



Potentiometric Titration of Aluminum Using Aluminum Electrode

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A new method was proposed for determination of aluminum by potentiometric titration using sodium fluoride as complexing titrant agent. The aluminum electrode was electrochemically prepared by coating a platinum electrode under suitable conditions. The electrolyte was 0.1 M acetate buffer pH = 4.5. The lowest concentration detected was 0.180 ppm, with a relative standard deviation of $\pm 3.865\%$.

Key Words: Aluminum, Determination, Aluminum electrode, Potentiometric titration.

INTRODUCTION

Aluminum is the third most abundant element in the Earth's crust and is a non-essential element to which humans are frequently exposed¹. During recent years, much interest has been raised by the toxicity and biological effects of aluminum². Some studies suggest that aluminum may be accumulated in the brain *via* different routes (drinking waters, food and medicines) and interfere with the normal activities of nervous system. This metal ion has been considered as a possible cause of renal osteodystrophy, Parkinson disease and Alzheimer's disease. The determination of low levels of aluminum has become increasingly very important in environmental and clinical chemistry since its negative role in the human life³⁻⁵.

Many methods have been used for the determination of aluminum such as graphite furnace atomic absorption spectrometry (GF-AAS), inductively coupled plasma-atomic emission spectrometry (ICP-AES), liquid chromatography, flow-injection, stripping voltammetry and spectrophotometry. Though these methods provide accurate results but are not very convenient for the analysis of large number of environmental samples as they require sample pretreatment and sufficient infrastructure back-up⁶⁻⁹.

Potentiometric titrations are used in the determination of aluminum. The fluoride ion-selective electrode (ISE) is most commonly used for the indirect determination of aluminum with fluoride. The initial formation rate of the aluminum-fluoride complex was proportional to the amount of aluminum⁶. Baumann has used the fluoride electrode as a potentiometric indicator of formation of slightly soluble sodium fluoroaluminat, Na_3AlF_6 , in ethanolic media⁷.

Unfortunately, there are not many previous methods using solid electrodes for the determination of aluminum ions. For this reason we review some selective electrodes which are being widely developed for aluminum ion. One of the electrodes is a PVC membrane electrode based on (5PHAZOSALNPHN)⁸. Another Al^{3+} selective sensor is PVC matrix membranes containing morin as ionophore⁹.

The only study we found using a solid electrode is a potentiometric system for the indirect flow determination of Al^{3+} with fluoride ions using an aluminum wire as indicating electrode at pH 5.0 in acetate buffer. The response was linear with concentration of aluminum in the range of 0.5-50 ppm¹⁰.

In the present work, a new potentiometric titration method for the determination of aluminum ions has been developed using an aluminum electrode.

EXPERIMENTAL

Potentiometric titration studies were carried out using Metrohm SM Titrino 702 instrument with an automatic burette and stirrer. It was kept in an air-conditioned room maintained at *ca.* 25 °C and the humidity was between 60-70 %.

The electrode used is a combined one. It consists of an Ag/AgCl (sat. KCl) electrode as a reference electrode and a platinum electrode electrochemically coated with aluminum as an indicating electrode. Coating was carried out by immersing the electrode in an electrochemical cell containing 9 mL aluminum nitrate 0.1 N and 1 mL nitric acid 0.1 N and passing voltage of -1.66 mV for 600 s.

All of the chemicals used were of AR grade. The solutions were prepared in double-distilled water. A stock solution of 0.1 N Al(III) was prepared and desired dilutions were made

as per the requirements. A 0.1 N solution of NaF was prepared in 100 mL of distilled water.

The buffer(1) was prepared by preparing a solution of 0.1 M sodium acetate in 100 mL of distilled water and adjusting pH to 4.5 with a few drops of concentrated acetic acid.

The buffer(2) was prepared by preparing a solution of 0.1 M ammonium acetate in 100 mL of distilled water and adjusting pH to 4.5 with a few drops of concentrated acetic acid.

Proposed methodology: In each determination, 1 mL (unless mentioned something else) of an aluminum nitrate solution of the desired concentration is added to 2 mL of acetic buffer in a 25 mL biker. Distilled water is used to complete the volume to 20 mL to achieve complete immersing of the electrode. Sodium fluoride solution is filled in the burette, which is added automatically. The stirrer is switched on. The titration was started after a pause of 25 s in order to achieve stability of the potential. The electrode is to be washed with distilled water after each titration or with concentrated aluminum nitrate solution when needed. Typical titration curve obtained for one concentration of Al(III) is shown in Fig. 1.

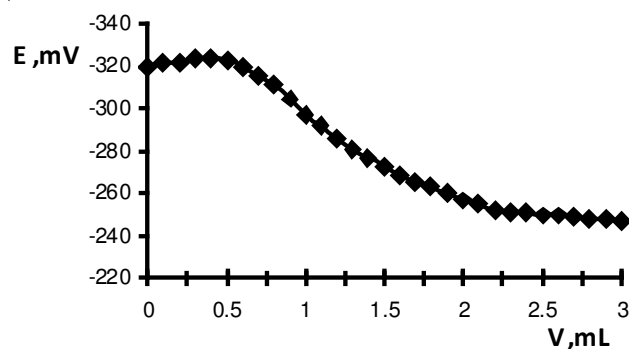
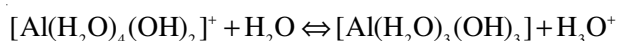
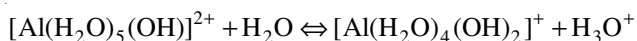


Fig. 1. Titration curve of 1 mL of aluminum nitrate 0.1 N with sodium fluoride 0.1 N in $\text{CH}_3\text{COONa-CH}_3\text{COOH}$ buffer (pH = 4.5)

RESULTS AND DISCUSSION

In aqueous solutions aluminum ions are present as $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$, which can be hydrolyzed to form $[\text{Al}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$, $[\text{Al}(\text{H}_2\text{O})_4(\text{OH})_2]^+$ and $[\text{Al}(\text{H}_2\text{O})_3(\text{OH})_3]$. Then reaction equations are as follows:



Only in acidic medium aluminum species be present mainly in the form of Al^{3+} (co-ordinated water has been omitted for simplicity). Al^{3+} can react with F^- to form the AlF_3 complex. This reaction can be monitored using an aluminum electrode⁶.

Effect of concentration of titrant (sodium fluoride): A solution containing 2 mL of aluminum nitrate 0.1 N, 2 mL acetate buffer 0.1 M (pH = 4.5) and sufficient quantity of distilled water to complete the volume to 20 mL was titrated with different concentrations of sodium fluoride such as (0.1, 0.2, 0.3, 0.4, 0.5 N). The titration curves obtained are shown in Fig. 2.

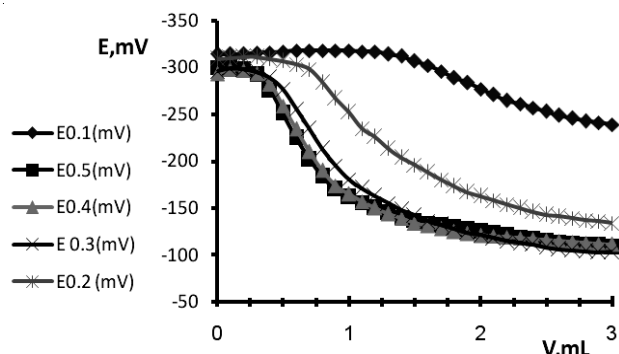


Fig. 2. Effect of the concentration of sodium fluoride on the titration curves in $\text{CH}_3\text{COONa-CH}_3\text{COOH}$ buffer (pH = 4.5)

When the concentration of F^- is low (0.1 N), a titration curve with a gentle wipe is obtained. When the concentration of F^- is high, a titration curve with a steep wipe is obtained. The dependence of potential wipe lengths on titrant concentration is shown in Fig. 3.

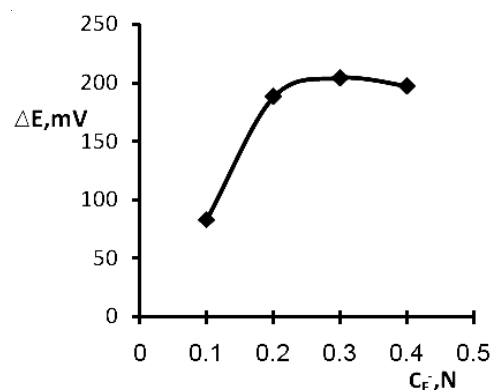


Fig. 3. Dependence of ΔE on titrant concentration of F^- ΔE : the potential range of the wipe

From Table-1 and Fig. 4, it is obvious that the equivalence point was not much affected by changing titrant rate, but the potential wipe was clearer when titrant rate concentration was three times bigger than sample. This has a great importance when titrating small concentrations of aluminum as illustrated in Fig. 4.

Effect of pH: The influence of pH on the determination of aluminum was investigated. The pH was varied from 2-7 using 0.1 M $\text{CH}_3\text{COONa-CH}_3\text{COOH}$ buffers solutions. The dependence of initial potentials on pH is shown in Fig. 5. The curve exhibits some stability between pH = 3-5. The best results with respect to enhancement, shape and reproducibility of the wipe potential were obtained at pH = 4.5.

Effect of titrant adding rate: A solution containing 1 mL of aluminum nitrate 0.1 N, 2 mL acetate buffer 0.1 M and sufficient quantity of distilled water to complete the volume to 20 mL was titrated with sodium fluoride at different titrant adding rates. The pH was 4.5. The titration equivalence points were not affected by increasing the rate up to 0.5 mL/min. The best rate is 0.2 mL/min. The titration curves obtained are shown in Fig. 6.

Effect of electrolyte

Effect of acetic acid-sodium acetate buffer concentration: A solution of 0.1 M of sodium acetate was prepared and the

TABLE-1
EFFECT OF THE CONCENTRATION OF SODIUM FLUORIDE ON THE
EQUIVALENCE POINTS IN CH₃COONa-CH₃COOH BUFFER (pH = 4.5)

Fluoride concentration (N)	0.1	0.2	0.3	0.4	0.5
Theoretical needed volume of titrant (mL)	2	1	0.66	0.5	0.4
Experimental consumed volume (mL)	1.96	0.964	0.64	0.56	0.52
Theoretical aluminum concentration (N)	0.1	0.1	0.1	0.1	0.1
Mean experimental aluminum concentration (N)	0.098	0.0964	0.096	0.112	0.13

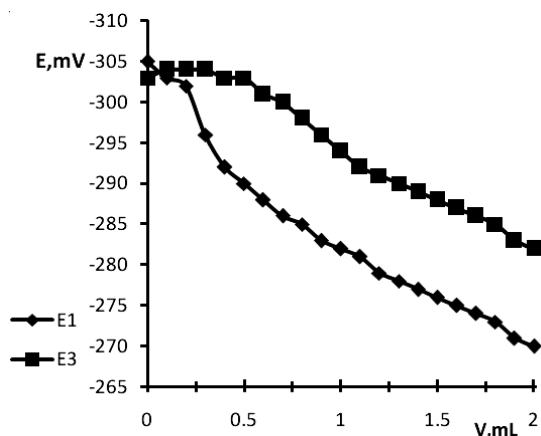


Fig. 4. E1: Titration curve of 1 mL Al³⁺ 5 × 10⁻³ N with F⁻ 5 × 10⁻³ N in CH₃COONa-CH₃COOH buffer (pH = 4.5). E3: Titration curve of 1 mL Al³⁺ 5 × 10⁻³ N with F⁻ 15 × 10⁻³ N in CH₃COONa-CH₃COOH buffer (pH = 4.5)

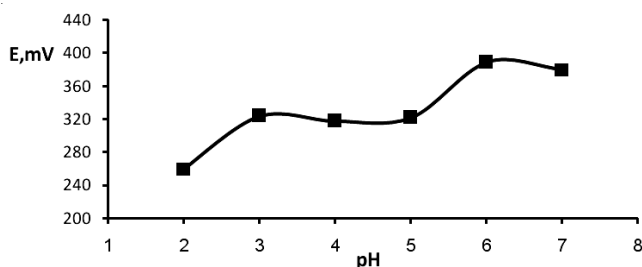


Fig. 5. Effect of pH on initial potentials

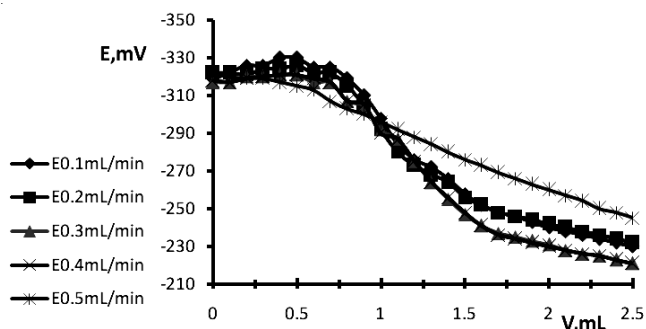


Fig. 6. Titration curves at different titrant adding rates in CH₃COONa-CH₃COOH buffer (pH = 4.5)

pH was adjusted to 4.5 with a few drops of concentrated acetic acid. From this buffer 1, 2, 4, 6, 8 and 10 mL were added, respectively to 1 mL of aluminum nitrate 0.1 N, the volume was completed with distilled water to 20 mL. Then the new concentrations of sodium acetate in 20 mL were 0.005, 0.01, 0.02, 0.03, 0.04 and 0.05 M, respectively. Another buffer with concentration 0.5 M and pH = 4.5 was prepared. From this buffer 4, 8 and 12 mL were added, respectively to 1 mL of aluminum nitrate 0.1 N, the volume was completed with

distilled water to 20 mL. Then the new concentrations of sodium acetate in 20 mL were 0.1, 0.2 and 0.3 M, respectively. Then the titrations were done and the curves obtained are shown in Fig. 7.

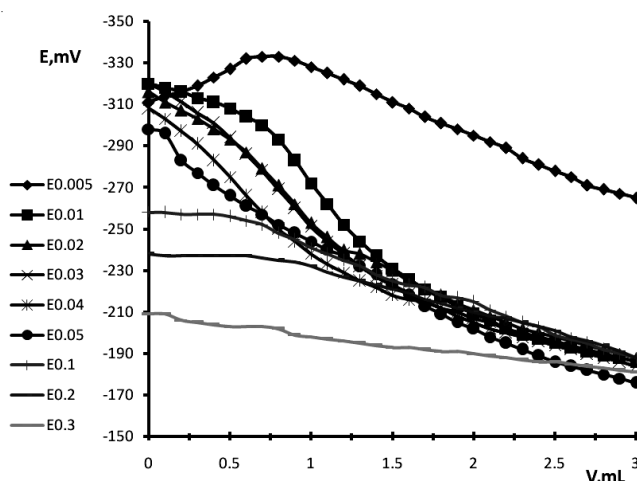


Fig. 7. Effect of CH₃COONa + CH₃COOH buffer concentration

From Fig. 7, it is clear that the electrolyte did not work effectively when its concentration was 0.005 M as the ionic force is weak. However, its range of action was 0.01-0.045 M. we chose 0.01 M because the wipe range was the widest. There is no typical titration curve above the concentration 0.05 M.

Effect of acetic acid-ammonium acetate buffer concentration: A solution of 0.1 M of ammonium acetate was prepared and the pH was adjusted to 4.5 with a few drops of concentrated acetic acid. From this buffer 1, 3, 5, 7 and 10 mL were added, respectively to 1 mL of 0.1 N aluminum nitrate, the volume was completed with distilled water to 20 mL. Then the new concentrations of ammonium acetate in 20 mL were 0.005, 0.015, 0.025, 0.035 and 0.05 M, respectively. Then the titrations were done and the curves obtained are shown in Fig. 8.

It is clear (Fig. 8) that with ammonium acetate buffer the wipe is less obvious than that of sodium acetate buffer. Therefore the latter is preferable.

Thus, CH₃COONa-CH₃COOH buffer was selected as the best electrolyte that gives a wide potential wipe, a good conductivity, a suitable ionic force and a suitable pH.

Effect of electrode: In order to study the effect of the electrode, titration of different aluminium nitrate solutions was carried out at the optimum conditions (2 mL of sodium acetate buffer pH = 4.5 adding rate 0.2 mL/min) using two different electrodes *i.e.*, the aluminum electrode and the platinum electrode. Fig. 9 shows the potential shift of the titration curves using the two electrodes at two different concentrations of aluminium nitrate.

TABLE-2
DETERMINATION OF ALUMINUM IONS BY POTENTIOMETRIC TITRATION
USING ALUMINUM ELECTRODE IN ACETATE BUFFER (n = 5, t = 2.776)

Concentration taken $\times 10^{-3}$ (N)	$\bar{X} \times 10^{-3}$ (N)	SD (N)	RSD (%)	$\frac{SD}{\sqrt{n}}$ (N)	$\frac{t \cdot SD}{\sqrt{n}} \pm \bar{X}^{***}$
0.025	0.0200	0.00070	3.865	0.00030	$0.00084 \pm 0.02000 \times 10^{-3}$
0.050	0.0444	0.00156	3.519	0.00070	$0.00194 \pm 0.0444 \times 10^{-3}$
0.250	0.2298	0.00668	2.910	0.00299	$0.00830 \pm 0.2298 \times 10^{-3}$
0.500	0.4730	0.00570	1.205	0.00255	$0.00708 \pm 0.4730 \times 10^{-3}$
1.000	0.9682	0.00748	0.773	0.00335	$0.00929 \pm 0.9682 \times 10^{-3}$
2.500	2.3995	0.01744	0.727	0.00780	$0.02166 \pm 2.3995 \times 10^{-3}$
5.000	4.8160	0.03299	0.685	0.01475	$0.04096 \pm 4.8160 \times 10^{-3}$
10.000	9.7700	0.04963	0.508	0.02220	$0.06162 \pm 9.7700 \times 10^{-3}$
25.000	24.255	0.09120	0.376	0.04079	$0.11322 \pm 24.255 \times 10^{-3}$

* \bar{X} : Found concentration in 20 mL; mean values represent five determinations. **Analytical standard error. ***Confidence limit.

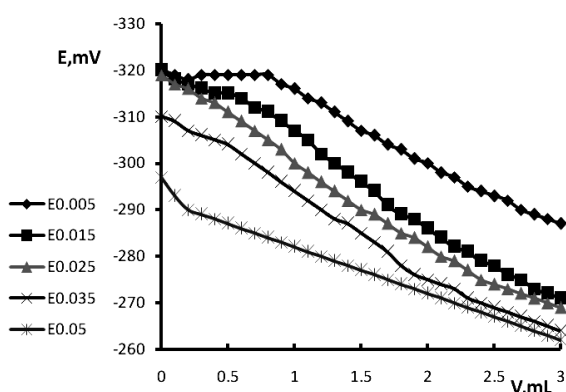


Fig. 8. Effect of $\text{CH}_3\text{COONH}_4 + \text{CH}_3\text{COOH}$ buffer concentration

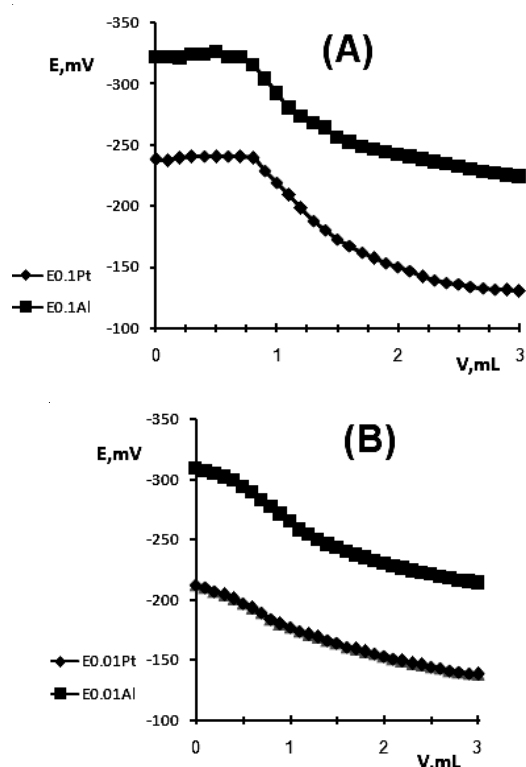


Fig. 9. Effect of electrode: (A): titration curves of 0.1 N of aluminum nitrate in acetate buffer pH = 4.5 using two electrodes. (B): titration curves of 0.01 N of aluminum nitrate in acetate buffer pH = 4.5 using two electrodes

At the concentration of 5×10^{-4} N of aluminium nitrate the aluminum electrode becomes more sensitive to potential variation. Thus, the aluminum electrode is preferable because its detection limit is smaller than the platinum one. And because solid electrodes have many properties over selective electrodes such as ready availability, simpler miniaturization, longer lifetimes, easier maintenance procedure and lower cost¹⁰.

Table-2 shows the results of Aluminum determination by potentiometric titration using sodium fluoride as complexing titrant agent, the aluminum electrode and the electrolyte was 0.1 M acetate buffer pH = 4.5.

It has been found that the lowest concentration detected was 0.180 ppm and the relative standard deviations were less than $\pm 3.865\%$ with five replicates measurements.

In this research work, aluminum electrode was used for direct determination of free (not bounded) aluminum ions while other's methods cannot determine its directly^{6,7,10}. The results are good and acceptable.

Conclusion

The proposed method in this research work for direct determination of aluminium ions by potentiometric titration was based on the reaction between aluminum ions and fluoride ions in acetate buffer using aluminium electrode. The method is simple, rapid, accurate, low cost and useful for further research works for determination of Al (III) in pharmaceutical compounds.

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