



Degradation of organothiophosphorous extractant Cyanex 301

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ABSTRACT

The resistance of extractants to light is important during industrial extraction processes. A photodegradation of the organothiophosphorous extractant Cyanex 301 in toluene and hexane as organic diluent and the identification of possible degradation products using FT-IR and GC-MS techniques were performed. The influence of copper(II) and cobalt(II) ions on the stability of the extractant under UV–vis light exposure was also studied. The changes in the percentage composition of individual components of the extractant depended on the types of organic diluents and copper or cobalt ions. During this process, copper complex irradiation precipitation of black powder and photooxidation of toluene were observed. Based on these results we proposed a hypothetical mechanism of photodegradation of extractant Cyanex 301.

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1. Introduction

In recent years, various sulphur-containing reagents such as Cyanex 301 have been given considerable attention both for their ability to extract soft transitional metal ions.

Cyanex 301 is a commercial extractant and the main ingredient is bis(2,4,4-trimethylpentyl)dithiophosphinic acid. The extractant has been noted by several authors to be of interest in the extraction of a wide range of metals: Rickelton and Boyle [1] on the extraction of zinc(II), Sole and Hiskey [2] and Fouad [3] on the extraction of Cu(II), Tait [4] and Tsakiridis and Agatzini [5] on the extraction of Co(II) and Ni(II). This extractant has also been considered in the selective extraction of actinides against lanthanides in acidic media in the frame of the studies dedicated to the reprocessing of irradiated nuclear fuels [6–10]. Cyanex 301 was also proposed as the extractant in the bulk extraction of nickel(II) and cobalt(II) in INCO's Goro project in New Caledonia [11]. However, Cyanex 301 was not stable and decomposed into a two stage process in which, in the first stage, that was reversible, the formation of disulphide was involved. The second stage, that was irreversible, involved the decomposition of disulphide to elemental sulphur and Cyanex 272. The change in the structure of the extractant could be attributed to the oxidation of Co(II) complexes with Cyanex 301, affected by the contact of the organic phase with air. The change in the composition of the complex during the extraction process by Grigorieva et al. [12] was also noted. During the observation, it was noted,

that the change of color loaded organic phase from blue (absorption band in the region 675 and 605 nm) to green (absorption band appeared in the region of 455 nm). With further contact with air the absorption band intensity in the region of 455 nm increased along with the dark brown color change.

The influence of mineral acids on the stability of Cyanex 301 was also studied [13]. The results showed that Cyanex 301 was rapidly oxidized to dialkylphosphinic acid (the active substance of Cyanex 272). The researches indicated that Cyanex 272 is very stable especially in acidic solutions; however, the compound could react with other byproducts, example, after degradation of tributyl phosphate [14].

The resistance of the extractant to light is important during industrial extraction processes in which extraction and stripping are carried out in installations with open mixers and settlers in countries where exposure to light is unavoidable. Our studies indicated that hydroxyoximes extractant degraded under the exposure to light and the rate of photodegradation was influenced by temperature, the presence of water and sulphuric acid [15–19]. Similar tests were performed for hydrophobic esters and amides of pyridine-3-carboxylic acid and pyridine-3,5-dicarboxylic acid. The obtained results indicated that all tested esters and amides, degraded under the exposure to UV light. The degree of degradation depended on the structure of the alkyl substituent of esters, the type of solvent and the presence of water or hydrochloric acid in the solution. There was no definite effect of metal on the photostability compounds but the reduction of Cu(II) ions to the copper mirror Cu(0) was detected as the result of the photochemical decarboxylation of mono- and di-esters. The survey also found out that pyridinecarboxamides are more stable to UV–vis light than esters of pyridinecarboxylic acid, but both tested derivatives

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of pyridinecarboxylic acid were more stable than hydroxyoximes extractant [20–22]. The influence of the presence of metal ions on the stability of other ligands was also noted [14,23] but only for derivatives of phosphoric acids the mechanism of the reaction was studied. The literature shows that degradation consists of metal-catalysed ester hydrolysis to alcohol and H_3PO_4 and the process depends on temperature, initial concentration of mineral acid and type of metal salts.

The aim of this work was to study the photostability of the organothiophosphorous extractant Cyanex 301 and the identification of possible degradation products. The research was carried out in an organic solvent (toluene and hexane) using UV–vis light irradiation. The influence of copper(II) and cobalt(II) ions on the stability of the extractant under UV–vis light exposure was also measured.

2. Experiment

2.1. Reagents

The commercial extractant Cyanex 301 was kindly supplied by Cytec Canada Inc., and was used directly without any further purification. Hexane and toluene (p.a., Chempur) were used as organic diluents proposed as potential diluents in extraction process [4,5,24]. N,O-bis(trimethylsilyl)acetamide (96%, Aldrich) and pyridine (p.a., Aldrich) were used as derivatisation reagents. Sulphate salts of metals and other chemicals were of analytical grade.

2.2. Photodegradation of extractant

Photo-degradation was carried out in the same way as previous studies of other pyridine derivatives and individual model hydroxyoximes, and commercial hydroxyoxime extractants [19–22]. Extractant samples (0.001 M) in hexane or toluene were irradiated in a Heraeus photoreactor of 120 cm³ volume containing medium pressure mercury lamp TQ 150 W (Heraeus) and a quartz filter ($\Phi = 0.6$ and 4.7 W for $\lambda = 270$ and 579 nm, respectively). The lamp was positioned within the inner part of the photoreactor and cooling water was circulated through a Pyrex jacket surrounding the tube. Argon was passed to the solutions with a stationary flow of 2 cm³ min⁻¹ at 20–23 °C during irradiation.

After photodegradation the samples were analysed using FT-IR technique in 0, 5, 10, 15, 30, 60, 120, 180, 240, 300, 360, 420, 480, 540 and 600 min exposure of UV–vis light. For the identification of the photoproducts the GC–MS technique was also applied.

2.3. Preparation and photodegradation of extractant complexes with metals

Complexes of Cyanex 301 with copper(II) or cobalt(II) ions were obtained in a standard extraction process at room temperature using organic phases containing 0.2 M of extractant dissolved in toluene and aqueous phases containing 0.1 M copper(II) sulphate or cobalt(II) sulphate and 0.5 M sodium sulphate at pH = 4 (the molar ratio ligand: metal (2:1) allowed to obtain a maximum concentration of complexes; pH = 4 allowed to complexation of copper(II) and cobalt(II) ions by Cyanex 301 without an influence of hydrogen ions on the degradation process) [2]; the volume ratio O/W was 1. Phases were mechanically shaken for 20 min and left to stand for separation. The metal concentration in the aqueous phase was determined by potentiometric titration (Mettler Toledo Titrator T50).

Before irradiation in a Heraeus photoreactor the organic phase was diluted to 0.001 M of ligand. The photodegradation was carried out as described for free extractant.

After photodegradation the samples were analysed after 0, 60, 120, 180 and 240 min exposure of UV–vis light. The samples of

Table 1

Names and retention times of detected compounds (GS–MS analysis using BSA as derivatisation reagents).

Components of the extractant	Short name	t_R (min)
<i>bis</i> (2,4,4-Trimethylpentyl)phosphinic acid	$\text{R}_2\text{P}(\text{O})\text{OH}$	19.68
<i>bis</i> (2,4,4-Trimethylpentyl)dithiophosphinic acid	$\text{R}_2\text{P}(\text{S})\text{SH}$	20.77
<i>tris</i> (2,4,4-Trimethylpentyl)phosphinesulphide	$\text{R}_3\text{P}=\text{S}$	24.24

organic phases containing extractant and its complexes with metal before GC–MS and FT-IR analysis before and after photodegradation were stripped twice for 30 min at 25 °C using 100 g dm⁻³ sulphuric acid, next washed, using 20 g dm⁻³ sodium sulphate and dried anhydrous sodium sulphate. The UV–vis analysis was performed without re-extraction

2.4. GC–MS analysis

GC–MS analyses were performed using a Varian CP3800 gas chromatography with 4000 MS mass spectrometer. Helium (1 cm³ min⁻¹) was used as the carrier gas. The transfer line and trap temperatures were 170 and 150 °C, respectively. A VF-5ms Varian CP8944 (30 m × 0.25 mm × 0.39 mm) column was used. After sample injection at 50 °C (injection port 250 °C), the oven temperature was increased to 330 °C at 10 °C min⁻¹.

To enable the detection of dithiophosphinic acid extractant, each sample (1 cm³) was typically derivatised by adding 0.3 cm³ of pyridine and 0.3 cm³ of N,O-bis(trimethylsilyl)acetamide (BSA) and heated (80 °C) for 30 min. Changes of the components were performed based on changes in the peak areas.

2.5. Spectrophotometric analysis

The transmittance FT-IR spectra were collected with a Vertex 70 spectrometer (Bruker optics). The spectra were collected over the 4000–400 cm⁻¹ wavenumber range, at a resolution of 4 cm⁻¹, and 48 scans were summed. KBr cells (0.68) with diluents were included to the reference scans.

The absorption spectrum of solutions before and after degradation was carried out in the UV–vis region (200–800 nm) by using a UV 1601PC Shimadzu spectrophotometer.

3. Results and discussion

3.1. Photodegradation of Cyanex 301

Cyanex 301 is a commercial extractant and its main ingredient is (~85%) *bis*(2,4,4-trimethylpentyl)dithiophosphinic acid. Previously performed studies, to determine the precise composition of the extractant Cyanex 301 showed, the presence in the largest quantities of *bis*(2,4,4-trimethylpentyl)dithiophosphinic acid and other additional pollutants: *bis*(2,4,4-trimethylpentyl)monothiophosphinic acid, *bis*(2,4,4-trimethylpentyl)phosphinic acid, *tris*(2,4,4-trimethylpentyl)phosphinesulphide and other unidentified compounds [2,25].

The GC–MS analysis of toluene and hexane solutions of Cyanex 301 after derivatisation and prior to photodegradation, showed that, apart from bands derived from the solvent and the main component of the extractant, the signals of other substances (derivatives of phosphinic acid) were also observed. The retention time of the peaks and detected compounds are presented in Table 1.

The FT-IR analysis confirmed the presence of *bis*(2,4,4-trimethylpentyl)dithiophosphinic acid as the main component of the solution. The signals that corresponded with the rest of the compounds were negligible. In the FT-IR spectra bands corresponding

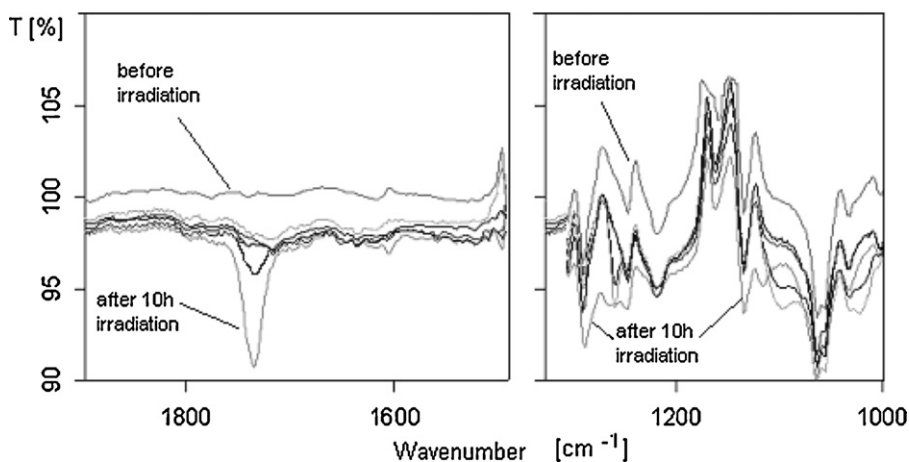


Fig. 1. The FT-IR spectrum of Cyanex 301 in hexane solution before and after irradiation of UV-vis light.

to vibrations of phosphinic moiety – $P-C(\nu)$ at 735 cm^{-1} , $P=S(\nu)$ at 612 cm^{-1} , $P-S(H)(\nu)$ at 524 cm^{-1} , $S-H(\nu)$ at 2413 cm^{-1} and $S-H(\delta)$ 913 cm^{-1} were observed. Cyanex 301 also displayed a vibration band, that corresponded to the vibrations of alkyl chain ($C-H(\nu)$ at 2954 cm^{-1} , $C-H(\delta)$ at 1385 , 1365 and 1469 cm^{-1} and $C-C(\nu)$ $1199-1286\text{ cm}^{-1}$).

As a result of the exposures to UV-vis light many changes were seen with Cyanex 301 dissolved in hexane, both on the GC-MS chromatograms and FT-IR spectrums. However, in the FT-IR spectrum, and after a 10 h irradiation, marked changes were observed at 1730 cm^{-1} (probably O-H band) and a change in the shapes of the bands in the $1300-1000\text{ cm}^{-1}$ (Fig. 1).

These changes suggest the degradation of *bis*(2,4,4-trimethylpentyl)dithiophosphinic acid and the creation of photoproducts. GC-MS analysis of hexane solution of Cyanex 301 during irradiation shows the changes in the intensity of signals corresponding to the components of extractant and also show the presence of another signal at $t_R = 25.39$ from a new unidentified compound, which probably resulted from the photodegradation of

diluents (Fig. 2). At $t_R = 19.72$, a signal that was not previously noted in such conditions was also observed, its spectrum mass suggested the formation of *bis*(2,4,4-trimethylpentyl)monothiophosphinic acid.

The GC-MS analysis of the solution after the UV-vis exposures that was based on the changes of the peak areas, showed that the highest degradation was observed for *tris*(2,4,4-trimethylpentyl)phosphine sulphide (after 4 h of exposure to UV-vis light the compound degraded to 80%). In the case of *bis*(2,4,4-trimethylpentyl)phosphinic acid, a slight degradation was initially observed, but eventually the dialkylphosphinic acid contents increased by 35%. The contents of *bis*(2,4,4-trimethylpentyl)dithiophosphinic acid changed for only few percents and the intensity of the signals of individual isomers were observed mainly (Fig. 3, Table 2).

The analysis of the FT-IR spectrums obtained after the irradiation of Cyanex 301 that was dissolved in toluene did not show any similar changes that were observed for hexane solutions. Changes that were observed within the range of $1200-600\text{ cm}^{-1}$ (a range of strong aromatic bands) suggested the degradation of toluene mainly. The results of GC-MS analysis of toluene solutions of Cyanex 301 after irradiation also differed from those of the analysis of hexane solutions. In the chromatogram of the solution, after 10 h of exposure to light, new signals at $t_R = 15.94$, 17.65 , 24.38 , 25.18 and 25.94 min were visible, and were as the result of photodegradation of the diluents: photooxidation or/and radical recombination (Fig. 4). The signals at $t_R = 15.94$ min and 17.65 min were identified as being the results of photodegradation of diluents:

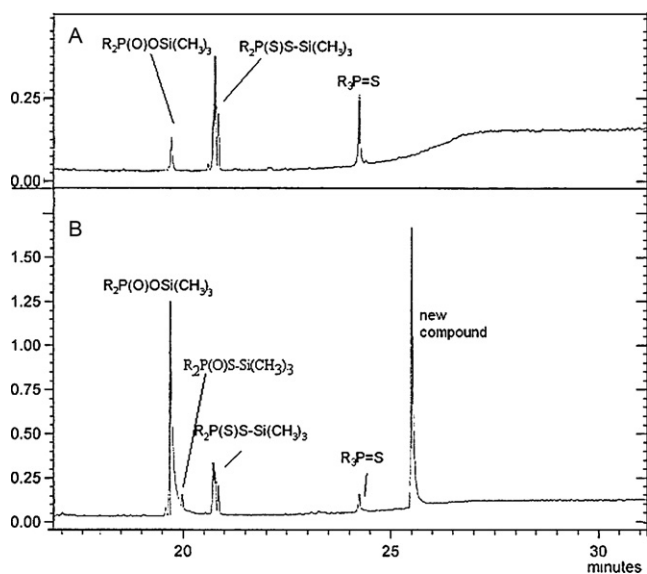


Fig. 2. The GC/MS chromatograms of Cyanex 301 in hexane solution before (A) and after (B) 10 h irradiation of UV-vis light. $R_2P(O)OSi(CH_3)_3$ – trimethylsilyl *bis*(2,4,4-trimethylpentyl) phosphinate, $R_2P(S)S-Si(CH_3)_3$ – trimethylsilyl *bis*(2,4,4-trimethylpentyl)dithiophosphinate, $R_3P=S$ – *tris*(2,4,4-trimethylpentyl)phosphine sulphide.

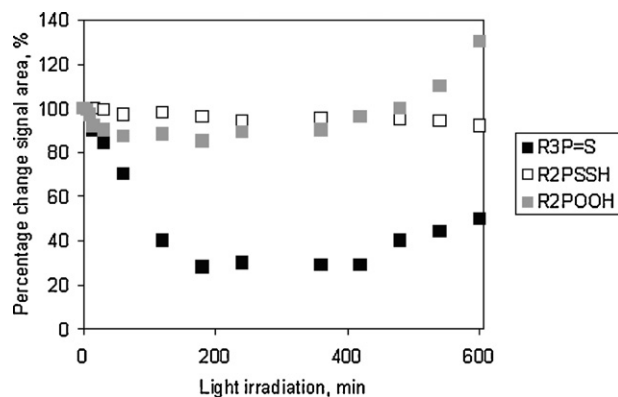


Fig. 3. The rate of photodegradation in hexane as diluents of each analysed compounds of extractant Cyanex 301 based on changes of peaks areas (GC/MS analysis).

Table 2

Analysis of GC/MS data before and after UV–vis irradiation of Cyanex 301 dissolved in hexane. $R_2P(O)OH$ – bis(2,4,4-trimethylpentyl)phosphinic acid, $R_2P(S)SH$ – trimethylsilyl bis(2,4,4-trimethylpentyl)dithiophosphinic acid, $R_3P=S$ – tris(2,4,4-trimethylpentyl)phosphine sulphide.

Compounds	t_R (min)	Signal area		Increase (+) or decrease (–) in the percentage of compound
		Before irradiation	After irradiation	
$R_2P(O)OH$	19.68	1.92×10^6	2.6×10^6	+35.4
New compound	19.72	–	0.59×10^6	–
$R_2P(S)SH$	20.77	3.18×10^6	2.94×10^6	–7.5
$R_3P=S$	24.24	1.39×10^6	0.70×10^6	–49.6
New compound	25.49	–	6.49×10^6	–

bibensyl and benzaldehyde molecules (Fig. 5). Whereas the signal at $t_R = 25.94$, that was derived from phthalic acid monoester resulted from the recombination of photooxidised solvent and extractant radicals.

The GC/MS analysis of toluene solution after UV–vis exposure, also showed the highest degradation of tris(2,4,4-trimethylpentyl)phosphine sulphide (35.7% degradation after 10 h exposure to light) and 20% degradation of bis(2,4,4-trimethylpentyl)dithiophosphinic acid. Bis(2,4,4-trimethylpentyl)phosphinic acid was the most resistance to light (Fig. 6, Table 3).

Literature reports on the photochemical reaction of phosphine oxide, phosphinic acid and thioanalogues are not sufficient enough. It has been reported that single molecular oxygen reacts with phosphines at room temperature and corresponding phosphine oxides are generated as dominating products [26]. Phosphinates, however, has also been produced, but in very small amounts only. Photochemical studies [27] also noted, that alkyl sulphides reacted readily with single molecular oxygen to form sulphoxides as the major product. The research also showed that in aprotic solvents, such as toluene, the reaction of photooxidation is very inefficient which was confirmed in the photodegradation of components of the extractant without an increase in the dialkylphosphinic acid content. However, these results did not explain the production of a large amount of dialkylphosphinic acid after irradiation in hexane. Differences were as a result of the ability of toluene to absorb radiation in the presence of UV–vis lamp. In literature the dimerisation of two thiyl radicals was also observed that caused the formation of disulphides, however in our research the dimer was not observed.

3.2. Photodegradation Cyanex 301 in the presence of metal

The influence of presence of copper(II) and cobalt(II) ions on the photostability of Cyanex 301 was also studied. Potentiometric analysis of aqueous phases before and after extraction allowed to determine the quantity of metal, that was transferred into the organic phase.

After shaking the organic phase containing 0.2 M of Cyanex 301 in toluene with the aqueous phase containing 0.1 M $CuSO_4$ and 0.5 M Na_2SO_4 copper ions were transported to organic phase to 56%. In the case of cobalt ions the extraction percentage was 62%.

After dissolution to 0.001 M ligand solutions were irradiated and analysed using FT-IR, UV–vis and GC–MS techniques (GC–MS analysis was performed after removing the metal from the solution).

The electronic spectra of the loaded organic phase containing copper(II) ions prior to photodegradation showed absorption in the 390–500 nm wavelength range, which confirms the presence of a complex metal in the solution. The complex was irradiated immediately after the extraction process, which did not allow the observation of the solution color over time. Also, during the sampling, after a hundredfold dilution of the solution the color changes were not observed. However, after an hour's exposure to UV–vis light, the band in the range 390–500 nm disappeared with a simultaneous increase at $\lambda_{max} = 286$ and 320 nm. The changes in the UV–vis spectra showed a complex destruction after an hour's exposure. Precipitate was also observed during the tests. A black precipitate was formed probably as a result of photoreduction of metal from Cu^{2+} on Cu^{1+} or formation CuS and/or CuO molecules.

The FT-IR analysis confirmed a photodegradation of Cyanex 301 complexes with copper(II) ions after an hour's exposure to light as

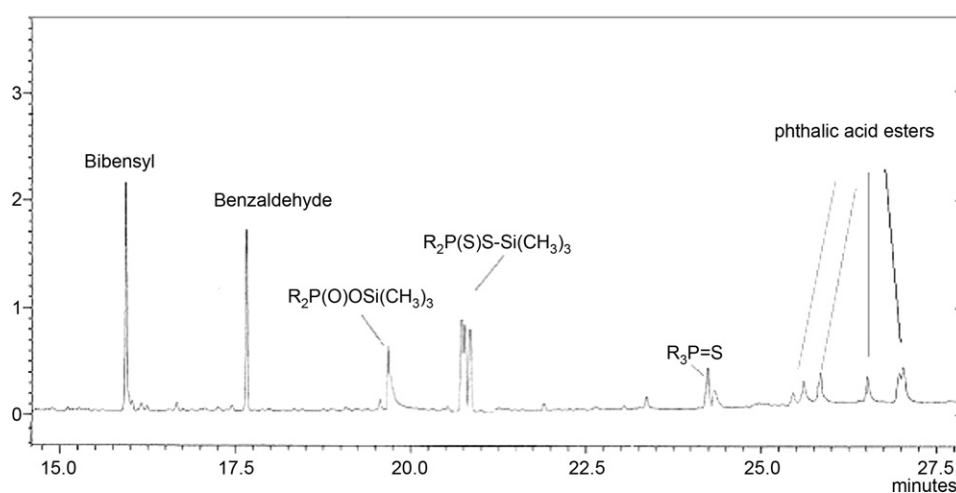


Fig. 4. The GC/MS chromatograms of Cyanex 301/toluene solution after 10 h irradiation UV–vis light. $R_2P(O)OSi(CH_3)_3$ – trimethylsilyl bis(2,4,4-trimethylpentyl) phosphinate, $R_2P(S)S-Si(CH_3)_3$ – trimethylsilyl bis(2,4,4-trimethylpentyl)dithiophosphinate, $R_3P=S$ – tris(2,4,4-trimethylpentyl)phosphine sulphide.

Table 3
Analysis of GC/MS data before and after UV–vis irradiation of Cyanex 301 dissolved in toluene. $R_2P(O)OH$ – bis(2,4,4-trimethylpentyl)phosphinic acid, $R_2P(S)SH$ – trimethylsilyl bis(2,4,4-trimethylpentyl)dithiophosphinic acid, $R_3P=S$ – tris(2,4,4-trimethylpentyl)phosphine sulphide.

Compounds	t_R (min)	Signal area		Increase (+) or decrease (–) in the percentage of compound
		Before irradiation	After irradiation	
Bibensyl	15.94	–	1.75×10^6	New compounds
Benzaldehyde	17.65	–	2.87×10^6	
$R_2P(O)OH$	19.68	2.07×10^6	2.08×10^6	No change
$R_2P(S)SH$	20.77	3.08×10^6	2.48×10^6	–19.5
$R_3P=S$	24.24	1.49×10^6	0.96×10^6	–35.7
Esters of phthalic acid	24.38	–	0.76×10^6	New compounds
	25.18	–	0.49×10^6	
	25.94	–	1.03×10^6	

evidenced by the band shift to lower value of wave number corresponding to vibrations of OH bonds $\sim 1780 \text{ cm}^{-1}$ (the band observed after metal complexation). In the region of about $1000\text{--}800 \text{ cm}^{-1}$ corresponding to vibrations of P=O and P=S moiety and aromatic bonds an increase of the bands were also observed.

The GC–MS analysis of samples, before and after photodegradation, after stripping process showed the presence of some new compounds that were formed during photodegradation and the percentage changes in the composition of the solution. The most intensive signals of the photoproducts were at $t_R = 15.94$ min and 17.65 min and were the products of photodegradation of the diluents: bibensyl and benzaldehyde. The rest of the new signals (above $t_R = 25$ min) were as the result of photodegradation of the solvent – derivatives of the phthalic acid (Fig. 7).

The quantitative analysis showed the highest decrease in content of all tested compounds after 10 h of irradiation: bis(2,4,4-trimethylpentyl)dithiophosphinic acid decreased to 65%, bis(2,4,4-trimethylpentyl)phosphinic acid to 92% and tris(2,4,4-trimethylpentyl)phosphine sulphide to 91% (Table 4).

Solutions of the complex Cyanex 301 and cobalt(II) before and after photodegradation were analysed using the FT-IR, UV–vis and GC–MS methods. The electronic spectra of the loaded organic phase containing cobalt(II) ions before photodegradation, showed a low intensity absorption at $\lambda_{\text{max}} = 457$ and 674 nm resulting metal coordination by Cyanex 301 (tetrahedral and octahedral complexes). After the first hour of photodegradation, just similar to the copper complex, similar like for copper complex, the disappearance of complexes' bands with a simultaneous increase in the bands of free ligand was observed. The FT-IR analysis of solutions before and after photodegradation showed only the evolution of the spectrum in the region typical for aromatic ring vibrations – no changes in the vibration OH group.

The GC–MS analysis of samples before and after photodegradation, regarding the copper complex, showed the presence of new compounds that were formed during photodegradation: bibensyl and benzaldehyde, but there were no derivatives of phthalic acid (Fig. 8).

The changes in the percentage composition of individual components of the extractant were lower than after the irradiation of copper-Cyanex 301 solutions. The content of bis(2,4,4-trimethylpentyl)dithiophosphinic acid after photodegradation in the presence of cobalt(II) ions decreased to 22.1% and the content of tris(2,4,4-trimethylpentyl)phosphine sulphide decreased to 38%. In the case of bis(2,4,4-trimethylpentyl)phosphinic acid no degradations were observed (Table 5).

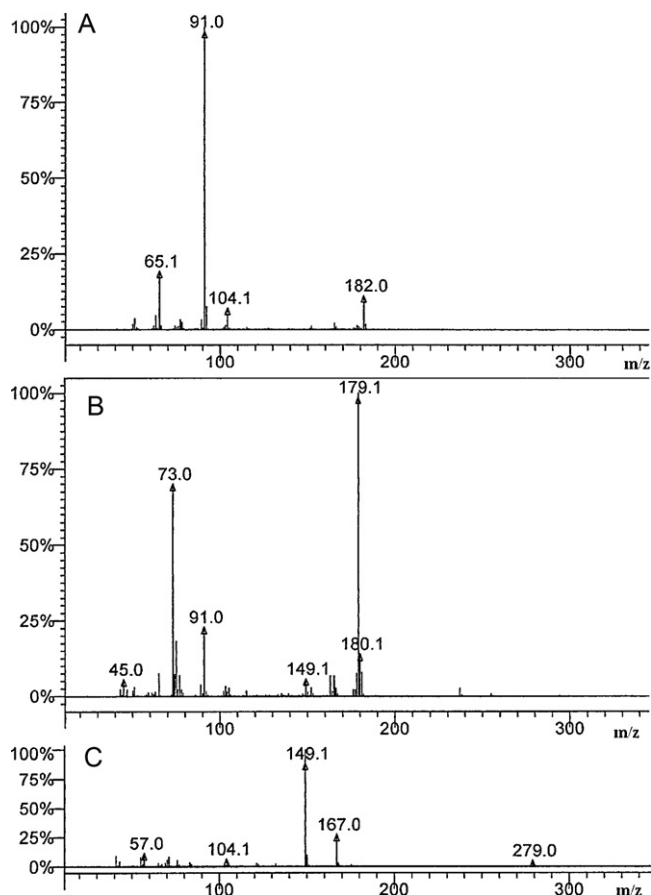


Fig. 5. Mass spectrum products of photodegradation of toluene (A) bibensyl, (B) benzaldehyde after silylation and (C) bis-octyl phthalate.

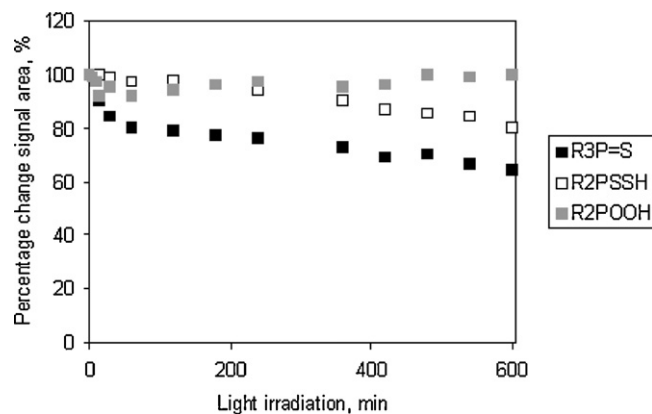


Fig. 6. The rate of photodegradation in toluene as diluents of each analysed compounds of extractant Cyanex 301 based on changes of peaks areas (GC/MS analysis).

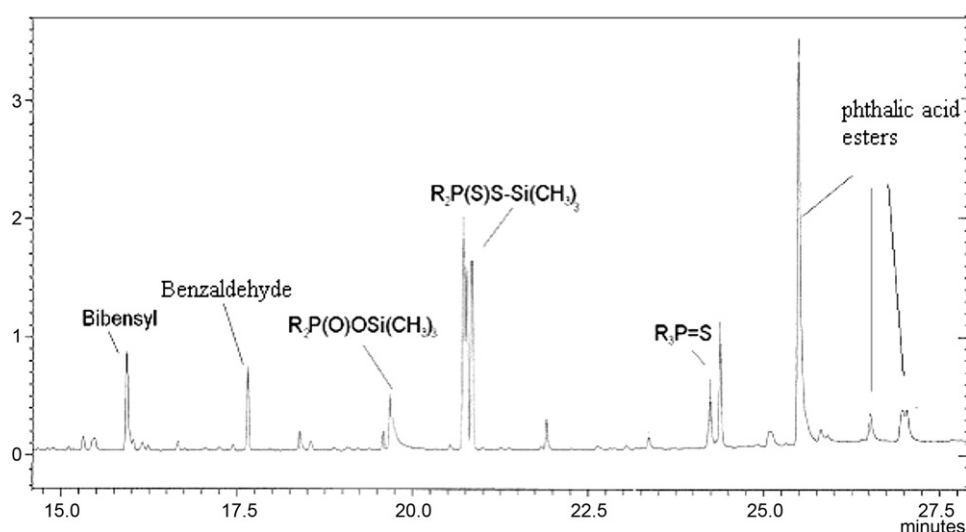


Fig. 7. The GC/MS chromatograms of Cyanex 301 and its complexes with copper(II) sulphate dissolved in toluene after irradiation UV–vis light. $R_2P(O)OSi(CH_3)_3$ – trimethylsilyl bis(2,4,4-trimethylpentyl) phosphinate, $R_2P(S)S-Si(CH_3)_3$ – trimethylsilyl bis(2,4,4-trimethylpentyl)dithiophosphinate, $R_3P=S$ – tris(2,4,4-trimethylpentyl)phosphine sulphide.

Table 4

Analysis of GC/MS data before and after UV–vis irradiation of Cyanex 301 and its complexes with copper(II) sulphate dissolved in toluene. $R_2P(O)OH$ – bis(2,4,4-trimethylpentyl)phosphinic acid, $R_2P(S)SH$ – trimethylsilyl bis(2,4,4-trimethylpentyl) dithiophosphinic acid, $R_3P=S$ – tris(2,4,4-trimethylpentyl)phosphine sulphide.

Compounds	t_R (min)	Signal area		Increase (+) or decrease (–) in the percentage of compound
		Before irradiation	After irradiation	
Bibensyl	15.94	–	1.99×10^6	New compounds
Benzaldehyde	17.65	–	1.49×10^6	
$R_2P(O)OH$	19.68	2.08×10^6	0.17×10^6	–91.8
$R_2P(S)SH$	20.77	3.08×10^6	1.08×10^6	–64.9
$R_3P=S$	24.24	1.49×10^6	0.13×10^6	–91.3
Esters of phthalic acid	24.38	–	2.87×10^6	
	25.49	–	1.20×10^7	
	27.02	–	0.90×10^6	

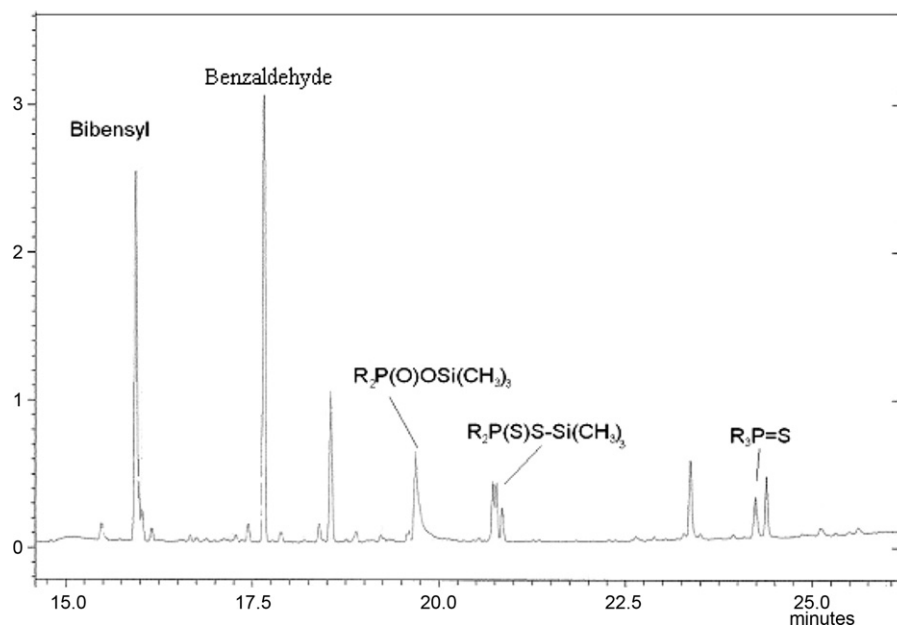


Fig. 8. The GC/MS chromatograms of Cyanex 301 and its complexes with cobalt(II) sulphate dissolved in toluene after irradiation UV–vis light. $R_2P(O)OSi(CH_3)_3$ – trimethylsilyl bis(2,4,4-trimethylpentyl) phosphinate, $R_2P(S)S-Si(CH_3)_3$ – trimethylsilyl bis(2,4,4-trimethylpentyl) dithiophosphinate, $R_3P=S$ – tris(2,4,4-trimethylpentyl)phosphine sulphide.

Table 5
Analysis of GC/MS data before and after UV–vis irradiation of Cyanex 301 and its complexes with cobalt(II) sulphate dissolved in toluene. $R_2P(O)OH$ – bis(2,4,4-trimethylpentyl)phosphinic acid, $R_2P(S)SH$ – trimethylsilyl bis(2,4,4-trimethylpentyl) dithiophosphinic acid, $R_3P=S$ – tris(2,4,4-trimethylpentyl)phosphine sulphide.

Compounds	t_R (min)	Signal area		Increase (+) or decrease (–) in the percentage of compound
		Before irradiation	After irradiation	
Bibensyl	15.94	–	5.05×10^6	New compound
Benzaldehyde	17.65	–	5.16×10^6	
$R_2P(O)OH$	19.68	2.08×10^6	2.06×10^6	0
$R_2P(S)SH$	20.77	3.08×10^6	2.40×10^6	–22.1
$R_3P=S$	24.24	1.49×10^6	0.92×10^6	–38.3

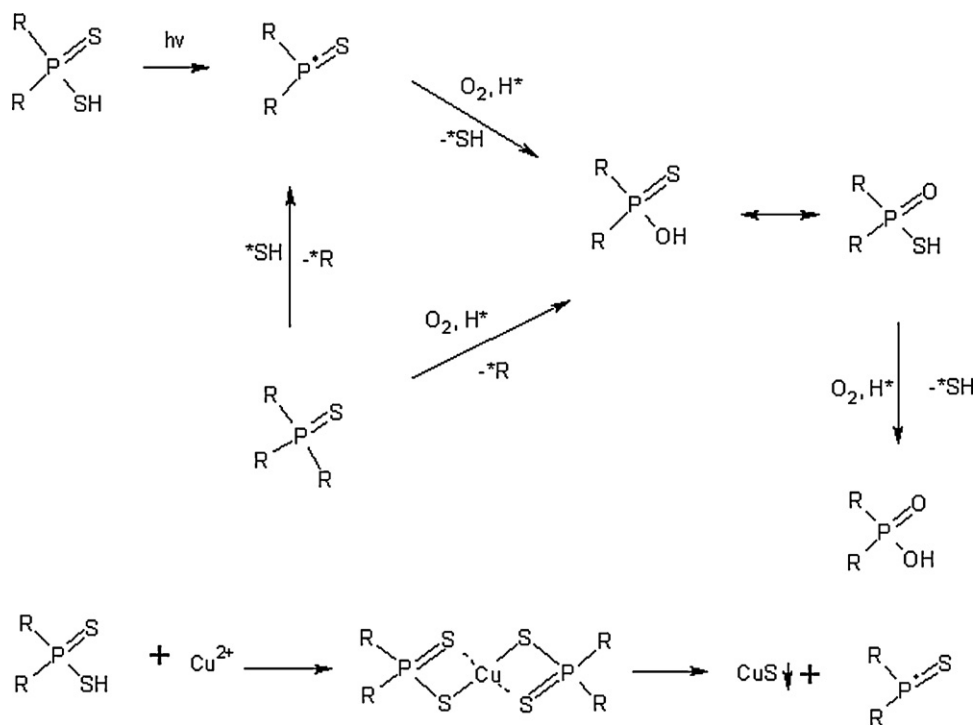


Fig. 9. Hypothetical mechanism of photodegradation of extractant Cyanex 301.

Analysing the impact of the presence of metal on the stability of the compound, only for copper complexes that the irradiation precipitation of black powder and photooxidation of toluene were observed. Menesi et al. [28] was also noted that in the presence of Cu(II) ions photocatalytic effect of oxidation was observed. Copper(II) is an efficient electron trap and is therefore capable of inhibiting recombination radicals, thereby significantly increasing the efficiency of photooxidation process.

Cobalt(II) ions also accelerated the photooxidation process especially by Co(III) cation that was formed during oxidation in the presence of air (generation OH radicals) or oxidation of Co(II) and forming of binuclear peroxobridged species described as intermediate products of catalytic oxidation of organic compounds [29]. However, cobalt complexes that were absorbed at 600–700 nm were stable and could behave as long-term stabiliser of ligand which explains, why the Cyanex 301 is more stable in the presence of cobalt than in the presence of copper ions.

Basing on the results, the mechanism of the photodegradation of each compound of Cyanex 301 was proposed (Fig. 9). The scheme showed that degradation of bis(2,4,4-trimethylpentyl)dithiophosphinic acid and tris(2,4,4-trimethylpentyl)phosphine sulphide might cause dialkylphosphinic acid formation and, as an intermediate, bis(2,4,4-trimethylpentyl)monothiophosphinic acid. CuS and CuO separation from the complex molecule also enabled the

formation of the phosphine radical, however, it did not explain the highest photodegradation of all analysed components' extractant.

4. Conclusion

The photodegradation of Cyanex 301 in toluene and hexane as organic diluents and the identification of possible degradation products using FT-IR and GC–MS techniques were performed. The influence of copper(II) and cobalt(II) ions on the stability of the extractant under UV–vis light exposure were also studied. The obtained results showed that the changes in the percentage composition of individual components of the extractant depended on the type of organic diluents and copper or cobalt ions present.

The quantitative analysis of solution after 10 h of exposures showed for hexane solutions a 35% increase in the content of bis(2,4,4-trimethylpentyl)phosphinic acid and a 50% lost of the content tris(2,4,4-trimethylpentyl)phosphine sulphide. For toluene solutions the GC–MS analysis showed a 19.5% decrease in the content of bis(2,4,4-trimethylpentyl)dithio-phosphinic acid and the decrease of 35.7%, regarding tris(2,4,4-trimethylpentyl)phosphine sulphide. In the chromatograms of the toluene and hexane solutions after 10 h of exposure to light the signals of photoproducts were visible; for toluene solutions signals at t_R = 24.38, 25.18 and 25.94 min for hexane solutions signal at 25.94 min.

The GC–MS analysis of samples before and after photodegradation of cobalt-complexes, showed an increase in the content of *bis*(2,4,4-trimethylpentyl)phosphinic acid to 24%, a decrease of 22%, regarding *bis*(2,4,4-trimethylpentyl)dithiophosphinic acid and the presence of new compounds. In the presence of copper ions after photodegradation the contents of *bis*(2,4,4-trimethylpentyl)dithiophosphinic acid decreased to 65% and the contents of other components of the extractant decreased to about 90%. During copper complexes irradiation precipitation of black powder and photooxidation of toluene were observed.

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