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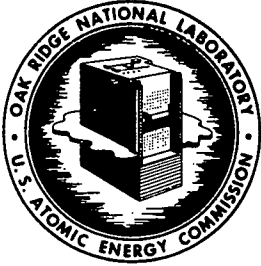
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EXTRACTION OF THE ELEMENTS WITH TRIOCTYLPHOSPHINE OXIDE
FROM ACIDIC SOLUTIONS

W. J. Ross

This report is a preliminary survey of the applicability of the tri-n-alkylphosphine oxides in the analytical separation of ions by solvent extraction.

Blake, Brown and Coleman¹ discovered that a number of these phosphine oxides, in particular, the trioctyl and tridecyl derivatives, were powerful extractants for uranium (UO_2^{++}) in a variety of media. In the application of the alkylphosphine oxides to the extraction of acidic leach liquors of uraniferous raw materials, they found that vanadium, aluminum, and iron were extracted to but a small fraction of the uranium that was extracted.

This work was undertaken to ascertain those ions that are extracted by the phosphine oxides in order that a cursory observation on the possible uses of these phosphine oxides as analytical extractants could be made. In this investigation only qualitative data were collected. It is obvious that any conclusions that may be drawn are tentative pending a quantitative study. A number of such studies are now either in progress or are contemplated.

It is the purpose of this report to acquaint the reader with the results of the qualitative study and perhaps stimulate more exhaustive research into their analytical uses. The investigation of the application of other phosphine oxides, particularly those with branched alkyl groups, is under way. The results reported by Blake et al on tris 2,ethylhexyl phosphine oxide and tris 3, 5, 5, trimethylhexyl phosphine oxide (the former being

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a poor extractant for uranium, the latter an excellent one), indicate that widely different extraction characteristics are to be expected. This work is under way and a brief preliminary report of this survey will be made in the near future.

Reagents

Trioctylphosphine oxide, 0.1 M solution in cyclohexane. Dissolve 38.6 g of $(C_8H_{17})_3PO$ in one liter of cyclohexane and store in an opaque container.

Al⁺³, 10 mg per ml. 8.93 g of $AlCl_3 \cdot 6H_2O$ in 100 ml of 0.5 M $HClO_4$.

Sb⁺³, 10 mg per ml. 2.39 g of Sb_2O_3 in 100 ml of 2.5 M HCl .

As⁺⁵, 10 mg per ml. 4.17 g of $NaHASO_4 \cdot 7H_2O$ in 100 ml of H_2O .

Ba⁺², 10 mg per ml. 1.78 g of $BaCl_2 \cdot 2H_2O$ in 100 ml of 0.5 M $HClO_4$.

Be⁺², 10 mg per ml. 1.00 g of Be in 100 ml of 2 M HCl and 2 M H_2SO_4 .

Bi⁺³, 5 mg per ml. 1.61 g of $Bi(NO_3)_3 \cdot 5H_2O$ in 2 M H_2SO_4 and 2 M HNO_3 .

B⁺³, 10 mg per ml. 5.72 g of H_3BO_3 in 100 ml of H_2O .

Cd⁺², 10 mg per ml. 2.03 g of $CdCl_2 \cdot 2-1/2 H_2O$ in 100 ml of 0.5 M $HClO_4$.

Ca⁺², 10 mg per ml. 2.78 g of $CaCl_2$ in 100 ml of 0.5 M $HClO_4$.

Ce⁺³, 2.0 mg per ml. Obtained as standard in HNO_3 .

Cr⁺⁶, 10 mg per ml. 14.14 g of $K_2Cr_2O_7$ in 500 ml of H_2O .

Co⁺², 10 mg per ml. 4.03 g of $CoCl_2 \cdot 6H_2O$ in 100 ml of 0.5 M $HClO_4$.

Cu⁺², 10 mg per ml. 2.12 g of $CuCl_2$ in 100 ml of 0.5 M $HClO_4$.

Dy⁺³, 1.0 mg per ml. Obtained as standard in HNO_3 .

Er⁺³, 0.2 mg per ml. Obtained as standard in HNO_3 .

Eu⁺³, 0.2 mg per ml. Obtained as standard in HNO_3 .

Gd⁺³, 0.2 mg per ml. Obtained as standard in HNO_3 .

Ga⁺³, 12 mg per ml. 1.23 g of Ga in 100 ml of 2.5 M HCl .

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Ge⁺⁴, 4.6 mg per ml. 0.165 g of GeO₂ in 25 ml of 12 M H₂SO₄.
Au⁺, 2.0 mg per ml. 0.200 g of Au in 100 ml of 1 M HNO₃ and 3 M HCl.
Hf⁺⁴, 8.9 mg per ml. 0.893 g of Hf in 100 ml of 2 M H₂SO₄.
Ho⁺³, 1.0 mg per ml. Obtained as standard in HNO₃.
In⁺³, 10 mg per ml. 0.995 g of In in 100 ml of 2.5 M HCl.
Fe⁺³, 10 mg per ml. 36.18 g of Fe(NO₃)₃·9H₂O in 500 ml of H₂O.
La⁺³, 10 mg per ml. 1.76 g of LaCl₃ in 100 ml of 0.1 M HCl.
Pb⁺², 10 mg per ml. 1.68 g of Pb(NO₃)₂ in 100 ml of 2 M HNO₃.
Mg⁺², 10 mg per ml. 8.50 g of MgCl₂·6H₂O in 100 ml of 2.5 M HCl.
Hg⁺², 10 mg per ml. 1.35 g of HgCl₂ in 100 ml of 2.5 M HCl.
Mo⁺⁶, 10 mg per ml. 9.18 g of (NH₄)₆Mo₇O₂₄·4H₂O in 500 ml of H₂O.
Nd⁺³, 1.0 mg per ml. Obtained as standard in HNO₃.
Ni⁺², 10 mg per ml. 24.77 g of Ni(NO₃)₂ in 500 ml of H₂O.
Pd⁺², 1.0 mg per ml. 0.100 g of Pd in 1 M HNO₃ and 3 M HCl.
Pt⁺², 10 mg per ml. 0.266 g of H₂PtCl₆·6H₂O in 100 ml of 2.5 M HCl.
Pr⁺³, 1.0 mg per ml. Obtained as standard in HNO₃.
Ru⁺², 0.4 mg per ml. 0.400 g fused in KOH and KNO₃ and dissolved in 100 ml of 2 M HCl.
Sm⁺³, 1.0 mg per ml. Obtained as standard in HNO₃.
Ag⁺, 10 mg per ml. 1.57 g of AgNO₃ in 100 ml of 2 M HNO₃.
Sr⁺², 10 mg per ml. 3.05 g of SrCl₂·6H₂O in 100 ml of 0.5 M HClO₄.
Tb⁺³, 0.5 mg per ml. Obtained as standard in HNO₃.
Th⁺⁴, 10 mg per ml. 2.38 g of Th(NO₃)₄ in 100 ml of 0.5 M HClO₄.
Tm⁺³, 0.2 mg per ml. Obtained as standard in HNO₃.
Sn⁺⁴, 10 mg per ml. 2.95 g of SnCl₄·5H₂O in 100 ml of 2.5 M HCl.
Ti⁺⁴, 5 mg per ml. 2.00 g of TiCl₄ in 100 ml of 4 M HCl.

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U⁺⁶, 10 mg per ml. 1.18 g of U₃O₈ in 100 ml of 2 M HNO₃.

V⁺⁴, 5 mg per ml. 0.89 g of V₂O₅ dissolved in 100 ml of 4 M H₂SO₄ after reduction of V⁺⁵ with SO₂ in 9 M H₂SO₄.

Yb⁺³, 0.1 mg per ml. Obtained as standard in HNO₃.

Y⁺³, 5 mg per ml. 0.65 g of Y₂O₃ in 2.5 M HCl.

Zn⁺², 10 mg per ml. 4.40 g of ZnSO₄·7H₂O in 100 ml of H₂O.

Zr⁺⁴, 10 mg per ml. 1.35 g of ZrO₂ in 100 ml of 4 M H₂SO₄.

Experimental

The ions to be investigated were divided into eight groups to minimize spectral interferences among elements during spectrographic determinations. This method of division was based on the total number of elements under study as well as on known spectral and chemical interferences that could be possible in such a diversity of cations and anions as were present in the reagent solutions. The ions were placed in the following groups:

- A. B⁺³, Mg⁺², Ca⁺², Sr⁺², and Ba⁺².
- B. Ti⁺⁴, Mo⁺⁶, As⁺⁵, Bi⁺³, V⁺⁴, Sb⁺³, Hf⁺⁴.
- C. Co⁺², Al⁺³, Y⁺³, La⁺³, Hg⁺², Ga⁺³, In⁺³.
- D. Pd⁺², Pt⁺², Ru⁺².
- E. Cu⁺², Zn⁺², Cd⁺², Au⁺, Sn⁺⁴, Ge⁺⁴, Be⁺².
- F. Ce⁺³, Pr⁺³, Nd⁺³, Sm⁺³, Eu⁺³, Gd⁺³, Tb⁺³, Dy⁺³, Ho⁺³, Er⁺³, Tm⁺³, Yb⁺³.
- G. Ag⁺, Pb⁺⁺, Th⁺⁴.
- H. Fe⁺⁺⁺, Ni⁺⁺, Cr⁺⁶, Zr⁺⁴, U⁺⁶.

Test solutions of the ion groups A through G were prepared by mixing the individual reagents so that the concentration of each ion was 1 mg per ml except for Au, the Pt group, and the rare earth group. The concentration of Au⁺ was 0.5 mg per ml, while the concentrations of Pd⁺², Pt⁺², and Ru⁺²

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were 0.45, 0.5, and 0.2 mg per ml. The standard solution of rare earths contained: 2 mg of Ce^{+3} per ml; 1 mg per ml of Pr^{+3} , Nd^{+3} , Sm^{+3} , Dy^{+3} , and Ho^{+3} ; 0.5 mg per ml of Tb^{+3} , 0.2 mg per ml of Y^{+3} , La^{+3} , Eu^{+3} , Gd^{+3} , Er^{+3} , and Tm^{+3} ; and 0.1 mg per ml of Yb. A two-ml test aliquot was taken and then diluted with three ml of acid of such concentration so as to yield final acid concentrations of: 1 and 7 M HCl, HNO_3 , and $HClO_4$ and 1 and 11 M H_2SO_4 .

Each test solution was equilibrated for ten minutes with 5 ml of 0.1 M trioctylphosphine oxide in cyclohexane by means of a Kahn shaker. The mixtures were allowed to stand until the phases were clear. Portions of both the organic and aqueous phases of each mixture were removed and analyzed by qualitative spectrographic procedures. The results of these analyses are reported in Table I 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.

The ions in Group H were investigated individually. These ions, Fe^{+3} , Ni^{+2} , Cr^{+6} , and Zr^{+4} , were determined colorimetrically; U^{+6} was determined fluorometrically.

Table I

Extraction of Ions from Acid Solution with 0.1 M Triocetylphosphine Oxide in Cyclohexane

Ion	HCl	H ₂ SO ₄	HClO ₄	HNO ₃
Al ³⁺	N	N	N	N
Sb ³⁺	P	E	P	P
As ⁵⁺	N	P	N	N
Ba ²⁺	N	-	N	N
Be ²⁺	N	N	N	N
Bi ³⁺	P	E	N	P
B ³⁺	N	-	-	N
Cd ²⁺	P	N	?	N
Ca ²⁺	N	-	-	N
Ce ³⁺	N	N	N	N
Cr ⁶⁺	E	E	E	E
Co ²⁺	N	N	N	N
Cu ²⁺	P	N	N	N
Dy ³⁺	N	N	N	N
Er ³⁺	N	N	N	N
Eu ³⁺	N	N	N	N
Gd ³⁺	N	N	N	N
Ga ³⁺	N	N	E	N
Ge ⁴⁺	?	?	?	?
Au ⁺	E	E	E	E
Hf ⁴⁺	E	E	E	E
Ho ³⁺	N	N	N	N
In ³⁺	P	E	P	N
Fe ³⁺	E	N	N	N
La ³⁺	N	N	N	N
Pb ²⁺	-	-	-	N
Mg ²⁺	N	-	-	N
Hg ²⁺	P	?	N	N
Mo ⁶⁺	E	E	E	E
Nd ³⁺	N	N	N	N
Ni ²⁺	N	N	N	N
Pd ²⁺	N	N	N	N
Pt ²⁺	P	P	N	N
Ru ²⁺	N	N	?	N
Sm ³⁺	N	N	N	N
Ag ⁺	-	-	-	N
Sr ²⁺	N	-	-	N
Tb ³⁺	N	N	N	N
Th ⁴⁺	-	-	-	?
Tm ³⁺	N	N	N	N
Sn ⁴⁺	E	E	E	E
Tl ⁴⁺	N	E	E	E
U ⁶⁺	E	E	E	E
V ⁴⁺	N	E	E	E
Y ³⁺	N	N	N	N
Zn ²⁺	N	N	N	N
Zr ⁴⁺	P	N	N	E

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

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Discussion

The data that are presented in Table I are qualitative in nature and are based only on the conditions used in these tests. As defined above, the designations E, P, and N are merely considered to be guides as to the efficiency of extracting each ion with trioctylphosphine oxide.

Definite spectral lines were obtained for each ion in the aqueous and/or the organic phases except in those cases, i.e. 11 M H_2SO_4 and 7 M HClO_4 , that a third phase formed during the extraction. This third, middle, phase is a result of the strong acid concentration and apparently consists mainly of trioctylphosphine oxide. The spectral lines of the elements in this middle phase and in the organic phase are the same but are much weaker than those found in the organic phase of two-phase systems containing the same ions.

Similar effects of concentrated acids (11 M H_2SO_4 and 7 M HClO_4) on the ions themselves were observed. A brown precipitate formed when the Group D ions were acidified to form a 11 M H_2SO_4 solution and the resulting spectral lines of Ru were very weak. White solids were observed in 11 M H_2SO_4 and 7 M HClO_4 solutions of the Group E ions; however, no diminution of spectral intensities were observed.

An effort was made to prepare solutions of each element in such a manner that the resulting ions would exist in their highest, stable oxidation states and thus preclude all redox reactions between the ions in any one solution. Inasmuch as V_2O_5 could be dissolved in H_2SO_4 only after the reduction of V^{+5} to V^{+4} , the resulting solution contained tetravalent vanadium (blue). This blue color persisted in all 1 M acid solutions and in 7 M HNO_3 , but changed to yellow on the addition of concentrated

HCl, H₂SO₄, and HClO₄. Apparently the vanadium that was extracted from 7 M HCl was V⁺⁵ (yellow). No other change in the oxidation state of any ion was observed although the color of such ions as Cu⁺² and Co⁺³ varied with type of acid media.

Many very interesting results are obvious from the data of Table I and a general conception of the applicability of trioctylphosphine oxide, as an extractant of metallic ions, can be obtained. Considerable investigation of a quantitative nature is, of course, required to supplement this qualitative data. The following classifications are included as a means of converting this qualitative data into forms that could stimulate further investigation in this field.

I. Elements that are extracted quantitatively:

Sb⁺³, Bi⁺³, Cd⁺², Cr⁺⁶, Ga⁺³, Au⁺, Hf⁺⁴, In⁺³, Fe⁺³, Mo⁺⁶, Sn⁺⁴, Ti⁺⁴, U⁺⁶, V⁺⁴, Zr⁺⁴.

II. Elements that are not extracted from any acid solution:

Al⁺³, Ba⁺², B⁺³, Ca⁺², Ce⁺³, Co⁺², Dy⁺³, Er⁺³, Eu⁺³, Gd⁺³, Ho⁺³, La⁺³, Pb⁺², Mg⁺², Nd⁺³, Ni⁺², Pd⁺², Pr⁺³, Ru⁺², Sm⁺³, Ag⁺, Sr⁺², Tb⁺³, Tm⁺³, Yb⁺³, Y⁺³.

III. Elements that are extracted from one acid solution only:

Be⁺², Cu⁺², Fe⁺³, V⁺⁴, Zn⁺².

IV. Elements that are extracted from two acid solutions only:

As⁺⁵, Cd⁺², Hg⁺², Pt⁺².

V. Elements whose extractions are dependent on acid concentration:

Bi⁺³, Cu⁺², Ga⁺², Pt⁺², Ti⁺⁴, V⁺⁴.

VI. Elements that are extracted from:

HCl		H ₂ SO ₄		HClO ₄		HNO ₃
Sb ⁺³	Hf ⁺⁴	Sb ⁺³	Hg ⁺²	Sb ⁺³	Hf ⁺⁴	Sb ⁺³
Bi ⁺³	In ⁺³	As ⁺⁵	Mo ⁺⁶	As ⁺⁵	In ⁺³	Bi ⁺³
Cd ⁺²	Fe ⁺³	Bi ⁺³	Pt ⁺²	Be ⁺²	Mo ⁺⁶	Cr ⁺⁶
Cr ⁺⁶	Hg ⁺²	Cr ⁺⁶	Sn ⁺⁴	Bi ⁺³	Sn ⁺⁴	Au ⁺
Cu ⁺²	Mo ⁺⁶	Ga ⁺³	Ti ⁺⁴	Cd ⁺²	Ti ⁺⁴	Hf ⁺⁴
Ga ⁺³	Pt ⁺²	Ge ⁺⁴	U ⁺⁶	Cr ⁺⁶	Zn ⁺⁴	Mo ⁺⁶
Ge ⁺⁴	Sn ⁺⁴	Au ⁺⁴	Zr ⁺⁴	Ga ⁺³		Sn ⁺⁴
Au ⁺	Ti ⁺⁴	Hf ⁺⁴		Ge ⁺⁴		Ti ⁺⁴
	U ⁺⁶	In ⁺³		Au ⁺		U ⁺⁶
	V ⁺⁴					Zr ⁺⁴
	Zn ⁺²					
	Zr ⁺⁴					

Recent quantitative investigations of a small number of these elements have shown that trioctylphosphine oxide is a powerful extracting and isolating reagent. Inasmuch as the extractability of some of these elements is changed radically when the oxidation state is altered, for example, trivalent chromium is not extracted at all, while the hexavalent state is readily extracted, an even greater versatility can be expected of trioctylphosphine oxide in separations by solvent extraction.

Reference

1. C. A. Blake, Jr., K. B. Brown, and C. F. Coleman, "Solvent Extraction of Uranium (and Vanadium) from Acid Liquors with Trialkylphosphine Oxides," ORNL-1964, August 26, 1955.

Acknowledgement

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