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SUBJECT: Extraction of the Elements with Tris-2-Ethylhexyl-
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TO: Distribution

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EXTRACTION OF THE ELEMENTS WITH TRIS-2-ETHYLHEXYL-
AND TRIHEXYLPHOSPHINE OXIDES FROM ACIDIC SOLUTIONS

W. J. Ross and J. C. White

This report is the second of a series which concerns the separation of ions by solvent extraction with trialkylphosphine oxides. Earlier work¹ has shown that considerable selectivity is exhibited in the extraction of ions from solutions of HCl, HNO₃, H₂SO₄, and HClO₄ with 0.1 M solutions of tri-octylphosphine oxide (TOPO) in a diluent of cyclohexane. An even greater selectivity was suggested by the pioneering investigations of Blake et al² into the characteristics of other organo-phosphine oxides. These investigators showed that, in comparison with TOPO, the extraction of uranium from acidic solutions was diminished when the extractant was a straight chain homolog of lower molecular weight and when the carbon atom was branched.

This investigation has consisted in the extraction of various ions from acidic solutions with extractants that are representative of these more specific phosphine oxides - trihexylphosphine oxide (THPO) and tris-2-ethylhexylphosphine oxide (TEHPO). These extractants were prepared as 0.1 M solutions in cyclohexane. The test solutions of the metals used in these tests were the same as those described previously¹ except for the standard solution of thorium. Since the amount of thorium, 2 mg, that was present in the extractions with TOPO was insufficient to permit satisfactory determination of the partitioning of this ion, the extractions in this experiment were performed with solutions containing a total of 25 mg of thorium. The procedure that was described for the extraction of ions with TOPO and

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qualitative determination by spectrographic methods¹ was duplicated in the present tests except that the ions: Fe^{+3} , Ni^{+2} , Cr^{+6} , and Zr^{+4} were extracted as a group instead of individually and 7 M H_2SO_4 was substituted for 12 M media in an effort to prevent the formation of a third phase during the extraction. The results of the extractions that were performed with TEHPO are reported in Table I and those with THPO in Table II wherein the designations E, P, and N are defined as follows: E = complete extraction, P = partial extraction, N = no extraction, or trace extraction, of the ion into the organic phase.

Table I

Extraction of Ions from Acid Solution with 0.1 M
Tris-2-Ethylhexylphosphine Oxide in Cyclohexane

Ion	HCl		H ₂ SO ₄		HClO ₄		HNO ₃	
	1 M	7 M	1 M	7 M	1 M	7 M	1 M	7 M
Al ⁺³	N	N	N	N	N	N	N	N
Sb ⁺³	P	P	P	E	P	E	P	P
As ⁺³	N	N	N	N	N	N	N	N
Ba ⁺²	N	N	-	-	N	N	N	N
Be ⁺²	N	N	N	N	N	N	N	N
Bi ⁺³	N	N	P	E	N	N	N	N
B ⁺³	N	N	-	-	N	N	N	N
Cd ⁺²	N	N	N	P	N	N	N	N
Ca ⁺²	N	N	-	-	N	N	N	N
Ce ⁺³	N	N	N	N	N	N	N	N
Cr ⁺⁶	P	P	P	-	P	P	P	N
Co ⁺²	N	N	N	N	N	N	N	N
Cu ⁺²	N	N	N	N	N	N	N	N
Dy ⁺³	N	N	N	N	N	N	N	N
Er ⁺³	N	N	N	N	N	N	N	N
Eu ⁺³	N	N	N	N	N	N	N	N
Gd ⁺³	N	N	N	N	N	N	N	N
Ga ⁺³	N	E	N	E	N	E	N	N
Ge ⁺⁴	?	P?	?	?	N	P?	N	N
Au ⁺	E	E	E	E	E	P	P	P
Hf ⁺⁴	N	E	N	E	P	E	P	E
Ho ⁺³	N	N	N	N	N	N	N	N
In ⁺³	P	P	N	E	N	P	N	N
Fe ⁺³	P	E	N	-	N	N	N	N
La ⁺³	N	N	N	N	N	N	N	N
Pb ⁺²	-	-	-	-	N	N	N	N
Mg ⁺²	N	N	-	-	N	N	N	N
Hg ⁺²	P	N	P	-	N	N	P	N
Mo ⁺⁶	P	E	P	E	P	P	P	P
Nd ⁺³	N	N	N	N	N	N	N	N
Ni ⁺²	N	N	N	-	N	N	N	N
Pd ⁺²	N	N	N	N	N	N	N	N
Pt ⁺²	N	N	N	P	N	N	N	N
Pr ⁺³	N	N	N	N	N	N	N	N
Ru ⁺²	N	N	N	N	N	N	N	N
Sm ⁺³	N	N	N	N	N	N	N	N
Ag ⁺	-	-	-	-	P	N	N	N
Sr ⁺²	N	N	-	-	N	N	N	N
Tb ⁺³	N	N	N	N	N	N	N	N
Th ⁺⁴	N	P	N	-	N	N	P	P
Tm ⁺³	N	N	N	N	N	N	N	N
Sn ⁺⁴	E	E	E	E	E	E	P	P
Ti ⁺⁴	N	P	N	E	N	E	N	P
U ⁺⁶	E	E	E	-	E	E	E	E
V ⁺⁴	N	N	N	P	N	N	N	N
Yb ⁺³	N	N	N	N	N	N	N	N
Y ⁺³	N	N	N	N	N	N	N	N
Zn ⁺²	P	N	N	N	N	N	N	N
Zr ⁺⁴	P	E	N	-	P	E	P	P

E = complete extraction P = partial extraction N = no extraction.

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Table IIExtraction of Ions from Chloride Solutions with 0.1 M
Trihexylphosphine Oxide in Cyclohexane

Ion	HCl		Ion	HCl	
	<u>1 M</u>	<u>7 M</u>		<u>1 M</u>	<u>7 M</u>
Al ⁺³	N	N	La ⁺³	N	N
Sb ⁺³	E	E	Mg ⁺²	N	N
As ⁺⁵	N	N	Hg ⁺²	N	N
Ba ⁺²	N	N	Mo ⁺⁶	E	E
Be ⁺²	N	N	Ni ⁺²	N	N
Bi ⁺³	E	N	Pd ⁺²	P	N
B ⁺³	N	N	Pt ⁺²	P	P
Cd ⁺²	P	P	Ru ⁺²	N	N
Ca ⁺²	N	N	Sr ⁺²	N	N
Cr ⁺⁶	E	E	Th ⁺⁴	P	E
Co ⁺²	N	N	Sn ⁺⁴	E	E
Cu ⁺²	N	N	Ti ⁺⁴	P	E
Ga ⁺³	N	E	U ⁺⁶	E	E
Ge ⁺⁴	?	E?	V ⁺⁴	N	P
Au ⁺	E	E	Y ⁺³	N	N
Hf ⁺⁴	E	E	Zn ⁺²	P	N
In ⁺³	P	N	Zr ⁺⁴	P	E
Fe ⁺³	P	E			

E = complete extraction P = partial extraction N = no extraction.

Discussion

The data in Tables I and II show that, in general, the selectivity of extraction of TEHPO and THPO is very similar and differs very little from that of TOPO. As a consequence, extractions with THPO from acidic systems other than HCl were not performed. Some differences in extraction among reagents are noteworthy, however. For example, Bi⁺³ is not extracted by TEHPO from 1M HCl, but it is extracted from the same media by THPO. Cadmium is not extracted from HCl or HClO₄ solutions by TEHPO, but is extracted by the same extractant from H₂SO₄ systems. Sexivalent chromium is readily extracted by TOPO even in HNO₃ media; no extraction occurs with

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TEHPO in an HNO_3 solution. Other examples are:

<u>Element</u>	<u>Acid</u>	<u>TEHPO</u>	<u>THPO</u>	<u>TOPO</u>
Hafnium	All acids	N	E	E
Indium	1 M H_2SO_4	N	E	E
Mercury(II)	HCl	E	N	P
Palladium(II)	HCl	N	P	N
Thorium	HCl , H_2SO_4 , HClO_4	N	E	E
Vanadium(IV)	7 M HCl	N	E	E
Zinc(II)	7 M H_2SO_4	E	N	N

E = complete extraction P = partial extraction N = no extraction.

In general, it is observed that:

- a. The order of increasing capacity of extraction is $\text{THPO} > \text{TOPO} > \text{TEHPO}$.
- b. No ion is extracted by THPO or TEHPO that is not extracted by TOPO under certain conditions.
- c. The effect of hydrogen ion concentration is greater in TEHPO systems than it is in the other two, which indicates greater selectivity of extraction with TEHPO.

As emphasized previously,¹ the results of these tests are qualitative in nature and do not represent absolute extraction coefficients. Quantitative studies have been performed in this laboratory with uranium, chromium, iron, nickel, and zirconium and will be reported separately. The possibility that even greater selectivity may be exhibited by other types of phosphine oxides will be investigated in future qualitative studies.

References

1. J. C. White, ORNL-CF-56-9-18, September 6, 1956 (WJR-114).
2. C. A. Blake, Jr., K. B. Brown, and C. F. Coleman, "Solvent Extraction of Uranium (and Vanadium) from Acid Liquors with Trioctylphosphine Oxide," ORNL-1964, August 26, 1955.

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