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NATIONAL STANDARD OF THE PEOPLE'S REPUBLIC OF CHINA

GB/T 14353.14-2014

Replacing GB/T 14353.14-1993

Methods for chemical analysis of copper ores, lead ores and zinc ore - Part 14: Determination of germanium content

铜矿石、铅矿石和锌矿石化学分析方法 第14部分：锗量测定

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1 Scope

This part of GB/T 14353 lays down the determination of germanium in copper ores, lead ores and zinc ores by atomic fluorescence spectrometry, and applies to that determination in copper ores, lead ores and zinc ores.

The measuring range is 0.060 μg/g to 100 μg/g and the detection limit of the method is 0.021 μg/g of germanium.

A warning printed above clause 1 states that the persons using this part shall have practical experience of regular laboratory work, that the part does not set out all the safety problems that may arise, and that the user is responsible for taking suitable safety and health

measures and for ensuring compliance with the conditions laid down by the relevant national regulations.

3 Principle

The test portion is decomposed with hydrofluoric acid, nitric acid and sulfuric acid and extracted with hot phosphoric acid. In a phosphoric acid (1+4) medium germanium reacts with potassium borohydride to form a hydride gas, which is carried by argon into an electrically heated quartz furnace. In the flame the hydrogen radicals collide with the hydride and dissociate it into free atoms. With a germanium high-intensity hollow-cathode lamp as the light source, the fluorescence intensity of germanium is measured on an atomic fluorescence spectrometer, and the germanium content of the test portion is calculated from that intensity.

4 Reagents

Unless otherwise stated, only reagents of analytical grade and water conforming to the specification for analytical laboratory water of GB/T 6682 shall be used.

4.1 Nitric acid, density 1.42 g/mL. 4.2 Hydrofluoric acid, density 1.13 g/mL, carrying the warning that hydrofluoric acid is toxic and strongly corrosive and that corrosion-proof gloves shall be worn to prevent contact with the skin. 4.3 Sulfuric acid (1+1), carrying the warning that improper dilution is dangerous. 4.4 Phosphoric acid solution (1+4).

4.5 Potassium borohydride solution, mass concentration 30 g/L: weigh 30 g of potassium borohydride into a beaker, dissolve it with stirring in potassium hydroxide solution of mass concentration 5 g/L, dilute to 1 000 mL and shake; the solution is prepared immediately before use.

4.6 Germanium standard solutions, prepared as follows. a) Germanium standard stock solution, mass concentration 100 μg/mL: weigh accurately 0.144 1 g of spectrally pure germanium dioxide that has been ignited at 600 °C into a 250 mL beaker, add about 50 mL of water and then about 3 grains of sodium hydroxide, dissolve by slow heating with stirring, cool, transfer with water to a 1 000 mL volumetric flask, dilute to the mark with water and shake; 1 mL of this solution contains 100 μg of germanium. b) Germanium standard working solution, mass concentration 0.1 μg/mL: pipette the germanium standard stock solution and dilute it stepwise with water so that 1 mL of the final solution contains 0.1 μg of germanium.

5 Apparatus

5.1 Atomic fluorescence spectrometer, fitted with a germanium high-intensity hollow-cathode lamp.

5.2 Analytical balance, class three, sensitivity 0.1 mg.

6 Test sample

6.1 The sample is prepared in accordance with the relevant provisions of GB/T 14505; the particle size of the prepared test sample shall be smaller than 97 μm.

6.2 The test sample is dried in an oven at 60 °C to 80 °C for 2 h to 4 h and then cooled to room temperature in a desiccator before use.

7 Analytical procedure

7.1 Test portion: weigh 0.1 g to 0.5 g of the test sample to the nearest 0.1 mg.

7.2 Blank test: carry out a blank test in duplicate alongside the test portion, taking the reagents used from the same reagent bottle and adding the same quantities.

7.3 Verification test: analyse a certified reference material of the same type of ore alongside the test portion.

7.4 Decomposition of the test portion. 7.4.1 Place the test portion (7.1) in a 50 mL polytetrafluoroethylene beaker, moisten it with a little water, add 10 mL of nitric acid (4.1), 10 mL of hydrofluoric acid (4.2) and 8 drops of sulfuric acid (4.3), and heat on a hotplate at 200 °C to 220 °C until white fumes are evolved; remove the beaker, rinse its wall with a little water, add 10 mL of phosphoric acid solution (4.4) and heat on the hotplate until the salts dissolve and the solution is clear. 7.4.2 Remove the beaker, transfer the test solution with phosphoric acid solution (4.4) into a 50 mL colorimetric tube, dilute to the mark, shake and keep for use.

7.5 Preparation of the calibration solution series: pipette 0.00 mL, 0.25 mL, 0.50 mL, 1.00 mL, 1.50 mL, 2.00 mL, 4.00 mL, 8.00 mL and 15.00 mL of the germanium standard working solution (4.6 b) into a set of 50 mL volumetric flasks, dilute to the mark with phosphoric acid solution (4.4), shake and keep for use.

7.6 Measurement: following the operating procedure of the instrument, adjust its parameters to bring it to the best measuring condition (see Annex A for reference values); with potassium borohydride solution (4.5) as reducing agent and phosphoric acid solution (4.4) as carrier stream, measure the fluorescence intensity of germanium in the calibration solutions and in the test solution, and measure at the same time the fluorescence intensity of the blank test solution.

7.7 Plotting of the calibration curve: with the quantity of germanium as the abscissa and the fluorescence intensity as the ordinate, plot the calibration curve and read the corresponding quantity of germanium from it.

8 Calculation of results

The germanium content is expressed as the mass fraction w(Ge) in μg/g and is calculated by formula (1). The symbols are: the mass concentration of germanium in the test solution read from the calibration curve, in nanograms per millilitre (ng/mL); the mass concentration of germanium in the blank test solution read from the calibration curve, in ng/mL; the volume of the test solution, in millilitres (mL); and the mass of the test portion, in grams (g).

The clause also prescribes how many decimal places the reported result carries according to its magnitude. The printed list of numeric formats could not be read digit by digit with certainty on the scan and is therefore not reproduced here.

9 Precision

Under repeatability conditions the absolute difference between the values of two independent test results obtained within the level range given in Table 1 shall not exceed the repeatability limit r; cases where it does exceed r shall not be more than 5 %. The repeatability limit r is calculated from the equation listed in Table 1 for that level range.

Under reproducibility conditions the absolute difference between the values of two independent test results obtained within the level range given in Table 1 shall not exceed the reproducibility limit R; cases where it does exceed R shall not be more than 5 %. The reproducibility limit R is calculated from the equation listed in Table 1 for that level range.

The statistical data obtained from the interlaboratory test results are given in Annex B.

Table 1 has four columns - element, level range m, repeatability limit r and reproducibility limit R - and one data row, for germanium, with the unit given as micrograms per gram. The level range is 0.91 to 26.1; the repeatability limit is given as r = 0.098 34 m + 0.014 9 and the reproducibility limit as R = 0.179 1 m - 0.056 2. A note states that the precision data were established by 7 laboratories on test samples at 5 levels.

10 Quality assurance and control

10.1 Each analytical measurement shall be quality-controlled by methods such as a blank test, replicate analysis and verification against a certified reference material.

10.2 Each analytical batch shall include 2 blank tests, replicate analysis of 20 % to 30 % of the samples and 1 or 2 verification tests on a certified reference material of the same type. Where the number of samples does not exceed 5, replicate analysis shall be carried out on 100 % of them.

10.3 In replicate analysis the absolute difference between the two determinations shall be smaller than the repeatability limit r given in Table 1; in reproducibility analysis the absolute difference between the determinations of different laboratories shall be smaller than the