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National Standard of the People’s Republic of China

GB/T 15072.4-2008

 Replaces GB/T 15072.4-1994

Test method of precious metal alloys

Determination of palladium content for palladium and silver alloys

Butanedione dioxime gravimetry

贵金属合金化学分析方法

钯、银合金中钨钯量的测定

二甲基乙二醛肟重量法

(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 fourth of GB/T 15072-2008.

This part replaces GB/T 15072.4-1994 (*Methods for Chemical Analysis of Precious Metals and Their Alloys Palladium, silver alloys Determination of palladium content*).

The following deviations have been made with respect to the GB / T 15072.4-1994(the previous edition):

—The title of standard is changed from *Methods for Chemical Analysis of Precious Metals and Their Alloys Palladium, silver alloys Determination of palladium content* to *Test method of precious metal alloys Determination of palladium content for palladium and silver alloys Butanedione dioxime gravimetry*.

—The scope of the standard is extended from PdIr10, PdIr18,PdAgCuAuPtZn30-14-10-10-1, PdAgCu69-27, PdAgCu58-32, PdAgCu65-20,PdAgCu52-28, PdAgCu54-21,AgPd20,AgPd60 of the previous edition to this standard is applicable to the determination of palladium content for alloys of PdIr, PdAgCu, PdAgCuAuPtZn and AgPd.  The determination range of this standard (mass fraction) is 4% to 92%.

—This part is drafted in accordance with the rules given in the GB/T20001.4-2001.

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.

This part is explained by the national non ferrous metal Standardization Technical Committee.

The previous edition of this standard is as follow:

—GB / T 15072.4-1994.

Test method of precious metal alloys

Determination of palladium content for palladium and silver alloys

Butanedione dioxime gravimetry

1. Scope

This part specifies a method for the determination of palladium content in palladium and silver alloys.

This part is applicable to determination of palladium contents between 4% - 92% in PdIr, PdAgCu, PdAgCuAuPtZn and AgPd alloys.

1. Normative references

The following normative documents contain provisions which, through reference in this, 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 recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies.

YS/T 371 *Methods for chemical analysis of precious metals alloys General rules and regulations*.

1. Method abstract

The test portion of PdIr and PdAgCuAuPtZn alloys shall be dissolved with mixture acid of hydrochloric acid and nitric acid. PdAgCu and AgPd alloys shall be dissolved with nitric acid. Gold alloy should be reduced and separated by sodium nitrite, and silver alloy should be separated by silver chloride precipitation. Pd alloy should be precipitated by butanedione dioxime in dilute hydrochloric acid. The mass fraction of palladium should be determined by gravimetry.

1. Reagent and material

Unless otherwise noted, reagents and utensil are in accordance with YS/T 371.

4.1 Sodium chloride.

4.2 Hydrochloric acid(ρ1.19g/mL).

4.3 Nitric acid(ρ1.42g/L).

4.4 Acetic acid(ρ1.05g/L).

4.5 Ammonium hydroxide(ρ0.90g/L).

4.6 Hydrochloric acid solution(1+1).

4.7 Hydrochloric acid solution(1+9).

4.8 Hydrochloric acid solution(2+98).

4.9 Mixed acid:3 unit volume hydrochloric acid(4.2)mixed with 1 unit volume nitric acid(4.3), prepare it just before using.

4.10 Mixed acid:30 unit volume hydrochloric acid(4.2)mixed with 1 unit volume nitric acid(4.3), prepare it just before using.

4.11 Ammonium hydroxide(1+1).

4.12 Sodium nitrite solution(100g/L).

4.13 Sodium nitrite solution(10g/L).

4.14 Sodium hydroxide solution(100g/L).

4.15 Butanedione dioxime ethanol solution(10g/L).

* 1. Thymol blue solution(1g/L):weigh 0.1g thymol blue in a 100mL beaker, add 2.2 mL sodium hydroxide solution(4.13)and dilute to 100mL with water.
1. Sample

Alloy sample should be  rolled into thin sheets of thickness not greater than 0.3mm, remove oil stains with acetone, and cut into debris, washed with water, dried and mixed well.

1. Analysis procedure

6.1 Test portion

Weigh the test portion according to Table 1, accurate to 0.00001g.

Table 1

|  |  |
| --- | --- |
| Mass fraction of palladium /% | Test portion /g |
| >4.00 to 10.00 | 0.40 |
| >10.00 to 40.00 | 0.13 |
| >40.00 to 92.00 | 0.03 |

6.2 Determination of the number

Two independent determinations should be required, and average the results.

6.3 Determination

6.3.1 Dissolving of the portion

6.3.1.1 The PdIr alloy portion should be placed in a 400mL beaker, then cover the surface dish and add 10mL mixed acid(4.9) which was mixed by hydrochloric acid and nitric acid, Heating the solution at low temperature until test portion completely dissolved, then remove, cool, wash surface dish and beaker wall with water. After that, adding 0.1g sodium chloride and evaporate the solution to precipitation of moist salt. Adding 10mL hydrochloric acid (4.2) and evaporate the solution to precipitation of moist salt. It should be repeated 2 times.

6.3.1.2 The PdAgCuAuPtZn alloy portion should be placed in a 250mL beaker, then cover the surface dish and add 10mL hydrochloric acid (4.10). Heating the solution at low temperature until test portion completely dissolved, then remove, cool, wash surface dish and cup wall with water. After that, adding 0.1g sodium chloride and evaporate the solution to precipitation of moist salt. Adding 10mL hydrochloric acid (4.2) and evaporate the solution to precipitation of moist salt. It should be repeated 2 times.

6.3.1.3 The PdAgCu and AgPd alloys portion should be placed in a 250mL beaker, then cover the surface dish and add 10mL nitric acid (4.3). Heating the solution at low temperature until test portion completely dissolved, then remove, cool, wash surface dish and cup wall with water. After that, adding 0.1g sodium chloride and evaporate the solution to precipitation of moist salt. Adding 10mL hydrochloric acid (4.2) and evaporate the solution to precipitation of moist salt. It should be repeated 2 times.

6.3.2 Separation

6.3.2.1 Adding 10mL hydrochloric acid (4.2) and 200mL water to the residue (6.3.1.1), and add 15mL butanedione dioxime ethanol solution (4.15) with agitate, stirring for 3min and still standing for 1h.

6.3.2.2 Adding 4mL hydrochloric acid solution (4.5) and 100mL water to the residue (6.3.1.2), It shall be heated to boil until silver chloride precipitated and agglomerated, placing the solution for 4h in the dark. Filtering with medium speed filter paper, washing the beaker and precipitate 6 times each with hydrochloric acid solution (4.8), washing the beaker and precipitate 2 times each with water, discarding the precipitate. Adding 2 drops of thymol blue solution (4.16) to the filtrate, the solution shall be adjusted from red to orange (pH2) with sodium hydroxide solution (4.14), heating to boil, adding 10mL sodium nitrite solution (4.12) with agitate, then boil the solution for 30min until gold was able to precipitated and agglomerated. Filtering with dense filter paper while it was hot, the beaker and precipitate shall be washed 5 times each with hot sodium nitrite solution (4.13). Adding 5 mL hydrochloric acid solution (4.6) into the beaker and filter paper, the beaker and precipitate shall be washed 10 times each with hot water, discarding the precipitate. Heating the filtrate and boil it for 1h. The solution shall be evaporated to precipitation of moist salt. Adding 10mL hydrochloric acid (4.2) and evaporate the solution to precipitation of moist salt. It shall be repeated 3 times. Adding 10 mL hydrochloric acid (4.2) and 200 mL water, then add 10 mL butanedione dioxime ethanol solution with agitate, stirring for 3min and still standing for 1h.

6.3.2.3 The PdAgCu residue (6.3.1.3 )shall be separated from silver in accordance with the operation (6.3.2.2), adding 8 mL hydrochloric acid (4.2) to the filtrate, and water was added to the total volume of 200 mL. Add butanedione dioxime ethanol solution (4.15) with agitate, stirring for 3min and still standing for 1h.

6.3.2.4 Adding 100 mL water to the AgPd residue (6.3.1.3), adding 10 mL ammonia solution (4.11) with agitate. Until yellow color of the solution disappears (if the pink precipitation is produced, it should be heated slightly to dissolved the precipitation), and then dropping acetic acid (4.4) to adjust the solution to pH6.Adding 5 mL hydrochloric acid solution (4.7), stirring for 3min, remove, and still standing for 4h in the dark. Filtering with medium speed filter paper, The beaker and precipitate shall be washed 6 times each with hydrochloric acid solution (4.8),After that, washing the beaker and precipitate 2 times each with water, discarding the precipitate. Adding 5 mL hydrochloric acid (4.2) with agitate, and heated to boil for 5min, remove and cool. Adding water until the total volume is 200 mL, adding butanedione dioxime ethanol solution with agitate, stirring for 3min and still standing for 1h.

6.3.3  Filtration

The precipitation of butanedione dioxime palladium (6.3.2.1, 6.3.2.2, 6.3.2.3, 6.3.2.4) shall be vacuum filtrated in a No.4 glass sand filter crucible which were dried at 110℃ to constant weight. The beaker and precipitate shall be washed 10 times each with hydrochloric acid solution (4.8). Scrubbing the edge of the beaker with a glass rod with rubber head, then wash the beaker and precipitate 5 times in hot water at about 85℃.

6.3.4 Constant weight

The crucible (6.3.3)shall be dried at 110℃ for 1h.Removing and place in the dryer for 30min. Then weigh the dryer many times until constant weight.

7 Calculation of analysis results

The mass fraction of palladium $ω\_{Pd}$ should be calculated according to formula (1), and the value is expressed as % :

 $ω\_{Pd}=\frac{（m\_{1}-m\_{2}）×0.3161}{m\_{0}}×100$ -- -- -- -- -- -- -- -- -- -- -- (1)

In the formula:

$m\_{1}$ is the mass of butanedione dioxime palladium and crucible in grams (g).

$m\_{2}$ is the mass of the crucible in grams (g).

$m\_{0}$ is the mass of portion in grams (g).

0.3161 is the conversion of butanedione dioxime palladium to palladium.

The results should be expressed to two decimal places.

8 Tolerance1

Differences between laboratory analysis results allowable should be not more than listed in table 2.

 Table 2. %

|  |  |
| --- | --- |
| Mass fraction of palladium | Tolerance1 |
| >4.00~10.00 | 0.10 |
| >10.00~40.00 | 0.20 |
| >40.00~92.00 | 0.30 |