Anion-exchange enrichment and spectrophotometric determination of traces of uranium in sea water

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Anreicherung durch Anionenaustausch und spektral-photometrische Bestimmung von Uranspuren in Meereswasser

The determination of U in sea water generally entails a concentration step. High concentrations of NaCl in sea water makes it difficult to achieve quantitative recovery of U by conventional ion-exchange techniques [1]. We found that the anion-exchange in $\text{Mg}(\text{NO}_3)_2$ media [2] permits enrichment of U even in the presence of high concentrations of NaCl, providing the basis for the determination of U in sea water.

Experimental

Procedure. Filter the sea water sample (acidified to 0.1 mol/l in HNO_3) through a 0.45 μm membrane filter. Take a 200 ml fraction of the filtrate and add 220 g of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ to it. Condition the anion-exchange column (2 g of Bio-Rad AG1-X8(Cl) contained; 12 mm i.d. $\times$ 28 mm) with 20 ml of 2.5 mol/l $\text{Mg}(\text{NO}_3)_2$ -0.5 mol/l NaCl-0.1 mol/l HNO_3 solution. Load the sample solution onto the column at a flow rate of 2 ml min^{-1} . Pass 30 ml of 6 mol/l HCl to remove Th. Strip U with

15 ml of 1 mol/l HCl and determine photometrically with Arsenazo III.

Results and discussion

The distribution coefficients of U(VI) in 0.5 mol/l NaCl-0.1 mol/l HNO_3 solution are obtained by a batch equilibrium study as a function of $\text{Mg}(\text{NO}_3)_2$ concentration. The coefficients obtained are 1800, 610, 210, 46, 13, and 4 for 3.0, 2.5, 2.0, 1.5, 1.0, and 0.5 mol/l $\text{Mg}(\text{NO}_3)_2$ concentrations, respectively. These values are higher than those obtained in the absence of NaCl [2], favourable for the sorption of U from sea water. Artificial sea water (4.6 $\mu\text{g U l}^{-1}$) was analyzed for U to confirm the procedure; the average recovery obtained was $102 \pm 2.0\%$ ($n = 3$). Possible interferences from Th, which is also sorbed from the nitrated media, can be avoided by simply washing the column with 6 mol/l HCl before the elution of U. The results of sea water analyses with and without addition tests were $3.54 \pm 0.10 \mu\text{g U l}^{-1}$ (Amatsukominato, Pacific Ocean, salinity 32.20‰; $n = 6$) and $3.01 \pm 0.20 \mu\text{g U l}^{-1}$ (Aburatsubo bay, Kanagawa, salinity 30.24‰; $n = 9$). No difference was found in the U results whether the acidification of the water sample with HNO_3 was made before or after the filtration of the collected samples.

References

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Benzoin oxime as a reagent for the separation of rhenium from Mo, W, V and others

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Benzoinoxim als Reagens zur Trennung des Rheniums von Mo, W, V und anderen

Amongst the oximes, dimethylglyoxime, α -furildioxime and salicylaloxime have often been used for extractive studies of transition metals in acid as well as alkaline media [1]. Though the highly specific nature of benzoin oxime as a gravimetric reagent [2] for molybdenum has long been known, there is, however, hardly any report available in literature which makes use of this reagent for the extractive separation of rhenium particularly from elements of analytical importance. Keeping this fact in view, a systematic investigation is desirable.

Experimental. To the sample solution containing 100 $\mu\text{g Re}$ and milligram amounts of other ions in a separatory funnel are added 4 ml 10 mol/l HCl, 1 ml $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (20%) and 2 ml 1% α -benzoin oxime solution in alcohol in a final 20 ml volume

and the rhenium complex thus formed is extracted once with an equal volume of chloroform for 3 min. The metal ion from the solvent is back-extracted with 1:1 NH_3 containing a few drops of 30% H_2O_2 . When Mo(VI) and W(VI) are also present in the sample, $\sim 100 \text{ mg NaF}$ are added initially to the aqueous solution. Microgram amounts of rhenium are determined by the thiocyanate method [3] and the presence or absence of other metal ions is tested by sensitive conventional methods [4].

It has been observed that rhenium in lower valency state, produced on reduction with stannous chloride, forms a colourless complex with α -benzoin oxime in hydrochloric acid solution which is highly extractable into chloroform. The extraction is influenced by various parameters, namely, acidity, reductant, reagent concentration etc. (Table 1) and under the optimum conditions chosen for the system, rhenium is transferred quantitatively into the solvent phase in a single extraction.

U(VI), V(V), Cr(III), Cd(II) (0.25 mg/ml); Fe(II), Ni(II), Co(II), Cu(II), Mn(II) (0.5 mg/ml); Cr(VI), Zr(IV) (0.1 mg/ml) do not interfere at all. Mo(VI) and W(VI) (0.5 mg/ml) are extracted only in traces, but the interference due to these ions is eliminated by masking with $\sim 100 \text{ mg of NaF}$. SO_4^{2-} , PO_4^{3-} , F^- do not influence the extraction; whereas Cl^- , $\text{C}_2\text{O}_4^{2-}$, CH_3COO^- and tartrate decrease it by 1, 5, 5 and 8%, respectively.

The ratio of metal to ligand in the complex formed is determined as 1:6 by conductometric titrations [5] using equimolar solutions of rhenium and α -benzoin oxime with concentrations of 0.004 and 0.005 mol/l in each set, respectively.

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