

Study on the Effect of Selection Point Range on the Specific Surface Area and External Surface Area of Carbon Black Samples

1. Introduction

Carbon black is produced through the incomplete combustion or thermal decomposition of hydrocarbon feedstocks and is widely used as a reinforcing agent in rubber. More than 90% of global carbon black output is consumed by the rubber industry. When incorporated into a rubber matrix, carbon black enhances key mechanical properties—including hardness, tensile strength, and abrasion resistance—while also improving compound processability and lowering overall formulation cost. Among commercial reinforcing fillers, carbon black remains the most important, and its specific surface area is a primary factor governing reinforcement performance.⁽¹⁾

The specific surface area of carbon black is typically divided into internal and external components. The external specific surface area is especially relevant for evaluating reinforcement because effective reinforcement requires intimate contact between carbon black particles and rubber polymer chains. When the pores on the carbon black surface are too small for rubber molecules to enter, the internal surface associated with these ultrafine pores does not contribute to reinforcement and must be excluded. Therefore, the external specific surface area is defined as the portion of the total surface area remaining after subtracting the internal surface area of pores with diameters ≤ 2 nm that are inaccessible to rubber.^(2,3)

This application note investigates how different selection-point ranges influence the measured total specific surface area and external specific surface area of carbon black samples.

2. Experiment

Nitrogen adsorption–desorption measurements were conducted on standard carbon black materials using the AMI Meso 400. The nitrogen specific surface area (NSA) was calculated using the Brunauer–Emmett–Teller (BET) model, which provides the total accessible surface area of each sample.

The statistical thickness surface area (STSA), representing the external surface area, was calculated using de Boer’s t-curve method together with the standard carbon black structural model.⁽⁴⁾

The STSA is determined from the functional relationship between the adsorbed nitrogen volume per gram of sample (V_a , in mL/g at STP) and the statistical thickness of the adsorbed layer (t). A V_a – t plot is generated using V_a as the ordinate and t (in 10^{-10} m) as the abscissa. The statistical thickness is computed using:

$$t = 0.088(p/p_0)^2 + 0.645\left(\frac{p}{p_0}\right) + 0.298$$

ASTM D6556-14 and ISO 18852:2015 specify that the t-value range for STSA determination corresponds to $P/P_0 = 0.2-0.5$, which gives $t = 0.43-0.65$.(4,5) The standards also define performance requirements for STSA measurements:

- ✓ Repeatability: $\leq 3.49\%$ of the mean
- ✓ Reproducibility: $\leq 6.87\%$ of the mean

3. Results

Table 1 lists the ASTM D6556-14 reference NSA and STSA values for four standard reference carbon black (SRB-8) materials: A8, C8, E8, and G8.⁽⁴⁾

SRB-8	Variety	NSA (m ² /g)	STSA (m ² /g)
A8	N326	76.2	76.7
		74.93-77.55	75.58-77.91
C8	HS-Tread	126.3	115.9
		124.72-127.92	114.40-117.46
E8	N660	36.5	35.6
		35.88-37.14	34.6-36.61
G8	N990	9.1	8.4
		8.74-9.46	7.80-9.00

Table 1: NSA and STSA values for standard reference carbon black materials

Sample	Surface Area Range (m ² /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 recommended pressure ranges for BET analysis

Table 2 summarizes the standard specific surface area ranges for carbon black and white carbon black, along with their recommended relative pressure ranges.

Table 3 compares the specific surface areas of A8, C8, E8, and G8 calculated using both the conventional BET range ($P/P_0 = 0.05-0.3$) and the standardized selection-point ranges. Except for G8, the correlation coefficient (C_c) obtained using the standard-specified range is slightly higher than that

Sample Name	BET Selection Range	NSA (m ² /g)	Repeatability (%)	BET Selection Range	NSA (m ² /g)	Repeatability (%)
A8-1	0.05-0.3	76.176	0.99997	0.1-0.3	76.621	0.99998
A8-2		75.946	0.99997		76.354	0.99999
C8-1		126.564	0.99999	0.05-0.2	126.667	1.00000
C8-2		126.273	0.99999		126.334	1.00000
E8-1		36.907	0.99998	0.1-0.3	37.062	1.00000
E8-2		36.248	0.99998		36.386	1.00000
G8-1		9.146	0.99997	0.1-0.3	9.110	0.99994
G8-2		9.016	0.99998		8.999	0.99997

Table 3: Specific surface areas of A8, C8, E8, and G8 calculated using the conventional BET range ($P/P_0 = 0.05-0.3$) and the standardized selection point ranges, including the measurement repeatability

obtained using the conventional range, although all values satisfy the required criterion of $C_c \geq 0.9999$. As shown in Figure 1, all measured specific surface areas for the four SRB-8 samples fall within their respective reference ranges.

Overall, both the conventional BET range ($P/P_0 = 0.05-0.3$) and the standard-specified ranges produce NSA values that meet test requirements. Users may select either approach based on analytical preference.

Sample Name	BET Selection Range	NSA (m ² /g)	C_c	BET Selection Range	NSA (m ² /g)	C_c
N115	0.05-0.3	137.607	0.99999	0.05-0.1	137.570	1.00000
N134		138.111	0.99999		135.734	0.99999
N234		120.981	0.99999	0.05-0.2	120.546	0.99998
N326		78.102	0.99997	0.1-0.3	78.644	0.99999
N339		87.575	0.99999		87.788	0.99999
N550		39.001	0.99997		39.233	0.99999
N660		34.874	0.99998		35.020	1.00000

Table 4: Specific surface areas of seven additional carbon black materials, BET selection ranges, and linear correlation coefficient

Table 4 presents the specific surface areas of seven additional carbon black samples evaluated using both range types. Except for N234, the standard-specified selection range gives slightly higher correlation coefficients. All results meet test requirements, and the differences between the two ranges are minimal.

Using the standard t-range of 0.43–0.65, the calculated STSA values for SRB-8 samples do not match the reference STSA values provided for these materials. Table 5 presents STSA results for C8 obtained using different t-ranges. While all ranges satisfy the repeatability criterion, the t-range of 0.35–0.55 yields the best repeatability and is the only range that produces STSA values consistent with the SRB-8 reference values.

Sample name	T: 0.43-0.65		T: 0.35-0.55		T: 0.35-0.65	
	STSA (m ² /g)	Repeatability (%)	STSA (m ² /g)	Repeatability (%)	STSA (m ² /g)	Repeatability (%)
C8-1	125.045	1.898	115.229	0.145	120.874	1.050
C8-2	124.855	1.860	114.873	0.223	120.617	0.997

Table 5: Calculated STSA values for C8-1 and C8-2 at different t-ranges and measurement repeatability

Additional standard carbon black materials were evaluated, as shown in Table 6. For seven samples (N115, N134, N234, N326, N339, N550, N660), the STSA values obtained using the standard t-range (0.43–0.65) differ significantly from the reference values. These results confirm that the choice of t-range has a substantial effect on calculated external surface area.

Based on the SRB-8 reference materials and customer carbon black samples, a recommended t-range is proposed for carbon blacks with different external surface area levels, as summarized in Table 7.

Sample Name	Adsorption Layer Thickness (t)	Calculated STSA (m ² /g)	Adsorption Layer Thickness (t)	Reference STSA (m ² /g)
N115	0.43-0.65	139.229	0.35-0.50	124.972
N134		141.593	0.35-0.50	133.404
N234		122.761	0.35-0.45	113.164
N326		85.163	0.35-0.55	78.071
N339		90.712	0.33-0.55	88.167
N550		41.110	0.33-0.50	38.791
N660		36.532	0.35-0.55	33.809

Table 6: Calculated STSA values for additional carbon black materials using the standard t-range compared to reference values

Sample External Surface Area Range	Adsorption Layer Thickness
$\leq 100 \text{ m}^2/\text{g}$ carbon black	0.33-0.50
$100 < \text{Surface Area} < 130 \text{ m}^2/\text{g}$ carbon black	0.35-0.55
$\geq 130 \text{ m}^2/\text{g}$ carbon black	0.35-0.50

Table 7: Recommended *t*-ranges for varying carbon black samples

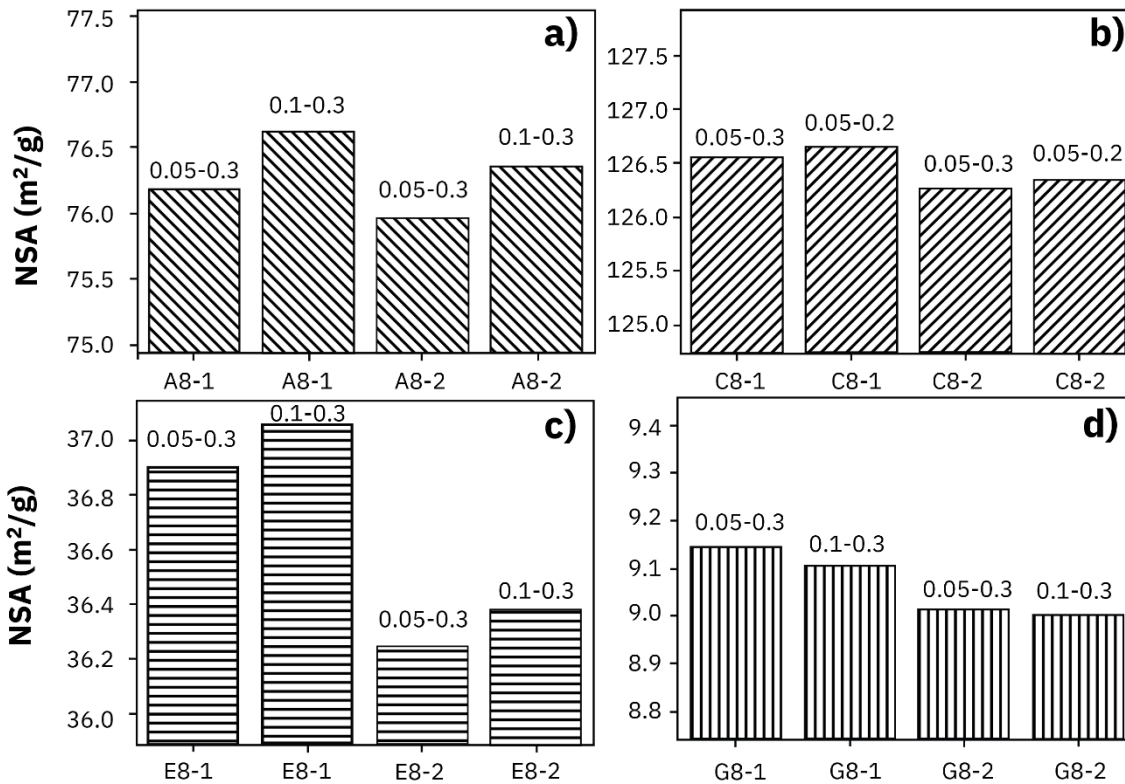


Figure 1: Effect of different selection points on measured values for four standard carbon black samples

4. Conclusions

Both the conventional BET selection-point range ($P/P_0 = 0.05-0.3$) and the standard-specified relative pressure range yield NSA values for SRB-8 carbon black that meet test requirements, with deviations $\leq 0.6\%$. STSA values obtained using the standard *t*-range (0.43–0.65) do not match the reference STSA values for SRB-8 materials. Both reference samples and customer samples demonstrate that the selected *t*-range significantly influences the calculated external surface area.

Recommended *t*-ranges:

- ✓ For carbon black samples with STSA $> 100 \text{ m}^2/\text{g}$: use $t = 0.35-0.55$
- ✓ For carbon black samples with STSA $< 100 \text{ m}^2/\text{g}$: use $t = 0.35-0.50$

The **AMI Meso 400** provides an excellent platform for accurately determining both total and external surface area in carbon black analysis. Its high accuracy pressure transducers deliver highly linear



AMI Meso 400

- ✓ Compact, high-performance sorption analyzer for mesoporous and microporous materials
- ✓ Fully autonomous operation in 4 independent analysis ports
- ✓ Precise analysis with 1000 torr pressure transducers

adsorption data—critical for reliable BET and t-plot calculations. The wide dynamic range of the instrument enables accurate characterization across diverse carbon black grades, from high-surface-area reinforcing materials to lower-surface-area semi-reinforcing types. Automated analysis workflows, robust thermal control, and multiport capability ensure consistent reproducibility and high sample throughput. Together, these capabilities make the **Meso**

400 exceptionally well suited for routine quality control, standards compliance, and advanced research applications in carbon black surface characterization.

5. References

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