

CYTEC



CYANEX[®] 471X Extractant

Solvent Extraction Reagent

- Selective for silver
- Separates palladium from platinum

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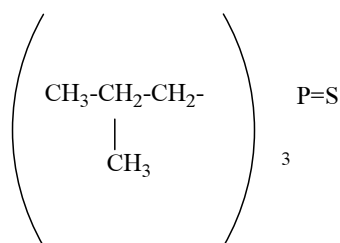
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CYANEX 471X extractant is a new phosphine-based extractant developed by Cyanamid for the hydrometallurgical industry.

This reagent is particularly useful for the selective recovery of silver and in the separation of palladium from platinum.

Chemical Structure



Triisobutylphosphine Sulfide (TIBPS)

Typical Properties

Appearance	: Off-white crystalline solid
Specific Gravity at 22°C	: 0.91
Melting Point	: 58-59°C
Solubility in Distilled Water	: 43 µg/mL at 24°C

Stability

Some hydrolysis of CYANEX 471X extractant (triisobutylphosphine sulfide) to the oxide or other oxygen bearing degradation products might be expected on continuous contact with sulfuric or hydrochloric acid systems. However, as can be seen in Tables 1 and 2, we found that no measurable degradation (detectable by gas chromatography) occurs even at elevated temperatures for 30-40 day exposure periods. Furthermore, gas chromatographic analysis of the aqueous phase at the completion of each test also failed to detect any degradation products.

TABLE 1 – IN CONTACT WITH SULFURIC ACID

Solvent	: 25.9 g/L CYANEX 471X extractant 5 v/o D2EHPA in Varsol* DX-3641 diluent
Aqueous	: 6N H ₂ SO ₄
Temperature	: 50°C
A/O	: 1

Solvent Analysis		
Contact time (hr)	CYANEX 471X Extractant (g/L)	Oxide Concentration (g/L)
0	25.9	<0.1**
2	24.7	<0.1
336	25.1	<0.1
676	26.4	<0.1

TABLE 2 – IN CONTACT WITH HYDROCHLORIC ACID

Solvent	: 142.7 g/L CYANEX 471X extractant, in Varsol DX-3641 diluent
Aqueous	: 1.1 g/L Pd (as PdCl ₂), 2N HCl
Temperature	: 50°C
A/O	: 1

Solvent Analysis		
Contact time (hr)	CYANEX 471X Extractant (g/L)	Oxide Concentration (g/L)
0	142.7	<0.1**
2	146.2	<0.1
158	142.7	<0.1
216	145.2	<0.1
844	143.9	<0.1
964	146.3	<0.1

* A product of Exxon Co., USA

** Detection limit of analytical method.

Toxicity

The acute oral (rat) and acute dermal (rabbit) LD₅₀ values for the active phosphine sulfide contained in CYANEX 471X extractant are 10,000 mg/kg of body weight. No significant skin irritation and only mild eye irritation were produced during primary irritation studies with rabbits. The sulfide was determined to be non-mutagenic in the Ames *Salmonella* Assay.

4 Silver Recovery

Background

CYANEX 471X extractant is a solvating reagent and will extract silver from sulfate, nitrate and chloride systems. Note that, although silver chloride is essentially insoluble in water, it does exhibit finite solubility in chloride solutions, as follows:

Temperature : 25°C		
HCl (g/L)	AgCl(g/L)	Specific Gravity
235	1.12	1.10
372	3.91	1.16
443	4.44	1.19

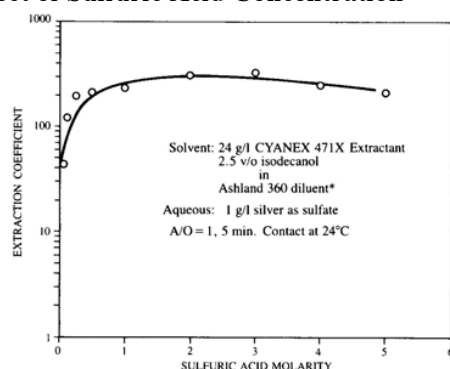
The majority of the world's silver is produced as a by-product from the mining of base metals. Silver may, therefore, form a component of many aqueous streams when the treatment of such ores or secondary sources involves hydrometallurgical processing.

While the source of silver may be a sulfate, chloride or nitrate liquor containing a combination of copper, lead, and other metals, the data cited describes specifically the selective recovery of silver from acid sulfate solutions of zinc or copper.

Effect of Acidity

Since acidity has a significant impact on the extraction power of solvating reagents in many systems (e.g., TBP-uranyl nitrate), the effect of sulfuric acid concentration on silver extraction with CYANEX 471X extractant was studied. Results and experimental conditions are given in Figure 1.

FIGURE 1
Effect of Sulfuric Acid Concentration



As can be seen, silver extraction was essentially quantitative for initial acid concentrations in excess of 0.015M. The small decrease in the extraction coefficient observed with the 4 and 5M acid solutions, may have resulted from a crowding effect due to co-extraction of sulfuric acid.

On the basis of these results the extraction of silver with CYANEX 471X extractant should not be affected by the different sulfuric acid concentrations which might be encountered in commercial practice.

Extraction tests with CYANEX 471X extractant dissolved in Ashland* 360 diluent produced emulsions even when isodecanol was used as a modifier. For this reason, a number of other diluent-modifier combinations were examined under the following conditions.

Solvent	: 24 g/L CYANEX 471X extractant, 0 and 5 v/o modifier in the diluent
Aqueous A/O	: 1 g/L Ag as Ag ₂ SO ₄ , 10 g/L H ₂ SO ₄ : 1
Contact Time	: 5 minutes
Temperature	: 24°C
Diluents	: Varsol DX-3641**, Kermac 470B***, Aromatic 150**
Modifiers	: Isodecanol, Tributylphosphate, D2EHPA

Silver extraction was essentially quantitative in all of the examined systems. However, only those solvents modified with D2EHPA solubilized the extracted complex. This may be due to the displacement of bonded water from the silver ion by the stronger OH ligand present in D2EHPA. The OH group in water is a stronger ligand than in isodecanol and, conceivably, could account for the failure of the alcohol modifier. In later experiments, p-nonylphenol, which like D2EHPA contains an acidic OH group, also proved to be an effective modifier.

* A product of Ashland Chemical Co.

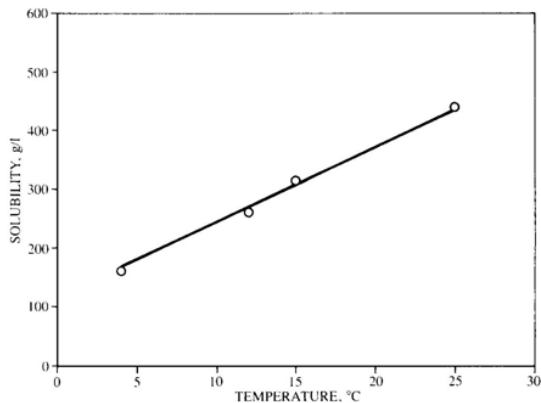
** A product of Exxon Co., USA.

*** A product of Kerr McGee Refining Corp.

Solvent poisoning may occur in a system where the pH is sufficiently high to allow D2EHPA to extract cations such as Fe^{3+} . In this event, p-nonylphenol is the phase modifier of choice.

Based on its performance, availability and the general preference for aliphatic over aromatic diluents, Varsol DX3641 is recommended. The solubility of CYANEX 471X extractant in this diluent is shown as a function of temperature in Figure 2.

FIGURE 2
Solubility in Varsol DX-3641 Diluent



Extraction Isotherms

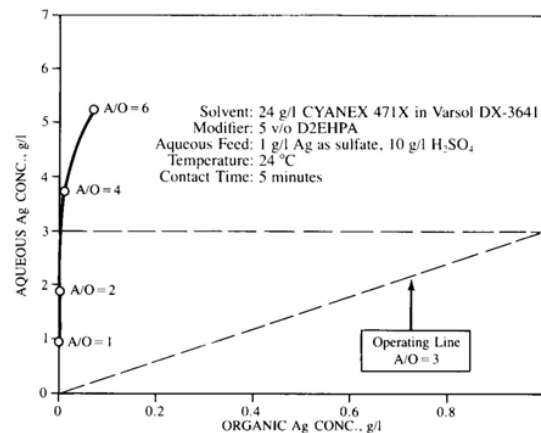
A silver extraction isotherm was generated by contacting an aqueous and solvent feed solution at several A/O ratios. This isotherm along with experimental conditions is shown in Figure 3.

McCabe-Thiele interpolations indicated essentially quantitative silver extraction in one theoretical stage at A/O = 3 from an aqueous solution containing 1 g/L silver. The inflexion in the isotherm suggested that the loading capacity of the solvent (0.1 M in extractant) was being approached at approximately 5.2 g/L Ag (0.024M Ag_2SO_4).

The solvent loaded to 5.2 g/L Ag darkened after several hours standing; possibly a result of the minimal amount of acid which would be expected to co-extract under these conditions and the consequent hydrolysis of the extracted silver complex.

The solvent loaded to 3.7 g/L Ag at A/O = 4 was observed for five days and remained homogeneous.

FIGURE 3
Silver Extraction Isotherm



Stripping Isotherm

Theoretically, stripping may be achieved with any compound which forms a strong ligand with silver. However, reagents proposed in the past for laboratory use have been unsatisfactory for a number of reasons; e.g. cyanide solutions in acid systems are toxic and ammonia tends to form explosively unstable fulminates.

For this reason, it was necessary to find a new stripping system for this class of compounds. The discovery that thiosulfate fixer solutions were effective made possible the commercialization of CYANEX 471X extractant. These reagents are non-toxic and form stable complexes with silver from which silver metal may be recovered by well established processes (see Appendix A). The recovery of metallic silver regenerates the strip liquor which can be recycled. This contributes significantly to lowering process costs.

6 | Silver Recovery

A silver stripping isotherm was constructed by contacting loaded solvents at various A/O ratios with a stabilized thiosulfate solution of the following composition:

COMPONENT	QUANTITY
Water (at 50°C)	: 600 mL
Sodium Thiosulfate, Na ₂ S ₂ O ₃ ·5H ₂ O	: 240 g
Sodium Sulfite Na ₂ SO ₃	: 15 g
Acetic Acid (28%)*, CH ₃ COOH	: 48 mL
Boric Acid (Crystal)**, H ₃ BO ₃	: 7.5 g
Aluminum Potassium Sulfate, AlK (SO ₄) ₂ ·12H ₂ O	: 15 g
Cold Water to make	: 1 liter

The following procedure was adopted to prepare the solution from its components.

- Sodium thiosulfate was dissolved in the specified volume of warm water.
- The remaining components were added in the given order; ensuring that each was dissolved before adding the next.

The isotherm, plotted in Figure 4, indicates efficient stripping.

* To make 28% acetic acid, dilute 3 parts of glacial acetic with 8 parts of water.

** Crystalline boric acid should be used as specified. Powdered boric acid dissolves only with great difficulty and its use should be avoided.

FIGURE 4
Silver Stripping Isotherm



The selective extraction of silver from a copper-zinc sulfate solution was investigated in a continuous, counter-current, mini-plant test using a Bell Engineering mixer-settler apparatus. The solvent was recycled through two extraction and two stripping stages. The thiosulfate strip feed was not recycled. Operating conditions and results are given in Table 3.

TABLE 3 - CONTINUOUS, COUNTER-CURRENT TESTING OPERATING CONDITIONS

Mixer Volume	: 180 mL			
Settler Volume	: 620 mL			
Settler Area	: 88.5 cm ²			
Solvent	: 24 g/L CYANEX 471X extractant, 5 v/o D2EHPA in Varsol DX-3641 diluent			
Aqueous Feed	: 0.97 g/L Ag ⁺ , 6.06 g/L Zn ²⁺ , 10.3 g/L, Cu ²⁺ (as sulfates) 10 g/L H ₂ SO ₄			
Extraction Stages	: 2			
Strip Stages	: 2			
Solution Flow- rates (mL/min)				
Aqueous Feed	: 50			
Solvent	: 50			
Strip Feed	: 50			
Continuous Phase	: Organic (extraction and stripping)			
Temperature	: 24°C			
Duration of Test	: 4 hours			
Analysis				
	Strip Liquor (g/L)			
Raffinate	Ag Recovery	Ag	Zn	Cu
<0.001 g/L Ag	99.9%	0.97	0.012	0.006
Separation Factors:	(Ag/Zn)=0.5 x 10 ⁶			
	(Ag/Cu)=1.5x10 ⁶			

The high separation factors are indicative of the extremely selective separations which can be achieved with CYANEX 471X extractant.

Aqueous Solubility

Although CYANEX 471X extractant has very little solubility in water, there will be some losses and these will vary from system to system depending upon the composition of the aqueous phase and other operating parameters.

For example, losses to the raffinate and strip liquor described in the continuous test were determined to be 6 µg/mL and <1 µg/mL, respectively. Solubility of the corresponding triisobutyl oxide in water is approximately 40 g/L. If any long-term hydrolysis to the oxide does occur, this compound will be lost to the aqueous phase through preferential solubility.

8 Separation of Palladium from Platinum

Background

CYANEX 471X extractant has potential in the separation of palladium from chloride solutions containing platinum (IV) and palladium (II). As with silver, palladium extraction occurs through a solvating mechanism. Similarly, stabilized thiosulfate solutions are an effective strip feed. If present, Ag, Hg (II), Au (III) will be co-extracted with palladium.

The following information on palladium extraction, stripping and palladium/platinum separation will be of use in the design of preliminary batch experiments.

Extraction Isotherms

The results of two extraction isotherms are shown in Table 4. One was generated with an unmodified solvent and the other using a solvent modified with p-nonylphenol.

In the absence of the modifier, the extracted palladium complex precipitated as a dark brown solid at loadings of 11.2 and 22.4 g/L Pd. The p-nonylphenol solubilized the compound to at least 22.4 g/L Pd in the solvent. This represents an 87% stoichiometric loading; assuming that 2 moles of CYANEX 471X extractant react with 1 mole of palladium.

TABLE 4 - EFFECT OF p-NONYLPHENOL ON THE LOADING CAPACITY

Solvent	: (A) 120 g/L CYANEX 471X extractant in Varsol DX-3641 diluent.
	: (B) As above, modified with 10 v/o p-nonylphenol.
Aqueous	: 2.24 g/L Pd (as PdCl ₂) in 2N HCl.
Temperature	: 50°C
Contact Time	: 20 minutes

Solvent	A/O	Organic [Pd] (g/L)	% Pd Extracted
A	1	2.24	100
	2	4.48	100
	5	11.20*	100*
	10	22.40*	100*
B	1	2.24	100
	2	4.48	100
	5	11.20	100
	10	22.40	100

*Precipitation of the extracted complex occurred.

Selectivity

Initial batch experiments to investigate Pd/Pt selectivity were made by contacting a solvent containing CYANEX 471X extractant with a Pd/Pt chloride solution. The results were as follows.

Solvent	: 300 g/L CYANEX 471X extractant, 10 v/o p-nonylphenol in Varsol DX-3641 diluent.
Aqueous	: 1.23 g/L Pd (II) < 2.54 g/L Pt(IV) as chloride 2N in HCl.
Contact Time	: 10 minutes
Temperature	: 50°C

% Extraction		
A/O	Pd	Pt
1	100	11
2	100	13

Higher selectivities will be obtained by reducing the concentration of CYANEX 471 X extractant in the solvent.

Kinetics

A study of the rate of Pd and Pt extraction has shown that the selective separation of these two metals is kinetically based; as illustrated in Figure 5. The results were obtained at 50°C and A/O = 2 by contacting an unmodified solvent (30g/L CYANEX 471X extractant in Varsol DX-3641 diluent) with an aqueous chloride solution containing 1 g/L Pd (II) and 1 g/L Pt (IV) in 2N HCl

Stripping

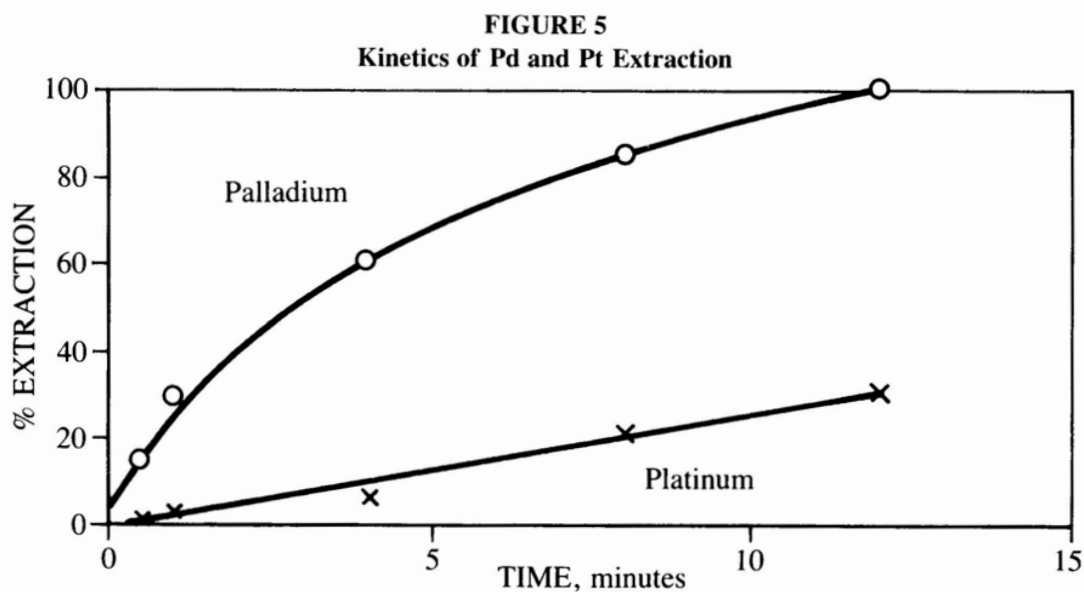
Palladium may be stripped from the loaded solvent using a sodium thiosulfate solution of the same composition as given in the section on silver recovery. The results of preliminary batch tests illustrating the utility of thiosulfates as strip feeds are as follows:

Solvent : 120 g/l CYANEX 471X extractant in Varsol DX-3641 diluent; loaded to 2.21 g/L Pd
 Strip Feed : Stabilized sodium thiosulfate solution
 Temperature : 50°C
 Contact Time : 20 minutes

A/O	% Pd Stripped
1	100
2	100

Ammonia has not been evaluated as a strip feed for palladium in our laboratories. However, its properties are such that it will probably be effective. Palladium-ammonia complexes are stable but care must be exercised to avoid complex formation with other metals which form explosively unstable fulminates; e.g. silver and mercury.

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10 Analytical Methods

Two gas chromatographic procedures have been developed for the determination of the active ingredient of CYANEX 471X extractant (triisobutylphosphine sulfide, or TIBPS). The first method is designed to analyze the concentration of TIBPS in process solvents and the second, to measure solubility losses in raffinate, strip liquors or other aqueous solutions.

Both procedures require the preparation of standard solutions of TIBPS. Typically, CYANEX 471X extractant will be 95% pure and this should be compensated for when preparing standard solutions from commercial product.

Alternatively and preferably, AR grade CYANEX 471X extractant may be prepared from CYANEX 471X by recrystallization from a 70 v/o solution of 2-propanol in distilled water. The recrystallization procedure is described in Appendix B.

Analysis in Organic Solvents

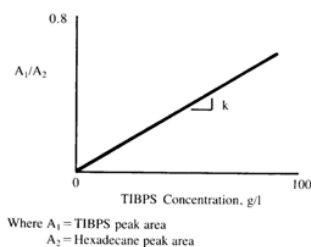
As described, the procedure is suitable for analyzing solvents containing between 20 and 100 g/L TIBPS. Other concentrations may be determined by making appropriate changes to the aliquots and/or dilutions which are cited.

Reagents

1. 25 v/o solution of hexadecane (internal standard) in toluene.
2. AR grade TIBPS.

Calibration

1. Make up 20, 40, 60, 80 and 100 g/L standard solutions of TIBPS in the appropriate diluent; e.g. Varsol DX-3641, Escaid 100, etc.
2. Prepare the analyte solutions by pipetting 10 mL of the hexadecane internal standard into a 50-mL volumetric flask and making up to volume with the standard solution. Analyze the solution as described under "Gas Chromatographic Conditions."
3. Plot the calibration curve as follows and determine the slope "k".



Hexadecane elutes before TIBPS. The calibration curve should be a straight line passing through the origin.

Procedure

1. Centrifuge the solvent to be analyzed or filter through PS paper to remove any entrained aqueous or suspended solids.
2. Pipette 10 mL of the hexadecane internal standard into a 50-mL volumetric flask and make up to volume with the process solvent. Determine the hexadecane and TIBPS peak areas as described under "Gas Chromatographic Conditions."

Calculation

$$\text{Concentration of TIBPS in the solvent (g/L)} = \frac{A_t}{A_h} \times \frac{1}{k}$$

Where A_t = TIBPS peak area
 A_h = Hexadecane peak area
 k = Slope of the calibration curve

Gas Chromatograph Conditions

Instrument	: Perkin Elmer, Sigma 115 or equivalent
Column	: 6' x 1/8" stainless steel, packed with 3% OV 17 on 80/100 Chromasorb W (AW)
Detector	: FIX (Air at 30 psig, H ₂ at 20 psig)
Carrier Gas	: Helium (22 mL/min)
Temperatures	: FID = 300°C Injection Port = 310°C
Program	: Column at 175°C for 4 min then raised to 250°C at 30°C/min and held for 5 min.
Sample Injection	
Volume	: 1 µL
Peak Areas	: Determined by electronic integration. hexadecane and TIBPS have approximate retention times of 3.6 and 5.6 min., respectively.

Notes

1. PS (Phase Separation) paper is available from Whatman, Inc., Clifton, NJ.
2. Escaid 110 diluent is available from Exxon Company, USA.
3. Varsol DX-3641 diluent is available from Exxon Company, USA.
4. Organic compounds generally exhibit high coefficients of volumetric expansion. Care should be taken to maintain all organic solutions at a controlled temperature to avoid errors induced by volume changes.
5. This method has not been validated.

Analysis in Aqueous Solution

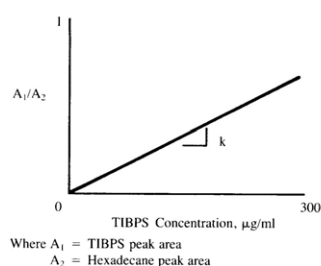
The procedure is designed for the analysis of raffinates or other aqueous solutions containing up to 15 $\mu\text{g/mL}$ of TIBPS. Detection limit is approximately 1 $\mu\text{g/mL}$.

Reagents

1. Cyclohexane
2. 3500 $\mu\text{g/mL}$ solution of hexadecane (internal standard) in cyclohexane.
3. 350 $\mu\text{g/mL}$ solution of hexadecane in cyclohexane.
4. 2000 $\mu\text{g/mL}$ solution of TIBPS in cyclohexane.
5. All reagents are AR grade.

Calibration

1. Pipette 1, 5, 10 and 15 mL aliquots of the 2000 $\mu\text{g/mL}$ solution of TIBPS into 100-mL volumetric flasks. Pipette 10 mL aliquots of the 3500 $\mu\text{g/mL}$ hexadecane solution into each of the flasks. Make up to volume with cyclohexane to prepare 20, 100, 200 and 300 $\mu\text{g/mL}$ TIBPS standard solutions each containing 350 $\mu\text{g/mL}$ of the internal standard, hexadecane.
2. Analyze the solutions as described under "Gas Chromatographic Conditions."
3. Plot the calibration curve as follows and determine the slope "k".



The calibration curve is a straight line passing through the origin.

Procedure

1. Filter the aqueous solution to remove entrained organic.
2. Pipette 100 mL of the aqueous and 5 mL of the 350 $\mu\text{g/mL}$ solution of hexadecane in cyclohexane into a 250 mL separatory funnel (or other suitable vessel) and equilibrate for 10 minutes at room temperature (24°C).
3. Allow 15 minutes to settle and transfer the organic (and any emulsion) to a glass vial and centrifuge for one hour at 1300 g to remove entrained aqueous. If no emulsion is present initially, filtration through PS paper is adequate.

4. Analyze the coalesced organic as described under "Gas Chromatographic Conditions".

Calculation

$$\text{Concentration of TIBPS in the Aqueous } (\mu\text{g/mL}) = \frac{A_t}{A_h} \times \frac{1}{k} \times \frac{Q}{A}$$

Where A_t = TIBPS peak area
 A_h = Hexadecane peak area
 k = Slope of the calibration curve
 Q/A = Organic/aqueous volume phase ratio for extraction (in this case 1/20)

Gas Chromatographic Conditions

Instrument	: Perkin Elmer, Sigma 115 or equivalent
Column	: 6' x 1/8" stainless steel, packed with 3% OV 17 on 80/100 Chromasorb W (AW)
Detector	: FID (Air at 30 psig, H_2 at 20 psig)
Carrier Gas	: Helium (10 mL/min)
Temperatures	: FID = 300°C Injection Port = 310°C
Program	: Column at 175°C for 6 minutes then raised to 200°C at 10°C/min and held for 5 minutes
Sample Injection	
Volume:	0.5 μL
Peak Areas	: Determined by electronic integration. Hexadecane and TIBPS have approximate retention times of 6.9 and 10.3 minutes, respectively.

Notes

1. The solubility of TIBPS in distilled water is approximately 43 $\mu\text{g/mL}$ at 24°C.
2. The solubility in TIBPS in a 10 g/L H_2SO_4 raffinate containing 6 g/L Zn^{2+} and 10 g/L Cu^{2+} , is 6 $\mu\text{g/mL}$ at 24°C. The solubility in a thiosulfate stripping solution (ibid) is <1 $\mu\text{g/mL}$ at 24°C. Solubilities will vary depending upon the composition of the solvent, aqueous feed, temperature etc.
3. PS (Phase Separation) paper is available from Whatman, Inc.
4. Organic compounds generally exhibit high coefficients of volumetric expansion. Care should be taken to maintain all organic solutions at a controlled temperature to avoid errors induced by volume changes.
5. This method has not been validated.

12 | Appendices

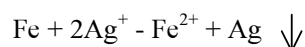
APPENDIX A Silver Recovery from Fixer Solutions

Two methods are widely used in the photographic industry to recover silver from fixer solutions used in film and paper processing. These are:

Electrolysis

Cementation

Electrolysis produces high purity silver cathodes. However, it is the more costly of the two alternatives. In cementation the fixer solution is passed through a filter cartridge containing spun steel and silver metal is precipitated according to the reaction:



Both methods can and are operated on a continuous basis. Occasional make-up of the thiosulfate solution is required.

APPENDIX B Purification of CYANEX 417X Extractant

1. At 40°C, dissolve 500 g of CYANEX 471X extractant in 150-200 mL of a 70 v/o solution of 2-propanol in distilled water.
2. Cool to room temperature and vacuum filter to remove undissolved solids.
3. Cool the filtrate to approximately 0°C and maintain at this temperature for 1 hour. Vacuum filter the recrystallized TIBPS and wash the filter cake with 100 mL of the 70 v/o 2-propanol solution (at 0 to 10°C).
4. Repeat the procedure for a total of 3 recrystallizations. Vacuum dry the final TIBPS filter cake at 25-30°C for 24 hours.
5. The final product should be >98% pure by total GC peak integration and have a melting point of 58-59°C.

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SPT-015-C