

CHROM. 4602

SEPARATIONS OF TRACE ELEMENTS FROM SEA WATER, BRINE AND SODIUM AND MAGNESIUM SALT SOLUTIONS BY CHROMATOGRAPHY ON CHITOSAN*

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(Received January 12th, 1970)

SUMMARY

Chitosan, a chelating polymer, has been used to collect traces of transition elements from salt solutions and sea water by column chromatography. Chitosan can be favorably compared with the chelating resin Chelex[®], and it is proposed as a chelating chromatographic support suitable for pollution detection survey and abatement, for waste water purification and recovery of trace metal ions for analytical purposes.

INTRODUCTION

Chitosan has recently been proposed as a chelating chromatographic support¹. Because this natural polymer does not appreciably collect sodium and magnesium, it should be applicable for the separation of small amounts of transition metals from sodium and magnesium matrices. In fact, these separations and preconcentrations are very often required for analytical and technological work, particularly in oceanography and waste water treatment; in biology, fluids are also analyzed for trace metals. In practice co-precipitation is the technique most widely used for preconcentration. The preconcentration of trace metals from sea water by co-precipitation with insoluble compounds or special reagents is widely published, but only a few papers present data obtained by chromatography.

Separation of trace metals from Mg and Na by chromatography on Chelex, a chelating artificial resin, has been proposed and performed in a few cases²⁻⁶; however, the resin stability, its relatively high affinity for Mg and its cost are main limitations. Other chelating resins have been proposed⁷, but no breakthrough is foreseen for the various prototypes of artificial chelating resins⁸. This applies for analysis in fields other than oceanography. For example, impurities in alkali metals have to be determined by carrier precipitation with special reagents previous to emission spectro-

* Paper presented at the Meeting on Analytical Methodology, sponsored by the C.N.R., Rome, Italy, December 1969.

graphy analysis⁹⁻¹¹. When neutron activation analysis is preferred, one must recognize that large amounts of Na or Mg disturb detection and quantitation of several trace metals, also when Ge(Li) detectors are used^{12,13}. The isotopic ion-exchange technique has been proposed, based on columns of ion-exchange resins^{13,14}; apparently it is not suitable for preconcentration from matrices in which Na and Mg are together as main constituents, as in sea water or biological fluids. The so-called "precipitation ion-exchange preconcentrations"¹⁵ present the same disadvantages; in the work cited above¹³⁻¹⁵ the very small amounts of matrices that can be manipulated are further drawbacks; moreover, the retention of trace metals on the resin is unfavorably dependent on the concentration of matrix salt in solution. We have therefore investigated some fast preconcentration techniques based on the use of chitosan columns, employing sea water, brine and artificial Na and Mg salt solutions.

EXPERIMENTAL

Reagents and tracers

All reagents used were analytical reagent grade. The polymer, 100-200 mesh, was prepared in this laboratory according to a published method¹. Radioactive isotope solutions were purchased from the Radiochemical Centre, Amersham. The amounts, expressed in micrograms, used for each experiment are as follows: Hg, 0.040; Co, 0.0104; Ag, 0.38; Mo, 0.02; In, 2.6; Cs, 0.004; Zn, 0.02; Au and Sb, carrier-free; Fe and Cr, not specified.

A ²³³U solution was kindly offered by Euratom BCMN, Geel, Belgium. Sea water was collected at a depth of 600 m in the Mediterranean, 100 km east of Naples during the NATO cruise aboard the ship "Bannock" of the C.N.R. (Italy). It was filtered through a 0.45- μ Millipore filter using a Teflon pump. Concentrated sea water was kindly supplied by the Istituto di Studio delle Acque, Rome, and came from the pilot desalination plant in Bari, Italy. The artificial solutions contained, respectively, in 60 ml of twice distilled water: 45 g of NaNO₃ at pH 4.5; 50 g of Mg(NO₃)₂ at pH 7.0; 50 g of NaCl at pH 5.5 and 15 g of MgCl₂·6H₂O at pH 4.5.

High precision Whatman columns fed by a peristaltic pump were filled with chitosan to form a 10-cm bed, I.D. 1 cm, and operated at 20°. Batch procedures were carried out by shaking 200 mg of chitosan in 50 ml of sea water at 20°. Mechanical stirring was employed.

Analytical procedures

The radiochemical techniques were those previously described¹. The ²³³U solutions have been measured by adding 3 ml to a solution of dioxane + PPO + naphthalene + TOPO. Each sample has been counted for 1000 min with a multichannel spectrometer. Energies higher than 1.0 MV have been counted.

The atomic absorption measurements were made with a Densatomic Spectrophotometer (manufactured by Optica, Milan) equipped with water-cooled lamps and an acetylene air burner.

RESULTS AND DISCUSSION

Firstly, the capacities of chitosan and the resin Chelex have been compared. The sorption curves in Figs. 1 and 2 refer to the collection of zinc and mercury ions

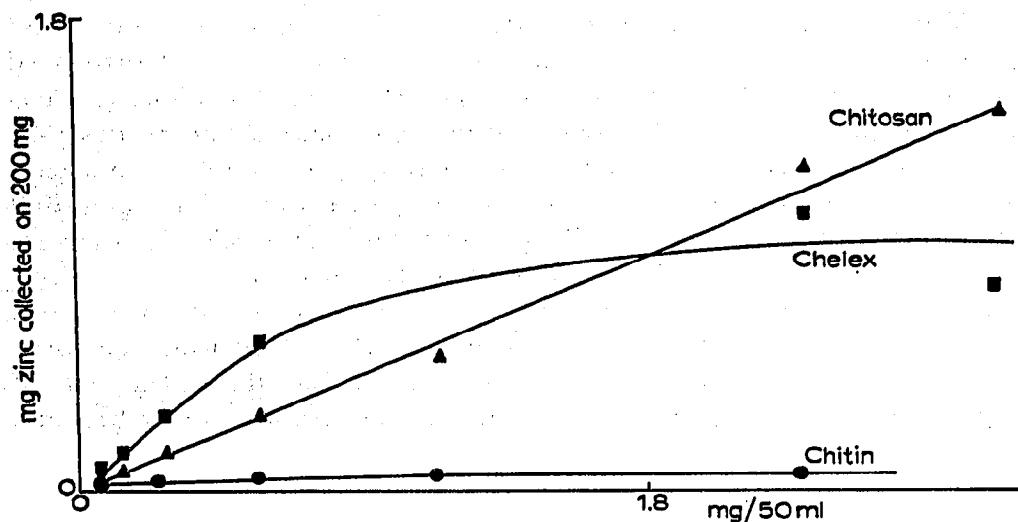


Fig. 1. Collection of zinc on chitosan and Chelex. Chitin is acetylated chitosan.

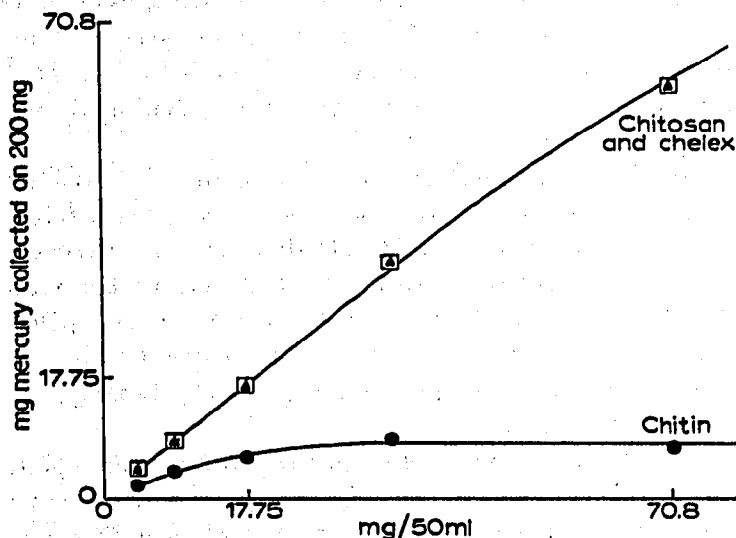


Fig. 2. Collection of mercury on Chitosan, chelex and chitin.

from water solutions. These ions are those for which Chelex exhibits the highest capacity¹⁸; therefore the comparison of Chelex with chitosan is of particular significance. These data show that chitosan is a good chelating polymer for collection of relatively large amounts of Hg and Zn ions. Therefore, trace amounts of radioactive elements have been added to the highly concentrated salt solutions reported under *Reagents and tracers*. The resulting solutions, 60 ml, were passed through the chitosan column. The column was then washed with a total of 740 ml of twice distilled water. These operations took less than 5 min. Sodium and magnesium were determined on the last water fractions by atomic absorption spectrometry. The results are tabulated in Table I, and the elution curves are presented in Fig. 3.

These results demonstrate that a very large amount of Na or Mg salt has no effect on the retention of traces of most transition elements on chitosan. The partial

TABLE I

SEPARATION OF TRACE ELEMENTS FROM Na AND Mg SALT SOLUTIONS IN TWICE DISTILLED WATER
Column: chitosan, 100 mesh, 10 × 1 cm.

Trace element	Total amount (μg)	Collected (%)	Eluting agent	Eluted (%)	Eluent volume (ml)
^{105}Au	c.f.	88	KCN 0.1 N	100	3
$^{110\text{m}}\text{Ag}$	0.38	100	HCl acetone	96	50'
^{60}Co	0.0104	100	KCN 0.1 N	100	3
^{203}Hg	0.040	100	EDTA 0.1 N	89	60
^{44}Cu	n.s.	100	KCN 0.1 N	100	3
$^{114\text{m}}\text{In}$	24	70	EDTA 0.1 N	100	60
^{65}Zn	0.02	100	EDTA 0.1 N	100	60
$^{59}\text{Fe(II)}$	n.s.	100	EDTA 0.1 N	79	60
^{125}Sb	c.f.	40	EDTA 0.1 N	100	60
^{137}Cs	c.f.	0			

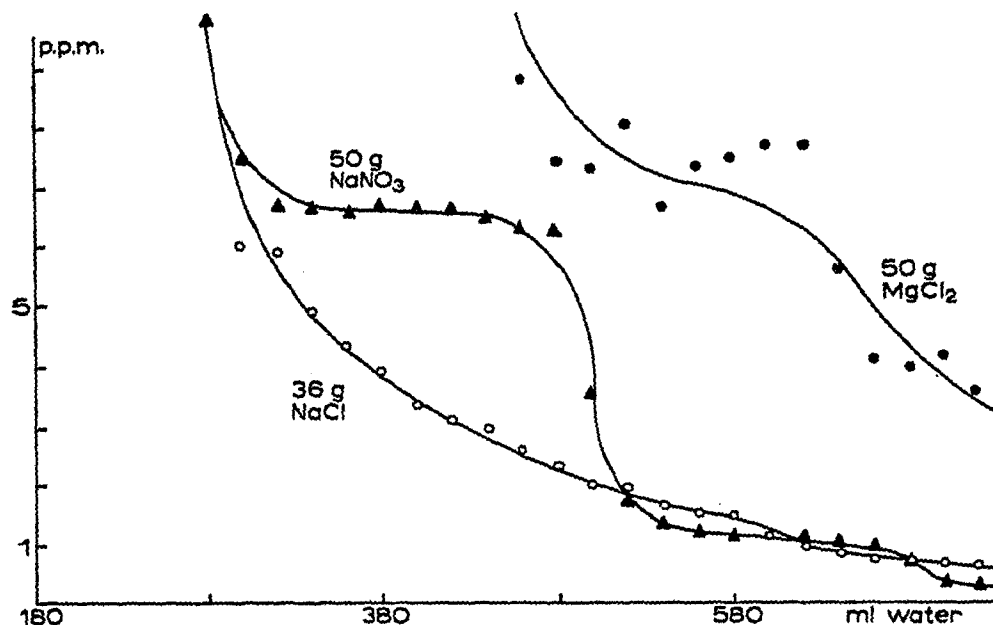


Fig. 3. Elution curves of Na and Mg from a chitosan column after passing concentrated salt solutions, followed by atomic absorption spectrometry.

collection of Au and In depends on the behavior of these elements and not only on the salt concentration. By washing the column with 740 ml of water, the Na concentration in the eluate dropped to 0.1 and 0.4 p.p.m. and the Mg concentration to 6.8 and 3.0 p.p.m. for the nitrate and chloride solutions, respectively. The Na and Mg content in mg/g of the column has been found to be the following, before and after chromatography respectively: Na, 1.5 and 1.4; Mg, 0.2 and 0.185.

The effectiveness of the separations reported in Table I can be appreciated in neutron activation analysis. Without separation the ^{108}Ag photopeaks are completely concealed by the Compton edge of the ^{27}Mg gamma ray spectrum, even when Ge(Li)

detectors are used. After having passed a solution containing both ^{27}Mg and ^{108}Ag through a chitosan column and having washed with a Mg solution for isotopic elution of ^{27}Mg , one can count the polymer blown out of the column and measure the ^{108}Ag photopeaks with accuracy. The total yield is 100% and the chromatographic procedures take less than 5 min and do not require special solutions or equipment. In this respect, this method compares most favorably with others¹⁴.

Some batch measurements were done on sea water and brine from a pilot desalination plant. Results are reported in Table II.

TABLE II

COLLECTION OF TRACE ELEMENTS FROM 50 ml OF BRINE (2-FOLD CONCENTRATED SEA WATER), pH 7.8, ON 200 mg OF CHITOSAN — 1 h SHAKING AT 20°

Trace element	Collected from brine (%)	Collected from sea water (%)
^{105}Au	72	63
^{60}Co	80	100
^{203}Hg	60	100
^{65}Zn	100	100
^{160}Tb	92	96
$^{110\text{m}}\text{Ag}$	100	100
^{125}Sb	100	37
$^{114\text{m}}\text{In}$	100	100

^{233}U tracer has been used to study the behavior of uranium towards chitosan in sea water. A 60-ml fraction of a solution containing a total of $5 \cdot 10^{-6}$ g U has been used for this measurement. 10 ml have been taken for reference, and 50 ml have been shaken with 200 mg of chitosan. After a measured time, a 10-ml fraction was taken and centrifuged. The liquid scintillation measurements are reported in Table III. On this basis, the adsorption of U on chitosan can be considered total and rapid.

TABLE III

COLLECTION OF ^{233}U FROM A 50-ml SOLUTION CONTAINING 4.2×10^{-6} g OF U ON 200 mg OF CHITOSAN, pH 5.5

Reference solution (c.p.s./g)	Treated solution (c.p.s./g)	Shaking time (h)	Collected (%)
27.2 ± 3.0	1.7 ± 0.5	1	94.3
31.7 ± 1.3	1.2 ± 0.5	2	96.0
30.2 ± 0.8	0.9 ± 0.5	18	97.0

A 7×0.5 cm column of chitosan in sea water has been prepared. 1 ml of a solution containing $5 \cdot 10^{-6}$ g U was diluted to 10 ml and passed through the column. The column was then washed with 30 ml of twice distilled water and 30 ml of a 1 N solution of sodium carbonate, which were collected in three 10-ml fractions.

TABLE IV

ELUTION PROFILE OF 5×10^{-6} g OF ^{233}U (90% ENRICHED) COLLECTED FROM SEA WATER
100-200 mesh chitosan column, 7×0.5 cm.

<i>Eluting solution</i>	<i>Fraction volume (ml)</i>	<i>Eluate (c.p.s./g)</i>
Dist. water	30	0 ± 0.5
Na_2CO_3 1 N	10	0 ± 0.5
Na_2CO_3 1 N	10	161.2 ± 4.3
Na_2CO_3 1 N	10	11.3 ± 2.8
Total:		172.5 ± 7.1
Expected:		178.2 ± 5.0

The results are shown in Table IV. Therefore it can be said that U is completely adsorbed on the column and can be eluted completely with sodium carbonate.

Field preconcentrations of trace elements from sea water have been carried out to confirm the evidence obtained from radiochemical data. The results reported in Table V are the most relevant because they have been obtained by emission spectrography, without introducing any chemical into water. The fact that water filtered through Millipore filters was used in one case allows one to conclude that the trace metals collected are chemically fixed on chitosan because the particulate matter has been removed.

TABLE V

TRACE ELEMENTS CONCENTRATIONS IN SEA WATER, AS CALCULATED AFTER ANALYSIS OF CHITOSAN AND COMPARED WITH MEAN REPORTED VALUES¹⁷

Values (p.p.m.) under column *Chitosan powder before use* are reported only to show its purity.

<i>Element</i>	<i>Millipore-filtered water from 600 m depth ($\mu\text{g/l}$)</i>		<i>Ref. 17 ($\mu\text{g/l}$)</i>	<i>Paper-filtered surface water ($\mu\text{g/l}$)</i>		<i>Chitosan powder before use (p.p.m.)</i>	
	<i>Spec.</i>	<i>NAA</i>		<i>Spec.</i>	<i>Spec.</i>	<i>NAA</i>	
Aluminium	0.3/3			12/120	5/50		45
Copper	0.03/0.3	0.7	3	0.4/4	~1		2.2
Iron	0.3/3	4.5	10	40	10/100		120
Lead	0.3		0.03	0.4/4	<10		
Manganese	0.03/0.3		2	0.4/4	<1		
Zinc		0.6	10	4	<100		0.3
Silicium	3/30		3000	40/400	10/100		
Titanium	0.03		1	0.12/1.2	<1		
Silver	0.03		0.3	0.04/0.4	<1		
Chromium		0.13	0.05				2.2
Cobalt		0.02	0.5				0.2

It has been observed that the upper layer (about 300 mg) of the column collects the trace metals, under our conditions and for 10-l of water.

It can be seen that very little of the original Mg and Na present in water is left on the column; the amounts retained are so low (microgram level) that they do

not disturb the determination of other trace metals which are present at the same level.

CONCLUSIONS

On the basis of the results reported, chitosan looks very promising as a chelating support for preconcentration of trace elements. The fact that traces of transition elements can be separated from sodium and magnesium salts makes it suitable for application in oceanography and, generally speaking, for detection, measurement and abatement of water pollution.

ACKNOWLEDGEMENTS

Thanks are due to Profs. G. SEMERANO and A. BRECCIA for their continued interest in this work.

The liquid scintillation measurements were done by R. VANINBROUKX, Euratom BCMN, Geel, Belgium. The neutron activation analyses were done by A. MALVANO, Sorin, Saluggia, Italy.

This work was performed under contract No. 115,3106 of the National Research Council of Italy. U.S.A. and Europe patent applications are pending.

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