

# Determination of aluminium in water samples by adsorptive cathodic stripping voltammetry in the presence of pyrogallol red and a quaternary ammonium salt

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## Abstract

A fast, sensitive and selective method for the determination of aluminium based on the reaction of the metal with pyrogallol red (PR) in the presence of tetrabutylammonium tetrafluoroborate (TBATFB) to form an  $\text{Al}(\text{PR})_3 \cdot 9\text{TBATFB}$  complex which is adsorbed on the mercury electrode is presented. Under these conditions complexation of aluminium is rapid and no waiting period or heating of the sample is required. The reduction current of the accumulated complex is measured by scanning the potential in the cathodic direction. The variation of peak current with pH, adsorption time, adsorption potential, ligand and quaternary ammonium salt concentration, and some instrumental parameters, such as stirring rate in the accumulation stage, and step amplitude, pulse amplitude and step duration while obtaining the square wave voltamperograms were optimized. The best experimental parameters were pH 8.5, ( $\text{NH}_4\text{Ac}-\text{NH}_3$  buffer),  $C_{\text{PR}} = 25 \mu\text{mol L}^{-1}$ ,  $C_{\text{TBATFB}}$  over  $75 \mu\text{mol L}^{-1}$ ,  $t_{\text{ads}} = 60 \text{ s}$ , and  $E_{\text{ads}} = -0.60 \text{ V}$  versus Ag/AgCl. A linear response is observed over the  $0.0\text{--}30.0 \mu\text{g L}^{-1}$  concentration range, with a detection limit of  $1.0 \mu\text{g L}^{-1}$ . Reproducibility for  $9.0 \mu\text{g L}^{-1}$  aluminium solution was 2.3% ( $n=6$ ). Synthetic sea water and sea water reference material CRM-SW were used for validation measurements. Aluminium in urine samples of a volunteer who ingested 800 mg of  $\text{Al}(\text{OH})_3$  was analyzed.

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## 1. Introduction

Aluminium occurs ubiquitously in the environment, in the form of salts and oxides. Aluminium is not an essential element in humans, and it has been linked with a number of disorders in man including Alzheimer's disease, Parkinson's dementia and osteomalacia. However, the potential contribution of aluminium in Alzheimer's disease and related disorders is not resolved. Some studies have found an increase of this element in the brain [1–4], whereas others have not [5–8]. On the other hand, several epidemiological studies have associated aluminium in drinking water with the incidence of Alzheimer's disease [9–13]; other studies have not found significant associations with similar levels of aluminium concentration [14–17]. On the other hand, the bioavailability of aluminium from water and foods is low. Studies of the relative bioavailability of aluminium naturally

present in aluminium treated drinking water were determined in healthy volunteers with normal renal function who consumed 1.6 L per day with  $140 \mu\text{g L}^{-1}$  aluminium. The bioavailability of aluminium from this treated water was 0.37%, similar to that from food (0.28–0.64%) [18].

Aluminium exhibits a complex chemistry in natural waters. Solution pH and the presence of fluoride, silicon, iron and natural chelating agents in the water may all influence the speciation of aluminium and consequently its bioavailability. Trivalent  $\text{Al}^{3+}$  and the hydrolyzed ions  $\text{Al}(\text{OH})^{2+}$  and  $\text{Al}(\text{OH})_2^+$  represent the species of principal concern, with organically bound Al and polymeric forms considered far less toxic [19].

Sensitive, selective and accurate methods are required for the determination of aluminium in biological and environmental matrices. Electroanalytical techniques have important advantages that include speed, high selectivity and sensitivity, low detection limit, relative simplicity, and low equipment cost compared to other techniques. Of these electroanalytical methods, stripping voltammetry is the most sensitivity one because it has a preconcentration step on the electrode surface prior to

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Table 1  
List of the adsorptive stripping voltammetric methods have been reported for determination of aluminium

Method	Ligand	pH	Linear range	Detection limit	Refs.
DPSV	Solochrome violet RS	4.5	0–30 $\mu\text{g L}^{-1}$	0.15 $\mu\text{g L}^{-1}$	[20]
LSV	Solochrome violet RS	5.2	$1 \times 10^{-8}$ – $8 \times 10^{-7}$ $\text{mol L}^{-1}$	$5.1 \times 10^{-9}$ $\text{mol L}^{-1}$	[21]
		8.5	$1 \times 10^{-8}$ – $1 \times 10^{-6}$ $\text{mol L}^{-1}$	$3.8 \times 10^{-9}$ $\text{mol L}^{-1}$	
DPAdSV	Solochrome violet	4.5		1.4 $\mu\text{g L}^{-1}$	[22]
	Palatine chrome black 6B	7.0		69.0 $\mu\text{g L}^{-1}$	
	Chromazul S	7.0		35.5 $\mu\text{g L}^{-1}$	
	Erochrome black T	4.5		49.2 $\mu\text{g L}^{-1}$	
AdCSV	Solochrome violet RS	8.8		$4.5 \times 10^{-9}$ $\text{mol L}^{-1}$	[23]
DPAdSV	DASA	7.1–7.3		1 n $\text{mol L}^{-1}$	[24]
AdCSV	DASA	7.1	0.8–30 $\mu\text{g L}^{-1}$	0.8 $\mu\text{g L}^{-1}$	[25]
AdCSV	Cupferron	7.0		30 ng $\text{L}^{-1}$	[26]
AdCSV	Alizarin S	8.2	$2.5 \times 10^{-8}$ – $3.5 \times 10^{-7}$ $\text{mol L}^{-1}$	$2.5 \times 10^{-8}$ $\text{mol L}^{-1}$	[27]
AdCSV	Morin	7.0	1–15 $\mu\text{g L}^{-1}$	0.11 $\mu\text{g L}^{-1}$	[28]
FSDPV	Arsenazo III	3.6	$0-6 \times 10^{-6}$ $\text{mol L}^{-1}$	$3.7 \times 10^{-8}$ $\text{mol L}^{-1}$	[29]
LSV	Norepinephrine	8.5	$4 \times 10^{-6}$ – $4 \times 10^{-5}$ $\text{mol L}^{-1}$	$1.8 \times 10^{-6}$ $\text{mol L}^{-1}$	[31]
SWAdSV	Cupferron	4.5	0.5–5.0 $\mu\text{g L}^{-1}$ (240 s)	1–10 $\mu\text{g L}^{-1}$	0.5 $\mu\text{g L}^{-1}$
			(120 s)	2–20 $\mu\text{g L}^{-1}$ (60 s)	

recording the voltammogram. The accumulation of metal ions can occur by electrolysis (anodic stripping voltammetry, ASV) or by adsorption (adsorptive stripping voltammetry, AdSV) after complexation with a surface active ligand. The quantitation of aluminium by ASV is difficult because it is reduced at  $-1.75$  V versus Ag/AgCl, close to hydrogen evolution. The presence of a ligand which forms a complex with aluminium displaces the potential to more positive values due to adsorption of the complex on the working electrode. AdSV is more sensitive than ASV, but the concentration range for its application is more limited because the surface area of the electrode is saturated and many ligands are adsorbed, competing with the complex. There are few reports on the application of adsorptive cathodic stripping voltammetry for the determination of aluminium; they use solochrome violet RS [20–23], 1,2-dihydroxy-anthraquinone-3-sulphonic acid (DASA) [24,25], cupferron [26], alizarin S [27], morin [28], arsenazo III [29], calmagite [30], and norepinephrine [31] with hanging mercury drop or mercury film electrodes, and recently cupferron [32] with bismuth film electrodes (Table 1). A good detection limit was obtained with solochrome violet RS, but it was necessary to heat the sample solution for 10 min at  $90^\circ\text{C}$  to ensure quantitative complexation [20–22]. On the other hand, the reduction potential of the free norepinephrine and the aluminium complex are very close, making difficult the quantitation of aluminium in real samples [31]. The main advantages of the use of DASA [24,25] as complexing agent for the voltammetric determination of aluminium is the low detection limit and the fast reaction kinetics, which obviate the need to heat the sample after addition of the reagent.

The present paper describes a sensitive and rapid adsorptive stripping procedure based on the reaction of the aluminium with pyrogallol red (3,4,5-trihydroxy-9-(2'-sulphophenyl)-6-isoxanthone, pyrogallolsulphophthalein, PR) in the presence of tetrabutylammonium tetrafluoroborate (TBATFB) to form an Al-PR-TBATFB complex, which is adsorbed, followed by reduction at  $-1.10$  V versus Ag/AgCl. PR has four groups capable of dis-

sociation with the abstraction of a proton: one sulfo group and three hydroxyl groups (Fig. 1). The dissociation constants were determined by spectrophotometric, computational and graphical methods and were calculated for different ionic strengths because cationic surfactants affect the dissociation of PR [33]. The pyrogallol structural group is found in many important natural and synthetic molecules, such as gallic acid, tannic acid and humic acid. Pyrogallol red has been used for the detection of aluminium and other metals via spectrophotometry and for other metal ions via adsorptive cathodic stripping voltammetry (copper [34], copper and molybdenum [35], antimony [36], germanium [37], and vanadium [38]), but this is the first report for the detection of aluminium via AdCSV in the presence of quaternary ammonium salt which it modifies acid–base properties of PR ligand and accelerating the complexation. The method was validated with synthetic sea water and sea water reference material CRM-SW, and it was also applied to the determina-

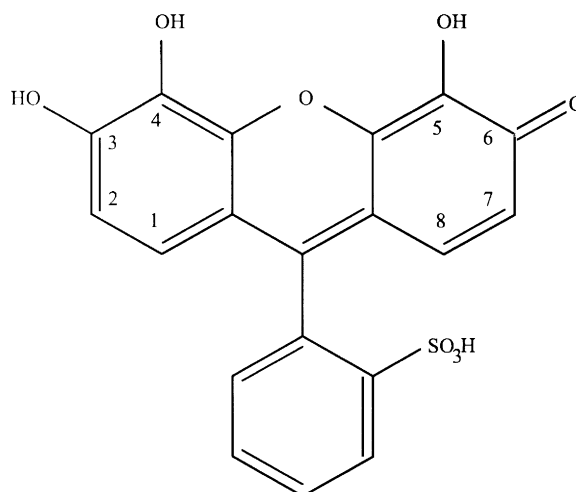


Fig. 1. Structural formula of pyrogallol red.

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