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PREPARATION OF A HEAVY METAL-REMOVED SEAWATER

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A purification procedure is described for preparing a heavy metal-removed blank seawater without altering its major compositions and pH. Coastal seawater is treated sequentially by passing through a charcoal column, shaking with a dense slurry of ferric hydroxide at pH 8, and passing the supernatant through a Chelex-100 chelating ion-exchange column. Experimental data show that this process efficiently removes Cd, Co, Cu, Cr(III), Fe, Mn, Ni, Pb, V and Zn from natural seawater at the spiking concentrations of 10 and 100 ppb levels.

INTRODUCTION

In developing methods for analyzing trace metals in seawater, a trace metal-free seawater is frequently required as a backgound matrix. For example, it can be used to study the effect of salt interference on heavy metal determinations using graphite furnace atomic absorption spectrometry.

Attempts to use an artificially prepared seawater for the above-mentioned purpose were abandoned because the metal impurities usually contained in the commercial laboratory grade chemicals may be several orders of magnitude higher than the trace metal contents in natural seawater, and also because the preparation of such an artificial seawater is tedious and expensive. In fact, the natural seawater, which usually contains ppb levels of heavy metals, is a convenient and less expensive source of the salt matrix if it is properly purified.

Several basic criteria were considered in searching for an ideal purification process: (1) The major salt compositions of seawater should be kept un-altered. (2) The pH of seawater should be maintained at its natural level after the whole process; (3) If extra reagents are added, they should be removed readily after purification.

Among the many available methods, the metal hydroxide co- precipitation and chelating ion-exchange techniques are likely to be the most applicable approaches for the purification. Since these methods are critically pH dependent, it is customary to adjust the pH of seawater to the optimal value. For example, to perform ferric hydroxide co-precipitacion the seawater is added with an acidic ferric chloride solution, then the pH is adjusted to the optimal pH ca. 9.5, and the precipitate is allowed to settle. This procedure is very effecient for removing Cu, Cr(III), Mn, Ni, Pb, Zn, but less effective for Mn and Cd.[1]

As to the Chelex-100 technique, the optimal pH. for metal removal varies from element to element, and the overall efficiency is related to the flow rate applied and the capacity of the column. In general, at pH 5.5-7 the resin sorbs Co, Cu, Ni, Pb and Zn completely, but loss of Mn, Fe, Cr(III) and probably Cd occurs, at pH 8 the resin quantitatively removes Cd, Co, Ni, Mn, Zn, but appears less efficient for Fe, Cu, Cr(III), and Pb.[2,3] The resin removes Cr(VI) at pH lower than 2[2] and sorbs Mo and V at pH around 5.[4]

Since the purpose of this study is to search for an easy-handle way to purify natural seawater and to cover as many elements as possible in a single treatment, the feasibility of using a combined procedure including both co-precipitation and Chelex-100 in a successive manner has been investigated. The former method provides a large metal-removing capacity, and therefore was arranged ahead of the latter Chelex-100 treatment.

During the early stages of developing such a combined purification process, the raw seawater was added with Fe(III) and pH was adjusted to the optimal value of 9.5 to form the hydroxy precipitates. However, experience showed that the pH of this mixture shifts drastically during the settling, and that to adjust it back to 8 or to 6.5 for the next Chelex-100 step might be somewhat difficult. To solve this problem the pH of the seawater is fixed at its natural value during the entire purification process, thus eliminating the tedious work of adjusting pH. In addition, a bufrered ferric hydroxide slurry is used, instead of adding acidic ferric solution and then NaOH to form ferric hydroxide, so that the purification process can be further simplified. This process, based on the adsorption mechanism of the ferric hydroxide slurry, should therefore be termed as "adsorption-precipitation" rather than "co- precipitation".

Considering the possibility that metal-removing efficiency of the adsorption procedure might not be as effective as that using the normal co-precipitation procedure, the concentration of the ferric hydroxide coagulant was raised to ca. 50 mg Fe per 1 liter of seawater. Even so, at the non-optimal pH(e.g. 8), satisfactory removal rate only applied to Cu, Cr, and Pb. The removal of Mn, Ni, Co, Cd and Zn by adsorption with the slurry was not complete.[1] Fortunately, this drawback can be compensated by the later Chelex-100 column treatment which removes those residual elements to a non-detectable level.

Apart from the inorganic metal species, natural seawater usually contains a substantial portion of organic metal species which might not be removed by the co-precipitation or the Chelex- 100 ion exchange treatment. For this reason, the seawater was first passed through a charcoal column before other treatments.

MATERIALS AND METHODS

Ferric Hydroxide Slurry

Five grams of ferric chloride and 0.5 g of boric acid were dissolved in ca. 100 mL of distilled water in a Pyrex glass beaker. The pH of the mixture was adjusted to ca. 8 with sodium hydroxide to form a brownish slurry. The reason for the addition of borate is simply to buffer the pH of the slurry.

Chelex-100 Column

Twenty grams of Chelex-100 resin(100-200 mesh, manufactured by Bio-Rad Laboratories, U.S.A.) were packed into a polypropylene column (10 cm x 3 cm ID). The column was activated by washing sequentialiy with two 10 mL portions of 2N nitric acid, two 10 mL portions of distilled water, two 10 mL portions of 1 N sodium hydroxide, five 10 mL portions of distilled water, two 10 mL portions of 1 M magnesium chloride, and at least 10 bed volumes of distilled water until the pH of the effluent dropped down to 8-9. The functional groups of the column were converted to magnesium form.

Purification of Acid

Nitric acid was sub-distilled[5] and then collected in the all-Teflon bottles. The purity check was made by direct g.f.a.a.s. using repeat deposition technique, i.e. twenty cycles of injections/dryings of 20 uL aliquots of the acid into the graphite furnace. The recorded signals for all element tested showed that the impurities in this sub-distilled acid were all below 0.05 μg/L level.

APDC + DDTC Reagent

Two grams of ammonium pyrrolidine-1-dithio- carbamate and 2 g of diethylammonium *N,N*-diethyldithiocarbamate were dissolved in 100 mL of distilled water. The mixture was filtered to remove undissolved particles, and then purified by consecutive extractions with three 10 mL portions of MIBK.

Atomic absorption spectrometry: A Hitachi model Z-8000 polarized Zeeman effect a.a.s. was used to detect heavy metals.

Test of Settling Time

Bulk of 10 L of filtered seawater was spiked with 100 ug each of Cd, Co, Cu, Cr(III), Mn, Mo, Ni, Pb, Zn, and 1 mg of V. Aliquot of 20 mL of ferric hydroxide slurry (containing 0.2 g Fe) was added. The mixture was shaken vigorously and the precipitates were allowed to settle. Portions of the supernatant were carefully withdrawn after 0.5, 1, 2, 4, 8, 16, 24, 48, 72, 96, and 120 hours, and were acidified to avoid further precipitation. The detection of metals was made by the direct graphite furnace a.a.s. in the begining stages when the concentrations of metals were high and detectable, and by pre-concentration/g.f.a.a.s. in the later stages when the concenlrations became very low.

Detection of Heavy Metals

The monitoring of heavy metal contents in seawater at different purification stages was carried out in three ways. For those elements(such as Cd, Co, Cu, Ni, Pb, and Zn) that suffer from strong salt matrix interference the seawater was preconcentrated by the APDC + DDTC/MIBK solvent extraction methods followed by the flame or graphite furnace a.a.s. For low concentrations (up to 50 ppb) or Mn, Mo and V the sample was pre-concentrated by the Chelex-100 technique at pH 6.5, 5 and 5, respectively. For Cr and high concentrations (above 50 ppb) of Mn, Mo, and V, the sample was detected directly by g.f.a.a.s. after evaporating most salts in the ashing stage.

The procedure for APDC + DDTC/MIBK extraction was similar to that described by Magnussen and Westerlund[6] but without back- extraction: Aliquot of 500 mL of sample was placed in a 1 L separatory funnel to which was added 5 mL of ammonium acetate bufrer (pH = 4.5) and 5 mL of APDC + DDTC reagent. The mixture was extracted with 30 mL MIBK. After phase separation, the organic fraction was collected in a 50 mL Pyrex beaker, then evaporated to almost dryness on a hot plate. The residue was redissolved in 0.5 mL of conc. nitric acid and 4.5 mL of distilled water. The recovered heavy metals in the final concentrate (100 fold) were detected by flame a.a.s or g.f.a.a.s. A parallel test using 500 mL of distilled water was also carried out to construct calibration curves and also to give reagent blank.

The procedures for pre-concentrating low concentrations of Mn, Mo, and V by the Chelex-100 technique were similar to those given in the previous work:[2,3,4] Aliquot of 500 mL of sample was added with 30 mL of ammonium maleate buffer (pH 6.5 for Mn) or ammonium acetate buffer (pH 5 for Mo and V), then loaded onto a Chelex-100 column (10 cm x 0.8 cm ID, containing 2 g of 100-200 mesh resin in ammonium form) at a flow rate of ca. 5 mL/min. The recovery was made by eluting with 4 portions of 1 mL of 2 N nitric acid then diluting to 5 mL.

The procedure for direct determination of Cr, Mn, Mo and V in seawater by the graphite furnace a.a.s. was as follows: Aliquot of 20 uL of seawater was injected into the pyro-coated graphite tube on the atomizer. It was dried at a ramp temperature (room- 120°C) for 30 s. The ashing temperature was set between 1600- 2200°C (depending on element) for 60 s in order to remove most of the salt matrix. The atomization temperature was set at 2500-3000 °C for 5 s as suggested by the manufacturer.

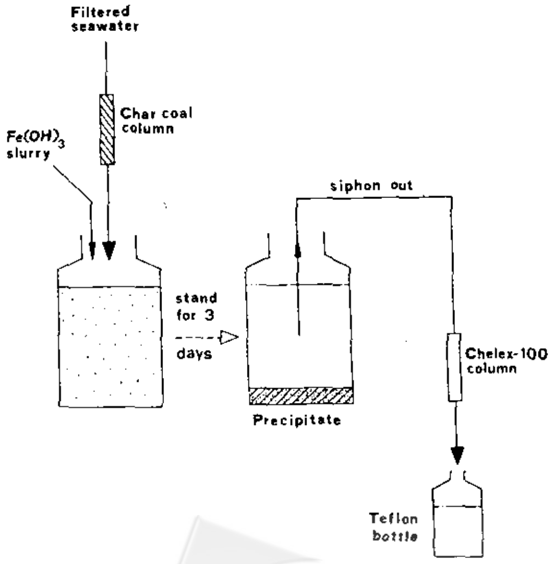

Fig. 1. Schematic layout of the proposed purification procedure.

Recommended Purification Procedure

The following procedure has been used in our laboratories for the preparation of the background seawater: Bulk of 25 L of freshly collected coastal seawater is stored in a PE tank. The seawater is filtered through Whatman GF/C glass fibre filter, then passed through a column containing activated charcoal (50 g) to remove the possible organic substances. Aliquot of 100 mL of the ferric hydroxide slurry (pH 8) is added and the mixture is shaken vigorously, allowed to stand for 3 days until the brownish slurry of ferric hydroxide precipitates has settled down at the bottom. The un-disturbed supernatant is siphoned out (see Fig. 1) and led to a 15 cm x 3 cm ID Teflon column packed with 20 g of Chelex-100 resins (100-200 mesh, magnesium form) at a flow rate no more than 10 mL/min. The first 200 mL of the effluent is discarded and the rest portion is collected and stored in 1 L Teflon bottles.

RESULTS AND DISCUSSION

Removal of Heavy Metal by Ferric Hydroxide Precipitate

The removal of heavy metals from seawater by mixing with ferric hydroxide slurry was identified from the measurement of heavy metal residues in the supernatant (Table 1). More than 80% of the absorbant, i.e. ferric hydroxide, settled rapidly within 1 hour. Comparatively, the removing rate of Cd, Co, Cr(III), Cu, Mn, Ni, Pb, Zn, and V was much slower. The supernatant became clear after 24 hours, and the residue of Cu, Cr(III), Pb, and V was nearly not detectable ($<1\%$). More than 90 % of Ni and Zn was removed after 48 hours. However, substantial amounts of Cd, Co, Cr(VI), Mn, and Mo still existed in the solution. The residual fractions for these elements were found to be 59%, 24%, 75%, 53%, and 30%, respectively. Additional tests showed that longer settling time or more absorbant could

Table 1. Effect of settling time on the removal of spiked heavy metals from seawater by mixing with ferric hydroxide slurry at pH 8.0

Element	Fe	Cd	Co	Cu	Cr(III)	Cr(VI)	Mn	Mo	Ni	Pb	V	Zn
Spike conc. (ppb)	(20ppm)	10	10	10	10	10	10	50	10	10	100	10
Settling time(h)	Residue (%) in solution											
0	100	100	100	100	100	100	100	100	100	100	100	100
0.5	19	76	87	82	81	91	85	60	24	51	55	68
1	13	71	74	71	71	88	74	53	18	37	17	47
2	8	69	68	53	63	85	70	49	15	33	6	34
4	4	67	60	33	52	83	63	43	13	26	5	25
8	3	66	52	20	30	79	58	36	12	19	2	20
16	2	64	43	15	14	78	57	32	11	10	1	16
24	1	61	29	9	6	78	57	30	11	4	1	11
48	<1	63	24	3	2	76	56	29	10	<1	<1	9
72	<1	59	24	1	<1	75	53	30	10	<1	<1	7
96	<1	61	25	1	<1	77	54	29	11	<1	<1	10
120	<1	58	23	<1	<1	76	52	28	10	<1	<1	8

Supernatant was withdrawn periodically and was acidified with HNO_3.

Detection of metals was made by direct g.f.a.a.s. in the beginning stages; whereas pre-concentrations were applied in later stages.

Both Cr(III) and Cr(VI) were measured by direct g.f.a.a.s., but the spiking was made in separate batches.

improve very little the removal rate of those elements. Since the ferric hydroxide flocs were pre-formed before adding to the seawater and the pH was maintained constant at 8 throughout the whole process, the metal removal was probably mainly controlled by the adsorption, rather than the inclusion or other mechanisms.

Removal of Heavy Metals by Chelex-100 Technique

Although the Chelex-100 column cannot remove completely Cu and Pb from seawater at pH 8, but it has very strong retention ability to Cd, Co, Mn, Ni, Zn[2,3] thus compensating the "weakness" for the prior adsorption-precipitation process. The resin bed also acts as a porous filter. If any ferric hydroxide floc exists in the supernatant, it will be stopped by the resin and forms a yellowish band at the top of resin bed. The size of column nominated was proven large enough to allow a high flow rate of even up to 20 mL/min without lossing its efficiency. However, the removal of Cr(VI) and Mo at pH 8 was not successful.

Removal of Heavy Metals by the Combined Process

A freshly collected, filtered, and charcoal treated coastal seawater was used to demonstrate the efficiency of heavy metal removal by the proposed precipitate-adsorption/chelating ion exchange combined process. The seawater was divided into three 10 L portions (Samples A, B and C) to give different spiking metal concentrations. Sample A was the original seawater, samples B and C were further spiked with 10 and 100 μg/L of each metal of interest. Measurement of heavy metal contents was made before and after purification, using different pre-concentration methods or direct injection to the g.f.a.a.s. The results are listed in Table 2. It can be seen that most heavy metals spiked (except for Cr(VI) and Mo) in samples B and C were removed to a non- detectable level. Even iron, the precipitation agent with high concentration, was completely removed. It is important to use Teflon labwares in the final stage of the purification, i.e. column, storing bottle, and the connecting tubings between them, otherwise leaching of Fe, Ni, and Zn from these vessel might occur. The collection of the purified seawater should also be freed from dust contamination. A hepa filter equipped laminar hood is highly recommended.

Table 2. Removal of spiked heavy metal contents in a coastal seawater using the proposed purification scheme

Element	Concentration found(μg/L) before/after purification					
	Sample A		Sample B		Sample C	
	before	after	before	after	before	after
Cd	0.16	<0.005	9.98	<0.005	98.8	<0.005
Cu	1.13	<0.03	11.3	<0.03	103.7	<0.03
Co	<0.02	<0.02	10.2	<0.02	102	<0.02
Cr(III)*	<0.5	<0.5	9.8	<0.5	99.6	<0.5
Cr(VI)	<0.5	<0.5	10.2	8.7	96.5	81.7
Fe	8.64	<0.1	17.9	<0.1	110.3	<0.1
Mn	7.65	<0.05	17.8	<0.05	112.5	<0.05
Mo	10.9	2.4	21.2	6.3	114	27.2
Ni	3.72	<0.1	14.0	<0.1	105.1	<0.1
Zn	16.5	<0.02	28.7	<0.02	121	<0.02
Pb	<0.02	<0.02	10.2	<0.02	101	<0.02
V	1.56	<0.05	12.0	<0.05	103	<0.05

Sample A: non-spiked natural coastal seawater.
Sample B: natural seawater spiked with 10 ppb of each metal.
Sample C: natural seawater spiked with 100 ppb of each metal.
*Cr(III) and Cr(VI) were spiked separately and the total Cr was detected by direct g.f.a.a.s.
"<": less than the detection limits indicated after this mark.

CONCLUSION

Although at the non-optimal pH 8 the metal-removing abilities of the ferric hydroxide co-precipitation and the Chelex-100 technique are only efficient for several selected elements, the over-all efficiencies can be much improved if these two procedures are operated in a successive manner. The proposed procedure provides a fast and low cost way to prepare large volume of the analytical grade blank seawater from natural seawater. Experimental results have shown that the combined procedure removes completely the spiked Cd, Co, Cu, Cr(III), Fe, Mn, Ni, Pb, V, and Zn at 10 and 100 ppb levels, but is not satisfactory for Cr(VI) and Mo. Additional treatments would be required for removing the latter two elements.

The major constitutes of seawater are only slightly changed after the purification (less than 0.5 % for Na, Cl, etc.) except for borate. Borate is added as a buffer in the ferric hydroxide slurry and the concentration is raised to 3.5 mmol/L from its natural level of 0.1 mmol/L. Natural seawater of most locations, if not seriously polluted, can therefore be used as the raw material to produce the purified blank seawater for further applications.

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Key Word Index-

Heavy metal; Seawater; Purification.

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