Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Site-Isolated Iridium Complexes on MgO Powder: Individual Ir Atoms Imaged by Scanning Transmission Electron Microscopy

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Experimental Section

Materials and sample preparation: Details of the sample preparation have been reported.[1] Sample syntheses and handling were performed with the exclusion of moisture and air by use of standard methods. The precursor $Ir(C_2H_4)_2(acac)$, which has been characterized by X-ray diffraction crystallography and ^1H and ^{13}C NMR, Raman, and IR spectroscopies, was synthesized as described elsewhere.[2] The MgO support was obtained from EM Science. Deionized water was added to the MgO to form a paste, which was dried overnight in air at 393 K. The solid was ground and calcined as O_2 flowed through a bed of the particles as the temperature was ramped linearly from room temperature to 973 K and then held for 2 h. The treatment in O_2 was immediately followed by evacuation of the sample for 14 h at 973 K. The resultant MgO was then cooled to room temperature under vacuum. To prepare the supported iridium complex, the precursor $Ir(C_2H_4)_2(acac)$ and calcined MgO were slurried in dried and deoxygenated *n*-pentane (Fisher, 99%) that was initially at dry-ice temperature. The stirred slurry was kept at this temperature for two days of mixing period, and thereafter the solvent was removed by evacuation for a day. The resultant solid, containing 1.0 wt% Ir, was light gray in color. It was stored in an argon-filled glove box.

In another preparation to make a sample for comparison with the supported iridium complex, the reaction of Hacac with calcined MgO was carried out in *n*-pentane with exclusion of air and moisture; the slurry was stirred for one day, and the solvent was removed by evacuation for one day.

H_2 was supplied by Airgas (99.999%) or was generated by electrolysis of water in a Balston generator (99.99%); it was purified by passage through traps containing particles of reduced Cu/Al_2O_3 and activated zeolite 4A to remove traces of O_2 and moisture, respectively. He (Airgas, 99.999%) and C_2H_4 (Airgas, 99.99%) were purified by passage through similar traps.

IR Spectroscopy. A Bruker IFS 66v/S spectrometer with a spectral resolution of 2 cm^{-1} was used to collect transmission spectra of powder samples. Approximately 10 mg of each sample, handled with exclusion of moisture and air, was pressed between two KBr windows for optical optimization that allowed detection of minor peaks. IR spectra were recorded with the samples at room temperature under vacuum, with an average of 128 scans per spectrum.

X-ray Absorption Spectroscopy. EXAFS spectra were collected at beamline X-18B at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory, and at beamline 10-2 at the Stanford Synchrotron Radiation Laboratory (SSRL), Stanford Linear Accelerator Center. The storage ring electron energy was 2.8 GeV at NSLS and 3 GeV at SSRL. The ring currents were 110–250 mA and 50–100 mA at NSLS and SSRL, respectively.

In a glove box at each synchrotron (filled with argon at NSLS and N_2 at SSRL), powder samples were loaded into an EXAFS cell.[3] The cell was evacuated to a pressure less than 1.3×10^{-5} mbar and aligned in the X-ray beam. Spectra were collected in transmission mode at the Ir L_{III} edge (11215 eV) with the sample cooled to approximately liquid-nitrogen temperature. In some experiments, spectra were collected with the sample at 298 K during treatment in flowing helium, C_2H_4, H_2, or $H_2 + C_2H_4$ in the EXAFS cell described elsewhere.[4]

For measurements of a sample working as an ethene hydrogenation catalyst, the sample was initially scanned in flowing helium, and then the flow of reactant gases was begun (40 mbar each of ethene and H_2, with the remainder being helium and the pressure atmospheric). After the measurement of an initial EXAFS spectrum, the steady flow of reactants continued for 2 h as XANES spectra were collected, followed by four EXAFS spectra at the end.

Ethene Hydrogenation Catalysis in a Tubular Plug-Flow Reactor. Ethene hydrogenation catalysis was also carried out in a conventional laboratory once-through tubular plug-flow reactor. The catalyst (30 mg), diluted with particles of inert, nonporous α-Al_2O_3 in a mass ratio of Al_2O_3 to catalyst of 30:1, was loaded into the reactor in a glove box. The feed ethene and H_2 partial pressures were 40 mbar each, and the temperature was 294 ± 1 K. Details of the reaction experiments and product analysis by gas chromatography are as described elsewhere.[5] Conversions of ethene to ethane were <5%, and the reactor operated in the differential mode, determining reaction rates directly.[6]

EXAFS Data Analysis. The X-ray absorption edge energy was calibrated with the measured signal of a platinum foil at the Ir L_{III} edge (11215 eV); this foil was scanned simultaneously with the sample. Ir L_{III} EXAFS data were collected at energies near that of the edge (11215 eV). The data were normalized by dividing the absorption intensity by the height of the absorption edge.

Analysis of the EXAFS data was carried out with the software ATHENA (part of the IFEFFIT package)[7] and the software XDAP.[8] Athena was used for data alignment, edge calibration, and deglitching. Data normalization, background subtraction, and conversion of the data into a chi file and data fitting were performed with XDAP,[8] which allows the efficient application of a difference-file technique[9] for the determination of optimized fit parameters and isolation of individual shells.

Reference files, used in the data analysis, were calculated by using the code FEFF7.0.[10] The phase shifts and backscattering amplitudes representing Ir–Ir and Ir–Mg were calculated from the structural parameters characterizing iridium metal and $IrMg_3$, respectively. The crystal structure of $Ir(C_2H_4)_2(acac)$[2] was used to calculate the phase shifts and backscattering amplitudes representing the Ir–C and Ir–O shells, as it was expected that the structure of the supported iridium species would be similar to that of this precursor.

Iterative fitting was carried out for various structural models of the supported iridium complex until the best agreement was attained between the calculated k^0-, k^1-, and k^2- weighted EXAFS data and the postulated model (k is the wave vector).[11]

In the analysis of the data characterizing the initially prepared sample, the fitting ranges in both momentum (k) and real (r) space (r is distance from the absorbing Ir atom) were determined by the data quality; the range in k was 2.9–12.0 Å^{-1} and the range in r was 0.7–4.0 Å. These values were used with the Nyquist theorem[12] to estimate the justified number of fitting parameters. The number of parameters used in fitting the data to each model (16) was always less than this number (approximately 20).

In the analysis of the data characterizing the sample under reaction conditions, as ethene reacted catalytically with H_2 at 293 K, the fitting ranges in k space were 2.9–13.1 Å^{-1} and the ranges in r space were 0.7–4.0 Å. Again, the number of parameters used in the fitting (20) was always less than that defined by the Nyquist theorem with these ranges (23).

The accuracies of the parameters are estimated to be as follows (with the exception of the Ir–Mg and longer Ir–O contributions): coordination number N, ± 10%; distance R, ± 0.02 Å; Debye-Waller factor $\Delta\sigma^2$, ± 20%; and inner potential correction ΔE_0, ± 20%.

We emphasize that attempts were made to include Ir–Ir contributions in all of the fits, even with a k^3 weighting of the data—but none was found; furthermore, we emphasize that it is difficult to distinguish Ir–Mg and long Ir–O contributions from each other (we refer to long Ir–O distances as those greater than an Ir–O bonding distance). Thus, the Ir–Mg and/or long Ir–O contributions are assigned only tentatively, and the errors characterizing such shells are greater than those stated above. Part of the challenge of analyzing these shells is obtaining a suitable reference that approximates the structure of the interface between the iridium complex and the support.[1]

Further details of the EXAFS analysis are as reported.[1]

Table SI-1. Qualitative summary of EXAFS fitting results for four candidate models characterizing the structure of MgO-supported iridium complex formed from the reaction of Ir(C_2H_4)$_2$(acac) with highly dehydroxylated MgO

Model	Absorber/backscaterrer contributions	Comments regarding the quality of fit of EXAFS data
I	Ir–C Ir–O Ir–Mg Ir-O$_l$	Good overall fit (as shown by goodness of fit parameter). Good individual fits for all contributions. Physically realistic values of all fit parameters. This is the preferred model.
II	Ir–C Ir–O Ir–Mg Ir-O$_l$	Adequate overall fit; however, poor fits of individual contributions (especially when the phase- and amplitude-correction is applied). Physically unrealistic values of the fit parameters: Unrealistic coordination numbers for Ir–O contribution, and ΔE_0 value
III	Ir–C Ir–O Ir–Mg Ir-O$_l$	Adequate overall fit; however, poor fits of individual contributions (especially when the phase- and amplitude-correction is applied). Physically unrealistic values of the fit parameters: Unrealistic coordination numbers for Ir–O contribution, and ΔE_0 value and poor fit of the long Ir–O shell
IV	Ir–O Ir–Mg Ir-O$_l$	Adequate overall fit; however, poor fits of individual contributions (especially when the phase- and amplitude-correction is applied). Physically unrealistic values of the fit parameters: Unrealistic coordination numbers for Ir–O contribution, and extremely high ΔE_0 and $\Delta\sigma^2$ values and poor fit of the long Ir–O shell

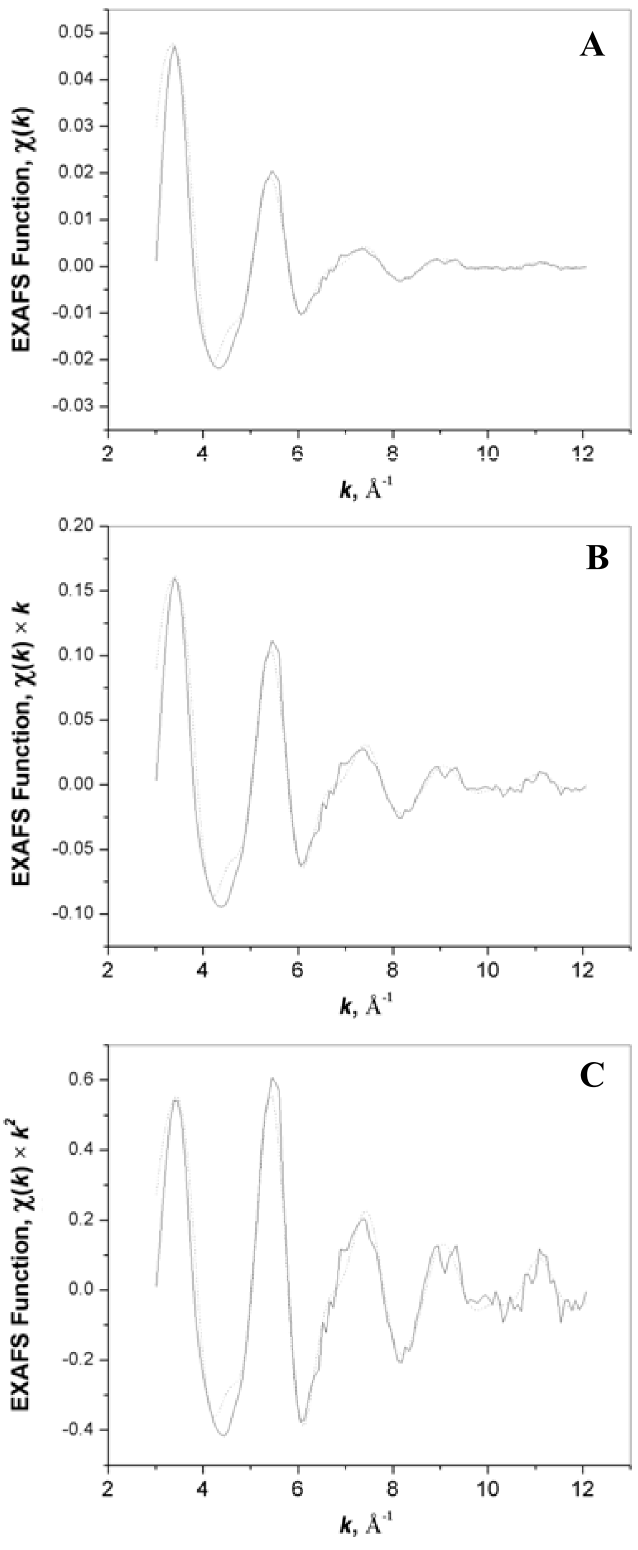


Fig. SI-1. Results of EXAFS analysis for the recommended model (Model I) characterizing the sample formed from the reaction of $Ir(C_2H_4)_2(acac)$ and MgO that had been calcined at 973 K. EXAFS function, χ (solid line), and calculated contribution (dotted line); A, k^1-weighted; B, k^2-weighted; and C, k^3-weighted (Δk = 3.0–12.1 $Å^{-1}$).

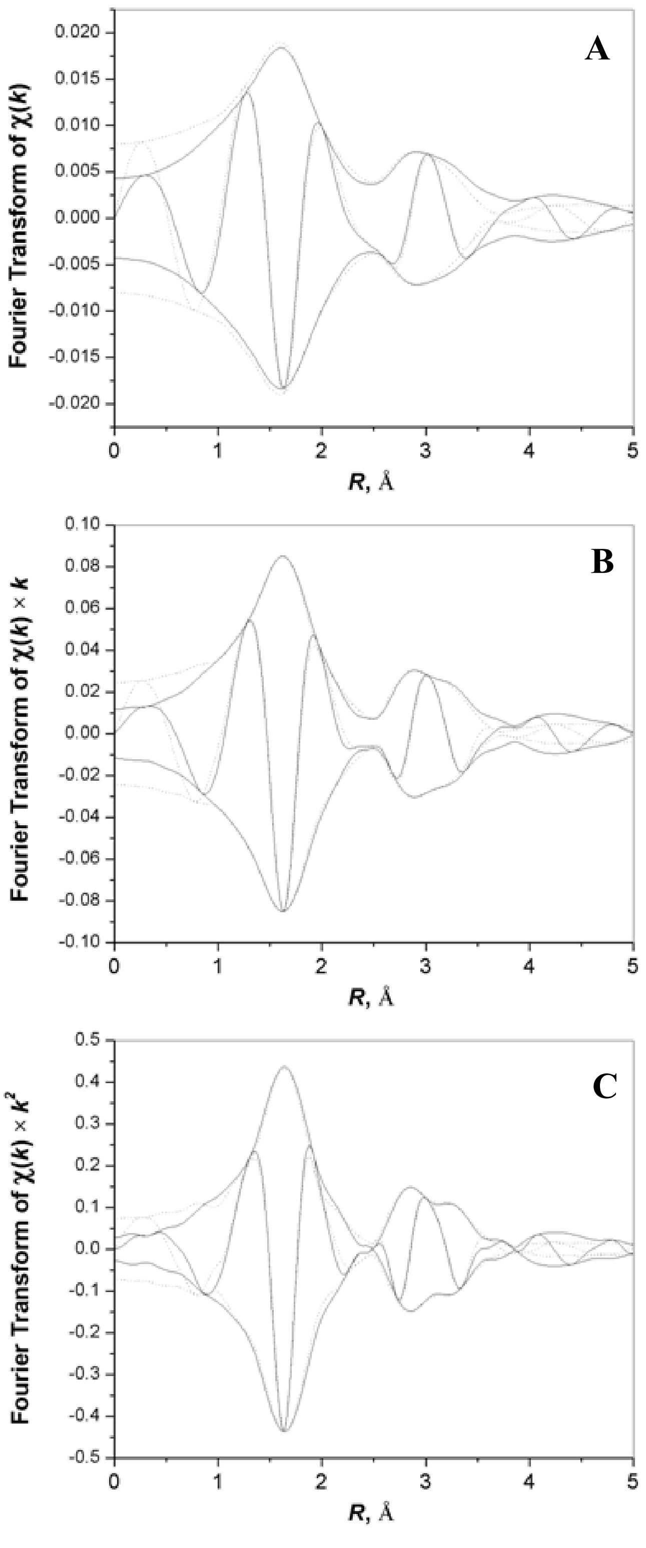


Fig. SI-2. Results of EXAFS analysis for the recommended model (Model I) characterizing the sample formed from the reaction of Ir(C_2H_4)$_2$(acac) and MgO that had been calcined at 973 K. Imaginary part and magnitude of the Fourier transform of data (solid lines) and calculated contributions (dotted lines): A, k^1-weighted; B, k^2-weighted; and C, k^3-weighted (Δk = 3.0–12.1 Å^{-1}).

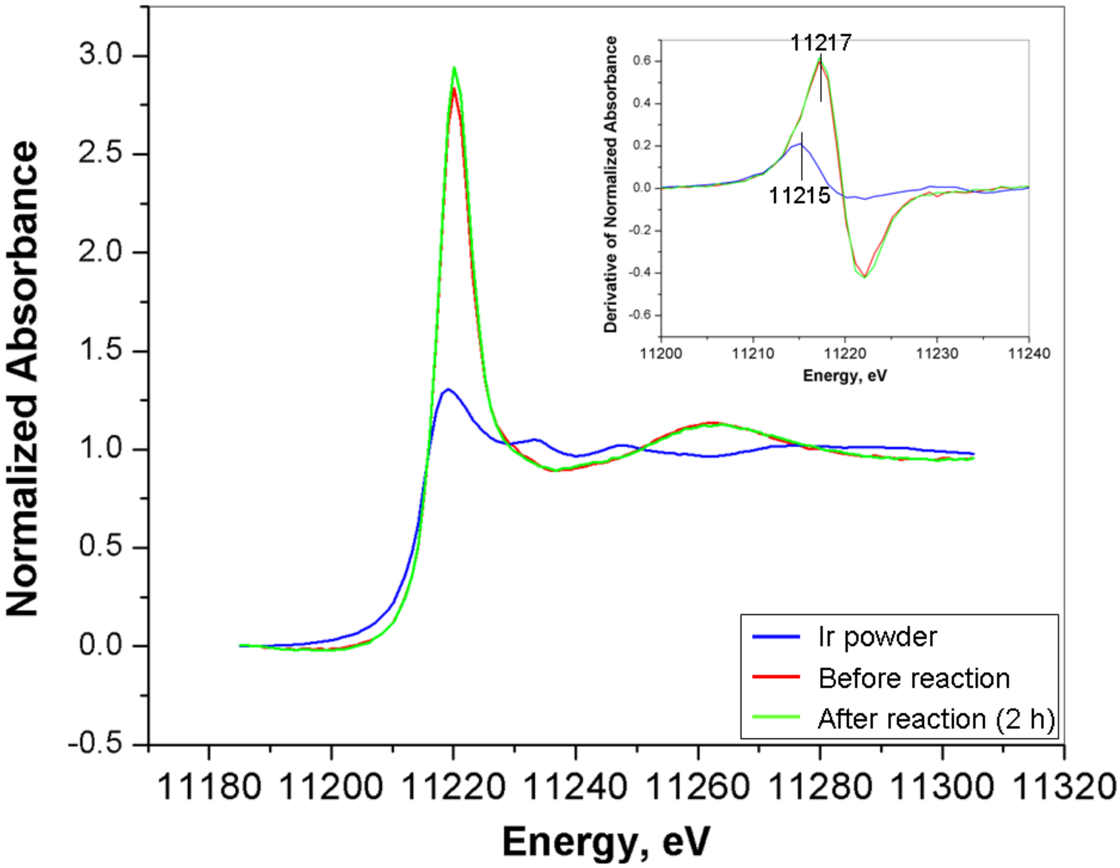


Fig. SI-3. Normalized XANES spectra at the Ir L_{III} edge of the sample formed from $Ir(C_2H_4)_2(acac)$ and MgO before and after reaction in equimolar ethene and H_2 at 293 K. For comparison, the spectrum of iridium powder is also shown. The inset indicates the derivatives of spectra illustrating the energy edge positions.

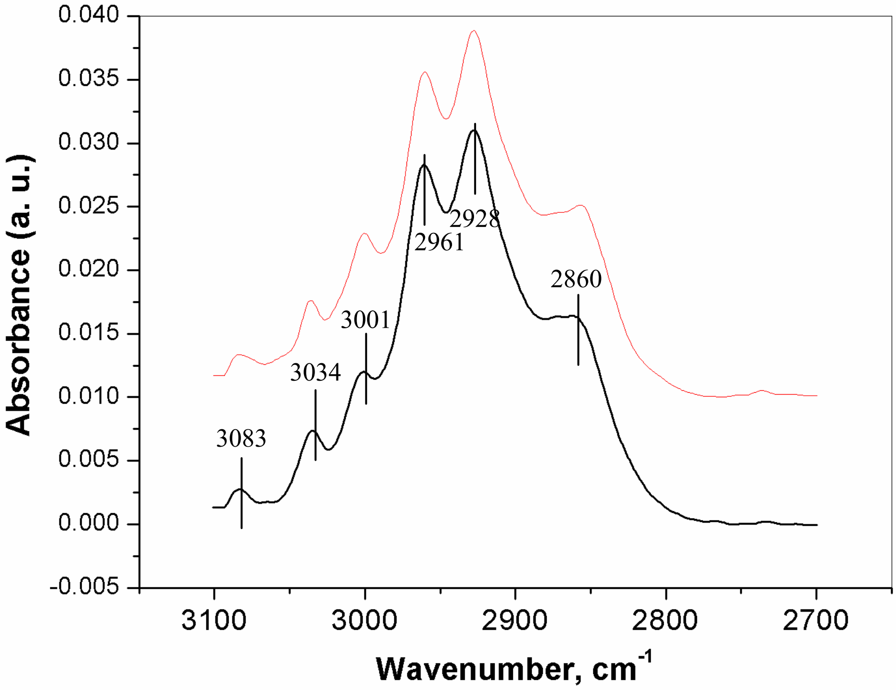


Fig. SI-4. IR spectra in the υ_{CH} region characterizing the ethene ligands in the sample formed by reaction of MgO (calcined at 973 K) with $Ir(C_2H_4)_2(acac)$ in *n*-pentane. Spectrum in red was obtained exposing the sample to air for 10 s.

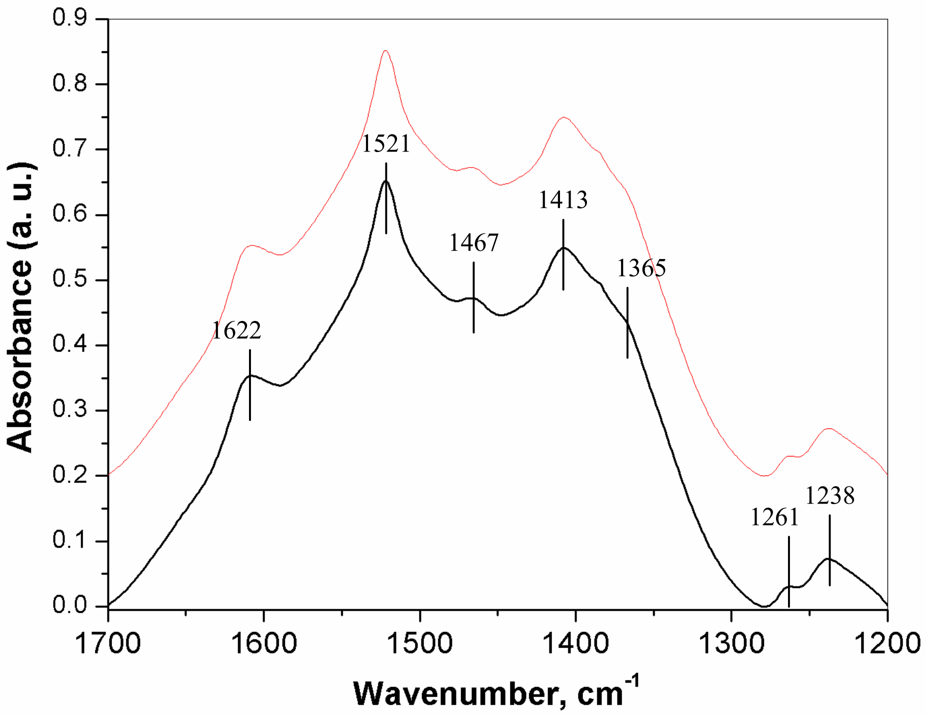


Fig. SI-5. IR spectra in the region of 1200 to 1800 cm^{-1} characterizing the sample formed by reaction of MgO (calcined at 973 K) with Ir(C_2H_4)$_2$(acac) in *n*-pentane. Spectrum in red was obtained exposing the sample to air for 10 s.

Table 4. Frequencies of IR bands observed in C–H stretching region and in acetylacetonate region characterising reference compounds and sample formed by adsorption of $Ir(C_2H_4)_2(acac)$ on highly dehydroxylated MgO

Sample				Assignment
$Mg(acac)_2$	Hacac/MgO	$Ir(C_2H_4)_2(acac)$	$Ir(C_2H_4)_2(acac)$ on MgO	
3128	-	-	-	not assigned
-	-	3045	3083	$\upsilon(CH_2)$ (π-bonded ethene)
-	-	3030	3034	$\upsilon(CH_2)$ (π-bonded ethene)
-	-	2981	3001	$\upsilon(CH_2)$ (π-bonded ethene)
2993	2993	-	-	$\upsilon(CH_3)$ (acac)
2970	2965	2935	2961	$\upsilon(CH_3)$ (acac)
2925	2920	2906	2928	$\upsilon(CH_3)$ (acac)
2866	-	2879	2860	not assigned
1623	1620	1576	1622	$\upsilon(C–C)$ {or $\upsilon(C–O)$}
1528	1521	1549	1521	$\upsilon(C–O)$ {or $\upsilon(C–C)$}
1489	1465	1486	1467	$\upsilon(C–C) + \delta(C–H)$
1423	1418	1424	1413	$\delta_d(CH_3)$
1371	1367	1361	1365	$\delta_s(CH_3)$
1263	1265	1276	1261	$\upsilon_s(C–C) + \upsilon(C–CH_3)$
1199	1199	1212	1238	$\upsilon_s(C–CH_3) + \delta(C–H)$

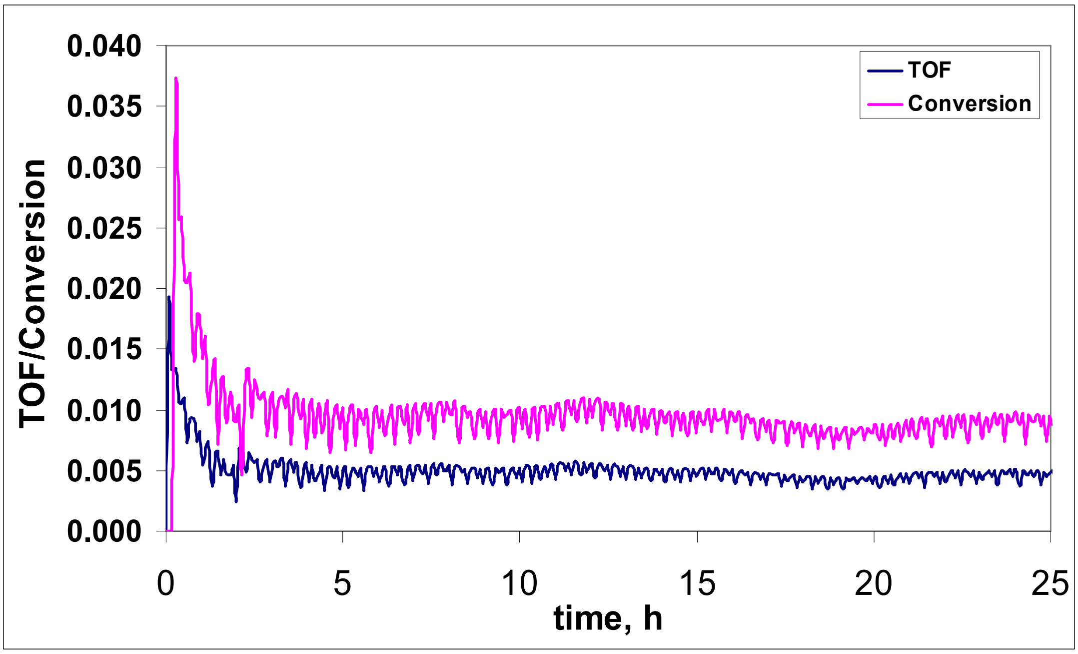
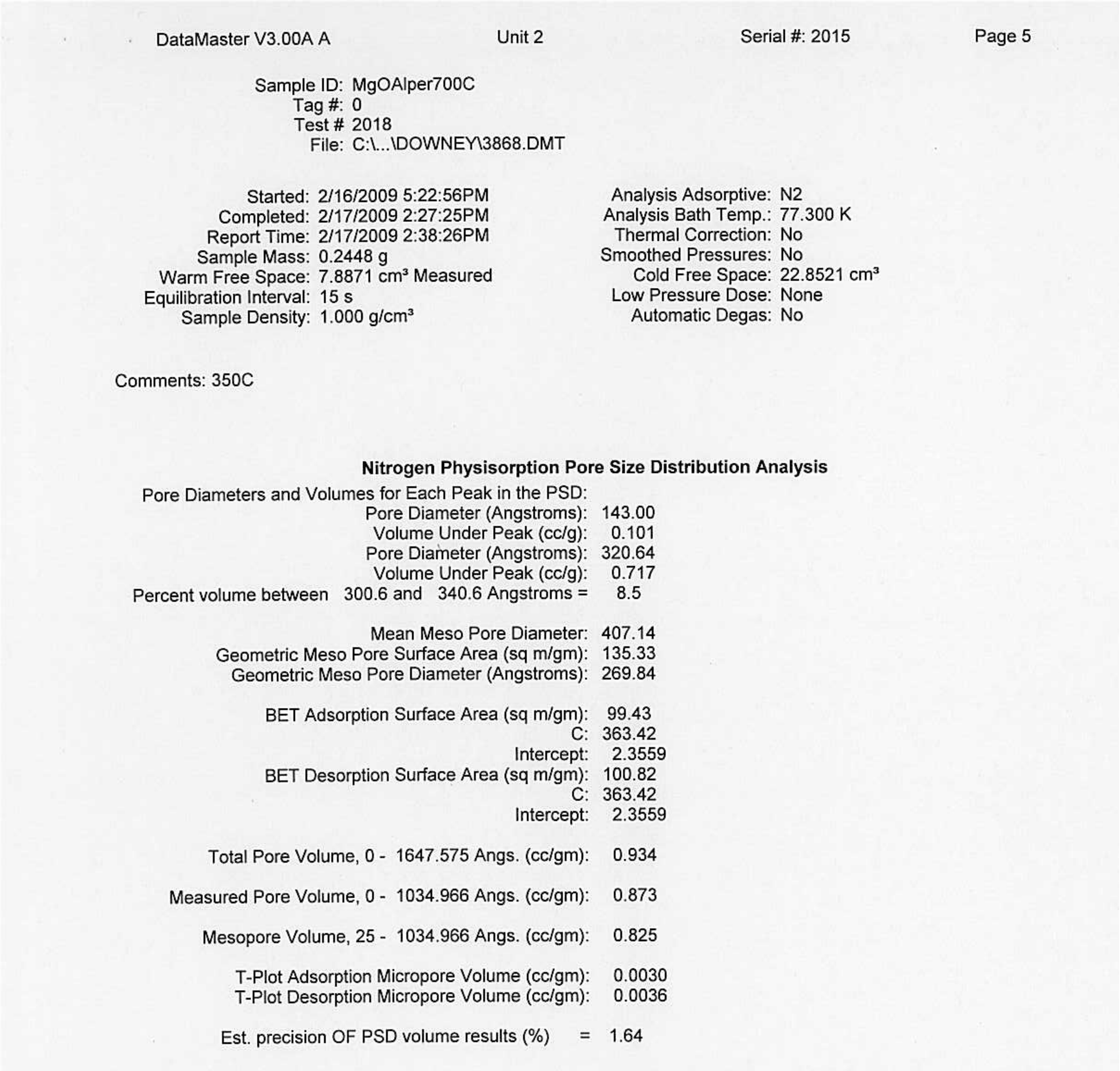


Fig. SI-6. Ethene hydrogenation catalyzed by sample formed from chemisorption of Ir(C_2H_4)$_2$(acac) on MgO: conversion of ethene and turnover frequency versus time on stream in a flow reactor with a total flow rate of 100 mL/min, in the presence of 40 mbar of ethene and 40 mbar of H_2 (in a balance of He) at 294 K and atmospheric pressure with 30 mg of catalyst.



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                   Sample ID: MgOAlper700C
                       Tag #: 0
                      Test # 2018
                        File: C:\...\DOWNEY\3868.DMT

               Started: 2/16/2009 5:22:56PM          Analysis Adsorptive: N2
             Completed: 2/17/2009 2:27:25PM         Analysis Bath Temp.: 77.300 K
           Report Time: 2/17/2009 2:38:26PM          Thermal Correction: No
           Sample Mass: 0.2448 g                    Smoothed Pressures: No
       Warm Free Space: 7.8871 cm³ Measured            Cold Free Space: 22.8521 cm³
  Equilibration Interval: 15 s                      Low Pressure Dose: None
        Sample Density: 1.000 g/cm³                   Automatic Degas: No

Comments: 350C

                    Nitrogen Physisorption Pore Size Distribution Analysis
  Pore Diameters and Volumes for Each Peak in the PSD:
                                    Pore Diameter (Angstroms):  143.00
                                      Volume Under Peak (cc/g):   0.101
                                    Pore Diameter (Angstroms):  320.64
                                      Volume Under Peak (cc/g):   0.717
 Percent volume between   300.6 and   340.6 Angstroms =   8.5

                                    Mean Meso Pore Diameter:  407.14
             Geometric Meso Pore Surface Area (sq m/gm):  135.33
               Geometric Meso Pore Diameter (Angstroms):  269.84

                    BET Adsorption Surface Area (sq m/gm):   99.43
                                                        C:  363.42
                                                Intercept:    2.3559
                    BET Desorption Surface Area (sq m/gm):  100.82
                                                        C:  363.42
                                                Intercept:    2.3559

         Total Pore Volume, 0 -  1647.575 Angs. (cc/gm):    0.934

      Measured Pore Volume, 0 -  1034.966 Angs. (cc/gm):    0.873

        Mesopore Volume, 25 -  1034.966 Angs. (cc/gm):    0.825

            T-Plot Adsorption Micropore Volume (cc/gm):    0.0030
            T-Plot Desorption Micropore Volume (cc/gm):    0.0036

         Est. precision OF PSD volume results (%)     =   1.64
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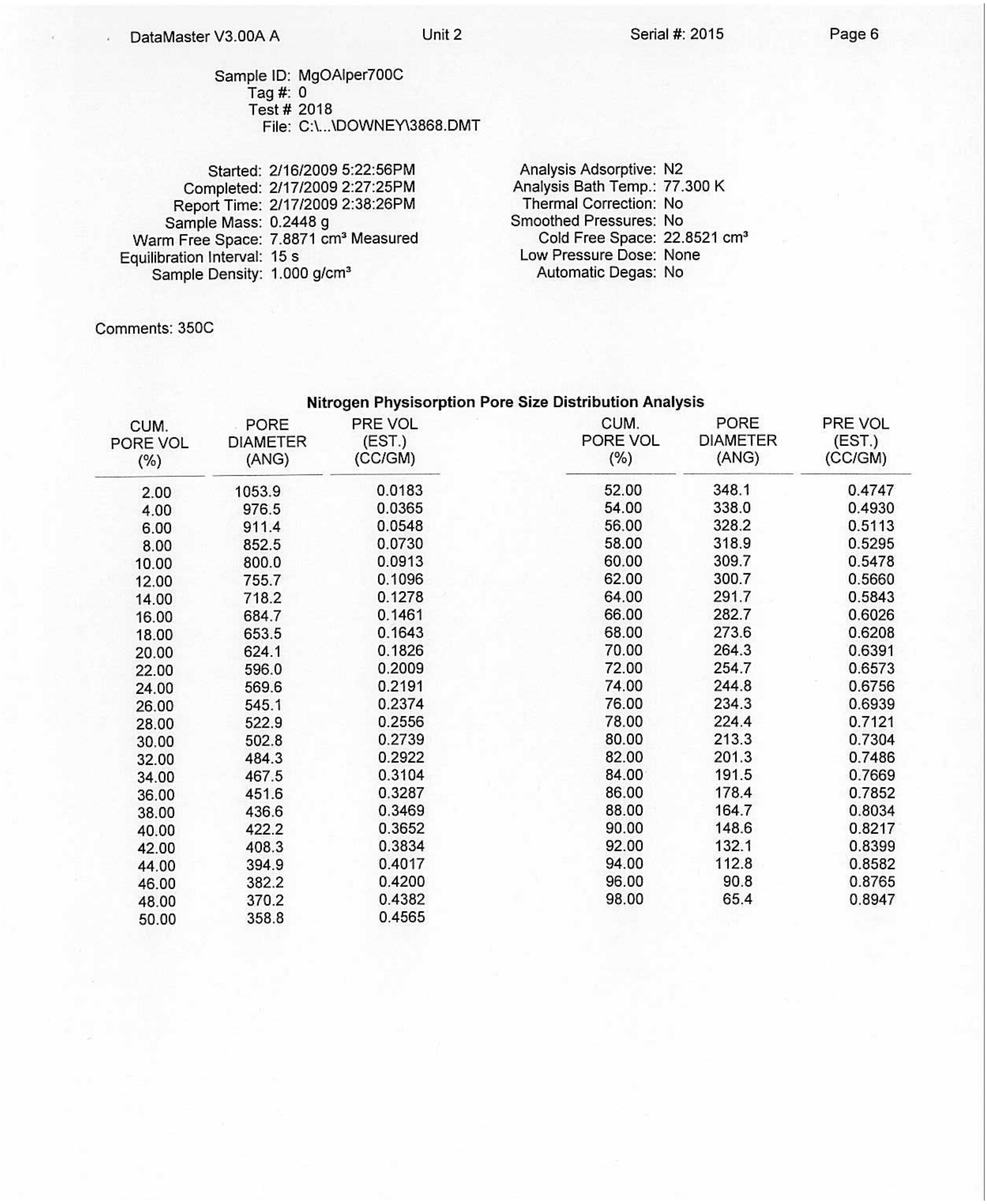

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Sample ID: MgOAlper700C
Tag #: 0
Test # 2018
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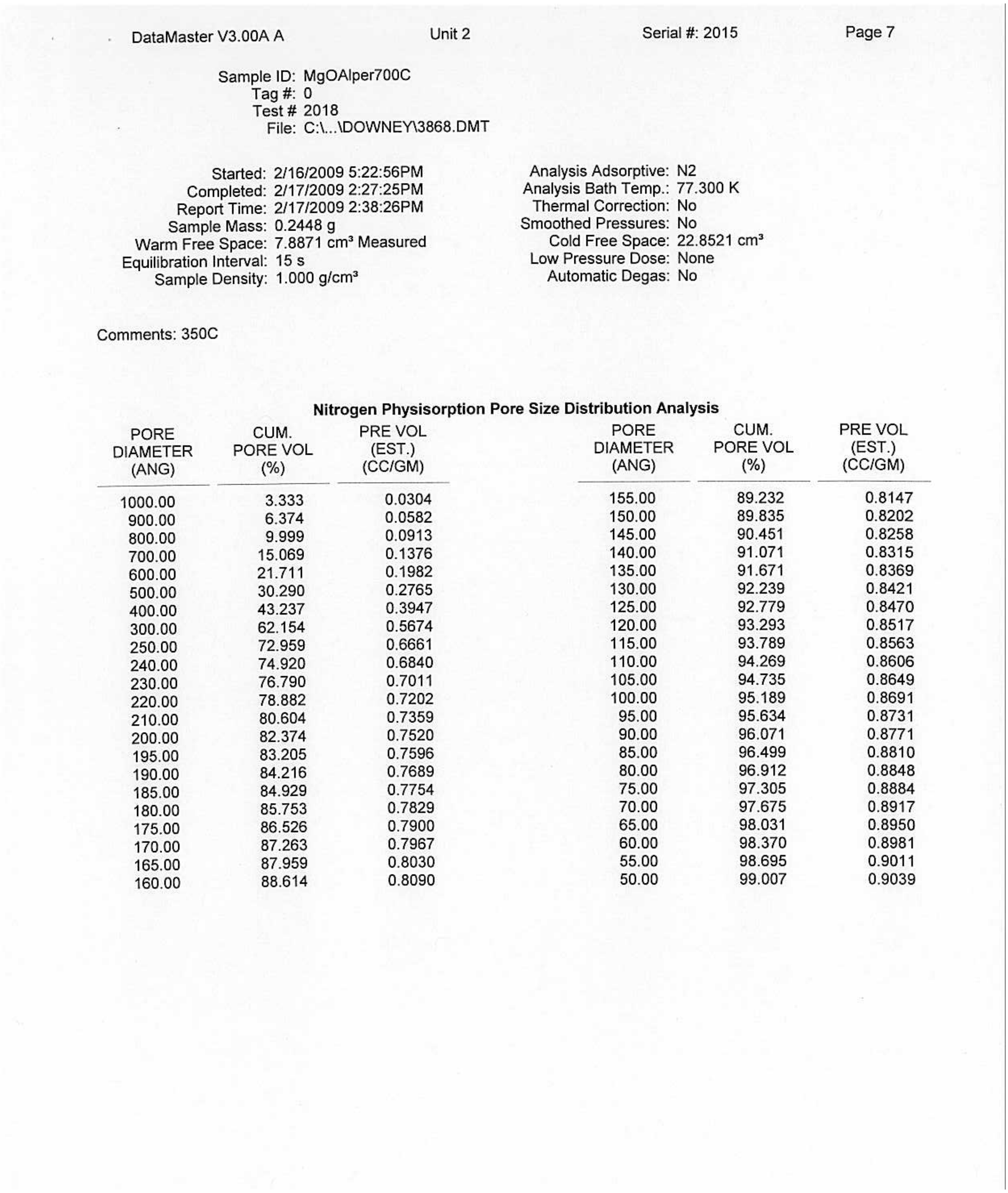
Report Time: 2/17/2009 2:38:26PM
Sample Mass: 0.2448 g
Warm Free Space: 7.8871 cm³ Measured
Equilibration Interval: 15 s
Sample Density: 1.000 g/cm³

Analysis Adsorptive: N2
Analysis Bath Temp.: 77.300 K
Thermal Correction: No
Smoothed Pressures: No
Cold Free Space: 22.8521 cm³
Low Pressure Dose: None
Automatic Degas: No

Comments: 350C

Nitrogen Physisorption Pore Size Distribution Analysis

CUM. PORE VOL (%)	PORE DIAMETER (ANG)	PRE VOL (EST.) (CC/GM)
2.00	1053.9	0.0183
4.00	976.5	0.0365
6.00	911.4	0.0548
8.00	852.5	0.0730
10.00	800.0	0.0913
12.00	755.7	0.1096
14.00	718.2	0.1278
16.00	684.7	0.1461
18.00	653.5	0.1643
20.00	624.1	0.1826
22.00	596.0	0.2009
24.00	569.6	0.2191
26.00	545.1	0.2374
28.00	522.9	0.2556
30.00	502.8	0.2739
32.00	484.3	0.2922
34.00	467.5	0.3104
36.00	451.6	0.3287
38.00	436.6	0.3469
40.00	422.2	0.3652
42.00	408.3	0.3834
44.00	394.9	0.4017
46.00	382.2	0.4200
48.00	370.2	0.4382
50.00	358.8	0.4565
52.00	348.1	0.4747
54.00	338.0	0.4930
56.00	328.2	0.5113
58.00	318.9	0.5295
60.00	309.7	0.5478
62.00	300.7	0.5660
64.00	291.7	0.5843
66.00	282.7	0.6026
68.00	273.6	0.6208
70.00	264.3	0.6391
72.00	254.7	0.6573
74.00	244.8	0.6756
76.00	234.3	0.6939
78.00	224.4	0.7121
80.00	213.3	0.7304
82.00	201.3	0.7486
84.00	191.5	0.7669
86.00	178.4	0.7852
88.00	164.7	0.8034
90.00	148.6	0.8217
92.00	132.1	0.8399
94.00	112.8	0.8582
96.00	90.8	0.8765
98.00	65.4	0.8947



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Sample ID: MgOAlper700C
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Test # 2018
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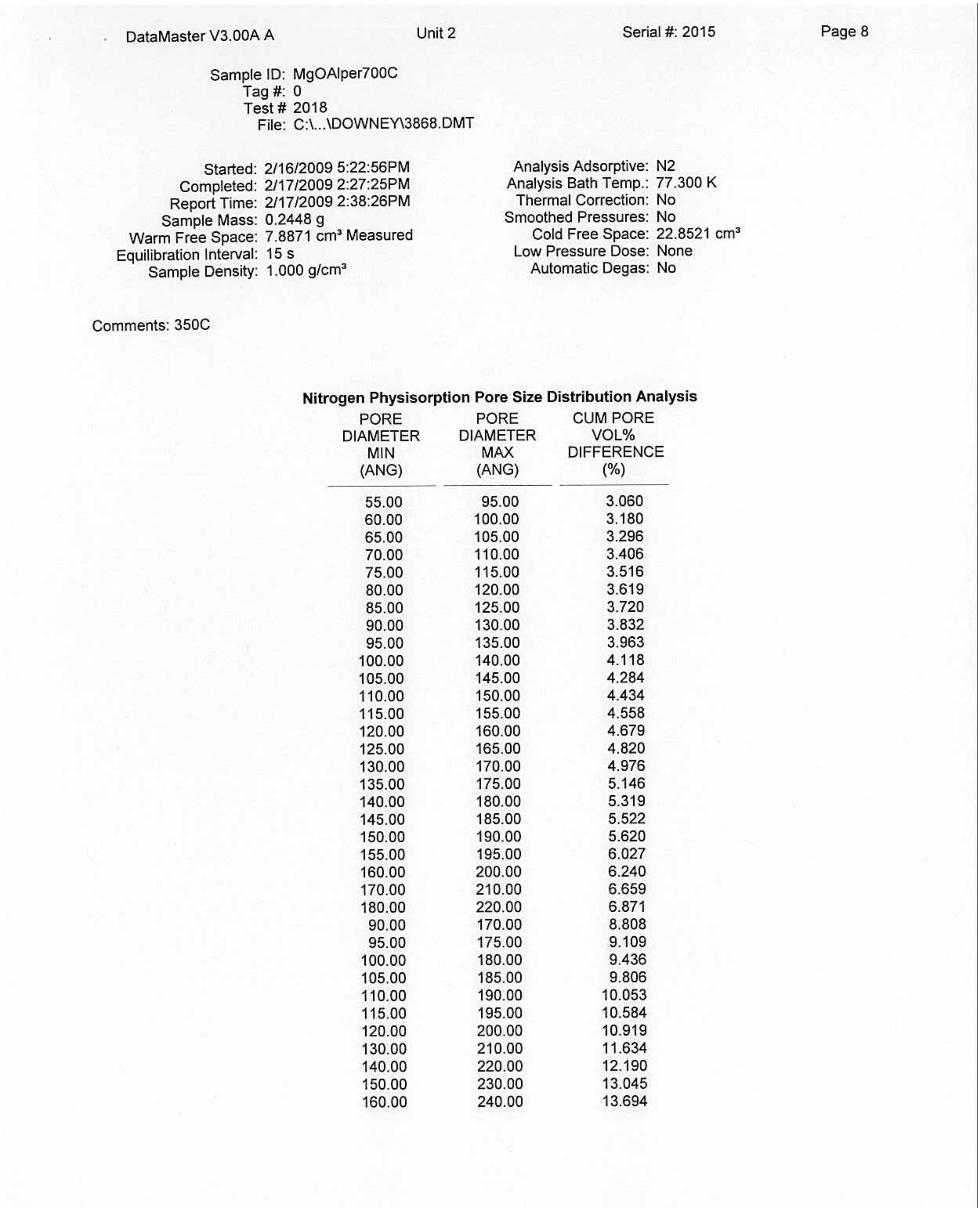
Completed: 2/17/2009 2:27:25PM
Report Time: 2/17/2009 2:38:26PM
Sample Mass: 0.2448 g
Warm Free Space: 7.8871 cm³ Measured
Equilibration Interval: 15 s
Sample Density: 1.000 g/cm³

Analysis Adsorptive: N2
Analysis Bath Temp.: 77.300 K
Thermal Correction: No
Smoothed Pressures: No
Cold Free Space: 22.8521 cm³
Low Pressure Dose: None
Automatic Degas: No

Comments: 350C

Nitrogen Physisorption Pore Size Distribution Analysis

PORE DIAMETER (ANG)	CUM. PORE VOL (%)	PRE VOL (EST.) (CC/GM)
1000.00	3.333	0.0304
900.00	6.374	0.0582
800.00	9.999	0.0913
700.00	15.069	0.1376
600.00	21.711	0.1982
500.00	30.290	0.2765
400.00	43.237	0.3947
300.00	62.154	0.5674
250.00	72.959	0.6661
240.00	74.920	0.6840
230.00	76.790	0.7011
220.00	78.882	0.7202
210.00	80.604	0.7359
200.00	82.374	0.7520
195.00	83.205	0.7596
190.00	84.216	0.7689
185.00	84.929	0.7754
180.00	85.753	0.7829
175.00	86.526	0.7900
170.00	87.263	0.7967
165.00	87.959	0.8030
160.00	88.614	0.8090
155.00	89.232	0.8147
150.00	89.835	0.8202
145.00	90.451	0.8258
140.00	91.071	0.8315
135.00	91.671	0.8369
130.00	92.239	0.8421
125.00	92.779	0.8470
120.00	93.293	0.8517
115.00	93.789	0.8563
110.00	94.269	0.8606
105.00	94.735	0.8649
100.00	95.189	0.8691
95.00	95.634	0.8731
90.00	96.071	0.8771
85.00	96.499	0.8810
80.00	96.912	0.8848
75.00	97.305	0.8884
70.00	97.675	0.8917
65.00	98.031	0.8950
60.00	98.370	0.8981
55.00	98.695	0.9011
50.00	99.007	0.9039



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Sample ID: MgOAlper700C
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Sample Mass:	0.2448 g	Smoothed Pressures:	No
Warm Free Space:	7.8871 cm³ Measured	Cold Free Space:	22.8521 cm³
Equilibration Interval:	15 s	Low Pressure Dose:	None
Sample Density:	1.000 g/cm³	Automatic Degas:	No

Comments: 350C

Nitrogen Physisorption Pore Size Distribution Analysis

PORE DIAMETER MIN (ANG)	PORE DIAMETER MAX (ANG)	CUM PORE VOL% DIFFERENCE (%)
55.00	95.00	3.060
60.00	100.00	3.180
65.00	105.00	3.296
70.00	110.00	3.406
75.00	115.00	3.516
80.00	120.00	3.619
85.00	125.00	3.720
90.00	130.00	3.832
95.00	135.00	3.963
100.00	140.00	4.118
105.00	145.00	4.284
110.00	150.00	4.434
115.00	155.00	4.558
120.00	160.00	4.679
125.00	165.00	4.820
130.00	170.00	4.976
135.00	175.00	5.146
140.00	180.00	5.319
145.00	185.00	5.522
150.00	190.00	5.620
155.00	195.00	6.027
160.00	200.00	6.240
170.00	210.00	6.659
180.00	220.00	6.871
90.00	170.00	8.808
95.00	175.00	9.109
100.00	180.00	9.436
105.00	185.00	9.806
110.00	190.00	10.053
115.00	195.00	10.584
120.00	200.00	10.919
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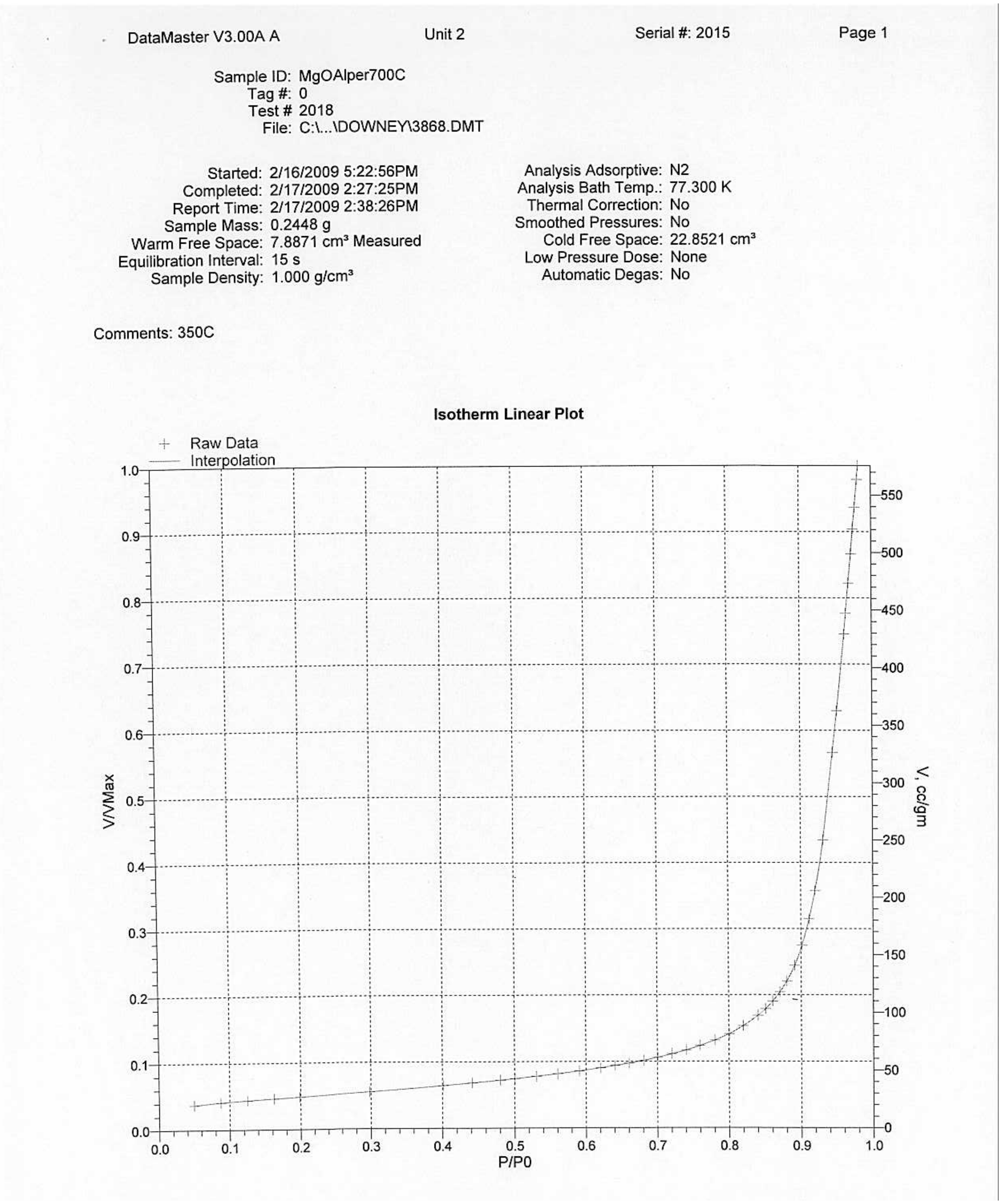
160.00	240.00	13.694



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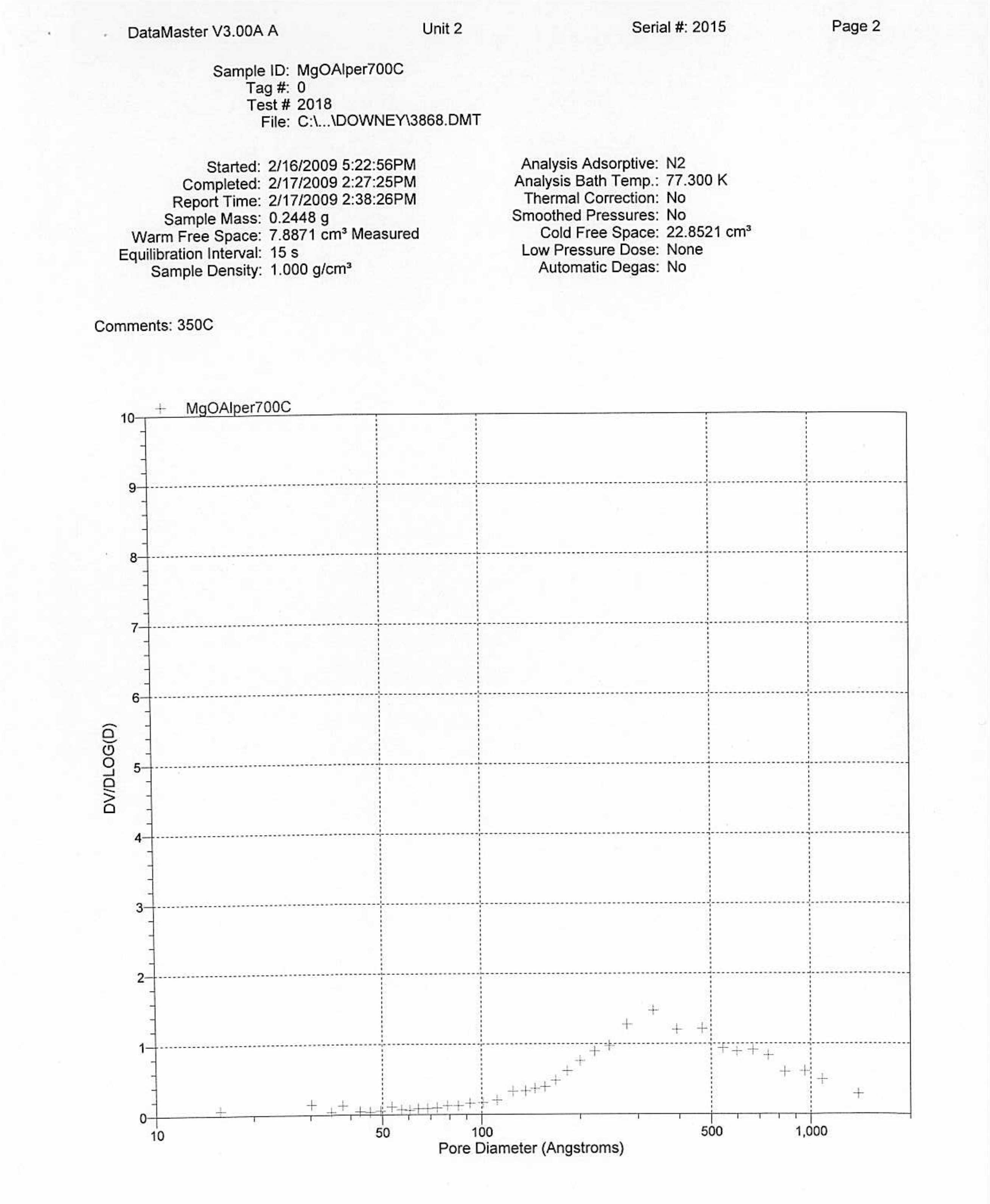
Low Pressure Dose: None
Automatic Degas: No

Comments: 350C

Isotherm Linear Plot

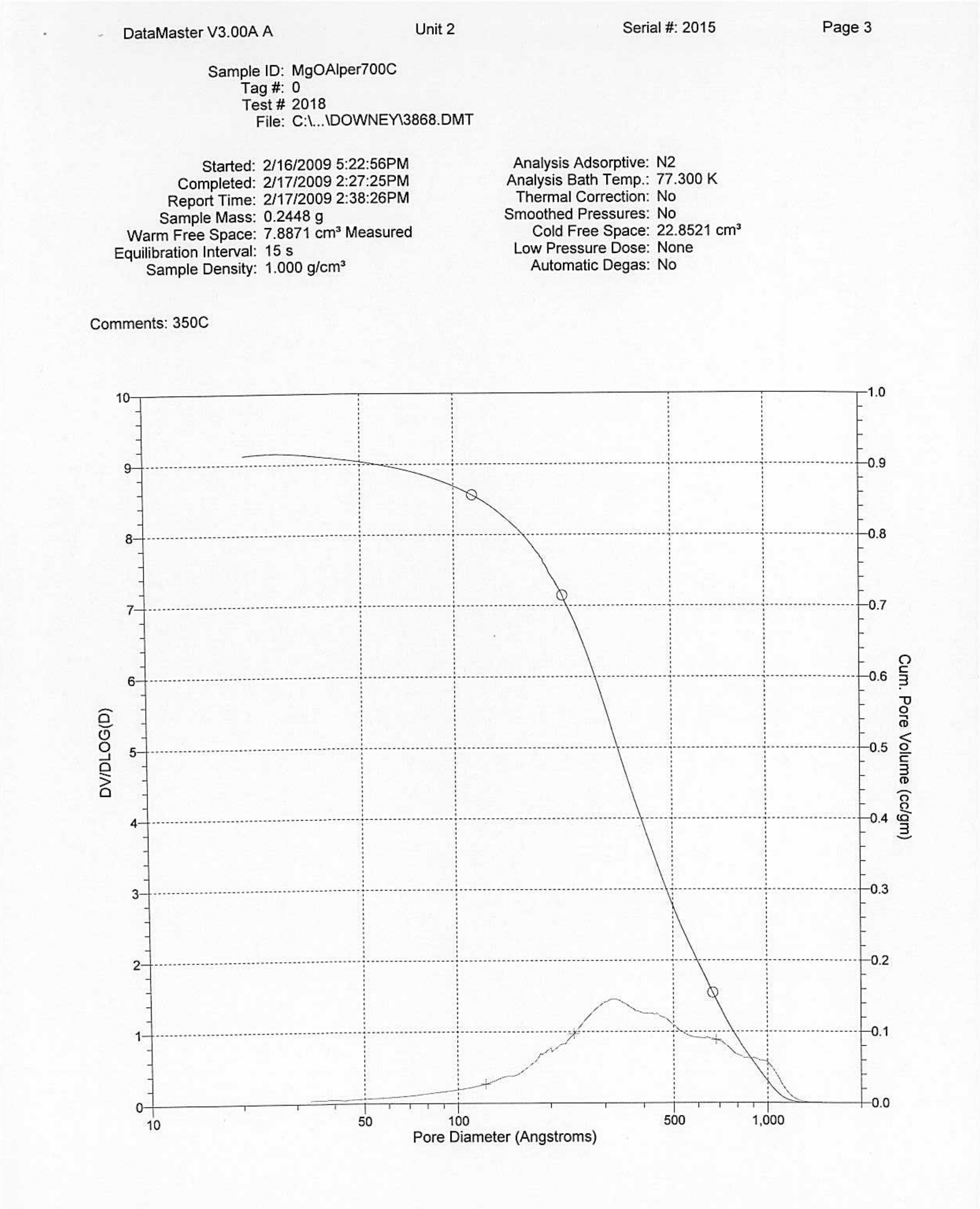


DataMaster V3.00A A   Unit 2   Serial #: 2015   Page 2

Sample ID: MgOAlper700C
Tag #: 0
Test # 2018
File: C:\...\DOWNEY\3868.DMT

Started:	2/16/2009 5:22:56PM	Analysis Adsorptive:	N2
Completed:	2/17/2009 2:27:25PM	Analysis Bath Temp.:	77.300 K
Report Time:	2/17/2009 2:38:26PM	Thermal Correction:	No
Sample Mass:	0.2448 g	Smoothed Pressures:	No
Warm Free Space:	7.8871 cm³ Measured	Cold Free Space:	22.8521 cm³
Equilibration Interval:	15 s	Low Pressure Dose:	None
Sample Density:	1.000 g/cm³	Automatic Degas:	No

Comments: 350C



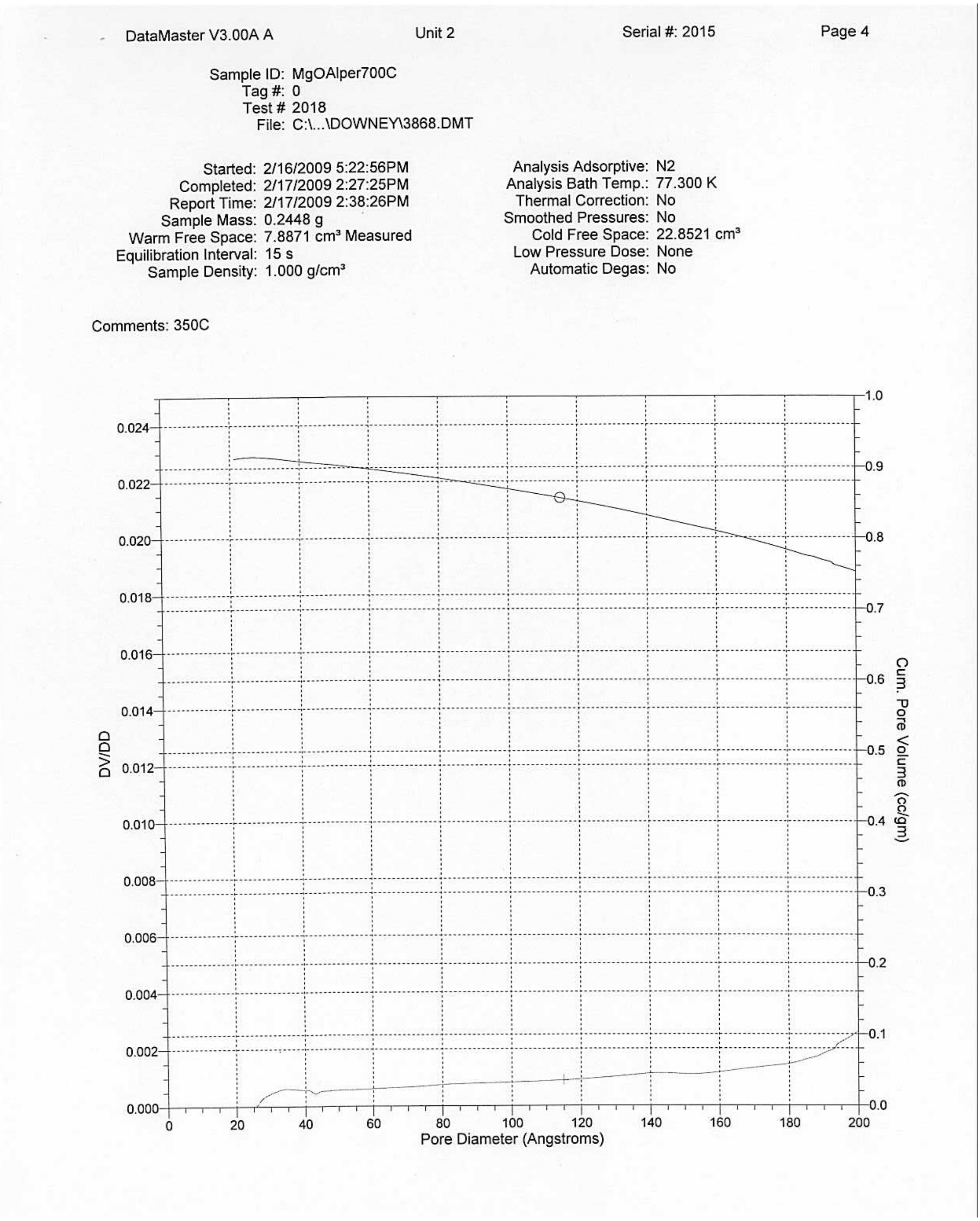
DataMaster V3.00A A Unit 2 Serial #: 2015 Page 3

Sample ID: MgOAlper700C
Tag #: 0
Test # 2018
File: C:\...\DOWNEY\3868.DMT

Started: 2/16/2009 5:22:56PM
Completed: 2/17/2009 2:27:25PM
Report Time: 2/17/2009 2:38:26PM
Sample Mass: 0.2448 g
Warm Free Space: 7.8871 cm³ Measured
Equilibration Interval: 15 s
Sample Density: 1.000 g/cm³

Analysis Adsorptive: N2
Analysis Bath Temp.: 77.300 K
Thermal Correction: No
Smoothed Pressures: No
Cold Free Space: 22.8521 cm³
Low Pressure Dose: None
Automatic Degas: No

Comments: 350C



DataMaster V3.00A A Unit 2 Serial #: 2015 Page 4

Sample ID: MgOAlper700C
Tag #: 0
Test # 2018
File: C:\...\DOWNEY\3868.DMT

Started: 2/16/2009 5:22:56PM
Completed: 2/17/2009 2:27:25PM
Report Time: 2/17/2009 2:38:26PM
Sample Mass: 0.2448 g
Warm Free Space: 7.8871 cm³ Measured
Equilibration Interval: 15 s
Sample Density: 1.000 g/cm³

Analysis Adsorptive: N2
Analysis Bath Temp.: 77.300 K
Thermal Correction: No
Smoothed Pressures: No
Cold Free Space: 22.8521 cm³
Low Pressure Dose: None
Automatic Degas: No

Comments: 350C

References

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