GB

NATIONAL STANDARD OF THE

PEOPLE'S REPUBLIC OF CHINA

ICS 77.120.99

H 68

GB/T 23277-2009

Chemical analysis methods of catalysts containing precious metals - Determination of platinum, palladium and rhodium in automobile exhaust-purifying catalysts - Spectrophotometry

贵金属催化剂化学分析方法 汽车尾气净化催化剂中铂、钯、铑量的测定 分光光度法

Issued on: January 05, 2009 **Implemented on: November 01, 2009**

Issued by: General Administration of Quality Supervision, Inspection and Quarantine;

Standardization Administration of the People's Republic of China.

Table of Contents

Chemical analysis methods of catalysts containing precious metals - Determination of platinum, palladium and rhodium in automobile exhaust-purifying catalysts - Spectrophotometry

1 Scope

This Standard specifies the determination method of platinum, palladium and rhodium in automobile exhaust-purifying catalysts.

This Standard applies to the determination of platinum, palladium and rhodium content in new and expired automobile exhaust-purifying catalysts. The determination range is 20g/t~5000g/t for Pt, Pd, 20g/t~600g/t for Rh.

2 Normative references

The following documents contain the provisions which, through reference in this Standard, become the provisions of this Standard. For dated references, their subsequent amendments (excluding corrigendum) or revisions do not apply to this Standard. However, the parties who enter into agreement based on this Standard are encouraged to investigate whether the latest versions of these documents are applicable. For undated reference documents, the latest versions apply to this Standard.

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

3 Method principle

The test material is dissolved in a Teflon sample-dissolving vessel sealed with hydrochloric acid and hydrogen peroxide under constant temperature heating. Use two-wavelength spectrophotometry of N,N'-Dibenzyldithiooxamide--potassium iodide-ascorbic acid system to determine the amount of platinum and palladium at the same time. Use potassium iodide-2-mercaptobenzothiazole-TBP-CCl_4 to extract and separate platinum and palladium. Use 2-mercaptobenzothiazole-stannous bromide extraction spectrophotometry to determine the amount of rhodium.

4 Reagents and materials

Unless otherwise specified, the reagents and utensils used in this Standard shall comply with the provisions of YS/T 371.

4.1 Hydrochloric acid (ρ1.19g/mL).

4.2 Nitric acid (ρ1.42g/mL).

4.3 Hydrochloric acid (8.4mol/L).

4.4 Mixed acid: Three unit volumes of hydrochloric acid (4.1) are mixed with one unit volume of nitric acid (4.2). Prepare as required.

4.5 Hydrogen peroxide (30%).

4.6 N,N'-Dibenzyldithiooxamide (DbDO) acetone solution (10g/L).

4.7 Potassium iodide solution (100g/L).

4.8 Ascorbic acid (Vc) solution (50g/L).

4.9 Trichloromethane.

4.10 Anhydrous sodium sulfate.

4.11 Hydrobromic acid (40%).

4.12 Stannous bromide solution: 22.5g of $SnCl_2 \cdot 2H_2O$ is dissolved in 100mL of hydrobromic acid. Prepare as required.

4.13 Sodium bromide solution (400g/L).

4.14 Acetic acid (36%).

4.15 Ammonium acetate solution (100g/L).

4.16 Sodium chloride solution (200g/L).

4.17 Ethyl acetate.

4.18 Tributyl phosphate (TBP)-carbon tetrachloride (CCl_4) mixed solution (1+1).

4.19 2-mercaptobenzothiazole (MBT) ethanol solution (0.1mol/L).

4.20 Platinum standard stock solution: Weigh 0.1000g of platinum wire (the mass fraction of Pt is not less than 99.99%) into a 200mL high beaker. Add 10mL of mixed acid. Cover the watch glass. Place on an electric hot plate to heat and dissolve at low temperature. Add 1 mL of sodium chloride solution. Evaporate to near dryness at low

temperature. Add 3mL~5mL of hydrochloric acid (4.1) to catch nitric acid twice. Add 10mL of hydrochloric acid (4.1). Transfer to a 100mL volumetric flask. Use water to dilute to the mark. Mix well. 1mL of this solution contains 1mg of platinum.

4.21 Platinum standard solution: Pipette 2.00mL of platinum standard stock solution into a 100mL volumetric flask. Add 10mL of hydrochloric acid (4.1). Use water to dilute to the mark. Mix well. 1mL of this solution contains 20μg of platinum.

4.22 Palladium standard stock solution: Weigh 0.1000g of palladium flakes (the mass fraction of Pd is not less than 99.99%) into a 200mL high beaker. Add 10mL of mixed acid. Cover the watch glass. Place on a hot plate for low temperature heating and dissolving. Add 1 mL of sodium chloride solution. Evaporate to near dryness at low temperature. Add 3mL~5mL of hydrochloric acid (4.1) to catch nitric acid twice. Add 10mL of hydrochloric acid (4.1). Transfer to a 100mL volumetric flask. Use water to dilute to the mark. Mix well. 1mL of this solution contains 1mg of palladium.

4.23 Palladium standard solution: Pipette 2.00mL of palladium standard stock solution into a 100mL volumetric flask. Add 10mL of hydrochloric acid (4.1). Use water to dilute to the mark. Mix well. 1 mL of this solution contains 20μg of palladium.

4.24 Rhodium standard stock solution: Weigh 0.1000g of sponge rhodium (Rh mass fraction is not less than 99.99%). Use 20mL of hydrochloric acid (4.1) and 4mL of hydrogen peroxide in a Teflon sample dissolution vessel with a steel protective jacket. Seal and dissolve completely at 180℃ ± 5℃. Take out the dissolution vessel. Cool to room temperature. Open the vessel. Transfer the solution to a 200mL beaker. Add 1mL of sodium chloride solution. Place on a hot plate and heat to boiling to remove chlorine gas. Transfer to a 100mL volumetric flask. Use water to dilute to the mark. Mix well. 1mL of this solution contains 1mg of rhodium.

4.25 Rhodium standard solution: Pipette 2.00mL of rhodium standard stock solution into a 100mL volumetric flask. Add 10mL of hydrochloric acid (4.1). Use water to dilute to the mark. Mix well. 1mL of this solution contains 20μg of rhodium.

4.26 Polytetrafluoroethylene sample dissolution vessel: The volume is 30mL~70mL.

4.27 Separation funnel: 60mL.

5 Instruments and equipment

UV visible dual wavelength spectrophotometer.

6 Specimen

The sample is dried in an oven at 100°C ± 5°C. After cooling, grind to about 74μm. Mix well.

5.5mol/L. Add 0.5mL of potassium iodide solution, 1mL of MBT solution. Mix well. Place 5min. Add 8mL of TBP-CCl4 mixed solution to shake and extract for 1min. After separation, discard the lower organic phase. Add 3mL of carbon tetrachloride to the aqueous phase. Shake and extract for 10s~15s. Discard the lower organic phase. Place the aqueous phase in a 50mL beaker. Add 0.5mL of hydrogen peroxide. Heat to near dry on a hot plate. Add 2mL of mixed acid. Cover the watch glass. Heat for 15min~20min. Blow and wash the watch glass. Evaporate the solution to near dryness. Add 2mL~3mL of hydrochloric acid (4.1) to catch nitric acid twice. Evaporate to dryness.

7.3.3.2 Add 2mL of hydrochloric acid (4.1), 10mL of water. Then add 0.5mL of acetic acid, 2mL of ammonium acetate solution, 4mL of sodium bromide solution, 2.5mL of stannous bromide solution, 1mL of MBT solution in sequence. Use a glass rod to stir well. Cover with a watch glass and heat to boiling on a hot plate. Immediately remove. Cool in cold water to room temperature. Transfer the solution into a separatory funnel. Use water to rinse the beaker once. Then use 8mL of ethyl acetate to wash the beaker three times. The washing solutions are combined into a separatory funnel. Shake and extract 30s. After phase separation, discard the lower aqueous phase. Use dry filter paper to absorb water droplets in the funnel neck. Put the organic phase into a 10mL dry volumetric flask. Add ethyl acetate to the mark. Mix well. Add a little anhydrous sodium sulfate powder (0.1g~0.5g). Mix well. Wait for the solution to clear. Take the reagent blank extract as a reference. Use a 10 mm absorption dish to measure the absorbance (A) at a wavelength of 476nm. Check the amount of rhodium from the working curve.

7.4 Drawing of working curve

7.4.1 Drawing of working curves of platinum and palladium: Use a graduated pipette to respectively pipette 0.50mL, 1.00mL, 1.50mL, 2.00mL, 2.50mL, 3.00mL of standard solutions of platinum and palladium into a 50mL colorimetric tube. Add water to the 10mL mark. The following is carried out according to 7.3.2. Take the amount of platinum and palladium as the abscissa, and the absorbance difference (ΔA) of platinum and palladium as the ordinate. Draw the working curve.

7.4.2 Drawing of rhodium working curve: Use a graduated pipette to respectively pipette 0mL, 0.25mL, 0.50mL, 1.00mL, 1.50mL, 2.00mL of rhodium standard solution into a 50mL beaker. Add 2mL of hydrochloric acid (4.1) and 10mL of water to each. The following measurement is carried out according to 7.3.3.2. Take the amount of rhodium as the abscissa, and the corresponding absorbance value (A) as the ordinate. Draw the working curve.

8 Calculation of analysis results

According to formula (1), calculate the mass fraction w_x of Pt, Pd and Rh. The value is expressed in (g/t):

This is an excerpt of the PDF (Some pages are marked off intentionally)

------ The End ------