VOLTAMMETRIC DETERMINATION OF ALUMINIUM IN HAEMODIALYSIS CONCENTRATES USING THE ADSORPTION OF THE Al(III)-1,2-DIHYDROXYANTRAQUINONE-3-SULPHONIC ACID COMPLEX IN PRESENCE OF CALCIUM.

KEYWORDS: Aluminium, Adsorption stripping voltammetry, Sensitization by calcium, Haemodyalisis concentrates.

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ABSTRACT

This paper describes a method for the quantitative determination of aluminium in haemodialysis concentrates, based on the adsorption on a static mercury drop electrode of the Al-1,2 dihydroxyantraquinone-3-sulphonic acid complex. The signal was notably increased in presence of calcium. The electrolysis was carried out at -0.900 V. After 60 sec the aluminium contents were measured by differential pulse voltammetry. In these conditions aluminium can be determined in the range 0.65 - 30 ng/ml with a detection limit (3σ) of 0.20 ng/ml. The relative standard deviation was in all instances less than 2.1 %.

INTRODUCTION

Studies on the toxicity of aluminium have revealed important health-related complaints. Certain disorders that have been observed in renal-failure patients undergoing regular dialysis are associated with the presence of aluminium in the human body.

The difficulty of determination of aluminium in dialysis concentrates is evidenced by the high level of dispersion observed in the results obtained from different laboratories for the same sample[1]. It has been observed, that the high saline content in the dialysis concentrates interferes with the determination of aluminium by electrothermal[2] and by graphite-furnace[3] atomic absorption spectrometry. However, this interference can be minimized by using on-line preconcentration of the aluminium on chelex-100 or amberlite IRA-400[1].

On the other hand, it is known that direct electrochemical methods for determination of aluminium are complicated because the reduction potential of the analyte is very negative (-1.75 V vs SCE, in 0.05 M $BaCl_2$ as supporting electrolyte[4]).

Adsorptive accumulation in stripping voltammetry has been used for aluminium using different organic chelates[5-7]. By way of example, the dye solochrome violet RS reacts with aluminium to form a complex which is easily adsorbed on a static mercury electrode[5]. The detection limit of this method was 0.15 µg/l, however the principal drawback of the method was the slow complex formation reaction, which need a previous heating of the sample for 10 min at 90 °C.

Similarly, Van den Berg et al.[6] reported the adsorption voltammetric determination of aluminium using the dye 1,2-dihydroxyantraquinone-3-sulphonic acid (DASA) as chelating agent. The method was successfully applied to the determination of the

analyte in sea water. However these authors did not consider the importance of alkaline earth ions in the sensitization of the determination.

The aim of this paper was to study the effect of some alkaline earth ions on the adsorption voltammetric determination of aluminium using the complex with 1,2-dihydroxyantraquinone-3-sulphonic acid. The optimum experimental conditions were also established in order to determine the analyte in haemodialysis concentrates.

EXPERIMENTAL

Reagents

All reagents were of analytical-reagent grade. All solutions were prepared with high purity water from a Millipore Milli-Q water purification system device.

Standard Aluminium (III) solution (Titrisol Merck, 1000 µg/ml). Other ranges of concentrations were prepared by appropriate dilution.

A 0.001 M of 1,2-dihydroxyantraquinone-3-sulphonic acid (DASA) solution was prepared by dissolving the compound in water.

A 0.1 M sodium diethylthiobarbiturate solution. (DETB)

A 0.1 M N,N'-bis-(2-hydroxyethyl)-2-amino-ethane sulphonic acid solution, neutralized with HCl solution to pH=7.0 (BES).

Foreign ions solutions. Solutions of diverse ions were prepared by dilution of 1000 µg/ml Titrisol (Merck)

Apparatus

All the determinations were carried out using a Princeton Applied Research (PAR) 174 A instrument. The working electrode was a static mercury drop electrode SMDE 303, an Ag/AgCl, KCL

saturated electrode as the reference electrode and a platinum wire as auxiliary.

Procedure

To an aliquot of sample solution containing aluminium complete at 5 ml with water. Then add 50 µl of DETB or BES solution to adjust pH 7, 50 µl of DASA solution and 50 µl of 1000 mg/l calcium solution. Purge oxygen-free nitrogen during 4 min. and electrolyse for 60 se at -0.900 V vs Ag/AgCl, KCl_{sat}. After 10 sec. record the voltammogram at 20 mV/s in differential pulse mode using an amplitude of 25 mV.

RESULTS & DISCUSSION

The interaction of calcium with the Al-DASA complex has been studied by spectrophotometry[8]. The spectrophotometric results suggested that there is established an equilibrium between Al ions (probably largely hydrolyzed) and DASA on the one hand and Al-DASA complexes on the other. The presence of calcium ions shifts the equilibrium far to the right owing to the formation of a complex between calcium, aluminium and two molecules of DASA.

Cyclic voltammograms were recorded in order to study the effect of calcium ion on the electrochemical behaviour of the DASA (fig. 1A and B) and Al-DASA complex (fig 1C and D). As can be seen in fig. 1A the DASA chelate shows a reduction peak at -0.720 V which corresponds to the reduction of the substituted antraquinones[4,6]. This reduction signal was higher and more negative (-0.790V) in presence of calcium (fig. 1B). The irreversible nature of the signal is evident in the reverse oxidative scan ($I_{pc} > I_{pa}$).

Similarly, the signal at -1.010 V corresponding to the reduction of the Al-DASA complex (fig. 1C) was notably increased

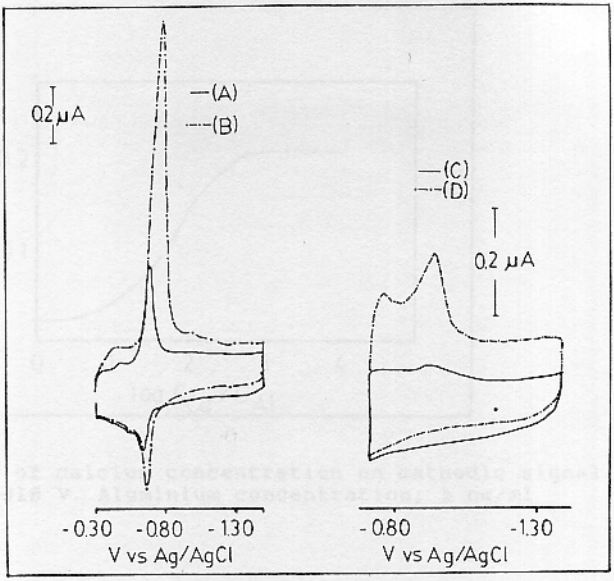

Figure 1: Cyclic voltammograms recorded in sodium diethylthiobarbiturate solution (pH=7). (A) DASA; (B) DASA-Ca; (C) Al-DASA and (D) Al(III)-DASA-Ca. Adsorption potential, -0.300V; adsorption time, 45 seg; scan rate, 100 mV/s. Aluminium concentration, 15 ng/ml; calcium concentration, 3 µg/ml

in presence of calcium (fig 1D). This cathodic peak was totally irreversible due to the slow complex formation between aluminium and DASA[6]. Further, subsequent repetitive scans yield significantly smaller cathodic peak, which indicates a rapid desorption of the complex from the electrode surface.

A similar effect on the reduction signal of Al-DASA complex was observed with other alkaline earth ions. Probably all the alkaline earth ions reacts with Al and two molecules of DASA to form a complex which is more easily adsorbed on the mercury surface. However the results show that higher analytical signal were obtained, in the order Ba < Mg < Ca for a same concentration of alkaline earth ion.

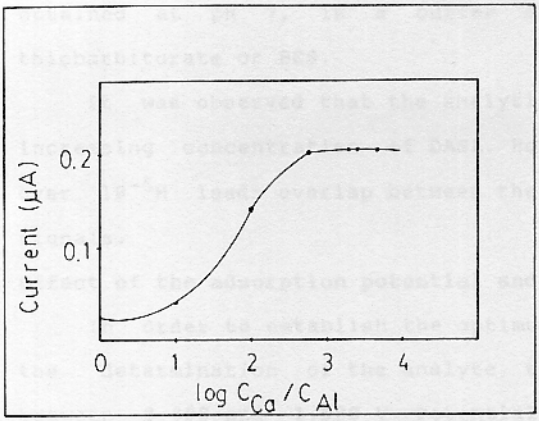

Figure 2: Effect of calcium concentration on cathodic signal of aluminium at - 1.010 V. Aluminium concentration; 5 ng/ml

Fig. 2 shows the effect of the calcium concentration on the determination of aluminium. The signal increased to reach a maximum at 500:1 (Ca:Al) ratio for 5 ng/ml aluminium. A concentration of 10 μg/ml was chosen for analytical determinations.

Effect of pH and DASA Concentration

The voltammetric behavior of the Al-DASA complex in presence of calcium was studied at selected pH values, without the addition of buffer. The reduction peak of the antraquinone is shifted cathodically as the pH increased, being the reduction reversible only in acidic media.

Similarly to the observed by Van den Berg et al[6], the signal obtained for aluminium was constant at pH values between 6.0 and 8.5, whereas at lower pH values the peak rapidly diminished and disappeared at pH 5.0. The best signal-to-background ratio was

obtained at pH 7, in a buffer system of sodium diethylthiobarbiturate or BES.

It was observed that the analytical signal increased with increasing concentration of DASA. However DASA concentrations over 10^{-5}M leads overlap between the analytical and the DASA signals.

Effect of the adsorption potential and time

In order to establish the optimum adsorption potential in the determination of the analyte, this variable was studied between -0.300 and -1.000 V. Potential values more positive than -0.800 V leads the reduction of the chelate, making the determination less sensitive. The maximum height of the reduction peak was obtained at an adsorption potential of -1.000 V, however, in this conditions the signal were neither well defined nor reproducible. An adsorption potential of -0.900 V was selected as a compromise between sensitivity and reproducibility.

The peak height increased with the adsorption time to reach a maximum at 90 sec for samples containing 5 ng/ml of aluminium. Over this value the electrode is saturated with the complex. An adsorption time of 60 s was selected as optimum for concentrations of aluminium lower than 30 ng/ml. For concentrations higher than this value the adsorption time could be decreased proportionally.

Figure 3 shows the adsorptive stripping voltammograms, in differential pulse mode, obtained in the conditions above mentioned.

Features of the method

Under the experimental conditions selected above and using the standard addition method, the recovery for eight replicate

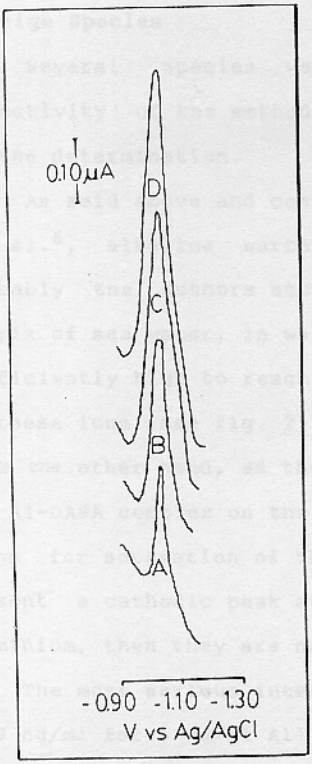

Figure 3. Adsorptive stripping voltammograms of Al-DASA in presence of calcium at different concentrations of Al (ng/ml). (A) 5, (B) 7.5, (C) 10, (D)12.5.

determinations at the 5 ng/ml level was found to be 101.1%, with a relative standard deviation of 2 %.

The sensitivity of the method was obtained from the slope of the calibration graph and it was found to be 0.040 µA·ml/ng.

The determination range, for the proposed method, was between 0.65 and 30 ng/ml, with a limit of detection (3 σ) of 0.2 ng/ml.

Foreign Species

Several species were studied in order to test the selectivity of the method. Alkaline metal ions had no influence in the determination.

As said above and contrarily to the information by Van den Berg et al.[6], alkaline earth ions increase the signal notably. Probably the authors studied the interferences directly in the matrix of sea water, in which the level of alkaline earth ions is sufficiently high to reach the maximum of sensitization produced by these ions (see fig. 2).

On the other hand, as the method is based on the adsorption of the Al-DASA complex on the electrode surface, its provides a good means for separation of the analyte from Fe, Mn, Cd, Cu, which present a cathodic peak at potential values more positive than aluminium, then they are not absorbed at -0,900 V.

The most serious interference was from zinc (tolerance limit = 60 ng/ml for 5 ng/ml Al) because the Zn-DASA complex presents a reduction peak which is only 50 mV more positive than that of the analyte. This interference can not be masked with $1 \cdot 10^{-4}$ M of EDTA[6] because it interferes at concentrations over $1 \cdot 10^{-5}$ M. However, the Zn signal was completely masked by addition of $4 \cdot 10^{-3}$ M of KCN. However, in this instance it was necessary to use a buffer BES, otherwise KCN reacts with DETB.

On the other hand, most of common anions do not to interfere.

Glucose is a major component of the haemodialysis concentrate, it was necessary to investigate its effect. It was found a tolerance limit of 7 g/l for 5 ng/ml Al.

Applications

A synthetic haemodialysis concentrate sample was prepared according to the contents given by the manufacturer (table 1).

TABLE 1

Typical composition of a haemodialysis concentrate sample

Compound	Content g/l
Sodium chloride	62.00 g
Potassium chloride	1.90 g
Calcium chloride 2-hydrate	2.62 g
Magnesium chloride 6-hydrate	1.04 g
Sodium Acetate 3- hydrate	54.14 g
Glucose	10.20 g

TABLE 2

Determination of aluminium in synthetical haemodialysis concentrates samples.

	Aluminium content/ng/ml			
Sample	Added&	Found*	Recovery /%	RSD/%
1	6.0	6.1	101.7	2.1
2	11.0	10.9	99.1	1,9
3	14.0	13.9	99.3	2.0
4	4.0	4.2	105.0	2.1

& 1 ml of sample
* Average of five determinations

Portions of the sample were spiked with standard Al in the concentration range of 6.0 to 19 ng/ml. The aluminium content was determined using the additions standard method (table 2).

The recovery and the RSD achieved indicates that the method is quite applicable for determination of aluminium in samples with a high saline content.

In this respect, the proposed method was applied to the determination of Aluminium in two commercial haemodyalisis concentrates. The aluminium contents were found to be 5.2 and 45.5 ng/ml with a relative standard deviation of 1.2 % and 0.5 %, respectively.

Finally, as the interference from zinc was masked with cyanide, the method could be applicable to the determination of the analyte in tap water.

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REFERENCES

1. Pereiro-García, M.R., López-García, A., Díaz-García, M.E., Sanz-Medel, A., J. Anal. At. Spectrom., 1990, 5, 15.

2. Gitelman, H. J., "Aluminium and Health. A Critical Review", Marcel Dekker, New York, 1988.

3. Slavin, W., J. Anal. At. Spectrom., 1986, 1, 281.

4. Kolthoff, I.M. and Lingane J.J., "Polarography", Vol II. Interscience, New York, 1952, pp. 513, 703.

5. Wang, J., Farias, P.A.M. and Mahmoud, J.S., Anal. Chim. Acta, 1985, 172, 57.

6. Van Den Berg, C.M.G., Murphy, K. and Riley, J.P., Anal. Chim. Acta, 1986, 188, 177.

7. Chiang, L. James, B.D., Magee, R.J., Mikrochim. Acta, 1989, II, 149.

8. Parker, C.A. and Goddard, A.P., Anal. Chim. Acta, 1950, 4, 517.