

Determination of Aluminum in Foods by Stabilized Temperature Platform Graphite Furnace Atomic Absorption Spectrometry

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A method for the determination of aluminum in foods by stabilized temperature platform graphite furnace atomic absorption spectrometry (STP-GFAAS) is described. Samples were digested in a mixture of HNO_3 - HClO_4 (5 + 1), and the digested residue was dissolved in 0.5% (w/v) $\text{Mg}(\text{NO}_3)_2$ -0.3% (v/v) HNO_3 . Aluminum in solution was measured at 237.5 nm with a Varian SpectraAA-40P spectrometer equipped with a DS-15 data station and a GTA-96 graphite furnace. The linear calibration curve ranged from 0.24 to 250 ng. The detection limit of aluminum was 0.24 ng. The accuracy of the method was evaluated by using NBS pine needles (SRM 1575) and spinach leaves (SRM 1570) as standard reference materials. The values obtained (562 $\mu\text{g/g}$) for pine needles and (854 $\mu\text{g/g}$) for spinach leaves are in good agreement with NBS SRM certified values. Sixteen different varieties of food samples were spiked, and the average recoveries of aluminum from the spiked samples ranged from 86% to 111%.

Aluminum is one of the most abundant metals on the surface of the earth. Thus, it is commonly found in the living organisms consumed as food by human beings. Over the past decade, it has been reported that abnormal accumulation of aluminum in certain tissues of the human body was associated with abnormal skeletal metabolism (Lione, 1983) and various diseases, such as Alzheimer's disease (Finberg et al., 1986; Petit et al., 1980), osteomalacia (Boyce et al., 1982) and Parkinsonism dementia (Perl et al., 1982). Interest in the possible biological function of aluminum has therefore continued to increase in recent years.

Previous reports indicate that aluminum intoxication may result from intravenous administration of aluminum through hemodialysis, heavy dosage of aluminum-containing drugs, and daily intake of foods that contain excessive aluminum originating from the use of aluminum as food additives, the leaching of aluminum during cooking, and natural foods having high levels of aluminum. The overdose of aluminum during medical treatment can be controlled by minimizing the dosage prescribed. To avoid excessive dietary intake of aluminum, data on the aluminum content of foods and the aluminum content of daily diets are wanted for making recommendations to the public. Unfortunately, there is no compilation of published data on the aluminum content in foods and diets in China to date. Hence, there is an urgent need to develop a sensitive and reliable method for the determination of aluminum for future survey and routine monitoring uses.

For decades, spectrophotometric (Froede and Rollin, 1982; Klaus and Quade, 1979; Sang et al., 1975) and flame atomic absorption spectrometric (Liu, 1981; Gorsky et al., 1978) methods have been widely used in China for the quantification of aluminum. However, these methods are subject to severe sample matrix interferences and poor sensitivity; therefore, they are not suitable for use in measuring aluminum in foods and diets. State-of-the-art techniques, e.g., ICP-MS and laser MS, are much more

sensitive, but they are too advanced to be practical for routine analytical use in China at this time.

This paper describes a stabilized temperature platform graphite furnace atomic absorption spectrometric (STP-GFAAS) procedure that combines excellent sensitivity with high specificity and speed of analysis and that is useful and applicable to the routine analysis of aluminum in foods and diets in our field laboratories.

MATERIALS AND METHODS

Precaution. Digestion uses perchloric acid, the properties of which the user should become familiar with before use. Use adequate safety equipment.

Apparatus. A Varian SpectraAA-40P atomic absorption spectrophotometer equipped with DS-15 data station, GTA-96 graphite furnace, aluminum hollow cathode lamp, and deuterium background correct lamp was used for the determination of aluminum. Pyrolytically coated furnace tubes fitted with pyrolytically coated graphite platforms were used for ashing the sample throughout the experiment. Conditions for sample analysis are listed in Table I.

Reagents. All reagents used were of analytical reagent grade unless otherwise specified. Nitric acid was further purified by distillation, and water used for the preparation of solutions was subboiling distilled water.

(a) *Nitric Acid-Perchloric Acid Mixture (5 + 1).*

(b) *10% (w/v) Magnesium Nitrate Solution.* Dissolve 10 g of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in water and dilute to 100 mL. Adjust pH to 7-9 and extract with 0.2 M 8-hydroxyquinoline in chloroform to remove any aluminum if presented.

(c) *Diluent.* Add 25 mL of 10% magnesium nitrate solution and 1.5 mL of nitric acid to 473.5 mL of water.

(d) *Aluminum Standard Solution.*

Stock Solution (1 mg/mL). The surface of aluminum foil (SP) is treated with hydrochloric acid for a few seconds and then washed with water and acetone or ethyl ether. The aluminum foil was dried at 105-110 °C for 5 min. One gram of the treated aluminum foil was dissolved in 100 mL (1 + 1) of hydrochloric acid (GR). The solution was transferred to a 1-L volumetric flask and diluted to volume with water.

Intermediate Solution (10 $\mu\text{g/mL}$). Ten milliliters of the stock solution was pipetted into a 1000-mL volumetric flask and diluted to volume with water.

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Table I. Instrumental Conditions for the Analysis of Al in Foods

wavelength, nm	237.5	injection vol, μL	10
slit width, nm	1.0	background correction on	
lamp current, mA	10	measurement mode	area integration
Furnace Parameter			
step	temp, $^{\circ}\text{C}$	ramp time, s	hold time, s
			internal Ar flow, L/min
drying	300	25	5
ashing	1000	15	5
atomization	2500	0.8	3
burn out	2600	2	1

Working Solution (1 $\mu\text{g}/\text{mL}$). This solution was prepared fresh by diluting the intermediate solution with water to a final concentration of 1 $\mu\text{g}/\text{mL}$.

Contamination Control. All glassware and polypropylene bottles were soaked in 20% HNO_3 containing 6 g of $\text{EDTA}-2\text{Na}/\text{L}$ and then rinsed several times with distilled water and stored under plastic cover until dry.

Procedure. Sample Preparation. Tea, rice, and soybean were ground in a stainless steel grinder. Fruit, vegetable, fish, egg, and meat samples were washed with water, air-dried at room temperature, and homogenized with a blender.

The following sample size was used: tea, rice, and soybean, 0.5 g; fish, egg, and meat, 1 g; fruits and vegetables, 8 g.

The sample was weighed and quantitatively transferred into a 100-mL conical flask. After 10–15 mL of the nitric-perchloric acids mixture was added, the mixture was allowed to stand for a few minutes or overnight. The sample was digested on a hot plate to colorless, and then the heat was increased to expel fumes of HClO_4 from the flask until dryness. The sample was cooled to room temperature, and the digested residues were dissolved in 25 mL of diluent. If the aluminum concentration in the solution exceeded the upper limit of the linear range, the solution was further diluted with the diluent; reagent blanks were carried through the entire procedure.

Determination. Standard or sample solutions were injected into the graphite furnace under conditions listed in Table I. The amount of aluminum present in the sample solution was determined by comparing the absorbance produced by each sample with those of known concentration standard solutions.

Liquid samples that do not require preliminary digestion are introduced directly into the graphite furnace.

RESULTS AND DISCUSSION

(1) Effect of Perchloric Acid on the Signal of Aluminum. Perchloric acid did not cause any interference at concentrations of 0.5% and lower, but a reduction of 30% in aluminum absorbance was noted when the perchloric concentration was 1% or higher. To avoid this interference, the digested sample residue should be evaporated to dryness (Caution).

(2) Selection of Analytical Wavelength. An analytical wavelength of 237.5 nm was chosen for the determination of aluminum in foods since the linear range at this wavelength was found to be much broader than that at 309.3 nm.

(3) Optimization of Experimental Parameters. A two factor–three level orthogonal experiment with the three most frequently used matrix modifiers [0.5% $\text{Mg}(\text{NO}_3)_2$ (Slavin et al., 1982), $\text{Cu} + \text{Ni} = 2 + 4 \text{ mg}/\text{L}$ (He, 1987), and 3% NH_4NO_3 (Smeysers and Verbeelen, 1988)] and three solution media (0.5% HCl , 0.5% HNO_3 , and 0.5% H_2SO_4) was performed. The optimal concentrations for the modifier and the solution medium were found to be at 0.5% magnesium nitrate and 0.5% nitric acid, respectively.

A four factor–three level orthogonal design was employed to optimize the assay conditions by using various

Table II. Accuracy Data in Determination of Standard Reference Materials

SRM	certified, $\mu\text{g}/\text{g}$	obtained, $\mu\text{g}/\text{g}$	RSD, %
pine needles 1575	545 \pm 30	562	2.1
spinach 1570	870 \pm 50	854	2.1

Table III. Recoveries of Aluminum in Representative Foods

sample	Al level, $\mu\text{g}/\text{g}$	added Al, μg	av recovery, %	RSD, %
rice	15.11	5.00	105	4.6
noodles	33.06	25.00	96	2.1
soya bean	24.10	4.00	95	4.6
corn powder	18.18	4.00	91	5.6
milk	0.24	1.50	100	8.1
milk powder	3.22	2.00	95	2.0
egg	1.57	4.00	91	3.2
meat	5.45	4.00	95	4.0
fish	1.52	2.00	94	6.0
kelp	180.5	100	86	3.2
tea	403.3	200	111	8.5
soy sauce	2.17	2.00	97	2.6
tomato	0.16	2.50	101	4.9
radish	0.11	2.00	101	8.4
Chinese cabbage	0.18	2.00	94	9.8
apple	0.26	2.00	98	4.5

concentrations of nitric acid and modifier as well as different ashing and atomization temperatures. The best conditions for the determination of aluminum appeared to be at 0.3% (v/v) for nitric acid, 0.5% (w/v) for magnesium nitrate, 1000 $^{\circ}\text{C}$ for ashing, and 2500 $^{\circ}\text{C}$ for atomization.

(4) Interference. Standard solutions A and B containing 2 ng of aluminum/mL and blank solutions C and D were prepared. Various ions were added into solutions B and D, respectively. Absorbances of A–D were determined and the relative absorbance (A_r) for each ion was calculated.

$$A_r = (B - D)/(A - C)$$

If the value of A_r was less than 0.9 or more than 1.1, the interference could not be tolerated. Maximum tolerances to various ions were 10 000-fold for K^+ , Na^+ , Cl^- , and ClO_4^- ; 1000-fold for Li^+ , Ag^+ , Zn^{2+} , Mg^{2+} , Mo^{2+} , Cr^{3+} , Cd^{2+} , Pb^{2+} , Cu^{2+} , Ni^{2+} , $\text{Te}(\text{IV})$, Fe^{2+} , Fe^{3+} , Ca^{2+} , Co^{2+} , Ga^{3+} , $\text{Se}(\text{IV})$, $\text{Se}(\text{VI})$, PO_4^{3-} , and SO_4^{2-} ; 500-fold for SiO_3^{2-} and VO_2^+ ; 200-fold for Sn^{2+} and $\text{Ti}(\text{IV})$; and 50-fold for Be^{2+} .

(5) Analytical Range. The calculated detection limit based on the recommendations given by IUPAC was 0.24 ng of Al. The calibration curve was linear within the range 0.24–250 ng of Al.

(6) Precision Study. The precision of the method was calculated on the basis of the results obtained from seven replicate analyses of rice 1 (6.51 μg of Al/g), rice 2 (15.8 μg of Al/g), and milk powder (3.37 μg of Al/g). The relative standard deviations for rice 1, rice 2, and milk powder were 4.5%, 4.2%, and 11%, respectively.

(7) Accuracy. The accuracy of the method was evaluated by using NBS SRM 1575 pine needles and NBS SRM 1570 spinach. The values obtained from triplicate analyses are in good agreement with the certified values (Table II). The accuracy of the method was also evaluated by using the recoveries of 16 different varieties of food samples spiked with aluminum (Table III). The average recoveries ranged from 84 to 111%.

(8) Analysis of Food Samples. Aluminum levels of 37 food samples obtained commercially were determined by using the method developed (Table IV).

Table IV. Aluminum Levels in Foods

food	Al level, μg/g	food	Al level, μg/g
rice	15.1	egg	1.57
noodles	33.1	meat (1)	5.45
flour	14.4	meat (2)	1.23
refined noodles	13.0	tomato	0.16
soya bean	24.1	radish	0.11
bean curd powder	9.4	Chinese cabbage	0.18
health corn powder	18.2	apple	0.26
pure soybean powder	51.2	dried apricot	47.0
milk, μg/mL	0.24	dried pear	7.44
milk powder	3.22	dried apricot ^a	104
fish	1.52	kelp	180
preserved vegetable	31.4	soy sauce, μg/mL	2.17
garlic powder ^a	58.3	white grape wine	0.61
baking powder ^a	2.84 × 10 ⁴	beer	1.08
deep-fried twisted dough sticks	227	Litchi drinks	0.36
green tea	403	Tianfu-cola	0.82
jasmine tea	319	Coca-Cola	0.13
red tea	485	orange juice	0.36
		gooseberry juice	0.34

^a Aluminum-containing food additives were used.

CONCLUSION

In general, aluminum content in natural foods such as fruits, vegetables, milk, and beverages is low. Among these, tea leaves contain the highest amount of aluminum. However, the aluminum content of processed foods that contain aluminum as part of a food additive is very high.

If an individual in China consumes 500 g of grains or grain products, 500 g of fruits and vegetables, and 200 g of animal products per day, the estimated daily aluminum intake is about 10 mg.

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