**N-n-HEPTYLANILINE AS A NEW REAGENT FOR THE LIQUID-LIQUID EXTRACTION OF THALLIUM(III)**

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**1. Introduction**

Thallium was discovered by the English chemist William Crookes in 1861 and metallic thallium was first prepared by a French scientist C Lamy in 1862 [1]. The name derives from the green spectral line, which initially identified the element. In the past, thallium was extensively used for medical purpose. It was given to children to produce hair loss in the treatment of ring worm of the scalp and widely used in the treatment of venereal diseases, tuberculosis and malaria [2]. It is bluish white, in elastic, soft and easily fusible heavy metal having common oxidation states +1 (thallous) and +3 (thallic). Thallium is a by-product metal recovered in some countries from flue dusts. Thallium is present in cadmium(II), lead(II), zinc(II) or indium(III) compounds as a trace constituent hence extraction and separation is important [3, 4].

Pure thallium is a soft, malleable, bluish-white metal that is found in trace amounts on the earth’s crust. In its pure form, thallium is odourless and tasteless. It can also be found combined with other substances such as bromine, chlorine, fluorine and iodine. When it combined, it appears colourless to white or yellow [5]. Thallium remains in the environment since it can not be broken down to simpler substances [6]. Thallium with an atomic number of 81 and a relative atomic mass of 204.37 is a trace element. On account of its density (11.83 g/cm3), it is classified as a heavy metal [7].

It occurs mostly in sulphur containing ores [8]. In the activation of enzymes Tl (I) is known to replace potassium ions [9]. With a number of metals such as lead, silver, antimony and thallium readily forms alloys. The commercial cost of thallium is more than $ 2000 per kg. The contamination of the environment with thallium results from coal combustion, nonferrous amines and cement plants [10].

Currently, thallium is used in the manufacture of electronic components, optical lenses, semiconductor materials, alloys, gamma radiation detection equipment, imitation jewellery, artist’s paints, low temperature thermometers and green fireworks. Thallium is also used as a radiological contrast agent in myocardial imaging and in the visualisation of tumors. Thallium exposure may occur at smelters, in the maintenance and cleaning of ducts and flues and through contamination of cocaine heroin and herbal products. The main source of exposure to thallium in the general population is due to atmospheric pollution from, e.g. coal-burning power plants [11]. Environmental concerns are growing, as thallium is both a waste product of coal combustion and also of the manufacture of cement.

The cumulative index of ‘Chemical Abstracts’ 1995, lists over 150 uses and potential applications for thallium and its compounds until the early years of the 20th century. Thallium salts were used extensively to treat syphilis (since 1883), to reduce night sweats in tuberculosis patients since 1898 [12]. The use of thallium salts as poisons for rodents and later as insecticides began in 1920 and for the next 45 years remained the principal use for this element [13]. Thallium also crosses the placenta freely and produces abnormalities as well as fatal death and congenital abnormalities [14]. The toxicity is due to destructive effects on enzyme systems in the body.

By considering all these, it is interesting to develop a extraction and separation method for thallium.

**2. Summary of the solvent extraction methods for thallium(III) and thallium(I)**

With high molecular weight amines, the solvent extraction of thallium(III) have been investigated. A rapid and simple method was used for the extraction separation of less amount of thallium(III) and indium(III) by extraction with trioctylamine from chloride and iodide media at various concentrations of sulphuric acid [15]. From 2 M hydrobromic acid using N-benzylaniline, thallium(III) was readily and quantitatively extracted [16]. Extraction of micro amounts of thallium(III) in the presence and absence of gallium(III), indium(III) and iron(III) macro amounts by using solutions of trioctylamine and aliquat 336 shown co-extraction and extraction suppression are taking place in the system studied [17]. With tribenzylamine a simple solvent extraction study for thallium has been conducted which based on the extraction of thallium which forms chlorocomplex. The recovery of thallium was found about 95 % [18]. N-n-octylaniline in benzene, was used for solvent extraction of thallium(III) from aqueous chloride media. For quantitative extraction of thallium(III) comparatively high concentration of this extractant (0.10 M) was required also the intereference of bismuth(III), citrate, ascorbate, thiourea, thiocyanate was observed [19]. Primary amine, n-octylaniline dissolved in toluene has been reported as effective extractant for thallium(III) by using salicylate media [20].

X. Zhang et al. [21] carried out extraction of thallium(III) and thallium(I) from chloride media. For the separation of Tl(I) and Ga(III) and Tl(I) and In(III), CA-12 was found to be effective extractant [22]. Thallium(I) could be extracted with a hexanoic acid, monocarboxylic acid dissolved in either benzene, 4-methyl-2-pentanone, chloroform or nitrobenzene [23]. Organophosphorus compounds have been found, which is useful for the extraction of thallium(III). At pH 2.0 the neutral extractant tri-n-octylphosphine oxide (cyanex 921) extract thallium(III) into toluene [24]. For the mutual separation of gallium(III) and indium(III) from thallium(III) the method was extended [25]. Thallium(III) was extracted from 1.3 × 10-3 – 3.1 × 10-3 M sodium salicylate solution with 10 mL 45 % tris (2-ethylhexyl) phosphate [26]. From hydrochloric acid solutions the extraction of thallium(III) was studied by trioctylphosphine oxide and tributyl phosphate [27, 28]. The extraction efficiency of thallium(III) with TOPO was found to be higher than tributyl phosphate. The extraction coefficient of thallium(III) with trioctyl amine was found to be increased with increasing acid concentration [29, 30]. Thermodynamic study of solvent extraction of thallium(I) was carried out with diethyl hexyl monothiophosphoric acid (D2EHMPTA) [31, 32] and di(2-ethyl hexyl) dithiophosphoric acid [33] in the organic phase at the temperatures from 278.15 to 303.15. A method used for the separation of thallium(I) from thallium(III) with crown ether [34]. By extraction with n-octylaniline in chloroform separation of gallium, indium and thallium carried out [35].

Thallium(III) was separated using methyl isobutyl ketone (MIBK) in hydrobromic acid from the geological material [36, 37]. Extraction of thallium(III) with isoamyl acetate from 10 M hydrochloric acid media was proposed [38]. Extraction of thallium(III) by LIX 63 from 0.1-10 M hydrochloric acid media showed that the distribution coefficient of thallium increases with increasing temperature [39]. The extraction was found as dispersion free [40, 41]. Using PVDF, i.e., polyvinylidine fluoride (hydrophobic) and polypropylene HF (hollow fibre), liquid-liquid extraction of thallium(III) from NaCl-H2SO4 solution in the butyl acetate have been investigated [42-45]. Fe(III) was partially coextracted with thallium(III) [46]. Using 2-octylaminopyridine in chloroform as an extractant rapid liquid-liquid extraction of thallium(III) from succinate media has been studied [47]. Selective solvent extraction methods which are previously reported used for extraction of thallium(III) are given in (Table No. 1).

Thermal decomposition of the solvent-extracted metal complexes with high molecular weight amines studied [48]. Using n-benzylaniline separation of thallium-201 from lead-201 carried out [49]. Liquid-liquid extraction of indium and thallium from chloride media by resin ion exchange method was investigated [50]. A study of liquid-liquid extraction behaviour of gallium(III), indium(III) and thallium(III) with cyanex-925 (Bis-2,4,4-trimethyl pentyl-n-octyl phosphine oxide) was undertaken [51]. Reverse phase separation of gallium(III), Indium(III) and thallium(III) was carried out by Kuchekar et al 52]. A selective method has been developed for extraction, chromatographic separation of thallium(III) with N-n-octylaniline as a stationary phase on silica gel [53]. A new, simple and efficient method for simultaneous preconcentration of ultratrace amounts of gold and thallium is developed using an ion pair based-ultrasound assisted emulsification-solidified floating organic drop microextraction procedure before graphite furnace atomic absorption spectrometry determination [54]. Methylene blue has been proposed as a new analytical reagent for the catalytic spectrophotometric determination of thallium(I) [55]. Complexometric determination of thallium(III) using bromide as masking agent and silver (I) as demasking agent were studied [56].

A separation method between Tl(I) and Tl(III) in the presence of other heavy metals has been developed under pseudo three-phase equilibrium [57].

Here we propose simple, rapid extraction of thallium(III). Selective and quantitative extraction of thallium(III) by N-n-heptylaniline in xylene, was investigated. The various parameters like reagent concentration, acid concentration, loading, volume ratio, contact time, temperature have been studied. Nature of extracted species was predicted with the help of log [D] Vs log [C] plot. Vary many cations and anions do not interfere. The proposed method was applied for binary, ternary mixtures and alloys successfully.

**3. Experimental**

**3.1 Instrumentation**

Elico pH meter model (LI-120) was used to read pH of the solution. Digital balance was used for the weighing purpose.

**3.2 Reagent and solution**

**3.2.1 Thallium(III) solution (1 mg/mL)**

Stock solution of thallium(I) was made by dissolving an adequate quantity of its nitrate salt in very dilute nitric acid. Further thallium (I) was converted to thallium(III) using saturated bromine water, then the solution was standardized complexometrically.

**3.2.2 (0.001 M) Solution of thorium (IV) nitrate**

0.01 M thorium nitrate solution was prepared by dissolving calculated quantity of its nitrate salt in double distilled water and standardized against standard zinc(II) solution. Working solution of thorium nitrate (0.001 M) was prepared by proper dilution.

**3.2.3 EDTA solution (0.001 M)**

A standard 0.01 M EDTA solution was prepared by dissolving 3.722g disodium salt of EDTA in 1.0 litre of double distilled water and standardized complexometrically. Working solution of EDTA (0.001 M) was prepared by proper dilution.

**3.2.4 N-n-heptylaniline solution**

N-n-heptylaniline was synthesized by the method of Z. G. Gardlund and its solution (%,v/v) was prepared by using xylene as the diluent.

**3.2.5 Indicator**

Prepared by as in chapter III.

Working solutions were prepared by accurate dilution. AR grade chemicals and very pure solvents were used.

**3.3 General extraction procedure**

To an aliquot of solution containing 1 mg of thallium(III), add sufficient quantity of hydrochloric acid to make the concentration of 1 M in a total volume of 15 mL. Transfer the solution into a 125 mL separating funnel and shake the solution for 1 minute with 10 mL of 0.10 M N-n-heptylaniline in xylene. The swirl the solution and allow to separate the two phases. The organic phase was stripped twice with 40mL of acetate buffer. The amount of thallium(III) was determined complexometrically, by adding excess of 0.001M EDTA and back titrating against 0.001M thorium nitrate using 0.1% xylenol orange indicator. The end point is yellow to red violet.

**4. Results and Discussion**

**4.1 Effect of acid concentration on extraction of thallium(III)**

The extraction of 1 mg of thallium(III) was studied from various acids like hydrochloric, hydrobromic, sulphuric, nitric and perchloric acid media in the range of 0.1 to 7.5 M with 0.10 M N-n-heptylaniline in xylene keeping the aqueous to organic volume ratio 1.5:1. The extraction of thallium(III) increases with increase in acid concentration and becomes quantitative in 0.5 to 7.5 M hydrochloric and hydrobromic acid media (Table No. 2 and Figure No.1), 1.0 M concentration of hydrochloric acid was used throughout the work, as it has a wide range of applications as compared with hydrobromic acid. In other acids incomplete extraction was observed.

**4.2 Effect of reagent concentration on extraction of thallium(III)**

Increase in N-n-heptylaniline concentration increased the extraction of thallium(III). The excess of reagent concentration had no adverse effect on magnitude of extraction (Table No. 3 and Figure No. 2). It was found that, 10 mL of 0.10 M N-n-heptylaniline was sufficient for the quantitative extraction of thallium(III) from 1.0 M hydrochloric acid. Therefore in the recommended procedure 0.10 M N-n-heptylaniline in xylene has to be used to ensure complete extraction of thallium(III).

**4.3 Effect of shaking time on extraction of thallium(III)**

Study of shaking time was carried out. A set of experiments has been performed at different intervals of shaking time at the fixed condition of aqueous : organic ratio 1.5:1, 0.10 M N-n-heptylaniline, hydrochloric acid 1.0 M . The effect of shaking time was observed on the system for a period of 10 s to 3 min. The extraction was found to be quantitative over a period of 15 s to 3 min (Table No. 4 and Figure No. 3). Therefore, for the proposed method, 1 minute shaking time was recommended for the quantitative extraction.

**4.4 Effect of various diluents on extraction of thallium(III)**

The selection of an appropriate solvent is essential for the solvent extraction method. At optimum condition the extraction of thallium(III) was studied with 0.10 M N-n-heptylaniline by changing solvents. The extraction of thallium(III) was quantitative in solvents having low dielectric constant with few exceptions such as carbon tetrachloride, amyl acetate, methyl isobutyl ketone and nitrobenzene. It was incomplete with ethyl acetate and n-butanol. The results are tabulated in (Table No. 5 and Figure No. 4). The xylene was selected as the diluent as it gives clear-cut separation of the phases. It may be because of its low dielectric constant.

**4.5 Effect of aqueous to organic volume ratio on extraction of thallium(III)**

Upto what extent aqueous to organic volume ratio could be tolerated for the successful extraction of thallium(III) by N-n-heptylaniline at optimum condition was investigated from 1:1 to 20:1. The study shows that quantitative extraction takes place with phase ratios upto 4:1, beyond 4:1 extraction decreases probably due to the less stability of ion pair formed (Table No. 6 and Figure No. 5).

**4.6 Effect of strippants**

In any commercial extraction process it becomes necessary to back strip the metal from the loaded organic phase. Hence, number of strippants were tried to strip thallium(III) from loaded N-n-heptylaniline. Thallium(III) was back stripped completely with acetate buffer (pH 4.63) (2×40 mL) solution while in other strippants like sulphuric acid, acetic acid, nitric acid, perchloric acid and water back stripping was incomplete (Table No. 7).

**4.7 Loading capacity**

Maximum capacity of the reagent to extract metal from aqueous to organic phase is studied. From the results it seems that the quantitative extraction of metal takes place upto 5 mg. At higher concentration of thallium(III), extraction decreased (Table No. 8 and Figure No. 6). Thus, this study indicates that 5 mg of thallium(III) was a loading capacity of 10 mL 0.10 M N-n-heptylaniline in xylene.

**4.8 Effect of temperature on extraction of thallium(III)**

The experiment started with 0.10 M N-n-heptylaniline in xylene and was carried out at 1.0 M HCl at different temperatures (298 to 323 K). It was found that in the extraction of thallium(III) by N-n-heptylaniline in xylene the distribution ratio increases with a rise in temperature. The (Kex) as a change of the extraction equilibrium constant with temperature is expressed by the Van’t Hoff equation

Here note that, instead of T, K is taken for graph, where K = absolute temperature.

The graph of log Kex vs 1000/K is a strait line having slope -4.10 (Figure No. 7) and the enthalpy ΔH = 78.31 KJ mol-1 which suggests the reaction is an endothermic process.

ΔG = -2.303 RT logKex  (II)

ΔS = ΔH-ΔG/T (III)

ΔG and ΔS values are calculated by using equations (II), (III) and results are tabulated in (Table No. 9). The reaction is spontaneous as the value of ΔG is negative. Enthalpy results show that the extraction of thallium(III) with N-n-heptylaniline in xylene is favourable with a rise in temperature.

**4.9 Nature of the extracted species**

The extraction mechanism of thallium(III) was determined by analyzing the experimental data. Stoichiometry was determined using the traditional slope analysis method. Extracted species was determined by using graph Log D[Tl(III)] vs log C[N-n-heptylaniline)] (Figure No. 8) 0.61 and 0.99 are the slopes of straight lines at 0.1 and 0.4 M HCl. Hence, it is evident that the species is 1:1.

The probable extraction mechanism may be as follows,

TlCl3 + HClHTlCl4

[RR'NH]org+ HClaq [RR'NH2+Cl-]org

[(RR'NH2+Cl-)]org+ HTlCl4  [RR'NH2+TlCl4-] + HCl

Here, R and R’ are organic gropus such as, -C6H5 and -C7H15.

**4.10 Effect of foreign ions**

The effect of various foreign ions commonly associated with the thallium(III) was studied by the recommended procedure. The tolerance limits for the test ions were given in (Table No. 10). When interference was found to be intensive, the tests were repeated with successively smaller amounts of foreign ion that could be present to give an error less than ± 2 % in the recovery of thallium(III). It was observed that the method is free of interference from a large number of cations and anions. Bismuth(III), zinc(II) and mercury(II) co-extract.

**5. Applications**

**5.1 Thallium(III) separation from binary mixtures**

The method was applied for the extraction and separation of thallium(III) from a number of synthetic binary mixtures. Metal under study was quantitatively extracted, separated from associated metal ion in binary mixture by proposed method. Associated metals were determined by separate methods (58, 59, 60). The results are given in (Table No. 11).

**5.2 Analysis of thallium(III) in synthetic ternary mixtures**

The validity of the proposed method was applicable for the analysis of synthetic mixtures of various compositions. From the results of triplicate analysis demonstrate that it is possible to separate and identify thallium(III) from the ternary mixtures (Table No. 12).

**5.3 Alloy analysis**

Synthetic mixtures of standard alloys were prepared. A known amount of alloy was dissolved in a dilute nitric acid (3.5 M) then the solution was boiled with 1:1 HNO3 (5 mL) and filtered. Further filtrate is made 100 mL in volumetric flask. Then, thallium(III) was determined by general extraction method (Table No. 13).

**6. Conclusion**

The influence of concentration of acid, N-n-heptylaniline concentration, solvents, contact time, phase ratio, metal loading capacity, temperature effect, stripping agent, foreign ions and synthetic mixtures have been analyzed. The thallium(III) was quantitatively extracted from HCl and HBr having concentrations 0.5 to 7.5 M using a xylene solution of 0.10 M N-n-heptylaniline. To strip thallium(III) from the organic phase acetate buffer (pH 4.63) solution was used. Then it was standardized complexometrically. The proposed method is used for selective and rapid separation of thallium(III) from associated ions in their alloy samples, binary and ternary synthetic mixtures.

**Table**

**Table No. 1 Summary of solvent extraction methods for thallium(III) and thallium(I)**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Sr. No.** | **System** | **Aqueous phase** | **Organic phase** | **Special features** | **Ref. No.** |
| 1) | Trioctylamine  (TOA) | HCl,  HI | - | * By using masking agents the co-extracted ions was removed. | 15 |
| 2) | N-benzylaniline | HBr | Chloroform | * By using masking agents, scrubbing of organic phase, interference of common ions was removed. | 16 |
| 3) | TOA,  Aliquat 336 | HCl | Nitrobenzene, benzene | * Extraction of thallium takes place in presence of macroamounts of other metals. | 17 |
| 4) | Tribenzylamine | NaCl, H2SO4 | MIBK, Chloroform, Toluene | * 95 % recovery of thallium(III) | 18 |
| 5) | N-n-octylaniline | HCl | Benzene | * Interference of ions studied. | 19 |
| 6) | n-octylaniline | Sodium salicylate | Toluene | * Separation of Tl(I) and Tl(III) | 20 |
| 7) | CA-12, CA-100, NA | NH4Cl | Kerosene | * Separation of thallium(III) from gallium(III) and indium(III) | 21 |
| 8) | CA-12 | Chloride | Kerosene | * Separation of Tl(I) from In(III) and Ga(III) | 22 |
| 9) | Hexanoic acid | Sodium perchlorate | 4-methyl-2-pentanone, benzene, nitrobenzene, chloroform | * Extracted species TIR(HR)n | 23 |
| **Sr. No.** | **System** | **Aqueous phase** | **Organic phase** | **Special features** | **Ref. No.** |
| 10) | Cyanex 921 | HCl | Toluene | * Separation of thallium from multicomponent mixtures | 24 |
| 11) | Cyanex 923 | pH 1.5-3.0 | Toluene | * Mutual separation of thallium(III) from In(III) and Ga(III) | 25 |
| 12) | Tris(2-ethylhexyl)phosphate | Sodium salicylate | Toluene | * Thallium recovered from alloys, Interference of cations | 26 |
| 13) | TOPO, TBP | HCl | - | * Extracted complex dimeric with TOPO | 27 |
|  |  | HCl, LiCl | Benzene | * Extraction efficiency of TOPO higher than TBP | 28 |
| 14) | TBP/TOA | HCl/LiCl | Benzene | * Extraction increases with acidity, Extraction efficiency of thallium compared with that of In(III) and Ga(III). | 29  30 |
| 15)  16) | D2EHMTPA | Na2SO4 | Octane | * Thermodynamic properties of extraction calculated. | 31  32 |
| 17) | Di(2-ethylhexyl) dithiophosphoric acid |  |  | * Standard extraction constants analyzed. | 33 |
| 18) | Crown ethers | - | - | * Separation of thallium(I) and thallium(III). | 34 |
| 19) | n-octylaniline | HCl, HBr, HI | Chloroform | * The reagent can be recovered for reuse. | 35 |
| 20) | Methyl Isobutyl Ketone (MIBK) | HBr | MIBK | * Analysis of geological samples. | 36 |
|  |  | HBr | MIBK | * Separation of Tl(III) from Ga(III) and In(III). | 37 |
| **Sr. No.** | **System** | **Aqueous phase** | **Organic phase** | **Special features** | **Ref. No.** |
| 21) | Isoamyl acetate | HCl | - | * Analysis of sulphide minerals | 38 |
| 22) | LIX 63 | HCl | - | * Extraction depends on acidity and temperature | 39 |
| 23) | Butyl acetate | NaCl, H2SO4 | - | * Two stage solvent extraction * Single stage, two stage extraction * Extracted species HTCl4 * Dispersion free extraction | 40-43 |
| 24) | 16 Butyl acetate | HCl | Propylene carbonate | * Separation of thallium(III) from other metals | 44 |
| 25) | Cellulose nitrate resin | pH 1.6 | - | * By using masking agents interfering ions removed | 45 |
| 26) | SRS – 100 | Sodium acetate, acetic acid, pH 5.0 – 6.0 | - | * Separation of thallium(III) from several metal ions | 46 |
| 27) | 2-octylaminopyridine | Sodium succinate | Chloroform | * The method was applied to the synthetic mixtures and alloys. * It is simple, rapid, selective and eco-friendly method. | 47 |

**Table No. 2 Effect of acid concentration**

**Parameters:**

Tl(III) = 1.0 mg Reagent = 0.10 M in xylene

Volume ratio : 1.5 : 1 Equilibriation time = 1 min

Stripping agent = (2×40 mL) Acetate buffer (AB)

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Sr.**  **No.** | **Acid**  **(M)** | **Hydrochloric** | | **Hydrobromic** | |
| **%Ea** | **Db** | **%Ea** | **Db** |
| 1) | 0.1 | 52.0 | 1.44 | 72.0 | 3.86 |
| 2) | 0.2 | 68.0 | 3.19 | 86.0 | 9.21 |
| 3) | 0.3 | 94.0 | 23.5 | 96.0 | 36.0 |
| 4) | 0.4 | 98.0 | 73.5 | 98.0 | 73.5 |
| 5) | 0.5 | 100.0 | ∞ | 100.0 | ∞ |
| 6) | 0.7 | 100.0 | ∞ | 100.0 | ∞ |
| 7) | 1 to 7.5 | 100.0 | ∞ | 100.0 | ∞ |

**% Ea = Percentage extraction Db = Distribution ratio**

Tl(III) was not extracted in HNO3, H2SO4, HClO4

**Table No. 3 Effect of reagent concentration**

**Parameters:**

All parameters are constant as table no. 2 only N-n-heptylaniline concentration is varied.

|  |  |  |  |
| --- | --- | --- | --- |
| **Sr. No.** | **Reagent (M)** | **%Ea** | **Db** |
| 1) | 0.025 | 82.0 | 8.83 |
| 2) | 0.050 | 92.0 | 17.3 |
| 3) | 0.075 | 98.0 | 73.5 |
| 4) | 0.100 to 0.250 | 100.0 | ∞ |

**% Ea = Percentage extraction Db = Distribution ratio**

**Table No. 4 Effect of shaking time**

**Parameters:**

Except for the shaking time, all of the parameters are same as those listed in table no. 2.

|  |  |  |  |
| --- | --- | --- | --- |
| **Sr. No.** | **Shaking time (Sec.)/(Min.)** | **% Ea** | **Db** |
| 1) | 10 sec. | 96.0 | 36.0 |
| 2) | 15 sec. | 100.0 | ∞ |
| 3) | 20 sec. to 3 min. | 100.0 | ∞ |

**% Ea = Percentage extraction Db = Distribution ratio**

**Table No. 5 Influence of solvents**

**Parameters:**

With the exception of N-n-heptylaniline dissolving in solvent, all of the parameters are the same as those listed in table no. 2.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Sr. No.** | **Solvents used** | **% Ea** | **Db** | **Dielectric constant** |
| 1) | Amyl Acetate | 92.0 | 17.25 | 5.000 |
| 2) | Benzene | 100.0 | ∞ | 2.280 |
| 3) | Carbon-tetrachloride | 94.0 | 23.50 | 2.240 |
| 4) | Chloroform | 100.0 | ∞ | 4.810 |
| 5) | Ethyl acetate | 86.0 | 9.21 | 6.020 |
| 6) | Methyl isobutyl ketone | 98.0 | 73.50 | 13.10 |
| 7) | n-butanol | 82.0 | 6.83 | 17.80 |
| 8) | Nitrobenzene | 92.0 | 17.25 | 34.82 |
| 9) | Toluene | 100.0 | ∞ | 2.380 |
| 10) | Xylene | 100.0 | ∞ | 2.300 |

**% Ea = Percentage extraction Db = Distribution ratio**

**Table No. 6 Effect of volume ratio**

**Parameters:**

Except for the ratio of aqueous to organic phases all other parameters are the same as those listed in table no. 2.

|  |  |  |  |
| --- | --- | --- | --- |
| **Sr. No.** | **Volume ratio** | **% Ea** | **Db** |
| 1) | 1:1 | 100.0 | ∞ |
| 2) | 1.5:1 to 4:1 | 100.0 | ∞ |
| 3) | 5:1 | 88.0 | 11.0 |
| 4) | 7.5:1 | 64.0 | 2.67 |
| 5) | 10:1 | 40.0 | 1.00 |
| 6) | 12.5:1 | 28.0 | 0.58 |
| 7) | 15:1 | 6.0 | 0.09 |
| 8) | 20:1 | 0.0 | - |

**% Ea = Percentage extraction Db = Distribution ratio**

**Table No. 7 Effect of strippant on extraction of thallium(III)**

**Parameters:**

All conditions are similar to one as described in table 2 only strippant is absent.

|  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Sr. No.** | **Stripping agent (M)** | **Nitric acid** | | **Sulphuric acid** | | **Perchloric acid** | | **Ammonia** | | **Acetic acid** | |
| **% Ea** | **Db** | **% Ea** | **Db** | **% Ea** | **Db** | **% Ea** | **Db** | **% Ea** | **Db** |
| 1) | 0.1 | 8.0 | 0.13 | 18.0 | 0.33 | 14.0 | 0.24 | **0.0** | - | 8.0 | 0.13 |
| 2) | 0.5 | 12.0 | 0.20 | 26.0 | 0.53 | 22.0 | 0.42 | 0.0 | - | 12.0 | 0.20 |
| 3) | 1.0 | 18.0 | 0.33 | 28.0 | 0.58 | 36.0 | 0.84 | 0.0 | - | 18.0 | 0.33 |
| 4) | 2.0 | 22.0 | 0.42 | 32.0 | 0.62 | 42.0 | 1.09 | 4.0 | 0.06 | 18.0 | 0.33 |
| 5) | 3.0 | 26.0 | 0.53 | 38.0 | 0.92 | 42.0 | 1.09 | 8.0 | 0.13 | 22.0 | 0.42 |
| 6) | 4.0 | 34.0 | 0.77 | 44.0 | 1.18 | 48.0 | 1.38 | 10.0 | 0.17 | 24.0 | 0.47 |
| 7) | 5.0 | 46.0 | 1.28 | 52.0 | 1.63 | 60.0 | 2.25 | 16.0 | 0.29 | 28.0 | 0.58 |
| 8) | 6.0 | 58.0 | 2.07 | 58.0 | 2.07 | 74.0 | 4.27 | 16.0 | 0.29 | 28.0 | 0.58 |
| 9) | 7.0 | 58.0 | 2.07 | 60.0 | 2.25 | 78.0 | 5.32 | 18.0 | 0.33 | 28.0 | 0.58 |
| 10) | 8.0 | 62.0 | 2.45 | 60.0 | 2.25 | 88.0 | 11.0 | 20.0 | 0.38 | 30.0 | 0.64 |
| 11) | 9.0 | 62.0 | 2.45 | 62.0 | 2.45 | 100.0 | ∞ | 0.0 | - | 30.0 | 0.64 |
| 12) | 10.0 | 62.0 | 2.45 | 64.0 | 2.67 | 100.0 | ∞ | 0.0 | - | 32.0 | 0.71 |

**% Ea = Percentage extraction Db = Distribution ratio**

**Stripping agent Percentage Recovery (% R)**

* (2×40 mL) Acetate buffer (pH 4.63) 100.0
* (H2O) Water 68.0

**Table No. 8 Loading study of N-n-heptylaniline**

**Parameters:**

With the exception of the varying quantity of Tl(III) in mg, all parameters are the same as those listed in table no. 2.

|  |  |  |  |
| --- | --- | --- | --- |
| **Sr. No.** | **Metal,**  **(mg)** | **% Ea** | **Db** |
| 1) | 0.50 | 100.0 | ∞ |
| 2) | 1.0 to 5.0 | 100.0 | ∞ |
| 3) | 6.0 | 78.0 | 5.32 |
| 4) | 7.0 | 62.0 | 2.45 |
| 5) | 8.0 | 46.0 | 1.23 |
| 6) | 9.0 | 38.0 | 0.92 |
| 7) | 10.0 | 32.0 | 0.71 |

**% Ea = Percentage extraction Db = Distribution ratio**

**Table No. 9 Effect of temperature**

Parameters : All parameters are same to the stated in table no. 2, with the exception that the hydrochloric acid concentration is taken 1.0 M.

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Sr. No.** | **Absolute Temperature**  **(K)** | **1000/K** | **% Ea** | **Db** | **Log D** | **Log Kex** | **ΔG** | **ΔS** | **ΔH** |
| 1) | 298 | 3.355 | 78.72 | 5.54 | 0.7441 | 0.7463 | -4258 | 14.55 |  |
| 2) | 303 | 3.300 | 85.10 | 8.56 | 0.9328 | 0.9350 | -5424 | 18.16 |  |
| 3) | 308 | 3.246 | 89.36 | 12.6 | 1.1002 | 1.1024 | -6501 | 21.36 | 78.31 |
| 4) | 313 | 3.194 | 93.61 | 21.9 | 1.3411 | 1.3433 | -8050 | 25.97 |  |
| 5) | 318 | 3.144 | 95.74 | 33.7 | 1.5277 | 1.5299 | -9315 | 29.54 |  |
| 6) | 323 | 3.095 | 97.87 | 68.9 | 1.8383 | 1.8405 | -1138 | 35.48 |  |

**% Ea = Percentage extraction Db = Distribution ratio**

**Table No. 10 Effect of foreign ions**

|  |  |  |
| --- | --- | --- |
| **Sr. No.** | **Diverse ion** | **Tolerance limit (mg)** |
| 1) | Al(III) | 2.5 |
| 2) | Mn(II) | 5.0 |
| 3) | Pb(II) | 5.0 |
| 4) | Cd(II) | 5.0 |
| 5) | Fe(III) | 5.0 |
| 6) | Ni(II) | 5.0 |
| 7) | Cr(III) | 5.0 |
| 8) | Cu(II) | 5.0 |
| 9) | Co(II) | 5.0 |
| 10) | Fe(II) | 5.0 |
| 11) | Ag(I) | 5.0 |
| 12) | Th(IV) | 10.0 |
| 13) | Ca(II) | 30.0 |
| 14) | Mg(II) | 30.0 |
| 15) | Ba(II) | 30.0 |
| 16) | Zn(II) | Co-extract |
| 17) | Hg(II) | Co-extract |
| 18) | Bi(III) | Co-extract |
| 19) | EDTA | 50.0 |
| 20) | Tartrate | 50.0 |
| 21) | Oxalate | 100.0 |
| 22) | Acetate | 100.0 |
| 23) | Nitrate | 100.0 |
| 24) | Nitrite | 100.0 |
| 25) | Phosphate | 25.0 |

**Table No. 11 Thallium(III) separation from synthetic binary mixtures**

|  |  |  |  |
| --- | --- | --- | --- |
| **Sr. No.** | **Metal** | **Composition, mg** | **Average % Recovery** |
| 1) | Tl(III)  Al(III) | 1.0  1.0 | 99.9  99.9 |
| 2) | Tl(III)  Cd(II) | 1.0  1.0 | 99.9  99.8 |
| 3) | Tl(III)  Fe(III) | 1.0  1.0 | 99.7  99.9 |
| 4) | Tl(III)  Pb(II) | 1.0  1.0 | 99.8  99.7 |
| 5) | Tl(III)  Sb(III) | 1.0  1.0 | 99.8  99.7 |
| 6) | Tl(III)  Th(IV) | 1.0  1.0 | 99.9  99.8 |

**Table No. 12 Analysis of thallium(III) from synthetic ternary mixtures**

|  |  |  |  |
| --- | --- | --- | --- |
| **Sr. No.** | **Composition of the mixture (mg)** | **Thallium(III) found, (mg)** | **% recovery** |
| 1) | Tl(III), 1; Ca(II), 1; Cd(II), 1 | 1.0 | 100.0 |
| 2) | Tl(III), 1; Cu(II), 1; Fe(III), 1 | 1.0 | 100.0 |
| 3) | Tl(III), 1; Ni(II), 1; Mg(II), 1 | 1.0 | 100.0 |
| 4) | Tl(III), 1; Mn(II), 1; Fe(II), 1 | 1.0 | 100.0 |
| 5) | Tl(III), 1; Ba(II), 1; Co(II), 1 | 1.0 | 100.0 |
| 6) | Tl(III), 1; Cd(II), 1; Th(IV), 1 | 1.0 | 100.0 |

**Table No. 13 Alloy analysis**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Sr. No.** | **Sample** | **Mixture,**  **%** | **Amount of Tl(III) Taken, (mg)** | **Percentage Recovery,**  **(% R)** | **Relative Standard Deviation**  **(%)** |
| 1) | Type metal alloy | Pb 80.0  Sn 17.0  Sb 3.0 | 1.0 | 99.4 | 0.6 |
| 2) | Non-ferrous (Brass) alloy | Pb 2.0  Cu 65.0  Zn 30.0  Sn 1.0 | 1.0 | 99.6 | 0.4 |

**Figure**

****

**Figure No. 1 Effect of acid concentration**

**F:\Graph TIF File\Tl (III) TIF\Graph 2.TIF**

**Figure No. 2 Effect of N-n-heptylaniline concentration**

F:\Graph TIF File\Tl (III) TIF\Graph5.TIF

**Figure No. 3 Influence of shaking time**

F:\Graph TIF File\Tl (III) TIF\Graph solvent effect.TIF

**Figure No. 4 Influence of solvents**

F:\Graph TIF File\Tl (III) TIF\Graph 5.TIF

**Figure No. 5 Influence of volume ratio**

F:\Graph TIF File\Tl (III) TIF\Graph 4.TIF

**Figure No. 6 Study of loading capacity**

F:\Graph TIF File\Tl (III) TIF\Graph2 temp.TIF

**Figure No. 7 Effect of temperature on extraction**

F:\Graph TIF File\Tl (III) TIF\Graph Log-log .TIF

**Figure No. 8 Log-Log graph of LogD[Tl(III)] Vs Log C [N-n-HA]**

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