Method of Test for Heavy Metals in Food Grade Salt

1. Scope

This method is applicable for the determination of copper, arsenic, cadmium, mercury and lead in food grade salt.

2. Method

After microwave assisted acid digestion, heavy metals are determined by inductively coupled plasma mass spectrometry (ICP-MS).

2.1. Equipment

2.1.1. Inductively coupled plasma mass spectrometer.

2.1.2. Microwave digester: > 1000 W with temperature control and pressure feedback system.

2.1.3. Blender.

2.1.4. Acid steam cleaning system.

2.2. Chemicals

Nitric acid, ultrapure grade (67-70%) and reagent grade;

Sodium chloride, reagent grade;

Deionized water, resistivity ≥ 18 MΩ • cm (at 25°C);

Copper, arsenic, cadmium, mercury, lead and gold, 1000 μg/mL, reference standards, ICP grade;

Scandium, germanium, rhodium, iridium and bismuth, 1000 μg/mL, internal standards, ICP grade.

2.3. Apparatus

2.3.1. Microwave digestion flask(Note): quartz or Teflon.

2.3.2. Volumetric flask(Note): 50 mL.

2.3.3. Storage tube: 50 mL, PP.

2.3.4. Membrane filter: 0.45 μm, PTFE.

Note: After cleaning, use an acid steam cleaning system to clean the apparatus with nitric acid (reagent grade) vapor for 2 hours, or soak the apparatus in nitric acid (reagent grade) : water (1:1, v/v) overnight. Take the apparatus out, wash away the residual nitric acid with deionized water and dry.

2.4. Reagents

2.4.1. 5% (w/w) nitric acid containing 1% (w/w) sodium chloride

Dissolve 10 g of sodium chloride with 800 mL of deionized water, add 50 mL of nitric acid (ultrapure grade) slowly, and dilute with deionized water to 1000 mL.

2.4.2. 1% (w/w) sodium chloride

Dissolve and dilute 10 g of sodium chloride with deionized water to 1000 mL.

2.5. Internal standard solution preparation

Accurately transfer 0.5 mL of scandium, germanium, rhodium, iridium and bismuth internal standards and 5 mL of gold reference standard(Note) to each 50-mL volumetric flask, make up to volume with 5% (w/w) nitric acid containing 1% (w/w) sodium chloride, and transfer to storage tubes as the internal standard stock solutions and the gold standard stock solution. When to use, mix appropriate amount of the internal standard stock solutions and the gold standard stock solution, then dilute with 5% (w/w) nitric acid containing 1% (w/w) sodium chloride to 1 μg/mL (containing 10 μg/mL gold reference standard) as the internal standard solution.

Note: The purpose of adding the gold reference standard is to form a complex of amalgams with mercury to stabilize the mercury element and reduce the memory effect or the carryover effect of mercury.

2.6. Standard solution preparation

Accurately transfer 0.5 mL of copper, arsenic, cadmium, mercury and lead reference standards to each 50-mL volumetric flask, make up to volume with 5% (w/w) nitric acid containing 1% (w/w) sodium chloride, and transfer to storage tubes as the standard stock solutions. When to use, mix appropriate amount of the standard stock solutions and the internal standard solution, dilute with 5% (w/w) nitric acid containing 1% (w/w) sodium chloride to 0-25 ng/mL (containing 10 ng/mL internal standard and 100 ng/mL gold reference standard), and transfer to storage tubes as the standard solutions.

2.7. Standard curve preparation

Inject the standard solutions into the ICP-MS at the appropriate rate, and operate according to the following conditions. Establish

the standard curves of copper, arsenic, cadmium, mercury and lead by the ratios of the signal intensity of copper, arsenic, cadmium, mercury and lead to that of the internal standard vs. the added concentrations.

ICP-MS operating conditions(Note):

Radiofrequency power: 1500 W.

Plasma argon flow rate: 15 L/min.

Auxiliary argon flow rate: 0.9 L/min.

Nebulizer argon flow rate: 1.0 L/min.

Dilution gas (argon) flow rate: 0.2 L/min.

Collision gas (helium) flow rate: 5 L/min.

Atomic mass (*m/z*):

Analyte		Internal standard	
Copper	65	Scandium	45
Arsenic	75	Germanium	74
Cadmium	114, 111, 112	Rhodium	103
Mercury	202, 200, 201	Iridium	193
Lead	208, 206, 207	Bismuth	209

Note: All the parameters can be adjusted depending on the instruments used if the above conditions are not applicable.

2.8. Sample solution preparation

Transfer about 0.5 g of the homogenized sample accurately weighed into a microwave digestion flask, add 0.5 mL of the internal standard solution and 6 mL of nitric acid (ultrapure grade), and then digest according to the following conditions. After cooling to room temperature, transfer to a 50-mL volumetric flask. Wash and rinse the residue in the digestion flask with 5 mL of deionized water several times. Add the washings to the same volumetric flask, and make up to volume with deionized water. Transfer to a storage tube, filter with a membrane filter, and take the filtrate as the sample solution. Take an empty microwave digestion flask, add 0.5 mL of the internal standard solution and 6 mL of nitric acid (ultrapure grade), and perform the same procedure except deionized water being replaced with 1% (w/w) sodium chloride

solution described above as the blank solution,.

Microwave digester operating conditions(Note):

Condition / Step	Power (W)	Heating time (min)	Duration time (min)	Temperature (°C)
1	1200	15	10	210

Note: All the parameters can be adjusted depending on the instruments used if the above conditions are not applicable.

2.9. Quantification

Inject the sample solution, the blank solution and the standard solutions into the ICP-MS separately at the appropriate rate, and operate according to the conditions in section 2.7. Calculate the amount of copper, arsenic, cadmium, mercury or lead in the sample based on the ratio of the signal intensity of copper, arsenic, cadmium, mercury or lead to that of the internal standard by the following formula:

The amount of copper, arsenic, cadmium, mercury or lead in the sample (mg/kg) = $\frac{(C - C_0) \times V}{M \times 1000}$

Where,

C: the concentration of copper, arsenic, cadmium, mercury or lead in the sample solution calculated by the standard curve (ng/mL)

C_0: the concentration of copper, arsenic, cadmium, mercury or lead in the blank solution calculated by the standard curve (ng/mL)

V: the final make-up volume of the sample (mL)

M: the weight of the sample (g)

Remark: 1. The limits of quantification (LOQs) are 0.05 mg/kg for copper and arsenic, and 0.02 mg/kg for cadmium, mercury and lead.

2. Further validation should be performed when interference compounds appear in samples.

3. When the test is conducted by other instruments, verification by the certified reference material (CRM) or the standard reference material (SRM), or validation of

the method should be performed.

Reference

1. Wu, J. and Boyle, E. A. 1997. Low black pre-concentration technique for the determination of lead, copper, and cadmium in small-volume seawater samples by isotope dilution ICPMS. Anal. Chem. 69: 2464-2470.
2. U.S. Food and Drug Administration. 2020. Elemental analysis manual for food and related products. 4.7. Inductively coupled plasma - mass spectrometric determination of arsenic, cadmium, chromium, lead, mercury, and other elements in food using microwave assisted digestion.
[https://www.fda.gov/media/87509/download]