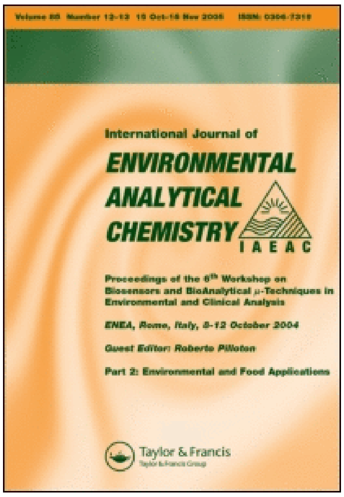

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IMPROVEMENTS IN USE OF CHELEX-100 RESIN FOR DETERMINATION OF COPPER, CADMIUM AND IRON IN SEA WATER*

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Tests have been carried out for copper and iron to determine the capacity of Chelex-100 resin in its "sea form", using a constant quantity of resin and variable volumes of sea water. For copper an asymptotic capacity curve is found analogous to the cadmium curve reported earlier, while for iron a maximum is observed. As Chelex-100 in its "sea form" appears useful for the determination of cadmium, but not for that of copper and iron, a preconcentration procedure utilising the Chelex-100 in its H^+ form is proposed. Using batch equilibration and a practical sea water/exchanger ratio, good recoveries and low blank values were obtained. The method was tested for sea water reference material.

KEY WORDS: Chelex-100, preconcentration heavy metals, sea water.

INTRODUCTION

Recent studies[1–3] on the application of Chelex-100 for the trace-level determination of elements in sea water, mostly use the procedure reported by Kingston *et al.*[4] with a column containing a cation-exchange resin in the NH_4^+ form, pre-elution of alkaline and alkaline earth metals with ammonium acetate and elution of heavy metals with nitric acid. Boniforti *et al.*[2] carry out preconcentration by batch equilibration, with a subsequent transfer to the resin column and elution with acid. The use of buffers for the elution of alkaline and alkaline earth metals can still create problems with the blank, which necessitates careful and laborious procedures of purification and further analytical processing.

Some time ago, we started a systematic study comparing preconcentration methods to determine "boxes" of heavy metal compounds dissolved in sea water, with the view of their determination by flameless AAS. The results obtained for cadmium[5] led us to continue this kind of research, using Chelex-100 for a study of iron and copper.

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EXPERIMENTAL

Sampling The sample of inshore water was filtered over a 0.45 μm Millipore filter in a nitrogen atmosphere, using a pressure difference of about 40 KPa. A 10-l volume of filtered sea water, at its natural pH, was stored at 4 °C. All experiments for recovery and loading tests were carried out using aliquots of the same stock.

Instrumentation A Varian Atomic Absorption Spectrophotometer 400 A with a graphite furnace GTA 96 and a DS 15 Computer were used.

Reagents Nitric acid 65% (Suprapur, Merck), hydrochloric acid 37% (RPE, Carlo Erba), sodium hydroxide 20% (RPE, Carlo Erba), and the 1000 ppm Titrisol Standards Solution (Merck) were used. We used also Chelex-100 (Bio Rad Laboratories) 50–100 mesh, Na^+ form.

Materials Containers, micropipette tips and other laboratory materials were of polythene. The filtration apparatus was of polycarbonate (Sartorius, mod. SM165.10); 60 μm Nylon and 0.45 μm Millipore filters were used.

Cleaning procedures Containers, filtration apparatus and micropipette tips were treated before use for 1 h with 1:1 HCl, washed with purified Milli-Q water, dried at 40 °C, washed with 1,1,2-trichloro-2,2,1-trifluoroethane (RPE, Carlo Erba) and stored in polythene bags. Nylon filters were washed with 1:1 NaOH and deionised and Milli-Q water. Millipore filters were washed with 1:1 HCl, and deionised and Milli-Q water.

Preparation of the exchanger in H^+ form Chelex-100 (10 g), Na^+ form, were equilibrated for 24 h with 50 ml of 2 M HCl, washed with deionised and Milli-Q water to pH 5, dried at 40 °C and stored in polythene bags over silica.

Preparation of the exchanger in "sea form" Dried Chelex-100 (0.1500 g) in the H^+ form was equilibrated with successive volumes of purified sea water (48 h for each step) until the pH attained a value of 6, using 800 ml per g of dried resin for every step.

Purified sea water was prepared as follows: 10 g of Chelex-100 (H^+ form) were equilibrated with 2 litres of filtered sea water for 48 h in a polythene container on a shaking plate. The sea water was then removed and stored in a polythene bottle at 4 °C.

Capacity experiments with Chelex-100 (sea form) Experiments were carried out by varying the ratio sea water volume/dried resin weight in order to verify the best operative conditions. Exchanger (0.1500 g) was used with sea water volumes increasing from 100 to 900 ml in the same kind of container.

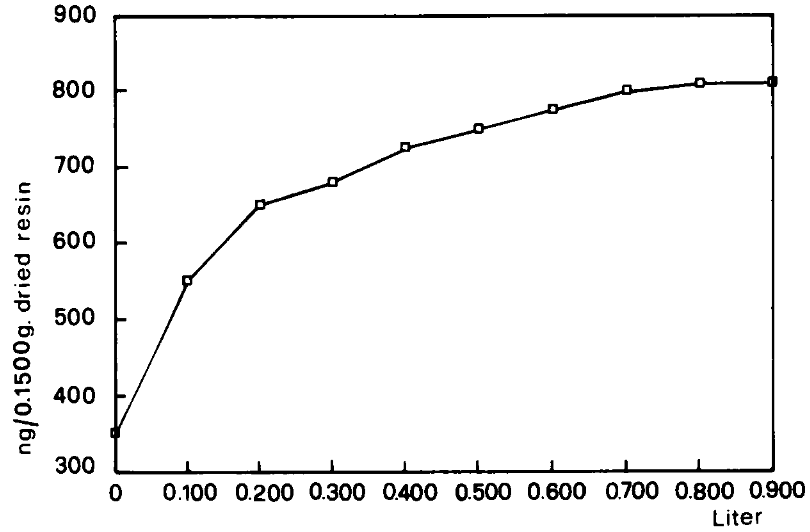

Figure 1 Loading curve of copper on Chelex-100 in its "sea form".

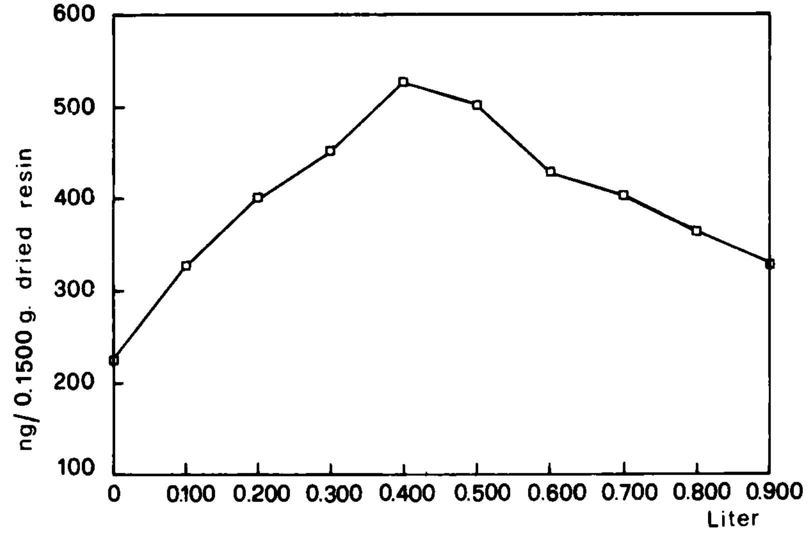

Figure 2 Loading curve of iron for Chelex-100 in its "sea form".

RESULTS

Initially we studied the possibility to use Chelex-100 in its "sea form" for the iron and copper preconcentration using the conditions earlier employed for cadmium.[5] Figures 1 and 2 show the results on the Chelex-100 "sea form" capacity for copper and iron, respectively. For copper, we note an asymptotic behaviour as was earlier observed for cadmium[5]—which reaches a plateau at about 800 ng of copper for 0.1500 g of dried resin. The blank value of the resin prepared in the "sea form", is

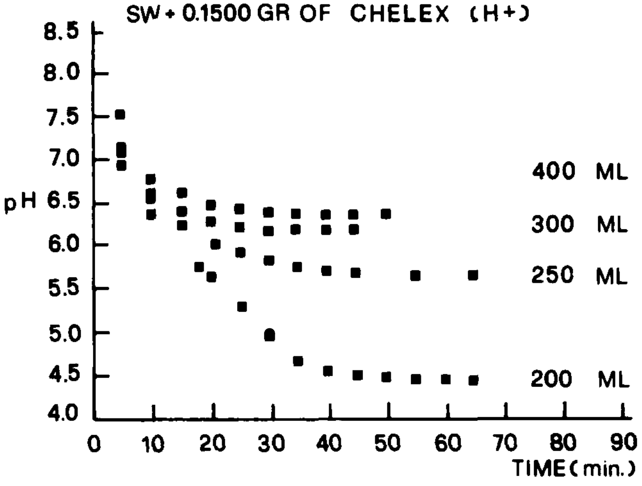

Figure 3 pH values of sea water in contact with Chelex-100 in H^+ form, for variable volumes of water *vs* time variation.

for copper 1.8 μg/l if we work with 200 ml of sea water and 0.1500 g of dried resin. This value is much too high because the mean value of the total dissolved concentration of copper today is about 0.2–0.5 μg/l.

For iron, the shape of the capacity curve is different from that of the copper curve: a maximum occurs at about 550 ng of iron, obtained by equilibration with 400 ml of sea water, and next, a decrease which probably indicates effects due to the salt matrix. The blank value (for 0.1500 g of dried resin treated with 200 ml of sea water) is 1.0 μg/l. This is too high compared with mean concentration values of about 0.50 μg/l. The blank data show that the Chelex-100 resin in the "sea form"—even though the resin is useful for the determination of cadmium—cannot be used for the determination of either total copper or iron.

To reduce the blank values for copper and iron a systematic study was carried out with Chelex-100 samples obtained by equilibration of the exchanger in the "sea form" with HNO_3 at varying concentrations. The blank values for both copper and iron decreased when increasing the HNO_3 concentration. In other words, in order to give low blank values, Chelex-100 has to be in the H^+ form, although such use was criticised by Florence and Batley.[6] This criticism is related to the low pH value obtained when the sea water passes through the column which may give a low degree of chelation for the metals. In order to test this by means of batch equilibrations, we carried out a series of experiments by treating 0.1500 g of Chelex-100 resin (H^+ form) with varying volumes of sea water (200, 250, 300, 400 ml) and plotted the pH as function of the time (Figure 3).

The graph shows that when treating 0.1500 g of dried resin with 300 ml of sea water in batch equilibration, the pH of the solution becomes constant with a value of 6.20 after about 1 h. At this value, heavy metal chelation during the contact time will no doubt be complete.

Table 1 Results obtained with the final procedure applied to sea water samples (Ligurian sea; recovery) and to a sea water standard (CASS-1)

Metal	*Recovery* (%)	*Bland values* ($\mu g/l$)	*CASS-1* ($\mu g/l$)	
			Found	*Certified*
Cd	97± 9	0.004±0.001	0.019±0.001	0.026±0.005
Cu	94± 5	d.l.	0.325±0.096	0.291±0.027
Fe	70±10	0.400±0.036	0.685±0.076	0.873±0.076

All results are the average of 4 subsamples drawn from an initial sample. The detection limits (2s on the value of blank) are 0.002, 0.018, and 0.072 μg/l for Cd, Cu and Fe, respectively.

Final procedure

On the basis of the above results the following procedure is proposed.

The preconcentration is carried out by a batch equilibration procedure using 0.1500 g of exchanger (H^+ form) and 300 ml of filtered sea water at its own pH in a 500 ml container, using a contact time of 30 h with shaking on a plate.

The exchanger is separated by decantation or by filtration over a 60 μm Nylon filter, washed with 100 ml MQ water, dried at 40 °C for 24 h and stored. For elution the exchanger is then transferred to a 50 ml container and eluted by 1 h contact with 2 ml of 1 M HNO_3. Table 1 gives the results obtained when applying the procedure to the sea water reference material CASS-1 from the National Research Council of Canada for the determination of copper, iron and cadmium. The recovery test was carried out with spiked sea water samples (iron and copper, 1 μg/l; cadmium, 0.1 μg/l).

CONCLUSION

Chelex-100 in its "sea form"—previously used for trace level cadmium determinations—is not suited for copper and iron determination because of high blank values. Working with Chelex-100 in the H^+ form, and using batch equilibration with a sufficient contact time, appears to allow the determination of cadmium and copper with good recovery. For iron, the blank value still is rather high and the recovery is not completely satisfactory, probably because of hydrolysis phenomena, as found by Riley *et al.*[7] and Sturgeon *et al.*[8] also.

In principle, the proposed preconcentration procedure is rather simple and the contamination risk is low. We therefore think this method to be useful for oceanographic studies when the laboratory conditions do not allow extensive and complex sample manipulation.

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