

THE DETERMINATION OF TRACE LEVELS OF ALUMINIUM BY DIFFERENTIAL PULSE POLAROGRAPHY

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SUMMARY

The direct determination of aluminium in aqueous solutions by differential pulse polarography is described. If the pH is carefully controlled to 4.00 ± 0.01 , there is a linear relationship between the peak height of the polarographic wave and the aluminium concentration up to $2.5 \times 10^{-5} \text{ mol dm}^{-3}$. The coefficient of variation is about 4% at the $10^{-5} \text{ mol dm}^{-3}$ level. With increasing aluminium concentrations, the relationship ceases to be linear, and above $9 \times 10^{-5} \text{ mol dm}^{-3}$, the peak splits, probably because of hydrolysis and polymerisation. Na^+ , NH_4^+ , Mg^{2+} and Ca^{2+} interfere at levels 100 times greater than that of the aluminium whereas Fe^{2+} , Fe^{3+} , Cu^{2+} , Zn^{2+} , Ni^{2+} , NO_3^- , ClO_4^- , Cl^- and SO_4^{2-} do not interfere.

The determination of aluminium in aqueous solutions is difficult, partly because there may be several aluminium species in solution, both monomeric and polymeric, and the rate of interconversion between these may be slow [1]. Methods for the determination of aluminium have been reviewed by Tikhonov [2]. Those commonly employed are atomic absorption spectrometry (a.a.s) and colorimetry with aluminon, 8-hydroxyquinoline or solochrome cyanine R. A.a.s. is only sensitive enough for determination of aluminium at levels of about $10^{-4} \text{ mol dm}^{-3}$ ($1 \text{ ppm} = 3.71 \times 10^{-5} \text{ mol dm}^{-3}$). At lower concentrations a heated graphite furnace can be used; this approach is relatively interference-free except that chloride causes low recoveries because of the volatility of aluminium chloride. Similarly, colorimetry is relatively insensitive unless the aluminium is extracted into organic solvents [3].

Kolthoff and Lingane [4] reviewed early work on the d.c. polarographic behaviour of aluminium in aqueous solution and reported a half-wave potential of -1.75 V vs. SCE for aluminium(III) in $5 \times 10^{-2} \text{ mol dm}^{-3}$ barium chloride with limits of detection exceeding $2 \times 10^{-4} \text{ mol dm}^{-3}$. Hodgson and Glover [5] found a half-wave potential of -1.63 V vs. SCE in a $2.5 \times 10^{-2} \text{ mol dm}^{-3}$ barium chloride at pH 4.5 with a detection limit of $4 \times 10^{-5} \text{ mol}$

dm^{-3} . Because the d.c. polarographic determination is unsuitable for aluminium in trace amounts, several workers [6–10] have determined aluminium by measuring the reduction waves of its complexes with solochrome violet RS and other compounds.

This paper describes a new direct method for the determination of aluminium by differential pulse polarography. It is suitable for concentrations less than $4 \times 10^{-5} \text{ mol dm}^{-3}$ and may have advantages compared with a.a.s. or colorimetry.

EXPERIMENTAL

Reagents

Analytical reagent-grade chemicals were used except where noted, and all solutions were stored in acid-washed polyethylene bottles. The water used was distilled and de-ionised.

Aluminium stock and standard solutions. Aluminium (99.999%; Koch-Light) was dissolved in a slight excess of purest-grade (1 + 4) hydrochloric acid (Hayashi Pure Chemical Industries) and the solution was diluted to a concentration of $3.71 \times 10^{-2} \text{ mol dm}^{-3}$ with $1.5 \times 10^{-2} \text{ mol dm}^{-3}$ nitric acid. A dilute stock solution was then prepared by diluting 3.37 cm^3 of the above to 100 cm^3 with $1.5 \times 10^{-2} \text{ mol dm}^{-3}$ nitric acid.

Aluminium standards were prepared by adding 0–2400 μl of the $1.25 \times 10^{-3} \text{ mol dm}^{-3}$ stock solution to 30 cm^3 of $7.5 \times 10^{-3} \text{ mol dm}^{-3}$ potassium nitrate.

Apparatus

A Metrohm E506 Polarecord was used with a dropping mercury electrode (DME) and a silver–silver chloride reference electrode dipping in a saturated potassium chloride solution.

Procedure

The standard or unknown sample (30 cm^3 , prediluted if necessary and made $7.5 \times 10^{-3} \text{ mol dm}^{-3}$ in KNO_3) was added to the polarographic cell and deoxygenated for 10 min with high-purity nitrogen. Since careful pH control was essential in obtaining reproducible polarograms, the pH was maintained during the analyses at 4.00 ± 0.01 by adding $3.0 \times 10^{-1} \text{ mol dm}^{-3}$ lithium hydroxide or $1.5 \times 10^{-2} \text{ mol dm}^{-3}$ nitric acid from microburettes; a combined glass electrode and pH meter were used with a chart recorder. Buffers were avoided because the hydrogen wave from weak acids is much broader than that of strong acids [4]; also, most buffers suitable for use at pH 4.00 have reduction potentials in the same region and would therefore mask the aluminium peak. A differential pulse polarogram was then run over the range -1.8 to -1.0 V vs. SCE at a constant scan rate for each sample, with a pulse amplitude of -50 mV and duration of 60 ms, and a drop time of 1 s. All experiments were done at ambient temperature (19 – 20°C).

RESULTS AND DISCUSSION

Electrode processes

A d.c. polarogram of aluminium in 7.5×10^{-3} mol dm $^{-3}$ potassium nitrate is shown in Fig. 1A. The gradual increase to the limiting current indicates an irreversible reaction. The resolution of the aluminium wave is greatly enhanced by using differential pulse polarography (Fig. 1B); the reduction wave for aluminium appears at -1.7 V, close to the hydrogen wave at -1.5 V. The increase in current at more negative values is due to reduction of potassium. As the aluminium peak is on the shoulder of the hydrogen wave, peak current values were calculated relative to the baseline obtained at more positive potentials than that of the hydrogen wave (-1.0 to -1.1 V). The peak current was found to be a linear function of the aluminium concentration up to about 2.4×10^{-5} mol dm $^{-3}$. Above this concentration, the slope of the line decreased (Fig. 2), Heyrovsky [11] showed, from current-time curves, that the aluminium wave was due to the evolution of hydrogen during the reduction of the hexaquo aluminium ion, the reaction being catalysed by the $\text{Al}(\text{OH})_3$ produced. The non-linearity of the curve at higher concentrations may be due to aluminium hydroxide forming a film on the mercury drop.

Peak splitting at high concentrations

As the aluminium concentration was increased above ca. 9×10^{-5} mol dm $^{-3}$, the peak split into two, with the new peak at a more positive potential (Fig. 3A). This phenomenon occurred in all the electrolytes investigated but at different initial aluminium concentrations. Peak splitting in potassium and lithium chlorides was observed at aluminium concentrations above ca.

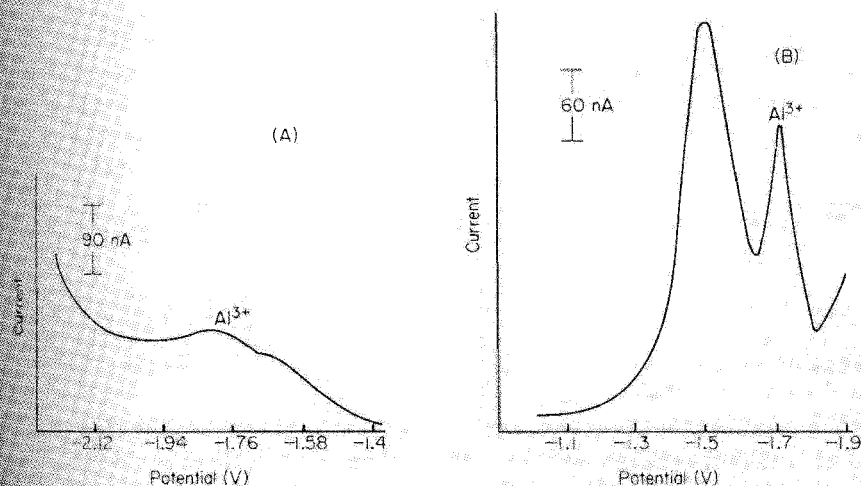


Fig 1. D.c. polarogram (A) and d.p. polarogram (B) for 1.2×10^{-5} mol dm $^{-3}$ in 7.5×10^{-3} mol dm $^{-3}$ KNO_3 at pH 4. All potentials are relative to the Ag/AgCl electrode.

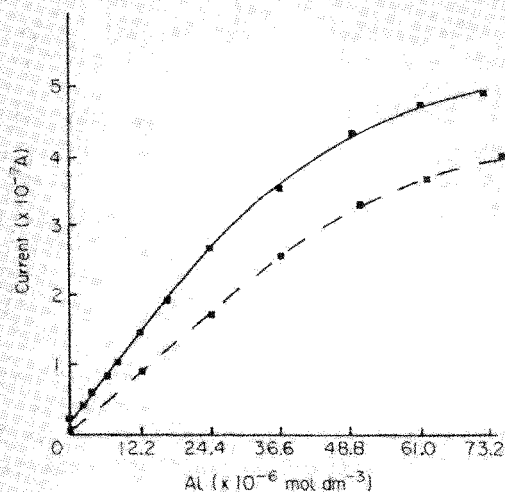


Fig. 2. Variation of peak current as a function of aluminium concentration in 7.5×10^{-3} mol dm $^{-3}$ KNO $_3$ at pH 4.00 ± 0.01 : (—) samples kept in the glass polarographic cell for <1 h; (---) samples kept in the cell for 1 h.

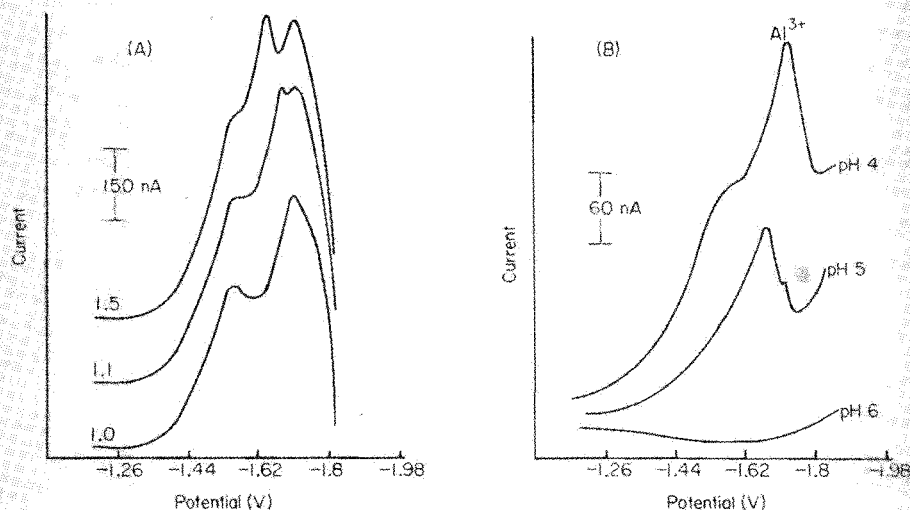


Fig. 3. Variation of peak shape with (A) increasing aluminium concentrations in the range $1.0\text{--}1.5 \times 10^{-4}$ mol dm $^{-3}$ aluminium at pH 4.0, and (B) increasing pH, at an aluminium concentration of 8×10^{-5} mol dm $^{-3}$. Supporting electrolyte, 7.5×10^{-3} mol dm $^{-3}$ KNO $_3$.

9.2×10^{-5} mol dm $^{-3}$. In potassium nitrate, resolution of the two peaks occurred at a slightly higher concentration than in the chloride electrolytes. In contrast, peak separation in lithium sulphate did not become obvious until the aluminium concentration exceeded ca. 1.3×10^{-4} mol dm $^{-3}$.

There are three possible explanations: complexation, adsorption or poly-

merisation of the aluminium. The only strong complexes of aluminium are with hydroxide and fluoride ions [12], but $\text{Al}(\text{SO}_4)$ and $\text{Al}(\text{SO}_4)_2^-$ can be formed with the sulphate ion. These sulphate species would predominate at pH 4 at sulphate concentrations of $7.5 \times 10^{-3} \text{ mol dm}^{-3}$ and less than 10% of the total aluminium would be present as free ions [1]. Complexes with chloride ions have not been detected, even in 12 mol dm^{-3} solutions. Thus, the peak splitting cannot be attributed to complex formation since it occurs in the presence and absence of complex-forming ions. Adsorption of aluminium onto the mercury drop is also unlikely as a cause of peak splitting. Adsorption could result in reduction peaks corresponding to free aluminium ions and to adsorbed Al^{3+} , but the phenomenon was found to depend on pH, which is not a characteristic of adsorption currents [13].

A more likely explanation is the increase in polymerisation and hydrolysis of aluminium with increasing concentration. In the linear part of the curve in Fig. 2, i.e. up to approximately $10^{-5} \text{ mol dm}^{-3}$, 95% of the aluminium in solution is present as Al^{3+} [12]. However, as the concentration increases, the proportion of polymerised species increases quite rapidly and eventually precipitation occurs. In reviewing research on the hydrolysis of aluminium, Baes and Mesmer [14] concluded that the form $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$ is the major polymeric species at equilibrium. Several monomeric species were considered possible depending on pH and concentration. Therefore, it seems probable that the peak splitting represents the formation of polymeric hydrated species and that the new peak occurs at more positive potentials because such larger species would tend to accept an electron more easily. The aluminium concentration at which peak splitting occurs in different electrolytes is consistent with this explanation. In sulphate electrolytes, some complex formation would occur (see above) and so higher aluminium concentrations would be required before polymerisation and splitting of the peak occurred. Nitrate and chloride ions do not form complexes [12] so that peak splitting occurs at lower concentrations of aluminium in these electrolytes. The variation of the aluminium wave with pH and ionic strength supports this hypothesis. As the pH is increased above 4, the peak shifts to more positive potentials and becomes broader, and the limiting current decreases (Fig. 3B). Below pH 4, the hydrogen wave increases rapidly and eventually obscures the aluminium peak. Changing the ionic strength had relatively little effect.

Choice of electrolyte and interference by other ions

Lithium and potassium are the most suitable cations for the supporting electrolyte as their reduction potentials (-2.3 and -2.1 V) are furthest from the reduction potential of aluminium [4]. Alkaline earth cations are less suitable although barium chloride has been used successfully [5]. The suitability of KCl , KNO_3 , K_2SO_4 , LiCl and Li_2SO_4 as background electrolytes was investigated. The reduction wave for aluminium was found to be very similar in each electrolyte and of sufficient resolution for analytical usage. KNO_3 was selected because of its use as an electrolyte in current research at

this laboratory, which involved the determination of low levels of aluminium. A concentration of $7.5 \times 10^{-3} \text{ mol dm}^{-3}$ was sufficient; as the concentration was increased, there was a gradual shift of the aluminium peak to more positive potentials.

The maximum tolerable concentration of Na^+ , NH_4^+ , Mg^{2+} or Ca^{2+} which could be present without interference were found to be ca. 8, 3, 0.4 or $0.7 \times 10^{-3} \text{ mol dm}^{-3}$, respectively. These ions were chosen because their reduction waves were close to that of aluminium. An ion was considered to interfere if the measured aluminium concentration in its presence was significantly different (by the "t" test) from the standard value obtained.

If identical solutions, containing no aluminium, are available for use as blanks, the background concentration of interfering ions can be much higher: ca. $5 \times 10^{-3} \text{ mol dm}^{-3}$ of Mg^{2+} and Ca^{2+} , $6 \times 10^{-3} \text{ mol dm}^{-3}$ NH_4^+ and $16 \times 10^{-3} \text{ mol dm}^{-3}$ Na^+ may be tolerated. At higher concentrations the aluminium peak is completely masked by the broad peaks from these cations. Few other ions interfere, either because they are not reduced (e.g., SO_4^{2-} , ClO_4^-) or are reduced at much more positive potentials (e.g., NO_3^- , Cl^- , Fe^{3+} , Fe^{2+} , Cu^{2+} , Zn^{2+} , Ni^{2+}).

Adsorption on glass

At these low aluminium levels, adsorption on the glass polarographic cell occurred if the solutions were in contact with them for more than 1 h. A calibration curve constructed by means of successive additions over a period of 2 h thus showed a reduced slope (Fig. 2). This problem was overcome by preparing separate standards and storing them in polyethylene bottles. Subsequently, all solutions were in contact with the glass cell for only ca. 15 min while the solutions were deoxygenated, the pH adjusted to 4.00 ± 0.01 and the polarogram run. There was no significant difference (at a probability level of 0.01) in peak current for two aluminium standards (8.2×10^{-6} and $2.4 \times 10^{-5} \text{ mol dm}^{-3}$) stored in polyethylene bottles over a six-day period. Subramanian et al. [15] found that approximately 40% aluminium was adsorbed from aqueous solutions at pH 4 by pyrex and other containers during the first five days of storage.

Precision and accuracy

The upper limit of the linear range of the calibration curve was somewhat arbitrarily chosen as $2.4 \times 10^{-5} \text{ mol dm}^{-3}$. Linear regression analysis of this part of the curve gave a correlation coefficient of 0.996 (calculated from 8 points). Table 1 gives the confidence limits and the precision for three points on the linear part of the curve, at a probability level of 0.01. The limit of detection (defined as twice the standard deviation of the blank) was $1.9 \times 10^{-7} \text{ mol dm}^{-3}$, and the sensitivity was $4 \times 10^{-8} \text{ mol dm}^{-3}$ at the largest scale expansion used. When known amounts of aluminium were added to samples, a mean recovery of 102% was found.

The new technique is convenient and should find wide application. It has

TABLE 1

Precision of peak current measurements for standard solutions

Al (mol dm ⁻³)	0	8.218×10^{-6}	2.433×10^{-5}
Mean current (nA)	23.1	135.7	394.6
Standard deviation	2.9	5.8	12.7
Confidence limits ^a	± 2.3	± 4.1	± 8.9
Coefficient of variation (%)	12.6	4.3	3.2
Degrees of freedom	14	17	17

^aAt a probability level of 0.01.

a higher detection limit than the graphite-furnace a.a.s. method but has better sensitivity. Since it has been shown that the likely cause of peak splitting is polymerisation and hydrolysis, it is possible that these phenomena could now be studied polarographically.

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