Analysis of Alum Content in Catering Foods Based on Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

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Abstract. The determination of alum in catering food was carried out by inductively coupled plasma mass spectrometry (ICP-MS) method, using nitric acid for Miss. Ü and microwave digestion, after the digestion, the samples were driven to acid for half an hour, and then the samples were fixed with ultrapure water and analyzed by ICP-MS. It was found that the calibration curve result of this experimental result was f (x)=119.1827*x+471.1455, where f(x)is the response value and x is the Al concentration, with linear R2=0.9994, linear range of 0~500ug/L, detection limit of 0.060mg/kg, and the recovery of more than 98%, which indicated that the method is simple, stable, reliable and able to accurately determine the aluminum in catering food. It was found that the probability of alum detection was as high as 80% with 2 batches exceeding the limit of detection, accounting for 4%, while alum was not detected in oil cakes, buns and steamed buns, and 10 batches of sesame balls were detected, accounting for 20%, but did not exceed the limit value of 100mg/kg in GB 2760-2024. In summary, the phenomenon of excessive use of alum in catering food should be emphasized.

Keywords: ICP-MS, Alum, Plasma mass spectrometry, GB 2760-2024.

1. Introduction

Food safety inspection is a comprehensive and meticulous process, which runs through the whole chain of food production, from farmland environment and agricultural production to the quality control of raw materials, production environment and equipment involved in food processing to the final product. [1] This process is very important to ensure food safety and consumers' health, because it can effectively prevent potential food safety risks. In recent years, with the frequent outbreak of food safety problems, especially the out-of-range and excessive use of food additives, people talk about food discoloration. Fried dough sticks, steamed buns, hemp balls and steamed bread in catering food are daily necessities in people's homes, but some lawless elements usually overuse some alum to make these foods more crisp, delicious and delicious. At present, the current effective GB 2760-2024 [2] stipulates that alum should not be higher than 100mg/Kg. In daily life, there are three main ways for consumers to ingest aluminum: First, aluminum naturally exists in food. Because aluminum ore comes from the earth's crust, there will be a small amount of aluminum in some edible economic crops and livestock, and the aluminum residue is generally less than 5 mg/kg, which is a very low level. However, some studies have shown that the soil properties have obvious influence on the aluminum residue of vermicelli products. Second, the aluminum from the aluminum cooker. In the traditional white electricity industry, there was an era when aluminum alloy was widely used. In the cooking process of aluminum products, a small amount of aluminum was bound to be mixed into the cooked food, but this amount was also very low and difficult to estimate. Aluminum-containing food additives added in the third food technology. This is the main source of aluminum intake by consumers at present. Because of its various good properties, aluminum compounds are widely used in pasta and baking fields, and the addition amount is not low. Therefore, aluminum is one of the key indicators of food safety control in China.

When aluminum enters the human body, it will be enriched in many organs in the human body, such as brain, liver, bones and kidneys. [3] First of all, aluminum will affect the human nervous system, attention and learning ability, which may seriously cause conformational degeneration of proteins in the brain, leading to Alzheimer's disease. Secondly, aluminum is the most abundant in bones, reaching 54%, which affects bone mineralization through coupling reaction with osteoclasts and osteoclasts, thus causing problems such as fractures, osteochondrosis and bone regeneration

disorders. Finally, long-term aluminum exposure will seriously damage human immune system and development system, and lead to hepatorenal toxicity, carcinogenesis and anemia.

Therefore, it is of great practical significance to analyze and investigate alum in catering food. At present, the detection methods of aluminum include spectrophotometer method, atomic absorption method and ICP-MS method, among which spectrophotometer method is a common one, but it is only suitable for products with high aluminum content, and the process steps are very complicated, time-consuming and requires high reagents. [4] Secondly, although atomic absorption spectrometry is more sensitive than spectrophotometer, it is easily influenced by complex matrix and unstable in the detection process. ICP-MS has the advantages of high sensitivity, high efficiency, high speed, high accuracy, wide linear range and stable results. Therefore, the determination of alum in catering food by ICP-MS in this experiment can provide data reference for subsequent investigation and research. [5]

2. Materials and Methods

2.1. Instruments and reagents

(1) Mettler Electronic Balance: mettler toledo Instruments (Shanghai) Co., Ltd.

(2) Microwave Digester: Anton Paar Co., Ltd.;

(3) Thermo Fisher Scientific Inductively Coupled Plasma Mass Spectrometer: Thermo Fisher Scientific Science and Technology Co., Ltd.;

(4) Nitric acid (excellent purity, Sinopharm Group);

(5) Argon: (99.9%, Beijing Hepu Beifen Gas Industry Co., Ltd.);

(6) Helium: (99.9%, Beijing Hepupeifen Gas Industry Co., Ltd.);

(7) Aluminum: (1000ug/ml, Tanmo Co., Ltd.);

(8) Internal standard element solution (10 mg/L, bismuth, rhenium, rhodium, etc., Tanmo Co., Ltd.).

2.2. Analytical Methods

2.2.1. Sample pretreatment

After the sample is dried to constant weight, weigh 0.5g (accurate to 0.001), add to PTFE into PTFE digestion tank, add 10ml of nitric acid, pre-dissolution on the heating plate at 120℃ for 1h, cooled with a lid to the microwave digestion instrument. After the digestion is completed, after the digestion tank is completely cooled down, slowly open the inner cover, and put the irrigation port toward the exhaust port, rinse the inner cover with a small amount of ultrapure water, then the digestion tank to the acid drive plate, 120℃ to drive the acid for 2h, then use ultrapure water to transfer to the centrifuge tube, and the volume is fixed. Blank for pure water in accordance with the above steps together.

Table 1. Microwave digestion procedure

Move	Temperature/°C	Temperature rise time/min	Constant temperature time/min
1	120	5	5
2	150	5	10
3	180	5	20

2.2.2. ICP-MS working conditions

The working principle of ICP-MS is that argon gas forms high-temperature plasma under the action of oscillating magnetic field [6]. After the sample enters the fog chamber at a constant rate and is atomized, it enters the plasma in the form of aerosol and is ionized. Then, the sample ions are focused through its unique interface cone and introduced into the vacuum system. After the ions are filtered by the deflection quadrupole, the ions with a specific mass-to-charge ratio are accurately

screened in the quadrupole mass filter, and finally the signals are amplified and output after reaching the detector. The main components of the instrument are shown in Figure 1.

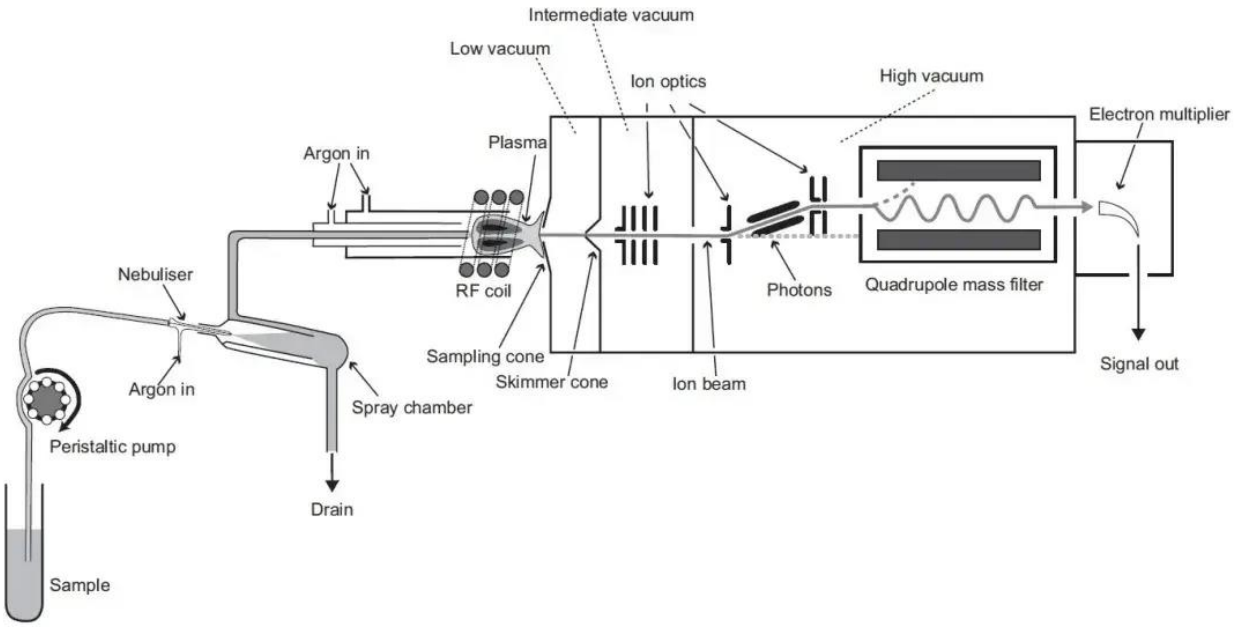

Figure 1. Main components of ICP-MS [7]

After the instrument is switched from standby state to analysis state, when the temperature of the atomization chamber is lowered to 2°C, insert the sample tube into the tuning liquid, insert the internal standard tube into pure water, and adjust the instrument parameters such as sampling depth, sampling cone position, carrier gas flow rate, make-up gas flow rate, emission power, etc. so that the counting rate of mass number 7 is greater than 2000, the counting rate of 89 is greater than 8000, the counting rate of oxide (156/205) is greater than 6000 in the collision-free mode. Adjust the lens voltage and collision gas flow rate to make the counting rate of mass number 56 less than 3000 and that of mass number 89 greater than 2000. The sample tube is inserted into pure water, and the internal standard tube is inserted into the internal standard solution. Observe the counting rate values and stability results of mass numbers 45, 115 and 209 on the tuning interface. If it is stable, the measurement can be started.

The mass-to-nucleus ratio of aluminum is 27, and the acquisition time is 0.1 second. After introducing the online internal standard and observing that the sensitivity of the internal standard meets the requirements, introduce the reagent blank, standard series and sample solution into the instrument respectively. Select Scandium (45Sc), the internal standard of aluminum element, input the concentration parameters of the standard curve, draw the standard curve by computer, and calculate the element concentration in the sample by instrument according to the linear regression equation obtained from the standard curve and the counting rate of the measured sample. Through experiments, the best instrument conditions for detecting aluminum in food are shown in Table 2.

Table 2. Reference conditions for ICP-Ms operation

Sports event	Parameters
RF power	15000W
Carrier gas flow	1.20L/min
Plasma gas	15L/min
Auxiliary gas	1.5L/min
Atomization chamber temperature	2.00℃
Cooling water temperature	20.00℃
Detector mode	Pulse mode
Integration time	0.1s
Repetition times	3 times
Plasma mode	High sensitivity
Peristaltic pump speed	0.15mL/min

2.2.3. Standard curve preparation

The Al standard solution was diluted with (5+95) nitric acid solution and the series concentrations were prepared as 0ng/ml, 100ng/ml, 500ng/ml, 1000ng/ml, 3000ng/ml, 5000ng/ml.

3. Results and Discussion

3.1. Sample pretreatment methods

Sample degradation usually includes dry degradation, wet degradation and microwave degradation, etc. However, wet degradation has the defects of high blank background value, incomplete degradation and hazardous exposure, resulting in a large error in the subsequent results. In the dry digestion process, there are problems such as localized explosion due to uneven heating of the sample, which leads to the lack of sample, resulting in small sample values. Therefore, the microwave digestion method, which can completely complete the digestion of samples with a small amount of nitric acid in a confined space, has become the first choice. In this microwave digestion process, the sample to be tested contains high oil and grease, so it is necessary to carry out pre-digestion, through 120℃ heating, so that the oil and grease substances are fully dissipated, and then again microwave digestion, you can avoid the explosion.

3.2. Selection of instrument conditions

The matrix of food contains a large number of interfering substances, which has a certain degree of interference with the determination of Al. In order to avoid this interference, through the CCT (collision mode), using ultra-pure helium as the collision gas, which is able to collide off most of the interfering substances.

3.3. Selection of internal standard elements

The internal standard is to cope with the changes of the element to be tested in different matrices. This time, sc was chosen as the internal standard, which is similar to Al in terms of ionization energy, chemical properties and molecular weight, and the deviation of Al in different matrices can be corrected by the element sc.

3.4. Linearity and detection limit

By determining different series of concentrations of Al, and the blank was determined continuously 11 this, the detection limit was calculated to obtain the linear equation of this time as f (x) = 119.1827*x + 471.1455, where f (x) is the response value, x is the concentration of Al, and the linearity R2 = 0.9994

The linear range was 0~500ug/L and the detection limit was 0.060mg/kg.

3.5. Method recovery and precision

Three different concentration levels of 100 ng/ml, 500 ng/ml and 3000 ng/ml were chosen to be added to the samples, and the recoveries and precision were calculated, as shown in Table 3.

Table 3. Precision and recovery (n=6)

Elemental	Spiked concentration (ng/ml)	Recovery rate	
		Average value/%	S_{RSD}/%
Al	100	107.6	1.56
	500	98.1	2.10
	3000	98.4	3.11

3.6. Sample data analysis

The samples of this experiment were purchased by the samplers from the circulation areas of breakfast stores, supermarkets as well as fast food stores, etc. The Al content and risk of these catering food products were preliminarily derived by testing the common ones such as drawsticks, oil cakes, sesame balls, buns and steamed buns. Usually, potassium aluminum sulfate is added to these noodle products during the production process, which will make the products more tasty, stable and crispy. However, long-term aluminum exposure can cause important damage to the human body. From the results of this test, Al element has not yet been detected in oil cakes, steamed buns and buns, while it was detected in doughnuts and sesame balls, with a detection rate of 40% and 10%, respectively, of which 4 batches of doughnuts had Al content exceeding the limit value of 100mg/kg in GB2760, which accounted for 2%, while the Al content detected in sesame balls did not exceed the limit.

Table 4. Results of sample data analysis

Food category	Number of samples	Monitoring value range (mg/Kg)	Mean value (mg/Kg)	Sample detected n (%)	Sample exceeded [n (%)]
Youtiao (deep-fried breadstick)	50	0~200	50	40 (80)	2 (4)
Oilcake (animal fodder)	50	0~80	ND	0	0
Sesame balls	50	0~80	15	10 (20)	0
Buns	50	0~80	ND	0	0
Steamed buns	50	0~80	ND	0	0

Note: ND indicates not detected.

4. Discussion and Conclusion

In the northern part of China, wheat-based food has almost become a necessary ingredient for people to eat every day. [8] However, with the development of industry, more and more businesses have begun to add contraband to pasta, the most common one is adding alum to pasta raw materials. As a food additive, alum can improve the taste in food processing. Aluminum is a chronic accumulative substance, and long-term excessive intake of aluminum will cause chronic toxicity to the body. After being ingested into human body, aluminum can combine with various substances such as protein, enzymes and adenosine triphosphate in cells, and gradually accumulate, and finally affect the activity of human cells, thus interfering with human functions and leading to metabolic abnormalities. Excessive accumulation of aluminum in human body will destroy the consciousness and memory function of brain. Alzheimer's disease is closely related to aluminum intake, and symptoms such as visual dyskinesia, osteomalacia, low immunity and embryonic dysplasia are also positively related to excessive aluminum intake. Aluminum is mainly metabolized by the kidney.

Excessive aluminum intake will involve the kidney, increase the burden on the kidney, and even cause irreversible damage to the kidney. Therefore, it is necessary to control aluminum intake.

Through this experimental study, it was found that aluminum would be added to fried dough sticks and hemp balls, and the probability of adding aluminum to fried dough sticks was as high as 40%, and two batches exceeded the threshold of 100mg/kg of dried samples in GB2760-2014. This high-content aluminum exposure risk brings serious harm to the health of small pilots, so it is an inevitable trend for the deep processing of catering and food industry to standardize and scientifically add and develop aluminum substitute products.

In addition, in this experiment, the pretreatment of samples was optimized, and based on the breakfast with high oil content such as hemp balls, the risk of oil explosion was eliminated by pre-digestion. Then further microwave digestion, so that the sample is completely digested. In addition, through CCT collision gas mode, using undisturbed high-purity helium as collision gas, the detection method of aluminum in catering food is effectively established. This method has the advantages of simple treatment, low possibility of sample pollution, high stability, good repeatability, high sensitivity and accuracy, and can quickly determine and investigate aluminum in food in circulation field, and then provide data reference for subsequent intervention measures.

References

[1] Barnes J, Whiley H, Ross K, et al. Defining food safety inspection [J]. International Journal of Environmental Research and Public Health, 2022, 19 (2): 789.

[2] https://www.gov.cn/zhengce/zhengceku/202403/content_7001729.htm.

[3] Yokel R A. Aluminum in food–the nature and contribution of food additives[M]. Rijeka, Croatia: Intech, 2012.

[4] Mittal M, Kumar K, Anghore D, et al. ICP-MS: analytical method for identification and detection of elemental impurities [J]. Current drug discovery technologies, 2017, 14 (2): 106 - 120.

[5] Limbeck A, Galler P, Bonta M, et al. Recent advances in quantitative LA-ICP-MS analysis: challenges and solutions in the life sciences and environmental chemistry [J]. Analytical and bioanalytical chemistry, 2015, 407: 6593 - 6617.

[6] Ammann A A. Inductively coupled plasma mass spectrometry (ICP MS): a versatile tool [J]. Journal of mass spectrometry, 2007, 42 (4): 419 - 427.

[7] Meermann B, Nischwitz V. ICP-MS for the analysis at the nanoscale–a tutorial review [J]. Journal of Analytical Atomic Spectrometry, 2018, 33 (9): 1432 - 1468.

[8] Gao Y, Wang X, Shi Y. The Types, Regional Distribution, and Consumption Trend of Chinese Traditional Wheat-Based Foods [J]. Journal of Food Quality, 2022, 2022 (1): 9986119.