



A Honeywell Company

Total Chloride in Alumina Supported Catalysts by WD-XRF

UOP Method 979-14

Scope

This method is for determining the total chloride content of fresh, regenerated, and spent alumina supported catalysts by wavelength dispersive x-ray fluorescence (WD-XRF) spectroscopy. The range of quantitation is from 0.01 to 3 mass-% and applies to samples containing less than 10 mass-% water and other volatiles as determined by loss on ignition (LOI) measurement at 900 °C. The upper concentration limit of the method can be extended if appropriate standard and reference materials can be obtained. See *Notes* for matrix-effect and other interferences.

References

UOP Method 291, "Total Chloride in Alumina and Silica-Alumina Catalysts by Potentiometric Titration," www.astm.org

UOP Method 954, "Loss on Ignition (LOI) for Fresh, Regenerated, Used, and Spent Catalysts, Catalyst Supports, and Adsorbents," www.astm.org

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

Outline of Method

A ground sample is introduced into a wavelength dispersive XRF spectrometer. It is irradiated with x-rays, exciting a large number of elements which will emit energy as "characteristic x-rays." The emitted x-ray intensity is detected and measured in a helium path at an angle specific to chloride. The signal intensity is proportional to concentration.

The XRF calibration curve is established using a series of matrix-matched catalyst samples whose chloride concentrations were obtained by potentiometric titration using UOP Method 291, "Total Chloride in Alumina and Silica-Alumina Catalysts by Potentiometric Titration," and UOP Method 954, "Loss on Ignition (LOI) for Fresh, Regenerated, Used, and Spent Catalysts, Catalyst Supports, and Adsorbents."

Apparatus

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used (see *Note 3*).

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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Grinding mill, ball, capable of grinding catalyst to finer than 325 mesh, Mixer/Mill, SPEX SamplePrep, Cat. No. 8000M

Grinding vials and balls, for grinding mill, Hardened Steel Vial Set, SPEX SamplePrep, Cat. No. 8001

Regulator, counting gas, two-stage, high purity, Matheson Tri-Gas, Model 3122-350

Regulator, helium, two-stage, high purity, Matheson Tri-Gas, Model 3122-580

Sieve, brass, No. 325, Fisher Scientific, Cat. No. 04-881EE

Sieve cover, brass, Fisher Scientific, Cat. No. 04-886A

Sieve receiver, brass, Fisher Scientific, Cat. No. 04-886B

Wavelength Dispersive X-ray Fluorescence Spectrometer (WD-XRF), equipped for x-ray detection in the 4.7 Å range, PANalytical. For optimum sensitivity to chloride, the instrument should be equipped with the following:

Analyzing crystal, suitable for the dispersion of chlorine $K\alpha$ x-rays within the angular range of the spectrometer employed. Germanium or other materials such as pentaerythritol can be used.

Gas proportional detector, designed for the detection of long wavelength x-rays

Optical path, helium

Pulse height analyzer, or other means of energy discrimination

X-ray tube, capable of exciting chlorine $K\alpha$ radiation. Tubes with anodes of rhodium or chromium are preferred although other anodes can be used.

Reagents and Materials

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

Catalysts, matrix-matched, containing various levels of chloride as analyzed by UOP Method 291, local supply. See *Procedure*, *Calibration Standards*, and *Reference*.

Counting gas, for instruments equipped with flow proportional counters, P-10 ionization gas, 90 vol.-% argon and 10 vol.-% methane

Helium gas, minimum purity 99.9%

Sample cells, compatible with the sample and the geometry requirements of the spectrometer; disposable cells are recommended, PANalytical, Cat. No. 9430-500-00521

X-ray transparent film, any film that resists attack by the sample, is free of chlorine, and is sufficiently x-ray transparent, compatible with the spectrometer. Six-micron Mylar™ film is recommended, PANalytical, Cat. No. 9425-888-00028

Procedure

The analyst is expected to be familiar with general laboratory practices, the technique of x-ray fluorescence, and the equipment being used. Dispose of used supplies and samples in an environmentally safe manner according to applicable regulations.