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On the lability of dissolved Cu, Pb and Zn in freshwater: Optimization and application to the Deûle (France)

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ABSTRACT

A procedure to determine lead and zinc by anodic stripping voltammetry and copper by cathodic stripping voltammetry in natural river samples was developed and validated. Cu determination involves the adsorption of Cu complexes with 8-hydroxyquinoline (oxine) onto a hanging mercury drop electrode. All samples were studied at natural pH and following optimal conditions were found: an accumulation step at −1.3 V (all potential values in the paper are given versus the Ag/AgCl, [KCl] = 3 M reference electrode) during 30 s for determination of Zn contents and at −0.7 V during 60 s for determination of Pb contents. Concerning Cu analysis, the optimal oxine concentration was found to be 10^{-5} M with a deposition potential of −1.1 V during 30 s followed by an adsorption step at −0.25 V during 15 s. This procedure was afterwards validated by using certified reference freshwater and performing an intercalibration exercise. Finally the method was successfully applied in the Deûle River, highly contaminated by dissolved Zn and to a lesser extent by Pb and Cu, due to past and present activities of metallurgical plants. Under these optimal conditions, metal concentrations measured by our voltammetric procedures in the Deûle River were found in the range 12.4–23.2 nM for Zn, 1.7–3.2 nM for Pb and 4.9–7.6 nM for Cu.

1. Introduction

The bioavailability and toxicity of dissolved trace metals in natural waters (the colloidal and particulate phases are by far less harmful [1,2]) are depending on their chemical speciation which is partly controlled by interactions with organic ligands (especially in freshwaters). Some studies showed indeed that metals such as Cu, Pb or Zn tend to be partially or fully complexed by organic matter reducing their bioavailability and toxicity [3–5].

Among speciation techniques like ion-selective electrodes [6], diffusive gradients in thin film (DGT) [7], permeation liquid membrane (PLM) [8] or Donnan-membrane technique (DMT) [9], anodic stripping voltammetry (ASV) is an attractive alternative method permitting high sensitivity, multielement quantification and a low risk of sample contamination during analysis. During ASV analysis, the analyte is accumulated in the liquid drop or film by reduction and amalgation with Hg. This step of deposition is followed by a voltammetric scan towards more positive potentials during which the metal is re-oxidized. When trace metals cannot be determined using a classical anodic stripping procedure (ASV) mainly due to a high organic matter/metal ratio and/or ultra low concentrations, adsorptive cathodic stripping voltammetry (AdCSV) can be used as a reliable and sensitive method. After addition of a specific ligand metal complexes that are able to interact with the mercury drop are formed. In CSV analysis, an adsorption potential slightly more positive than the reduction potential of the metal–ligand complex is chosen [10,11] and the voltammetric scan is conducted towards more negative potentials. In this paper, we opted for 8-hydroxyquinoline (oxine) as the Cu complexing ligand [12] but in the literature several other ligands such as catechol [13], salicylaldoxime [14] or tropolone [15] have been reported for Cu determination using CSV. However, these latter are, according to the literature, less stable as a function of time especially cathecol which is known for its instability against oxidation by dissolved oxygen [12,14]. Furthermore, in preliminary experiments, oxine has been tested to detect other metals such as Cd because the speciation of this metal in addition to the one of copper enters in the framework of TIMOTHY project (Tracing and integrated modeling of natural and anthropogenic effects on hydrosystems: the Scheldt river basin and adjacent coastal North Sea). Oxine is known to be a ligand allowing the detection of several metals such as Pb, Cd, Zn and Mo [12,16] in a single scan while salicylaldoxime is only specific to Cu.

In the present work differential pulse anodic and cathodic stripping voltammetry methods, DPASV and DPCSV, respectively, are described to assess electrolabile Zn, Pb and Cu concentrations in

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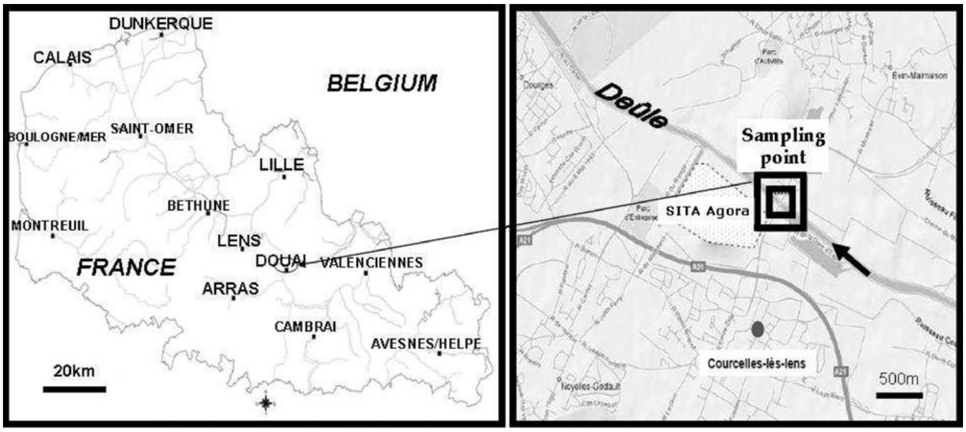

Fig. 1. Location of the sampling area.

a polluted river, the Deûle canal located in northern France. These metals are present at different total dissolved concentrations in this river being necessary a modification of previously reported stripping method procedures in order to obtain reproducible and fast results on the sample without any preliminary dilution or tedious pre-treatment at natural pH.

2. Materials and methods

2.1. Location and sampling

The Deûle River is located in the Scheldt basin and is one of the main tributaries of the Leie River. It is also connected via the Spiere canal with the Upper-Scheldt River. The former smelter Metaleurop located near Douai (a city in northern France) was one of the major metallurgical industries in the area and has strongly impacted the river from 1894 to 2003 by lead and zinc discharges.

Metaleurop was a European leader for the production of metals such as Pb and Zn with a typical value of 150,000 and 100,000 tons per year respectively which corresponds to 2/3 for Pb and 1/3 for Zn of the national production of France [17]. Metaleurop has caused a large pollution of its surroundings, particularly soils, shallow groundwaters, and also the Deûle canal, in which lead and zinc sulphide ores and slags were inadvertently directly discharged [18,19]. Since 2003, Metaleurop was closed down and Sita France (Suez Environnement) via the AGORA project is decontaminating the area and is installing eco-industries involved in waste recovery at the site.

Water samples from the Deûle River were collected from the river bank at the Metaleurop area close to the former discharge point of the factory (50°25′ N/03°01′ E) (Fig. 1) by using a telescopic sampling system on which was fixed a high density plastic container. Prior to use, it was cleaned with 2% nitric acid (Suprapur, Merck) and rinsed several times with Milli-Q water prior to use. The container was held in the river at about 50 cm below the water surface and while the first water sample was used to rinse the container, the second one was transferred to 1 L clean polyethylene bottles. Immediately after, water was filtrated in the field with a decontaminated 20 mL syringe through a clean 0.45 μm cellulose acetate filter (Millipore) under pressure; filtrates were collected in 30 mL clean polyethylene bottles. In order to check the risk of contamination, 20 mL of Milli-Q water was also filtrated in the field with the same procedure. The results showed no increase of metal concentrations in the filtrate of Milli-Q water sample.

Samples serving for total metal dissolved analysis with ICP-MS were acidified with 1% nitric acid; samples serving for analysis of the labile metal fraction were kept at natural pH and analyzed within maximum 2 days to avoid the redistribution of metal species in the solution. All samples were transported to the laboratory and stored at 4 °C.

2.2. Experimental

2.2.1. Reagents

All solutions were prepared with deionised water (Milli-Q, Millipore, 18.2 MΩ cm) and all reagents (NaOH, HNO_3, KCl) used were of analytical grade (Merck).

Standard solutions of copper, lead and zinc were prepared by dilutions of a stock solution of 1000 mg L^{-1} (Spectrosol grade, Merck) in 2% HNO_3. A stock solution of 0.01 M of 8-hydroxyquinoline (oxine) ligand (Analar grade, Merck) was prepared in 0.15 M HCl. Fresh standard solutions were prepared daily for metals and weekly for oxine.

A pH buffer stock solution of pH 7.9 was prepared by mixing 1 M boric acid (Analar grade, Merck) and 0.25 M NaOH. 200 μL of the buffer solution were added to 20 mL of each Deûle sample keeping approximately the initial value of the pH in the solution (pH around 8) constant.

2.2.2. Apparatus

Voltammetric measurements were performed using a 663 VA stand (Metrohm, Switzerland) equipped with electrodes, a μAutolab III potentiostat and GPES 4.9 software. A hanging mercury drop electrode (HMDE) with a surface of 0.52 mm^2 (size 3) was used as a working electrode. The potential was measured against a Ag/AgCl, KCl = 3 M reference electrode (E = +0.208 V vs. NHE at 25 °C) and a glassy carbon rod was used as counter electrode.

pH values were measured with a WTW 330i pH meter by using a combined glass electrode with a Ag/AgCl [KCl] = 3 M reference electrode. The calibration of the electrode was performed each time with 2 buffer solutions (WTW) at pH 7 and 10.

HR-ICP-MS measurements (Thermo Finnigan Element II) were carried out to determine the total dissolved metal concentrations in the previously filtrated samples at 0.45 μm and acidified at pH ~2 with 1 M suprapur nitric acid solution (Merck); 1 ppb of indium was used as internal standard. For a multi-element analysis, three standards were necessary to carry out an external calibration (XIII from Merck, ICM-224 and SM70 from Radion). The detection limits of this apparatus were 0.1 nM for Pb and 0.01 nM for Cu and Zn in the high resolution mode.

2.2.3. General procedure

The term “electrolabile” is used in this paper to define the amount of metal reduced at the electrode at natural pH and at a specified deposition potential. Concerning copper that is measured by DPCSV, even if oxine is a quite strong ligand for it, a fraction of the Cu burden parent may still remain associated with even stronger ligands as described hereafter in Section 3. As a consequence the term “L-electrolabile” (where L means the oxine Ligand) will be preferred to define the copper concentration estimated by DPCSV since the initial speciation in the sample has been modified.

All trace metal concentrations were measured in the same filtered sample solution. Prior to the measurement, dissolved oxygen was removed by purging the solution with nitrogen for 10 min and for an additional 20 s before each scan.

The DPASV procedure to determine electrolabile lead and zinc concentrations was adapted from Duinker and Kramer [20] and more recently from Cukrov et al. [21] in the Krka River. A 20 mL aliquot of the filtered sample was pipetted into the voltammetric cell and 200 μL of 1 M borate buffer were added. After the mercury drop has been formed, the potential was set to −1.3 V for 30 s for Zn and to −0.7 V for 60 s for Pb while the solution was stirred at 1500 min^{-1}. After a rest period of 5 s, the stripping step occurred in positive direction. After the electroactive species accumulation at the mercury drop electrode the differential pulse ramp employed for the redissolution process was used with the following parameters: a pulse amplitude of 20 mV, a potential step increment of 2 mV, a time between pulses of 0.1 s and a pulse duration of 0.04 s.

The procedure to determine the L-electrolabile copper concentration by DPCSV (Differential Pulse Cathodic Stripping Voltammetry) was adapted from the method developed by van den Berg [12]. In addition to the 200 μL of 1 M borate buffer solution (see the determination of Pb and Zn), 20 μL of 0.01 M oxine solution were added to 20 mL of filtered sample. This solution was then allowed to equilibrate for 24 h to achieve a new thermodynamic equilibrium previously disturbed by the ligand addition. After this rest period, the solution was transferred into the voltammetric cell and purged with nitrogen. The voltammetric cell potential was set to −1.1 V for 30 s while stirring at 1500 min^{-1}. The potential was in a second phase switched to −0.25 V during 15 s in a quiescent solution before starting the cathodic scan from −0.25 V down to −0.9 V by using the differential pulse method described previously. Note that the first step at −1.1 V permits to avoid some interferences [12]. Afterwards, when the potential is switched to −0.25 V, all copper reduced during the first step is reoxidized and complexed again with oxine onto the mercury drop electrode.

In order to determine the electrolabile Pb and Zn concentrations by DPASV that includes the free hydrated cations and weak organic and inorganic complexes in equilibrium with non-electrolabile organically complexed metal, titration of a Deûle river sample has been carried out with Zn or Pb additions. The theory used is analogous to that described by [22] for Zn speciation in the North Pacific. With this technique, the concentration of the electrolabile fraction [Me]labile corresponds to

$$[\text{Me}]\text{labile} = \frac{i_\text{p}}{S} \quad (1)$$

where i_p is the metal reduction peak current (A) in the sample and S the slope (A mol^{-1}) of the linear portion of the metal titration curve where the added metal is supposed not to be complexed anymore with the “strong” (also called “non electroactive”) complexing organic ligands.

With the DPCSV method, the added oxine ligand and naturally occuring organic ligands enter in competition. The concentration of electrolabile copper [Cu]labile corresponds approximately to:

$$[\text{Cu}]\text{labile} = [\text{Cu'}] + [\text{Cu–oxine}] \quad (2)$$

where [Cu′] is the remaining concentration of inorganic copper and [Cu–oxine] the concentration of copper complexed by oxine. With this technique, the labile copper concentration is equal to the ratio of the copper reduction peak current (A) by the sensitivity S (A mol^{-1}) of the Cu–oxine titration curve [23].

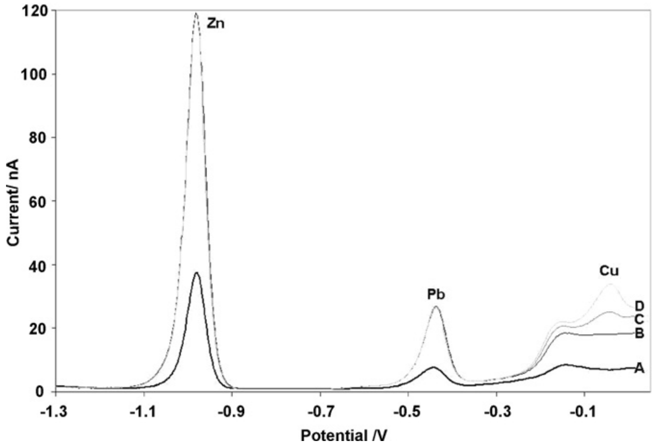

Fig. 2. Typical differential pulse anodic stripping voltammogram obtained from Deûle river sample containing (A) 2.0 nM of Pb, 17.2 nM of Zn and 6 nM of Cu with $E_\text{dep} = -1.3$ V, $t_\text{dep} = 60$ s, (B) the same sample than in (A) with $E_\text{dep} = -1.3$ V, $t_\text{dep} = 300$ s, (C) the same sample than in A with addition of 31.5 nM of Cu ($E_\text{dep} = -1.3$ V, $t_\text{dep} = 300$ s) and (D) the same sample than in A with addition of 63 nM of Cu ($E_\text{dep} = -1.3$ V, $t_\text{dep} = 300$ s). All samples contain borate buffer as supporting electrolyte (pH 7.9). The other parameters relative to the electrochemical analysis are mentioned in Section 2.

3. Results and discussion

3.1. Electrochemical responses

Preliminary measurements have been carried out to check the possibility to determine Zn, Pb and Cu concentrations in Deûle river samples by differential pulse anodic stripping voltammetry (DPASV) in the presence of only a borate buffer. At natural pH, Zn, Pb and Cu peaks are respectively detected at −0.98 V, −0.45 V and −0.04 V (Fig. 2). It appeared that in these samples Pb and Zn concentrations could be easily detected with DPASV but it was obviously not the case for Cu, where a signal of Cu redissolution should have appeared at −0.04 V. This redissolution potential was clearly revealed after Cu(II) standard addition in a Deûle river sample.

Longer deposition times were explored to improve the detection of Cu by DPASV in Deûle samples at natural pH; a small peak sometimes appears (depending on the Cu sample concentration) for a deposition time of 300 s but it is only from 600 s or higher deposition times that the method starts to be sensitive enough. However, due to the weak signal and the presence of high dissolved organic matter content in the river (5–20 mg L^{-1} [24,25]) compared to the concentration of copper, replicates were not reproducible and the relative standard variation was very high. In these conditions a reproducible method for copper by using differential pulse cathodic stripping voltammetry (DPCSV) with oxine as added ligand was selected, optimized and finally validated for our samples.

Oxine is an organic ligand containing an aromatic ring structure with N and O donors. Ligand adsorption onto the HMDE is influenced by effects such as electrostatic or π–electron interactions [26,27]. Oxine forms 2 complexes with copper according 1:1 and 1:2 stoichiometries; reactions are expressed as:

$$\text{Cu}^{2+} + \text{OxH} \leftrightarrows \text{CuOx}^{+} + \text{H}^{+} \quad (3)$$

$$\text{CuOx}^{+} + \text{OxH} \leftrightarrows \text{CuOx}_2 + \text{H}^{+} \quad (4)$$

In presence of a large excess of oxine, Garay et al. [28] have used calculations based on Laplace transforms to assume that a two-electron quasi-reversible process was involved. In buffered

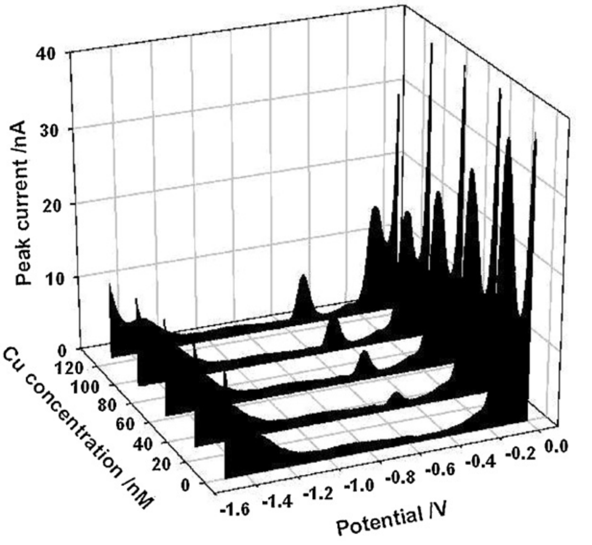

Fig. 3. DPCS voltammograms of deionised water with 0.01 M borate buffer obtained with 1×10^{-5} M oxine in presence of 0, 31.5, 63, 94.5 and 126 nM Cu. Experimental parameters were: $E_{\mathrm{acc}} = -1.1$ V; $t_{\mathrm{acc}} = 30$ s; $E_{\mathrm{ads}} = -0.25$ V; $t_{\mathrm{ads}} = 15$ s.

solution, they assumed that the peak detected at −0.48 V corresponds to the electroreduction (there is a direct transfer of two electrons [28]) of $\mathrm{Cu(Ox)_2}$ following this equation:

$$\mathrm{Cu(Ox)_{2\,(sol)}} \leftrightarrow \mathrm{Cu(Ox)_{2\,(ad)}} + 2e^- \leftrightarrow \mathrm{Cu(Hg)} + 2\mathrm{Ox}^-_{\mathrm{(sol)}} \tag{5}$$

This study also showed a predominance for $\mathrm{CuOx_2}$ at pH > 4 under equilibrium conditions.

Two free oxine peaks have been detected at −0.13 V and −1.27 V in Milli-Q water solution containing 0.01 M borate buffer (Fig. 3). This suggests that 2 redox couples are involved. Beltagi et al. [29] explain the peak at −1.27 V as a reduction of the N=C double bond of the pyridine ring. Metal chelation is established through the nitrogen and phenolic oxygen atoms of oxine [27]. The second peak at −0.13 V can be related to the quinoline group reduction of the ligand involved in the complexation permitting the detection of Cu. A decrease of the oxine peak at −0.13 V is confirmed by Cu additions (Fig. 3). Additionally, Abollino et al. [27] showed that the quinoline reduction was pH dependent. Between pH 8 and 9 this reduction could vary from −0.10 to −0.26 V.

The cathodic peak of Cu(II)-oxine appears at −0.5 V in Milli-Q water sample (Fig. 3) and at −0.43 V in a Deûle river sample because Cu(II)–oxine is more difficult to reduce compared to free $\mathrm{Cu^{2+}}$ that is reduced at around −0.05 V. Similar results were obtained by Jin et al. [30] and van den Berg [12], respectively in freshwater and seawater.

3.2. *Effect of accumulation potential*

The influence of the accumulation potential on Zn and Pb peak currents was studied in a Deûle river sample by pseudopolarography with deposition potentials varying from −1.6 V to 0 V in order to determine the deposition potential where only the labile metal complexes are reduced in the time scale related to the applied technique [31–33]. Concerning the zinc pseudopolarograms, the peak current begins to increase from −1 V to −1.1 V and reaches a plateau from −1.1 V till −1.3 V. Then for potentials between −1.3 V and −1.6 V there is an increase in the peak current which can be explained as follows: for very negative potential, the reduction of strong organic-Zn complexes starts to occur as already observed in previous papers [33–36] but other causes are not excluded. According to this observation, the deposition potential of −1.3 V was chosen as the best option of accumulation potential for the labile zinc measurement in this study.

Similarly as the pseudopolarograms obtained for Zn, those of Pb shows an increase for deposition potential from 0 to −0.5 V, as we are using only 30 s of deposition time, the stripping step also cause an additional deposition time conducing to this wide range of deposition potential observed for the intensity increase. However, a plateau for deposition potentials more negative than −0.6 V is observed. As we work with natural samples, it is obvious that a slight shift of the wave to a more or a less negative value is possible. For that reason, we decided to work with a slightly more negative deposition potential of −0.7 V to keep a safety margin.

These deposition potentials chosen for Zn and Pb are in accordance with those usually used in voltammetry as they are only −0.2 to −0.3 V more negative than the reoxidation peak of the considered metal. At this potential range, only electroreduction of the most labile species including some weak organic complexes are taken into account [37]. Conversely, at more negative deposition potentials stronger metal complexes would also have been reduced such as explained here above for strong organic-Zn complexes when using a deposition potential of −1.6 V.

The effect of accumulation potential was also studied on the Cu peak current over the range of −0.25 V to −1.3 V. During the deposition period, copper can be accumulated as $\mathrm{Cu^0}$ in the mercury drop and/or directly adsorbed on the mercury drop as a complex with oxine, according to the value of E_{d} chosen. As the rest period before the scan is in all cases set up at −0.25 V, all the copper accumulated is finally associated with the oxine on the mercury electrode. That explains why the sensitivity of the cathodic redissolution intensity does not change drastically with the variation of the deposition potential. Similar experiment was carried out by van den Berg [12] and confirmed this finding. Moreover, at a deposition potential of −1.1 V, possible interferences coming from U and V are eliminated [12]. For that reason, the deposition potential was chosen at −1.1 V in this paper to determine Cu concentrations.

3.3. *Effect of accumulation time*

The effect of the accumulation time on the DPASV peak heights of Zn and Pb (up to 600 s) was studied under stirring condition (Fig. 4). For both metals, it was found that peak heights increase linearly with time at least until 600 s ($R^2 = 0.9999$ for Zn and $R^2 = 0.9977$ for Pb). In Deûle river samples, Zn concentrations are about 5 times higher than those of Pb. The choice of the

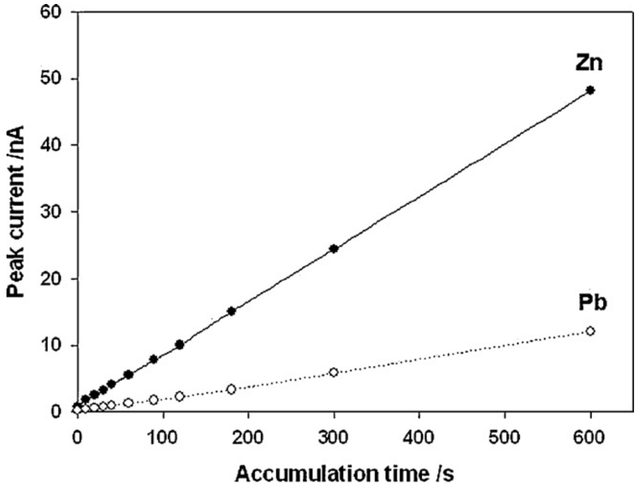

Fig. 4. Effect of accumulation time on 2.0 nM of Pb and 17.2 nM of Zn peak heights obtained for a Deûle river sample containing 0.01 M borate buffer with optimal DPASV conditions described in the Section 2.

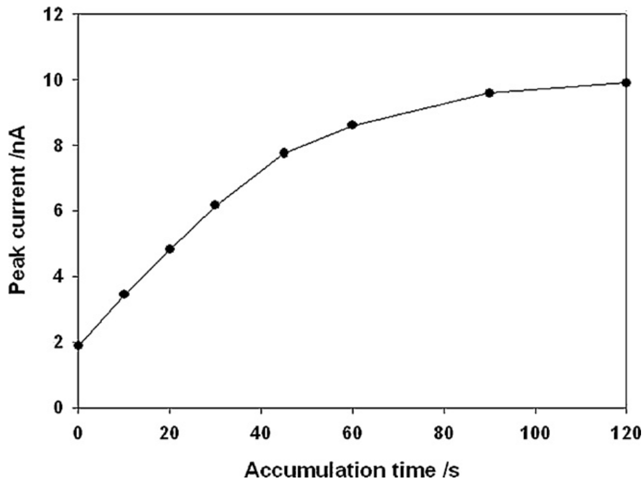

Fig. 5. Effect of adsorption time on Cu peak height obtained for a Deûle river sample containing 0.01 M borate buffer, 10^{-5} M oxine and 31.5 nM Cu^{2+}.

accumulation time has then been adapted to levels of both metals: 60 s and 30 s were chosen as optimal deposition times to analyze Pb and Zn, respectively.

The effect of accumulation time was also studied on the DPCSV Cu peak height in presence of oxine (Fig. 5). The accumulation potential was −1.1 V and it was found that the peak height increased linearly up to approximately 40 s while after 60 s, the signal continues increasing slowly probably until reaching the deposition saturation onto the surface electrode. An appropriate accumulation time for Cu determination was 30 s.

3.4. Effect of oxine concentration for Cu analysis

The effect of oxine concentration on DPCSV Cu peak height was studied in the range of 10^{-8}–10^{-3} mol L^{-1}. Fourteen subsamples of a Deûle river sample were prepared with different oxine concentrations containing 0.01 M of borate buffer and with 31.5 nM added Cu. All samples were analyzed after 24 h of equilibrium. The deposition time was carried out at −1.1 V with an adsorptive accumulation of 30 s. Results are displayed in Fig. 6.

The stripping peak current increases from 0.01 nA (10^{-8} M) to 2.8 nA ($1–2 \times 10^{-5}$ M). The maximum sensitivity was obtained between 0.8×10^{-5} and 5×10^{-5} M of oxine. Similar results have been observed by van den Berg [12] in seawater samples at pH 7.7. At low concentration, oxine can be bound to inorganic copper complexes and to copper bound to weak natural ligands. When the oxine concentration increases, the thermodynamic equilibrium is displaced and stronger natural Cu complexes are also dissociated and therefore detected by DPCSV. The peak current decrease related to Cu for oxine concentrations higher than 5×10^{-5} M could be explained by a competitive adsorption of free oxine and Cu–oxine complexes onto the mercury drop electrode [30], the free oxine acting in this case as a surfactant. As a consequence, to ensure an efficient complexation of all the “L-electroactive” copper fraction in our samples the oxine concentration was chosen at 10^{-5} M.

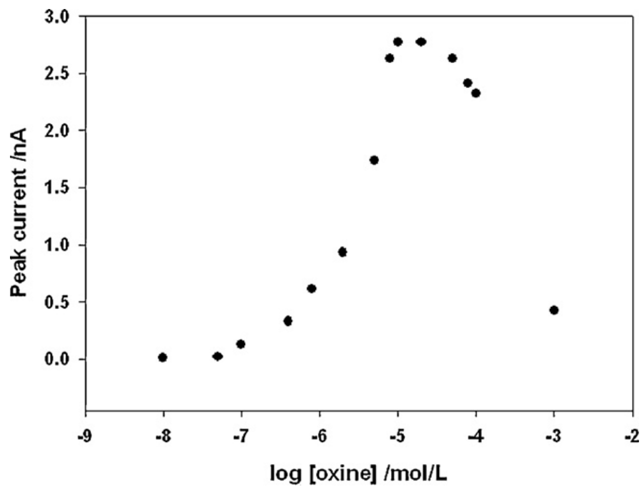

Fig. 6. Effect of oxine concentration on Cu peak height in a Deûle river sample.

3.5. Linearity and interferences

Under optimal conditions rigorously established in the previous sections, a linear concentration range was obtained for each metal titration curve in a Deûle river sample at natural pH. Using DPASV, the linear range corresponds to the end of the titration curve where the metal addition is supposed not to be complexed anymore with the natural complexing organic ligands. Zn and Pb responses were found to increase linearly with added Zn between 1.53 and 4.59 μM ($R^2 = 0.998$) and with added Pb between 0.82 and 2.90 μM ($R^2 = 0.999$), with corresponding detection limits of 2.91 nM for Zn and 0.03 nM for Pb. Using DPCSV, the linear range corresponds to the situation where all of the stronger natural ligands present in our samples have been saturated with Cu. Cu response was increasing linearly to 57.9 nM ($R^2 = 0.9997$) with a corresponding detection limit of 0.6 nM.

Moreover the reproducibility of our methods was estimated on 21 measurements from a Deûle sample containing initially 12.4 nM of Zn, 1.71 nM of Pb and 4.93 nM of Cu. The relative standard deviations calculated in this experiment were 4.0% for Zn, 2.0% for Pb and 1.3% for Cu.

Possible interferences can affect the determination of metals because metal ions compete for complexation with ligands (natural or added) and for adsorption onto the mercury drop. Peaks from our voltammograms are at the expected potential, well-defined and no displacement of the peak potential has been noticed. Therefore, the presence of organic matter does not affect metal determination in our samples. In the case where adsorption of natural organic matter affects voltammograms, a more negative deposition potential can be applied to eliminate artifacts [36]. Interferences can also be due to the formation of intermetallic compounds or to the mutual overlap of peak potentials preventing a correct determination of trace metals.

The influence of several trace metals on the peak heights of Pb, Zn and Cu (in presence of oxine) was studied. Realistic concentrations of trace metals found in natural aquatic systems have been added to our samples. Results presented in this section correspond to the maximum concentration for which no significant interferences have been observed (<5%). It appears that additions of 63 nM of Cu, 45 nM of Cd, 48 nM of Pb and 170 nM of Ni do not interfere with the redissolution peak of Zn; the variation of its intensity was each time lower than 5%. As for Cu, addition of 121 nM of Pb, 382 nM of Zn, 426 nM of Ni and 445 nM of Cd do not affect significantly its quantification. Additions of 79 nM of Cu, 45 nM of Cd and 85 nM of Ni in the solution do not interfere with Pb determination. Only Zn seems affecting the lead redissolution peak: for instance, addition of 77 nM of Zn makes the Pb voltammetric signal increased by 15%. To our best knowledge, only the paper of El tall et al. [38] underlined an interaction between Pb and Zn by using a boron-doped diamond electrode and assumed the formation of intermetallic Zn–Pb species. From these results, it was decided to analyze first Pb at a deposition potential of −0.7 V (to hinder Zn deposition in the mercury electrode) during 60 s and afterwards, to determine Zn at a deposition potential of −1.3 V during 30 s.

Table 1
Results obtained for electrolabile Zn, Pb and Cu concentrations by both laboratories (VUB and Lille University). Concentration values are given in nM.

Metal	Lab	Conc.	St. dev	RSD (%)
Zn	VUB	24.2	1.3	5.5
	Lille	25.2	1.1	4.1
Pb	VUB	3.2	0.1	2.5
	Lille	3.1	0.1	3.8
Cu	VUB	7.6	0.8	10.9
	Lille	9.1	1.0	10.8

Natural organic surfactants can also interfere in the determination of trace metals because at high concentrations they can compete for adsorption on the Hg drop and can lead to a significant decrease or suppression of the signal. For this reason, triton-X concentrations from 0.2 mg L^{-1} to 5 mg L^{-1} were added to the Deûle sample. This concentration range was chosen because it corresponds to the main adsorption stages of the adsorption of triton-X monomers onto the electrode surface. The first range from 0.2 mg L^{-1} to 0.8 mg L^{-1} corresponds to the transformation phase where adsorbed molecules are oriented perpendicular to the electrode while the second range from 0.9 mg L^{-1} to 4 mg L^{-1} indicates an adsorption of the molecules in the same orientation forming a relatively homogenous layer [39]. The effect of triton X was studied by DPASV for Pb and Zn and by DPCSV in presence of oxine for Cu. Results show a peak decrease of 97%, 99% and 84%, respectively for Cu, Zn and Pb in presence of 5 mg L^{-1} of triton-X. A peak shift from −1 V (without triton-X) to −0.84 V (with triton-X addition) was observed for Zn peak and no significant shift for Pb and Cu has been noted. As no shift was observed for the Zn redissolution peak during our DPASV experiments, we can conclude that organic surfactants comparable to triton-X do not seem to interfere significantly (or are not present at high concentrations) during metal determinations in our samples.

3.6. Method validation

3.6.1. Intercalibration

An intercalibration exercise between the VUB and University of Lille I for the analysis of electrolabile Zn, Pb and Cu was performed. The same analytical procedure, 2 voltammetric instruments and two different operators have been used for this experiment.

The following results were obtained (Table 1) showing good agreement between both laboratories.

3.6.2. Certified reference material

To validate the method, metals were determined in certified reference materials (BCR-505, estuarine water and SLRS-4, river water). Results are summarized in Table 2. Results obtained by voltammetry show good agreement with certified data indicating the good accuracy of the technique used and confirming that all the metal species in the certified waters are present under labile forms.

3.7. Sample analysis

The described method was applied to determine labile fractions of Zn and Pb by DPASV and Cu by DPCSV in Deûle river samples. Labile metal concentrations were determined from titration curves which are presented in Fig. 7.

The total dissolved concentration of these 3 metals was measured by HR-ICP-MS. Results are presented in Table 3. Lability results show that organic complexation and colloids dominate trace metal speciation of these 3 metals (80–98.5%). The Deûle River is a river system exposed to important shipping which implies a continuous sediment resuspension into the water column. Hence, the adsorption of metals on colloids and the binding with strong complexing ligands dominate the metal speciation. In the literature, lability percentages of lead and zinc complexes in freshwaters are very variable. Pei et al. [40] found a lability percentage equal to 18% and 31.2%, respectively for Pb and for Zn in the Arve River (Switzerland) using a Gel-Integrated Hg plated Microelectrode (GIME) with square wave anodic stripping voltammetry while Unsworth et al. [41] using a GIME determined a lead lability equal to 2% in the Wyre River (United Kingdom). Botelho et al. [42] obtained an average lead lability around 24% by DPASV in the Este River (Portugal).

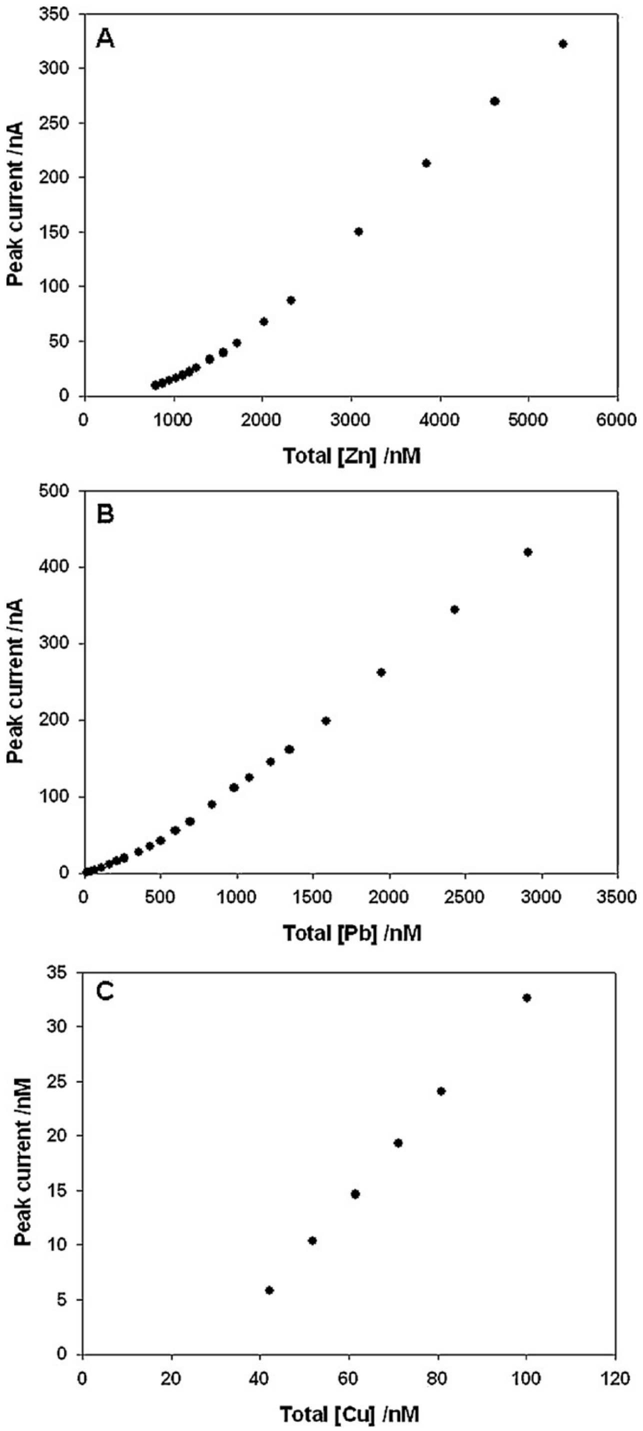

Fig. 7. (A) DPASV zinc titration with E_{acc} = −1.3 V, t_{acc} = 30 s, (B) DPASV lead titration with E_{acc} = −0.7 V, t_{acc} = 60 s and (C) DPCSV copper titration with [oxine] = 1×10^{-5} M, E_{acc} = −1.1 V, t_{acc} = 30 s. All samples contain 0.01 M borate buffer, pH 8.2.

Table 2
Analytical results of total Zn, Pb and Cu concentrations in certified reference materials (in nM).

		Reference material			Voltammetry		
		Conc.	St. dev	RSD (%)	Conc.	St. dev	RSD (%)
BCR-505	Zn	172.0	11.0	6.4	177.4	4.8	3.0
BCR-505	Cu	29.4	1.5	5.1	29.4	1.0	3.4
SLRS-4	Pb	0.415	0.034	8.2	0.396	0.029	7.3

Table 3
Zn, Pb and Cu concentrations in Deûle river samples (in nM).

	August-09			February-10			June-10		
	pH 8.02			pH 8.06			pH 8.22		
	Zn	Pb	Cu	Zn	Pb	Cu	Zn	Pb	Cu
ICP-MS	510.00	15.15	36.67	889.9	67.76	41.70	797.06	13.34	42.17
voltatnmetry	17.17	2.04	6.04	24.23	3.24	7.64	12.40	1.71	4.93
% Lability	3.37	13.47	16.47	2.72	4.78	18.32	1.56	9.32	11.69

In our study, the lability of copper appears higher compared to others because it does not take into account only inorganic Cu but also Cu–oxine complexes which displace the equilibrium towards the labile fraction. For comparison, in the Scheldt estuary van den Berg et al. [43] determined the organic complexation of copper by DPCSV in presence of cathecol as added ligand; the average value found for the electrolabile fraction was around 33%.

Additionally, a study performed by Waeles et al. [44] using ultrafiltration and stripping chronopotentiometry showed that Cu and Pb were mainly found as colloidal compounds in the Penzé estuary (France), 94% and 91%, respectively. It appeared that both metals dominate the size range of 0.22 μm–300 kDa for salinity 0 and that they are mainly associated with high-molecular weight colloids.

4. Conclusion

In this study, DPASV and DPCSV methods were closely investigated with the aim of determining Pb, Zn and Cu electrolabile fractions at natural pH in a polluted river (the Deûle River). Preliminary experiments clearly display the difficulty to measure the Cu electrolabile fraction by using DPASV, whereas DPCSV by using oxine gives much more sensitive and reliable results. For each metal, variations of accumulation potential and accumulation time were investigated (by DPASV for Zn and Pb and by DPCSV for Cu). Interference studies showed an effect of Zn on Pb determination. For this reason, Pb concentrations were not measured at the same time than Zn concentrations: a first DPASV procedure permitting to accumulate Pb in the mercury electrode without Zn at a deposition potential of −0.7 V during 60 s while a second DPASV procedure was dedicated to Zn determination at −1.3 V during 30 s. To determine Cu concentrations in presence of oxine, a deposition potential at −1.1 V during 30 s under stirring was chosen, followed by an adsorption process at −0.25 V during 15 s in the quiescent solution. Moreover, various oxine concentrations were also tested and the best peak current related to Cu reduction was obtained between 0.8×10^{-5} and 5×10^{-5} M.

Finally, the method validation showed good agreement between values from an intercalibration with University of Lille 1 and from certified reference materials. The proposed method has been successfully applied to Pb, Zn and Cu determination at natural pH in a polluted area, the Deûle River. Lability results showed that organic complexation and/or colloids were dominant for Zn, Pb and Cu species. Moreover, electrolabile copper appeared higher compared to electrolabile Pb and Zn due to the presence of oxine in DPCSV measurements.

The two next milestones relative to this research are now: (i) to apply our voltammetric procedures to detect daily, monthly and seasonal variations of electrolabile Cu, Zn and Pb in the Deûle River and (ii) to pay more attention to the "non electrolabile fraction" of trace metals because it represents more than 80% of the total dissolved metal concentrations in the Deûle River.

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References

[1] A. Tessier, D.R. Turner (Eds.), Metal Speciation and Bioavailability in Aquatic Systems, IUPAC Series on Analytical and Physical Chemistry of Environmental Systems, vol. 3, Wiley, Chichester, 1995.
[2] W. Stumm, J.J. Morgan, Aquatic Chemistry: Chemical Equilibria and Rates in Natural Water, 3rd ed., John Wiley & Sons, New York, 1996.
[3] Y. Louis, C. Garnier, V. Lenoble, S. Mounier, N. Cukrov, D. Omanovic, I. Pizeta, Mar. Chem. 114 (2009) 110–119.
[4] R. Nicolau, Y. Louis, D. Omanovic, C. Garnier, S. Mounier, I. Pizeta, Anal. Chim. Acta 618 (2008) 35–42.
[5] K. Hirose, Appl. Geochem. 22 (2007) 1636–1645.
[6] E. Bakker, E. Pretsch, Trends Anal. Chem. 24 (3) (2005) 199–207.
[7] H. Zhang, W. Davison, Anal. Chem. 67 (1995) 3391–3400.
[8] N. Parthasarathy, M. Pelletier, J. Buffle, J. Chromatogr. A 1025 (2004) 33–40.
[9] E.J.M. Temminghoff, A.C.C. Plette, R. van Eck, W.H. van Riemsdijk, Anal. Chim. Acta 417 (2000) 149–157.
[10] E.P. Achterberg, C. Braungardt, Anal. Chim. Acta 400 (1999) 381–397.
[11] C.M.G. van den Berg, Analyst 117 (1992) 589–593.
[12] C.M.G. van den Berg, J. Electroanal. Chem. 215 (1986) 111–121.
[13] C.M.G. van den Berg, Anal. Chim. Acta 164 (1984) 195–207.
[14] M.L.A.M. Campos, C.M.G. van den Berg, Anal. Chim. Acta 284 (1984) 481–496.
[15] J.R. Donat, C.M.G. van den Berg, Mar. Chem. 38 (1992) 69–90.
[16] Y.C. Sun, J. Mierzwa, C.H. Lan, Talanta 52 (2000) 417–424.
[17] T. Sterckeman, F. Douay, N. Proix, H. Fourrier, Environ. Pollut. 107 (2000) 377–389.
[18] N. Vdović, G. Billon, C. Gabelle, M. Wartel, J.L. Potdevin, Environ. Pollut. 141 (2006) 359–369.
[19] A. Boughriet, N. Proix, G. Billon, P. Recourt, B. Ouddane, Water Air Soil Pollut. 180 (2007) 83–95.
[20] J.C. Duinker, C.J.M. Kramer, Mar. Chem. 5 (1977) 207–228.
[21] N. Cukrov, P. Cmuk, M. Mlakar, D. Omanovic, Chemosphere 72 (2008) 1559–1566.
[22] J.R. Donat, K.W. Bruland, Mar. Chem. 28 (1990) 301–323.
[23] L.M. Laglera, C.M.G. van den Berg, Mar. Chem. 82 (2003) 71–89.
[24] AEAP 2011 http://donnees.eau-artois-picardie.fr/.
[25] J. Lions, V. Guérin, P. Bataillard, J. van der Lee, A. Laboudigue, Environ. Pollut. 158 (2010) 2857–2867.
[26] C.M.G. van den Berg, Analyst 114 (1989) 1527–1530.
[27] O. Abollino, M. Aceto, C. Sarzanini, E. Mentasti, Electroanalysis 11 (1999) 870–878.

[28] F. Garay, V. Solis, M. Lovric, J. Electroanal. Chem. 478 (1999) 17–24.
[29] A.M. Beltagi, M.M. Ghoneim, J. Appl. Electrochem. 39 (2009) 627–636.
[30] L. Jin, N.J. Gogan, Anal. Chim. Acta 412 (2000) 77–88.
[31] S. Bubić, M. Branica, Thalassia Jugoslavica 9 (1973) 47–53.
[32] O. Omanović, M. Branica, J. Electroanal. Chem. 543 (2003) 83–92.
[33] O. Omanović, M. Branica, J. Electroanal. Chem. 565 (2004) 37–48.
[34] B.L. Lewis, G.W. Luther III, H. Lane, T.M. Church, Electroanalysis 7 (1995) 166–177.
[35] J.J. Tsang, T.F. Rozan, H. Hsu-Kim, K.M. Mullaugh, G.W. Luther III, Environ. Sci. Technol. 40 (2006) 5388–5394.
[36] Y. Louis, P. Cmuk, D. Omanović, C. Garnier, V. Lenoble, S. Mounier, I. Pižeta, Anal. Chim. Acta 606 (2008) 37–44.
[37] P.B. Kozelka, K.W. Bruland, Mar. Chem. 60 (1998) 267–282.
[38] O. El Tall, N. Jaffrezic-Renault, M. Sigaud, O. Vittori, Electroanalysis 19 (2007) 1152–1159.
[39] B. Gasparović, D. Risovic, B. Cosovic, Electrochim. Acta 49 (2004) 3383–3396.
[40] J. Pei, M.L. Tercier-Waeber, J. Buffle, Anal. Chem. 72 (2000) 161–171.
[41] E.R. Unsworth, K.W. Warnken, H. Zhang, W. Davison, F. Black, J. Buffle, J. Cao, R.F.M.J. Cleven, J. Galceran, P. Gunkel, E.J.J. Kalis, D. Kistler, H.P. van Leeuwen, M. Martin, S. Noel, Y. Nur, N. Odzak, J. Pauy, W.H. van Riemsdijk, L. Sigg, E.J.M. Temminghoff, M.L. Tercier-Waeber, S. Topperwien, R.M. Town, L. Weng, H. Xue, Environ. Sci. Technol. 40 (2006) 1942–1949.
[42] C. Botelho, R. Boaventura, M.L. Simoes Goncalves, Electroanalysis 13 (2001) 1497–1504.
[43] C.M.G. van den Berg, A.G.A. Merksb, E.K. Duursmab, Estuarine Coastal Shelf Sci. 24 (1987) 785–797.
[44] M. Waeles, V. Tanguy, G. Lespes, R.D. Riso, Estuarine Coastal Shelf Sci. 80 (2008) 538–544.