HJ

NATIONAL ENVIRONMENTAL PROTECTION STANDARD

OF THE PEOPLE’S REPUBLIC OF CHINA

HJ 491-2019

Replacing HJ 491-2009

Soil and sediment - Determination of copper, zinc, lead, nickel and chromium - Flame atomic absorption spectrophotometry

土壤和沉积物 铜、锌、铅、镍、铬的测定

火焰原子吸收分光光度法

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Soil and sediment - Determination of copper, zinc, lead, nickel and chromium - Flame atomic absorption spectrophotometry

Warning: Since the perchloric acid and nitric acid used in the experiment are highly oxidizing and corrosive, and the hydrochloric acid and hydrofluoric acid are highly volatile and highly corrosive, reagent preparation and sample digestion shall be carried out in a fume hood; during the operation, protective equipment shall be wore as required to avoid inhalation into respiratory tract or contact with skin and clothing.

1 Scope of application

This Standard specifies the flame atomic absorption spectrophotometry for the determination of copper, zinc, lead, nickel and chromium in soil and sediment.

This Standard applies to the determination of copper, zinc, lead, nickel and chromium in soil and sediment.

When the sample volume is 0.2 g and the constant volume after digestion is 25 ml, the method detection limits for copper, zinc, lead, nickel and chromium are 1 mg/kg, 1 mg/kg, 10 mg/kg, 3 mg/kg and 4 mg/kg, respectively, and the lower limits of determination are 4 mg/kg, 4 mg/kg, 40 mg/kg, 12 mg/kg and 16 mg/kg, respectively.

2 Normative references

This standard refers to the following documents or clauses therein. For undated references, the valid edition applies to this Standard.

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

HJ 494, Water quality - Guidance on sampling techniques

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

HJ 832, Soil and sediment - Digestion of total metal elements - Microwave assisted acid digestion method

HJ/T 166, Technical specification for soil environmental monitoring

3 Principle of the method

After the soil and sediment are digested by acid, the copper, zinc, lead, nickel and chromium in the sample are atomized in the air-acetylene flame, and the ground state atoms have selective absorption of the characteristic spectral lines of copper, zinc, lead, nickel and chromium respectively; the absorption intensity is proportional to the concentration of copper, zinc, lead, nickel and chromium within a certain range.

4 Interference and elimination

4.1 Iron below 1 000 mg/L does not interfere with the determination of zinc.

4.2 Potassium, sodium, magnesium, iron and aluminum below 2 000 mg/L, as well as calcium below 1 000 mg/L, do not interfere with the determination of lead.

4.3 When using 232.0 nm as the absorption line to measure nickel, it is influenced by the nickel three-line spectrum of similar wavelength, and the selection of 0.2 nm spectral passband can reduce the influence.

4.4 Under the conditions of this Standard, when using a reducing flame, the common elements coexisting in soil and sediment do not interfere with the determination of chromium.

5 Reagents and materials

Unless otherwise stated, use guaranteed reagents that meet national standards in the analysis, and use freshly prepared deionized water as the experimental water.

5.1 Hydrochloric acid: $\rho(HCl) = 1.19$ g/ml.

5.2 Nitric acid: $\rho(HNO_3) = 1.42$ g/ml.

5.3 Hydrofluoric acid: $\rho(HF) = 1.49$ g/ml.

5.4 Perchloric acid: $\rho(HClO_4) = 1.68$ g/ml.

5.5 Metal copper: spectral pure.

5.6 Metal zinc: spectral pure.

5.7 Metal lead: spectral pure.

5.8 Metal nickel: spectral pure.

5.9 Metal chromium: spectral pure.

Accurately pipette 10.00 ml of zinc standard stock solution (5.14) into a 100 ml volumetric flask; use nitric acid solution (5.12) to dilute to the mark; shake well. Store in a polyethylene bottle; refrigerate below 4 °C, valid for one year.

5.20 Lead standard working solution: ρ(Pb) = 100 mg/L.

Accurately pipette 10.00 ml of lead standard stock solution (5.15) into a 100 ml volumetric flask; use nitric acid solution (5.12) to dilute to the mark; shake well. Store in a polyethylene bottle; refrigerate below 4 °C, valid for one year.

5.21 Nickel standard working solution: ρ(Ni) = 100 mg/L.

Accurately pipette 10.00 ml of nickel standard stock solution (5.16) into a 100 ml volumetric flask; use nitric acid solution (5.12) to dilute to the mark; shake well. Store in a polyethylene bottle; refrigerate below 4 °C, valid for one year.

5.22 Chromium standard working solution: ρ(Cr) = 100 mg/L.

Accurately pipette 10.00 ml of chromium standard stock solution (5.17) into a 100 ml volumetric flask; use nitric acid solution (5.12) to dilute to the mark; shake well. Store in a polyethylene bottle; refrigerate below 4 °C, valid for one year.

5.23 Gas: acetylene, purity ≥99.5%.

5.24 Supporting gas: air, where water, oil and other impurities shall be removed before entering the burner.

6 Instruments and apparatuses

6.1 Flame atomic absorption spectrophotometer.

6.2 Light source: sharp line source or continuous light source of copper, zinc, lead, nickel and chromium elements.

6.3 Electrothermal digestion device: temperature-controlled electric heating plate or graphite electrothermal digestion instrument, with a temperature control accuracy of ±5 °C.

6.4 Microwave digestion device: power 600 W ~ 1 500 W, equipped with microwave digestion tank.

6.5 Polytetrafluoroethylene crucible or polytetrafluoroethylene digestion tube: 50 ml.

6.6 Analytical balance: sensitivity 0.1 mg.

6.7 Utensils and equipment commonly used in general laboratories.

7 Sample

7.1 Sample collection and storage

Soil samples shall be collected and stored in accordance with the relevant requirements of HJ/T 166; sediment samples shall be collected and stored in accordance with the relevant requirements of GB 17378.3 or HJ 494.

7.2 Sample preparation

Remove foreign matter (such as sticks, leaves, stones) in the sample; in accordance with the requirements of HJ/T 166 and GB 17378.3, air-dry, crush, and sieve the collected samples in the laboratory, and save them for future use.

7.3 Determination of moisture

Measure the dry matter content of soil samples according to HJ 613; determine the moisture content of sediment samples according to GB 17378.5.

7.4 Preparation of test pieces

7.4.1 Electrothermal digestion method

7.4.1.1 Hot plate digestion method

Weigh 0.2 g ~ 0.3 g (accurate to 0.1 mg) of the sample (7.2) into a 50 ml polytetrafluoroethylene crucible (6.5); use water to wet it; then, add 10 ml of hydrochloric acid (5.1); put it on the electric heating plate in the fume hood at 90 °C ~ 100°C to decompose the sample initially; when the digestion solution evaporates to about 3 ml remaining, add 9 ml of nitric acid (5.2); cover and heat until there are no obvious particles; add 5 ml ~ 8 ml of hydrofluoric acid (5.3); uncover the lid; heat to remove silicon at 200 °C for 30 minutes; cool slightly; add 1 ml of perchloric acid (5.4); heat at 150 °C ~ 170 °C until white smoke comes out; shake the crucible frequently during heating. If there are black carbides on the crucible wall, add 1 ml of perchloric acid (5.4); cover and continue to heat until the black carbides disappear; then, uncover; heat to remove the acid until the contents are in the shape of liquid beads that do not flow (observe while it is hot). Add 3 ml of nitric acid solution (5.12); warm to dissolve the soluble residue; transfer the entire amount to a 25 ml volumetric flask; use nitric acid solution (5.12) to dilute to the mark; shake well; store in a polyethylene bottle; let stand; take the supernatant liquid for later testing. Complete the analysis within 30 days.

7.4.1.2 Graphite electrothermal digestion method

Weigh 0.2 g ~ 0.3 g (accurate to 0.1 mg) of the sample (7.2) into a 50 ml polytetrafluoroethylene digestion tube (6.5); use water to wet it; then, add 5 ml hydrochloric acid (5.1); put it on the graphite electrothermal digestion instrument in the fume hood to heat at 100 °C for 45 min. Add 9 ml of nitric acid (5.2) and heat for 30

w_{H2O} – moisture content of the sediment sample, %.

9.3 Result expression

When the measurement result is less than 100 mg/kg, keep the result to an integer; when the measurement result is greater than or equal to 100 mg/kg, keep the result to three significant figures.

10 Precision and accuracy

10.1 Precision

Six laboratories shall respectively perform six repeated determinations on the uniform samples of yellow soil with copper content of 22 mg/kg, brown soil of 106 mg/kg, river sediment of 16 mg/kg and lake sediment of 63 mg/kg, where the intra-laboratory relative standard deviation ranges are 1.4% ~ 4.0%, 1.6% ~ 3.9%, 1.1% ~ 6.7% and 1.0% ~ 3.0%, respectively; the inter-laboratory relative standard deviation ranges are 3.7%, 2.3%, 4.0% and 3.0%, respectively; the repeatability limits r are 2 mg/kg, 8 mg/kg, 2 mg/kg and 4 mg/kg, respectively; the reproducibility limits R are 3 mg/kg, 10 mg/kg, 3 mg/kg and 7 mg/kg, respectively.

Six laboratories shall respectively perform six repeated determinations on the uniform samples of yellow soil with zinc content of 49 mg/kg, brown soil of 165 mg/kg, river sediment of 61 mg/kg and lake sediment of 190 mg/kg, where the intra-laboratory relative standard deviation ranges are 1.0% ~ 3.5%, 1.1% ~ 3.6%, 1.1% ~ 3.8% and 1.3% ~ 4.5%, respectively; the inter-laboratory relative standard deviation ranges are 3.2%, 4.7%, 4.0% and 4.3%, respectively; the repeatability limits r are 4 mg/kg, 11 mg/kg, 5 mg/kg and 15 mg/kg, respectively; the reproducibility limits R are 6 mg/kg, 24 mg/kg, 8 mg/kg and 27 mg/kg, respectively.

Six laboratories shall perform six repeated measurements on the certified standard samples GSS-5 and GSD-5a, as well as the uniform samples of brown soil with a lead content of 116 mg/kg, and river sediment with a lead content of 152 mg/kg, where the intra-laboratory relative standard deviation ranges are 1.8% ~ 4.7%, 0.7% ~ 3.1%, 2.9% ~ 6.5% and 2.1% ~ 6.4%, respectively; the inter-laboratory relative standard deviations are 1.3%, 2.0%, 5.4% and 3.1% respectively; the repeatability limits r are 48 mg/kg, 6 mg/kg, 16 mg/kg and 16 mg/kg, respectively; the reproducibility limits R are 49 mg/kg, 8 mg/kg, 23 mg/kg and 20 mg/kg, respectively.

Six laboratories shall respectively perform six repeated determinations on the uniform samples of yellow soil with nickel content of 24 mg/kg, brown soil of 35 mg/kg, river sediment of 20 mg/kg and lake sediment of 36 mg/kg, where the intra-laboratory relative standard deviation ranges are 1.8% ~ 7.0%, 1.9% ~ 4.0%, 2.2% ~ 8.1% and 2.1% ~ 6.7%, respectively; the inter-laboratory relative standard deviation ranges are 3.4%, 2.9%, 4.2% and 3.7%, respectively; the repeatability limits r are 3 mg/kg, 3 mg/kg and 42 mg/kg: the additional-standard recovery ranges are 88.9% ~ 105% and 92.7% ~ 98.5% respectively; the additional-standard recovery final values are 96.9%±12.4% and 95.5%±4.2%, respectively. Six laboratories shall respectively conduct six repeated measurements on the river sediment sample with copper content of 16 mg/kg – with additional-standard amount of 17 mg/kg and 42 mg/kg: the additional-standard recovery ranges are 87.4% ~ 100% and 91.1% ~ 102%, respectively; the additional-standard recovery final values are 94.3%±9.0% and 96.0%±9.0%, respectively.

Six laboratories shall respectively conduct six repeated measurements on the yellow soil sample with zinc content of 49 mg/kg – with additional-standard amount of 17 mg/kg and 42 mg/kg: the additional-standard recovery ranges are 90.5% ~ 108% and 86.7% ~ 104%, respectively; the additional-standard recovery final values are 98.1%±13.8% and 95.4%±12.6%, respectively. Six laboratories shall respectively conduct six repeated measurements on the river sediment samples with zinc content of 61 mg/kg – with additional-standard amount of 17 mg/kg and 42 mg/kg: the additional-standard recovery ranges are 88.7% ~ 102% and 90.0% ~ 109% respectively; the additional-standard recovery final values are 96.2%±9.8% and 98.4%±14.2%, respectively.

Six laboratories shall respectively conduct six repeated measurements on the brown soil samples with lead content of 116 mg/kg – with additional-standard amount of 125 mg/kg and 250 mg/kg: the additional-standard recovery ranges are 90.3% ~ 104% and 94.1% ~ 99.8% respectively; the additional-standard recovery final values are 97.5%±10.2% and 97.5%±5.2%, respectively. Six laboratories shall respectively conduct six repeated measurements on the river sediment sample with lead content of 152 mg/kg – with additional-standard amount of 83 mg/kg and 167 mg/kg: the additional-standard recovery ranges are 87.2% ~ 106% and 84.7% ~ 101%, respectively; the additional-standard recovery final values are 92.8%±8.2% and 92.5%±12.6%, respectively.

Six laboratories shall respectively conduct six repeated measurements on the yellow soil sample with nickel content of 24 mg/kg – with additional-standard amount of 17 mg/kg and 42 mg/kg: the additional-standard recovery ranges are 87.6% ~ 100% and 93.6% ~ 100%, respectively; the additional-standard recovery final values are 95.9%±10.4% and 97.6%±5.0%, respectively. Six laboratories shall respectively conduct six repeated measurements on the river sediment samples with nickel content of 20 mg/kg – with additional-standard amount of 17 mg/kg and 42 mg/kg: the additional-standard recovery ranges are 91.5% ~ 101% and 84.9% ~ 104% respectively; the additional-standard recovery final values are 97.7%±7.0% and 95.0%±13.6%, respectively.

Six laboratories shall respectively conduct six repeated measurements on the yellow soil sample with chromium content of 68 mg/kg – with additional-standard amount of 17 mg/kg and 42 mg/kg: the additional-standard recovery ranges are 89.2% ~ 105% and 90.8% ~ 104%, respectively; the additional-standard recovery final values are

96.9%±11.4% and 96.1%±9.6%, respectively. Six laboratories shall respectively conduct six repeated measurements on the river sediment samples with chromium content of 60 mg/kg – with additional-standard amount of 17 mg/kg and 42 mg/kg: the additional-standard recovery ranges are 92.0% ~ 102% and 88.8% ~ 109% respectively; the additional-standard recovery final values are 98.5%±7.6% and 96.2%±19.6%, respectively.

See Appendix A for accuracy data.

11 Quality assurance and quality control

11.1 Make at least 2 laboratory blanks for each batch of samples. The determination result of zinc in the blank shall be lower than the lower detection limit, and the determination results of other elements shall be lower than the detection limit of the method.

11.2 A standard curve shall be established for each analysis, and its correlation coefficient shall be ≥0.999.

11.3 After the analysis of every 20 samples or each batch (less than 20 samples/batch), it is necessary to check the zero-concentration point and intermediate concentration point of the standard series. The measurement result at the zero-concentration point shall be lower than the detection limit of the method, and the relative error between the measured value of the intermediate concentration and the standard value shall be within ±10%.

11.4 For every 20 samples or each batch (less than 20 samples/batch), a parallel sample shall be analyzed, and the relative deviation of the parallel sample determination results shall be ≤20%.

11.5 For every 20 samples or every batch (less than 20 samples/batch), one certified standard sample shall be measured at the same time, and the relative error between the measurement result and the guaranteed value shall be within ±15%; alternatively, for every 20 samples or each batch (less than 20 samples/batch), one substrate additional-standard sample shall be analyzed, and the additional-standard recovery rate shall be 80% ~ 120%.

12 Waste disposal

The waste generated in the experiment shall be classified and collected, marked accordingly, and entrusted to a qualified unit for disposal.

------ The End ------