

PLATINUM IN SPENT CATALYST

UOP Method 896-93

SCOPE

This method is for determining platinum in spent catalysts or catalyst residues at concentrations from approximately 0.05 to 1.0 mass-% by spectrophotometry. The method is applicable to catalysts that may range from *gamma*- or *alpha*-alumina to pure silica, aluminum silicates, corderite, mullite and cristobalite, etc. Catalyst residues containing high concentrations of barium sulfate cannot be analyzed.

OUTLINE OF THE METHOD

An unground, weighed representative sample of the spent catalyst is ignited at 900°C by a specified procedure to remove moisture, volatile matter and carbon. After cooling, the catalyst is ground in a specified fashion.

Two procedures are given for the dissolution of the catalyst samples. Method A applies to catalysts that are composed of alumina only. Method B can be applied to any sample but is specifically for samples containing silica. It requires quartz glassware and the use of hydrofluoric acid.

After dissolution, a weighed aliquot of the resultant solution is treated with stannous chloride to form a yellow colored complex. A portion of the solution is extracted with isoamyl acetate to remove the platinum-tin color, leaving other colored ions and impurities in the aqueous phase. Spectrophotometric measurements are made of the original and extracted sample solutions at 403 nm. The difference in absorbance is attributable to the platinum content.

The concentration of the platinum is determined by comparing the difference in absorbance to a calibration curve prepared from standard platinum solutions. The platinum content of the catalyst is calculated on a volatile-free basis at 900°C.

APPARATUS

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

Balance, electronic, readability 0.1-mg

Balance, electronic, top loading, readability 0.01-g

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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Beaker, Berzelius, tall form, 300-mL, calibrated 25- to 250-mL, with spout, borosilicate glass, Fisher Scientific, Cat. No. 02-546C. Each beaker must be marked with an identification number.

Beaker, quartz-Pyrobeaker, flared, with pour spout, calibrated 50- to 200-mL, 64-mm (2.5-inch) ID × 112-mm (4.41-inch) high, 250-mL volume, Pyromatics, Cat. No. PSC, Part No. 7205-Pt77. Before use, weigh new beakers to the nearest 0.1 g and inscribe the mass and an identification number onto the beakers using a tungsten carbide scribe. Silica containing catalysts require the use of HF, which will cause chemical attack of the wetted quartz surface. Therefore, the beaker must never be used for more than 8 HF digestions in Method B, or to a maximum mass loss of 45 g.

Beakers, borosilicate glass, 50-, 250-, and 400-mL, Fisher Scientific, Cat. Nos. 02-540G, K and L, respectively

Bottle, narrow mouth, round, amber glass, 237-mL, with molded plastic conical, polyethylene-lined cap, Fisher Scientific, Cat. No. 03-320-6C

Bottle, reagent, borosilicate glass, with stopper, 1000-mL, Fisher Scientific, Cat. No. 02-940E

Bottle, washing, polyethylene, 500-mL, Fisher Scientific, Cat. No. 03-409-10E

Brush, scrubbing

Buret, weighing, 10-mL, Kimble Science Products, Cat. No. 17200F-10

Calculator, or computer, capable of least squares analysis

Cells, spectrophotometric, 10-mm path length, near-UV glass, rectangular, sold as a set of two matched, although only one is required, Fisher Scientific, Cat. No. 14-385-910A. Alternatively, a stationary flow cell may be used (see Note 1).

Crucible, low, wide-form, porcelain, 30-mL, with cover, Fisher Scientific, Cat. Nos. 07-955E and 07-970G, respectively. Each crucible must be inscribed with an identification number using a tungsten carbide scribe or if preferred, Coors ceramic marking ink.

Cylinders, graduated, plastic, polymethylpentene (PMP), 25-, 50-, 100- and 500-mL, Fisher Scientific, Cat. Nos. 08-572-5B, C, D and F, respectively

Desiccator, with plate, Fisher Scientific, Cat. Nos. 08-631B and 08-641D, respectively

Dish, Vycor, 45-mL, Fisher Scientific, Cat. No. 08-708A. Each dish must be inscribed with an identification number using a tungsten carbide scribe.

Flask, Kjeldahl, 100-mL, Fisher Scientific, Cat. No. 10-110C

Flasks, volumetric, Class A, 50-, 100-, 200- and 1000-mL, Fisher Scientific, Cat. Nos. 10-210-5B, -5C, -5D and -5G, respectively

Funnel, filter, 58° angle bowl, short stem, 75-mm diameter, Fisher Scientific, Cat. No. 10-322E

Funnel, separatory Squibb, borosilicate glass, with polyethylene stopper and PTFE-plug stopcock, 60-mL, Fisher Scientific, Cat. No. 10-437-5A

Furnace, programmable, electric, chamber 360-mm wide × 300-mm deep × 330-mm high, lined with molded refractory ceramic, capable of maintaining 1000 ± 10°C, Fisher Scientific, Cat. No. 10-650-126

Glass beads, 3-mm, solid, borosilicate, Kimble Scientific Products, Cat. No. 13500-3. Rinse with water to remove glass chips and allow to dry before use. Alternatively, use of a small magnetic stirring bar is preferred for preparation of the platinum standard.

Gloves, Fisher brand, nonsterile, powdered, Fisher Scientific, Cat. No. 11-394-103, size A to H

Gloves, high temperature, Zetex, to withstand temperatures up to 593°C, Fisher Scientific, Cat. No. 11-392-15

Hot plate-stirrer, remote control, adjustable heat and stirrer, ceramic top, heating range 65 to 510°C, Fisher Scientific, Cat. No. 11-495-59A.

Pipets, Mohr, 5-, 10- and 25-mL, Fisher Scientific, Cat. Nos. 13-665K, M and N, respectively

Pipet, Pasteur, borosilicate glass, Fisher Scientific, Cat. No. 13-678-20C

Pipet, repeater, dispensing capacity 15-mL, Fisher Scientific, Cat. No. 13-683-10D

Riffler, precision sample splitter, Gilson, Model SP-1613X

Scoop, weighing, 20-g capacity, nickel alloy, Fisher Scientific, Cat. No. 01-914-38

Scriber, tungsten carbide pencil, Fisher Scientific, Cat. No. 13-378. Alternatively, Coors ceramic marking ink may be used.

Spectrophotometer, minimum absorbance repeatability of ± 0.0003 at 0.1 Abs, noise less than 0.00005 Abs (rms) at 0.0 Abs, and 0.0006 Abs (rms) at 2.0 Abs, minimum stability of 0.0003 Abs per hour, readability to 0.0001 Abs, Varian Instrument Group, Cary Model 4 (Note 2)

Standards, absorbance, spectrophotometric, certified, glass filters, 10-30% transmittance, 440- to 635-nm wavelength range, NIST, Cat. No. SRM-930-D

Stirring bars, magnetic, borosilicate glass, 6-mm OD $\times$ 21-mm and 9.5-mm OD $\times$ 25.4-mm, Baxter Scientific Products, Cat. Nos. S8313-31 and -33, respectively. Only borosilicate glass or Teflon stirring bars can be used in borosilicate beakers.

Stirring bar, magnetic, quartz, Alnico magnet, 10-mm OD $\times$ 35- to 40-mm, Pyromatics, Cat. No. PI-8789. Due to HF attack, periodic replacement is necessary.

Thermometer, electronic, with surface temperature probe, Omega Engineering, Cat. Nos. HH81 and 88108K, respectively

Tray, quartz, Pyrosil, opaque, 121- $\times$ 121- $\times$ 16-mm high, Pyromatics, Cat. No. PI-7321

Watch glass, Pyro-quartz, triple-rib, 90-mm diameter, rim to center-curvature height approximately 25-mm, Pyromatics, Cat. No. PI-7206. Due to HF attack, periodic replacement is necessary.

REAGENTS AND MATERIALS

All reagents shall conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, when such specifications are available, unless otherwise specified. References to water mean deionized or distilled water, except where noted.

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

Acetone, 99% minimum purity

Catalyst support, silica-alumina, UOP

Catalyst support, gamma-alumina, UOP

Ceramic marking ink, Coors, Fisher Scientific, Cat. No. 11-734 (optional)

Desiccant, indicating Drierite, 8-mesh, Fisher Scientific, Cat. No. 07-578-3A

Filter paper, whatman No. 50, quantitative, hardened, low-ash, 18.5-cm diameter, Fisher Scientific, Cat. No. 09-865G

Glass wool, borosilicate glass, Fisher Scientific, Cat. No. 11-388

Hydrochloric acid, concentrated, 37%

Hydrochloric acid, 1:1. Add 500 mL of concentrated hydrochloric acid, measured in a graduated cylinder, to an equal volume of water and mix.

Hydrochloric acid, 10 vol-%. Dilute one volume of concentrated hydrochloric acid, with nine volumes of water, measured with a graduated cylinder, and mix. (Used for cleaning glassware, see Note 3)

Hydrofluoric acid, concentrated, 48-51%

Hydrogen peroxide, 30%

Ice

Isoamyl acetate, 99% minimum purity, Mallinckrodt, Baxter Scientific Products, Cat. No. 2491

Lens paper, optical, Fisher Scientific, Cat. No. 11-996

Nitric acid, concentrated, 70%

Phosphoric acid, concentrated, 85%

Platinum wire, 99.998% minimum purity, Puratronic, 0.25-mm OD, Aesar, Cat. No. 10958

Sodium hydroxide, pellets

Sodium hydroxide, solution, approximately 10 mass-%. Dissolve approximately 50 g of sodium hydroxide pellets in approximately 450-mL of water. Prepare only when needed and use while still warm, from a polyethylene wash bottle for glass cleaning (see Note 3).

Solvent acid. In a 1000-mL glass stoppered bottle, combine 300 mL each of 1:1 sulfuric acid, 1:1 hydrochloric acid and concentrated phosphoric acid. Mix well. This acid mixture is stable indefinitely.

Stannous chloride, dihydrate, Baker Analyzed Reagent Grade, lot analysis provided, 99.9% minimum purity, J.T. Baker, Cat. No. 3980 (see Note 4)

Stannous chloride, solution. In a beaker, while stirring, dissolve 50 ± 0.01 g of the stannous chloride in 50 mL of concentrated hydrochloric acid with gentle warming, if necessary. Transfer the solution to a 100-mL volumetric flask and dilute to approximately 95 mL with water. Allow to cool to ambient temperature, dilute to the mark with water, stopper and mix by inverting several times. Filter the solution through a fluted Whatman No. 50 filter paper into a second 100-mL volumetric flask. This solution must be prepared daily.

Sulfuric acid, concentrated, 98%

Sulfuric acid, 1:1. Carefully, and with ice-cooling, pour 500 mL of concentrated sulfuric acid into 500 mL of water, mix and allow to cool.

Test paper, potassium iodide-starch, Fisher Scientific, Cat. No. 14-860

STANDARDIZATION

To avoid errors introduced by weighing volumetric flasks with stoppers that can be mismatched to another flask in a subsequent weighing step, it is recommended that all weighings of volumetric flasks, from initial taring to weighing of the final solution volume, be performed without stoppers in place. This proviso is applicable to all sections of this method involving weighing of volumetric flasks.

All subsequent steps involving handling and heating of concentrated acids or acid solutions must be performed in a fume hood.

Preparation of Standard Platinum Solution

Prepare a standard platinum solution containing 1.0 mg platinum/g as follows:

1. Weigh 1.0 g of 99.998% platinum wire to the nearest 0.1 mg.
2. Transfer the platinum wire quantitatively into a 100-mL Kjeldahl flask. Place the flask in a 400-mL beaker. Add either glass beads or, preferably, a small borosilicate glass magnetic stirring bar.
3. Add 10 mL of concentrated nitric acid and 25-mL of concentrated hydrochloric acid.
 - Treatment of the platinum is conducted at ambient temperature until evolution of chlorine has subsided.
4. Place the solution on a stirrer hot plate and heat to a gentle boil.
 - Stirring slowly with a magnetic stir bar prevents bumping.
5. Maintain the solution volume at approximately 30 mL by the dropwise addition of concentrated nitric and hydrochloric acids in a ratio of 1 to 3, until the platinum wire dissolves.
 - When adding the acids, take care that no solution is lost by spattering.
6. Evaporate the acid solution slowly to a syrup, approximately 3 mL, by gently boiling.
 - It is imperative that the solution does not go to dryness during the volume reduction. Platinum losses will result.
7. Add 1 to 2 mL of concentrated hydrochloric acid, slowly with a Pasteur pipet, and then add 1 to 2 mL of hydrogen peroxide, dropwise with a Pasteur pipet, to the evaporating solution and boil gently. Repeat the addition and boil until evolution of the brown nitrogen dioxide fumes ceases.
8. Add 10 mL of concentrated hydrochloric acid and 50 mL of water to the solution.
9. Remove the flask from the hot plate and allow the platinum solution to cool to ambient temperature.
10. Transfer the platinum solution quantitatively to a one-liter volumetric flask, tared to the nearest 0.01 g.
11. Add 15 mL of concentrated hydrochloric acid to the solution.

12. Dilute with water to a mass that will produce a platinum concentration as close as possible to 1.0000-mg platinum per gram of solution, weighed to the nearest 0.01 g.
 - Calculate the Pt concentration on a mass basis by dividing the mass of Pt in mg by the net solution mass in grams for use in Equation 2. For example, if 1.0034 g of platinum wire was dissolved, and the final mass of the platinum solution was 1003.21 g, the Pt concentration would be 1.0002 mg Pt/g.
13. Cap and mix the solution thoroughly by shaking and inverting the flask at least 10 times.
14. Subdivide the standard platinum solution, without dilution, into separate 237-mL (or smaller), amber glass bottles and seal with polyethylene lined caps for storage.
 - The stability of the solution in an unopened bottle is not known.
 - Once opened, the standards cannot be used for more than four weeks.

SAMPLE PREPARATION

Whole Pill Catalyst

1. Obtain a representative sample of whole pill spent catalyst utilizing UOP Method 918 without loss of sample to dusting.
2. Riffle the representative sample down to 400 mL (about 200 g).
 - If the catalyst is to be ignited in vertical quartz tubes, continue as described in the *APPENDIX* (optional).
3. Riffle the 400 mL portion further to obtain a 200-mL (100 g) portion for ignition, if the catalyst is to be ignited in quartz trays. Continue as described in *Carbon Ignition*.

Dust or Broken Catalyst with Fines

1. Riffle the representative sample of broken catalyst with fines to obtain a 200-mL (100 g) portion for ignition and continue as described in *Carbon Ignition*.
2. Transfer the dust obtained from the baghouse to an appropriate sized mixing container. Thoroughly homogenize and continue as described in *Carbon Ignition*.

Carbon Ignition

1. Distribute the 200-mL (100 g) portion of whole pill catalyst or broken catalyst with fines into three quartz trays.
 - A smaller sample may be used if sufficient sample is unavailable (see UOP Method 918).
 - The catalyst sample bed should only be a few pills thick, and is limited to approximately 30 g/tray.
2. Transfer a representative 10-g portion of the dust to a Vycor dish.
3. Place each quartz tray or Vycor dish on a hot plate at ambient temperature in a hood.
4. Increase the hot plate temperature gradually to $450 \pm 50^{\circ}\text{C}$.
5. Maintain the catalyst at this temperature until all indication of vapor emissions ceases.
6. Place the quartz trays or Vycor dishes containing the preignited spent catalyst into a furnace at 500°C .

7. Increase the furnace temperature at a maximum rate of 10°C per minute to 900°C and ignite for a minimum of 3 hours at 900°C.
 - The time required to reduce the carbon content to less than the 0.1%, which is required for the analysis, is determined by the composition of the sample; some samples may require more than 3 hours.
 - Carbon can be determined on the ground ignited sample by UOP Method 703.
8. Decrease the furnace temperature to 200°C and allow the samples to equilibrate to this temperature.
 - The furnace temperature is lowered to allow removal of the ignited catalyst.
9. Remove the quartz trays or Vycor dishes from the furnace using high temperature gloves, place in a desiccator and allow to cool to ambient temperature.
10. Combine portions of the same catalyst sample in an appropriate container. Thoroughly homogenize dust samples by random shaking for 5 minutes. For all other samples proceed with *Grinding*.

Grinding

1. Clean the pulverizer and grind the broken or whole pill catalyst samples as described in UOP Method 918.
 - No grinding is needed for dust. Continue as described under *PROCEDURE*.
2. Mix the collected, ground sample thoroughly by randomly shaking it for 5 minutes in an appropriate container.
 - Once the mixing is complete, the homogenous powder must not be agitated again until after the sample is taken.
3. Verify that the carbon content of the sample is below 0.1 mass-% using UOP Method 703.
 - If the carbon content is greater than 0.1 mass-%, the ignition must be repeated on the same sample using a longer time at final temperature.

PROCEDURE

Sample Analysis

Sample Weighing

1. Scoop a sample approximately 2.0-2.1 g of the ground catalyst or dust into a weighing scoop.
2. Tare the weighing scoop on the analytical balance to read zero.
3. Transfer the catalyst sample carefully, to avoid dust loss, into the bottom of a 250-mL quartz beaker.
 - If the catalyst is known to be an easily dissolved alumina (Method A), a Pyrex beaker may be used in place of quartz.
4. Place the empty weighing scoop onto the analytical balance and record the differential mass to the nearest 0.1 mg.
 - The sample mass will be read as a minus value on the balance.

5. Scoop separate 2-g portions of spent catalyst into two tared, pre-ignited ceramic crucibles for determination of the LOI by UOP Method 275, for noble metal containing catalyst.
 - Samples for the LOI must be taken at the same time the sample is weighed for the platinum determination.
 - The two LOI's are calculated to three significant figures and the results must agree within 5% relative standard deviation or the analysis, beginning with Step 1, must be repeated.
6. Prepare the required volume of matrix matching solution as follows.
 - The required volume depends on the platinum content of the samples (see Table 1) and the number of samples to be analyzed. In addition, each of the four platinum standards also requires 65 mL of solution for a total of 260 mL.
7. Weigh multiple portions of 2.0 to 2.1 g of alumina or silica-containing ground catalyst support (depending on sample composition) into 250-mL quartz beakers.
 - A borosilicate beaker and magnetic stirrer may be used for easily dissolved alumina catalysts (without silica) in Method A.
 - Multiple portions are required because only two grams can be processed per beaker.
 - Each portion produces 200 mL of matrix-matched solution. The number of portions to be weighed depends on the total volume required as described in Step 6.
 - The individual portions of matrix-matched solution are combined in a one-liter volumetric flask after dissolution is complete.
8. Place a quartz enclosed, magnetic stirring bar into each quartz beaker and cover with a quartz watch glass.
 - A borosilicate beaker and magnetic stirrer may be used for easily dissolved alumina catalysts (without silica) in Method A.
9. Digest and dissolve the samples and catalyst support as described under *Dissolution of Catalysts*.

Dissolution of Catalysts

All subsequent steps involving handling and heating of concentrated acids or acid solutions must be performed in a fume hood.

Method A, Alumina Samples

1. Add 40 mL of 1:1 sulfuric acid to each sample and also to each catalyst support through the spout of the covered beaker and gently hand swirl until all the powder is wetted.
2. Add through the spout, 60 mL of the solvent acid followed by 5 mL of concentrated nitric acid using graduated cylinders. Swirl gently, until most gas evolution has subsided.
 - For easy to dissolve catalysts, more dilute acid mixtures may be substituted for the solvent acid mentioned here and elsewhere below, provided the dilute acids are shown to effectively dissolve the sample completely without any haze remaining undissolved.
3. Place the covered beaker on the stirrer hot plate and gradually increase the heat to a gentle boil while slowly stirring.
 - The stirring speed is crucial; too slow causes bumping – too fast causes sample spatter.

4. Continue boiling and stirring until the mixture begins to fume at a hot plate temperature of approximately 400-450°C.
5. Continue fuming until the entire sample has dissolved to produce a crystal clear solution and the volume has been reduced to about 35 to 40 mL (see Note 5).
 - At temperatures below 400-450°C, the dissolution time increases.
 - The resulting solution is composed of approximately equal portions of concentrated sulfuric and phosphoric acids.
6. Continue as described under Method B, starting at Step 10.

Method B, Silica-Containing Samples

1. Add 40 mL of 1:1 sulfuric acid to each sample and also to each catalyst support through the spout of a covered quartz beaker and gently hand swirl until all the powder is wetted.
2. Add through the spout, 10 mL of concentrated hydrochloric acid and 5 mL of concentrated nitric acid, using graduated cylinders.
3. Swirl gently until most gas evolution has subsided and then add 25 mL of concentrated hydrofluoric acid with a plastic graduated cylinder.
 - Appropriate safety precautions must be taken when handling hydrofluoric acid.
4. Place the covered beaker on the stirrer hot plate and while slowly stirring, gradually increase the heat to a gentle boil.
 - The stirring speed is crucial; too slow causes bumping – too fast causes sample spatter.
5. Continue boiling and stirring until the mixture begins to fume, approximately 60 minutes.
 - At temperatures below 400-450°C, the dissolution time increases and the chemical attack on the quartz beaker by HF also increases.
 - The sample is fumed for no longer than five minutes. If sudden precipitation of white anhydrous aluminum sulfate is noted, immediately stop fuming and proceed to Step 6.
 - The residual concentrated sulfuric acid volume will be approximately 20 mL after fuming.
 - If liquid droplets are observed where the watch glass contacts the rim of the beaker, rotate and reposition the watch glass. If white silica gel is observed on the beaker rim, the dissolution must be started over.
6. Allow the acid slurry to cool until the beaker is warm to the touch. Carefully add several mL of water through the spout of the covered beaker while stirring and then rinse down the beaker walls and watch glass with water to a maximum volume of 50 mL.
 - Care should be exercised on adding water to concentrated acid.
7. Add 60 mL of the solvent acid to the covered beaker using a plastic graduated cylinder.
8. Add 5 mL of concentrated nitric acid through the spout of the covered beaker, swirl, and return the beaker to the hot plate at medium heat. Gently stir until the sample begins to boil and reflux.
9. Increase the heat gradually over a period of approximately 30 minutes or until fuming begins at approximately 400-450°C. Continue fuming for an additional 15-25 minutes until the solution is crystal clear (see Note 5).

- The solution contains approximately equal proportions of sulfuric and phosphoric acids and the volume is approximately 35 to 40 mL.
10. Allow the clear sample solution to cool to a temperature at which the beaker can be handled, then slowly and cautiously, add water through the spout of the covered beaker while stirring, to a total volume of 125 mL.
 - Care should be exercised on adding water to concentrated acid.
 11. Add 25 mL of concentrated hydrochloric acid through the spout followed by 5 mL of hydrogen peroxide, stir and wait until most of the chlorine evolution has subsided.
 12. Reheat, boil and evaporate the clear sample solution with a vigorous stirring vortex until the solution volume is approximately 100 mL. Allow the solution to cool to room temperature.
 13. Transfer the sample and catalyst support solutions quantitatively with water into separate pre-weighed (to the nearest 0.01 g on a top-loading balance), 200-mL volumetric flasks.
 - Any residual trace particles are removed by passing the solution through a very small pad of glass wool inserted into the stem of the funnel used to transfer the solutions to the volumetric flasks.
 14. Fill each flask to approximately 180 mL, swirl to mix and allow to cool to room temperature. Fill to the mark with water and then reweigh (to the nearest 0.01 g on a top-loading balance) the flasks containing the samples to obtain the net sample dilution mass. Stopper the flasks and thoroughly mix.
 15. See Table 1 for the proper aliquot to withdraw from each sample flask.
 - If the platinum content is unknown, use a 50-mL aliquot.
 - If platinum values other than those shown are expected, the aliquot size can be obtained by interpolation.
 16. Measure the proper aliquot into a 50-mL plastic graduated cylinder, place the cylinder on a balance capable of weighing to the nearest mg and tare the balance to read zero.
 - Most 50-mL graduated cylinders will hold 65 mL of solution. Mark the 65 mL position on the cylinder, as measured with water, and reserve the cylinder for this measurement.
 17. Pour the solution into a labeled, pre-weighed (to the nearest 0.01 g on a top-loading balance) 100-mL volumetric flask. Return the graduated cylinder to the balance and record the differential mass to the nearest mg (mass will be a minus value).
 18. Add the corresponding volume of catalyst support solution shown in Table 1 to each 100-mL sample flask.
 - Use the same type of catalyst support solution as the spent catalyst to be analyzed.
 19. Rinse down the neck of the volumetric flask with 1:1 hydrochloric acid to a volume of no more than 80-85 mL and swirl to mix. Continue as described under *Color Development* along with the platinum standard solutions.
 - It is essential that the hydrochloric acid is added prior to color development.

Table 1
Aliquots for Analysis

Estimated Pt Content, mass-%	Approximate sample Aliquot for Analysis, mL	Matrix-Matching Solution, ML
0.05	65	0
0.25	65	0
0.40	40	25
0.80	20	45
1.00	16	49
Unknown	50	15

Platinum Standards for Absorbance Calibration

Prepare platinum standards as follows:

1. Fill a weighing buret with the standard platinum solution containing 1.0 mg Pt/g and weigh to the nearest 0.1 mg.
2. Transfer 0.8-, 1.2-, 1.6- and 2.0-g aliquots of the solution to four 250-mL tall form beakers, respectively, weighed to the nearest 0.1 mg for catalysts exceeding 0.25% Pt, and transfer 0.3-, 0.7- 1.2- and 1.6-g aliquots for catalysts containing less than 0.25% Pt.
 - The platinum contents must span the platinum content expected in the catalyst.
 - No separate blank is required for Method A or B, since the isoamyl acetate extracted solutions become the blanks.
3. Add to each beaker, 3 glass beads. Cover with a watch glass and add, through the beaker spout, 25 mL of concentrated hydrochloric acid followed by 2 mL of hydrogen peroxide and swirl.
 - A borosilicate magnetic stirring bar may replace the glass beads. Stirring will eliminate all bumping. Quartz enclosed stirring bars must not be used in borosilicate beakers to prevent turbidity due to abrasion. Only non-abraded, new beakers can be used.
4. Allow most of the chlorine evolution to subside, then place the beakers on the hot plate, gently boil and evaporate the solution down to approximately 10 mL.
5. Add 25 mL of concentrated hydrochloric acid and again boil to evaporate the solution to about 10 mL in order to remove all traces of hydrogen peroxide.
6. Repeat the above step, while testing one drop of condensate from the underside of the watch glass with a strip of potassium iodide test paper. If it remains white, all traces of oxidizing agents have successfully been removed. Otherwise, repeat Step 5.
7. Allow the standards to cool, then quantitatively transfer them into four pre-weighed (to the nearest 0.01 g on a top-loading balance) 100-mL volumetric flasks, rinsing each beaker several times by using 65 mL of the same type of the catalyst support solution as that of the spent catalyst to be analyzed (see Table 1).
 - Use of the catalyst support solution to rinse the standard during transfer is required due to the limited volume of the 100-mL volumetric flask.

8. Rinse the beaker with 1:1 HCl acid, taking care not to exceed a total volume of 80-85 mL in the volumetric flask, then swirl to mix.
 - The glass boiling beads or any residual trace particles are removed by passing the solution through a very small pad of glass wool inserted into the stem of the funnel used to transfer the solutions to the volumetric flask. If a magnetic stirring bar is used, it is held back with a second magnet outside the beaker.
9. Continue as described for *Color Development*, simultaneously with the samples.

Color Development

1. Add 8-mL of stannous chloride solution to each standard and sample using a Mohr pipet and swirl to mix.
2. Dilute to a volume of approximately 95 mL with 1:1 hydrochloric acid, rinsing down the neck of the flask, then swirl to mix and stopper the flask.
3. Allow the color of the standards and samples to develop at the same temperature for 1-1/2 hours.
4. Dilute to the mark with 1:1 hydrochloric acid, reweigh the flask (to the nearest 0.01 g on a top-loading balance), then stopper and thoroughly mix the solutions by inverting the volumetric flasks several times.
5. Designate these solutions, “*Before Extraction*” and *immediately* proceed with *Extraction of the Pt-Sn Complex*.

Extraction of the Pt-Sn Complex

1. Transfer approximately 25 mL of the color developed sample and standard solutions, with a graduated cylinder, into separate, 60-mL separatory funnels.
 - The platinum is only to be extracted with isoamyl acetate after color development for 1.5 hours.
2. Add 15 mL of isoamyl acetate by repeater pipet to each separatory funnel, stopper and shake for 2 minutes.
3. Allow the liquid phases to completely separate, approximately 2 minutes, and draw off most of the aqueous lower layer into a 50-mL beaker.
 - Loss of a few drops of aqueous phase at this stage is not critical.
4. Discard the upper isoamyl acetate layer containing the yellow platinum complex through the stopcock, then return the aqueous phase in the beaker to the original separatory funnel.
5. Add 15 mL of fresh isoamyl acetate by repeater pipet to the separatory funnel, stopper and shake for 2 minutes.
6. Allow the two phases to completely separate as before, then drain the lower aqueous phase into a 50-mL volumetric flask and stopper.
 - Prior to collecting the aqueous phase in the 50-mL volumetric flask, pre-rinse the stem of the separatory funnel with the aqueous phase into the 50 mL beaker with a few quick rotations of the Teflon stopcock.
 - Loss of 1 to 3 mL of aqueous phase is not significant for this analysis.
 - The second isoamyl acetate layer is also discarded (see Note 3).

7. Designate the extracted, aqueous solution collected, “*After Extraction*”.

Spectrophotometric Measurement of Solutions

1. Calibrate the spectrophotometer once a week at a wavelength of 440 nm with the certified NIST glass filter absorbance standard as outlined in the instrument manual.
 - Spectrophotometers that utilize internal calibration cannot be calibrated with an external standard. In this case the NIST standard can be used as a performance check.
 - The certified solid standards must be periodically recertified.
2. Adjust the spectrophotometer using the specific instructions supplied by the manufacturer.
3. Zero the spectrophotometer with water in a 10-mm cell on the sample side and air, without a cell, in the reference side.
 - If a flow cell is used, see Note 1.
4. Read the absorbance of each standard and sample solution, before extraction using a 10-mm cell at a wavelength of 403 nm (Notes 1 and 2).
 - The absorbance of all the solutions must be measured within one hour of the extraction, and the temperature of all solutions must be the same within one degree C.
5. Read each standard and sample solution, after extraction, in the same manner.
6. Check the spectrophotometer zero to verify that the values are constant within the precision of the instrument.
 - If the zero is not constant (± 0.001 for a 3-place instrument or ± 0.0003 for a 4-place instrument), repeat Steps 3 through 6.
7. Calculate the net platinum absorbance (A) of the standards and samples using the following equation:

$$A = B - C \quad (1)$$

where:

- A** = net absorbance of platinum in standard or sample
- B** = absorbance of sample or standard *Before* extraction
- C** = absorbance of sample or standard *After* extraction

CALCULATIONS

Spectrophotometer Response

Calculate the concentrations of platinum in the color developed Pt standards to five significant figures as follows:

$$D = \frac{EF}{G} \quad (2)$$

where:

- D** = concentration of platinum in the color developed platinum standard, mg/g

- E** = mass of platinum standard taken, g
F = concentration of platinum standard solution, mg/g
G = total mass of color developed standard solution, g

Calculate the best straight line from the four net absorbances (Eq. 1) and the corresponding concentrations of the platinum standards in mg/g by performing a least squares analysis and obtain the correlation coefficient (Q) to 8 decimal places. Use a calculator capable of least squares analysis or the data reduction system on the spectrophotometer, if available. If the correlation coefficient (Q) is less than 0.99986, one suspect standard may be safely discarded and the best straight line recomputed to obtain a correlation coefficient of 0.99986 or larger. In no case can a two-point calibration, obtained by using the “best” two of the standards, be used.

Platinum in Catalysts

Calculate the platinum concentration of the color developed sample solution (I), mg/g, by using the computation algorithm of the calculator or computer used to calculate the best straight line and entering the net absorbance of the sample.

Calculate the platinum content of the spent catalyst sample, on a volatile-free basis at 900°C to the nearest 0.001 mass-% as follows:

$$\text{Pt, mass - \%} = \frac{IKL}{10MN \left(\frac{100_A - P}{100} \right)} \quad (3)$$

where:

- I** = platinum concentration of the color developed sample solution, mg/g
K = mass of color developed solution, g
L = mass of dissolved, diluted sample solution, g
M = mass of dissolved, diluted sample solution aliquot in graduate, g
N = mass of spent catalyst taken for analysis, g
P = the loss on ignition of the ground, spent catalyst at 900°C as measured by UOP Method 275 for noble metal containing catalyst, mass-%
10 = factor to convert from mg/g to mass-%
100 = factor to convert mass-% residue after ignition to a decimal fraction
100_A = factor to convert mass-% residue after ignition

NOTES AND PRECAUTIONS

1. The same cell must be inserted in the same way in the light beam each time a measurement is made using air as a reference. Alternatively, a flow-through sample cell, which is never moved from the spectrophotometer, might be used providing conditions are arranged to ensure complete removal of the previous sample each time spectrophotometric data are measured. Proper use of a flow-through cell requires thorough clean-out between blanks, standards and samples. The cell must first be flushed five times with a 1:1 mixture of concentrated hydrochloric acid and water, followed by five rinses with water. The instrument is then zeroed with water in the sample cell, versus air. Then flush the cell five times with 1:1 hydrochloric acid/water. Follow this with five flushes (to a constant optical density reading) for each of the standards and samples using the next standard or sample solution to rinse out the previous one from the flow cell. After the last sample has been measured, flush the cell with five flushes of 1:1 hydrochloric acid/water, followed by five flushes with water, ending with a recheck of the instrument zero at 403 nm.

2. If the spectrophotometer does not fulfill *all* of the specifications, a spectrophotometer capable of accurate and precise measurement of the absorbance to 3-decimal places (i.e., 0.001 Abs) may be used. But, each absorbance *must* be determined a minimum of 9 times. The nine absorbance readings are then averaged to obtain the absorbance that would be equivalent to that read with a 4-decimal place instrument.

3. After an isoamyl acetate extraction, the separatory funnels often contain a thin film of water- and acid-insoluble hydrolyzed tin oxide. This can be removed by rinsing with warm caustic, then water, dilute hydrochloric acid and again water. Finally rinse with acetone and allow the separatory funnels to air dry.

4. Oxidation or hydrolysis of the stannous chloride renders the reagent unusable. The reagent must not be used if it has any yellow color, does not dissolve easily in concentrated hydrochloric acid or has remained more than 6 months in an opened bottle.

5. It is recommended that the analysis of samples be completed within a single day. If necessary, the analysis may be stopped at this point before the final oxidation steps are started (Steps 10 to 12). Store the undiluted sample in the beaker used for digestion, covered with a watch glass.

PRECISION

Repeatability

Based on two tests performed by each of two analysts on each of two different days (8 tests), the within-laboratory estimated standard deviations (esd) were calculated for components at specific concentrations and are listed in Table 2. Two tests performed in one laboratory by different analysts on different days should not differ by more than the allowable differences in Table 2 at the concentrations listed (95% probability).

Table 2

Sample Type	Platinum Concentration, mass-%	Repeatability	
		Within-Lab esd, mass-%	Allowable Difference, mass-%
Cat. 1	0.36	0.0030	0.010
Cat. 2	0.29	0.0011	0.004
Cat. 3	0.25	0.0052	0.021
Cat. 4 (Dust)	0.26	0.0017	0.006

Reproducibility

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

TIME FOR ANALYSIS

The elapsed time for one sample analysis including carbon ignition and grinding is 12.5 hours. The labor requirement is 5.5 hours.

REFERENCES

UOP Method 275, "Loss on Ignition of Catalyst at 900°C"

UOP Method 703, "Carbon on Catalyst by Combustion and IR Detection"

UOP Method 918, "Collection and Grinding of Adsorbents and Catalysts for Analysis"

SUGGESTED SUPPLIERS

Aesar/Johnson Matthey, 892 Lafayette Rd., P.O. Box 1087, Seabrook, NH 03874-1087 (508-521-6300)

J.T. Baker, Inc., 222 Red School La., Phillipsburg, NJ 08865 (908-859-2151)

Baxter Scientific Products, 1430 Waukegan Road, McGaw Park, IL 60085-6787 (708-689-8410)

Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA 15219 (412-562-8300)

Gilson Co., Inc., P.O. Box 677, Worthington, OH 43085-677 (800-431-5935)

Kimble Science Products, Crystal Ave., Vineland, NJ 08360 (609-794-5560)

National Institute of Standards and Technology (NIST), Gaithersburg, MD 20899 (301-975-6776)

Omega Engineering, Inc., One Omega Dr., P.O. Box 4047, Stamford, CT 06907 (203-359-1660)

Pyromatics, Inc., P.O. Box 764, Willoughby, OH 44094 (216-951-3985)

UOP, Process Performance Systems & Equipment, 25 E. Algonquin Rd., Des Plaines, IL 60017-5017
(708-391-2529)

Varian Instrument Group, 220 Humboldt Ct., Sunnyvale, CA 94089 (408-734-5370)

APPENDIX

IGNITION OF SPENT CATALYST

SCOPE

This procedure is for removing carbon from spent catalyst using a tube furnace.

OUTLINE OF THE METHOD

Carbon ignition of the broken and whole pill spent catalyst is accomplished in as many as 8 vertically arranged quartz tubes simultaneously. A flow of air is passed from the bottom up through a 400-mL (~ 200 g) column of sample contained in each quartz tube.

APPARATUS

The apparatus listed is in addition to that listed in the body of the method.

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

Controller, with over-temperature protection, Lindberg/Blue M, Model No. 58124-P-B

Clamp, joint, Fisher Scientific, Cat. No. 05-885E (for 18/9 ball socket of sample tubes)

Exhaust hood, stainless steel, custom built for removal of combustion gases

Flowmeter, rotometer, Matheson Gas Products, Model EZ1130-G, 8 required

Flowmeter, electronic, Matheson Gas Products, Model 8112-0424, 8 required (optional)

Gas purifier, in-line, Alltech Associates, Cat. No. 8128

Regulator, air, two-stage, Matheson Gas Products, Model 3121-590

Sample tubes, quartz, Fig. A-1, special order from Reliance Glass, 8 required. Each tube must be inscribed with an identification number using a tungsten carbide scriber.

Stand, furnace, Lindberg/Blue M, Model No. 556-VFS

Support plates, furnace sample tube, custom made, top and bottom, stainless steel, see Fig. A-2

Tube adapter, one ring, Moldatherm, 152-mm diameter, with eight 24-mm diameter holes, Lindberg/Blue M, Model No. 59538. Install at the lower inlet end of the furnace above the *bottom* furnace sample tube support plate as shown in Fig. A-3.

Tube adapter, solid type (blank), Moldatherm, 152-mm diameter, Lindberg/Blue M, Model No. 59539. Drill eight 32-mm diameter holes to exactly coincide with the eight-hole positions of the *top* furnace sample tube support plate as shown in Fig. A-2. Install at the upper exit end of the furnace. This upper adapter acts as an insulator around the quartz tubes and prevents undesirable heat losses due to a chimney effect.

Tube furnace, split hinge, vertical mount, 1200°C, single zone, 610-mm heated length, bore diameter 152-mm, 533-mm high by 508-mm wide by 940-mm long, Lindberg/Blue M, Model No. 55642

Valve, metering, 6.35-mm (1/4-inch), straight, Nupro, Cat. No. B-554

REAGENTS AND MATERIALS

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

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

Air, dry, Matheson Gas Products, or pressurized laboratory air (free of oil vapor)

PROCEDURE

1. Transfer as many as eight 400-mL (200-g) portions of the whole pill catalyst into separate, quartz tubes.
 - The bed height above the quartz disc must not exceed 460 mm.
 - Only whole pill catalysts can be ignited in the tube furnace. All finer fractions must be ignited in quartz trays or Vycor dishes as described under *Carbon Ignition* in the method proper.
 - To assure proper ignition, the catalyst must be centered within the effective hot zone of 610 mm.
2. Position the quartz tubes vertically in the furnace, as shown in Fig. A-3, supporting the tubes with the upper and lower support plates.
3. Connect the air inlet tube to the ball joint at the inlet of each quartz tube below the furnace and adjust the dry air flow to approximately 3 L/min for each tube as indicated by the flowmeter.
 - The 3 L/min flow rate must be maintained at all times to moderate exothermic reactions, prevent condensation and back flash or fires.
4. Verify that the exhaust gases are safely vented by visual inspection and adjustment of the apparatus and the exhaust hood.
5. Set the furnace programmer to a heating rate of 30°C/min and the furnace controller set point to 1000°C so that in approximately 30 minutes the final ignition temperature of 900°C is reached. Hold this temperature for a minimum of 3 hrs.
 - Because of variable temperature profiles, from the top to the bottom of the bed, a 1000°C controller set point is required.
6. Turn off the furnace and open one half of the split-hinge furnace to allow the samples to cool, while continuing to pass air through the samples until the samples reach room temperature.
 - Cooling can be accelerated by removing the quartz tubes from the furnace while at 400°C and reestablishing the air flow.
 - If the tubes are removed at 400°C, most samples can be ignited and cooled in 4.5 hours.
7. Recombine all portions of the same ignited sample when cool into a single appropriate container for mixing and proceed as described in *Grinding* in the method proper.

SUGGESTED SUPPLIERS

Alltech Associates, Inc., 2051 Waukegan Rd., Deerfield, IL 60015-1899 (708-948-8600)
 Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA 15219 (412-562-8300)
 Lindberg/Blue M, 304 Hart St., Watertown, WI 53094 (414-261-7000)
 Matheson Gas Products, Inc., P.O. Box 96, Joliet, IL 60434 (815-727-4848)
 Nupro Co., 4800 E. 345th St., Willoughby, OH 44094 (216-951-7100)
 Reliance Glass Works, Inc., P.O. Box 825, Bensenville, IL 60106-0825 (708-766-1816)

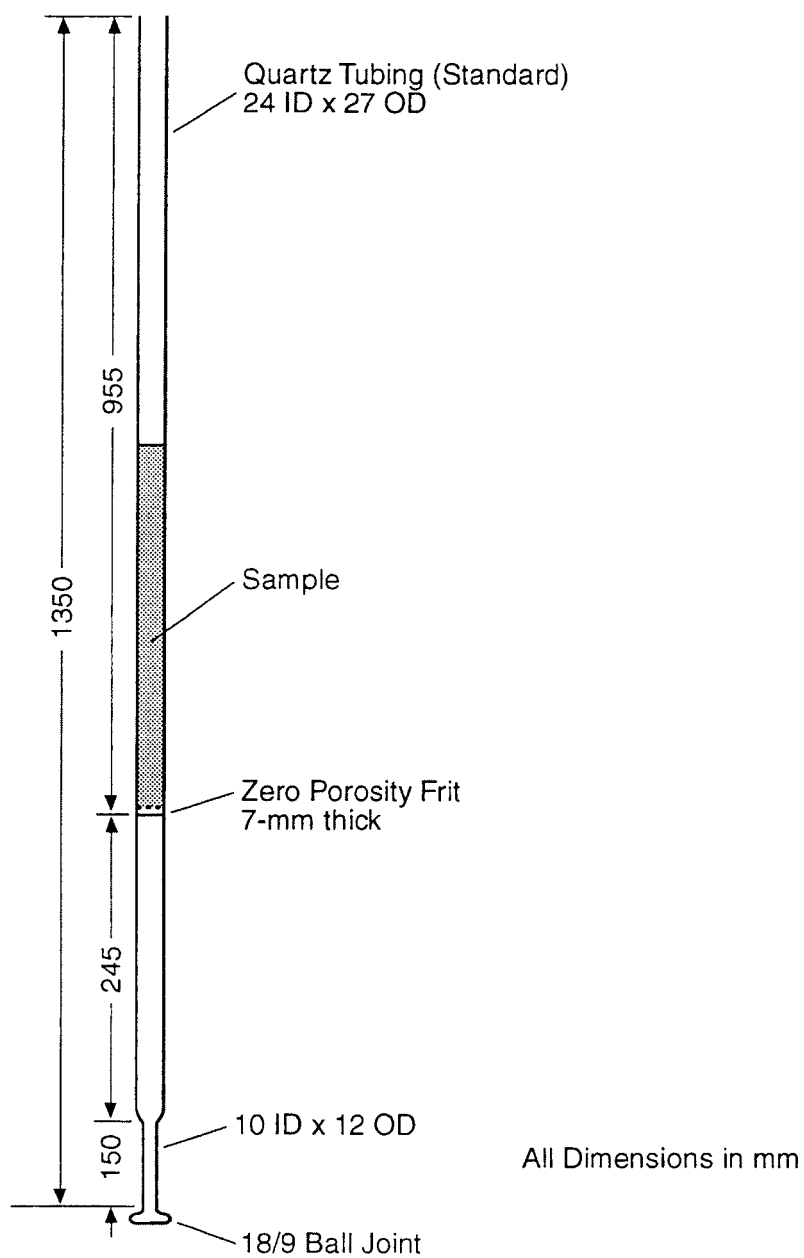
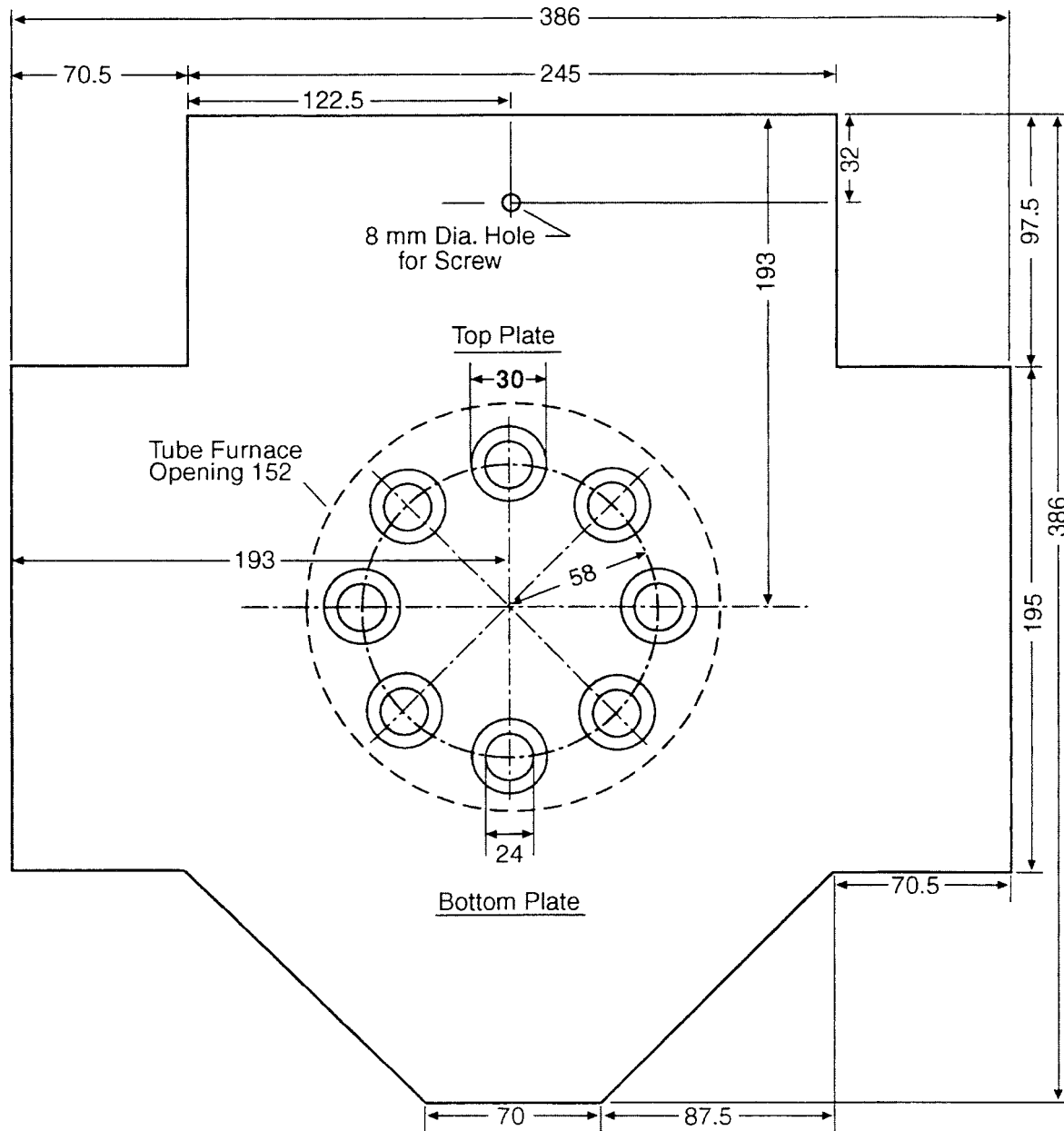


Figure A-1
Sample Tube

**Two Plates Required**

Top Plate: 8 Holes x 30 mm Diameter

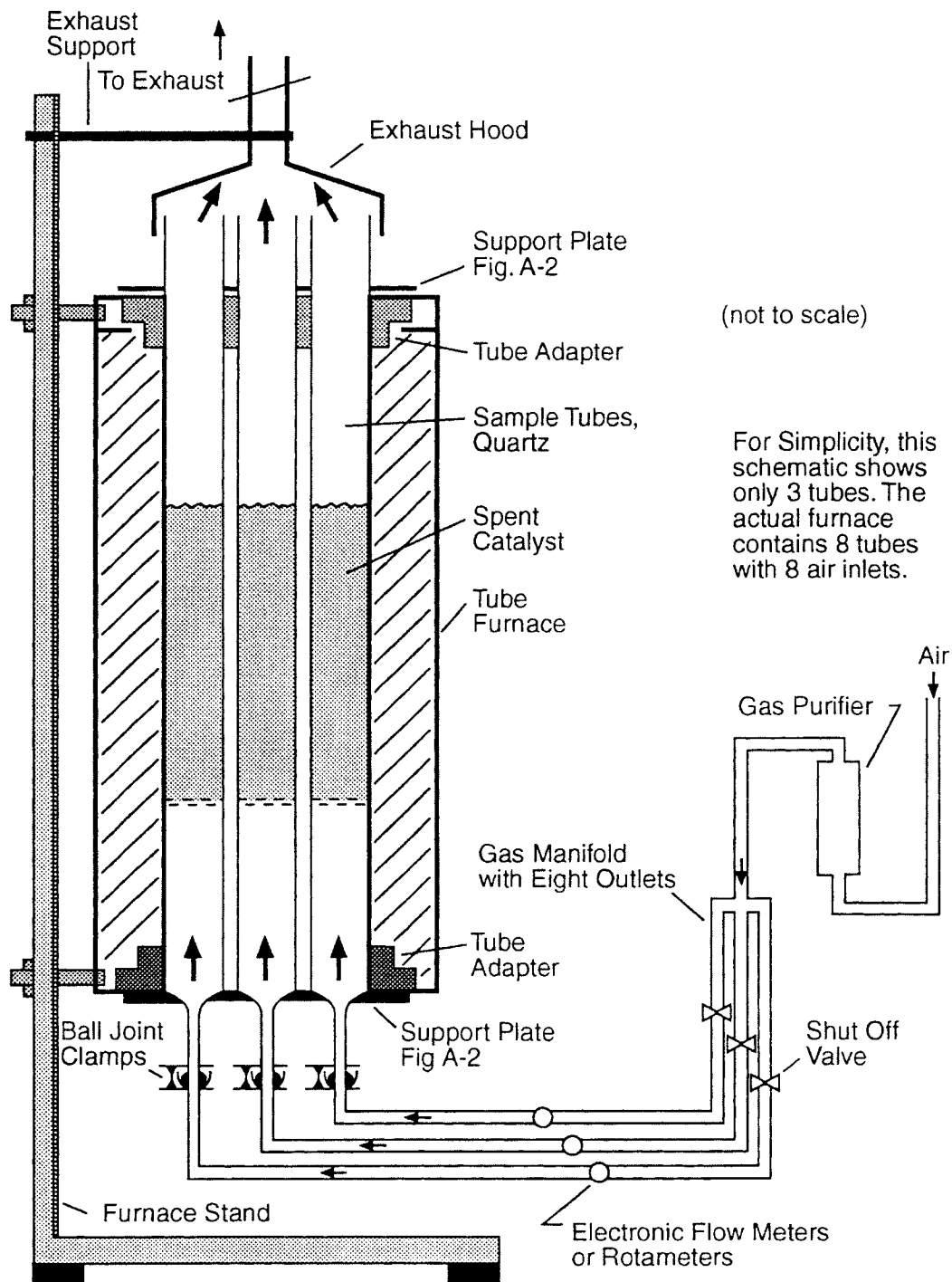
Bottom Plate: 8 Holes x 24 mm Diameter

Stainless Steel, 1-mm thick

All Dimensions in mm

Figure A-2

Furnace Sample Tube Support Plates

**Figure A-3**

Multiple Sample Tube Ignition Apparatus