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Methods for chemical analysis of tungsten concentrates - Part 19: Determination of fluoride content - Ion selective electrode method

钨精矿化学分析方法 第19部分：氟含量的测定 离子选择电极法

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Table of Contents

1 Scope

This document describes a method for the determination of the fluoride content of tungsten concentrates.

This document applies to the determination of the fluoride content of tungsten concentrates. Determination range: 0.020 percent to 2.00 percent.

2 Normative references

The contents of the following documents constitute indispensable provisions of this document through normative reference in the text. For dated references, only the edition corresponding to that date applies to this document; for undated references, the latest edition, including all amendments, applies to this document.

GB/T 6682 Water for analytical laboratory use - Specification and test methods

GB/T 8170 Rules of rounding off for numerical values and expression and judgement of limiting values

3 Terms and definitions

There are no terms and definitions that need to be defined in this document.

4 Principle

The test portion is decomposed by fusion with sodium hydroxide. The melt is leached with water and the solution is filtered. In a sodium citrate and triethanolamine medium at pH 6.5 to pH 7.0, with a saturated calomel electrode as the reference electrode and a fluoride ion selective electrode as the indicator electrode, the fluoride content is measured on a potentiometer.

5 Reagents or materials

Unless otherwise stated, only reagents confirmed to be of analytical grade are used in the analysis.

5.1 Water, GB/T 6682, grade 2.

5.2 Sodium hydroxide.

5.3 Nitric acid (1+4).

5.4 Sodium citrate solution (294 g/L).

5.5 Triethanolamine solution: add 64 mL of hydrochloric acid to 100 mL of triethanolamine, adjust to pH 6.5 to pH 7.0 with hydrochloric acid (1+1) and ammonia water (1+1), dilute to 500 mL with water and mix.

5.6 Fluoride standard stock solution: weigh 1.105 5 g of sodium fluoride that has been dried for 2 h at 120 degrees Celsius, dissolve it in water, transfer to a 500 mL volumetric flask, dilute to the mark with water, mix, and store in a polyethylene bottle. One millilitre of this solution contains 1 000 micrograms of fluoride. A commercially available certified reference material may also be purchased.

5.7 Fluoride standard solution A: pipette 10.00 mL of the fluoride standard stock solution (5.6) into a 100 mL plastic volumetric flask, dilute to the mark with water and mix. One millilitre of this solution contains 100 micrograms of fluoride.

5.8 Fluoride standard solution B: pipette 10.00 mL of fluoride standard solution A (5.7) into a 100 mL plastic volumetric flask, dilute to the mark with water and mix. One millilitre of this solution contains 10 micrograms of fluoride.

5.9 Phenol red indicator (2 g/L): weigh 0.1 g of phenol red, add 6 mL of sodium hydroxide solution (2 g/L), dilute to 50 mL with water and mix.

6 Apparatus

6.1 Potentiometer: accuracy better than 0.1 mV.

6.2 Fluoride ion selective electrode: over a fluoride ion concentration of one times ten to the power minus six mol/L to one times ten to the power minus one mol/L, the electrode potential shows a good linear relationship with the negative logarithm of the concentration. Before use the electrode shall be activated by soaking for 1 h in sodium fluoride solution of one times ten to the power minus three mol/L, then washed with water until the potential of the washings is not lower than the potential value corresponding to a fluoride ion concentration of one times ten to the power minus six mol/L.

6.3 Saturated calomel electrode.

6.4 Magnetic stirrer.

7 Sample

7.1 The particle size of the sample shall be less than 0.074 mm.

7.2 The sample shall be dried for 1 h in an oven at 100 degrees Celsius to 105 degrees Celsius and cooled to room temperature in a desiccator before use.

8 Test procedure

8.1 Test portion. Weigh the sample in accordance with Table 1, to the nearest 0.000 1 g. Table 1 relates the expected fluoride mass fraction to the mass of test portion: for a mass fraction of 0.020 percent to 0.50 percent the test portion is 0.50 g; for a mass fraction above 0.50 percent and up to 2.00 percent the test portion is 0.15 g.

8.2 Parallel tests. Carry out the test on two portions in parallel.

8.3 Blank test. Carry out a blank test alongside the test portion.

8.4.1 Place the test portion (8.1) in a 30 mL nickel crucible, add 5 g of sodium hydroxide (5.2), heat on a low temperature hot plate until it melts and dehydrates, then transfer to a high temperature furnace already at 700 degrees Celsius and fuse for 10 min. Remove and allow to cool slightly.

8.4.2 Place the crucible in a 250 mL beaker containing 50 mL of warm water, cover with a watch glass and heat to leach the melt. Wash the watch glass and the crucible clean with water and cool to room temperature. Transfer the solution together with the precipitate into a 100 mL volumetric flask, dilute to the mark with water, shake, filter dry, and take 10.00 mL of the filtrate into a 50 mL volumetric flask.

8.4.3 Add 15 mL of sodium citrate solution (5.4) and mix. Add one drop of phenol red indicator (5.9), adjust with nitric acid (5.3) until the solution has just turned yellow, add 5 mL of triethanolamine solution (5.5), dilute to the mark with water and mix.

8.4.4 Pour the test solution (8.4.3) into a dry 100 mL beaker in which a stirring bar has been placed beforehand, insert the fluoride ion selective electrode and the saturated calomel electrode, and, with magnetic stirring, measure the equilibrium potential on the potentiometer. Note: the equilibrium potential is the potential at which, under stirring, the electrode potential changes by no more than 0.2 mV/min.

8.5.1 Plotting of the low concentration working curve. Pipette 0.50 mL, 1.00 mL, 2.00 mL, 5.00 mL and 10.00 mL of fluoride standard solution B (5.8) into a set of 50 mL volumetric flasks, add 10 mL of the blank solution (8.3), and proceed as in 8.4.3 and 8.4.4. Measure under the same conditions as the test solution, in order of increasing fluoride ion concentration. On semi-logarithmic graph paper, plot the working curve with the logarithm of the mass of fluoride ion on the horizontal axis and the potential value on the vertical axis.

8.5.2 Plotting of the high concentration working curve. Pipette 1.00 mL, 1.50 mL, 2.00 mL, 2.50 mL and 3.00 mL of fluoride standard solution A (5.7) into a set of 50 mL volumetric flasks, add 10 mL of the blank solution (8.3), and proceed as in 8.4.3 and 8.4.4. Measure under the same conditions as the test solution, in order of increasing fluoride ion concentration. On semi-logarithmic graph paper, plot the working curve with the logarithm of the mass of fluoride ion on the horizontal axis and the potential value on the vertical axis.

9 Processing of test data

The fluoride content is expressed as the mass fraction of fluoride and is calculated by formula (1). In the formula the symbols have the following meanings: the mass of fluoride ion read off the working curve, in micrograms; the total volume of the test solution, in millilitres; the volume of filtrate taken, in millilitres; and the mass of the test portion, in grams.

When the calculated result is less than 1.00 percent, two significant figures are retained; when the calculated result is not less than 1.00 percent, the result is expressed to two decimal places. Rounding of numerical values is carried out in accordance with GB/T 8170.

10 Precision

10.1 Repeatability. The absolute difference between the measured values of two independent test results obtained under repeatability conditions, within the range of mean values given in Table 2, shall not exceed the repeatability limit r; cases in which the repeatability limit is exceeded shall not be more than 5 percent. The repeatability limit is obtained from the data of Table 2 by linear interpolation or extrapolation. The raw data of the precision test are given for information in Annex A. Table 2 pairs each fluoride mass fraction