

PHOSPHORUS IN CATALYSTS BY VISIBLE SPECTROPHOTOMETRY

UOP Method 865-86

SCOPE

This method is for determining total phosphorus in catalyst containing 0.01 to 1.0 mass-% phosphorus. Interferences are removed by an electrolytic analyzer. Samples containing higher concentrations of phosphorus can be analyzed by UOP Method 378.

OUTLINE OF METHOD

The sample is dissolved with dilute hydrazine solution and sulfuric acid under reflux. The sample is then filtered and the filtrate treated with concentrated nitric acid and 30% hydrogen peroxide to oxidize phosphorus to *ortho*-phosphate. If the catalyst contains metals such as nickel or molybdenum, the sample solution is placed on an electrolytic analyzer to remove the metal interferences. The treated sample is then color-developed using ammonium vanadate and ammonium molybdate. Matched matrix standards treated in the same manner are used to develop a calibration curve that is used to determine the phosphorus content.

APPARATUS

Analyzer, electrolytic, motor stirred, two position, 5 ampere, with heaters (see Fig. 2), Sargent-Welch Scientific, Cat. No. S-29465, or equivalent

Anode, platinum, gauze, corrugated form, 45 mesh, for electrolytic analyzer, Sargent-Welch Scientific, Cat. No. S-29632, or equivalent

Balance, readability 0.1-mg

Beakers, electrolytic, extra high form, without pour-out, 250-mL, Sargent-Welch Scientific, Cat. No. S-4715-B, or equivalent

Beakers, Griffin, 400-mL, Sargent-Welch Scientific, Cat. No. S-4675-L, or equivalent

Bottle, washing

Cathode, mercury, for electrolytic analyzer, Sargent-Welch Scientific, Cat. No. S-29678, or equivalent

Cells, spectrophotometric, 10-mm path length, UV Silica, Beckman Instruments, Inc., Cat. No. 580012, or equivalent

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).

Condenser, acorn type, to fit electrolytic beaker (see Fig. 1)

Cylinder, graduated, 25-mL, Sargent-Welch Scientific, Cat. No. S-24674-C, or equivalent

Flasks, volumetric, 100- and 1000-mL, Sargent-Welch Scientific, Cat. Nos. S-34855-20G and S-34855-20L, or equivalent

Funnels, analytical, fluted 60°, long stem, Sargent-Welch Scientific, Cat. No. S-35345-E, or equivalent

Hot plate, Lindberg, Sargent-Welch Scientific, Cat. No. S-41220-C, or equivalent

Pipet, measuring, Mohr type, graduated in tenths, 1.0-mL

Pipets, volumetric transfer, 2-, 4-, 5-, 8-, 10-, 15-, 20-, 25-, 30- and 75-mL

pH meter, Beckman Model pH 170, Cat. No. 123002, or equivalent

Spectrophotometer, minimum of $\pm 0.5\%$ photometric accuracy, double-beam

“*Transite*”, 2-cm thick, 760-mm long by 300-mm wide, or equivalent, to fit top of hot plate

REAGENTS

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.

Ammonium molybdate solution, 4-hydrate, $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}]$. Dissolve 500 ± 1.0 g of ammonium molybdate in warm water and dilute to one liter with water. Filter through Whatman 42 filter paper before use.

Ammonium vanadate solution, meta, (NH_4VO_3) . Dissolve 2.5 ± 1.0 g of ammonium vanadate in 500 mL of hot water. Add 20 mL of concentrated nitric acid and dilute to one liter with water.

Boiling chips, carborundum, Thomas Scientific, Cat. No. 1590-D30, or equivalent

Buffer solutions, pH reference, 4.01 and 7.00, Sargent-Welch Scientific, Cat. Nos. S-30141-10A and 10B, or equivalent

Catalyst base, alumina (Al_2O_3)

Filter paper, Whatman No. 42, 12.5-cm diameter, Sargent-Welch Scientific, Cat. No. S-33175-F, or equivalent

Hydrazine, (NH_2NH_2) , 95% minimum purity

Hydrazine solution. Dilute 5 ± 0.1 g of hydrazine to one liter with water.

Hydrochloric acid, concentrated

Hydrogen peroxide, 30%

Mercury metal, triple distilled

Nitric acid, concentrated

Platinum standard. Prepare a platinum standard as described in UOP Method 274, *STANDARDIZATION*

Potassium phosphate monobasic, (KH_2PO_4) , Sargent-Welch Scientific, Cat. No. SC-14266, or equivalent

Phosphorus standard, 0.100 mg P/mL. Dissolve 0.4393 g $\pm$ 0.1 mg of potassium phosphate monobasic in water and dilute to one liter with water.

Sodium hydroxide, 50%, Sargent-Welch Scientific, Cat. No. SC-14836, or equivalent

Sodium hydroxide, 25%. Mix equal volumes of 50% sodium hydroxide and water

Sulfuric acid, concentrated

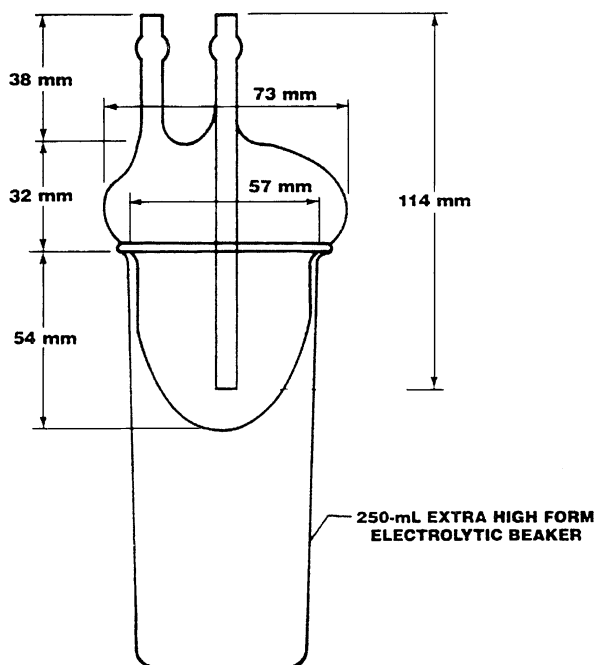


Figure 1

Reflux Vessel



Figure 2

Electrolytic Analyzer

Sulfuric acid, 70 vol-%. Add 7 parts concentrated sulfuric acid to 3 parts water.

PROCEDURE

Preparation of Standard Calibration Curve

Weigh into each of seven 250-mL electrolytic beakers $0.7 \text{ g} \pm 2 \text{ mg}$ of ground catalyst base. Pipet 17.5 mL of the previously prepared platinum standard into each of the beakers. Pipet 5, 10, 15, 20, 25 and 30 mL of the previously prepared phosphorus standard into six of the beakers. In the 7th beaker prepare a reagent blank by omitting only the phosphorous standard.

Add 10 mL of the hydrazine solution, 10 mL of the 70 vol-% sulfuric acid and several boiling chips to each beaker. In a hood or well ventilated area reflux using the apparatus shown in Fig. 1 until the catalyst base is in solution (typically 4 hours or less). Cool the beaker and rinse the acorn condenser with water. Filter the standard solution through Whatman No. 42 filter paper into a 400-mL beaker to remove the reduced Pt and any insoluble fines, quantitatively rinsing the electrolytic beaker and filter paper with water. Add several boiling chips and, in a hood, concentrate to white fumes of sulfur trioxide. Add, dropwise, 1-2 mL of concentrated nitric acid over a ten-minute period. Then, add dropwise 30% hydrogen peroxide until evolution of nitric fumes ceases. Remove the beaker from the hot plate and allow it to cool. Dilute to approximately 200 mL with water. If the samples are to be treated with the electrolytic analyzer, then the standards must be processed in the same manner. Attach the platinum anode to the center post on the electrolytic analyzer and the mercury cathode to the outer post. Fill the cathode with triple-distilled mercury. Place the cathode and anode in the sample solution. Set the voltage switch to NORMAL and turn the motor and current switches ON. Allow the reaction to proceed for four hours. At the end of four hours, turn the motor switch OFF and raise the cathode and anode assembly. Quantitatively rinse the anode and cathode with water and remove the beaker from under the assembly. Turn the current switch OFF.

Adjust the pH to 1.0 with 25% sodium hydroxide using a pH meter. Concentrate by boiling to 50 mL, allow to cool and quantitatively transfer to a 100-mL volumetric flask with water, leaving room for the later addition of reagents. Pipet 10 mL of the ammonium vanadate solution and 10 mL of the ammonium molybdate solution into each flask. Mix by inverting the flask several times between additions. Allow to stand for 45 minutes, but no longer than 60 minutes, bring to volume with water, and mix. Read the absorbance of the standards at 460 nm in 10-mm cells, using the matrix blank as the reference. Plot a graph of absorbance versus concentration in mg phosphorus/100 mL for use in the calculations.

Analysis of Catalyst

Weigh $0.7 \text{ g} \pm 2 \text{ mg}$ of ground catalyst into a 250-mL electrolytic beaker. Analyze the sample by the procedure described in *Preparation of Standard Calibration Curve* beginning with the paragraph, "Add 10 mL of hydrazine solution...", with the exception that all samples are refluxed for 4 hours even though they may not be totally soluble.

Samples that contain metals such as nickel and vanadium above a concentration of 0.1 mass-% must be placed on an electrolytic analyzer to remove interferences as follows. After the nitric acid and hydrogen peroxide treatment, dilute the sample to 200 mL with water. Attach the platinum anode to the center post on the electrolytic analyzer and the mercury cathode to the outer post. Fill the cathode with triple-distilled mercury. Place the cathode and anode in the sample solution. Set the voltage switch to NORMAL and turn the motor and current switches ON. Allow the reaction to proceed for four hours. At the end of four hours, turn the motor switch OFF and raise the cathode and anode assembly. Quantitatively rinse the anode and cathode with water and remove the beaker from under the assembly. Turn the current switch OFF.

Continue with the analysis as described under *Preparation of Standard Calibration Curve*, beginning with the paragraph “Adjust the pH to 1.0 with 25% sodium hydroxide...”.

CALCULATIONS

Calculate the phosphorus on an “as received” basis as follows:

$$\text{Phosphorus, mass-\%} = \frac{100 A}{1000 W}$$

where:

A = phosphorus, mg/100 mL (from graph)

W = mass of ground sample, g

100 = factor to calculate mass-%

1000 = conversion factor from mg to g

PRECISION

Based on 6 replicate determinations, the estimated standard deviation for phosphorus at the 0.3 mass-% level was calculated to be 0.0017%. Duplicate results by the same operator should not differ by more than 0.0062 mass-% (95% probability) at the stated level.

Based on 6 replicate determinations using an electrolytic analyzer, the estimated standard deviation for phosphorus at the 0.2 mass-% level was calculated to be 0.0056%. Duplicate results by the same operator should not differ by more than 0.020 mass-% (95% probability) at the stated level.

TIME FOR ANALYSIS

The labor requirement is 0.55 hour when the electrolytic analyzer is not used or 0.8 hour when it is required. The elapsed time in either case is 14 hours.

REFERENCES

ASTM Method D 1091, www.astm.org

UOP Method 274

UOP Method 378

SUGGESTED SUPPLIERS

Beckman Instruments, Inc., Scientific Instruments Div., 2500 Harbor Blvd., Fullerton, CA 92634

Sargent-Welch Scientific Co., 7300 N. Linder, Skokie, IL 60077

Thomas Scientific, P.O. Box 99, Swedesboro, NJ 08085-0090