

## Determination of Trivalent Aluminum and Divalent Zinc in Drinking Waters by Differential Pulse Stripping Voltammetry

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**Abstract:** A Sensitive and precise differential- pulse stripping voltammetric method at static mercury dropping electrode (SMDE) has been applied to measure zinc(II) by anodic stripping at pH~4 and aluminum(III) by adsorptive cathodic stripping mode in presence of  $1 \times 10^{-3}$  M N,N'-bis-2-hydroxyethyl-2-amino-ethane sulphonic acid (BES) buffer at pH~7.1 and  $2 \times 10^{-5}$  M of alizarin red S as a ligand in drinking water samples purchased in Egypt. The optimal preconcentration potentials and times for the detection of these metal ions in all samples have been studied. The concentrations of metal ions were determined by standard addition method. The statistical parameters i.e. standard deviation, correlation coefficient, slope and confidence have been calculated. The limits of detection for Zn and Al were 2.5 and  $10 \mu\text{g l}^{-1}$ , respectively.

**Keywords:** Aluminum, Zinc, Electroanalytical determination, waters

### INTRODUCTION

Aluminum is an abundant element. It is distributed among the body tissues, organs and bones, but its exact biological functions are not known fully. Abnormal amounts of aluminum have been detected in the brains of dead patients suffering from Alzheimer's disease<sup>[1,2]</sup>, Parkinson's disease<sup>[3]</sup> and dialysis encephalopathy<sup>[4-6]</sup>. In fact, the element zinc is an essential element for man and is necessary for the functioning of various enzyme systems, including alkaline phosphatase, carbonic anhydrase and alcohol dehydrogenase<sup>[7]</sup>.

Stripping voltammetry has been widely used to measure the low concentration of metal ions such as Aluminum and Zinc in natural waters as no preconcentration step is required even for saline waters. In addition to conventional anodic stripping voltammetry (ASV), cathodic stripping voltammetry (CSV) with adsorptive collection is very useful<sup>[8]</sup>.

Anodic stripping voltammetry (ASV) has been widely used for the trace determination of several metal ions, including zinc, in different matrices. The advantages of ASV are high sensitivity, low maintenance costs, rapidity and minimal sample preparation<sup>[9]</sup>.

Because of the environmental and biological significance of aluminum, a highly sensitive method is required for its reliable measurement. The

electrochemical behaviour of aluminum makes its voltammetric quantitation difficult<sup>[10]</sup>.

Aluminum is reduced at -1.75V, yielding an irreversible wave, distorted by the hydrogen evolution background current<sup>[11]</sup>. Especially useful in this respect seems to be adsorptive stripping voltammetry which has been known to give excellent sensitivity for the determination of a variety of trace metals at a mercury electrode<sup>[12]</sup>. This method consists of an aluminum complex compound with organic ligands. This complex is accumulated adsorptively at a chosen potential on the cathode. Then, currents are directly proportional to Al concentrations<sup>[13]</sup>.

Solochome Violet SR<sup>[14-17]</sup>, calmagit<sup>[18-21]</sup>, cupferro<sup>[10]</sup> and alizarin-S [1,2-dihydroxyanthraquinone-3-sulphonic acid]<sup>[22,23]</sup> are most frequently used for aluminum complexation. Out of all these complex compounds the most suitable seems to be alizarin-S. its complex with Al is obtainable for several seconds at room temperature, without heating. Alizarin-S in BES buffer (N, N'-bis-2-hydroxyethyl-2-amion-ethane sulphonic acid) was used to determine Al in sea water<sup>[22,23]</sup>. However, the application of BES solution as a supporting electrolyte causes production of the aliz./Al peak at the potential of -1.25V versus Ag/AgCl which causes interference by high concentrations of zinc ( $>50 \text{ nM}$ )<sup>[22]</sup>.

In this study, the employment of sensitive and reproducible method of cathodic adsorptive stripping

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voltammetry in differential pulse technique using alizarin-S as a complexing agent and BES buffer as a supporting electrolyte was successfully performed for monitoring trace amounts of Al(III) in mineral water samples containing low concentrations of zinc <50nM. In addition the work presented here focuses on applying sensitive and precise procedure of differential pulse anodic stripping voltammetry (DPASV) for the direct determination of Zn(II) ions in samples under investigation. The detection limits achieved are comparable to, or better than, those reported in previous literature.

## MATERIALS AND METHODS

### Apparatus

- Polarographic analyzer/stripping voltammeter-EG & G Princeton Applied Research corp. (PAR, Princeton, NJ) Model 264A stripping analyzer, coupled with a PAR 303A static mercury drop electrode (SMDE; drop size, medium; area of drop, 0.014 cm<sup>2</sup>) had been used. The polarographic cell (PAR Model K0060) was fitted with Ag/AgCl saturated KCl and used as a reference electrode with a platinum wire as a counter electrode. A PAR 305 stirrer was connected to the 303A SMDE. A PAR Model RE0089X-Y recorder was used to collect experimental data.
- pH meter - pH values of different solutions and reagents were measured with a fischer scientific (Pittsburgh, PA) Accument, Digital pH Meter Model 810.

**Solutions and reagents:** The electrolysis cell, volumetric flasks and pipettes were thoroughly cleaned with dilute nitric acid (6M) by soaking over night and then washed with bidistilled water. All reagents are of analytical grade. The following solutions were prepared with bidistilled water.

- Stock solution of 0.1M nitric acid was prepared by diluting of a definite volume of concentrated acid (BDH) with bidistilled water. The solution was standardized using standard solution of sodium hydroxide (BDH) free carbonate<sup>[24]</sup>.
- An aqueous solution of 10<sup>-3</sup>M alizarin red S (Merck) was prepared by dissolving the appropriate mass in bidistilled water. The aqueous stock pH buffer solution prepared was 1M solution of BES buffer (Sigma) in 0.5M sodium hydroxide.
- 0.1M of potassium nitrate and 0.01M of each of zinc nitrate and aluminum nitrate solutions (BDH) were prepared by dissolving the appropriate amount of each one in bidistilled water.

All measurements were made at 25±1°C with a nitrogen atmosphere maintained over the solution surface.

**Analytical procedure:** The following parameters were used to perform differential pulse anodic stripping voltammetry (DPASV). Pulse amplitude(ΔE) 25 mV and scan rate 10 mVs<sup>-1</sup> with pulse duration for 1 sec.

For determination of Zn(II) in mineral water samples. 5 mL of the sample, 10μl of 0.1 M. HNO<sub>3</sub> and 1 mL of 0.1 M KNO<sub>3</sub> were transferred to the electrolysis cell and diluted to 10 mL using bidistilled water (pH~4). The solution was deaerated by passing pure nitrogen for 16 minutes. The deposition potential was controlled at (-1.15 V vs. Ag/AgCl saturated KCl) and applied to a fresh mercury drop while the solution was stirred. After the deposition step and further 15 sec. (equilibrium time), the voltammogram was recorded. Aliquots from the stock solutions of the Zn(II) were spiked to the same cell, then repeating the procedure as above (standard addition method).

For determination of Al(III), the sample (5 mL) is pipetted into the electrolysis cell, 10μl of the BES buffer is added (giving pH =7.1) followed by 200 μl of 10<sup>-3</sup>M of alizarin-S stock solution, giving a working concentration of 2×10<sup>-5</sup>M. After deaeration of the solution with nitrogen as an inert gas for 16 minutes, the stirrer is started and the potentiostat is set to -0.9V. A new mercury drop is then extruded which signifies the beginning of the adsorption time. 15 sec. is allowed for the solution to become quiescent. The differential pulse cathodic stripping scan is then started, at a rate of 20 mVs<sup>-1</sup>, with a pulse height of 25mV and a pulse time of 1sec. Aliquots from the Al(III) solution were spiked to the same cell, then repeating the procedure as above.

## RESULTS AND DISCUSSION

Preliminary experiments have been carried out to investigate the effect of various operational parameters on the differential pulse anodic stripping response. The influence of supporting electrolyte was studied using DPASV technique. Generally, the electrolyte chosen was 0.001M HNO<sub>3</sub> and 0.01M KNO<sub>3</sub> used as supporting electrolyte which brought the pH of solution to pH~4 to determine Zn<sup>2+</sup> trace in mineral water samples. [In this medium, no organic matter or other materials capable of forming inert complexes with zinc<sup>[25]</sup>. The effect of deposition potential was studied and it was observed that the highest and best shape peak for Zn<sup>+2</sup> was at deposition potential -1.15V. The effect of deposition time on the anodic peak current of Zn(II)

Table 1: Zinc content of different water samples, confidence level is 95%, number of repetition, n=3

Sample	Deposition time sec.	conc. $\mu\text{g l}^{-1}$	Regression parameter			Confidence	
			Slope $\text{nA}/\mu\text{g l}^{-1}$	St. dev.	Corr. Coeff.	Lower 95%	Upper 95%
Aqua	90	6.03	2.39	1.01	0.9991	2.21	2.57
Baraka	60	5.11	1.36	1.22	0.9999	1.35	1.37
Delta	60	11.32	1.55	2.03	0.9997	1.51	1.59
Nestle	60	4.01	4.17	1.05	0.9998	4.04	4.29
Nubia	60	17.47	1.86	3.11	0.9999	1.82	1.89
Safi	15	64.17	0.74	5.06	0.9996	0.72	0.76
Schweppes	60	16.22	1.69	2.85	0.9998	1.66	1.74
Tap water	5	345.62	2.29	11.28	0.9999	2.27	2.31

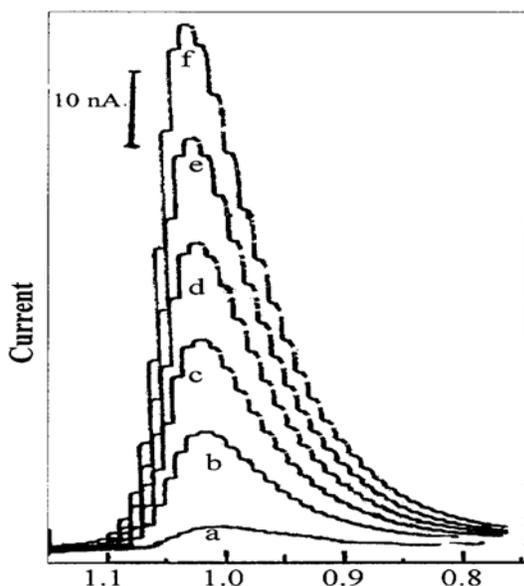


Fig. 1: DPAS Voltammograms for different deposition times of Zn(II) in Schweppes sample, a) Zero sec. b) 30 sec., c) 60 sec. d) 90 sec e) 120 sec and f) 150 sec.

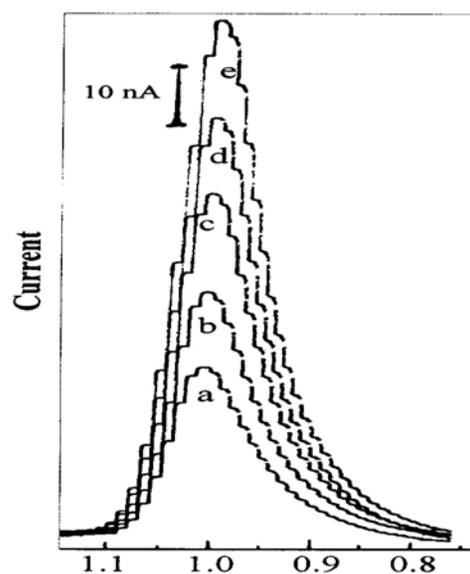


Fig. 2: DPAS Voltammograms for determination of Zn(II) in Schweppes sample spiked with different concentrations of Zn(II) ions, deposition time 60 sec. a) sample, S., b) S.+10, c) S.+20, d) S. +30, e) S. +  $40 \times 10^{-8}$  M Zn(II)

was investigated and the optimal deposition times required were listed in Table 1. However, the deposition time was selected in a manner that linear relation must be established between deposition time and the current signals as shown in Fig. 1. While, Fig. 2 shows the differential pulse anodic stripping voltammograms of the addition of standard zinc nitrate. The plots of peak current against concentration are given in Fig. 3. From the interception of the line with the concentration axis at zero current signal gives the concentration of the analyte in the voltammetric cell for each sample, these concentration values multiplied by the factor 2 since the original volume of the sample taken is 5 mL. After correction for the background current of blank experiments. The limits of detection of the proposed procedure for zinc ions under investigation were calculated<sup>[26]</sup>. Table 1 shows the

concentrations of Zn(II) ions in all samples under consideration using DPASV.

Preliminary measurements were made to obtain the highest peak signal for Al(III) ions in five mineral water samples under consideration. In this work, a procedure is described for determination of aluminum ions in drinking waters by cathodic stripping voltammetry of its complex with alizarin-S. The reduction currents of the ligand in the adsorbed complex are indication of the aluminum concentration. In this aspect, the method differs from the determination by cathodic stripping voltammetry of other metals such as copper<sup>[27]</sup> or nickel<sup>[28]</sup> in which the current arises from the reduction of the metal in the adsorbed complex<sup>[29]</sup>. Alizarin-S is adsorbed on a mercury drop electrode forms a cathodic peak at the potential of -0.63V and two anodic peaks at

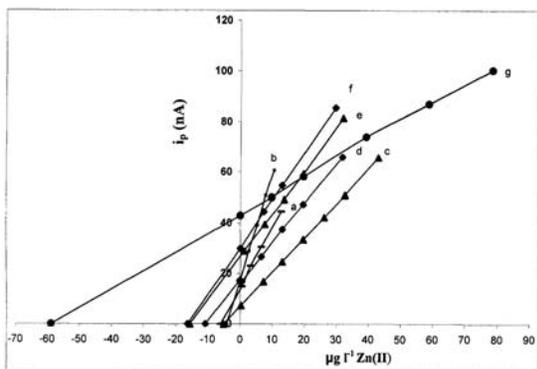


Fig. 3:  $i_p$  vs. concentration for Zn(II) in: a) Aqua, b) Nestle, c) Baraka, d) Delta, e) Schweppes, f) Nubia and g) Tap water

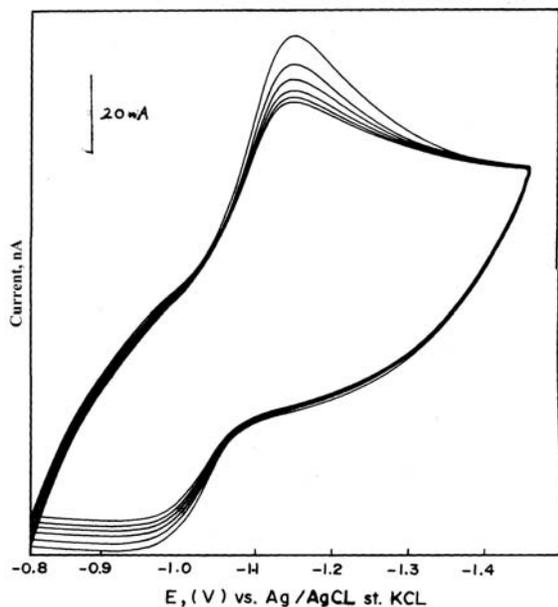


Fig. 4: Cyclic voltammograms for  $1 \times 10^{-3}$  M BES buffer at pH~7.1 containing  $2 \times 10^{-5}$  M alizarin-S and  $25.58 \text{ mg l}^{-1}$  Al(III) while scan rate was  $100 \text{ mVs}^{-1}$

the potentials of -0.63 and -0.55V. The main reduction peak appeared at -0.63V is in agreement with half-wave potentials quoted for substituted anthraquinones<sup>[30]</sup>. A repeated cycle on the same mercury drop affects an increase in the peak height due to alizarin-S adsorption onto the electrode surface and causes the appearance of more cathodic peak at the potential of -0.51V. These voltammograms are consistent with those obtained in previous literature<sup>[22]</sup>. They indicate a reversible reduction of free ligand (alizarin-S) on a mercury drop electrode surface. In the presence of  $25.58 \text{ µg l}^{-1}$  aluminum and after stirred adsorption for 5 sec. at -0.8V, a peak related to aliz. Al complex appears at -1.11V.

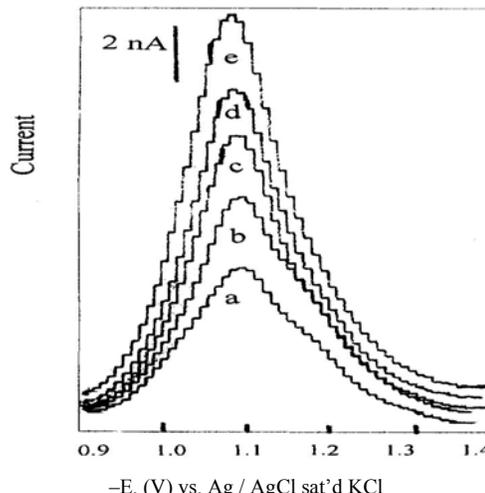


Fig. 5: DPCS Voltammograms for determination of Al(III) in delta sample spiked with different concentrations of Al(III) ions, preconcentration potential -0.9 V and accumulation time 10 sec. a) Sample, S., b) 5, c) 10, d) 15, e)  $20 \times 10^{-7}$  M

Figure 4 represents cyclic voltammograms for  $1 \times 10^{-3}$  M BES buffer at pH~7.1 containing  $2 \times 10^{-5}$  M alizarin-S and  $25.58 \text{ mg l}^{-1}$  Al(III) while scan rate was controlled at  $100 \text{ mVs}^{-1}$ .

This reduction step is irreversible; the returning scan reveals only a poorly defined and broad peak. This irreversibility may be due to slow formation of the aliz. Al complex, as the reduction of alizarin-S itself is reversible. The reduction peak does not shift in a negative direction when the scan rate is increased to 200 or  $500 \text{ mVs}^{-1}$ , confirming that the reduction step itself is fast and that irreversibility is due to relatively slow complexation kinetics. Upon operating the scan, the reduction peak is smaller because the diffusion of the ligand and the metal away from the electrode. The effect of pH on the peak height obtained for the aluminum in mineral water was investigated and it was found that the peak height was constant at pH values between 5.5 and 8.5, whereas, at lower pH values the peak rapidly diminished and disappeared at pH~5.2. However  $1 \times 10^{-3}$  M BES buffer giving a pH of 7.1 (neutral medium) was selected to give excellent separation of the aliz. Al peak. The process of adsorptive accumulation of aluminum depends on many parameters. One of them is the accumulation potential. No peak for aluminum is visible when adsorption potentials near to more positive than the reduction peak for the free ligand is selected at -0.7V, under these conditions the aliz Al peak is masked as a result of saturation of the drop surface by free ligand. The peak height diminishes when adsorption potentials nearer to

Table 2: Aluminum content of different water samples, confidence level is 95%, number of repetition, n=3

Sample	Accumulation time sec.	conc. $\mu\text{g l}^{-1}$	Regression parameter			Confidence	
			Slope $\text{nA}/\mu\text{g l}^{-1}$	St. dev.	Corr. Coeff.	Lower 95%	Upper 95%
Aqua	10	8.04	3.18	1.91	0.9939	2.31	2.52
Delta	10	5.53	2.51	1.85	0.9999	1.81	1.85
Nestle	10	25.58	1.86	2.56	0.9987	4.31	4.51
Nubia	10	39.96	4.01	3.37	0.9999	4.01	4.05
Schweppes	10	36.67	5.02	3.12	0.9999	4.02	4.51

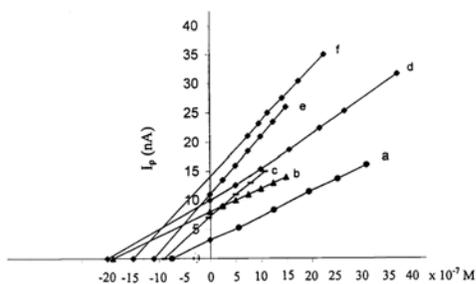


Fig. 6:  $I_p$  vs. concentration for Al(III) in: a) Delta, b) Schweppes, c) Baraka and d) Nubia e) Nestle and f) Aqua samples

the aliz. Al peak (at -1.11V), whereas, the greatest peak height is obtained when adsorption potential is controlled at -0.9V. The peak height of aliz. Al complex was measured as a function of ligand concentration. It was found that the peak height is increased strongly with the ligand concentrations up to  $2.2 \times 10^{-5} \text{M}$ . This increase reflects the increase formation of the aliz. Al complex in solution at higher ligand concentrations. At ligand concentrations  $> 2.2 \times 10^{-5} \text{M}$  the background current increases. The optimal ligand concentration for the determination of aluminum using  $1 \times 10^{-3} \text{M}$  BES buffer (pH~7.1) in mineral water samples is  $2 \times 10^{-5} \text{M}$  ligand. Another important factor is the accumulation time. The optimal time of adsorptive accumulation at alizarin-S concentration  $2 \times 10^{-5} \text{M}$  is 10 sec. However, the accumulation time was selected to reduce the analysis time and linearity should be established between accumulation time and current signals and the suitable accumulation times are listed in Table 2. The dependence of the voltammograms on the scan rate for the aliz. Al complex was illustrated and it was found that, the optimized differential pulse cathodic stripping scan is started at a scan rate of  $20 \text{mVs}^{-1}$ , with a pulse height of 25mV and pulse time of 1 sec. the influence of major cations Cr(III), Cd(II), Pb(II), Cu(II), Ni(II), Co(II) and Fe(III) on the height of aliz. Al peak was examined. As shown by experiments. The additions of  $10^{-7} \text{M}$  of each of Cu(II), Cr(III) and Fe(III) or  $10^{-8} \text{M}$  of each of Ni (II), Co(II), Cd(II) and Pb(II) have no effect

on the determination of 15nM aluminum in water samples. Only zinc was found to interfere as it may be present at enhance levels ( $>50 \text{nM}$ ) and could be masked by initiating the scan from -0.9 to -1.0V. It was also found that addition of  $10^{-4} \text{M}$  EDTA to fresh water completely masked zinc without affecting the aluminum response. In the present work, Zinc levels are less than 50nM in mineral water samples except tap water; there is no need to add masking agent. Organic matter often interferes with voltammetric determinations and therefore sample solutions usually have to be digested. Samples of Ground water, drinking water and mineral water ran usually be analyzed without pretreatment. On the basis of this study, the optimal conditions for aluminum determination in mineral water samples are as follows:

1. Analysis can be carried out directly without pretreatment.
2. BES buffer concentration was  $1 \times 10^{-3} \text{M}$  giving pH~7.1.
3. Alizarin-S concentration was  $2 \times 10^{-5} \text{M}$ .
4. Adsorption potential was -0.9V.
5. Accumulation time was 10 sec.
6. Scan rate was  $20 \text{mVs}^{-1}$ .

Figure 5 shows the standard addition method for Al(III) determination using adsorptive cathodic differential pulse stripping voltammetry (AdCDPSV) in water samples. By plotting the peak current values against the standard concentration added to obtain the Al content in different water samples as shown in Fig. 6. Table 2 shows the concentrations of aluminum in all samples using (AdCDPSV). The limits of detection for Al and Zn were found to be 1 and 2.5  $\text{mg l}^{-1}$ . These values achieved are better than, those reported in literature. The results obtained using AdCDPSV indicate that, aluminum contents in mineral water samples under investigation were ranged from 5.53-39.96  $\text{mg l}^{-1}$ . While, the results obtained using DPASV indicate that, the concentrations of zinc in the samples under consideration were ranged from 4.01-17.47  $\mu\text{g l}^{-1}$  and 345.62  $\mu\text{g l}^{-1}$  for tap water sample. The precision and reproducibility of the selected procedure were investigated by measuring the

concentration of Al(III) and Zn(II) in all mineral water samples under consideration for (n=3), the confidence intervals and the standard deviations obtained indicate the good reproducibility and high precision of the selected voltammetric procedures as shown in Table 1 and 2. In conclusion, our selected procedure is rapid, sensitive, reproducible, precise and can be usefully performed to determine trace aluminum and zinc ions in mineral water samples purchased in Egypt.

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