# HJ

NATIONAL ENVIRONMENTAL PROTECTION STANDARD

OF THE PEOPLE'S REPUBLIC OF CHINA

**HJ 803-2016**

# Soil and sediment - Determination of aqua regia extracts of 12 metal elements - Inductively coupled plasma mass spectrometry

土壤和沉积物 12 种金属元素的测定

王水提取-电感耦合等离子体质谱法

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**WARNING: Nitric and hydrochloric acids are highly corrosive and oxidizing. Wear protective equipment as required during operation. Avoid contact with skin and clothing. Sample pretreatment shall be performed in a fume hood.**

## 1 Scope

This Standard specifies the inductively coupled plasma mass spectrometry method for the determination of 12 metal elements in aqua regia extracts of soil and sediment.

This Standard applies to the determination of 12 metal elements -- cadmium (Cd), cobalt (Co), copper (Cu), chromium (Cr), manganese (Mn), nickel (Ni), lead (Pb), zinc (Zn), vanadium (V), arsenic (As), molybdenum (Mo), and antimony (Sb) -- in soil and sediment. If verified, this Standard can also be applied to the determination of other metal elements.

When the sampling volume is 0.10g and the constant volume after digestion is 50ml, the detection limits and lower determination limits of the 12 metal elements are shown in Table 1.

**Translator NOTE:** In the table, A: cadmium B: cobalt C: copper D: chromium E: manganese F: nickel G: lead H: zinc I: vanadium J: arsenic K: molybdenum L: antimony.

## 2 Normative references

This Standard refers to the following documents or their clauses. For undated references, the latest edition of the referenced document applies.

HJ/T 166, *Technical specification for soil environmental monitoring*

HJ 613, *Soil - Determination of dry matter and water content - Gravimetric method*

GB 17378.3, *The specification for marine monitoring - Part 3: Sample collection, storage and transportation*

GB 17378.5, *The specification for marine monitoring - Part 5: Sediment analysis*

## 3 Method principle

Soil and sediment samples are digested by a mixed solution of hydrochloric acid/nitric acid (aqua regia) on an electric heating plate or microwave digestion apparatus. Use an inductively coupled plasma mass spectrometer to test. Qualification is based on the mass spectrum or characteristic ions of the element. Use internal standard method for quantification.

The specimen is brought into the atomization system by the carrier gas for atomization. The target element goes into the axial channel of the plasma in the form of aerosol. It is fully evaporated, dissociated, atomized and ionized at high temperature and inert gas. It is then converted into charged positive ion. It enters the mass spectrometer through the ion acquisition system. The mass spectrometer separates and analyzes qualitatively and quantitatively according to the mass-to-charge ratio of the ion. Within a certain concentration range, the response value corresponding to the mass-to-charge ratio of an ion is proportional to its concentration.

## 4 Interference and elimination

### 4.1 Mass spectrum interference

Mass spectrum interference mainly includes polyatomic ion interference, isobaric interference, oxide and doubly charged ion interference.

Polyatomic ion interference is the most important source of interference in ICP-MS. It can use interference correction equations, instrument optimization, and collision-reaction cell techniques to resolve. See Table A.1 in Annex A for common polyatomic ion interferences. Isobaric interferences can be corrected using the interference correction equation. Or before the analysis, eliminate the sample by chemical separation and other methods. See Table A.2 in Annex A for the main interference correction equations. Oxide interference and double charge interference can be reduced by adjusting the instrument parameters.

### 4.2 Non-mass spectrum interference

It can use high-purity metals (purity is greater than 99.99%) or metal salts (baseline or high-purity reagents) to prepare. Commercially available certified reference materials can also be purchased for preparation. The medium is nitric acid solution (5.4).

**5.7.5** Internal standard reference use solution: ρ = 100μg/L.

Use nitric acid solution (5.4) to dilute the internal standard reference stock solution (5.7.4) and prepare the internal standard reference use solution. Due to the different diameters of peristaltic pump tubes used in different instruments, when adding internal standard online, the concentration added is also different. Therefore, when preparing the internal standard reference use solution, the concentration of the internal standard element in the specimen shall be 10~50μg/L.

**5.7.6** Tuning solution: ρ = 10μg/L.

It is advisable to choose a solution containing Li, Be, Mg, Y, Co, In, Tl, Pb and Bi elements as the tuning solution of the mass spectrometer. It can use high-purity metals (purity is greater than 99.99%) or corresponding metal salts (baseline or high-purity reagents) to prepare. Commercially available certified reference materials can also be purchased

**NOTE 1:** Reference solutions of all elements shall be stored in sealed polyethylene or polypropylene bottles after preparation.

**5.8** Slow quantitative filter paper.

**5.9** Carrier gas: Argon, purity ≥99.999%.

# 6 Instruments and equipment

**6.1** Inductively coupled plasma mass spectrometer: The mass range that can be scanned is 5~250u. The peak width at a resolution of 10% peak height shall be between 0.6~0.8u.

**6.2** Temperature control electric heating plate: The control accuracy is ±0.2°C. The maximum temperature can be set up to 250°C.

**6.3** Microwave digester: The output power is 1000~1600W. It has programmable control function. It can carry out full monitoring of temperature, pressure and time (heating time and holding time). It has safety protection function.

**6.4** Analytical balance: The accuracy is 0.0001g.

**6.5** Teflon closed digestion vessel: It can resist pressure, acid and corrosion. It has the function of pressure relief.

**6.6** Erlenmeyer flask: 100ml.

**6.7** Glass funnel.

**6.8** Volumetric flask: 50ml.

**6.9** Nylon sieve: 0.15mm (100 mesh).

**6.10** General laboratory instruments and equipment.

# 7 Sample

### 7.1 Sample collection and storage

Collect and preserve soil samples in accordance with the relevant regulations of HJ/T 166. Collect and preserve sediment samples in accordance with the relevant provisions of GB 17378.3. Contamination and loss of analyte elements shall be avoided during sample collection, transportation and storage.

### 7.2 Determination of moisture

Determination of dry matter of soil samples is carried out in accordance with HJ 613. The moisture content of sediment samples shall be carried out in accordance with GB 17378.5.

### 7.3 Sample preparation

Remove sticks, leaves, stones and other foreign objects in the sample. According to the requirements of HJ/T 166 and GB 17378.5, the collected samples are air-dried, coarsely ground, and finely ground to pass through a sieve (6.9) with an aperture of 0.15mm (100 mesh). The sample preparation process shall avoid contamination and loss of analyte elements.

### 7.4 Specimen preparation

### 7.4.1 Hot plate heating and digestion

Pipette 15ml of aqua regia (5.3) into a 100ml Erlenmeyer flask. Add 3 or 4 small glass beads. Put on the glass funnel (6.7). Heat to a slight boil on a hot plate. Let the aqua regia vapor infiltrate the inner wall of the Erlenmeyer flask for about 30min. Discard after cooling. Use experimental water to wash the inner wall of the Erlenmeyer flask. Let dry and set aside.

Weigh 0.1g of the sample to be tested (accurate to 0.0001g). Place in the 100ml Erlenmeyer flask prepared above. Add 6ml of aqua regia solution (5.3). Put on the glass funnel (6.7). Heat on the hot plate. Keep the aqua regia in a slightly boiling state for 2h (keep the aqua regia vapor refluxing on the flask wall and glass funnel, but the reaction shall not be so violent that the sample overflows). Place and cool to room temperature after digestion. Use slow quantitative filter paper (5.8) to filter the extract. Collect it in

## 10 Precision and accuracy

### 10.1 Precision

6 laboratories use the electric hot plate digestion method and microwave digestion method to measure 5 kinds of unified standard soil samples and sediment samples with different content levels. For the precision and total data of the hot plate digestion method, see Table B.1 in Annex B. See Table B.2 in Annex B for summary data on the viscosity of the microwave digestion method.

### 10.2 Accuracy

6 laboratories use electric heating plate digestion method and microwave digestion method to measure 2 kinds of unified standard soil samples and sediment samples with different content levels. See Table B.3 in Annex B for summary data on the accuracy of the hot plate digestion method. See Table B.4 in Annex B for summary data on the accuracy of the microwave digestion method.

## 11 Quality assurance and quality control

**11.1** Make at least 2 laboratory blank samples for each batch of samples. The determination results shall be lower than the lower limit of determination.

**11.2** A standard curve shall be established for each analysis. Its correlation coefficient shall be greater than 0.999. For every 20 samples or every batch (at least 20 samples/batch) of samples, a middle concentration point of the standard curve shall be analyzed. The relative deviation between the determination result and the actual concentration shall not exceed 10%. Otherwise, find out the reason or reestablish the standard curve. After every 20 samples or each batch (less than 20 samples/batch) samples are analyzed, a zero-point analysis of the standard curve shall be performed. The relative deviation between the measurement result and the actual concentration value shall not exceed 30%.

**11.3** At least 10% of each batch of double samples shall be tested in parallel. When the number of samples is less than 10, at least one parallel double sample shall be determined. In the parallel double-sample determination results, the relative deviation of cobalt (Co), copper (Cu), chromium (Cr), manganese (Mn), nickel (Ni), lead (Pb), zinc (Zn), vanadium (V), arsenic (As) determined by hot plate digestion shall be less than 30%. The relative deviation of cadmium (Cd), molybdenum (Mo) and antimony (Sb) shall be less than 40%. The relative deviation of the 12 metal elements determined by microwave digestion shall be less than 30%.

**11.4** For each batch of samples, analyze at least 10% of spiked recovery samples. When the number of samples is less than 10, at least one spiked recovery sample shall be made. In the determination results of the spiked recovered samples, the spiked recovery rate of cadmium (Cd), cobalt (Co), copper (Cu), chromium (Cr), manganese (Mn), nickel (Ni), lead (Pb), zinc (Zn), vanadium (CV) and arsenic (As) determined by the electric hot plate digestion shall be controlled between 70%~125%. The spiked recovery rate of molybdenum (Mo) and antimony (Sb) shall be controlled between 50%~125%. The spiked recovery rate of 12 metal elements determined by microwave digestion shall be controlled between 70%~125%.

**11.5** ICP-MS requires high purity of reagents. Reagents with high purity shall be used. Each batch of reagents must pass the blank test. The reagent blank value shall not exceed the detection limit of the method. The same batch of samples shall use the same batch of experimental water. Experimental water shall be used for blank experiments. The blank value shall not exceed the detection limit of the method.

**11.6** The intensity of the response to the internal standard shall be determined for each analysis. The response value of the internal standard in the specimen shall be between 70%~130% of the response value of the standard curve. Otherwise, it means that the instrument drifts or there is interference. The cause shall be found and reanalyzed. If matrix interference is found, the specimen must be diluted for determination. If it is found that the specimen contains internal standard elements, the internal standard must be replaced, or the concentration of internal standard elements must be increased.

## 12 Waste disposal

Waste liquid and waste generated during the experiment shall be stored in airtight containers. Entrust qualified agencies to handle.

## 13 Precautions

**13.1** The glassware used in the experiment must be soaked in nitric acid solution (5.6) for 24h. Wash with tap water and experimental water in turn before use.

**13.2** To ensure the stability of the instrument and the accuracy of the experiment, refer to the instrument manual. Clean the atomizer, torch, sampling cone and extraction cone of the instrument periodically or after measuring a certain number of samples.

**13.3** When using microwaves to digest samples, be aware of the temperature and pressure limitations of the digestion vessel used. Check the tightness of the digestion vessel before and after digestion. The check method is: When the digestion vessel is filled with sample and digestion solution, cover the digestion vessel tightly and weigh it (accurate to 0.01g). After the sample is digested, wait for the digestion vessel to cool down to room temperature, then weigh again. Record the weight of each vessel. If the post-digestion weight decreases by more than 10% from the pre-digestion weight, discard the sample and investigate the cause.

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