

# PLATINUM DISPERSION ON PLATINUM OR PLATINUM/TIN CATALYST BY HYDROGEN-OXYGEN TITRATION

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## UOP Method 945-96

### SCOPE

This method is for determining the dispersion of alumina supported platinum (Pt) on fresh or regenerated catalyst containing Pt alone or Pt plus tin. Catalyst, such as presulfided or spent, containing sulfides, carbon, or greater than 1.5 mass-% chlorides, cannot be reliably analyzed. This method is applicable to catalyst sizes ranging from 0.29 mm (50 mesh) to 3.99 mm (5 mesh).

The results are expressed as the ratio of the number of moles of hydrogen chemisorbed to the number of moles of Pt in the catalyst. A ratio of 1.00 is defined as 100% dispersion (all the Pt atoms are available for catalysis). Values less than 1.00 may indicate crystallite growth or a surface interference. Also, the resulting  $H_2/Pt$  values can be affected by elements other than Pt on the catalyst. The Pt content of the test sample is determined by the appropriate UOP Method for the catalyst type.

### OUTLINE OF METHOD

A sample of catalyst is placed in a quartz reactor tube and reduced with hydrogen at 500°C for prereduced catalyst, or 565°C for an oxidized or regenerated catalyst. The sample is purged with helium to remove the residual hydrogen, allowed to cool to ambient temperature and then treated with air. The oxygen in the air is chemisorbed onto the catalyst, reacted (titrated) with hydrogen to form water, and then the platinum becomes available to chemisorb hydrogen. The moles of hydrogen consumed, determined using a hydrogen transfer tube and a thermal conductivity detector, are compared to the moles of platinum in the sample. The results are reported as the ratio of hydrogen adsorbed to the Pt in the sample.

### APPARATUS

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

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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The apparatus listed below is for the construction of a system capable of simultaneously analyzing two catalyst samples as shown in Fig. 1. If a low workload is expected, the construction of a single system is satisfactory, or the system can be expanded to meet heavier workloads. A single reactor system can be constructed by utilizing only one of each of the following: Sample Valve, Stream Select Valve, Detector Select Valve, 3-way Valve, Filter, Oven, Temperature Controller, Temperature Sensor and Reactor Tube. Along with these, use only the required number of fittings, toggle valves, needle valves and flow controllers.

*Balance*, readability 0.1-mg

*Barometer*, dual-scale dial type, Fisher Scientific, Cat. No. 02-404

*Clamp*, ground joint, 18A, Thomas Scientific, Cat. No. 2841-D33 (4 required)

*Detector*, thermal conductivity (TCD), gas chromatographic, EG & G Chandler Engineering, Cat. No. 70303-74

*Enclosure box*, approximately 300- x 215- x 150-mm, fabricated from metal and insulated with rock wool or similar material, having appropriate holes for tubing to connect the sample valves, HTT and TCD, which are contained in the box, to other equipment. A GC oven can also be used for this purpose.

*Filter*, 60- $\mu$ m, Dearborn Valve and Fitting, Cat. No. SS-2F-60

*Fittings*, tubing, Swagelok, available from Dearborn Valve and Fitting. Additional fittings may be required depending on the specific installation.

*Reducer*, 1/4-inch tube stub to 1/16-inch tube, Cat. No. SS-100-R-4 (4 required)

*Reducer*, 1/16-inch to 1/8-inch, Cat. No. SS-200-6-1 (14 required)

*Tee*, branch, 1/4-inch, Cat. No. SS-400-3 (2 required)

*Tee*, male branch, 1/8-inch, Cat. No. SS-200-3TTM (3 required)

*Tee*, tube, 1/8-inch, Cat. No. SS-200-3 (7 required)

*Union*, tube, 1/16-inch, Cat. No. SS-100-6 (10 required)

*Union*, tube, 1/8-inch female NPT to 1/8-inch tube, Cat. No. SS-200-7-2 (6 required)

*Flow controller*, with flow element A-110, Porter Instrument, Cat. No. VDC 1000A (8 required)

*Flowmeter*, soap film, 25 cc, Alltech Associates, Cat. No. 4043

*Gas purifier*, in-line, packed with drierite and 5A molecular sieves, Alltech, Cat. No. 8125 (4 required)

*HTT pyrometer module*, EG & G Chandler Engineering, Cat. No. 72090-22

*Hydrogen transfer tube (HTT)*, with heater, EG & G Chandler Engineering, Cat. No. 70304-51

*Integrator*, electronic, for obtaining peak areas

*Joints*, stainless steel, greaseless O-ring, 5-mm ID, threaded, Kontes Glass, Cat. NO. K-674850, construct as shown in Fig. 2

*Needle*, syringe, 22-gauge, point style 2, 50-mm length, Hamilton, Cat. No. 90122

*O-ring*, duro viton 60, Tech-Syn, Cat. No. 203

*Oven*, reactor heater, construct as shown in Fig. 3. Attach two heater half-shells together and attach a bottom to it cut from insulation board. Wire the two halves in parallel, connecting them to a power cord equipped with an end terminal compatible with the output connection on the temperature controller. Insulate the outside of the oven with a suitable material and cover the coils on the inside with high temperature bonding cement. Place the temperature sensor inside along the wall approximately 2/3 of the way down. Two ovens are required. The heater half-shells are available from Lindberg, hevi-duty, type 74-S, Cat. No. 50011.

*Reactor tubes*, construct as shown in Fig. 4, UOP

*Recorder*, 1-mV, 1-sec full-scale response

*Regulator*, air, two-stage, high purity, Matheson Gas Products, Cat. No. 3122-590

*Regulator*, helium and nitrogen, two-stage, high purity, Matheson Gas Products, Cat. No. 3122-580 (2 required)

*Regulator*, hydrogen, two-stage, high purity, Matheson Gas Products, Cat. No. 3122-350

*Sample loop*, 0.25-mL, Valco Instrument, Cat. No. SL250C6W

*Syringe*, 1.0-mL, Teflon, Luer Lock Chaney, gas-tight, Hamilton, Cat. No. 81324

*Temperature controller*, programmable, with read-out, LFE, Inotek-Pacific Indicator, Cat. No. 05-5201-5600 (2 required)

*Temperature sensor*, J-type, iron constantan, 1.6-mm (0.062-inch) diameter, 2.4-m (96-inches) long, for use with temperature controller, Durex, Cat. No. DC-6-8M2J (2 required)

*Thermometer*, total immersion, 0.1°C graduations, -1 to 51°C, Fisher Scientific, Cat. No. 15-043A

*Transformer*, variable, powerstat, 3-wire, to control heater on HTT, Wilkens-Anderson, Cat. No. 30872-01

*Tubing*, stainless steel, 3.2-mm (1/8-inch) OD, and 1.6-mm (1/16-inch) OD x 1.0-mm (0.040-inch) ID, Alltech Associates, Cat. Nos. 30103 and 30033, respectively (6 m of each required)

*Valve*, check, 35-kPa gauge (5-psig) release, Nupro, Cat. No. SS-4CP2-5 with female tubing adapter, Swagelok, Cat. No. SS-2-TA-7-4 and union tee, Swagelok, Cat. No. SS-200-3, available from Dearborn Valve and Fitting (2 of each required)

*Valve*, flow controlling, needle, Nupro, Dearborn Valve and Fitting, Cat. No. SS-2MG (2 required)

*Valve*, pressure relief, Nupro, Dearborn Valve and Fitting, Cat. No. SS-2CA4-3 (3 required)

*Valve*, sample, 6-port, EG & G Chandler Engineering, Cat. No. 72301-00 (2 required)

*Valve*, stream select, 5-port, Valco Instrument, Cat. No. CSD-4HPA (2 required)

*Valve*, switching, 4-port, side select and detector select, EG & G Chandler Engineering, Cat. No. 72300-00 (2 required)

*Valve*, toggle, Nupro, Dearborn Valve and Fitting, Cat. No. SS-OGS2 (6 required)

*Valve*, 3-way ball, stainless steel, two required, Whitey, Cat. No. SS-41XS2, available from Dearborn Valve and Fitting

## REAGENTS AND MATERIALS

Unless otherwise specified, all reagents shall conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society when such specifications are available.

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

*Acetone*, 99.5% minimum purity

*Air*, less than 2.0-ppm H<sub>2</sub>O

*Alumina*, catalyst support, spherical, UOP

*Drierite*, absorbent, indicating, Fisher Scientific, Cat. No. 07-578-3B

*Glass wool*, quartz, Alltech Associates, Cat. No. 4033

*Helium*, high purity, less than 1.0-ppm oxygen, less than 1.0-ppm water

*Hydrogen*, high purity, less than 1.0-ppm oxygen, less than 1.0-ppm water

*Leak detector*, liquid detergent, Leak-Check, Alltech Associates, Cat. No. 2025

*Molecular sieves*, Type 5A, 4-8 mesh beads, Fisher Scientific, Cat. No. M521

*Nitrogen*, high purity, less than 1.0-ppm oxygen, less than 1.0-ppm water

*Septum*, 9.5-mm (3/8-inch) diameter, Alltech Associates, Cat. No. 6516

## PREPARATION OF APPARATUS

Assemble the apparatus on a panel or grill as schematically shown in Fig. 1. Install the sample valves, hydrogen transfer tube (HTT) and detector (TCD) in an enclosure box to reduce variations in temperature. The heat given off from the HTT heater warms the enclosure box to an equilibrium temperature of 40 to 45°C. The exact temperature is not critical but should be constant. Attach the enclosure box to the panel or grill at a location that will result in short tubing connections to the other apparatus.

Use 3.2-mm (1/8-inch) OD tubing and fittings from the regulated gas sources to the flow controlling needle valves. Make the remaining connections with 1.6-mm (1/16-inch) tubing and fittings and always keep the length of the connecting tubing as short as possible. Thoroughly clean all tubing with acetone and air dry prior to using. Connect the pressure relief valves into the incoming carrier gas lines using the 1/8-inch male branch tees, after adjusting them to a 175 kPa gauge (25 psig) relief pressure setting. Set each incoming gas pressure at 140 kPa gauge (20 psig).

Modify four of the stainless steel, O-ring joints by welding a 100-mm, 8-14 threaded stud to the middle of each (see Fig. 2). These studs can be used to mount the joints to the grill or panel. Connect the joints to the rest of the system using the 1/8-inch female NPT to 1/8-inch tube union, a 1/16-inch tube to 1/8-inch tube stub reducer, and 1.6-mm (1/16-inch) tubing. Where the distance is short enough, the reducers may be joined directly to the tubing on the valves. Install the 60- $\mu$ m filters immediately following the 3-way valves (See Fig. 2) to prevent catalyst dust from entering the detector system.

Immediately upstream of the joint where the inlet of the reactor tube is to be connected, install a 1/4-inch male branch tee equipped with a septum (see Fig. 1). This is the calibration tee where aliquots of hydrogen are injected into the system during the calibration procedure. Install a check valve that is set to release at 35 kPa gauge (5 psig) to vent, just upstream of each reactor ahead of the calibration tee.

The Stream Select valves have five connections, of which three are used as stream inlets for each of the gases, and one (located in the offset position relative to the other connections) is used for the stream outlet. The fifth (another inlet) is not used and is left open.

To install the hydrogen transfer tube (HTT), connect the helium inlet line to the line from the Detector Select valve, the nitrogen inlet line to the reference side outlet of the detector, and the nitrogen outlet line to the sample inlet line of the detector. The helium outlet line is connected to vent.

All connections to vent may be made to a common vent manifold, but this must be of sufficient size to accommodate all flows without causing back pressure on any of the lines. Care must be taken to vent these flows properly as they contain hydrogen and are potentially explosive.

Connect the recorder and integrator to the detector controller at the appropriate outlet terminals, and connect the detector to the controller. The detector bridge current should be left on continuously unless there is a loss of N<sub>2</sub> flow to it. Connect the ovens to their respective temperature controllers. Insert the J-Type temperature sensors inside the ovens, near the wall (See Fig. 3) and connect them to the temperature controllers.

Connect the HTT to the pyrometer module by attaching the thermocouple wires to the pyrometer, connecting the yellow to the plus (+) side and the red to the minus (-) side. Connect the power wires to each of the terminal connections that have wires from the temperature controlling powerstat connected to them.

When the system is properly connected, and the nitrogen flow has been set, turn the HTT heater on and adjust the powerstat to maintain the HTT at  $515 \pm 5^\circ\text{C}$ . The nitrogen flow must be maintained while the HTT is at temperature. The HTT heater is to be left on continuously due to the long stabilization time required.

Check the apparatus *thoroughly* for leaks with a liquid detergent or electronic device and for proper flow patterns. Set the gas flow rates as shown in Table 1.

**Table 1**

**Gas Flow Rates**

|                                 |                   |
|---------------------------------|-------------------|
| <b>Air (Stream select)</b>      | <b>100 mL/min</b> |
| <b>Helium (Stream select)</b>   | <b>40 mL/min</b>  |
| <b>Helium (Detector select)</b> | <b>40 mL/min</b>  |
| <b>Hydrogen (Stream select)</b> | <b>100 mL/min</b> |
| <b>Hydrogen (Sample valve)</b>  | <b>100 mL/min</b> |
| <b>Nitrogen (TCD)</b>           | <b>60 mL/min</b>  |

The flow rates of the gases that flow through the Stream Select valve can be checked at the reactor tube inlet connection (from the sample valve). The flow rates of each of the other streams can be checked at the vent of the detector or valve to which they are attached. These flow rates are critical. They must be checked each day and they must be within 1% of the values shown in Table 1.

## **PROCEDURE**

### **Calibration of Hydrogen Injection Loop**

The volume of the hydrogen injection loop must be less than 0.4 mL because a larger volume will be beyond the linear range of the HTT and produce a non-linear detector response. The volume of any loop, purchased or locally fabricated, is determined using the following calibration procedure:

1. Place approximately 2 g of the alumina catalyst support spheres in a reactor tube.
2. Attach the reactor to the O-ring joints and secure the reactor with the clamps.
3. Start the helium flow through the reactor with the Stream Select valve.
4. Place the Side Select valve in the appropriate position for the side to be calibrated.
5. Set the Detector Select to connect to the detector.
  - If necessary, disable any automated injection device at this point.
6. Make a series of five replicate injections through the septum in the male branch tee, using the 1.0-mL gas sampling syringe for each given volume of hydrogen gas covering a range from 0.1 through 0.4 mL, incrementing each volume by 0.05 mL.
  - When making these injections, minimize the transfer of heat from the hands to the barrel of the syringe.
  - The gas syringe should be filled by inserting the syringe needle through the septum in a 1/4-inch male branch tee into a flowing stream of hydrogen which is going to vent.

7. Allow the detector signal to return to baseline between injections and keep the time between injections consistent.
  - All injections including the sample loop must be made on the same day.
8. Obtain a peak area for each injection.
9. Calculate the average peak area for each injection volume from the series.
  - All injections in a series must be within  $\pm 1\%$  of the average area or the series should be repeated.
10. Prepare a calibration graph by plotting the average area versus volume of hydrogen injected.
  - A typical calibration curve is shown in Fig. 5.
11. Make 5 injections of hydrogen using the hydrogen injection loop for the side being calibrated.
12. Obtain a peak area for each injection and calculate an average peak area.
13. Refer to the calibration curve and read the volume of the loop to three significant figures.
14. Repeat the entire procedure for the other loop in a dual system.

### Equipment Preconditioning

The following blank run procedure is performed on each reactor in the system each day an analysis is to be performed.

1. Set the Stream Select valve so that helium is flowing through the manifold.
2. Secure the empty reactor tube to the manifold using the ground joint clamps, making sure that the frit is on the side opposite the gas inlet.
3. Set the Stream Select valve so that hydrogen flows through the empty reactor tube for approximately 4 seconds and set the 3-way valve to vent.
4. Switch the Stream Select valve to helium flow for approximately 5 minutes. Leave the 3-way valve in the vent position.
5. Switch to air flow for  $90 \pm 2$  seconds with the 3-way valve remaining in the vent position.
6. Return to helium flow for approximately 4 seconds.
  - The system is now ready for hydrogen injection.
7. Set the Side Select valve to connect to the detector and set the Detector Select valve for flow to the detector.
8. Verify that the detector current is switched on.
9. Turn on the recorder and check for a stable baseline.

10. Set the integrator in the run mode after the baseline has stabilized.
11. Inject a series of three hydrogen aliquots using the sample valve.
12. Observe the three hydrogen injection peaks.
  - A smaller or non-existent No. 1 peak indicates that hydrogen is being absorbed by the system.

### Sample Analysis

Either a reduced or oxidized platinum only reference catalyst should be used for quality control. One or both of these references must be run routinely, e.g., twice per week when samples are being analyzed. If a consistent value for either reference is obtained that varies from the established value by more than  $\pm 0.05$ , see Note 1.

For multiple reactor systems, Steps 1 through 15 may be carried out simultaneously while Steps 16 through 24 must be performed sequentially for each reactor.

1. Set the Stream Select valve so that helium is flowing through the reactor tube.
2. Remove the reactor tube from the system and weigh the empty tube to the nearest 0.1 mg. Place approximately 1.0 g of catalyst into the reactor tube.
  - This is equivalent to approximately 3.75 mg of platinum. For catalysts with greater than or less than 0.375 mass-% Pt, adjust the sample mass accordingly. Under no circumstances should the reactor tube be filled more than 2/3 full.
  - Before a catalyst is analyzed, the concentrations of all constituents on the catalyst must be known or at least closely approximated. This includes concentrations of platinum and tin as well as halides, acids, or other electrolytes and promoters. If the as-received catalyst contains more than 1.5 mass-% halides, more than 100 mass-ppm sulfur or carbon contamination, it cannot be run by this method.
3. Attach the reactor tube to the manifold using the ground joint clamps, making sure that the frit is on the side opposite the gas inlet so there is an upflow of gas through the sample.
4. Set the Stream Select valve so that hydrogen flows through the reactor tube, and set the 3-way valve to vent.
  - The effluent is vented to prevent contamination of the transfer lines by volatilized elements.
5. Bring the oven up into position around the reactor tube using adequate support.
6. Cover the open area around the top of the oven with a quartz glass wool pad or another insulation.
7. Begin temperature programming of the oven from ambient temperature to  $200 \pm 5^\circ\text{C}$  at  $15^\circ\text{C}/\text{min}$  and hold at  $200^\circ\text{C}$  for two minutes.
8. Increase the oven temperature from  $200^\circ\text{C}$  to the maximum desired temperature ( $500 \pm 5^\circ\text{C}$  for prereduced and  $565 \pm 5^\circ\text{C}$  for oxidized or regenerated catalyst) at a rate of  $20^\circ\text{C}$  per minute.

9. Set the temperature programmer on HOLD, when the maximum temperature is reached, and maintain the catalyst under hydrogen flow at this temperature.
  - Pre-reduced catalysts are maintained at this temperature for a minimum of 45 minutes under hydrogen. Catalysts that have not been pre-reduced require a minimum hold of 55 minutes under hydrogen.
10. Switch the Stream Select valve to helium flow after the reduction period is completed while the oven is still at temperature. Leave the 3-way valve in the vent position.
  - Make sure that there is always a hydrogen or helium flow through the reactor tube when it is at elevated temperature since the introduction of air during the heating process will cause an erroneous analysis.
11. Purge the sample with helium for five minutes.
12. Turn off the heater and remove the oven.
13. Set the 3-way valve so the helium flows to the Side Select valve and the Side Select valve is set to vent.
14. Allow the reactor tube and catalyst to cool to room temperature and then switch to air flow for  $90 \pm 2$  seconds.
15. Return to helium flow.
  - The catalyst is now ready for hydrogen titration.
16. Set the Side Select valve to connect to the detector and set the Detector Select valve for flow to the detector.
17. Verify that the detector current is switched on.
18. Turn on the recorder, and check for a stable baseline.
19. Set the integrator in run mode after the baseline has stabilized.
20. Inject a series of eleven hydrogen aliquots using the sample valve.
  - Sufficient time must be allowed between injections for the detector response to return to baseline.
  - The injections may be automated to provide precise timing between injections and consistent injection volumes. This can be accomplished by adding appropriate valve activators and the proper timer controllers. Some integrators also have valve control capacity.
21. Obtain peak areas for each injection.
  - The first injection is often completely chemisorbed and in this case no peak area will be obtained (see Fig. 6).
22. Record the room temperature and barometric pressure from the thermometer and barometer, respectively.

23. After the analysis is complete, remove the reactor tube containing the sample and weigh it to the nearest 0.1 mg.
24. Determine the sample mass by subtracting the reactor mass (Step 2) from the final mass (Step 23).

## CALCULATIONS

Calculate the micromoles of hydrogen in each sample loop injection to the nearest 0.01 as follows:

$$S = \frac{10^6 P V}{(62.36)(10^3) T} \quad (1)$$

where:

- P** = barometric pressure, mm Hg
- S** = H<sub>2</sub> contained in loop, micromoles
- T** = temperature in °K (°C + 273)
- V** = volume of loop, mL
- 62.36** = molar gas constant, liter mm Hg/mole K
- 10<sup>3</sup>** = factor to convert mL to L
- 10<sup>6</sup>** = factor to convert moles to micromoles

Average the areas of the last five peaks of the series of eleven. Compare the area for the sixth peak to the average area of the last five peaks. If it is greater than 97% of the average, recalculate the average including this area, i.e., obtain an average of the last six peaks. If it is less than 97% of the average, do not include it in the average but use it in the same manner as the first five peaks in Eq. 2. Calculate the number of micromoles of H<sub>2</sub> chemisorbed to three significant figures as follows:

$$A = \frac{[(B - C_1) + (B - C_2) + (B - C_3) + (B - C_4) + (B - C_5)]S}{B} \quad (2)$$

where:

- A** = total micromoles of H<sub>2</sub> chemisorbed by the catalyst
- B** = average peak area of last five peaks
- C<sub>1-5</sub>** = peak area of first, second, third, fourth and fifth peaks, respectively
- S** = previously defined, Eq. 1

Calculate the number of micromoles of platinum in the sample to three significant figures using the following equation:

$$D = \frac{10^6 WR}{(195)(10^2)} \quad (3)$$

where:

- D** = platinum on catalyst, micromoles (see Note 2)
- R** = Pt in the catalyst sample, mass-%
- W** = mass of catalyst analyzed, g
- 195** = atomic mass of platinum, g/mole
- 10<sup>2</sup>** = factor to convert % to a decimal
- 10<sup>6</sup>** = factor to convert moles to micromoles

Calculate the hydrogen to platinum ratio to the nearest 0.01 using the following equation:

$$\text{H}_2/\text{Pt} = \frac{\text{A}}{\text{D}} \quad (4)$$

where:

- A** = previously defined, Eq. 2
- D** = previously defined, Eq. 3
- H<sub>2</sub>/Pt** = hydrogen-to-platinum ratio

## INTERPRETATION OF RESULTS

This direct ratio is indicative of the dispersion of the platinum on the catalyst. For a catalyst containing only platinum, a H<sub>2</sub>/Pt ratio of 1.00 is arbitrarily equated to 100% dispersion (all Pt atoms are available for catalysis). A lower value can indicate poorer dispersion (crystallite growth), surface interference or other elemental interference.

## REPORT

Report the calculated H<sub>2</sub>/Pt value and add the following statement for all catalyst:

“H<sub>2</sub>/Pt values can be affected by a variety of sample contaminants, such as high levels of Fe. Samples containing levels of carbon or sulfur in excess of 0.01 mass-% cannot be reliably analyzed, and reported values may be low due to these interfering contaminants.”

## NOTE

1. If a consistent value for either the reduced reference or for the oxidized reference is obtained that varies from the established value by more than  $\pm 0.05$ , the apparatus should be checked for the following: leaks, proper flow rates, HTT operating temperature and back pressure, or head pressure on the sample loop. The analytical procedure should also be checked out. If no discrepancies can be found in any of these areas, then the HTT should be checked for leaks. This can be done by placing an empty reactor tube on the manifold. Select the appropriate side and switch the detector into the system. Turn on the recorder and check that the detector is on. Select, alternatively, air and then helium with the Stream Select valve. Watch the baseline on the recorder. If it changes as the valve is switched, up for helium and down for air, there is a leak in the HTT and the tube must be replaced.

2. The calculated platinum concentration may be biased slightly because the sample in this method is heated to 500 or 565°C, whereas a LOI is obtained at 900°C. This difference is not considered to have a significant effect on the H<sub>2</sub>/Pt results.

## PRECISION

### Repeatability

Based on two tests performed by each of two analysts on each of two different days (8 tests per lab) and using data collected from each of 3 laboratories, the within-laboratory estimated standard deviations (esd) were calculated at the hydrogen-to-platinum ratios (H<sub>2</sub>/Pt) for the catalysts shown in Table 2. Two tests performed in the one laboratory by different analysts on different days should not differ by more than the allowable differences shown (95% probability).

### Reproducibility

The between laboratory estimated standard deviations (esd) were calculated for the H<sub>2</sub>/Pt levels shown in Table 2. Two tests performed in different laboratories by different analysts, on different days, should not differ by more than the allowable differences shown (95% probability).

**Table 2**

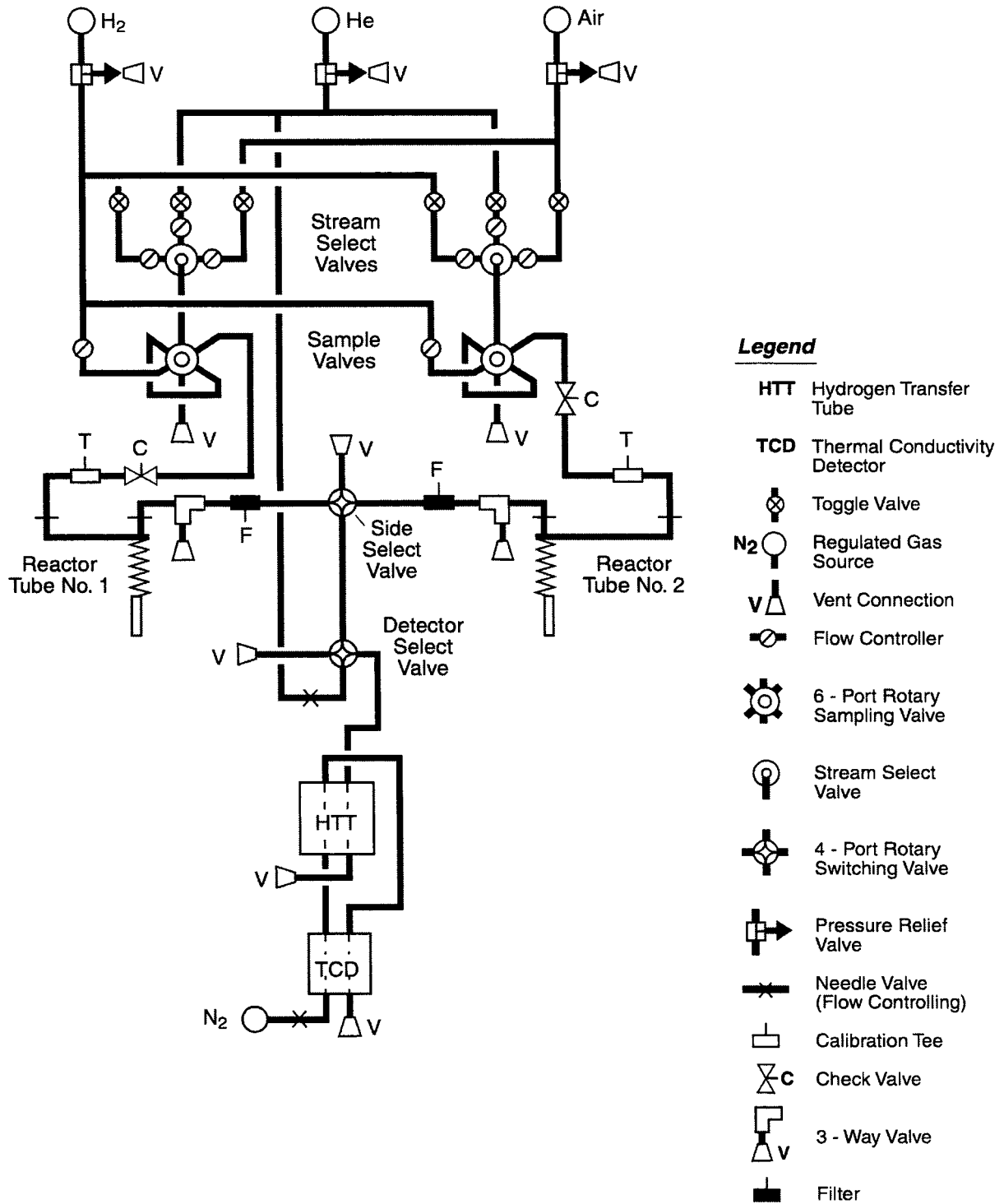
| <b>Catalyst</b>                     | <b>H<sub>2</sub>/Pt</b> | <b>Repeatability</b>      |                                 | <b>Reproducibility</b>      |                                 |
|-------------------------------------|-------------------------|---------------------------|---------------------------------|-----------------------------|---------------------------------|
|                                     |                         | <b>Within-Lab<br/>esd</b> | <b>Allowable<br/>Difference</b> | <b>Between-<br/>Lab esd</b> | <b>Allowable<br/>Difference</b> |
| <b>Platinum Only<br/>(Reduced)</b>  | <b>0.93</b>             | <b>0.011</b>              | <b>0.03</b>                     | <b>0.011</b>                | <b>0.07</b>                     |
| <b>Platinum Only<br/>(Oxidized)</b> | <b>0.91</b>             | <b>0.017</b>              | <b>0.05</b>                     | <b>0.026</b>                | <b>0.16</b>                     |

## TIME FOR ANALYSIS

The elapsed time for one analysis of a pre-reduced catalyst is 2 hours. The elapsed time for an oxidized or regenerated catalyst is 2.5 hours. In either case, the labor requirement is 0.5 hour.

## **SUGGESTED SUPPLIERS**

Alltech Associates, Inc., 2051 Waukegan Rd., Deerfield, IL 60015 (847-948-8600)  
Dearborn Valve and Fitting Co., 1540 N. Old Rand Rd., Wauconda, IL 60084 (847-526-6900)  
Durex, 190 Detroit St., Cary, IL 60013 (847-639-5600)  
EG & G Chandler Engineering, 7707 E. 38th St., Tulsa, OK 74145 (918-250-7200)  
Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA 15219 (412-562-8300)  
Hamilton Co., P.O. Box 10030, Reno, NV 89502 (702-786-7077)  
Inotek-Pacific Indicator, 5320 East Ave., Countryside, IL 60525 (708-352-3500)  
Kontes Glass, P.O. Box 729, Vineland, NJ 08360 (609-692-8500)  
Lindberg, a Unit of General Signal, 304 Hart St., Watertown, WI 53094 (414-261-7000)  
Matheson Gas Products, Inc., P.O. Box 96, Joliet, IL 60434 (815-727-4848)  
Porter Instrument Co., Township Line Rd., Hatfield, PA 19440 (215-723-4000)  
Tech-Syn Corp., 225 E. Prospect Ave., Mt. Prospect, IL 60056 (847-774-1600)  
Thomas Scientific, P.O. Box 99, Swedesboro, NJ 08085 (609-467-2000)  
UOP, Process Information and Control, 25 E. Algonquin Rd., Des Plaines, IL 60017-5017 (847-391-2529)  
Valco Instruments Co., P.O. Box 55603, Houston, TX 77255 (713-688-9345)  
Wilkens-Anderson Co., 4525 W. Division St., Chicago, IL 60651 (312-384-4433)



**Figure 1**  
Schematic System

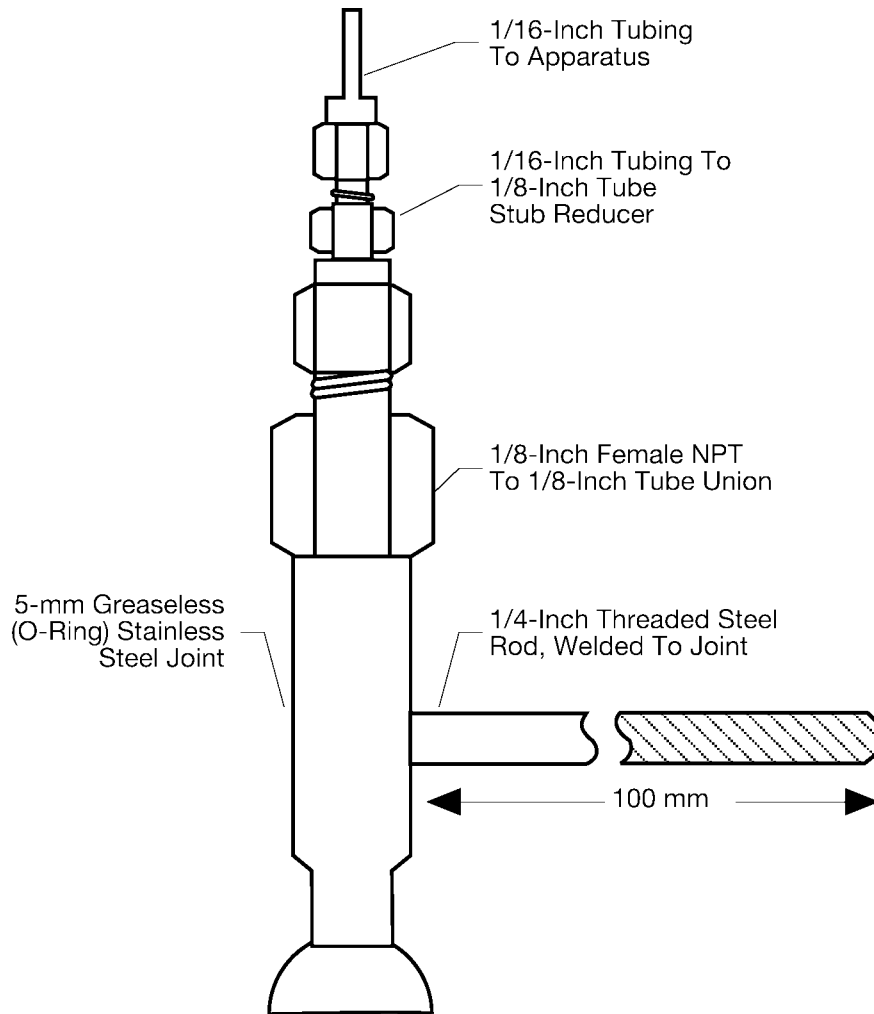


Figure 2  
Greaseless Joint Modification  
and Construction

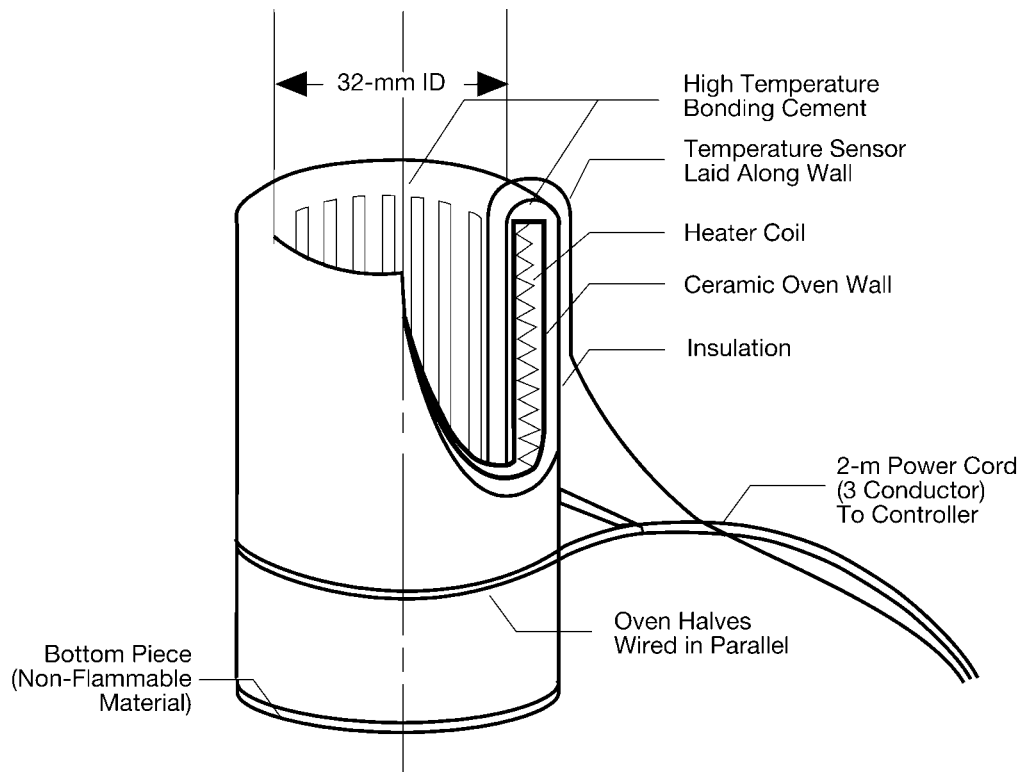


Figure 3  
Reactor Heater Oven

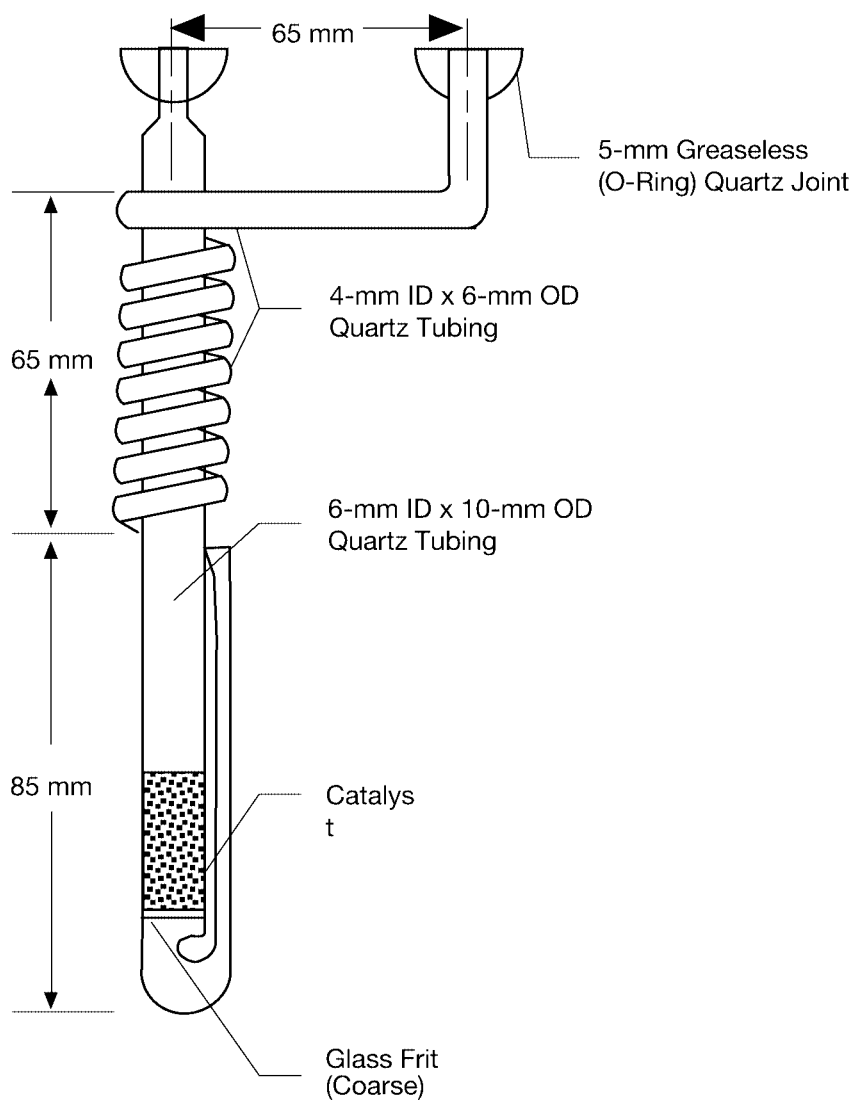


Figure 4  
Reactor Tube

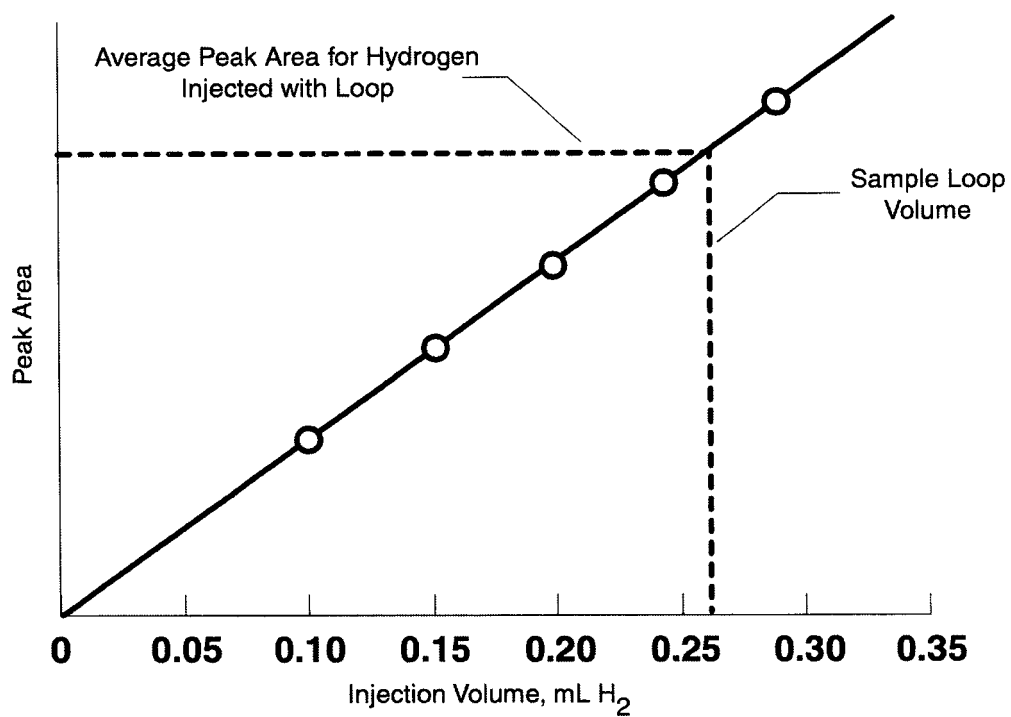


Figure 5

Typical Calibration Curve

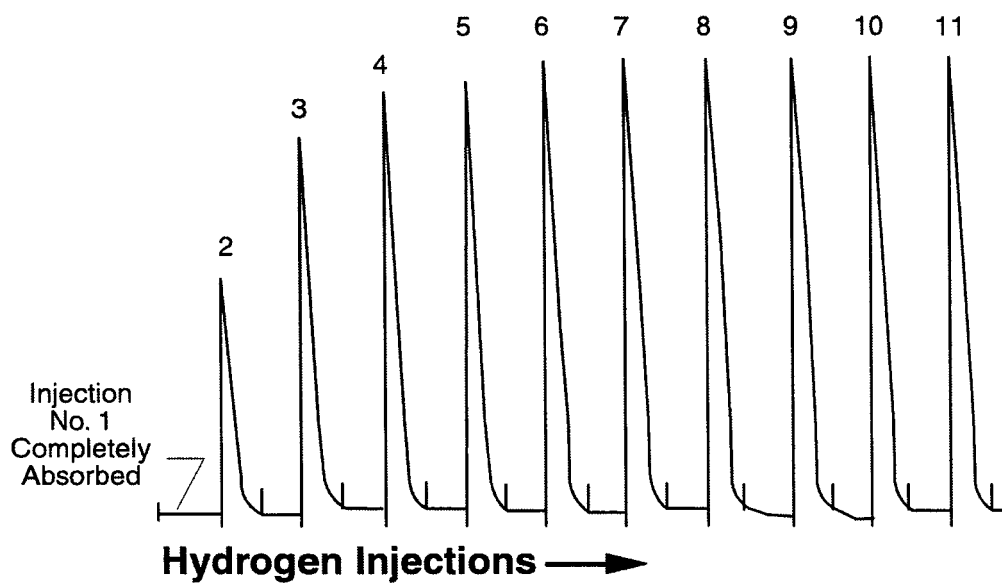


Figure 6

Typical Chromatogram