

Thermo. Titr. Application Note No. H-082

Title: Determination of surface acidity in Zeolites and other materials with a high specific surface area.

Scope: Determination of total acidic surface active sites in natural and synthetic surface-active materials

Principle: A weighed sample of surface-active material is suspended in dry cyclohexane or toluene, and reacted with a known volume of standard n-butylamine in cyclohexane or toluene. The excess base is back-titrated with standard methane sulfonic acid in dry 2-propanol

Reagents: *0.1 mol/L n-butylamine solution:* Dispense 10mL 99.5% n-butylamine (e.g., Aldrich cat. no. 471305, FW=73.08914) into a dry 1000mL volumetric flask, and make to volume with dry cyclohexane or toluene. Protect the reagent with a freshly filled soda-lime guard tube.

0.1 mol/L methanesulfonic acid, CH₃SO₃H. Weigh accurately approximately 9.6g 99.5+% methane sulfonic acid (e.g., Aldrich cat. no. 471356, FW=95.98812) into a dry 1000mL volumetric flask, and make to volume with dry 2-propanol. Protect the reagent with a freshly filled molecular sieve 3A guard tube. *Note: other strong organic acids such as trifluoromethanesulfonic acid might prove suitable as a back-titrant.*

Method: *Basic Experimental Parameters:*

Titration delivery rate (mL/min.)	4
No. of endothermic endpoints	1
Data smoothing factor	88
Stirrer speed	15

Basic Procedure: Weigh approximately 1 - 2 g of sample (depending on the nature of the sample) into a clean, freshly oven-dried 100mL glass vessel provided with a stopper. Immediately pipette in 75mL cyclohexane, and then accurately dispense (by pipette or Dosino) in 15mL of 0.1mol/L n-butylamine solution. Add a dry magnetic spin bar, and stir on a magnetic stirrer for 30 minutes. Take off the stirrer, and allow any fine solids to settle. Pipette 30mL of clear supernatant solution into a freshly dried titration vessel. Back-titrate with 0.1 mol/L methane sulfonic acid to a slight exothermic endpoint.

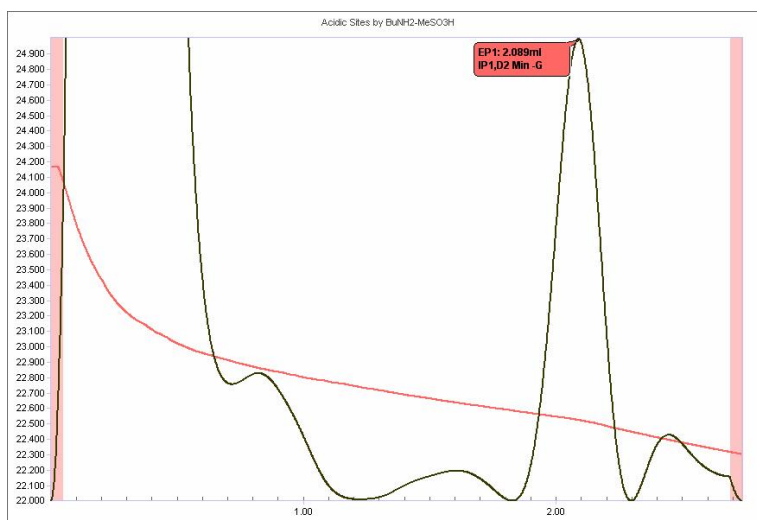
Blank determination: Accurately dispense 5mL of 0.1mol/L n-butylamine solution into a clean, freshly dried titration vessel. Add 25mL of dry cyclohexane, and titrate to a slight exothermic endpoint. Perform this determination at least in triplicate, and use the mean mL value .

Results: All samples were dried at 200°C for 4 hours immediately prior to analysis.

Sample	Acid Sites, mmol/g
Zeolite (unknown provenance)	0.584, 0.585
Silica gel (from drying sachet)	0.575, 0.573
Smelter grade alumina, 35m ² /g	0.107, 0.107
Smelter grade alumina, 107m ² /g	0.237, 0.235

Calculation: acid sites, mmol/g = $\frac{((\text{blank} - \text{titre}) \times \text{mol/L CH}_3\text{SO}_3\text{H})}{\text{sample mass, g}}$

Thermometric Titration Plot:



Legend:

Red = solution temperature curve

Black = second derivative curve