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National Standard ofthe People’s Republic of China

GB/T 15072.1-2008

Replaces GB/T 15072.1-1994

Methods for chemical analysis of precious metals alloys

Determination of gold content for gold, platinum and palladium alloys

Potentiometric titration using ferrous sulfate

贵金属合金化学分析方法

金、铂、钯合金中金量的测定

硫酸亚铁电位滴定法

(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 an integrated revision of GB/T 15072-1994(*Chemical analysis methods for precious metals and their alloys*)(all parts), which is divided into 19 parts:

—GB/T 15072.1-2008 *Test methods of precious metal alloys Determination of gold content for gold, platinum and palladium alloys Potentiometric titration with ferrous sulfate*.

—GB/T 15072.2-2008 *Test methods of precious metal alloys Determination of silver content for silver alloys Potentiometric titration with sodium chloride*.

—GB/T 15072.3-2008 *Test methods of precious metal alloys Determination of platinum content for gold, platinum and palladium alloys Current titration with potassium permanganate*.

—GB/T 15072.4-2008 *Test methods of precious metal alloys Determination of palladium content for palladium and silver alloys Butanedione dioxime gravimetry*.

—GB/T 15072.5-2008 *Test methods of precious metal alloys Determination of silver content for gold and palladium alloys Potentiometric titration with potassium iodide*.

—GB/T 15072.6-2008 *Test methods of precious metal alloys Determination of iridium content for platinum and palladium alloys Potentiometric titration with ferrous sulfate*.

—GB/T 15072.7-2008 *Test methods of precious metal alloys Determination of chromium and iron contents for gold alloys Inductively coupled plasma atomic emission spectrometry*.

—GB/T 15072.8-2008 *Test methods of precious metal alloys Determination of copper content for gold, palladium and silver alloys EDTA complexometric back titration with thiourea precipitation*.

—GB/T 15072.9-2008 *Test methods of precious metal alloys Determination of indium content for gold alloys EDTA complexometric back titration*.

—GB/T 15072.10-2008 *Test methods of precious metal alloys Determination of nickel content for gold alloys EDTA complexometric back titration*.

—GB/T 15072.11-2008 *Test methods of precious metal alloys Determination of gadolinium and beryllium contents for gold alloys Inductively coupled plasma atomic emission spectrometry*.

—GB/T 15072.12-2008 *Test methods of precious metal alloys Determination of vanadium content for silver alloys Hydrogen peroxide spectrophotometry*.

—GB/T 15072.13-2008 *Test methods of precious metal alloys Determination of tin, cerium and lanthanum contents in silver alloys Inductively coupled plasma atomic emission spectrometry*.

—GB/T 15072.14-2008 *Test methods of precious metal alloys Determination of aluminium and nickel contents for silver alloys Inductively coupled plasma atomic emission spectrometry*.

—GB/T 15072.15-2008 *Test methods of precious metal alloys Determination of nickel, zinc and manganese contents for gold, silver and palladium alloys Inductively coupled plasma atomic emission spectrometry*.

—GB/T 15072.16-2008 *Test methods of precious metal alloys Determination of copper and manganese contents for gold alloys Inductively coupled plasma atomic emission spectrometry*.

—GB/T 15072.17-2008 *Test methods of precious metal alloys Determination of tungsten content for platinum alloys Tungsten trioxide gravimetry*.

—GB/T 15072.18-2008 *Test methods of precious metal alloys Determination of zirconium and gallium contents for gold alloys Inductively coupled plasma atomic emission spectrometry*.

—GB/T 15072.19-2008 Test methods of precious metal alloys Determination of vanadium and magnesium contents for silver alloys Inductively coupled plasma atomic emission spectrometry.

This part is the first of GB/T 15072-2008.

This part replaced GB/T 15072.1-1994(*Methods for Chemical Analysis of Precious Metals and Their Alloys Gold , palladium alloys Determination of gold content*).

The following deviations have been made with respect to the GB / T 15072.1-1994(the previous edition):

—The title of standard is changed from *Methods for Chemical Analysis of Precious Metals and Their Alloys Gold , palladium alloys Determination of gold content* to *Test method of precious alloys Determination of gold content for gold platinum and palladium alloys Potentiometric titration using ferrous sulfate*.

—Inductively potentiometric titration replaces coulometry of the previous standard for determination of gold content in gold and palladium alloys.

-- The scope of the method is extended from 15 alloy brands to 22 alloy series which are containing the same component elements, for detail: The original brands including AuNi9.0,AuNiCu7.5-1.5,AuNiCr5.0-1.0,AuNiCr5.0-2.0,AuNiIn9.0-8.0,AuCuNiZn22.0-.5-1.0,AuCuNiZnMn8.0-1.8-0.7-0.2,AuNiFeZr5.0-1.5-0.3,AuNiFeZr9.0-2.0-0.3,AuAgCu20.0-3.0,AuAgCu35.0-5.0,AuAgCuGd35.0-5.0-0.5,AuAgCuMnGd35.5-3.0-2.5-0.5,AuAgPt25.0-6.0,PdAgCuAuPtZn30.0-14.0-10.0-10.0-1.0,Revised to the following alloy series AuAg ,AuAgPt, AuAgCu, AuAgCuMnGd, AuCu, AuCuPtAgZn, AuNi, AuNiIn, AuNiCu, AuNiCr, AuNiGd, AuNiFeZr, AuFeCr, AuBe, AuGeNi, AuIr, AuSn, PtAu, PtRhAu, PdAu, PdAgCuAuPtZn, SnPbAuSb and other alloys containing the above elements.

——The range of gold content(mass fraction) is extended from 5% ~95% to 3% ~99.5%.

This part was proposed by Nonferrous Metals Industry Association of China.

This part was prepared by SAC/TC 243 Chinese Nonferrous Metal Standardization Technical Committee.

The previous editions of this part are as follows:

——GB / T 15072.1-1994.

Methods for chemical analysis of precious metals alloys

Determination of gold content for gold- Platinum and palladium alloys

Potentiometric titration with ferrous sulfate;

1. Scope

This part specifies a method for the determination of gold contents in gold, platinum and palladium alloys.

This part is applicable to the determination of gold contents between5% to 99.5%(mass fraction) in AuAg, AuAgPt, AuAgCu, AuAgCuMnGd, AuCu, AuCuPtAgZn, AuNi, AuNiIn, AuNiCu, AuNiCr, AuNiGd, AuNiFeZr, AuFeCr, AuBe, AuGeNi, AuIr, AuSn, PtAu, PtRhAu, PdAu, PdAgCuAuPtZn, SnPbAuSb and other alloys containing the above elements.

2 Normative references

The following normative documents contain provisions which, through reference in this test, constitute provisions of this part. For dated references, subsequent amendments (excluding corrections), or revisions, of any of these publications do not apply to this part. However parties to agreements based on this part are encouraged to investigate the possibility of applying the most resent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies.

GB/T 9725 Cemical reagent General for potentiometric titration

Y/T 371 General and general rules for chemical analysis of noble metal alloys

1. Method abstract

Gold alloy, palladium alloy portion were dissolved by mixture of hydrochloric acid and nitric acid. Platinum alloy which was containing rhodium alloy, iridium alloy were dissolved by hydrochloric acid and hydrogen peroxide solution in closed container. Rhodium, iridium, tin and a high amount of platinum and palladium alloys were separated from gold by reduction of cuprous chloride. In sulfuric acid and phosphoric acid medium, the gold was reduced Au (Ⅲ) to Au (0) by ferrous sulfate standard titration solution. The mass fraction of gold was determined by potentiometric indication.

1. Reagents and materials

Unless otherwise stated, use only reagents and materials as specified in YS/T 371.

* 1. Hydrochloric acid, （ρ about 1.19 g/mL）
  2. Nitric acid,（ρabout1.42 g/mL）
  3. Sulfuric acid, （ρ about 1.84 g/mL）
  4. Phosphoric acid,（ρ about 1.70 g/mL）
  5. Hydrogen peroxide, amass fraction of 30 %.
  6. Potassium permanganate solution(KMnO4),（ 20 g/L.）
  7. Sulfuric acid solution (4 + 96).
  8. Hydrochloric - nitric acid mixture:3 unit volumes of hydrochloric acid (4.1) mixed with 1 unit

volume of nitric acid(4.2),prepared it just before using.

* 1. Hydrochloric - nitric acid mixture:30 unit volumes of hydrochloric acid (4.1) mixed with 1 unit

volume of nitric acid(4.2), prepared it just before using.

* 1. Sulfuric - phosphoric acid mixture: measure out 200mL sulfuric acid(4.3)into a porcelain

evaporating dish, heat to produce white dense smoke, dropwise add potassium permanganate solution with stirring until the red colour fastness ,remove and cool .Add isopyknic phosphoric acid, mix them well, transfer into a 500mL one-mark volumetric flask.

4.11. Hydrochloric acid diluted (1+ 9).

4.12. Sodium chloride solution, 250 g/l.

4.13. Cupric chloride solution.

Weighing 3.0 g of cupric chloride, transfer into a 50 mL beaker .Adding 30 mL of hydrochloric acid (4.1). Transfer the solution quantitatively into a 1 00 mL one-mark volumetric flask, dilute to the mark with water and mixit well, It should be prepared it just before using.

4.14 Gold standard solution

Weighing 0.2500g of pure gold (purity ≥ 99.99% (mass fraction)).Transfer into a 400 mL beaker and add 10 mL of hydrochloric-nitric acid mixture (4.8). Cover with a watch-glass and heat the solution in a water bath gently to complete dissolution. Rinse the watch-glass and beaker wall with a little water, added 4.0mL Sodium chloride solution (4.12). Evaporate the solution to precipitation of moist salt in a water bath. Added 4.0mLhydrochloric acid (4.1), Rinse the watch-glass and beaker wall with a little water. Evaporate the solution to precipitation of moist salt in a water bath. Repeat it 4 to 5 times. After that, added 50mLhydrochloric acid(4.1), transfer the solution to a 250 mL one-mark volumetric flask, dilute to the mark with water and mix it well.1 mL of this solution contained 1mg of gold.

4.15 Ferrous sulfate titrand

4.15.1 Preparation

Dissolving 10.5 g of ferrous sulfate (FeSO4.7H20) in5000 mL sulfuric acid (4.7) and mix them well. Standardization of the solution shall be taken after one week.

4.15.2 Standardization: The standardization shall be carried out in parallel with the determination of test portion.

Transfer 10.00mL to 20.00mL gold standard solution into a 100mL beaker, add 0.5mL sodium chloride solution (4.12), evaporated the solution to precipitation of moist salt in the water bath, and remove. Adding 5mL sulfuric -phosphoric acid mixture (4.10), added water to about 40mL.According to the operation of GB/T9725, a platinum indicating electrode and a saturated potassium chloride reference electrode were inserted into the solution, under electromagnetic stirring, titrated with ferrous sulfate titrand (4.15) to the end point, then titrated with a microburette, The end point of titration was the potential abrupt to the maximum.

Parallel standardization in triplicate, the volume difference of the consumed ferrous sulfate titrand should not exceed 0.02rnL, and the average value should be taken.

The concentration of ferrous sulfate titrand should be calculated according to formula (1):

-------------------------------------- (1)

In the formula:

C is the concentration of ferrous sulfate titrand, the unit is moles per liter (mol/L).

C0is the concentration of gold standard solution, the unit is milligrams per milliliter (mg/mL).

V1is the volume of gold standard solution, the unit is in milliliters (mL).

V2is the volume of ferrous sulfate titrand which is consumed in standardization, the unit is milliliters (mL).

196.966 is the molar mass of gold, the unit is grams per mill (g/mol).

1. Apparatus
   1. Potentiometer (or acidity meter with potential measurement function), the minimum potential

detection accuracy is not more than 1mV.

* 1. Magnetic stirrer.
  2. Indicating electrode: platinum electrode.

5.4 Reference electrode, saturated potassium chloride calomel electrode.

5.5 Microburette, minimum scale is 0.0050mL.

5.6 Oven.

5.7 Polytetrafluoroethy lene sample tank, volume is 30mL.

1. Sample

The alloy samples should be made into a thin sheet with a thickness of about 0.3mm.Remove the oil stain with acetone, cut it into debris, wash it with water and mix it after drying.

7 Analysis procedure

7.1 Test portion

Take the portion according to Table 1, accurate to 0.00001g.

Table 1

|  |  |
| --- | --- |
| Mass fraction of gold/% | Mass of test portion/g |
| >3.00 to 5.00 | 0.20 |
| >5.00 to 10.00 | 0.15 |
| >10.00 to 20.00 | 0.10 |
| >20.00 to 50.00 | 0.25 |
| >50.00 to 99. 50 | 0.20 |

Measure independently two times and calculate the mean value.

7.2 Blank test

Blank test shall be done along with the test portion.

7.4 Determination

7.3.1 Dissolving of the portion

7.3.1.1 The test portion of AuAg, AuAgPt, AuAgCu, AuAgCuMnGd and AuCuPtAgZn alloys should be placed in a 400mL beaker, add 30 mL of hydrochloric acid - nitric acid mixture (4.9), cover the beaker with a watch glass, heating to complete dissolution at low temperature. Remove and cool. Wash the watch glass and beaker wall with water.

7.3.1.2 The test portion of PdAu, PdAgCuAuPtZn and SnPbAuSb alloys should be placed in a 100mL beaker, add 10 mL to 30 mL of hydrochloric -nitric acid mixture(4.9), cover the beaker with a watch glass, heating to complete dissolution at low temperature. Remove and cool. Wash the watch glass and beaker wall with water.

7.3.1.3 The test portion of AuCu, AuNi, AuNiIn, AuNiCu, AuNiCr, AuNiGa, AuNiFeZr, AuGeNi, AuFeCr, AuBe and AuSn alloys should be placed in a 400mL beaker, add 10 mL of hydrochloric -nitric acid mixture (4.8), cover the beaker with a watch glass, heating to complete dissolution at low temperature. Remove and cool. Wash the watch glass and beaker wall with water. Transfer the gold-tin solution into a certain volumetric flask(make the mass concentration of gold to 1mg/mL～2 mg/mL), dilute to the mark with water and mix it well.

7.3.1.4 The test portion of AuIr, PtAu and PtRhAu alloys should be placed in a polytetrafluoroethylene sample tank, add 15 mL of hydrochloric acid (4.1) and 5 mL hydrogen peroxide(4.5),put in oven at 150℃±5℃ for 6h to 8h,cool it to the room temperature and remove the solution. Transfer the gold-iridium test portion into a certain volumetric flask(make the mass concentration of gold to 1mg/mL to 2 mg/mL), dilute to the mark with water and mix. Transfer the platinum-gold and platinum-rhodium-gold test portion into a 100mL beaker.

7.3.2 Treatment of test portion

7.3.2.1 Adding 4.0 mL sodium hydride solution (4. 12) to the test portion (7. 3.1.1, 7.3.1.3), The solution should be evaporated to precipitation of moist salt in the water bath, and remove it. Adding 5 mL hydrochloric acid (4. 1), washing beaker wall with a little water, and evaporating the solution to precipitation of moist salt in the water bath. Repeat 4 to 5 times, and taken it off. Transfer the residue into a 100 mL volumetric flask with water, fixed the volume, taken the test portion containing 10 mgto20 mg of gold in a 100 mL beaker, add 5 mL mixing acid of sulfuric acid and phosphoric acid (4. 10), and adding water to about 40 mL to obtain the solution to be titrated.

7.3.2.2 Adding 0.5 mL sodium chloride solution (4. 12) to the test portion obtained in (7. 3. 1. 2)

and the test portion of PtAu and PtRhAu obtained in (7. 3. 1. 4), the solution should be evaporated to precipitation of moist salt in the water bath. Take it off. Adding 2 mL hydrochloric acid (4. 1) and washing the beaker wall with a little water, evaporating the solution to precipitation of moist salt in a water bath. Repeat 4 to 5 times (PtAu and PtRhAu test portion should be repeated once), and remove it.

7.3.2.3 Removing gold containing about 10 mg to 20 mg of AuSn test portion (7.3.1.3) and AuIr test portion

(7.3.1.4) in 100 mL beaker, add 0.5 mL of sodium chloride solution (4.12), evaporate the solution to precipitation of moist salt in a water bath, and take it off. Adding 2 mL hydrochloric acid (4.1) and washing the beaker wall with a little water, and evaporating the solution to precipitation of moist salt in a water bath. Repeat it 4 to 5 times (the test portion of AuIr should be repeated once), and remove it.

7.3.3 Separation

Adding 2mL hydrochloric acid (4.1) and 8mL cuprous chloride solution (4.13) into the residue (7.3.2.2 and 7.3.2.3), cover the surface dish, boil it at low temperature for 2min, take it off , washing the surface dish and break wall with water. Filtrating with 3# glass sand funnel, washing the precipitate and beaker 4 to 5 times with hydrochloric acid solution (4.11), discard the washing liquid. Dissolve the precipitate for 4 times with 20mL hydrochloric acid (4.1) and 4mL hydrogen peroxide (4.5), washing the funnel for 4 to 5 times. The solution and washing solution were combined into the original beaker. Adding 0.5mL sodium chloride solution (4.12), evaporating the solution to precipitation of moist salt in the water bath, and remove. Add 5mL sulfuric -phosphoric acid (4.10) to the residue, adding water to about 40mL to get the titrant solution.

7.3.4 Titration

According to the operation of GB/T9725, the indicating electrode of platinum and reference electrode of saturated potassium chloride were inserted into the titrant (7.3.2.1 and 7.3.3), and then titrated with the ferrous sulfate titrand (4.15) to the nearly end point under electromagnetic stirring, and then titrated with the micro-burette, The end point of titration is the potential abrupt to the maximum.

1. Calculation of analysis results

The mass fraction of palladium should be calculated according to formula (2), and the value is expressed as %,

In the formula:

C is the concentration of ferrous sulfate titrand, the unit is moles per liter(mol/L).

V3 is the total volume of the test portion, the unit is milliliters (mL)

.

V4 is divide the volume of test portion, the unit is milliliters (mL).

V5is the volume of ferrous sulfate titrand consumed in the titrate solution, the unit is mL.

m0 is the mass of the test portion, the unit is gram(g).

196.966 is the molar mass of gold, the unit is gram per mole (g/mol).

103 is the conversion factor between a liter and a milliliter.

The results should be expressed to two decimal places.

1. Tolerance
   1. Repeatability

Within the mean values given below, the absolute difference in results of two parallel determinations under repeatability conditions shall not be greater than repeatability limit. If the difference exceeds the limit, it shall be not more than 5%.The repeatability limit is obtained by linear interpolation according to the data in Table 2.

Table 2 in %

|  |  |  |  |
| --- | --- | --- | --- |
| Mass fraction of gold /% | 9.98 | 60.16 | 90.85 |
| Repeatability limit (R)/% | 0.060 | 0.084 | 0.128 |

9.2 Tolerance

The difference in analysis results between laboratories shall not be greater than tolerance given in Table 3.

Table 3 in %

|  |  |
| --- | --- |
| mass fraction of gold/% | relative tolerance |
| >3.00 to10.00 | 0.07 |
| >10.00 to 30.00 | 0.15 |
| >30.00 to 60.00 | 0.20 |
| >60.00 to 99.5 | 0.30 |