



A Honeywell Company

Platinum Agglomeration by X-Ray Diffraction

UOP Method 905-08

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 can also be used 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.

Reference

UOP Method 274, "Platinum in Fresh Catalysts by Spectrophotometry," www.astm.org

UOP Method 896, "Platinum in Spent Catalyst," www.astm.org

UOP Method 999, "Precision Statements in UOP Methods," www.astm.org

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.

Blade, utility knife, round point, Runco, Cat. No. BOS11987, or other sharp, straight edge such as a single edge razor blade

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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Nonconfidential UOP Methods are available from ASTM International, 100 Barr Harbor Drive, P.O. Box C700, West Conshohocken, PA 19428-2959, USA. The UOP 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.

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

Hood, dust, with HEPA filter, VWR, Cat. No. 30140-258

Sample holders, specific to instrument used, see *Note*

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

Software, Jade (version 8.5.3 was in use at this writing), MDI Materials Data

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, using the fixed slit Bragg-Brentano geometry and either a scintillation or peltier cooled detector, Scintag/Thermo Scientific, see *Note*

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

Procedure

The analyst is expected to be familiar with general laboratory practices, the technique of x-ray diffraction, and the equipment being used.

Calibration of Apparatus

1. Set the slits to assure that the x-rays do not go outside the sample area of the holder at the angles that are being run.
 - For the Scintags, 2° and 4° slits are on the tube side and 0.5° and 0.3° slits are on the receiving slit side. This can be verified by running a fluorescent sample (typically supplied with the instrument for alignment procedures).
2. Prepare the diffractometer for operation according to the manufacturer's instructions.
 - Steps 3 through 7 are done once each day that analyses are performed.
3. Prepare a standard *alpha*-alumina sample holder or slide following the instructions in "Sample Preparation".
 - Once a standard α -alumina sample holder or slide has been prepared, it may be stored and used repeatedly.
4. Scan the α -alumina standard using the conditions shown in Table 1 (Figures 1, 2, and 3).
5. Integrate the intensities of the (012), (104) and (113) peaks by whatever means appropriate and record the sum as Istd.
6. Measure the peak position of the (113) peak of the *alpha*-alumina at 43.36° 2 θ (Figure 3).

7. If there is a shift in the d-spacing of more than 0.02 Å, as determined by Bragg's Law (Equation 1), or a drop in the intensity of more than 15% from the previous calibration, check the X-ray tube and/or the instrument alignment.

$$d = \frac{\lambda}{2 \sin \theta} \quad (1)$$

where:

d = d-spacing

λ = 1.54059 Å (CuKα₁)

θ = peak position of the (113) peak of the *alpha*-alumina at 43.36° 2θ (Figure 3)

Table 1
Scanning Conditions, α-Alumina Standard

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

Sample Preparation

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.

- Prepare the samples in a dust hood wearing gloves.
- Grind the sample to a fine powder, to 150 mesh or smaller, that packs easily and contains no grit that can be felt (through gloves).

Packing of Sample

The sample must be carefully packed into the sample holder for the best precision and accuracy. The procedure for packing a sample into the sample holder is dependent on the type of sample holder supplied with the XRD equipment. Most likely either backloading or frontloading of the sample holder will be utilized. The equipment described in the *Note* uses the frontloading procedure.

Frontloading Procedure

1. Pour some powder into the sample holder (cup), being careful not to overfill the sample holder.
2. Take a glass slide and flatten the powder into the sample holder, scrape off excess or add more powder as needed.
3. Check to see that the powder is at the same height as the edges of the sample holder. If not, add or remove powder as necessary.
4. Use glass slide to flatten surface of powder so that it is smooth.

Backloading Procedure

1. 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".

2. Place the taped slides, glass side down, on a flat surface and pour an excess of the powdered sample into the cavity.
3. Tamp the surplus gently but thoroughly with the edge of a spatula.
 - This step is important because it causes the cavity to fill evenly.
4. Slice off the excess powder with a blade.
5. Add a loose layer of powder about 1.5-mm thick.
6. Press gently but firmly with the flat blade of the spatula to compress the powder.
7. Slice off the excess powder with the blade again and repeat a third time with a fresh layer.
8. Loosen the tape at each end and slice off any excess powder remaining on the aluminum slide.
9. Cover the back of the aluminum slide with a clean glass slide.
10. 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.
11. Turn the assembly over and remove the tape from one end of the face.
12. Hold the assembly down and by slipping the 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.

Sample Analysis

1. Place the sample holder or 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.
 - 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.

Table 2
Scanning Conditions, Sample

Scan	2θ Range, degrees	Step Time, sec	Step Width, degrees
1	5 - 90	8	0.05
2	24 - 27	50	0.04
3	49 - 54	50	0.04
4	79.5 - 83.5	200	0.04

3. Inspect Scan 1 for the presence of any peaks other than those associated with γ (gamma)-alumina (Figure 4). Additional peaks indicate the presence of platinum, platinum alloy, α (alpha)-alumina and/or θ (theta)-alumina (Figure 5).
 - 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 (Figures 6 and 7).

- 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 (Figures 8 and 9), proceed to "Report".
 7. Measure the position of the Pt (311) peak (Figure 9).
 - If the peak maximum is outside the range of 81.2° to 81.4° (Figure 10), 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° 2θ (Figure 9), the α -alumina (012) peak at 25.6° 2θ (Figure 6), and the θ -alumina peak at 50.8° (Figure 7). Record as R_T , R_α and R_θ , respectively.
 - The α -alumina peak area at 52.6° 2θ is not included.
 - Due to the curved background in the region of the Pt (311) peak (Figure 9) 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 known. If the target platinum concentration is known for the sample, that may be used. Alternatively, the level of platinum may be determined by UOP Method 274, "Platinum in Fresh Catalysts by Spectrophotometry" or by UOP Method 896, "Platinum in Spent Catalyst."

Calculations

Correct the intensity of the platinum peak at 81.3° for difference in step time using Equation 2:

$$I_T = 0.25 R_T \quad (2)$$

where:

I_T = total intensity in the Pt (311) region

R_T = integrated intensity in the Pt (311) region

0.25 = 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 Equation 3:

$$I_\alpha = 0.105 R_\alpha \quad (3)$$

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 Equation 4:

$$I_\theta = 0.023 R_\theta \quad (4)$$

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 Equation 5:

$$I_s = I_T - I_\alpha - I_\theta \quad (5)$$

where:

I_s = intensity of Pt (311) peak corrected for interferences and step time
 I_T, I_α, I_θ = previously defined

Calculate the percent platinum agglomeration using Equation 6:

$$\text{Pt agglomeration, \%} = \frac{297 I_s}{M I_{\text{std}}} \quad (6)$$

where:

I_s = previously defined, Equation 4
 I_{std} = sum of the integrated intensities of the standard α -alumina peaks (012), (104) and (113), Figures 1, 2, and 3, respectively
 M = platinum in sample, mass-%
297 = constant derived using Equation 7

$$297 = 100 IP \quad (7)$$

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 Equations 6 and 7 may be used to calculate the percent Pt agglomeration of the sample.

Report

From Equation 6 of *Calculations*, report the result as an estimate of % Pt Agglomeration by X-ray Diffraction, to the nearest whole number.

From Step 5 of *Procedure, Sample Analysis*, report the alumina types found and an estimate of the amount, based upon signal intensities, e.g., major, moderate, or trace.

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

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

Note

The x-ray diffractometers used to update this method and for the precision determination are Scintag XDS 2000 (theta-theta) goniometers with Peltier-cooled detectors, fixed slit, copper tube, with standard quartz slide and aluminum sample holder. Scintag was purchased by Thermo Scientific so a comparable XRD system should be available from them. Other manufacturers such as Rigaku, Bruker, and PANalytical also could supply comparable systems. The main features that need to be duplicated are the fixed slit Bragg-Brentano geometry and either a scintillation or peltier cooled detector.

Precision

Precision statements were determined using UOP Method 999, "Precision Statements in UOP Methods."

Repeatability and Site Precision

A nested design was carried out by two analysts in the same laboratory, with each analyst performing analyses on two samples on two different instruments on two separate days, performing one analysis each day for a total of 16 analyses. Using a stepwise analysis of variance procedure, the within-day estimated standard deviations (esd) were calculated at the concentration means listed in Table 3. Two analyses performed in one laboratory by the same analyst should not differ by more than the repeatability allowable differences shown in Table 3 with 95% confidence. Two analyses performed in one laboratory by different analysts on different instruments should not differ by more than the site precision allowable differences shown in Table 3 with 95% confidence.

Table 3
Repeatability and Site Precision, Agglomeration, mass-%

	<u>Mean</u>	<u>Repeatability</u>		<u>Site Precision</u>	
		<u>Within-Day esd</u>	<u>Allowable Difference</u>	<u>Within-Lab esd</u>	<u>Allowable Difference</u>
Sample 1	5	1.6	6	2.3	10
Sample 2	23	2.7	11	2.6	14

The data in Table 3 represent short-term estimates of the repeatability of the method. When the test is run routinely, use of a control standard and a control chart is recommended to generate an estimate of long-term repeatability.

Reproducibility

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

Time for Analysis

The elapsed time is 12 hours and the labor requirement is 1.5 hours.

Suggested Suppliers

Fisher Scientific, 585 Alpha Dr., Pittsburgh, PA 15238 (412-490-8300) www.fishersci.com

MDI Materials Data, 1224 Concannon Blvd., Livermore, CA 94550 (925-373-1659)
www.materialsdata.com

National Institute of Standards and Technology, Standard Reference Materials Group, 100 Bureau Drive, Stop 2322, Gaithersburg, MD 20899-2322 (301-975-6776) www.nist.gov

Runco Office Supply, 1655 Elmhurst Road, Elk Grove Village, IL 60007 (847-437-4300)
www.runcoonline.com

SPEX CertiPrep, Inc., 203 Norcross Ave., Metuchen, NJ 08840 (732-549-7144) www.spexcsp.com

Thermo Scientific, 5225 Verona Road, Madison, WI 53711-4495 (608-276-6100)
www.thermo.com

VWR International, 1310 Goshen Parkway, West Chester, PA 19380 (610-431-1700) www.vwr.com

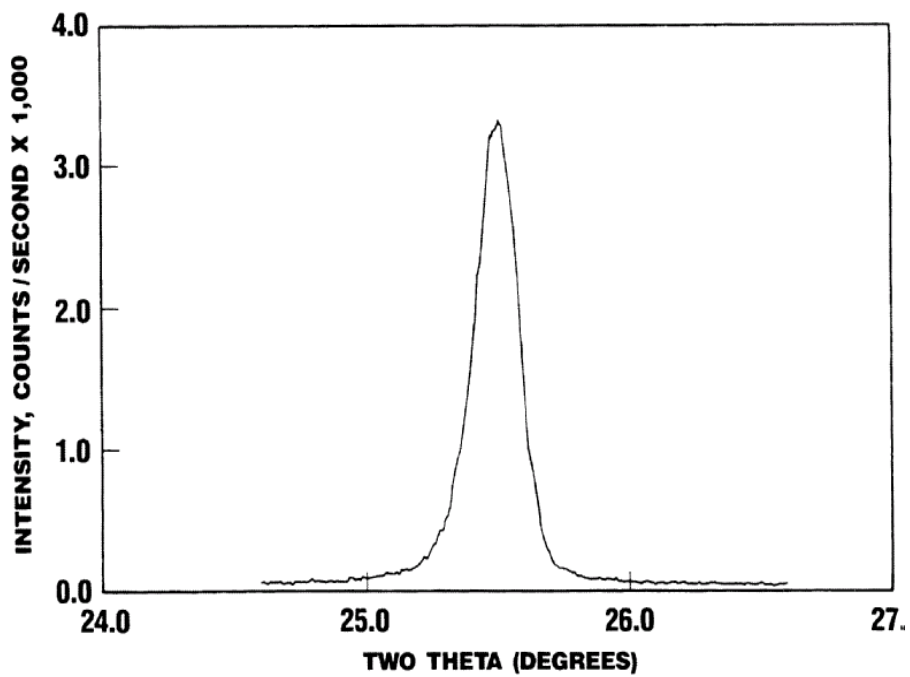


Figure 1
alpha-Alumina (012) Peak – Standard

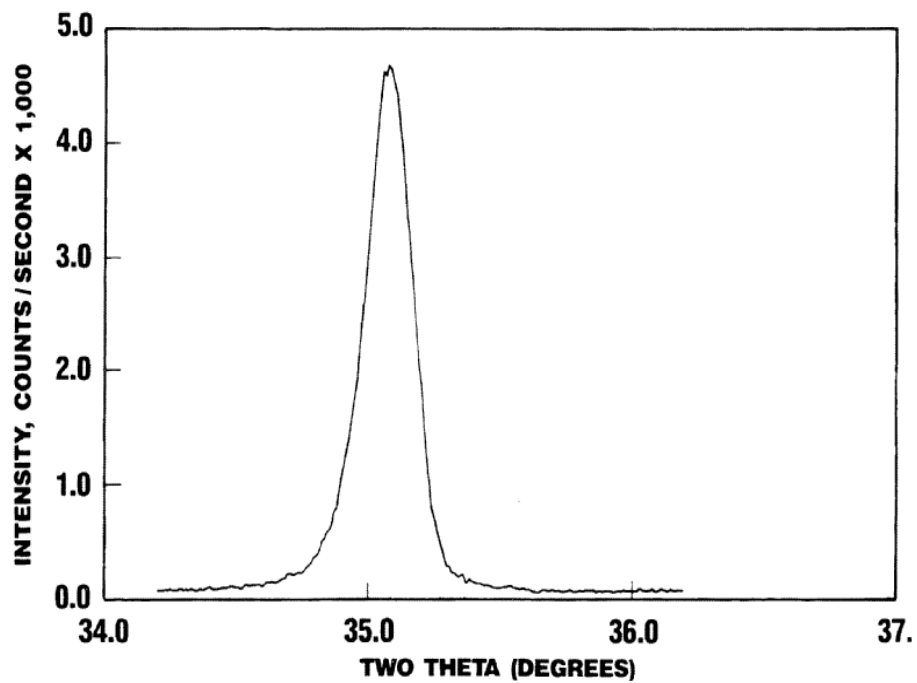


Figure 2
alpha-Alumina (104) Peak - Standard

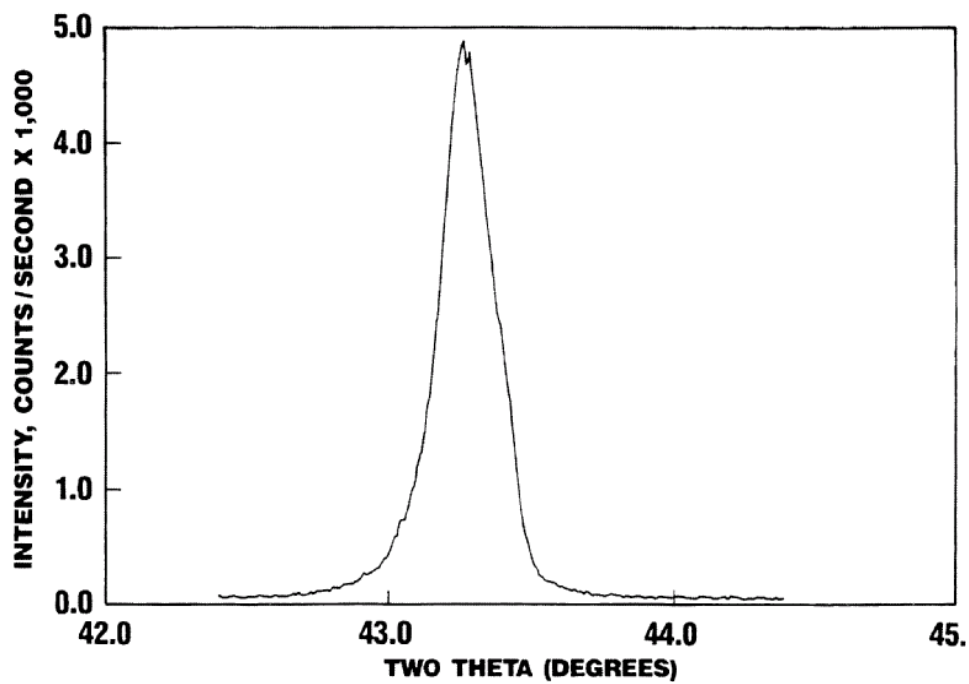


Figure 3
alpha-Alumina (113) Peak – Standard

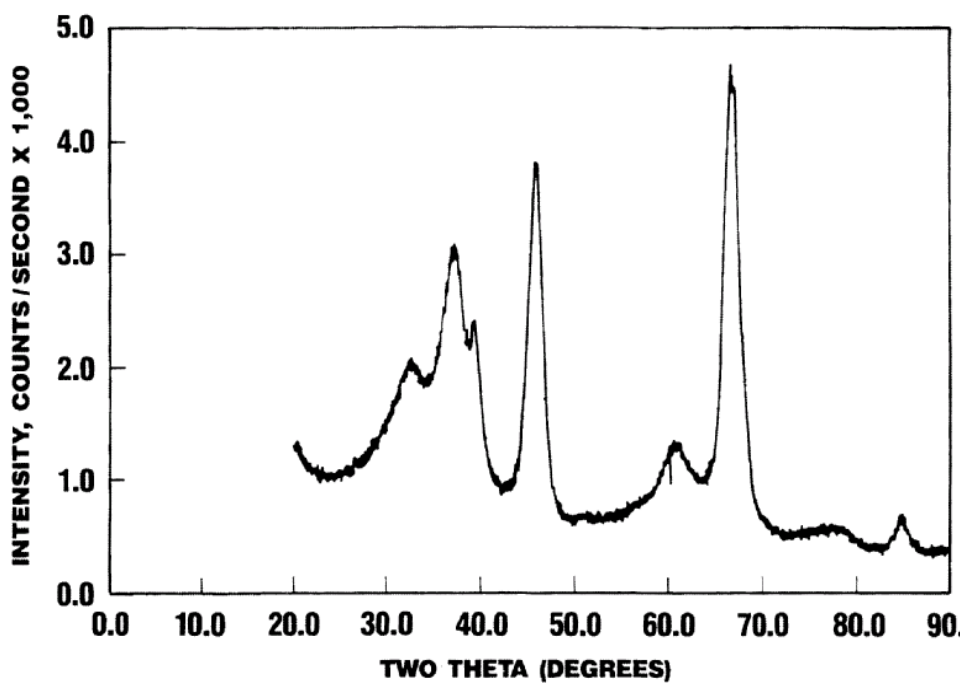


Figure 4
gamma-Alumina Only

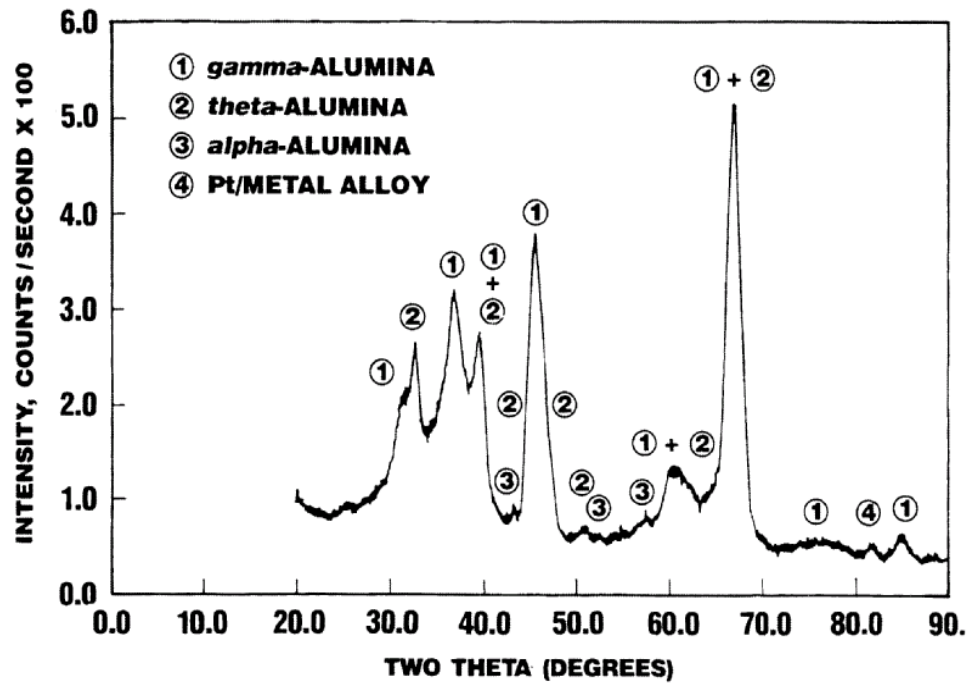


Figure 5
 α - γ -, θ -Alumina and Pt/Metal Alloy

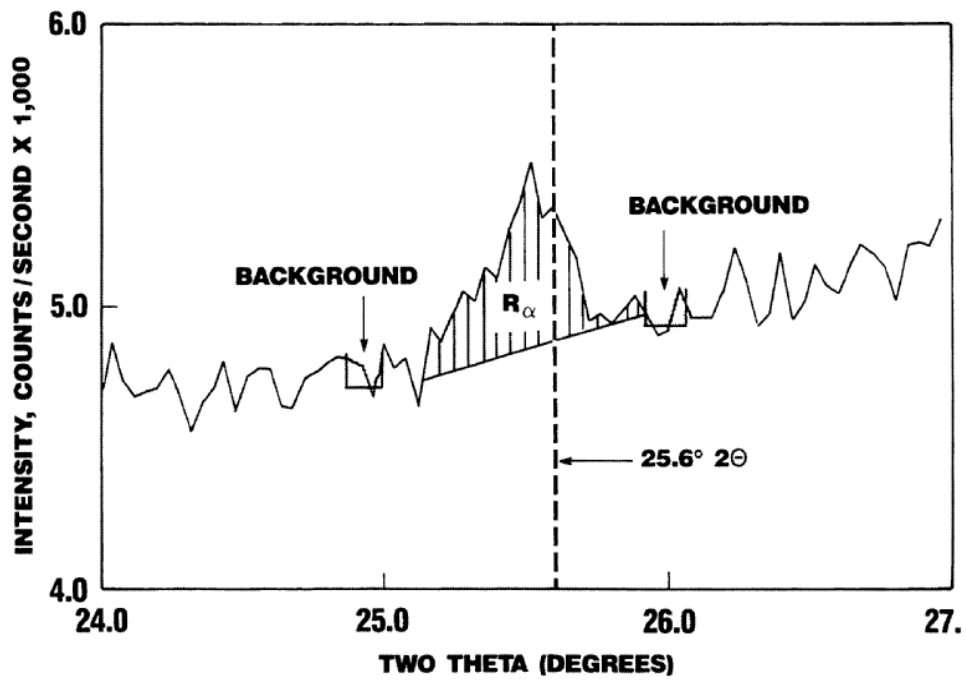


Figure 6
 α -Alumina (012) Peak - Sample

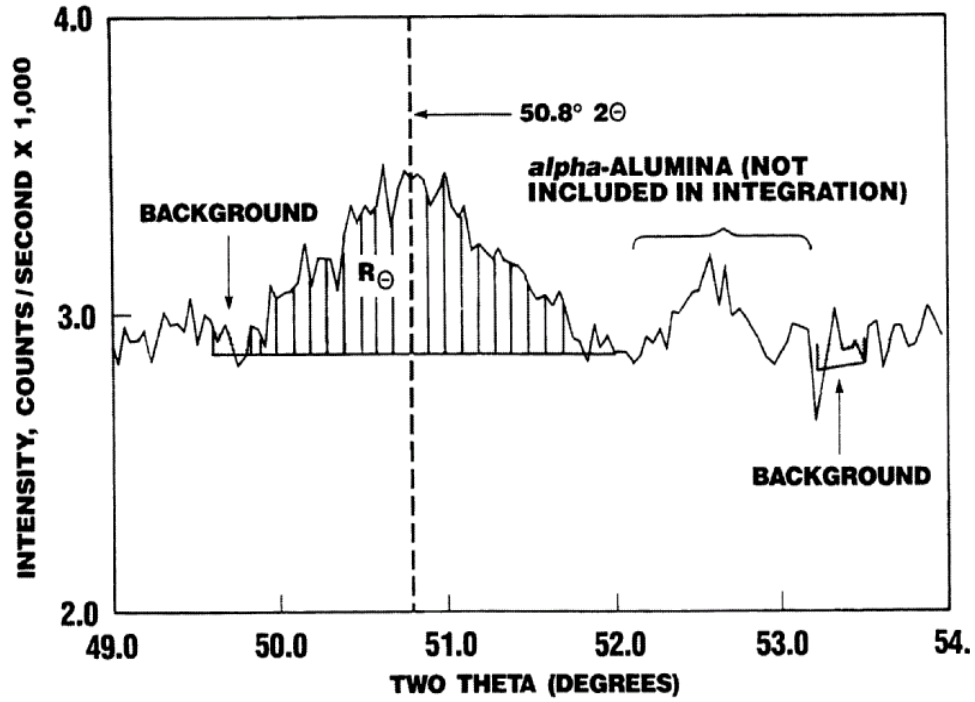


Figure 7
theta-Alumina - Sample

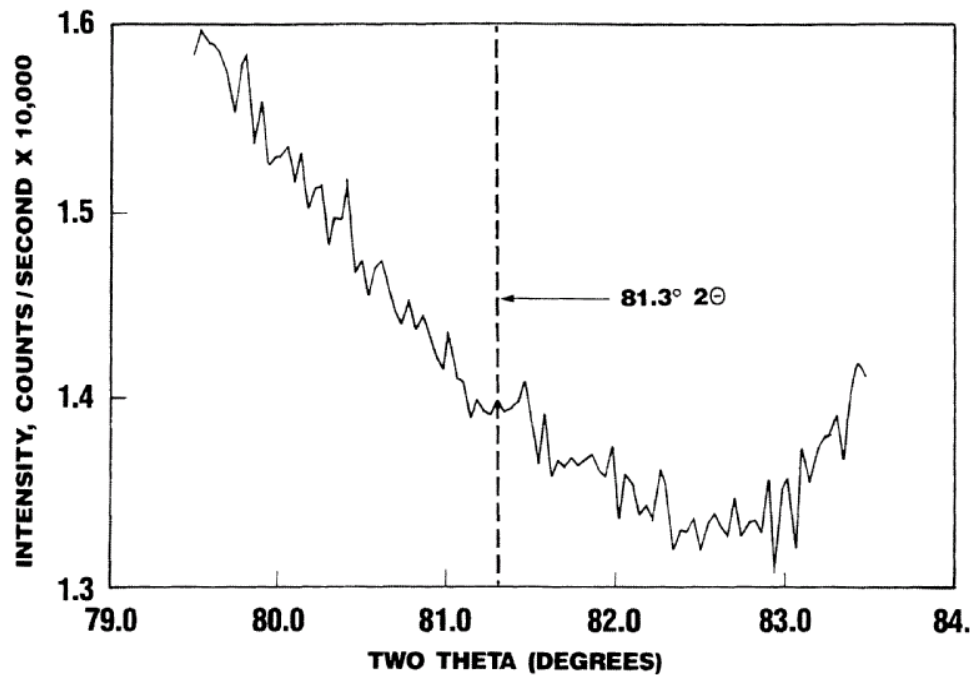


Figure 8
No Crystalline Platinum

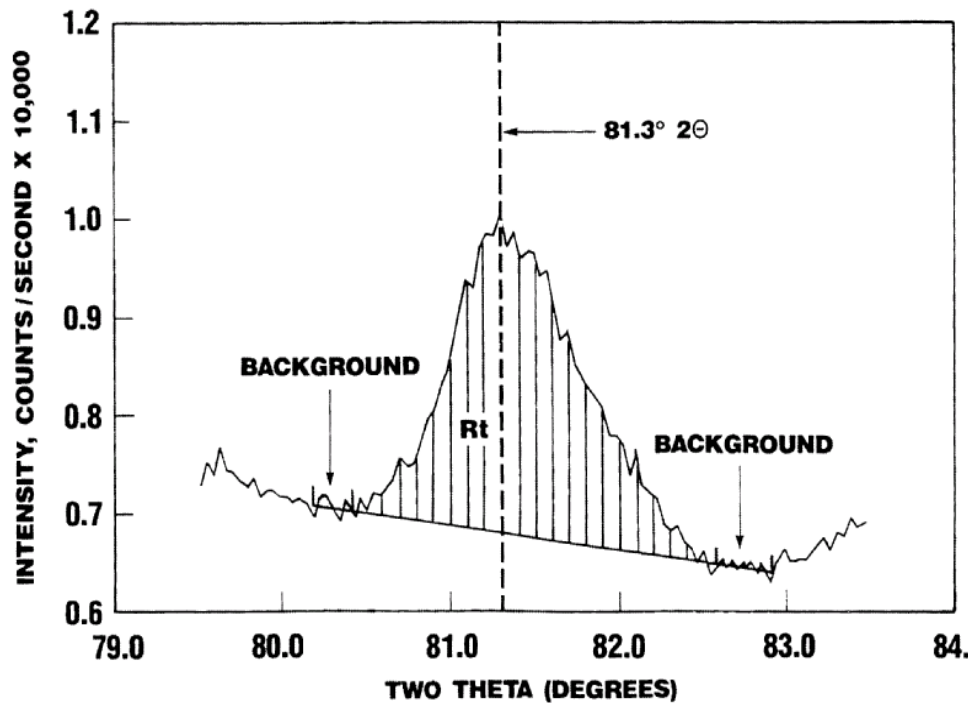


Figure 9
Platinum Crystalline Peak

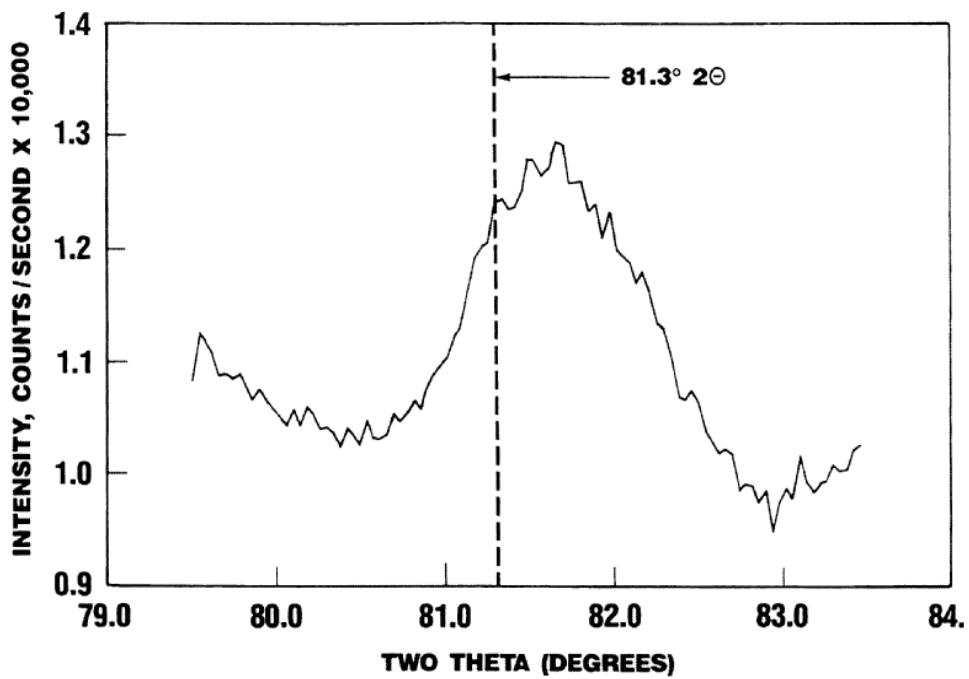


Figure 10
Platinum/Metal Alloy