Influencing Factors in Nitrogen Physisorption for Measuring Specific Surface Area and Pore Volume of Amorphous Silica

1. Background

Amorphous silica, commonly known as precipitated silica or white carbon black, features a highly interconnected three-dimensional network formed through tetrahedral coordination of silicon atoms. The aggregation of its primary particles into larger agglomerates produces complex capillary channels, which create a highly porous internal architecture with a notably large specific surface area. These characteristics contribute to its exceptional adsorption capacity, reinforcement behavior, thickening properties, and its high chemical and thermal stability. Because of these advantageous traits, amorphous silica is widely used in industries such as rubber manufacturing, plastics, coatings, pharmaceuticals, food processing, catalysis, and personal care formulations.(1-6)

Nitrogen physisorption remains one of the most important analytical methods for determining the specific surface area, pore size distribution, and pore volume of amorphous silica. Among existing analytical approaches, BET surface area and mesoporous/pore structural analyses are often the most sensitive to pretreatment method, degassing temperature, measurement window selection, and sample storage history. This application note discusses how these parameters affect measured results and provides guidance for optimizing measurement quality when using the **AMI Micro 300 Series** physisorption analyzer.

2. Experiment

Measurements were conducted using the **AMI Micro 300** physisorption analyzer. Four commercial amorphous silica samples representing different product categories and performance requirements were selected for analysis, shown in Table 1. These samples were pretreated and tested across a range of temperatures, times, and degassing methods to evaluate how these variables influence BET-specific surface area and total pore volume.

Application Industry	**Toothpaste**	**Food**	**Animal Feed**	**Rubber**
Sample Number	A	B	C	D
Specific Surface Area Range	260-280	210-230	180-200	160-180

Table 1: Industrial applications and specific surface area ranges of amorphous silica samples A-D

BET calculations followed the recommended relative pressure window of $P/P_0 = 0.05–0.20$ for amorphous silica, consistent with established adsorption standards for carbon black and white carbon black, shown in Table 2. Several pretreatment workflows were evaluated, including in-situ vacuum degassing performed directly on the analyzer manifold and external oven drying prior to sample transfer. Degassing temperatures ranged from 105 °C to 300 °C, with durations of 1–4 hours.

Sample	Surface Area Range (m²/g)	Relative Pressure Range (P/P_0)
Carbon black	≤100	0.1-0.3
	100 - 130	0.05-0.2
	≥130	0.05-0.1
White carbon black	140-450	0.05-0.2

Table 2: Typical surface area ranges and measurement pressure ranges for various carbon black and white carbon black materials

The **AMI Micro 300** analyzer provides exceptionally stable pressure control, which ensures highly linear BET plots even in low-pressure regions. Its integrated high-vacuum pretreatment station also eliminates complications arising from transfer exposure, making it ideal for materials such as silica that are sensitive to ambient moisture and weakly bound contaminants.

3. Results and Discussion

3.1 Pretreatment Method: In-situ Vacuum vs. Oven Drying

The choice of pretreatment method significantly affected the measured BET surface area. When samples were degassed in-situ under vacuum at 105 °C for two hours, the resulting nitrogen adsorption isotherms showed higher uptake in the low-pressure region compared to samples dried in a conventional laboratory oven. To confirm, this experiment was conducted twice. Although both isotherms exhibited similar shapes overall, as seen in Figure 1, the suppressed adsorption in the oven-dried samples at $P/P_0 < 0.2$ directly reduced the calculated BET surface area (Table 3).

Pretreatment Method	Specific Surface Area (m²/g)	Pore Volume (cm³/g)
In-situ at 105° C for 2 hours	268.989	0.979
	270.155	0.975
Oven at 105° C for 2 hours	173.813	0.933

Table 3: Comparison of pretreatment methods on calculated specific surface area and pore volume for Sample A

This behavior can be explained by the surface chemistry of silica. Its surface contains multiple types of silanol groups, including isolated hydroxyls, vicinal hydrogen-bonded groups, and geminal pairs. These sites readily adsorb water vapor and other weakly bound gases from the environment. Oven drying removes moisture slowly and often incompletely, and samples may readsorb contaminants while being transferred to the analyzer. In contrast, in-situ vacuum pretreatment removes physisorbed species more completely and minimizes airborne contamination.

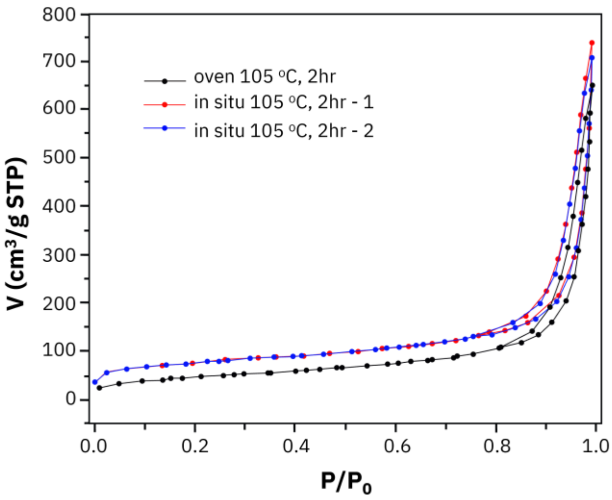

Figure 1: Effect of pretreatment method on adsorption-desorption isotherm for Sample A

Differences in pore volume between the two pretreatment methods were comparatively small.

This is consistent with the mechanistic expectation that pore volume is governed by adsorption in the capillary condensation region, typically at P/P_0 values above 0.4, where the primary determinant of uptake behavior is total pore volume rather than the availability of surface adsorption sites. In-situ degassing is therefore essential for obtaining consistent and accurate BET surface area values. For materials susceptible to moisture uptake, such as amorphous silica, the use of in-situ vacuum degassing is strongly recommended.

3.2 Effect of Pretreatment Temperature

Degassing temperature strongly influenced the measured BET surface area. Across samples A–D, pretreatment temperatures of 105–160 °C produced highly consistent total surface area values with excellent repeatability. However, increasing the temperature to 180 °C or above caused the BET surface area to rise by approximately six to seven percent, depending on the sample. The effects of pretreatment temperature on specific surface area and pore volume for samples A-D are shown in Table 4.

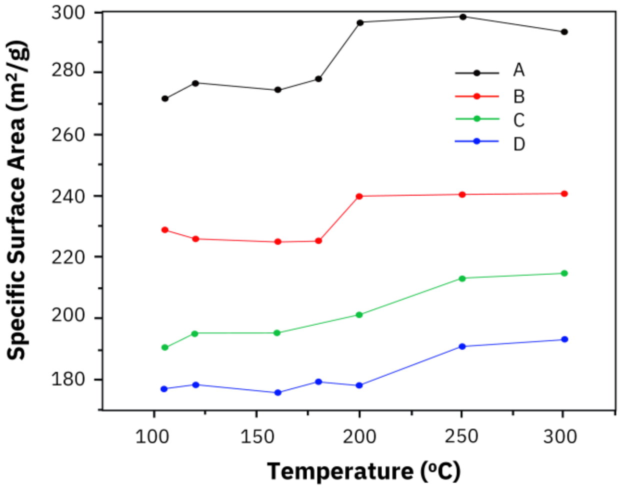

Figure 2: Effect of pretreatment temperature on specific surface area for samples A-D

These increases are attributed to progressive desorption of more strongly bound species and partial structural rearrangements of hydrogen-bonded silanol groups. Literature reports indicate that physisorbed water desorbs below roughly 200 °C, while vicinal hydroxyl groups begin to reorganize around 170–400 °C. At higher temperatures, deeper dehydroxylation may occur. Thus, elevated temperatures can open additional adsorption sites for nitrogen, altering measured BET values.

Pretreatment Temperature (°C)	**Specific Surface Area (m²/g)**				**Pore Volume (cm³/g)**			
	A	B	C	D	A	B	C	D
105	271.572	228.635	190.876	176.919	0.979	1.296	0.954	0.742
120	276.439	226.041	195.200	178.474	0.968	1.302	0.941	0.763
160	274.333	224.895	195.430	176.024	1.037	1.285	0.964	0.757
180	278.296	225.449	-	179.371	1.082	1.287	-	0.760
200	296.547	239.939	201.156	178.117	1.04	1.301	0.962	0.787
250	298.497	240.503	213.035	191.062	1.008	1.288	0.99	0.783
300	293.32	240.723	214.837	193.495	1.049	1.383	0.961	0.756

Table 4: Effect of pretreatment temperature on calculated specific surface area and pore volume

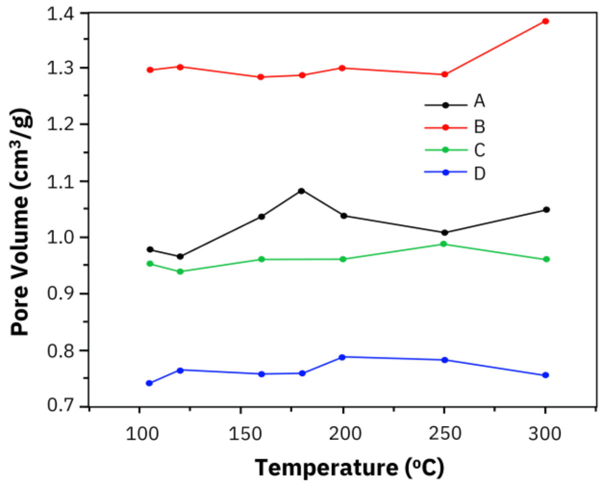

Figure 3: Effect of pretreatment temperature on pore size for samples A-D

Despite changes in BET area, total pore volume remained relatively stable across all temperatures (Figure 3). The only exception was Sample A, which exhibited slightly larger fluctuations in pore volume due to its less stable formulation. This indicates that while elevated temperatures alter the number of active adsorption sites, the overall pore structure remains largely intact.

Considering these results, a pretreatment temperature of 160 °C represents an optimal compromise between effective desorption and preservation of surface chemistry. It provides stable BET results while minimizing unnecessary structural changes to surface hydroxyl groups and supports higher throughput by allowing shorter degassing times where appropriate.

3.3 Effect of Pretreatment Time

Pretreatment time was evaluated at 160 °C for durations of one, two, and four hours. For samples with moderate moisture content, BET surface area and pore volume values varied only slightly across the tested times, with deviations typically below two percent (Table 5).

This stability suggests that for most commercial silica materials, one hour of in-situ degassing is sufficient to achieve complete desorption of physisorbed contaminants. Longer degassing times offer minimal additional benefit unless samples are exceptionally moisture-laden or freshly synthesized.

Pretreatment Time (h)	Specific Surface Area (m²/g)			Pore Volume (cm³/g)		
	B	C	D	B	C	D
1	220.019	196.817	172.003	1.274	0.934	0.763
2	224.859	195.430	176.024	1.285	0.964	0.757
4	221.963	192.052	178.805	1.325	0.959	0.712

Table 5: Effect of pretreatment time on calculated specific surface area and pore volume

3.4 Influence of Sample Storage Time

Storage time had a pronounced effect on BET surface area but little effect on pore volume, as shown in Table 6. Over time, specific surface area decreased steadily, with literature reporting noticeable declines within the first month of storage and further reductions over a year.(7,8)

Storage Time (Months)	Specific Surface Area (m²/g)	Pore Volume (cm³/g)
0	276.439	0.968
1	272.566	1.036
2	277.082	0.981
3	258.556	0.939
5	233.532	0.904

Table 6: Effect of storage time on calculated specific surface area and pore volume of Sample A

The reduction in surface area is likely due to a combination of moisture readsorption and gradual structural rearrangement of silanol groups, which reduces the number of accessible adsorption sites for nitrogen at low relative pressures. Because pore volume depends more on geometric pore structure than on surface chemistry, it remained mostly unaffected by storage.

To minimize storage-related drift in BET values, samples should be stored in airtight containers with desiccant and handled to minimize exposure before analysis. For long-term studies or quality-control monitoring, recording sample age and applying consistent pretreatment protocols are essential for maintaining data reliability.

4. Conclusions

Micro 300

- ✓ High precision physisorption instrument designed for:
  - ✓ Adsorption-desorption isotherms
  - ✓ Specific surface area
  - ✓ Pore size analysis
- ✓ Three independently operating analysis ports for simultaneous experiments

Figure 4: Highlighted features of the ***Micro 300*** *from* ***AMI***

Pretreatment method, temperature, time, and storage conditions each exert a distinct influence on nitrogen adsorption measurements of amorphous silica. In-situ vacuum degassing provides the most reliable and reproducible approach for sample preparation, particularly when low-pressure nitrogen uptake is critical for BET analysis. Temperatures between 105 and 160 °C offer an effective balance between completeness of desorption and preservation of surface chemistry, while a pretreatment duration of one hour is generally sufficient for routine analyses.

Although pore volume remains relatively stable across processing conditions, BET surface area can be strongly affected by surface contamination, hydroxyl restructuring, and sample aging. Careful control of environmental exposure and consistent analytical procedures are therefore essential for ensuring data accuracy. The **AMI Micro 300** physisorption analyzer, shown in Figure 4, is well-suited for these analyses due to its precise pressure control, stable transducer performance, and integrated high-vacuum degassing system, which together enable high-quality BET and pore-volume measurements for research and industrial applications.

5. References

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