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Progress Report on Uranium Recovery from Wet-Process Phosphoric Acid with Octylphenyl Acid Phosphate

W. D. Arnold
D. R. McKamey
C. F. Saes

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CHEMISTRY DIVISION

PROGRESS REPORT ON URANIUM RECOVERY FROM WET-PROCESS
PHOSPHORIC ACID WITH OCTYLPHENYL ACID PHOSPHATE

W. D. Arnold
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ABSTRACT

Studies were continued to complete development of a process for recovering uranium from wet-process phosphoric acid with octylphenyl acid phosphate (OPAP), a mixture of mono- and dioctylphenyl phosphoric acids. The mixture was found to contain at least nine impurities, the principal one being octyl phenol. It also contained material that readily hydrolyzed to octyl phenol and orthophosphoric acid. The same impurities were present in all the OPAP batches examined, although the relative amounts varied. The combination of mono- and dioctylphenyl phosphoric acids was the principal uranium extractant in the OPAP mixture, but some of the impurities also extracted uranium. Hydrolysis of the extractant had little effect on uranium extraction, as did the presence of moderate concentrations of octyl phenol and trioctylphenyl phosphate. Diluent choice among refined kerosenes, naphthenic mixtures, and paraffinic hydrocarbons also had little effect on uranium extraction, but extraction was much lower when an aromatic diluent was used. Purified OPAP fractions were sparingly soluble in aliphatic hydrocarbon diluents. The solubility was increased by the presence of impurities such as octyl phenol, and by the addition of water or an acidic solution to the extractant-diluent mixture.

In continuous stability tests, extractant loss by distribution to the aqueous phase was much less to wet-process phosphoric acid than to reagent grade acid. Uranium recovery from wet-process acid decreased steadily because of the combined effects of extractant poisoning and precipitation of the extractant as a complex with ferric iron. Unaccountable losses of organic phase volume occurred in the continuous tests. While attempts to recover the lost organic phase were unsuccessful, the test results indicate it was not lost by entrainment or dissolution in the phosphoric acid solutions.

1. INTRODUCTION

Phosphate rock deposits represent one of the nation's largest known uranium resources. Published estimates of the U_3O_8 contained in these deposits range from 600,000 tons to 1,000,000 tons.¹⁻³ Most of the uranium dissolves and becomes available for recovery as a by-product when phosphate rock is acidulated to produce wet-process phosphoric acid, an intermediate in fertilizer manufacture. Recent trends toward the use of higher-analysis fertilizers have resulted in greatly increased production of wet-process phosphoric acid. Production in 1975 was about 6.8 million tons (as P_2O_5), and current production capacity is more than 9 million tons.⁴ Although the uranium concentration in wet-process acid is only 0.1 to 0.2 g/liter, the large tonnages of acid produced represent a significant amount of uranium that is available for recovery. For example, the acid produced in 1976 contained an estimated 3000 tons of U_3O_8 and this amount is projected to increase to about 8000 tons per year by the end of the century.⁵ This uranium, which is equivalent to about 15% of the present annual domestic production from sandstone ores, can be recovered without any additional mining, leaching, or tailings disposal.

Two processes have been developed at ORNL to recover uranium from wet-process phosphoric acid. These are the DEPA-TOPO process,⁶⁻⁸ which uses a mixture of di(2-ethylhexyl) phosphoric acid and trioctylphosphine oxide as the extractant, and the OPAP process,⁷⁻⁹ which uses octylphenyl acid phosphate, a mixture of mono- and dioctylphenyl phosphoric acids.

The DEPA-TOPO process is a two-cycle process. In the first or concentration cycle, hexavalent uranium is extracted from the acid and then stripped from the extract with phosphoric acid containing a reductant, concentrating the uranium by a factor of 50 or more. The second or purification cycle consists of oxidizing the uranium in the first cycle strip solution followed by uranium extraction with the DEPA-TOPO reagent, scrubbing with water, and stripping-precipitation with ammonium carbonate. The ammonium uranyl tricarbonate product can be calcined to U_3O_8 and fed directly to a uranium refinery for conversion to UF_6 . This process has

been successfully tested at pilot scale and full-size plants based on it are presently in the early stages of commercial operation.

The OPAP process offers several potential advantages for alternative use in the first cycle. This reagent extracts U^{4+} , which is the prevailing uranium valence in freshly-produced phosphoric acid, and oxidation of the uranium before recovery is not required. Uranium is stripped from the OPAP extract with phosphoric acid containing an oxidant to produce a feed solution that does not require oxidation before processing in the second cycle with DEPA-TOPO. OPAP is a stronger uranium extractant than DEPA-TOPO, allowing the use of lower extractant concentration and/or fewer extraction stages; it is less expensive by about a factor of three at the concentrations needed for process use and is commercially available in large quantities.

This report describes recent progress in a program that is underway at ORNL to complete development of the OPAP process. Emphasis in the program is on separating and identifying the components of the OPAP mixture and determining their role in the behavior of the extractant, and on measuring the long-term stability and extraction performance of the extractant.

We wish to thank Faith I. Case for assistance in some of the continuous tests and F. J. Hurst for helpful comments and suggestions. The OPAP samples were provided by Mobil Chemical Company, and diluent samples were provided by American Mineral Spirits Company, Exxon Company, Humble Oil and Refining Company, Kerr-McGee Solvent and Refining Company, and Mobil Oil Company. Uranium and iron analyses were made by members of the ORNL Analytical Chemistry Division under the direction of L. J. Brady and R. R. Rickard.

2. DESCRIPTION OF OPAP

2.1 Structure and Composition

Octylphenyl acid phosphate is a commercially available* mixture of mono-octylphenyl phosphoric acid (MOPPA) and dioctylphenyl phosphoric

* Mobil Chemical Company, Richmond, Virginia

acid (DOPPA). The commercial material, an approximately equimolar mixture of the two esters, is prepared by reacting p-octyl phenol with phosphorous pentoxide (Fig. 1). The octyl group is 1,1,3,3-tetramethylbutyl. Formula weights are 286.31 for MOPPA and 474.63 for DOPPA.

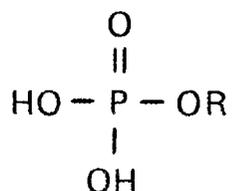
The composition of commercial OPAP varies considerably, as shown by titrations of the 23 samples listed in Table 1. These samples were produced over a span of at least 10 years. Batch A is the material that was used in earlier development studies at ORNL and was produced in 1967. The production dates of batches B through G are unknown. Batches H, I, and J were produced in 1975-76, and batches K-W were produced in 1977. As described below, commercial OPAP contains readily-hydrolyzable acidic impurities that interfere with the MOPPA-DOPPA assay. The compositions in Table 1 are therefore reported as apparent concentrations of MOPPA and DOPPA. The apparent MOPPA concentration ranged from 32 to 44 wt % and the apparent DOPPA concentration ranged from 53 to 75%; the MOPPA/DOPPA mole ratio ranged from 0.7/1 to 1.3/1. The samples also contained small concentrations (0.2 to 0.6%) of orthophosphoric acid and up to 5% of nonacidic impurities.

The assays were made by titration of weighed samples in an acetone-water medium with standard NaOH. The titration curves were characterized by two breaks, the first (pH 6 to 7) indicating neutralization of the DOPPA and the strongly acidic hydrogen of the MOPPA, and the second (pH about 11) indicating neutralization of the weakly acidic hydrogen of the MOPPA. Orthophosphoric acid concentrations were measured by adding silver nitrate to the sample at the middle of the second end-point and titrating the liberated HNO_3 as the third end-point. The concentrations of nonacidic impurities were obtained by difference. In many of the samples, the sum of the apparent MOPPA and DOPPA concentrations is greater than 100%. This is due to the presence of acidic impurities that have lower equivalent weights than MOPPA and DOPPA.

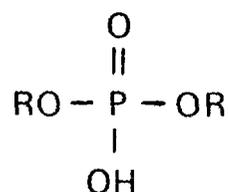
2.2 Identification of Impurities

Zangen, et al, found that the pyrophosphoric acid esters studied in the 1950's and 1960's as extractants for uranium from phosphoric acid

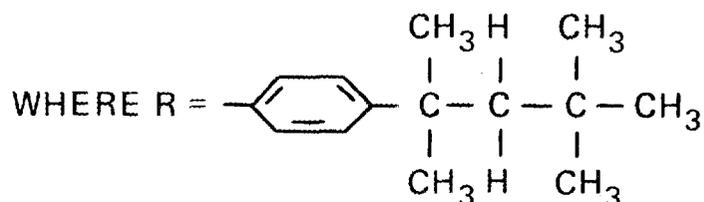
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MONOOCTYLPHENYL
PHOSPHORIC ACID
(MOPPA)



DIOCTYLPHENYL
PHOSPHORIC ACID
(DOPPA)



OCTYLPHENYL ACID PHOSPHATE IS AN APPROXIMATELY
EQUIMOLAR MIXTURE OF MOPPA AND DOPPA PREPARED
BY REACTING OCTYL PHENOL WITH P_2O_5 :

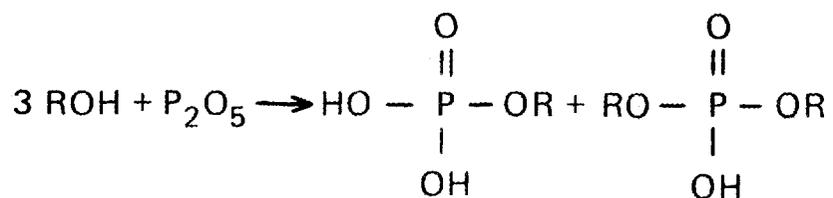


Fig. 1. Structure and preparation of octylphenyl acid phosphate.

Table 1. Titration of OPAP samples

Procedure: 0.1 g samples of as-received OPAP were dissolved in 50 ml acetone + 25 ml H₂O and titrated with 0.1 N NaOH

Batch	Year produced	Apparent concentration (wt %)				MOPPA DOPPA mole ratio
		MOPPA	DOPPA	H ₃ PO ₄	Other ^a	
A	1967	43.4	54.8	0.4	1.4	1.3
B	—	42.7	58.8	<i>b</i>	—	1.2
C	—	42.0	61.4	<i>b</i>	—	1.1
D	—	44.3	55.6	<i>b</i>	0.1	1.3
E	—	42.6	52.9	<i>b</i>	4.5	1.3
F	—	41.6	60.0	<i>b</i>	—	1.2
G	—	37.6	67.8	<i>b</i>	—	0.9
H	1975	34.3	65.0	0.6	0.1	0.9
I	1976	32.6	64.8	0.2	2.4	0.8
J	1976	32.3	67.5	0.4	—	0.8
K	1977	34.2	69.2	<i>b</i>	—	0.8
L	1977	34.1	69.4	<i>b</i>	—	0.8
M	1977	33.7	75.2	<i>b</i>	—	0.7
N	1977	33.0	63.9	<i>b</i>	3.1	0.9
O	1977	36.7	60.0	<i>b</i>	3.3	1.0
P	1977	34.4	62.0	<i>b</i>	3.6	0.9
Q	1977	35.4	63.8	<i>b</i>	0.8	0.9
R	1977	33.8	64.2	<i>b</i>	2.0	0.9
S	1977	37.7	57.0	<i>b</i>	5.3	1.1
T	1977	35.4	61.9	<i>b</i>	2.7	1.0
U	1977	33.6	67.9	<i>b</i>	—	0.8
V	1977	37.3	59.0	<i>b</i>	3.7	1.0
W	1977	34.1	62.5	<i>b</i>	3.4	0.9

^aBy difference

^bH₃PO₄ not determined; any present in the samples would be reported as MOPPA

are complex mixtures of organophosphorous esters. Since the OPAP preparation is basically the same, the reaction of a phenol or alcohol with phosphorous pentoxide, it is subject to the same chances for incomplete or side reactions that produce other than the desired products. Our liquid chromatographic analyses show that MOPPA and DOPPA are the major constituents of OPAP but that the mixture contains at least 11 components (Fig. 2).

Two columns are used in the analysis, with detection at 275 nm. Nonacidic and weakly acidic materials elute with absolute methanol from strong base anion exchange resin, while more strongly acidic materials are retained. Five peaks are separated with this column, and the identity of four of them is known. Peak A is trioctylphenyl phosphate, peak B is an impurity in commercial octyl phenol that carries through the OPAP preparation, peak C is octyl phenol, and peak E is phenol. Eight peaks are separated by a column containing silica coated with C₁₈-hydrocarbon (ODS column) and elution with a 25% H₂O-methanol mixture containing tetrabutyl ammonium phosphate. The identity of only three of the eight peaks is presently known; peak 2 is MOPPA, peak 5 is octyl phenol, and peak 8 is DOPPA. No other peaks elute at longer times. Compounds such as trioctylphenyl phosphate and the octyl phenol impurity are retained. Octyl phenol is the only material that we are certain is separated by both columns, although peaks D and 3 may be the same. We have found the same materials, with some variations in the relative amounts, in all of the OPAP batches we have analyzed by this technique. The chromatograms in Figure 2 are for Batch I, which was used in most of our tests.

2.3 Effect of Hydrolysis

Commercial OPAP contains a significant amount of readily-hydrolyzable acidic material. Figure 3 shows the results of tests in which OPAP batch I was hydrolyzed five successive times by gently refluxing with water. Titrations of the OPAP show a decrease in the apparent concentrations of both MOPPA and DOPPA in the initial hydrolysis treatments. The MOPPA concentration decreased slightly in subsequent treatments, indicating additional hydrolysis and/or solubility in the aqueous phase,

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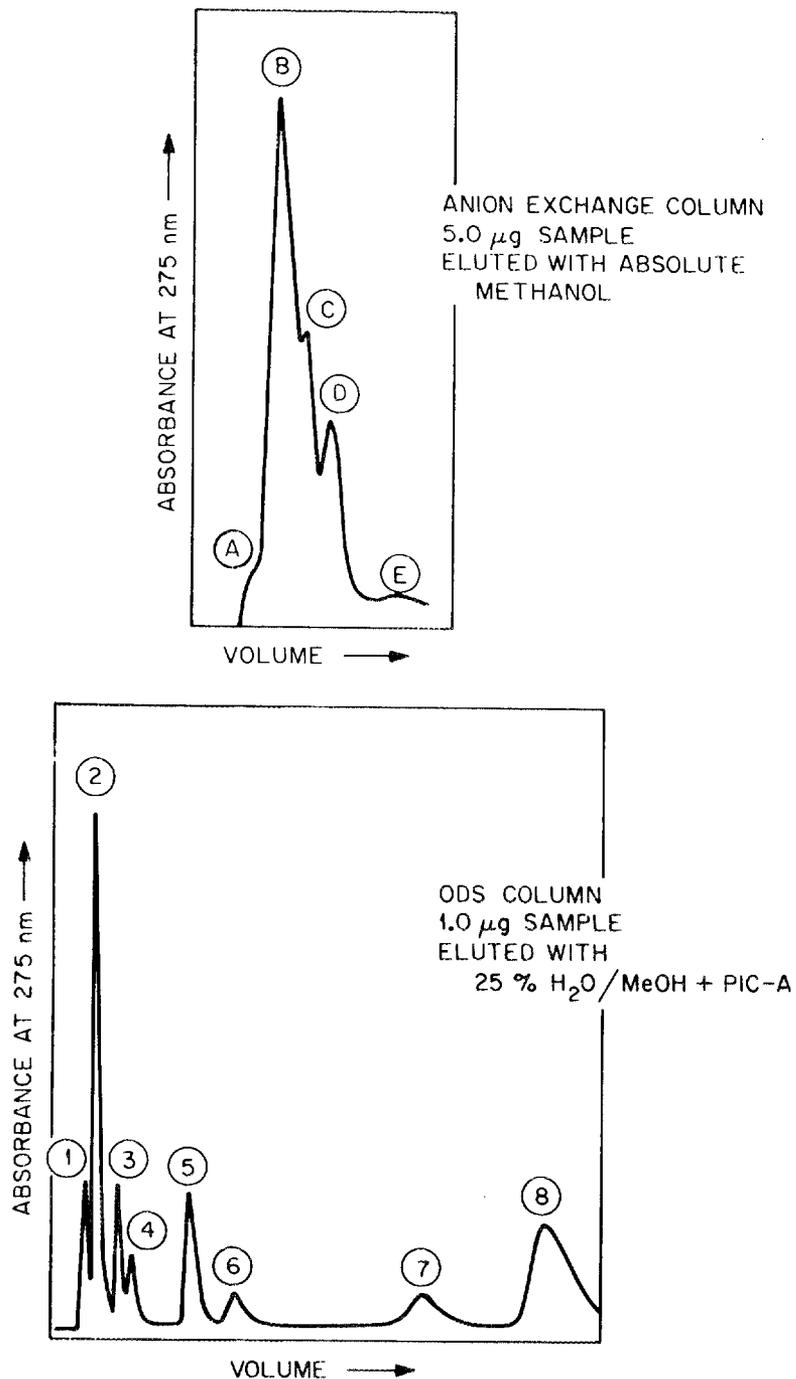
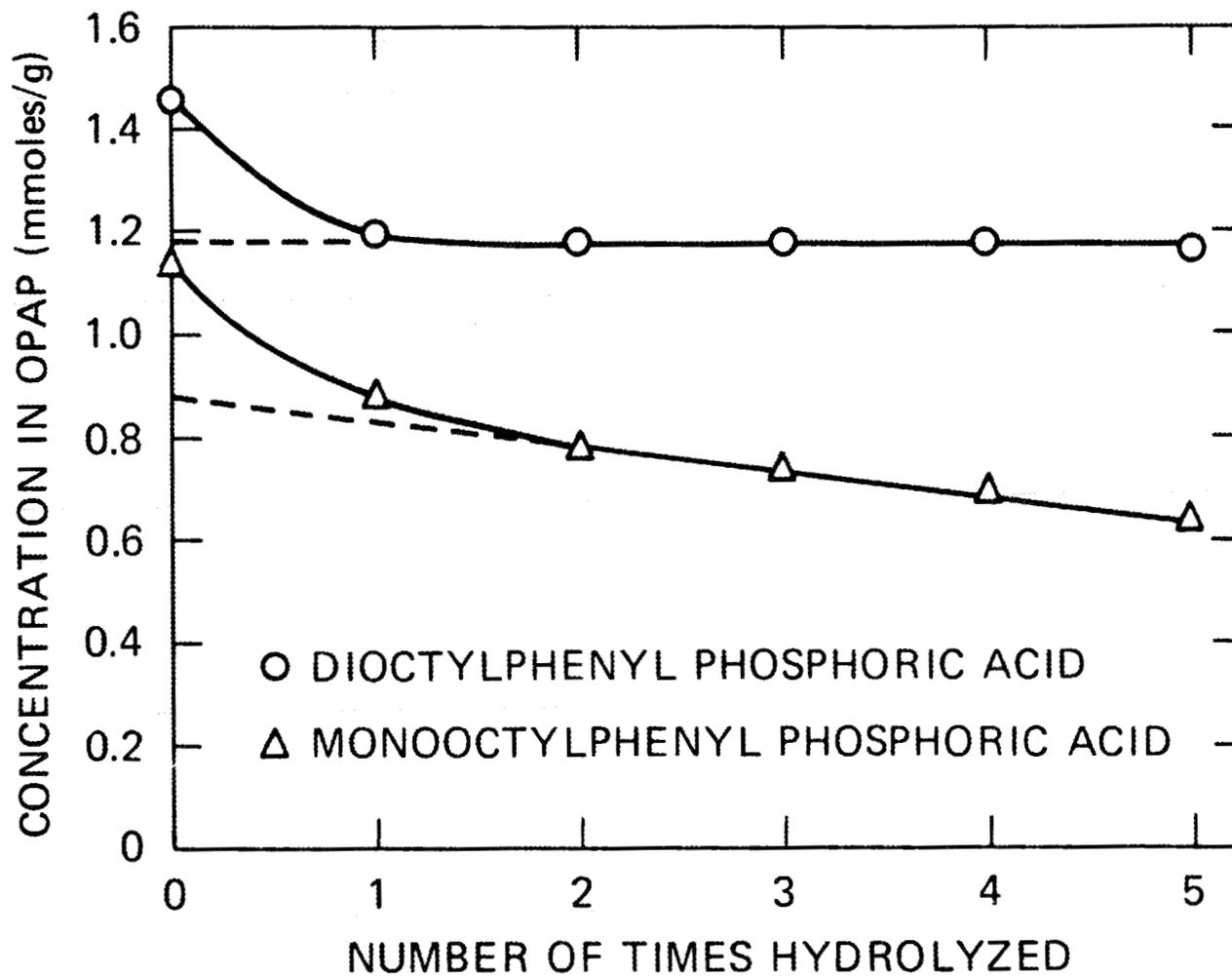


Fig. 2. Liquid chromatographic analysis of OPAP. Identification of peaks: A trioctylphenyl phosphate, B octyl phenol impurity, C octyl phenol, D unknown, E phenol; 1 unknown, 2 MOPPA, 3 unknown, 4 unknown, 5 octyl phenol, 6 unknown, 7 unknown, 8 DOPPA.



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Fig. 3. Effect of hydrolysis on OPAP composition-titrations. OPAP batch I was hydrolyzed 5 times by gentle reflux for 20 hr with 1 ml H₂O/g OPAP. Samples of the hydrolyzed OPAP were titrated.

but the DOPPA concentration did not change. The difference between the apparent initial concentration and the intercept of the straight portion of the lines represents decomposition of readily-hydrolyzable acidic material. It amounts to 24% of the apparent initial MOPPA concentration and 19% of the apparent initial DOPPA concentration. Other batches subjected to the same treatment lost somewhat smaller amounts of readily-hydrolyzable material:

OPAP batch	Apparent initial loss on hydrolysis (%)	
	MOPPA	DOPPA
A	20	0
I	24	19
M	26	10
P	7	7
S	10	0

Chromatograms of the hydrolyzed samples of Batch I (Fig. 4) show that the peak 1 and the MOPPA concentrations decreased and that the peak 3 and the octyl phenol concentrations increased. Peak D with the anion exchange column increased the same way as peak 3, which indicates they may represent the same material. Orthophosphoric acid was the major product that formed in the aqueous samples, which also contained lower concentrations of MOPPA.

On the basis of these results, a process extractant would contain higher concentrations of octyl phenol and the unidentified material represented by peak 3 than would be indicated by analysis of the starting material. We would expect the readily-hydrolyzable material to decompose in plant use, but later results (Sect. 4.1) show that hydrolysis of the major OPAP components does not occur with phosphoric acid.

3. PROPERTIES OF OPAP

The uranium extraction properties of OPAP and its solubility in organic diluents were studied in a series of batch tests.

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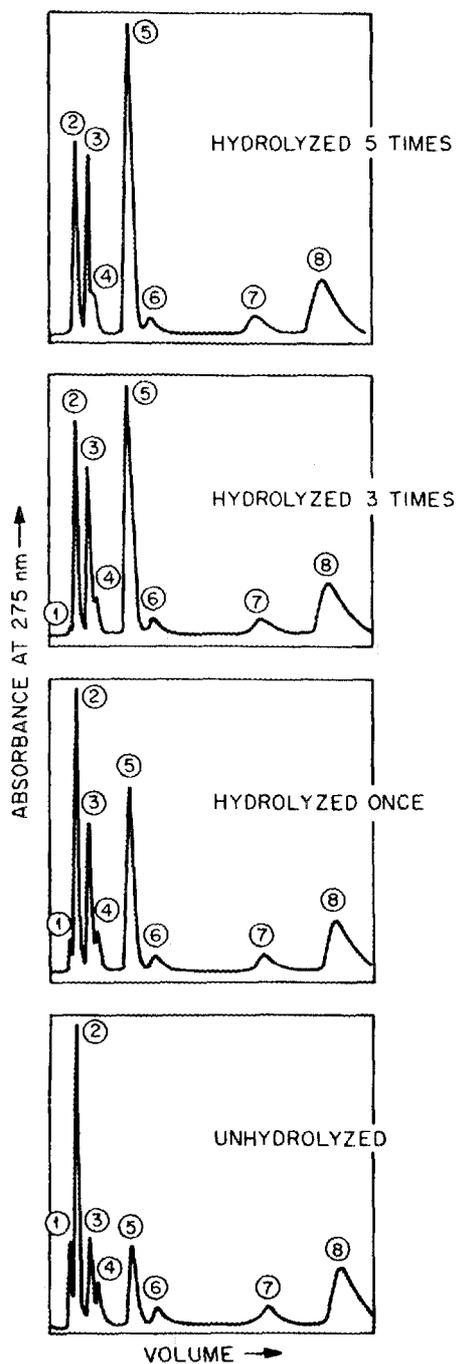


Fig. 4. Effect of hydrolysis on OPAP composition-liquid chromatographic analysis. OPAP batch I was hydrolyzed 5 times by gentle reflux for 20 hr with 1 ml H₂O/g OPAP. Samples of the hydrolyzed OPAP were dissolved in 25% H₂O-methanol and analyzed with the ODS column. Identification of peaks: 1 unknown, 2 MOPPA, 3 unknown, 4 unknown, 5 octyl phenol, 6 unknown, 7 unknown, 8 DOPPA.

3.1 Uranium Extraction

3.1.1 Screening Tests

Uranium extraction with the OPAP batches was compared in standardized batch extraction tests. The tests were all made with a sample of wet-process acid that was set aside for this purpose. It was 5.8 M in H_3PO_4 and contained 0.12 grams of uranium and 8.6 grams of ferric iron per liter. Before the extraction tests, the uranium valence in the phosphoric acid was reduced to +4 by dissolving 1 gram per liter of iron metal in the acid. The emf of the solution dropped from +520 mv to +230 mv.* The organic solutions were 0.20 M OPAP dissolved in a hydrocarbon diluent, Amsco 450 in most cases. Unhydrolyzed OPAP was used, with purified (>99.5%, purified as described in Appendix A) MOPPA or DOPPA added to adjust the apparent concentration of each major component to 0.10 M. Equal volumes of the reduced acid and the organic solutions were equilibrated for 10 minutes at room temperature with a wrist-action shaker. Extraction coefficients were calculated as the ratio of the uranium concentrations in the organic and aqueous phases at equilibrium.

As shown in Table 2, the most recent OPAP batches (1977) gave higher uranium extraction coefficients than the earlier batches. The reason for this is not evident; we did not measure significant differences in the composition of these samples by titrations or liquid chromatographic analyses. Extraction with purified MOPPA and DOPPA fractions was higher than with the commercial OPAP batches produced before 1977. There was little difference in uranium extraction when the purified MOPPA-DOPPA fractions were dissolved in either of three refined kerosene diluents. With commercial batch A, extraction was much lower with an aromatic diluent (Solvesso 100) than with an aliphatic diluent.

3.1.2 Effect of diluent

The diluent can have an important effect on uranium extraction, as illustrated by the above results with Amsco 450 and Solvesso 100. The

* Measured with a 2 M KCl-Ag/AgCl electrode

Table 2. Uranium extraction with OPAP

Organic: 0.20 M unhydrolyzed OPAP (0.10 M MOPPA + 0.10 M DOPPA) in indicated diluent

Aqueous: wet-process green acid, 5.8 M H_3PO_4 , 0.12 g U/liter, 8.6 g Fe^{3+} /liter

Contact: 10 minutes at organic/aqueous phase ratio of 1, temperature $\approx 23^\circ\text{C}$

OPAP batch	Diluent	Uranium extraction coefficient, E_a^0
Purified fractions	Amsco 450	12.2
	Kermac 470B	12.0
	Exxon LOPS	13.0
A	Amsco 450	9.3
C		7.5
D		8.6
E		8.0
F		8.6
G		8.2
H		Amsco 450
I	9.5	
J	9.0	
K	Amsco 450	14.5
L		11.7
M		15.3
N		15.3
P		17.1
Q		15.5
R		14.4
S		17.7
T		18.6
U		15.9
V	16.7	
W	15.0	
A	Solvesso 100	3.2

effect of diluent structure was studied with a series of commercial and laboratory diluents. The OPAP used in this test was Batch I that had been hydrolyzed once with water. The 0.2 M solutions (0.087 M MOPPA plus 0.117 M DOPPA) were prepared in the various diluents and equilibrated at room temperature with the wet-process acid at an organic/aqueous phase ratio of 1. With the paraffinic diluents, uranium extraction decreased slightly as the diluent chain length was increased (Table 3). In this series of diluents, the hexane is a mixture of isomers. The octane and dodecane are normal paraffins and the Escaid 200 and "n-paraffin" are mixtures of normal paraffins; the average number of carbons is 11.5 for Escaid 200 and 13.3 for "n-paraffin". Three diluents containing naphthenes and aromatics had the following approximate compositions:

	Concentration (%)		
	Kermac 627	Kermac 470B	Escaid 110
Naphthenes	13	49	58
Aromatics	6	17	2
Paraffins	79	34	40

The uranium extraction coefficients with these diluents were slightly lower than with the paraffins. There was very little difference between the naphthenic diluents, although the extraction increased slightly with increasing paraffin content of the diluent. Extraction was high with one isoparaffin and two refined kerosenes. The exact structure of these diluents is not known.

3.1.3 Effect of impurities

Octyl phenol and trioctylphenyl phosphate are two of the impurities identified in commercial OPAP. Both of these have a slight depressing effect on uranium extraction, as shown in Fig. 5. In these tests, octyl phenol or trioctylphenyl phosphate was added to Amsco 450 solutions containing 0.10 M MOPPA + 0.10 M DOPPA and uranium extraction from the standard wet-process acid was measured at room temperature. No other

Table 3. Effect of diluent on uranium extraction with OPAP

Organic phase: 0.20 M OPAP Batch I (0.087 M MOPPA + 0.117 M DOPPA) in indicated diluent

Aqueous phase: wet-process green acid, 5.8 M H_3PO_4 , 0.12 g U/liter, 8.6 g Fe^{3+} /liter

Contact: 10 minutes at organic/aqueous phase ratio of 1, temperature $\sim 23^\circ\text{C}$

Diluent	Chain length	Uranium extraction coefficient
<u>Paraffins</u>		
Hexane	~ 6	8.4
n-octane	8	7.1
Escaid 200	11.5	7.5
n-dodecane	12	6.5
"n-paraffin"	13.3	5.6
<u>Isoparaffins</u>		
Isopar M	—	8.1
<u>Naphthenic diluents</u>		
Kermac 627	—	7.6
Escaid 110	—	6.8
Kermac 470B	—	6.7
<u>Refined Kerosenes</u>		
LOPS	—	8.2
Certrex 39	—	8.5

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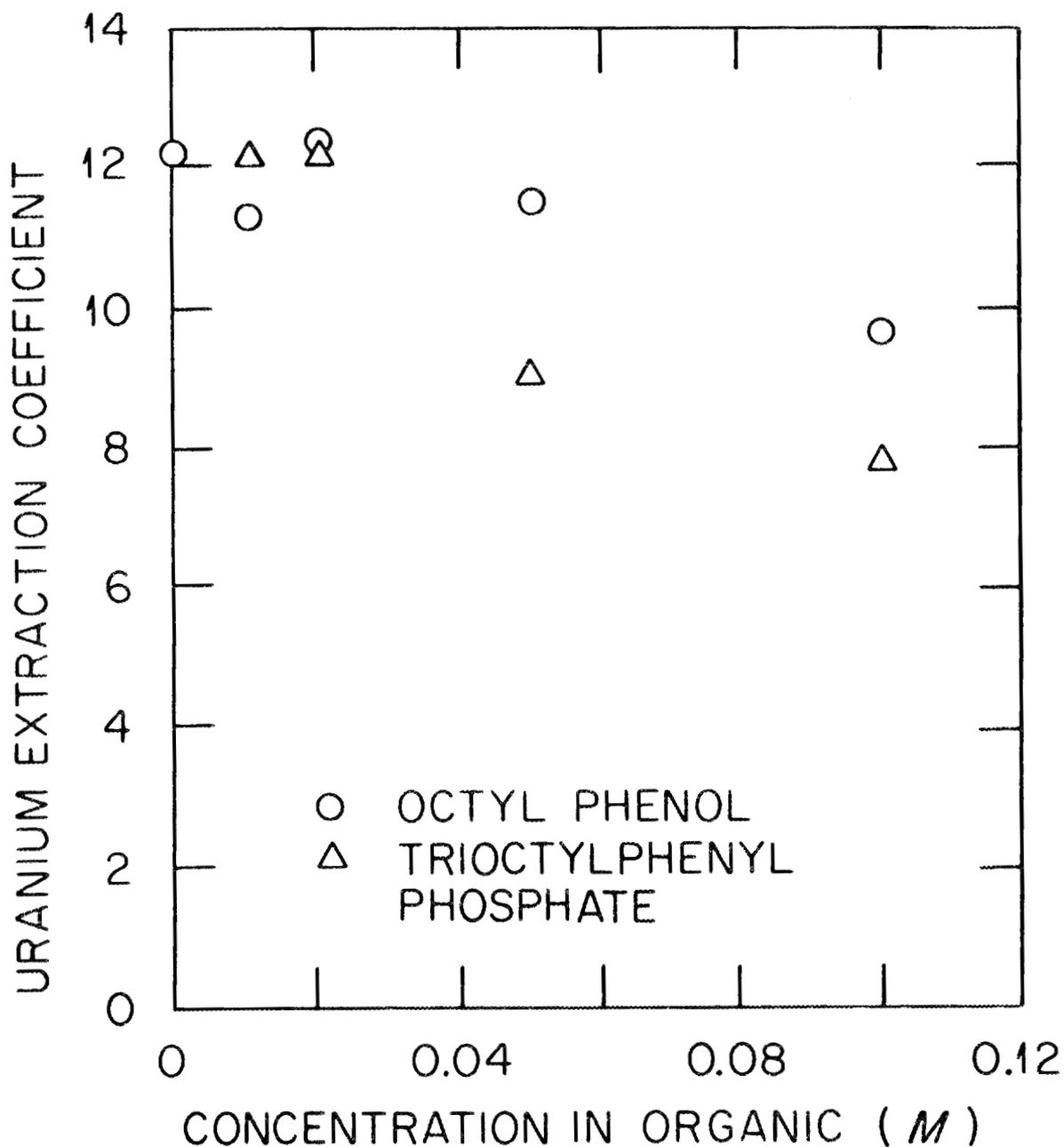


Fig. 5. Effect of octyl phenol and trioctylphenyl phosphate on uranium extraction with OPAP. Octyl phenol or trioctylphenyl phosphate was added to an organic phase containing 0.10 M MOPPA + 0.10 M DOPPA in Amsco 450. Uranium extraction was measured by equilibrating the organic phase with an equal volume of wet-process green acid (5.8 M H_3PO_4 , 0.12 g U/liter, 8.6 g Fe^{3+} /liter) at room temperature.

impurities were present. There was little effect at the lower concentrations of the impurities, but the extraction coefficients were depressed by 20-30% when the impurity concentration was 0.10 M, or half that of the MOPPA + DOPPA. Based on chromatographic analyses, we estimate that process solutions of 0.3 M once-hydrolyzed commercial OPAP would contain 0.06 M or less of either of these impurities. Their effect on the uranium extraction power of the extractant should therefore be small.

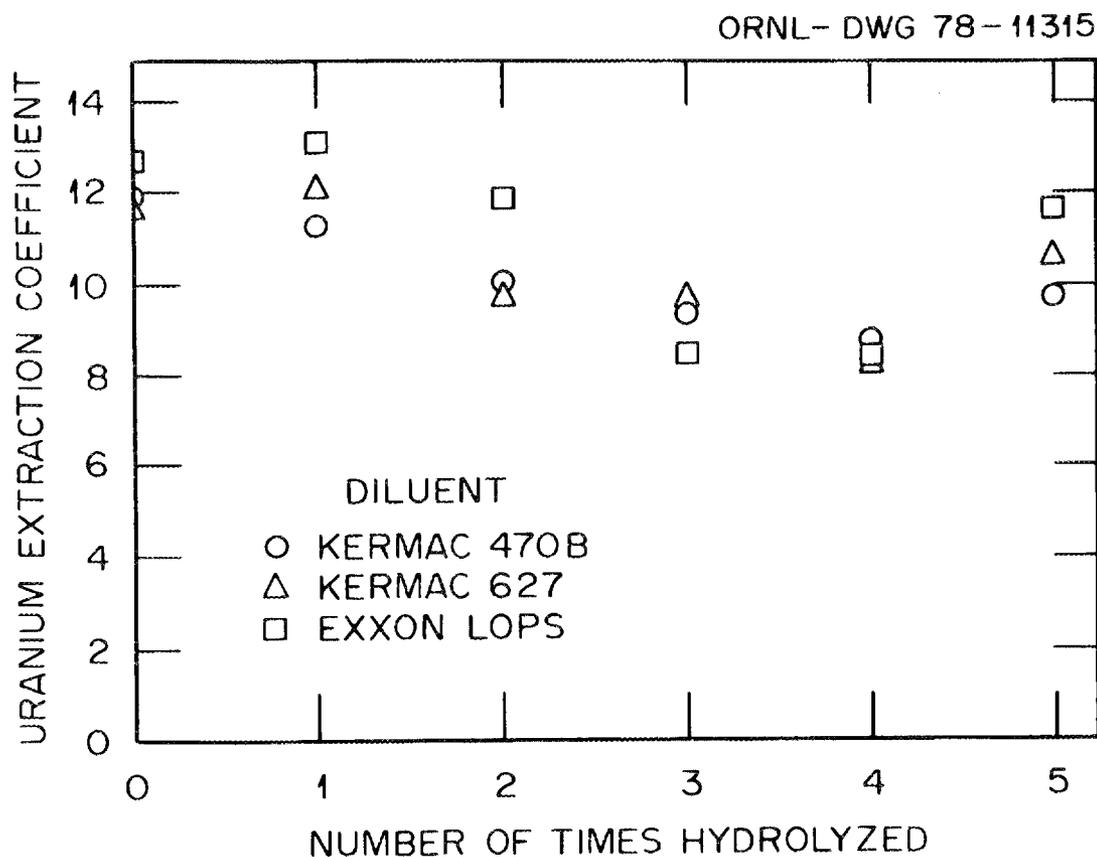
3.1.4 Effect of hydrolysis

As described earlier, OPAP contains a readily-hydrolyzable acidic fraction that is lost to the aqueous phase. The effect of hydrolysis on uranium extraction power was measured with the OPAP from the hydrolytic stability tests (Sect. 2.3). Solutions of OPAP were prepared in three diluents to be 0.20 M in combined MOPPA plus DOPPA, based on the apparent concentrations indicated by titrations of the hydrolyzed and unhydrolyzed OPAP samples. When these solutions were equilibrated with the standard wet-process acid, uranium extraction decreased slightly with increasing hydrolysis (Fig. 6). The reduced extraction with the more-extensively hydrolyzed samples was possibly caused by the higher concentrations of octyl phenol and the unidentified impurity (see Sect. 2.3). The diluent choice had little effect on the extraction power.

3.2 Solubility in Organic Diluents

OPAP solubility in organic diluents is an important consideration for process application. We have had problems in a few instances with dissolving OPAP and with precipitation from solution after the OPAP has been dissolved. The tests described below, which were made to try to define the factors that control OPAP solubility, indicate that impurities such as octyl phenol and the presence of an aqueous phase have a significant effect on the solubility of the major OPAP components. Additional work on this subject is needed and is being done.

Purified fractions of MOPPA and DOPPA are sparingly soluble in n-dodecane, as shown by Fig. 7. The solubility of DOPPA (no MOPPA



Effect of OPAP Hydrolysis on Uranium Extraction
 ORGANIC - 0.2 M OPAP (MOPPA + DOPPA) IN INDICATED
 DILUENT
 AQUEOUS - WET-PROCESS GREEN ACID, 5.8 M H_3PO_4 ,
 0.12 g U/liter
 CONTACT - 1^a/1^o, ROOM TEMPERATURE

Fig. 6. Effect of hydrolysis on uranium extraction with OPAP. OPAP batch I was hydrolyzed 5 times by gentle reflux for 20 hr with 1 ml H_2O /g OPAP. Samples of the hydrolyzed OPAP (0.20 M MOPPA + DOPPA) in the indicated diluents were equilibrated with an equal volume of wet-process green acid (5.8 M H_3PO_4 , 0.12 g U/liter, 8.6 g Fe^{3+} /liter) at room temperature.

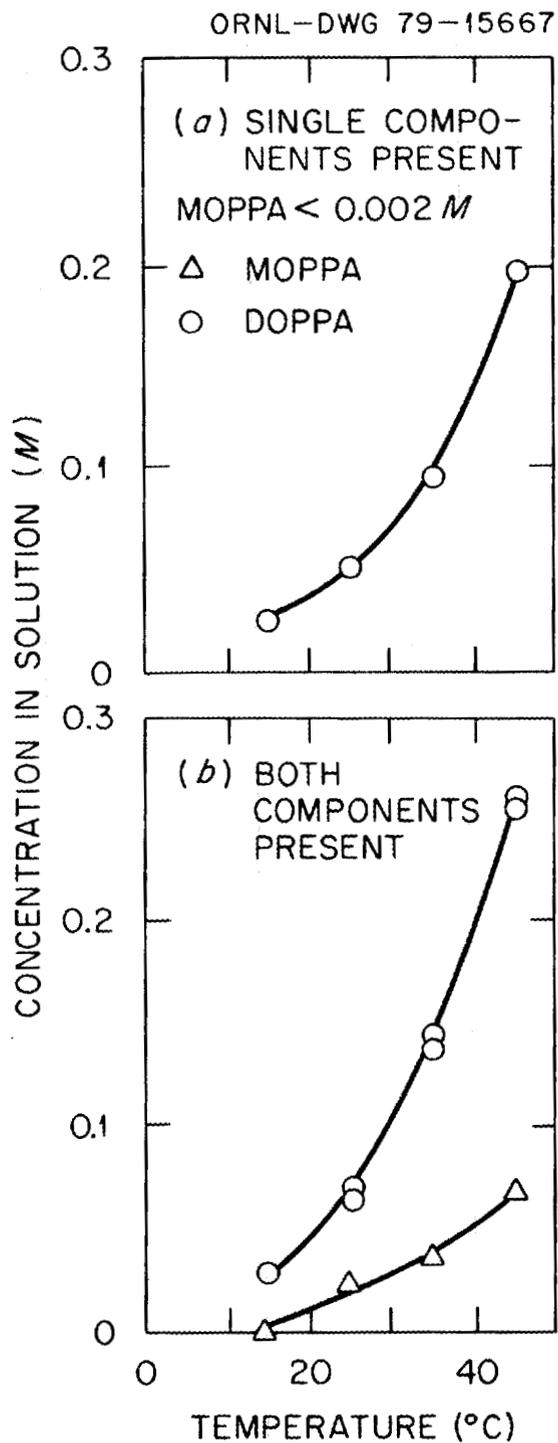


Fig. 7. Solubility of purified OPAP fractions in n-dodecane. Purified (>99%) MOPPA or DOPPA was scrubbed with n-dodecane and excess solid was equilibrated with n-dodecane at the indicated temperature. The concentration of the OPAP fractions in solution was measured by titration.

present) increased from 0.028 M at 15°C to 0.20 M at 45°C, while MOPPA alone had no measurable solubility in this temperature range. When both MOPPA and DOPPA were present, the DOPPA solubility was the same at 15°C (0.028 M) but slightly higher at 45°C (0.28 M). The MOPPA solubility was increased by the presence of DOPPA but remained lower than that of DOPPA; the MOPPA/DOPPA ratio in solution was about 0.25 in the temperature range from 25°C to 45°C. In these tests, purified fractions of MOPPA and DOPPA were washed with n-dodecane to remove any remaining impurities that might affect the solubility. The washed material (1 g in the case of MOPPA, 3 g in the case of DOPPA) was equilibrated for at least 24 hours at each temperature with 10 ml of n-dodecane and aliquots of the solution were titrated. For the test with both components present, the mixture contained about 0.8 g MOPPA, 2 g DOPPA, and 15 ml n-dodecane.

The saturation solubility at room temperature of several OPAP batches in commercial diluents was measured by equilibrating 3 g of unhydrolyzed OPAP with 10 ml of diluent. In every case, all of the OPAP dissolved in 10 to 15 minutes, but solids started precipitating from the solutions in 1/2 to 1 hour. After 24 hours of agitation, the mixtures stood for several days at room temperature and were agitated again and centrifuged before the solutions were titrated for MOPPA and DOPPA content.

The concentrations of MOPPA and DOPPA in solution appeared to depend on the OPAP batch and were about the same for the diluents tested (Table 4). The concentrations of both MOPPA and DOPPA in solution were much higher than obtained with the purified fractions; the difference was a factor of 10 to 12 for MOPPA and a factor of about 4 for DOPPA. The MOPPA/DOPPA ratio in solution was also much higher in these tests; it ranged from 0.7 to 1.0 depending on the OPAP batch. The ratio in solution was different in each case from the ratio in the OPAP solids; it was lower in the solution with batch A and higher for the other three.

Additional tests with batch A showed that the saturation solubility is a function of the amount of OPAP present (Fig. 8). When 1, 3, or 5 grams of OPAP was equilibrated with 10 ml of Amsco 450 as described above, the concentrations of both MOPPA and DOPPA in solution increased as

Table 4. Solubility of commercial OPAP in organic diluents

Procedure: 3.0 g of commercial OPAP was added to 10 ml of the indicated diluent. The concentrations of the major OPAP components in solution were measured after several days equilibration at room temperature ($\sim 23^{\circ}\text{C}$)

OPAP batch	Diluent	Concentration in solution (M)		MOPPA/DOPPA ratio	
		MOPPA	DOPPA	Initial solid	Solution
A	Amsco 450	0.21	0.28	1.3	0.8
	Kermac 470B	0.20	0.28		0.7
	Kermac 627	0.21	0.27		0.8
H	Amsco 450	0.27	0.27	0.9	1.0
	Kermac 470B	0.27	0.28		1.0
I	Amsco 450	0.28	0.28	0.8	1.0
	Kermac 470B	0.28	0.28		1.0
	Kermac 627	0.27	0.28		1.0
J	Amsco 450	0.27	0.29	0.8	0.9
	Kermac 470B	0.28	0.28		1.0

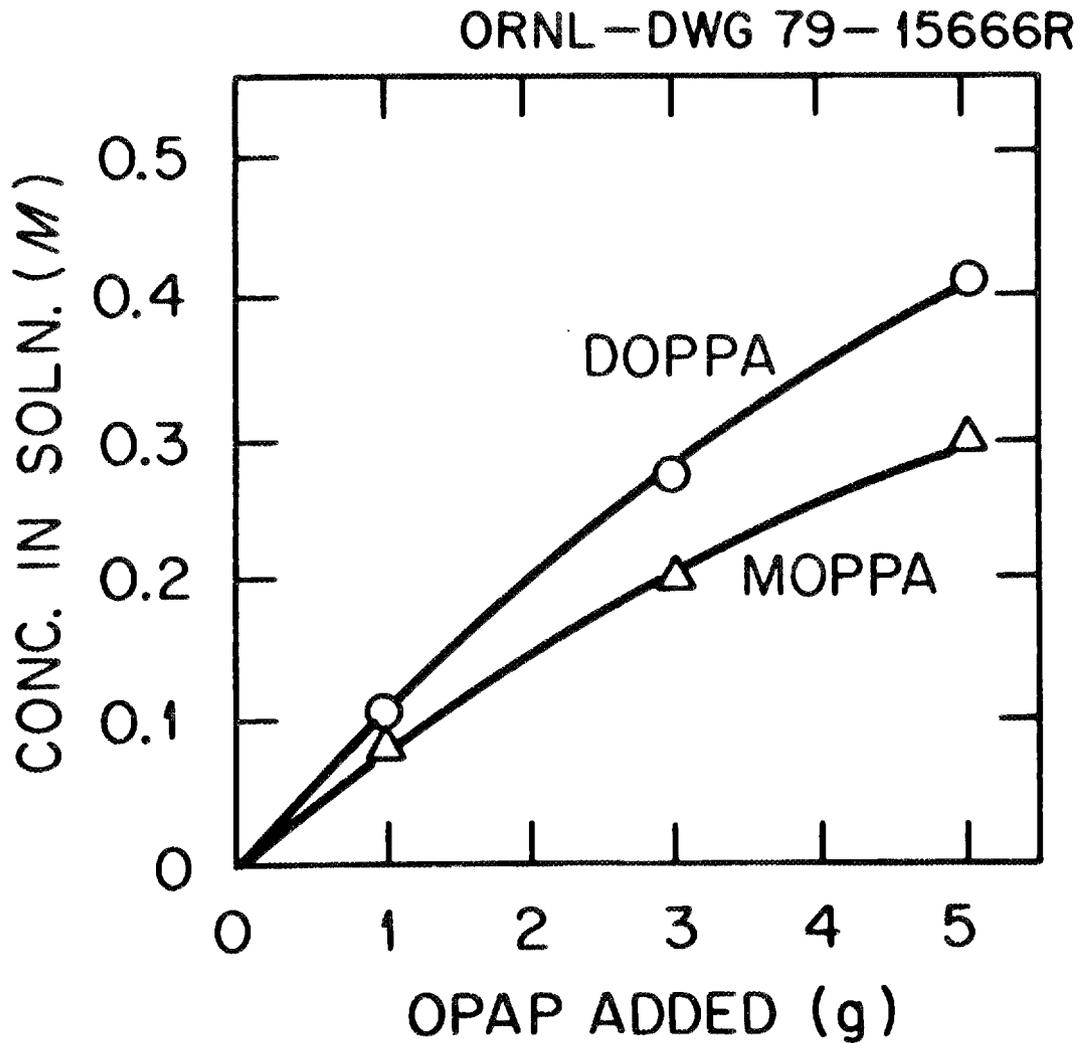


Fig. 8. Solubility of OPAP in Amsco 450. OPAP batch A was equilibrated at room temperature with 10 ml of Amsco 450. Concentrations of MOPPA and DOPPA in solution were measured by titration.

the amount of OPAP was increased. The MOPPA/DOPPA ratio in solution was the same (0.7) for the three samples.

These results indicate that some impurities in OPAP affect the solubility of the major components in organic diluents, although our chromatographic analyses do not show any major differences in the amounts of impurities present in the OPAP. We have also observed that the solubility of OPAP is increased by the presence of an aqueous phase; addition of water or acidic solutions causes OPAP solids that are insoluble to dissolve in the organic phase. The effect appears to be greater with MOPPA, i.e., it is solubilized to a greater extent than DOPPA by the aqueous phase. The DOPPA solubility is then increased by the presence of the MOPPA-aqueous phase complex.

4. STABILITY OF OPAP

Studies of the stability and long-term performance of OPAP are a major part of our program. These studies include measurements of organic losses by distribution to the aqueous phase and by physical entrainment as well as measurements of factors that affect the extraction power of the extractant on long-term use.

4.1 Distribution to the Aqueous Phase

Batch measurements showed that MOPPA is lost by distribution to the aqueous phase but that DOPPA is not (Fig. 9). The distribution coefficients (calculated as the ratio of the MOPPA concentrations in the organic and aqueous phases) were 2250 with wet-process brown acid, 1750 with wet-process green acid, and 530 with 6 M reagent grade phosphoric acid. The MOPPA concentrations in the aqueous phase indicated by these distribution coefficients are as follows:

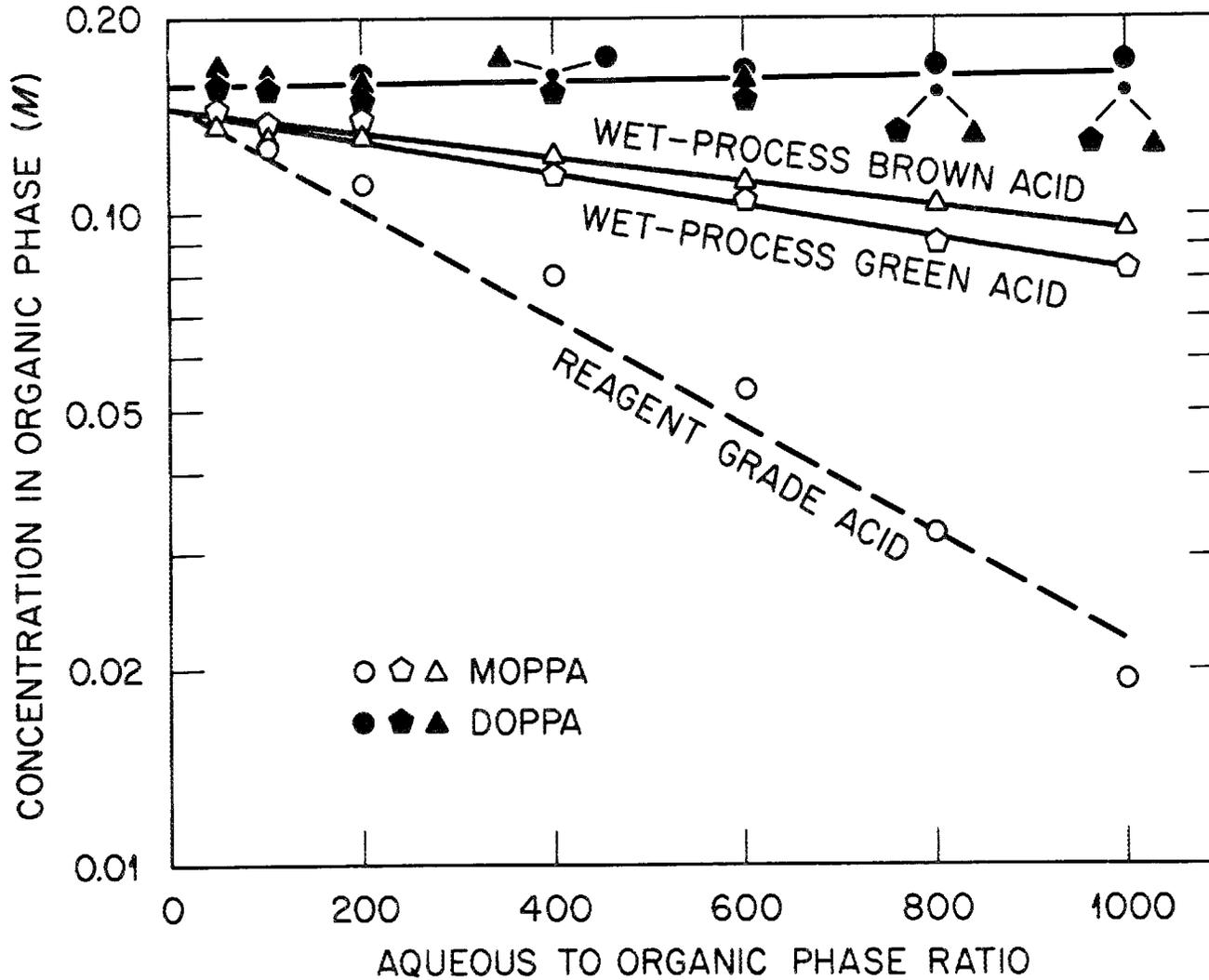


Fig. 9. Aqueous phase distribution loss of OPAP-batch tests. OPAP batch A in Amsco 450 (0.15 M MOPPA + 0.16 M DOPPA) was equilibrated with wet-process and reagent grade phosphoric acid solutions at aqueous/organic phase ratios to 1000/1. Concentrations of MOPPA and DOPPA in the equilibrated organic phase samples were measured by titration.

MOPPA concentration in organic phase (M)	Type of phosphoric acid	MOPPA concentration in phosphoric acid (ppm)
0.15	Brown	19
	Green	24
	Reagent	81
0.10	Brown	13
	Green	16
	Reagent	54

The iron and uranium extracted from the wet-process acids probably complexed part of the MOPPA and reduced its aqueous phase distribution loss. These results indicate a slow decrease of the MOPPA concentration in the organic phase would occur in process use of the OPAP extractant, and makeup would eventually be needed to maintain the extraction power of the reagent mixture. The MOPPA would be distributed in the phosphoric acid going to rubber-lined evaporators for concentration to ~54% P_2O_5 .

The tests were made by cascading organic phase that initially contained 0.149 M MOPPA and 0.156 M DOPPA in Amsco 450 with the phosphoric acid solutions up to a total aqueous to organic phase ratio of 1000/1. Aliquots of the organic phase were scrubbed twice with 10 M H_3PO_4 and titrated between equilibrations. The bulk organic phase was not stripped or scrubbed between contacts with the phosphoric acid solutions.

Distribution to the aqueous phase was also studied in continuous cyclic tests. A flowsheet for the continuous system is shown in Fig. 10. It contained 2 extraction stages and 2 stripping stages. Feed ratios (aqueous:organic) were 4:1 to the extraction section and 1:20 to the stripping section. Tests were made with purified OPAP fractions in n-dodecane and reagent grade phosphoric acid and with commercial OPAP in Kermac 470B and wet-process phosphoric acid. The extract was stripped with 10 M H_3PO_4 that contained $NaClO_3$ to oxidize the uranium; about 8 times the stoichiometric amount was added. In order to assure an adequate oxidant supply, about 1/3 of the $NaClO_3$ was added to the second stage with

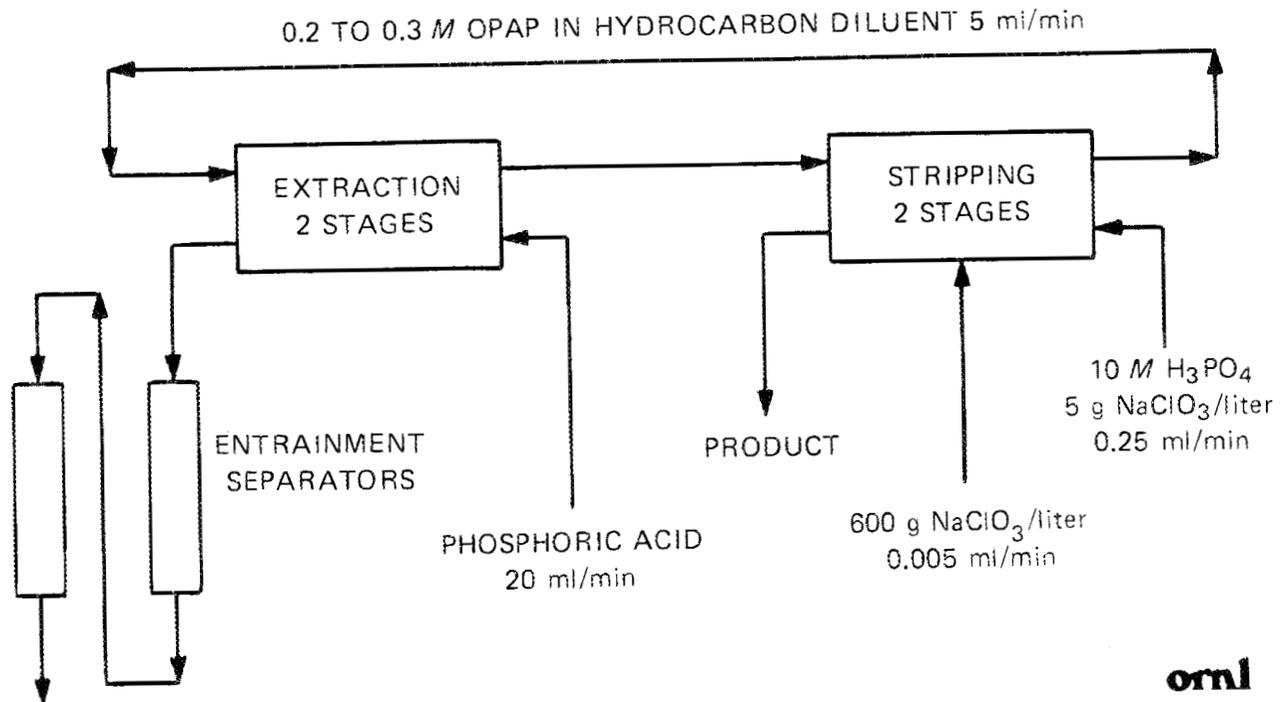


Fig. 10. Flowsheet for continuous tests.

the 10 M H_3PO_4 strip solution and about 2/3 was added to the first stage as a concentrated (4.5 M) solution. The temperature was controlled at 45°C. The system was filled and the tests were completed without any further addition of organic phase. Reagent composition and uranium recovery were measured as a function of operating time.

The organic phase for the initial test was prepared by dissolving purified MOPPA and DOPPA fractions in n-dodecane to make the extractant about 0.09 M in each component. The aqueous phase was 6 M reagent grade phosphoric acid that contained 0.15 g uranium and 2.0 g Fe^{2+} per liter. The system was operated for 260 hr with the results shown in Fig. 11. The MOPPA content of the organic phase decreased rapidly from the start of the test and was less than 10% of its initial value at the end. The measured DOPPA concentration increased by about 5% during the test but dropped sharply due to precipitation near the end, after essentially all of the MOPPA had been lost. After precipitation started, about 20% of the DOPPA in the organic inventory was lost in 24 hours; the crystallized solids contained >96% DOPPA.

The MOPPA loss rate was at least twice as high as the loss rate to reagent grade acid in the batch tests. There was a substantial loss of organic phase volume (see Sect. 4.4) which makes accurate calculation of the MOPPA distribution coefficient difficult. By making assumptions as to the organic phase volume based on beginning and ending inventories, the estimated o/a distribution coefficient for this test was 100-200, compared to 530 measured in the batch tests. Liquid chromatographic analyses of organic phase samples taken during the test show that the MOPPA loss was by distribution to the aqueous phase and not by degradation or hydrolysis (Fig. 12). The MOPPA peak decreased in size and no decomposition products, e.g., octyl phenol, formed.

Uranium recovery in the system, based on raffinate analysis, was more than 99% for the first 150 hours of the test. The recovery decreased in the last 100 hours, and was about 47% at the end of the test. The MOPPA/DOPPA ratio in the organic phase when uranium recovery started to drop was between 0.25/1 and 0.35/1, well below the effective extraction range

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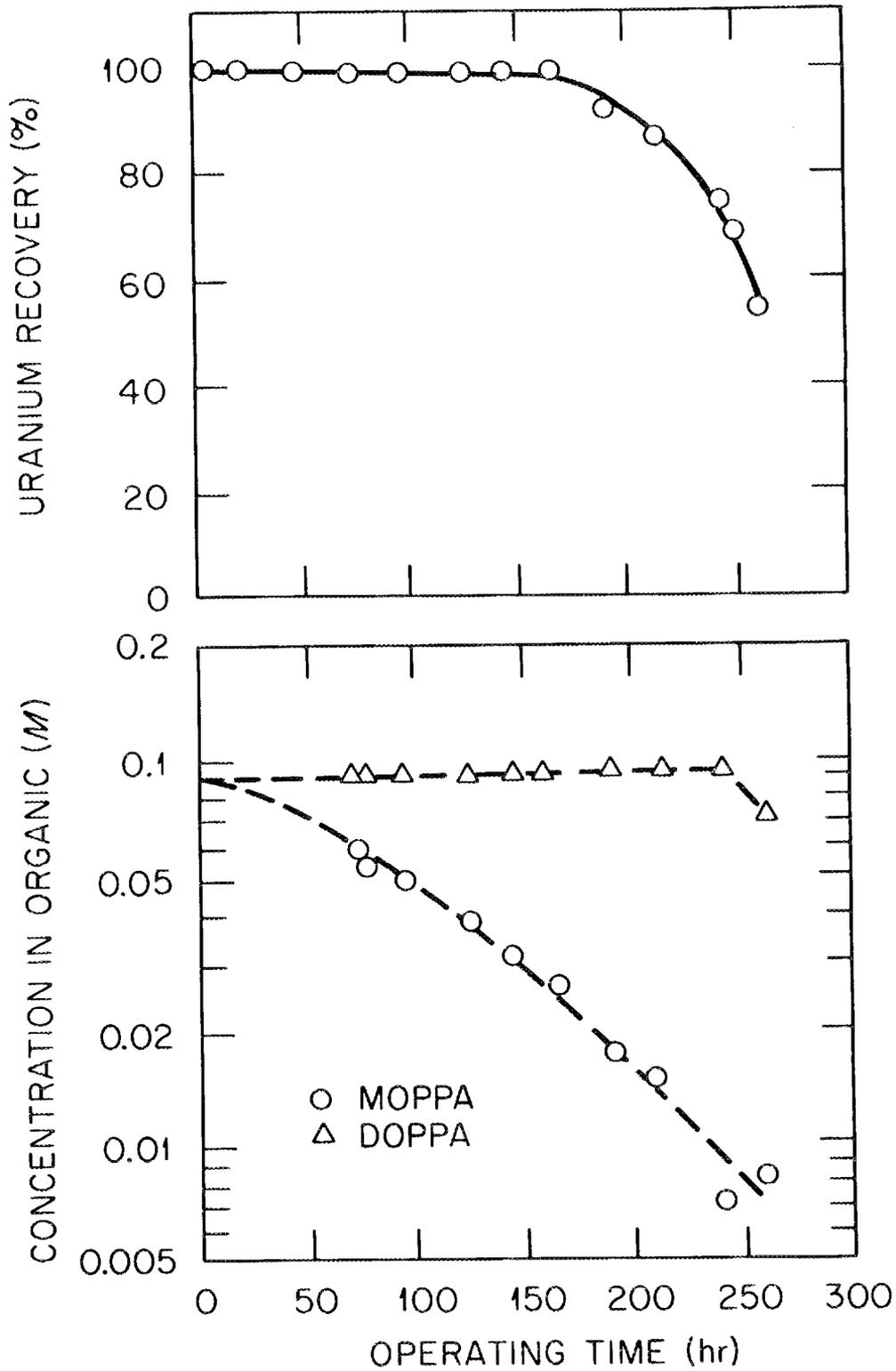


Fig. 11. Uranium recovery and organic phase composition in continuous test with reagent grade phosphoric acid.

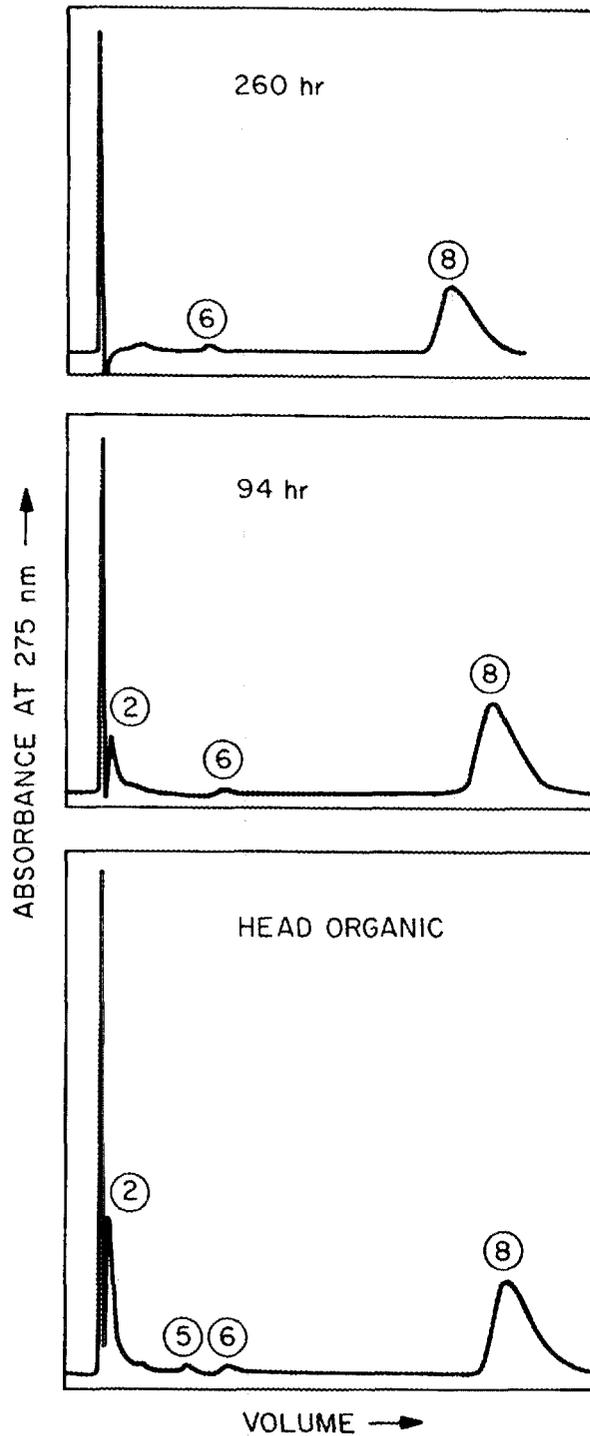


Fig. 12. Liquid chromatographic analysis of organic phase samples from continuous test with reagent grade phosphoric acid. Identification of peaks: 2 MOPPA, 5 octyl phenol, 6 unknown, 8 DOPPA.

indicated by Hurst and Crouse.⁷ Uranium stripping efficiency was 95 to 98%. Not all of the NaClO_3 added to the system was consumed; the aqueous phase in both stripping stages contained from 2 to 4 grams per liter of NaClO_3 equivalent throughout most of the test.

The results of an abbreviated test with 0.1 M octyl phenol added to the organic phase show no effect by the octyl phenol on the MOPPA loss rate. Titrations of two organic phase samples and the head organic indicate essentially the same MOPPA loss rate that was measured with no octyl phenol present. The system, which was shut down after 37 hours because of mechanical problems, was not operated long enough to measure any effect of octyl phenol on uranium extraction; about 98% recovery was indicated by analysis of the raffinate samples taken.

OPAP stability was also studied in the continuous system with commercial OPAP in commercial diluent and wet-process phosphoric acid. The organic phase, prepared from twice-hydrolyzed OPAP batch I, contained 0.120 M MOPPA and 0.188 M DOPPA in Kermac 470B. The commercial wet-process acid, which was obtained from a company that processes calcined rock, contained 30% P_2O_5 , 0.17 grams of uranium per liter, and 13.7 grams of iron per liter. Most of the iron in the acid was oxidized since the ferrous iron concentration was only about 0.6 g/liter. The uranium valence was reduced by dissolving 1 gram per liter of iron metal powder in the acid before it was fed to the extraction system. The system was operated for 440 hours, under the same conditions as the previous test, with the results shown in Fig. 13.

Uranium recovery, based on analyses of the aqueous feed and raffinate samples, decreased from about 70% at the start of the test to about 50% at the end (70% recovery indicates high stage efficiency; this is about the best recovery that could be expected in two stages under the test conditions used). The extraction power of the extractant, as measured in batch tests by the extraction coefficient from the "standard" wet-process green acid that was used in the OPAP screening tests, decreased by about half during the test. Titrations of organic phase samples, after

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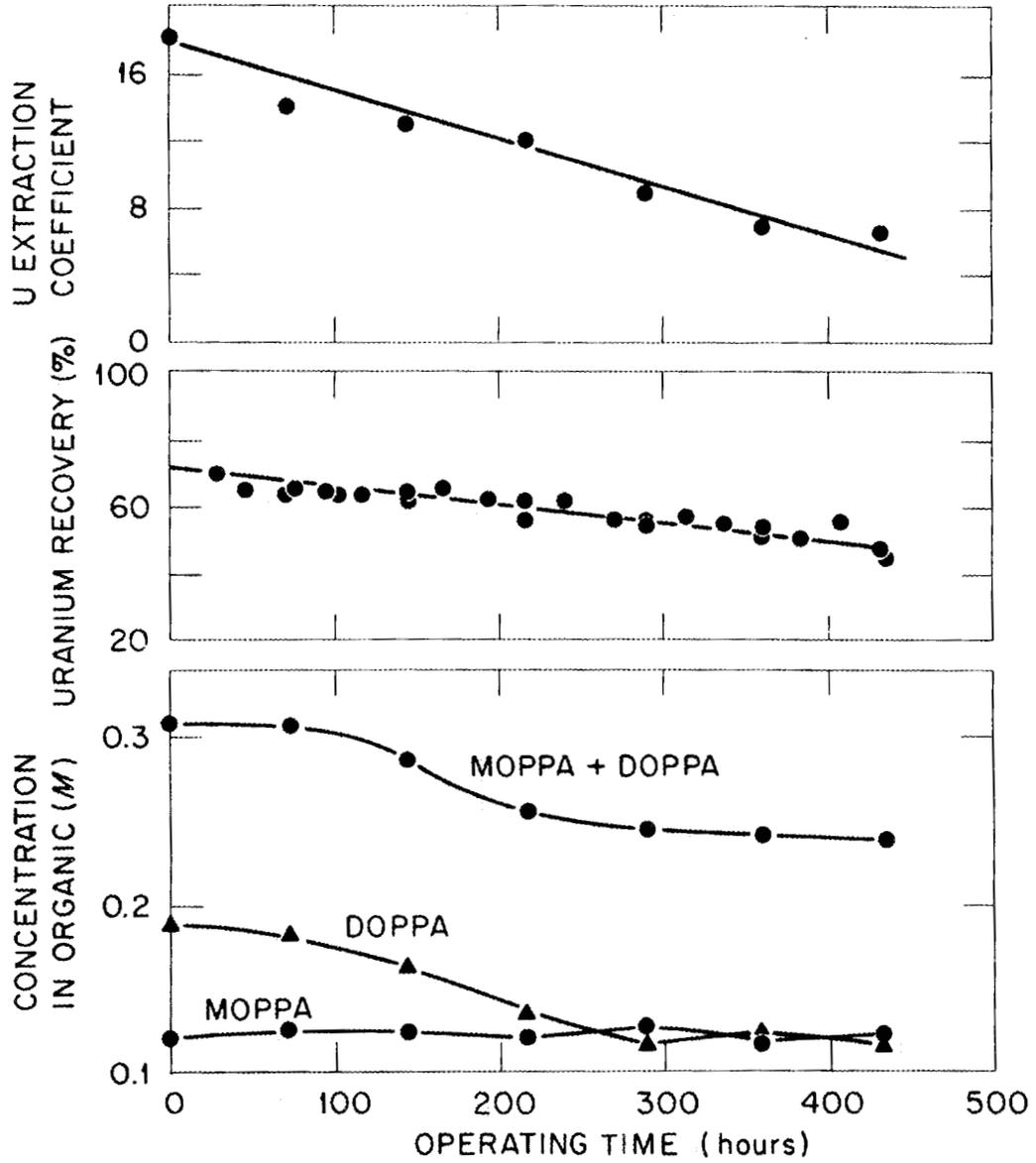


Fig. 13. Uranium recovery and organic phase composition in continuous test with wet-process phosphoric acid.

scrubbing with 10 M H_3PO_4 to remove extracted uranium and iron, indicated no significant change in MOPPA concentration during the test but showed a decrease in DOPPA concentration in the period from about 100 hours to 250 hours. The apparent DOPPA concentration stabilized when the MOPPA/DOPPA mole ratio reached 1/1, and did not change for the remainder of the test.

The period of DOPPA concentration change corresponds to the time that crystallization was observed in the extraction system. The solids that formed were found to be a complex of ferric iron that contained both MOPPA and DOPPA, which disagrees with the constant MOPPA concentration indicated by the organic phase titrations. As described below, the loss of extractant to the solids was large enough to contribute to the loss of uranium extraction power. In addition, some material that poisoned the extractant was apparently extracted from the phosphoric acid; this contributed to the loss of uranium extraction power and also interfered with the titrations of the organic phase samples.

As described in Sect. 2, the concentrations of MOPPA and DOPPA in the organic phase are determined by titration with standard NaOH. The MOPPA concentration is calculated from the volume of titrant consumed between the second and first end-points, and the DOPPA concentration is calculated from the titrant volume consumed to the first end-point minus the amount consumed between the second and first. If part of the material that should titrate at the first end-point is complexed and does not titrate, and then does titrate at the second end-point, the results will be high in MOPPA and low in DOPPA. Titrations of initial and final organic phase samples indicate that this possibly happened in our test (Fig. 14). Both end-points are sharp and well-defined in the titration of the head organic. For the final organic, the shape of the first end-point is not much changed but the second end-point has a lower slope and is poorly defined, possibly because the interfering material is being neutralized or precipitated there.

The solids were analyzed by equilibrating a weighed sample with 6 M HCl and an aromatic diluent such as toluene, causing the iron to

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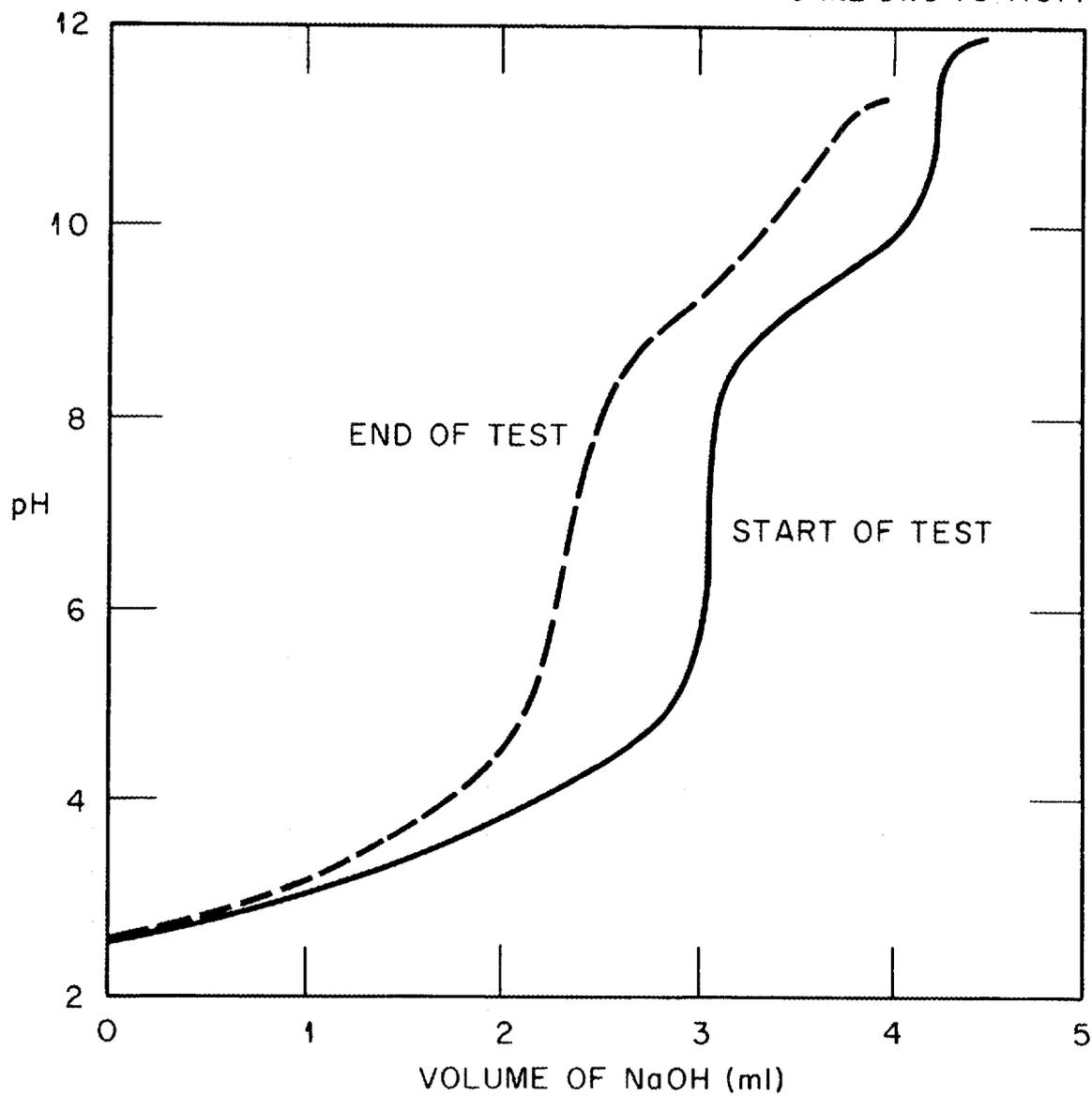


Fig. 14. Titration of organic phase samples from continuous test with wet-process phosphoric acid.

distribute to the aqueous phase and the extractant to distribute to the organic phase. Extractant concentrations were then determined by titrating aliquots of the organic phase. The solids recovered from the system at the end of the test contained a total of 79.7 milliequivalents of the extractant (41.7 meq of MOPPA and 38.0 meq of DOPPA). Titrations of the initial and final organic phases indicate an extractant loss of 76.7 meq, which is in good agreement with the solids analysis. However, the extractant loss based on the titrations was all DOPPA, which suggests the MOPPA loss was masked by extractant poisoning as described above.

These results indicate that the solids formed with iron account for most of the extractant concentration losses in the test, and that both MOPPA and DOPPA were lost. They also indicate that the MOPPA distribution loss to wet-process acid is much lower than indicated by results of the batch and continuous tests with reagent grade acid. The loss of uranium extraction power is thought to be due to the combined effects of the extractant loss and poisoning of the extractant with material extracted from the phosphoric acid.

4.2 Extractant Poisoning

The major symptoms of extractant poisoning, which were described above, were the steady decline in uranium recovery during the continuous test with wet-process green acid and the interference with titrations of organic phase samples. In addition, the color of the organic phase darkened in the first part of the continuous test from light straw to a dark red (it appeared black in large volumes). The color lightened somewhat after part of the extractant crystallized as a ferric iron complex.

The identity of the poisoning material is not known at the present time. We do not know whether it originates in the phosphate rock or in chemicals added during beneficiation or acid production. We also do not know whether it is extracted by one of the major OPAP components or by one or more of the impurities. Our test results indicate that the poisoning is not due to irreversible extraction of metals. Iron was the only

metal detected in significant concentrations in a spectrographic analysis of the ash from a sample of the poisoned organic phase from the continuous test.

We were unable to regenerate the poisoned organic by scrubbing with solutions of H_3PO_4 , HNO_3 , HCl , or H_2SO_4 (Table 5). The acid scrubs did not improve the uranium extraction, titration characteristics, or color of the organic phase. Scrubbing with ammonium carbonate solution and then with acid improved the titration; both end-points were sharper and the apparent concentrations of MOPPA and DOPPA were near those estimated from reagent losses by crystallization. However, the uranium extraction and the color of the organic phase were not affected by this treatment.

Additional work is needed to identify the source of the poisoning material and to find ways to minimize its effect. This includes studies of the effect on uranium extraction of humic materials separated from phosphate rock and of beneficiation and defoamer chemicals added to reagent grade phosphoric acid. Tests with wet-process phosphoric acid that has a known history of chemicals addition will also be made. The acid sample used in the continuous test was prepared from calcined rock and its concentration of organic matter (humic material) should be low; this suggests the poison is something other than organic matter from the phosphate rock. Tests with purified OPAP fractions and with commercial material that contains different impurities can help to identify the part of OPAP that extracts the poison.

4.3 Precipitation with Iron

The crystalline material that formed in the extraction section of the continuous system was found to be a complex of ferric iron that contained both major components of the OPAP reagent. It deposited from the organic phase, i.e., the iron extracted into the organic phase and then the complex crystallized on the settler walls and in the organic lines and collected at the interfaces. The solids were observed to be forming during the period of apparent DOPPA concentration decrease and

Table 5. Regeneration tests with poisoned organic

Procedure: Organic phase from the continuous test with wet-process acid was scrubbed 3 times with 10 M H_3PO_4 at an organic/aqueous phase ratio of 1/1 and filtered. The regeneration tests were made by scrubbing this organic phase 3 times at 1^a/1^o with the indicated acid. The tests with $(\text{NH}_4)_2\text{CO}_3$ included 3 scrubs at 1^a/1^o with 4 M $(\text{NH}_4)_2\text{CO}_3$ followed by 3 scrubs at 1^a/1^o with the indicated acid. The uranium extraction tests were made at 1^a/1^o with the standard wet-process green acid.

Scrubbing solutions	Uranium extraction coefficient	Apparent concentration (M)	
		MOPPA	DOPPA
Head organic before test, scrubbed with 10 M H_3PO_4	18.9	0.120	0.188
Organic at end of test	6.5	0.122	0.115
1 M HNO_3	6.1	0.129	0.103
6 M HNO_3	4.9	0.123	0.126
1 M HCl	5.6	Not titrated	
6 M HCl	5.4	Not titrated	
1 M H_2SO_4	5.9	Not titrated	
4 M $(\text{NH}_4)_2\text{CO}_3$, 10 M H_3PO_4	5.3	Not titrated	
4 M $(\text{NH}_4)_2\text{CO}_3$, 6 M HNO_3	5.0	0.102	0.138

precipitation appeared to stop after about 250 hr, when the apparent DOPPA concentration had stabilized.

A total of 27.6 g of solids was recovered from the two extraction settlers after completion of the continuous test. The material from the first stage (22.6 g) was a brown granular material with the appearance of topsoil, and the material from the second stage had the same texture but was lighter in color. The difference in appearance was due to dissolved or suspended mineral matter in the acid; the first stage was "dirtier" because the acid entered the system there. The samples were combined for analysis. The combined sample (8.2 grams) from the organic lines, the settler walls, and the interface of the first entrainment separator was about the same color as the solids from the second stage interface, but was more crystalline.

Although the solids did not cause any operational problems, they contained a substantial amount of the extractant, and undoubtedly contributed to the loss of uranium extraction power seen in Fig. 13. The recovered solids contained 16% of the MOPPA and 19% of the DOPPA that was added to the system in the initial organic phase inventory (Table 6). The MOPPA/DOPPA/Fe ratio (milliequivalent basis) was 0.55/0.52/1 in the interfacial solids and 0.71/0.58/1 in the combined solids from the lines, walls, and entrainment separator. No metals other than iron were found in significant concentrations in a spectrographic analysis of the solids. Other samples that we prepared or obtained from other sources varied somewhat in composition, but all contained primarily MOPPA, DOPPA, and Fe.

Before analysis, the solids were blotted with filter paper to remove entrained liquid (organic or aqueous). Even after blotting, the solids contained a substantial amount of entrained phosphoric acid. Washing with water reduced the weight by as much as 20%. Most of the material removed by the wash was H_3PO_4 . Both samples lost about 75% of their weight when they were heated to 1000°C, with most of the weight loss occurring between 125°C and 400°C.

Table 6. Composition of solids from continuous system

Solids were removed from the continuous system, blotted dry with filter paper, and weighed. Analyses for MOPPA and DOPPA were made by adding samples of the solids to toluene and 6 M HCl, equilibrating the phases, and titrating an aliquot of the toluene phase.

	Extraction settler interfaces	Entrainment separator, organic lines, extraction settler walls
Weight of solids, grams	27.6	8.2
MOPPA in solids		
concentration, wt %	15.3	21.2
weight, grams	4.2	1.7
milliequivalents	29.5	12.2
% of initial inventory	11.3	4.6
DOPPA in solids		
concentration, wt %	48.1	58.0
weight, grams	13.3	4.8
milliequivalents	28.0	10.0
% of initial inventory	13.8	5.0
Iron in solids		
concentration, wt %	3.6	3.9
weight, grams	1.0	0.3
milliequivalents	53.5	17.3

The major factors that affected formation of the precipitate in batch tests were the concentrations of ferric iron and phosphoric acid in the aqueous phase. Precipitation decreased with decreasing Fe^{3+} concentration and with increasing H_3PO_4 concentration. The precipitate did not form with ferrous iron, and the tendency to form was less with reagent-grade H_3PO_4 than with wet-process acid at the same Fe^{3+} concentration. Hydrolyzed commercial OPAP was more resistant to formation of the precipitate than purified OPAP fractions (MOPPA and DOPPA separated and purified, then recombined), and the purified fractions were more resistant than unhydrolyzed commercial OPAP. Commercial diluents were better than aliphatic hydrocarbons. The OPAP concentration and the MOPPA/DOPPA ratio had little effect within the ranges we tested.

Varying the ferric iron concentration and the phosphoric acid concentration in the directions that reduced the tendency to form the precipitate also would reduce extraction of iron into the organic phase. This suggests that the crystallization could be minimized by inhibiting iron extraction, e.g., by controlled reduction of the iron valence in the phosphoric acid. Reduction of the iron valence would also increase uranium extraction by lowering competition for the extractant. This would allow the use of lower extractant concentration or fewer extraction stages for uranium recovery. Some balance would be needed, however, because complete reduction of the iron could result in higher MOPPA distribution loss to the aqueous phase (see Sect. 4.1). The uranium valence in wet-process phosphoric acid is reduced by dissolving iron metal to produce ferrous iron, which then reduces the uranium. This treatment also reduces part of the ferric iron, but it is a poor method for bulk reduction of the iron valence because it also increases the total iron concentration of the acid. An alternate method of valence control that is efficient and economical is needed.

4.4 Organic Phase Volume Loss

Organic phase entrainment in solvent extraction should be kept as low as possible to minimize loss of extractant and to minimize

contamination of downstream processing operations and waste treatment facilities. This is particularly important in uranium recovery from phosphoric acid because the next processing step is evaporation of the acid to 54% P_2O_5 . Most evaporators are lined with a rubber material that can be severely damaged by excessive entrained organic phase. Most operators try to keep the entrainment at less than 0.1 ml of organic phase per liter of aqueous phase passed through the extraction system.

The loss rate in the 2-stage continuous tests (Sect. 4.1) was about eight times higher than this rate, and the rate in several tests in a 1-stage system was about four times higher. The 1-stage system did not contain a stripping section. The organic phase (0.2 M commercial, once-hydrolyzed OPAP in n-dodecane) was cycled at an organic/aqueous phase ratio of 1/4 against reagent grade H_3PO_4 (6 M) that contained 2 g Fe^{2+} /liter. While the losses from both systems were of the total organic phase, they were not "normal" entrainment losses. The extraction systems included columns of teflon turnings to separate entrained organic phase and return it to the system. Organic phase was recovered and decanted with the first entrainment separator but none ever collected in the second. The phosphoric acid solutions leaving both systems were slightly opaque; there was little settling on long standing.

The losses in the tests, summarized in Table 7, are the volumes of organic phase that we cannot account for on the basis of the beginning and ending organic phase inventories. The losses do not include the volumes of samples removed for analysis, or our estimates of the volumes lost in small spills that occurred in some of the tests. The magnitude of the unaccountable loss ranged from 23 ml in a 23-hr test in the 1-stage system to 450 ml in the 440-hr test in the 2-stage system.

The losses show a linear relationship to the volume of phosphoric acid passed through the recovery systems (Fig. 15). The slope of the lines could represent the rate of organic phase volume loss to the phosphoric acid, and the intercepts could represent a constant unrecoverable loss that is a function of the system, i.e., the volume that remains on equipment surfaces when the system is disassembled. We measured this

Table 7. Organic phase volume loss in continuous tests

OPAP	Diluent	Acid	No. of extraction stages	Acid volume (liters)	Organic phase volume (ml)	
					Initial inventory	Loss
Commercial, hyd	Kermac 470B	wet-process	2	520	1080	451 ± 29
Purified, M + D	n-dodecane	reagent, U + Fe ²⁺	2	311	1075	350 ± 9
Purified, M + D + OP	n-dodecane	reagent, U + Fe ²⁺	2	45	1080	59 ± 10
Commercial, hyd	n-dodecane	reagent, Fe ²⁺	1	121	390	65 ± 3
Commercial, hyd	n-dodecane	reagent, Fe ²⁺	1	89	381	49 ± 2
Commercial, hyd	n-dodecane	reagent, Fe ²⁺	1	72	350	43 ± 3
Commercial, hyd	n-dodecane	reagent, Fe ²⁺	1	63	540*	40 ± 2
Commercial, hyd	n-dodecane	reagent, Fe ²⁺	1	28	346	23 ± 2
None	n-dodecane	reagent, Fe ²⁺	1	57	346	7 ± 1
DEPA-TOPO	n-dodecane	reagent, Fe ³⁺	1	117	544*	42 ± 5

* Organic continuous mixing; others aqueous continuous

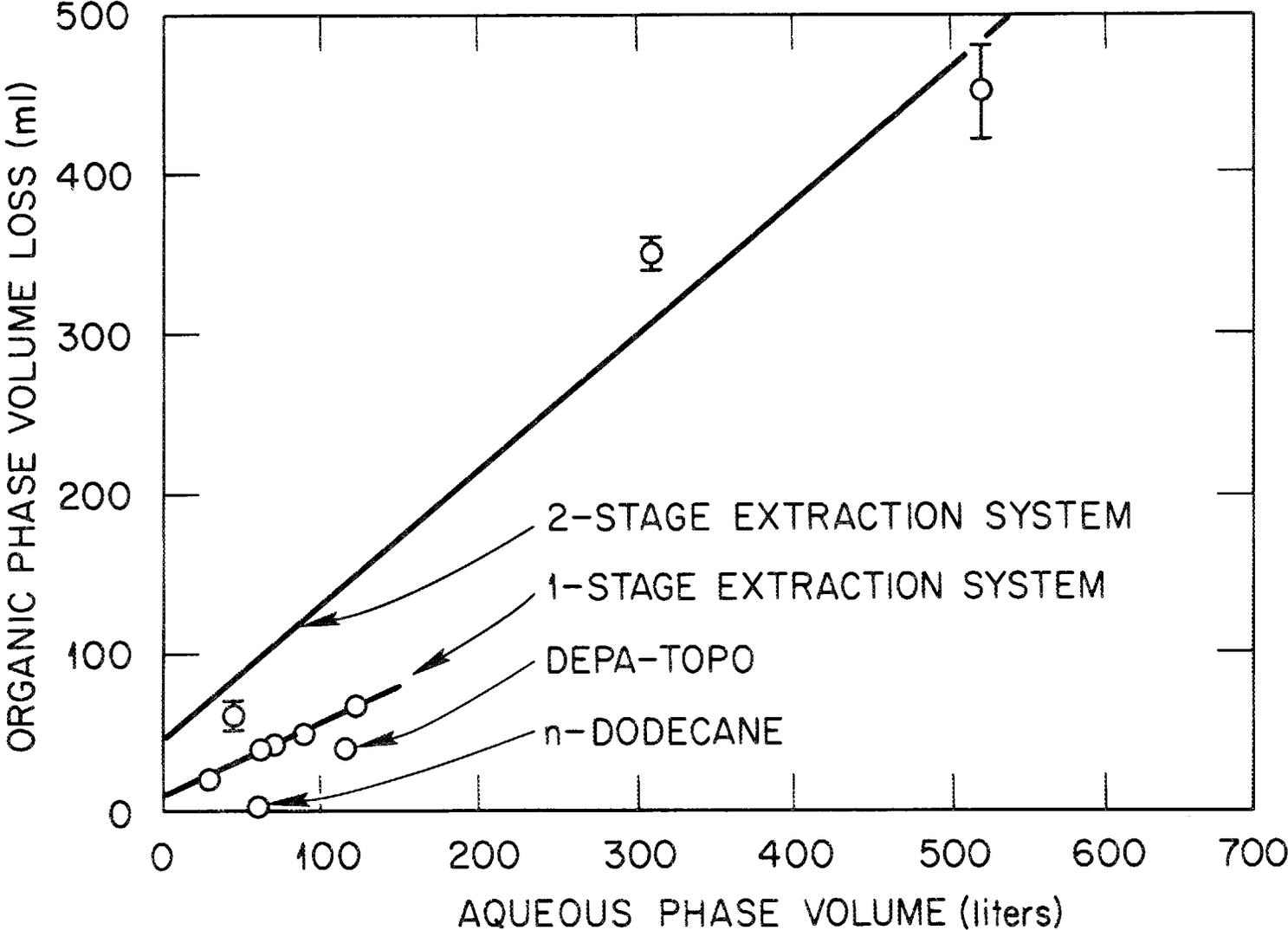


Fig. 15. Organic phase volume losses in continuous tests.

volume to be 11 ml, the same as the intercept of the line, for the 1-stage system. The indicated losses for the two systems are:

Number of extraction stages	Organic phase volume loss	
	On equipment surfaces (ml)	To phosphoric acid (ml/liter)
1	11	0.44
2	42	0.84

Since the flow rates and the mixer volumes were the same in all of the tests, it is also possible the results of Fig. 16 indicate a relationship of the organic phase volume loss and the contact time with the phosphoric acid rather than the acid volume. Both the loss rate and the total contact time were about a factor of 2 higher in the 2-stage system.

In the tests with reagent-grade acid, there was significant distribution of MOPPA to the aqueous phase in addition to the organic phase volume loss (Fig. 16). The MOPPA distribution coefficient (organic/aqueous) in this 1-stage test was 150; it ranged from 125 to 240 in the others. This loss to reagent grade acid was about the same in the 2-stage and 1-stage systems, although it was much lower to wet-process acid as discussed in Sect. 4.1. The concentrations of DOPPA and octyl phenol in the organic phase did not change in this or other tests with reagent grade acid, which indicates the volume loss was of the total organic phase and not by evaporation of the diluent. The extractant must be present for the loss to occur, since only 7 ml was lost in a test with n-dodecane as the organic phase. The loss in a test with 0.5 M DEPA-0.125 M TOPO in n-dodecane was higher than with n-dodecane alone but was lower than with OPAP in n-dodecane. The composition of the organic phase (OPAP concentration, purified fractions or commercial OPAP, n-dodecane or commercial diluent) had little effect on the loss rate, and there was little difference in the loss to reagent grade and wet-process phosphoric acid. The loss rate was the same with organic- or aqueous-continuous mixing, although the amount of organic recovered in the entrainment separator was 20 to 30 times higher with aqueous continuous mixing.

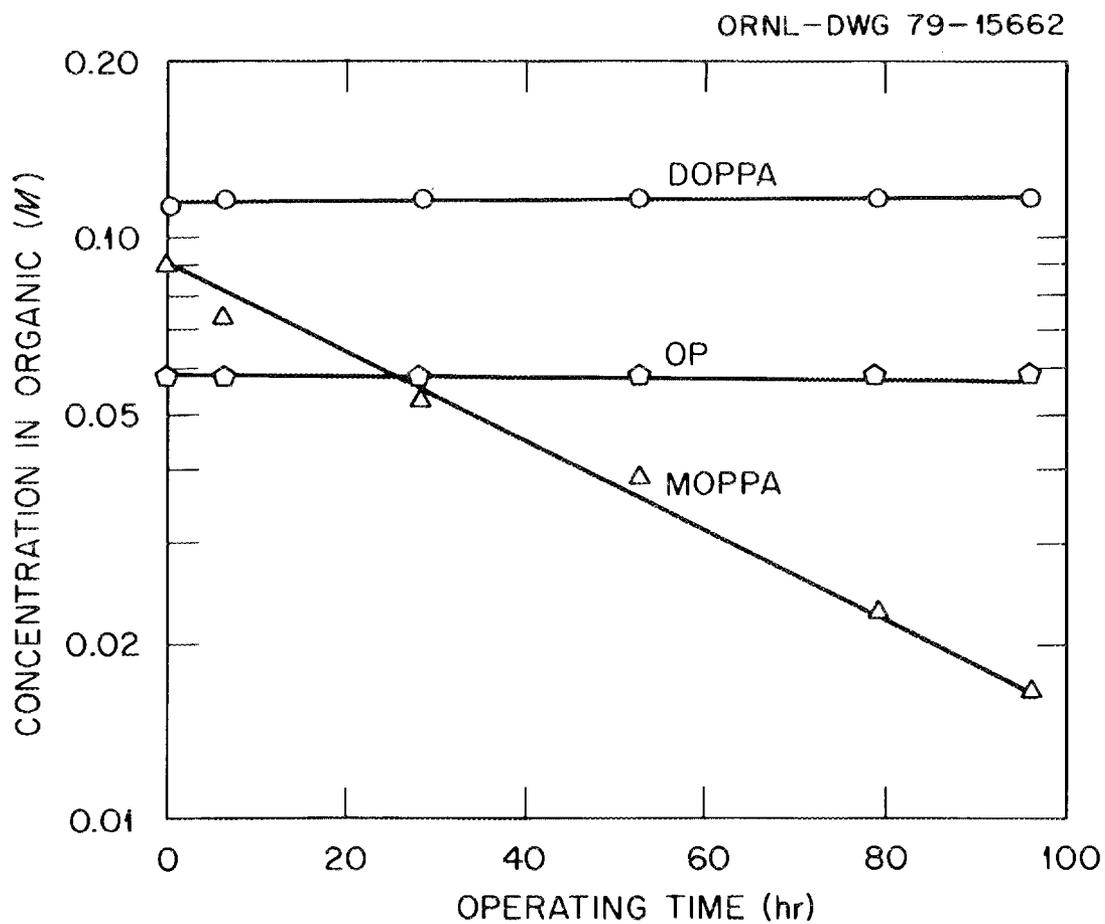


Fig. 16. Organic phase composition in 1-stage continuous test with reagent grade phosphoric acid. MOPPA and DOPPA concentrations were measured by titration and OP concentrations were measured by liquid chromatographic analysis.

We have not been able to recover the lost organic phase or to measure it in the phosphoric acid solutions. Recovery methods attempted include distillation, extraction, adsorption, and air flotation. Titration, UV absorption, liquid chromatographic analysis, total carbon analysis, and measurement of changes in turbidity and surface tension were used to try to detect the organic phase in the phosphoric acid.

Distillation worked well for known samples; over 90% of the added organic phase was recovered in the first 100 ml of distillate from 3-liter samples of phosphoric acid. Further distillation did not increase the yield of organic phase. Titrations of the distilled organic phase indicated that it was primarily diluent; it did not contain any MOPPA or DOPPA, but did contain some OP. The recovery was the same from reagent grade and wet-process acids. Distillations of 3- ℓ phosphoric acid samples from one of the 1-stage continuous tests indicated that the acid leaving the settler contained 1.1 ml of entrained organic phase per liter and the acid leaving the second entrainment separator contained less than 0.05 ml per liter.

We were not able to detect the extractant in phosphoric acid samples by direct UV absorption measurements or by liquid chromatographic analysis. Extraction with CHCl_3 followed by titration or liquid chromatographic analysis of the extract gave erratic results; we could not obtain complete or reproducible recovery of MOPPA or DOPPA with known solutions. An attempt to "salt out" dissolved or distributed organic phase by saturating the phosphoric acid with NaCl was unsuccessful. Essentially no OPAP was recovered in continuous tests by scrubbing the effluent phosphoric acid with n-dodecane in a column containing berl saddles or in a mixer-settler. Passing the phosphoric acid through a column of glass beads or filtering it through glass wool were also completely ineffective.

Some recovery of organic phase was achieved by passing the phosphoric acid through a bed of activated carbon or XAD-2, a polymeric adsorbent for water-soluble organic substances, or by sparging the phosphoric acid with air. The results indicate, however, that the material removed from the acid by these treatments was distributed MOPPA rather than the total

organic phase. These tests were made as part of the 1-stage continuous tests. The effluent phosphoric acid was treated as it left the system, after passing through the entrainment separator filled with teflon turnings. The phosphoric acid solutions were monitored by light scattering, aqueous phase surface tension, and total carbon analysis.

A turbidimeter/nephelometer was used to measure light scattering by the phosphoric acid solutions. The results, in nephelometric turbidity units (NTU), are based on comparison with liquid latex suspensions, which in turn are based on comparison with formazin suspensions. The measured turbidities in our tests were about 4 NTU in the acid leaving the settler, about 1 NTU in the acid leaving the first entrainment separator, and about 0.5 NTU in the acid leaving the adsorbent column or the air treatment column.

The surface tension measurements were made by the drop volume method with a precision microsyringe. In this method, the surface tension is calculated from the volume of drops that just fall from a glass tip of known diameter.¹² The surface tension of the phosphoric acid solutions (wet-process or reagent grade) was about 77 dynes/cm and this was reduced to about 35 dynes/cm by equilibration with the OPAP solutions. The surface tension was restored to its initial value by passage through the carbon or XAD-2 column and it was raised to about 45 dynes/cm by the air treatment. Surface tension lowering as a function of distributed organic phase concentration is shown in Fig. 17. In these tests, equilibrated phosphoric acid (surface tension 34 dynes/cm) was diluted with unequilibrated acid and the surface tension of the mixed solutions was measured. The surface tension decreased as the fraction of equilibrated acid was increased, more at the lower fractions than at the higher ones. On the basis of these results, the carbon and XAD-2 removed all of the distributed organic phase that affects the surface tension, and the air removed about 2/3 of it.

Surface tension lowering was not affected significantly by the diluent choice (Table 8). Wet-process and reagent grade acid were equilibrated with 0.2 M OPAP in a series of diluents and the surface tension of the

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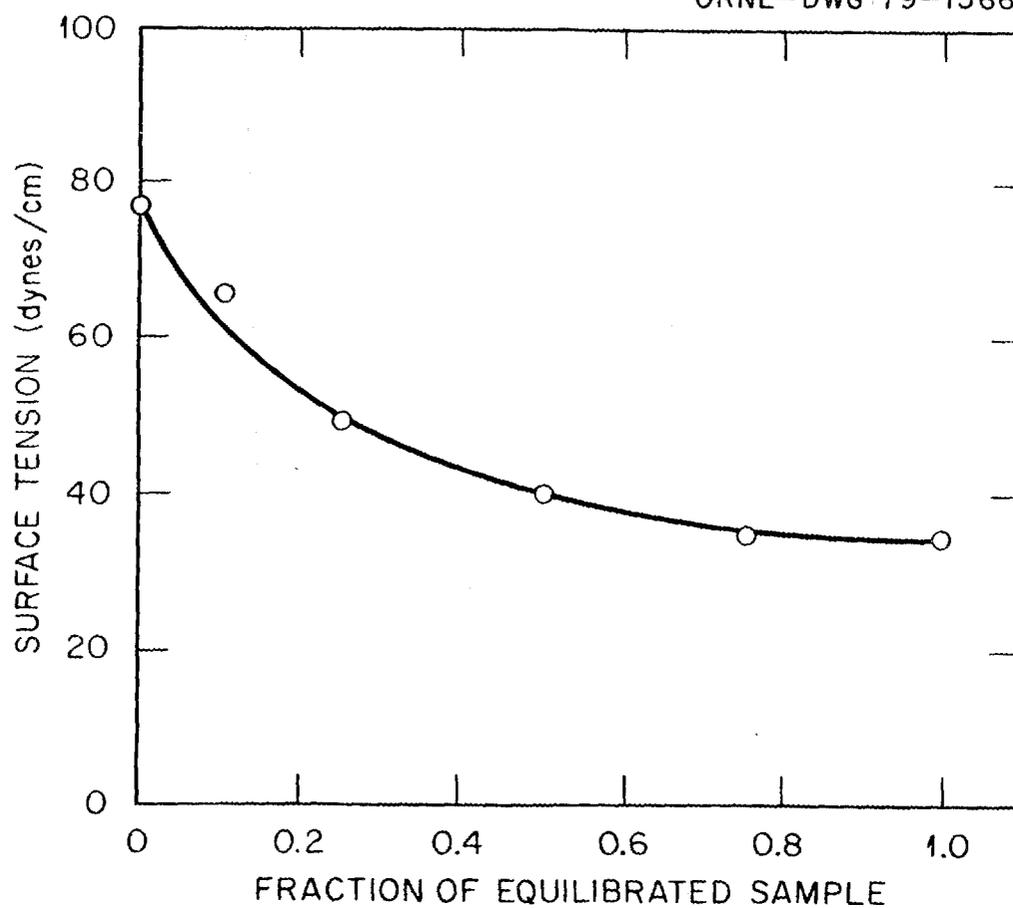


Fig. 17. Effect of distributed organic phase on surface tension of phosphoric acid solutions. Reagent grade phosphoric acid that had been equilibrated with 0.2 M OPAP in n-dodecane was diluted with unequilibrated acid solution and the surface tension of the diluted solutions was measured.

Table 8. Effect of diluent on surface tension lowering of phosphoric acid solutions with OPAP

Procedure: Phosphoric acid solutions were equilibrated at an organic/aqueous phase ratio of 1/1 with 0.2 M OPAP (0.09 M MOPPA + 0.12 M DOPPA) in the indicated diluent. The surface tension of the equilibrated phosphoric acid solutions was measured.

Diluent	Surface tension (dynes/cm)	
	Reagent grade acid	Wet-process acid
None	77.2	77.8
Hexane	35.4	40.7
Octane	—	39.4
Escaid 200	—	37.0
n-dodecane	32.5	36.6
n-paraffin	—	37.6
Kermac 627	—	36.8
Escaid 110	—	37.7
Kermac 470B	32.5	39.8
Isopar M	—	37.4
LOPS	—	38.1
Certrex 39	—	37.7

equilibrated aqueous phases was measured. The results show little diluent effect, with perhaps slightly more surface tension lowering with increasing n-paraffin chain length. The surface tension of the equilibrated reagent grade acid solutions was slightly lower than that of the wet-process acid solutions.

A total carbon analyzer was used to measure carbon concentration in the phosphoric acid solutions. The analyzer was standardized with solutions of potassium acid phthalate in 0.6 and 6.0 \underline{M} H_3PO_4 (Fig. 18). The measured carbon concentrations in the test solutions were about 100 ppm leaving the settler and about 60-70 ppm leaving the entrainment separator. The concentration in the acid leaving the system was reduced to about 40 ppm in the test with the air column and to 5-15 ppm in the tests with the carbon and XAD-2. These concentrations are close to those the acid would contain if the carbon was due to MOPPA distribution loss, but are considerably lower than the 280 ppm that would be present if the carbon was due to the organic phase volume loss measured in the test (Fig. 19).

Titration and chromatographic analyses of the organic material removed from the phosphoric acid showed that it was essentially all MOPPA and that it contained little or no DOPPA. The carbon and XAD-2 columns were eluted with acetone. Titration of the residues after removal of the acetone indicated the following composition:

Column	Amount of material recovered (g)	Concentration (%)		Estimated MOPPA distribution loss (g)	MOPPA recovered (g)
		MOPPA	DOPPA		
Carbon	1.96	96.5	1.5	3.1	1.9
XAD-2	1.04	76	<0.1	0.3	0.7

Chromatographic analyses showed that MOPPA, OP, and peak 3 (see Sect. 2.2) were present in both samples of recovered material, but DOPPA was not detected. The amounts of MOPPA recovered are in fair agreement with the amounts lost by distribution to the phosphoric acid. In the test

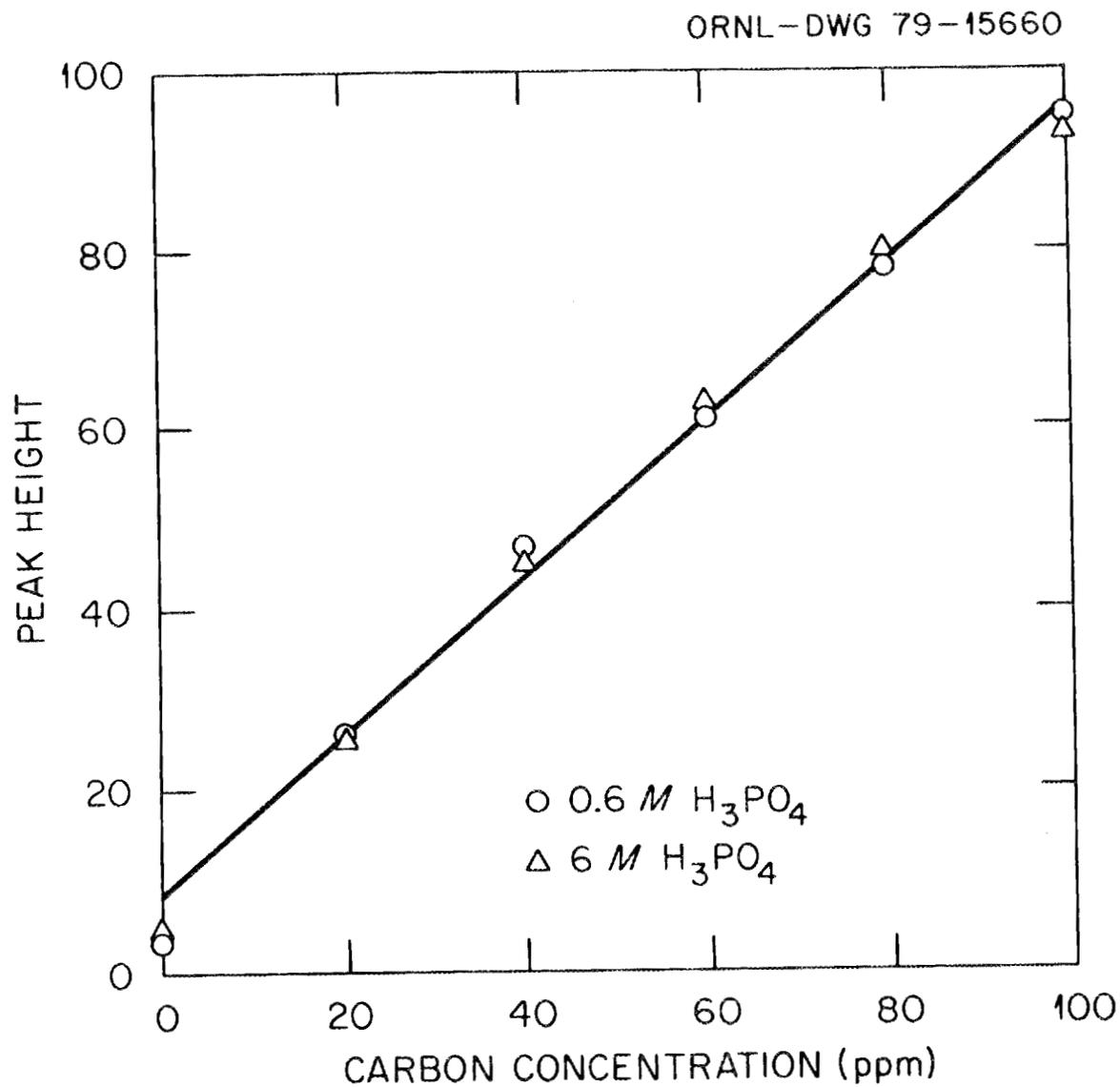


Fig. 18. Standard curves for total carbon analyzer. Standard solutions were potassium acid phthalate in 0.6 or 6 M H₃PO₄.

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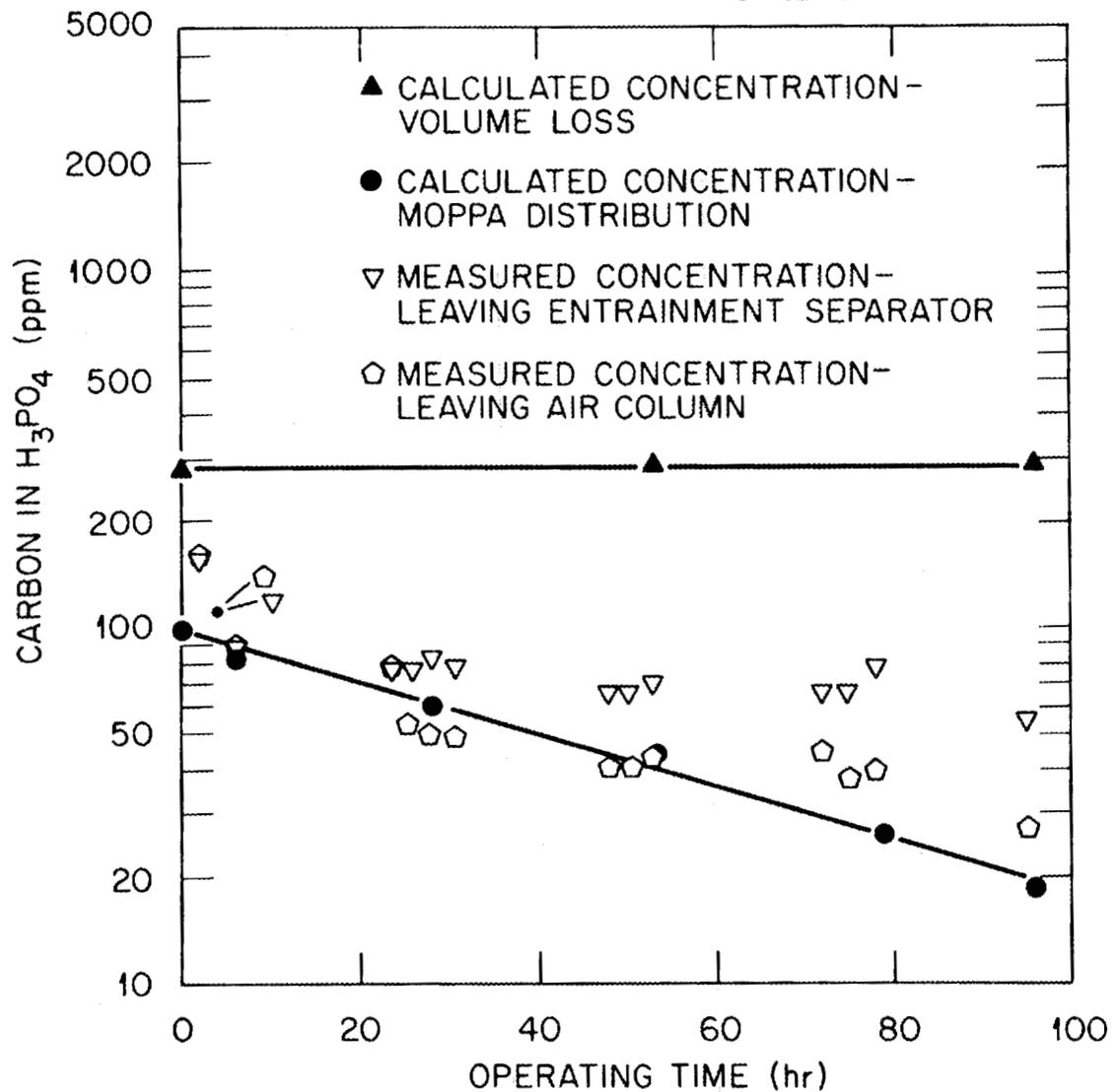


Fig. 19. Measured and calculated carbon concentrations in phosphoric acid solutions from 1-stage continuous test.

with air, about 50 cc/min of compressed air was introduced through a frit at the bottom of the column, and passed up the column countercurrent to the acid flow. About 20 ml of a waxy emulsion that contained air and aqueous phase collected on top of the acid in the column in the 73 hr that it was in operation. The emulsion could not be broken by centrifugation and the addition of hexane was required to separate it into two phases. Although the color of the emulsion was the same as the color of the bulk organic phase, titration of the recovered material showed that it contained 2.3 g of MOPPA and less than 0.1 g of DOPPA. A liquid chromatographic analysis indicated that the material was predominantly MOPPA but that it also contained smaller concentrations of the other OPAP components. The recovered material did not contain nearly enough DOPPA to account for the organic phase volume loss, but it contained more MOPPA than was lost as organic phase volume. This suggests the recovered material was mostly MOPPA that had been lost by distribution to the aqueous phase, along with a small amount of entrained organic phase, which agrees with the data of Fig. 19.

The organic phase volume losses are substantial and real. They are systematic, reproducible losses that apparently are a function of phosphoric acid volume and/or contact time. Our tests to measure or recover it have been made on the assumption that the mechanism of the losses is by entrainment in the phosphoric acid. Our test results indicate, however, that this is not the case. Although it is possible the organic leaves the system as a spray into the air or somehow remains in the equipment when it is disassembled, neither of these mechanisms has yet been substantiated.

APPENDIX

Appendix

Purification of OPAP Fractions

As described in Sect. 2.1, OPAP is prepared by reacting octyl phenol with phosphorous pentoxide to form an approximately equimolar mixture of MOPPA and DOPPA. The reaction mixture also contains impurities such as unreacted octyl phenol, trioctylphenyl phosphate, hydrolyzable material that is probably pyrophosphoric acids, and other unidentified impurities. Peppard et al., separated the major fractions from each other by partitioning the acid form of OPAP or its sodium salt between ethylene glycol and organic diluents.^{15,16} The MOPPA distributes primarily to the ethylene glycol and the DOPPA distributes primarily to the organic phase. The separated DOPPA was purified by scrubbing the organic phase and evaporating the diluent; in some cases it was further purified by recrystallization from heptane. The MOPPA was extracted from the ethylene glycol (after dilution with water) into diethyl ether and a purified product was prepared by scrubbing the ether extract and then evaporating the ether.

The basic separation in our first preparation, for the earlier process development studies,⁹ was made by partitioning the acid form of OPAP between ethylene glycol and hexane. The separated DOPPA was converted to the sodium salt, diluted with ethylene glycol, and scrubbed with hexane in a continuous extractor¹⁷ to remove nonacidic impurities. The product prepared by acidifying the scrubbed sodium salt, extracting it into hexane, and evaporating the hexane contained 1.5% MOPPA and 93.3 % DOPPA. The DOPPA yield was about 60%. The same procedure was used to purify the MOPPA sodium salt. Stable emulsions formed when the scrubbed Na salt was acidified, and the addition of EtOH was required to break them. The acidified sodium salt was extracted into benzene and the final MOPPA product was prepared by evaporating the benzene. It contained 90.4% MOPPA and 1.0% DOPPA; the MOPPA yield was about 50%.

A more efficient primary separation was obtained by precipitating the MOPPA sodium salt from ethyl alcohol.¹⁸ The MOPPA sodium salt is essentially insoluble in 97-98 vol % ethanol (Fig. A-1), and can be

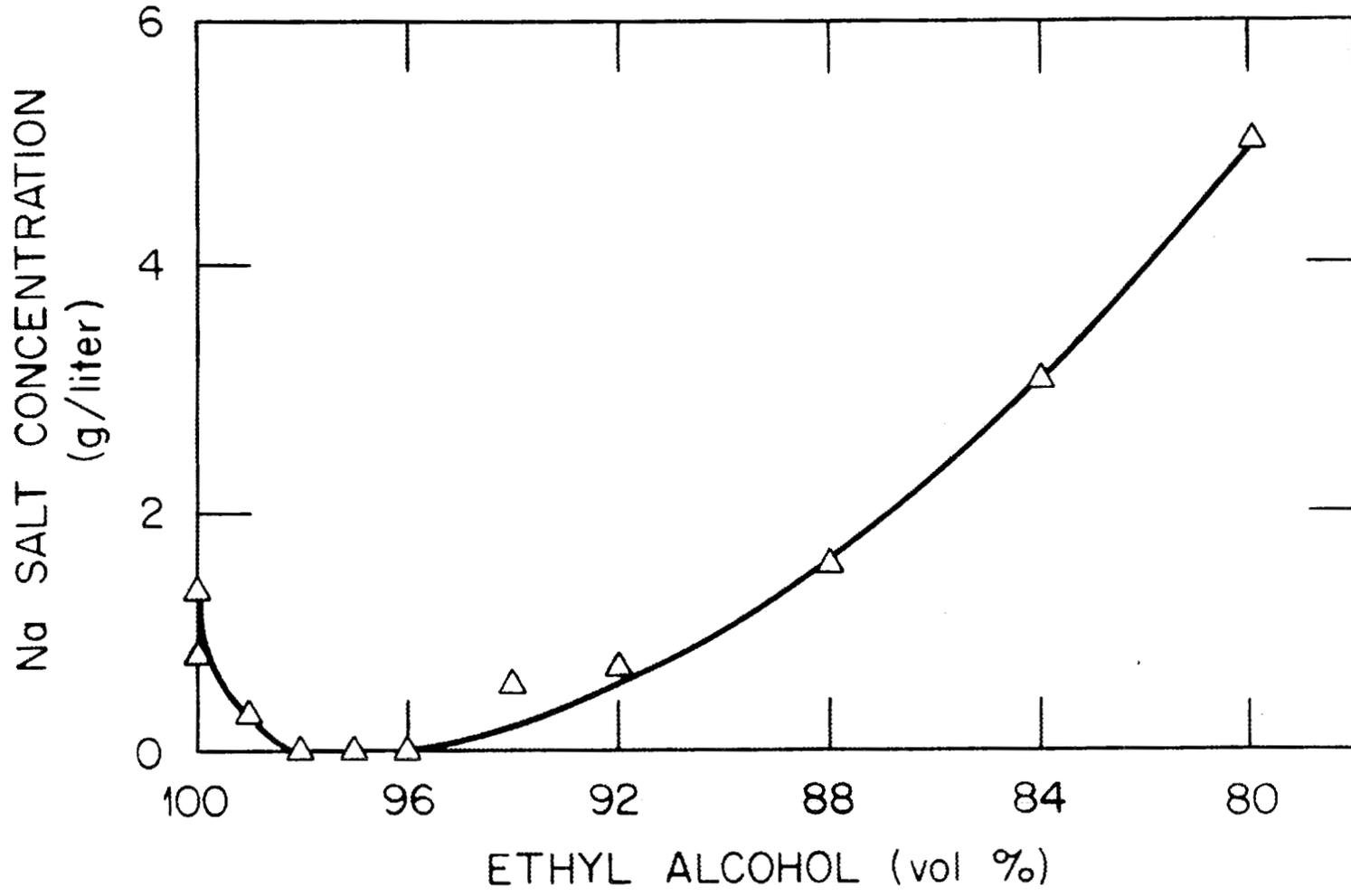


Fig. A-1. Solubility of MOPPA sodium salt in ethanol-water solutions.

obtained as a bulky, easily filtered solid by dissolving OPAP in absolute ethanol and converting to the sodium salt with 10 M NaOH. The DOPPA sodium salt and most of the impurities remain in solution.

Essentially pure (>99%) MOPPA was prepared from the sodium salt by acidification, extraction into diethyl ether, evaporation of the ether, and a final wash with petroleum ether (MOPPA has limited solubility in this solvent) to remove residual impurities.

DOPPA was purified by precipitating the copper salt as described by Partridge and Jensen.¹⁹ The alcohol was evaporated from the DOPPA sodium salt; it was dissolved in toluene, and converted to the copper salt by equilibration with CuSO_4 solution. Most of the toluene was evaporated and the copper salt solution was added to chilled acetone. The precipitated copper salt was filtered, washed, dissolved in toluene and converted to the acid form. After evaporation of the toluene, final purification of the product was made by recrystallization from hexane or dodecane. The product was >99% pure and the yield was about 40%. The copper salt of DOPPA (or of some of the impurities) is somewhat gummy and much harder to handle than the copper salt of di(2-ethylhexyl) phosphoric acid.

Chromatograms of the purified products, both >99% pure by titration, are shown in Fig. A-2. The DOPPA chromatogram contains an injection artifact but neither shows any impurities.

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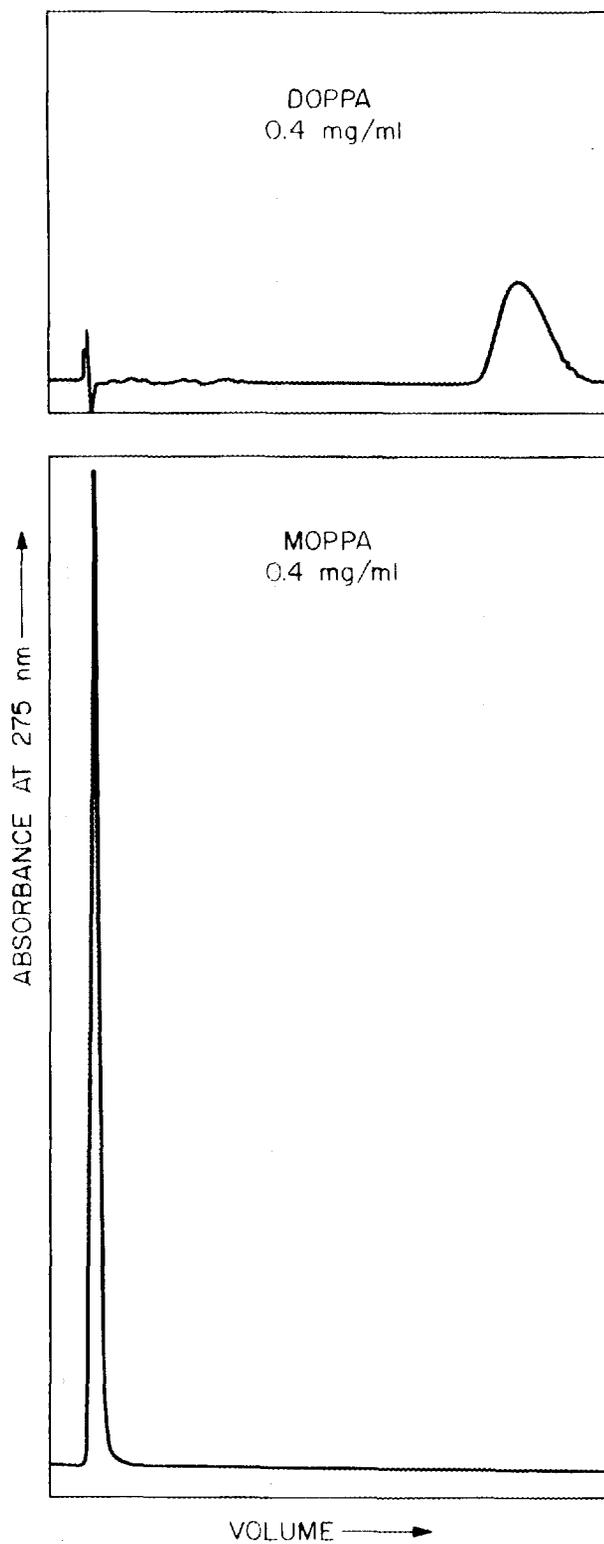


Fig. A-2. Liquid chromatographic analysis of purified MOPPA and DOPPA.

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