

PLATINUM AGGLOMERATION BY X-RAY DIFFRACTION

UOP Method 905-91

SCOPE

This method is for determining the extent of platinum agglomeration in reforming catalysts, i.e., the fraction of the platinum in the sample that has agglomerated into crystallites larger than 3.5 nm, using X-ray diffraction. These materials generally contain between 0.2 to 0.4 mass-% platinum on predominantly *gamma*-alumina support. This method is also for qualitatively determining the alumina types present in the sample.

Catalyst samples may be either fresh, spent or regenerated, as typical levels of carbon, sulfur and moisture associated with these samples do not interfere. Reforming catalysts containing less than 2% zeolitic materials may also be analyzed. Samples where the platinum has formed an alloy with other metals such as tin, rhodium, rhenium or iron cannot be analyzed by this method.

OUTLINE OF METHOD

A sample of ground catalyst is packed into an aluminum sample holder, placed in the instrument and irradiated by Cu K α X-rays. The sample is scanned in four regions of interest. If the Pt (311) peak is present, the intensity is integrated and ratioed to the empirical value that was obtained for a sample known to be fully (100%) agglomerated. In cases where *theta*- and *alpha*-alumina are also present in the sample, the alumina types are reported and the integrated intensity of the Pt (311) peak is corrected.

APPARATUS

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

Gloves, disposable, polyethylene, Fisher Scientific, Cat. No. 11-394-100

Grinder, mixer/mill, SPEX Industries, Cat. No. 8000

Grinding balls, tungsten carbide, 11-mm (7/16-inch) diameter, SPEX Industries, Cat. No. 8004A

Mask, dust respirator, Fisher Scientific, Cat. No. 17-653

Razor blades, single-edged carbon steel, Fisher Scientific, Cat. No. 12-640

Slides, glass, plain, for sample preparation, 75 mm x 25 mm, Fisher Scientific, Cat. No. 12-550A

IT IS THE USER'S RESPONSIBILITY TO ESTABLISH APPROPRIATE PRECAUTIONARY PRACTICES AND TO DETERMINE THE APPLICABILITY OF REGULATORY LIMITATIONS PRIOR TO USE. EFFECTIVE HEALTH AND SAFETY PRACTICES ARE TO BE FOLLOWED WHEN UTILIZING THIS PROCEDURE. FAILURE TO UTILIZE THIS PROCEDURE IN THE MANNER PRESCRIBED HEREIN CAN BE HAZARDOUS. MATERIAL SAFETY DATA SHEETS (MSDS) OR EXPERIMENTAL MATERIAL SAFETY DATA SHEETS (EMSDS) FOR ALL OF THE MATERIALS USED IN THIS PROCEDURE SHOULD BE REVIEWED FOR SELECTION OF THE APPROPRIATE PERSONAL PROTECTION EQUIPMENT (PPE).
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UOP Methods are available through ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken PA 19428-2959, United States. The Methods may be obtained through the ASTM website, www.astm.org, or by contacting Customer Service at service@astm.org, 610.832.9555 FAX, or 610.832.9585 PHONE.

Spatula, stainless steel blade, Fisher Scientific, Cat. No. 14-365A

Vials, grinding, polystyrene, 30-mL capacity, with caps, SPEX Industries, Cat. Nos. 6135 and 6135C, respectively

X-ray diffractometer, fixed slit, copper tube, with standard quartz slide and aluminum sample slides

REAGENTS AND MATERIALS

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

alpha-Alumina, intensity standard, NIST, SRM 674A

Tape, labeling, 12.6-mm (0.5-inch), Fisher Scientific, Cat. No. 11-880-A

CALIBRATION OF APPARATUS

1. Prepare the diffractometer for operation according to the manufacturer's instructions.
 - Steps 2 through 7 are done once each day that analyses are performed.
2. Place the standard quartz slide that came with the instrument into the sample chamber of the diffractometer.
3. Measure the peak position and integrated intensity of the (101) peak of the standard quartz slide at $26.6^\circ 2\Theta$ (Fig. 1).
 - If there is a shift in the d-spacing of more than 0.002 nm or a drop in the intensity of more than 15% from the previous calibration, check the X-ray tube and/or the instrument alignment.
4. Set the divergence slit for 1° and the receiving slit for 0.2 mm.
5. Prepare a standard *alpha*-alumina slide following the instructions in "Sample Preparation".
 - Once a standard α -alumina slide has been prepared, it may be stored and used repeatedly.
6. Scan the α -alumina standard using the conditions shown in Table 1 (Figs. 2, 3 and 4).

Table 1

Peak	2Θ Range, degrees	Step Time, sec	Step Width, degrees
(012)	24.6 - 26.6	1	0.01
(104)	34.2 - 36.2	1	0.01
(113)	42.4 - 44.4	1	0.01

7. Integrate the intensities of the (012), (104) and (113) peaks by whatever means appropriate and record the sum as I_{std} .

SAMPLE PREPARATION

1. Grind an amount of as-received sample in excess of the volume of the hole in the aluminum sample slide, in a polystyrene vial with a tungsten carbide grinding ball for approximately 2 minutes.
 - Wear gloves and dust mask for sample grinding and packing.
2. Cover one side of the aluminum sample slide with a clean glass slide and bind firmly at each end with tape.
 - Double the ends of the tape to aid in removing later.
 - The covered side is considered the “face”.
3. Place the taped slides, glass side down, on a flat surface and pour an excess of the powdered sample into the cavity.
4. Tamp the surplus gently but thoroughly with the edge of a spatula.
 - This step is important because it causes the cavity to fill evenly.
5. Slice off the excess powder with a razor blade.
6. Add a loose layer of powder about 1.5-mm thick.
7. Press gently but firmly with the flat blade of the spatula to compress the powder.
8. Slice off the excess powder with the razor blade again and repeat a third time with a fresh layer.
9. Loosen the tape at each end and slice off any excess powder remaining on the aluminum slide.
10. Cover the back of the aluminum slide with a clean glass slide.
11. Tape two diagonally opposite corners of the aluminum slide to the back glass slide.
 - Be careful to keep the tape out of the path of the x-ray beam.
12. Turn the assembly over and remove the tape from one end of the face.
13. Hold the assembly down and by slipping the razor blade between the aluminum slide and the glass slide covering the face, lift off the glass slide without disturbing the sample.
 - This maintains a smooth surface at the face.

PROCEDURE

1. Place the slide into the sample chamber of the diffractometer.
 - Maintain the same slit settings that were used for the standard.
2. Scan the sample using the conditions shown in Table 2.

Table 2

<u>Scan</u>	<u>2Θ Range, degrees</u>	<u>Step Time, sec</u>	<u>Step Width, degrees</u>
1	20 - 90	10	0.05
2	24 - 27	50	0.04
3	49 - 54	50	0.04
4	79.5 - 83.5	250	0.04

- Longer step times are required for these scans than for the standards.
 - The use of a position sensitive detector or a rotating anode is acceptable and greatly reduces the length of the run time required to get equivalent data.
3. Inspect Scan 1 for the presence of any peaks other than those associated with γ -alumina (Fig. 5). Additional peaks indicate the presence of platinum, platinum alloy, α -alumina and/or Θ -alumina (Fig. 6).
 - Generally the sample contains γ -alumina with no crystalline platinum present.
 4. Inspect Scans 2 and 3 for the presence of α - and/or Θ -alumina (Figs. 7 and 8).
 - Both α - and Θ -alumina have peaks in the Pt region of interest. If these phases are present correction factors are applied (see "Calculations").
 5. Report the types of alumina found (see "Report").
 6. Inspect Scan 4 for the presence of crystalline platinum.
 - If no crystalline platinum is present (Fig. 9), proceed to "Report".
 7. Measure the position of the Pt (311) peak (Fig. 10).
 - If the peak maximum is outside the range of 81.2° to 81.4° (Fig. 11), the platinum has formed an alloy with another metal. Proceed to "Report".
 8. Integrate the peak areas of the crystalline platinum (311) peak at 81.3° 2 Θ (Fig.6), the α -alumina (012) peak at 25.6° 2 Θ , and the Θ -alumina peak at 50.8° 2 Θ by whatever means available. Record as R_T , R_α and R_Θ , respectively.
 - The α -alumina peak area at 52.6° 2 Θ is not included.
 - Due to the curved background in the region of the Pt (311) peak, it has been found that it is best to take the background of the peak as close to the peak as possible. A computer program that does background subtraction alleviates this problem.
 - For samples where agglomeration is indicated, the platinum content must be determined. Alternatively, the level of platinum may be known by experience with the catalyst type.

CALCULATIONS

Correct the intensity of the platinum peak at 81.3° for difference in step time using the following equation:

$$I_T = 0.20 R_T \quad (1)$$

where:

- I_T = total intensity in the Pt (311) region
- R_T = integrated intensity in the Pt (311) region
- 0.20** = step time for α - and Θ -alumina divided by step time for the sample

Calculate the intensity of the interference from α -alumina in the 79-84° region, if present, using the following equation:

$$I_{\alpha} = 0.105 R_{\alpha} \quad (2)$$

where:

I_{α} = intensity of the interfering α -alumina (220) peak

R_{α} = integrated intensity of the non-interfering α -alumina (012) peak

0.105 = constant derived from the ratio of the intensity of the (220) peak to the (012) peak in a pure α -alumina standard

Calculate the intensity of the interference from Θ -alumina in the 79-84° region, if present, using the following equation:

$$I_{\Theta} = 0.023 R_{\Theta} \quad (3)$$

where:

I_{Θ} = intensity of the interfering Θ -alumina peak

R_{Θ} = integrated intensity of the non-interfering Θ -alumina (50.8°) peak

0.023 = constant derived from the ratio of the intensity of the (79°-83°) peak to the (50.8°) peak in a pure Θ -alumina standard

Calculate the intensity of the peak in the 79-84° region due to crystalline platinum using the following equation:

$$I_s = I_T - I_{\alpha} - I_{\Theta} \quad (4)$$

where:

I_s = intensity of Pt (311) peak corrected for interferences and step time

$I_T, I_{\alpha}, I_{\Theta}$ = previously defined

Calculate the percent platinum agglomeration using the following equation:

$$\text{Pt agglomeration, \%} = \frac{297 I_s}{M I_{\text{std}}} \quad (5)$$

where:

I_s = previously defined, Eq. 4

I_{std} = sum of the integrated intensities of the standard α -alumina peaks (012), (104) and (113)

M = platinum in sample, mass-%

297 = constant derived using Eq. 6

$$297 = 100 IP \quad (6)$$

where:

I = the empirically determined ratio (3.89) of the sum of the intensities of the standard α -alumina peaks to the intensity of the platinum peak for a fully agglomerated sample

P = mass-% of platinum (0.763) of the fully agglomerated sample used in the empirical determination, g

100 = percentage constant

Alternatively, a computer program based on Eqs. 5 and 6 may be used to calculate the percent Pt agglomeration of the sample.

REPORT

From Eq. 5 of the “Calculations”, report the result as % Pt Agglomeration by X-ray Diffraction.

From Step 5 of the “Procedure”, report the alumina types found and whether each is characterized as major, minor or trace.

From Step 6 of the “Procedure”, if no crystalline platinum is found, report <1% Pt Agglomeration by X-ray Diffraction, crystallite size <3.5 nm.

From Step 7 of the “Procedure”, if the platinum has formed a metal alloy, report % Pt Agglomeration cannot be determined due to the presence of metal alloy.

PRECISION

Repeatability

Based on two tests performed by each of two analysts on four different days in one laboratory (8 tests), the within-laboratory estimated standard deviation (esd) was calculated for the percent platinum agglomeration at the levels listed in Table 3. Two tests performed in one laboratory by different analysts on different days should not differ by more than the allowable difference shown in the table at the levels listed (95% probability).

Table 3

Agglomeration, %	Within-Lab esd, %	Allowable Difference, %
10	1.02	3.5
27	1.40	4.7

Reproducibility

There is insufficient data to calculate the reproducibility of the test at this time.

TIME FOR ANALYSIS

The elapsed time is 16 hours and the labor requirement is one hour.

SUGGESTED SUPPLIERS

Fisher Scientific, 1600 W. Glenlake Ave., Itasca, IL 60143
 National Institute of Standards and Technology (NIST), Office of Standard Reference Materials,
 Gaithersburg, MD 20899
 SPEX Industries, Inc., 3880 Park Ave., Edison, NJ 08820

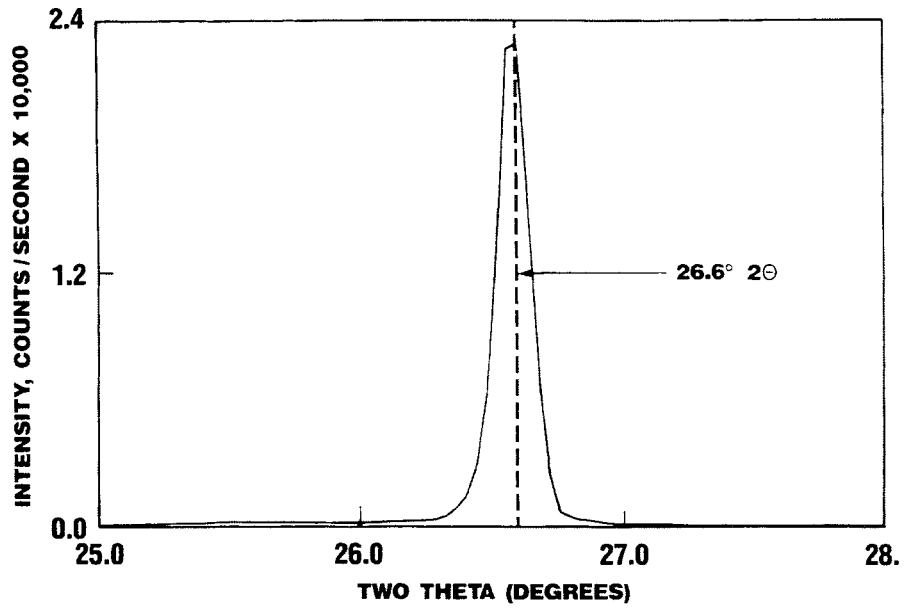


Figure 1

Standard Quartz Slide

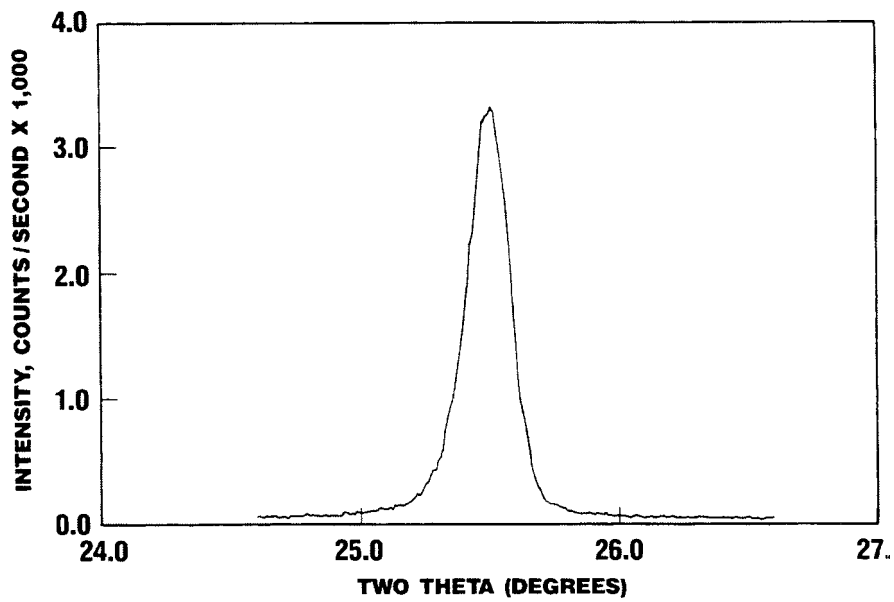


Figure 2

alpha-Alumina (012) Peak - Standard

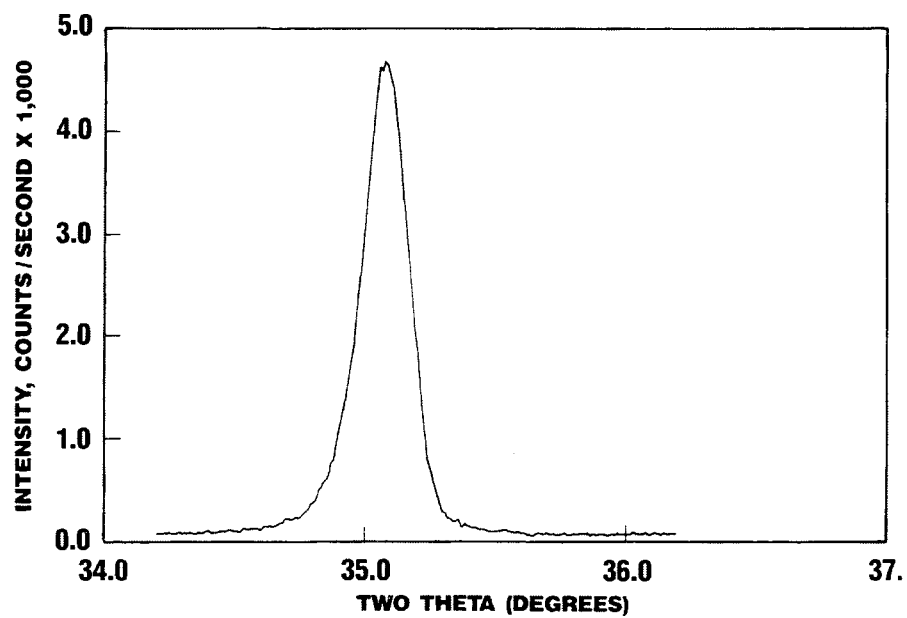


Figure 3

alpha-Alumina (104) Peak - Standard

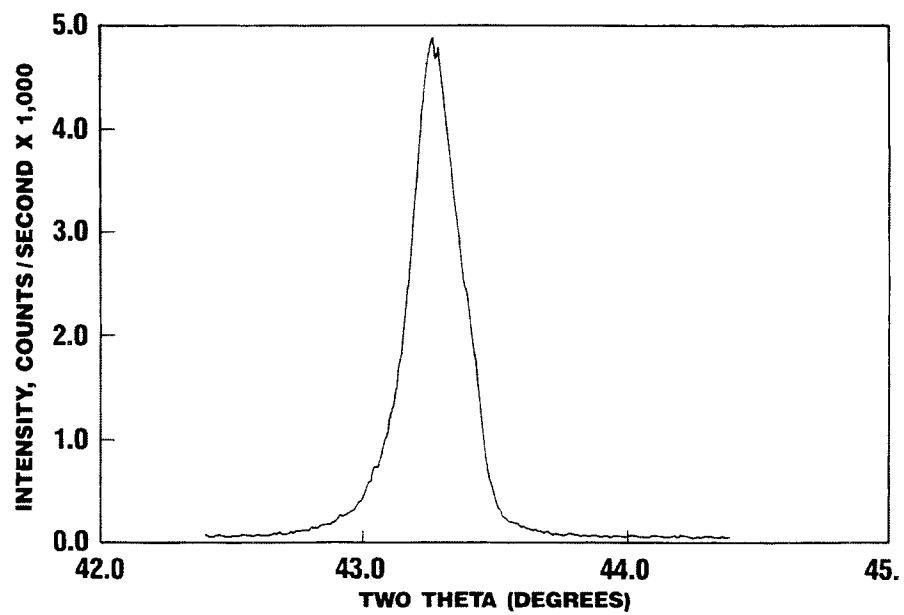


Figure 4

alpha-Alumina (113) Peak - Standard

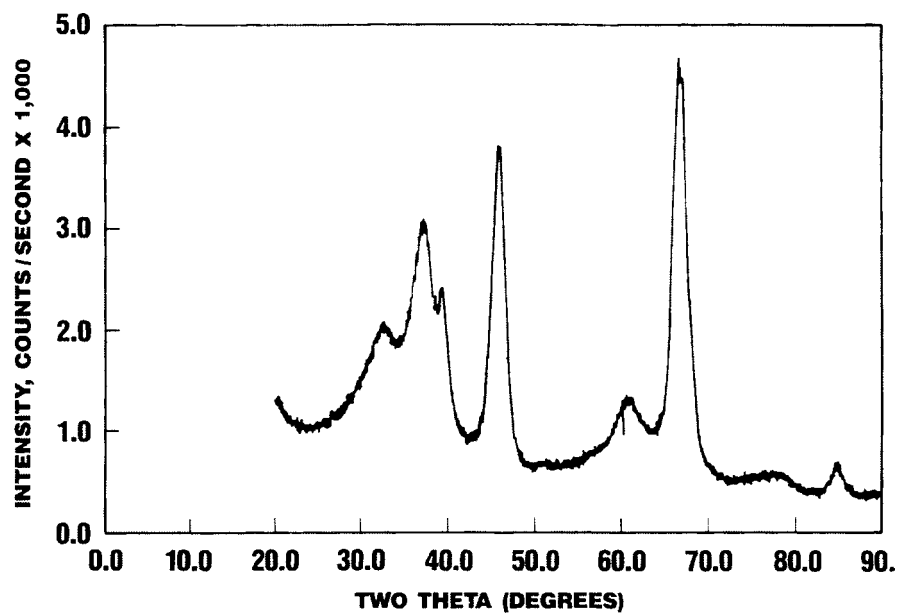


Figure 5
gamma-Alumina Only

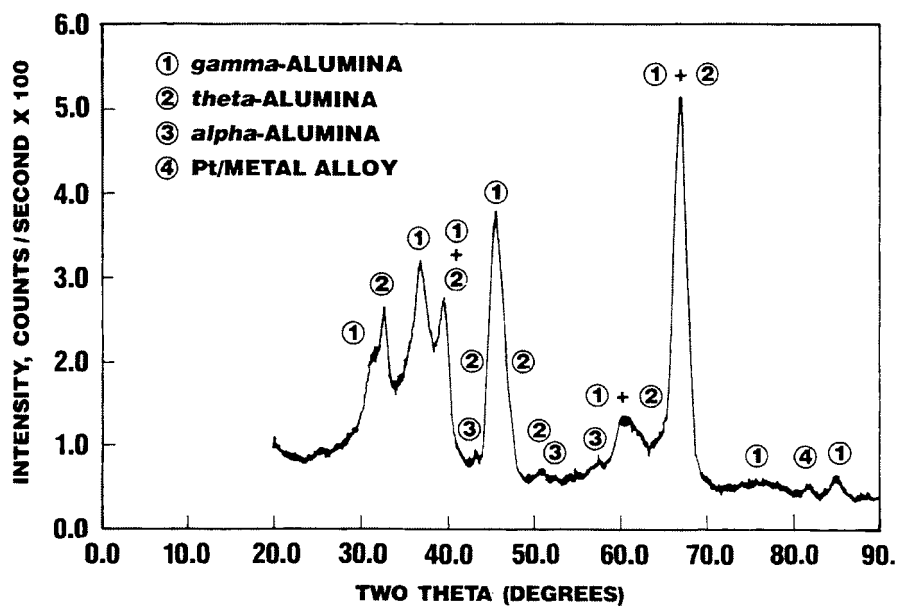


Figure 6
 α - γ -, θ -Alumina and Pt/Metal Alloy

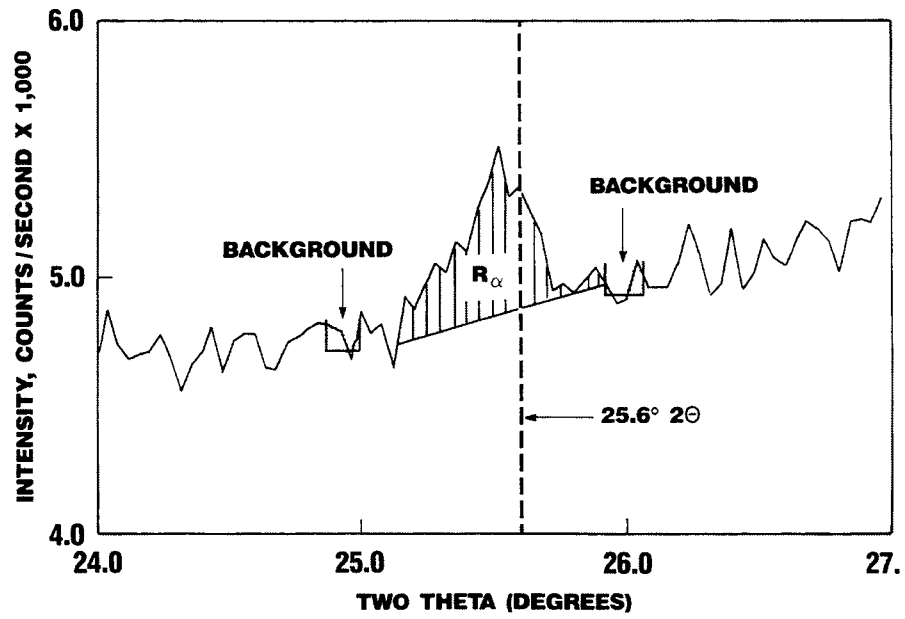


Figure 7

alpha-Alumina (012) Peak - Sample

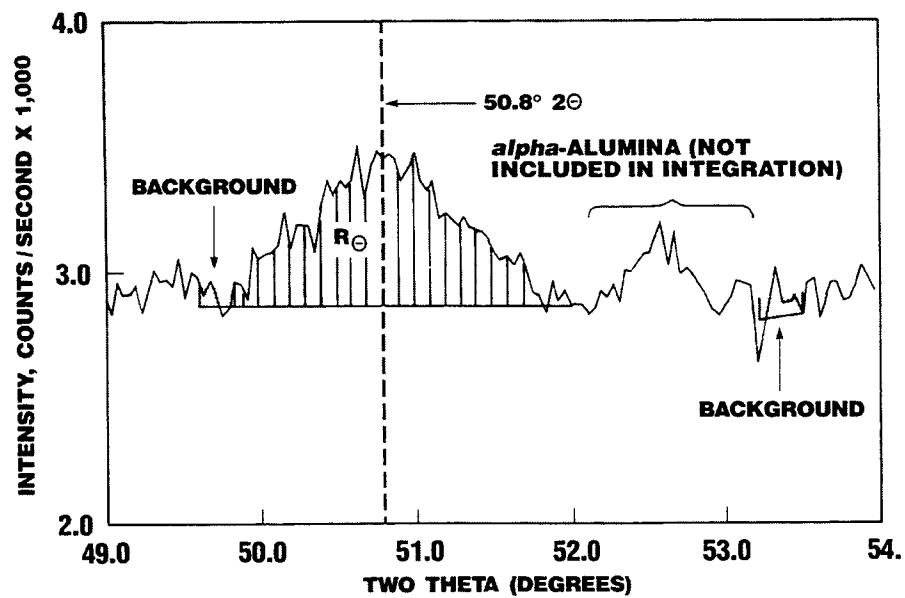


Figure 8

theta-Alumina - Sample

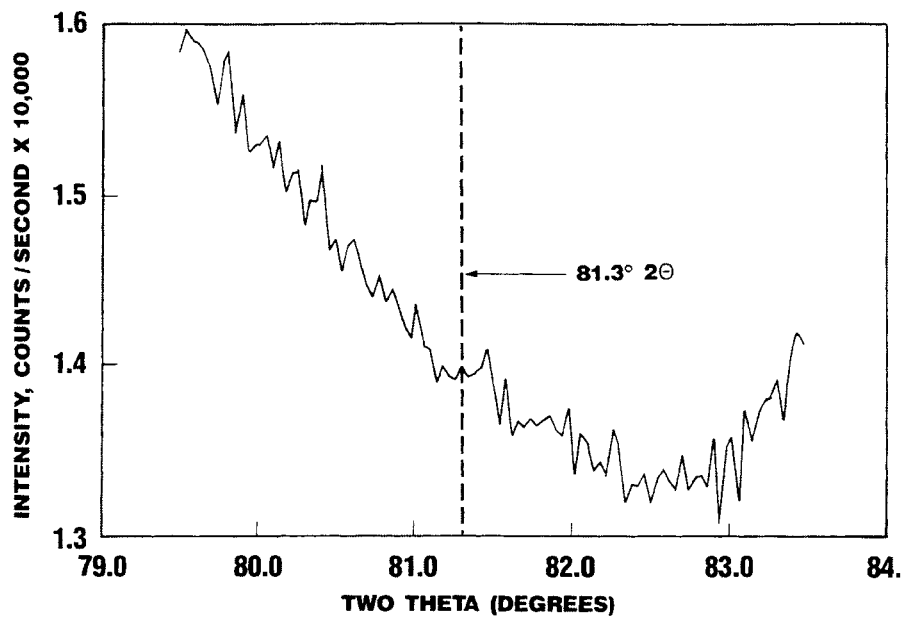


Figure 9

No Crystalline Platinum

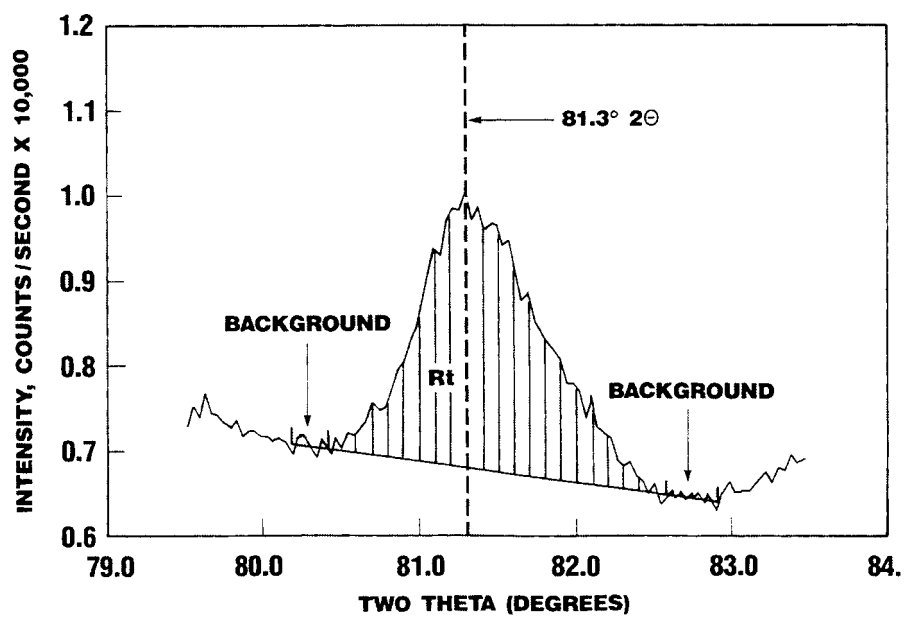


Figure 10

Platinum Crystalline Peak

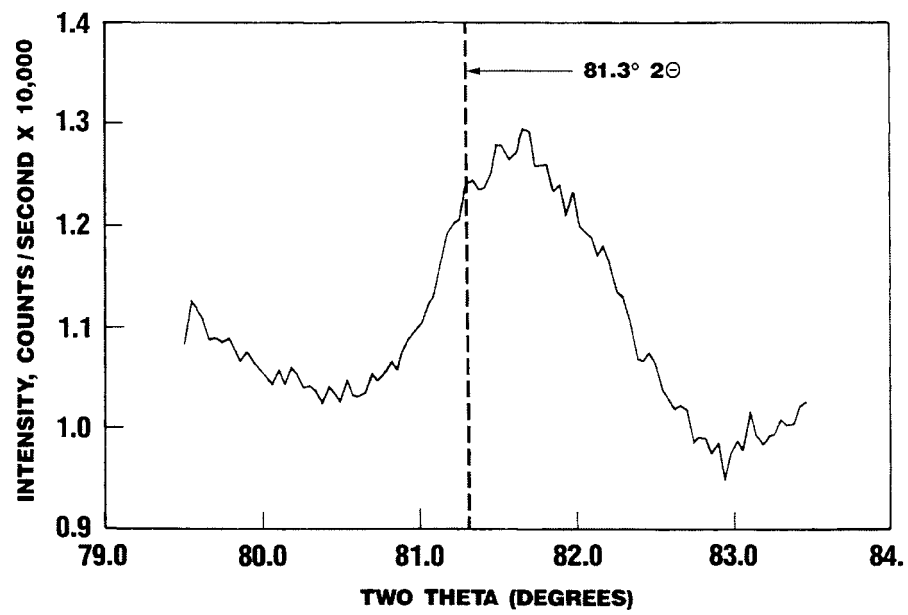


Figure 11

Platinum/Metal Alloy