



A Honeywell Company

Water in Solids by Furnace Desorption with Volumetric Karl Fischer Titration

UOP Method 993-15

Scope

This method is for determining total water in solid materials such as catalysts and zeolites (molecular sieves). Other materials may be applicable. This test is quantitative over a range of 0.2 to approximately 30 mass-% water. Common interferences are discussed in *Notes*.

References

ASTM Method D1364, "Water in Volatile Solvents (Karl Fischer Reagent Titration Method)," www.astm.org

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

Outline of Method

The sample is introduced into a furnace and ramped to 900°C. The water liberated from the sample is carried by a dry nitrogen stream to the detection cell. The water is titrated volumetrically by the Karl Fischer method and reported as mass-%.

Apparatus

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

Balance, readability 0.0001 g

Beaker, 50-mL, VWR, Cat. No. 13912-149

Desiccator, plastic, Fisher Scientific, Cat. No. 08-642

Drier, for nitrogen, VWR, Cat. No. 22891-090

Electrode, Detector Elec./BNC F/CA-20/100, COSA Xentaur, Cat. No. MC12006

Regulator, nitrogen, two-stage, high purity, delivery pressure range 30-700 kPa (4-100 psi), Matheson Tri-Gas, Model 3122-580

Spatula, VWR, Cat. No. 82027-526

Stirrer, magnetic, with stir bar, VWR, Cat. No. 89090-988

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Titration, amperometric, with titration cell, designed to perform titrations to pre-set endpoints with a polarizing current capable of maintaining approximately 1 V across two platinum electrodes and a sensitivity capable of indicating an endpoint based on a 50 mV change. Included is a dispenser having a volume readout of 0.001-99.999 mL with a 0.01% resolution, and a 10-mL buret. The Mitsubishi, Model CA-200, Mitsubishi Chemical Analytech, is satisfactory.

Oven/Vaporizer, Model VA-121, Mitsubishi Chemical Analytech, Cat. No. MC60025

Quartz boats, Mitsubishi Chemical Analytech, Cat. No. VAHSB

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 deionized or distilled, unless otherwise specified.

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

Cleanser, mildly abrasive, Comet™, Runco Office Supply, Cat. No. PAG-02255

Desiccant, 8-mesh, indicating, Fisher Scientific, Cat. No. NC9979539

Hydrogen peroxide (30%), ACS Grade, VWR, Cat. No. JT2186-1

Karl Fischer solvent, Aquamicon GEX, Mitsubishi Chemical Analytech, available from COSA Xentaur, Cat. No. MC02044 (See Note)

Karl Fischer titrant, SS-Z 5mg, Mitsubishi Chemical Analytech, available from COSA Xentaur, Cat. No. SS-Z 5mg Titrant

Molecular sieve, Mitsubishi Chemical Analytech, available from COSA Xentaur, Cat. No. MC02025

Nitrogen, 99.999% minimum purity (passed through Molecular Sieve/Desiccant prior to use), local supply

Reference standard, powder standard, Cosa Instruments, Cat. No. MC02022 or Hydranal standard sodium tartrate-2-hydrate, Sigma-Aldrich Cat. No. 34803

Sulfuric acid, concentrated, 95-98%, ACS Grade, VWR, Cat. No. JT9681-2

Transfer pipets, disposable, Fisher Scientific, Cat. No. 13-711-9AM

Water, deionized or distilled

Water, tap, warm

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

Procedure

The analyst is expected to be familiar with general laboratory practices, the technique of Karl Fischer titration, and the equipment being used. Refer to ASTM Method D1364, "Water in Volatile Solvents (Karl Fischer Reagent Titration Method)," for additional information regarding Karl Fischer

titration. Caution: hot surfaces when instrument in operation. Provide signage and access controls appropriate to good lab practices and applicable regulations.

Instrument Setup

1. The instrument should be set up as per manufacturer's specifications. Connect the drier listed in *Apparatus*, filled with desiccant, in the nitrogen line before the instrument. This is in addition to the driers in the instrument. General guidelines for operating conditions for the instrument referred to under *Apparatus* are shown in Table 1. However, these conditions may be optimized to meet the user's specific needs/requirements.
2. Pipet 100 mL of the titration solvent into the 250-mL titration cell.
 - Replace the titration solvent when the solution becomes cloudy, or the drift becomes excessive.
3. Adjust the stirring speed to create a vortex in the solvent such that bubbles do not develop at its center. Allow the drift reading of the solution to stabilize.

Table 1
Typical Operating Conditions for Volumetric Titration

Delay	3 minutes
Minimum titration time	27 minutes
End sensitivity	30 seconds
Furnace temperature	900°C
Nitrogen flow rate	250 mL/min

Electrode Preparation

Clean the double platinum electrode using the following procedure:

1. Use a mildly abrasive cleanser to prepare a "paste" with warm tap water.
2. Load a wiper or a cleaning pad with the paste. Polish the platinum tips of the detector electrode with the paste and wiper or cleaning pad.
3. Rinse the residue off the electrode with warm tap water, then with deionized water.
 - If required sensitivity is not achieved with cleaning, the electrode tip can be immersed in a solution of equal parts of concentrated sulfuric acid and hydrogen peroxide in a small beaker and stirred for approximately one hour or more to remove any residual organic coating on the platinum. Great care should be taken with this solution, and it is strongly recommended to wear heavy nitrile or neoprene gloves.

Standardization for Titration

1. On the analytical balance, tare, to the nearest 0.0001 g, a transfer pipet with a few mL of de-ionized water.
2. Remove the titration vessel stopper and add one drop of water using the tared dropper, titrate the water as per manufacturer instructions.
 - The drop of water must be added directly to the titration solvent and must not contact any part of the glass titration vessel.
3. Replace the dropper on the analytical balance, record the weight to the nearest 0.0001 g, and enter the weight into the titrator.
4. When the first titer is complete, repeat Steps 1-3.
 - Run titers until there are three consistent values
5. Average the titer results.

- Make sure the three titers are within 1% relative standard deviation.
- Titer values are good for the day, and should not be used for more than one day.

Blank Analysis

1. Turn on furnace and nitrogen.
 - Temperature should be below 100°C at the start.
 - Good laboratory practices should be exercised when working with elevated temperatures.
 - Although 900°C is the typical temperature utilized in this procedure, other temperatures may be used. Investigation and development may be necessary to determine performance for specific sample types.
 - Nitrogen flow is approximately 250 mL/min and passes through the desiccant and/or molecular sieve drier. The desiccant/molecular sieve should be replaced after approximately 4-6 months, when the indicator shows more than 75% spent, or when the instrument drift remains high after replacing the titration solvent.
2. Place an empty quartz boat into the oven and ramp the temperature to 900°C. Analyze the blank as per manufacturer instructions.
 - Quartz boats should be kept in a desiccator when not in use
3. Record the mL titrant consumed for the blank as indicated by the titrator.
 - Blank values are good for the day, and should not be used for more than one day.
 - The blank value is primarily due to moisture entering the system when it is opened to insert the boat.
4. Turn off the power to the furnace and cool to below 100°C.

Reference Standard Analysis

1. Place an empty quartz boat on the balance and tare.
2. Using a spatula, transfer an aliquot of reference standard into the quartz boat and record the weight to the nearest 0.0001 g.
 - A reference standard should be selected that contains a known amount of water, ideally similar to the level expected in the samples, and of sufficient quantity to determine long term repeatability. It may be the reference standards listed in *Reagents and Materials*, or a material similar to the types of samples routinely analyzed that has a stable water content.
3. Insert the quartz boat into the oven and ramp to 900°C. Analyze as per manufacturer instructions.
4. Record the volume (mL) of titrant consumed for the sample as indicated by the titrator.
5. Calculate the water content (see *Calculations*).
 - Reference standard results should match the theoretical result within the limits listed in the method precision statement or long term control limits established by the lab.

Sample Analysis

1. Place an empty quartz boat on the balance and tare. Furnace temperature should be 100°C or lower before weighing the sample.
2. Transfer the sample by spatula into the quartz boat and record the weight of the quartz boat with the sample to the nearest 0.0001 g.
 - The sample size needed is dependent on the expected water concentration. The optimum sample amount results in at least a 1 mL titration. Suggested sample sizes are shown in Table 2.

Table 2
Sample Sizes Guidelines for Expected Water Content

<u>Expected Water Concentration, mass-%</u>	<u>Sample Amount, g</u>
0.2-0.5	1-2
0.5-5	1
5-10	0.5
10-30	0.1-0.2

3. Insert the quartz boat into the oven and ramp the oven temperature to 900°C. Analyze as per manufacturer instructions.
4. Record the volume (mL) of titrant consumed for the sample as indicated by the titrator.
5. Calculate the water content (see *Calculations*).

Calculations

Automatic titrators are often capable of performing the calculations required. If the titrator used is not capable of performing the calculations, use the equations below.

Calculate the titer of the titrant using Equation 1:

$$\text{Titer, mg H}_2\text{O/ mL of reagent} = \frac{1000 S}{V} \quad (1)$$

where:

S = mass of water used in the standardization, g

V = volume of titrant used, mL

1000 = conversion from g to mg

Calculate the mass-% water, to the nearest 0.01 mass-%, using Equation 2:

$$\text{Water, mass-\%} = \frac{(A - B) C}{10 W} \quad (2)$$

where:

A = sample titration value, mL

B = blank value, from *Blank Analysis*, mL

C = average titer value (from Standardization or Equation 1), mg H₂O/ mL of reagent

W = mass of sample, g

$$10 = \frac{1000}{100} \quad (2a)$$

where:

100 = conversion to %

1000 = convert g to mg

Note

Common interferences include: aldehydes, ketones and mercaptans.

Special Karl Fischer reagents may be purchased to allow for water determination in the presence of ketones and aldehydes. Such reagents include Dehydrated Solvent KTX, Cosa Instrument, Cat. No. MC02046.

Mercaptans oxidize to disulfides concurrently with the water determination. This gives a false high water content. The measured water concentration can be mathematically corrected for mercaptans if the concentration of the mercaptans is known. Calculate the water, corrected for mercaptan interference, using Equation 3:

$$\text{Corrected water, mass-\%} = (\text{mass-\% water, from Equation 2}) - (0.281 S) \quad (3)$$

where:

S = mercaptan sulfur, mass-%

$$0.281 = \frac{18}{(32)(2)} \quad (3a)$$

where:

2 = correction for the $2 e^-$ reaction in the presence of water, $1 e^-$ oxidation of RSH

18 = molecular weight of water

32 = atomic mass of sulfur

Other interferences and their corrections are beyond the scope of this method, but may be available in the literature.

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 water in two solid samples by two analysts, with each analyst performing analyses on two separate days, performing three analyses each day for a total of 24 analyses. Using a stepwise analysis of variance procedure, the within-day estimated standard deviations (esd) were calculated at the concentration means listed in Table 3. 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 3 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 3 with 95% confidence.

Table 3
Repeatability and Site Precision, Water, mass-%

<u>Sample</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>
A	2.6	0.05	0.2	0.05	0.2
B	25.1	0.29	1.0	0.30	1.0

The data in Table 3 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 2 hours. The labor requirement to prepare the volumetric titrator and oven is 1.5 hours. The labor requirement is 0.5 hours and the elapsed time is 1 hour for each analysis.

Suggested Suppliers

Cosa Instrument Corp., 84G Horseblock Rd. Yaphank, New York 11980, USA, 1-631-345-3434, www.cosaxentaur.com, distributor for Mitsubishi Chemical Analytech, 370 Enzo, Chigasaki, Kanagawa Pref., 253-0084, Japan, +81- 467-86-3864, www.dins.jp/dins_e/index_e.htm

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

Matheson Tri-Gas, 166 Keystone Dr., Montgomeryville, PA 18936, USA, 1-215-641-2700, www.mathesontrigas.com

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

Sigma-Aldrich, 3050 Spruce St., St. Louis, MO 63103, USA, 1-314-771-5765, www.sigma-aldrich.com

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