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A routine speciation method for a pollution survey of coastal sea water

ASV
Zn, Cd, Pb, Cu
Sb, Bi
Speciation
Coastal waters
ASV
Zn, Cd, Pb, Cu
Sb, Bi
Spéciation
Eaux côtières

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ABSTRACT

A simplified speciation scheme for routine analysis is illustrated which includes rapid and simple sample treatment with a subsequent quantitative determination by anodic stripping voltametry methods (DPASV at a HMDE and DCASV with a RRDE).
The classification used has a practical utility in studies of the effects and chemical composition of local pollution sources within the framework of a routine survey.
The scheme permits discrimination between oxidation state antimony (III and V), so-called labile, weakly and strongly bound Zn, Cd, Pb, Cu, Sb and Bi in the dissolved fraction of the sea.

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RÉSUMÉ

Obtention d'un modèle simple et rapide de la répartition des métaux lourds dissous sous leurs différentes formes chimiques en milieu côtier marin par polarographie de redissolution anodique.

Un modèle simple et rapide de la répartition du Zn, Cd, Pb, Cu, Sb et Bi (fraction ionique, faiblement et fortement complexée) et de Sb (III et V) basé sur l'utilisation de techniques voltamétriques (DPASV-HMDE et DCASV-RRDE) est proposé dans le but pratique de déterminer les effets et la nature chimique des sources locales de pollution au cours de campagnes côtières.

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INTRODUCTION

The total content in the water column is distributed between the dissolved state and the suspended matter phase.

As the dissolved state is the predominant phase by which transfers and interactions between heavy metals and suspended matter, organisms and sediments occur; the elucidation of chemical states and forms (speciation) in which heavy metals are involved is particularly significant (Allen *et al.*, 1970; Batley, Florence, 1976; Brezonik, 1974; Florence, Batley, 1976; 1977; Long, Angino, 1977; Mackey, 1982; Rohl, 1982; Gillain, Duyckaerts, 1977).

The various anodic stripping techniques meet the combined requirements of sensitivity, accuracy, rapidity and simplicity necessary for the execution of speciation studies of heavy metals (Duinker, Kramer, 1977; Figura, Mc Duffie, 1980; Gillain, Duyckaerts, 1979; Nürnberg, 1983; Odier, Pichon, 1977; Schonberger, Pickering, 1980).

During a routine monitoring program, a simplified speciation method was applied where differentiation was made by measurement of concentration of some elements by anodic stripping voltametry after filtration, acidification, reduction of antimony (V) to antimony (III) by sulfur dioxide and UV-irradiation.

The combination of two ASV techniques, *i.e.* differential pulse anodic stripping voltametry (DPASV) at a hanging mercury drop electrode (HMDE); and direct current anodic stripping voltametry (DCASV) at a rotating ring-disc electrode (RRDE), permitted the definition of a simple approach to soluble metal speciation (free ionic, weakly and strongly bound Zn, Cd, Pb, Cu, Sb and Bi).

The limits between each fraction are difficult to determine but the principal purpose is the practical application of this speciation method to the survey of local pollution sources in the North Sea (Belgian coast).

MATERIALS AND METHODS

The combination of DPASV at a HMDE and linear ASV with collection at a RRDE was used for an approach to soluble Zn, Cd, Pb, Cu, Sb and Bi trace metals speciation.

The techniques and materials were described previously by Gillain and Duyckaerts (1979) and Brihaye and Duyckaerts (1982 *a* and *b*).

Ultra-violet irradiation was required for the degradation of organic substances binding trace metals as inert complex species (Afghan *et al.*, 1970; Armstrong *et al.*, 1966; Bartlett, 1975; Gershey *et al.*, 1979; Gillain, Duyckaerts, 1977; Menzel, Vaccaro, 1964).

The irradiation unit (Fig. 1) is a closed system which permits the treatment of six sea samples simultaneously with a minimum sample manipulation and negligible reagent blanks. A volume of 30 ml of acidified sea water (pH = 1.5) is treated with 0.05 ml of 30% hydrogen peroxide suprapur Merck and irradiated in a slowly rotating 15 mm diameter quartz tube for a night under the light of 30 W TUV germicide tubes.

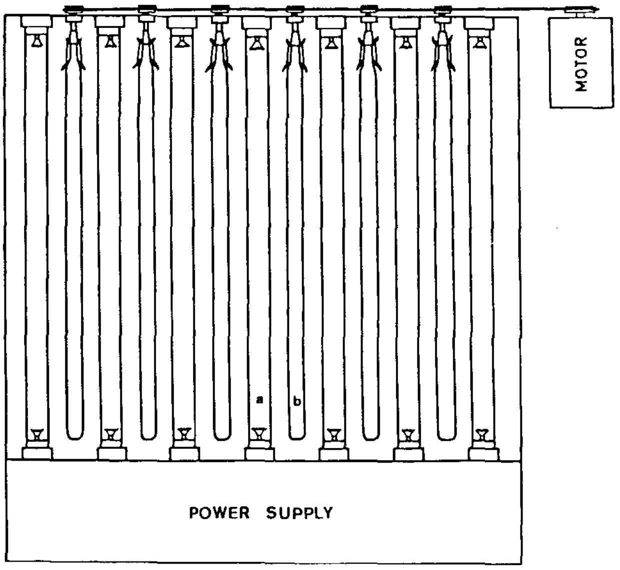


Figure 1

UV-irradiation system: a) TUV germicide tubes; b) rotating quartz tubes containing the sea water sample.

Système d'irradiation UV : a) tubes germicides TUV; b) tubes rotatifs en quartz contenant l'échantillon.

Antimony (V) is not electroactive at the electrode and must be reduced to antimony (III) by saturating the solution with sulfur dioxide, the excess of which is easily eliminated by bubbling nitrogen through the solution at 90°C.

SPECIATION PROCEDURE AND DISCUSSION

A flow chart for the speciation method is shown in Figure 2. The sequence of operations is as follows:

The first measurement by ASV at a HMDE at natural pH gives ionic species and other very labile forms (I).

The voltametric measurement at pH = 1.5 will give the concentration of free metals and weakly complexed cations $(II)_a$ (antimony being present as Sb (III)). The difference between the concentration of $(II)_a$ and (I) represents the fraction corresponding to the metal bound in weak complexes at the natural sea water pH. Given that the concentrations of Sb (III) and Bi are very low, measurements are made by linear ASV at a RRDE after electrolysis at —0,40 V.

After treatment with sulphur dioxide, the value obtained for antimony includes the sum of the free metal ions and weak complexes of Sb(III) and (Sb(V)) (II_b). From the difference between (II_b) and (II_a) the concentration of antimony in the pentavalent state is obtained.

As UV-irradiation destroys organic matter, the total metal concentrations of Zn, Cd, Pb, Cu, Sb and Bi in the solution (III) are measured when irradiation is followed by reduction with sulphur dioxide. The fraction given by the difference $(III)-(II)_b$ is called strongly complexed cations. Under these conditions, the Sb and Bi concentrations are higher than with measurement at pH = 1.5 and direct measurement at a HMDE is easier than at a RRDE.

Comparison between various stripping techniques has shown DPASV at a HMDE (Gillain, Duyckaerts, 1979) in combination with linear ASV with collection at a RRDE (Brihaye, Duyckaerts, 1982), to comprise those most convenient for our purpose. The former is suitable for measurement of concentrations of 1 to 0.1 $\mu g\ l^{-1}$ and the latter for lower concentrations. The advantages of ASV with RRDE are the following (Brihaye, Duyckaerts, 1982 *b*):

— the base line is a straight line with zero slope permitting the most accurate peak-height measurement;

— this base line is not influenced by adsorbable organic matter. It is quite significant in natural water analysis.

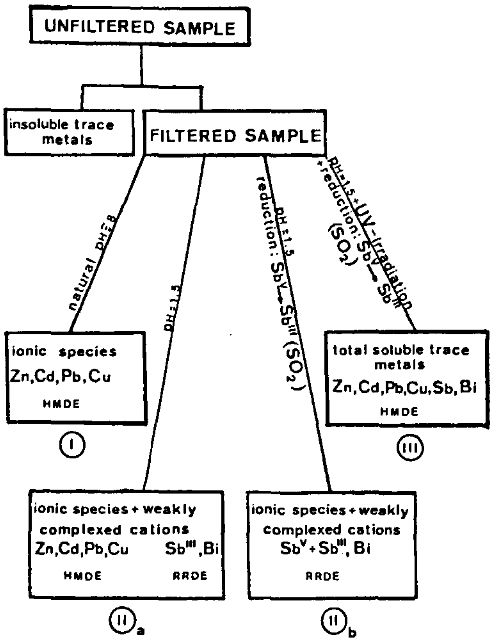


Figure 2

Chemical speciation scheme.

Schéma de la répartition des métaux sous leurs différentes formes chimiques.

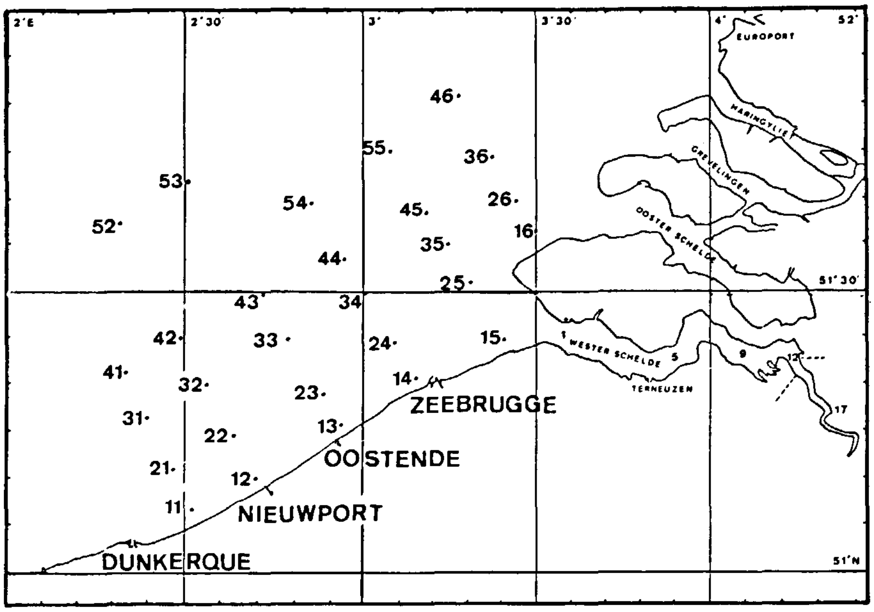


Figure 3
Location of sampling stations in the North Sea (Belgian coast).
Position géographique des stations de prélèvement le long de la côte belge.

RESULTS

The full scheme was applied in the Belgian Southern Bight coastal waters contaminated by urban pollution, industrial dumping and a polluted river (Scheldt). The stations are located along grid lines perpendicular to the coast (Fig. 3).

The results given in the Table were used to discriminate between four different metal fractions. Due to the wide scattering of the results, possible local effects such as dumping, remobilization from the sediments or effects related to increased biological activities are not evident. However, the highest values corresponding to local pollution were recorded along the coast and in the vicinity of the Scheldt estuary.

Representative voltamograms are shown for different sea water pretreatments (Fig. 4).

At pH of sea water the peak heights for Cd and Pb are often very low. Sb and Bi cannot be measured because of hydrolysis of their salts under these conditions and consequently, because of the lack of value at pH 8, the ionic form of these ions cannot be differentiated from their weak complexes.

A marked increase in the Zn, Cd, Pb and Cu concentrations is observed, when the sample is acidified at pH 1.

Speciation of dissolved heavy metals in sea water (µg l^{-1}) (*July* 1983).

	Cu			Sb			Bi	
Stations	pH *in situ* I	pH acid II_a	UV III	pH acid II_a	pH acid $+SO_2$ II_b	UV + SO_2 III	pH acid II°	UV III
11	0.20	0.40	1.10	<0.005	0.020	0.06	0.005	0.150
12	0.10	0.20	0.95	<0.005	0.067	0.10	0.005	0.120
13	0.10	0.25	1.40	0.013	0.092	0.12	0.012	0.090
14	0.30	0.60	1.80	0.039	0.092	0.12	0.005	0.100
15	0.20	0.80	1.60	0.005	0.062	0.11	0.014	0.130
24	0.15	0.40	0.96	0.005	0.100	0.12	N.D.	N.D.
25	0.25	0.55	1.30	0.008	0.250	0.38	0.005	0.070
26	0.18	0.38	1.10	0.007	0.120	0.24	0.010	0.100
33	0.13	0.30	0.88	<0.005	0.010	0.05	0.008	0.080
34	0.15	0.35	0.75	—	—	—	—	—
41	0.10	0.28	0.68	<0.005	0.020	0.05	N.D.	N.D.
42	0.08	0.25	0.70	<0.005	0.015	0.05	N.D.	0.110
45	0.06	0.40	1.20	0.008	0.200	0.28	N.D.	0.150
46	0.12	0.38	1.40	<0.005	0.150	0.23	N.D.	N.D.
52	0.10	0.08	0.40	<0.005	0.020	0.06	N.D.	N.D.
53	<0.05	0.15	0.65	<0.005	0.020	0.08	N.D.	N.D.
54	<0.05	0.20	0.60	<0.005	0.080	0.13	N.D.	N.D.
55	0.10	0.25	0.70	<0.005	0.160	0.21	N.D.	N.D.
56	0.12	0.20	0.45	<0.005	0.050	0.15	N.D.	N.D.

N.D. = no detected.
I = ionic species.
II_a = ionic species + weak organic and inorganic complexes (for Sb, II_a = Sb^{III}).
II_b = $Sb^V + Sb^{III}$.
III = total concentration.
°II_a = II_b for Bi (pH acid).

Figure 4

(a) and (b) Voltamogram of Zn, Cd, Pb and Cu at pH in situ *(a) and at pH acid (b) by DPASV with HMDE.*
Deposition time: 30 min. (a) and 10 min. (b); pulse amplitude: 50 mv; scan rate: 2 mv s^{-1}.
Zn=0.30 μg l^{-1} *(a),* *Pb=0.05 μg* l^{-1} *(a),*
0.50 μg l^{-1} *(b),* *0.09 μg* l^{-1} *(b).*
Cd=0.20 μg l^{-1} *(a),* *Cu=0.18 μg* l^{-1} *(a),*
0.030 μg l^{-1} *(b),* *0.38 μg* l^{-1} *(b).*

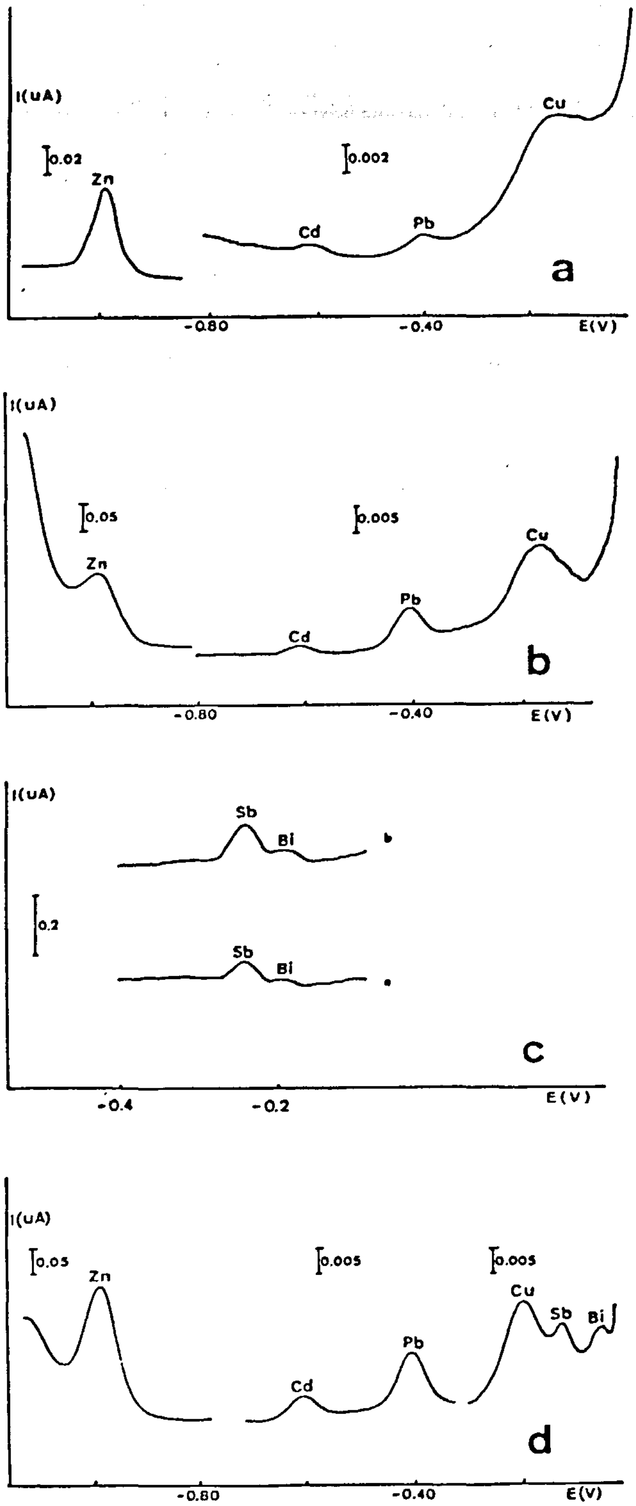
(c) Voltamogram of Sb and Bi for sea water by ASV with collection.
1.63 10^{-5} *M Hg;* $\omega = 1\,500$ *rpm;* $v = 3$ *V min.*$^{-1}$; *deposition time: 15 min.;* $E_R = -0.5$ *V.*
$Sb^{III} = 0.07$ *μg* l^{-1}; $Sb^{III} + Sb^{V} = 0.12$ *μg* l^{-1}.
Bi = 0.010 *μg* l^{-1}.

(d) Voltamogram of Zn, Cd, Pb, Cu, Sb and Bi for sea water at pH 1 *containing 2M chloride and after UV-irradiation by DPASV with HMDE.*
Deposition times: 20 min. (Zn, Cd, Pb) and 40 min. (Cu, Sb, Bi); pulse amplitude: 35 mv (Zn, Cd, Pb) and 10 mv (Cu, Sb, Bi); scan rate: 2 mv s^{-1} *(Zn, Cd, Pb) and 0.5 mv (Cu, Sb, Bi); Zn=1.60 μg* l^{-1}; *Cd=0.130 μg* l^{-1}; *Pb=0.18 μg* l^{-1};*Cu=1.10 μg* l^{-1}; *Sb=0.24 μg* l^{-1}; *Bi=0.10 μg* l^{-1}.

(a) et (b) Voltammogramme du Zn, Cd, Pb et Cu à pH *in situ* (a) et à pH acide (b) par redissolution anodique en mode impulsionnel sur goutte pendante de mercure.
Temps d'électrolyse : 30 min (a) et 10 min (b); amplitude d'impulsion: 50 mv; vitesse de balayage : 2 mv s^{-1}.
Zn=0.30 μg l^{-1} (a), Pb=0.05 μg l^{-1}(a),
0.50 μg l^{-1} (b), 0.09 μg l^{-1} (b).
Cd=0.020 μg l^{-1} (a), Cu=0.18 μg l^{-1} (a),
0.030 μg l^{-1} (b), 0.38 μg l^{-1} (b).

(c) Voltammogramme de Sb et du Bi obtenu sur une eau de mer à pH acide par redissolution anodique avec collection.
1.63 10^{-5} M Hg; $\omega = 1500$ rpm; v = 3 V min^{-1}; temps d'électrolyse : 15 min; $E_R = -0.5$ V.
$Sb^{III} = 0.07$ μg l^{-1}; $Sb^{III} + Sb^{V} = 0.12$ μg l^{-1}.
Bi = 0.010 μg l^{-1}.

(d) Voltamogramme du Zn, Cd, Pb, Cu, Sb et Bi obtenu sur une eau de mer à pH acide et après irradiation aux UV par redissolution anodique en mode impulsionnel sur goutte pendante de mercure.
Temps d'électrolyse : 20 min (Zn, Cd, Pb) et 40 min (Cu, Sb, Bi); amplitudes d'impulsion : 35 mv (Zn, Cd, Pb) et 10 mv (Cu, Sb, Bi); vitesses de balayage : 2 mv s^{-1} (Zn, Cd, Pb) et 0.5 mv s^{-1} (Cu, Sb, Bi).
Zn = 1.60 μg l^{-1}; Cd = 0.130 μg l^{-1}; Pb = 0.18 μg l^{-1}.
Cu = 1.10 μg l^{-1}; Sb = 0.240 μg l^{-1}; Bi = 0.10 μg l^{-1}.



The data for Sb and Bi show concentrations below detection limit (< 0.005 μg l^{-1}), except for samples close to the coast and in the vicinity of the mouth of the Scheldt. They might indicate that Bi diffuses from the coast and is rapidly diluted or removed by unknown processes from the offshore water column.

Further significant increase of metal concentration are measured after irradiation for all samples, indicating that an acidification to pH = 1 does not release all the metal present in the dissolved fraction of these water samples. The content of Zn, Cd, Pb and Cu involved in strong organic complexes represents an important fraction of the total concentration and shows large variations from one sampling site to another: 40-90% for Zn, 20-80% for Cd, 33-87% for Pb and 50-80% for Cu.

Antimony is present in the greatest fraction as antimony (V) and the percentage of Sb complexed by organic matter can be estimated to vary between 20 and 60% of the total concentration.

CONCLUSION

The speciation method is simple and rapid. The low blanks make the concentrations relatively certain. The concentrations of each metal species are obtained from each measurement or calculated by simple substraction so that errors are significantly reduced. The scheme permits the discrimination between so-called labile, weakly and strongly bound Zn, Cd, Pb, Cu, Sb and Bi in the dissolved fraction as well as between the oxidation states (III) and (V) for antimony.

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