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The determination of trace metals in sea water and suspended matter by classical anodic stripping (Zn, Cd, Pb, Cu) or differential pulse anodic stripping voltammetry with a hanging mercury drop electrode (Zn, Cd, Pb, Cu, Sb and Bi).

An approach to speciation.

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1.- Sampling methodology

Sampling appears to be the most hazardous step in the determination of trace metals at the ppb level in sea-water because of contamination problems. Classically, Niskin bottles can be used with Teflon coated messengers and hydrowire ; water can be collected with Teflon centrifugal pumps. The next step is filtration which usually is carried out on Millipore filters (0.45 µm pore size), the final product being stored on board the ship at -20°C in polyethylene bottles carefully washed with pure HCl and tridistilled water. Filtration can also be carried out after thawing before analysis in the laboratory on land. Contamination is of course possible at any step and the ship itself is probably the main cause of trouble if not some other ship leaving behind herself a cload of Zn, Cu, Pb, etc from propellers, zinc anodes, paint, engine exhausts among other sources. Airborn material, careless handling by unskilled experimenters, the depth at which the sample is taken versus the ship's draught, the location on board of sampling system, atmospheric conditions, non homogeneity of the water, etc are all possible causes of difficulties piling up in an almost infinite list. To make sampling and filtrations more reliable the following system has been tested by

Gillain (personal communication) and shown to give far more better results than those described above which get easily out of control. Better results means that in some cases the trace metals concentrations are one order of magnitude lower than with the conventional methods.

The principle is to continuously collect small samples of water from a very large volume screened from atmospheric pollution. A peristaltic pump draws continuously 6 ℓ water per min at 5 m depth (2 m below the ship's keel);[in the North Sea (Southern Bight) the water column is taken as homogeneous] through a PVC tube previously soaked in 6 N HCl , rinsed with tridistilled deionized water. The ship is adrift and the tube is on the lee side so that it meets water masses not polluted by the vessel. A second peristaltic pump draws 0.5 ℓ per min from the main flow which is returned to the sea. The unfiltered sea water is kept in a 5 ℓ polyethylene bottle and magnet stirred continuously. Pure nitrogen (0.3 kg/cm^2 pressure) is used to drive the water to an ultrafiltration kit (0.45 µm millipore filter) where the liquid is stirred to reduce filter clogging and filtration proceeds under nitrogen pressure. The filtered samples are collected in 1 ℓ bottles each finally representative of about 60 ℓ water, excess water from the filter being discarded by simple bypass. The samples are immediately frozen at -20°C. Thawing is carried out in the laboratory immediately before analysis.

2.- Analytical techniques

2.1.- CLASSICAL ANODIC STRIPPING VOLTAMMETRY

The method has been described in detail by Duyckaerts and Gillain (1977). It allows to measure Cu, Pb, Cd and Zn not only in sea-water but also in plankton and/or suspended matter, first lyophilized and then ashed with microwave activated oxygen, followed by dissolution in concentrated HCl.

The interesting point is that besides being very sensitive (0.5 to 0.1 ppb), the method allows an approach to speciation. Carried out at *in situ* pH it gives an evaluation of the ionic species (I) ; at pH 3 metals forming "weak" complexes are released (II) ; at pH 3.5-4 samples first irradiated by U.V. during 12 hours at pH 1 show the release of

"strongly" complexed cations (III). The differences (II) - (I) and (III) - (II) can be used together with (I) to approach speciation.

2.1.- DIFFERENTIAL PULSE ANODIC STRIPPING VOLTAMMATRY

Differential pulse anodic stripping voltammetry receives considerable attention as a convenient technique for the simultaneous determination of heavy metals at the microtrace level. A review of its application to sea-water together with a complete description of the technique adapted by the authors has been recently described by Gillain et al.(1979).

The method can be used to perform the same sort of analysis as indicated for classical anodic stripping but the sensitivity is about one order of magnitude higher (0.05 to 0.01 ppb).

Further it can be used in well controlled conditions to determine simultaneously Zn, Cd, Pb, Cu, Sb and Bi.

Gillain et al have shown that a very good resolution of the peaks can be obtained by carefully studying the effects of both pH and NaCl concentrations. The optimal conditions, illustrated by fig.1, show the

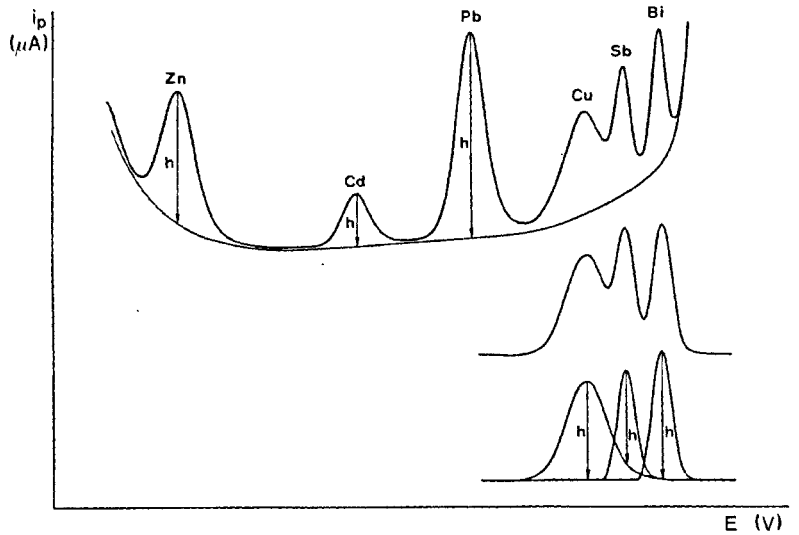

fig. 1.

Evaluation of stripping peaks (differential voltammetry) to measure simultaneously Zn , Cd , Pb , Cu , Sb , Bi .

results obtained at pH 1 and NaCl 2M concentration and how the height of the peaks are determined. The pH and the NaCl concentrations are adjusted by adding suprapure HCl and NaCl to the sea-water samples. The analysis takes only 2 hours.

Under these conditions it should be kept in mind that the metal concentrations which are measured correspond to the sum of the ionic species and the weakly bound ones, or if U.V. irradiation is used, to the sum of all species.

Typical values for North Sea water samples (ionic + weakly bound species) are given in table 1 together with indications on the precision of the method.

Table 1

Metals	Concentration (ppb)	Standard deviation (ppb)
Zn	5.2	0.26
Cd	0.6	0.06
Pb	6.2	0.70
Cu	4.3	0.40
Sb	0.4	0.06
Bi	0.3	0.04

3.- Results

3.1.- METALS IN SOLUTION

The data presented here correspond to samples taken during September, October and November 1978 in the coastal region off the Belgian coast between Dunkerque and the Scheldt estuary (51°07'20"-51°20'40"N, 51°25'00"-51°39'25"N ; five transects). The depth of sampling is 5m, the improved sampling system is used on board as well as the differential pulse technique in the laboratory.

Table 2 gives the mean values for Zn, Cd, Pb and Cu, as well as the extreme concentrations detected (20 samples per cruise).

Table 2

Mean values and extreme values (µg/ℓ) for Zn, Cd, Pb, Cu off the Belgian coast

	Metals	(I) pH *in situ*		(II) pH 3		(III) U.V. irradiation	
		Mean	Range	Mean	Range	Mean	Range
September 1978	Zn	0.48	0.10 - 1.50	2.48	1.00 - 5.43	6.7	2.6 - 14.5
	Cd	0.02	0.01 - 0.05	0.05	0.03 - 0.09	0.10	0.04 - 0.23
	Pb	0.75	0.10 - 1.60	2.55	0.90 - 5.80	5.10	0.90 - 9.10
	Cu	0.55	0.30 - 1.10	1.45	0.45 - 2.46	2.50	0.60 - 4.70
October 1978	Zn	2.45	0.50 - 4.30	6.60	2.50 - 10.0	10.6	2.5 - 23.0
	Cd	0.03	0.01 - 0.10	0.09	0.04 - 0.30	0.11	0.04 - 0.32
	Pb	0.70	0.30 - 1.30	2.50	1.10 - 4.80	5.10	3.00 - 9.70
	Cu	1.00	0.30 - 2.00	2.15	1.20 - 4.30	3.20	1.10 - 8.50
November 1978	Zn	1.60	0.35 - 3.60	4.0	1.80 - 8.50	6.5	2.5 - 10.6
	Cd	0.03	0.01 - 0.06	0.08	0.03 - 0.10	0.10	0.05 - 0.18
	Pb	1.50	0.20 - 1.90	3.40	2.20 - 4.50	5.00	2.30 - 7.90
	Cu	0.60	0.20 - 1.90	1.70	1.10 - 4.00	2.50	0.80 - 6.00

Note : (I), (II), (III) refer to concentrations of heavy metals in ppb ; (I) corresponds to ionic species, (III) to the total amount of metal, (II) - (I) to the weakly bound species, (III) - (II) to the strongly complexed cations (see text).

The values of column (II) (ionic species + weakly bound ones) are lower but not systematically, considering the ranges, with the data published in 1979 by the authors for 5 samples from the North Sea taken with conventional methods in 1977 (table 3).

Table 3

Metals	Metal content (ppb)				
	1	2	3	4	5
Zn	7.00	2.66	14.20	22.00	14.00
Cd	0.40	0.30	0.20	0.95	0.30
Pb	1.80	7.44	7.26	3.60	6.38
Cu	2.82	9.70	5.70	8.00	9.12
Sb	0.30	0.45	0.82	0.30	0.42
Bi	0.20	0.68	0.55	0.20	0.28

It is too early to compare the new results with the thousands of data collected in the North Sea off the Belgian coasts since 1971 (J.C. Nihoul and I. Elskens, 1978) because the bettered sampling technique has not been used long enough to detect the general pattern of distribution, the seasonal fluctuations, which considerably affect the amounts of heavy metals in this region.

At the international level, some intercomparisons can be made. For instance the mean values obtained by Duinker and Kramer in 1975 by polarographic analysis in the vicinity of the Rhine estuary (ppb) are given in table 4.

Table 4

	Mean	Range
Zn	9.9	3 - 20
Cd	0.20	0.10 - 0.30
Pb	2.5	1.7 - 3.3
Cu	1.7	1.0 - 2.5

These data were obtained at pH 3 and should be compared to column (II) in table 2.

Abdullah and Royle (1972) report polarographic results after preconcentration on chelating resin for mean values (10 samples) collected in the North Sea (table 5). The results again have to be compared with the data of column (II) of table 2 (ppb).

In 1973, Dutton and Jefferies, using atomic absorption spectroscopy after extraction with APDC-MIBK (ammonium pyrrolidine dithiocarbamate-methylisobutylketone)give the following values (ppb) for North Sea samples collected in May-June 1971 in a region rather close to the one investigated where we obtained the results quoted table 2 :

	Mean	Range
Zn	6.3	3 - 16
Cd	0.5	0.1 - 6.2
Pb	-	-
Cu	1.4	1 - 3

Table 5

		Mean	Range
Liverpool Bay	Zn	11.86	2.3 - 47.6
	Cd	0.27	0.14 - 0.74
	Pb	1.74	0.66 - 4.17
	Cu	1.45	0.30 - 3.03
Tardigan Bay	Zn	7.46	3.6 - 19.6
	Cd	1.11	0.50 - 2.41
	Pb	2.24	1.12 - 3.53
	Cu	1.72	0.98 - 4.02
Bristol Channel	Zn	10	3.6 - 21.4
	Cd	1.13	0.28 - 4.20
	Pb	1.2	0.40 - 5.00
	Cu	2.10	1.00 - 4.70

More recently, Burda et al.(1978) found at station 60°00'N, 0°30'E in the North Sea, after concentration on chelating resin and analysis by fluorescence : Zn 5.7 ppb, Pb 1.2 ppb, Cu 2.7 ppb (mean of 3 samples).

These results are difficult to compare to those of table 2 , as is with those of Abdullah et al., Dutton et al., because of the extraction or preconcentration techniques used. However they should also be compared in first analysis with column (II) of table 2.

Valenta et al.(1977) find at 13 km off the Island of Walcheren, probably in 1976, using anodic stripping for Cd : 0.028 ppb, Pb : 0.077 ppb, Cu : 1.22 ppb.

Although all these informations fall practically within the range of the determinations given in table 2 or are within the same order of magnitude, there is a rather wide scattering of the results indicating either unproper sampling or analytical techniques, correct measurements but referring to metals involved in different complexes or speciation, seasonal changes, horizontal inhomogeneity of water, effects related to biological activities (plankton - blooms, etc), local effects because of river discharge, dumping, atmospheric effects related to rain, transport of airborn material, etc.

Only long temporal series, correlated to other major events in the ecosystem will allow to understand the meaning of these fluctuations, provided proper intercalibration is carried out to ascertain the funda-

mental equivalent validity of the different methods actually used not only in the analytical chemistry laboratory but on board the ships used to collect the samples.

3.2.- METALS IN SUSPENDED MATTER

After calcination under microwave activated oxygen, the material soluble in suprapure concentrated HCl is analysed by the same techniques at sea-water ; 70% of Sb being lost during ashing, there is no reason to adjust the NaCl concentration. The results of table 6 refer to samples collected in September, October and November 1978 as reported for the data on the metals in solution.

Table 6

Concentration (ppm)
(Dry weight)

		Zn	Cd	Pb	Cu
September 1978	Mean	202	1.40	42	32
	Range	48 - 500	0.40 - 2.70	12 - 115	13 - 66
October 1978	Mean	130	0.78	35	38
	Range	13 - 300	0.30 - 1.70	3 - 110	22 - 75
November 1978	Mean	107	0.80	30	32
	Range	21 - 240	0.40 - 2.00	1 - 60	4 - 70

The values are of the same order of magnitude as those reported by Duinker and Nolting in 1973 as minimum values in the region of the Scheldt and Rhine estuaries :

Zn : 100 - 200 µg/g Cu : 30 - 50 µg/g	minimum values
Zn : 4800 µg/g Cu : 800 - 1000 µg/g	maximum values

The maximum values observed by Duinker and Nolting are probably due to the input of the Rhine.

Conclusions

Anodic stripping voltammetry is well suited for sea-water trace metal analysis ; it further allows to have an insight into chemical speciation however rudimentary : ionic species, weakly bound ones, strongly bound ones, by only changing one parameter, that is pH. This subdivision of the total metal content might prove very usefull to biologists if some differences appear at the toxicity level, or rate of accumulation of heavy metals, depending on a crude knowledge of speciation. This is the case as indicated in the paper of Bouquegneau et al. on "The fate of heavy metals in aquatic food chains, uptake and release of Hg and Cd by some marine organisms, role of metallothioneins" in this same issue.

It is obvious that atomic absorption analysis after extraction by solvents or by chromatography on chelating ion exchange resins will give different results.

This together with the problem of uniformization of sampling techniques are extremely important points ; intercalibration, choice of analytical method, preparation of standardized samples, etc are topics about which chemists interested in marine chemistry and related problems should come to a world-wide agreement.

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