Extraction and Spectrophotometric Assay of Yttrium (III) with TOPO, Application to Water Samples and Alloys

Salim Ali Mohammad, Samiea Yaseen Sharaf Zeebaree *

Department of Chemistry, College of Science, Mosul University, Mosul, Iraq

Email address:
Salimsalah813@yahoo.com (S. A. Mohammad), Samie.yasin@dpu.edu.krd (S. Y. Zeebaree)

*Corresponding author

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Abstract: An easy, accurate, selective and sensitive method for extraction and spectrophotometric determination of yttrium (III) in aqueous solution has been determined. The procedure is based on the extract of yttrium (III) with Trioctylphosphine oxide (TOPO) reagent from the aqueous medium followed reaction of extracted yttrium (III) in organic layer with alizarin red s (ARS) reagent at pH 4.9 to form a red carmine complex which has maximum absorption at 519 nm. Beer’s law is obeyed over the concentration range 10-260 µg yttrium (III) /10 ml, (i. e., 1-26 ppm) with a determination coefficient of (0.991) and molar absorptivity of $0.53 \times 10^4$ l.mol$^{-1}$.cm$^{-1}$. The recoveries are obtained in the range of 98.7 - 100.01% and a relative standard deviation is better than ±2.33%. The method has been successfully applied to the determination of yttrium (III) in natural waters and magnesium alloys.

Keywords: Yttrium (III), Extraction, TOPO, Spectrophotometric, Alloys

1. Introduction

Yttrium is an important member of rare-earth family. It is more abundant than the heavy lanthanides, resembles them in Properties, and occurs with them in nature. Yttrium is never found in nature as the free element. It is found in the three main minerals supplying lanthanides, xenotime, monazite and bastnaesite. Yttrium has silvery-metallic luster and spontaneously igniting in air [1]. In many neutral phosphorus extractant TBP is the earliest applied in rare earth extraction separation [2]. A selective method is presented the solvent extraction of yittrium (III) from salicylate media by using triphenylphosphine oxide [3]. TOPO has been widely used for solvent extraction separation and distribution ratio for most element in the system 5% TOPO – HCl have been determined in the rang 1-12N HCl [4]. Solvent extraction of yttrium (III) and trivalent metal ions in weakly acidified 1 mol dm$^{-3}$ NaClO$_4$ solution with trioctylphosphine oxide in hexane was studied [5]. A batch solvent extraction process has been developed for the specific purpose of separating Y$^{91}$ and Ce$^{144}$ from the gross rare earth fission products fraction. It involves the extraction of these two elements into di(2-ethylhexyl)- phosphoric acid (D2EHPA) in Amsco [6]. The extraction behavior of lanthanides and yttrium using CYANIX925 (mixture of branched chain alkylated phosphine oxide in n-heptane from nitrate medium has been studied [7]. Extraction behavior of some tervalent lanthanides from acidic media like HCl, H$_2$SO$_4$, HNO$_3$ and H$_3$PO$_4$ in a toluene solution of cyanix 923 have been studied [8]. A new kind of hydrophobic ionic liquids [1-alkyl-3-(1-carboxylpropyl)imid][PF6] has been synthesized and their extraction properties for Y (III) in the nitric acid medium was also investigated [9].

2. Experimental

2.1. Apparatus and Reagents

Spectral and absorbance measurements are executed using JASCO V-630 double beam UV-Visible spectrophotometer (Japan) with 1-cm quartz cells. The pH measurements are carried out using HANNA instruments pH 211. All chemical used are of the highest purity available.

Standard Y (III) solution (100 µg /ml). It was prepared by dissolving 0.341 g of yttrium chloride hexahydrate (Fluka) in 100 ml distilled water using a volumetric flask.

Dilute Y (III) solution It is prepared by diluting the
Alizarin red S reagent solution ($2 \times 10^{-3}$ M). This solution is prepared by dissolving 0.0342 g of ARS reagent (Fluka) in 50 ml distilled water using a volumetric flask and then is transferred to a dark bottle. This solution is stable for at least one week.

**TOPO reagent solution 2%** is prepared by dissolving 2 gm of TOPO in 100 ml chloroform.

Sodium salicylate 0.5 M solution is prepared by dissolving 8.005 gm of sodium salicylate salt in 100 ml distilled water using volumetric flask.

Composite mixture solution have prepared by dissolving 1.5 gm of ascorbic acid and 0.02 gm of sodium florid in 50 ml of distilled water and the mixture solution should be used immediately.

Buffer solution (pH4.9). This solution is prepared by mixing 11 ml of 0.1M formic acid with 10.5 ml of 0.1 M sodium hydroxide and the volume is completed to 100 ml with distilled water [10].

### 2.2. Preliminary Study

#### 2.2.1. Effect of Ethanol Quantity

In order to develop the complex color produced between yttrium (III) and ARS reagent in the organic layer it should be form a homogeneous solution that is accomplished when addition of aqueous solution (contain ARS) to the extracted organic layer which contain complex of (Y-TOPO) dissolved in toluene, however, the final mixture of reaction must be diluted as less as possible by addition of ethanol instead of water, the effect of added (ethanol 96% ) to the final mixture have been studied establishing that mixing 2 ml of toluene with 3 ml of water followed completing the volume with ethanol to mark of volumetric flask gave a homogeneous solution with high solubility could be depended at adjusting the optimum condition of procedure.

#### 2.2.2. Recommended Procedure

A 2.5 ml of 0.5 M of sodium salicylate solution has been added to the 50 ml separatory funnel containing 200 µg of yttrium (III), then the volume of aqueous layer is completed to the 25 ml with distilled water, after that a 5 ml of 2% of TOPO dissolved in toluene must be added with shaking the separatory funnel within 1 minute, the organic layer was separated and 1 ml (contain 40 Mg of $Y^{3+}$) was taken and transferred into 10 ml calibrated flasks with addition 2 ml of $1 \times 10^{-3}$M ARS reagent and 1 ml of buffer solution pH 4.7, The solutions are mixed and completed to the mark with ethanol. The absorbance of coloured solution is measured at 523 nm against the reagent blank solution.

Recommended procedure for the extraction of Y (III) in natural waters

After filtering the sample, aliquots of not more than 5 ml are taken, and the above procedure described was followed.

### 3. Results and Discussion

The spectrophotometric properties of the extracted product as well as the different parameters affecting the extraction process and colour development of the complex and its stability are studied and optimized. For the following experiments, 1ml of organic separated layer is taken in a final volume of 10 ml.

#### 3.1. Effect of pH

In order to detect the ideal pH of extraction process The addition effect of acid and base in aqueous layer was studied by monitor the absorption of Y (III)-ARS complex after extraction process. The results indicated that the optimum pH range for aqueous layer was found to be 3.95 – 6.22 at which the colour intensity has a Constance maximum absorption at 523 nm (Figure 1). pH 4.8 is considered the optimum because of the high extraction and good colour contrast.

![Figure 1. Effect of pH on absorbance.](image)

Therefore, the experimental data of this investigation indicated that 1.5 ml of 0.01 HCl solution lead to optimum pH, therefore it has been selected for the subsequent experiments.

#### 3.2. Effect of Sodium Salicylate Concentration

The previous studies point out to the composition of extracted specious as $Y\text{(Hsal)}_3\text{2TPPO}$ and favouring the extraction by adduct formation. The bis adduct $Y\text{(Hsal)}_3\text{2TPPO}$ is presumably more hydrophobic than the parent complex $Y\text{(Hsal)}_3$, thus favouring its extraction into an organic phase [11].

Any way the effect of sodium salicylate concentration on the extraction of yttrium by TOPO was studied by addition various quantity of it showing that 3 ml of 0.5 M of sodium salicylate gave the better extraction.

| ml of Sodium salicylate (0.5 M) | Absorbance |
|--------------------------------|------------|
| 1                              | 0.1728     |
| 1.5                            | 0.1886     |
| 2                              | 0.2002     |
| 2.5                            | 0.2005     |
| 3                              | 0.2439     |
| 3.5                            | 0.2300     |
| 4                              | 0.2310     |
| 4.5                            | 0.2290     |

#### 3.3. Effect of Organic Solvent

Influence of variety organic solvent employed to prepare
TOPO solution has been studied to identify the better efficiency extraction process, a lot of solvents classes was experienced such as xylene, chloroform, cyclohexane, tetrachlorocarbon and toluene, the results indicates that dissolving of TOPO in chloroform solvent gave much more extracted yttrium than another solvents by measuring the absorptivity of extracted species. So it has been selected for the subsequent experiments.

### 3.4. Effect of Masking Agent

In order to enhance the selectivity the effect of common masking agents NaF and ascorbic acid has been investigated. The experimental data showed that the masking agents used was not effect on the absorbance of the extracted yttrium.

| ml of 3% ascorbic acid | Absorbance at $\lambda_{max}$ 519 nm |
|------------------------|-------------------------------------|
| 1                      | 0.3022                              |
| 2                      | 0.3020                              |
| 3                      | 0.3028                              |
| 5                      | 0.2911                              |

During the addition of ascorbic acid it's showing decreasing in pH of aqueous phase so the pH should be adjusted by addition a portion of 0.01 M NaOH.

Also the table below showing the effect of NaF addition

| ml of 0.01 M NaF | Absorbance |
|-----------------|------------|
| 0.5             | 0.3019     |
| 1               | 0.3001     |
| 1.5             | 0.2793     |
| 2               | 0.2716     |
| 2.5             | 0.2623     |

### 3.5. Effect of Composite Mixture Solution

A composite mixture of NaF and ascorbic acid was prepared and experienced to investigate their effect on the extraction process, the results indicate that there is no effect of this mixture solution on extraction of yttrium.

### 3.6. Effect of TOPO Concentration

The influence of various concentration of TOPO reagent (1% - 3%) on the efficiency of yttrium extraction have been studied. The table below show that the 5 ml of 2% show better absorbance therefor it's collected in the next experience.

| Concentration of TOPO (%) | Absorbance |
|---------------------------|------------|
| 1.0                       | 0.1561     |
| 1.5                       | 0.1688     |
| 2.0                       | 0.3014     |
| 2.5                       | 0.3009     |
| 3.0                       | 0.3012     |

### 3.7. Effect of Volume Ratio

A several time periods (0.5 – 10) minutes was studied to identify the best shaking time of mixture reaction in separatory funnel and showed that the 1 minute is suitable time for shaking to own the best extraction.

| ml of aqueous phase (Va) | ml of organic phase (Vo) | $Va / Vo$ ratio | Absorbance |
|-------------------------|--------------------------|-----------------|------------|
| 15                      | 5                        | 3:1             | 0.2635     |
| 20                      | 5                        | 4:1             | 0.2911     |
| 25                      | 5                        | 5:1             | 0.3098     |
| 30                      | 5                        | 6:1             | 0.2460     |

### 3.8. Effect Time of Shaking

A several time periods (0.5 – 10) minutes was studied to identify the best shaking time of mixture reaction in separatory funnel and showed that the 1 minute is suitable time for shaking to own the best extraction.

| Time of shaking (min.) | 0.5 | 1.0 | 1.5 | 2.0 | 3.0 | 5.0 | 10 |
|------------------------|-----|-----|-----|-----|-----|-----|----|
| Absorbance             | 0.2878 | 0.3099 | 0.3057 | 0.3085 | 0.3006 | 0.3010 | 0.2985 |
3.9. Effect of pH on the Extraction Process

After adjusting the optimum condition the efficiency of extraction was studied one more time by addition of acid and base to the aqueous phase, it have showed that efficiency of extraction was reached to 99.2% while the pH of aqueous layer is 4.88.

Table 9. Effect of pH on the extraction process.

| (ml of HCl solution 0.01M) | pH of the aq. Layer | Absorbance |
|---------------------------|---------------------|------------|
| 0                         | 4.32                | 0.3001     |
| 0.5                       | 3.83                | 0.2922     |
| 1                         | 3.38                | 0.2612     |
| ml of NaOH solution (0.01M) | pH of the aq. Layer | Absorbance |
| 0.5                       | 4.54                | 0.2998     |
| 1                         | 4.88                | 0.3101*    |
| 1.5                       | 5.25                | 0.2911     |
| 2                         | 5.69                | 0.2509     |

* A= 0.3106 without extraction, [Y^3+] = 40 µg, D = 620.2, E %=99.2, Vaq. = 25 ml, Vorg. = 5 ml.

3.10. Effect of pH on the Complex Formed Between Y^{3+} and ARS

The absorption value of Y-ARS complex was experienced by measuring the pH of mixture during addition diluted solution of acid and base. The table below show that the highest value of complex absorption was at the pH 4.9.

Table 10. Effect of pH on the complex of Y-ARS.

| ml of 0.01M HCl solution | pH of final solution | Absorbance |
|---------------------------|----------------------|------------|
| 0.0                       | 4.80                 | 0.3069     |
| 0.5                       | 4.41                 | 0.2902     |
| 1.0                       | 3.95                 | 0.2711     |
| 1.2                       | 3.44                 | 0.2131     |
| ml of 0.01M NaOH solution | pH of final solution | Absorbance |
| 0.2                       | 4.90                 | 0.3112     |
| 0.3                       | 5.07                 | 0.3101     |
| 0.4                       | 5.22                 | 0.2714     |

In order to protect the pH changing of complex mixture the buffer solution have been prepared (formic acid – NaOH) and determined the suitable volume by addition a various quantity of buffer solution and show that 1 ml of buffer solution could maintain the pH value.

Table 11. Effect of buffer solution.

| ml of buffer solution (pH4.9) | Absorbance |
|------------------------------|------------|
|                              | Sample solution | Blank solution |
| 0.5                          | 0.3011       | 0.0136        |
| 0.7                          | 0.3142       | 0.0144        |
| 1                            | 0.3145       | 0.0141        |
| 1.2                          | 0.3100       | 0.0170        |
| 1.5                          | 0.2956       | 0.0200        |

3.11. Effect of ARS Reagent Amount

The effect of different amounts (0.3-1.8 ml) of 2×10^{-3} M ARS on the absorbance of the resulting complex Y (III)-ARS have been studied. The results in Table show that 1.3 ml of 2×10^{-5} M ARS solution show better absorbance at 519 nm therefore it is recommended for the subsequent experiments.

Table 12. Effect of ARS reagent.

| ml of 2×10^{-5}M ARS reagent | Absorbance |
|------------------------------|------------|
| 0.3                          | 0.2821     |
| 0.5                          | 0.3412     |
| 0.8                          | 0.3663     |
| 1                            | 0.3774     |
| 1.3                          | 0.3801     |
| 1.5                          | 0.3751     |
| 1.8                          | 0.3556     |

3.12. Effect of CTAB Surfactant

To know the influence of surfactant solution on the absorption value of complex formed the series of test have been done and show that there is a negative effect was achieved while addition of CTAB surfactant so it have been excluded.

Table 13. Effect of surfactant.

| ml of CTAB solution (1×10^{-2} M) | Absorbance |
|-----------------------------------|------------|
| 0.3                               | 0.3638     |
| 0.5                               | 0.3771     |
| 0.8                               | Turbid     |
| 1                                 | Turbid     |
| 1.5                               | Turbid     |

3.13. Effect of Time on the Stability of Complex

After adjusting the optimum condition of the color reaction between yttrium (III) and ARS reagent the effect of time on the stability of complex have been studied, its show that the complex is stable for 1 hour.

Table 14. Stability of complex.

| Time (min) | Absorbance / µg of Y (III) extracted |
|------------|-------------------------------------|
|            | 25                                  |
|            | 50                                  |
| Immediately| 0.1791                              |
| 2          | 0.1815                              |
| 5          | 0.1853                              |
| 10         | 0.1911                              |
| 15         | 0.1912                              |
| 20         | 0.1912                              |
| 25         | 0.1933                              |
| 30         | 0.1935                              |
| 40         | 0.1983                              |
| 50         | 0.1985                              |
| 60         | 0.1997                              |

3.14. Final Absorption Spectrum

The final spectrum has been drew after set the optimum condition by transfer 1 ml of extracted yttrium (40 µg) to the volumetric flask of 10 ml followed by addition 1.3 ml of (2×10^{-3} M) ARS and 1 ml of buffer solution (pH=4.9) then the volume was completed with ethanol to the mark to form a red carmine complex which has maximum absorption at 519 nm.
4. Quantification

In order to investigate the range in which the colored complex adheres to Beer's law, the absorbance of the complex is measured at 519 nm after extraction of yttrium and developing the colour by following the suggested procedure for a series of solutions containing increasing amounts of Y (III) (Figure 3).

The Beer's law limits, molar absorptivity, Sandell's sensitivity, (LOD) and (LOQ) values [12] are evaluated and are given in Table 15 which indicates that the method is sensitive. Linearity is represented by the regression equation and the corresponding determination coefficient for BH determined by the proposed method represents excellent linearity ($R^2=0.9954$). The relative standard deviation (RSD) and accuracy (recovery %) for the analysis of five replicates of each of the three different concentrations of BH indicates that the method is precise and accurate.

Table 15. Summary of optical characteristics and statistical data for the proposed method.

| Parameter                                      | Values of method |
|------------------------------------------------|------------------|
| Beer's law limits (ppm)                       | 1-26             |
| Molar absorptivity (Lmol$^{-1}$.cm$^{-1}$)     | 0.53×10$^4$      |
| Sandell's sensitivity (µg.cm$^{-2}$)           | ------           |
| Slope                                          | 0.006            |
| Intercept, $b$                                 | ------           |
| Determination coefficient                      | 0.991            |
| Range of recovery (%)                          | 94.73 - 103.77%  |
| RSD (%)                                        | Better than ±2.33% |

* Average of five determinations in sea water.

Effect of Foreign Ions

The effect of various amounts of many foreign ions on the extraction of Y (III) are examined using the recommended procedure. The results obtained are summarized in Table 16.

Table 16. Individual tolerance limit of foreign ions on the extraction of 40µg Y (III).

| Foreign ion added | Tolerance limit, µg |
|-------------------|---------------------|
| Mg$^{2+}$, Mo$^{6+}$, SO$_4^{2-}$, Fe$^{3+}$ | 2000                |
| Al$^{3+}$, Co$^{2+}$, Cu$^{2+}$, Fe$^{2+}$, Ni$^{2+}$, Ti$^{4+}$, W$^{6+}$, Zn$^{2+}$, Zr$^{4+}$ | 1500                |
| Bi$^{3+}$, Th$^{4+}$, PO$_4^{3-}$, La$^{3+}$, Sn$^{2+}$ | 200                 |

As shown in Table 16, the largest interfering species are found to be Bi$^{3+}$, La$^{3+}$, Th$^{4+}$, PO$_4^{3-}$ ions.

5. Application

5.1. Determination of Yttrium in Water Samples

The present method has been applied to determination of Y (III) at three different concentrations added to appropriate volumes of river and sea waters. The results are compiled in Table 17 and showed that the proposed method is suitable for determining Y (III) with satisfactory recovery.

Table 17. Determination of yttrium in natural waters.

| Sample solution | ml of sample | Amount of Y (III) added (µg) | Recovery (%) |
|-----------------|--------------|------------------------------|--------------|
| Sea water**     | 5            | 100                          | 94.73        |
|                 |              | 200                          | 99.46        |
|                 |              | 500                          | 103.77       |
|                 | 10           | 100                          | 97.75        |
|                 |              | 200                          | 99.91        |
|                 | 15           | 100                          | 95.26        |
|                 |              | 200                          | 99.56        |
5.2. Determination of Yttrium in Prepared Magnesium Alloys

Yttrium has been determined in a sample contain a various ions that prepared in lab.

| Sample of synthetic mixture** | Sample composition (µg) | Amount of Y (III) found (µg) | Recovery* (%) |
|-----------------------------|-------------------------|-----------------------------|---------------|
| SMI                         | Mg^{2+} (3000), Zr^{4+} (200), Y^{3+} (200) | 206.02                     | 103.01        |
| SMII                        | Fe^{3+} (50), Mg^{2+} (2000), Y^{3+} (200), SO_4^{2-} (50) | 197.40                     | 98.70         |

*Average of three determinations.
**Magnesium alloys, are used in aircraft and high performance vehicles [14].

5.3. Comparison of Methods

Table (19) shows the comparison of spectrophotometric methods for Yttrium (III) determination based on chelating with some organic reagents.

| Analytical parameter | Present method | Literature method [14] |
|----------------------|----------------|------------------------|
| Reagent              | ARS            | ARS                    |
| pH of colure development | 4.9         | 4.7                    |
| λ_{max} (nm)         | 519            | 535                    |
| Determination coefficient (r^2) | 0.9910      | -                      |
| Beers law rang (µg/ml) | 1-26        | -                      |
| Molar absorptivity (l. mol^{-1}.cm^{-1}) | 0.53×10^4 | -                      |
| Solvent used         | Chloroform     | Xylene                 |
| Extraction reagent   | TOPO           | N-n-octylaniline       |
| Equilibrium time (min) | 1           | 5                      |
| Time of color development | Immediately | Immediately          |
| Recovery (%)         | 98.7-100.01    | 98.5-99.5              |
| Surfactant           | none           | None                   |
| Stripping agent      | none           | HCl                    |
| Application          | Determination of Y (III) in natural waters and Magnesium alloys | Determination of Y (III) in synthetic mixtures |

6. Conclusion

A sensitive and selective spectrophotometric method has been developed for the extraction and determination of yttrium in aqueous solution using TOPO as extraction agent and alizarin red S as chelating agent at pH4.9. The coloured complex exhibits a molar absorptivity 0.53×10^4 l.mol^{-1}.cm^{-1} at 519 nm, Beer’s law is obeyed over the concentration range 1-26 ppm. The method has been applied successfully to the determination of yttrium (III) natural waters and synthetic alloys.

References

[1] Osman, A., D., (2006). Ph. D. Thesis, Liquid-Liquid Extraction of Rare Earth Elements from Sulfuric Acid Solutions. Department of Chemistry, University of Leeds. p. 48.

[2] Li deqian, (2017), A review on yttrium solvent extraction chemistry and separation process, journal of rare earths, 35(2), 107.
[3] N., G., Bhilare, V., M., Shinde, (1996), Liquid-liquid extraction and separation studies of yttrium, Fresenius J Anal Chem, 354, 122-124.

[4] E., Steinnes, O., R., Birkelund, O., Johansen, (1971), Determination of trace element in biological material by neutron activation and extraction with TOPO, journal of radioanalytical chemistry, 9, 267-272.

[5] M., Yamada, S., Kusakabe, J., Prekopova And T., Sekine, (1996), Solvent Extraction of Seven Trivalent Metal Ions in Aqueous Perchlorate Solutions with Trioclylphosphine Oxide in Hexane and Rapid Extraction of Chromium (III), Analytical science, 12, 405.

[6] T., A., Butler, E., E., Ketchen, (1961), Solvent Extraction Separation of Cerium and Yttrium from Other Rare Earth Fission Products, Industrial and engineering chemistry, 53(8), 651-654.

[7] W., Li, X., Wang, H., Zhang, S., Meng, D., Li, (2007), Solvent extraction of lanthanides and yttrium from nitrate medium with cyanex 925 in heptane, Chemical technology and biotechnology, 82(4), 376-381.

[8] B., Gupta, P., Malak and A., Deep, (2003), Solvent extraction and separation of tervalent lanthanides and yttrium using cyanix 923, solvent extraction and ion exchange, 21(2), 239-258.

[9] W., Wei, L., Yu, X., Aimei, Y., Hualing, C., Hongmin and C., Ji, (2012), Solvent extraction of yttrium by task–specific ionic liquid bearing carboxylic group, Chinese journal of chemical engineering, 20(1), 40-46.

[10] D., D., Perrin, B., Dempsy, 1974. Buffers for pH and metal Ion Control. Champan and Hall Ltd., London, 132.

[11] International Conference on Harmonization (2005), ICH Harmonized Tripartite Guide-line: Validation of Analytical Procedures Text and Methodology, Q2 (R1), Current Step 4 Version, 11-13.

[12] Henriksen, A., 1965. An Automatic Method for Determining Nitrate and Nitrite in Fresh and Saline Waters, Analyst, 90, 83-88.

[13] https://en.wikipedia.org/wiki/Magnesium_alloy/ (accessed 15 April 2015).

[14] B., N., Kokare, A., M., Mandthare, S., S., Kolekar and M., A., Anuse, N-octylaniline as a New reagent for analytical Liquid-liquid extraction of yttrium (III) from matrices of various metal ions, Macedonian Journal of Chemistry and Chemical Engineering, (2011), 30 (2) p. 151-162.