ADSORPTIVE STRIPPING VOLTAMMETRIC DETERMINATION OF ALUMINIUM USING ARSENAZO III

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A new analytical method for the indirect determination of trace amounts of aluminium(III) is based on the adsorptive accumulation of an azo dye, Arsenazo III, on the hanging mercury drop electrode. In the presence of Al(III) forming complexes with the dye, its peak occurring at –330 mV decreases. Optimized experimental conditions were found as follows: supporting electrolyte, acetate or chloroacetate–acetate buffer (pH 3.6); accumulation potential, –50 mV *vs* SCE; accumulation time, 120 s; Arsenazo III concentration, $5 \cdot 10^{-7}$ mol l^{-1}; scan rate, 20 mV s^{-1}; initial potential, –500 mV; final potential, 0 mV; FSDPV mode; pulse amplitude, 50 mV; pulse duration, 100 ms; pulse interval, 10 ms. Under these experimental conditions, the calibration dependence was linear in the concentration range 0–6 μmol l^{-1} with a detection limit of $3.7 \cdot 10^{-8}$ mol l^{-1} (1 ppb, calculated as 3σ for $n = 10$). Interference of iron(III) can be suppressed by addition of L-ascorbic acid, the effect of numerous divalent metal ions is negligible. Serious interfering effects were observed for U(VI) as UO_2^{2+}, both Cr(III) and Cr(VI), and F^-. The method developed was verified using a certified reference material (SRM 1575 Pine Needles); no statistically significant differences between the determined and declared contents were found.

Keywords: Stripping voltammetry; Electrochemistry; Hanging mercury drop electrode; Adsorption; Azo dyes; Al complexes.

It is not known if aluminium belongs to the trace elements essential for the human body. Pathological changes of human lung, central nervous system, and bones related to a long-term exposure to aluminium are controversely discussed[1]. Several methods are available for the determination of total aluminium, graphite furnace atomic absorption spectrometry (GFAAS) being

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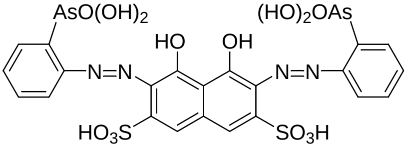
the most widely used technique and producing reliable results[2]. However, the technique is relatively expensive.

Concerning polarographic or voltammetric methods, it is necessary to mention that direct determination of aluminium is difficult. In acid media, the corresponding irreversible reduction signal is overlapped by the hydrogen wave and, in alkaline media, Al(III) can not be reduced[3,4]. For that reason, methods for trace analysis of Al(III) are usually based on its complexation and adsorptive properties of the complexes formed with some organic ligands. Quinalizarin[5], Eriochrome Black T[6], Calmagite[7–9], Cupferron[10], quinolin-8-ol[11], 4-nitrocatechol[12], Morin[13], Lumogallion[14], Solochrome Violet RS[15–20] and Alizarin Red S[21–28] were suggested as complexing agents. In particular, the last two reagents rank among the most frequently used for the determination of aluminium in different matrices like snow[19,20], sea water[23], soil[21], hemodialysis concentrates[18,22], membrane electrolyser liquors[24], tree samples (wood, leaves, roots)[25], *etc.* Disadvantageous is that the organic reagents used are often impure. In addition, sample solutions using procedures with Solochrome Violet RS must be heated to complete the complex formation.



Arsenazo III

We observed recently that Arsenazo III [2,2′-(1,8-dihydroxy-3,6-disulfonaphthalene-2,7-diylbisazo)bis(phenylarsonic acid) or its sodium salt] can also be used for some indirect voltammetric determinations[29,30]. The compound was synthesized at the end of the fifties in search for new metallochromic indicators and organic reagents[31,32] as an azo dye derived from chromotropic acid. The analytical significance of this compound follows from its ability to form complexes with numerous cations which can be used for detection tests as well as for spectrophotometric determinations of uranium, titanium, zirconium, hafnium and thorium, lanthanoids, and others[33,34] (see also ref.[29] and references therein). Its solutions are stable and the reagent is available as a very pure substance[35].

EXPERIMENTAL

Apparatus

A PC-controlled polarograph (model Eco-Tribo, Polaro-Sensors, Prague, Czech Republic) was used for all voltammetric measurements carried out in three-electrode configuration using a platinum plate and a saturated calomel electrode (SCE) as auxiliary and reference electrodes, respectively, and a pen-type renewed hanging mercury drop microelectrode (UMμE, Polaro-Sensors) as a working electrode. The electrodes were in a conical glass vessel (50 ml). pH measurements were carried out with a Gryf 107A pH meter equipped with a combined HC113 glass electrode (Gryf, Havlíčkův Brod, Czech Republic), and calibrated with standard buffer solutions. For samples mineralization, a two-stand microwave digestion unit BM-1S (Plazmatronika, Wroclaw, Poland) was used.

Chemicals and Reagents

Arsenazo III was of analytical-reagent grade (Fluka). Its stock 1 mM solution was prepared in acetate buffer (pH 3.6). All other chemicals were of analytical grade (Lachema, Brno, Czech Republic) and were used without further purification. A stock 1 mM aluminium(III) solution was prepared by dissolving an appropriate amount of $AlCl_3 \cdot 6H_2O$ in acetate buffer just before use. A 0.1 M acetate or chloroacetate–acetate buffer (pH 3.6) was used for pH adjustment. Double-distilled water was used throughout.

Pine needles (Standard Reference Material SRM 1575, National Institute of Standards & Technology, U.S.A.) were used for the method validation.

Procedure

General procedure of adsorptive voltammetry. A portion (20 ml) of the buffer was placed into a voltammetric cell, then the Arsenazo III stock solution (10 μl) was added, the stirrer was switched on and the mixture was purged with argon for 15 min. Subsequently, the parameters found during optimization steps were applied, *i.e.*, accumulation potential –50 mV, initial potential –500 mV, final potential 0 mV, accumulation time 120 s, and scan rate 20 mV s^{-1}. A fast-scan differential-pulse-voltammetric (FSDPV) mode was generally used with a pulse amplitude of 50 mV; pulse duration was 100 ms and pulse interval 10 ms.

Mineralization of solid samples. A sample of pine needles (0.1–0.2 g) in a mixture of concentrated nitric acid (1 ml) and hydrogen peroxide (2 ml) in a 110 ml Teflon vessel was mineralized using the microwave digestion unit. The power of 150 W per vessel was applied for 20 min. After the mineralization was finished, the solution was transferred into a 25 ml volumetric flask and filled with acetate to the mark.

Evaluation. To evaluate the Al(III) concentration in the sample, a modified multiple standard addition method was used: both sample and standard Al(III) solutions were added to the supporting electrolyte alternately and the decrease in the peak height was evaluated.

RESULTS AND DISCUSSION

Electrochemical Behaviour of Arsenazo III

Chemical equilibria of Arsenazo III are rather complex as the dye (H_8L) is able to form ten species from H_9L^+ to L^{8-}, liable to dissociation/protonation[36]. Complexation equilibria of the dye are also quite complex as it affords a rich offer of several chelate rings due to the presence of numerous donor atoms[37,38]. Having in mind the dye structure including a number of possible electroactive centres, the abundance of several dissociation degrees in solution, the presence of several tautomeric forms, the adsorption abilities of the dye at the electrode surface, as well as the incidental formation of the complexes with electrode material, extremely complex behaviour of Arsenazo III could be expected. The cyclic voltammogram of Arsenazo III shows several cathodic peaks in the potential range from –1 000 to +150 mV and their gradual changes indicate quite a lot of electrochemical processes affected by probable desorption when the cycle is repeated[30]. The shape of a cyclovoltammogram depends on many experimental conditions, such as pH of the supporting electrolyte, dye concentration, scan rate, *etc.* In the presence of Al(III), the peak occurring at –330 mV (pH 3.6) decreases significantly. This anodic peak of the adsorbed dye is observable also in FSDPV records and can therefore be exploited for the indirect determination of aluminium(III).

Effects of Experimental Conditions

The effect of accumulation time on the saturation of the electrode surface is presented for Arsenazo III alone in Fig. 1. The dependence is nearly linear within the wide range of 40–160 s. In view of that fact, the optimum time for the adsorptive accumulation of the dye (at concentration $5 \cdot 10^{-7}$ mol l^{-1}) lies within the range of 80–140 s. The accumulation time of 120 s seemed the best compromise from the viewpoint of both sensitivity and time of analysis.

The variation of the accumulation (adsorption) potential between –800 and +100 mV (pH 3.6, scan from –500 to 0 mV, FSDPV mode, Fig. 2) shows that the current response exhibits two maxima, a higher one at *ca* –50 mV and the other, significantly lower, at *ca* –600 mV. This is probably accompanied with complex (and not known) electrode processes and each attempt to discuss them – at least qualitatively – would be disputable. For

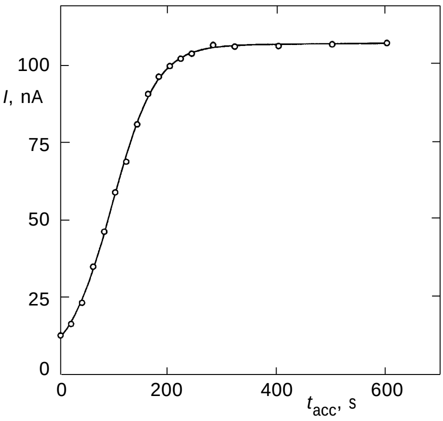


FIG. 1
Dependence of the Arsenazo III peak height on accumulation time. Reagent concentration $5.0 \cdot 10^{-7}$ mol l^{-1}, supporting electrolyte 0.1 M acetate buffer (pH 3.6), scan rate 20 mV s^{-1}, accumulation potential –50 mV, initial potential –500 mV, final potential 0 mV, pulse amplitude 50 mV

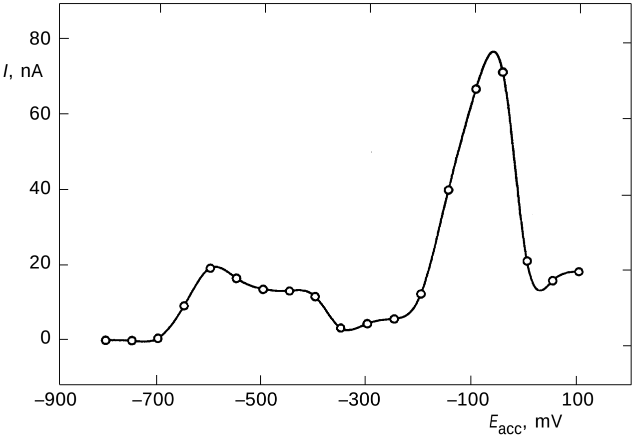


FIG. 2
Dependence of the Arsenazo III peak height on accumulation potential. Reagent concentration $5.0 \cdot 10^{-7}$ mol l^{-1}, supporting electrolyte 0.1 M acetate buffer (pH 3.6), scan rate 20 mV s^{-1}, accumulation time 120 s, initial potential –500 mV, final potential 0 mV, pulse amplitude 50 mV

further measurements, the potential at which the higher maximum appeared was applied.

The influence of the dye concentration on the peak height is illustrated in Fig. 3. It is evident from the figure that for Al(III) determination, a concentration of Arsenazo III must be chosen from the interval of $1.5 \cdot 10^{-7}$–$6.5 \cdot 10^{-7}$ mol l^{-1}. At higher values than $8 \cdot 10^{-7}$ mol l^{-1}, a limiting current response is achieved which is almost independent of the dye concentration. In addition, extremely high dye concentrations may cause a break-down of an adsorption isotherm which can be explained by multilayer adsorption. The $5 \cdot 10^{-7}$ M Arsenazo III concentration was finally taken as an optimum.

The pH dependence of the peak current gives a parabolic curve. Although the maximum peak current is achieved at pH 1.8–2.2, higher pH values are recommended because of the complex formation of the dye with Al(III). This is why 0.1 M acetate buffer (pH 3.6) was used as a compromise.

Based on the above studies, the procedure for aluminium(III) determination was finally used as described in Experimental. The current response of the dye decreases linearly with increasing Al(III) concentration, and a linear calibration curve can be obtained (Fig. 4).

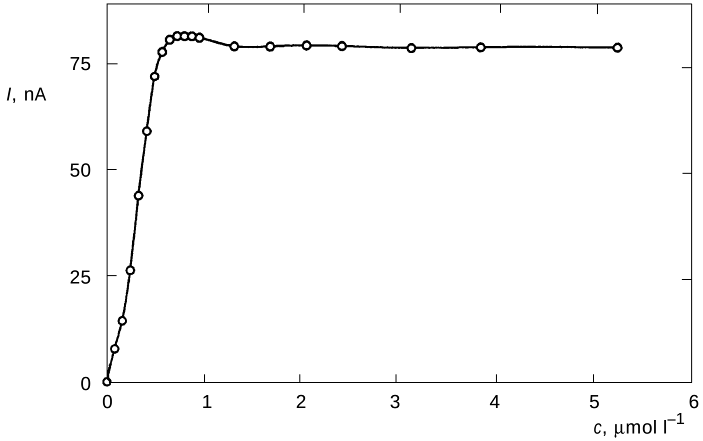


FIG. 3

Dependence of the current response on Arsenazo III concentration. Supporting electrolyte 0.1 M acetate buffer (pH 3.6), scan rate 20 mV s^{-1}, accumulation potential –50 mV, accumulation time 120 s, initial potential –500 mV, final potential 0 mV, pulse amplitude 50 mV

Detection Limit and Reproducibility

In the final procedure, *i.e.*, for $5 \cdot 10^{-7}$ M Arsenazo III concentration, the dependence of the peak current is linear below $1 \cdot 10^{-6}$ M Al(III) concentration, and the detection limit in real matrices (calculated as 3σ for 10 measurements) is $3.7 \cdot 10^{-8}$ mol l^{-1} (1 ppb). When lower concentrations of Arsenazo III are used, the current response is also lower and the working range decreases. Reproducibility of the determination was checked at $5 \cdot 10^{-8}$ M Al(III) level with relative standard deviation (RSD) of 3.0% (*n* = 10), while the signal of the dye alone was measured with RSD of 0.8% (*n* = 20).

Analytical Applications and Interferences

Using optimized experimental conditions as described above, a linear calibration curve can be expected in a wide concentration range. However, to determine the Al(III) content in real matrices, a modified standard addition procedure should be applied.

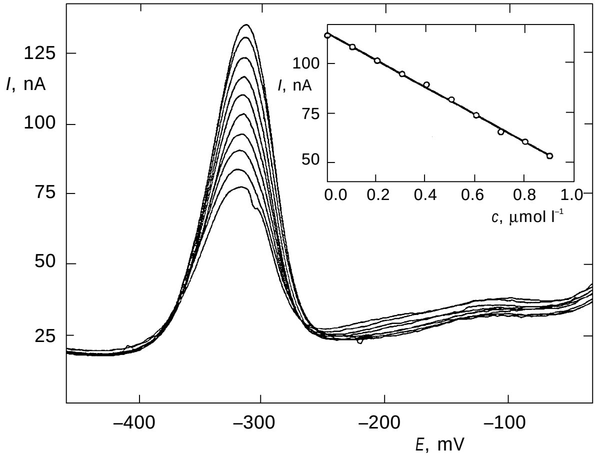


FIG. 4

Differential pulse voltammograms in the presence of aluminium(III). Both current response and Al(III) concentration correspond to those indicated on the calibration graph given in the insert. Reagent concentration $5.0 \cdot 10^{-7}$ mol l^{-1}, supporting electrolyte 0.1 M acetate buffer (pH 3.6), scan rate 20 mV s^{-1}, accumulation potential –50 mV, accumulation time 120 s, initial potential –500 mV, final potential 0 mV, pulse amplitude 50 mV

The accuracy of the method developed was tested by determination of Al(III) in a certified reference material, pine needles (SRM 1575), where the declared content of aluminium was 545 ± 30 μg g^{-1} (mean ± RSD). Having worked under conditions of the optimized procedure, we found 549 ± 14 μg g^{-1} (n = 8) which was in an unexpected but excellent agreement.

Concerning the Al(III) determination in other real matrices, it should be mentioned that there are numerous ions forming complexes with Arsenazo III but their stability generally increases with increasing ion valency. At pH 3.6, the values of the conditional stability constants for divalent cations are so small that their interference is negligible. Serious interference was observed in the presence of iron(III) but that could be successfully eliminated by addition of L-ascorbic acid (L-ascorbic acid alone did not influence the electrochemical behaviour of Arsenazo III). Regarding other ions, the most important finding was not to use the method in the presence of UO_2^{2+} which forms a very stable complex with the dye (for the determination of uranium based on a similar principle, see ref.[30]). Measurements were also problematic in the presence of both Cr(III) and Cr(VI). Finally, fluorides present in concentrations higher than 1 mmol l^{-1} decrease the peak height significantly as the stability of Al(III) fluoro complexes is higher than that of Al(III)–Arsenazo III complexes. The effect of other anions was more or less insignificant.

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