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Determination of Ni (II) in Beverages without Any Sample Pretreatment by Adsorptive Stripping Chronopotentiometry (AdSCP)

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The purpose of this paper was to use adsorptive stripping chronopotentiometry for the determination of Ni (II) in worldwide consumed beverages without any sample pretreatment, using dimethilglyoxime (DMG) as complexing agent and a glassy carbon mercury film electrode as the working electrode. Ni $(DMG)_2$ complex is adsorbed onto the mercury film at an electrolysis potential of −500 mV for 60 s and then reduced by a −5 μA constant cathodic current. The sensitivity of the method was studied for certified reference water and black tea in the pH range 6.5−11. At pH 9.5 in ammonia buffer, a detection limit of 0.2 μg L^{-1} was achieved; the instrumental precision (expressed as rsd %) was 1.5%, and the accuracy, expressed as obtained recoveries both from certified and not certified matrixes, ranged from 93.0 to 95.5 %. The chronopotentiometric analysis executed on commercial beverages provided evidence that black tea samples were the richest source of Ni (II) (1500−3700 μg L^{-1}), followed by coffee (100.0−300.5 μg L^{-1}); bottled mineral water showed a Ni (II) concentration lower than 4.6 μg L^{-1}. Among alcoholic beverages, red wines presented the highest content of Ni (II) (55.5−105.0 μg L^{-1}). Significant differences were noticed between Ni (II) levels of fermented and distillated alcoholic beverages; moreover, canned cola and beer did not show higher Ni (II) levels with respect to the glass-bottled products.

KEYWORDS: Adsorptive stripping chronopotentiometry; beverages; nickel

INTRODUCTION

Nickel is an ubiquitarious trace metal of prime environmental and alimentary concern. Nickel is used in many products for consumers, industrial, military, and transport. The biggest use, however, is as an alloying metal along with chromium and other metals in the production of stainless and heat-resisting steels. Stainless steel is widely used in the alimentary industries in food processing and storage. Nickel has not been yet demonstrated to be an essential nutrient for humans, but it is considered to be a normal constituent of the diet; the human requirement for nickel does not exceed 100 μg/day. Rich food sources of nickel are green leafy vegetables, oatmeal, beans, dried beans and peas, nuts, and chocolate. Recent studies demonstrated that the Ni absorption from meals is about 1%, and up to 27% is absorbed from water, but the daily intake of water provides only 1−2 μg of Ni. (*1*). The WHO has recommended a TDI (tolerable daily intake) of 5 μg/Kg body weight/day (equivalent to 350 μg/day for a 70-Kg adult) (*2*). Nickel has long been recognized as a contact irritant, causing a reaction called systemic contact dermatitis. It was not proven that nickel ingested in food can cause persons to become sensitized, but it was demonstrated that the oral exposure to high levels of nickel may invoke an eruption or aggravate dermatitis in sensitized individuals. Therefore, for those persons, acid foods cooked in stainless steel or canned food may need to be avoided (*3*). Moreover, Haber et al. (*4*) assessed the nickel toxicity from oral exposure both in animals and humans at concentrations higher than 50.0 mg/Kg/day and showed systemic effect on the kidney, immune system depression, and particularly in animals, neonatal mortality; carcinogenic effects from oral exposure are unproven. Nevertheless, an appropriate knowledge of nickel content in beverages daily consumed worldwide, as bottled mineral water, fruit juice, wine, beer, spirits, tea, coffee, and cola, is of great concern for the daily control of Ni assumption, particularly for eczema patients. The most common techniques used to determine nickel in food, biological, and environmental matrixes are atomic absorption spectroscopy (AAS), inductive coupling plasma atomic emission spectroscopy (ICP-AES), and voltammetry. All these techniques require a sample pre-treatment suitable to destroy the organic molecules that cause interferences. Particularly, flame atomic absorption spectroscopy (FAAS) is subjected to less interferences respect to electrothermal atomic absorption spectroscopy (ETAAS) or inductive coupling plasma mass atomic emission spectroscopy (ICP-AES-

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MS), but requires the use of a preconcentration step to reach an appropriate level of sensitivity (*3*, *5*, *6*). Moreover, ICP-AES-MS shows very low limits of detection but is a very expensive technique both for instrumentation costs and its maintenance. Several stripping voltammetric (SV) methods for trace nickel determination in various matrixes have been proposed using their organometallic complexes adsorbed onto the hanging mercury drop electrode (HMDE) (*7*−*9*). It was demonstrated that SV is more susceptible than stripping chronopotentiometry (SCP) to interferences by electro-active organic molecules and by capacitive currents, which caused a sensitivity decrease (*10*). The transformation of SCP *E*/*t* data into d*t*/d*E* format allows the elimination of capacitive current and reduces the impact of induced adsorption of organic molecules onto the working electrode surface (*11*). The area under the peaks in *E* versus d*t*/d*E* plots correspond to the time taken for faradic reduction process, while the area under the baseline is the time for double layer charging (*10*, *11*). Nevertheless SCP is more suitable than SV for analysis of samples containing significant amounts of organic matter (*12*−*15*). Literature does not report data about the use of adsorptive stripping chronopotentiometry for Ni (II) determination in food matrixes. The purpose of this paper is to use adsorptive chronopotentiometric stripping analysis (AdSCP) to determine the concentration of nickel in various commercial beverages as mineral water, pure fruit juice, wine, beer, tea, coffee, and coke without any sample pretreatment. Particularly, the content of nickel found in some canned beverages and in glass bottled beverages were compared. A mercury film glassy carbon electrode (MF) was used as the working electrode; it is widely employed for the electro-analytical stripping determination of mercury soluble elements (*7*−*9*). Nickel was determined in the commercial beverages as its dimethilglyoxime complex that was previously adsorbed onto the mercury film at a constant potential and then reduced by a cathodic constant current and redissolved (stripping). Prior to each analysis, the sample was spiked with ammonia buffer and an excess of DMG that out competed the natural complexing matter present in the sample, making virtually all nickel labile. The sensitivity of the determination depends on the amount of the Ni $(DMG)_2$ adsorbed onto the electrode surface, which is controlled by the diffusion coefficient of the complex in the sample solution; the sensitivity may be increased by enhancing the deposition time (*11*, *14*). The reported method combines low maintenance costs with excellent sensitivity, good accuracy, and precision. Adsorptive stripping chronopotentiometry enables the determination of trace nickel concentrations without the need for any sample extraction procedure and preconcentration step, thus reducing the samples handling that may cause analyte loss or contamination.

MATERIALS AND METHODS

Reagents. All the reagents used were of analytical grade. The 10 mg/g Ni (II) certified standard solution (NIST 3136), 10%HNO_3, purchased from Promochem (Milan, Italy) was diluted with ultrapure water to obtain 0.05, 0.10, 0.25, 1.00, and 5.00 mg L^{-1} solutions. The 0.5 M ammonia buffer and the 0.05 M ethanolic solution of dimethylglioxime were obtained from Panreac (Barcellona, Spain). Sodium hydroxide (Baker J. T., Deventer, Holland) and hydrochloric acid (34−37%) (Panreac), were used to prepare 0.5 M aqueous solutions. The accuracy of the method described was tested with black tea certified reference matrix (NRMGBW 07605) purchased from Promochem. Saccharose standards solutions were prepared by dilution of extra-pure saccharose (Merk, Darmstadt, Germany). Ultrapure water (18.2 MΩ/cm) was prepared by a Pure Lab RO and a Pure Lab UV system (USF, Ransbach-Baumbach, Germany).

Samples. All the studied commercial beverages were purchased from a super market in September, 2003 and stored at 4°C until the analysis. Five samples of different glass-bottled Italian mineral water, five samples of glass bottled Coca Cola and five of canned Coca Cola, five samples of different tea and coffee, and six samples of different pure fruit juice were studied. Among the alcoholic beverages, five different bottled beers and the corresponding canned products, five samples of different Italian red wines and five of Italian white wines, five samples of different brandy, whiskeys, and vodkas were analyzed. A 3-g sample of dried tea and a 2-g sample of dried coffee were placed in a glass beaker, extracted in 100 mL and 250 mL of boiling ultrapure water, respectively, for 5 min, and filtered through filter paper.

Apparatus. Nickel (II) analyses were carried out on a PSA ION 3 potentiometric stripping analyzer (Steroglass, S. Martino in Campo, Perugia, Italy), which was controlled by NEOTES 2.0.1 software (Steroglass) run on an IBM-compatible personal computer. The working electrode was a glassy carbon electrode coated with a thin mercury film; an Ag/AgCl electrode (3M KCl) and a platinum wire were also used as the reference and the auxiliary electrode, respectively. A pH meter MI229 BDH equipped with glass + combination pH electrodes (BDH, Milan, Italy) was used to measure the pH values of the samples.

Adsorptive Chronopotentiometric Stripping Analysis of Commercial Beverages. After the plating of the working electrode (*12*−*15*), 2.0 mL of sample was put into the electrochemical cell together with 0.5 mL of 0.05 M DMG, 0.5 mL of 0.5 M ammonia buffer, and 17.4 mL of ultrapure water and deoxigenated by 10 min of nitrogen purging. Mineral water was not diluted. A 10.0-mL aliquot of sample, spiked with ammonia buffer and DMG, was analyzed. The Ni $(DMG)_2$ complex was preconcentrated onto the working electrode at the adsorption potential of −500 mV for 60 s, while the agitation speed was 1000 rpm, then the stirrer was stopped and the potential was scanned toward the final acquisition potential fixed at −1400 mV; the sampling time was 300 μs. The nickel stripping peak was registered around −1060 mV (**Figure 1**). The nickel peak may appear at less or more negative potential, according to the pH value of the aqueous sample and the presence of organic compounds. Quantitative analysis was executed by the multiple point standard additions method: optimum precision and accuracy were obtained by executing two additions of an appropriate volume of 2.5 mg L^{-1} Ni (II) standard solution to double the analyte concentration, and performing the measurements five times (*16*). Calibration curves with a correlation coefficient > 99.5% were obtained. The linear concentration range was 0−5000 μg L^{-1}.

Precision, Limits of Detection (LOD), and Limits of Quantification (LOQ). The instrumental precision was determined by six determinations, both on water and the certified black tea, and expressed as relative standard deviation of the measurements.

LOD and LOQ were calculated by the expressions $3\sigma/S$ and $10\sigma/S$, respectively (*17*). σ indicated the standard deviation of the response (set at 80 ms) obtained by 10 measurements on the standardized aqueous matrixes, and S (ms L μg^{-1}) was the sensitivity obtained from the slope of the calibration curve ($R^2 \geq 0.995$).

Effect of pH on the Stripping Potential and Sensitivity. The effect of pH in the presence of ammonia buffer on the stripping potential, sensitivity and accuracy of the determination were investigated both on water and certified black tea (ORM = organic reference matrix). The effect of pH on stripping potential and sensitivity was assessed by analyzing ammonia buffered standard solutions containing 70.0 μg L^{-1} Ni (II) and 0.50 mM of DMG and adjusting the pH in the range 6.5−11 by adding aliquots of HCl or Na (OH), 1 M (**Figure 2**).

Effect of Deposition Time, Deposition Potential, and Stripping Current. The effect of deposition time, deposition potential, and stripping current on the sensitivity of Ni (II) determination was valued analyzing a 70.0-μg L^{-1} Ni (II) aqueous standard solution, 0.5 mM DMG, and 0.01 M ammonia buffer (pH 9.5) in the range 30−660 s., (**Figure 3**).

Effect of Ligand Concentration. The effect of increasing DMG concentration on the analytical response and on the stripping potential was investigated both in water and tea reference matrix. The water reference used contained only Ni(II) as inorganic cation, whereas the certified tea was used as a model matrix, containing also several organic and inorganic species that may compete with Ni (II) and DMG, respectively, for the Ni $(DMG)_2$ complex formation, thus influencing the analytical response. The analysis were performed in 0.01 M (pH

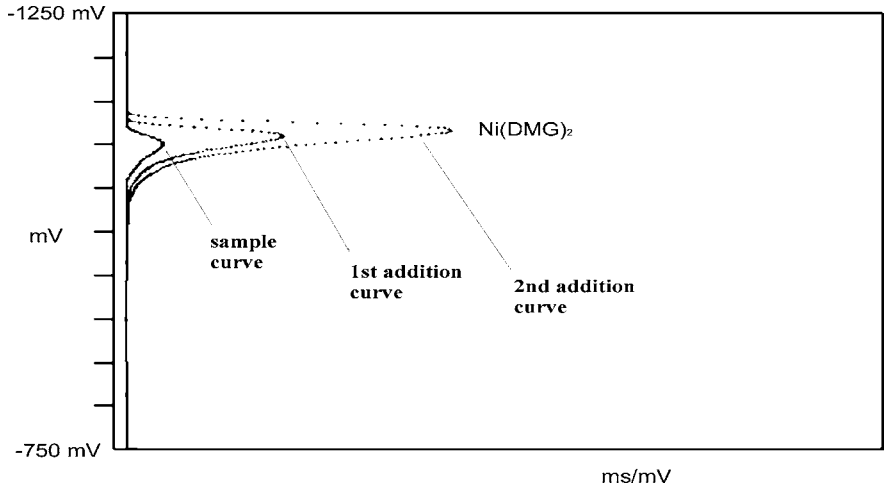

Figure 1. Ni (II) $(DMG)_2$ peak obtained from adsorptive stripping chronopotentiometric analysis of a 70.0-μg L^{-1} Ni (II) certified water, 0.01 M ammonia buffer (pH 9.5), 0.5 mM DMG; E_{dep}= –500 mV, t_{dep} = 60 s, I = –5 μA.

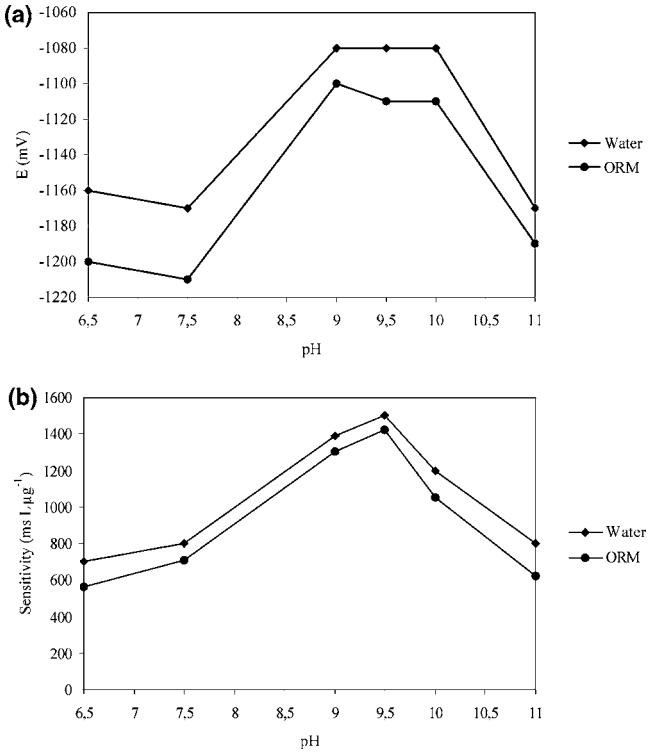

Figure 2. Dependence of Ni (II) $(DMG)_2$ (**a**) stripping potential and (**b**) sensitivity on pH, both for water and organic reference matrix (ORM).

9.5) ammonia buffered solutions containing 70.0 μg L^{-1} Ni (II) and increasing amounts of DMG; the deposition potential was −500 mV for 60 seconds, the cathodic current was −5 μA. The obtained results are illustrated in **Figure 4** .

Spike and Recovery Test. To confirm that a Ni (II) extraction procedure was not necessary and that Ni (II) loss did not occur during the electro-deposition step, spike and recovery tests were executed both on a 4600-μg Kg^{-1} Ni (II) certified black tea, and on different not certified beverages. The Ni (II) concentration originally present in the not certified commercial beverages was determined by the proposed method. Then, the samples were spiked at different levels with Ni (II) standard solution and analyzed by AdSCP using the electrochemical conditions described earlier. Both not spiked and spiked certified black tea solutions were analyzed by AdSCP, the obtained recoveries represent the accuracy of the proposed method. The results are given in **Table 1**.

Effect of Saccharose and Ethanol Concentration. The effect of saccharose and ethanol concentrations, present in many studied beverages, on nickel determination by AdSCP was studied on a 70.0-μg L^{-1}Ni (II) standard aqueous solution, 0.01M ammonia buffer and 0.5

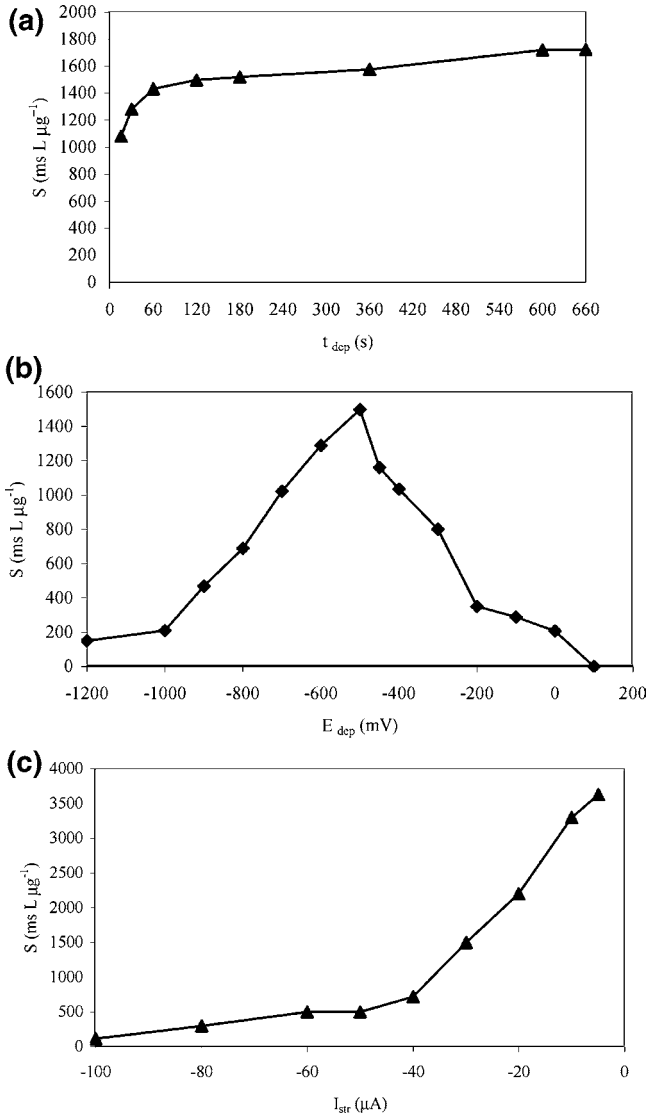

Figure 3. Dependence of sensitivity of Ni (II) analysis by AdSCP on (**a**) deposition time, E_{dep}= –500 mV, I = –5 μA; (**b**) deposition potential, t_{dep} = 60 s, I = –5 μA; (**c**) stripping current, E_{dep}= –500 mV, t_{dep} = 60 s, in a 70.0 μg L^{-1} Ni (II) standard water reference, 0.01 M ammonia buffer (pH 9.5), 0.5 mM DMG.

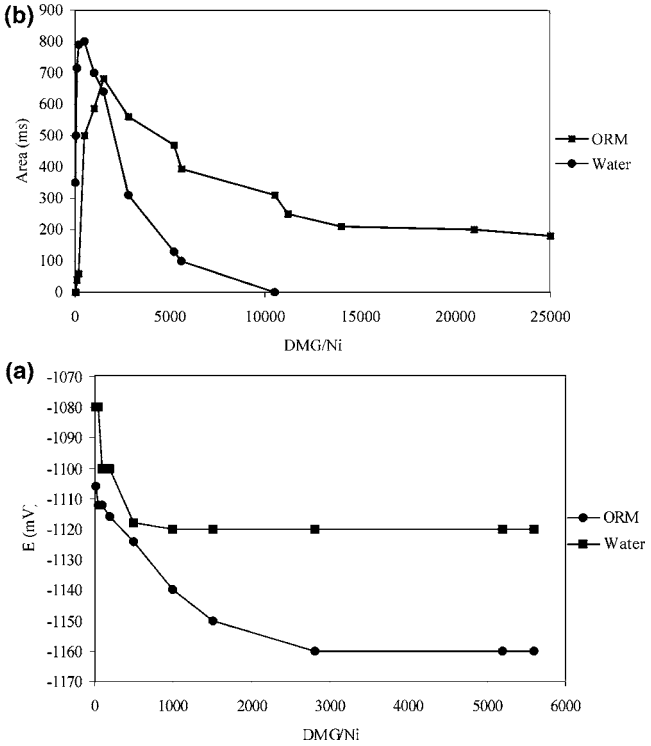

Figure 4. Influence of DMG to Ni (II) ratio on (**a***)* sensitivity and (**b***)* stripping potential both for water and organic reference matrix (ORM) at pH 9.5; $E_{dep} = -500$ mV, $t_{dep} = 60$ s, $I = -5$ μA.

Table 1. Spike and Recovery Test on Certified Black Tea and Other Not Certified Beverages[a]

	Ni μg L^{-1}	added μg L^{-1}	expected μg L^{-1}	found μg L^{-1}	mean recov %
certified tea	4600.0	0	4600.0	4370.1 ± 70.3	
	4600.0	2000.0	6600.0	6340.1 ± 100.2	95.5 ± 0.5
	4600.0	5000.0	9600.0	9120.4 ± 140.1	
pure orange	40.3	20.0	60.3	57.0 ± 0.7	
juice	40.3	40.0	80.3	77.2 ± 1.0	95.0 ± 1.0
	40.3	100.0	140.3	145.0 ± 1.7	
red wine	55.5	20.0	75.5	72.1 ± 1.1	
	55.5	50.0	105.5	100.2 ± 1.5	95.5 ± 1.0
	55.5	100.0	155.5	150.7 ± 2.4	
whisky	1.0	1.0	2.0	1.8 ± 0.04	
	1.0	4.0	5.0	4.8 ± 0.07	93.0 ± 3.0
	1.0	10.0	11.0	10.3 ± 0.15	

[a] The Ni (II) concentration originally present in the certified black tea was determined by ICP-MS. The recoveries obtained by AdSCP represent the accuracy of the proposed method. The Ni (II) concentration originally present in commercial orange juice, wine, and whisky was determined by AdSCP. Percent recovery values are the mean of four determinations. The analyses were performed in 0.01 M ammonia buffer (pH 9.5), 0.5 mM DMG solutions; $E_{dep} = -500$ MV, $t_{dep} = 60$ s, $I = -5$ μA.

mM DMG. The effect of saccharose was valued in the concentration range 0−800 g L^{-1} (**Figure 5**). Because ethanol caused the dissolution of the mercury film of the working electrode influencing the analytical response, the accuracy, sensitivity, and detection limits of Ni (II) determination were assessed in the concentration range 0−30% v/v. (**Table 2**).

RESULTS AND DISCUSSION

To gain further insight into Ni determination in aqueous matrixes by adsorptive stripping chronopotentiometry in the constant cathodic current mode, some important parameters such as pH, deposition time and potential, ligand concentration, and matrix effect were optimized.

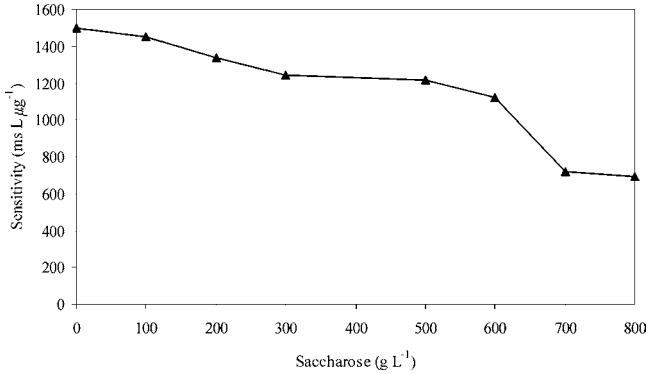

Figure 5. Effect of increasing saccharose concentration on sensitivity of Ni (II) determination by AdSCP in a 70.0 μg L^{-1} Ni (II) standard water reference, 0.01 M ammonia buffer (pH 9.5), 0.5 mM DMG; $E_{dep} = -500$ mV, $t_{dep} = 60$ s, $I = -5$ μA.

Table 2. Recovery Test from Alcoholic Solutions, Sensitivity of AdSCP Ni (II) Determinations and LOD[a]

ethanol % v/v.	Ni μg L^{-1}	found[b] μg L^{-1}	recov %	sensitivity ms μg L^{-1}	LOD μg L^{-1}
0	70.0	68.1 ± 1.2	97.2	1500	0.16
6.3	70.0	67.1 ± 1.2	95.8	1100	0.21
12.7	70.0	66.5 ± 1.1	98.0	625	0.38
20.0	70.0	66.8 ± 1.1	95.5	590	0.40
25.4	70.0	60.2 ± 1.0	86.0	300	0.80
30.0	70.0	51.3 ± 0.8	73.1	95	2.50

[a] Analyses were performed in 0.01 M ammonia buffer (pH 9.5), 0.5 mM DMG Solutions; $E_{dep} = -500$ MV, $t_{dep} = 60$ s, $I = -5$ μA. [b] Each value was the mean of three determinations.

Figure 2a shows that when the pH was increased from 6.5 to 11, slight variations of the stripping potential were observed in the range −1170 to −1080 mV in water and −1200 to −1100 in the certified black tea (ORM). The presence of organic compound in ORM caused the peak potential to be shifted toward more negative values with respect to water. The pH value of the sample significantly influenced the analytical response of Ni (II) determination, as its DMG complex presented the highest value at pH 9.5 (**Figure 2b**).

In a simplified manner, the proposed electrode reaction mechanism can be written as (*18*)

electrodeposition:

$$Ni(II)(DMG)_{2\ sol} + Hg^0 \rightarrow Ni(II)(DMG)_{2\ ads}\ (Hg^0)$$

cathodic stripping:

$$Ni(II)(DMG)_{2\ ads} + 2e^- \rightarrow Ni^0\ (DMG)_{2\ sol} + Hg^0$$

These electrodic reactions indicate that the analytical response of Ni (II) can be influenced remarkably by the choice of electrochemical parameters such as the deposition time, the deposition potential, and the stripping current. Many data were reported concerning the dependence of the sensitivity of the analysis on deposition time in electroanalytical stripping techniques (*9*, *14*, *18*, *19*). **Figure 3a** shows the influence of deposition time upon the chronopotentiometric stripping response, and the sensitivity (ms L μg^{-1}) was observed to linearly increase due to longer deposition time in the range 15−60 upon applying deposition time longer than 60 seconds. The sensitivity become almost independent of the deposition time, suggesting

a saturation of the electrode surface (*19*). The plot of the sensitivity versus deposition potential (**Figure 3b**) shows that the highest response for the adsorption of Ni(II) $(DMG)_2$ complex was observed at deposition potential of −500 mV. The decrease in the analytical response for potential more negative and more positive than −500 mV was due to preferential adsorption of water molecules and interfering ions, eventually present in the sample solution (*19*). **Figure 3c** provides evidence that the optimum sensitivity for Ni (II) response was achieved with the application of a stripping current of −5 μA; upon applicatio of a current more negative than −30 μA, the peak was shifted toward more negative values, and the resolution was not good. As a compromise between reasonable analysis time and sensitivity, a deposition time of 60 s, deposition potential of −500 mV, and a stripping current of −5 μA were selected as the most appropriate electrochemical parameters for further applications, obtaining LOD and LOQ of 0.16 μg L^{-1} and 0.53 μg L^{-1}, respectively, for both water and tea certified reference matrixes. The effect of increasing ligand concentration on the analytical response and on the stripping peak was investigated. **Figure 4a** shows that in the tea reference matrix (ORM) there is the need for an higher concentration of DMG with respect to the water sample to obtain the highest responses, which were observed at a DMG to Ni (II) ratio of 1500:500. The obtained results provided evidence that a high concentration of DMG in the ORM was needed to compete with the natural complexing matter, making virtually all Ni (II) labile. Peak potential was also found to shift toward more negative potentials with increasing ligand concentration, particularly in the ORM (**Figure 4b**). The effect of saccharose concentration on the analytical response of Ni (II) determination by AdSCP is illustrated in **Figure 5**. The analytical sensitivity was found to decrease by 3% in the presence of 100 g L^{-1} of saccharose, by 20% in the presence of 500 g L^{-1}, and by 54% in the presence of 800 g L^{-1}. This interference was likely due to the increase of solution viscosity with increasing sugar concentration, as the Fick law shows, resulting in a more difficult diffusion of the metal toward the electrode surfaces (the diffusion coefficient decreased) (*20*). Peak potential was also found to shift from −1090 mV to −1190 mV when sugar concentration was incerased from 0 to 800 g L^{-1}. The negative influence of saccharose on the analytical sensitivity was negligible for the beverage samples of this study, because their total sugars contents were in the range 0−100 g L^{-1} (*21*); however, this interference can be avoided by opportunely diluting the sample. The effect of ethanol concentration on the analytical response of Ni (II) determination by AdSCP is given in **Table 2**. Poor recoveries and a very low sensitivity were observed at ethanol concentrations higher than 20 % v/v. Therefore, beverages with a high alcoholic content, such as whisky and vodka (about 40%) and brandy (30 %), were diluted 2.0 times, as described earlier, to obtain 20 and 15% ethanolic solutions, respectively. In these conditions, recoveries within 95.5% and detection limits lower than 0.40 μg L−1 were achieved. The mean recoveries obtained from the not-spiked and from the spiked certified black tea (**Table 1**) demonstrated the good accuracy (95.5%) of the proposed method and confirmed that the extraction procedure was not necessary prior to the AdSCP analysis. Recoveries within 95.5 % were also obtained from the spiked commercial beverages.

Application. The content of Ni (II) was determined by AdCSP in 11 types of alcoholic and non-alcoholic commercial beverages. Five samples from different trademarks of each type of beverage were analyzed; **Table 3** illustrates the obtained nickel concentration ranges. Among the studied beverages, black tea was the richest source of nickel, followed by coffee. The concentrations found in black tea spanned from 1500 to 3700 μg L^{-1}; considering the mean content of 2400 ± 875 μg L^{-1} ($n = 5$), a daily assumption of more than 0.15 L of tea should exceed the TDI established for a 70 Kg b.w. adult (350.0 μg). Coffee samples showed an average nickel content of 204.4 ± 76.5 μg L^{-1} ($n = 5$), 12 times lower than that found in tea, with a maximum value of 300.5 μg L^{-1}. Pure fruit juices showed a nickel concentration range of 33.7−70.3 μg L^{-1}; particularly pineapple juices presented a higher mean content of Ni (II) (62.6 ± 6.9 μg L^{-1}, $n = 3$) with respect to orange juice (39.9 ± 4.9 μg L^{-1}, $n = 3$). Glass bottled and canned Coca Cola had very similar Ni (II) mean contents of 19.4 ± 2.2 μg L^{-1} ($n = 5$) and 17.0 ± 2.7 μg L^{-1} ($n = 5$), respectively. Even though Coca Cola is an acid beverage (pH < 3), the storage process does not influence the nickel content of the product. Among the studied non-alcoholic beverages, bottled mineral water showed the lowest mean content of nickel, 2.5 ± 2.0 μg L^{-1} ($n = 5$), confirming the literature data (*1*). Among the studied alcoholic beverages, significant differences were observed between fermented products (wine and beer) and distillated ones (brandy, whiskey, and vodka). Differences were also observed between red and white wines; the former showed a mean nickel content of 78.9 ± 21.5 μg L^{-1} ($n = 5$), the latter of 17.2 ± 3.5 μg L^{-1} ($n = 5$). Further studies concerning a larger number of red and white wine samples should confirm whether these differences are correlated to the nature of soil, grape variety, or the wine-making process. Bottled and canned beers showed similar nickel contents, respectively of 15.6 ± 3.7 μg L^{-1} ($n = 5$) and 18.3 ± 4.1 μg L^{-1} ($n=5$), respectively. Distillates contained very low amounts of Ni (II) (<1.0 μg L^{-1}).

Coca Cola and pure fruit juice are beverages abundantly consumed by young people. Considering the TDI of 150 μg for a 30 Kg b.w. child, according to this study, a 0.33-L can or bottle of Coca Cola or the same quantity of pure pineapple or orange fruit juice provides about 6.0 μg, 20.5 μg, and 13.0 μg of Ni (II), respectively, which represent, at maximum, 10% of the TDI. On the other hand, wine and beer are consumed by adults. Thus, considering the TDI of 350 μg, a 0.33-L can or bottle of beer or the same quantity of red or white wine provides about 5.6 μg, 26.0 μg, and 13.0 μg of Ni (II), respectively, which reaches, at maximum, 23.6% of the TDI. However, it is very

Table 3. Nickel Concentrations Range Found for Some Beverages[a]

beverage	sample no.	Ni (II) (μg L^{-1})
bottled mineral water	5	n.d.[b]–4.6
tea	5	1500–3700
coffee	5	100.0–300.5
bottled 100% pineapple juice	3	57.0–70.3
bottled 100% orange juice	3	33.7–43.3
bottled coca cola	5	17.0–22.9
canned coca cola	5	13.5–20.7
bottled red wine	5	55.5–105.0
bottled white wine	5	12.0–21.0
bottled beer	5	10.9–20.0
canned beer	5	12.6–23.4
brandy	5	n.d.[c]
whisky	5	n.d.[c]-*1.0*
vodka	5	n.d.[c]

[a] Five different samples of each beverage were analyzed, each analysis was performed in triplicate and the rsd% of the measurements was 1.5%. Analyses were performed in 0.01 M ammonia buffer (pH 9.5), 0.5 mM DMG solutions; E_{dep} = –500 mV, t_{dep} = 60 s, I = –5 μA. [b] n.d. = not detectable, <0.2 μg L^{-1}. [c] n.d. = not detectable, <0.4 μg L^{-1}.

difficult to correctly estimate the dietary assumption of Ni (II) because many toxicological studies demonstrated that the adsorption of ingested Ni (II) is lower when it is administered in food than when it is administered in water to fasted subjects (*1*, *22*−*24*).

This paper describes the use of adsorptive stripping chronopotentiometry for Ni (II) determination in alcoholic and non alcoholic commercial beverages without any sample pretreatment. The direct determination of Ni (II) was not affected by interference from the organic substances naturally present in beverages; the observed sensitivity decrease caused by saccharose and ethanol can be avoided by diluting the sample. Due to its accuracy, high sensitivity, short time of analysis, and low instrumental costs, AdSCP can be considered as a practical and valid technique for reliable nickel determination in commercial beverages and particularly prone for routine analysis. From the nutritional point of view, this paper provides some information about the Ni (II) content of worldwide consumed beverages: black tea presented the highest levels (> 1000 μg L^{-1}), followed by coffee. All the other non alcoholic and alcoholic studied beverages showed Ni (II) concentrations lower than 100 μg L^{-1}, and their correct consumption provides Ni (II) intakes much lower than the TDI.

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