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Soil quality - Determination of total mercury - Cold atomic absorption spectrophotometry

土壤质量 总汞的测定 冷原子吸收分光光度法

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3.4 Nitric acid (HNO_3), ρ = 1.42 g/ml.

3.5 Sulfuric acid-nitric acid mixture, 1 + 1.

3.6 Potassium dichromate ($K_2Cr_2O_7$).

3.7 Potassium permanganate solution: Use distilled water (3.1), to dissolve 20 g of potassium permanganate ($KMnO_4$, recrystallized and refined if necessary); dilute it to 1000 ml.

3.8 Hydroxylamine hydrochloride solution: Use distilled water (3.1), to dissolve 20 g of hydroxylamine hydrochloride ($NH_2OH·HCI$); dilute it to 100 ml.

3.9 Vanadium pentoxide (V_2O_5).

3.10 Stannous chloride solution: Put 20 g of stannous chloride ($SnCl_2•2H_2O$) in a beaker. Add 20 ml of hydrochloric acid (3.3). Heat slightly. After completely dissolving, cool down. Use distilled water (3.1) to dilute it to 100 ml. If there is mercury, it can be bubbled with nitrogen gas to remove mercury. Prepare it before use.

3.11 Mercury standard fixative: Dissolve 0.5 g of potassium dichromate (3.6) in 950 ml of distilled water (3.1). Add 50 ml of nitric acid (3.4).

3.12 Diluent: Dissolve 0.2 g of potassium dichromate (3.6) in 972.2 ml of distilled water (3.1). Add 27.8 ml of sulfuric acid (3.2).

3.13 Mercury standard stock solution, 100 mg/L: Weigh 0.1354 g mercuric chloride ($HgCl_2$), which has been fully dried in a silica gel (3.16) desiccator. Use mercury standard fixative solution (3.11) to dissolve it. Transfer it into a 1000 ml volumetric flask. Then use mercury standard fixative solution (3.11), to dilute it to the mark. Shake well.

3.14 Mercury standard intermediate solution, 10.0 mg/L: Pipette 10.00 ml of mercury standard stock solution (3.13), into a 100 ml volumetric flask. Add mercury standard fixative solution (3.11) to dilute to the mark. Shake well.

3.15 Mercury standard use solution, 0.100 mg/L: Pipette 1.00 ml of mercury standard intermediate solution (3.14), into a 100 ml volumetric flask. Add mercury standard fixative solution (3.11), to dilute to the mark. Shake well.

3.16 Color-changing silica gel: Φ3 ~ 4 mm, for drying.

3.17 Activated carbon treated with iodine: Take 1 part of iodine, 2 parts of potassium iodide, 20 parts of distilled water by weight. Prepare a solution in a glass beaker. Then add about 10 parts of columnar activated carbon (for industrial use, Φ3 mm, length 3 ~ 7 mm). Stir vigorously, until the solution is decolorized. Take out the activated carbon from the beaker. Use glass fiber to filter the solution. Then dry it at about 100 °C, for 1

5 ml of sulfuric acid (3.2), 3 ~ 5 glass beads. Shake well. Insert a small funnel into the mouth of the bottle. Place it on an electric heating plate, to heat it to near boiling. Keep it for 30 ~ 60 minutes. Take it out and let it cool slightly. Add 20 ml of distilled water (3.1). Continue to heat and boil for 15 minutes. At this time, the specimen is light off-white (if the specimen is dark in color, nitric acid shall be added appropriately to decompose it). Remove it for slightly cooling. Add potassium permanganate solution (3.7) dropwise, until the purple color does not fade. Before the measurement, add the hydroxylamine hydrochloride solution (3.8) dropwise while shaking, until the excess potassium permanganate and the hydrated manganese dioxide, on the wall of the vessel, are completely discolored.

6.2 Determination

6.2.1 Connect the instrument. Replace the silica gel (3.16) in the U-shaped tube. Adjust the mercury meter and recorder, according to the instructions. Select the sensitivity gear and carrier gas flow rate. Turn the three-way valve (4.5) to the "zero calibration" end.

6.2.2 Take out the blowing head of the mercury reducer (4.3). Transfer all the test solution (including residue) into the mercury reduction bottle. Use distilled water, to rinse the conical flask for 3 ~ 5 times. Combine the rinsing liquid into the reduction bottle. Add distilled water to 100 ml. Add 1 ml of stannous chloride solution (3.11). Quickly insert the gas blowing head. Then turn the three-way valve (4.5) to the "sample injection" end, to let the carrier gas flow into the mercury reducer (4.3). At this time, the mercury in the test solution is reduced and vaporized into mercury vapor, which flows into the absorption pool of the mercury meter with the carrier gas flow. The meter pointer and the recorder pen rise rapidly. Record the highest reading or peak height. After the pointer and recorder pen return to zero, turn the three-way valve (4.5) to the "zero calibration" end. Take out the blowing head. Discard the waste liquid. Use distilled water (3.1), to clean the mercury reducer (4.3) twice. Then use diluent (3.11) to rinse it once, to oxidize the possible residual divalent tin. Then carry out the determination of another specimen.

6.3 Blank specimen

For each batch of specimens analyzed, prepare at least two sets of blank specimens according to step (6.1). Perform determination according to step (6.2).

6.4 Calibration curve

Accurately pipette 0.00, 0.50, 1.00, 2.00, 3.00, 4.00 ml of mercury standard solution (3.15) into 150 ml conical flask. Add 4 ml of sulfuric acid and nitric acid mixture (3.5). Add 5 drops of potassium permanganate solution (3.7). Add 20 ml of distilled water (3.1). Shake well. Before measurement, add dropwise hydroxylamine hydrochloride solution (3.8) for reduction. Subsequently, perform the determination, according to the steps described in 6.2.

Appendix B

(Normative)

Purification of hydroxylamine hydrochloride solution

Mercury is often contained in the hydroxylamine hydrochloride reagent and must be purified. When the mercury content is low, mercury can be removed by using sulfhydryl cotton fiber tube. When the mercury content is high, first remove a large amount of mercury by extraction, then use sulfhydryl cotton fiber tube to remove mercury.

B1 Mercury removal method by sulfhydryl cotton fiber tube: Fill 0.1 ~ 0.2 g of sulfhydryl cotton fiber, into a one-end thinned glass tube, which has an inner diameter of 6 ~ 8 mm and a length of about 100 mm, OR into a 500 ml separatory funnel. Make the reagent to be purified flow through it, at a speed of 10 ml/min, for 1 ~ 2 times, to remove all mercury.

Preparation of sulfhydryl cotton fiber (abbreviated as S.C.F):

Add 100 ml of thioglycolic acid ($CH_2SHCOOH$, analytically pure), 60 ml of acetic anhydride [$(CH_3CO)_2O$], 40 ml of 36% acetic acid (CH_3COOH), 0.3 ml of sulfuric acid (3.2), into a brown jar with ground mouth. Mix well. After cooling to room temperature, add 30 g of long-fiber absorbent cotton. Soak it completely. Use water to cool it. After the heat of reaction dissipates, put it in an oven at 40 ± 2 °C for 2 ~ 4 days. Take it out. Use an acid-resistant filter funnel, for suction filtration. Use mercury-free distilled water (3.1) to fully rinse it, until neutral. Spread out. Dry it at 30 ~ 35 °C. Place the finished product in a brown ground jar. Protect it from light. Store it at a lower temperature.

B2 Extraction method: Take 250 ml of hydroxylamine hydrochloride solution (3.8). Inject it into a 500 ml separating funnel. Add 15 ml of 0.1 g/L carbon tetrachloride (CCl_4) solution, which contains diphenylthiazone (dithizone $C_{13}H_{12}N_4S$) each time. Perform repeated extraction, until the carbon tetrachloride solution containing dithizone remains green. It is then extracted by carbon tetrachloride, to remove excess dithizone.

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