Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Investigation of High-Performance Adsorption for Benzene and Toluene Vapors by Calix[4]arene based Organosilica (CBOS)

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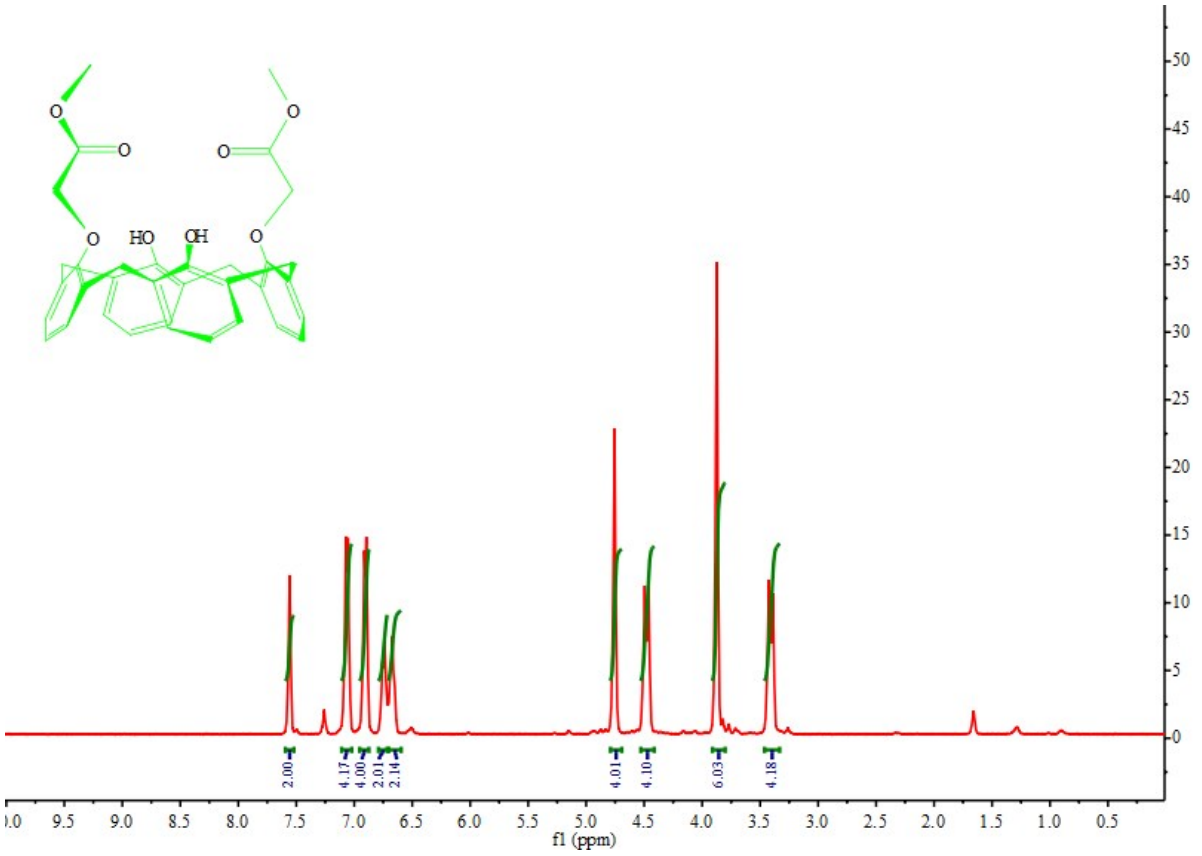


Fig. S1. The ^{1}H NMR spectra of calix-3.

^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.59 (s, 2H, OH), 7.11 (s, 4H, ArH), 6.95 (s, 4H, ArH), 6.79 (s, 2H, ArH), 6.70 (s, 2H, ArH), 4.79 (s, 4H, OCH_2), 4.53 (d, 4H, $ArCH_2Ar$), 3.91 (s, 6H, OCH_3), 3.46 (d, 4H, $ArCH_2Ar$). Anal. Calcd for $C_{34}H_{32}O_8$: C, 71.82; H, 5.67; O, 22.51; Found: 72.91; H, 5.08; O, 22.01.

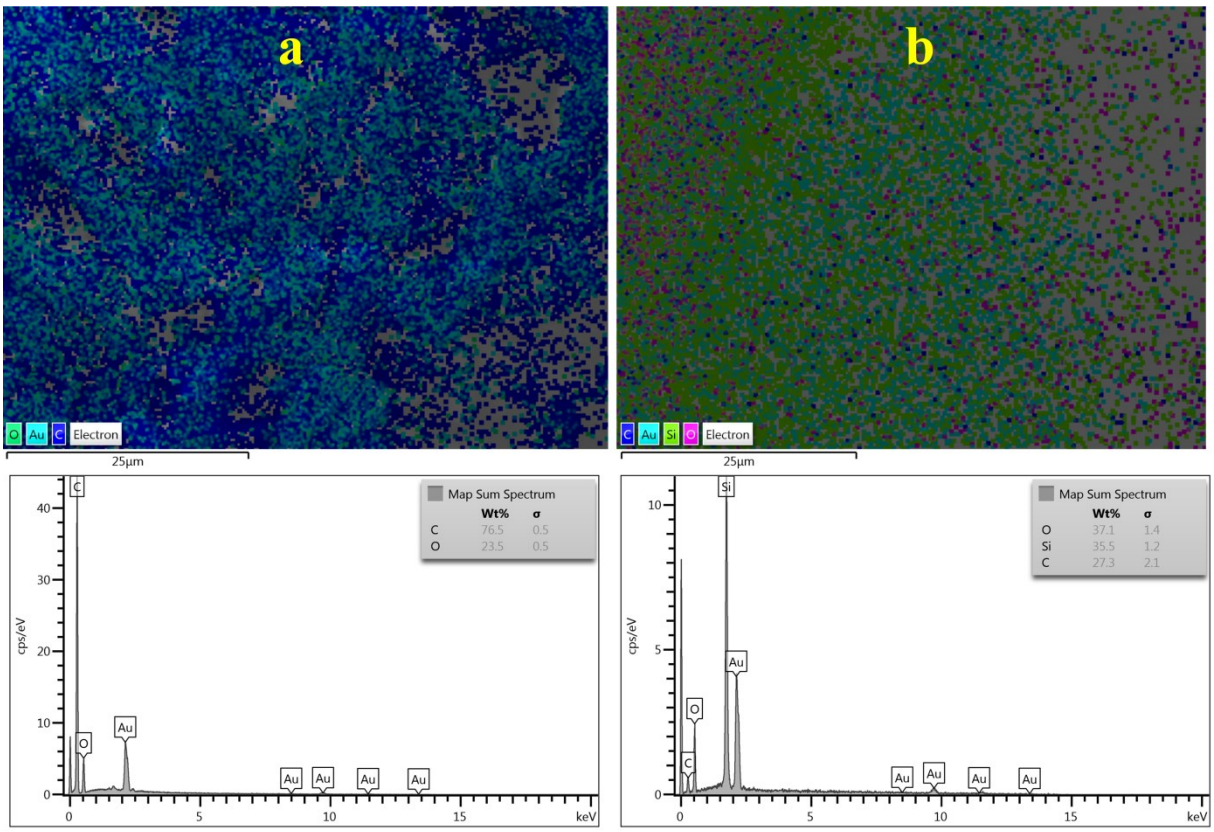


Fig. S2. EDS mapping of the calix-3 (a) and CBOS (b).

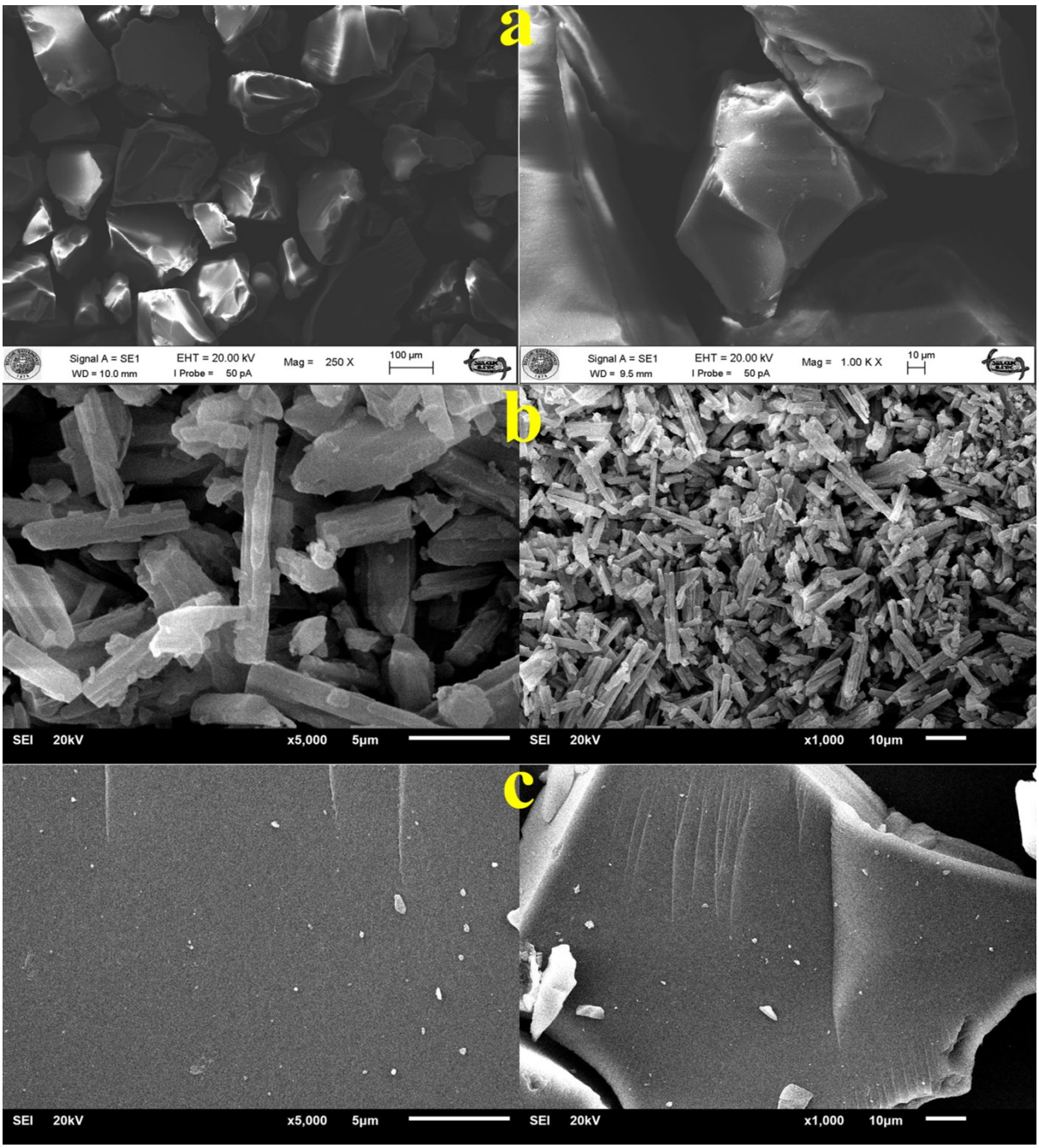
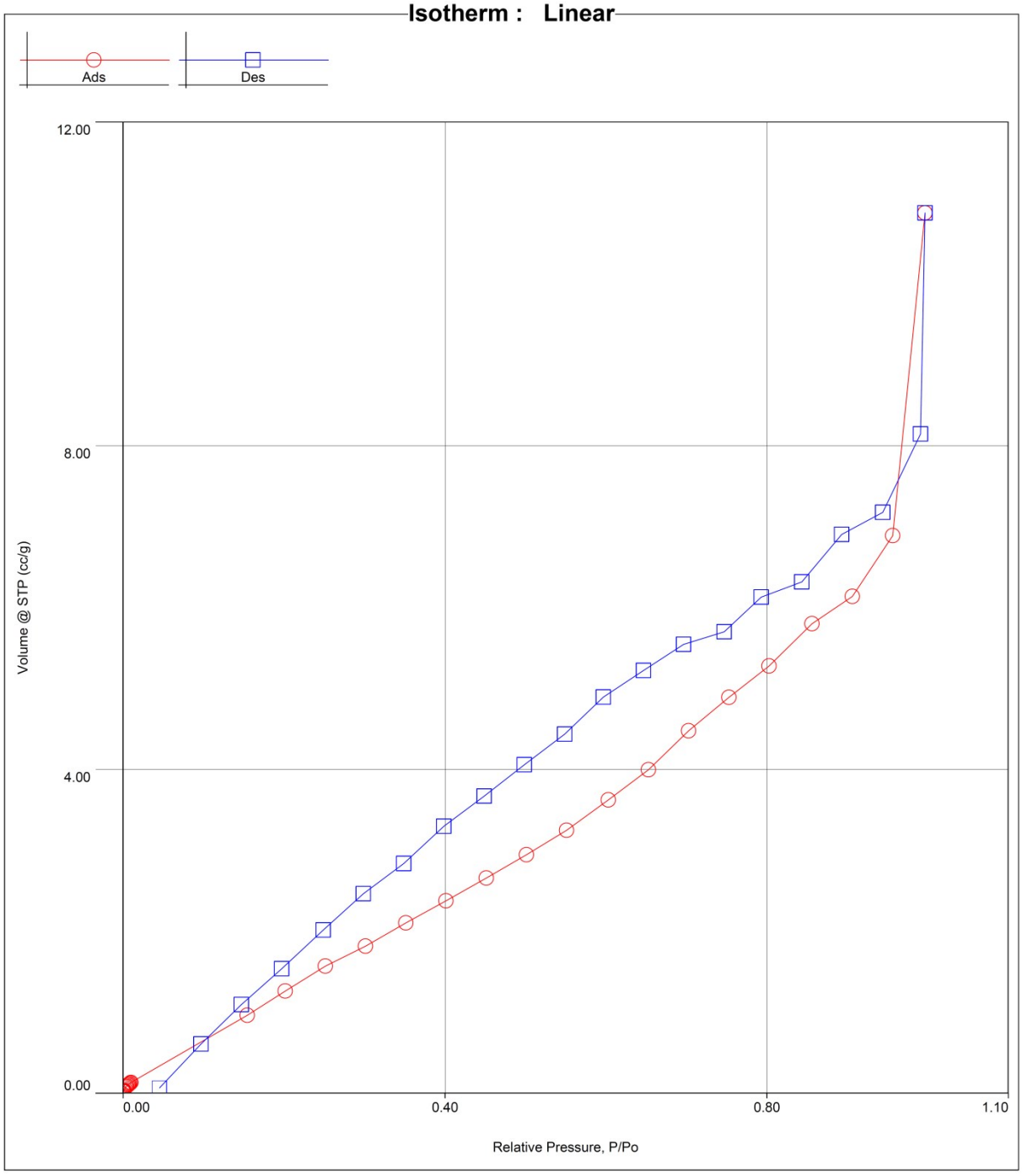
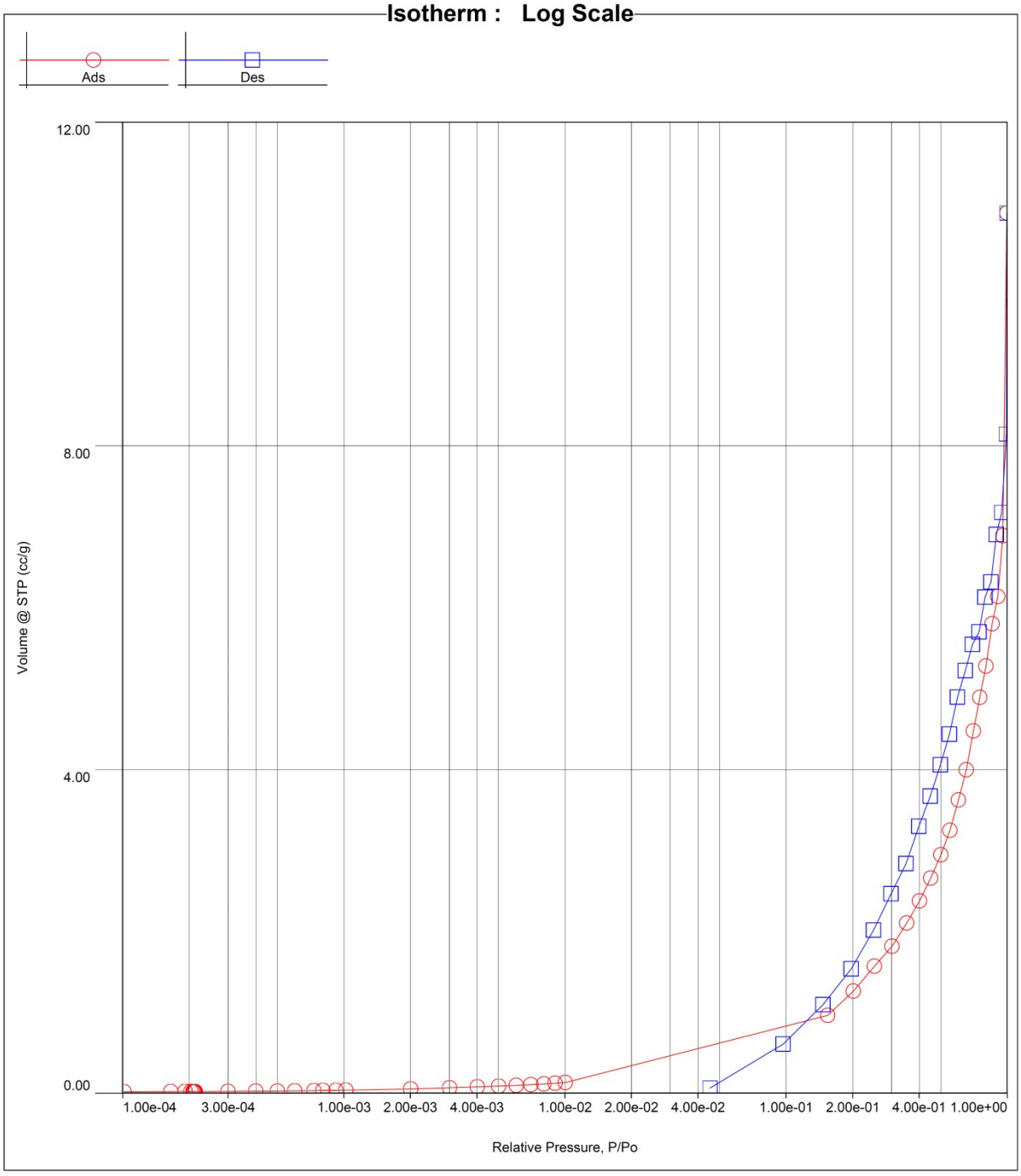
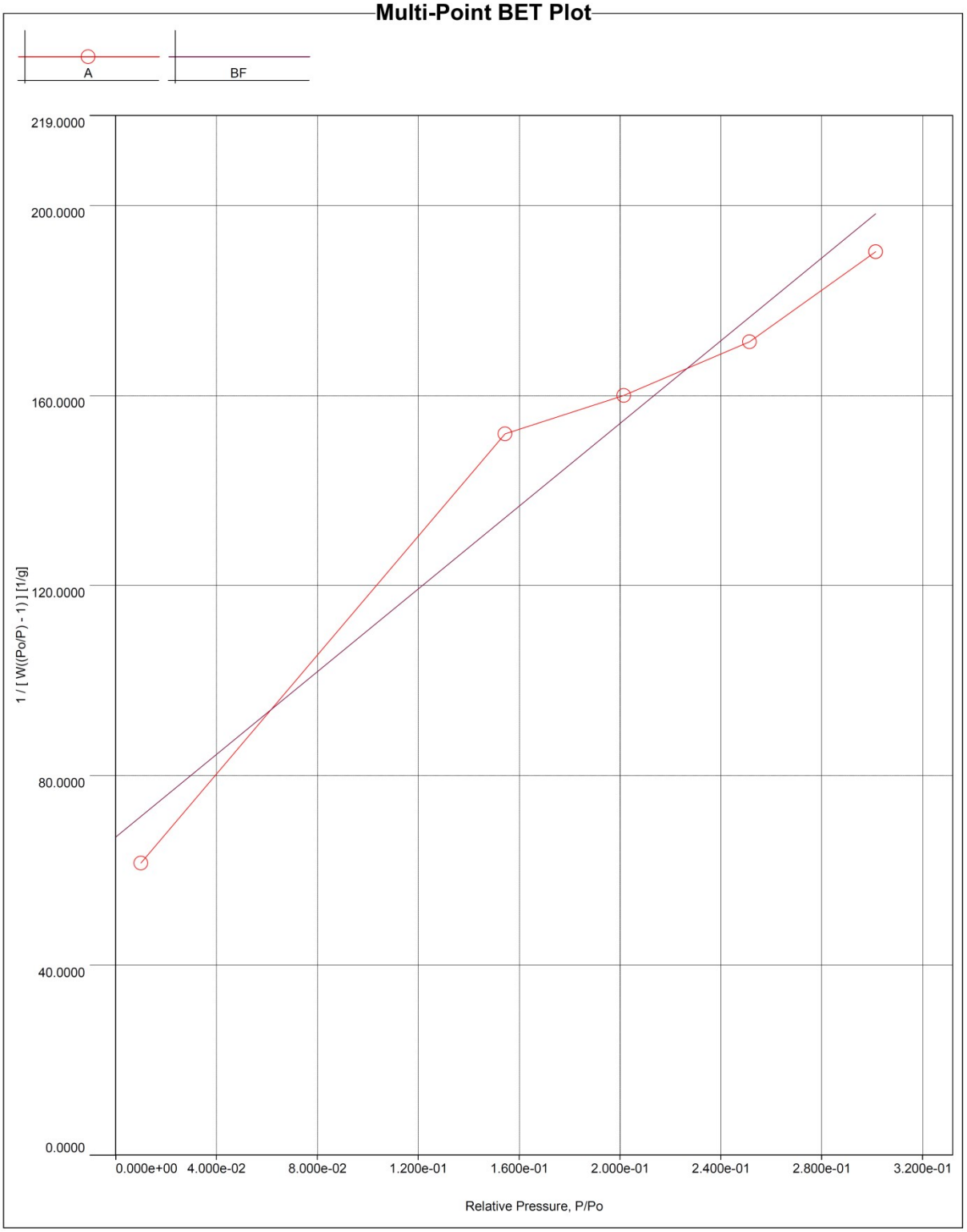
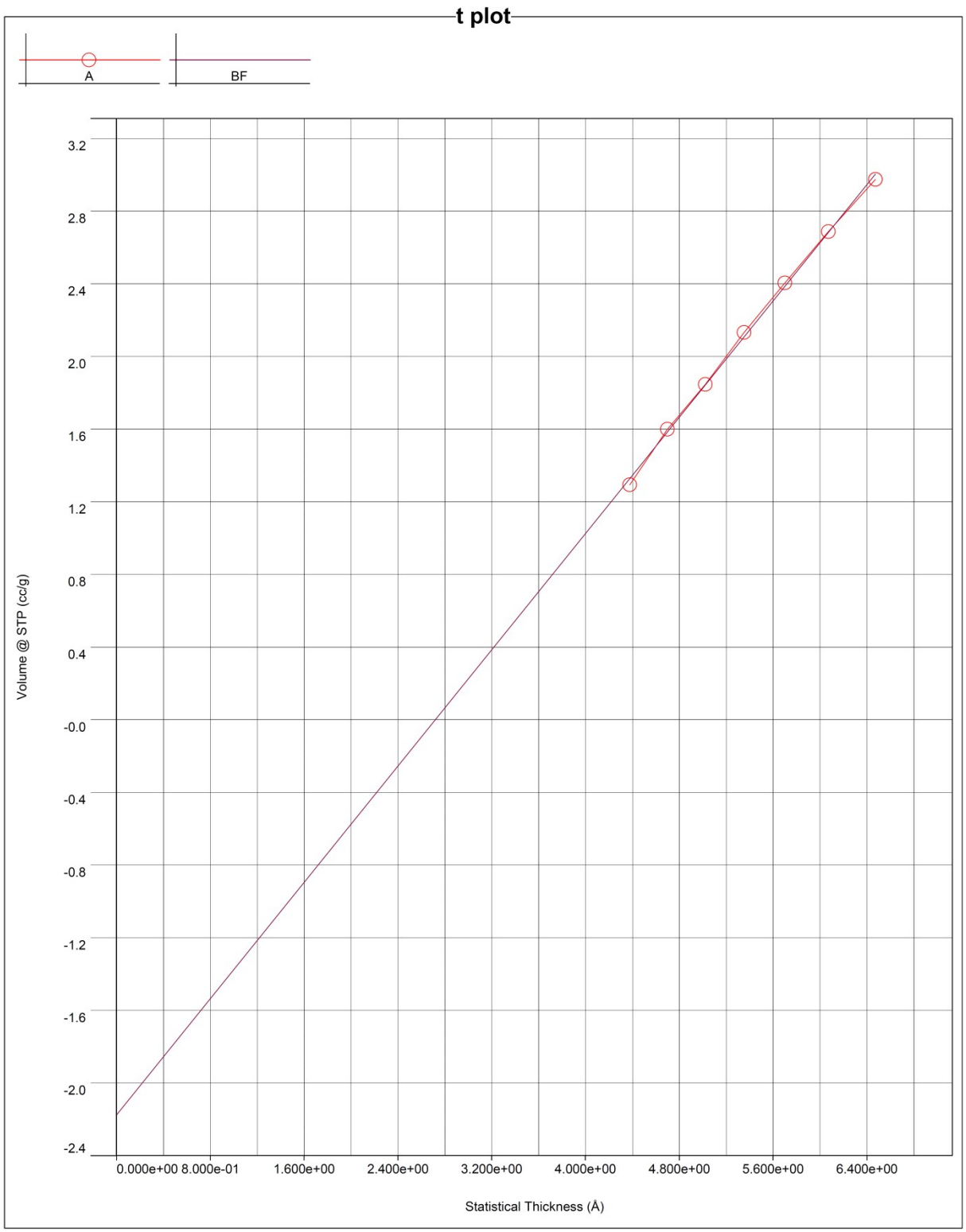


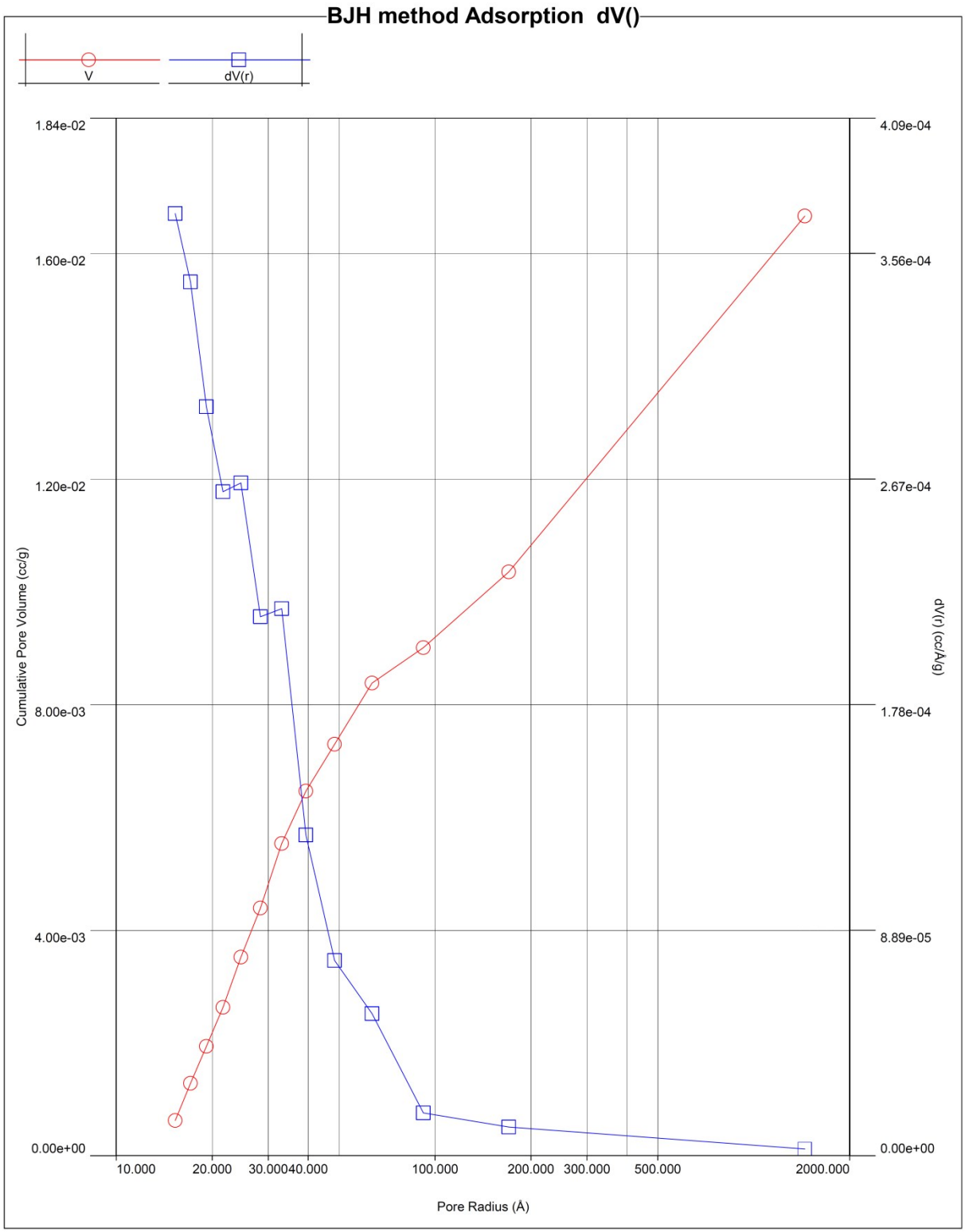
Fig. S3. SEM images of mesoporous silica (a), calix-3 (b), CBOS (c).

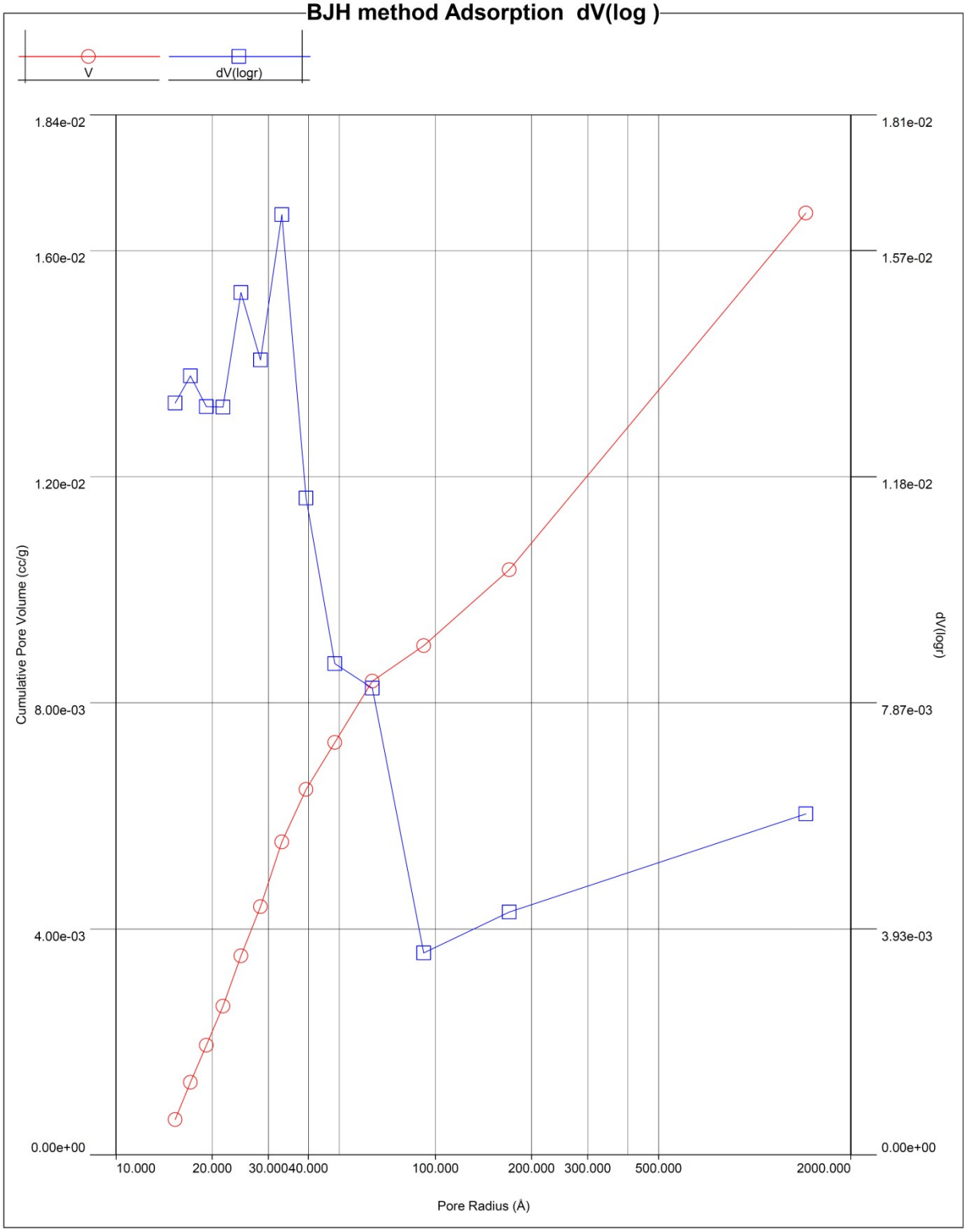

Isotherm : Linear
Ads
Des
12.00
8.00
4.00
0.00
Volume @ STP (cc/g)
0.00
0.40
0.80
1.10
Relative Pressure, P/Po

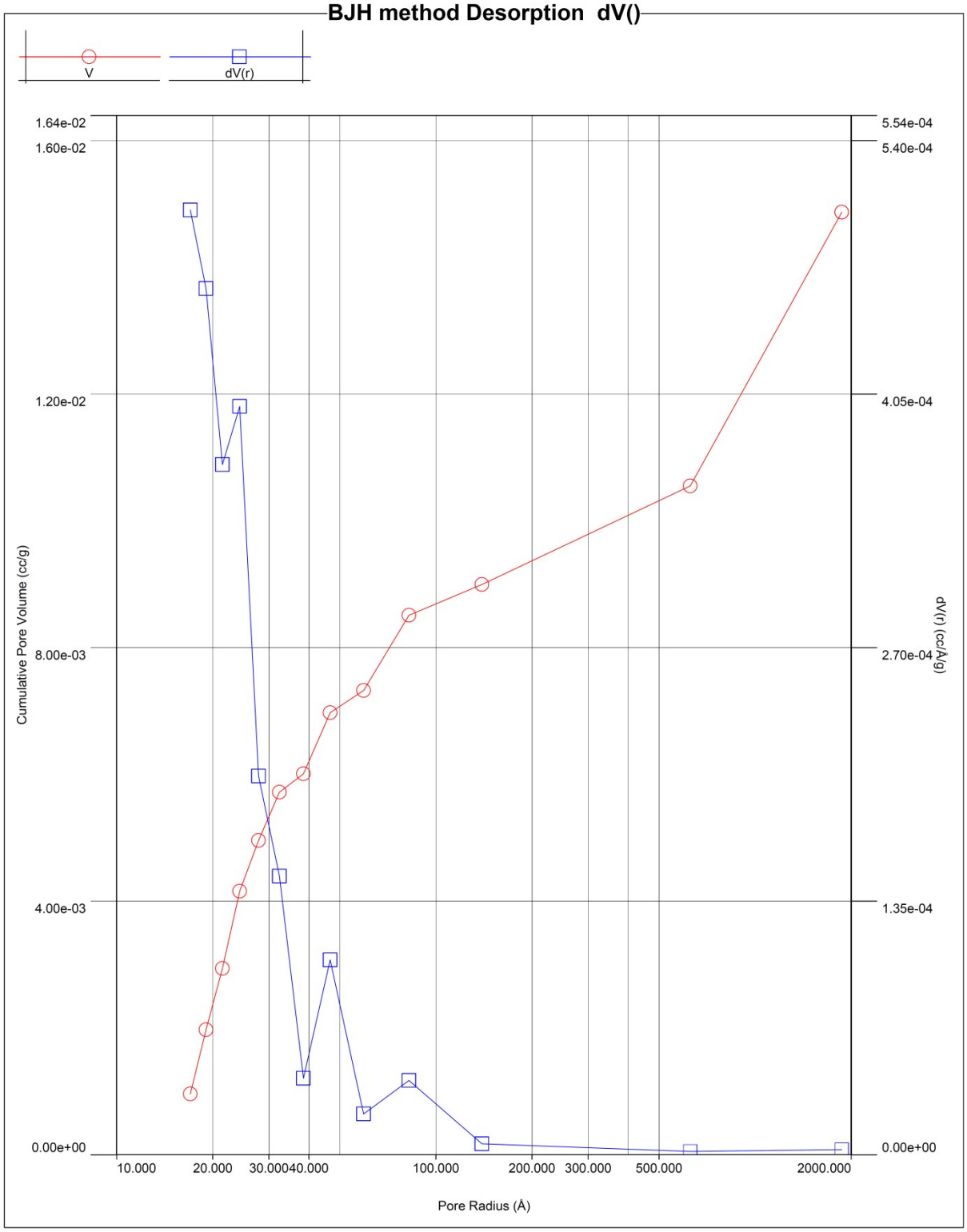

Isotherm : Log Scale
Ads
Des
12.00
8.00
4.00
0.00
Volume @ STP (cc/g)
1.00e-04
3.00e-04
1.00e-03
2.00e-03
4.00e-03
1.00e-02
2.00e-02
4.00e-02
1.00e-01
2.00e-01
4.00e-01
1.00e+00
Relative Pressure, P/Po

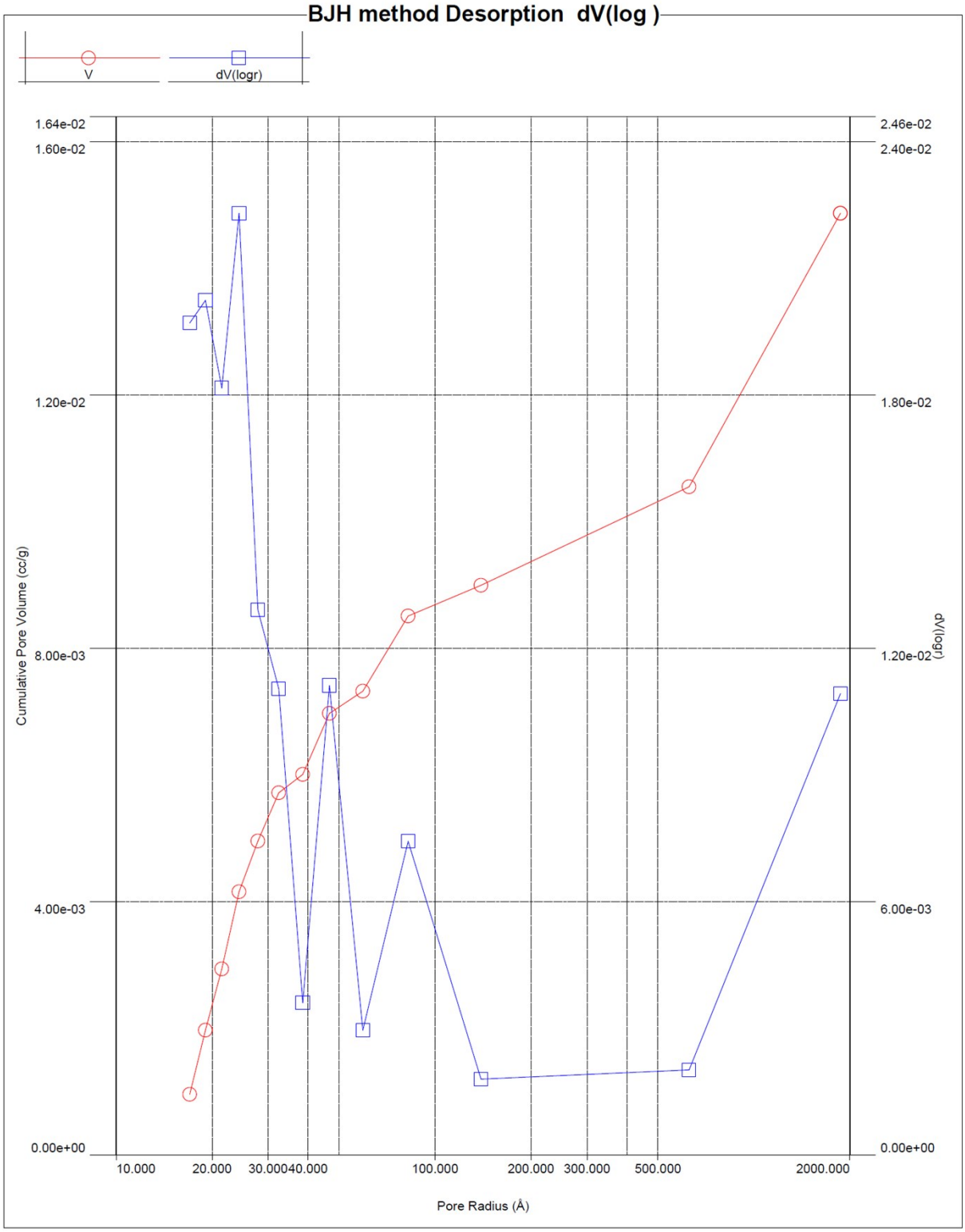

Multi-Point BET Plot
A
BF
219.0000
200.0000
160.0000
120.0000
80.0000
40.0000
0.0000
1 / [W((Po/P) - 1)] [1/g]
0.000e+00
4.000e-02
8.000e-02
1.200e-01
1.600e-01
2.000e-01
2.400e-01
2.800e-01
3.200e-01
Relative Pressure, P/Po

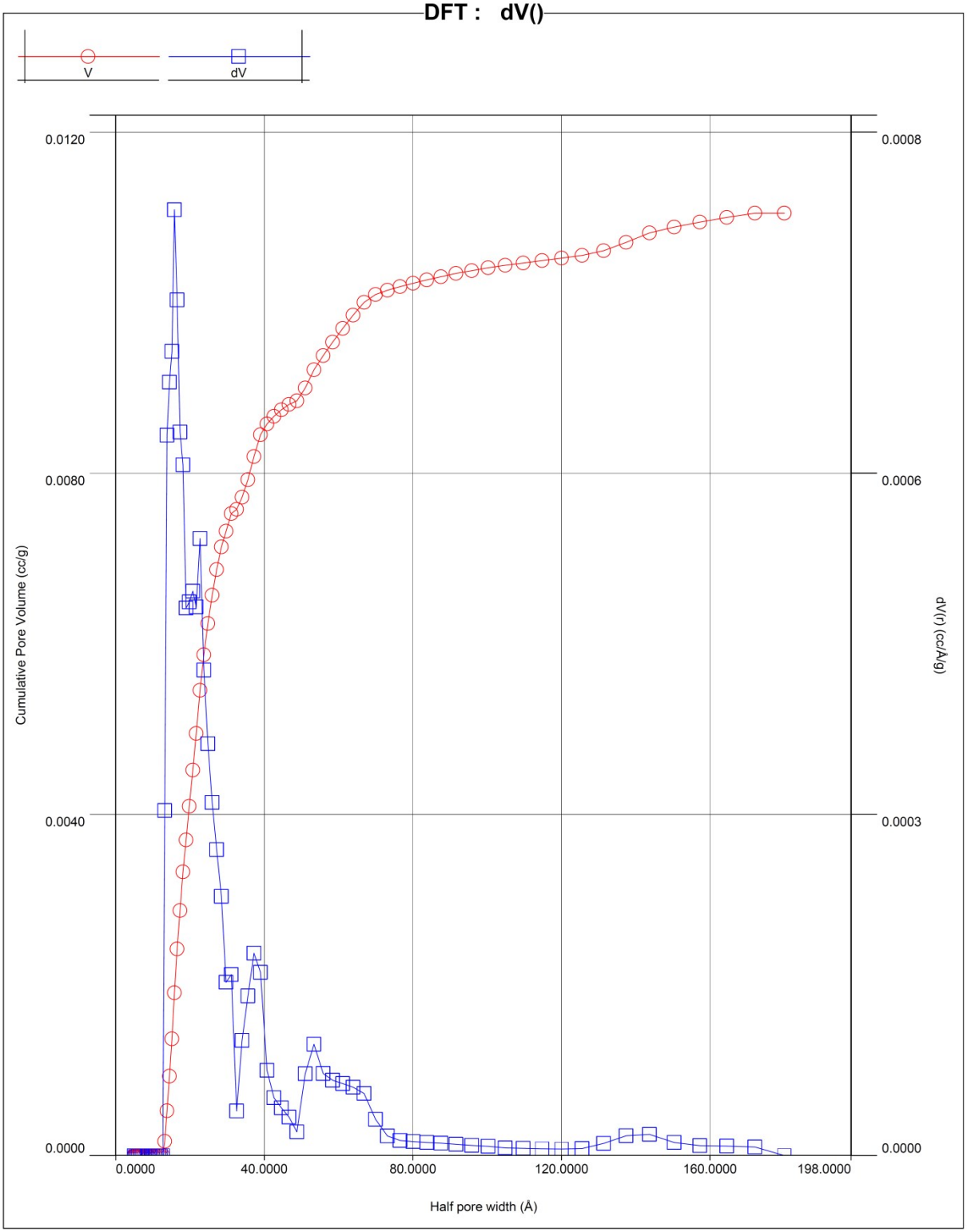

t plot
A
BF
Volume @ STP (cc/g)
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
-0.0
-0.4
-0.8
-1.2
-1.6
-2.0
-2.4
0.000e+00 8.000e-01 1.600e+00 2.400e+00 3.200e+00 4.000e+00 4.800e+00 5.600e+00 6.400e+00
Statistical Thickness (Å)


BJH method Adsorption dV()
V
dV(r)
1.84e-02
1.60e-02
1.20e-02
8.00e-03
4.00e-03
0.00e+00
4.09e-04
3.56e-04
2.67e-04
1.78e-04
8.89e-05
0.00e+00
Cumulative Pore Volume (cc/g)
dV(r) (cc/Å/g)
10.000
20.000
30.000
40.000
100.000
200.000
300.000
500.000
2000.000
Pore Radius (Å)

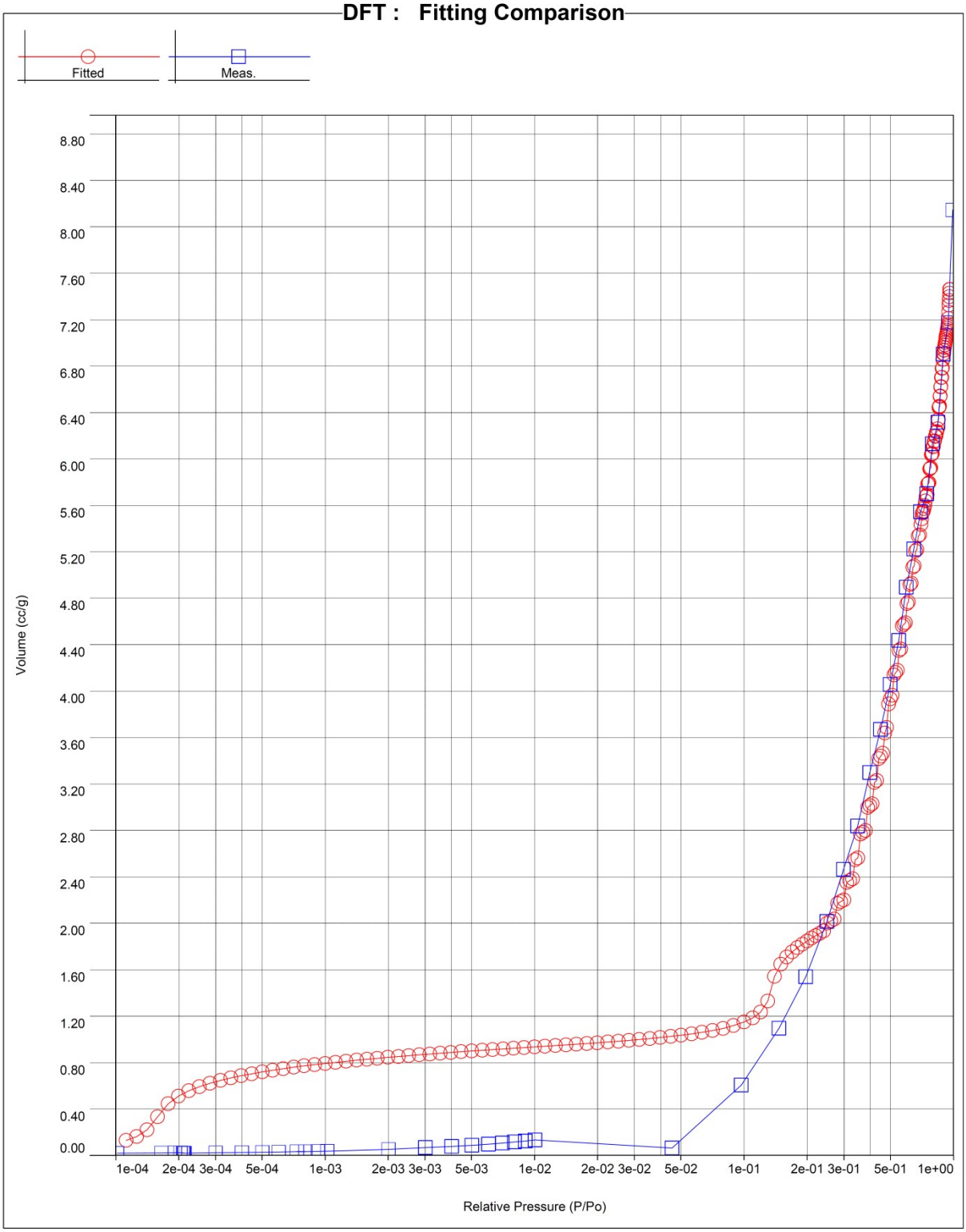

BJH method Adsorption dV(log)
V
dV(logr)
1.84e-02
1.60e-02
1.20e-02
8.00e-03
4.00e-03
0.00e+00
1.81e-02
1.57e-02
1.18e-02
7.87e-03
3.93e-03
0.00e+00
Cumulative Pore Volume (cc/g)
dV(logr)
10.000
20.000
30.000
40.000
100.000
200.000
300.000
500.000
2000.000
Pore Radius (Å)

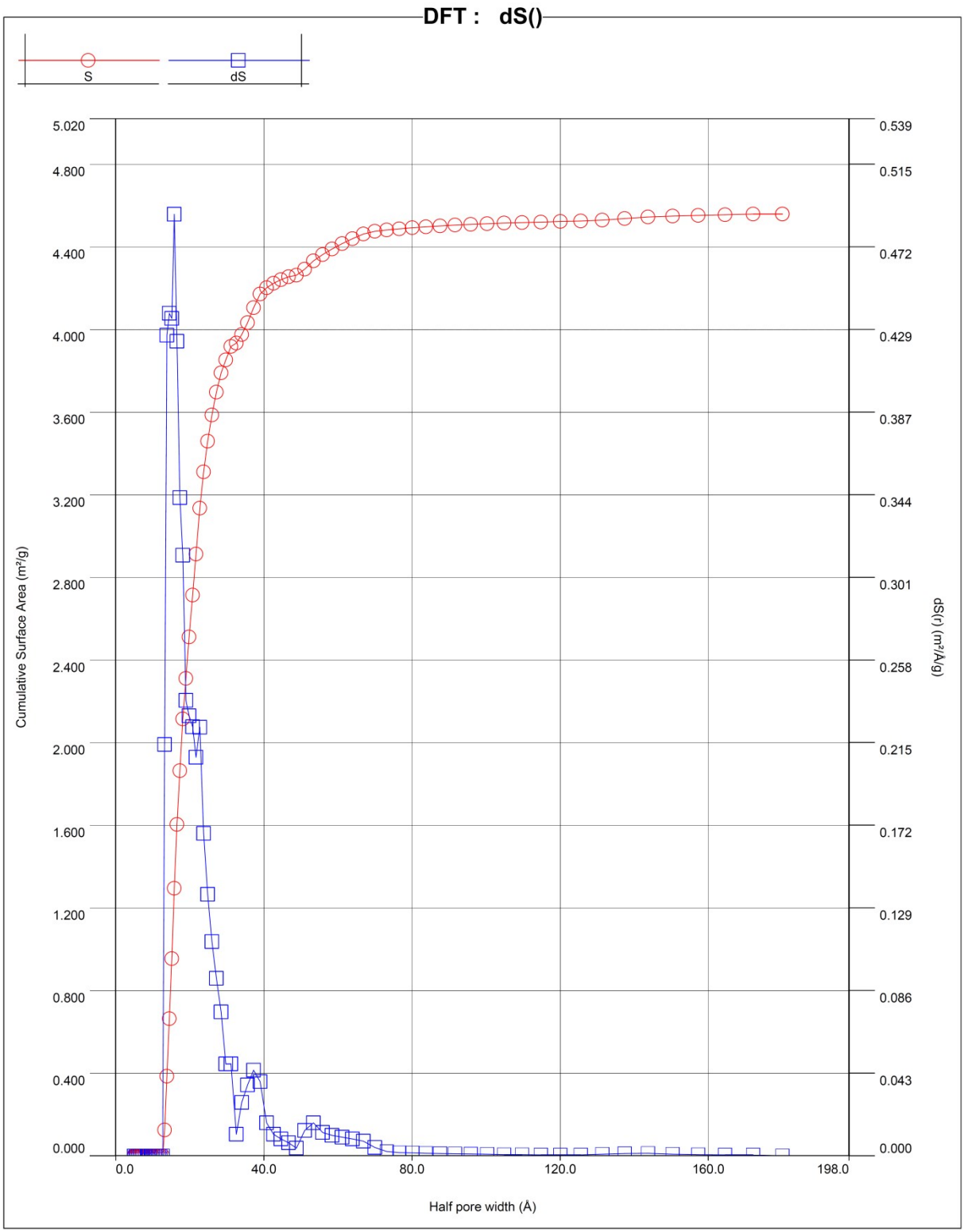

BJH method Desorption dV()
V
dV(r)
1.64e-02
1.60e-02
1.20e-02
8.00e-03
4.00e-03
0.00e+00
5.54e-04
5.40e-04
4.05e-04
2.70e-04
1.35e-04
0.00e+00
Cumulative Pore Volume (cc/g)
dV(r) (cc/Å/g)
10.000
20.000
30.000
40.000
100.000
200.000
300.000
500.000
2000.000
Pore Radius (Å)

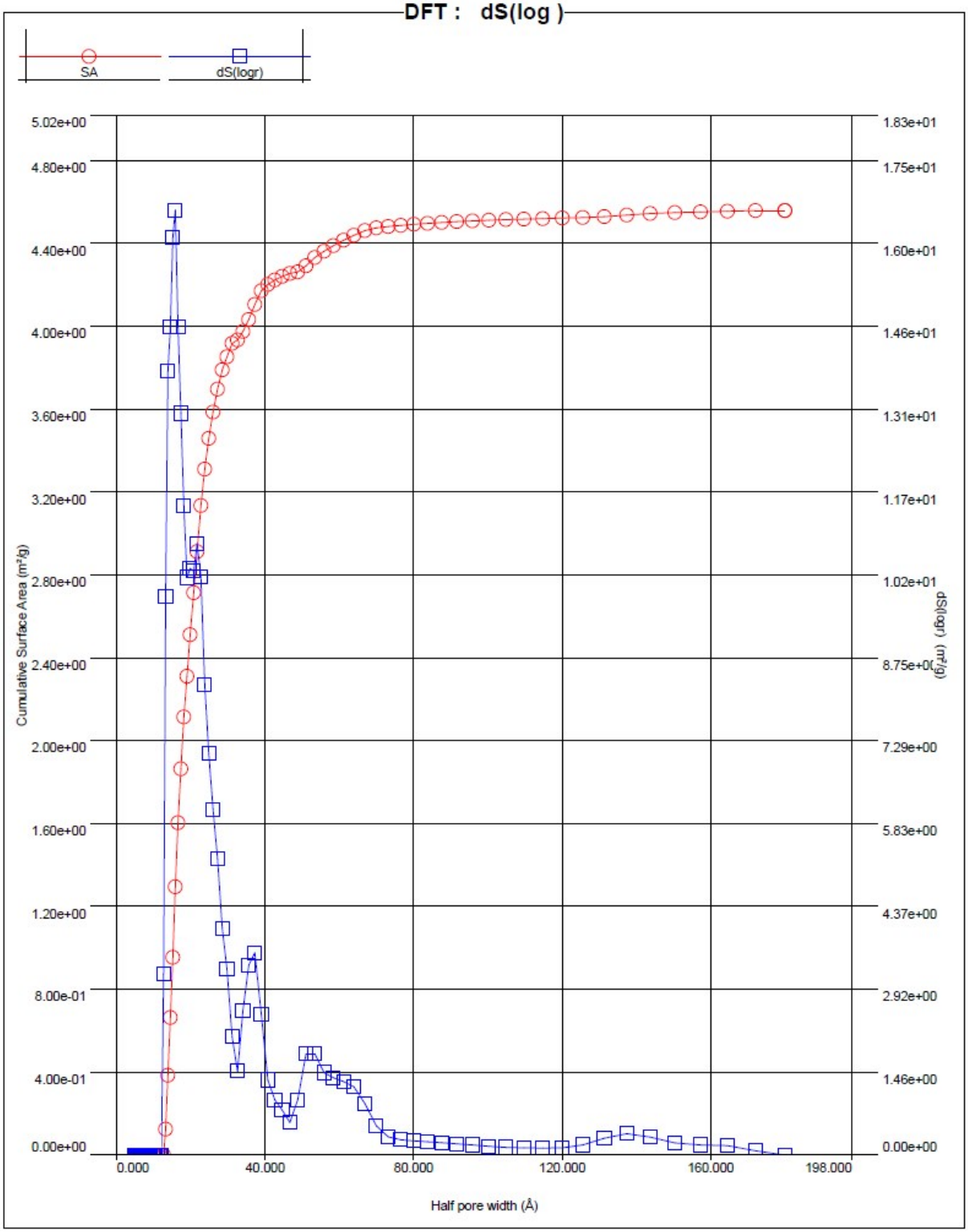

BJH method Desorption dV(log)
V
dV(logr)
1.64e-02
1.60e-02
1.20e-02
8.00e-03
4.00e-03
0.00e+00
2.46e-02
2.40e-02
1.80e-02
1.20e-02
6.00e-03
0.00e+00
Cumulative Pore Volume (cc/g)
dV(logr)
10.000
20.000
30.000
40.000
100.000
200.000
300.000
500.000
2000.000
Pore Radius (Å)


DFT : dV()
V
dV
0.0120
0.0080
0.0040
0.0000
0.0008
0.0006
0.0003
0.0000
Cumulative Pore Volume (cc/g)
dV(r) (cc/Å/g)
0.0000
40.0000
80.0000
120.0000
160.0000
198.0000
Half pore width (Å)

DFT : Fitting Comparison




DFT : dS()
S
dS
5.020
4.800
4.400
4.000
3.600
3.200
2.800
2.400
2.000
1.600
1.200
0.800
0.400
0.000
0.539
0.515
0.472
0.429
0.387
0.344
0.301
0.258
0.215
0.172
0.129
0.086
0.043
0.000
Cumulative Surface Area (m²/g)
dS(r) (m²/Å/g)
0.0
40.0
80.0
120.0
160.0
198.0
Half pore width (Å)


DFT : dS(log)
SA
dS(logr)
5.02e+00
4.80e+00
4.40e+00
4.00e+00
3.60e+00
3.20e+00
2.80e+00
2.40e+00
2.00e+00
1.60e+00
1.20e+00
8.00e-01
4.00e-01
0.00e+00
Cumulative Surface Area (m²/g)
1.83e+01
1.75e+01
1.60e+01
1.46e+01
1.31e+01
1.17e+01
1.02e+01
8.75e+00
7.29e+00
5.83e+00
4.37e+00
2.92e+00
1.46e+00
0.00e+00
dS(logr) (m²/g)
0.000
40.000
80.000
120.000
160.000
198.000
Half pore width (Å)

Multi-Point BET

Relative Pressure [P/Po]	Volume @ STP [cc/g]	1 / [W((Po/P) - 1)] [1/g]	Relative Pressure [P/Po]	Volume @ STP [cc/g]	1 / [W((Po/P) - 1)] [1/g]
1.00529e-02	0.1321	6.1507e+01	2.51416e-01	1.5687	1.7131e+02
1.54432e-01	0.9619	1.5191e+02	3.01487e-01	1.8150	1.9027e+02
2.01540e-01	1.2624	1.5998e+02			

MBET summary

Slope =	435.370 1/g
Intercept =	6.698e+01 1/g
Correlation coefficient, r =	0.973157
C constant=	7.500
Surface Area =	6.932 m²/g

Total Pore Volume data

Total Pore Volume

Total pore volume = 1.682e-02 cc/g for pores smaller than 2660.8 Å (Radius) at P/Po = 0.99639

Average PoreSize data

Average pore Radius = 4.85356e+01 Å

Single Point Surface Area

Relative Pressure [P/Po]	Volume @ STP [cc/g]	1 / [W((P/Po) - 1)]	Slope	Surf. Area [m²/g]
3.01499e-03	0.0665	3.6394e+01	12071.1264	0.2885
4.02271e-03	0.0774	4.1728e+01	10373.0756	0.3357
5.02977e-03	0.0873	4.6344e+01	9214.0394	0.3780
6.02829e-03	0.0958	5.0664e+01	8404.3486	0.4144
7.02700e-03	0.1053	5.3760e+01	7650.5087	0.4552
8.02484e-03	0.1151	5.6219e+01	7005.6147	0.4971
9.03171e-03	0.1232	5.9168e+01	6551.1703	0.5316
1.00529e-02	0.1321	6.1507e+01	6118.3167	0.5692
1.54432e-01	0.9619	1.5191e+02	983.7030	3.5402
2.01540e-01	1.2624	1.5998e+02	793.7939	4.3872
2.51416e-01	1.5687	1.7131e+02	681.3636	5.1111
3.01487e-01	1.8150	1.9027e+02	631.1063	5.5181
3.51471e-01	2.1020	2.0629e+02	586.9313	5.9334
4.01494e-01	2.3740	2.2609e+02	563.1194	6.1843
4.51354e-01	2.6569	2.4774e+02	548.8922	6.3446
5.01473e-01	2.9445	2.7334e+02	545.0750	6.3891

Thickness summary

Thickness method: DeBoer

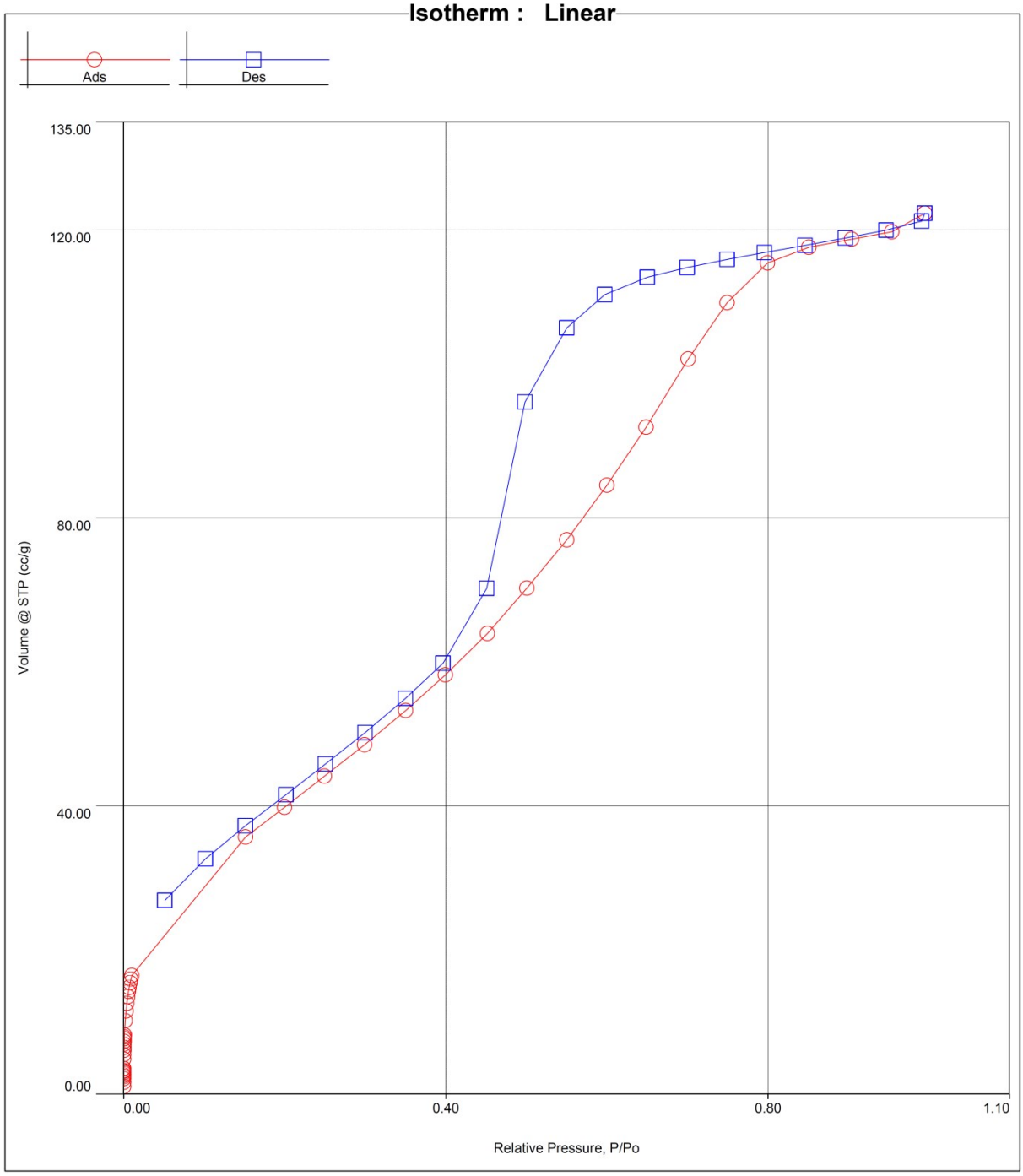
Slope =	0.800
Intercept =	-2.206
Correlation coefficient, r =	0.999237

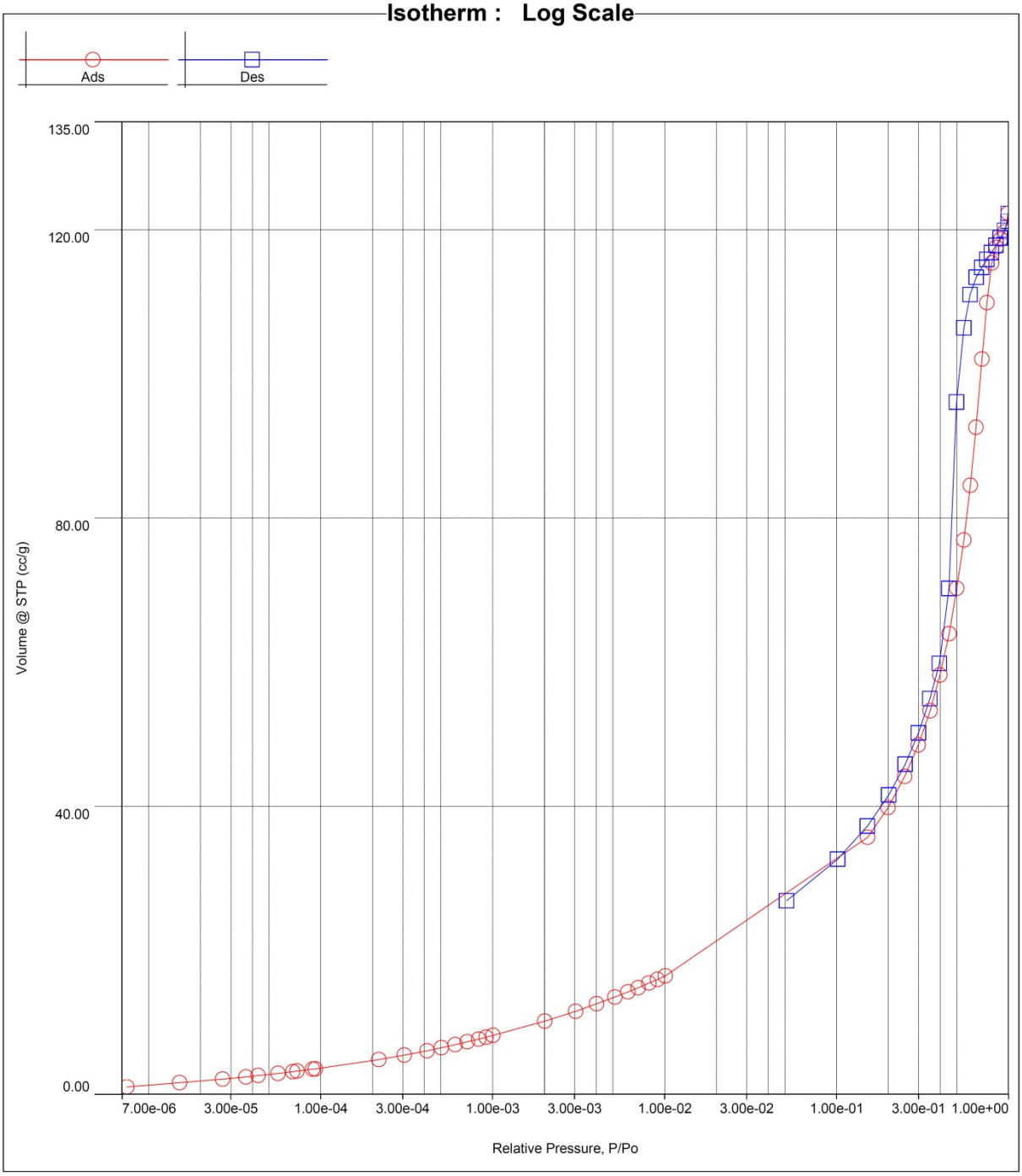
V-t method summary

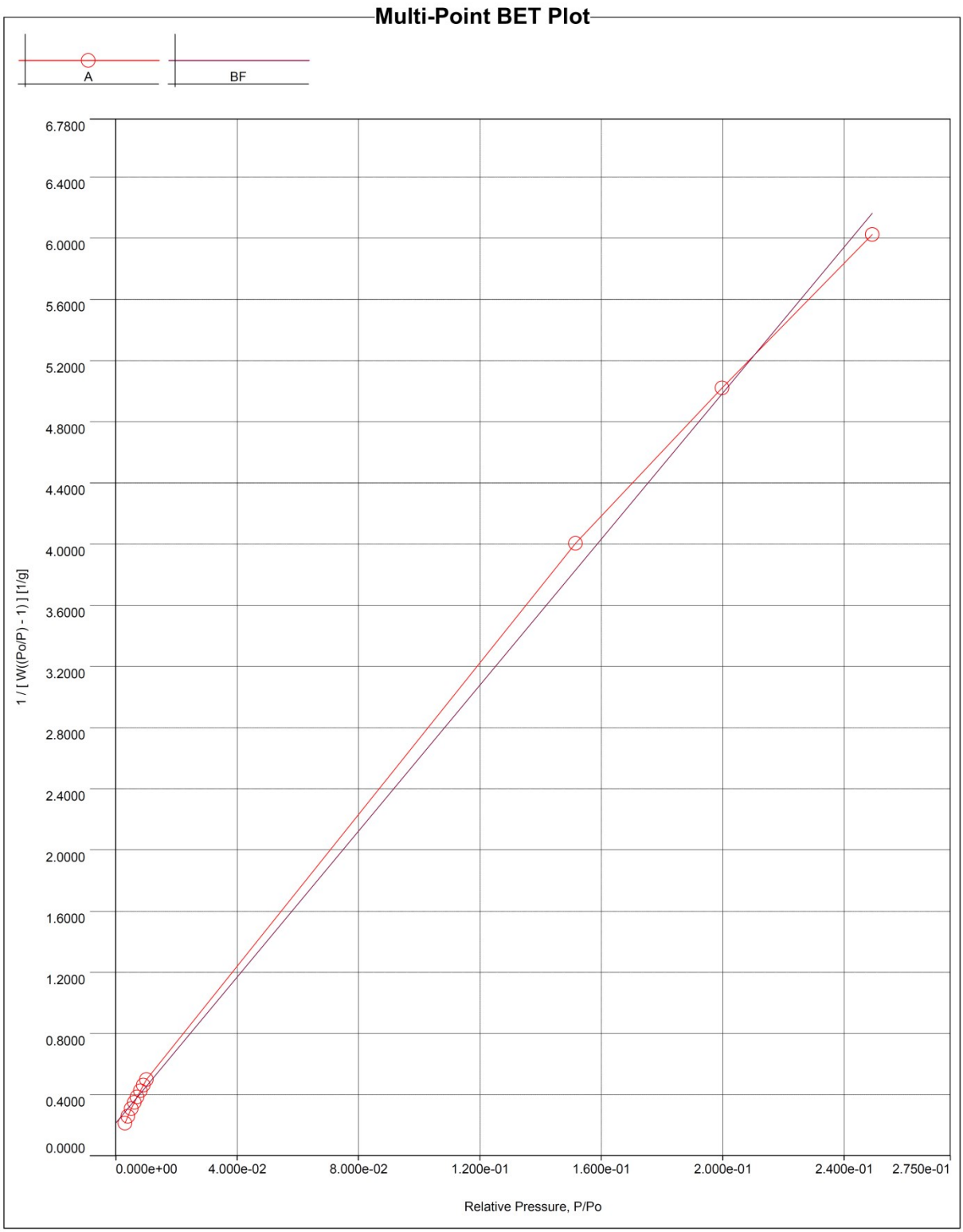
Thickness method: DeBoer

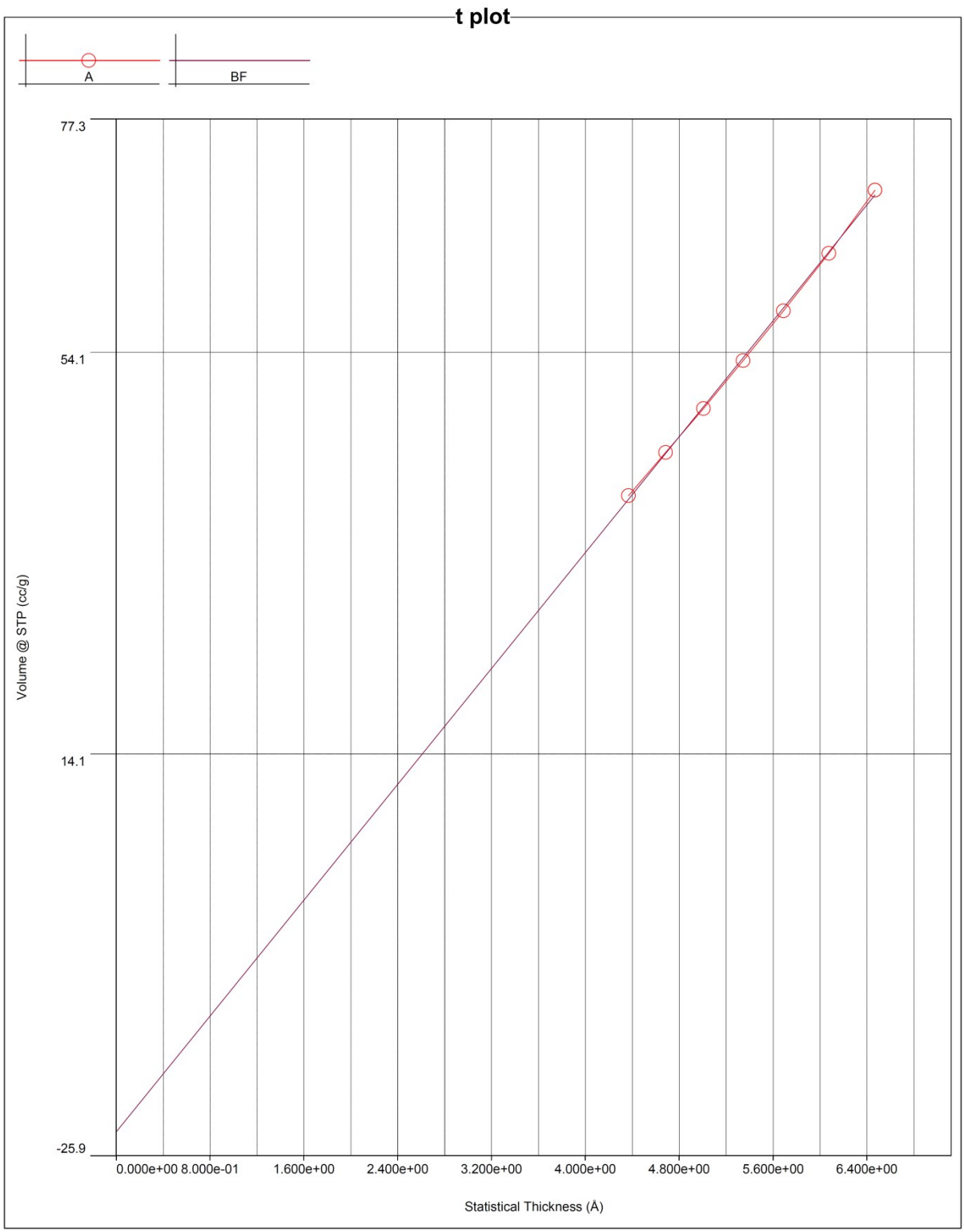
Slope =	0.800
Intercept =	-2.206
Correlation coefficient, r =	0.999237
Micropore volume =	0.000 cc/g
Micropore area =	0.000 m²/g
External surface area =	6.932 m²/g

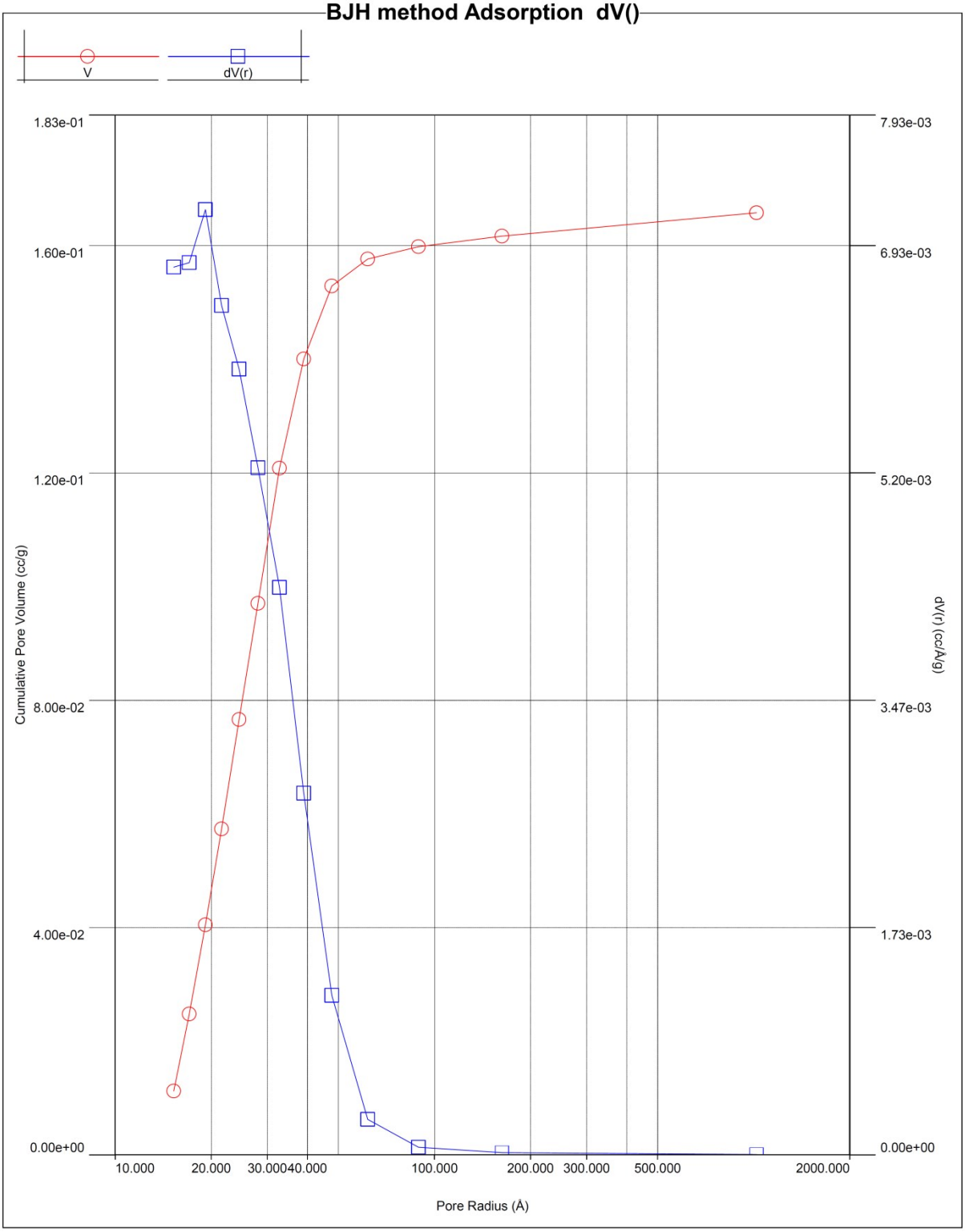
Fig. S4. The BET plot and analysis data for calix-3 precursor.

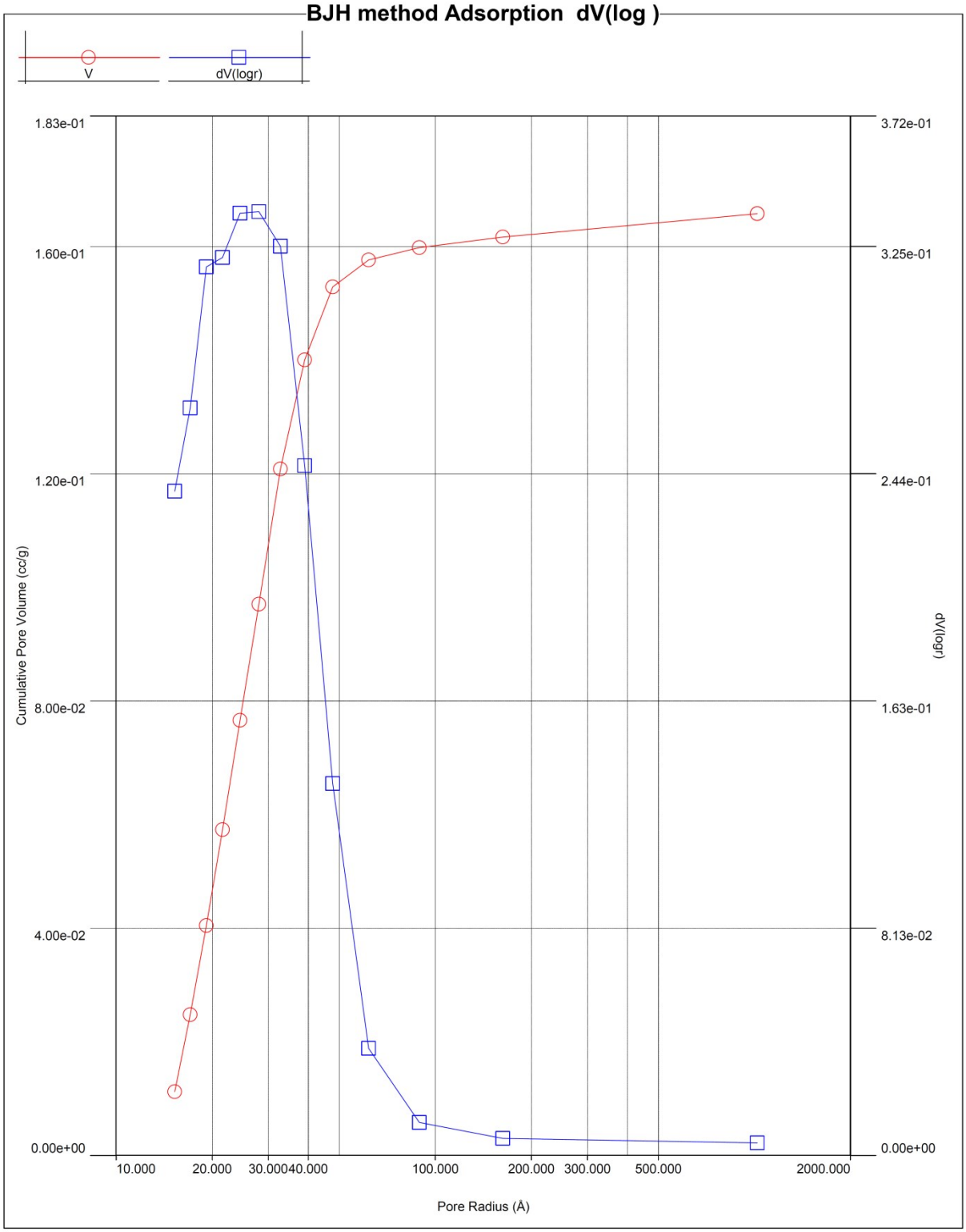

Isotherm : Linear
Ads
Des
135.00
120.00
80.00
40.00
0.00
Volume @ STP (cc/g)
0.00
0.40
0.80
1.10
Relative Pressure, P/Po

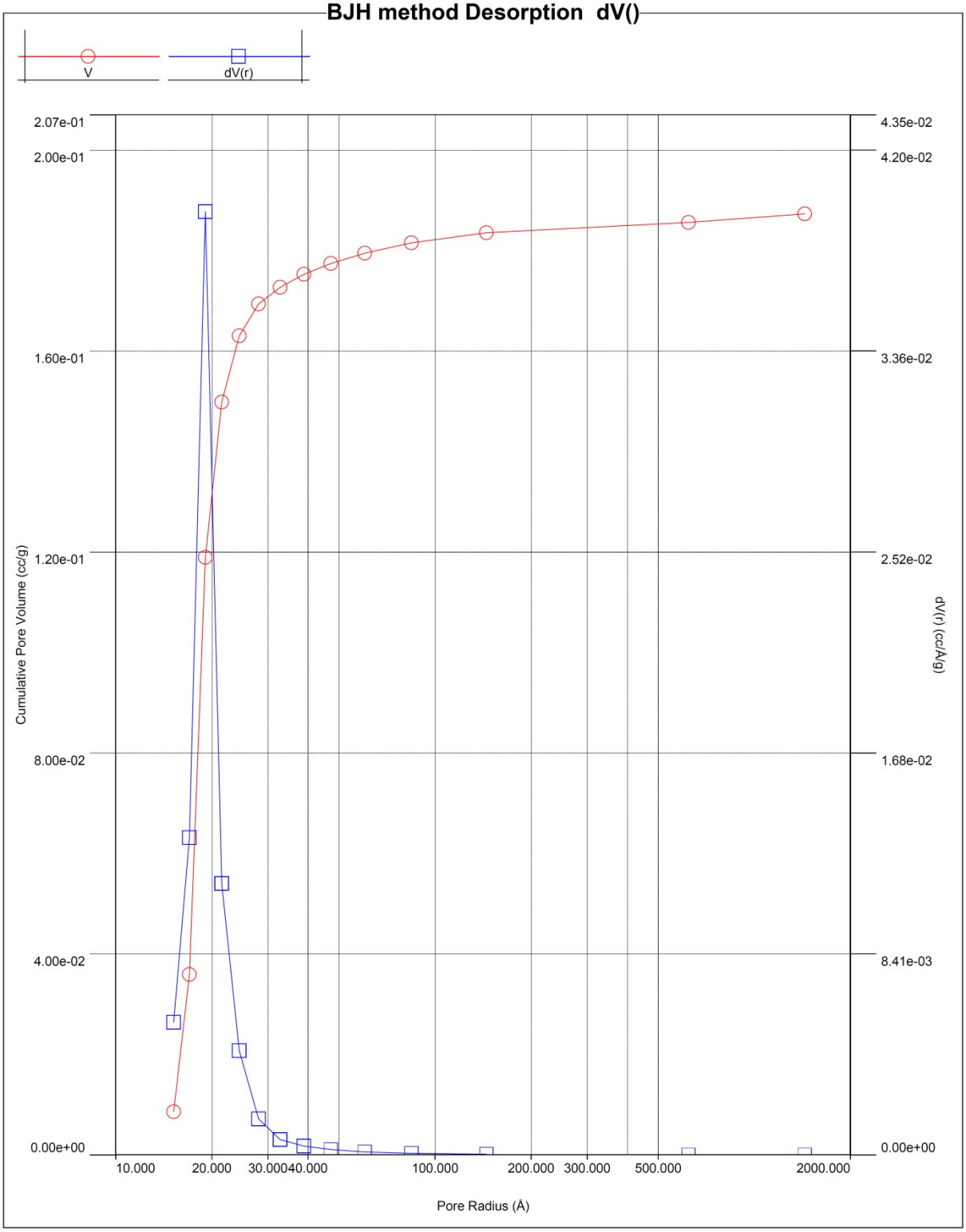

Isotherm : Log Scale
Ads
Des
135.00
120.00
80.00
40.00
0.00
Volume @ STP (cc/g)
7.00e-06
3.00e-05
1.00e-04
3.00e-04
1.00e-03
3.00e-03
1.00e-02
3.00e-02
1.00e-01
3.00e-01
1.00e+00
Relative Pressure, P/Po

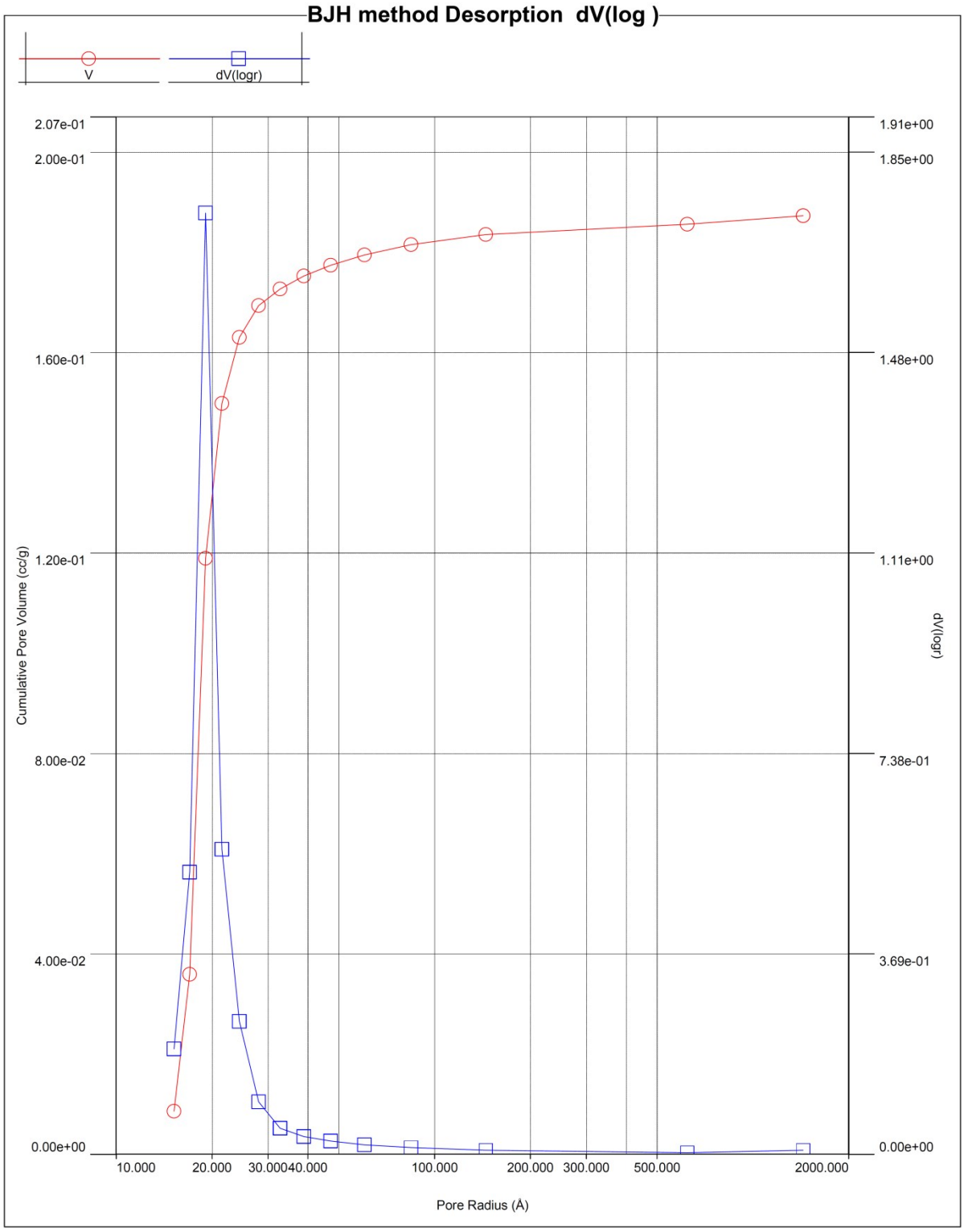

Multi-Point BET Plot
A
BF
6.7800
6.4000
6.0000
5.6000
5.2000
4.8000
4.4000
4.0000
3.6000
3.2000
2.8000
2.4000
2.0000
1.6000
1.2000
0.8000
0.4000
0.0000
1 / [W((Po/P) - 1)] [1/g]
0.000e+00
4.000e-02
8.000e-02
1.200e-01
1.600e-01
2.000e-01
2.400e-01
2.750e-01
Relative Pressure, P/Po

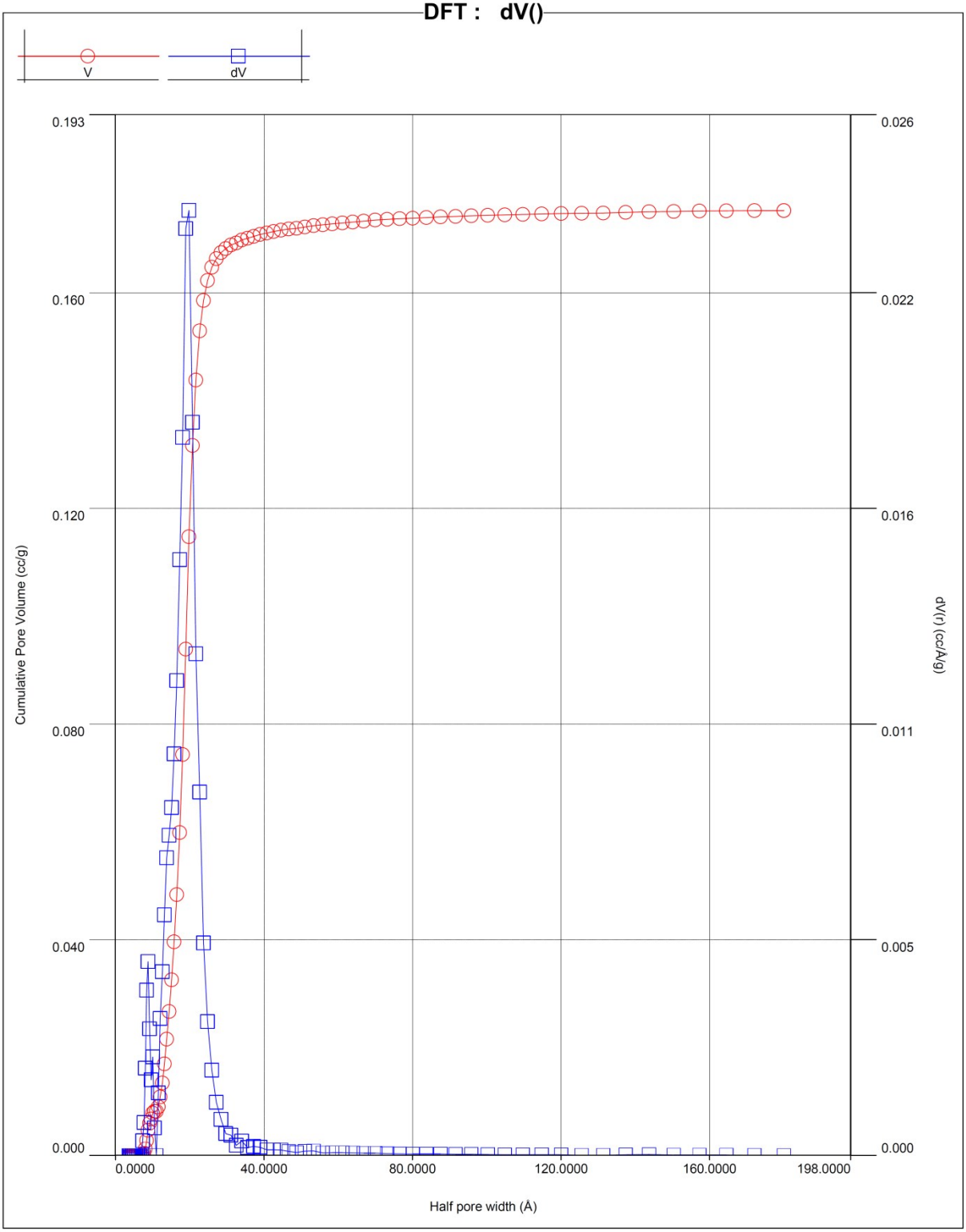

t plot
A
BF
77.3
54.1
14.1
-25.9
Volume @ STP (cc/g)
0.000e+00 8.000e-01 1.600e+00 2.400e+00 3.200e+00 4.000e+00 4.800e+00 5.600e+00 6.400e+00
Statistical Thickness (Å)

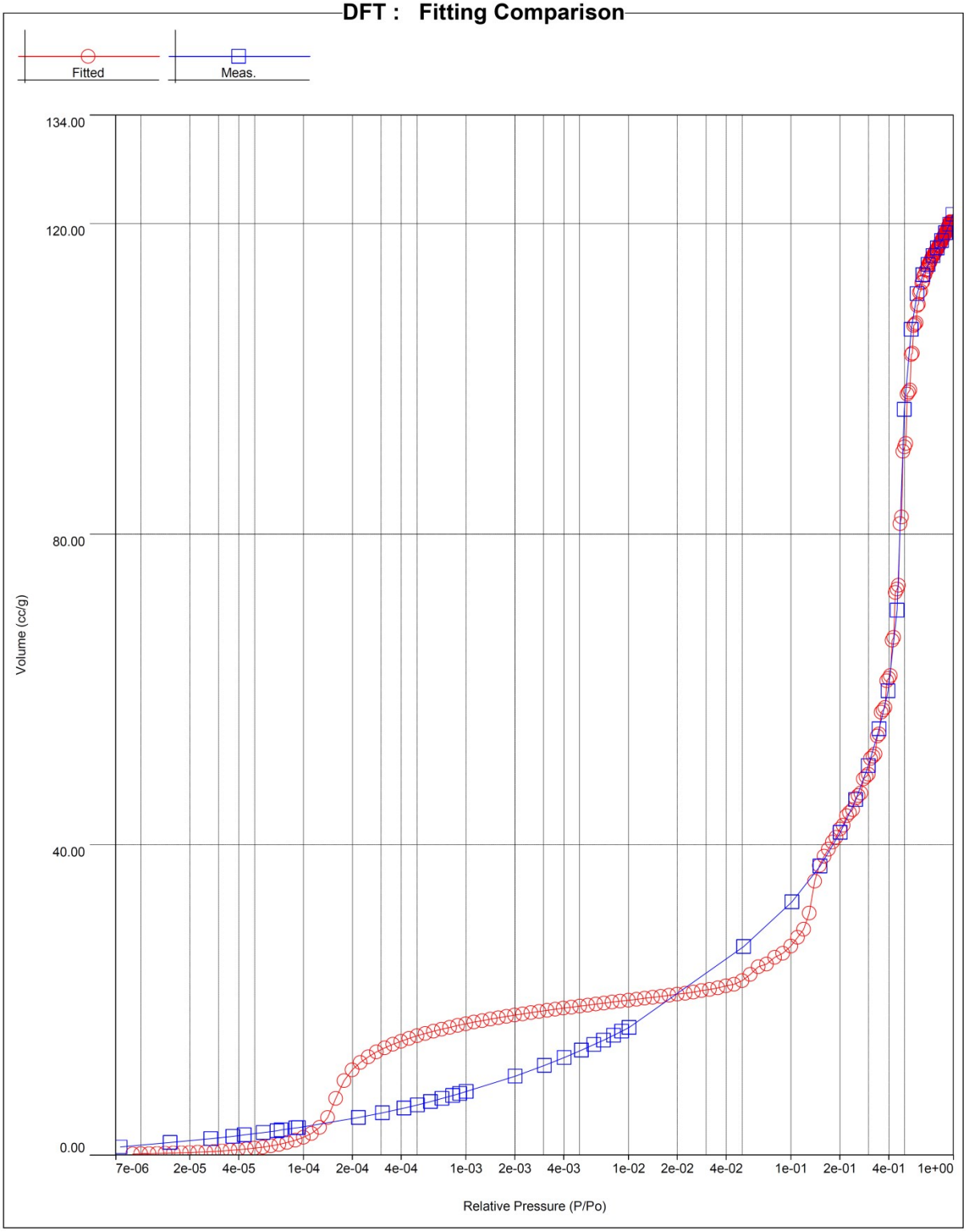

BJH method Adsorption dV()
V
dV(r)
1.83e-01
1.60e-01
1.20e-01
8.00e-02
4.00e-02
0.00e+00
7.93e-03
6.93e-03
5.20e-03
3.47e-03
1.73e-03
0.00e+00
Cumulative Pore Volume (cc/g)
dV(r) (cc/Å/g)
10.000
20.000
30.000
40.000
100.000
200.000
300.000
500.000
2000.000
Pore Radius (Å)

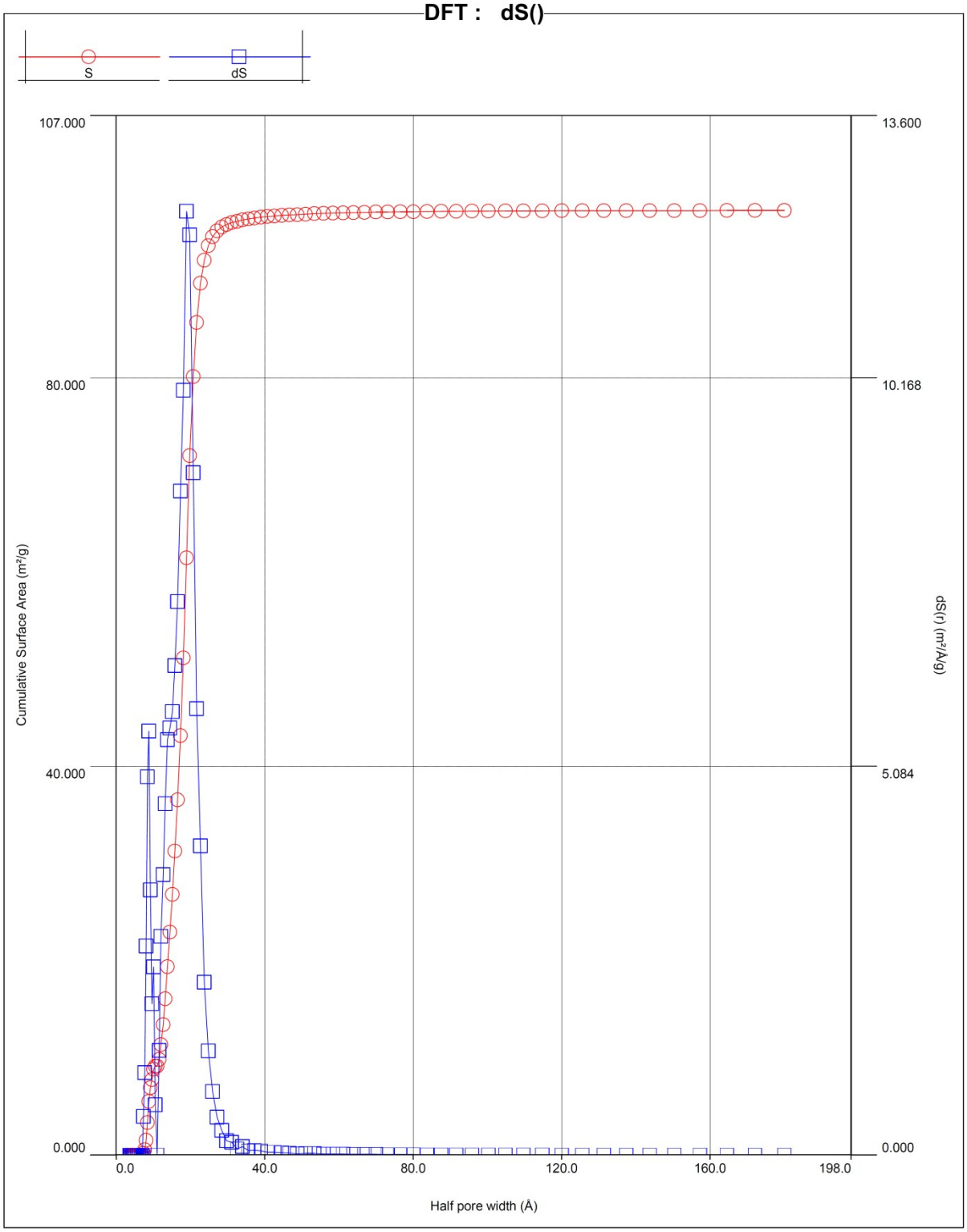

BJH method Adsorption dV(log)
V
dV(logr)
1.83e-01
1.60e-01
1.20e-01
8.00e-02
4.00e-02
0.00e+00
3.72e-01
3.25e-01
2.44e-01
1.63e-01
8.13e-02
0.00e+00
Cumulative Pore Volume (cc/g)
dV(logr)
10.000
20.000
30.000
40.000
100.000
200.000
300.000
500.000
2000.000
Pore Radius (Å)

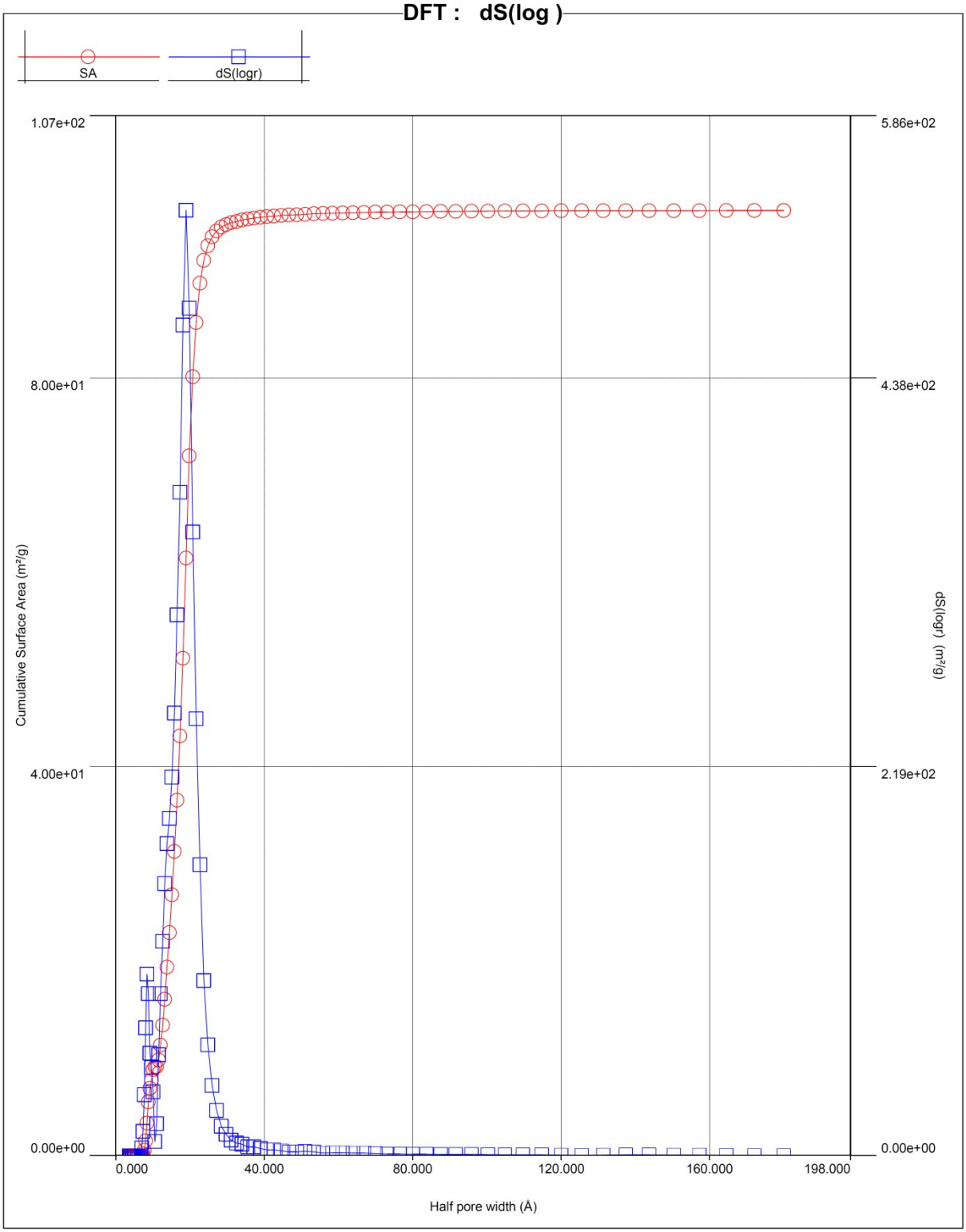

BJH method Desorption dV()
V
dV(r)
2.07e-01
2.00e-01
1.60e-01
1.20e-01
8.00e-02
4.00e-02
0.00e+00
4.35e-02
4.20e-02
3.36e-02
2.52e-02
1.68e-02
8.41e-03
0.00e+00
Cumulative Pore Volume (cc/g)
dV(r) (cc/Å/g)
10.000
20.000
30.000
40.000
100.000
200.000
300.000
500.000
2000.000
Pore Radius (Å)


BJH method Desorption dV(log)
V
dV(logr)
2.07e-01
2.00e-01
1.60e-01
1.20e-01
8.00e-02
4.00e-02
0.00e+00
Cumulative Pore Volume (cc/g)
1.91e+00
1.85e+00
1.48e+00
1.11e+00
7.38e-01
3.69e-01
0.00e+00
dV(logP)
10.000
20.000
30.000
40.000
100.000
200.000
300.000
500.000
2000.000
Pore Radius (Å)


DFT : dV()
V
dV
0.193
0.160
0.120
0.080
0.040
0.000
0.026
0.022
0.016
0.011
0.005
0.000
Cumulative Pore Volume (cc/g)
dV(r) (cc/Å/g)
0.0000
40.0000
80.0000
120.0000
160.0000
198.0000
Half pore width (Å)


DFT : Fitting Comparison
Fitted
Meas.
134.00
120.00
80.00
40.00
0.00
Volume (cc/g)
7e-06
2e-05
4e-05
1e-04
2e-04
4e-04
1e-03
2e-03
4e-03
1e-02
2e-02
4e-02
1e-01
2e-01
4e-01
1e+00
Relative Pressure (P/Po)


DFT : dS()
S
dS
107.000
80.000
40.000
0.000
13.600
10.168
5.084
0.000
0.0
40.0
80.0
120.0
160.0
198.0
Cumulative Surface Area (m²/g)
dS() (m²/Å/g)
Half pore width (Å)


DFT : dS(log)
SA
dS(logr)
1.07e+02
8.00e+01
4.00e+01
0.00e+00
5.86e+02
4.38e+02
2.19e+02
0.00e+00
Cumulative Surface Area (m²/g)
dS(logr) (m²/g)
0.000
40.000
80.000
120.000
160.000
198.000
Half pore width (Å)

Multi-Point BET

Relative Pressure [P/Po]	Volume @ STP [cc/g]	1 / [W((Po/P) - 1)] [1/g]	Relative Pressure [P/Po]	Volume @ STP [cc/g]	1 / [W((Po/P) - 1)] [1/g]
3.04515e-03	11.5254	2.1204e-01	9.09683e-03	15.9404	4.6080e-01
4.03642e-03	12.5579	2.5822e-01	1.01236e-02	16.4313	4.9800e-01
5.14660e-03	13.4983	3.0664e-01	1.51489e-01	35.6733	4.0043e+00
6.13671e-03	14.2184	3.4746e-01	1.99807e-01	39.7915	5.0208e+00
7.02144e-03	14.7876	3.8259e-01	2.49312e-01	44.1070	6.0246e+00
8.12461e-03	15.4301	4.2474e-01			

MBET summary

Slope =	23.865 1/g
Intercept =	2.135e-01 1/g
Correlation coefficient, r =	0.999354
C constant=	112.785
Surface Area =	144.633 m²/g

Total Pore Volume data

Total Pore Volume

Total pore volume = 1.891e-01 cc/g for pores smaller than 1825.8 Å (Radius) at P/Po = 0.99473

Average PoreSize data

Average pore Radius = 2.61543e+01 Å

Single Point Surface Area

Relative Pressure [P/Po]	Volume @ STP [cc/g]	1 / [W((P/Po) - 1)]	Slope	Surf. Area [m²/g]
3.04515e-03	11.5254	2.1204e-01	69.6337	50.0120
4.03642e-03	12.5579	2.5822e-01	63.9722	54.4380
5.14660e-03	13.4983	3.0664e-01	59.5814	58.4497
6.13671e-03	14.2184	3.4746e-01	56.6205	61.5062
7.02144e-03	14.7876	3.8259e-01	54.4895	63.9117
8.12461e-03	15.4301	4.2474e-01	52.2787	66.6145
9.09683e-03	15.9404	4.6080e-01	50.6546	68.7503
1.01236e-02	16.4313	4.9800e-01	49.1923	70.7940
1.51489e-01	35.6733	4.0043e+00	26.4332	131.7479
1.99807e-01	39.7915	5.0208e+00	25.1285	138.5886
2.49312e-01	44.1070	6.0246e+00	24.1648	144.1154
2.99142e-01	48.4679	7.0460e+00	23.5541	147.8520
3.50211e-01	53.2253	8.1020e+00	23.1345	150.5337
3.99716e-01	58.1846	9.1567e+00	22.9079	152.0224
4.51855e-01	63.9190	1.0319e+01	22.8362	152.4997
5.00869e-01	70.2177	1.1434e+01	22.8291	152.5472

Thickness summary

Thickness method: DeBoer	
Slope =	14.414
Intercept =	-23.515
Correlation coefficient, r =	0.999575

V-t method summary

Thickness method: DeBoer	
Slope =	14.414
Intercept =	-23.515
Correlation coefficient, r =	0.999575
Micropore volume =	0.000 cc/g
Micropore area =	0.000 m²/g
External surface area =	144.633 m²/g

Fig. S5. The BET plot and analysis data for CBOS precursor.

Table S1. ANOVA results of the quadratic surface model for the benzene adsorption process.

Source	Sum of Squares	Degree of Freedom	Mean Square	*F*-value	*p*-value	
Model	6.722E+05	9	74688.59	81.89	< 0.0001	significant
X_1-Time	2.238E+05	1	2.238E+05	245.42	< 0.0001	
X_2-Concentration	1.627E+05	1	1.627E+05	178.36	< 0.0001	
X_3-Temperature	55919.32	1	55919.32	61.31	< 0.0001	
$X_1 X_2$	10989.03	1	10989.03	12.05	0.0060	
$X_1 X_3$	5371.66	1	5371.66	5.89	0.0356	
$X_2 X_3$	127.20	1	127.20	0.1395	0.7166	
X_1^2	1.062E+05	1	1.062E+05	116.46	< 0.0001	
X_2^2	1.098E+05	1	1.098E+05	120.37	< 0.0001	
X_3^2	35291.14	1	35291.14	38.70	< 0.0001	
Residual	9120.21	10	912.02	-	-	
Lack of Fit	122.79	5	122.79	0.1269	0.8215	insignificant
Pure Error	6.25	5	1.25	-	-	
Cor Total	6.813E+05	19	-	-	-	
R^2 = 0.9866, Adjusted R^2= 0.9746, Predicted R^2 = 0.8994, Adequate Precision = 28.2665						

Table S2. ANOVA results of the quadratic surface model for the toluene adsorption process.

Source	Sum of Squares	Degree of Freedom	Mean Square	*F*-value	*p*-value	
Model	8.065E+05	9	89606.56	72.92	< 0.0001	significant
X_1-Time	2.661E+05	1	2.661E+05	216.53	< 0.0001	
X_2-Concentration	2.082E+05	1	2.082E+05	169.43	< 0.0001	
X_3-Temperature	60054.58	1	60054.58	48.87	< 0.0001	
$X_1 X_2$	14377.84	1	14377.84	11.70	0.0065	
$X_1 X_3$	6191.06	1	6191.06	5.04	0.0486	
$X_2 X_3$	0.0003	1	0.0003	2.543E-07	0.9996	
X_1^2	1.339E+05	1	1.339E+05	108.98	< 0.0001	
X_2^2	1.264E+05	1	1.264E+05	102.83	< 0.0001	
X_3^2	34457.52	1	34457.52	28.04	0.0003	
Residual	12288.28	10	1228.83	-	-	
Lack of Fit	117.58	5	117.58	0.1023	0.9510	insignificant
Pure Error	1.05	5	0.2097	-	-	
Cor Total	8.187E+05	19	-	-	-	
R^2 = 0.9850, Adjusted R^2= 0.9715, Predicted R^2 = 0.8854, Adequate Precision = 26.9512						