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Speciation studies of nickel and chromium in wastewater from an electroplating plant

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Abstract

A speciation scheme involving the use of flame atomic absorption spectrometry (FAAS) and differential pulse adsorptive cathodic stripping voltammetry (DPAdCSV) techniques was applied to studies of nickel and chromium in wastewater from a nickel–chrome electroplating plant. Dimethylglyoxime (DMG) and diethylenetriaminepentaacetic acid (DTPA) were employed as complexing agents for adsorptive voltammetric determination of Ni and Cr, respectively. Cr(III) and Cr(VI) were determined by exploiting differences in their reactivity towards DTPA at HMDE. Total dissolved metal content was in the range 2906–3141 and 30.7–31.2 $\mathrm{mg\,l^{-1}}$ for Ni and Cr, respectively. A higher percentage of the metal was present as labile species (mean value of 67.9% for Ni and 79.8% for Cr) suggesting that strongly binding ligands are not ubiquitous in the sample. About 77.8% of Cr was found to exist in the higher oxidization state, Cr(IV). Results on effect of dilution on lability of the metal forms in the sample using DPAdCSV showed slight peak shifts to a more negative (cathodic) value by -0.036 V for Ni and -0.180 V for Cr with a dilution factor of 100, while peak intensity (cathodic current) remained fairly constant.

Keywords: Metal speciation; Labile forms; Electroplating plant wastewater; Adsorptive stripping voltammetry

1. Introduction

The occurrence of heavy metals in industrial wastewater is of interest because they are often present at significant levels and if discharged into surface waters can have severe effects on the environment and public health [1]. In addition, toxic levels inhibit biological processes with adverse effects on sewage treatment plants [1]. Some metals such as Cr are mobile in geological systems and can penetrate into the underground water aquifers [2]. Therefore, monitoring of levels of toxic metals and determination of their physicochemical forms is critical. It is now well known [3–5] that the toxicity, bioavailability, mobility, and other critical properties of elements depend on their speciation rather than their total concentrations only. The term speciation is understood to mean the occurrence of different chemical and/or physical forms or 'species' of an element in a sample. With reference to metals it is often useful to make a distinction between physical speciation (distribution among dissolved, colloidal or particulate forms) and chemical speciation (distribution among various distinct chemical species in solution including 'uncomplexed' and 'complexed' forms such as $NiCl_2$ and Ni–FA/HA complexes) [6]. Chemical speciation also includes the distinction between different oxidation states of an element, e.g. Cr(III) and Cr(VI) or As(III) and As(V). Thus speciation analysis is the process of identification and determination of different physical and/or chemical species in a sample. The most toxic forms are the free metal ions and the labile complexes, while the least toxic forms are the strongly bound metal complexes as well as metals adsorbed on colloidal particles [7].

This work is part of an environmental impact assessment study of the operations of small scale industries in Botswana. These industries include Ni–chrome electroplating plants utilizing nickel ($NiCl_2$, $NiSO_4$) and chromium salts ($CrCl_3$) as well as chromic acid (H_2CrO_4) and boric acid (H_3BO_3) as plating agents. The plant whose effluent was sampled for this work, has however complied with the guidelines for effluent discharges in Botswana [8] by constructing underground settling tanks lined with polyvinyl chloride (PVC) material to ensure there is no soakaway of the wastewater.

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The objective of our study was therefore to determine the composition of the labile forms of Ni and Cr in the wastewater. The labile forms of the metals in this study are defined as those electroactive species that are detectable by the cathodic stripping voltammetry (CSV). These labile species include hydroxo, chloro, sulphato, oxo as well as simple organic complexes from the organic cleaning agents used in the plating industry. Ni and Cr are both suspect carcinogens [9]. In addition, the properties of Cr(III) and Cr(VI) differ considerably in that while Cr(III) is an essential element, Cr(VI) is toxic [10,11].

Several analytical methods have been used in speciation studies of metals in water systems [3,12–15]. Electrochemical techniques are considered to be the most powerful methods [3]. In particular, anodic stripping voltammetry (ASV) is of interest due to its high sensitivity and selectivity. However, some metals such as Ni are not suitable for detection by ASV, and therefore, adsorptive stripping voltammetry (AdSV) becomes a method of resort [7] when used in combination with complexing agents, also making it possible to differentiate between the oxidation states of elements in some cases [16]. Our study utilized differential pulse adsorptive cathodic stripping voltammetry (DPAdCSV) with dimethylglyoxime (DMG) and diethylenetriaminepentaacetic acid (DTPA) as the complexing agents for the determination of the labile forms of both Ni (based on DMG) and Cr (based on DTPA) at a hanging mercury electrode (HMDE) [16–18]. Most studies using adsorptive voltammetry [7,16,18–20] have applied the technique to metal speciation investigations at trace levels. However, we demonstrate that this highly sensitive method albeit suitable for trace analysis, can also be successfully applied to wastewater analysis. With the DPAdCSV method, it was possible to distinguish between Cr(III) and Cr(VI) because the former forms a complex with DTPA that is electrochemically active but becomes inactive after 30 min, leaving Cr(VI) in solution uncomplexed [16–18]. To determine the total dissolved Ni and Cr, flame atomic absorption spectrophotometer (FAAS) has been used.

2. Experimental

2.1. Instrumentation

The determination of total dissolved metal after acid digestion of filtered samples was performed on a Varian Spectra AA 220 FS atomic absorption spectrometer (Varian, Australia) equipped with a deuterium background correction. The operational parameters are provided in Table 1. An electrochemical analyzer comprising of Autolab recorder (PGSTAT10, Ecochemie, Netherlands) and voltammetric stand (663 VA, Metrohm, Switzerland) was used for determination of labile forms of both Ni and Cr. A software (757 VA Computrace, Metrohm, Switzerland) running in a Dell Dimension V400 was used for data acquisition and manipulation. The voltammetric cell, 150 ml capacity (Metrohm, Switzerland) consisting of the normal three electrodes was employed. The working electrode was HMDE. A carbon rod and Ag/AgCl (saturated KCl_{aq}) auxiliary and reference electrodes, respectively, were used.

Table 1
FAAS instrumental parameters

	Parameters			
	Wavelength (nm)	Lamp current (mA)	Spectral band pass	Fuel composition
Ni	232.0	3.5	0.2	Air–acetylene
Cr	357.9	7.0	0.2	Air–acetylene

2.2. Reagents

Ultrapure water was obtained by passing tap water through a reverse osmosis system (Milli-Q water system, millipore). Nitric, perchloric and hydrochloric acids used in the digestion process were of spectral purity (Fluka, Switzerland). Other reagents (analar grade) used were: dimethyl glyoxime (SAARCHEM, South Africa), diethylenetriaminepentaacetic acid (Aldrich, USA), methanol (Aldrich, USA), ammonia, sodium acetate and sodium nitrate (SAACHEM, South Africa). Ni and Cr stock standards ($1000\,mg\,l^{-1}$) were purchased from SAACHEM, South Africa.

2.3. Sample collection

Wastewater samples were collected from the settling tank of a nickel–chrome electroplating plant in Gaborone, Botswana. The samples were put in plastic containers initially rinsed three times with the wastewater.

2.3.1. Total dissolved metal

The wastewater samples were filtered through a 0.45 μm membrane filter paper. An aliquot of the filtered sample (10 ml) was put into a 250 ml conical flask and digested with 5 ml mixture of concentrated nitric acid (65%) and perchloric acid (70%). When digestion was complete, 10 ml of 0.5 M HCl was added to redissolve the residue and the resultant solution filtered into a 50 ml volumetric flask. Ultrapure water was used to bring the volume to the mark. Total dissolved Ni and Cr were determined conventionally by FAAS.

2.3.2. Dissolved labile metal

Ammonia buffer was prepared by mixing 26 ml of conc. HCl (32%) and 44 ml of ammonia (25%) in a 100 ml volumetric flask. The volume was made up to 100 ml with ultra pure water. Fifty microliters of the sample (diluted 500 times with ultrapure water) was placed in a voltammetric cell containing 20 ml of ultrapure water, 50 μl of ammonia buffer and 10 μl of 0.1 M DMG in 95% methanol. The pH was adjusted to 9.2 ± 0.1 by addition of either NH_3 or HCl. After purging with nitrogen for 5 min, the DPAdCSV determination of Ni was accomplished under the following instrumental conditions:

Adsorption potential	−700 mV
Adsorption time	60 s
Equilibration period	10 s
Scan rate	6 mV s^{-1}
Step height	4 mV
Pulse height	50 mV
Starting potential	−0.7 V
End potential	−1.25 V

For Cr determination, a mixture containing sodium acetate (0.2 M), DTPA (0.05 M), and sodium nitrite (2.5 M) was used as the background electrolyte. The pH of the solution was adjusted to 6.2 ± 0.1 by addition of minimum amount of 30% NaOH in ultra pure water prior to analysis. Twenty milliliters of ultra pure water was put in the cell followed by 100 μl of the sample (diluted 10 times) and 5 ml of the background electrolyte. The pH of the resulting solution was adjusted by addition of sodium hydroxide solution (30%). N_2 was passed for 5 min and then Cr determined by DPAdCSV method. Total labile Cr was determined immediately after addition of DTPA. Cr(VI) was determined by delaying the analysis for 30 min to allow the Cr(III) complex to be converted into its electrochemically inactive form [16]. The instrumental settings were: pulse amplitude, −50 mV; voltage step time, 0.3 s; adsorption potential, −1.0 V; starting potential, −1.0 V; and end potential, −1.45 V. The effect of dilution on the composition of the labile metal forms in the wastewater samples was investigated by varying the dilution factor from 0 to 2000.

3. Results and discussion

The levels of total dissolved metal determined using FAAS after acid digestion were in the range 2906–3141 mg l^{-1} for Ni (Table 2) and 30.7–31.2 mg l^{-1} for Cr (Table 3), with percent relative standard deviations (%R.S.D.) of 1.3–2.8% and 3.5–6.4% for Ni and Cr, respectively. These levels compare well with other studies on similar effluents [21]. Results by DPAdCSV show peaks at −0.98 V for Ni (Fig. 1) and −1.26 V for Cr (Fig. 2) indicating a good resolution between metal peaks of −0.28 V (that is, $\Delta E > 0.1$ V). The peak values are in close agreement with those reported by other workers [18,20] using similar methods. Values for AdCSV-labile metal fractions were 1976–2148 mg l^{-1} for Ni (Table 2) and 23.5–26.4 mg l^{-1} for Cr (Table 3).

Table 2
Concentrations (FAAS for total metal and DPAdCSV for labile forms) of nickel in wastewater from electroplating plant

Sample identity	Total dissolved Ni (FAAS, mg l^{-1})	CSV-labile Ni (mg l^{-1})	Total labile fraction (%)
S1	2906 ± 38	2089 ± 6	71.9
S2	3054 ± 39	2147 ± 61	70.3
S3	3141 ± 78	2100 ± 101	66.8
S4	3116 ± 88	2121 ± 63	68.0
S5	3098 ± 65	1976 ± 76	63.8
S6	3088 ± 59	2051 ± 109	66.4

Although the complexation kinetics of nickel has been reported to be slow [22], the uptake of nickel by DMG is fast enough to complex all ‘free’ nickel in solution within a few minutes [23], especially when DMG is present in large excess as was the case in this work. AdCSV can detect kinetically fast components such as aqua species and other labile species. Thus the AdCSV values reported in this work represent the free hydrated metal ions as well as weakly bound metal (hydroxo, chloro, sulphato complexes, etc.) that undergo fast ligand exchange kinetics. Complexation between DTPA and Cr(III) is kinetically fast and spontaneous [16,18]. The Cr species determined immediately after addition of DTPA include, the free and weakly bound Cr(VI) and Cr(III). It should be noted that Cr(VI) does not form a complex with DTPA, but Cr(III) does. The Cr(III)–DTPA complex formed immediately after adding the ligand, is the electrochemically labile form. During the deposition stage, Cr(VI) is reduced to Cr(III) at the HMDE, which is then complexed by DTPA *in situ* giving electrochemically active complex [18]. The peak current recorded during the reduction of Cr(III) in the complexed form (with DTPA), is proportional to the concentration of the total labile Cr (III and VI) in the sample.

The percentage composition of CSV-labile fraction in the sample was obtained by expressing the CSV-labile values as a percentage of the total dissolved metal based on the FAAS values (Tables 2 and 3). The results show that a greater proportion of the metals exist in the labile forms (63.8–71.9% for Ni with %R.S.D. of 0.75–5.3; and 76.8–85.2% for Cr

Table 3
Concentrations (FAAS for total metal and DPAdCSV for labile forms) of chromium, Cr(III) and Cr(VI), in wastewater from electroplating plant

Sample identity	Total dissolve Cr (FAAS, mg l^{-1})	CSV-labile Cr (mg l^{-1})	CSV-labile Cr(VI) (mg l^{-1})	% CSV-labile Cr(VI)	% Total labile Cr
S1	30.7 ± 1.2	24.7 ± 1.7	20.7 ± 0.9	83.8	80.5
S2	31.2 ± 1.5	24.0 ± 1.1	18.3 ± 1.5	76.2	76.8
S3	31.0 ± 1.1	26.4 ± 2.3	21.2 ± 1.1	80.3	85.2
S4	31.0 ± 1.8	23.5 ± 1.1	16.1 ± 0.4	68.5	74.2
S5	30.8 ± 2.0	24.3 ± 1.4	21.3 ± 1.3	87.6	79.0
S6	31.1 ± 1.4	25.8 ± 1.6	18.1 ± 0.8	70.1	83.0

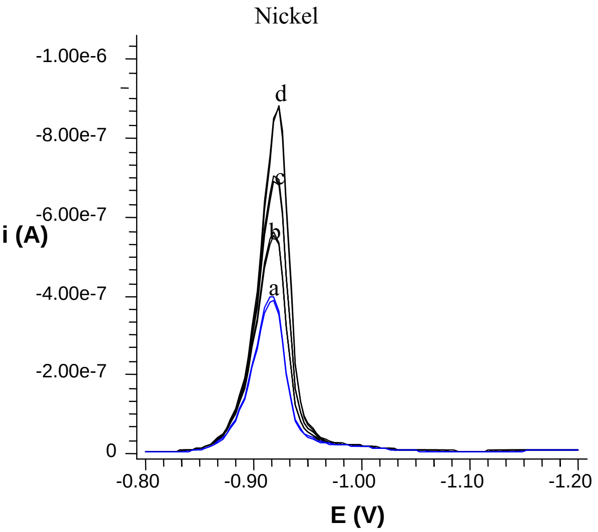

Fig. 1. DPAdCSV voltammogram of nickel at a HMDE: (a) sample peak; and (b–d) standard additions.

with %R.S.D. of 2.5–8.2). The high proportion of labile metal suggests that strongly binding ligands such as humic and fulvic acids are not ubiquitous in the wastewater samples unlike in freshwater systems where it has been reported that up to 99.9% of dissolved Ni is strongly bound to organic ligands [22]. Thus metals in the freshwater systems are strongly bound by organic compounds and hence exist largely as non-labile forms that are electrochemically inactive. The total labile metal reported in this work is likely to be predominantly in the form of free hydrated metal ions as well as chloro, hydroxo, amino, and sulphato complexes because of the use of ammonia, chloride, and sulfate salts as raw materials. The pale-green color of the samples shows that the aquo ion $[Ni(H_2O)]^{2+}$ and its derivatives dominate the chemistry of nickel in the wastewater. Stabilization of the free metal ions can be attributed to the acidic conditions in the samples (pH 5.1–5.3), owing to the use of acids during the plating process. Although the alkaline conditions (pH 9.2) employed in the voltammetric measurements are likely to cause hydrolysis and hence modify speciation in the original sample, nickel hydrolysis however is not extensive [24] and the time period elapsed during voltammetric measurements is not sufficient for new equilibria to be attained. In addition only the simple hydroxo complexes of nickel undergo relatively fast ligand exchange unlike their polynuclear counterparts, which can form only at high nickel concentrations [24]. The low pH of the samples (5.1–5.3), owing to the use of acids in the plating process, could also be playing a role in stabilizing the free metal ions. The fact that Ni undergoes slower ligand exchange reactions [24] relative to Cr is demonstrated by the fact that only 71.9% of Ni compared to 85.2% of Cr exists in the labile forms. The occurrence of non-labile fractions of the metals could be due to metal complexation with non-labile organic or inorganic materials in the cleaning agents such as “activax cleaner” used in the plant. Table 3 shows that both Cr(III) and Cr(VI) species are present in the sample. This arises from the use of chromic acid and Cr(III) salts as plating agents. However, most of the Cr exists as Cr(VI) (68.5–87.6%), which is an environmentally undesirable situation. Given the pH range of the wastewater samples coupled with the absence of strongly binding organic ligands, the expected dominant Cr(III) species are the aquo Cr(III) as well as its hydroxides namely, $Cr(OH)^{2+}$, $Cr(OH)_2{}^+$ including those for Cr(VI) namely, $CrO_4{}^{2-}$ and $Cr_2O_7{}^{2-}$ [20]. We note that, the change of sample pH (from 5.2 to 6.2) during voltammetric measurements may not significantly alter the speciation of chromium and in particular that of Cr(III) which exhibits slow hydrolysis kinetics [24]. The presence of labile-Cr(VI) in greater proportions (an average of 77.7%) raises environmental concerns due to its toxicity coupled with the generally high mobility of labile metal forms in the environment. In view of the relatively high levels of Cr(VI) in the wastewater, our study recommends pre-treatment of the wastewater to reduce Cr(VI) to Cr(III) before disposal.

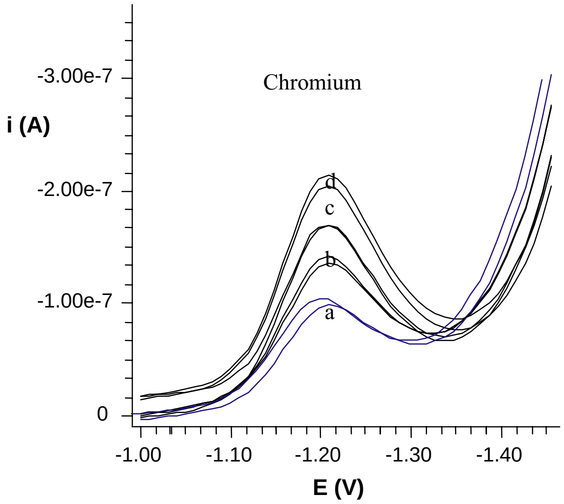

Fig. 2. DPAdCSV voltammogram of chromium, Cr(III) at a HMDE: (a) sample peak; and (b–d) standard additions.

Results (Fig. 3) obtained from the investigation of the effect of sample dilution on the lability of metal forms showed that the cathodic peak potentials shifted to more negative values by −0.036 V for Ni and −0.18 V for Cr with dilution (up to a factor of 100) at fairly constant peak intensity. However, above a dilution factor of 100 and up to 2000, there was minimal peak shift (±0.005 V). The implication to environmental samples is that at trace metal concentrations, a predominant labile metal species (i.e. electrochemically active) that is relatively stable exists. The observation that dilution had minimal effect on peak current intensities implies that the overall percentage lability remains fairly constant in dilute samples. In order to understand the implications of the electrochemical behavior (i.e. shifts in peak potentials and variation in peak current intensities) on the dynamics of environmental pollution, the following suggestions are made. The shifts in peak po-

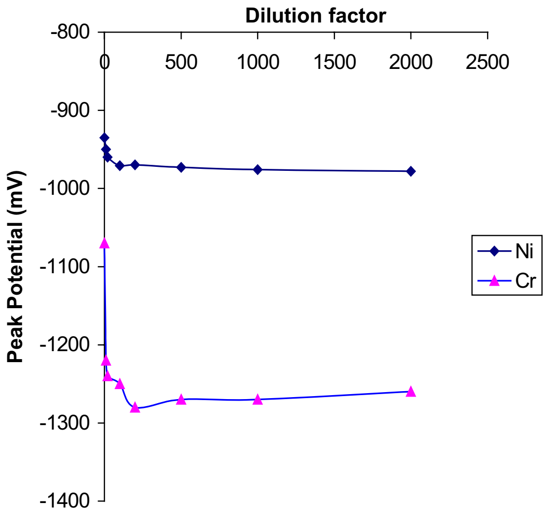

Fig. 3. Effect of wastewater sample dilution—plot of peak potentials of Ni (◆) and Cr (▲) versus dilution factor using DPAdCSV.

tentials with dilution can be attributed to, firstly, possible changes in metal speciation upon dilution. For instance, at higher concentrations (>0.1 M) hydrolysis products such as $[Ni(H_2O)_5OH]^{+}$, $[Ni(H_2O)(OH)_3]^{-}$, $[Ni(OH)6]4^{-}$, $[Ni_4(OH)_4]^{4+}$, $[Cr(H_2O)_5OH]^{2+}$, $[Cr(H_2O)_4(OH)_2]^{+}$, $[Cr_4(OH)_6]^{6+}$, etc. may be present [25]. The hydroxide species, particularly polynuclear complexes, undergo very slow ligand exchange reaction owing to their slow dissociation. In the diluted samples the aquo species, $[Ni(H_2O)_6]^{2+}$ and $[Cr(H_2O)_6]^{3+}$, as well as the oxo anions of Cr(VI), $CrO_4{}^{2-}$ and $Cr_2O_7{}^{2-}$ predominate to a large extend and undergo fast ligand exchange reactions. Secondly, the effect of dilution could be explained by changes in the ratio of the concentration of supporting electrolyte to that of the analyte. Thus, in voltammetric analysis, a large excess of the supporting electrolyte to analyte (usually a ratio greater than 10) is desirable to eliminate migration as a mode of mass transport of analyte species to the electrode surface [26]. Changes in the composition and concentration of supporting electrolyte and hence ionic strength, have been shown to affect currents as well as peak potentials in voltammetric analysis [26]. In our study, we suspect that during the analysis of undiluted samples, the ratio of supporting electrolyte to analyte may have been less than the recommended value of 10. This may have led to the observed changes in peak characteristics of the electroactive analyte during the dilution experiments. Thirdly, incomplete metal complexation as a result of insufficient ligand concentration, may also explain the observed changes in peak characteristics. In order to promote fast ligand exchange kinetics and formation of stable complexes, it is important that the stoichiometric ratio of ligand to metal ion concentration be high [26]. This may have not been the case with the undiluted wastewater samples during the measurements of stripping potentials. In such a case, not all the metal ions present in the sample are complexed by the added reagent (DMG for Ni and DTPA for Cr). Therefore, the presence of “uncomplexed” nickel and chromium, presumably the aqua forms, might have contributed to observed changes in potentials with sample dilution. The reduction of the metal aquo species occurs at cathodic potential values different from those of their respective DMG and DTPA complexes. Considering the overall shifts in peak potentials (for dilution factor from 0 to 2000) for the two metals, we note that the changes in speciation upon dilution were less significant for Ni which showed potential shift of about 4.5% compared to Cr with 19.6%. However, for dilution factor between 100 and 2000, the shifts were not significant for both metals, as potential shifts of less than 5% (0.7% for Ni and 2.8% for Cr) were observed. Comparing the two metals with respect to effect of dilution, we note that chromium showed a significant change in speciation. This may be explained by the difference in the hydrolysis chemistry for the two metals. Thus Cr ions exhibit two dominant oxidation states (III and VI) compared to only one oxidation state (II) for Ni ions. These observations do have implications on environmental pollution when dynamic physicochemical changes are considered.

Analyzing the FAAS and DPAdCSV results, we report that the former has higher values than the latter. This, as expected, is due to the fact that acid digestion releases the fraction of the metal that is bound or adsorbed to inorganic or organic particles. The FAAS values therefore refer to the sum of all the various physicochemical forms of the dissolved metal whereas the DPAdCSV represents the weakly bound (electrochemically active) labile forms. We note that, ideally UV-digestion [27] should be employed to enable total metal determination by voltammetry, hence provide a level ground for comparison between FAAS and DPAdCSV. However, we regret that this facility was not available in our laboratory. UV-digestion is particularly important for analysis of natural waters where organic ligands play a major role in metal complexing [28]. Thus most studies on adsorptive voltammetry have applied the technique to metal speciation investigations at trace levels [7,16,18–20]. In this work we demonstrate that this highly sensitive method albeit suitable for trace analysis, can also be successfully applied to wastewater analysis.

4. Conclusions

Results obtained in this study show that most of the dissolved metals were found to exist in labile forms for both metals (average of 67.9% Ni and 79.8% Cr). This could be attributed to both the low pH of the sample and the fact that the wastewater is not rich in strongly binding ligands such as humic substances usually found in freshwater systems. A high percentage of the labile fraction is of environmental concern since these species are generally more mobile in the environment and also more toxic to organisms. We note that, the wastewater samples contain significantly high levels of both metals that exceed the Botswana Bureau of Standards [8] and WHO [29] guidelines for wastewater and thus recommend pre-treatment of the effluent prior to its final disposal. The two techniques used (FAAS and DPAdCSV) are complementary tools for determination of metal speciation, particularly in wastewaters containing elevated levels of metals where the distinction between labile and non-labile fractions may be sufficient reason for environmental impact assessment of wastes. In this study, we have demonstrated that DPAdCSV even though useful particularly for analysis of natural waters where metals occur in trace levels, can also be applied for the analysis of wastewater containing high levels of metals, if factors such as pH, ionic strength, and dilution effect are taken into account during the potential measurements.

References

[1] International Programme on Chemical safety (IPCS), Environmental Health Criteria 61: Chromium, WHO, Geneva, 1988.
[2] D. Oktavec, J. Lehotay, E. Hornackova, At. Spectrosc. 16 (1995) 92.
[3] T.M. Florence, Analyst 111 (1986) 489.
[4] M. Scoullos, A. Pavlidou, Croat. Chim. Acta 70 (1997) 299.
[5] E. Lores, J. Penncock, Chemosphere 37 (1998) 861.
[6] M.R. Twiss, O. Errécalde, C. Fortin, P.G.C. Campbell, C. Jumarie, F. Denizeau, E. Becrkelaar, B. Hale, K. van Rees, Guidelines for Studies of Metal Bioavailability and Toxicity—Why Metal Speciation should be Considered and How? Canadian Network of Toxicology Centres (CNTC), Metal Speciation Team, 2000.
[7] A.W. Bott, Curr. Sep. 14 (1) (1995) 24–30.
[8] Department of Water Affairs, Guidelines for Effluent Discharges, Botswana, 1992.
[9] S. Langard, T. Norseth, Handbook on the Toxicology of Metals, Elsevier, Amsterdam, 1979, p. 383.
[10] O. Domínguez, M.J. Arcos, Anal. Chim. Acta 470 (2002) 241.
[11] D.T. Gjerde, D.R. Wiederin, F.G. Smith, B.M. Mahson, J. Chromatogr. A 640 (1993) 73.
[12] M. Hiraide, T. Ueda, A. Mizuike, Anal. Chim. Acta 227 (1989) 421.
[13] M. Soylak, L. Elci, Int. J. Environ. Anal. Chem. 66 (1997) 51.
[14] S. Tokalioglu, S. Kartal, L. Elci, Anal. Sci. 16 (2000) 1169.
[15] T.M. Florence, G.E. Batley, CRC Crit. Rev. Anal. Chem. 9 (1980) 219.
[16] J. Golimowski, P. Valenta, H.W. Nürnberg, Fresenius J. Anal. Chem. 322 (1985) 315.
[17] J.A. Herrera-Melián, J.M. Doña-Rodríguez, J. Hernández-Brito, J. Pérez-Peña, J. Chem. Educ. 74 (12) (1997) 1444.
[18] Metrohm Application Bulletin No. 116/2e, Metrohm Ltd., Herisau, Switzerland.
[19] S.B. Adeloju, A. Hadjichari, Anal. Sci. 15 (1999) 95.
[20] Y. Li, H. Xue, Anal. Chim. Acta 448 (2001) 121.
[21] H.D. Revanasiddappa, T.N.K. Kumar, J. Anal. Chem. 56 (12) (2001) 1084.
[22] H.B. Xue, S. Jansen, A. Prash, L. Sigg, Environ. Sci. Technol. 35 (2001) 539.
[23] M. Lam, J. Murimboh, N.M. Hassan, C.L. Chakrabarti, Anal. Chim. Acta 402 (1999) 195.
[24] D.T. Richens, The Chemistry of Aqua Ions, John Wiley & Sons Publications, New York, 1997, p. 491.
[25] J.C. Myland, K.B. Oldham, J. Electroanal. Chem. 347 (1993) 49.
[26] K.B. Oldham, J.C. Myland, Fundamentals of Electrochemical Science, Academic Press, CA, 1994.
[27] M. Kolb, P. Rach, J. Schafer, A. Wild, Fresenius J. Anal. Chem. 342 (1992) 341.
[28] J.H. Reuter, E.M. Perdue, Geochim. Cosmochim. Acta 41 (1977) 325.
[29] WHO, Guideline for Raw-Water Quality, Geneva, vol. 12, 1971, pp. 1084–1988.