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Extraction and Separation of Germanium(IV) with 4-Pyridone Derivatives

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Extraction of germanium(IV) from aqueous hydrochloric, sulphuric and phosphoric acid solutions with 3-hydroxy-2-methyl-1-phenyl-4-pyridone (HX) and 3-hydroxy-2-methyl-1-(4-tolyl)-4-pyridone (HY) dissolved in chloroform was studied. Extraction with HX took place in the acidity range 1–3 M H_2SO_4 or 0.5–9.5 M HCl and that with HY in the range 0.5–5 M H_2SO_4 or 0.2–9.5 M HCl. Separation of germanium(IV) from a large excess of zinc(II), arsenic(III) and gallium(III) by extraction with HX and HY was simple and fast. Formation of a Ge^{IV}-HX(HY) complex from sulphuric acid solution was applicable for spectrophotometric determination of germanium(IV) in the organic phase at the maximum absorption at 299 nm. Extraction of germanium(IV) with chloroform, in the absence of HX or HY, from hydrochloric and sulphuric acid solutions, in dependence on acid concentration and on addition of lithium chloride, was also studied.

Key words: germanium, 4-pyridone derivatives, extraction, separation, zinc, arsenic, gallium, spectrophotometric determination.

INTRODUCTION

In continuation of our investigations of metal extraction and separation with 4-pyridone derivatives, 3-hydroxy-2-methyl-1-phenyl-4-pyridone (HX) and 3-hydroxy-2-methyl-1-(4-tolyl)-4-pyridone (HY),[1–10] the present experiments were undertaken to study the extraction of germanium(IV) with HX and HY from different aqueous solutions. The results described here show

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that this element can be quantitatively extracted with HX and HY from hydrochloric and sulphuric acid solutions. The presence of germanium in a number of industrial products, such as, among others, semiconductors, special optical glasses, alloys and organometallic compounds, has increased interest in its determination in a variety of samples. Germanium can also occur as a byproduct of hydrometallurgical zinc processing operations. There is a void in the domestic process technology for recovering germanium from this type of material. Separation of germanium from copper, zinc, arsenic, lead and antimony is interesting because these elements are usually associated with one another in minerals. Similarly, separation of germanium from gallium, indium and thalium is important because of their appreciable use in semiconductors. For this reason, we have studied the extraction of germanium(IV) with HX and HY in the presence of a large excess of zinc(II), arsenic(III) and gallium(III).

Formation of a Ge^{IV}-HX(HY) complex from sulphuric acid solution is also applicable for the spectrophotometric determination of germanium(IV) in the organic phase at the maximum absorption at 299 nm in the presence of large amounts of zinc, arsenic and gallium.

Quantitative extraction of germanium(IV) with carbon tetrachloride from 9 M HCl has been reported.[11] Literature data also refer to germanium(IV) extraction as $GeCl_4$ from hydrochloric acid solution by several solvents such as benzene, bis(2-chloroethyl)ether, chloroform, carbon tetrachloride, toluene, and kerosene.[12–15] Our investigation was therefore focussed on the extraction of germanium(IV) with chloroform, in the absence of HX or HY, from hydrochloric and sulphuric acid solutions, in dependence on acid concentration and addition of lithium chloride.

EXPERIMENTAL

Reagents

A standard germanium(IV) solution (4×10^{-3} M) was prepared by dissolving GeO_2 (Aldrich Chem. Co., Milwaukee, USA) in 5 M NaOH. By addition of H_2SO_4 or HCl, the pH was adjusted to 5.5. The solution was standardized spectrophotometrically by the phenylfluorone method.[16] Solutions of lower concentrations were prepared by diluting the standard solution with deionized-distilled water.

HX and HY were synthesized as described previously.[17] Solutions of the two pyridone derivatives were prepared by dissolving weighed amounts of HX or HY in chloroform (containing 0.5% of ethanol and used without purification or drying).

Other chemicals were of analytical reagent grade.

Apparatus

A Varian Cary 3 spectrometer was used to determine absorption spectra and to perform absorbance measurements of organic and aqueous phases. A Griffin flask shaker with a time switch served for extraction. Germanium determinations were performed by means of inductively coupled plasma atomic emission spectrometry using a Jobin-Yvon 50P ICP spectrometer with a specialized computer program. The pH of the aqueous phase was measured with a Radiometer PHM 85 Precision pH-meter.

Extraction Procedures

The germanium(IV) distribution ratio was determined at room temperature by shaking equal volumes (5 mL) of organic and aqueous phases of a given composition with a mechanical shaker in a 50 mL conical flask for 20 minutes. After the phases were separated by gravity for each experimental point their aliquots were used. Germanium(IV) concentrations in the aqueous phase were determined spectrophotometrically by the phenylfluorone method[16] and by atomic emission spectrometry (ICP-AES) after appropriate dilution. The difference between the initial and final concentrations of the metal in the aqueous phase was assumed to be equal to the concentration of the metal in the organic phase.

RESULTS AND DISCUSSION

Optimum Conditions for Extraction

The degree of germanium(IV) extraction with HX and HY dissolved in chloroform was investigated as a function of the initial sulphuric, hydrochloric or phosphoric acid concentration. From solutions to which no acids were added (pH ~5.5, as a result of acidity from stock solution), about 80% of germanium was extracted with HX and about 90% with HY. The results were independent of the pH of the stock solution being adjusted with

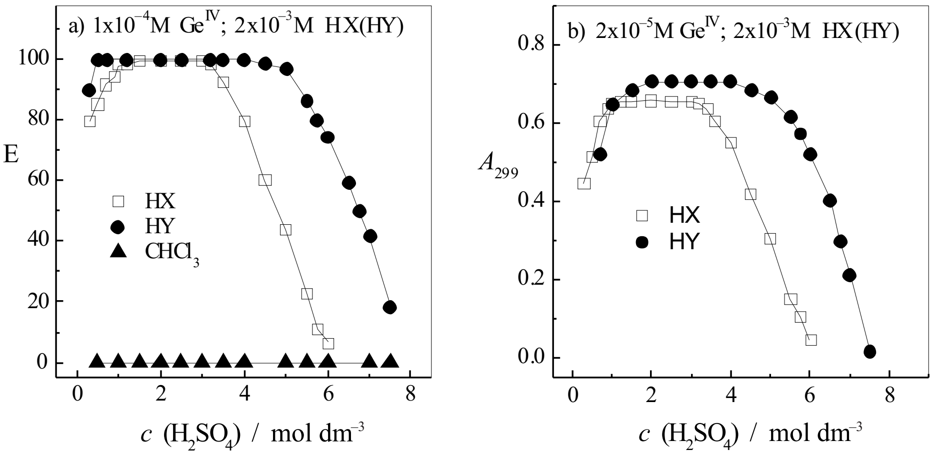

Figure 1. Dependence of (a) per cent extraction of germanium and (b) absorbance of Ge^{IV}-HX(HY) complex on the initial sulphuric acid concentration.

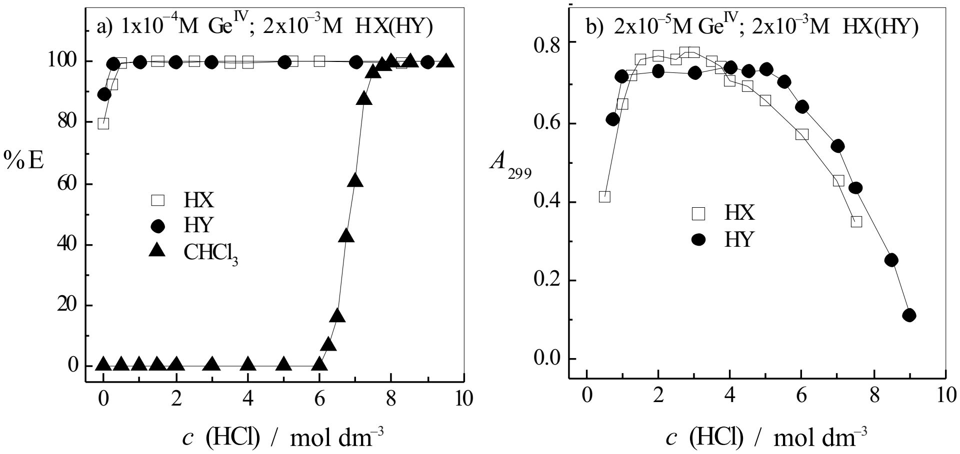

Figure 2. Dependence of (a) per cent extraction of germanium and (b) absorbance of Ge^{IV}-HX(HY) complex on the initial hydrochloric acid concentration.

sulphuric or hydrochloric acid. The acidity range in which quantitative extraction from sulphuric acid solution took place was 1–3 M H_2SO_4 for HX and 0.5–5 M H_2SO_4 for HY (Figure 1). From the hydrochloric acid solution, germanium(IV) was quantitatively extracted in a wider acidity range, from 0.5 to 9.5 M HCl with HX and from 0.2 to 9.5 M HCl with HY (Figure 2). Extraction from the phosphoric acid solution was less efficient. At a 400-fold excess of the reagent, maximum germanium extraction was about 40% for HX in the acidity range 1.0–2.5 M H_3PO_4 and about 92% for HY in the acidity range 2.5–3.5 M H_3PO_4. The effect of the HX and HY concentrations in the organic phase on germanium(IV) extraction from the aqueous phase at optimum acidity was also studied (Table I). For the quantitative extraction from both sulphuric and hydrochloric acid solutions, the molar ratio of HX to Ge^{IV} had to be at least 15 and that of HY to Ge^{IV} at least 10.

The germanium(IV) extracted from sulphuric or hydrochloric acid could be stripped quantitatively with sulphuric acid at a concentration of 8 M H_2SO_4 or higher.

Absorption Spectra of Extracted Complexes

The solution of the Ge-HX and Ge-HY complexes extracted in chloroform from sulphuric or hydrochloric acid had maximum absorption at 299 nm if H_2SO_4 concentration was higher than 0.3 M and HCl concentration higher than 0.4 M. The absorbances of the Ge-HX (HY) complex extracted from hydrochloric acid solution were maximal in the concentration range of 2–5 M HCl but were not reproducible (Figure 2). They were maximal, constant and

TABLE I

Dependence of germanium extraction on HX and HY concentration in the organic phase

HX or HY conc. / mol dm^{-3}	HX(HY) : Ge molar ratio	A_{299}		E (%)	
		HX	HY	HX	HY
2.0×10^{-5}	1	0.029	0.092	6.1	15.1
4.0×10^{-5}	2	0.036	0.185	13.3	34.0
8.0×10^{-5}	4	0.072	0.315	36.3	54.1
1.2×10^{-4}	6	0.129	0.439	53.4	74.9
1.6×10^{-4}	8	0.195	0.551	75.3	96.4
1.8×10^{-4}	9	0.211	0.593	84.9	98.7
2.0×10^{-4}	10	0.232	0.597	94.0	100.0
2.4×10^{-4}	12	0.332	0.700	95.6	100.0
2.8×10^{-4}	14	0.285	0.705	98.3	100.0
3.0×10^{-4}	15	0.372	0.706	100.0	100.0
4.0×10^{-4}	20	0.481	0.706	100.0	99.7
5.0×10^{-4}	25	0.555	0.706	100.0	99.9
6.0×10^{-4}	30	0.616	0.705	99.5	100.0
8.0×10^{-4}	40	0.671	0.704	99.8	99.9
1.0×10^{-3}	50	0669	0.706	100.0	99.8
1.2×10^{-3}	60	0.669	0.707	100.0	99.9
1.6×10^{-3}	80	0.668	0.706	99.9	100.0

reproducible in the concentration range of 1.0–3.0 M H_2SO_4 for HX and 2.0–4.5 M H_2SO_4 for HY (Figure 1).

Therefore, germanium(IV) could be determined spectrophotometrically in the organic phase after extraction from sulphuric acid solution with HX or HY at the maximum absorption occurring at 299 nm. The absorption *vs.* concentration calibration graph was linear all over the range suitable for spectrophotometric measurements, corresponding to $5 \times 10^{-6} - 5 \times 10^{-5}$ M of germanium(IV) in the measured solution. The effective molar absorptivity was 3.5×10^4 L mol^{-1} cm^{-1} (for Ge-HY) and 3.33×10^4 L mol^{-1} cm^{-1} (for Ge-HX). Absorbance of the organic phase was stable for 60 minutes. For maximum and constant absorbances at optimum acidity (2.3 M H_2SO_4), the molar ratio of HX to Ge^{IV} had to be at least 40 and that of HY to Ge^{IV} (3 M H_2SO_4) at least 15 (Table I).

TABLE II

Effect of foreign ions on the spectrophotometric determination of germanium(IV) with HX and HY dissolved in chloroform

Foreign ions	Tolerance limit [Ion] / [germanium]
Sulphate, phosphate, Ni^{II}, Mn^{II}, K^{I}, Cr^{III}, Cd^{II}, Mg^{II}	10^4
Nitrate, acetate, chloride, As^{III}, Ga^{III}, Zn^{II}	10^3
Co^{II}, Al^{III}	750
Ti^{IV}	500
Tartarate, citrate, Ta^{V}, V^{V}, Cu^{II}	250
Mo^{VI}	150
Sn^{IV}, Nb^{V}	100
In^{III}, Bi^{III}, Zr^{IV},	50
Ag^{I}	25
Thiocyanate, oxalate, Fe^{III}	1

A detailed study of the interference effect on the spectrophotometric determination of germanium(IV) was performed. Ions were considered to be non-interfering when they produced an error of less than ± 2% in the analyte determination. The results are summarized in Table II.

Germanium can be determined spectrophotometrically at trace concentrations by a variety of reagents.[18–27] Most of these methods are not selective if common species, which are generally found to be associated with germanium such as Zn^{II}, Ga^{III}, Ti^{IV}, Sn^{IV}, As^{III}, are present. A preextraction step is therefore required to separate germanium from the interfering ions.[23] Table III summarizes the analytical characteristics of the proposed method along with some other spectrophotometric methods. The proposed method is more sensitive if compared with those of other authors[18–20] and generally more selective than other.[18–23,25–27]

Separation of Germanium(IV) from Zinc(II), Arsenic(III) and Gallium(III)

Separation of germanium(IV) from zinc(II), arsenic(III) and gallium(III) is of large practical importance in the field of analytical chemistry, radiochemistry and high purity germanium technology. The varying behaviour of germanium(IV), zinc(II), arsenic(III) and gallium(III) in extraction with HX and HY can be utilized for their separation. Germanium(IV) was quantitatively extracted from 2.5 M H_2SO_4 with HX and from 3 M H_2SO_4

TABLE III

Comparative evaluation of various spectrophotometric determinations of germanium

Reagent	Medium	λ/nm	$\varepsilon \times 10^{-4}$	Linear range μg Ge^{IV} / mL^{-1}	Tolerance limits (excess of ions to germanium)	Ref.
N-hydroxy-*N*, *N*'-diphenylbenzamidine	$CHCl_3$	395	1.5	up to 10	As^{III}, Cu^{II} (15); Sn^{IV}, Sb^{III} (7.5)	18
Bromparogallol Red +CTMB	Aqueous	500	2.8	up to 7.5	As^{III} (500); Zn^{II} (100); Cu^{II} (1)	19
Phenylfluorone	Cyclohexanol	525	0.175	0.4–4.8	Zn^{II}, Ni^{II}, Cu^{II} (1000); As^{III} (50); Ti^{IV} (2)	20
Catechol violet + CTMB	Aqueous	655	8	0.1–1.0	As^{III}(1000); Zn^{II}, Cu^{II}, Ni^{II}, Ti^{IV}(100)	21
Phenylfluorone	Toluene	525	7.08	up to 1.8	Zn^{II}, Cu^{II} (1000); Sn^{II}, Sn^{IV}, Ti^{IV} (10)	22
Phenylfluorone + ZEPH	Aqueous	505	13.8	up to 0.4	As^{III} (100)	23
Phenylfluorone + SLS	Aqueous	504	11.8	up to 0.2	Zn^{II}, $Ga^{III,}$ Cu^{II}, Ni^{II} (1000); Sn^{II}(1)	24
N-*p*-chlorophenyl-2-furohydroxamic acid	$CHCl_3$	495	12	0.02–0.64	Zn^{II}, Sn^{IV}(375); Cu^{II} (300); As^{III}(185); Ti^{IV}, Ga^{III} (250)	25
Malachite Green	Chlorobenzene	628	11.3	0.012–0.63	As^{V} (500); Zn^{II}, As^{III}, Cu^{II}, Ni^{II} (100)	26
Methylene Blue	Acetone	660	45	0.007–1.2	Ga^{III}(100); As^{V} (10); Cu^{II}(large amount)	27
3-Hydroxy-2-methyl-1-phenyl-4-pyridone (HX)	$CHCl_3$	299	3.35	0.36–3.6	Zn^{II}, Ga^{III}, As^{III} (1000); Ti^{IV}(500); Cu^{II}(250); Sn^{II} (100)	*
3-hydroxy-2-methyl-1-(4-tolyl)-4-pyridone (HY)	$CHCl_3$	299	3.5	0.36–3.6	Zn^{II}, Ga^{III}, As^{III} (1000); Ti^{IV}(500); Cu^{II}(250); Sn^{II} (100)	*

* This work.
CTMB – Cetyltrimethylammonium bromide; ZEPH – Zephiramine; SLS – Sodium lauryl sulphate;
TDAB – Tridodecylethylammonium bromide.

with HY (Figure 1), while zinc(II) and gallium(III) remained in the aqueous phase.[10] Investigation of arsenic(III) extraction with HX and HY dissolved in chloroform was carried out in the range from pH 1 to 6 M sulphuric acid. Under these conditions, arsenic(III) was not extracted and remained in the aqueous phase. The influence of large amounts of zinc(II), arsenic(III) and gallium(III) on the extraction of germanium(IV) was studied. The results confirmed that germanium(IV) extraction was not affected, regardless of the zinc, arsenic or gallium concentrations in the investigated concentration range. The molar ratio for zinc, arsenic or gallium relative to germanium was from 10 to 1000. To test the separation of germanium(IV) from zinc(II), arsenic(III), and gallium(III) the experiments were carried out in duplicate, and atomic emision spectrometry was applied.

The simple and fast separation of germanium(IV) from zinc(II), arsenic(III) and gallium(III) by extraction with HX or HY has the advantage over the other methods,[28–30] because large amounts of zinc, arsenic and gallium, relative to germanium, (1000-fold excess) can be separated.

Extraction of Germanium(IV) Chloride with Chloroform Alone

Extraction of germanium(IV) with chloroform started at an HCl concentration higher than 6M (Figure 3). An increase in HCl concentration was

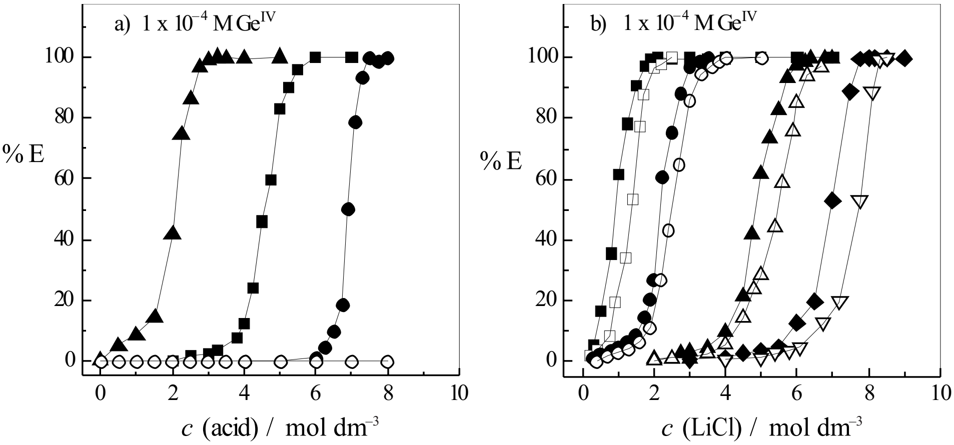

Figure 3. Dependence of per cent extraction of germanium with chloroform on the initial acid concentration (a) and LiCl concentration (b).
a) HCl (●), H_2SO_4 (○), HCl or H_2SO_4 with 3 M LiCl (■), HCl or H_2SO_4 with 6 M LiCl (▲).
b) 6 M HCl (■), 6 M H_2SO_4(□), 4.5 M HCl (●), 4.5 M H_2SO_4 (○), 3 M HCl (▲), 3 M H_2SO_4 (△), 1 M HCl (◆), 1 M H_2SO_4 (▽).

followed by a rapid increase in germanium(IV) extraction and at an HCl concentration above 7.5 M, germanium(IV) was quantitatively extracted very likely as $GeCl_4$. Absorbances at 299 nm, which showed formation of a Ge^{IV}-HX(HY) complex, descreased at the HCl concentration higher than 6 M (Figure 2). This indicated a possible presence of a mixture of the Ge^{IV}-HX (HY) complex and $GeCl_4$ in the organic phase in the concentration range of 6–7.5 M HCl. At the HCl concentration above 8 M, germanium(IV) was extracted as $GeCl_4$ and the Ge^{IV}-HX(HY) complex was not present in the organic phase (Figures 2 and 3). Germanium(IV) extraction with chloroform from sulphuric or phosphoric solutions did not take place in the whole acidity range from 0.5 to 9 M H_2SO_4 or H_3PO_4. On the other hand, addition of LiCl to sulphuric acid solution increased the extraction. As a result of the increase in LiCl concentration, germanium(IV) was quantitatively extracted from lower acidity regardless of the presence of hydrochloric or sulphuric acid (Figure 3). At 1 M sulphuric or hydrochloric acid solution, the quantitative extraction of germanium(IV) with chloroform required an LiCl concentration higher than or equal to 8 M to be comparable to the one taking place at the HCl concentration of 8 M or higher without addition at LiCl. At 6 M HCl, where germanium(IV) extraction started without addition of chloride, in the presence of LiCl ≥ 2 M, germanium(IV) was quantitatively extracted from hydrochloric or sulphuric acid solution. If conducted at constant ionic strength (H, Li)Cl = 6 M, germanium(IV) extraction was above 5.6% in the whole acidity range at the HCl concentration ≥ 1M. Without addition of HCl (the pH was 5.5 from the standard solution of germanium), germanium(IV) was not extracted. This shows that the chloroform extraction of germanium(IV) depended on chloride concentration but also called for the presence of an acid. Without addition of the acid (hydrochloric or sulphuric), germanium(IV) was not extracted regardless of chloride concentration.

CONCLUSION

3-Hydroxy-2-methyl-1-phenyl-4-pyridone (HX) and 3-hydroxy-2-methyl-1-(4-tolyl)-4-pyridone (HY) have been used as new reagents for the extraction of germanium from sulphuric acid media and for the spectrophotometric determination of germanium in the organic phase. Separation of germanium(IV) from zinc(II), arsenic(III), and gallium(III) is of large practical importance in many fields such as analytical chemistry, radiochemistry and high purity germanium technology. The described separation of germanium(IV) from zinc(II), arsenic(III) and gallium(III) by extraction with HX and HY is simple and fast and has the advantage over the other described methods[28–30] because large amounts of zinc, arsenic and gallium, relative to germanium, can be separated.

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SAŽETAK

Ekstrakcija i odvajanje germanija(IV) derivatima 4-piridona

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Proučavana je ekstrakcija germanija(IV) iz otopina koje su sadržavale sumpornu, klorovodičnu ili fosfornu kiselinu s 1-fenil-3-hidroksi-2-metil-4-piridonom (HX) i 3-hidroksi-2-metil-1-(4-tolil)-4-piridonom (HY) otopljenim u kloroformu. Germanij se kvantitativno ekstrahira s HX u području koncentracija 1–3 mol dm^{-3} (H_2SO_4) ili 0,5–9,5 mol dm^{-3} (HCl), a s HY u području 0,5–5 mol dm^{-3} (H_2SO_4) ili 0,2–9,5 mol dm^{-3} (HCl). Predloženom ekstrakcijskom metodom moguće je jednostavno i potpuno odvajanje germanija(IV) od velikog suviška cinka(II), arsena(III) i galija(III). Nastajanje kompleksa Ge^{IV}-HX(HY) u otopinama koje sadržavaju H_2SO_4 može se primijeniti za spektrofotometrijsko određivanje germanija(IV) u organskoj fazi pri čemu se mjeri apsorbancija pri 299 nm. Također je proučavana ekstrakcija germanija(IV) kloroformom, bez prisutnosti HX ili HY, iz otopina koje su sadržavale HCl ili H_2SO_4, u ovisnosti o koncentraciji kiseline i litijeva klorida u vodenoj fazi.