



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).

© COPYRIGHT 2002, 2014 UOP LLC. All rights reserved.

Nonconfidential UOP Methods are available from ASTM International, 100 Barr Harbor Drive, P.O. Box C700, West Conshohocken, PA 19428-2959, USA. The UOP Methods may be obtained through the ASTM website, www.astm.org, or by contacting Customer Service at service@astm.org, 610.832.9555 FAX, or 610.832.9585 PHONE.

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 α 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 α 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.

Spectrometer Conditions for Chloride Analytical Program

Set up the instrument according to the instrument manufacturer's instructions for chloride. Actual settings are instrument dependent.

For correct operation of the x-ray instrument, assemble the required measurement program and calculation program as suggested by the manufacturer.

Calibration Standards and Reference

Obtain a series of alumina supported catalysts containing various levels of chloride and analyze them using UOP Method 291. Calculate the results as volatile free, using loss on ignition at 900 °C as determined by UOP Method 954. Select six catalysts spanning the chloride concentration range of 0.01 to 3 mass-% for use as the calibration standards. Select a seventh catalyst for use as the reference.

Preparation and Analysis of Calibration Standards, Reference, and Samples

1. Grind the calibration standards, reference, and sample catalysts (having loss on ignition at 900 °C of less than 10 mass-%) in a mill to a uniform powder (finer than 325 mesh).
 - The grinding capability of the mill can be determined by pulverizing and then screening similar catalyst types prior to performing this method.
 - Samples found to have greater than 10 mass-% LOI, cannot be analyzed by this method, and must be analyzed by UOP Method 291.
2. Assemble a disposable sample cell.
 - Ensure that the x-ray transparent film is free of wrinkles. Wrinkles in the film will affect the intensity of the x-rays transmitted.
 - Oil from fingerprints contains Cl and can affect the reading when analyzing low levels of chloride. Care must be taken to avoid touching the inside of the sample cell or the portion of the window film in the cell.
3. Place the ground sample in the assembled disposable sample cell. Lightly tap the cups on a clean flat surface prior to analysis to ensure a smooth, level sample surface on the Mylar film.
 - Although x-rays will only penetrate a short distance into the sample, scatter from the sample cell and sample can vary. Ensure the sample is filled above a minimum depth, about 1 cm, beyond which additional sample does not significantly affect the count rate.
4. Analyze the sample according to the manufacturer's instructions.

Establishing the Calibration Curve

1. Analyze the six calibration standards.
2. Measure the intensity of the emitted chloride radiation from each of the standards.
3. Input the measured chloride x-ray intensities along with the chloride concentrations for each standard into a calibration model, according to the manufacturer's instructions.
 - Use the instrument software to calculate a linear regression model, with the intercept not forced through zero. The RMS for the regression (a measure of the quality of fit) should be less than 0.1.

Reference Analysis

Analyze the reference catalyst. Determine if the calculated value agrees with the previously determined value within the allowable difference shown in *Precision*. If the reference value does not fall within these specified limits, reconfirm the integrity of the calibration standards and check the instrument for proper setup and operation. Then re-establish the calibration curve as described above.

Measure the reference sample at the beginning of each day that samples are analyzed and verify that the result lies within specified limits before proceeding to routine samples.

Sample Analysis

Analyze the prepared samples. Determine the level of chloride using the calibration. Ensure that the calculated results are within the range of the calibration; otherwise, the samples must be analyzed by UOP method 291.

Calculations

All calculations are performed by the instrument software.

Report

Report results to the nearest 0.01 mass-%.

Notes

1. An effect on the chlorine emission intensities is expected when water is present (as LOI) in the sample; however, at concentration levels less than 10%, the error is minor. Samples found to have greater than 10 mass-% LOI cannot be analyzed by this method, and must be analyzed by UOP Method 291.
2. When the elemental composition of samples differs significantly from the standards, errors in the chloride determination can result. The applicability of the method should be verified using matrix-matched standards and references.
3. Energy Dispersive Equipment (ED-XRF) has undergone many recent technological improvements. ED-XRF may be a suitable alternative technique. However, as instruments vary widely, the user must ensure that the ED-XRF instrument meets the precision criteria stated in this method. In case of dispute, UOP Method 291, from which the calibration is derived, shall be the referee.

Precision

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

Repeatability and Site Precision

A nested design was carried out for determining chloride on two catalyst samples. The samples were analyzed on two instruments (4.0 kW and 2.4 kW) by two analysts, with each analyst performing two analyses on two separate days for a total of 32 analyses. Separately, a third sample was analyzed on a third instrument (1.0 kW) by two analysts, with each analyst performing four analyses on two separate days for a total of 16 analyses. Using a stepwise analysis of variance procedure, the within-day and within-lab estimated standard deviations (esd) were calculated at the concentration means listed in the Table. Two analyses performed in one laboratory by the same analyst on the same day should not differ by more than the repeatability allowable differences shown in the Table with 95% confidence. Two analyses performed in one laboratory by different analysts on different days should not differ by more than the site precision allowable differences shown in the Table with 95% confidence.

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

Table
Repeatability and Site Precision, mass-%

<u>Catalyst</u>	<u>Instrument</u>	<u>Mean</u>	<u>Repeatability</u>		<u>Site Precision</u>	
			<u>Within- Day esd</u>	<u>Allowable Difference</u>	<u>Within- Lab esd</u>	<u>Allowable Difference</u>
Spent	4.0 kW	0.81	0.005	0.02	0.006	0.03
Regenerated	4.0 kW	1.38	0.014	0.06	0.016	0.09
Spent	2.4.kW	0.82	0.008	0.03	0.009	0.05
Regenerated	2.4.kW	1.38	0.019	0.09	0.023	0.11
Fresh	1.0 kW	1.22	0.008	0.02	0.009	0.03
The 4.0 kW instrument was a PANalytical Axios MAX						
The 2.4 kW instrument was a PANalytical Axios MAX						
The 1.0 kW instrument was a PANalytical Axios						

Reproducibility

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

Time for Analysis

The elapsed time and labor requirement for a single chloride analysis are the same, 0.5 hour.

Suggested Suppliers

Fisher Scientific, 300 Industry Dr., Pittsburgh, PA 15275, USA, 1-412-490-8300,
www.fishersci.com

Matheson Tri-Gas, 150 Allen Rd. #302, Basking Ridge, NJ 07920, USA, 1-908-991-9200,
www.mathesontrigas.com

PANalytical, 117 Flanders Rd. Westborough, MA 01581 USA, 1-508-647-1100, or, Lelyweg 1,
7600 AA Almelo, The Netherlands, +31 5465 34 444, www.panalytical.com

SPEX SamplePrep LLC, 65 Liberty St, Metuchen, NJ 08840, USA, 1-732-623-0465,
www.spexsampleprep.com