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EXTRACTION OF CHROMIUM WITH TRIOCYTLPHOSPHINE OXIDE

J. C. White
W. J. Ross

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ANALYTICAL CHEMISTRY DIVISION

M. T. Kelley, Director
C. D. Susano, Associate Director

EXTRACTION OF CHROMIUM WITH TRIOCTYLPHOSPHINE OXIDE

J. C. White, W. J. Ross

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ABSTRACT

Chromium in the hexavalent state is readily extracted by tri-n-octylphosphine oxide (TOPO) from acidic sulfate and chloride solutions. When present in the trivalent form, chromium is not extractable under any condition tested. Thus TOPO provides an excellent reagent for the separation by solvent extraction of the two common oxidation states of chromium.

Chromium is quantitatively extracted in a single equilibration from chloride solutions that are 1 to 7 M HCl and from sulfate solutions that are 1 to 4 M H_2SO_4. In hydrochloric acid, approximately 12 mg of chromium are extracted quantitatively by 0.5 millimole of TOPO; in sulfuric acid, nearly 20 mg are extractable with the same concentration of reagent. The loading capacity of this concentration of reagent is 21 mg for hydrochloric acid solutions, 30 mg for sulfuric acid solutions.

The time required to reach equilibration is extremely short; for example, 10 mg of chromium are extracted completely after equilibration for one minute.

Extremely large volume phase ratios are tolerable, particularly in hydrochloric acid solutions. Complete extraction is attainable in a single equilibration from a V_a/V_o ratio of 10. In sulfate solutions the maximum phase ratio is three. The addition of excess anion in the form of a neutral salt retards extraction in both chloride and sulfate media. The extraction coefficient for chromium is 2.6 for a solution 1 M HCl, and 0.1 to 2 M NaCl as compared to about 100 for 1 M HCl alone. In 1 M H_2SO_4, 0.5 to 2 M Na_2SO_4, the extraction coefficient is approximately 15 as compared to 30 for 1 M H_2SO_4.

In both chloride and sulfate systems the extractable species is $H_2Cr_2O_7 \cdot 2TOPO$.

The extraction of chromium from nitrate, phosphate and perchlorate systems is incomplete. In nitrate systems at high acidities, the hexavalent chromium acts as a strong oxidant. For this reason, although considerable chromium is extracted under favorable conditions, extraction is not recommended from nitrate solutions. In neither perchlorate nor phosphate systems, is the extraction sufficiently complete for efficient application.

The solvent in which the TOPO is dissolved has little effect on the extraction of chromium. Essentially,no difference in the degree of extraction is obtained if the TOPO is dissolved in cyclohexane, carbon tetrachloride, or nitrobenzene. This relationship is in sharp contrast to the effect of solvent on the extraction of uranium with TOPO where, in general, the higher the polarity of the solvent the lower the extraction coefficient.

EXTRACTION OF CHROMIUM WITH TRIOCTYLPHOSPHINE OXIDE

J. C. White, W. J. Ross

INTRODUCTION

In the course of their systematic study of organic complexing agents for uranium, Brown and his coworkers[1] have found a number of promising reagents among the organo-phosphorous compounds. One class of these compounds, the tri-n-alkylphosphine oxides, was found to have an extremely high extraction coefficient for uranium, significantly greater than the coefficient for iron, aluminum, thorium, and vanadium.

On the basis of this work, White and his coworkers[5] made a comprehensive qualitative investigation of the extraction of some 40 additional metal ions from acidic solutions by tri-n-octylphosphine oxide to obtain a general picture of the selectivity of these compounds as solvent extractants. Among those metal ions that were extracted under these conditions was chromium. This investigation concerns a study of the effects of many variables on the extraction of chromium from acidic solutions. These include concentration of hydrogen ion, concentration of anion, concentration of reagent, phase ratio, equilibration time, etc. On the basis of these studies, conditions will be established for the separation of chromium by solvent extraction and its application in analytical chemistry, which will be the subject of future work.

REAGENTS

Potassium dichromate solution. Dissolve 14.57 grams of National Bureau of Standards $K_2Cr_2O_7$ in 500 ml of water to prepare a solution that contains 10.3 mg of chromium(VI) per ml. A similar solution which contained 49.6 mg of chromium(VI) per ml was also used.

Chromic sulfate solution. Dissolve 23.18 grams of reagent grade $Cr_2(SO_4)_3 \cdot 5H_2O$ in 500 ml of water to prepare a solution that contains 10.0 mg of chromium(III) per ml. Pass sulfur dioxide through the solution for a few minutes to insure the absence of any dichromate. Boil the solution to remove excess sulfur dioxide. Standardize by oxidizing the chromium(III) to chromium(VI) with perchloric acid and titrating with a standard solution of iron(II).

Tri-n-octylphosphine oxide (TOPO), 0.1 M solution. Dissolve 39.6 grams of TOPO in one liter of diluent and store in a brown-glass container. Cyclohexane was used as a diluent in this work although other diluents, such as kerosene, or benzene are equally satisfactory in many respects. Cyclohexane is particularly ideal because of its high purity and excellent spectral characteristics. Carbon tetrachloride and nitrobenzene are satisfactory diluents, each with a specific gravity greater than one, although these solvents are not attractive from a toxicological viewpoint. Alcohols cannot be used as diluents since such compounds readily reduce chromium(VI) in acidic systems. If desired, the concentration of TOPO in cyclohexane can be increased as high as 0.2 M at 25° C. The TOPO used was 99.4 per cent pure; its melting point was 50.8° to 51.5° C. The combined acidity was 0.2 per cent; total acidity was 0.4 per cent.

GENERAL PROCEDURE

All extractions that are described in the following tests (except for those tests which involved the use of more than 20 ml of liquid) were performed in specially designed glass containers. The containers were fabricated from 40/50 ₮ male ground glass joints and were approximately 1-1/2 inches in diameter and 3 inches long (excluding the joint). The containers were closed with caps which consisted of 40/50 ₮ female ground glass joints which were sealed on to five-inch test tubes (15 mm O.D.). When the total volume of the two phases exceeded 20 ml, the extractions were performed in separatory funnels.

The test mixture was prepared by transferring the desired volume of the standard solutions of chromium(VI) (10.3 or 49.6 mg of chromium(VI) per ml) or chromium(III) (9.6 mg of chromium(III) per ml) to the extraction container and then adding sufficient acid to produce the desired concentration of acid. In most tests the volume of the aqueous phase was five ml. Five ml of the TOPO solution (usually 0.1 M in cyclohexane) was then added to the extraction container. The container was capped and placed in a perforated wooden block that was mounted on a Kahn shaker. Extraction was achieved by mechanically agitating the mixtures on this Kahn shaker for predetermined lengths of time.

After equilibration, the container was removed and inverted so that the mixture was transferred to the narrow test tube portion of the cap where it was allowed to remain until the phases were completely separated and the solutions were clear. Test portions were taken from both phases.

The organic test portion was removed from the organic phase, the organic diluent evaporated and the residual TOPO destroyed by heating with HNO_3 and $HClO_4$ prior to the determination of chromium. Such decomposition left a small white residue of oxides of phosphorus that was readily soluble in dilute HCl. The aqueous phase was analyzed directly. Chromium was determined either by standard volumetric[4] or colorimetric[3] methods.

The value of the extraction coefficient, E_a^o, was calculated from the concentrations of chromium in the two phases after extraction and is defined as

$$E_a^o = \frac{\text{Concentration of Cr in organic phase}}{\text{Concentration of Cr in aqueous phase}} .$$

EXTRACTION OF CHROMIUM FROM CHLORIDE SOLUTIONS

Effect of Concentration of Hydrochloric Acid

The results of the tests to determine the effect of concentration of acid on the extraction of hexa- and trivalent chromium are presented in Table I.

Table I

Extraction of Chromium from Hydrochloric Acid with TOPO
Effect of Acid Concentration

Cr^{+6} - 10.3 mg
Cr^{+3} - 9.6 mg
TOPO - 5 ml, 0.1 M in cyclohexane
Phase ratio, aqueous/organic - 6/5
Equilibration time - 10 minutes

Chromium, Oxidation State	HCl Molarity	Chromium, mg Organic	Chromium, mg Aqueous	E_a^o
+6	10	4.5	5.76	0.93
	7	10.0	0.26	47
	3.5	10.3	0.04	307
	1	10.2	0.14	73
+3	10	7×10^{-4}	9.6	7×10^{-5}
	7	14×10^{-4}	9.6	14×10^{-5}
	4	19×10^{-4}	9.6	19×10^{-5}
	1	14×10^{-4}		14×10^{-5}

Hexavalent chromium is extracted quantitatively from solutions as highly concentrated as 7 M HCl. At higher concentrations the extraction diminishes markedly; for example, the E_a^o at 10 M HCl is only 0.9. This decrease in extraction of chromium with increasing acid concentration is in part due to the formation of a third, intermediate, phase wherein a large fraction of the TOPO is concentrated. The volume of this third phase, evidently a factor that is dependent on the effect of hydrogen ions on the solubility of TOPO in the organic phase, becomes greater with increasing concentration of HCl.

Several extractions were made from chloride solutions in which the acidity was markedly lower than in the above tests. At pH 0.3, the E_a^o was found to be only 0.2 as compared to approximately 100 at 1 M HCl. When the

pH was 3.2 no hexavalent chromium was extracted into the organic phase. Similar results were found for tests which were conducted in a basic solution at pH 10. These results demonstrate the effect of acidity on the extraction and indicate that the dichromate ion is the actual species extracted.

Trivalent chromium was not extracted at any of the acid concentrations tested. Hexavalent chromium is thus quantitatively separated from trivalent chromium in chloride solutions that are 1 to 7 M HCl by extraction with TOPO.

Effect of Concentration of Chromium

The effect of concentration of chromium on the extraction with TOPO was determined through a series of extractions of varying amounts of chromium with five ml of 0.1 M TOPO in cyclohexane. The results are tabulated in Table II.

Table II

Extraction of Chromium from Chloride Solutions
Effect of Concentration of Chromium

HCl - 1 M
TOPO - 5 ml, 0.1 M in cyclohexane
Equilibration time - 10 minutes
Phase ratio, aqueous/organic - 1

Chromium, mg			
Present	Found		E_a^o
	Organic	Aqueous	
5.2	5.2	0.002	2600
6.2	6.2	0.025	248
7.2	7.2	0.038	190
8.2	8.1	0.050	164
9.3	9.2	0.100	92
10.3	10.1	0.150	67
11.3	11.1	0.240	46
12.4	12.0	0.425	28
13.4	12.6	0.775	16
14.4	13.2	1.20	11
15.5	13.8	1.73	8.0
16.5	14.0	2.46	5.7
17.5	14.2	3.31	4.3
18.5	14.9	3.58	4.1
19.6	15.3	4.25	3.6
20.6	15.2	5.44	2.8
25.8	15.3	10.5	1.5
30.9	16.5	14.4	1.1
36.1	17.2	18.9	0.9
41.2	17.4	23.8	0.7
98.0	18.0	80.0	0.2
147.0	21.0	126.0	0.2
198.3	20.6	177.7	0.1

The extraction of chromium from chloride solutions is presented graphically in Figure 1. The loading capacity of 0.5 millimoles of TOPO, that is, the maximum amount of chromium that is extracted by the reagent, is approximately 21 mg. Of more importance to its potential analytical use as an extractant, however, is the maximum amount of chromium that is extracted quantitatively

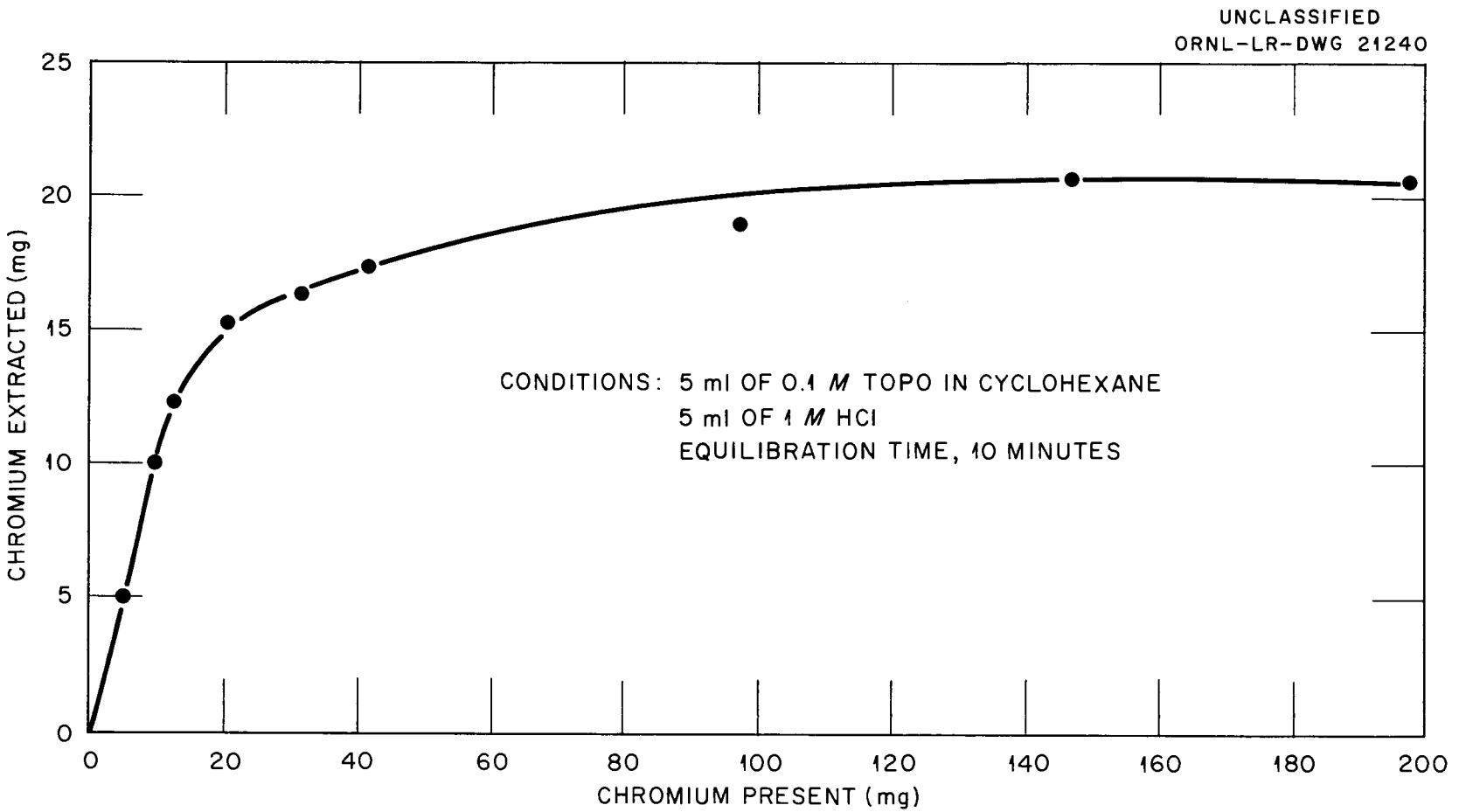

Fig. 1. Extraction of Chromium(VI) from Chloride Solutions with Trioctylphosphine Oxide.

by a given amount of reagent in a single equilibration. The linear portion of the isotherm extends to approximately 10 mg of chromium. A quantitative separation of approximately 12 mg of chromium can, therefore, be achieved in a single extraction, although the loading capacity, 0.5 millimoles of TOPO, is approximately twice as large. This loading value is equivalent to approximately one mole of TOPO per mole of chromium. Inasmuch as the primary purpose of this test was to establish the portion of the isotherm that is applicable to quantitative separation no attempt was made to compare the significance of the value of the extraction coefficient in nearly saturated media with that which would be obtained in mixtures wherein the concentration of TOPO was in large excess.

Effect of Concentration of Trioctylphosphine Oxide

The data that are presented in Table III were obtained from a series of tests that was designed to identify the complex that is extracted into the organic solvent with TOPO. Various concentrations of extractant were used in the equilibration of a constant amount of chromium.

Table III

Extraction of Chromium(VI) from Chloride Solutions
Effect of Concentration of Trioctylphosphine Oxide

Cr^{+6} - 198.3 mg
HCl - 1 M
Equilibration time - 10 minutes
Phase ratio, aqueous/organic - 1

TOPO, Molarity	Chromium, mg		$\frac{(TOPO)}{(Cr^{+6})}$
	Organic	Aqueous	
0.01	3.6	194.7	0.72
0.05	10.9	187.4	1.19
0.10	20.6	177.7	1.26
0.15	34.0	164.3	1.15
0.20	42.0	156.3	1.24

These results show that the amount of chromium which is extracted into cyclohexane is a function of the concentration of TOPO and also that the molar ratio, (TOPO)/(Cr), of the components in the organic phase is approximately 1.2 when the concentration of TOPO is varied from 0.05 to 0.2 M. The ratio found with 0.01 M TOPO is less than unity.

Effect of Equilibration Time

The rate with which equilibration of the phases is achieved was determined by shaking the two phases mechanically for predetermined periods of time. Approximately 10 mg of hexavalent chromium in 1 M HCl was extracted with 0.5 millimoles of TOPO. Several tests were also made with trivalent chromium under similar conditions. The results are shown in Table IV.

Table IV

Extraction of Chromium from Chloride Solutions
Effect of Equilibration Time

Cr^{+6} - 10.3 mg
Cr^{+3} - 9.6 mg
HCl - 1 M
TOPO - 5 ml, 0.1 M in cyclohexane
Phase ratio, aqueous/organic - 6/5

Chromium, Oxidation State	Time, Minutes	Chromium, mg		E_a^o
		Organic	Aqueous	
+6	1	9.8	0.5	25
	5	10.1	0.2	67
	20	10.1	0.2	67
+3	1	9×10^{-4}	9.6	9×10^{-5}
	20	5×10^{-4}	9.6	5×10^{-5}
	60	5×10^{-4}		5×10^{-5}

A very short equilibration time is indicated inasmuch as 95 per cent of the chromium was extracted in one minute and 98 per cent in five minutes.

Essentially no trivalent chromium was extracted even after 60 minutes, which eliminates the possibility of slow formation of an extractable complex between trivalent chromium and TOPO.

Effect of Phase Ratio

Since one of the major attractions of extraction as a means of separation or isolation is its ability to effect a simultaneous concentration of the desired ion, a series of tests was performed to determine the extraction of chromium into the organic phase at large aqueous and organic volume ratios. The results are presented in Table V.

Table V

Extraction of Chromium from Chloride Solutions
Effect of Phase Ratio

Cr^{+6} - 10.3 mg
HCl - 1 M
TOPO - 5 ml 0.1 M in cyclohexane
Equilibration time -10 minutes

V_a/V_o	Chromium, mg		E_a^o
	Organic	Aqueous	
1	10.1	0.2	60
2	10.0	0.3	80
3	9.9	0.4	86
5	9.9	0.4	94
10	9.5	0.8	119
20	9.1	1.2	152

These results show that the value of E_a^o becomes larger as the phase ratio, V_a/V_o, is increased. These data reveal the applicability of TOPO as a means of concentrating chromium(VI) through extraction from large volumes of aqueous solution. At $V_a/V_o = 20$, approximately 90 per cent of the chromium is extracted in a single equilibration. Quantitative

removal of chromium from large volumes of acidic solutions would be feasible with only two extractions at most.

Effect of Concentration of Chloride

The effect of concentration of chloride on the extraction of chromium from 1 M HCl solution was determined. The results are shown in Table VI.

Table VI

Extraction of Chromium from Chloride Solutions
Effect of Chloride

Cr^{+6} - 20.6 mg
HCl - 1 M
TOPO - 5 ml, 0.1 M in cyclohexane
Equilibration time - 10 minutes
Phase ratio, aqueous/organic - 6/5

Sodium Chloride		Chromium, mg		E_a^o
mg	Molarity	Organic	Aqueous	
0	0	18.6	2.0	9.3
35	0.1	14.2	6.4	2.7
175	0.5	14.0	6.6	2.5
350	1	14.1	6.5	2.6
700	2	14.2	6.4	2.7

The presence of as little as 35 mg of NaCl, 0.1 M chloride, reduces the loading capacity of five ml of 0.1 M TOPO by approximately 20 per cent. Additional chloride has no further effect on the extraction.

Identification of the Extracted Species

Inasmuch as the extraction of chromium by TOPO is affected by the concentrations of TOPO, hydrogen ion, chloride ion, and chromium that exist in the mixture before equilibration, an attempt was made to determine if these effects are due to variations in the composition of the species that is extracted. The concentration of various constituents of the organic

phases which were obtained after equilibrating the organic phase with solutions of chromium in various concentrations of hydrochloric acid were determined as follows: The hydrogen ion concentration in the organic phase was determined by forming a water-miscible solution of the cyclohexane solution of TOPO, ethanol, and benzene and then titrating with standard sodium hydroxide. The chloride content was determined potentiometrically with standard silver nitrate after an aliquot of the organic phase had been stripped with 0.1 M sodium hydroxide and aqueous strip solution was neutralized with sulfuric acid. The chromium content of the organic phase was calculated by difference after determination of chromium in the aqueous phase. The results of these experiments are presented in Table VII.

Table VII

Extraction of Chromium from Chloride Solutions
Identification of Extracted Species

TOPO - 0.5 millimoles
Phase ratio, aqueous/organic - 1

HCl, Molarity	Chromium Present mg	Found in Organic Phase, Millimoles			Molar Combining Ratio
		Hydrogen	Chloride	Chromium	$TOPO:HCl:H_2Cr_2O_7$
2	0	0.02	0.04	-	10:1:0
2	20.6	0.33	0.0	0.28	10:0:3
4	0	0.11	0.22	-	5:2:0
4	20.6	0.33	0.22	0.30	10:4:3
7	0	0.30	0.35	-	10:7:0
7	20.6	0.47	0.27	0.32	10:5:3

Since the species extracted must be electrically neutral, the assumptions were made that each chloride ion must be accompanied by a hydrogen ion and that each mole of chromium, as $Cr_2O_7^{=}$, is bonded to two hydrogen ions. The total concentration of hydrogen ions found in each test was

slightly deficient to fulfill this postulation; however, this paucity of hydrogen ion is considered to be due to experimental errors that are involved in the titration of an organic solution with an aqueous alkaline solution.

The calculated combining ratios show that both hydrochloric acid and chromium are extracted by TOPO. When 2 M HCl is equilibrated with TOPO, the molar ratio of HCl to TOPO in the organic phase is 0.1. For 4 M HCl the ratio is increased to 0.4 and for 7 M HCl it is 0.7. These ratios are altered surprisingly when chromium is present in the solution. For example, in 2 M HCl solution, no chloride is extracted at all. In 4 M HCl the ratio remains at 0.4 but in 7 M it is 0.5. In all the tests with chromium present, the identical molar combining, 0.3 ratio of $H_2Cr_2O_7$ to TOPO was observed. These ratios demonstrate the dual capacity of TOPO as an extractant of mineral acid as well as chromium. The absolute values of the ratios would undoubtedly be altered if the concentration of chromium in the original aqueous solution were varied.

EXTRACTION OF CHROMIUM FROM SULFATE SOLUTIONS

Effect of Concentration of Sulfuric Acid

The effect of acid concentration on the extraction of chromium from sulfate solutions is presented in Table VIII.

Table VIII

Extraction of Chromium from Sulfate Solutions
Effect of Concentration of Sulfuric Acid

Cr^{+6} - 10.3 mg
Cr^{+3} - 9.6 mg
TOPO - 5 ml, 0.1 M in cyclohexane
Equilibration time - 10 minutes
Phase ratio, aqueous/organic - 6/5

Chromium Oxidation State	H_2SO_4 Molarity	Chromium, mg Organic	Chromium, mg Aqueous	E_a^o
+6	12[a]	2.1	8.16	0.3
	8[a]	7.3	3.00	2.9
	4	9.9	0.36	33
	1	9.9	0.45	26
+3	10	9×10^{-4}	9.6	9×10^{-5}
	7	38×10^{-4}	9.6	38×10^{-5}
	4	21×10^{-4}	9.6	21×10^{-5}
	1	14×10^{-4}	9.6	14×10^{-5}

[a] Three-phase system.

The extraction of chromium decreases with increasing acidity similar to the results obtained in hydrochloric acid solutions. An abrupt decrease in the value of E_a^o commences when the concentration of H_2SO_4 is increased to eight molar. Again, this drastic change in extraction can be correlated with the formation of a third phase which results in strongly acid solution. Most of the chromium that is extracted is retained in this third phase and thereby vitiates complete extraction from the aqueous phase.

The extraction of trivalent chromium is negligible except in the 12 M H_2SO_4 medium. The peculiar solubility phenomena with the formation of a third phase apparently permits the transfer of a small amount of chromium into the organic phase.

When the aqueous phase was less acidic than those described in Table VIII, the fraction of chromium that was extracted decreased rapidly, i.e., E_a^o 2.3 at pH 1.1 and 0 at pH 2.0. These results also parallel those found in chloride systems.

Effect of Concentration of Chromium

The effectiveness of TOPO as an extractant of chromium from sulfuric acid solution was determined from the extractions of various amounts of chromium in 1 M H_2SO_4. The results are presented in Table IX and Figure 2.

Table IX

Extraction of Chromium from Sulfate Solutions
Effect of Concentration of Chromium

TOPO - 5 ml, 0.1 M in cyclohexane
Equilibration time - 10 minutes
Phase ratio, aqueous/organic - 1

Chromium, mg			E_a^o
Present	Found		
	Organic	Aqueous	
6.19	5.98	0.213	28.1
9.26	7.95	0.313	25.4
10.32	9.91	0.413	24.0
12.38	11.85	0.525	22.6
14.45	13.82	0.625	22.1
16.51	15.78	0.725	21.7
18.58	17.60	0.973	18.1
20.64	19.49	1.15	16.9
25.80	23.12	2.68	8.63
30.96	25.46	5.50	4.63
36.12	26.59	9.53	2.79
41.28	25.60	15.68	1.63
49.0	26.5	22.5	1.18
98.0	26.5	71.5	0.37
147	26.0	131.0	0.22

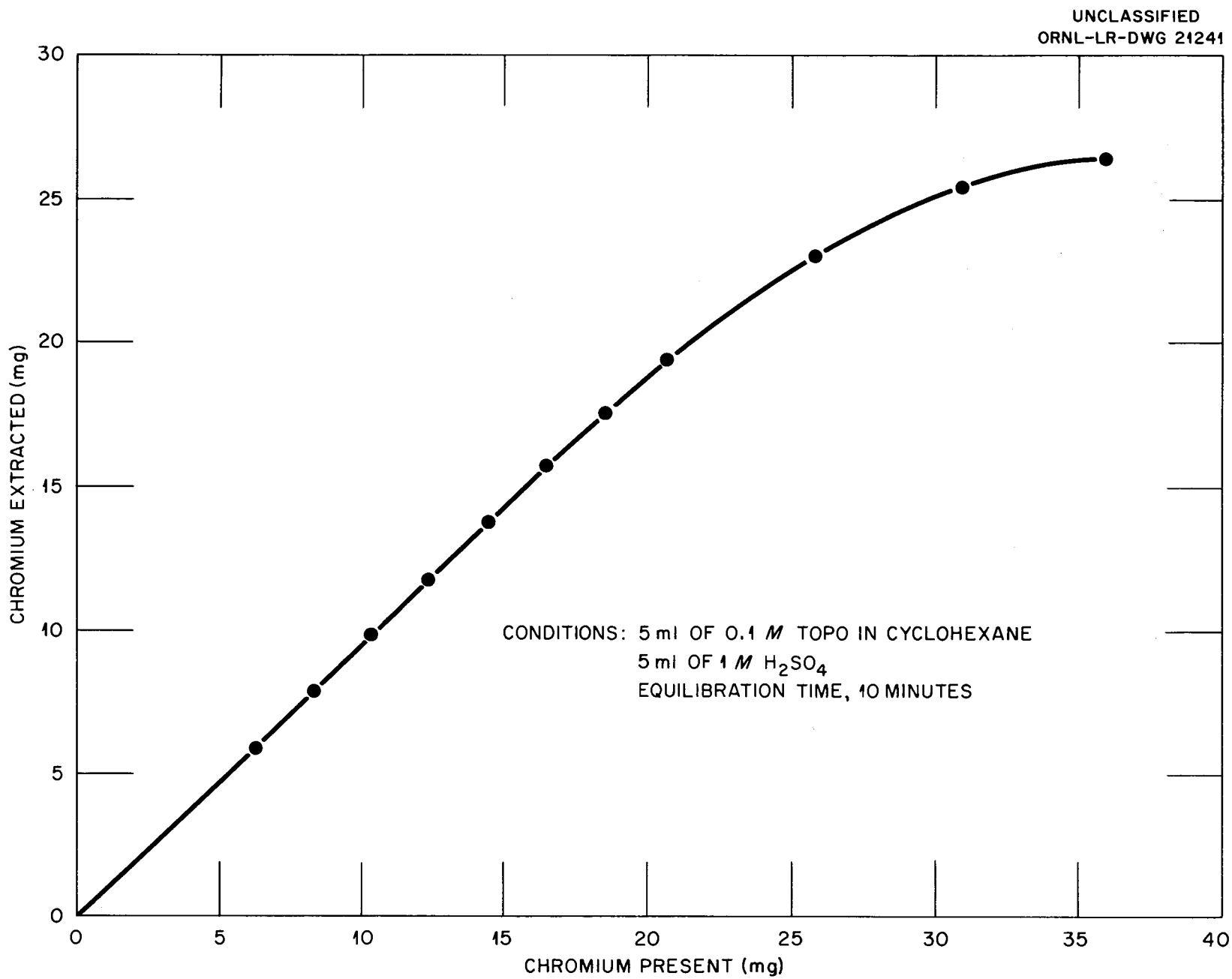

Fig. 2. Extraction of Chromium(VI) from Sulfate Solutions with Trioctylphosphine Oxide.

The results in Table IX show that chromium is not quantitatively extracted from 1 M H_2SO_4. The data reveal , however, that the extraction of as much as 20 mg of Cr^{+6} is 95 per cent complete in one equilibration. The loading capacity of 0.5 millimoles of TOPO in sulfuric acid is 26 mg of chromium. Loading is achieved when about 30 mg of chromium are present. This rather rapid loading from sulfate solutions indicates that sulfuric acid is not readily extracted by TOPO.

Effect of Concentration of Trioctylphosphine Oxide

The effect of concentration of TOPO on the extraction of chromium was investigated through a series of extractions with varying concentrations of TOPO in cyclohexane. The loading capacity of the TOPO was greatly exceeded in all cases, so that the amount of acid that might be extracted was minimized. The results of these tests are presented in Table X.

Table X

Extraction of Chromium from Sulfate Solutions
Effect of Concentration of Trioctylphosphine Oxide

Cr^{+6} - 198.3 mg
H_2SO_4 - 1 M
Equilibration time - 10 minutes
Phase ratio, aqueous/organic - 1

TOPO, M	Chromium, mg		$\frac{(TOPO)}{(Cr^{+6})}$
	Organic	Aqueous	
0.01	5.6	192.7	0.46
0.05	14.6	183.7	0.89
0.10	29.3	169.0	0.89
0.15	35.0	163.3	0.89
0.20	57.0	141.3	0.91

These data prove that the amount of chromium that is extracted is directly proportional to the concentration of TOPO. When the concentration

of extractant exceeds 0.05 M, the molar ratio of TOPO to chromium approximates unity, thus indicating the complex to be $2TOPO \cdot H_2Cr_2O_7$ except in the 0.01 M TOPO system where the ratio indicates a complex: $TOPO \cdot H_2Cr_2O_7$.

Effect of Equilibration Time

The effect of time of equilibration on the extraction of chromium in sulfate solutions was investigated over the period of one to 20 minutes. The results are shown in Table XI.

Table XI

Extraction of Chromium from Sulfate Solutions
Effect of Equilibration Time

Cr^{+6} - 10.3 mg
Cr^{+3} - 9.6 mg
H_2SO_4 - 1 M
TOPO - 5 ml, 0.1 M in cyclohexane
Phase ratio, aqueous/organic - 6/5

Chromium Oxidation State	Equilibration Time, Minutes	Chromium, mg Organic	Chromium, mg Aqueous	E_a^o
+6	1	9.8	0.5	25
	5	9.8	0.5	25
	20	9.8	0.5	25
+3	1	5×10^{-4}	9.6	5×10^{-5}
	20	7×10^{-4}	9.6	7×10^{-5}
	60	7×10^{-4}	9.6	7×10^{-5}

Variation of the time of equilibration had no effect on the extraction of chromium. Maximum extraction was attained after only one minute contact, which indicates the extreme rapidity with which equilibration is attained in sulfate solutions. Trivalent chromium is not extracted after equilibration for one hour.

Effect of Phase Ratio

The applicability of TOPO as a means of concentrating chromium, through extraction of chromium from sulfate solution, was established through a series of extractions wherein the phase ratio, aqueous/organic, was varied. The data in Table XII represent the results of these tests.

Table XII

Extraction of Chromium from Sulfate Solutions

Effect of Phase Ratio

Cr^{+6} - 10.3 mg
H_2SO_4 - 1 M
TOPO - 5 ml, 0.1 M in cyclohexane
Equilibration time - 10 minutes

V_a/V_o	Chromium Distribution, mg		E_a^o
	Organic	Aqueous	
1	10.0	0.31	32
2	9.7	0.56	34
3	9.6	0.74	38
5	8.7	1.63	21
10	7.1	3.23	22
20	5.6	4.65	24

These data, although somewhat inconsistent, indicate that the value of E_a^o is not affected by the phase volume ratio to the extent found in chloride systems.

Effect of Concentration of Sulfate

A series of extractions, in which the sulfate concentration of the aqueous phase was varied through the addition of Na_2SO_4, was carried out to investigate the effect of sulfate on the extraction of chromium. The results are shown in Table XIII.

Table XIII

Extraction of Chromium from Sulfate Solutions
Effect of Concentration of Sulfate

Cr^{+6} - 20.6 mg
H_2SO_4 - 3 M
TOPO - 5 ml, 0.1 M in cyclohexane
Equilibration time - 10 minutes
Phase ratio, aqueous/organic - 1

Na_2SO_4, M	Chromium, mg		E_a^o
	Organic	Aqueous	
0.1	19.29	1.35	14.3
0.5	19.45	1.19	16.3
1.0	19.53	1.11	17.6
2.0	19.11	1.53	12.5

These results furnish further proof that sulfate ions do not affect the extraction of chromium, through competitive complexing of TOPO, since the variations in sulfate concentration have little effect on the value of E_a^o.

EXTRACTION OF CHROMIUM FROM NITRATE SOLUTIONS

Effect of Concentration of Nitric Acid

The results that were obtained when chromium was extracted from solutions of HNO_3 into TOPO in cyclohexane are presented in Table XIV.

Table XIV

Extraction of Chromium from Nitrate Solutions
Effect of Concentration of Nitric Acid

Cr^{+6} - 10.3 mg
Cr^{+3} - 9.6 mg
TOPO - 5 ml, 0.1 M in cyclohexane
Phase ratio, aqueous/organic - 6/5
Equilibration time - 10 minutes

Chromium, Oxidation State	HNO_3, M	Chromium, mg Organic	Chromium, mg Aqueous	E_a^o
+6	10	0.6	9.7	0.1
	7	5.2	5.1	1.2
	5	5.5	4.8	1.4
	3.5	6.6	3.7	2.1
	1	8.3	1.9	4.3
+3	10	22×10^{-4}	9.6	22×10^{-5}
	7	24×10^{-4}	9.6	24×10^{-5}
	4	26×10^{-4}	9.6	26×10^{-5}
	1	27×10^{-4}	9.6	27×10^{-5}

These data show that trivalent chromium is not extracted by TOPO from nitrate solutions. The extraction of hexavalent chromium decreases with increasing acidity of the aqueous phase at a much more rapid rate than was observed in either the chloride or sulfate systems. This effect of acid concentration is attributed to partial reduction of chromium to the trivalent state in HNO_3 media. As the molarity of HNO_3 is increased, a change in color of the solution from yellow-brown to blue-green becomes more pronounced with time. In 10 M HNO_3, the aqueous phase exhibits a blue color immediately after extraction. After extraction from solutions of lower molarities, the yellow-brown color of the organic phase also changes to blue upon standing for several hours. This color change is accompanied by a shift in the maxima of the spectra of the solution from approximately 365 to much

lower wavelengths and is presumed to be the result of gradual reduction of hexavalent chromium to the trivalent state.

The decrease in extraction of chromium due to relatively high concentrations of nitric acid is apparently the result of oxidation of TOPO by the chromium-nitric acid solution. The instability of such a system precludes the use of acid concentrations higher than 1 M and, even with weakly acid media, the determination of chromium in the organic phase by spectrophotometric methods is not feasible.

Effect of Concentration of Chromium

A series of extractions, in which the concentration of chromium was varied, was performed to determine the applicability of TOPO as an extractant of chromium from nitrate solutions. The results are tabulated in Table XV and presented graphically in Figure 3.

Table XV

Extraction of Chromium from Nitrate Solutions
Effect of Concentration of Chromium

HNO_3 - 1 M
TOPO - 5 ml, 0.1 M in cyclohexane
Equilibration time - 10 minutes
Phase ratio, aqueous/organic - 1

Chromium, mg			
Present	Found		E_a^o
	Organic	Aqueous	
6.19	5.24	0.95	5.5
8.26	7.03	1.23	5.7
10.32	8.72	1.60	5.5
12.38	10.35	2.03	5.1
14.45	12.12	2.33	5.2
16.51	13.46	3.05	4.4
18.58	14.69	3.89	3.8
20.64	15.84	4.80	3.3
25.80	18.15	7.65	2.4
30.96	19.71	11.25	1.8
36.12	20.64	15.48	1.3
49.0	22.5	26.5	0.9
98.0	24.0	74.0	0.3
198.3	26.1	172.2	0.2

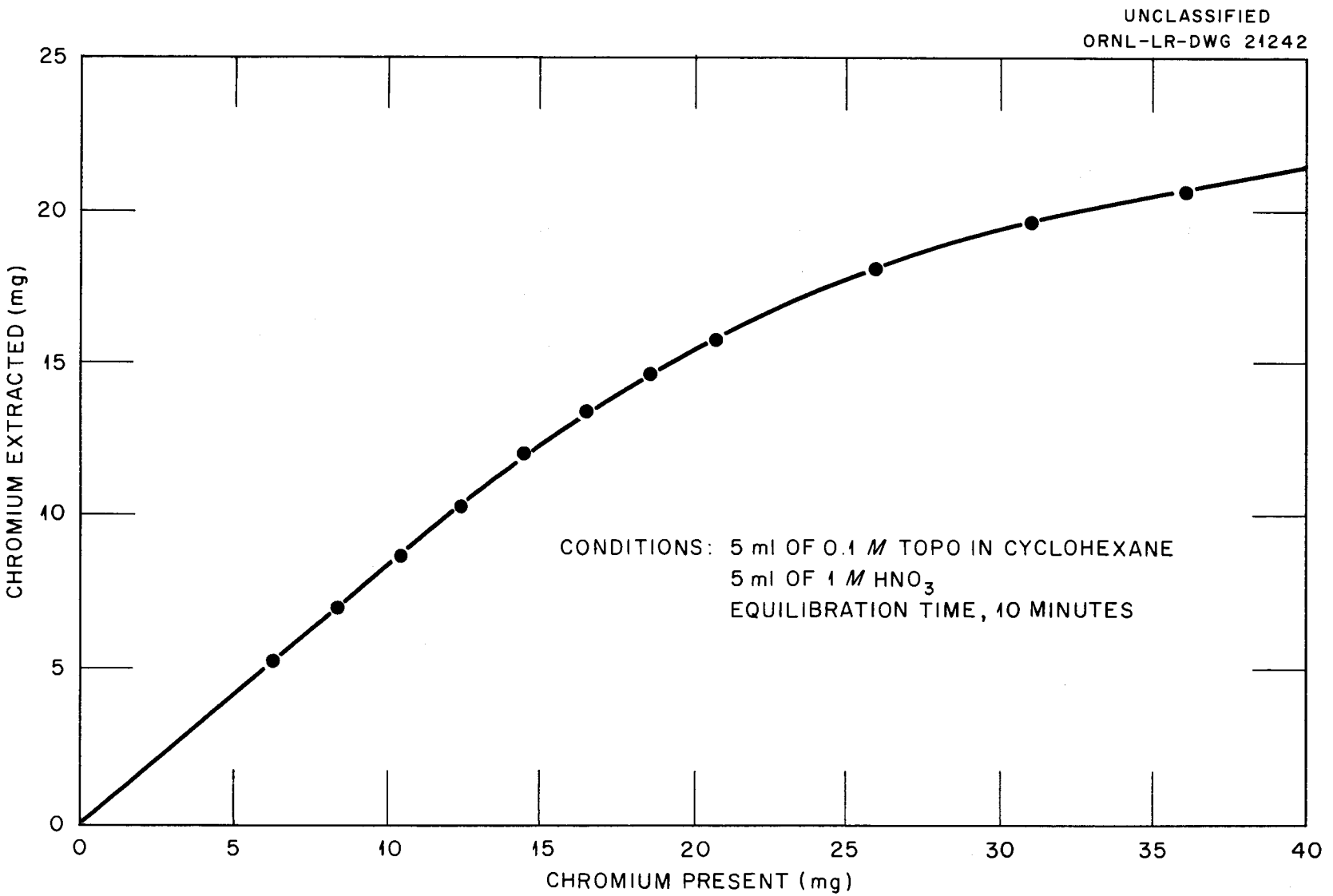

Fig. 3. Extraction of Chromium(VI) from Nitrate Solutions with Trioctylphosphine Oxide.

The data in Table XV show that quantitative extraction of chromium is not achieved. The values for E_a^o are correspondingly smaller than those found for chloride and sulfate systems, although the coefficient remains essentially constant when less than 14 mg of chromium are present. Approximately 85 per cent of the chromium is extracted. These results indicate that partial reduction of chromium may occur even in 1 M HNO_3 with subsequent retention of trivalent chromium in the aqueous phase after extraction.

The theoretical loading value, 26 mg of chromium, is attained only when approximately 200 mg is present in the system. Thus, the loading of chromium by TOPO from nitrate solutions is far less than in sulfate systems but greater than in chloride media. This trend is postulated to be indicative of the tendency of TOPO to form complexes with the mineral acids as well as with chromium.

Effect of Concentration of Trioctylphosphine Oxide

A study of the composition of the species, that is extracted from nitrate solution by TOPO, was performed through a series of extractions with various concentrations of TOPO. The results are shown in Table XVI.

Table XVI

Extraction of Chromium from Nitrate Solutions
Effect of Concentration of Trioctylphosphine Oxide

Cr^{+6} - 198.3 mg
HNO_3 - 1 M
Equilibration time - 10 minutes
Phase ratio, aqueous/organic - 1

TOPO, M	Chromium, mg Organic	Chromium, mg Aqueous	$\frac{(TOPO)}{(Cr^{+6})}$
0.01	6.1	192.2	0.43
0.05	14.8	183.5	0.88
0.10	26.1	172.2	1.00
0.15	44.8	153.5	0.87
0.20	58.5	139.8	0.89

These data are comparable to those obtained with sulfate systems and prove that the amount of chromium that is extracted is a function of the concentration of TOPO. The stoichiometry of the complex is approximately one mole of TOPO per mole of chromium or 2 TOPO·$H_2Cr_2O_7$. The much lower value of the ratio obtained with 0.01 M TOPO is thought to represent a limiting value of the stoichiometry for a large excess of chromium so that the extracted complex is TOPO·$H_2Cr_2O_7$ under this condition.

Effect of Equilibration Time

A series of extractions for varying lengths of time was carried out in an effort to elucidate the effect of HNO_3 on the extraction of chromium by TOPO as a function of time. The results are shown in Table XVII.

Table XVII

Extraction of Chromium from Nitrate Solutions
Effect of Equilibration Time

Cr^{+6} - 10.3 mg
Cr^{+3} - 9.5 mg
HNO_3 - 6 M
TOPO - 5 ml, 0.1 M in cyclohexane
Phase ratio, aqueous/organic - 6/5

Chromium, Oxidation State	Equilibration Time, Minutes	Chromium, mg		E_a^o
		Organic	Aqueous	
+6	20	5.6	4.7	1.21
	10	5.7	4.6	1.5
	5	5.5	4.8	1.4
	1	5.6	4.8	1.4
+3	20	-	9.5	-
	10	-	9.5	-
	5	0.3	9.2	0.1
	1	0.4	8.6	0.1

The extraction coefficient is obviously not time-dependent. These results indicate that the cause of the decrease in extractability of chromium in nitrate systems must occur nearly instantaneously after the extraction was begun. Only about half of the chromium is extracted from 6 M HNO_3.

Effect of Phase Ratio

The applicability of TOPO as a means of concentrating chromium through extraction from nitrate solutions was investigated with a series of extractions from 1 M HNO_3 in which the phase ratio, aqueous/organic, was varied. The results of these tests are presented in Table XVIII.

Table XVIII

Extraction of Chromium from Nitrate Solution
Effect of Phase Ratio

Cr^{+6} - 10.3 mg
HNO_3 - 1 M
TOPO - 5 ml, 0.1 M in cyclohexane
Equilibration time - 10 minutes

V_a/V_o	Chromium Distribution, mg		E_a^o
	Organic	Aqueous	
1	9.2	1.14	8
2	8.1	2.19	7
3	7.3	3.02	7
5	5.3	5.04	4
10	5.8	4.45	13
20	3.1	7.20	9

The values for E_a^o are much smaller in nitrate systems than in chloride or sulfate systems and do not vary with the ratio V_a/V_o.

Effect of Concentration of Nitrate

The effect of added nitrate ion on the extraction of chromium with TOPO in 1 M HNO_3 is illustrated by the data in Table XIX.

Table XIX

Extraction of Chromium from Nitrate Solutions
Effect of Concentration of Nitrate

Cr^{+6} - 20.6 mg
HNO_3 - 1 M
TOPO - 5 ml, 0.1 M in cyclohexane
Equilibration time - 10 minutes
Phase ratio, aqueous/organic - 1

$NaNO_3$, M	Chromium, mg		E_a^o
	Organic	Aqueous	
0.5	15.0	5.61	2.7
1.0	13.3	7.31	1.8
2.0	12.7	7.95	1.6
3.0	12.3	8.30	1.5

The addition of $NaNO_3$ to 1 M HNO_3 caused the extraction to become continuously less. This trend is compatible with the postulation that nitrate is intermediate between chloride and sulfate in ability to complex with TOPO.

EXTRACTION OF CHROMIUM FROM PHOSPHATE SOLUTIONS

Effect of Concentration of Phosphoric Acid

The extraction of chromium from phosphate solutions is revealed in Table XX. The magnitude of the extraction ratio is much less than those in HCl or H_2SO_4 and only slightly greater than that found in HNO_3 systems. The reduction of hexa- to trivalent chromium in phosphate systems also occurs.

The extraction of trivalent chromium from H_3PO_4 solutions is negligible.

Table XX

Extraction of Chromium from Phosphate Solutions
Effect of Concentration of Phosphoric Acid

Cr^{+6} - 10.3 mg
Cr^{+3} - 9.5 mg
TOPO - 5 ml, 0.1 M in cyclohexane
Equilibration time - 10 minutes
Phase ratio, aqueous/organic - 6/5

Chromium, Oxidation State	H_3PO_4, M	Chromium, mg Organic	Chromium, mg Aqueous	E_a^o
+6	12	7.8	2.5	2.7
	8	8.5	1.8	5.7
	4	7.7	2.6	3.6
	1	6.1	4.2	1.5
+3	12	0	9.5	0.1
	8	0.1	9.4	0.1
	4	0.2	9.3	0.1
	1	0.1	9.4	0.1

EXTRACTION OF CHROMIUM FROM PERCHLORATE SOLUTIONS

Effect of Concentration of Perchloric Acid

The effect of perchloric acid on the extraction of chromium is shown in Table XXI. The values for E_a^o that were obtained in 1 and 4 M $HClO_4$ systems approximated those that were obtained with H_3PO_4. An effect previously not observed was noted when the concentration of $HClO_4$ was increased to 7 M or greater. The chromium was rapidly precipitated in these solutions as an orange-red solid that was presumed to be chromium trioxide. When the mixtures that contained CrO_3 were equilibrated with five ml of 0.1 M TOPO in cyclohexane, chromium reported to a third, intermediate phase, and the other two phases were colorless. No determination of chromium in aqueous phase was performed, although there was evidently little or no chromium remaining in this phase. Again, trivalent chromium was not extracted.

Table XXI

Extraction of Chromium from Perchlorate Solutions
Effect of Concentration of Perchloric Acid

Cr^{+6} - 10.3 mg
Cr^{+3} - 9.6 mg
TOPO - 5 ml, 0.1 M in cyclohexane
Equilibration time - 10 minutes
Phase ratio, aqueous/organic - 1

Chromium, Oxidation State	$HClO_4$, M	Chromium, mg Organic	Chromium, mg Aqueous	E_a^o
+6	10	-	(a)	-
	7	-	(a)	-
	4	9.0	1.3	6.9
	1	8.8	1.5	5.9
+3	10	10×10^{-4}	9.6	10×10^{-5}
	7	10×10^{-4}	9.6	10×10^{-5}
	4	14×10^{-4}	9.6	14×10^{-5}
	1	15×10^{-4}	9.6	15×10^{-5}

(a) Chromium precipitated.

EFFECT OF SOLVENT

In their study on the extraction of uranium with TOPO, Blake et al[1] found that the extraction coefficient was affected by the polarity of the solvent in which the TOPO was dissolved: the more polar the solvent, the lower the extraction coefficient. They concluded that the best diluents were aromatic and kerosene-range aliphatic hydrocarbons. Other workers[2] found similar effects for extraction of uranium with tributylphosphate (TBP) and postulated that highly polar diluents depress the electronegativity of the phosphorus atom, and thus diminish the possibility of formation of coordinate bonds between the phosphorus atom of an organophosphorus extractant and metal ions.

As a consequence of these observations, extractions of chromium were made with TOPO dissolved in carbon tetrachloride and also in nitrobenzene. The latter is an example of a highly polar solvent, its dielectric constant being 34.8. The results were rather striking in that the extraction coefficients of chromium by TOPO in nitrobenzene were higher in both 1 M HCl and 1 M H_2SO_4 solutions than for TOPO dissolved in cyclohexane. The extraction coefficient for chromium in 1 M HCl by TOPO in carbon tetrachloride solution was significantly lower than for TOPO in cyclohexane. There was little difference in extraction from 1 M H_2SO_4.

It is obvious that the polarity of the solvent is not an important factor in the extraction of chromium with TOPO. These results would indicate that the extraction of chromium and uranium proceed by different mechanisms. A summary of the effect of solvent on the extraction of chromium is shown in Table XXII.

Table XXII

Extraction of Chromium from Acidic Solutions
Effect of Solvent

Cr^{+6} - 10.3 mg
Acid - 5 ml of 1 M
Phase ratio, aqueous/organic - 1
Equilibration time - 10 minutes
TOPO - 0.1 M

Solvent	Dielectric Constant at 25° C	Acid	E^o_a
Cyclohexane	2.015	HCl	102
		H_2SO_4	17
		HNO_3	4.3
Carbon Tetrachloride	2.298	HCl	18
		H_2SO_4	11
		HNO_3	4.2
Nitrobenzene	34.82	HCl	1140
		H_2SO_4	280

SUMMARY

Extraction of Chromium from Chloride Solutions

The extraction of hexavalent chromium from chloride solutions is quantitative over a wide range of hydrochloric acid concentrations from 1 to 7 M HCl. In 10 M HCl, approximately 45 per cent of the chromium is extracted in a single pass. At concentrations less acidic than one molar, the extraction is markedly decreased. Under no acid concentration tested was trivalent chromium extracted.

The loading capacity of 0.5 millimole of TOPO is approximately 21 mg of chromium from 1 M HCl. Quantitative separation of at least 10 mg is possible from 1 M HCl in a single equilibration.

The molar combining ratio of TOPO to chromium $\frac{(TOPO)}{(Cr^{+6})}$ is 1.2 for a range of 0.05 to 0.2 M TOPO. For 0.01 M TOPO the ratio is less than unity. Under these conditions in which the loading capacity of the TOPO is far exceeded, the extracted species is $H_2Cr_2O_7 \cdot 2TOPO$.

Equilibration is reached extremely rapidly; quantitative extraction of chromium is achieved in one minute from 1 M HCl. The possible slow formation of an extractable species of trivalent chromium is not indicated even after 60 minutes contact time between phases.

Approximately 90 per cent of the chromium is extracted from 1 M HCl at a phase ratio of V_a/V_o as large as 20.

The addition of sodium chloride to a 1 M HCl solution retards the extraction of chromium. Only 70 per cent of chromium is extracted when the solution is 1 M HCl and 0.1 to 2 M NaCl.

Tri-n-octylphosphine oxide extracts hydrochloric acid as well as hexavalent chromium. However, the extraction affinity for hexavalent chromium is much more pronounced. For example, in 2 M HCl, the ratio of HCl to TOPO in the organic phase is 0.1. When 20 mg of chromium are present in the 2 M HCl, equivalent to approximately the loading capacity, no chloride is extracted. As the HCl concentration is increased, the amount of chloride extracted increases. The molar combining ratio of $H_2Cr_2O_7$ to TOPO is 0.3 in all cases, however.

Extraction of Chromium from Sulfate Solutions

The extraction of chromium from sulfate solutions is approximately 97 per cent complete from 1 to 4 M H_2SO_4. Extraction decreases markedly with increasing H_2SO_4 concentration. In less acidic systems, extraction decreases sharply when the system is less than 1 M H_2SO_4.

The loading capacity of 0.5 millimole in 1 M H_2SO_4 is about 26 mg of chromium. Nearly 20 mg are extracted to approximately 95 per cent in a single equilibration, however. The rate with which loading is reached is such that little sulfuric acid is being extracted simultaneously.

The molar combining ratio of TOPO to chromium in 1 M H_2SO_4 for TOPO concentration exceeding 0.05 M is unity, which indicates the extracted species to be $H_2Cr_2O_7 \cdot 2TOPO$.

Equilibrium is attained within one minute. Trivalent chromium was not extracted even when the phases were in contact for as long as 60 minutes.

At phase ratios, V_a/V_o, less than three, quantitative extraction is achieved in a single pass in 1 M H_2SO_4. At $V_a/V_o = 20$, extraction is 56 per cent complete.

Addition of sulfate as sodium sulfate has little beneficial effect on the extraction of chromium from 1 M H_2SO_4.

Extraction of Chromium from Nitrate Solutions

The extraction of chromium from nitrate solutions is incomplete at all acid concentrations tested. Increasing nitric acid concentration further retards extraction. This vitiation is probably the result of reduction of chromium in the strong acid solutions. Trivalent chromium is not extracted from nitrate solutions.

The theoretical loading value of 0.5 millimole of TOPO is 26 mg of chromium. However, an excess of 200 mg must be present which indicates the slow rate with which loading is achieved.

The composition of the extracted species is $H_2Cr_2O_7 \cdot 2TOPO$ when the concentration of TOPO exceeds 0.01 M.

Equilibration is reached rapidly in nitrate solution. Essentially the same extraction coefficient is found after one minute as that after 20 minutes of contact.

The addition of nitrate as sodium nitrate has little effect on the extraction of chromium.

Extraction of Chromium from Phosphate and Perchlorate Solutions

The extraction of chromium from phosphate and perchlorate solutions is not complete. Under the optimum conditions, approximately 80 to 90 per cent is extracted in a single equilibration.

Effect of Solvent for Tri-n-octylphosphine Oxide

The polarity of the solvent for TOPO apparently has no effect on the extraction of chromium. Essentially the same coefficients were obtained for cyclohexane, carbon tetrachloride, and nitrobenzene solutions of TOPO.

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APPENDIX

ABSORPTION SPECTRA OF TRI-N-OCTYLPHOSPHINE OXIDE-CYCLOHEXANE EXTRACTS OF CHROMIUM

The absorption spectra of the organic phase from the extraction of chromium from both hydrochloric and sulfuric acid solutions is shown in Figure 4. The spectra of a 1 M H_2SO_4 solution of potassium dichromate is included for comparative purposes.

The spectra of the TOPO extract is not affected by the acidic medium from which the extraction was made. The spectra is identical whether the extraction is made from sulfuric or hydrochloric acid solutions, which substantiates the postulation that $H_2Cr_2O_7$ is the species being extracted. Furthermore, there is little significant difference in the spectra of the TOPO extract and that of the dichromate-sulfuric acid solution. Three distinct maxima are noted in the spectra of the TOPO extract between 350 and 375 mμ in contrast to the single broad absorption peak at 350 mμ in the aqueous dichromate spectra.

Another absorption peak was found in the ultraviolet region at 285 mμ. The molar absorbance index at this wavelength is about 1800. Since Beer's law relationship is followed at this wavelength, a direct determination of chromium in the TOPO extract is feasible. Cyclohexane must be used as the solvent for TOPO since it does not absorb at this wavelength.

Investigation of the analytical possibilities of the 285 mμ absorption peak will be the subject of a future report.

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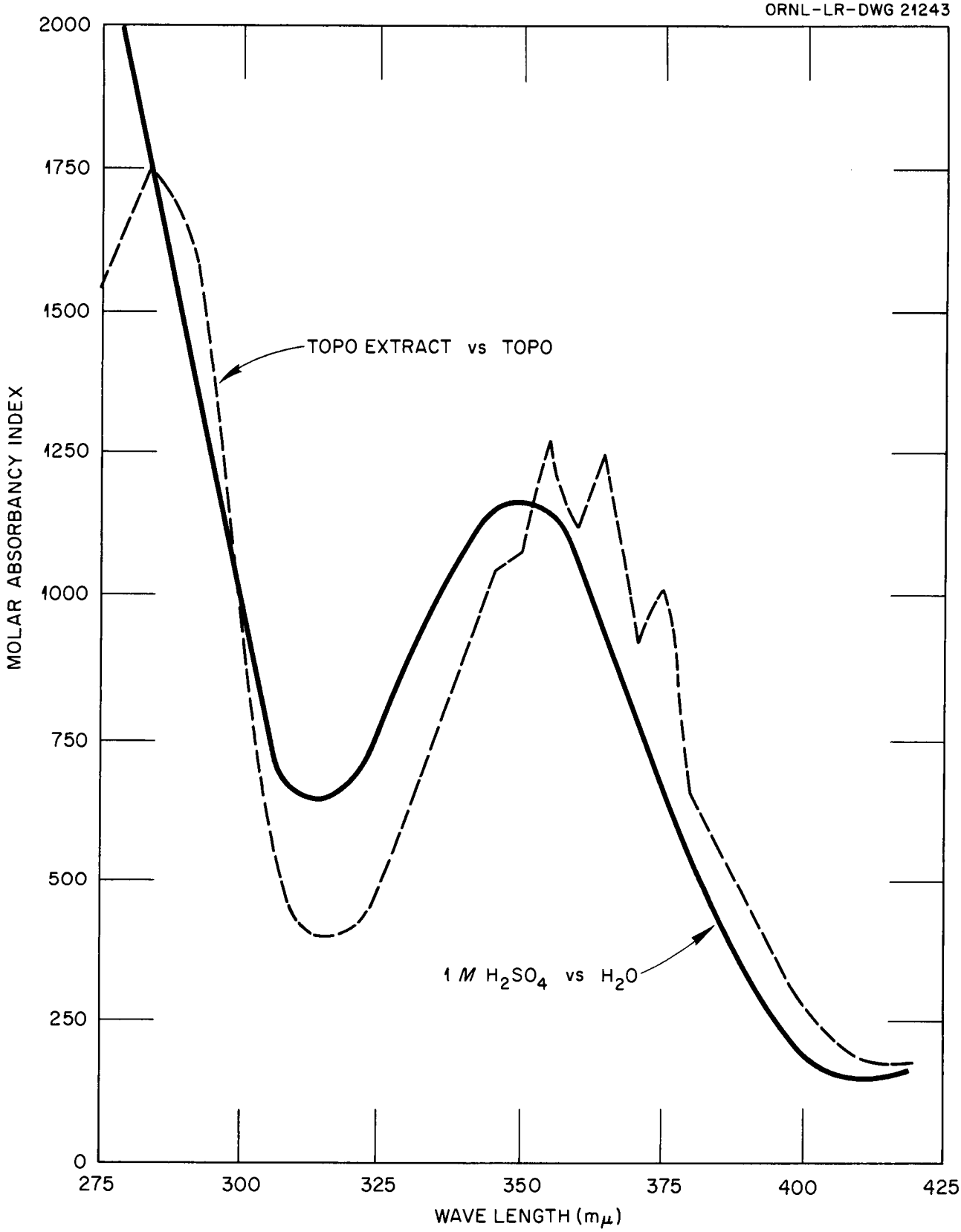

Fig. 4. Spectra of Chromium(VI) Solutions