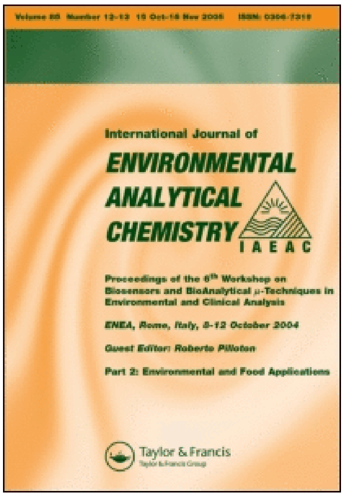

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Comparison of APDC/FREON Extraction and Chelex-100 Ion Exchange Chromatography for Preconcentration of Heavy Metals from Seawater

C. Díaz-romero[a]
[a] Department of Analytical Chemistry, Food Science & Toxicology, University of La Laguna, La Laguna, Spain

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COMPARISON OF APDC/FREON EXTRACTION AND CHELEX-100 ION EXCHANGE CHROMATOGRAPHY FOR PRECONCENTRATION OF HEAVY METALS FROM SEAWATER

C. DÍAZ-ROMERO

Department of Analytical Chemistry, Food Science & Toxicology, University of La Laguna, 38071-La Laguna, Spain

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Two methods for preconcentration of heavy metals from seawater: APDC/Freon extraction and CHELEX-100 ion exchange chromatography, have been compared. Retention of heavy metals on a CHELEX-100 resin in the acid form was not complete. Consistent and reliable results were obtained for Ni, Cd, Pb, and Zn by both studied preconcentration methods. CHELEX-100 ion exchange chromatography is not suitable for Fe and Cu preconcentration because of the low recoveries obtained, 79 and 72% respectively. Applying the CHELEX-100 ion exchange chromatography method, the preconcentration factor and the consuming time were higher than when the APDC/Freon extraction method was used.

KEY WORDS: Heavy metals, seawater, preconcentration techniques.

INTRODUCTION

A search of the literature for concentration of heavy metals which might be regarded as baseline in seawater reveals a great deal of variability. This is due to the compositions of different types of seawater (coastal and open seawater) as well as problems related to the analysis such as contamination or losses of the element of interest during sampling, storage or analysis. Also, the use of several methods of analysis can produce different results[1,2].

Several methods have been used for analysing heavy metals in seawater such as neutron activation analysis (NAA)[3,4], differential anodic stripping voltametry (DASV)[3,5–8], cathodic stripping voltametry (CSV)[9] or inductively coupled plasma atomic emission spectrometry (ICP-AES)[10–15]. But the most widely used method is probably atomic absorption spectrometry with flame (F-AAS)[16,17] or graphite furnace (GF-AAS)[18–27] technique. The use of the graphite furnace improves the sensitivity but the analysis is then more expensive than with the use of the flame technique.

The main problems in analysis of heavy metals in seawater are the low levels (usually sub µg/l for most heavy metals) and interferences due to salt matrix. Although some authors[1,8,14,18,19,26] have proposed the direct determination of heavy metals in seawater, preconcentration and/or separation steps such as chelating ion exchange[4,6,7,11,23] extraction[3,7,9,21,23–25,27] or coprecipitation[5,12,21] have frequently been recommended for their determination.

In this paper, two methods to preconcentrate heavy metals in seawater, APDC/Freon-TF extraction and Chelex-100 ion exchange chromatography, have been compared.

EXPERIMENTAL

Apparatus

Pye-Unicam SP-100 and Varian atomic absorption spectrophotometers, provided with deuterium arc background correction. Hollow-cathode lamps for Cd, Pb, Ni, Zn, Fe, and Cu.

Radiometer PH M84 digital pH-meter equipped with glass-calomel combination electrode.

Milli-Q water system OM-140.

Reagents and solutions

1000 µg/l Cd, Pb, Ni, Zn, Fe, and Cu Fisher certified standard solutions for AAS. Appropiate dilutions with milli-Q water were carried out for preparing the calibration curves.

Ammonium pyrrolidine dithiocarbamate (APDC), 2% aqueous solutions purified by repeated extractions with Freon-TF.

Ammonium citrate buffer (pH = 5) purified by extraction with Freon-TF.

CHELEX-100 resin Bio-rad (200–400 mesh, sodium form). 10 ml (≈5 g) of wet resin were introduced in an exchange column (10 cm × 2 cm i.d.). The resin was repeatedly (10 fold) precleaned with 10 ml hydrochloric acid (6 M) by suspension, decantation and addition of fresh acid. It was then rinsed with milli-Q water and treated with 50 ml of calcium acetate (0.5 M) in order to change the acid form to the Ca^{+2} form of the resin. Finally, the resin was cleaned with milli-Q water (250 ml) until Ca^{+2} ions were not detectable in the eluate.

Sodium 5,5-diethylbarbiturate/5,5-diethylbarbituric acid buffer (pH = 7.6).

Other reagents used were of analytical quality.

All equipment used in the analysis and containers was precleaned with an ordinary wash, and subsequently treated with HNO_3 1:1, and repeatedly rinsed with milli-Q water.

Seawater samples

25 l sample seawater was collected in polypropylene containers in the docks of Santa Cruz de Tenerife which was used for optimization and comparison of the two studied preconcentration methods. This sample were stored in polypropylene containers, acidified (5 ml of concentrated nitric acid/1 l of seawater) to pH = 1–1.5.

Procedures of determination compared

1) Preconcentration by APDC/Freon-TF extraction: This method is similar to that described by L. G. Danielson *et al.*[24] but the initial volume of seawater is doubled in

order to increase the concentration factor. Also, the shaking time and volume of extractants were twice those recommended by the authors[24].

In outline, transfer and filter 1 l of seawater to a separatory funnel. Adjust the acidified sample to pH = 5 with 6 ml of purified ammonium citrate buffer and sodium hydroxide. Add 6 ml of purified APDC (2%) and 40 ml of Freon-TF, and shake vigorously for 3 min. Allow the phases to separate and drain the lower organic layer into a stoppered test tube. Add another 20 ml of Freon-TF and shake the funnel for 1 min. Combine the two extracts and add 0.4 ml of concentrated nitric acid. Shake the tube for 30 sec. and let it stand for at least 5 min. Add 10 ml of milli-Q water and shake for 20 sec. The acid extract is now ready for determination by AAS.

2) Preconcentration by CHELEX-100 exchange chromatography:
This method is analogous to that described by Lamathe[18], decreasing the final volume to 10 ml to improve the concentration factor.

Previously, the resin must be changed to the Ca^{+2} form by treatment with calcium acetate which as described above. Take 5 l of seawater and acidify it to pH 1.5 to store. Adjust the pH to 7.7–7.8 with sodium hydroxide and pass this solution at 5 ml/min through a CHELEX-100 column. Sucessively, wash the column with acetic acid and milli-Q water in order to eliminate interferent ions, mainly Ca^{+2}. Eluate (2.5 ml/min) the retained heavy metals with 50 ml of HNO_3 (2 M) and evaporate carefully to near dryness. Dissolve quantitatively the residue with 1–2 ml of nitric acid (0.1 M), adjust to 10 ml with milli-Q water and measure by AAS.

Blanks of seawater

Samples of seawater were treated according to the described procedures to eliminate the heavy metals from seawater. After, these samples were analyzed again to determine the blank values; they were also used in spiking experiments for recovery studies.

RESULTS AND DISCUSSION

The CHELEX-100 resin can be used in several forms: Ca^{+2} [18,20] H^+ [18,25]and NH_4^+ [22,23,25]. CHELEX-100 resin in the acid form was used to investigate the retention of the studied heavy metals (Table 1). The retention of heavy metals on a CHELEX-100 in acid form was not complete, which has been observed by other authors[18,20]. The obtained recoveries decreased when the concentration of Cu decreased. The observed average recoveries for Cu(0.5 μg/l), Cd(0.5 μg/l), and Pb (5 μg/l) were 36.9, 60.0, and 45.1% respectively. Lamathe[18,20] has found complete recoveries for Pb and Cu, obtaining recoveries for Cd and Zn of 35.2 and 82.6% respectively. Sturgeon *et al.*[25] have reported recoveries for Fe and Cu of 55 and 77%, using a column of CHELEX-100 in the acid form to preconcentrate the heavy metals from seawater. The production of H^+ ions in the exchange process, progressively decreased the pH (≈3) of the eluate and therefore, the retention of heavy metals was not effective. Moreover, traces of Cu could be detected in the last 250 ml of seawater after they passed through the resin. Thus, the CHELEX-100 resin in acid form is not suitable for quantitatively separating heavy metals of seawater.

The CHELEX-100 column was therefore changed to the Ca^{+2} form according to the procedure described by Lamathe[18]. Several pHs between 5–6 have been used in order to take advantage of the maximum distribution coefficients for heavy metals relative to alkaline and alkaline earth metals in the retention on the CHELEX-100 resin[12,16,22,25]. However, other authors have preferred to pass the seawater through the CHELEX-100

Table 1 Recovery of some heavy metals from seawater using CHELEX-100 resin in the acid form.

Metal	*n°*	*Initial volume (l)*	*Spiked concentration (μg/l)*	*Recovery (%)*	*pH**	*Concentration (μg/l)**
Cu	1	1	1000	93.4**	2.95	60
	1	1	500	83.8**	3.00	50
	1	1	200	67.2**	3.03	48
	7	5	0.5	36.9 ± 4.6 (30–43)	3.11	n.d.
Cd	7	5	0.5	60.0 ± 8.6 (50–73)	3.08	n.d.
Pb	7	5	5	45.1 ± 5.3 (38–53)	3.14	n.d.

*pH and concentration of the metal in the last 250 ml of seawater passed through the resin.
**The measurement was carried out directly on the 50 ml of HNO_3 (2 M) used for elution.

resin at natural pH (pH ≈ 8)[20]. But most laboratories[18,20] appear to use a pH similar to that described originally. A study of the influence of the pH on the retention of heavy metals by CHELEX-100 resin in the Ca^{+2} form has been carried out. 1 l of aqueous solutions of all the studied heavy metals (2 mg/l) were adjusted to different pHs with barbituric/barbiturate buffer. Then, these solutions were passed through the resin. The retained heavy metals were eluted with 50 ml of nitric acid 2 M and the maximum absorbance for each metal was directly measured in this solution. Figure 1 shows that the maximum value of absorbance for all the studied metals was between 7.7 and 7.8. However, the changes of absorbances through the interval of pH considered were not very high for most metals studied. Metal concentrations usually present in seawater could be assayed in order to evaluate their retention on the CHELEX-100 column in more realistic conditions.

Some authors[16,18] have studied the possibility of selective elution of heavy metals from CHELEX-100 resin, using increasing concentrations of nitric acid. Several volumes of nitric acid (2.5 M) have been recommended for total elution of heavy metals previously retained on the CHELEX-100 column: 7.5[28], 10[7,12,16], 25[29] and 30[25] ml of nitric acid (2.5 M). Flow rate during elution can influence the total volume necessary to complete elution of heavy metals from the CHELEX-100 resin[12]. Thus, the volume of nitric acid (2.5 M) for complete elution of heavy metals has been studied. Recoveries found in the first 25 ml were not complete (≈ 70% for Cu and Cd), using a flow rate for elution of 2.5 ml/min. Therefore, 50 ml were employed to ensure a total recovery of the studied heavy metals. In order to increase the concentration factor, the eluate was taken to near dryness and the saline residue dissolved and adjusted to 10 ml with diluted nitric acid. No losses of the studied heavy metals were observed in this process.

Recoveries of Cd, Pb, Ni, Zn, Fe, and Cu from seawater after both preconcentration methods are shown in Table 2. Several blanks of seawater [5 l (CHELEX-100) or 1 l (APDC/Freon)] were spiked with amounts of metals commonly present in seawater as indicated in Table 2. Then, analysis of the studied heavy metals in seawater was carried out using both methods. When the APDC/Freon-TF extraction was used, good mean values of recovery were obtained. These mean recoveries ranged from 95% for Ni to 101% for Cd. Furthermore, the analytical results for Cd ($P > 0.5$), Pb ($P > 0.05$), and Fe

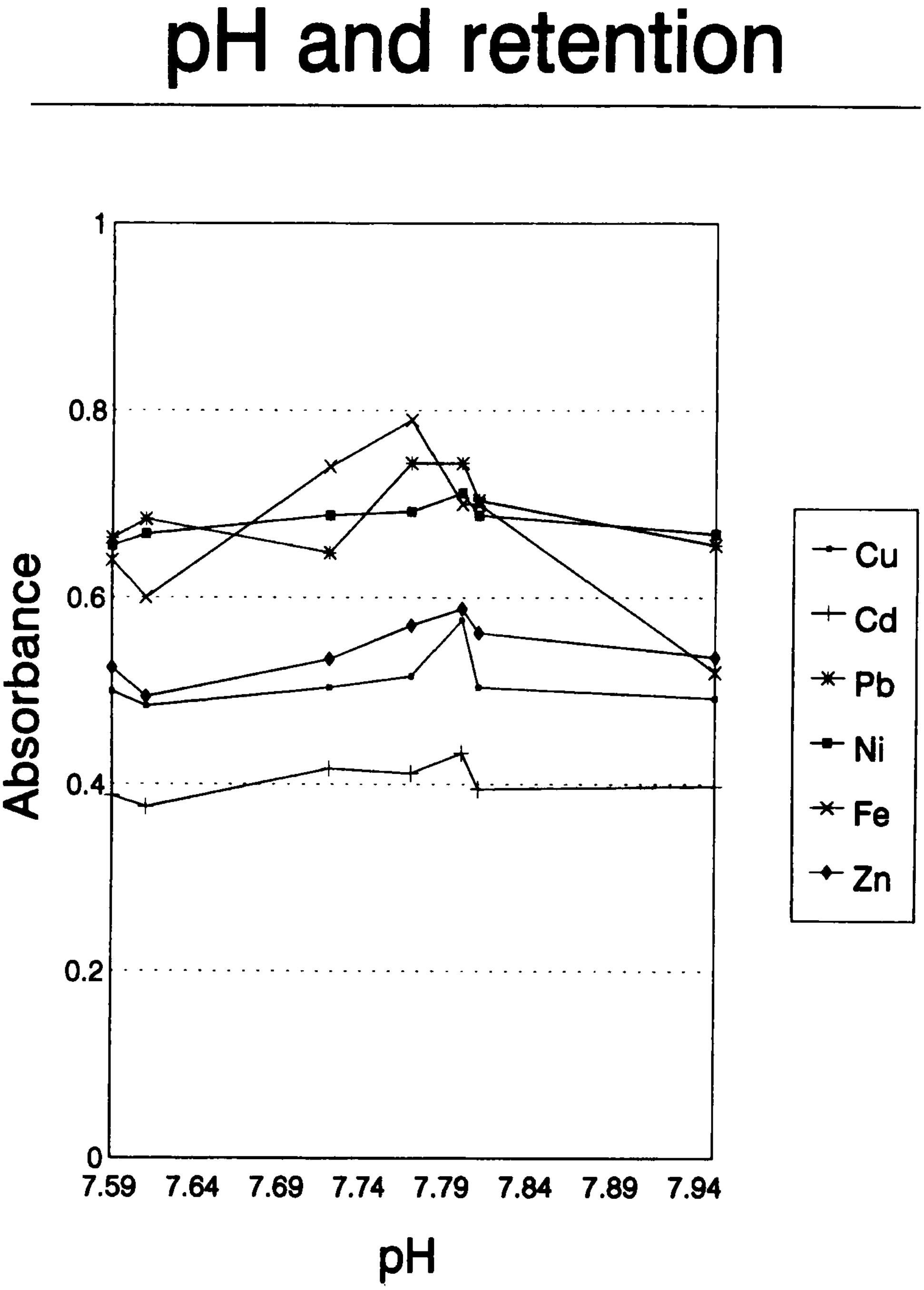

Figure 1 Influence of the pH on the retention of heavy metals in the CHELEX-100 resin.

Table 2 Recovery of the studied heavy metals by the described preconcentration methods.

Metal	*Statistics**	*CHELEX-100*	*APDC/Freon*
Cd	n	11	17
(0.25–2)**	X ± SD	97.9 ± 3.8	100.9 ± 3.7
	m–M	91.3–103.2	94.0–107.5
Pb	n	11	17
(2–16)**	X ± SD	94.0 ± 3.8	98.3 ± 3.32
	m–M	91.3–103.2	92.3–108.7
Ni	n	11	17
(1–8)**	X ± SD	96.0 ± 3.7	94.9 ± 5.18
	m–M	90.4–101.7	89.2–103.1
Zn	n	11	17
(10–50)**	X ± SD	98.6 ± 3.6	97.5 ± 3.08
	m–M	94.2–103.9	93.4–105.3
Fe	n	6	11
(15–35)**	X ± SD	79.0 ± 4.9	99.3 ± 4.93
	m–M	73.7–86.3	90.9–106.8
Cu	n	9	22
(1–10)**	X ± SD	71.6 ± 4.5	98.1 ± 4.0
	m–M	65.8–76.8	91.2–106.8
			91.3–103.2

*n = number of data; X ± SD = mean ± standard deviation; m–M = minimum–Maximum.
**range of concentrations spiked (in µg/l).

($P > 0.5$) did not present systematic differences between the methods. Acceptable recoveries were also found for Cd, Pb, Ni, and Zn using CHELEX-100 ion exchange chromatography, with no systematic differences between the methods for Cd ($P > 0.05$) and Zn ($P > 0.2$). When both methods of preconcentration are compared, the mean values for Cd, Pb, Ni, and Zn are not statistically ($P < 0.05$) different. However, the differences observed between the results for Fe and Cu were statistically significant ($P > 0.05$). When the CHELEX-100 method was employed, the recoveries found for both metals were not complete (70–80%). This agrees with other authors[6,16,23] who reported that a fraction of Cu in seawater is not removed by the CHELEX-100 technique. These authors assumed that a fraction of Cu is associated with colloidal and fine particulate matter and is not affected by the chelating resin. Similar considerations can be deduced for Fe[22]. But the previous acidification process for storing of the samples should liberate this fraction. However, the pH of the seawater before passing through the column CHELEX-100 must be 7.7–7.8. As the time needed to pass 51 of seawater through the column is long (16.7 hr), the Cu and Fe could be recombined with the colloidal fraction in which case the results for both metals would be lower. Data for precision for the studied metals analyzed by both preconcentration methods ranged between 3–5%, which is better than those published by other[12,14,16,21]. However, our data for precision were similar to those obtained by Tao *et al.*[15] and Danielsson *et al.*[24].

The detection limits observed in this paper were sensitively lower than those found using direct ICP-AES[15]. However, these were higher than the observed using GF-AAS with a lower preconcentration factor[21,27] (Table 3). Similar detection limits to those

Table 3 Comparison of detection limits* of metals in seawater published in the literature.

Analytical technique	*Concentration factor*	*Cd*	*Pb*	*Ni*	*Zn*	*Cu*	*Fe*	*Ref.*
Extraction/ AAS	100	0.08	3	0.4	0.2	0.3	1	Present work
CHELEX-100/ AAS	500	0.016	0.6	0.08	0.04	0.06	0.2	Present work
-/ ICP-AES	1	7.5	24	9	4.5	3	-	14
Extraction/ ICP-AES	100	0.017	0.52	0.13	0.11	0.047	0.048	15
Extraction/ ICP-AES	100	0.022	0.60	0.11	0.084	0.051	0.075	13
Extraction/ GF-AAS	50	0.0006	-	0.048	0.024	0.009	-	21
Extraction/ GF-AAS	40	0.003	0.03	0.10	0.03	0.05	0.20	27

*Detection limits were defined as the metal concentrations (in µg/l) which give a signal (absorption or emission) equal to three fold the standard deviation of the background noise.

obtained in ICP-AES[13,15] (preconcentration factor = 100) have been reached using the described CHELEX-100 preconcentration technique/AAS (preconcentration factor = 500). Analysis times with direct injection methods are extremely short compared to the separation-preconcentration techniques studied here. A preconcentration factor of 500 could be achieved with CHELEX-100. However, the use of volumes larger than 1 l for APDC/Freon-TF extraction was impractical and it was thus difficult to obtain a factor higher than 100. This factor is not sufficient to determine Cd, Ni, and Pb, in unpolluted or open ocean seawaters when flame AAS techniques are used. Therefore, the CHELEX-100 procedure could be recommended in these cases. Calibration curves to determine the concentration of the studied heavy metals in seawater were obtained by treating spiked seawater using the described procedure of extraction. The linearity of the calibration graph was good ($r > 0.99$ for all preconcentrated studied metals previously) and the lineal intervals were confirmed from the detection limits up to the following values: 10, 2, 80, 16, 8, and 35 µg/l of Cu, Cd, Zn, Pb, Ni, and Fe respectively. These intervals include the metal concentrations commonly present in seawater.

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