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SEPARATION OF TRACES OF METAL IONS FROM SODIUM MATRICES

by

J. Korkisch and K. A. Orlandini

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TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	3
I. INTRODUCTION.	3
II. EXPERIMENTAL PROCEDURE	4
A. Reagents and Solutions	4
1. Ion-exchange Resin	4
2. Extractants and Eluents	4
3. Sodium Acetate.	4
B. Tracers.	4
C. Apparatus	4
D. Determination of Distribution Coefficients	5
E. Working Procedure	5
1. Isolation of Metal Ions Forming Stable TTA Complexes in Acetic Acid Solution.	5
2. Isolation of Metal Ions Forming Stable Dithizonates in Acetic Acid Solution	5
3. Separation of the Extracted Metal Ions from Coextracted Traces of Sodium.	5
III. RESULTS AND DISCUSSION	6
A. TTA Extraction.	6
B. Dithizone Extraction	7
C. Ion-exchange Separation	7

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ABSTRACT

This report describes a rapid and quantitative method for the isolation of traces of metal ions from sodium matrices (e.g., sea water). The technique consists of two extractions and an ion-exchange step. In the first extraction, metal ions which form stable TTA-complexes in sodium chloride solutions, which are buffered with sodium acetate to a pH of 4.7-6.1, are extracted with 0.1M TTA in benzene-tetrahydrofuran. More than 30 elements, including rare earths, uranium, thorium, titanium, zirconium, and hafnium, are completely extracted under these conditions. Following this extraction, other traces of metal ions (i.e., silver, mercury, and cadmium) are extracted from the same aqueous solution using 0.001M dithizone in benzene as the extractant. To remove residual sodium ion from the two organic extracts, this element is selectively adsorbed on the strongly acidic cation exchanger Dowex 50 from the organic phases after the addition of pyridine. Following this final purification step, the elements thus isolated can be determined radiometrically.

I. INTRODUCTION

Previous investigations* have shown that from organic solvent media containing 2-thenoyltrifluoroacetone (TTA) and pyridine, alkali metal ions such as those of sodium and cesium are very strongly retained on the strongly acidic cation exchange resin Dowex 50, while practically all other elements are not adsorbed under these conditions. Alkali metal ions are also completely removed by this technique from organic solvents immiscible with water (e.g., benzene). This method is therefore suitable to remove residual sodium or other alkali metals after the extraction of traces of metal ions using as an extractant a TTA solution in benzene and/or dithizone dissolved in the same solvent. In the presence of pyridine, the extracted metal ions are then separated from alkali metal ions by cation exchange. This report describes this technique of extraction,

* J. Korkisch and K. A. Orlandini, Selective Cation Exchange Separation of Carrier-free Cesium-137 and Sodium-22, Anal. Chem., submitted for publication.

followed by the ion exchange procedure, as applied to the isolation of traces of metal ions from sodium matrices, using as an example the quantitative isolation of radiotracers of numerous elements from sea water.

II. EXPERIMENTAL PROCEDURE

A. Reagents and Solutions

1. Ion-exchange Resin

The ion-exchange resin used was the air-dried, strongly acidic, cation exchange resin Dowex AG50W-X8 (100-200 mesh; hydrogen form).

2. Extractants and Eluents

The following extractants and eluents were used:

Extractant I: 0.1M thenoyltrifluoroacetone (TTA) in 90% benzene-10% tetrahydrofuran (THF) (v/v).

Extractant II: 0.001M dithizone (diphenylthiocarbazone) in benzene.

Eluent I: extractant I plus pyridine (proportion in mixture: 10 + 1, e.g., 10 ml extractant I + 1 ml pyridine).

Eluent II: benzene plus pyridine (proportion in mixture: 10 + 1, e.g., 10 ml benzene + 1 ml pyridine).

3. Sodium Acetate

The sodium acetate used was analytical grade $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$.

B. Tracers

Hydrochloric acid and nitric acid solutions of many radioactive tracers were used. These included: ^{233}U , ^{46}Sc , ^{144}Ce , ^{169}Yb , ^{89}Sr , ^{95}Zr , ^{95}Nb , ^{106}Ru , ^{99}Tc , ^{181}Hf , ^{124}Sb , ^{54}Mn , ^{110}Ag , ^{204}Tl , ^{60}Co , ^{59}Fe , ^{192}Ir , ^{109}Cd , ^{207}Bi , ^{44}Ti , and ^{241}Am .

The radioactive measurements were performed by using standard counting techniques.

C. Apparatus

For the ion-exchange separations, ion-exchange columns of 0.5-cm diameter and 25-cm length were used.

D. Determination of Distribution Coefficients

The distribution coefficients of the radiotracers were determined using steps 1 and 2 of the working procedure described in Section E below.

$$\text{Distribution coefficient} = \frac{\text{counts of tracer/ml organic extract}}{\text{counts of tracer/ml aqueous phase}}$$

E. Working Procedure

The entire working procedure described here can be completed in less than 4 hr.

1. Isolation of Metal Ions Forming Stable TTA Complexes in Acetic Acid Solution

First the radiotracer and then sodium acetate are added to 10 ml of the acidified sample of sea water (in a centrifuge tube of 40 ml) until the solution shows a pH of 4.7 to 6.1. [For example, with sea water having a pH of 1.5 (acidified with hydrochloric acid when the sample was taken), the addition of 1 ml 1M sodium acetate raises its pH to 4.7.] Then 10 ml of extractant I are added and the mixture vigorously stirred for 10 min. Afterwards the mixture is centrifuged for about 2-5 min, and the phases are separated. The organic phase is stored in a polyethylene bottle, and the aqueous phase is used for step 2.

2. Isolation of Metal Ions Forming Stable Dithizonates in Acetic Acid Solution

Ten ml of extractant II are added to the aqueous phase obtained after step 1, and the extraction is carried out as described in step 1.

3. Separation of the Extracted Metal Ions from Coextracted Traces of Sodium

a. Pretreatment of Resin

One gram of the resin is slurried with a few milliliters of eluent I. After about 20-30 min, the slurry is transferred to the ion-exchange column. Subsequently, the resin bed is washed with 10-15 ml of the same eluent.

b. Separation of Sodium

One ml of pyridine is added to the organic phase obtained after step 1, and this solution is passed through the ion-exchange column using a flow rate corresponding to the back-pressure of the resin bed.

Afterwards, the resin is washed portionwise with 10 ml of eluent I. (This effluent fraction 1 contains all the metal ions that are extractable according to step 1.)

Subsequently 1 ml of pyridine is added to the dithizone-extract obtained after carrying out step 2, and the mixture is passed through the column at the same rate. This is followed by a 10-ml wash with eluent II. (This effluent fraction 2 contains all the metal ions extracted in step 2.)

In the effluent fractions 1 and 2, the metal ions are determined by measurement of their radioactivity.

To remove the adsorbed sodium from the column, the resin bed is first washed with 10 ml of acetone, and then the sodium is eluted with 15 ml of 6N hydrochloric acid.

III. RESULTS AND DISCUSSION

A. TTA Extraction

From sea water buffered with acetate to a pH of 4.7-6.1 (see working procedure in Section II), trace amounts of many elements are virtually completely extracted into an equal volume of extractant I. The results of these investigations using step 1 of the working procedure are recorded in Table I, which also includes the extraction behavior of poorly extractable elements. Also partly extractable are V(IV and V), Mo(VI), Cr(III), Pd(II), and Np. Under these conditions, Na, K, Cs, Ca, Mg, Sr, Ir, Ag, Sb, Sn, Cd, Tl, and Tc, as well as anions such as chloride, sulfate, and nitrate are virtually nonextractable (distribution coefficients of less than 0.1). Gold is also not extracted because it is reduced to the elemental state during the extraction.

TABLE I. Extraction of Traces of Metal Ions (present in millicurie quantities) from Sea Water by Means of 0.1M TTA in 90% Benzene-10% Tetrahydrofuran (v/v)

Metal Ion	Distribution Coefficient	Percentage Extracted into Organic Phase (single equilibration with an equal volume of extractant)	Metal Ion	Distribution Coefficient	Percentage Extracted into Organic Phase (single equilibration with an equal volume of extractant)
Fe(III)	460	>99.9	Th(IV) ^a	>10 ²	>99.9
Co(II)	370	>99.9	Bi(III)	66	>98
Ni(II) ^a	>10 ²	>99	Cu(II) ^a	>10 ²	>99
Ti(IV)	366	>99.9	Zn(II)	59	98
Zr(IV)	>>10	>99	Be(II) ^a	>50	98
Hf(IV)	>>10	>99	Al(III) ^a	>50	98
Sc(III)	>10 ³	>99.9	Pb(II) ^a	>10 ²	>99
Y(III) ^a	>10 ³	>99.9	Mn(II)	7.2	85
Ce(III)	>10 ³	>99.9	Nb(V)	0.5	30
Yb(III)	>10 ³	>99.9	Ru(III and IV)	-0.1	15
Am(III)	>10 ³	>99.9	In(III)	-0.1	15
UO ₂ (II)	400	>99.9	Hg(II)	-0.1	15
Pu(III and IV)	>10 ²	>99.9			

^aNo suitable radioactive tracers of these metal ions were available. They were present in amounts ranging from 100 to 1,000 µg, and were determined spectrographically.

The presence of 10% tetrahydrofuran in extractant I serves the purpose of dissolving a white organic precipitate, which is sometimes formed if the organic extract is stored longer than for about 1 hr. If the extract is kept for longer than 1 day, this precipitate forms, even in the presence of THF, but is readily soluble on addition of pyridine, as described in step 3.b of the working procedure. This compound causes no interference in the column operation.

B. Dithizone Extraction

Among the elements that are partly or not at all extracted with TTA-benzene, only a few are removed by dithizone extraction as described in step 2 of the working procedure. Silver, cadmium, and mercury, with distribution coefficients of 150, $>10^3$, and $>10^3$, respectively, are completely extracted into dithizone-benzene. Antimony is partially extracted (distribution coefficient = 0.37). Most elements that are also not extracted as TTA-chelates are virtually nonextractable (see Section III.A above).

C. Ion-exchange Separation

With the ion-exchange operation described in step 3 of the working procedure, the last traces of sodium and other alkali metal ions are removed from the organic extracts. In these two extracts, the presence of TTA and dithizone prevents the adsorption of the extracted metal ions on the cation exchanger. However, sodium is strongly retained (distribution coefficient greater than 600,000), so that an absolute removal of this element is achieved. Therefore it is expected that this method, in combination with the preceding two extraction steps, may be particularly useful in radiochemical work involving the determination of traces of elements after neutron-activation of matrices consisting predominantly of sodium. Examples are: sea water, brines (e.g., oil-well brines), alkali metal reactor coolants, and certain biological fluids.

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