



A Honeywell Company

Total Chloride in Alumina and Silica-Alumina Catalysts by Microwave Digestion and Potentiometric Titration

UOP Method 291-15

Scope

This method is for determining the total inorganic chloride content of fresh or spent alumina and silica-alumina catalysts or catalyst supports. The range of quantitation is 0.01 to 10 mass-%.

Reference

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

The as-received sample is weighed into a Teflon™ vessel and 20% sulfuric acid is added. The vessel is placed in a specially configured microwave oven and heated for a pre-determined amount of time. If promoter metals are present, such as Pt, Pd, etc., the metals are reduced with magnesium as described under *Procedure, Sample Analysis, Reduction*. Chloride is determined potentiometrically by titration with a silver nitrate solution using a silver-silver chloride indicating electrode system.

Apparatus

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

Balance, readable to 0.0001 g

Beakers, sample, 250-mL, Metrohm USA, Cat. No. 6.1432.320

Bottle, washing, 500-mL, Nalgene™, Fisher Scientific, Cat. No. 03-409-17E

Crucible, 30-mL, Fisher Scientific, Cat. No. FB965E

Cylinders, graduated, 100- and 250-mL, Fisher Scientific, Cat. No. 08-550E and -550F, respectively

Dispenser, bottle-top, 10-50-mL, VWR, Cat. No. 40000-068

Electrode, combination silver/glass Titrode 6.0430.100, Metrohm USA, Cat. No. 6.0430.100

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. SAFETY DATA SHEETS (SDS) OR EXPERIMENTAL 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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Flask, volumetric, Class A, 1000-mL, Fisher Scientific, Cat. No. 10-210-5G

Microwave, 600 watt, Milestone Ethos Microwave Digestion System, with Carousel (turntable), 24-position with Teflon vessels, and Pro24 High Throughput Rotors (Pro2425M)

Oven, drying, capable of operation at 105°C

Pipet, volumetric transfer, Class A, 100-mL, Fisher Scientific, Cat. No. 13-650-2U

Pipet filler, Fisher Scientific, Cat. No. 13-681-102A

Stir bar, magnetic, Fisher Scientific, Cat. No. 14-513-59

Stir plate, Thermo Scientific™ Super-Nuova™ Multi-Position Digital Stir Plate, Fisher Scientific, Cat. No. 11-475-32Q

Titration, potentiometric, recording, ± 2000 -mV range, 1-mV, resolution with dispenser having a volume readout of 0.00 to 99.9 mL and 0.01% resolution, Titration Model 904, Metrohm USA

Watch glass, glass, 65 mm diameter, Fisher Scientific, Cat. No. 02-610B

Reagents and Materials

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used. References to water mean distilled water, except where noted.

Cleaning pad, synthetic, mildly abrasive, Scotch-Brite™, Runco Office Supply, Cat. No. MMM-96

Filter aid, Whatman ashless clippings, Fisher Scientific, Cat. No. 09924542

Magnesium, metal turnings, Sigma-Aldrich, Cat. No. 200905-500G

Potassium chloride, primary standard, oven dried at 105°C for 2.5 hours, Fisher Scientific, Cat. No. P217-500

Potassium chloride solution, saturated, Fisher Scientific, Cat. No. SP138-500

Silver nitrate, 0.1N standard aqueous solution, Fisher Scientific, Cat. No. SS72-4

Silver nitrate, 0.01N standard aqueous solution. Pipet 100 mL of the 0.1N aqueous solution into a 1000-mL flask and dilute to volume with distilled water. The exact normality is one-tenth that of the certified or standardized value of the nominally 0.1N silver nitrate standard solution.

Sulfuric acid, 20%(v/v), Reagent Grade, Fisher Scientific, Cat. No. 816532

Water, distilled

Wiper, Kimwipes™, Fisher Scientific, Cat. No. 06-666A

Procedure

The analyst is expected to be familiar with general laboratory practices, the techniques of microwave digestion and potentiometric titration, and the equipment being used. Dispose of used reagents, materials, and samples in an environmentally safe manner according to local regulations.

Silver–Silver Chloride Electrode Preparation and Reconditioning

Proper electrode preparation is essential to obtain reproducible and noise-free titration curves having good endpoints. An electrode should be dedicated to chloride analysis. Prepare and recondition the silver-silver chloride electrode as follows:

1. Clean the silver surface with a Scotch-Brite pad. Rinse with distilled water.
2. Weigh approximately 0.1 g of potassium chloride and place in a beaker. Using a graduated cylinder, add 20 mL of 20% sulfuric acid and 80 mL of distilled water to the beaker. Immerse the electrode, and titrate to the endpoint with 0.1N silver nitrate.
3. Remove the electrode from the solution and rinse with distilled water.
4. Wipe the excess silver chloride from the electrode with a wiper.
 - The electrode should be cleaned after each titration by rinsing with distilled water.

The freshly coated silver-silver chloride electrode may be stored in distilled water or carefully dried using tissues and stored for future use. It is necessary to repeat the electrode preparation when the AgCl begins to peel from the surface.

Silver Nitrate Standardization

The 0.1N silver nitrate solution may be purchased at a certified concentration. Alternatively, the solution may be standardized as follows:

1. Weigh 0.10 ± 0.01 g of dried potassium chloride to the nearest 0.0001 g into a clean, dry 250-mL beaker.
2. Using a graduated cylinder, add 100 mL of distilled water. Add a stirring bar. Acidify with 20 mL of 20% sulfuric acid.
3. Titrate the potassium chloride solution, while stirring, with 0.1N silver nitrate solution.
4. Calculate the normality of the silver nitrate solution to 3 significant figures using Equation 1.

$$N = \frac{A}{0.07455B} \quad (1)$$

where:

A = mass of potassium chloride weighed into beaker, g

B = volume of silver nitrate solution used in titration, mL

N = normality of the silver nitrate solution

0.07455 = molecular weight of the potassium chloride multiplied by 0.001, the factor to convert milliliters to liters

Sample Analysis

Sample digestion/reduction can be accomplished by microwave heating, as follows, or by conventional heating (see *Note* and *Appendix*).

Samples of fresh or spent catalyst that contain promoter metals (usually noble metals) must be reduced as described under *Reduction*. Catalyst bases do not require reduction.

Microwave Digestion of Catalyst

1. Weigh approximately 2 g of the as-received catalyst or catalyst support to the nearest 0.0001 g into a 120-mL Teflon vessel.
 - When results are to be reported on a volatile-free basis, weigh out a separate portion of the sample for the determination of LOI at 900°C as directed in UOP Method 954, "Loss on Ignition (LOI) for Fresh, Regenerated, Used, and Spent Catalysts, Catalyst Supports, and Adsorbents," at the same time the sample is weighed for chloride.
2. Using a graduated cylinder or a bottle-top dispenser, add 30 mL of 20% sulfuric acid to the Teflon vessel.

3. Cap and place the vessel in the holder and place on the carousel.
4. Secure and tighten the vessel as per the manufacturer's instructions.
5. Repeat the above procedure with additional samples until the carousel contains up to 24 sample vessels.
6. Place the carousel in the microwave oven.
7. Set the power and time program for the appropriate number of samples as suggested by the manufacturer and include at the end of the timing sequence a 20-minute period at 0% power for cooling.
 - Ramp temperature from ambient to 170°C at approximately 10°C per minute.
 - Hold at 170°C for a minimum of 20 minutes.
 - Cool for 20 minutes at 0% power.
8. Remove the carousel from the microwave oven. Remove the vessel from the carousel and make certain the vessel is cool before releasing any pressure.
9. Remove the cap. Carefully rinse the cap with water, catching the rinsings in a 250-ml sample beaker.
10. Quantitatively transfer the solution in the vessel into a 250-mL sample beaker. Rinse the vessel several times with 10-15 mL of distilled water, being careful not to cause any splashing. If any aluminum sulfate crystals form in the sample solution, warm slightly on a hot plate or in an oven to dissolve.

Reduction

Catalyst bases do not require reduction.

1. Add an additional 15 mL of 20% sulfuric acid into the sample beaker to assist with the digestion of the magnesium turnings.
2. Add a stirring bar to each beaker and start the magnetic stirrer.
3. Add approximately 0.3 g of magnesium turnings and cover with a watch glass. When the magnesium has completely dissolved, add an additional 0.3 g of magnesium turnings to ensure complete reduction.
4. When the magnesium has completely dissolved, rinse the watch glass with distilled water, catching the rinsings in the sample beaker.
5. Continue the sample analysis as described under *Titration*.

Titration

1. Assemble and operate the titrator and the electrode according to the manufacturer's instructions.
2. Condition the electrode as needed prior to running samples as described in *Silver–Silver Chloride Electrode Preparation and Reconditioning*.
3. Prior to titration, add sufficient distilled water to ensure complete electrode immersion, typically to about 100-mL total volume.
4. Add a small amount (~0.2 g) of filter aid to assist in keeping the electrode clean and free from silver chloride precipitate.

5. Titrate the sample with 0.1N silver nitrate at a titration rate of about 2.5 mL/min using a moderately fast stirring rate (no vortex or splashing). As the endpoint is approached, reduce the titration rate to approximately 0.1 mL/min. For chloride levels below 0.05 mass-%, titrate with 0.01N silver nitrate.
 - The endpoint of the titration corresponds to that volume of titrant at which the rate of change of potential, $\Delta \text{EMF}/\Delta \text{mL}$, reaches a maximum. Observe inflections and record the corresponding volume of titrant dispensed.
6. Clean the electrodes after each titration by rinsing with distilled water.

Calculations

Calculate the chloride content of the sample to the nearest 0.01 % as follows:

A) As-received basis:

$$\text{Chloride, mass-\%} = \frac{3.545 \text{ C N}}{W} \quad (2)$$

B) Volatile-free basis:

$$\text{Chloride, mass-\%} = \frac{3.545 \text{ C N}}{W \left(\frac{100 - V}{100} \right)} \quad (3)$$

where:

C = volume of silver nitrate to reach the chloride endpoint, mL

N = normality of silver nitrate

V = loss on ignition determined by UOP Method 954, mass-%

W = sample mass, g

3.545 = 0.03545 times 100, factor combining the millimolar weight of chlorine and the factor to convert mass fraction to mass-%

100 = 100%

Note

An alternative digestion procedure using acorn condensers is described in the *Appendix*. Data from a comparative study has shown that microwave or hot plate heating produce equivalent results.

Precision

The precision statements were determined using UOP Method 999.

Repeatability and Site Precision

A nested design was carried out for determining chloride in two reduced catalysts with two analysts in one laboratory. Each analyst carried out tests on two separate days, performing two tests each day per sample. The total number of tests performed was 16. 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 Table 1. Two tests performed by the same analyst on the same day should not differ by more than the repeatability allowable difference with 95% confidence. Two tests performed in one laboratory by different analysts on different days should not differ by more than the site precision allowable difference with 95% confidence.

Table 1
Repeatability and Site Precision, mass-%

<u>Catalyst Sample</u>	<u>Chloride Concentration</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>
Reduced	0.85	0.004	0.01	0.007	0.02
Reduced	0.95	0.006	0.02	0.008	0.02

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.

Time for Analysis

The total elapsed time for a set of 12 samples is 7 hours. The labor requirement per analysis is 1.6 hours when done singly or 0.8 hour when done in groups of 6 or more.

Suggested Suppliers

Fisher Scientific Co., 711 Forbes Ave., Pittsburgh, PA 15219-4785, USA, 1-412-490-8300,
www.fishersci.com

Lab Line Instruments, 1999 N 15th and Bloomingdale Avenue, Melrose Park, IL 60160, USA, 1-708-450-2600

Metrohm USA, 6555 Pelican Creek Circle, Riverview, FL 33578, USA, 1-813-316-4700,
www.metrohmusa.com

Milestone Inc. 25 Controls Dr. Shelton, CT 06484, USA, 1-866-995-5100, www.milestonesci.com

Runco Office Supply, 1655 Elmhurst Road, Elk Grove Village, IL 60007, USA, 1-847-437-4300,
www.runcoonline.com

Sigma-Aldrich, Milwaukee, WI 53201, USA, 1-414-438-3850, www.sigma-aldrich.com

Wilmad/Lab-Glass, 1002 Harding Hwy., Buena, NJ 08310, USA, 1-856-697-3000, www.wilmad-labglass.com

Appendix

Acorn Condenser Digestion of Catalyst

Scope

This appendix describes an alternative catalyst digestion procedure using an acorn condenser heating technique. Data from a comparative study has shown that conventional or microwave heating produce equivalent results.

Outline of Method

The as-received sample is weighed into a sample beaker and digested with hot dilute sulfuric acid. Promoter metals, if present, are reduced with aluminum pellets. The sample is then titrated as described in the body of the method.

Apparatus

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used. The following apparatus is in addition to or a substitution of those listed in the body of the method:

Condenser, acorn type (see Figure), Wilmad LabGlass, Custom order

Forceps, stainless steel, Fisher Scientific, Cat. No. 13-812-38

Hood, laboratory

Hot plate, stirring, Fisher Scientific, Cat. No. 11-300-49SHP

Stir bar, magnetic, 38-mm length, Fisher Scientific, Cat. No. 14-513-60

Tubing, Tygon, VWR, Cat. No. 63009-174, to fit condenser

Reagents and Materials

Aluminum pellets, Sigma-Aldrich, Cat. No. 338788-50G

Boiling chips, Fisher Scientific, Cat. No. 09-191-12

Water, tap, cold

Procedure

Digestion

1. Weigh approximately 2 g of the as-received catalyst or catalyst base to the nearest 0.0001 g into a 250-mL sample beaker. When results are to be reported on a volatile-free basis, weigh out a separate portion of the sample for the determination of LOI at 900°C, as directed in UOP Method 954, at the same time the sample is weighed for chloride.
2. Using a graduated cylinder or a bottle-top dispenser, add 75 mL of 20% sulfuric acid to the beaker containing the sample for chloride determination. Add several boiling chips.
3. Place the beaker on a cool hot plate, located in a hood or well-ventilated area, and place an acorn condenser in the top of the beaker (see Figure).
4. Start cold tap water running through the condenser and turn on the hot plate. Heat the sample to just below the boiling point (do *not* allow to boil) until the catalyst is completely digested, or for a maximum of 6 hours. Fresh alumina catalyst or base will usually require about 2 hours

for complete digestion, while used alumina catalyst or any silica-alumina catalyst may not completely dissolve, even after 6 hours.

5. Turn off the hot plate and allow the sample to cool.
6. Lift off the acorn condenser and rinse with distilled water, catching the rinsings in the sample beaker. If promoter metals are present, the sample needs to be reduced. Follow the procedure below described under *Reduction*. If no promoter metals are present, proceed with Step 7.
7. Continue the sample analysis as described under *Titration* in the body of the method.

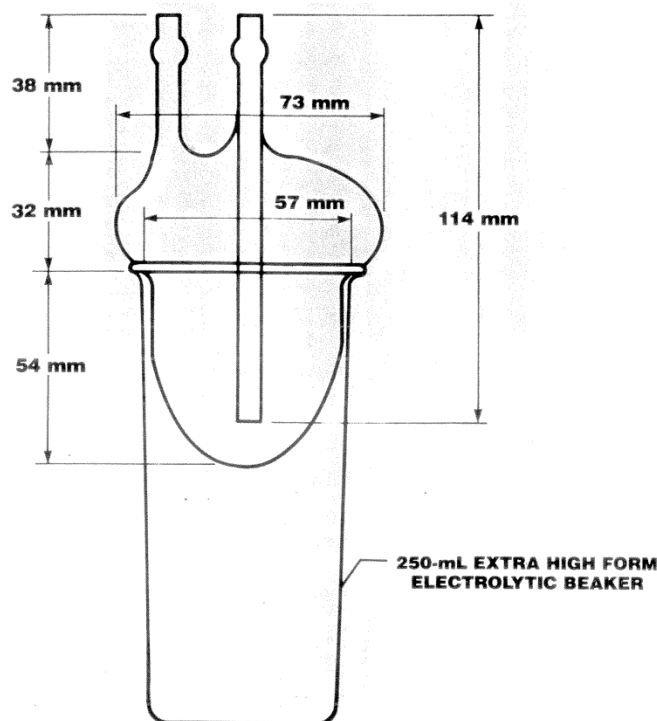


Figure
Condenser-Beaker Assembly

Reduction

1. Add 1-2 aluminum pellets to the sample beaker and replace the acorn condenser in the top of the beaker.
2. Turn the heat back on to a medium setting. Do not allow the sample to boil.
3. Let the sample reduce for ~30 minutes.
4. Turn off the heaters and allow the sample to cool.
5. Lift off the acorn condenser and rinse with water, catching the rinsings in the sample beaker.
6. Remove the aluminum pellets with forceps, rinse the pellets and forceps with water, catching the rinsings in the sample beaker.
7. Continue the sample analysis as described under *Titration* in the body of the method.

Precision

The precision statements were determined using UOP Method 999.

Repeatability, Site Precision, and Reproducibility

A nested design was carried out for determining chloride in oxidized and reduced catalysts with two analysts in five laboratories. Each analyst carried out tests on two separate days, performing two tests each day. The total number of tests performed was 120. Using a stepwise analysis of variance procedure, the within-day, within-lab, and between-lab estimated standard deviations (esd) were calculated at the concentration means listed in Table A1. Two tests performed by the same analyst on the same day should not differ by more than the repeatability allowable difference with 95% confidence. Two tests performed in one laboratory by different analysts on different days should not differ by more than the site precision allowable difference with 95% confidence. Two tests performed by different analysts in different laboratories on different days should not differ by more than the allowable difference shown in Table A1 with 95% confidence.

Table A1
Repeatability and Site Precision, mass-%

Catalyst Sample	Chloride Conc.	<u>Repeatability</u>		<u>Site Precision</u>		<u>Reproducibility</u>	
		<u>Within- Day esd</u>	<u>Allowable Difference</u>	<u>Within- Lab esd</u>	<u>Allowable Difference</u>	<u>Between- Lab esd</u>	<u>Allowable Difference</u>
Oxidized	1.18	0.012	0.04	0.014	0.04	0.017	0.05
Oxidized	1.10	0.016	0.05	0.016	0.05	0.020	0.06
Reduced	1.05	0.015	0.05	0.014	0.04	0.023	0.08

The data in Table A1 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.

Time for Analysis

The elapsed time for an analysis is up to 8 hours. The labor requirement is 0.8 hour.