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Selective Extraction of Mercury(II) by 1-Naphthylthiourea–Methyl Isobutyl Ketone System

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Abstract: Selective extraction of Mercury(II) using 1-naphthylthiourea–methyl isobutyl ketone (ANTU-MIBK) system from hydrochloric acid solutions (0.1–10 M) has been studied. Influence of foreign ions, acid and ligand concentrations has been investigated. Addition of ANTU in MIBK enhanced, extraction capacity of MIBK to several times. Low effect of foreign ions and high separation factors for a number of metal ions determined at 0.5 M hydrochloric acid concentration evaluated the proposed method efficient and selective. The experimental data obtained from application of the method for extraction of mercury from a synthetic aqueous solution reveal that more than 99% mercury can be separated from cadmium, zinc and selenium in a single step with five minutes equilibration.

Keywords: Extraction, selectivity, mercury(II), 1-naphthylthiocarbamide (ANTU), methyl isobutyl ketone (MIBK)

INTRODUCTION

Mercury is a naturally occurring element that is present throughout the environment and in plants and animals. Human activities have increased the

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amount of mercury that is currently cycling in the atmosphere, in soils, and in lakes, streams, and oceans. Mercury in these locations increases risks to people and wildlife. Coal burning is the major source of human–caused mercury emission in the atmosphere. In the atmosphere, mercury is transported by wind either as a vapor or as particles. Mercury reaches waters either through direct deposition or as run-off from soil after rain.

When mercury is deposited into water, microorganisms help convert it to methylmercury, a highly toxic form of mercury. Small organisms and plants take up mercury as they feed. As animals higher up in the food chain eat those plants and organisms, they, too, take in methylmercury. The process continues, with levels of mercury increasing up the food chain. This process is known as bioaccumulation. Fish higher in the food chain, such as sharks and swordfish, have much higher mercury concentrations than those lower on the food chain.

Mercury reacts with thiol group of most readily available thiol-reactive proteins like tubulin and inhibits multiple enzyme systems (1). At high doses, its exposure can cause damage to our senses and brain, cause tremors, inability to walk, convulsions, and even death. The developing fetus is most sensitive to the effects of mercury, and so women of child-bearing age in populations are of the greatest concern. Children exposed to methylmercury have exhibited delays and deficits in learning ability.

Because of its threatening toxicity, tremendous interest has been developed in extraction-preconcentration and removal of widespread mercury in the environment including waters, polluted effluents, and waste streams. In addition to activated carbon and ion exchange process (2), solvent extraction is considered to be an effective and energy saving separation technique suitable for this purpose (3). Literature survey shows that a number of reagents like triphenylphosphine oxide (TphPO) (4), 2-benzylpyridine (5), di-isopropylaminoethanol (6), bis(2-ethylhexyl) sulphoxide (7), substituted pyrimido[1,6]benzimidazole-1-thiol (PBT) (8), triphenylphosphine sulphide (9), dibenzo-18-crown-6 (10), dihexyl sulfoxide (11), dicyclohexano-18-crown-6 (12), Cyanex 923 (13) and Cyanex 471X (14) have been used for extraction of Hg(II).

Thiourea based extractants (soft bases) such as *N*-benzoyl-*N′*,*N′*-diheptadecylthiourea (15) alkylthiourea (16) and α-butylthiolauric acid (17) have been reported for extraction of Hg(II) (soft metal).

1-Naphthylthiourea (ANTU) also known as α-naphthylthiourea and 1-naphthylthiocarbamide being used as a pesticide (rodenticide) for rats but it is safe for domestic animals (18). ANTU-MIBK system has not yet been reported for extraction of mercury. Therefore, this present study focuses on the application of ANTU-MIBK system for extraction of mercury. Extraction data suggest that the proposed method is selective, fast in equilibration, and can be applied for separation of metal ions from hydrochloric acid solutions.

EXPERIMENTAL

Reagents and Procedure

1-Naphthylthiocarbamide was obtained from E. Merck and used as such. The reagent is being use as a pesticide and is almost insoluble in water but soluble in some organic solvents: acetone, triethylene glycol, and hot alcohol (18–20). The extractant has limited solubility in organic solvents like xylene, benzene and toluene observed during in preliminary experiments. Laboratory double distilled water was used. ^{203}Hg tracer solutions were prepared by dissolving a known amount of irradiated HgO in high purity acids and diluting it to a known volume with double distilled water.

The distribution ratios were measured by equilibrating 2 ml of aqueous phase containing approximately 10^5 gamma counts at room temperature (25 ± 3°C) with equal volumes of ANTU/MIBK in 20 ml glass vials. A five minute mixing period was selected, although equilibrium was attained sooner. After equilibration, vials were centrifuged and aliquot parts from each phase were analyzed for mercury-203 by counting in a γ-scintillation counter already described elsewhere (5).

Gamma-spectra were taken by employing a 4K series 85 Canberra multichannel analyzer and a Ge(Li) detector. This system has a resolution of 2.0 Kev with respect to 1332.5 KeV peak of Co-60 and a peak to Compton ratio is 40:1.

RESULT AND DISCUSSION

Different organic solvents were tested as diluents for ANTU. It was found that the reagent has limited solubility in solvents like benzene, toluene, and xylene but is very soluble in MIBK. MIBK selection was based to avoid any third phase formation. The extraction of 9.95×10^{-4} mmole mercury(II) with (0.003 and 0.005) M ANTU in MIBK from different hydrochloric acid solutions (0.1–10 M) is illustrated in Fig. 1. The extraction of mercury with 0.005 M ANTU in MIBK is $>99\%$ from 0.1–1 M and then decreases slightly with increase of HCl acid concentration. Decrease in extraction becomes very sharp from 8–10 M HCl acid concentration.

The extraction data obtained from extraction of mercury by 0.003 M in MIBK show that extraction decreases with increase of acid concentration in the low acidity range then curve attains plateau form presenting that extraction of Hg^{2+} is not significantly affected by increase in this HCl acid concentration range. When the acidity of solution is further increased to 8 M, a sharp decrease in the extraction of mercuric ions has been observed.

Decrease in extraction of mercury with increase of acidity can be attributed to the decrease in the formation of free Hg^{+2} and increase in the less

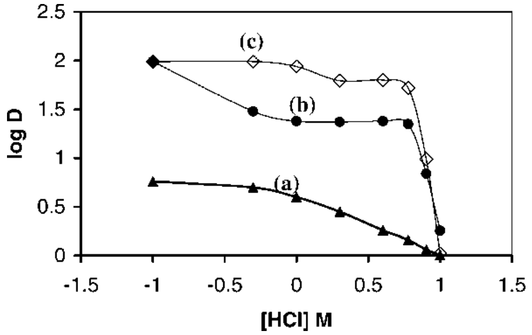


Figure 1. Effect of the extraction of mercuryhydrochloric acid concentration on (a) without ANTU, (b) 0.003 M ANTU, (c) 0.005 M ANTU in MIBK.

extractable mercuric anionic complexes $HgCl_4^{-4}$ and $HgCl_3^{-3}$ at higher HCl acid concentration.

The decrease in mercury extraction with increase of HCl acid can be further explained by effect of chloride ion concentration in the aqueous phase on the extraction of mercury and keeping the HCl acid concentration constant. As is clear from Fig. 2, that distribution value for mercury decreases with increase in chloride ion concentration. This decrease is considered to be due to the increase in anionic mercury chloride complexes, $HgCl_3^{-3}$ and $HgCl_4^{-2}$ which are not extracted by neutral ANTU.

The decrease of extraction of mercury with increase of HCl acid concentration and dependent on Cl^- concentration suggests that ANTU do not behave as cation exchange extractant but as solvating extraction reagent (17). Similar mechanism was proposed for extraction of mercury by thiourea based extractants (16, 17). In ANTU-MIBK complex, it is expected that coordination of mercury takes place through sulfur atom of ANTU, as reported in the literature (21).

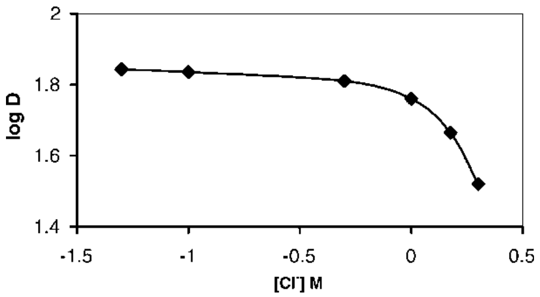


Figure 2. Equilibrium distribution of mercury(II) from sodium chloride solutions with ANTU.

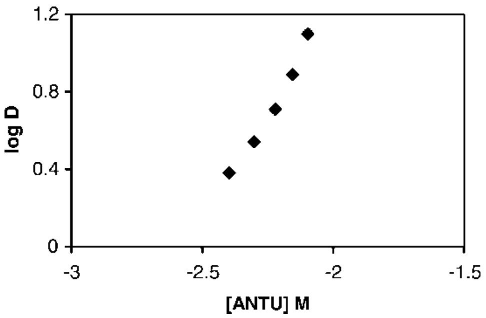


Figure 3. Dependency of distribution ratio of mercury on the concentration of ANTU in MIBK [HCl] = 0.5 M.

The stoichiometry of the extracted species was determined by analyzing experimental data obtained from extraction of 0.005 M mercury by varying reagent concentration from 0.001 M to 0.1 M while keeping acidity of aqueous solution constant at 0.5 M and results are presented in Fig. 3. The conventional slope analysis was used and plot of log D versus log [ANTU]

Table 1. Effect of foreign ions (5 mg/ml) in the determination of 0.1 mg/ml Hg(II) from 0.5 M HCl acid solution

Substance added	Hg^{+2} extraction %	Substance added	Hg^{+2} extraction %
Aluminum sulphate	99.4	Zinc sulphate	99.7
Strontium chloride	99.2	Zirconium nitrate	99.5
Barium nitrate	99.6	Sodium chloride	99.3
Bismuth nitrate	99.6	Sodium EDTA	98.4
Cadmium chloride	98.2	Sodium fluoride	98.9
Cobalt acetate	98.8	Sodium disulphite	71.1
Copper sulphate	98.0	Sodium iodate	82.6
Iron(III) nitrate	99.2	Sodium molybdate	99.8
Iron(II) sulphate	99.1	Sodium nitrate	98.7
Lead nitrate	99.4	Sodium sulphate	99.5
Manganese chloride	99.2	Sodium tartrate	99.6
Magnesium chloride	97.9	Sodium thiocyanate	99.5
Nickel chloride	98.7	Sodium thiosulphate	99.54
Potassium chromate	24.3	Sodium bromate	23.2
Potassium iodide	99.7	Sodium bromide	99.5
Potassium oxalate	99.5	Urea	99.8
Sodium acetate	99.5	Sodium ascorbate	99.6
Gold chloride	59.7	Sodium cyanide	0.0
Sodium peroxydisulphite	99.4	di-Ammonium hydrogen orthophosphate	99.5

gives a slope of 2.2 and suggests the involvement of two molecules of the extractant in the formation of Hg(II)-ANTU complex. 1 : 2 molar ratio was also suggested for mercury to sulphur containing extractants such as BHTE (22), trialylphosphine sulphides (23) and substituted thiourea (17).

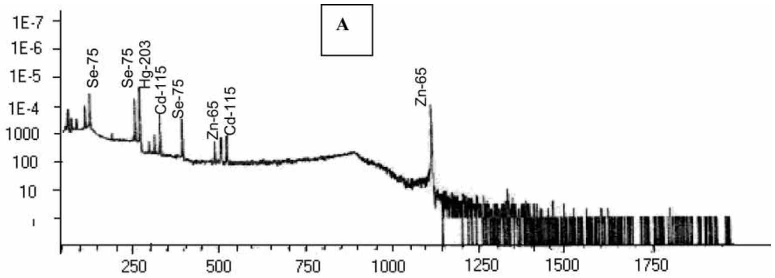
The presence of foreign ions may influence extraction of metal ions because of competition for the extraction sites, complex formation, dissociation, and precipitation. Generally, the higher the influence of foreign ions the lesser will be practical application of solvent extraction system. To evaluate the selectivity of the current system, the effects of various anions, cations and complexing agents on the extraction of mercury(II) conditions were investigated and the results are presented in Table 1. The extraction results depicts that extraction of 0.1 mg/ml of mercury in the presence of 5 mg/ml of foreign ions is not affected by most of diverse compounds studied. However, ions such as $S_2O_5^{2-}$, IO_3^-, BrO_3^- and CrO_4^{2-} reduce extraction of Hg(II) to some degree. The fast equilibration and extraction of mercury in the presence of foreign agents like $S_2O_5^{2-}$, IO_3^- and EDTA show a strong complexing affinity of ANTU for mercury.

Distribution ratios and separation factors for a number of metal ions were also determined and the results are tabulated in Table 2. The separation factors of most of the tested elements, including Fe(III), were greater than 10^3 therefore, present system seems to be very selective for separation of mercury in the presence of studied metal ions. The results also present the idea about the order of stability of some species $Hg^{+2} > Cd^{+2} > Zn^{+2}$ that is in good agreement with the order of stability of metal-thiourea complexes in aqueous solutions, for Hg^{+2}, Cd^{+2}, and Zn^{+2} reported (16).

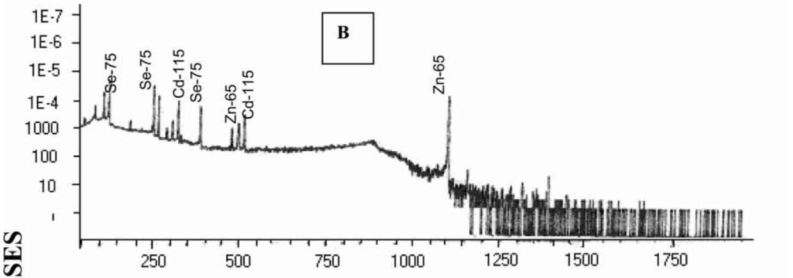
Table 2. Distribution coefficient and separation factors of different metal ions with respect to Hg(II) from 0.5 M HCl solution

Metal ions	Concentration (mol/L)	Distribution coefficients	Separation factors
Hg(II)	10^{-7}	657	—
Cd(II)	10^{-6}	1.3×10^{-1}	$>10^3$
Co(II)	10^{-6}	1.0×10^{-4}	$>10^6$
Cr(III)	10^{-3}	3.0×10^{-2}	$>10^4$
Eu(III)	10^{-6}	8.0×10^{-4}	$>10^5$
Fe(III)	10^{-5}	1.8×10^{-1}	$>10^4$
Hf(IV)	10^{-5}	1.0×10^{-5}	$>10^6$
Se(II)	10^{-5}	1.0×10^{-2}	$>10^4$
Sn(II)	10^{-3}	6.0×10^{-3}	$>10^5$
Sc(II)	10^{-5}	1.0×10^{-3}	$>10^5$
Sb(IV)	10^{-5}	4.0×10^{-2}	$>10^4$
Zn(II)	10^{-5}	8.0×10^{-3}	$>10^5$

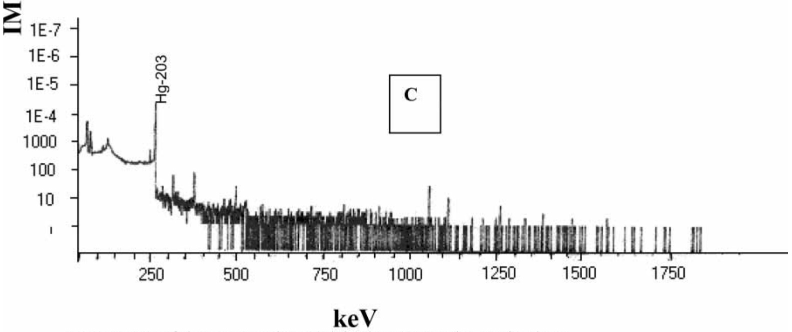
Various stripping agents of different concentrations such as 1 M HNO_3, 5 M HNO_3, 10 M HCl acid, 5 M $HClO_3$, 0.5 M thiourea in 0.5 M HCl acid, and 0.5 M NaCN in 0.5 M HCl were examined for the back extraction of the metal ions from the organic phase. Hg(II) is stripped quantitatively >99% by 10 ml of 0.5 M thiourea in 0.5 M HCl acid and 10 ml of 0.5 M NaCN in 0.5 M HCl.



γ-Spectrum of aqueous mixture of radioisotopes before extraction



γ-Spectrum of mixture radioisotopes in aqueous phase after extraction



γ-Spectrum of the separated Hg (II) in the extracted organic phase

Figure 4. Separation of Hg(II) from Zn, Cd and Se. Spectrum (A) γ-spectrum of aqueous mixture before extraction, Spectrum (B) γ-spectrum of aqueous mixture after extraction and spectrum (C) γ-spectrum of the separated Hg(II) in extracted organic phase.

To make the method more practical, the proposed method was applied for separation of ^{203}Hg from a synthetic solution consisting of Zn-65, Se-75, Cd-115 and Hg-203 radioisotopes. First, gamma spectrum (A) of a synthetic solution consisting of Zn-65, Se-75, Cd-115 and Hg-203 radioisotopes was taken, then this mixture was equilibrated with ANTU-MIBK mixture for five minutes and gamma spectrum of aqueous (B) and organic (C) phases were taken separately. By comparing, energy peaks for mercury in these spectra shown in Fig. 4, it has been concluded that the proposed method can successfully separate more than 99% mercury, leaving other selenium, cadmium, and zinc ions in aqueous phase.

CONCLUSIONS

These results underline the potential of the proposed method for quantitative, selective separation-preconcentration of Hg(II) from HCl media containing low or high concentration of mercury. Low effect of diverse ions, high separation factors, fast equilibration rendering this method attractive for environmental studies (preconcentration-separation-determination) and in the designing of a process for removal of mercury from nuclear waste and extraction of mercury from hydrochloric acid solutions.

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