



A Honeywell Company

Sodium in Catalysts by AAS

UOP Method 410-14

Scope

This method is for determining low levels of sodium in gamma- and theta-alumina and silica-alumina base catalysts using atomic absorption spectrophotometry (AAS). Results can be reported on an as-received or on a volatile-free basis. The lower limit of detection is approximately 0.0002 mass-%.

References

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 representative portion of catalyst is digested in hot sulfuric acid. The sodium concentration is measured by using an atomic absorption spectrophotometer in the flame emission mode. Loss on ignition is determined by UOP Method 954, "Loss on Ignition (LOI) for Fresh, Regenerated, Used, and Spent Catalysts, Catalyst Supports, and Adsorbents," to permit the calculation of results on a volatile-free basis.

Apparatus

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

Atomic absorption spectrophotometer, PerkinElmer AAnalyst 200 or AAnalyst 800

Balance, readable to 0.0001 g

Beaker, quartz, low form, 250-mL, Ace Glass, Inc., Cat. No. 5334-14

Beaker, PTFE, 250-mL, Fisher Scientific, Cat. No. 02-586-1H

Bottles, polypropylene, narrow mouth, round, with screw cap, 125-mL, Fisher Scientific, Cat. No. 02-925C

Bottles, washing, polypropylene, 500-mL capacity, labeled "Deionized Water," Fisher Scientific, Cat. No. 02-897-3

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. SAFETY DATA SHEETS (SDS) OR EXPERIMENTAL SAFETY DATA SHEETS (ESDS) 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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Cylinders, graduated, 25-, 50-, and 100-mL, VWR, Cat. Nos. 89001-112, -114, and -116, respectively

Flasks, volumetric, 100-, 500-, and 1000-mL, VWR, Cat. Nos. 89041-930, -936, -938, respectively

Flask, volumetric, 100-mL, polymethylpentene (PMP), Fisher Scientific, Cat. No. 10-198-52C

Funnel, polypropylene, analytical, 75-mm diameter, with external ridges, Fisher Scientific, Cat. No. 10-500-15

Hood, laboratory

Hot plate, variable heat, Corning Model PC-500, Fisher Scientific, Cat. No. 11-495-52A

Pipet, single channel, variable volume, 1-10-mL, VWR, Cat. No. 89079-978,

Pipets, volumetric, transfer, Class A, 1-, 5-, and 10-mL, Fisher Scientific, Cat. Nos. 13-650-2B, -2F, and -2L, respectively

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

Watch glass, PTFE, to cover 250-mL beaker, Fisher Scientific, Cat. No. 02-617-1G

Reagents and Materials

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used. Unless otherwise specified, references to water mean deionized water.

Acetylene, cylinder, compressed gas, local supply

Air, compressed, filtered and dried, minimum of 483 kPa (70 psig) to AAS instrument

Aluminum solution, 10,000 µg/mL, SPEX CertiPrep, Cat. No. PLAL1-3X

Gloves, disposable, nitrile, Fisher Scientific, Cat. Nos. 11-390-13A (small) through -13D (x-large)

Gloves, neoprene/natural rubber, VWR, Cat. No. 32917-212 (size 10)

Hydrofluoric acid, concentrated, trace metals grade, VWR, Cat. No. EM-HX0628-7

Nitric acid, concentrated, trace metals grade, VWR, Cat. No. EM-NX0408-2

Pipet tips, for pipettor, 1-10-mL, VWR, Cat No., 53495-706

Pipets, volumetric, transfer, Class A, 1-, 5-, and 10-mL, Fisher Scientific, Cat. Nos. 13-650-2B, -2F, and -2L, respectively

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

Potassium solution, 10,000-µg/mL, SPEX CertiPrep, Cat. No. PLK1-3X

Sodium stock solution, 1000-µg/mL, SPEX CertiPrep, Cat. No. PLNA1-2X

Sodium stock solution, 100-µg/mL. Pipet 50 mL of the 1000-µg/mL sodium stock solution into a 500-mL volumetric flask, dilute to the mark with water and mix. Store in a polypropylene bottle.

Sulfuric acid, concentrated, trace metals grade, VWR, Cat. No. EM-SX1248-6

Water. Unless otherwise indicated, references to water throughout this method shall be understood to mean distilled or deionized water which has a sodium concentration of less than 0.06 ppm. Should the available supply of water have a sodium content in excess of this level, some process of demineralization should be employed to attain water of this desired purity. Water that is demineralized or deionized and stored in polypropylene bottles is relatively sodium-free.

Distilled water stored in glass bottles is not of sufficient purity. When checking water for sodium content, readings of 2% (0.0088) absorbance or less will indicate the water is of sufficient purity for this method. Water should be checked prior to any sodium determinations.

Procedure

The analyst is expected to be familiar with general laboratory practices, the technique of atomic absorption spectrophotometry, and the equipment being used. Dispose of used supplies and samples in an environmentally safe manner according to applicable regulations. Wear disposable nitrile gloves throughout the analysis to avoid sodium contamination from the hands.

CAUTION: All subsequent steps involving additions of reagents and heating of samples must be performed in a properly operating fume hood, and appropriate personal protective equipment must be worn. See the safety data sheet (SDS) and any applicable requirements for each material used.

Care and Cleaning of Glassware

Beakers and other labware should be reserved exclusively for sodium determination. Pretreat beakers and watch glasses to be used for the first time in this analysis by refluxing for 4 hours with 40% sulfuric acid.

Preparation of Calibration Standards

Prepare a blank and three calibration standards containing sodium at the following concentrations: 1-, 5-, and 10- $\mu\text{g/mL}$.

1. Into each of four 100-mL volumetric flasks, pipet 10 mL of the 10,000- $\mu\text{g/mL}$ potassium solution, 50 mL of 10,000- $\mu\text{g/mL}$ aluminum solution, and then 5 mL of concentrated H_2SO_4 .
 - The 50-mL addition of aluminum is for matrix matching, and matches catalyst that is alumina based. For silica-alumina catalyst, reduce the volume of aluminium solution added appropriately. The silica portion does not need to be matrix-matched, as the silica is lost in the sample preparation.
2. To the first three flasks add consecutively by volumetric pipets 1-, 5-, and 10-mL aliquots of the 100 $\mu\text{g/mL}$ sodium stock solution. No sodium is added to the fourth flask since it serves as the blank.
3. Dilute the contents of each flask to the mark with water and mix well. Store in polypropylene bottles.

Sample Preparation, Alumina Base

1. Weigh, to the nearest 0.0001 g, 1.00 ± 0.05 g of sample into a tared 250-mL quartz or PTFE beaker.
2. Add 10 mL of deionized water and then 5 mL of concentrated sulfuric acid to the beaker. Swirl to mix the contents of the beaker.
3. Place on a hot plate at 275 $^{\circ}\text{C}$ temperature. Heat until white fumes of sulfuric acid appear.
4. Remove the beaker from the hot plate and allow it to cool. There should not be particulate matter in the solution. If there is particulate matter in the solution, add 1-2 mL of concentrated nitric acid, and return the beaker to the hot plate and heat until white fumes of sulfuric acid reappear. Remove the beaker from the hot plate and allow it to cool. If particulate matter still remains, take a fresh aliquot of sample and prepare it as described in *Sample Preparation, Silica-Alumina Base*.

5. Slowly rinse the sides of the beaker with deionized water. Add about 20 mL of water, cover with the PTFE watch glass, and return to the hot plate.
6. Boil the solution gently for 10 minutes; then, using the funnel, quantitatively transfer the contents into a 100-mL PMP volumetric flask, rinsing the beaker and watch glass several times with deionized water. Be sure to allow sufficient room in the flask for the addition of the potassium solution (Step 7).
7. Cool the solution by placing the flask in a cold water bath. Then add 10 mL of 10,000- $\mu\text{g}/\text{mL}$ potassium solution.
8. Dilute to the mark with water and mix well.

Sample Preparation, Silica-Alumina Base

1. Weigh, to the nearest 0.0001 g, 1.00 ± 0.05 g of sample into a tared 250-mL PTFE beaker.
2. Add 10 mL of deionized water, 5 mL of concentrated sulfuric acid, and 3 mL of hydrofluoric acid to the beaker. Swirl to mix the contents of the beaker.
 - Caution: Wear neoprene/natural rubber or other suitable gloves whenever working with HF or HF-containing samples.
3. Place on a hot plate at 275 °C temperature. Heat until white fumes of sulfuric acid appear. If undissolved material remains, rinse down the sides of the beaker with water and add another 3 mL of hydrofluoric acid. Reheat until white fumes of sulfuric acid appear.
4. Remove the beaker from the hot plate and allow it to cool.
5. Slowly rinse the watch glass and sides of the beaker with deionized water. Add about 20-mL of water, cover with the PTFE watch glass, and return to the hot plate.
6. Boil the solution gently for 10 minutes; then, using the funnel, quantitatively transfer the contents into a 100-mL PMP volumetric flask, rinsing the beaker and watch glass several times with water.
7. Cool the solution by placing the flask in a cold water bath. Then add 10 mL of 10,000- $\mu\text{g}/\text{mL}$ potassium solution.
8. Dilute to the mark with water and mix well.

Sample Analysis

The analysis is performed by flame emission using an atomic absorption spectrophotometer.

Approximate operating conditions are listed in Table 1 for the particular instrument referred to under *Apparatus*. Optimum conditions should be established for each instrument.

Table 1
General AAS Conditions of Operation

Wavelength	589 nm
Slit width	0.7 nm

Consult the manufacturer's instruction manual for best operating conditions, as well as adjustments necessary to realize maximum sensitivity.

1. Set up the instrument in the emission mode and enter the concentrations of the standards. The specified instrument will internally plot calibration data as the standards are run, and indicate the concentration of unknown solutions in $\mu\text{g}/\text{mL}$.

2. Ignite the flame, stabilize the instrument for approximately five minutes, and then start the readings.
3. Analyze in the following order: blank, standards, samples and then repeat the standards. The final standards should read within 3%, or approximately 1 µg/mL, of its original concentration. If not, rerun the series.
4. Samples that have a higher sodium content than 10 µg/mL will indicate over calibration and must be aliquoted and diluted with the blank. Apply an appropriate dilution factor (X/Y) in calculating results in such cases.

Calculations

Calculations are normally performed by the computer data reduction software after the analyst enters the appropriate values for the mass of the sample taken and the dilution volume.

The equivalent manual calculation is shown in Equation 1:

$$\text{Sodium, volatile- free basis, mass-\%} = \left(\frac{C D}{10,000 G V} \right) \left(\frac{X}{Y} \right) \quad (1)$$

where:

C = concentration of sodium in final solution as determined by the instrument, µg/mL

D = volume of final dilution, mL

G = sample mass, g

V = $1 - \frac{\% \text{ loss on ignition}}{100}$

X = volume to which sample aliquot is diluted, mL

Y = volume of aliquot taken from sample solution, mL (if no aliquot is taken X/Y will be one)

10,000 = factor used to convert µg to % sodium

Report sodium to the nearest 0.0001 mass-%, but do not exceed three significant figures. To convert mass-% sodium to sodium oxide, multiply mass-% sodium by 1.348.

Notes

1. The presence of tungsten or other elements may cause precipitation in the final sample solution. If this occurs, add 3 mL of hydrofluoric acid to the beaker. In this case, HF should also be added to the calibration standard for matrix matching.
2. This method is not suitable for use with barium-containing catalysts, as barium will not dissolve using the specified sample preparation.

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 n-dodecane in sodium by two analysts, with each analyst performing analyses on two separate days, performing four analyses each day for a total of 32 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 Table 2. 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 Table 2 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 Table 2 with 95% confidence.

Table 2
Repeatability and Site Precision, mass-%

Sodium Concentration	<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>
0.0142	0.00049	0.0019	0.00106	0.0041
0.1044	0.00362	0.0142	0.00259	0.0102

The data in Table 2 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.

Reproducibility

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

Time For Analysis

The elapsed time for one analysis is two hours. The labor requirement is 0.7 hour excluding the loss of ignition determination which requires an additional 0.4 hour.

Suggested Suppliers

Ace Glass, Inc., P.O. Box 688, 1430 North West Blvd., Vineland, NJ 08362-0688, USA, 1-856-691-3333, www.aceglass.com

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

PerkinElmer Analytical Instruments, 710 Bridgeport Ave., Shelton, CT 06484-4794, USA, 1-203-925-4600, www.perkinelmer.com

SPEX CertiPrep, Inc., 203 Norcross Ave., Metuchen, NJ 08840, USA, 1-732-549-7144, www.spexcsp.com

VWR International, 1310 Goshen Parkway, West Chester, PA 19380, USA, 1-610-431-1700, www.vwr.com