Column Separation and Preconcentration
of Copper(II), Lead(II) and Zinc(II) from Seawater

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**Trennung und Anreicherung von Kupfer(II),
Blei(II) und Zink(II) aus Meereswasser
mit Hilfe eines Trennsäulensystems**

Zusammenfassung. Die Probe Meereswasser (5 l) wird nach Entfernen der festen Teilchen auf einen pH-Wert von 5,6 gepuffert und durch eine Trennsäule mit ED_3A geführt. Die angereicherten Metallionen werden mit 15 ml 1 M HCl-Lösung eluiert. Anschließend erfolgt die Bestimmung durch Flammenatomabsorption. Die Methode erfordert insgesamt weniger als 15 min Arbeitszeit. Die Standardabweichungen (4 Best.) betragen für Cu, Pb und Zn (im normalen Bereich von etwa $2-6 \mu g \cdot l^{-1}$) etwa $2-5\%$, 5% und $1-10\%$, die Wiederfindungsraten 100%, 102% bzw. 104%. Der Konzentrationskoeffizient beträgt 300 bis 500.

Summary. The sample of seawater (5 l) is freed from solid particles, buffered at pH 5.6 and percolated through a column filled with ED_3A. After sample passage 15 ml 1 M hydrochloric acid solution are pumped through the column to dissolve the concentrated ions. The final measurement using flame atomic absorption is carried out in the hydrochloric acid solution. The total labour time is less than 15 min. The standard deviations (4 analyses) for the determination of Cu, Pb and Zn (in the normal concentration range of $2-6 \mu g \cdot l^{-1}$) were $2-5\%$, 5% and $1-10\%$, the recoveries 100%, 102% and 104%, respectively. A concentration coefficient of $300-500$ was obtained.

Key words: Best. von Kupfer, Blei, Zink; Spektralphotometrie, Atomabsorption; Flamme, chromatogr. Trennung

Due to the increasing number and complexity of pollution problems monitoring or at least frequent analysis of seawater at certain places is necessary. Analyses of a number of metals have been shown to be of great importance. From these metals, Cu(II), Pb(II) and Zn(II) were chosen as indicators giving information on the total pollution with metal ions.

Many methods for the analysis of metals in seawater are in use or have been proposed, e.g. anodic stripping differential pulse polarography [15], direct [4] or indirect [12] flameless atomic absorption spectrometry, X-ray fluorescence spectrometry and neutron activation [3]. Dybczyński et al. [6] gave a brief comparison of various analytical methods.

Electrochemical methods although promising, are not widely used in environmental routine analysis. This may be caused by the fact that experienced and skilled personnel is necessary, especially in this field. Flameless atomic absorption spectrometry has a sufficient sensitivity but matrix interferences, light scattering and background molecular absorption cause problems in the direct determination [1, 5]. Therefore its use in routine environmental analysis is troublesome. Flameless atomic absorption spectrometry gives good results if a proper matrix separation is carried out [13]. But once using a separation step in the procedure of the analysis, one may use, in stead of flameless atomic absorption, the more conventional flame absorption technique, which takes less labour time. X-ray fluorescence spectrometry and neutron activation analysis give good results but the techniques are somewhat out of the scope of a normal laboratory analyzing seawater.

Routine analysis of many seawater samples requires a simple final determination in combination with an automated sample pretreatment step. Such a simple and cheap method could be flame atomic absorption spectrometry. A pretreatment involving a matrix separation and concentration step should be automated and require no attention during the operation.

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Commonly used pretreatments are extraction [13], precipitation or coprecipitation [9] or electrodeposition [10]. These batch-wise methods are time and labour consuming and many times the concentration coefficients are small. Column pretreatments, in which the sample to be cleaned up is poured over a column containing some active material, are more promising and more easily automated.

Many active materials have been proposed. Braun and Farag [2] present a survey of several kinds of column materials. Immobilized reagents insuring a certain selectivity should be preferred. A drawback of many of the known immobilized reagents is their leaching out from the column. Ion exchangers on the contrary have less selectivity [14] which involves more external reagents and subsequently the ion exchange methods require more labour time and are more complicated [8]. Further, ion exchangers do not always release all the ions trapped before [11]. Burba et al. [3] present a discussion on several ways of pretreatment.

As an outcome of our considerations we feel that a group-selective immobilized reagent, which is free of any leaching-out effect should be chosen as a column filling in an automated procedure. A fairly new reagent, ED_3A, of which some properties already are known [7], was investigated. ED_3A consists mainly of EDTA chemically bound on a glass support. The material is commercially available.

1. Principle

Solid particles are removed from the seawater sample by any appointed method e.g. centrifugation or filtration. Then some buffer is added to adjust the pH value to 5.6 and the sample is pumped over a column filled with ED_3A. The metal ions are retained on the column. After sample passage the metal ions are dissolved in a small amount of a hydrochloric acid solution which passes through the ED_3A column in turn. Finally, the ions are measured in this solution using flame atomic absorption.

2. Experimental

2.1. Reagents. All chemicals were "Baker analyzed reagents"; deionized water was used.

The stock solutions of the metal ions were prepared by dissolving Cu(II), Pb(II) and Zn(II) nitrates to an amount of 2000 ppm in 6 M HCl. These solutions were diluted with water for use in the calibrations and standard additions. The diluted solutions were 1 M in HCl.

Acetate buffer: 0.1 M acetic acid and 1 M sodium acetate.

Column material: CPG-ED_3A (controlled pore glass-ethylene diamine triacetic acid; Pierce 23520).

Simulated seawater consisted of a 3 % (w/v) NaCl solution or a 2 % (w/v) artificial sea salt (Diwex) solution, intended for use in marine aquaria.

2.2. Apparatus. Sample centrifugation was carried out with 2 l of the sample during 15 min at about 10,000 g (vacuum; 15°C), using a Prepspin 50 Ultracentrifuge (MSE). A cellulose nitrate membrane filter (0.45 µm; SM 11306; Sartorius) in a filtration device (SM 16317; Sartorius) was used for sample filtration.

The peristaltic pumps (Gilson Minipuls II, model HP-1) had a controllable flow rate. Metal concentrations were measured using an atomic absorption spectrophotometer (Varian Techtron 1200) with an air/acetylene flame.

2.3. Procedure. Solid particles were removed from the sample (5 l) either by centrifugation or by filtration. The sample pH is adjusted by adding 500 ml buffer solution (pH 5.6). The prepared samples were kept in polythene vessels. The sample was pumped over the column [2] which was filled to a length of 10 cm with the immobilized reagent. The column consisted of a glass tube (inner diam. 0.6 cm; length 14 cm) closed on both ends with a Quickfit SQ 13 screw cap in which the tubings were fixed. The flow rate was 5 ml · min^{-1}. The pumping was stopped after the passage of 5 l of buffered sample. This procedure, which took about 17 h, was carried out over night.

The metal ions were dissolved by pumping a hydrochloric acid solution (1 M) over the column; the solution was collected in a 10 or 15 ml calibration flask. Then the column was cleaned with 100 ml of hydrochloric acid 1 M. The column material was used continuously for 3 – 6 months.

Atomic absorption measurements of Cu(II), Pb(II) and Zn(II) were carried out at wavelengths of 324.7, 217.0 and 213.9 nm resp., using an air/acetylene flame.

3. Results

Table 1 presents the results obtained from solutions of Cu(II), Pb(II) and Zn(II) in a 3 % (w/v) sodium chloride solution. The mean (13 analyses) recovery was 100, 102 and 104 %, respectively. Other solutions resembling seawater were made by dissolving "sea salt for marine aquaria". The results found upon standard addition of the three metal ions are presented in Table 2.

Table 3 presents the results found upon standard additions to North Sea water from which the investigated ions were previously removed by ED_3A column percolation. The water originates from the Eems-Dollard estuary (polluted area).

These results suggest again that the column traps all the naturally occurring "free" metal ions. Table 4 deals with the measurement of standard additions to real seawater (Source: North Sea near Oostvoorne). Table 5 finally presents analyses of seawater from various sampling spots from the North Sea west and north of the Netherlands. The same samples were analyzed by RIZA (the Netherlands' "Government Institute of Sewage and Waste Water Treatment") using an entirely different method. The results of both methods agreed well.

4. Discussion

Several factors influence the method and have to be discussed here. The molarity of the hydrochloric acid

Table 1. Determination of Cu(II), Pb(II) and Zn(II) in the presence of 3% (w/v) NaCl

Given ($\mu g \cdot l^{-1}$)			Found means ($\mu g \cdot l^{-1}$)			Number of detns.	Stand. dev. (%)		
Cu(II)	Pb(II)	Zn(II)	Cu(II)	Pb(II)	Zn(II)		Cu(II)	Pb(II)	Zn(II)
2	2	4	2.0	1.9	4	4	5	5	10
4	4	8	4.0	4.2	8	4	3	5	4
6	6	12	6.0	6.3	13	5	2	5	1

Table 2. Determination of Cu(II), Pb(II) and Zn(II) dissolved in a 2% (w/v) solution of a mixture of salts resembling seawater

Added ($\mu g \cdot l^{-1}$)			Found means ($\mu g \cdot l^{-1}$)			Number of detns.	Stand. dev. (%)		
Cu(II)	Pb(II)	Zn(II)	Cu(II)	Pb(II)	Zn(II)		Cu(II)	Pb(II)	Zn(II)
0	0	0	5.3	4.2	8	2	—	—	—
2	2	4	2.0	2.0	3	6	9	7	12
4	4	8	4.1	4.1	8	4	4	4	7
6	6	12	6.1	6.1	10	6	2	4	6

Table 3. Determination of Cu(II), Pb(II) and Zn(II) dissolved in seawater, from which these ions previously were removed

Added ($\mu g \cdot l^{-1}$)			Found means ($\mu g \cdot l^{-1}$)			Number of detns.	Stand. dev. (%)		
Cu(II)	Pb(II)	Zn(II)	Cu(II)	Pb(II)	Zn(II)		Cu(II)	Pb(II)	Zn(II)
0	0	0	0.7	1.1	1^5	2	—	—	—
2	2	4	1.7	1.9	4	4	5	5	2
4	4	8	3.6	3.8	8	4	4	11	2
6	6	12	5.6	5.4	12	3	3	9	2

Table 4. Analysis of seawater with standard additions

Added ($\mu g \cdot l^{-1}$)			Found ($\mu g \cdot l^{-1}$)		
Cu(II)	Pb(II)	Zn(II)	Cu(II)	Pb(II)	Zn(II)
0	0	0	0.9	0.1	10
2	2	4	2.5	2.2	14
4	4	8	4.4	4.2	20
6	6	12	6.9	6.8	24

Table 5. Some typical results of analyses of seawater samples

Sample origin	Year/ month/ day	Found ($\mu g \cdot l^{-1}$)		
		Cu(II)	Pb(II)	Zn(II)
North sea channel (Velsen)[a]	78/07/13	5.7	0.4	23.0
Waddenzee (Dutch Shallows)[a]	78/07/20	0.6; 0.7	0.6; 0.7	4.6; 5.5
Waddenzee[a]	78/07/20	1.3; 1.4	3.7; 3.9	12.4; 13.4
Waddenzee[a]	78/07/20	1.9; 2.3	0.4; 0.7	9.8; 10.7
Eems-Dollard I	78/08/09	2.3; 2.5	0.1; 0.3	8.0; 8.0
Eems-Dollard II	78/08/09	1.8; 2.0	0 ; 0.1	9.3; 9.6
Eems-Dollard III	78/08/09	1.4; 1.4	0 ; 0	6.2; 6.9
Eems-Dollard IV	78/08/10	2.3; 2.4	0.3; 0.3	13.9; 14.2
Eems-Dollard V	78/08/10	1.3; 1.4	0.4; 0.4	6.9; 7.3
Eems-Dollard I	78/09/11	2.6; 2.6	0 ; 0.1	12.0; 12.2
Eems-Dollard II	78/09/11	1.6; 1.6	0.1; 0.3	20.4; 21.0
Eems-Dollard III	78/09/11	1.4; 1.5	0 ; 0	6.6; 6.6
Eems-Dollard IV	78/09/13	2.2; 2.4	0 ; 0	11.6; 12.1
Eems-Dollard V	78/09/13	1.1; 1.3	0.1; 0.3	14.6; 14.8

[a] Centrifuged sample

solution used to strip the metal ions from the column should not be too low. Table 6 gives a summary of the influence of the molarity of hydrochloric acid on the recovery for the various metal ions. Especially the recovery of copper is highly affected by the acid strength. The chosen acid strength of 1 M is at the safe side.

The flow rate of the sample solution through the column is an other important experimental parameter. At very low flow rates all equilibria are set well and the metal ions are retained to the highest possible degree.

**Table 6.** Influence of acid strength on the recovery of Cu(II), Pb(II) and Zn(II) in 3% (w/v) NaCl solutions

Acid strength $(mol \cdot l^{-1})$	Given $(\mu g \cdot l^{-1})$			Number of detns.	Stand. dev. $(\mu g \cdot l^{-1})$			Recovery (%)		
	Cu(II)	Pb(II)	Zn(II)		Cu(II)	Pb(II)	Zn(II)	Cu(II)	Pb(II)	Zn(II)
0.10	5	5	10	5	0.9	0.3	0.1	26	100	93
0.10	5	5	10	5	0.7	0.1	0.4	12	102	100
0.01	5	5	10	4	–	0.5	1.1	0	30	61
0.01	5	5	10	5	–	0.6	1.2	0	34	62

Flow rate $(ml \cdot min^{-1})$	Recovery (%)
3	100
5	95
10	89

Table 7
Recovery of copper(II) at various sample flow rates

Table 8. Determination of Cu(II), Pb(II) and Zn(II) using different eluent (1 M HCl) volumes

Eluted volume (ml)	Given (μg)			Found (μg)			Number of detns.	Stand. dev. (%)		
	Cu(II)	Pb(II)	Zn(II)	Cu(II)	Pb(II)	Zn(II)		Cu(II)	Pb(II)	Zn(II)
10	20	20	40	21.0	21.4	40.1	5	4	4	2
15	20	20	40	21.0	21.9	39.1	5	2	4	1
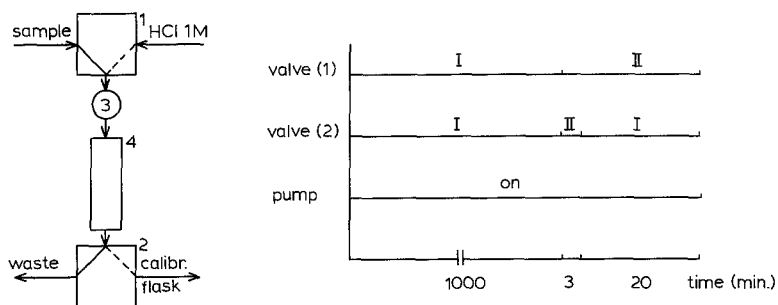
Fig. 1
Left: Flow scheme: (*1,2*) three-way valves (full line: position I; dotted line: position II) (*3*) peristaltic pump; (*4*) column.
Right: Time setting of valves and pump

However, a very low flow rate is impractical because of the long total time of analysis involved and because of the high equipment cost per analysis. Thus an optimal sample flow rate has to be found. Table 7 presents some recoveries of copper at various flow rates indicating that the finally selected flow rate of 5 ml · min^{-1} allows acceptable recoveries in an acceptable amount of time.

The recovery usually is improved by using a longer column. In orientating experiments some column lengths were studied. The advantage of a longer column, however, are restricted. As in a longer column more acid solution is needed to strip off the metal ions, a more diluted final solution results. The chosen column length was optimal in practice. Investigations were made to establish the minimal amount of acid solution needed to liberate all metal ions from the column. As a general outcome an amount of three times the column volume is sufficient, provided that the flow rate is moderate (e.g. appr. 5 ml · min^{-1}). Table 8 presents some figures on the recovery obtained for a column length of 10 cm and a flow rate of 5 ml · min^{-1}.

The accuracy of the lead determination is less than the accuracy found for the other metals. This may be caused by the better accuracy for Cu and Zn in flame atomic absorption. As the concentration coefficient obtained in daily practice is relatively high (appr. 400) we could use flame atomic absorption as a final

determination. If one likes to use flameless atomic absorption methods one may collect and pump less sample and the accuracy especially in the lead determination can be improved. But, as stated before, the whole procedure would consume more labour time.

In the completely automated mode (Fig. 1) the method is not labour consuming [7]. The overall labour time per sample in a series is 10 − 15 min. The most time consuming step is the filling of the calibrated flask prior to the final determination.

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