

Analytical, Nutritional and Clinical Methods

# Determination of trace aluminum in foods by stripping voltammetry

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## Abstract

The study of electrochemical behavior of aluminum–cupferron complex indicated that aluminum and cupferron formed complex in 0.4 mol/L (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> solution. Accumulation potential of –0.95 V (vs. SCE) was applied, while the solution was stirred for 60 s. The response curve was recorded by scanning the potential to the negative direction and the peak current of –1.18 V (vs. SCE) was recorded. This complex absorbed in hanging mercury drop electrode (HMDE) and create a sensitive peak current. The peak current and concentration of aluminum accorded with linear relationship in the range of  $4.0 \times 10^{-8}$ – $2.0 \times 10^{-9}$  g/mL. The relative standard deviation (at 10 µg/L) is 3.0% and the detection limit is  $8 \times 10^{-10}$  g/mL. The interference of some common ions was studied. This method has been used to determine trace aluminum in foods and water.

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**Keywords:** Aluminum; Food; Cupferron; Stripping voltammetry

## 1. Introduction

Aluminum is an essential metal element in biological systems. It exists in nature extensively and it is one of the most abundant elements in the earth's crust (Alfrey, 1986). Before 1970s, aluminum and aluminates were treated as substances which could not be absorbed, and were safe without any poisonous effects. Therefore, aluminum and aluminates were widely used in food additives, medicines, water coagulants and all kinds of cookers and containers. From mid-70s, with the development of analytical techniques and the increasing reports about the poisonous effects of aluminum, the study about the poisonous effects of aluminum to human beings had been further developed. In fact, when people ingested amounts of aluminum ions, aluminum

would deposit in the human bodies, and interfered with the normal activities of nervous system (Alfrey, 1986; Belitz & Crosn, 1987; Berman, 1980; Stocpler, 1992), and the worse effects would be brain diseases, which would clinically present as language difficulties, movement obstructions and abnormal electroencephalogram (Zhang, 1998). So, the determination of aluminum exhibits its extraordinary importance. The determination of aluminum has been reported much. Determination of aluminum in flour by spectrophotometry had low detection limit of 45 µg/mL (Li, 2004). In the catalytic spectrophotometric method, the detection limit of aluminum could be 1.2 ng/mL (He & Wang, 2000). Several methods were used to determine aluminum based on atomic absorption spectrum (Campillo, Vinas, Lopez, & Hernandez, 1999; Goncalves, Alves, & Aparecida, 2002; Luccas, Nobrega, Dliveira, & Krug, 1999), but these methods need costly apparatus. Some people applied flow-injection and liquid chromatography to determine trace aluminum (Albendin, Manuel-vez,

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Moreno, & Garcia-Vargas, 2003; Lian et al., 2004). The method of using  $F^-$  ion-selective electrode to determine trace aluminum in teas was simple and fast, but it was interfered with fluorine ions, and had low sensitivity (Wang, Zhang, Sun, Liu, & Liu, 1996). Stripping voltammetry has been widely used because of its high sensitivity (Wang, 1985). Wang, Percio, Farias, and Mahmoud (1985) applied stripping voltammetry to determine trace aluminum by using solochrome violet RS (SVRS) as ligand. The detection limit was  $0.15 \mu\text{g/L}$ . But this method was too complicated to operate. Downard, Kipton, Powerll, and Xu (1992) controlled pH 8.8 to determine trace aluminum by cathodic stripping voltammetry, when SVRS existed. The detection limit could be  $4.5 \times 10^{-9} \text{ mol/L}$ . Wang, Lei, Bi, Gan, and Wei (2001) used stripping voltammetry to determine aluminum in natural water in the same system. Balbo, Orto, Sobral, and Rezzano (1998) used linear scan stripping voltammetry at glassy-carbon based thin mercury film electrodes to determine aluminum in dialysis fluids, but the preparation of working electrode was too complicated. Wang, Lu, and Setiadji (1993) used adsorptive stripping to determine trace aluminum in the presence of cupferron, but this method was not used to determine aluminum in samples.

The present paper describes a highly sensitive adsorptive stripping procedure for determining trace aluminum in foods with cupferron. Cupferron and aluminum formed a complex in  $(\text{NH}_4)_2\text{SO}_4$  solution. Aluminum-cupferron complex absorbed in hanging mercury drop electrode (HMDE) and produced a sensitive peak current in  $-1.18 \text{ V}$  (vs. SCE). The increase of peak current was linear with the concentration of aluminum in the range of  $4.0 \times 10^{-8}$ – $2.0 \times 10^{-9} \text{ g/mL}$ . The detection limit was  $8 \times 10^{-10} \text{ g/mL}$ . This method was simple to operate, which did not need steps of heating, cooling and so on, and it could be used to determine trace aluminum in hair, water, tea leaves and flour with satisfactory results.

## 2. Materials and methods

### 2.1. Apparatus and electrode

Experiments were performed on a CHI 604A Electrochemical Analyzer (CH Instrument, USA) equipped with a computer as control and recorder. A hanging mercury drop electrode (HMDE) was used as the working electrode, the reference and counter electrodes were saturated calomel and platinum wire electrodes. A 50-mL beaker was used as the electrolytic cell. All potentials were measured vs. the saturated calomel electrode (SCE).

A 600-W MK-III microwave sample preparation system (Xin-Ke Institute of Applied Microwave Technology, Shanghai, China) was used for pretreatment of

the samples. Airtight and pressure-resisting vessels made of Shanghai were employed to hold the samples and a turntable was used to hold the vessels. Adjusting the pressure controlled the extent of the samples decomposition.

### 2.2. Reagents

A standard aluminum solution ( $1 \text{ mg/mL}$ ) was prepared by dissolving  $0.1000 \text{ g}$  aluminum in hydrochloric acid and then diluting with water in  $100\text{-mL}$  volumetric flask. A  $3.2 \times 10^{-3} \text{ mol/L}$  cupferron stock solution was prepared by dissolving  $0.0497 \text{ g}$  cupferron in water and then diluting it in  $100 \text{ mL}$  volumetric flask.  $(\text{NH}_4)_2\text{SO}_4$  solution ( $2.0 \text{ mol/L}$ ) was prepared by adjusting the pH to 5.4. All the reagents used are of analytical reagent grade. Triply distilled water is used for the preparation of all solutions.

### 2.3. Procedure

Pipette out the standard solution of aluminum into a  $50\text{-mL}$  volumetric flask, add  $10.00 \text{ mL}$  of  $2.0 \text{ mol/L}$   $(\text{NH}_4)_2\text{SO}_4$  solution,  $3.50 \text{ mL}$  of  $3.2 \times 10^{-3} \text{ mol/L}$  cupferron solution, diluting to  $50 \text{ mL}$ . Allow the solution to stand for about  $10 \text{ min}$  and then transfer to the electrolytic cell. Each measurement was carried out after an accumulation step while the solution was stirred for a given time; the accumulation potential of  $-0.95 \text{ V}$  (vs. SCE) was applied. After a rest period of  $10 \text{ s}$ , the response curve was recorded by scanning the potential to the negative direction and the peak current of  $-1.18 \text{ V}$  (vs. SCE) was recorded (Fig. 1). Each measurement was performed with a fresh drop and always of the same size.

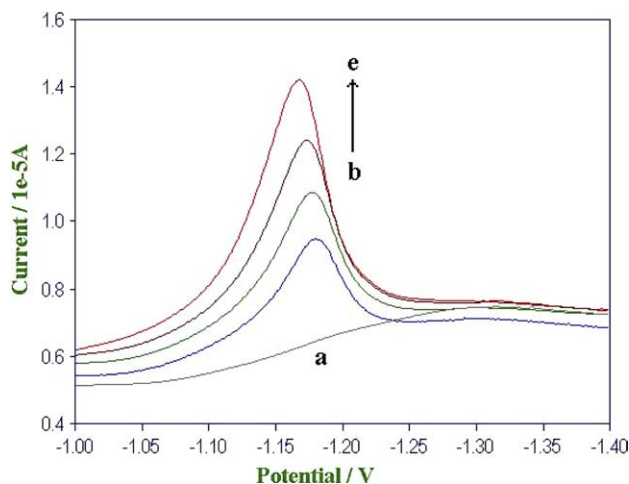


Fig. 1. Stripping voltammogram: (a)  $2.2 \times 10^{-4} \text{ mol/L}$  cupferron +  $0.4 \text{ mol/L}$   $(\text{NH}_4)_2\text{SO}_4$ ; (b) a +  $8 \times 10^{-9} \text{ g/mL}$  aluminum; (c) a +  $1.2 \times 10^{-8} \text{ g/mL}$  aluminum; (d) a +  $1.6 \times 10^{-8} \text{ g/mL}$  aluminum; (e) a +  $2.0 \times 10^{-8} \text{ g/mL}$  aluminum. Accumulation time is  $60 \text{ s}$ , preconcentration potential is  $-0.95 \text{ V}$ , scan rate is  $100 \text{ mV/s}$ .

## 2.4. Sample treatment

A 0.5–1 g sample was accurately weighted and transferred to the PTFE lined vessel. 4.0–6.0 mL nitric acid and 1.0 mL H<sub>2</sub>O<sub>2</sub> solution were added. The vessel was placed on the microwave turntable, the pressure was increased to 2 MPa for 5 min. After completion, the vessel was taken out to cool to room temperature. When a clear solution was obtained, the solution was transferred to a beaker and heated to near dryness. After cooling, the solution was neutralized using 1.0 mol/L NaOH to weak acidic (pH 5.0) and transferred to a volumetric flask and diluted to 25 mL with water.

## 3. Results and discussion

### 3.1. Effect of pH on the peak current

In experiments, we could get the stripping peak of aluminum–cupferron complex in the range of pH 3.8–6.0 and the pH 5.4 was found with maximum peak current. When pH was lower than 3.8, hydrogen wave was created. While pH was higher than 6, aluminum would create deposit. So the optimum pH was 5.4.

### 3.2. Effect of the concentration of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> solution on the peak current

The concentration of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> solution has a great effect on peak current. With the increase of the concentration of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> solution, the peak current increased. When the concentration of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> solution was 0.4 mol/L, the maximum peak current was obtained. While using the Na<sub>2</sub>SO<sub>4</sub> solution with the same concentration in the same experiments, no peak currents were created. So we used 0.4 mol/L (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> solution as the supporting electrolyte.

### 3.3. Effect of the concentration of cupferron solution on the peak current

The stripping peak was related with the concentration of cupferron solution. No peak current created in the (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> solution. While adding cupferron, we could get the stripping peak of aluminum because of aluminum and cupferron forming a complex. When the concentration of cupferron solution reached  $2.2 \times 10^{-4}$  mol/L, the peak current was maximum.

### 3.4. Effect of accumulation potential on the peak current

The effect of the accumulation potential on the stripping peak current was examined over the range –0.70 to –1.0 V. With the decrease of the accumulation potential, the peak current increased, and the peak current

reached the maximum at –0.95 V. Thus, an optimal accumulation potential of –0.95 V was selected.

### 3.5. Formation of stripping peak

The standard potential of aluminum is about –1.66 V, so the peak current in –1.18 V (vs. SCE) could not be the reduction peak current of aluminum. There was no peak in –1.18 V observed when cupferron existed without aluminum, which indicates that aluminum–cupferron complex produced the peak current in –1.18 V (vs. SCE). The aluminum–cupferron complex has strong adsorption at a mercury electrode and produces the reductive peak current. In order to prove the formation of aluminum–cupferron complex, we carried out the UV–Vis spectrometry experiments (Fig. 2). Cupferron produced the maximum adsorption peak in 300 nm and aluminum produced no peak in (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> solution. When we added aluminum with different concentrations, an adsorption peak was produced in 250 nm and the absorbance increased with the increasing of the concentration of aluminum, while the maximum adsorption wavelength remained without changes. All the above indicate that aluminum and cupferron really produced a new complex, and this complex was electro-active. So the aluminum–cupferron complex

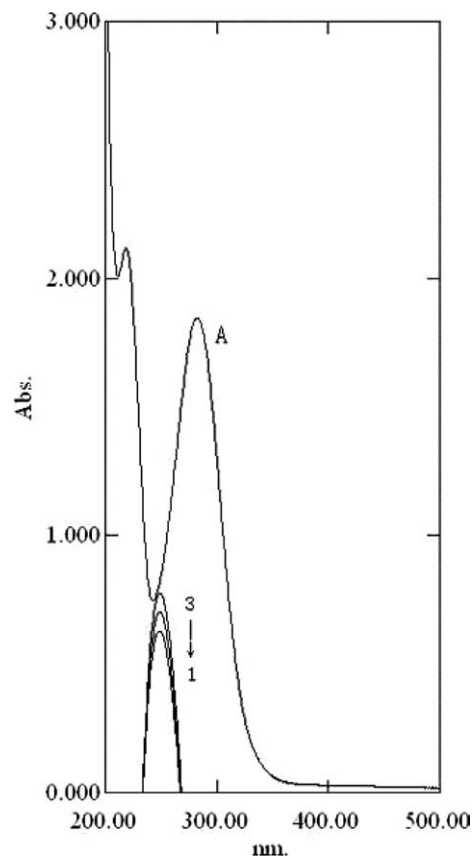


Fig. 2. UV–Vis adsorption spectra: (A)  $2.2 \times 10^{-4}$  mol/L cupferron + 0.4 mol/L (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, (1) A +  $6 \times 10^{-7}$  g/mL aluminum; (2) A +  $1.2 \times 10^{-6}$  g/mL aluminum; (3) A +  $1.8 \times 10^{-6}$  g/mL aluminum.

could produce a reduction peak current in  $-1.18$  V (vs. SCE). In order to prove its adsorption, we carried out accumulation time and cyclic voltammetry experiments. In experiments, with the increase of accumulation time, aluminum–cupferron complex adsorbed at the electrode increased and the peak current also increased. When the accumulation time reached 60 s, the complex adsorbed at the electrode reached saturation with maximum peak current, and the peak current did not increase with any longer accumulation time. If the electrode process is controlled by diffusion, the peak current will not change with different accumulation times. So the electrode process is controlled by adsorption. On the other hand, from cyclic voltammograms, we could observe that by scanning four cycles after accumulating 60 s, the peak current of first cycle was much higher than the next curves. Because there were no accumulation processes before the next scanning processes, the peak currents in the next curves descended. On the other hand, by scanning in the reverse direction, no oxidation peak was observed, which indicated the irreversibility of the electrode process. From all the above, we could draw the conclusion that the peak current was produced by the reduction of aluminum–cupferron complex adsorbed at the mercury electrode.

### 3.6. Analytical application

Under the optimum conditions, there was a linear relationship between the concentration of aluminum and the peak currents in the range of  $4 \times 10^{-9}$ – $2 \times 10^{-8}$  g/mL with the correlation coefficient of 0.9994. The detection limit was  $8 \times 10^{-10}$  g/mL, which was lesser than the reported method (Zhang, Wang, Zhang, & Wang, 1987).

To evaluate the selectivity of this method, the interference of other ions was studied. The tolerance ion concentration is 200-fold for  $F^-$ ,  $NO_2^-$ ,  $NO_3^-$ , Ca(II), Mg(II) and 100-fold for Ni(II), Cu(II), Sr(II), Mo(IV), Zn(II) and Co(II). Cd(II), Pb(II), Bi(III) and V(V) created the stripping peak in  $-0.60$ ,  $-0.58$ ,  $-0.33$  and  $-0.76$  V, respectively, but did not interfere with the stripping peak of aluminum in  $-1.18$  V (vs. SCE).

### 3.7. Determination of aluminum in tap water

We determined the presence of aluminum by boiling normal tap water in an aluminum pot. The results obtained are given in Table 1.

### 3.8. Determination of aluminum in bread, cookies, fry, tap water, flour, rice and tea leaves

We determined aluminum in the worked sample solutions by the experimental method. The results obtained are given in Table 2.

Table 1  
Determination of aluminum in tap water ( $n = 4$ )

Samples	Found (ppb)	Previous values in spectrophotometry (ppb)
Tap water	$14.78 \pm 1.12^a$	–
Tap water of boiling 10 min	$165 \pm 4.3$	$161 \pm 3.6$
Tap water of boiling 20 min	$201 \pm 2.8$	$198 \pm 3.4$
Tap water of boiling 30 min	$240 \pm 3.8$	$235 \pm 4.1$

<sup>a</sup>  $\pm$ Standard deviation.

Table 2  
Determination of aluminum in samples ( $n = 4$ )

Samples	Found ( $\mu$ g/g)	Previous values in spectrophotometry ( $\mu$ g/g)
Flour	$15.0 \pm 1.6^a$	$15.5 \pm 1.3$
Tea	$150.0 \pm 3.9$	$148.6 \pm 4.1$
Bread	$24.5 \pm 1.8$	$23.6 \pm 1.8$
Fry	$202.3 \pm 4.3$	$205.2 \pm 3.8$
Cookies	$59.8 \pm 2.2$	$61.2 \pm 2.4$
Rice	$21.3 \pm 1.3$	$20.1 \pm 1.7$

<sup>a</sup>  $\pm$ Standard deviation.

## 4. Conclusion

In the  $(NH_4)_2SO_4$  solution, cupferron and aluminum form an electro-active complex, which produces a sensitive peak current in  $-1.18$  V (vs. SCE), controlled by adsorption. UV–Vis spectrometry experiments prove the formation of aluminum–cupferron complex, and the electrochemical characteristics of stripping peak were studied by electrochemical methods. In addition, the results of determination of aluminum in hair, flour and tea by this method accord with the results reported in (Hu, Zhai, Wang, & Jiang, 2004). From Table 1, we can observe that the boiling water contained more aluminum than tap water, and the amount of aluminum in the water increased with the increase of boiling time. So the cookers made of aluminum should not be used again, in order to prevent more aluminum accumulating in the human body.

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