CYANEX®301 Extractant

Solvent Extraction Reagent

- Extracts zinc, cadmium and many other metals at low pH.
- Selective for heavy metals vs alkaline and alkali earths.

CYTEC

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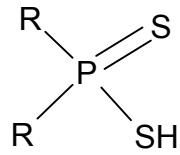
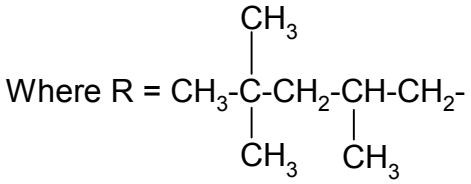
INTRODUCTION

CYANEX 301 is a dialky1dithiophosphinic acid extractant. This sulfur-containing compound is a much stronger acid than its analogous oxy-acid, CYANEX 272. As such, it is capable of extracting many metals at lower pH (<2). CYANEX 301 extractant does not discriminate between heavy metals in this pH range, however, a high degree of selectivity of extraction of heavy metals vs the alkaline earths is observed. This reagent was originally developed for the selective extraction of zinc from effluent streams also containing calcium, such as those generated in the manufacture of rayon by the viscose process.

Chemical Structure

The active component of CYANEX 301 extractant is bis(2,4,4-trimethylpentyl)dithiophosphinic acid.





Molecular Weight = 322

Typical Properties

Appearance	:	Green mobile liquid
Odor	:	Faintly characteristic of hydrogen sulfide
Assay	:	75-80% Bis(2,4,4-trimethyl pentyl) dithiophosphinic acid
Specific Gravity	:	0.95 at 24°C
Viscosity	:	78 centipoise at 24°C
Boiling Point	:	Decomposes at 220°C
Pour Point	:	-34°C
Flash Point (Closed Cup)	:	165°F(74°C)
Solubility in Water	:	7 mg/L*

**Solubility will be lower in aqueous solutions* containing dissolved *salts.*

MATERIALS OF COMPATIBILITY

Plastics

Samples of the following plastics and rubbers, in the form of tubing, were immersed for 1000 hours at 50°C in glass vessels containing CYANEX 301. The weights and dimensions of the test samples were determined before and after immersion. The following observations were made.

Material	Remarks
PVC (Solvent Grade)	No change in weight or dimensions. Loss of plasticity. Short-term suitability only.
PVC (Heavy Duty Chemical Grade)	15% loss in weight. Color change from transparent to black. Loss of plasticity. Short term suitability only.
PVC (Laboratory Grade)	20% loss in weight. Loss of plasticity. Short term suitability only.
Polyethylene	Suitable. No change significant changes in weight or dimensions
Polypropylene	Suitable. No change in weight or dimensions.
Teflon Fluorocarbon Film*	Suitable. No change in weight or dimensions.
Latex	Unsuitable. Twofold increase in dimensions.
Viton Fluoroelastomer*	15% increase in weight. Some loss of flexibility. Short term suitability only.

Metals

Samples of stainless steel (316 and 304) and mild steel in the form of coupons (approximate dimensions 50 mm x 20 mm x 3 mm) were immersed for 24 hours at 50*C in glass vessels containing CYANEX 301. No detectable corrosion was observed in this period. However, the shiny surfaces of the test samples became dull and the CYANEX 301 was severely discolored. None of the test metals are recommended for extended service.

**Product of E.L Dupont de Nemours & Co.*

HYDROLYTIC STABILITY

Experiments were conducted to investigate the stability of CYANEX 301 extractant in contact with hydrochloric and sulfuric acid.

A solvent containing CYANEX 301 extractant was contacted with 75 g/L HCI or 300 g/ L H_2SO_4 in a stirred resin flask at A/O=1 and 50°C for a total of 411 hours (HCI) and 466 hours (H_2SO_4).

The flask was equipped with a condenser to minimize diluent evaporation.

Samples of the dispersed phase were removed periodically and the coalesced solvent analyzed by base titration. The results are given in Table 1 and Figure 1.

Although some degradation did occur, the rate appeared to decrease after approximately 300-350 hours in both sulfuric and hydrochloric acids. The observed degradation is approximately equivalent to a plant residence time of 200-250 days.

FIGURE 1
HYDROLYTIC STABILITY

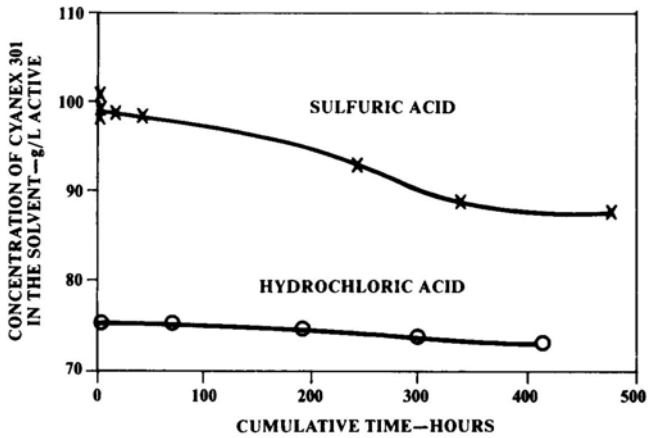


TABLE 1 - STABILITY TESTING

Solvent	:	CYANEX 301 extractant in Exxsol D-80 diluent*
Aqueous	:	75 g/L HCI or 300 g/L H_2SO_4
A/O	:	1
Temperature	:	50°C

	Cumulative Time (Hours)	Solvent Analysis (g/L Active)
Hydrochloric Acid	0	75.6
	62	75.3
	196	74.5
	300	73.8
	411	73.6
Sulfuric Acid	0	98.1
	1	100.3
	2	99.1
	4	98.3
	15	97.9
	52	97.4
	235	91.5
	338	88.4
	466	88.1

**A product of Exxon Co., U.S.A.*

PERFORMANCE DATA

General Extraction Properties

CYANEX 301 extractant is capable of the selective recovery of heavy metals at low pH in the presence of alkaline earths. This is illustrated by the data obtained in some batch, shake-out tests and given in Table 2.

It is also known that this type of compound is capable of extracting cadmium from wet process phosphoric acid[1] and amino acids from fermentation broths.[2]

TABLE 2 - EFFECT OF pH ON METAL EXTRACTION

Solvent	:	160 g/L CYANEX 301 extractant in toluene
Aqueous	:	0.015 M in Zn^{2+}, Ca^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} Mg^{2+} and Fe^{3+} as their sulfate salts
Temperature	:	50°C
Time	:	5 minutes
A/O	:	1
pH Adjustment	:	H_2SO_4 or NH_4OH, as appropriate

% Extraction

Equilibrium pH	Zn^{2+}	Ca^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Mg^{2+}	Fe^{3+}
0.48	100	0.8	87.6	99.1	100	0	37.6
0.90	100	0.6	98.2	100	100	0	55.2
1.55	100	0.7	99.9	100	100	0	97.1
2.15	100	1.1	100	100	100	0	99.5
2.55	100	1.0	100	100	100	0	100

Zinc-Calcium Separation

CYANEX 301 extractant was originally developed to recover zinc from the effluent streams of viscose rayon plants.[3] Zinc and calcium are present in this effluent in the form of their sulfate salts at a pH between one and two. The objective was to recover the zinc and recycle it for use in the viscose process acid bath.

It is important to make a highly selective zinc-calcium separation because, if calcium is recycled to the acid bath, gypsum forms and its precipitation has a deleterious effect on the rayon product. One further constraint is that the solvent extraction process must operate at the pH of the effluent. The low dollar value of the zinc and the comparatively low solution tenors, <1 g/L, make it uneconomical to adjust the pH.

[1] *Process For the Recovery of Cadmium and Other Metals From Solution. L W Bierman, et al, U.S. Patent 4,511,541 (1985)*
[2] *Extraction of Amino Acids ftom an Aqueous Solution with Dithiophosphinates. C. Savides and J. H. Bright, U.S. Patent 4,536,596 (1985)*
[3] *Selective Removal of Metals From Aqueous Solutions With Dithiophosphinic Acids. R.J. Boyle, et al, U.S. Patent 4,721,605 (1988)*

Zinc-calcium separation can be effected by such organophosphorus extractants as CYANEX 272 but pH adjustment to approximately 3 is required for complete recovery. In contrast, CYANEX 301 is a stronger acid and complete zinc extraction is possible in the pH range 1-2. Additionally, this reagent exhibits a high selectivity for zinc versus calcium.

This is illustrated by the pH isotherms for CYANEX 301 and CYANEX 272 extractants which are shown in Figure 2. The corresponding data are given in Table 3.

FIGURE 2
ZINC-CALCIUM SEPARATION COMPARING CYANEX 301 AND CYANEX 272

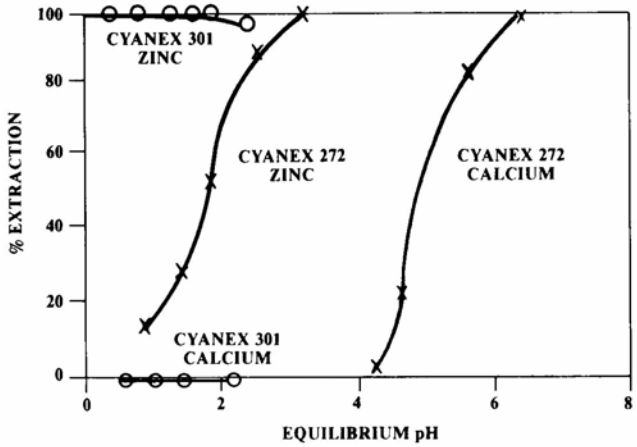


Table 3
ZINC-CALCIUM SEPARATION WITH CYANEX 301 AND CYANEX 272 EXTRACTANTS

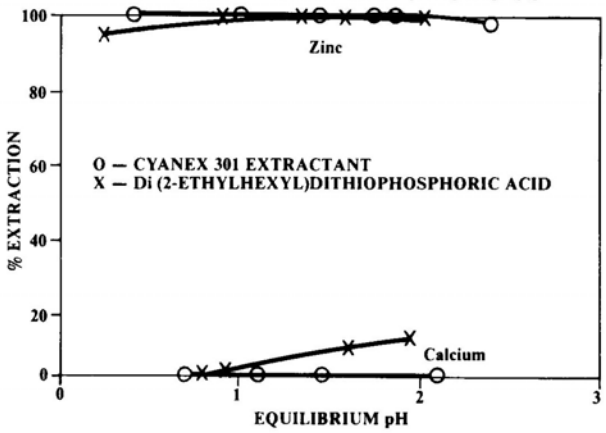
Solvent	:	0.6 M extractant in Kermac 470B diluent*
Aqueous	:	Single metal sulfate solutions, 0.015 M in metal ion
Temperature	:	50°C
pH control	:	H_2SO_4 or NH_4OH appropriate
A/O	:	1

CYANEX 301 Extractant				CYANEX 272 Extractant			
Zn		Ca		Zn		Ca	
Equilibrium pH	**% Extraction**	**Equilibrium pH**	**% Extraction**	**Equilibrium pH**	**% Extraction**	**Equilibrium pH**	**% Extraction**
0.41	99.9	0.62	0	0.90	14.6	4.15	3.4
0.91	100	1.11	0	1.42	24.2	4.53	20.4
1.42	100	1.50	0	1.88	53.3	5.38	81.7
1.67	100	2.06	0	2.40	87.7	6.52	99.6
1.87	100			3.08	99.4		
2.35	97.5						

** A product of Kerr-McGee Corp. U.S.A.*

Dithiophosphoric acids are also commercially available. However, acids of this type do not exhibit the high selectivity for zinc versus calcium which is associated with CYANEX 301. This is illustrated by the pH isotherms for di (2-ethylhexyl) dithiophosphoric acid and CYANEX 301 which are plotted in Figure 3. The isotherms were obtained under the same conditions as outlined in Table 3.

FIGURE 3
Zn—Ca SEPARATION
A COMPARISON OF
PHOSPHINIC & PHOSPHORIC ACIDS



Zinc Extraction and Stripping

A zinc extraction isotherm for a solvent containing 100 g/ L CYANEX 301 is plotted in Figure 4 using the data given in Table 4. The isotherm has an almost ideal shape; indicative of low staging requirements. For example, the McCabe-Thiele construction in Figure 4 implies complete recovery from a stream containing 6 g/ L Zn in two theoretical stages at A/O=1.

FIGURE 4
ZINC EXTRACTION ISOTHERM

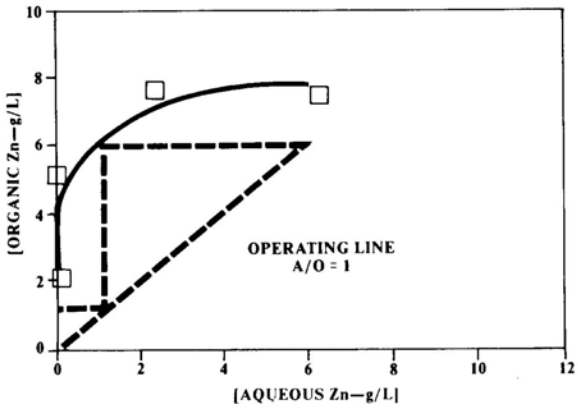


TABLE 4 - ZINC EXTRACTION ISOTHERM

Solvent	:	100 g/L CYANEX 301 extractant in Exxsol D-80 diluent
Aqueous	:	9.95 g/L Zn^{2+} as the sulfate
Temperature	:	50°C
pH	:	Controlled to 1.50 ± 0.05 with 200 g/L NaOH
Time	:	2 minutes contact after obtaining a stable equilibrium pH

	Equilibrium Zn Concentration (g/L)	
A/O	Organic	Aqueous
0.2	1.99	0
0.5	4.98	0
1	7.58	2.37
2	7.64	6.13

CYANEX 301 is not readily stripped as indicated by the stripping isotherm obtained using 300 g/L H_2SO_4 as the strip feed (Table 5 and Figure 5). Isotherms of this type are difficult to interpret using standard McCabeThiele constructions. However, a continuous, countercurrent, mini-plant test did reveal that a strip liquor containing in excess of 20 g/ L Zn could be produced (Table 6 and Figure 6). A solution of this composition is suitable for recycle in the viscose process.

TABLE 5 - ZINC STRIPPING ISOTHERM

Solvent	:	100 g/L CYANEX 301 extractant in Exxsol D-80 diluent loaded to 7.29 g/L Zn by contact with a $ZnSO_4$ solution
Strip Feed	:	300 g/L H_2SO_4
Temperature	:	50°C
Time	:	5 minutes

	Equilibrium Zn Concentration (g/L)	
A/O	Organic	Aqueous
5	1.84	1.09
2	2.85	2.22
1	3.59	3.70
0.5	4.24	6.10
0.2	4.93	11.8
0.1	5.45	18.4
0.05	5.71	31.6

FIGURE 5
ZINC STRIPPING ISOTHERM

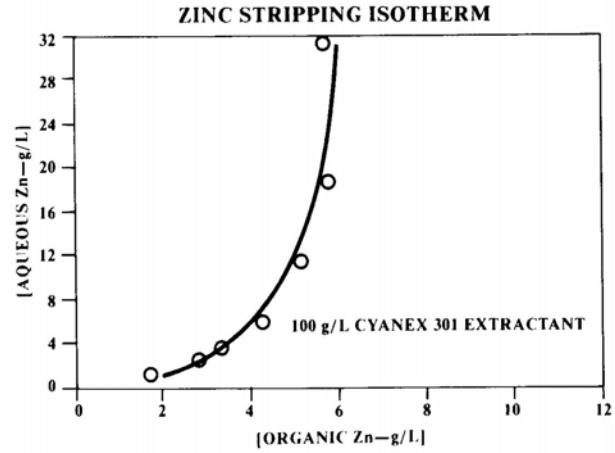
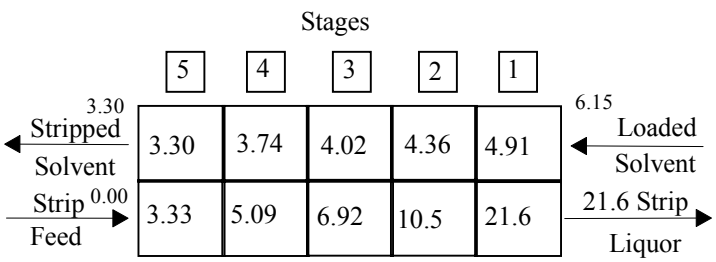


TABLE 6 - CONTINUOUS, COUNTER CURRENT TESTING: EXPERIMENTAL CONDITIONS

Stages	:	5
O/A	:	10
Solvent	:	100 g/L CYANEX 301 extractant In Exxsol D-80 diluent, loaded To 6.15 g/L Zn
Strip Feed	:	300 g/L H_2SO_4
Duration of Test	:	4 hours
Temperature	:	40°C

Figure 6
Continuous Stripping Test: Circuit Profile

Strip Feed = 300 g/L H_2SO_4



Numbers Refer to Zinc Solution Tenors IN g/L

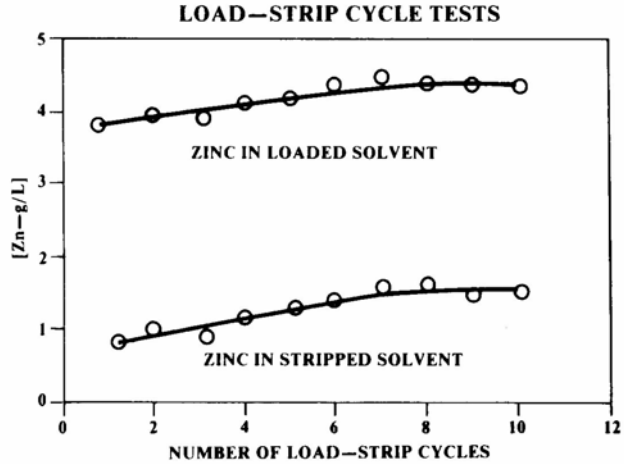
Although zinc is not readily stripped from CYANEX 301, there is no evidence of a zinc accumulation on the solvent which would lead to poisoning. This is illustrated by the results of some cycle tests where zinc was repeatedly loaded and stripped from a solvent containing CYANEX 301. The results are given in Table 7 and plotted in Figure 7.

TABLE 7 - LOAD-STRIP CYCLE TESTS

Solvent	:	50 g/L CYANEX 301 extractant In Exxsol D-80 diluent
Aqueous	:	10 g/L Zn as sulfate (loading)
pH	:	1.50±0.05 (loading): controlled with 200 g/L NaOH
Strip Feed	:	500 g/L H_2SO_4
Temperature	:	50°C (loading and stripping)
A/O	:	1 (loading and stripping)
Phase Continuity	:	Aqueous continuous (loading And stripping)

Load-Strip Cycle	Zinc In Loaded Solvent (g/L)	Zinc In Stripped Solvent (g/L)
1	3.90	0.78
2	3.95	0.89
3	3.92	0.84
4	4.08	1.06
5	4.18	1.21
6	4.35	1.33
7	4.45	1.44
8	4.42	1.46
9	4.35	1.40
10	4.32	1.39

FIGURE 7
LOAD—STRIP CYCLE TESTS



Recovery of Amino Acids

Dialky1dithiophosphinic acids, or their salts, have been shown to be effective in extracting a number of α-amino acids from fermentation broths. This will be illustrated with particular reference to the recovery of L-phenylalanine using CYANEX 301 extractant.

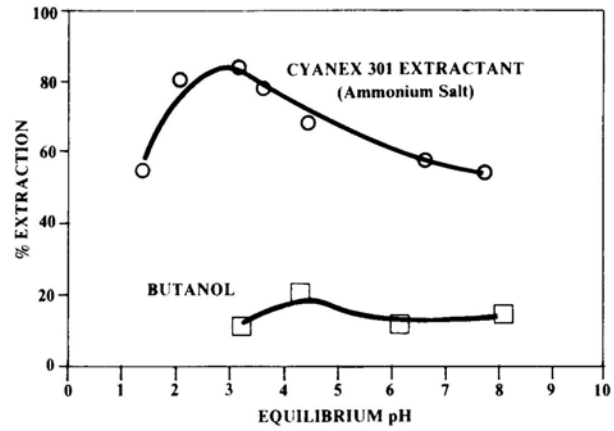
CYANEX 301 is more powerful and less water soluble than other extractants which might be used for the same purpose e.g. butanol. This can be seen by the results of shake-out tests (Table 8 and Figure 8) which show the effect of pH on the extraction of L-phenylalanine with CYANEX 301 and butanol.

TABLE 8 - EFFECT OF pH ON THE EXTRACTION OF L-PHENYLALANINE

Solvent : (1) 283 g/ L CYANEX 301 extractant (ammonium salt) in decanol
(2) butanol (undiluted)
(3) decanol (undiluted)
Aqueous : 25.5 g/L L-phenylalanine
Temperature : 25°C
A/O : 1
Contact Time : 5 minutes

	% Extraction	Equilibrium pH
	55	1.5
	80	2.3
	84	3.1
CYANEX 301	80	3.5
	69	4.5
	58	6.5
	54	7.6
	13	3.4
Butanol	20	4.2
	15	6.1
	16	8.1
Decanol	2	3.0
	1	6.7

FIGURE 8
EFFECT OF pH ON THE EXTRACTION OF PHENYLALANINE



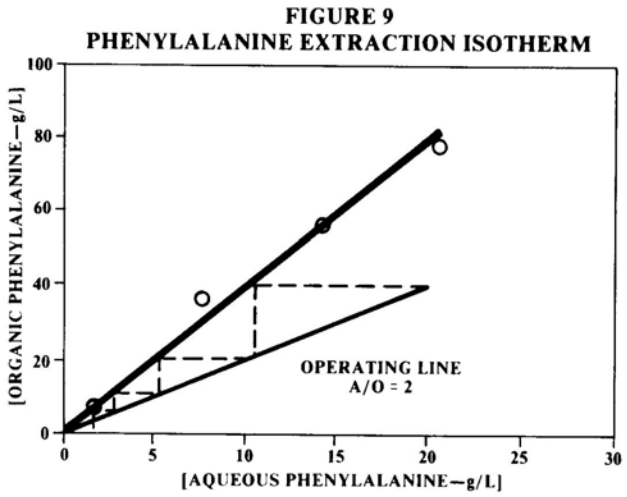
Additionally, interpolations from an extraction isotherm obtained with CYANEX 301 (Table 9 and Figure 9) indicate essentially quantitative recovery at A/O=2 in five or six theoretical stages from a fermentation broth containing 20 g/L L-phenylalanine. A polar diluent, such as decanol, is required for good extraction performance. CYANEX 301 was used in its ammonium salt form in the above two series of tests.

TABLE 9 -L-PHENYLALANINE EXTRACTION ISOTHERM

Solvent : 283 g/ L CYANEX 301 extractant (ammonium salt) in decanol

Aqueous : 25.5 g/L L-phenylalanine
Equilibrium pH : 3.0-3.3
Temperature : 25°C
Contact Time : 5 minutes

	Equilibrium Concentration (g/L)	
A/O	Organic	Aqueous
0.2	4.8	14.0
2	36.0	79.0
5	56.0	14.4
15	78.0	20.4



Dialky1dithiophosphinic acids extract α-amino acids through a pH dependent mechanism. Extraction is favored at a pH of approximately 3 while stripping is favored at both higher and lower pH (Figure 8). Water, at a pH of approximately 1.3-1.7, has been used successfully to strip L-phenylalanine from reagents similar in composition to CYANEX 301 extractant. A salting-out agent in the strip feed, e.g. 10-20% $(NH_4)_2SO_4$ or NH_4Cl, is required to maintain good phase disengagement characteristics. Data indicate that the amino acid may be selectively separated from the strip liquor by fractional crystallization due to its comparatively low aqueous solubility (approximately 30 g/ L at 25°C).

ANALYTICAL METHODS

ANALYSIS IN ORGANIC SOLVENTS

The gas chromatographic procedure described below is suitable for the accurate determination of the concentration of CYANEX 301 in organic solvents, typically containing 5-50 (v/o) CYANEX 301.

The active ingredient present in CYANEX 301 is bis(2,4,4-trimethylpentyl) dithiophosphinic acid. This acid is converted to the corresponding methyl ester for analytical purposes. Trioctylphosphine oxide (TOPO) is employed as an internal standard (ISTD).

Reagents

1. TOPO (purified-see note 1)
2. Methyl-8® (dimethylformamide dimethylacetal, Pierce Chemical Co.)

Calibration

The relative response factor of the dithioacid vs. TOPO must be determined. For the analytical conditions below, the RRF was found to have a value of 1.09 (see note 2).

Procedure

1. Accurately weigh 0.10 g of TOPO and combine with a 1.0 mL aliquot of the organic solution of CYANEX 301 in a Pierce 3 mL Reacti-vial®.
2. Add 0.4 mL of Methyl-80 (see note 3) and maintain the mixture at 65°C, with occasional swirling, for 1 hour.
3. Allow the mixture to cool to ambient temperature, then analyze as described under "Gas Chromatographic Conditions".

Calculations

$$\text{Concentration of } R_2PSSH \text{ (g/L)} = \frac{\text{Area of } R_2PSSCH_3 \times 1000 \times 1.09 \times \text{wt. ISTD}}{\text{Area of TOPO}}$$

Where wt. ISTD = wt. TOPO (g)

Gas Chromatographic Conditions

Instrument	:	Perkin-Elmer Sigma 115 or equivalent
Column	:	Supelco SPB-1 (100% methyl silicone) fused silica capillary column, 30 m x 0.32 mm I.D., 0.25 µ film thickness
Injection Volume	:	0.1 µL
Detector	:	FID
Carrier Gas	:	Helium at 70 psi
Auxiliary Gas	:	Nitrogen at 16 psi
Column Flow	:	1.0 mL/min
Split Ratio	:	60.1
Temperatures	:	°C
Detector	:	290
Injector	:	290
Oven	:	220 (0 min.) programmed to 300 At 10°C/min
Peak Areas	:	Determined by electronic intregation

Notes

1. Pure TOPO can be obtained by recrystallizing commercial grade TOPO from hexane (three recrystallizations are necessary).
2. The RRF value for R2PSSH vs. TOPO used here was found to be constant for 5-50 (v/o) solutions of CYANEX 301 in Exxsol D-80.
3. Methyl-8® or equivalent methylating agent is employed to prepare the methyl ester of R_2PSSH.
4. This method has not been validated.

ANALYSIS IN AQUEOUS SOLUTION

The procedure is based upon extracting the reagent into methylene chloride and determining the concentration of bis(2,4,4-trimethylpentyl) dithiophosphinic acid by gas chromatography. Trioctylphosphine oxide (TOPO) is used as an internal standard (ISTD).

The solubility of CYANEX 301 extractant in water is 7 mg/L. Soluble losses to a raffinate may be expected to be lower.

Reagents

1. Methyl-8® Concentrate. Pierce Chemical Co.
2. TOPO (purified-see note 1)

Calibration

1. Prepare a stock solution of TOPO (ISTD) by accurately weighing (± 1 mg) approximately 100 mg of TOPO into a 10 mL volumetric flask. Dilute to 10 mL with methylene chloride and dissolve the TOPO.

2. Determine the relative response factor of the dithiophosphinic acid with respect to the internal standard (TOPO). This is accomplished by accurately weighing these materials, combining with excess Methyl-8® Concentrate, and analyzing as described under "Gas Chromatographic Conditions".

Procedure

1. A 100 mL aliquot of the aqueous solution is adjusted to pH 1.5 with concentrated HCI and extracted with methylene chloride (3 x 35 mL).

2. The organic extracts are combined and evaporated to 2 mL, transferred to a 3 mL Pierce Reacti-Vial and concentrated with nitrogen to 0.5 mL.

3. Add 70 µL of Methyl-8® concentrate, followed by 100 µL, of TOPO stock solution (ca. 100 µg TOPO).

4. Inject 0.1 µL of this solution and analyze as described under "Gas Chromatographic Conditions".

Calculations

1. Concentration of dithiophosphinic acid in aqueous sample (g/L)

$$= \text{RRF} \times 1.25^{*} \times \frac{\text{area of methyl dithophosphinate}}{\text{area of TOPO (ISTD)}} \times \text{wt. ISTD (g)} \times 10$$

** See note 2*

Gas Chromatographic Conditions

Instrument	:	Perkin-Elmer Sigma 115 or equivalent
Column	:	Supelco SPB-1 (100% methyl Silicone) fused silica capillary Column, 30 m x 0.32 mm I.D., 0.25 µ film thickness
Detector	:	FID
Carrier Gas	:	Helium at 70 psi, flowrate 1.0 mL/minute
Temperatures	:	^{o}C
FID	:	290
Injection Port	:	290
Oven	:	100 to 300 at 15oC/minute, hold Final temp. for 2 minutes
Sample Injection Volume	:	0.1 µL, splitless injection with septum Purge after 30 seconds
Peak Areas	:	Determined by electronic integration

Notes

1. Pure TOPO can be obtained by recrystallizing commercial grade TOPO from hexane (three recrystallizations are necessary).

2. A factor (1.25) is used to correct for an incomplete extraction of the dithiophosphinic acid from aqueous solutions. If extraction efficiency is 100%, then the factor is unity. It may be determined by spiking the aqueous feed solution with a known quantity of CYANEX 301 and following the steps as described in "Procedure".
3. Retention times for TOPO and methyl dithiophosphinate are approximately 14 and 10 minutes, respectively.
4. The detection limit is approximately 1 mg/L.
5. This method has not been validated.

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