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Determination of Cu, Pb, Cd, Zn in sea water by anodic stripping voltammetry.

A first approach to the problem of the speciation of heavy metals in sea water.

by

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Introduction

Many publications in recent years are dealing with different methods proposed for the determination of heavy metals in sea water [Dyrssen *et al.* (1972)] : as the concentrations are normally very low, in the $\mu\text{g}/\ell$ range, a preconcentration step is often necessary (coprecipitation, solvent extraction, anion exchange, chelating ion exchange) and because of the presence of high concentration of salts, some methods like activation analysis require removal of the main constituents. In our case, we shall limit our interest only in the four heavy metals : copper, lead, cadmium and zinc. Beyond the fact that the concentrations of these heavy metals are very low ($\mu\text{g}/\ell$ or sub- $\mu\text{g}/\ell$ level) which means that contamination during collection and analysis (filters, glassware, chemicals, air-borne

dust, a.s.o. or loss during preservation and shipping of the sample) may easily lead to meaningless values, especially if preconcentration steps are necessary, this analytical problem is still more complicated by the fact that these metals are present in the Sea Liquid Medium in different forms : soluble species like Cu^{++} , CuOH^+ , CuOHCl , CuCO_3 , CuCl^+ , complexed amino acids and those associated with suspended particulate organic and inorganic matter [Dyrssen *et al.* (1974)].

It is therefore not surprising that the results found in the literature differ so greatly from one method to an other, even when they are obtained in the same laboratory on the same sample, mainly because each method gives the results for different species. The situation is still worse if the results concern samples resulting from different sampling or storing techniques. Nevertheless, as it is pointed out in many recent publications [Laitinen (1974)], the understanding and the evaluation of pollution by metals require from the analytical chemist not only the determination of their bulk concentration in the water phase, the planktons, the organisms, the sediments but, in each compartment the discrimination among various species in which the metal is present. Evidently, this represents an enormous task for the analytical chemists [Dyrssen (1972, 1974), Laitinen (1974)].

Among the multi-element methods of analysis that may be considered for the heavy metals or some of those we are considering, one finds, neutron activation analysis, mass spectrometry, arc, spark or flame emission spectrometry or anodic stripping voltammetry. We adopted like several others [Whitnack (1961, 1964), Sinko and Dolezal (1970), Macchi (1965), Ariel *et al.* (1964), Naumann and Schmidt (1971), Baric and Branica (1967), Whitnack and Sasselli (1969), Ariel and Eisner (1963), Odier and Pichon (1963), Florence (1972), Nikelly and Cooke (1957), Le Meur and Courtot-Coupez (1973)] the last technique for different reasons : the equipment is rather simple and inexpensive, the method does not require preliminary concentration or separation of the main salts which means a minimum contamination risk during analysis. On the other hand, as we shall see later, this method seemed to offer a rather simple, although crude, approach to the problem of the speciation of those heavy metals in sea water.

In the second part, some preliminary results concerning comparison between atomic absorption and anodic stripping will be mentioned in order to find out if the results obtained by both methods are reliable; a systematic difference between the results of both methods would perhaps allow us to find more informations about the species given by each method.

1.- Determination of Cu , Cd , Pb , Zn in sea water

1.1.- Sampling, storage and filtration of the samples

The sea water samples were collected by a centrifugal pump made of teflon, stored in polythene bottles, rapidly frozen at - 40 °C and maintained at - 20 °C , prior to analysis.

We have observed, as many others did before [Robertson (1968a,b)] that sea water samples stored in a polythene bottle at room temperature and sea pH undergo after three days a noticeable loss probably by adsorption on the vessel walls (table 1).

Table 1

Dates	Cu (µg/l)	Pb (µg/l)	Cd (µg/l)	Zn (µg/l)	Conditions
19- 1 -72	30.2	5.5	1.7	76	Room temperature pH = 8
21- 1 -72	13.2	2.6	1.0	39	
1-7-71	17.6	7.0	0.20	84.5	Stored at - 20°C pH = 8
8-9-71	18.2	6.4	0.19	91	
21- 1 -72	19.5	6.6	0.22	80	
18- 1 -72	30	5.5	1.0	66	Room temperature pH = 1
20- 3 -72	29	5.3	1.0	68	
26- 6 -72	30	5.8	1.2	65	

Storage at room temperature after acidifying at pH = 1 with HCl or at a temperature of - 20 °C does not indicate (in that concentration range) any noticeable loss even after several months.

All our samples have been stored at - 20 °C ; they are quickly thawed immediately before they are required for analysis and filtered through a 0.22 µm pore size Millipore filter. Here again, it is

important to wash the filters [Tolg (1972), Burrel (1972)] with 100 ml of a 10^{-2} M DTPA solution before filtering the sea water (table 2). The results on the heavy metal content of these Millipore filters were obtained by anodic stripping after dry ashing with microwave-activated oxygen and dissolving the residue with 2 ml of suprapur HCl .

Table 2

	$\mu\text{g Cu}$	$\mu\text{g Pb}$	$\mu\text{g Cd}$	$\mu\text{g Zn}$	Weight of Millipore filters in mg
Analysis of unwashed Millipore filters	1.15	0.01	0.01	0.52	82
	1.25	0.50	0.05	0.91	83
	3.0	0.06	0.32	19.7	83.4
	1.25	0.01	0.22	0.30	83
	2.3	0.07	0.23	0.27	83.4
Millipore filter washed with DTPA	0.01	0.005	0.02	0.01	83

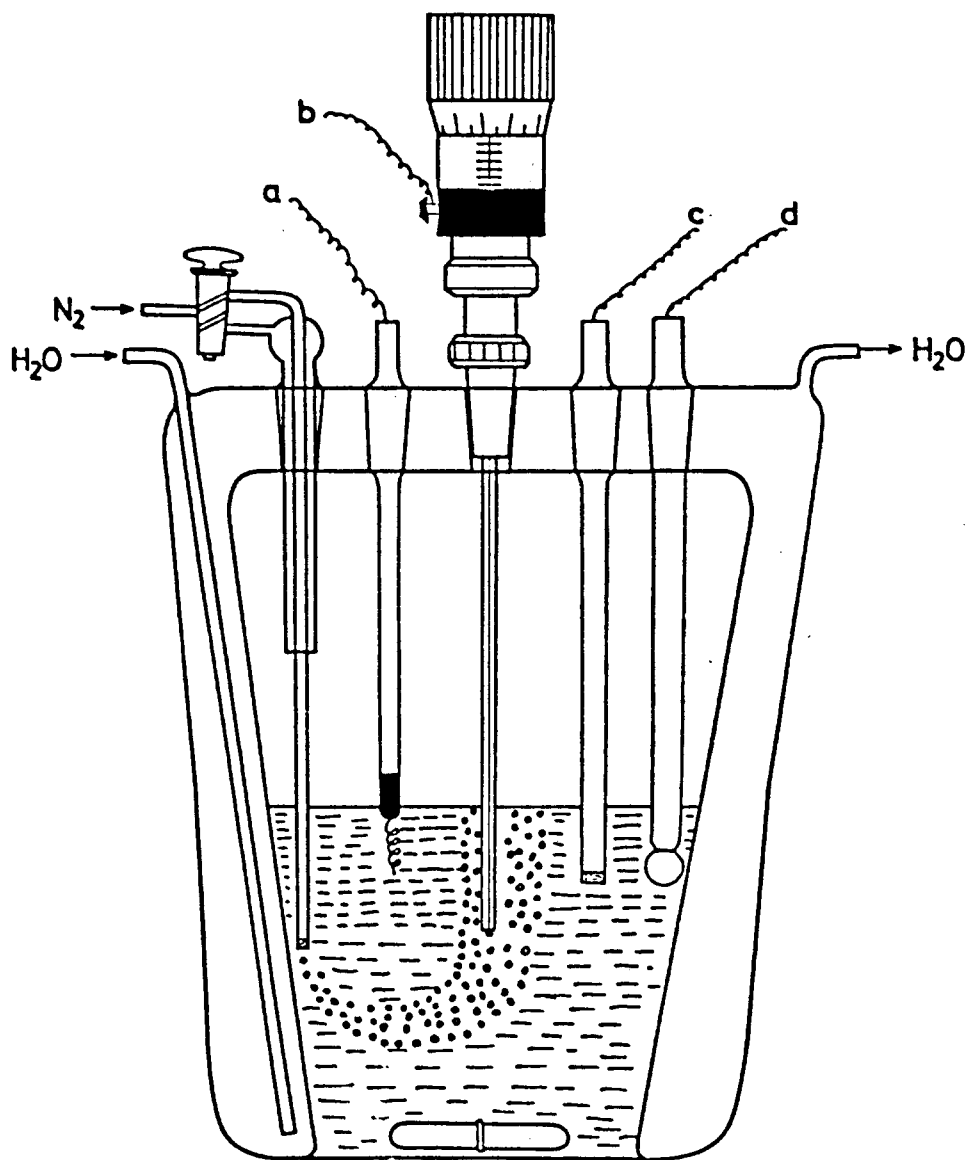
N.B. These values are corrected for the blank coming from the 2 ml of HCl used in dissolving the residue from dry ashing.

1.2.- Instrumentation

The determination of the four heavy metals is carried out on the freshly obtained filtrate by anodic stripping voltammetry with a hanging mercury drop electrode (HMDE).

The experiments were performed with the electronic unit (E.S.A. Multiple Anodic Stripping Analyzer Model 2014 - ESA Inc. Mass. U.S.A.) allowing the use of four cells simultaneously : it contains four units for electrolysis and one unit for the redissolution step. Instead of using the original cell of the manufacturer containing a mercury coated graphite cathode of large area, we preferred to adapt a more elaborate cell with a mercury drop cathode (HMDE).

Fig. 1 shows a drawing of our cell consisting of a Metrohm hanging mercury drop electrode, a platinum working electrode and a silver-silver chloride reference electrode. The glass electrode proved to be useful for our experiments at different pH. The cell temperature was adjusted



a : counter electrode
b : hanging mercury drop electrode

c : reference electrode : silver-silver chloride
d : glass electrode

fig. 1.

at $25^{\circ}C$ by a thermostat. The details of the procedure we have finally adopted are best illustrated by referring to fig. 2.

The cell contains 30 ml of solution; the distance between the mercury drop electrode and the magnetic stirrer is 25 mm. The diameter

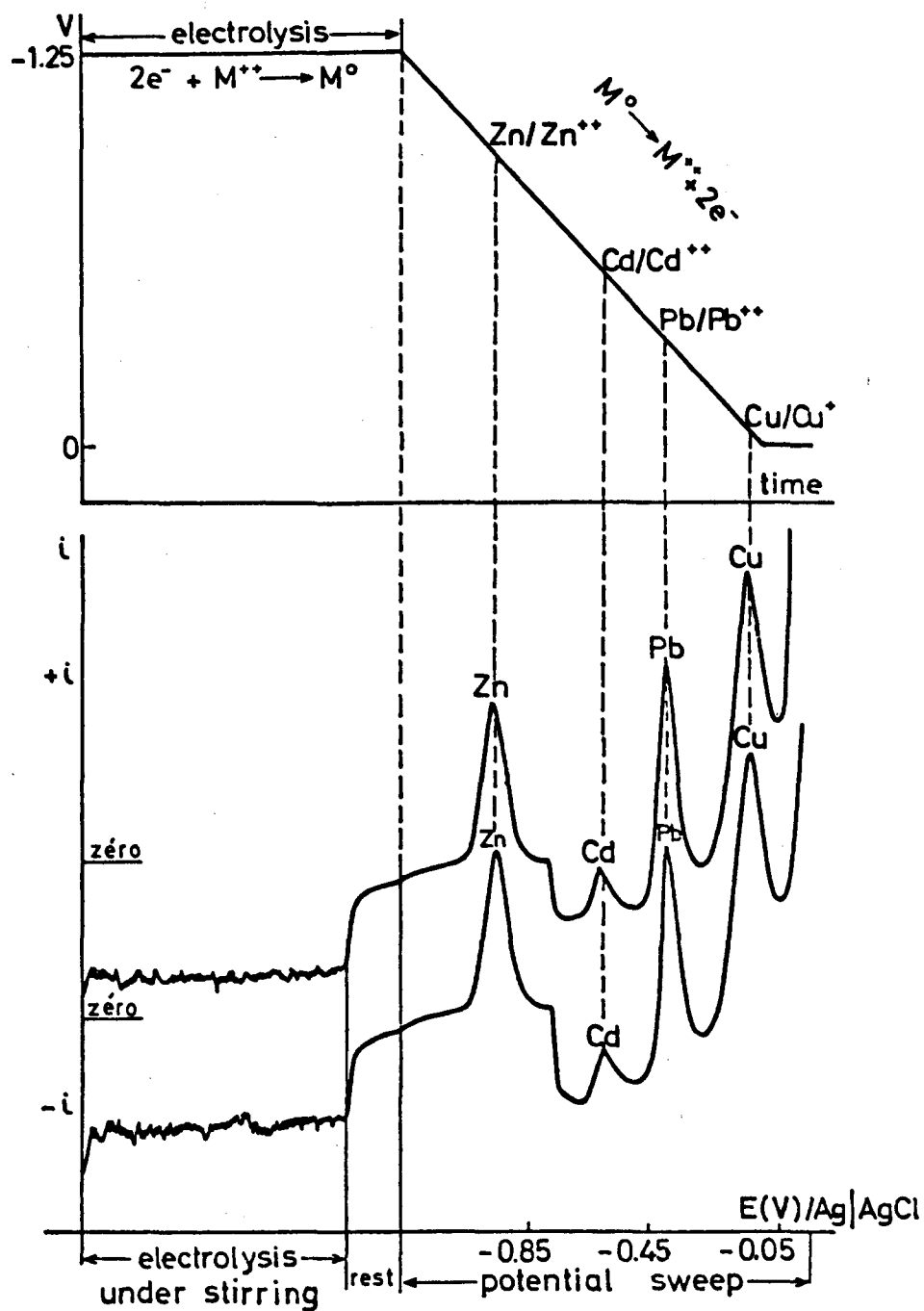


fig. 2.

of the drop is 0.76 mm . After bubbling very pure nitrogen through the solution for at least 30 minutes in order to remove oxygen, electrolysis is started at a constant potential of - 1.25 volt versus reference electrode, the magnetic stirrer being in steady state at 550 revolutions per minute; electrolysis is carried out for a precisely measured time ranging from 10 to 15 minutes depending on the concentrations of the metals to be determined.

After that time, the stirrer motor is stopped and after one more minute, the metals concentrated in the mercury drop are dissolved by linear sweep voltammetry at a rate of 200 mV/min .

In order to obtain the concentration of the four elements in the solution, we adopted the standard addition method, the volume of the injected standard solutions being adapted to the concentrations to be evaluated. This equipment allowed us to carry out the analysis of twelve samples per day with one operator.

1.3.- Reproducibility of the method

The reproducibility of the method has been tested on a sea water sample by carrying out five experiments and two recordings on each solution. The results are given in table 3.

Table 3

Number	Cu ($\mu\text{g}/\text{l}$)	Pb ($\mu\text{g}/\text{l}$)	Cd ($\mu\text{g}/\text{l}$)	Zn ($\mu\text{g}/\text{l}$)
1	3.0	5.1	1.25	5.2
2	2.8	5.7	1.35	4.5
3	3.0	5.6	1.55	4.8
4	2.9	6.1	1.5	4.4
5	2.6	6.1	1.45	5.0
Standard deviation (%) for 95 % confidence limits	7.0	8.5	13	6.5

1.4.- Influence of the pH on the results [Duursna and Seven Huysen (1966); Mancy]

As we have mentioned previously, the heavy metal content in the filtered sea water sample is distributed among different soluble species and perhaps some inorganic and organic particulate matter which passed through the filter.

The distribution between these species depending on the solution pH and the reduction rate on the mercury drop being different from one to another, one would expect an influence of the pH on the analytical result. This influence is illustrated in figure 3.

These results were obtained by starting with an acidified sea water sample and by increasing progressively the pH by NaOH addition. As pointed out by Dyrssen and Wedborg (1974), most complexation of heavy metal ions with organic ligands probably occurs within particulate matter of biological origin even if the amount of dissolved organic matter may be considerably larger. A part of this is certainly collected on the Millipore filter but as we shall see later, a not negligible amount remains in the filtered sample. Concerning the rest of the soluble species, we must consider, beside the free ions, those complexed by inorganic and organic ligands. The authors just mentioned above have evaluated the percentage speciation for those inorganic complexes (table 4).

Table 4

Percentage speciation in sea water at natural pH

Complex	Cu	Pb	Cd	Zn
M ⁺⁺	0.7	4.5	1.8	16.1
MOH ⁺	3.7	10.2	-	2.3
MHCO ₃ ⁺	-	1.4	-	0.3
MCO ₃	21.6	0.4	0.2	3.3
MSO ₄	-	0.5	0.2	1.9
MF ⁺	-	-	-	-
MCl ⁺	5.8	18.9	29.2	44.3
MCl ₂	1.6	42.3	37.5	15.4

peak heights
in mm

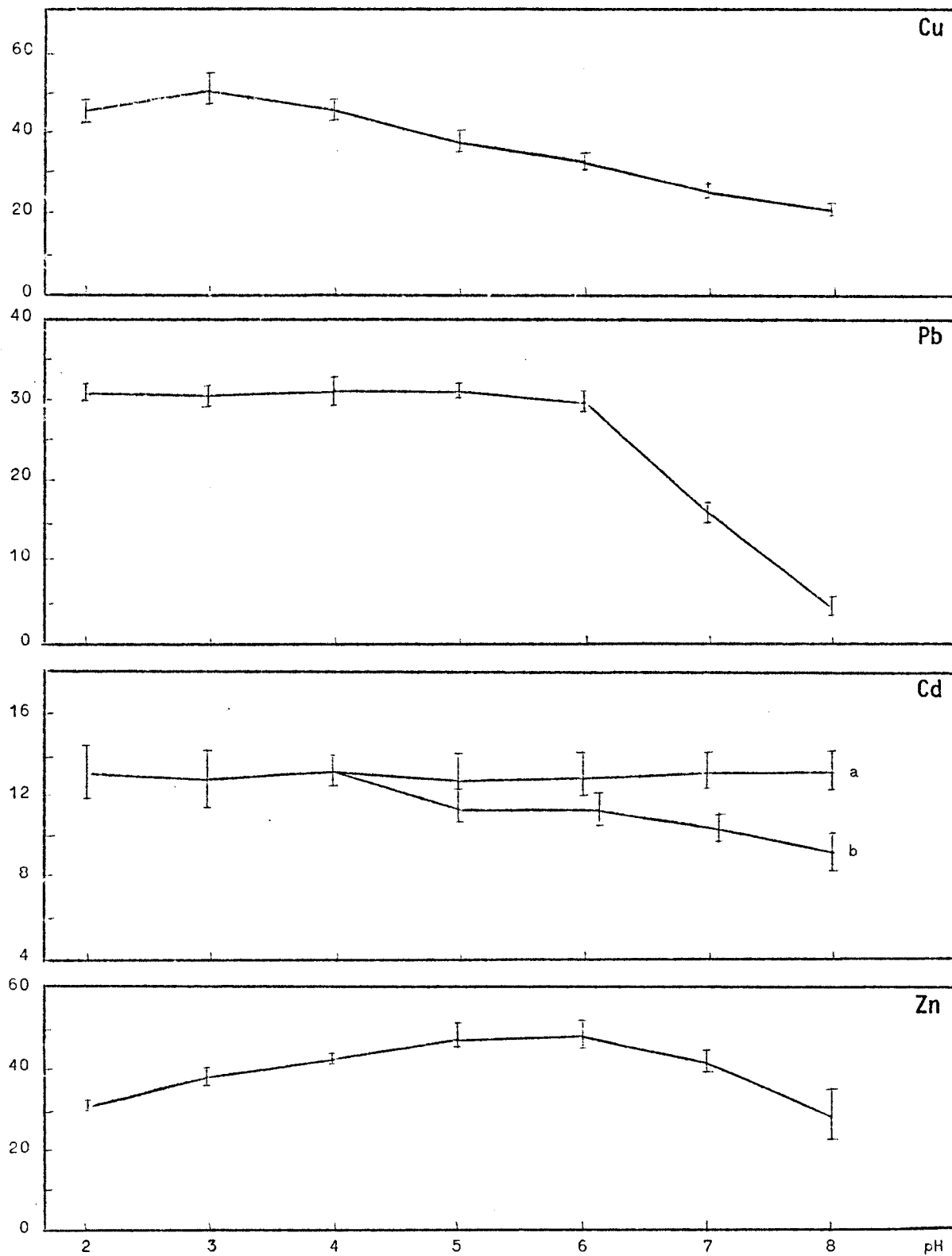


fig. 3.

Table 4
(continuation)

Complex	Cu	Pb	Cd	Zn
MCl_3	0.7	9.2	27.9	1.7
MCl_4^{--}	0.5	3.6	-	2.3
$MOHCl$	65.2	8.8	2.9	12.5
MBr^+	-	0.15	0.2	-

(Taken from The Sea, vol. 5, Marine Chemistry, Dyrssen and Wedborg).

It should be noticed from fig. 3 that the behaviour differs for the four cations : between the limits of errors, the concentration of cadmium given by this method is more or less independent of the pH between 2 and 8 , a result which is not too surprising since the chlorocomplexes are the main constituents (in some samples, a decrease with pH is observed nevertheless).

For lead and copper, we observe a progressive decrease of the measured content with increasing pH ; this could perhaps be more or less related with the percentage of hydroxychlorocomplexes.

The curve for zinc looks, at first sight, more surprising, but the decrease with decreasing pH is probably partly due to the interference of proton reduction at - 1.25 volt .

Beside these mentioned effects, it is quite reasonable to assume that this increase in heavy metal content observed for copper, lead and zinc by acidifying the sea water may be partly due to the dissociation of some organic complexes.

In order to give some very crude evaluation of the relative importance of the labile complexes with respect to the soluble species which are reducible at the pH of sea water, we decided to carry out, for each sample, an evaluation of the four cations respectively at pH = 3 and pH = 8 .

1.5.- Effect of irradiation by ultraviolet light

Armstrong has shown that irradiation of the sea water by ultraviolet light gives rise to some decomposition of the organic material [Johnston (1964), Pocklington (1971)] with liberation of complexed metallic ions [Armstrong *et al.* (1966)]. We therefore decided to analyze again the sample after irradiation for 12 hours under the light of germicide tubes TUV of 30 watts; the 30 ml sample is contained in a slowly rotating quartz tube of 15 mm diameter (fig. 4). pH of sample = 1.

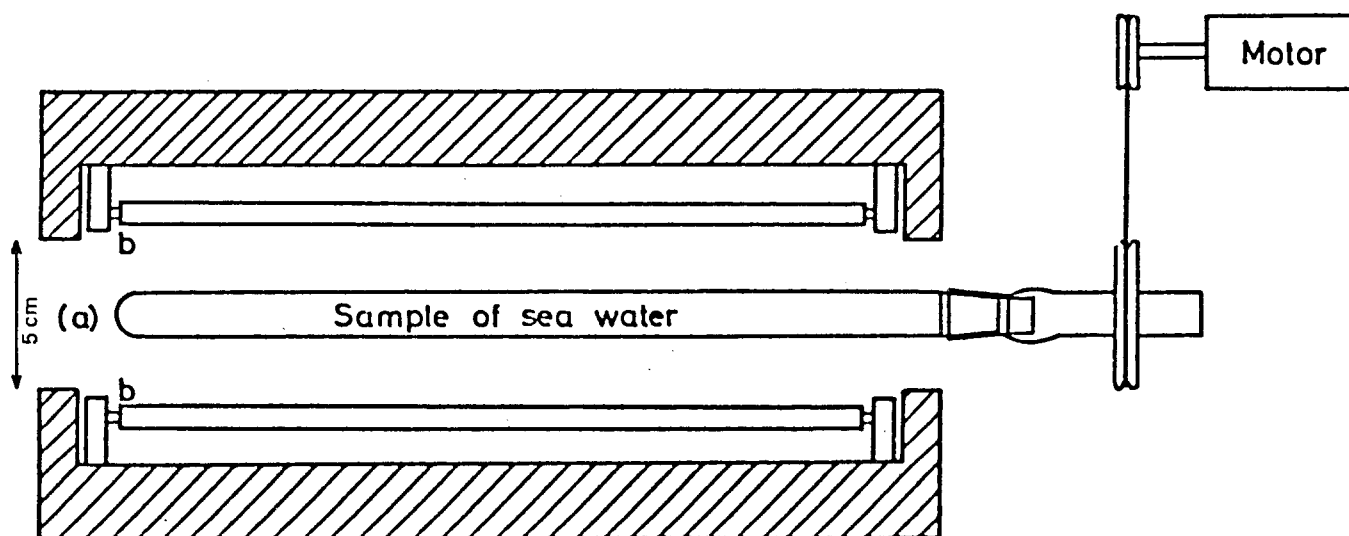


fig. 4.

UV Irradiation system.

a : quartz tube containing the sea water sample pH = 1

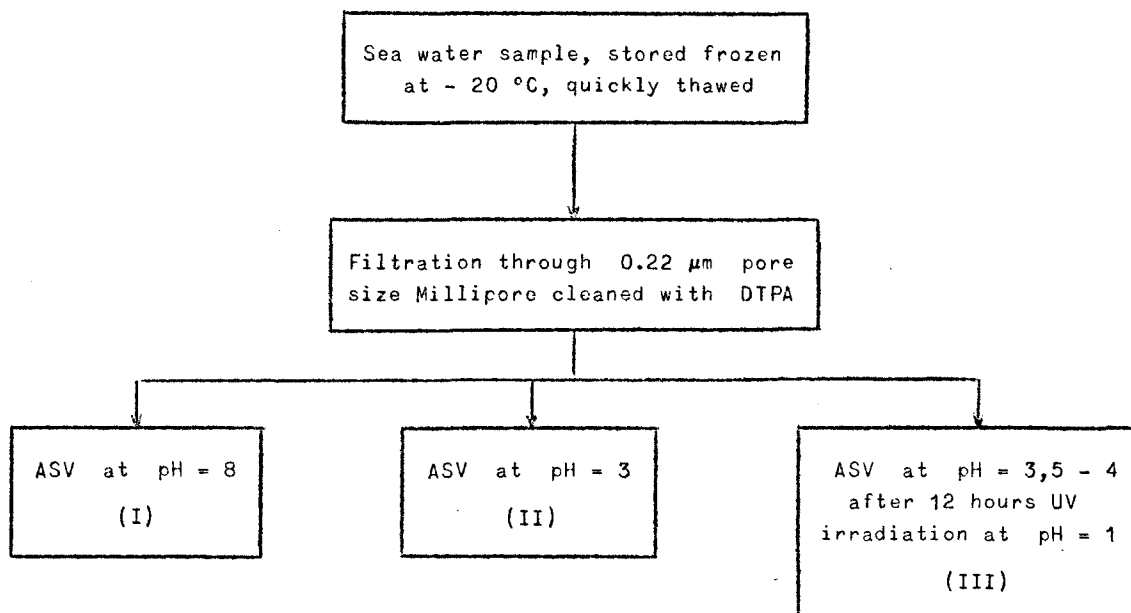
b : germicide-TUV lamps

As we shall see later, the heavy metal content observed by anodic stripping voltammetry (ASV) in acid medium has increased systematically after irradiation¹.

1. Some authors propose the destruction with persulfuric acid of the organic ligands causing the masking of a more or less important fraction of the heavy metal content [Noakes and Wood (1961); Slowey, Jeffery and Wood (1967)].

1.6.- Analysis schema

These considerations led us to the following scheme of analysis :



Those three results (I), (II) and (III) expressed in $\mu\text{g}/\text{l}$ allowed us to make a rough estimate of a certain speciation of those metals in the filtered sea water [Rozhanskaya (1970), William (1969), Barker and Ryther (1969)]; the fraction corresponding to the result (I) will be called arbitrarily "ionic species"; the difference between the concentrations of (II) and (I) represents the fraction corresponding to the metals bonded in weak complexes at the pH of sea water : we indicate this by "weakly-complexed cations" and finally the fraction given by the difference (III) - (II) is called "strongly-complexed cations". The figure given by (III) represents of course the maximum concentration of dissolved metals we could detect by our method of analysis.

1.7.- Results

More than one thousand sea water samples were analyzed by this method during the last three years; these samples were collected in the North Sea at different locations, periods of the year and depths.

As a matter of illustration of the method we have just described, we represent in tables 5 and 6 and in figures 5 to 8, the analytical results obtained for "solution species" of copper, lead, cadmium and zinc in the three compartments - ionic, weakly-complexed and strongly-complexed.

Tables 5 and 6 indicate the location reported on the map (figures 5 to 8) as well as the date and hour of sampling.

It is not our intention to discuss in this place the results in connexion with the problem of pollution or with the question of retention of heavy metals by microorganisms or inorganic particulates.

Table 5

Cruise of May 27th, 1974

Identification	Cu ($\mu\text{g}/\text{l}$)			Pb ($\mu\text{g}/\text{l}$)		
	I pH in situ	II pH = 3	III U.V.	I pH in situ	II pH = 3	III U.V.
M01.270574.1300.05	1.9	7.9	12.2	2.3	5.3	9.3
M02.270574.1530.05	1.4	7.3	17.6	2.9	5.1	4.9
M04.270574.1900.05	1.0	7.9	11.6	3.0	4.3	21.8
M20.280574.0830.05	1.8	5.5	5.2	3.8	5.0	10.7
M25.280574.1200.05	2.9	5.8	6.1	2.6	4.0	8.3
M22.280574.1600.05	2.9	5.8	8.4	3.0	4.4	7.8
M05.290574.0700.05	2.7	6.6	6.4	2.2	17.7	25.8
M55.290574.1030.05	2.5	9.3	12.5	5.0	5.1	13.0
M09.290574.1400.05	1.5	5.5	8.6	2.0	3.5	13.0
M15.290574.1700.05	2.1	3.0	3.1	3.1	7.9	8.1
M21.300574.0700.05	4.0	6.0	11.0	9.0	13.0	15.0
M16.300574.1030.05	2.9	5.2	4.8	2.4	4.0	7.1
M11.300574.1600.05	1.3	6.5	6.7	3.7	5.5	6.0
M12.300574.1800.05	2.8	5.5	8.7	3.5	4.7	5.1

M05.290574.0700.05 means a sample taken by the Mechelenship at point 05, the 29th May 1974, at 7.00 a.m. and at five meter depth.

Table 5 (continuation)

Identification	Cd ($\mu\text{g}/\text{L}$)			Zn ($\mu\text{g}/\text{L}$)		
	I pH in situ	II pH = 3	III U.V.	I pH in situ	II pH = 3	III U.V.
M01.270574.1300.05	0.08	0.22	0.45	0.5	3.5	3.8
M02.270574.1530.05	0.26	0.31	1.39	1.0	2.6	16.6
M04.270574.1900.05	0.07	0.23	0.66	0.9	1.3	2.6
M20.280574.0830.05	0.11	0.53	0.77	1.4	4.0	13.3
M25.280574.1200.05	0.15	0.46	0.40	0.6	2.7	4.7
M22.280574.1600.05	0.33	0.38	0.38	5.8	7.2	10.0
M05.290574.0700.05	0.08	0.21	1.00	0.5	2.3	5.0
M55.290574.1030.05	0.07	0.64	1.00	0.8	4.4	6.0
M09.290574.1400.05	0.17	0.29	0.81	2.5	3.5	18.3
M15.290574.1700.05	0.10	0.35	0.30	0.8	1.5	4.2
M21.300574.0700.05	0.20	0.22	1.30	1.5	2.4	9.6
M16.300574.1030.05	0.18	0.18	0.30	3.0	4.6	5.5
M11.300574.1600.05	0.10	0.75	0.68	2.3	5.0	11.1
M12.300574.1800.05	0.13	0.72	0.68	1.6	7.2	8.5

Table 6

	Cu ($\mu\text{g}/\text{L}$)				Pb ($\mu\text{g}/\text{L}$)				Cd ($\mu\text{g}/\text{L}$)				Zn ($\mu\text{g}/\text{L}$)			
	a	b	c	III	a	b	c	III	a	b	c	III	a	b	c	III
M01	1.9	6.0	4.3	12.2	2.3	3.0	4.0	9.3	0.08	0.14	0.23	0.45	0.5	3.0	0.0	3.8
M02	1.4	5.9	10.3	17.6	2.9	2.2	0.0	5.1	0.26	0.05	1.08	1.39	1.0	1.6	14.0	16.6
M04	1.0	6.9	3.7	11.6	3.0	1.3	17.5	21.8	0.07	0.16	0.43	0.66	0.9	0.4	1.3	2.6
M20	1.8	3.7	0.0	5.5	3.8	1.2	5.7	10.7	0.11	0.42	0.24	0.77	1.4	2.6	8.7	13.3
M25	2.9	2.9	0.0	5.8	2.6	1.4	4.3	8.3	0.15	0.31	0.00	0.46	0.6	2.1	2.0	4.7
M22	2.9	2.9	2.6	8.4	3.0	1.4	3.4	7.8	0.38	0.00	0.00	0.38	5.8	1.4	2.8	10.0
M05	2.7	3.9	0.0	6.6	2.2	15.5	8.1	25.8	0.08	0.13	0.79	1.00	0.5	1.8	2.7	5.0
M55	2.5	6.8	3.2	12.5	5.0	0.0	8.0	13.0	0.07	0.57	0.36	1.00	0.8	3.6	1.6	6.0
M09	1.5	4.0	3.1	8.6	2.0	1.5	9.5	13.0	0.17	0.12	0.52	0.81	2.5	1.0	14.8	18.3
M15	2.1	1.0	0.0	3.1	3.1	4.8	0.0	7.9	0.10	0.25	0.00	0.35	0.8	0.7	2.7	4.2
M21	4.0	2.0	5.0	11.0	9.0	4.0	2.0	15.0	0.20	0.00	1.10	1.30	1.5	1.0	7.2	9.7
M16	2.9	2.3	0.0	5.2	2.4	1.6	3.1	7.1	0.18	0.00	0.12	0.30	3.0	1.6	1.0	5.5
M11	1.3	5.2	0.0	6.5	3.7	1.8	0.0	6.0	0.10	0.65	0.00	0.75	2.3	2.7	6.1	11.1
M12	2.8	2.7	3.2	8.7	3.5	1.2	0.0	4.7	0.13	0.59	0.00	0.72	1.6	5.6	1.3	8.5

Column a : concentration of ionic species; column b : concentration of "weakly-complexed cations"; column c : concentration of "strongly complexed cations"; column III : maximum concentration observed. The samples correspond to those of table 5.

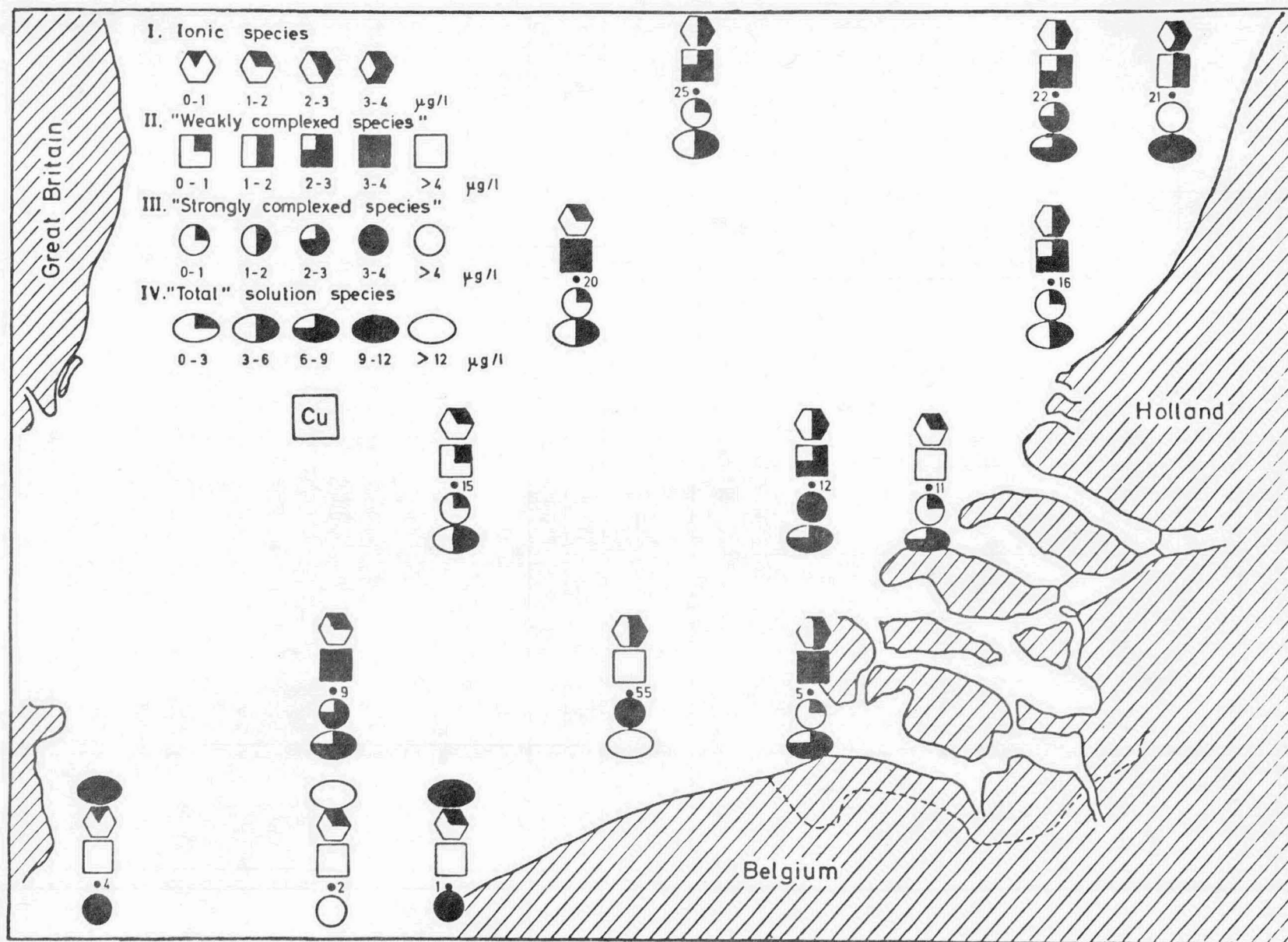


fig. 5.

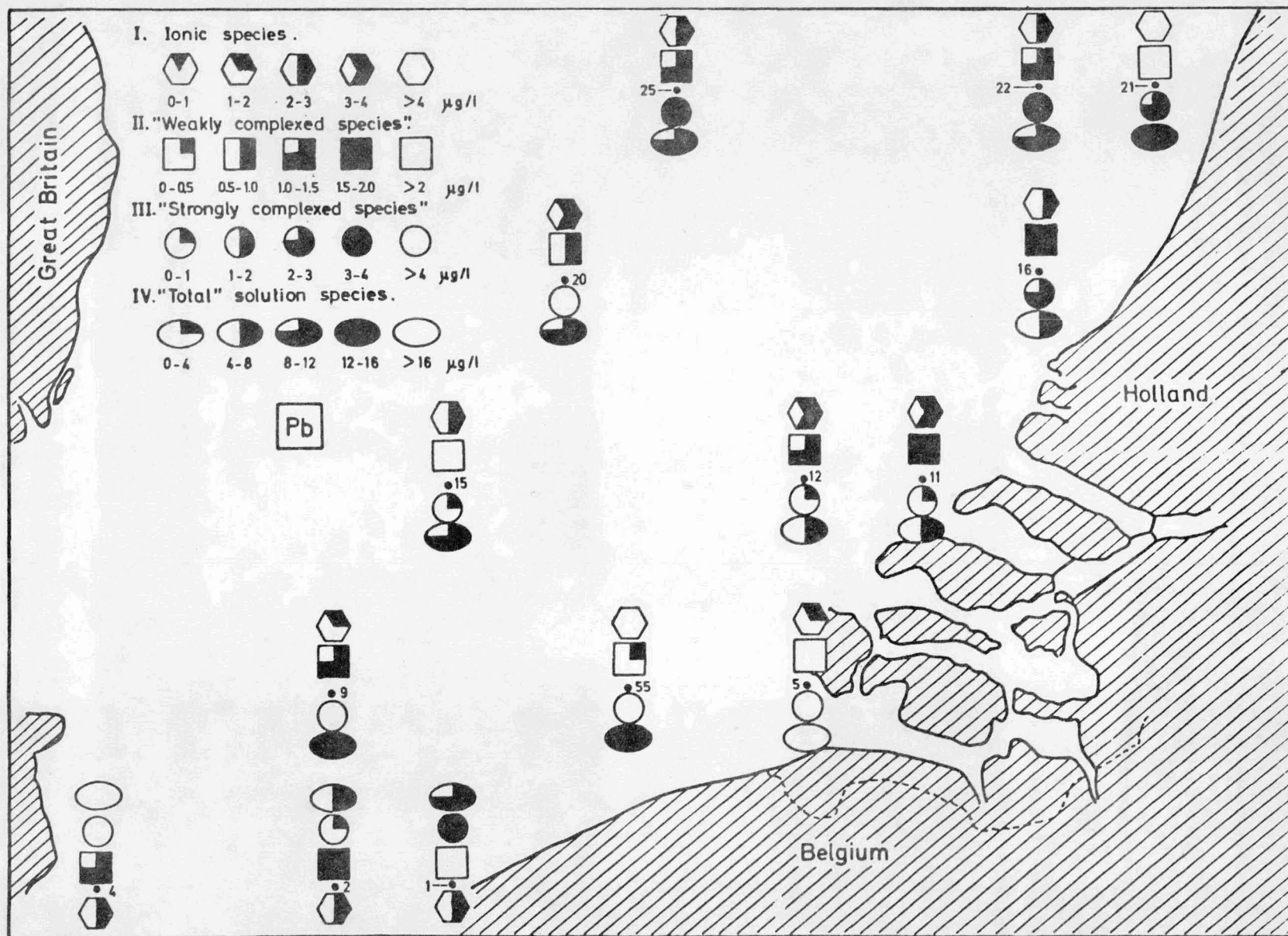


fig. 6.

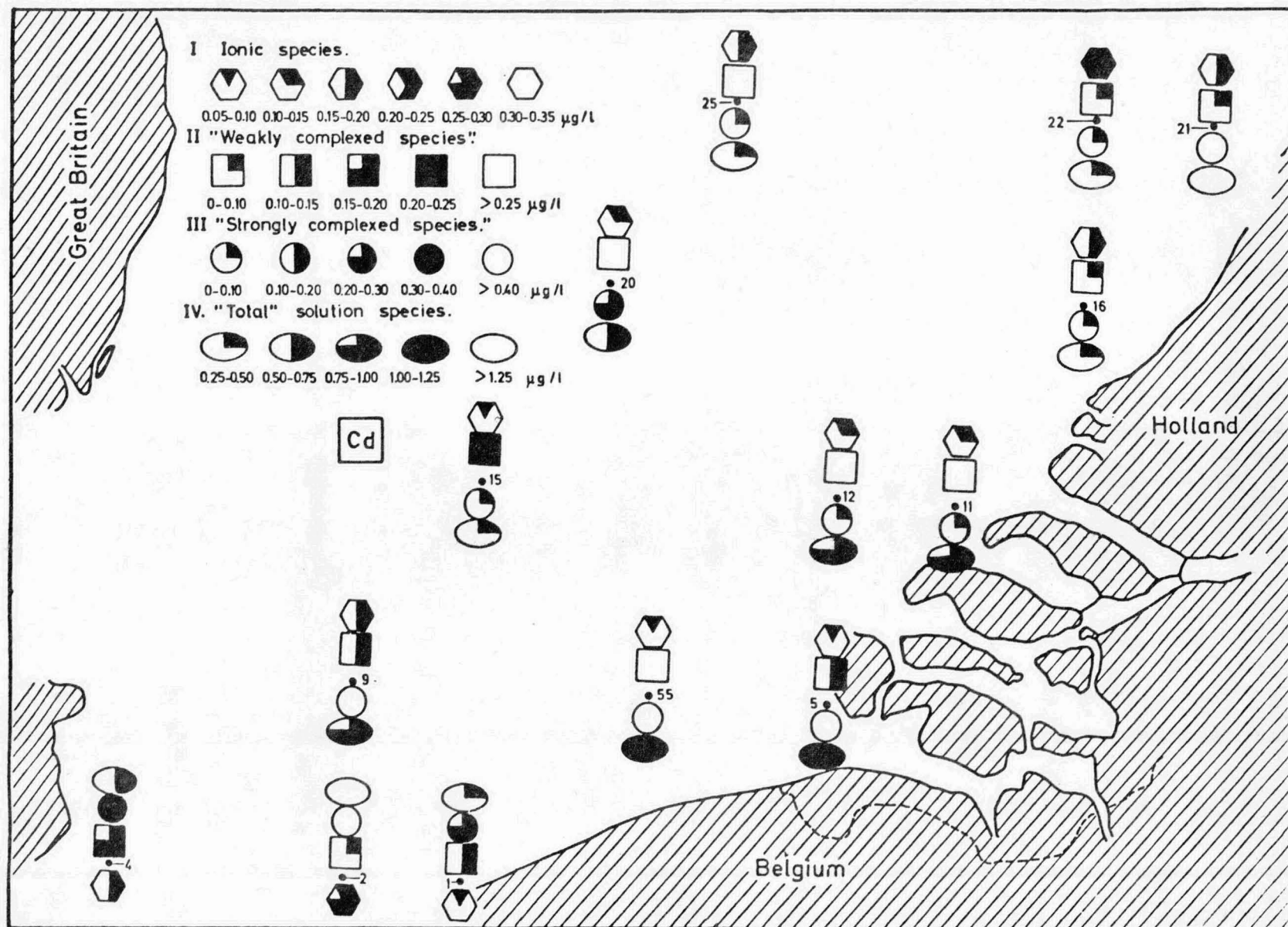


fig. 7.

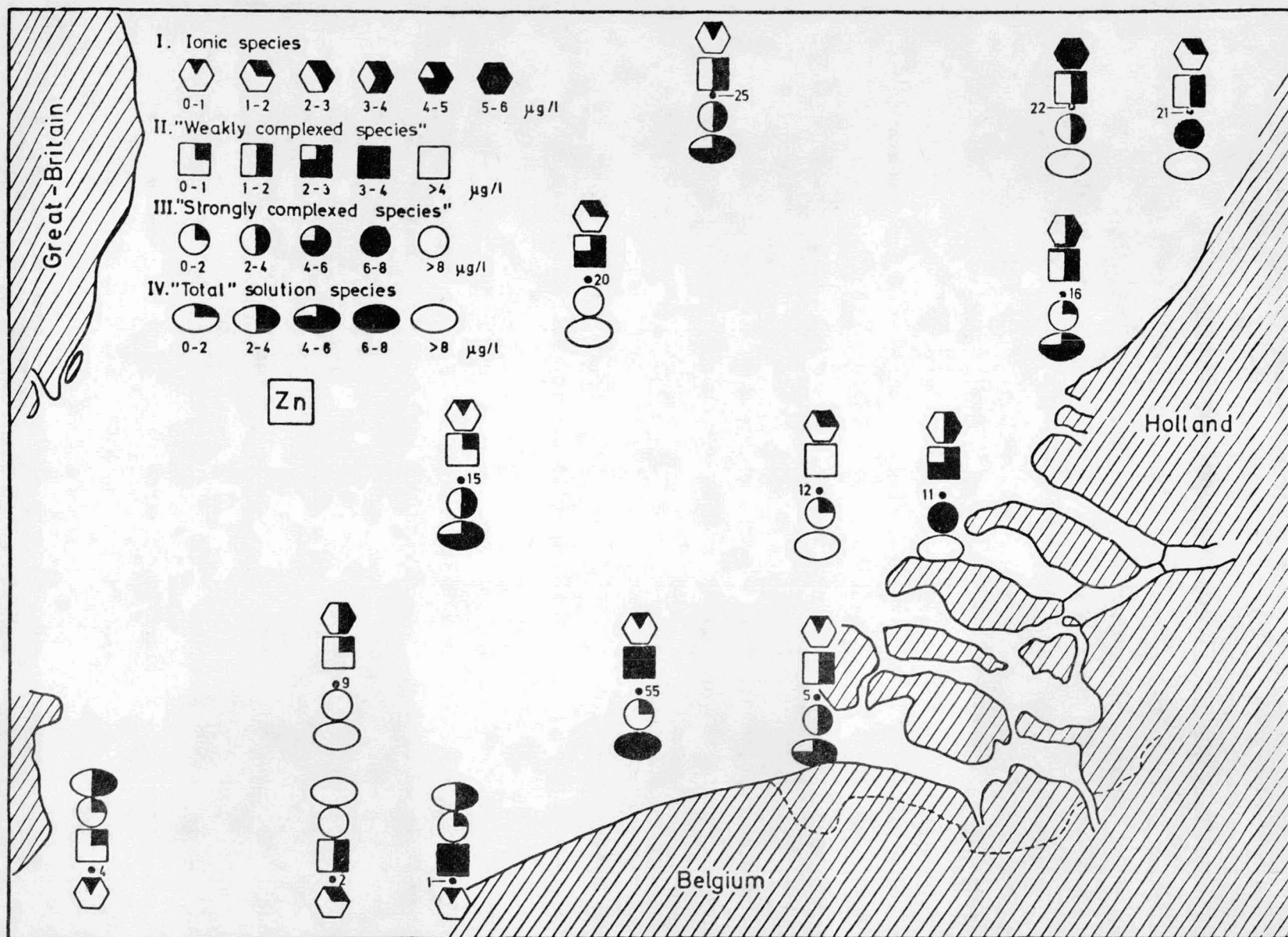


fig. 8.

2.- Preliminary comparison between ASV and atomic absorption

Atomic absorption spectrometry is used by many laboratories [Segar and Gonzales (1972), Fabricand, Sawger, Ungar and Adler (1962), Burrel and Wood (1969)] for heavy metals determination in sea water, the solution injected in the flame or in the graphite furnace being an extract obtained either by solvent extraction usually with APDC-MIBK [Paus (1973), Burrel (1967), Kuwata *et al.* (1971), Magnee and Rahman (1965), Armitage and Zeitlin (1971), Brooks *et al.* (1967)] (ammonium pyrrolidine dithiocarbamate - methylisobutylketone) or by chromatography on a chelating ion-exchange resin [Riley and Taylor (1968), Le Meur et Courtot-Coupez (1973)] (chelex-100 or Dowex A1). This preliminary extraction step is required by the necessity to remove the salt matrix for atomic absorption and to concentrate the solution in heavy metals. A great deal of literature exists on this subject. Intercalibration of different methods between different laboratories has been carried out in the USA recently for lead in ocean water [Patterson (1974)] and a project between several laboratories in Great Britain, Holland and Belgium is considering this problem; from the results already obtained, it seems that some very general conclusions can be drawn. One should mention first of all that three methods were used on the same samples :

- 1) Heavy metal extraction by APDC-MIBK or APDC- CHCl_3 at the pH of sea water followed by atomic absorption with the graphite furnace;
- 2) Heavy metal extraction by Chelex 100 (50-100 mesh Bio-Rad Lab) at pH = 7.6 eluted with HNO_3 .2N and analysis by flame or graphite furnace atomic absorption;
- 3) Anodic stripping voltammetry on the sample acidified until pH = 3 .

These three methods, applied in different laboratories on the same samples, gave, except for zinc, results which are significantly different. In general, the concentrations found for copper, lead and cadmium by ASV are higher than those obtained by AA-Chelex concentration and the latter are often higher than those by AA-extraction APDC. This observation is probably not too surprising by considering the fact that on one side AA gives the concentration of those species which are extracted at pH = 8

by APDC or by Chelex and on the other side, ASV gives the concentration of those species which are reduced to metal at - 1,25 volts and at pH = 3 .

As we know that the pH influences considerably the distribution of the heavy metal ions between different species, it seemed worth comparing these three methods on the same sea water solution at the same moment in the same laboratory.

The results presented in table 7 were carried out by Machiroux *et al.* (1973) for APDC-MIBK extraction and AA and by Machiroux et Dupont (1974) for Dowex A1 extraction and AA.

Table 7

Comparison of the results obtained by the three methods

N°	Cu ($\mu\text{g/l}$)			Pb ($\mu\text{g/l}$)		Cd ($\mu\text{g/l}$)		Zn ($\mu\text{g/l}$)	
	ASV	AAS	AAR	ASV	AAS	ASV	AAS	ASV	AAS
427	5.2	4.8		6.3	2.7	0.91	0.86	6.2	5.9
428	4.2	4.0		1.4	1.5	0.45	0.43	1.2	1.1
429	1.5	1.3		4.3	4.9	2.4	2.1	41.2	29.2
430	4.7	4.5		1.5	1.7	0.28	0.20	3.5	3.3
432	3.8	1.1		1.2	1.4	0.33	0.14	1.9	
433	4.1	1.6		2.6	0.4	0.14	0.16	2.2	
1	6.5		7.1						
2	15.2		13.8						
3	6.9		7.2						
4	14.8		11.6						
5	3.5		3.3						

ASV : anodic stripping voltammetry

AAS : atomic absorption after solvent extraction with APDC-MIBK

AAR : atomic absorption after Dowex A1 separation

The experimental conditions adopted are briefly the following :
the sea water samples are quickly thawed, immediately filtered through a 0.22 μm pore size Millipore and divided in three parts for analysis :
1) Anodic stripping voltammetry at pH = 3.5 - 4 (ASV);

- 2) Atomic absorption with the graphite furnace on the organic phase obtained by extracting three times by 5 ml MIBK 20 ml of sea water at pH = 4 containing 2 ml of APDC 1 % (AAS);
- 3) Atomic absorption with the graphite furnace on the following eluted solution : 100 ml of sea water pH = 8 passed through a column of Dowex A1 50-100 mesh with a flow rate of 0,5 ml/min \times cm² ; the elution is performed with 100 ml of HNO₃.2N at the same flow rate (AAR).

Considering the fact that the greatest discrepancies between different methods occur generally for copper, we carried out the comparison between ASV and AAR only on that element.

The results are presented in table 7.

Keeping in mind the low concentrations we are dealing with and the fact that atomic absorption requires a series of operations subject to contaminations and considering the errors inherent to each method, it seems reasonable to conclude that all three methods are capable to give, *under the described conditions*, the same result.

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