessary sensitivity, selectivity and lack of matrix interferences. The application of these methods to determine even milligram levels of Co or Ni is also limited considering the great influence of matrix effects originating from highly concentrated solutions such as seawater. Therefore, the determination of Co and Ni ultratraces should be preceded by a concentration step involving coprecipitation, solvent extraction, or cheating/chelating resin.

Furthermore, optical methods require expensive instrumentation. In contrast, voltammetric techniques utilize relatively inexpensive devices and are sufficiently sensitive to allow direct analyte determination without separate preconcentration. Moreover, the highly concentrated solutions used in the determination of Co and Ni, e.g. in seawater are very suitable supporting electrolytes for voltammetry. However, due to the extreme irreversibility of the electrode processes of Co and Ni the sensitivity of the voltammetric determination of these elements in non-complexing media is rather poor.

This disadvantage was overcome by Nürnberg's team, who introduced the adsorptive stripping voltammetric method of Ni and Co determination in the form of complexes with dimethylglyoxime (DMG) [1,2]. The method features the adsorption of complexes of Co and Ni with DMG onto the HMDE, followed by the development of a reductive stripping step. After adding DMG to the solution and applying the stripping procedure well-developed responses of Ni and Co were obtained. Although this excellent method, which enabled a significant enhancement of the sensitivity and selectivity of the determination of these elements, became a standard procedure [3] and was applied for the determination of Ni and Co in various environmental samples [4], there still remained some limitations in the determination of Co traces connected with an insufficient detection limit and selectivity against Zn and Ni. Due to small differences in the peak potentials of Co and Zn (ca 50 millivolts), the Zn wave can seriously overlap with the Co wave, especially in the presence of a large excess of Zn. An excess of Ni also interferes with the Co peak.

The third unsolved problem was connected with the explanation of the mechanism of Co-DMG and Ni-DMG reduction process. The observed voltammetric signals of Ni and Co were much higher than the ones expected under the assumption that the entire electrode surface is covered by the adsorbed complexes. According to Nurnberg’s group, current enhancement has an exclusively adsorptive nature [5].

As opposed to the above, the investigators from the Russian electrochemical school maintained that hydrogen ions undergo catalytic reduction [6]. Neither of the concepts fully explained the observed phenomenon.

The authors of this presentation and their collaborators proposed a different mechanism of electrode reaction [7,8]. During detailed electrochemical and spectroscopic studies we found that both the central metal ions, Co(II) or Ni(II), and the surrounding DMG ligands are simultaneously reduced in an overall 10-electron process [8]. The presence of Co(II) or Ni(II) ions, which form complexes with DMG, induces a non-cyclic catalytic reduction of two DMG ligands bound in the complexes at a potential more positive by ca. 600 mV than that in the absence of Co(II) or Ni(II). The above findings have also been confirmed by Jagner and co-workers [9].

To meet both analytical objectives, that is to increase the Co response and to dramatically improve selectivity against Zn and Ni, in the preliminary study the DMG ligand was replaced with other dioximes, such as 1,2-cyclohexanedione dioxime (nioxime), α-benzil dioxime (α-BD) and α-furil dioxime (α-FD) [7]. This improved peak separation between Co and Zn. Then, after introducing nitrite to the solutions containing Co(II) and Ni(II) ions in the presence of the investigated dioximes and ammonia buffer a great increase in the Co signal was observed [7]. This effect occurred thanks to the catalytic reduction of nitrite in the presence of complexes of Co with dioximates. Surprisingly, this effect was induced only by Co-dioxime complexes, but not by those with Ni.

Based on the above observations, new, original catalytic voltammetric or catalytic adsorptive stripping voltammetric methods (CAdSV) have been developed by one of the authors [7, 10-13]. In general, the methods exploit the catalytic effects which appear during the reduction of complexes of Co and such dioximes as DMG, aBD, aFD and nioxime in the presence of high concentrations (from 0.05 to 1M) of nitrite ions [4,10-14]. In optimal conditions the catalytic effect the Co polarographic response increased 100 to 10 000 times in the presence of both dioxime and nitrite in relation to the simple Co diffusion current. As a result of the catalytic effect induced by the dioximate Co-complexes in the presence of nitrite, Co traces at the levels of 10^{-10}-10^{-9} M may be determined using DPP polarography or even DC polarography with high sensitivity, precision and selectivity [7,15]. Adsorptive preconcentration using the techniques of adsorptive voltammetry makes it possible to further increase the sensitivity and decrease the detection limit of Co determination in catalytic systems [10-14].

The significant sensitization of the Co voltammetric signal is a result of three effects: reduction of the Co and Ni complexes with the participation of dioxime ligands, adsorptive preconcentration of Co-dioxime complexes onto the surface of the working electrode (HMDE or various solid electrodes) and catalytic reduction of nitrite anions induced by the reduction of Co-dioxime complexes [4,12,14].

The elaborated CAdSV systems of Co or Co and Ni determination at the hanging mercury drop electrode [10-27], amalgam [28,29] and mercury film electrodes [30] or bismuth film [31-34] and lead film electrodes [28,35-39] have found wide application in the environmental [4,10,12,17-39] and industrial analyses of Co or Co and Ni ultratraces [11,14,16,21] due to an enormous increase in the sensitivity of Co catalytic peak current. In the vast majority of the cited papers voltammetric adsorptive stripping was applied; however, an attempt to quantify of these elements by means of the potentiometric adsorptive stripping method was also undertaken [30,33]. Such enhancing effect and the sensitivity and selectivity against Zn, Ni and Cu are dependent on the type of dioxime, concentration of the components of the supporting electrolyte (such as sodium nitrite, ammonia and ammonium chloride), the pH, the voltammetric mode and conditions as well as accumulation time and potential. For this reason, the methods can be applied to solve various analytical problems, and the applicability of individual methods utilizing different the types of dioximes and different voltammetric techniques depends on Co, Ni and Zn contents, their mutual concentration relations and the matrix composition [14].

The highest sensitivity may be obtained for Co(II)-nioxime-nitrite and Co(II)-αBD-nitrite systems. Therefore, for simultaneous determination of Co and Ni traces in the selected biological materials, the most sensitive and selective catalytic-adsorptive system with nioxime and nitrite has been selected. The purpose of the present paper was to optimize the analytical parameters for simultaneous CAdSV determination of Co and Ni in human hair, oyster tissue, bovine liver and oriental tobacco leaves, with validation of the voltammetric results.

Experimental

Chemicals, Reagents, Stock and Standard Solutions

All solutions were prepared with deionized water with a resistivity of 18.2 MΩ (*Millipore*, Simplicity UV). A stock solution of 4 M ammonia buffer was prepared from *Merck* Suprapur analytical-grade purity reagents: ammonia and ammonia chloride. Nioxime was recrystallized from ethanol and a stock solution of $1 \cdot 10^{-2}$ M was prepared by dissolving an appropriate amount of reagent in 96% ethanol.

$NaNO_2$ was recrystallized via dissolution in bidistilled hot water followed by adding ethanol and cooling to 0 °C. The Co(II) and Ni(II) standards were prepared daily from reagents of analytical grade purity (*Merck*) by appropriate dilution of the stock solutions. Certified reference materials of Human Hair GWB 09101, Oyster Tissue SRM 1566a, Bovine Liver SRM 1577a and Oriental Tobacco Leaves CTA-OTL-1, were used to validate the accuracy and precision of the method. The solutions were deaerated with argon for 5 min.

Electrochemical Apparatus and Other Instrumentation

Voltammetric experiments were carried out with an *Ecochemie* Autolab PGSTAT 20 equipped with the GPES software package (Utrecht, The Netherlands) or a PP-04 Pulse Polarograph, *Unitra Telpod* Poland. The electrochemical cell consisted of a Control Growth Mercury Drop Electrode (*MTM* Krakow, Poland) or a Static Mercury Drop Electrode SMDE-2 (*Laboratorni Pristroje*, Prague), both used as a working electrodes in the HMDE mode, silver-silver chloride (3M KCl) as a reference electrode and platinum wire as an auxiliary electrode. High performance microwave digestion system, *MILSTONE* MLS-1200 MEGA was used.

Digestion Procedure

In order to decompose the biological materials, the sample (in an amount of 0.3 – 0.5 g) was digested in the microwave system when using 5 ml of concentrated nitric acid (65% HNO_3) as the mineralisation agent (65%).

Voltammetric Procedure

A solution containing 10 ml of 0.1 M ammonia buffer (pH 9.4), $5 \cdot 10^{-5}$ M nioxime and 0.2 M sodium nitrite was prepared by mixing appropriate volumes of each stock solution in the electrochemical cell. Then, the appropriate volume (250 µl) of the digested biological sample and 150 µl of 25% NH_3 were added to adjust the pH to 9.2 - 9.4. The solution was deaerated with pure argon for 5 minutes. Quantitative measurements were performed by means of the differential pulse mode (DPV) using the standard addition procedure.

After each standard addition the solution was deaerated for one minute. Accumulation was performed by applying a potential of E_{acc} = -0.75 V for t_{acc} = 60 s with stirring and, after a resting period of 10 s, the voltammograms were recorded in the cathodic direction from -0.75 V to –1.25 V. The other experimental parameters were as follows: step potential pulse potential ΔE = 50 mV, scan rate v = 40 mV/s.

Results and Discussion

Metrological Characteristics of the Method

To adopt the CAdSV method with nioxime and nitrite for the simultaneous determination of Co and Ni in the analyzed biological materials an optimization study was performed. The study comprised the investigation of the composition of the supporting electrolyte, the pH, and of instrumental parameters such as accumulation time and potential, voltammetric mode and scan rate.

In the course of study the optimal values of the concentration and pH of the supporting electrolyte, and the optimal accumulation time and potential were established (see Fig. 1 overleaf). The signal originating from the reduction of the Ni-nioxime complex was influenced significantly neither by nitrite nor accumulation potential. Only the prolongation of accumulation from 0 to 120 s caused a significant (16 times) increase in the Ni response. The cobalt signal was influenced to the largest degree by nitrite concentration. The introduction of nitrite to the supporting electrolyte caused a substantial (30 times for 0.2 M $NaNO_2$) multiplication of the Co peak current (Fig. 1, inset).

It was found that the optimal composition of the supporting electrolyte was 0.1 M ammonia buffer (pH 9.2 – 9.4), $5 \cdot 10^{-5}$ M nioxime and 0.2 M $NaNO_2$. The best experimental conditions for the simultaneous determination of Co and Ni are: accumulation potential E_{acc} = –0.75 V, accumulation time t_{acc} = 60 sec, with stirring. In the above-described solution, the CAdSV curve of Co is then sufficiently separated from that of Ni ($\Delta E^p_{Ni\text{-}Co}$ = 160 mV) and of Zn ($\Delta E^p_{Zn\text{-}Co}$ = 95 mV).

The CAdSV response of Co was ca. 10000 times higher than the signal for pure Zn diffusion and ca. 20 times higher than the CAdSV signal for Ni. The sensitivity corresponds to 120 nA/nM for Co and to 5.2 nA/nM for Ni for the accumulation time of 60 s. The relative standard deviations for blank concentrations (8 repetitions) are of the order of 2.8 % (for Co) and 3.8 % (for Ni).The reproducibility of the measurement of 8 subsequent DP CAdSV voltammetric peak currents of Co and Ni blank concentration was equal to s_r = 2.8% and s_r = 3.8%, respectively.

The limits of detection (LODs) of $8.9 \cdot 10^{-12}$ M (0.00053 µg/L Co) for Co and $2.2 \cdot 10^{-10}$ M (0.013 µg/l Ni) for Ni were estimated from the signal-to-noise ratios (S/N = 3). The detection limit was restricted by the Co and Ni blank, whose value was limited by the purity of the reagents applied.

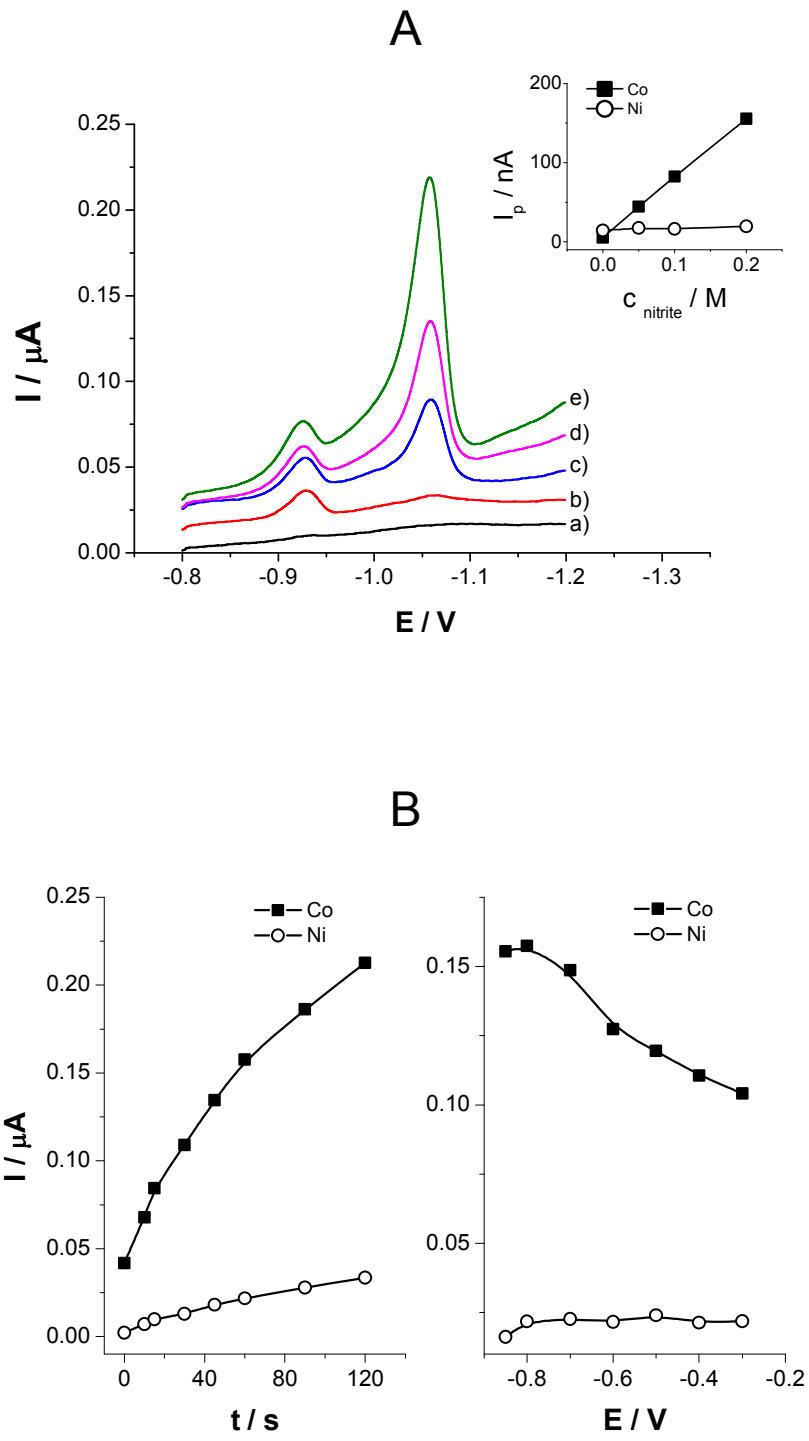

Fig. 1: *Simultaneous determination of Ni and Co - optimization of nitrite concentration (A) and instrumental parameters (B).* Legend: **A**) DPV voltammograms a) 0.06 µg/L Co, 0.3 µg/L Ni in 0.1 M ammonia buffer, b) solution a) and $5 \cdot 10^{-5}$ M nioxime, c) solution b) and 0.05 M $NaNO_2$, d) solution b) and 0.1 M $NaNO_2$, e) solution b) and 0.2 M $NaNO_2$, *inset*: peak currents of Ni and Co vs. $NaNO_2$ concentration. **B**) Solution e). Instrumental parameters: E_{acc} = -0.8V, t_{acc} = 60 s, t_{eq} = 5 s, ΔE = 50 mV, E_S = 2 mV.

The calibration plot for the accumulation time of 60 s was linear from $2 \cdot 10^{-10}$ M to $7 \cdot 10^{-9}$ M for Co (the correlation coefficient r = 0.999) and from $8 \cdot 10^{-10}$ M to $1 \cdot 10^{-7}$ M Ni (r = 0.999). However, the linear range of concentration is dependent on the applied voltammetric conditions. It was the higher for shorter preconcentration times, larger electrode surfaces and higher concentrations of the ammonia buffer. For example, in the supporting electrolyte of composition of 0.5 M ammonia buffer, $2 \cdot 10^{-5}$ M nioxime, 0.5 M nitrite and after a short accumulation time 10s without stirring the solution the upper linear range increased up to $3 \cdot 10^{-8}$ M Co (r = 0.999) and up to $1.5 \cdot 10^{-6}$ M Ni (r = 0.999).

Method Validation

The elaborated method was verified using certified reference materials and good agreement between the voltammetric results and the certified values was obtained (Table 1). Examples of the nickel and cobalt CAdSV determination in selected biological samples by CAdSV procedure are presented in Fig. 2.

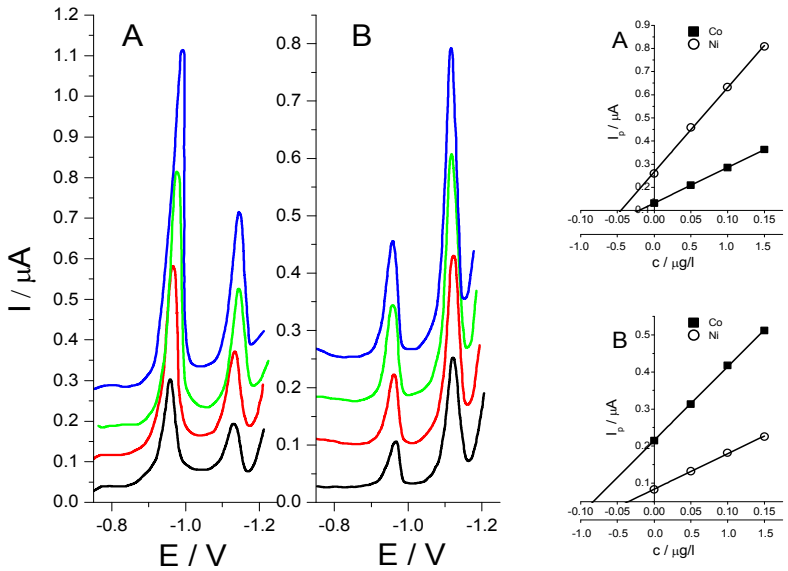

Fig. 2: *CAdSV quantification of nickel and cobalt in biological materials using the standard addition method*. Legend: (**a**) 250 µl of the digested sample of oriental tobacco leaves with addition of the supporting electrolyte to the final volume of 10 ml and with subsequent additions of 0.5 µg/L Ni and 0.05 µg/L Co. E_{acc} = - 800 mV, t_{acc} = 60 s. (**b**) 250 µl of the digested sample of human hair with addition of the supporting electrolyte to the final volume of 10 ml and with subsequent additions of 0.5 µg/L Ni and 0.025 µg/l Co. E_{acc} = - 750 mV, t_{acc} = 60 s.

Table I: *Results of CAdSV determination of Co and Ni in biological certified reference materials*.

CRM	Co ($\bar{x} \pm s$), μ/g		Ni ($\bar{x} \pm s$), μ/g	
	DP CAdSV Found	Certified	DP CAdSV Found	Certified
Human hair (GWB 09101)	0.124 ± 0.01	0.135 ± 0.008	2.47 ± 0.19	3.17±0.04
Bovine liver (SRM 1577a)	0.201± 0.011	0.21 ± 0.05	1.32 ± 0.10	none
Oyster tissue (SRM 1566a)	0.55 ± 0.11	0.57 ± 0.11	2.99 ± 0.30	2.25 ± 0.44
Oriental Tobacco Leaves (CTA-OTL-1)	0.849 ± 0.036	0.879 ± 0.039	6.01 ± 0.43	6.32 ± 0.65

Conclusions

The catalytic-adsorptive stripping voltammetric method with nioxime and nitrite is the most sensitive and selective electrochemical method currently available for the determination of Co and Ni traces. It was demonstrated that the method may be used to successfully determine low cobalt and nickel concentrations in biological samples such as human hair, oyster tissue, bovine liver and oriental tobacco leaves. The procedure is characterized by good precision, very low limits of detection of both investigated elements and ensures Co determination with excellent selectivity versus Zn and Ni, attained due to extremely high sensitivity of the Co catalytic response. The elaborated method has been verified using CRMs and good agreement between the voltammetric results and the certified values has been obtained. Moreover, one of the advantages of the method is the relatively low cost of instrumentation compared to ICP-MS, another very sensitive method for the quantification of low Co and Ni concentrations.

Likewise, when using spectrometric methods (ICP-MS, ICP-AES, or AAS) the voltammetric technique requires preliminary digestion and mineralization of the biological material; *e.g.*, in a microwave system, which was applied also in this work.

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