

TOTAL CHLORIDE IN ALUMINA SUPPORTED CATALYSTS BY WAVELENGTH DISPERSIVE X-RAY FLUORESCENCE

UOP Method 979-02

SCOPE

This method is for determining the total chloride content of fresh, regenerated, and spent alumina supported catalysts by wavelength dispersive x-ray fluorescence (XRF) spectroscopy. The range of quantitation is from 0.01 to 3 mass-% and applies to samples containing less than 10 mass-% water. 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.

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 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, (U291), and UOP Method 275, Loss on Ignition of Catalyst at 900°C (U275).

APPARATUS

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

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

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

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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UOP Methods are available through ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States. The 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).

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

Regulator, helium, two-stage, high purity, Matheson Gas Products, 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 (WDXRF), 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. 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, Chemplex Industries, Cat. No. 1830

X-ray transparent film, any film that resists attack by the sample, is free of chlorine, is sufficiently x-ray transparent, and is compatible with the spectrometer. Mylar™ film is recommended, Chemplex Industries, Cat. No. 157.

PROCEDURE

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 U291. Calculate the results as volatile free, using loss on ignition at 900°C as determined by U275. 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 (containing less than 10% water) 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.
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 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 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.

Reference Analysis

Analyze the reference catalyst. Determine if the calculated value is within ± 3 esd of chloride value obtained by U291. If the reference value does not fall within control limits, check the instrument for possible required maintenance, confirm the integrity of the standards, and re-establish the calibration curve. Run the reference each day samples are analyzed.

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 in the sample; however, at concentration levels less than 10 %, the error is minor.
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.

PRECISION

Precision statements were determined using UOP Method 999.

ASTM and UOP Repeatability

Precision data were obtained in two sets. Set 1: Four analysts in one laboratory carried out a precision study for determining chloride in one catalyst using two different instruments. Two analysts carried out tests on two days on each instrument, performing four tests each day. The total number of tests was 32. Set 2: Two analysts in one laboratory carried out a precision study for determining chloride in two catalysts at two concentrations using one instrument. Each analyst carried out two tests on each of two days. The total number of tests at each concentration was 8. The precision data are summarized in Table 1. Two tests performed by the same analyst on the same day should not differ by more than the ASTM allowable difference with 95% confidence. Two tests performed in one laboratory by different analysts on different days should not differ by more than the UOP allowable difference with 95% confidence.

The data in Table 1 are a short-term estimate of repeatability. When the test is run routinely, a control standard and chart should be used to develop a better estimate of the long-term repeatability.

Reproducibility

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

Table 1
ASTM and UOP Repeatability, mass-%

Set/Instrument*	Mean Conc.	<u>ASTM Repeatability</u>		<u>UOP Repeatability</u>	
		<u>Within- Day esd</u>	<u>Allowable Difference</u>	<u>Within- Lab esd</u>	<u>Allowable Difference</u>
Set 1					
Instrument D	1.02	0.011	0.03	0.014	0.05
Instrument R	1.03	0.0079	0.024	0.0087	0.027
Instruments D and R	1.03	0.0097	0.028	0.013	0.04
Set 2					
Instrument R	1.09	0.0079	0.031	0.0071	0.028
Instrument R	2.83	0.018	0.07	0.028	0.13

*Instrument D was a Philips MagiX PRO. Instrument R was a Philips PW1400.

TIME FOR ANALYSIS

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

REFERENCES

UOP Method 275, "Loss on Ignition of Catalyst at 900°C," www.astm.org
 UOP Method 291, "Total Chloride in Alumina and Silica-Alumina Catalysts by Potentiometric Titration," www.astm.org
 UOP Method 999, "Precision Statements in UOP Methods," www.astm.org

SUGGESTED SUPPLIERS

Chemplex Industries, 3091 S.E. Waaler Street, Stuart, Florida 34997-5923 (561-283-2700)
www.chemplex.com
 Fisher Scientific, 585 Alpha Dr., Pittsburgh, PA 15238 (412-490-8300) www.fishersci.com
 Matheson Tri-Gas, 166 Keystone Drive, Montgomeryville, PA 18936 (215-641-2700)
www.mathesontrigas.com
 PANalytical Inc., 12 Michigan Dr., Natick, MA 01760 (508-647-1100), or, Lelyweg 1, 7602 EA
 Almelo, The Netherlands (31 5465 34 444) www.panalytical.com
 SPEX CertiPrep, Inc., 203 Norcross Ave., Metuchen, NJ 08840 (732-549-7144) www.spexcsp.com