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Non-ferrous Metals Industry Standard of People's Republic of China

YS/T 958-2014

Methods for chemical analysis of silver­—­­Determination of copper, bismuth, iron, lead, antimony, palladium, selenium and tellurium contents­—­­Inductively coupled plasma-atomic emission spectrometry

银化学分析方法

铜、铋、铁、铅、锑、钯、硒

和碲量的测定

电感耦合等离子体原子发射光谱法

*(English Translation)*

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Foreword

SAC/TC 243 is in charge of this English translation. In case of any doubt about the contents of English translation, the Chinese original shall be considered authoritative.

This standard is drafted in accordance with the rules given in GB/T 1.1-2009.

This standard was proposed by the National Nonferrous Metals Standardization Technical Committee.

This standard was prepared by National Standardization Technical Committee 243 on Nonferrous Metals of SAC/TC.

Methods for chemical analysis of silver—­­­Determination of copper, bismuth, iron, lead, antimony, palladium, selenium and tellurium contents­—­­Inductively coupled plasma-atomic emission spectrometry

**1 Scope**

This standard specifies the analysis procedure for the determination of impurity elements in silver.

This standard is applicable to the determination of impurity elements in silver. The test range is shown in Table 1.

**Table 1**

|  |  |  |  |
| --- | --- | --- | --- |
| Element | test range ω/% | Element | test range ω/% |
| Cu | 0.0003-0.0500 | Sb | 0.0003-0.0050 |
| Bi | 0.0003-0.0100 | Pd | 0.0003-0.0100 |
| Fe | 0.0003-0.0050 | Se | 0.0003-0.0100 |
| Pb | 0.0003-0.0100 | Te | 0.0003-0.0100 |

**2 Summary**

The sample is decomposed by nitric acid-hydrogen peroxide (HNO3-H2O2) mixed solution and reduced with ascorbic acid solution. Then the reduced silver is decomposed with HNO3-H2O2 mixed solution again, and the matrix silver is precipitated by hydrochloric acid (HCl). Collect the filtrate twice and concentrate at a low temperature. Finally, the amount of each element is tested in a HCl medium by inductively coupled plasma atomic emission spectrometer (ICP-AES).

**3 Reagents and materials**

During the analysis, unless otherwise stated, use guaranteed reagents and distilled water or water of equivalent purity only.

3.1 HCl, ρ= 1.19 g/mL.

3.2 HCl (1+1): mix 1 portion of HCl solution (3.1) and 1 portion of water.

3.3 HCl (1+9): mix 1 portion of HCl solution (3.1) and 9 portions of water.

3.4 HCl (1+19): mix 1 portion of HCl solution (3.1) and 19 portions of water.

3.5 HNO3, ρ=1.42 g/mL.

3.6 HNO3 (1+1): mix 1 portion of HNO3 solution (3.5) and 1 portion of water.

3.7 Mixed acid: mix 1 portion of HNO3 solution (3.5), 3 portions of HCl solution (3.1) and 3 portions of water.

3.8 H2O2, mass fraction of 30%.

3.9 Ascorbic acid solution (0.11 g/mL): accurately weigh 11.00 g of ascorbic acid, dissolve in water, and dilute to a 100 mL volumetric flask. The solution should be prepared before use.

3.10 HNO3-H2O2 mixed solution: mix 1 portion of HNO3 solution (3.5) and 1 portion of H2O2 solution (3.8). The solution should be prepared before use.

3.11 Tartaric acid solution (100 g/L).

3.12 Copper standard stock solution:weigh 1.000 0 g of metallic copper (mass fraction≥99.99%), place in a 100 mL beaker, add 20 mL of HNO3(3.6). Heat gently until complete dissolution of sample and then heat to expel the nitrogen oxide. Rinse the watch glass and beaker wall with water. After cooling to room temperature, transfer the solution into a 1000 mL volumetric flask, dilute to volume with water and mix thoroughly. This solution contains 1 000 μg of copper per milliliter.

3.13 Bismuth standard stock solution: weigh 0.100 0 g of metallic bismuth (mass fraction≥99.99%), place in a 100 mL beaker, add 20 mL of HNO3(3.6). Heat gently until complete dissolution of sample and then heat to expel the nitrogen oxide. After cooling to room temperature, transfer the solution into a 100 mL volumetric flask, dilute to volume with water and mix thoroughly. This solution contains 1 000 μg of bismuth per milliliter.

3.14 Iron standard stock solution: weigh 1.429 7 g of ferroferric oxide (mass fraction≥99.99%), place in a 250 mL beaker, covered with a watch glass and then add 50 mL of HCl (3.2). Heat gently until complete dissolution of sample. Rinse the watch glass and beaker wall with water. After cooling to room temperature, transfer the solution into a 1000 mL volumetric flask, dilute to volume with water and mix thoroughly. This solution contains 1000 μg of iron per milliliter.

3.15 Lead standard stock solution:weigh 0.100 0 g of metallic lead (mass fraction≥99.99%), place in a 100 mL beaker, add 20 mL of mixed acid (3.7). Heat gently until complete dissolution of sample and then heat to expel the nitrogen oxide. After cooling to room temperature, transfer the solution into a 100 mL volumetric flask, dilute to volume with water and mix thoroughly. This solution contains 1 000 μg of lead per milliliter.

3.16 Antimony standard stock solution: weigh 0.100 0 g of metallic antimony (mass fraction≥99.99%), place in a 100 mL beaker, add 20 mL of mixed acid (3.7). Heat gently until complete dissolution of sample and then heat to expel the nitrogen oxide. After cooling to room temperature, transfer the solution into a 100 mL volumetric flask, dilute to volume with HCl (3.2) and mix thoroughly. This solution contains 1 000 μg of antimony per milliliter.

3.17 Palladium standard stock solution: weigh 0.100 0 g of metallic palladium (mass fraction≥99.99%), place in a 100 mL beaker, add 20 mL of mixed acid (3.7). Heat gently until complete dissolution of sample and then heat to expel the nitrogen oxide. After cooling to room temperature, transfer the solution into a 100 mL volumetric flask, dilute to volume with water and mix thoroughly. This solution contains 1000 μg of palladium per milliliter.

3.18 Selenium standard stock solution: weigh 0.100 0 g of metallic selenium (mass fraction≥99.99%), place in a 100 mL beaker, add 20 mL of HCl (3.2). Heat gently until complete dissolution of sample. After cooling to room temperature, transfer the solution into a 100 mL volumetric flask, dilute to volume with water and mix thoroughly. This solution contains 1000 μg of selenium per milliliter.

3.19 Tellurium standard stock solution: weigh 0.100 0 g of metallic tellurium (mass fraction≥99.99%), place in a 100 mL beaker, add 20 mL of HNO3 (3.6). Heat gently until complete dissolution of sample and then heat to expel the nitrogen oxide. After cooling to room temperature, transfer the solution into a 100 mL volumetric flask, dilute to volume with water and mix thoroughly. This solution contains 1000 μg of tellurium per milliliter.

3.20 Copper, iron, lead, palladium, selenium, tellurium, bismuth and antimony mixed standard solution: accurately transfer 10.00 mL of copper standard stock solution (3.12), 10.00 mL of bismuth standard stock solution (3.13), 10.00 mL of iron standard stock solution (3.14), 10.00 mL of lead standard stock solution (3.15), 10.00 mL of antimony standard stock solution (3.16), 10.00 mL of palladium standard stock solution (3.17), 10.00 mL of selenium standard stock solution (3.18) and 10.00 mL of tellurium standard stock solution (3.19) to a 200 mL volumetric flask, add 10 mL of nitric acid (3.5), dilute to volume with water and mix thoroughly. This solution contains 50 μg of copper, 50 μg of bismuth, 50 μg of iron, 50 μg of lead, 50 μg of antimony, 50 μg of palladium, 50 μg of selenium and 50 μg of tellurium per milliliter, respectively.

3.21 Argon, ΦAr≥99.99%.

**4 Apparatus**

ICP-AES. Refer to Annex A for recommended instrument operating conditions and elemental spectral lines.

Light source: plasma light source, using power not less than 0.75 kW.

**5 Sample**

In order to avoid surface contamination, the sample is slightly boiled with 20 mL of HCl solution (3.3) for 5 min, then washed with water until no chloride ion is present, and finally rinsed with alcohol or acetone twice and dried in an oven at 105℃-110℃.

**6 Analysis**

**6.1 Sample**

The sample is weighed according to Table 2 to the nearest 0.0001 g.

**Table 2**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Mass fraction  % | Sample mass  g | Ascorbic acid solution (3.9)  mL | HCl solution (3.3)  mL | Tartaric acid solution (3.11)  mL | HCl solution (3.1)  mL | Constant volume  mL |
| 0.0003-0.0030 | 2.00 | 20.0 | 16.0 | 0.5 | 5 | 50 |
| >0.0030-0.010 | 1.00 | 10.0 | 8.0 | 0.5 | 5 | 50 |
| >0.010-0.030 | 1.00 | 10.0 | 8.0 | 1 | 10 | 100 |
| >0.030-0.050 | 0.50 | 5.0 | 4.0 | 1 | 10 | 100 |

**6.2 Number of tests**

The tests shall be carried out twice independently and take the average.

**6.3 Blank test**

Carry out a blank test with the sample.

**6.4 Test procedure**

6.4.1Transfer the sample (6.1) into a 250 mL beaker, add 5 mL of HNO3-H2O2 mixed solution (3.10), and covered with a watch glass. Heat gently to near dryness, and then wash the watch glass and beaker wall with water, controlling the volume of the solution to about 30mL. Put the solution on a low temperature electric heating plate, and slowly add ascorbic acid solution (3.9) while stirring according to Table 2. 1 mL of tartaric acid solution (3.11) is added and set it still at low temperature for 10 minutes and then shake several times. Filtration is carried out with a slow quantitative filter paper, and the filtrate is collected by a 150 mL beaker. The beaker and filter paper are washed 3 times with a small amount of water. The filtrate shall be heated to a slight boiling, and then HNO3 solution (3.5) is slowly added dropwise until the solution becomes bright yellow. Finally the solution is concentrated on the low temperature electric heating plate to about 10 mL.

6.4.2 Put the filter paper into the original 250 mL beaker, add 2 mL of tartaric acid solution (3.11), and then add 20 mL of HNO3-H2O2 mixed solution (3.10). Place the solution on the low temperature electric heating plate, dissolve the precipitate until no bubble is generated. Then add water to 50 mL and covered with a watch glass. After heating to a slight boiling, remove the watch glass, slowly add HCl solution (3.3) dropwise while stirring according to Table 2. Then heat to a slight boiling and place the solution in the boiling water for 1 h. Filtration is carried out with a slow quantitative filter paper, then the precipitate is washed 6 times with warm diluted HCl solution (3.4) and the filter paper is washed three times. Finally, two filtrates are combined.

6.4.3 The filtrate shall be placed on a low temperature electric heating plate to evaporate to 1 mL-2 mL. According to Table 2, tartaric acid solution (3.11) and hydrochloric acid solution (3.1) are added, and the wall of the beaker is washed with a small amount of water to dissolve the residue at a low temperature. After cooling to room temperature, transfer the solution into the corresponding volumetric flask according to Table 2 and dilute to volume with water and mix thoroughly.

6.4.4 The ICP-AES is used to test mass concentration of the elements. Under the same conditions for the preparation of working curve, when the linearity of the working curve is greater or equal to 0.999 8, the mass concentration of the elements can be found on the working curve by subtracting the intensity of the blank solution from the intensity of sample solution.

**6.5 Preparation of working curve**

6.5.1 Transfer 0 mL, 1.00 mL, 2.00 mL, 4.00 mL, 12.00 mL, 20.00 mL of copper, iron, lead, palladium, selenium, tellurium, bismuth and antimony mixed standard stock solution (3.20) to a set of 200 mL volumetric flasks, add 6.0 mL of tartaric acid solution (3.11), dilute to volume with HCl solution (3.3) respectively and mix thoroughly. The mass concentration of each element is 0 μg/mL, 0.25 μg/mL, 0.50 μg/mL, 1.00 μg/mL, 3.00 μg/mL, and 5.00 μg/mL, respectively.

6.5.2 Under the recommended operating conditions, zero reference is used for zero adjustment and the intensity of each element in the standard solution is measured. The working curve is automatically drawn by the instrument with mass concentration as axis and intensity as vertical, respectively.

**7 Calculation**

Calculate the mass fraction (ω(X)) of copper, iron, lead, palladium, selenium, tellurium, bismuth and antimony according to Formula (1), and the values shall be expressed as percentage.

ω(X) = × 100 (1)

where

X is the test element；

ρX is the mass fraction of the test element in the sample solution, in μg/mL;

VX is the volume of the sample solution, in mL;

ρ0 is the mass fraction of the test element in the blank solution, in μg/mL;

V0 is the volume of the blank solution, in mL;

m is the mass of the sample.

The results shall be accurate to four decimal places.

**8 Precision**

**8.1 Repeatability**

The absolute difference between the two test results from two independent tests under the repetitive conditions within the average range given in Table 3 shall not be greater than repeatability limit (r). The case of exceeding the repeatability limit does not exceed 5%, and the repeatability limit is obtained by linear interpolation according to the data of Table 3.

**Table 3**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| ω(Cu)/% | 0.000 5 | 0.002 3 | 0.007 3 | 0.015 2 | 0.044 0 |
| r/% | 0.000 2 | 0.000 3 | 0.000 7 | 0.001 2 | 0.002 4 |
| ω(Bi)/% | 0.000 7 | 0.001 7 | 0.005 6 | ­­­- | - |
| r/% | 0.000 2 | 0.000 3 | 0.000 5 | - | - |
| ω(Fe)/% | 0.001 0 | 0.001 6 | 0.002 9 | - | - |
| r/% | 0.000 2 | 0.000 3 | 0.000 5 | - | - |
| ω(Pb)/% | 0.000 8 | 0.005 6 | 0.019 5 | - | - |
| r/% | 0.000 2 | 0.000 5 | 0.001 6 | - | - |
| ω(Sb)/% | 0.000 4 | 0.001 1 | 0.003 8 | - | - |
| r/% | 0.000 2 | 0.000 3 | 0.000 5 | - | - |
| ω(Pd)/% | 0.000 9 | 0.002 2 | 0.009 4 | - | - |
| r/% | 0.000 2 | 0.000 3 | 0.000 8 | - | - |
| ω(Se)/% | 0.000 4 | 0.001 5 | 0.002 8 | 0.009 9 | - |
| r/% | 0.000 2 | 0.000 3 | 0.000 4 | 0.000 8 | - |
| ω(Te)/% | 0.000 7 | 0.003 5 | 0.008 4 | - | - |
| r/% | 0.000 2 | 0.000 4 | 0.000 8 | - | - |

**8.2** **Reproducibility**

The absolute difference between the two test results from two independent tests under reproducible conditions within the average range given in Table 4 shall not be greater than reproducibility limit (R). The case of exceeding the reproducibility limit does not exceed 5%, and the reproducibility limit is obtained by linear interpolation according to the data of Table 4.

**Table 4**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| ω(Cu)/% | 0.000 5 | 0.002 3 | 0.007 3 | 0.015 2 | 0.044 0 |
| r/% | 0.000 3 | 0.000 5 | 0.001 0 | 0.001 6 | 0.003 0 |
| ω(Bi)/% | 0.000 7 | 0.001 7 | 0.005 6 | ­­­- | - |
| r/% | 0.000 3 | 0.000 4 | 0.000 8 | - | - |
| ω(Fe)/% | 0.001 0 | 0.001 6 | 0.002 9 | - | - |
| r/% | 0.000 3 | 0.000 4 | 0.000 6 | - | - |
| ω(Pb)/% | 0.000 8 | 0.005 6 | 0.019 5 | - | - |
| r/% | 0.000 3 | 0.001 0 | 0.002 3 | - | - |
| ω(Sb)/% | 0.000 4 | 0.001 1 | 0.003 8 | - | - |
| r/% | 0.000 2 | 0.000 3 | 0.000 7 | - | - |
| ω(Pd)/% | 0.000 9 | 0.002 2 | 0.009 4 | - | - |
| r/% | 0.000 3 | 0.000 5 | 0.001 0 | - | - |
| ω(Se)/% | 0.000 4 | 0.001 5 | 0.002 8 | 0.009 9 | - |
| r/% | 0.000 2 | 0.000 4 | 0.000 7 | 0.001 1 | - |
| ω(Te)/% | 0.000 7 | 0.003 5 | 0.008 4 | - | - |
| r/% | 0.000 3 | 0.000 6 | 0.001 0 | - | - |

**9 Test report**

The test report shall contain at least the following information:

* Samples;
* Standards (YS/T 958-2014);
* Results and representation;
* Discrepancy from basic analysis steps;
* Anomalies observed in the test;
* Date of test.

Annex A

(informative annex)

**Recommended instrument operating conditions**

The recommended operating parameters of the instrument are shown in Table A.1, and the elemental spectral lines are shown in Table A.2.

**Table A.1**

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Power  W | Spray chamber gas  flow  L/min | Observation height  mm | Pump flow  mL/min | Plasma flow  L/min | Auxiliary gas flow  L/min | Integra-tion time  s | Observa-tion method |
| 1 300 | 0.80 | 15 | 1.50 | 15 | 0.2 | 25 | Axial |

**Table A.2**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Element | Cu | Fe | Pb | Bi |
| Wavelength  nm | 327.393 | 238.204 | 220.353 | 223.061 |
| Element | Sb | Se | Te | Pd |
| Wavelength  nm | 206.836 | 196.026 | 214.281 | 340.458 |