## Data Section

## RADIOCHEMICAL SEPARATIONS BY RETENTION ON IONIC PRECIPITATE ADSORPTION TESTS ON 11 MATERIALS

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The retention of different radio-ions on columns of eleven ionic precipitates from different acid media was studied, in view of possible applications for radiochemical separations. The results of about 2,000 adsorption experiments, carried out in a standardized way, are presented schematically in periodic tables.

### Introduction

Inorganic ion exchangers have been applied for a long time in the nuclear energy field particularly when their outstanding resistance to high temperatures and high radiation doses made them preferable to organic ion exchangers (separation of fission products from spent fuel elements, deionization of reactor cooling water at high temperature). Many materials have been developed for such uses.<sup>1,2</sup> They have seldom been used for radiochemical separations applied to neutron activation analysis, despite the fact that a high selectivity for a few ions was often demonstrated.

In a few preceding works<sup>3-6</sup> we showed that the retention behaviour of many inorganic materials, not usually employed as ion exchangers, was interesting enough for many practical applications in destructive activation analysis.

Indeed, inorganic materials, not especially prepared as ion exchangers, can react with a solution containing trace ions with a number of possible reaction mechanisms, such as isotopic exchange, redox reactions, precipitation, formation of mixed crystals by recrystallization, and, of course, ion exchange. All these mechanisms can contribute to a different extent to the retention of different ions on a column of that material in an adsorption-elution experiment.

Often it is difficult to clarify the actual retention mechanisms and describe them with comprehensive chemical laws; and the possibility of extrapolating the behaviour of ionic precipitates to different experimental conditions can be greatly hindered by the intervention of different reaction mechanisms in different media and different concentrations. This does not prevent, however, the analyst from taking advantage of the unusual retention properties of many ionic precipitates, if the experimental conditions are kept as close to the original ones as possible.

When a wanted chemical separation is still feasible under standardized working conditions (the large variety of ionic precipitates which can be used compensate for the limitations in the experimental conditions), then the drawback turns out to be an advantage, as the materials and columns can be prepared in advance and kept as stock items, and the execution can be left to less specialized personnel. The construction of automated machines can also be greatly simplified.

Recently about 3,000 adsorption-elution cycles were carried out in a standardized way over different ionic precipitates from various media for a preliminary screening of possible useful materials for radiochemical separations.<sup>7</sup>

Here we report schematically the results obtained on nine inorganic materials which were retained as potentially useful after the screening tests. The results obtained with organic cation and anion exchange resins are also reported.

Possible analytical applications can be inferred from the behaviour of different ions in each couple column/medium and methods by which the task of developing chemical separation schemes based on the data reported here is greatly simplified, will soon be published.

The experiments were carried out with radioactive tracers which were obtained by neutron activation in a nuclear reactor, with irradiation times ranging from minutes to three weeks, depending on the half-life of the radionuclides. The amount of tracer used was that required to obtain a reasonable counting rate on a  $\gamma$ -spectrometer, by counting the column or the eluted solution. In this way the actual carrier concentration varies greatly from one radiotracer to another depending mainly on its activation cross section. While this is certainly a drawback in understanding the reaction mechanisms, in the practical analytical use it can be considered an advantage, as a relatively close simulation of a destructive activation analysis is thus obtained.

The application of the reported results to actual separation cases is, of course, not entirely straightforward.

The retention capacity of inorganic ion exchangers or ionic precipitates, in general, are lower than those of the organic exchangers, and moreover they vary considerably from ion to ion. For example, the retention capacity of hydrated antimony pentoxide for the alkaline ions in 0.1M HNO<sub>3</sub> (in milliequivalents per gram) has the following values: Na<sup>+</sup>: 2.61, K<sup>+</sup>: 1.7, Rb<sup>+</sup>: 1.45, Cs<sup>+</sup>: 0.15.<sup>8</sup>

As a consequence, ions for which the material has a low retention capacity can exhibit a different behaviour for different ion concentrations. Also ions present in extremely low concentrations or in a carrier-free state can frequently show unusual retentions or long elution 'tails'. The addition of  $50-100 \mu g$  of carrier when elution is wanted is a recommended practice to avoid both difficulties.

Elements present in large concentrations (matrix elements) can also alter the behaviour of the exchanger, as it happens with organic exchangers.

J. Radioanal. Chem. 5 (1970)

Even with these limitations, we found that the behaviour indicated in the tables is very often exactly respected in many practical applications for activation analysis, where ion concentrations are often rather small.

This report is far from an exhaustive study of analytical applications of ionic precipitates, and indeed it is little more than an introduction to that study. However, the possibility of applying directly the data as they are presented here to the development of separation schemes, has convinced us that the presentation of these results was worth while.

The data presented here are not correlated with each other enough to make the detection of possible mistakes easy. The number of data is also high enough to make possible and even probable the occurrence of such mistakes, even if most of the experiments were repeated at least twice. We shall be grateful to those, who will inform us of such errors.

### Experimental

The ionic precipitates proposed here as potentially useful for radiochemical separations are mostly of commercial origin. Many of them were previously known to exhibit ion exchange properties. Others had been studied by us for some special radiochemical applications.

Data on Dowex 1 and Dowex 50 are also reported, which were obtained both in view of their possible use together with inorganic exchangers, and as control data for anion and cation exchange in the study of reaction mechanisms.

The materials were used as received from the manufacturer eventually after sieving to eliminate finer particles to improve the elution flow-rate.

The radioactive tracers (except <sup>22</sup>Na and <sup>54</sup>Mn, which were of commercial origin), were prepared by neutron activation of the stable elements, in form of solid salts, in the Ispra 1 reactor. The irradiation times ranged from a few minutes eto sveral weeks, depending on the activation cross section and the half-life of the radionuclide formed. The irradiated salts were then dissolved and stored, generally as a 1M HCl solution.

The solutions for the adsorption step were prepared by taking aliquots from the mother solution (generally  $10-100 \lambda$ ) and diluting them to 30-50 ml with the required acid. From this second stock 5 ml fractions were taken for each tracer experiment.

The tracer used, and the approximate final carrier concentrations, are reported in Table 1.

The tracer experiments were carried out in the following way: disposable polyethylene columns, prepared by VEMOR (Monvalle, Varese, Italy) (Fig. 1) were used (internal diameter 7 mm). They include a 15 ml reservoir, and can be easily stacked one on top of the other when a series of column is needed.

The columns were prepared by putting a quartz wool plug (or a Teflon wool plug for the tracer experiments in HF) at the bottom, and filling the column with the exchanger up to a 3 cm level.

### Table 1

Radiotracer	Concentration, µg/cm <sup>3</sup>	Radiotracer	Concentration, µg/cm <sup>3</sup>
<sup>18</sup> F(—I)	0.02	<sup>110m</sup> Ag(I)	0.02
<sup>22</sup> Na(I)	0.02	<sup>115</sup> Cd(II)	5
<sup>28</sup> Al(III)	1	<sup>114m</sup> In(III)	0.06
<sup>27</sup> Mg(II)	1	$117^{m}Sn(+)$	10—40
$^{32}P(V)$	0.02	124Sb(+)	0.05
<sup>85</sup> S(VI)	0.02	<sup>131</sup> Te(IV)	15
<sup>8</sup> Cl(-I)	0.4	<sup>131</sup> I(—I)	0.1
$^{12}K(I)$	10	<sup>134</sup> Cs(I)	0.02
<sup>17</sup> Ca(II)	400	<sup>131</sup> Ba(II)	30—100
<sup>46</sup> Sc(III)	0.02	<sup>140</sup> La(III)	0.02
<sup>a</sup> Ti(IV)	1	<sup>141</sup> Ce(III)	0.2
$^{52}V(+)$	0.005	<sup>147</sup> Nd(III)	0.1-0.5
<sup>1</sup> Cr(III)	0.2	<sup>151</sup> Pm(III)	carrier free
<sup>4</sup> Mn(II)	0.02	<sup>152</sup> Eu; <sup>154</sup> Eu(III)	0.02
<sup>9</sup> Fe(III)	20	<sup>160</sup> Tb(III)	0.01
°Co(II)	0.05	<sup>169</sup> Yb(III)	0.01
<sup>5</sup> Ni(II)	20	<sup>177</sup> Lu(III)	0.002-0.01
<sup>4</sup> Cu(II)	0.8	<sup>181</sup> Hf(IV)	0.01
<sup>5</sup> Zn(II)	2	<sup>182</sup> Ta(V)	0.01
<sup>2</sup> Ga(III)	0.2	185W(VI)	2
<sup>7</sup> Ge(IV)	20	<sup>186</sup> Re(VII)	0.1—1
$^{6}As(+)$	0.2	<sup>191</sup> Os(IV)	0.050.1
<sup>75</sup> Se(IV)	0.2	<sup>192</sup> Ir(III)	0.001
$^{2}Br(-I)$	0.05	<sup>199</sup> Pt(IV)	2-3
<sup>66</sup> Rb(I)	1	<sup>198</sup> Au(III)	0.02-0.1
<sup>5</sup> Sr(II)	10	<sup>203</sup> Hg(II)	0.05
°Y(III)	0.05	<sup>233</sup> Th(IV)	0.1
<sup>5</sup> Zr(IV)	1—10	<sup>233</sup> Pa(V)	carrier free
<sup>5</sup> Nb(V)	0.02	<sup>239</sup> U(VI)	0.02-0.1
<sup>9</sup> Mo(VI)	0.2	<sup>239</sup> Np(IV)	carrier free
<sup>9m</sup> Tc(VII)	carrier free		
<sup>03</sup> Ru(IV)	0.1		
<sup>03</sup> Pd(II)	1		

## Radiotracer used, valence states, and carrier concentrations

(+) Uncertain oxidation state.

A preliminary wash with 5 ml of the eluting solution was done before the adsorption step, to wet and settle the column bed. The adsorption step (5 ml) was then carried out, and two successive 15 ml fractions were passed through. The eluted solutions were collected into two 20 ml polyethylene bottles, the first collecting the adsorption and first 15 ml fraction, the second collecting the successive 15 ml fraction. The second fraction was diluted to 20 ml and both bottles were analyzed by  $\gamma$ -ray spectroscopy, or  $\beta^-$  counting.

J. Radioanal. Chem. 5 (1970)

The column bed was transferred into a third bottle and analyzed in the same way. An experimental correction factor was used to relate the counting rate of the column to the counting rate of the eluted solutions.

 $\gamma$ -Ray spectroscopy was preferred to gross  $\gamma$ -counting, after realizing that occasionally what appeared by gross  $\gamma$ -counting as repartition of the tracer between column and solution was actually a complete separation of the tracer



from an impurity which could not be detected by  $\gamma$ -ray spectroscopy of the mother solution. A  $3'' \times 3''$  NaI(Tl) scintillator coupled with a LABEN 200 channel analyzer was used as a  $\gamma$ -ray spectrometer.

In tracer experiments with pure  $\beta^-$  emitters (<sup>32</sup>P, <sup>35</sup>S, <sup>90</sup>Y, <sup>233</sup>Th), counting was done with a Geiger counter. The sources were prepared by taking 1 ml of solution and drying it under an infrared lamp.

To count the columns, they were dissolved when possible and treated as the eluted solutions, otherwise they were carefully dried and stirred, and a weighed

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146

symbols used in the periodic tables

							Medium					
Material	Code word	HCI, 1 <i>M</i>	HCI, 6 <i>M</i>	HCI, 12M	HNO <sub>3</sub> , 0.1 <i>M</i> 65°C	HNO <sub>3</sub> , 1M	HNO <sub>3</sub> .	HNO <sub>3</sub> , 14 <i>M</i>	HCIO., 1M	HCIO., 6M	HF, 6M	H <sub>2</sub> SO,, 1 <i>M</i>
		1 C	6 C	12 C	0.1 N	z -	7 N	14 N	1 P	6 Р	6 F	1 S
Hydrated manganese dioxide	HMD				×	x		×	x		x	
(C. Erba, Milano, Italy) Anhydrous manganese dioxide	AMD							×	×		×	
(C. Erba, Milano, Italy) Hydrated antimony pentoxide	НАР		×	×		×	×	×	×	×	x	
(C. Erba, Milano, Italy) Acid aluminium oxide	AAO				-	×	×		×			
(M. woelm, Eschwege, W. Ger.) Tin dioxide	TDO	×			×	×	×	×	×		×	
(C. Erba, Milano, Italy) Zirconium phosphate	HdZ	,	x				×		· <u> </u>	×		×
(Bio Rad Laboratories, USA) Cupric sulphide	CUS		×				×	····		×		×
(B. D. H., Dorset, U. K.) Cuprous chloride	cuc									×	×	×
(B. D. H. Dorset, U. K.) Cerous oxalate	COX										×	×
(B. D. H. Dorset, U. K.) Anion exchange resin (Bio P ed I shoreforias 115A)	AER		×	- ·			×			×	×	
Cation exchange resin (Bio Rad Laboratories, USA)	CER		×				×			×	×	
Symbols in the periodic tables: 0	<ul> <li>completely re</li> <li>partially retain proportional 1</li> </ul>	tained ( ned (the o the ar	over 99 black a nount r	/%) trea is etained)		ୁ କୁ ୁ କ୍ତି -	ompletly shaviou	' eluted r not w	over 9' (over 9' ell repro	7 %) ducible		_

### F. GIRARDI et al.: RADIOCHEMICAL SEPARATIONS

part was spread over the counting tray. The 1 ml aliquot from the eluted solution was then added to an identical weight of fresh exchanger, which was then stirred, dried and spread over a counting tray in the same way as described above.

### Results

The materials and the media of the tests are summarized in Table 2, together with their code words and the symbols used in the periodic tables. The results of the tracer experiments are then reported.

These data are the basis for a methodology of development of chemical separation schemes based on logical mathematics, which is being prepared. In the same paper many typical applications of the materials presented here will also be reported.

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## Hydrated manganese dioxide 0.1M HNO<sub>3</sub> at 65 °C

Hydrated manganese dioxide 1M HNO<sub>3</sub>

HMD/1 N



HMD/0.1 N



## Hydrated manganese dioxide 1M HClO<sub>4</sub>

Hydrated manganese dioxide 6M HF

HMD/6 F



149

HMD/1 P



## 14M HNO<sub>3</sub>

## AMD/1 P

HMD/14 N



Hydrated manganese dioxide

Anhydrous manganese dioxide

1M HClO<sub>4</sub>



### Anhydrous manganese dioxide 6M HF

Anhydrous manganese dioxide 14M HNO<sub>3</sub>

AMD/14 N



AMD/6 F



## Hydrated antimony pentoxide 1M HNO<sub>3</sub>

Hydrated antimony pentoxide 1M HClO<sub>4</sub>

HAP/1 P

HAP/1 N



J. Radioanal. Chem. 5 (1970)



## Hydrated antimony pentoxide 6M HCl

Hydrated antimony pentoxide 6M HClO<sub>4</sub>

HAP/6 P



HAP/6 C



# Hydrated antimony pentoxide 6M HF

Hydrated antimony pentoxide 7M HNO<sub>3</sub>

HAP/7 N



HAP/6 F



## Hydrated antimony pentoxide 12M HCl

Hydrated antimony pentoxide 14M HNO<sub>3</sub>

### HAP/14 N



HAP/12 C



## Acid aluminium oxide 1*M* HNO<sub>3</sub>

Acid aluminium oxide 1M HClO<sub>4</sub>

AAO/1 P



AAO/1 N



## Acid aluminium oxide 7M HNO<sub>3</sub>

Tin dioxide 0.1M HNO<sub>3</sub> at 60 °C

TDO/0.1 N



AAO/7 N

### Tin dioxide 1M HCl

### TDO/1 C



## Tin dioxide 1M HNO<sub>3</sub>

TDO/1 N



Tin dioxide 1M HClO<sub>4</sub>

### В C N 0 F Li Be Si Ρ S CI Na Mg Al С О Κ Ga Ge As Se Br Ca Sc Tí Cr Mn Fe Co Ni Cu Zn V $\bigcirc$ $\bigcirc$ $\bigcirc$ О Ю С О С $\bigcirc$ Rb Sr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Y Zr Te Ι Ó Ο Ø С O|O|O|C ()()4 Pb Bi Po At Cs Ba R.E. Hf Ta W Re Os Ir Pt Au Hg TI ٢ O|O $\bigcirc$ $\bigcirc$ Ø $\bigcirc$ Ø C Ra Ac Fг Th Pa U Np Pu Am Cm Bk Cf $\cap$ La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu Ο (

### Tin dioxide 1*M* HF

TDO/6 F



TDO/1 P

## Tin dioxide 7M HNO<sub>3</sub>

### TDO/7 N



### Tin dioxide 14M HNO<sub>3</sub>

TDO/14 N





## Zirconium phosphate $1M H_2SO_4$

Zirconium phosphate 6M HCl

ZPH/6 C



J. Radioanal. Chem. 5 (1970).

ZPH/1 S

### Вe В С N Li 0 F Na Mg A۱ Si Ρ S CL $\bigcirc$ Cr Mn Fe Co Ni Cu Zn Ga Ge ĸ Ca Sc Ti ٧ As Se Br 0 O|O| $\bigcirc$ O О () Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I OlO O|O|O٢ $\bigcirc$ ()()C Cs Ba R.E. Hf Ta W Re Os Ir Pt Au Hg TI Pb Bi Po At O|O $\bigcirc$ $\bigcirc$ $\cap$ O | OFr Ra Ac Th Pa U Np Pu Am Cm Bk Cf Nd Pm Sm Eu Gd Tb Dy Ho Er Pr Tm La Ce Yb Lu O Ο

## Zirconium phosphate 6M HClO<sub>4</sub>

Zirconium phosphate 7M HNO<sub>3</sub>

ZPH/7 N



J. Radioanal. Chem. 5 (1970)

ZPH/6 P

## Cupric sulphide $1M H_2SO_4$



### Cupric sulphide 6M HCl

CUS/6 C



163

CUS/1 S

Cupric sulphide 6M HClO<sub>4</sub>



Cupric sulphide 7*M* HNO<sub>3</sub>

CUS/7 N

CUS/6 P



J. Radioanal. Chem. 5 (1970)

### Li Be В С Ν 0 F S CI Na Mg AI Si P ()()ĸ Cα Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Sc Ti V ( :)Ο |O|O|О $\cap$ Rb Sr Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Y 000 $\mathbf{O}$ $\cap$ Ο $\cap$ () $\bigcirc$ ()Ba R.E. Hf Ta W Re Os Ir Pt Au Hg TI Pb Bi Po At Cs С О $\bigcirc$ О Ο С ()Ra Ac Th Pa U Fr Np Pu Am Cm Bk Cf $\cap$ ( )Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu La Ce С C ()

## Cuprous chloride $1M H_2SO_4$

Cuprous chloride 6*M* HClO<sub>4</sub>





CUC/1 S

J. Radioanal. Chem. 5 (1970)

## Cuprous chloride 6M HF

### CUC/6 F



## Cerous oxalate $1M H_2SO_4$

COX/1 S



### Li Be В С N 0 F AI Si S CI Na Mg Ρ Ga Ge As Se Br Κ Ca Sc Tī ۷ Cr Mn Fe Co Ni Cu Zn ${}^{\odot}$ 0 С Ο Ο - $\bigcirc$ Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I $\bigcirc$ ${}^{()}$ 0 $\odot$ C()()Hg Pb Bi Po Ał Cs Ba R.E Hf Τa W Re Os I٢ Pt Au ΤI Ο Ο С Ο Ο С Fr Np Pu Am Cm Bk Cf Ra Ac Th Pa U La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu

### Cerous oxalate 6M HF

Anion exchange resin 6M HCl

### AER/6 C



COX/6 F



## Anion exchange resin 6M HClO<sub>4</sub>

Anion exchange resin 6M HF

AER/6 F



AER/6 P

J. Radioanal. Chem. 5 (1970)



## Anion exchange resin 7M HNO<sub>3</sub>

Cation exchange resin 6M HCl

CER/6 C

	_															
Li	Be											В	С	N	0	F
Na O	Mg											Al	Si	P	S	CI
к	Ca	Sc ()	Tí	V	Cr	Mn	Fe O	Co O	Ni	Cu	Zn	Ga	Ge	As	Se O	Br
Rb	Sr O	Y	Zr O	Nb ()	Mo	Тс	Ru	Rh	Pd	Ag ()	Cd	In O	Sn ()	Sb	Te	I ()
Cs O	Ba O	R.E.	Hf O	τ <sub>α</sub> Ο	w •	Re ()	0s O	Ir O	Pt	Au 🕐	Hg O	τı	РЬ	Bi	Po	At
Fr	Ra	Ac	Th	Pa	U	Np	Pu	Am	Ст	8k	Cf					
ία	Ce O	Pr	Nd	Pm	Sm	Eu	Gd	ТЬ	Dy	Но	Er	Tm	Yь	Lu		

J. Radioanal. Chem. 5 (1970)

AER/7 N



## Cation exchange resin 6M HClO<sub>4</sub>

Cation exchange resin 6M HF

CER/6 F

CER/6 P



Li	Be											В	С	N	0	F
Να Ο	Mg											Αl	Si	Ρ	S	СІ
K	Са	Sc O	Ti	V	Cr O	Мп	Fe	Co O	Ni	Cu	Zn	Gα	Ge	As	Se O	Br
Rь О	Sr ()	Y	Zr ()	NЬ	Mo	Тс	Ru	Rh	Pd	Ag O	Cd	In O	Sn O	Sb O	Te	I
Cs ()	Ba O	R.E.	нf	Ta	w D	Re ()	0s O	Ir O	Pt	Au O	Hg O	τı	РЬ	Bi	Po	At
Fr	Ra	Ac	Th	Pa D	υ	Np	Pu	Am	Ст	Bk	Cf					
La	Ce O	Рг	Nd	Pm	Sm	E B	Gd	ТЬ	Dy	Ηǫ	Er	Τm	Yb ⊖	Lu		

# Cation exchange resin 7M HNO<sub>3</sub>

J. Radioanal. Chem. 5 (1970)

CER/7 N