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# Chemical Characterization of Al-Li Alloys for Scandium by Hyphenated Technique using Ion Exchange Chromatography

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A simple method is developed for separation of scandium in Al-Li alloys using anion exchange chromatographic technique in ammonium sulphate medium. Scandium is strongly adsorbed on basic anion exchange resin, Dowex 1, X-8 (sulphate form) in 0.1 M ammonium sulphate and in 0.025 M sulphuric acid medium. In such condition, Al, Fe, Cu, Mn, Cr, Mg, Ti and Li are not adsorbed. The adsorbed scandium is eluted by ammonium sulphate and estimated by complexometric technique using 0.01 M EDTA.

**Key Words: Scandium, Al-Li Alloys, EDTA, Ion exchange chromatography.**

## INTRODUCTION

Aluminium base alloys are widely used for aeronautical applications. Especially, precipitation strengthened alloys are used to fabricate number of components of aircrafts. The development of Al-Li alloys resulted in the replacement of conventional Al-alloys because 1 % addition of Li reduces the density by 3 % and increases elastic modulus about 6 %[1]. A number of other alloying elements are added to achieve the required properties. Elements such as Cr and Ti are added to increase corrosion resistance, Zr for fine grain size, Mg for modification of precipitates and scandium to improve formability and welding strength of Al-alloys. On weight basis scandium imparts largest increases in strength of alloy and inhibits recrystallization due to interaction with other dispersoid formers like Cu, Mg and Zr[2]. It is therefore required to optimize scandium additions in Al alloys, which calls for accurate determination of scandium in Al-Li alloys.

Generally gravimetry, complexometry and colorimetry methods are used to determine scandium. In gravimetric method, 8-hydroxyquinalidine[3] and oxine[4] are few reagents used for analysis of pure scandium and interferences due to many elements like Al, Mg, Mn, *etc.* are reported. EDTA and CDTA are used in complexometry technique where Al, Ti and Zr interfere in the liberation of scandium by ammonium fluoride. Colorimetric regents such as xylenol orange and arsenazo-III[5], *ortho*-chlorophenylfluorone, cetyltrimethylammonium bromide[6] and disodium 3-hydroxy-4-[(6-methyl-2-pyridyl)azo]-2,7-naphthalenedisulfonate N-oxide[7] are used for spectrophotometric estimation of scandium. However these regents were not suitable for scandium in Al-Li alloy where other elements like Cu, Zr, Mn, Mg and Cr that are also present form colour complexes and interfere in the analysis. Separation of scandium by solvent extraction methods were tried using tri-*n*-butyl orthophosphate[8], mesityl oxide[9] and di (2-ethylhexyl)phosphoric acid[10] but Al was found to be interfering in the analysis. Minowa and Ebihara[11] studied the separation of rare earth elements from scandium by anion and extraction chromatography. Ramanaiah[12] proposed the determination of scandium, yttrium and other rare earth elements by ICP-AES. Separation of scandium and rare earth elements by reversed phase HPLC was reported by Lambrini[13]. Shang *et al.*[14] studied separation of scandium, yttrium and lanthanum by high performance centrifugal partition chromatography. The present work report an anion exchange separation of scandium from Al and other associated elements using Dowex 1, X-8 and estimation by complexometric method. Studies on distribution coefficient, concentration of eluent, flow rates, *etc.* for quantitative separation of scandium are also reported.

## EXPERIMENTAL

Stock solutions of all the elements were prepared from SPEC pure metal powder. A.R. grade acids were used for dissolution. Millipore water with 18-mega ohms resistance was used for diluting the solutions.

**Stock solution of scandium:** 0.1 g of scandium metal was dissolved in 10 mL HCl (1:1). After complete dissolution the contents were transferred to standard flask and made up to 100 mL using distilled water. The solution corresponds to 1 mg $mL^{-1}$.

**Stock solution of Al, Mg, Fe, Zr, Ti, Mn, Cu, Cr and Li:** 1.0 g Al, Mg, Ti and 0.1 g Fe, Zr, Mn, Cr and Li were dissolved separately in 20 mL 1:1 hydrochloric acid. 0.1g of Cu was dissolved in 10 mL nitric acid (1:1). After complete dissolution the contents were transferred to standard flask and made up to 100 mL using distilled water. The final concentration of Al, Mg and Ti were 10 mg $mL^{-1}$ and Fe, Zr, Mn, Cr, Li and Cu were 1 mg $mL^{-1}$.

### Preparation of resin and ion exchange column:

**Resin:** 10 g of resin of Dowex 1, X-8, 100 mesh, chloride form was converted to sulphate form by equilibrating with 3 M excess sulphuric acid until the effluent gave negative test for chloride with silver nitrate. Finally the resin was washed with distilled water to remove excess sulphate ion until the effluents gave negative test with barium chloride. The resin thus obtained was used for separation of scandium from Al and other elements.

**Column:** Conventional ion exchange column of 9 mm dia and 40 cm long was used. 10 mm layer glass wool was placed at the bottom of ion exchange column. The column was prepared by loading suspension of resin (10 g of sulphate form) in water to obtain a settled resin bed of 20 cm long.

### Preparation of solutions

**Synthetic standard solutions:** Synthetic standard solutions were prepared for calibration. The solutions of Al, Mg, Fe, Zr, Ti, Mn, Cu, Cr and Li were mixed to match alloy composition (Table-1). Aliquots of scandium and other associated elemental solutions mixed as per Table-2 were transferred to 250 mL beaker. The volume of the solution was reduced to 10 mL and 5 mL of sulphuric acid (0.25 M) was added to bring the solution into sulphate form. The solution fumed to remove excess of acid and cooled to room temperature. The salts were dissolved in 10 mL distilled water, 0.26 g of ammonium sulphate was added and made up to 50 mL (to maintain 0.1 M ammonium sulphate).

TABLE-1
PERCENTAGE COMPOSITION OF ELEMENTS IN Al-Li ALLOYS

| Element | Sc | Cu | Mn | Cr | Ti | Mg | Zr | Fe | Li | Al |
|---|---|---|---|---|---|---|---|---|---|---|
| Composition (%) | 0.27 | 0.01 | 0.26 | 0.031 | 0.09 | 4.60 | 0.17 | 0.11 | 2.0 | Balance |

TABLE-2
PREPARATION OF SYNTHETIC STANDARD SOLUTION

| *Elements (mL) | Sc | Al | Mn | Fe | Cu | Cr | Mg | Zr | Ti | Li |
|---|---|---|---|---|---|---|---|---|---|---|
| Blank | 0.0 | 9.0 | 1.0 | 1.0 | 1.0 | 1.0 | 2.5 | 1.0 | 1.0 | 1.0 |
| Synthetic std. 1 | 1.0 | 9.0 | 1.0 | 1.0 | 1.0 | 1.0 | 2.5 | 1.0 | 1.0 | 1.0 |
| Synthetic std. 2 | 2.0 | 9.0 | 1.0 | 1.0 | 1.0 | 1.0 | 2.5 | 1.0 | 1.0 | 1.0 |
| Synthetic std. 3 | 3.0 | 9.0 | 1.0 | 1.0 | 1.0 | 1.0 | 2.5 | 1.0 | 1.0 | 1.0 |

*Sc, Mn, Fe, Cu, Cr, Zr and Li were taken from stock solution of 1 mg $mL^{-1}$ and Al, Mg and Ti were taken from 10 mg $mL^{-1}$.

**Sample solutions:** 1.0 g of sample was dissolved in 20 mL hydrochloric acid (1:1). After complete dissolution, the volume of the solution was reduced to 10 mL. 5 mL of sulphuric acid (0.25 M) was added, fumed to remove the excess of acid and cooled to room temperature. The salts were dissolved in 10 mL distilled water, 0.26 g of ammonium sulphate was added and made up to 50 mL (to maintain 0.1 M ammonium sulphate).

## Analysis

**Separation of scandium from associated elements:** The ion exchange column was pre equilibrated with the mixture of 0.1 M ammonium sulphate and 0.025 M sulphuric acid solution (5 times). The synthetic standard solution was loaded slowly on the column. The column was eluted with the mixture of 0.1 M ammonium sulphate and 0.025 M of sulphuric acid (60 mL) and the effluent was collected in 100 mL standard flask. This fraction contained elements like Al, Mg, Cu, Cr, Li, Ti, Mn and Fe that were not adsorbed on resin. The eluted elements were analyzed after suitable dilution on flame atomic absorption spectrometer. Scandium was eluted by 0.1 M ammonium sulphate -0.025 M sulphuric acid (200 mL) and collected in conical flask for estimation by titrating with 0.01M EDTA. Finally Zr was eluted by 4 M hydrochloric acid (60 mL) and analyzed by inductively coupled plasma spectrometer.

**Estimation of scandium:** The separated scandium collected in conical flask was estimated by complexometry. 10 mL of 0.01 M EDTA (excess) was added to scandium solution and pH of the solution was adjusted to 5 to 5.5 using hexamine and hydrochloric acid. The excess EDTA was titrated against 0.01 M lead nitrate using xylenol orange indicator. 5 mL of 10 % ammonium fluoride was added to release scandium from EDTA complex. The solution was boiled, cooled to room temperature and adjusted the pH to 5.5. The released EDTA was titrated with lead nitrate (5 mL). Scandium was calculated as follows:

$$\text{Scandium (\%)} = V \times F / \text{wt. of sample}$$

where, F = Factor (0.4495).

**Estimation of associated element:** The associated elements like Al, Fe, Mn, Cr, Li, Mg, Cu and Ti in the effluents were estimated by flame atomic absorption spectrophotometry technique. Zr was separated by 4 M HCl (50 mL) and analyzed in the original solution by inductively coupled plasma spectrometry technique. The pure solution of Zr was used for calibration and the analysis was carried out at wavelength 343.8 nm, photo-multiplier tube at 1000 V and sample uptake rate 3 mL min$^{-1}$. The elements like Al, Mg in 10-fold diluted solution and Ti, Mn, Cu, Li, Cr and Fe in original solution were analyzed on flame atomic absorption spectrophotometer. The instrumental parameters used for analysis were presented in Table-3.

TABLE-3
PARAMETERS USED FOR DETERMINATION OF ASSOCIATED ELEMENTS ON FAAS

| Element | Wavelength in nm | Lamp current in mv. | Fuel used |
|---|---|---|---|
| Al | 309.3 | 8.0 | $C_2H_2/N_2O$ |
| Mg | 285.2 | 8.0 | $C_2H_2/N_2O$ |
| Cr | 357.9 | 8.0 | $C_2H_2$ / air |
| Cu | 324.7 | 8.0 | $C_2H_2$ / air |
| Li | 670.8 | 8.0 | $C_2H_2$ / air |
| Mn | 279.5 | 8.0 | $C_2H_2$ / air |
| Ti | 364.3 | 8.0 | $C_2H_2/N_2O$ |
| Fe | 248.3 | 8.0 | $C_2H_2$ / air |

## RESULTS AND DISCUSSION

It was found that scandium and zirconium show strong adsorption on the anion exchanger in sulphate medium. This method is useful for separation of scandium from associated elements and its estimation in Al-Li alloys. The following parameters were studied for quantitatively separation of scandium using Dowex 1, X-8.

**Distribution coefficient ($K_d$):** Distribution coefficient of scandium was calculated by taking 1 mL of stock solution of scandium and other elements like Al, Fe, Cu, Ti, Li, Mg and Cr (20 mg of each) in a beaker and evaporated to dryness. Ammonium sulphate solution (30 mL) of different concentration, *ca.* 0.025 M sulphuric acid and 1 g of dried resin were added to the beaker. These solutions were equilibrated at room temperature for 20 h. The resin was removed by filtration and filtrate was analyzed. The distribution coefficient of scandium can calculated as follows:

$$K_d = \frac{\text{Amount of metal ion/gram of dry resin}}{\text{Amount of metal ion/mL of solution}}$$

It must be noted that distribution coefficient of scandium depends markedly on the free sulphuric acid. When the free acid concentration increases to 0.5 M sulphuric acid the distribution coefficient of scandium becomes partially zero regardless the concentration of ammonium sulphate.

**Studies of eluents:** It was found that 1 M of hydrochloric acid eluted both scandium and zirconium. In the absence of zirconium, scandium was eluted by 1 M HCl but in presence of zirconium, scandium was eluted by 0.1 M ammonium sulphate - 0.025 M sulphuric acid (200 mL) and zirconium was eluted by 4 M HCl (50 mL).

**Effect of flow rate:** The effect of flow rate on scandium separation was studied by manipulation of stopcock of column burette. 1.0 mg of scandium was loaded and collected for constant time of 1 min and varying the flow rate from 0.25, 1.00 and 2.00 mL min$^{-1}$. Separation of scandium was found to be quantitatively at 1 mL min$^{-1}$.

TABLE-4
DISTRIBUTION COEFFICIENT OF SCANDIUM AT VARYING CONCENTRATION OF AMMONIUM SULPHATE

| Concentration of ammonium sulphate (M) | 0.01 | 0.03 | 0.10 | 0.30 | 1.00 | 2.00 |
|---|---|---|---|---|---|---|
| Distribution coefficient of Sc | 90.50 | 76.00 | 55.00 | 28.00 | 9.00 | 5.00 |

TABLE-5
RESULTS OBTAINED

| Standards | Scandium taken (mg) | Scandium found (mg) |
|---|---|---|
| Synthetic std. 1 | 1.0 | 1.05 |
| Synthetic std. 2 | 2.0 | 1.95 |
| Synthetic std. 3 | 3.0 | 3.05 |
| Standard | 2.7 | 2.70 |
| Standard | 2.1 | 2.05 |

## Conclusion

The quantitative separation of scandium from Al, Li, Fe, Cu, Mg, Zr, Cr, Mn and Ti were carried out successfully on anion exchange column on Dowex 1, X-8 resin (100 mesh) with successive determination by complexometry. Parameters like effect of flow rate, distribution of coefficient, *etc.* were optimized. In all instances, the recovery ranges from 95-99 % and each cycle takes 40 min from dissolution to titration. This method can be applied for estimation of scandium in Al-Li alloys.

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