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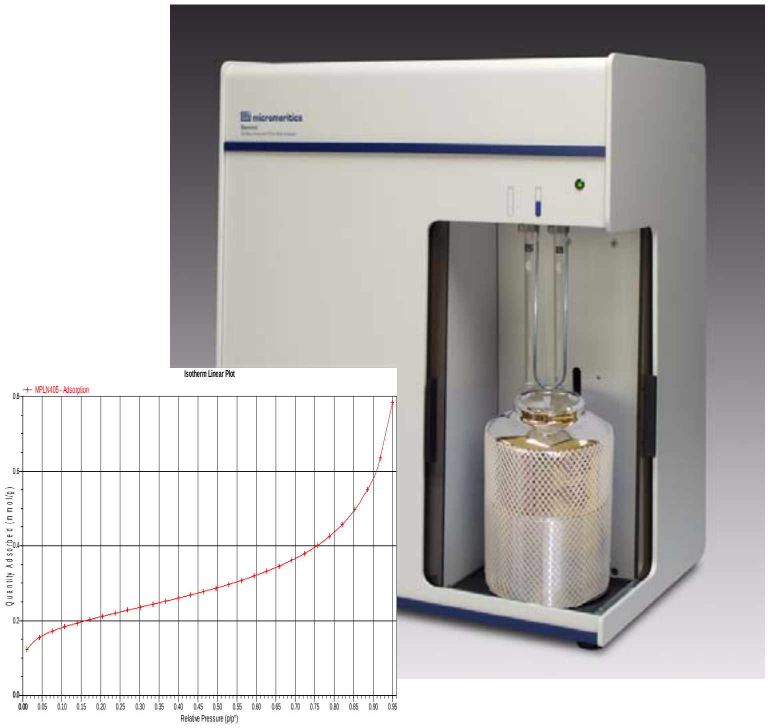
Initial testing and a laboratory manual for the Micromeritics Gemini VI physisorption system

Laboratory Operations Programme

Internal Report IR/08/086



BRITISH GEOLOGICAL SURVEY

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Initial testing and a laboratory manual for the Micromeritics Gemini VI physisorption system

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Micromeritics Gemini VI physisorption system

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Foreword

This report is the published product of a study by the British Geological Survey (BGS) and was produced under the Laboratory Operations Programme’s Maintenance and Development of Capability (MaDCap) project.

This report aims to provide a procedural manual for the newly acquired physisorption system and details of initial testing on a range of Earth Science materials including soils, mudstones and starting materials from hydrothermal experiments.

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Summary

This report describes initial testing of the newly acquired Micromeritics Gemini VI physisorption system as part of the Laboratory Operations Programme's Maintenance and Development of Capability (MaDCap) project.

The report firstly introduces the technique of surface area analysis and BGS's capabilities and then proceeds to present a user manual and suggested working methodologies for the new system.

The report also presents data produced from a range of sample types including soils, mudstones and experimental starting materials to demonstrate the capabilities of the system to various BGS project leaders. Reliable data were generated in all cases, although very low surface areas close to the system's lowest detection limit (c.0.05 m^2/g) appear to be slightly less reliable.

Multi-point BET analyses provide more accurate but slightly larger surface areas than those derived from single-point measurements for the same sample.

On the basis of the samples tested here, sample heterogeneity would not appear to be a significant problem for 'routine' samples. However, analysis of ground material from the same samples revealed a wider spread of results. Sample heterogeneity may also be a greater problem when analysing very low surface area materials.

For surface areas in the range 0.1-60 m^2/g, errors appear to be better than ±2% (of the value) which concurs with data for the supplied carbon black Surface Area Reference Material. For lower surface areas (<0.1 m^2/g) these errors can increase to ±6%.

Analysis of soils suggests that the technique may be useful in characterising black carbon contents. Interestingly, the surface area for the ground materials appears lower than that produced for the corresponding <2 mm size fraction. This is the reverse of the expected result and requires further investigation.

For mudstone samples, surface areas appear to correspond to the total concentration of clay minerals present with some influence from the presence of smectite. Surprisingly, the lowest surface area in this suite of mudstone samples was produced by the Bentonite (?Sweden) sample. This may relate to the degassing regime employed.

Users are advised to follow the protocols outlined in this report and the analysis programs setup. It is also advised that filler rods are used to reduce free-space and error for low surface area materials (<50 m^2/g).

Further work, beyond the scope of this initial study, is required to identify the effects of different degassing routines and the differing surface areas obtained when analysing ground and crushed samples. Additional work is also necessary to more fully explore the pore size distribution functions of the physisorption system.

1 Introduction

Surface area and porosity are two critical physical properties that determine the nature and reactivity of materials. In the Earth Sciences, surface area and porosity are important parameters when considering the characteristics of rocks and soils particularly with regard to their engineering properties, industrial mineral use, water/hydrocarbon potential, gas storage and possible effects on soil quality and human health.

Two different procedures are employed to determine surface area in Earth Science materials which utilize the adsorption of either gases or polar liquids.

The most common method is to derive the amount of adsorbed nitrogen (or other inert gas) on a solid surface at monolayer coverage from either a single-point analysis or a multipoint plot of adsorption isotherm data using the nitrogen/BET method, named after its inventors Brunauer, Emmett and Teller (Brunauer *et al.*, 1938). From a knowledge of the projected cross-sectional area per molecule in the monolayer and the quantity of gas adsorbed, the surface area of the material may be calculated. The method is described by the equation:

$$\frac{(P/Pø)}{V[1-P/Pø]} = \frac{1}{(VmC)} + \frac{\left[\frac{(C-1)}{(VmC)}\right]}{P/Pø}$$

where ***V*** is the volume (at standard temperature and pressure, STP) of gas adsorbed at pressure ***P***, $\boldsymbol{P_ø}$ is the saturation pressure, which is the vapour pressure of liquefied gas at the adsorbing temperature, $\boldsymbol{V_m}$ is the volume of gas (STP) required to form an adsorbed monomolecular layer, and ***C*** is a constant related to the energy of adsorption.

The surface area ***S*** of the sample giving the monolayer adsorbed gas volume ***Vm*** (STP) is then calculated from:

$$S = \frac{VmAN}{M}$$

where ***A*** is Avogadro's number, which expresses the number of gas molecules in a mole of gas at standard conditions, ***M*** is the molar volume of the gas, and ***N*** is the area of each adsorbed gas molecule.

By extending the process of gas adsorption so that gas is allowed to condense in material pore spaces, the fine pore structure of a material may be evaluated. As pressure is increased, the gas condenses in pores of increasing dimensions until saturation is reached when all pores are filled with liquid. Incremental reduction in the pressure of the adsorbed gas then evaporates the condensed gas. By comparison of the adsorption and desorption isotherms and the hysteresis between them using a range of different models (e.g. BJH method; Barrett, Joyner and Halenda, 1951) reveals information about the material's pore size distribution, pore volume, pore area and pore shape.

However, since inert gases do not penetrate between layers of expanding clay minerals in general, only the external surface area is determined using the BET method. To measure the total (internal and external) surface area of clay-bearing samples, a different technique is employed requiring the adsorption of polar molecules such as, for example, 2-ethoxyethanol (ethylene glycol monoethyl ether, EGME, Carter *et al.*, 1965).

The BGS laboratories are equipped to carry out both the gas and polar molecule adsorption methodologies but the capability to perform gas adsorption analyses has been restricted by a relatively old system. This report presents the results of a small study carried out during 2008 under the Maintenance and Development of Capability (MaDCap) project which aimed to:

- familiarise BGS staff with a newly-purchased physisorption system
- produce a user manual
- advertise the abilities of the new system to BGS project leaders
- establish some degree of error for the technique
- study the possible effects of sample heterogeneity

2 Background

The BGS have provided nitrogen/BET surface area analyses since the mid-1980s when a Micromeritics Flowsorb II 2300 system was purchased by the Mineralogy & Petrology Group and installed at the Grays Inn Road office, London. The system was subsequently moved to the Keyworth site and ultimately located in P Block.

During this time the system has been sporadically but often intensively used to provide single-point BET surface area data to a variety of projects such as:

- Industrial mineral characterisation and beneficiation projects
- Characterisation of lithologies for radioactive waste research
- Characterisation of materials before and after hydrothermal laboratory experiments relating to radioactive waste and CO_2 capture and storage
- Characterisation of soils
- Direct consultancy service to industry and consultancies

Despite remaining functional, the Flowsorb II 2300 increasingly suffered from its inability to offer anything other than single-point analyses. In addition, its lack of computer control and manual operation resulted in relatively slow analyses and high unit costs. Also, despite regular servicing, it appeared that most recently, the results obtained for low surface area materials had became inconsistent and therefore suspect.

A capital bid was therefore successfully submitted for a replacement system in the 2007/08 Capital Bid Round, and a Micromeritics Gemini VI 2385C instrument was installed in March 2008. This system offered:

- Both single- and the more reliable, multi-point BET analyses
- Total pore volume determinations
- Pore volume distribution determinations
- Full computer control to enable data collection, presentation and interpretation of generated data
- A dedicated vacuum preparation system

2.1 GEMINI VI 2385C SYSTEM

The Gemini series of surface area analyzers use the Static Volumetric Technique and a twin-tube design to generate high-speed surface area and porosity data (Figure 1).

Figure 1. Micromeritics Gemini VI series physisorption system (Micromeritics, 2008)

The Gemini uses an adaptive rate, static volumetric technique of operation which adapts the required rate at which gas is supplied for equilibration. As shown in Figure 2, the instrument has two gas reservoirs (A) which are filled with equal volumes of the desired adsorptive, usually nitrogen. Gas is dosed into the sample from the reservoirs, and balance tubes and a transducer (B) on the sample side monitors the target pressure.

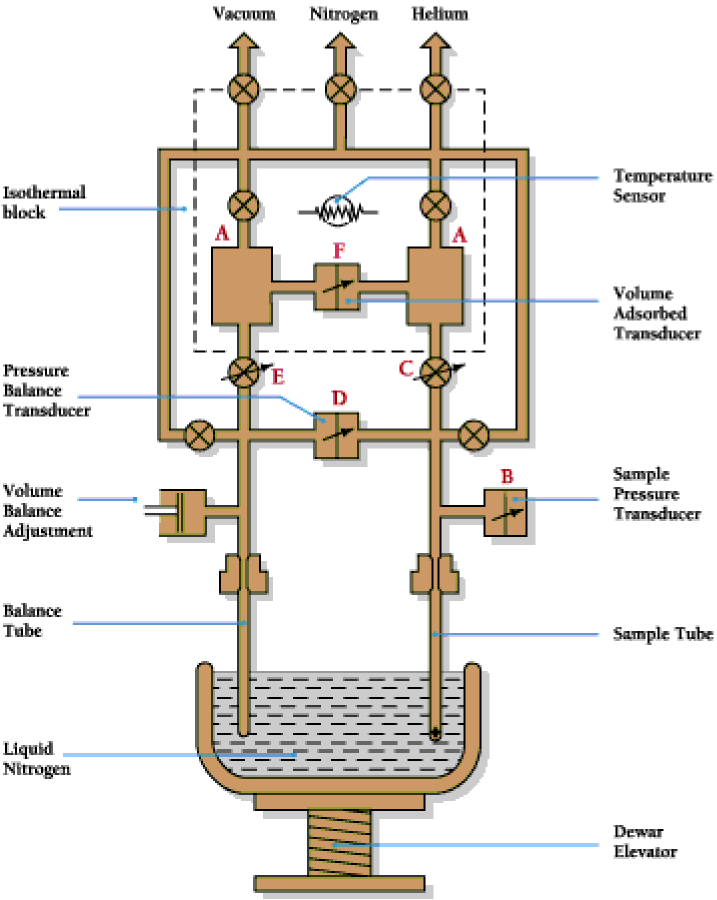


Figure 2. Schematic for the Gemini VI (Micromeritics, 2008)

As the sample adsorbs gas, the pressure would tend to decrease in the sample tube were it not that transducer (B) causes a fast response servo valve (C) to hold the pressure constant. Transducer (D) located between the sample and balance tubes detects any pressure difference between the two tubes and causes another servo valve (E) to balance the pressures in both tubes. A third pressure transducer (F) monitors the pressure between the two reservoirs to determine the amount of gas that is adsorbed on the sample. This method of dosing and accounting for the volume of gas uptake enables the Gemini to produce highly accurate, highly reproducible results in the minimum time.

The sample and balance tubes are identical in every way. Conditions within one tube exactly reproduce the conditions within the other, the only difference being associated with the presence of the sample in the sample tube. Free-space errors introduced by thermal gradient variations are cancelled because the balance tube essentially has the same free space variation as the sample tube and no pressure differential is produced. Since free-space error is the limiting factor in measuring low surfaces with nitrogen, common mode rejection of free-space variation in the Gemini allows accurate measurements to be performed with nitrogen on low surface area materials. Other static volumetric techniques would usually require the use of krypton.

The sample uptake rate therefore controls the rate at which the gas is delivered through a servo valve, therefore the adsorptive is delivered as fast as the sample can adsorb it. In this manner of dosing, there is no under-dosing in which the sample waits for more adsorptive, nor over-dosing in which case the target pressure is exceeded. The result is a surface area analyzer that is as fast as the physics of adsorption allows and yet retains accuracy and reproducibility.

The Windows-based software allows the Gemini to be controlled from a PC, thus providing more versatility in data archiving, networking, and printer options. In addition, the software extends the choices of data reduction methods in each Gemini model to include:

- Single- and Multipoint BET surface area
- Langmuir surface area
- Pore volume and pore area distributions in the mesopore and macropore ranges by the BJH (Barrett, Joyner, and Halenda) method using a variety of thickness equations including a user-defined, standard isotherm
- Pore volume (distribution and total pore volume) in a user-defined pore size range
- Micropore distribution by the MP-method and total micropore volume by the t-Plot and as Plot methods
- Halsey, Harkins-Jura, Carbon Black STSA, Broekhoff-de Boer and user-entered thickness curves

The larger cabinet design of the Gemini VI 2385C model allows extended analysis time, greater stability and improved repeatability due to its longer sample tubes and a larger dewar. It also allows continuous monitoring of the saturation vapour pressure ($P\o$) of the adsorptive using a dedicated $P\o$ tube and transducer. This feature allows the instrument software to accommodate, at each data point, any minute change in the saturation vapour pressure that may occur during the course of the analysis, resulting in a more meticulously determined relative pressure.

2.2 VACPREP DEGASSER

The VacPrep Degasser prepares samples for surface area and pore structure analysis using both the flowing gas method and a vacuum mode which prepares samples by heating and evacuation. The VacPrep removes contaminants such as water vapour and adsorbed gases from samples to avoid interference with surface area measurements. It features six degassing stations and a choice of vacuum or gas flow preparation on each of the six stations and minimises the chance of sample contamination during transfer from the degas-to-analysis. The VacPrep allows the operator to select the temperature and preparation technique best suited to the sample type and application.

Figure 3. Micromeritics VacPrep system (Micromeritics, 2008)

3 Methods and materials

Samples for analysis were submitted by BGS colleagues; Drs. Barry Rawlins (Soils Team), Chris Rochelle (Energy Theme) and Jon Harrington (Radwaste Team). Sample details are shown in Table 1.

Table 1. Sample details

MPL no	Incoming sample name	Sample type	Submitted by
MPLN405	610155 <2 mm	Black carbon-bearing soil samples. Crushed and ground subsamples.	Barry Rawlins
MPLN406	611353 <2 mm		
MPLN407	611495 <2 mm		
MPLN408	610155 ground		
MPLN409	611353 ground		
MPLN410	611495 ground		
MPLB464	Quartz 125-250 µm	Starting materials for hydrothermal laboratory experiments	Chris Rochelle
MPLB465	Albite 125-250 µm		
MPLG922	Chemgrade quartz (Fluka) 150 -400 µm		
MPLL081	Casablanca cap rock 250-500 µm		
MPLL082	Casablanca reservoir rock 250-500 µm		
MPLN411	Bentonite (?Sweden)	Mudstone core samples associated with containment projects	Jon Harrington
MPLN412	Lias Clay Liner		
MPLN413	Nordland Shale 15/9-A-11 (NS-S2) 907.4-907.49 Tin 5		
MPLN414	Ball Clay		
MPLN415	German Blue Clay		
MPLN416	Callovo-Oxfordian Paris Basin EST 27350 (ANDRA)		
MPLN417	Opalinus Clay off-cut OPA-2 Bewken Borehole		
MPLN418	London Clay (Landfill Liner) off-cuts Tin X19 13/5/97		
MPLN419	Boom Clay offcuts T4S2		
MPLN420	Opalinus Clay Mont Terri		
MPLN421	Gault Clay		

The samples from Drs. Barry Rawlins and Chris Rochelle (ground or granular materials) were analysed as received but the core samples received from Dr. Jon Harrington were first dried at 55˚C overnight and then stage crushed to produce a 1-2 mm fraction for analysis.

As well as learning how to use the instrument for Earth Science samples, the range of sample types submitted allowed the project to explore several lines of investigation:

- To establish analytical reproducibility, the same subsample from one of the mudstone samples was analysed three times.

- The soil samples were analysed both as <2 mm size fractions and ground powders to establish whether sample particle-size had any noticeable effect on surface area. Similarly the bentonite sample was analysed as a 1-2 mm fraction and a <125 µm powder.
- To establish whether sample heterogeneity produced any substantial errors, separate sub-samples were run for one of the soils (both <2 mm and ground materials) and one of the quartz samples.

All samples were prepared using a Micromeritics Gemini VacPrep Degasser and analyses were carried out on the Micromeritics Gemini VI 2385C system. All the samples were run on a 5 pressure point program to determine BET surface area. One sample, was also run on an extended 30-pressure point program to additionally determine pore volume distribution.

4 Results

A methodology for analysis of Earth Science materials was devised and implemented for all the samples in this study and is shown in Appendix 1. A sample preparation sheet with example data is shown in Appendix 2.

Correlation co-efficients for BET analyses provide an indication of the quality and reliability of the data produced. The majority of the samples analysed here produced co-efficients of better than 0.999 suggesting high quality analyses. However, the two quartz samples (MPLB464 and MPLG922) characterised by very low surface areas (c.0.07 m^2/g) produced lower coefficients of 0.99 suggesting poorer quality analyses.

Reporting of results from the Gemini software can be tailored to the needs of the particular analysis. Example output for a typical multi-point BET analysis is shown in Appendix 3 and that from a full adsorption isotherm and pore volume distribution in Appendix 4.

4.1 SOIL SAMPLES

The results of surface area analyses on the soils samples submitted by Dr Barry Rawlins are summarised in Table 2.

Table 2. Summary of results for soil samples

Incoming sample name	BET surface area (m2/g)									
	Run 1		Run 2		Run 3		Mean		Std Dev	
	value	+/- error	value	+/- error	value	+/- error	value	+/- error	value	+/- error
610155 <2 mm	16.2691	0.28	16.5814	0.27	16.1768	0.25	16.3424	0.2667	0.2120	0.0153
611353 <2 mm	5.8671	0.08					5.8671	0.0800		
611495 <2 mm	6.7906	0.08					6.7906	0.0800		
610155 ground	10.0930	0.06	13.8094	0.16	13.5109	0.15	12.4711	0.1233	2.0649	0.0551
611353 ground	5.5448	0.01					5.5448	0.0050		
611495 ground	6.0386	0.03					6.0386	0.0300		

Mean surface areas for the soil samples range from c.5.86-16.34 m^2/g (<2 mm fraction) and c.5.54-12.47 m^2/g (ground material). Soil 610155 shows the greatest surface area for both sample types and soil 611495 shows the lowest surface areas. Interestingly, in each case the surface area for the ground material is lower than that produced for the corresponding <2 mm size fraction. This is the reverse of the expected result whereby a greater surface area would be expected to be exposed by grinding material to a powder.

Sample heterogeneity would not appear to be a significant problem for the <2 mm material as the standard deviation value represents only a 1.3% differential, but as a result of the low surface area measured in Run 1 for the ground material, there appears to be a greater problem with these samples (16.6% differential). This is again the reverse of the expected result whereby it would be expected that a more homogeneous sample would be created by grinding to a powder.

The high surface area sample (610155) corresponds to the sample containing the highest levels of black carbon (6.44%, B. Rawlins pers. comm.) but the impact of black carbon is more difficult to discern in the remaining samples (611353, 2.09% and 611495, 0.5%). At these lower levels, the presence of small quantities of black carbon appear to be obscured by the presence of other phases such as clay minerals. Further samples will be run to explore the link between surface area and black carbon content in soils.

4.2 HYDROTHERMAL LABORATORY EXPERIMENTAL MATERIALS

The results of surface area analyses on the hydrothermal laboratory experimental samples submitted by Dr Chris Rochelle are summarised in Table 3.

Table 3. Summary of results for the hydrothermal laboratory experimental samples

Incoming sample name	BET SA (m^2/g)									
	Run 1		Run 2		Run 3		Mean		Std Dev	
	value	+/- error	value	+/- error	value	+/- error	value	+/- error	value	+/- error
Quartz 125-250 µm	0.0710	0.0022					0.0710	0.0022		
Albite 125-250 µm	0.6386	0.0112					0.6386	0.0112		
Chemgrade quartz (Fluka) 150-400 µm	0.0427	0.0042	0.0928	0.0028	0.0704	0.0050	0.0686	0.0040	0.0251	0.0011
Chemgrade quartz (Fluka) 150-400 µm (Using filler tubes)	0.0603	0.0041	0.0493	0.0033	0.0527	0.0031	0.0541	0.0035	0.0056	0.0005
Casablanca cap rock 250-500 µm	2.1448	0.0234					2.1448	0.0234		
Casablanca reservoir rock 250-500 µm	0.8437	0.0080					0.8437	0.0080		

In comparison to the soil samples, the hydrothermal laboratory experimental samples produced low or very low surface areas ranging from 0.07-2.14 m^2/g.

The two quartz samples produced particularly low surface areas (c.0.07 m^2/g) and correlation co-efficients of only 0.99 suggesting relatively poor-quality data compared to the remaining dataset. Such surface areas would appear to be close to the lower limit of accurate surface area detection using the Gemini VI.

The albite and Casablanca reservoir rock show also show low surface areas (c.0.64 and 0.84 m^2/g respectively) but these are an order of magnitude higher than the quartz samples. Previous X-ray diffraction (XRD) analyses of the Casablanca reservoir rock (Rochelle *et al.*, 2007) suggest that it is predominantly composed of calcite (95.9%) with traces of dolomite (3%) and quartz (1.1%). Such a mineralogy would be expected to produce a low surface area.

The Casablanca cap rock produced the highest surface area for the hydrothermal laboratory experimental samples, although at 2.14 m^2/g, this would still be described as a low value. The higher value compared to the reservoir rock is almost certainly due to the presence of phyllosilicates and clay minerals in the cap rock. Previous XRD analyses (Rochelle *et al.*, 2007) confirm that although the cap rock is also carbonate-dominated (calcite 55.9%, dolomite 5.8%, ankerite 1.6%) with minor quartz (14.3%), pyrite (3.8%) and albite (0.8%), it also contains undifferentiated mica including illite/smectite (15.4%) and chlorite (2.4%) species.

Three repeat runs for separate sub samples of the very low surface area Chemgrade quartz sample produced a mean surface area of 0.069 m^2/g and standard deviation of 0.025. This relatively large standard deviation value represents a large 36.6% differential and may result from the free space errors or indicate that sample heterogeneity presents a significant problem in low surface area materials.

In order to improve the quality of analysis of low surface area materials, Micromeritics suggest (but did not originally supply BGS) the use of filler tubes. Solid glass filler tubes, with a fine capillary down their lengths, are fitted to both the reference and sample tubes to exclude as much free space as possible and therefore ensure optimum precision and accuracy. Having obtained the filler tubes at a later date, only limited testing was carried out using the filler tubes. Three separate subsamples from the Chemgrade quartz sample were re-analysed and results show similar correlation coefficients of c.0.99, a mean surface area of 0.054 m^2/g but a smaller standard deviation of 0.005 suggesting more precise data.

Comparison of the multi-point surface area data produced by the Gemini with previously obtained values from single-point analyses performed on the Flowsorb II indicate a strongly positive correlation (Table 4 and Figure 4). The albite sample lies farthest from the overall trend. It is noticeable that for all the samples, with the exception of the Quartz 125-250 µm sample, the multi-point data produces a larger surface area than the previous single-point data. This concurs with standard data such as that supplied with Surface Area Reference Materials, e.g. carbon black standard multi-point surface area 30.6 ± 0.75 m^2/g, single-point surface area 29.9 ± 0.75 m^2/g).

Table 4. Comparison of multi-point and single-point BET data hydrothermal laboratory experimental samples

	BET SA (m2/g)	
	Gemini VI multi-point (this investigation)	**Flowsorb II single-point (previous investigations)**
Quartz 125-250 µm	0.0710	0.0824
Albite 125-250 µm	0.6386	0.1674
Chemgrade quartz (Fluka) 150-400 µm	0.0686	0.06
Casablanca cap rock 250-500 µm	2.1448	1.93
Casablanca reservoir rock 250-500 µm	0.8437	0.57

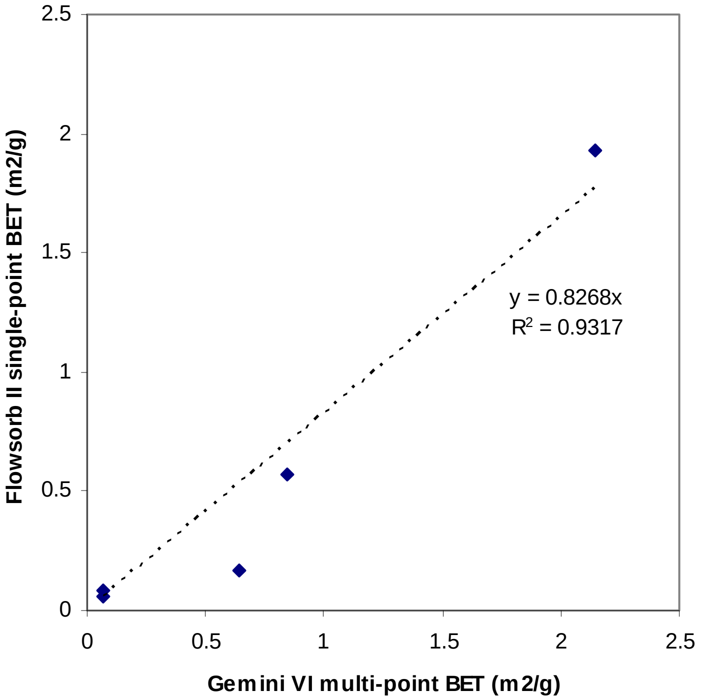


Figure 4. Cross-plot of multi-point and single-point BET data for the hydrothermal laboratory experimental samples

4.3 MUDSTONE CORE SAMPLES

The results of surface area analyses on the mudstone core samples submitted by Dr Jon Harrington are summarised in Table 5.

Table 5. Summary of results for the mudstone samples associated with containment projects (all are 1-2 mm fractions except where indicated)

Incoming sample name	BET SA (m2/g)									
	Run 1		Run 2		Run 3		Mean		Std Dev	
	value	+/- error	value	+/- error	value	+/- error	value	+/- error	value	+/- error
Bentonite	20.4925	0.3027					20.4925	0.3027		
Bentonite <125 µm	17.6855	0.0813					17.6855	0.0813		
Lias Clay Liner	24.0139	0.2240					24.0139	0.2240		
Nordland Shale	26.7313	0.1566					26.7313	0.1566		
Ball Clay	34.2023	0.0895					34.2023	0.0895		
German Blue Clay	53.8411	0.4279					53.8411	0.4279		
Callovo-Oxfordian	28.1373	0.4982	28.054	0.4882	27.8875	0.4823	28.0264	0.4896	0.1272	0.0080
Opalinus Clay	21.7706	0.1184					21.7706	0.1184		
London Clay	58.5419	0.7338					58.5419	0.7338		
Boom Clay	26.9840	0.1212					26.9840	0.1212		
Opalinus Clay	30.9592	0.2548					30.9592	0.2548		
Gault Clay	54.0795	1.0344					54.0795	1.0344		

The surface areas obtained for the mudstone core samples (1-2 mm fractions) were the highest for the samples analysed in this project and ranged from c.20.49 (Bentonite) to 58.54 m^2/g (London Clay). However, as mineralogical data were not available for the same samples, discussion of the surface area data is limited to general statements.

In general terms, the surface areas appear to correspond to the total concentration of clay minerals present with some influence from the presence of smectite. The higher surface areas therefore appear to correspond to the more clay-rich samples where smectite forms a significant proportion of the clay mineral assemblage and the lower surface areas are produced by samples with lower clay contents where smectite is largely absent.

The London Clay and Gault Clay samples present the highest BET surface areas for the sample batch at c.58.54 and 54.08 m^2/g respectively. Typically the London Clay shows high clay (20-81%, mean 57%; Kemp & Wagner, 2006) and smectite contents (5-30%, mean 17%; Kemp & Wagner, 2006) with moderate 2-ethoxyethanol total surface areas (74 – 260 m^2/g, mean 176 m^2/g; Kemp & Wagner, 2008). Similarly, the Gault Clay is characterised by high clay contents (up to 65%, Forster *et al.*, 1994) and highly-smectitic clay mineral assemblages (Jeans, 2006).

The German Blue Clay (c.53.84 m^2/g) and the Ball Clay (c.34.20 m^2/g) samples also present relatively high BET surface areas. These clays are most likely to be predominantly composed of disordered kaolinite with minor smectite (e.g. Konta, 1963). Typical ball clays contain >70% <2 µm material.

The majority of the mudstone samples (Boom Clay, Opalinus Clay, Callovo-Oxfordian Clay, Nordland Shale, Lias Clay) produce moderate BET surface areas in the range 20-30 m^2/g. Literature sources suggest that these lithologies are typically composed of c.50% clay minerals and usually illite- or illite/smectite-dominated clay mineral assemblages (e.g. Wenk *et al.*, 2008;

Kemp *et al.*, 2001; 2002; 2005). The Boom Clay differs in possessing a smectite-dominated clay mineral assemblage (Decleer *et al.*, 1983).

Surprisingly, the lowest surface area in this suite of samples was produced by the Bentonite (?Sweden) sample at c.20.49 m2/g. However, the BET surface area for standard bentonite (CMS source clay SWy-2) can produce relatively low 22.7m2/g (Umran Dogan *et al.*, 2006). As commercial bentonites are usually composed of high proportions of smectite-group minerals (rarely less than 60% and usually more than 70%), such low BET surface areas are puzzling. A possible cause of the low surface area may be the inadequate degassing of the sample prior to analysis. Further work is necessary to explore the effects of degassing procedures on 'difficult' samples such as bentonites.

Analytical reproducibility was examined by analysing the same Callovo-Oxfordian Clay sub-sample, three times. The three values (28.1373, 28.054 and 27.8875 m^2/g) indicate a mean surface area of 28.0264 m^2/g with a standard deviation of 0.4896. These values produce a coefficient of variance (standard deviation/mean) of 1.75%, suggesting good analytical reproducibility.

5 Conclusions

- The Micromeritics Gemini VI physisorption system has been successfully installed and a BGS user manual has been written and working methodologies implemented.
- A range of sample types have been analysed for various BGS project leaders, with reliable data being generated in all cases. Very low surface areas (<0.1 m^2/g) appear to be slightly less reliable, although these results may be improved by employing filler rods.
- Results indicate the lowest detectable surface area is of the order of c.0.05 m^2/g.
- Multi-point BET provide more accurate surface areas than those derived from single-point measurements. Multi-point surface areas appear to be slightly larger than those derived from single-point values for the same sample.
- On the basis of the samples tested here, sample heterogeneity would not appear to be a significant problem for 'routine' samples. However, analysis of ground material from the same samples revealed a wider spread of results. Sample heterogeneity may also be a greater problem when analysing very low surface area materials, although this may be accounted for by free space errors.
- For surface areas in the range 0.1-60 m^2/g, errors appear to be better than ±2% (of the value) which concurs with data for the supplied carbon black Surface Area Reference Material. For lower surface areas (<0.1 m^2/g) these errors can increase to ±6%. Surface areas are reproducible within the same degree of error.
- Analysis of soils suggests that the technique may be useful in characterising black carbon contents. Interestingly, the surface area for the ground materials appears lower than that produced for the corresponding <2 mm size fraction. This is the reverse of the expected result and requires further investigation.
- For mudstone samples, surface areas appear to correspond to the total concentration of clay minerals present with some influence from the presence of smectite. Surprisingly, the lowest surface area in this suite of mudstone samples was produced by the Bentonite (?Sweden) sample. This may relate to the degassing regime employed.

6 Recommendations

- Users are advised to follow the protocols outlined in this report and the analysis programs setup. This report should be quoted when reporting data produced by the physisorption system.
- For low surface area materials (<50 m^2/g), it is recommended that filler rods are used to reduce free-space and error.
- Further work, beyond the scope of this initial study, is required to identify the effects of different degassing routines and the differing surface areas obtained when analysing ground and crushed samples. Additional work is also necessary to more fully explore the pore size distribution functions of the physisorption system.

References

British Geological Survey holds most of the references listed below, and copies may be obtained via the library service subject to copyright legislation (contact libuser@bgs.ac.uk for details). The library catalogue is available at: http://geolib.bgs.ac.uk.

BARRETT, E.P., JOYNER, L.G. AND HALENDA, P.P. 1951. The determination of pore volume and area distributions in porous substances. I. Computations from nitrogen isotherms, *Journal of the American Chemical Society*, 73, 373–380.

BRUNAUER, S, EMMET, P H AND TELLER, E. 1938. Adsorption of Gases in Multimolecular Layers. *Journal of the American Chemical Society*, 60, 309-319.

CARTER, D.L., HEILMEN, M.D. AND GONZALEZ, F.L. 1965. Ethylene glycol monoethyl ether for determining surface area of silicate minerals. *Soil Science*, 100, 356-360.

DECLEER, J., VIAENE, W. and VANDENBERGHE, N. 1983. relationships between chemical, physical and mineralogical characteristics of the Rupelian Boom Clay, Belgium. *Clay Minerals*, 18, 1-10.

FORSTER, A., HOBBS, P.R.N., CRIPPS, A.C., ENTWISLE, D.C., FENWICK, S.M.M., RAINES, M.R., HALLAM, J.R., JONES, L.D., SELF, S.J. & MEAKIN, J.L. 1994. Engineering geology of British rocks and soils: Gault Clay. *British Geological Survey Technical Report*, WN/94/31. 60pp.

JEANS, C.V. 2006. Clay mineralogy of the Cretaceous strata of the British Isles. *Clay Minerals*, 41, 47-150.

KEMP, S.J. AND WAGNER, D. 2008. The mineralogy, geochemistry and surface area of mudrocks from the London Clay Formation of southern England. *British Geological Survey Internal Report*, IR/06/060. 81pp.

KEMP, S.J., TURNER, G. AND WAGNER, D. 2001. Mineralogical characterisation of the Nordland Shale, UK Quadrant 16, northern North Sea. *British Geological Survey Commissioned Report*, CR/01/136. 52pp.

KEMP, S J, PEARCE, J M and STEADMAN, E J. 2002. Mineralogical, geochemical and petrographical characterisation of Nordland Shale cores from well 15/9-A-11, Sleipner field, northern North Sea. *British Geological Survey Commissioned Report*, CR/02/313. 40pp.

KEMP, S.J., MERRIMAN, R.J. and BOUCH, J.E. 2005. Clay mineral reaction progress - The maturity and burial history of Lias Group of England and Wales. *Clay Minerals*, 40, 43-61.

KONTA, J. 1963. Quantitative mineralogical analysis of 'Blue clay' from Vonsov, Bohemia" a comparative study by nine laboratories. *Clay Minerals Bulletin*, 30(5), 255-264.

MICROMERITICS. 2008. Gemini VI Windows – Operator’s manual v2.00.

ROCHELLE, C.A, TURNER, G., PEARCE, J.M., TAYLOR, H., KEMP, S.J., SHAW, R AND WILLIAMS, C. 2007. Geochemical interactions between CO_2 and host rocks at the Casablanca field: Results of fluid-rock interaction experiments. *British Geological Survey Internal Report*, CR/07/015. 53pp.

DOGAN, A.U., DOGAN, M., ONAL, M., SARIKAYA, Y., ABURUB, A. AND WURSTER, D.E. 2006. Baseline studies of The Clay Minerals Society source clays: SSA by the Brunauer Emmett Teller (BET) Method. *Clays and Clay Minerals*, 54, 62-66.

WENK, H.R., VOLTOLINI, M., MAZUREK, M., VAN LOON, L.R. AND VINSOT, A. 2008. Preferred orientations and anisotropy in shales: Callovo-Oxfordian Shale (France) and Opalinus Clay (Switzerland). *Clay Minerals*, 56, 285-306.

Appendix 1 BGS methodology

OPERATING INSTRUCTIONS
FOR THE
MICROMERITICS
GEMINI VI
SURFACE AREA AND PORE SIZE ANALYZER
(ROOM P029)

1 SAMPLE PREPARATION (DAY BEFORE ANALYSIS)

1.1 Turn on VacPrep 061 on the rear panel.

1.2 Set temperature to desired value to most effectively remove moisture and adsorbed gases without changing the nature of the material (e.g. 300ºC for the carbon black standard; 60ºC for geological samples). The carbon black standard must be run before each batch of samples. *Note that the heating element takes a long time to cool down!*

1.3 Label the sample tubes and enter the sample number and description onto the BET sample sheet (shown in Appendix 3).

1.4 Using a 4 decimal place balance, weigh the sample into a balance boat, c.0.5 g for samples expected to have a high (>50 m^2/g) surface area and c.1.0 g for samples expected to have a low (<50 m^2/g) surface area. Set the sample aside.

1.5 Select a labelled sample tube. Fit the tube into the foam base and insert a rubber 'ear' into the tube. Using a 4 decimal place balance, weigh the tube, foam base and rubber 'ear' and note weight on the BET sample sheet (shown in Appendix 3).

1.6 Remove the tube, foam base and rubber 'ear' assembly from the balance. Remove the rubber 'ear' from the tube and attach the 'tube filler' funnel. Carefully pour the sample from balance boat into the tube.

1.7 Repeat steps 1.3 to 1.6 for up to 6 samples.

1.8 Attach each sample tube to the Vac Prep unit using the stainless steel connectors. First slacken the connector nut, then insert the sample tube securely and re-tighten the nut (finger-tight).

1.9 Turn on rotary pump at the wall socket.

1.10 Ensure all the needle valves at the 'T' pieces above the connectors are closed.

1.11 Turn the 'gas/off/vac' switch to the 'vac' position.

1.12 **Slowly** open each needle valve, ensuring that the sample is not drawn up the sample tube.

1.13 Place the sample tubes in their heating stations (at 60ºC or desired temperature) and leave overnight.

1.14 Repeat steps 1.3 – 1.6 using between 0.5-0.6 g of carbon black standard. Place to one side for the next day.

2 PREPARATION FOR ANALYSIS (ANALYSIS DAY)

2.1 Wearing gloves, eye protection and a lab coat, obtain a dewar of liquid N_2 from the K-block supply using established procedures.

2.2 Switch on the Gemini VI Surface and Pore Size Analyzer at the rear of machine. The green light on the front of the cabinet should glow green.

2.3 Open the He and N_2 gas supplies by releasing the valve on the top of each cylinder. The regulators should be set to read between 1.1 – 1.2 bar (**check!**).

2.4 Wearing gloves, eye protection and a lab coat, fill the instrument dewar with liquid N_2 to a level 5 cm from the top and place the dewar on the instrument elevator.

2.5 Transfer all the sample tubes from the VacPrep heating stations to their cooling positions.

2.6 Increase the VacPrep temperature to 300ºC, place the carbon black sample tube in a heating position and leave for 1 hour.

2.7 Ensure that an empty sample tube is placed in the instrument balance tube.

2.8 Wearing heat-resistant gloves, carefully remove the carbon black sample tube (**HOT!**) from its heating station, attach a rubber ‘ear’ to the tube and place the sealed tube in the cooling station for a few minutes.

2.9 Using a 4 decimal place balance, weigh the carbon standard, tube, ‘ear’ and foam base. Record the weight on the BET sample sheet.

2.10 Start up the instrument PC. Double-click on the desktop ‘Gemini’ icon.

2.11 Allow the software initialisation to complete [the Initialisation Window will close automatically].

2.12 Using the Gemini software, under the ‘Unit1’ dropdown menu, select ‘Show Instrument Schematic’. A window showing an interactive schematic for the instrumental settings will appear.

3 ANALYSIS OF CARBON BLACK STANDARD

3.1 Using the Gemini software, under the ‘File’ dropdown menu, select ‘Open’ and then ‘Sample Information’. Alternatively press ‘F2’ on the keyboard.

3.2 The ‘Open Sample Information File’ window will appear. Select the directory: C:\GEMINI\DATA\BGSDAT~1 and then Click the ‘OK’ button.

3.3 A further ‘Open Sample Information File’ window will appear indicating ‘File C:\GEMINI\DATA\BGSDAT~1***.SMP does not exist. Do you wish to create it ?’ Click the ‘Yes’ button.

3.4 A multi-tabbed window will appear. On the ‘Sample Information’ tab, click the ‘Replace All’ button.

3.5 The ‘Open Sample Information File’ window will appear. Navigate to the C:\GEMINI\DATA\METHODS directory and select the 004.SMP ‘BET Surface Area Method’. Click the ‘OK’ button.

3.6 On the ‘Sample Information’ tab, in the MPL sample: box, overtype ‘BET surface area method’ with ‘CARBON BLACK + date’ and overtype the sample mass (shown as 500.0000 g) with the value produced on the Excel BET sample sheet.

3.7 Using the buttons at the base of the tab, click ‘Save’ and then click ‘Close’.

3.8 Under the ‘Unit1’ dropdown menu, select ‘Start Analysis’. A ‘Start Analysis’ window will appear. Navigate to the C:\GEMINI\DATA\BGSDAT~1 directory and select the entry for ‘CARBON BLACK + date’. Click the ‘OK’ button.

3.9 Check the information in the new window is correct and click the ‘Start’ button at the bottom of the window. A new window will appear which asks you to remove the sample tube from its port.

3.10 On the instrument, ensure that the top of dewar is covered (e.g. with a blank CD) to prevent objects from falling into the liquid N_2.

3.11 Disconnect the sample tube from the instrument by releasing the tube nut. Note the position of the ferrule and O-ring. Click the ‘OK’ button.

3.12 A new window will then appear requesting that you re-attach the sample tube.

3.13 Place the tube nut, ferrule and O-ring (in this order) onto the sample tube.

3.14 Insert the sample tube into the instrument housing and tighten the nut to finger tight plus a quarter-turn.

3.15 Check that the bases of the sample and reference tubes are level.

3.16 Place the dewar cover over the sample, reference and saturation tubes and push to the top. Close the protection doors.

3.17 Click the ‘OK’ button.

3.18 Following completion of the analysis, to view the results, under the ‘Reports’ dropdown menu, select ‘Start Reports’ and then select the appropriate file from the C:\GEMINI\DATA\BGSDAT~1 directory.

3.19 Check that the carbon black standard produces a BET surface area within specifications (30.6 ± 0.75 m^2/g). If the value obtained is outside these specifications, repeat the procedure with fresh carbon black sample.

4 ANALYSIS OF SAMPLES

4.1 On the instrument, ensure that the top of dewar is covered (e.g. with a blank CD) to prevent objects from falling into the liquid N_2.

4.2 Disconnect the sample tube containing the carbon black standard from the instrument by releasing the tube nut. Discard the carbon black standard material.

4.3 On the VacPrep unit, turn the 'gas/off/vac' switch to the 'gas' position for 30 seconds

4.4 Turn the gas/off/vac switch to the 'off' position.

4.5 Disconnect the sample tube from the instrument by releasing the tube nut. Attach 'ear' immediately. Using a 4 decimal place balance, weigh the sample, tube, 'ear' and foam base assembly. Record the weight on the BET sample sheet. Note: The weight of sample produced on the BET sample sheet is required when completing the 'Sample Information' tab later.

4.6 Follow the same procedure as that for the carbon black standard [steps 3.1 -3.18] substituting the appropriate MPL number when completing the 'Sample Information' tab [step 3.6].

5 TUBE CLEANING AFTER ANALYSIS

5.1 Rinse each of the sample tubes with weak detergent.

5.2 Place the tubes in an ultrasonic bath filled with RO water and sonicate for c.5 minutes.

5.3 Rinse the tubes with acetone and leave in an oven set at 50ºC until dry.

Appendix 2 BET sample sheet with example data

SAMPLE PREPARATION FOR GEMINI VI SUARFACE AREA AND PORE SIZE ANALYSER

Day before analysis

Weigh sample approximately into a balance boat, i.e. 0.5g (for samples with high surface areas) and 1.0g (for samples with low surface areas). Set sample aside.

Select a labelled sample tube. Fit tube into foam base and insert rubber ear into tube. Weigh all 3 components together and note weight in table below.

Remove components from scales and fill tube with sample by first removing rubber ear and attaching the 'tube filler' to tube, then carefully pouring sample from balance boat into it.

Repeat the above steps for all samples and finally weigh out between 0.5g and 0.6g Carbon Black* reference material into tube and leave in 50^{o}C oven overnight.

Finally, place filled sample tubes in Vac-Prep unit and evacuate overnight at 60^{o}C - see section 1.4 in operating instructions.

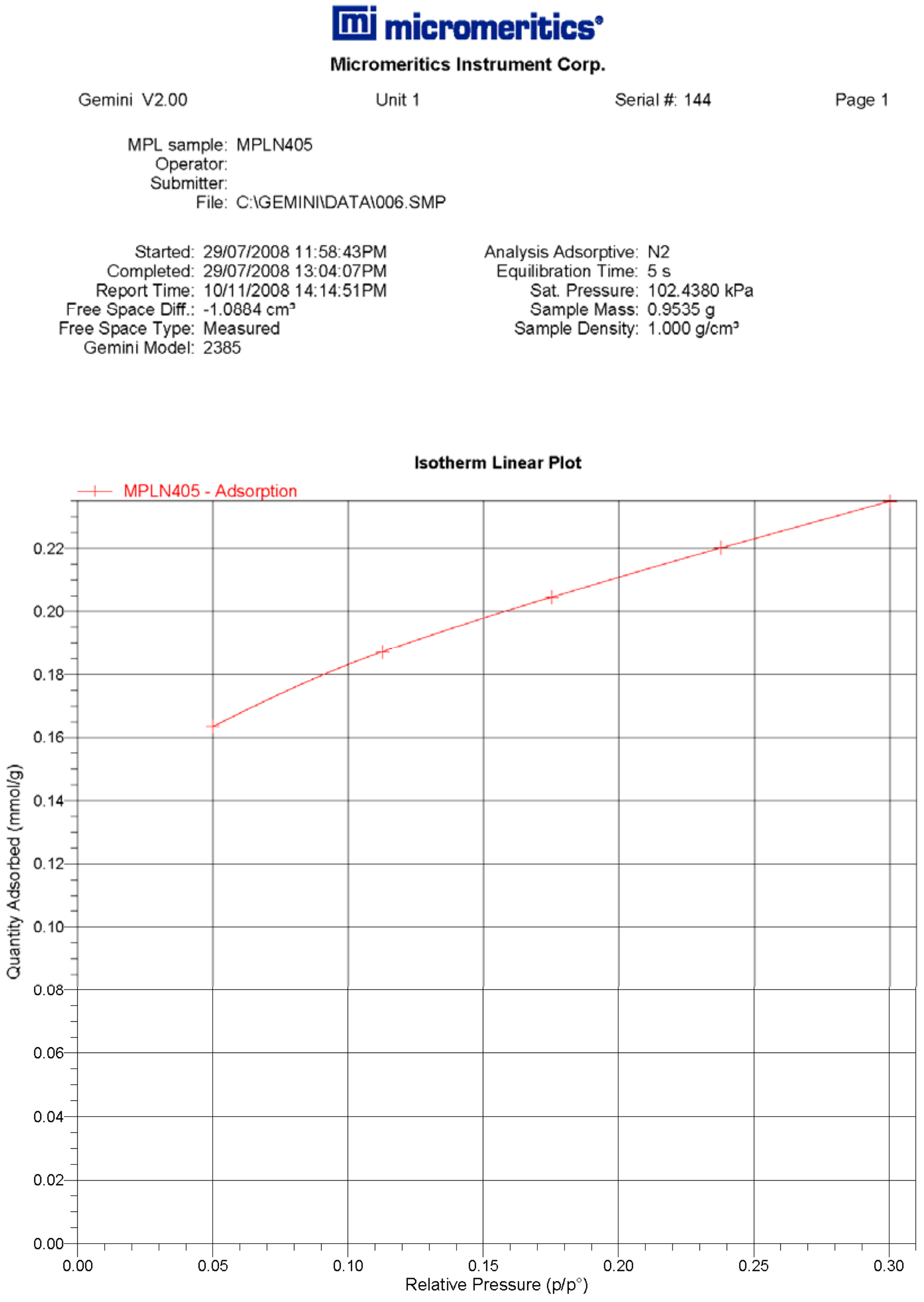
Day of analysis

Prior to analysis, remove a sample tube containing a sample to be analysed from the Vac-Prep (after allowing to cool) and insert rubber ear, thus ensuring that the sample remains dry. Determine the sample weight by fitting the **tube + sample + ear** into the **base**, weighing all components and entering and the weight into the table. The sample weight calculated in the final column should be approximately 0.5g or 1.0g.

TUBE No.	MPL No.	Alternative Sample No./Description (if applicable)	Weight (g) **TUBE+EAR+BASE**	Weight (g) **TUBE+SAMPLE+EAR+BASE** (after removal from vac prep **on day of analysis**)	Sample Weight (g)
1	N418	London Clay	20.1689	21.2635	1.0946
2	N419	Boom Clay	20.1376	21.2145	1.0769
3	N420	Opalinus Clay	20.1143	21.2004	1.0861
4	N421	Gault Clay	20.1196	21.2682	1.1486
5	N411	Bentonite <125um	20.1805	20.6818	0.5013
6					0
7					0

**** Carbon Black reference sample should always be run prior to any unknown samples and the result verified to ensure that the instrument is operating correctly.***

Appendix 3 Example multi-point BET report (3 pages)



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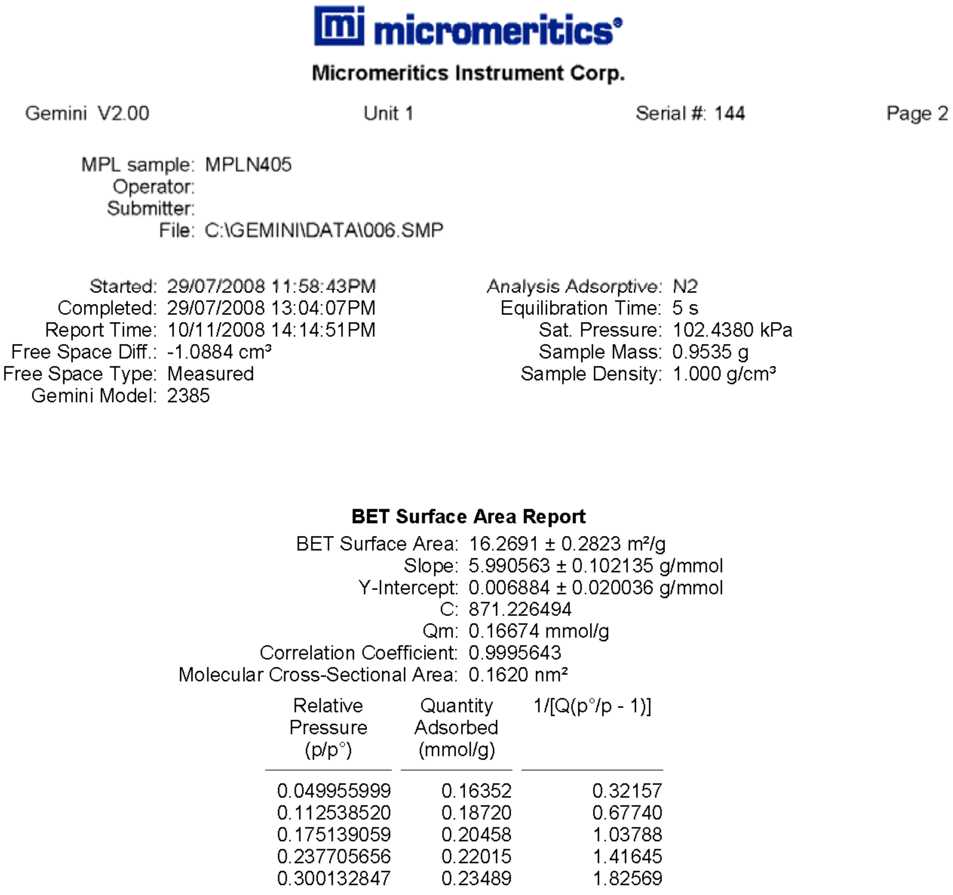
Gemini V2.00 Unit 1 Serial #: 144 Page 1

MPL sample: MPLN405
Operator:
Submitter:
File: C:\GEMINI\DATA\006.SMP

Started: 29/07/2008 11:58:43PM
Completed: 29/07/2008 13:04:07PM
Report Time: 10/11/2008 14:14:51PM
Free Space Diff.: -1.0884 cm³
Free Space Type: Measured
Gemini Model: 2385

Analysis Adsorptive: N2
Equilibration Time: 5 s
Sat. Pressure: 102.4380 kPa
Sample Mass: 0.9535 g
Sample Density: 1.000 g/cm³

Isotherm Linear Plot



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Micromeritics Instrument Corp.

Gemini V2.00 Unit 1 Serial #: 144 Page 2

MPL sample: MPLN405
Operator:
Submitter:
File: C:\GEMINI\DATA\006.SMP

Started: 29/07/2008 11:58:43PM
Completed: 29/07/2008 13:04:07PM
Report Time: 10/11/2008 14:14:51PM
Free Space Diff.: -1.0884 cm³
Free Space Type: Measured
Gemini Model: 2385

Analysis Adsorptive: N2
Equilibration Time: 5 s
Sat. Pressure: 102.4380 kPa
Sample Mass: 0.9535 g
Sample Density: 1.000 g/cm³

BET Surface Area Report

BET Surface Area: 16.2691 ± 0.2823 m²/g
Slope: 5.990563 ± 0.102135 g/mmol
Y-Intercept: 0.006884 ± 0.020036 g/mmol
C: 871.226494
Qm: 0.16674 mmol/g
Correlation Coefficient: 0.9995643
Molecular Cross-Sectional Area: 0.1620 nm²

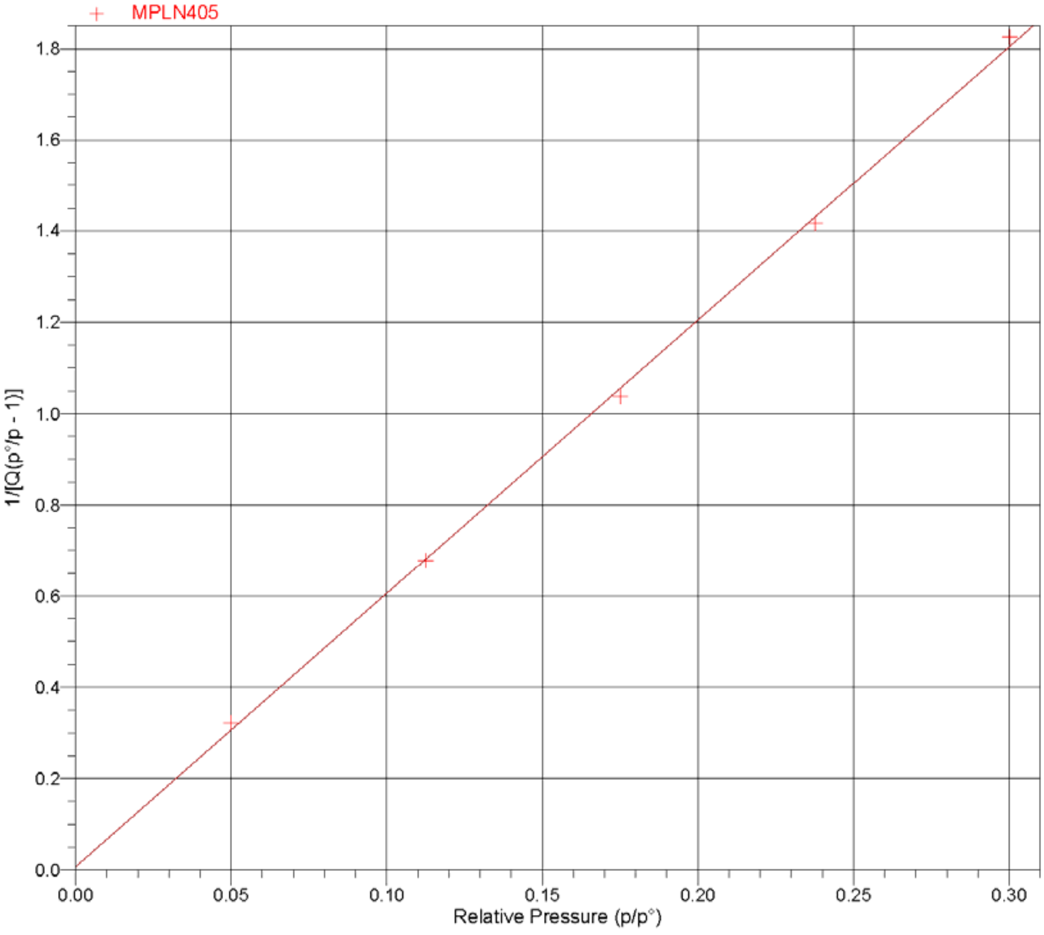
Relative Pressure (p/p°)	Quantity Adsorbed (mmol/g)	1/[Q(p°/p - 1)]
0.049955999	0.16352	0.32157
0.112538520	0.18720	0.67740
0.175139059	0.20458	1.03788
0.237705656	0.22015	1.41645
0.300132847	0.23489	1.82569

MPL sample: MPLN405
Operator:
Submitter:
File: C:\GEMINI\DATA\006.SMP

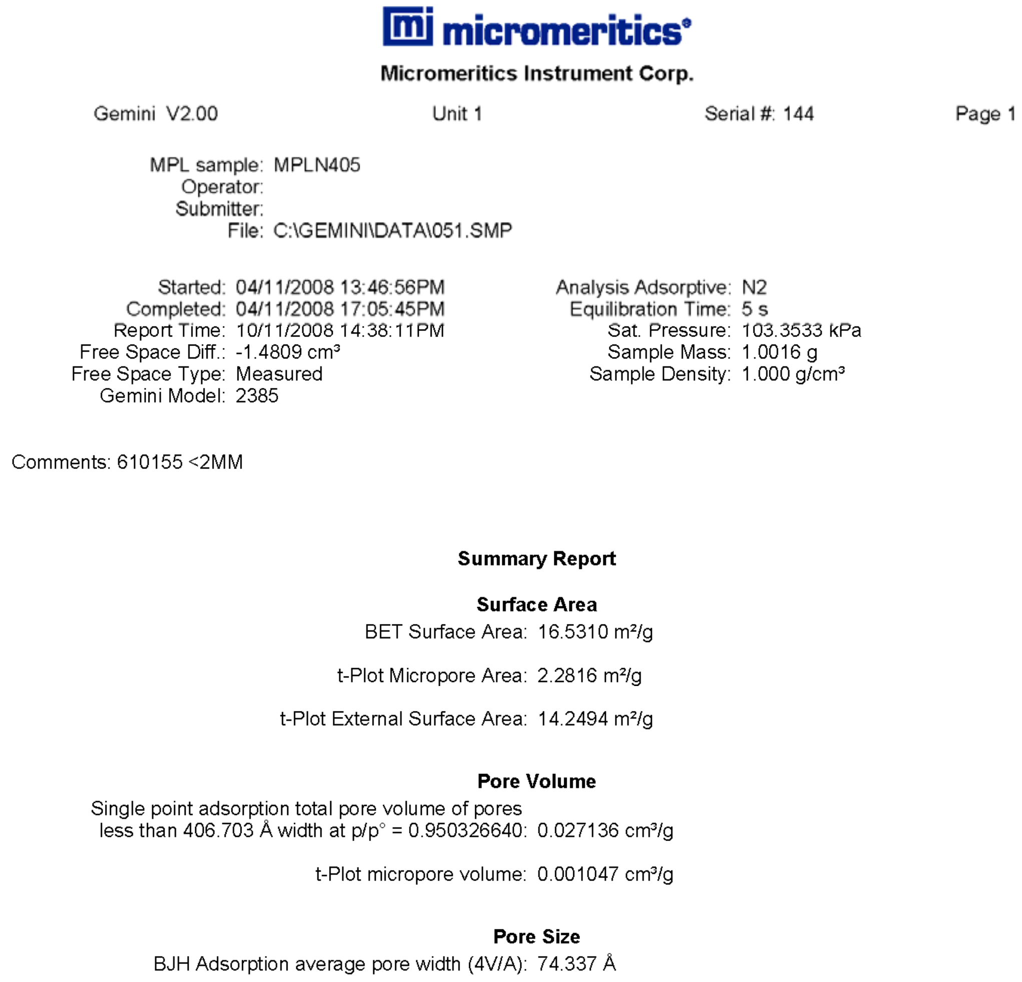
Started: 29/07/2008 11:58:43PM
Completed: 29/07/2008 13:04:07PM
Report Time: 10/11/2008 14:14:51PM
Free Space Diff.: -1.0884 cm³
Free Space Type: Measured
Gemini Model: 2385

Analysis Adsorptive: N2
Equilibration Time: 5 s
Sat. Pressure: 102.4380 kPa
Sample Mass: 0.9535 g
Sample Density: 1.000 g/cm³

BET Surface Area Plot



Appendix 4 Example full isotherm and pore volume distribution report (9 pages)



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Gemini V2.00 Unit 1 Serial #: 144 Page 1

MPL sample: MPLN405
Operator:
Submitter:
File: C:\GEMINI\DATA\051.SMP

Started: 04/11/2008 13:46:56PM
Completed: 04/11/2008 17:05:45PM
Report Time: 10/11/2008 14:38:11PM
Free Space Diff.: -1.4809 cm³
Free Space Type: Measured
Gemini Model: 2385

Analysis Adsorptive: N2
Equilibration Time: 5 s
Sat. Pressure: 103.3533 kPa
Sample Mass: 1.0016 g
Sample Density: 1.000 g/cm³

Comments: 610155 <2MM

Summary Report

Surface Area

BET Surface Area: 16.5310 m²/g

t-Plot Micropore Area: 2.2816 m²/g

t-Plot External Surface Area: 14.2494 m²/g

Pore Volume

Single point adsorption total pore volume of pores
less than 406.703 Å width at p/p° = 0.950326640: 0.027136 cm³/g

t-Plot micropore volume: 0.001047 cm³/g

Pore Size

BJH Adsorption average pore width (4V/A): 74.337 Å micromeritics®

Micromeritics Instrument Corp.

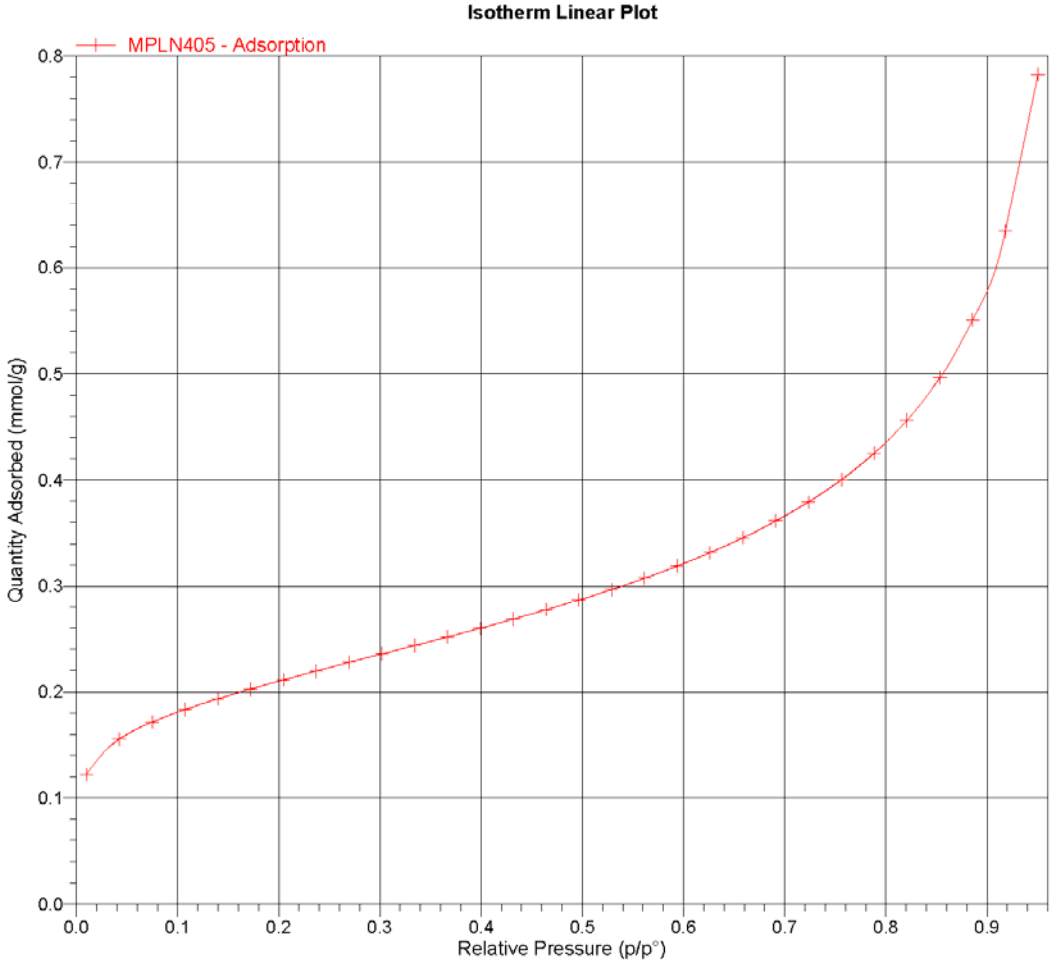
Gemini V2.00 Unit 1 Serial #: 144 Page 2

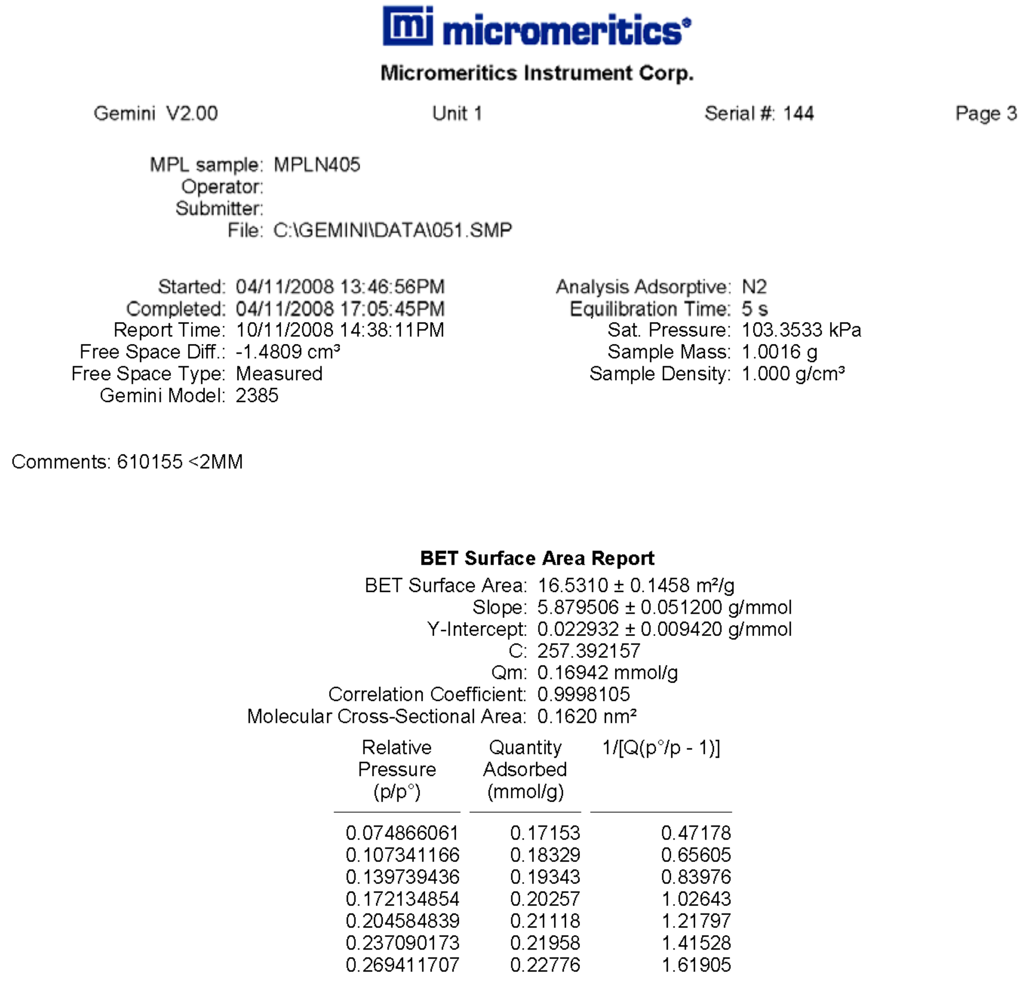
MPL sample: MPLN405
Operator:
Submitter:
File: C:\GEMINI\DATA\051.SMP

Started: 04/11/2008 13:46:56PM
Completed: 04/11/2008 17:05:45PM
Report Time: 10/11/2008 14:38:11PM
Free Space Diff.: -1.4809 cm³
Free Space Type: Measured
Gemini Model: 2385

Analysis Adsorptive: N2
Equilibration Time: 5 s
Sat. Pressure: 103.3533 kPa
Sample Mass: 1.0016 g
Sample Density: 1.000 g/cm³

Comments: 610155 <2MM





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Gemini V2.00 Unit 1 Serial #: 144 Page 3

MPL sample: MPLN405
Operator:
Submitter:
File: C:\GEMINI\DATA\051.SMP

Started: 04/11/2008 13:46:56PM
Completed: 04/11/2008 17:05:45PM
Report Time: 10/11/2008 14:38:11PM
Free Space Diff.: -1.4809 cm³
Free Space Type: Measured
Gemini Model: 2385

Analysis Adsorptive: N2
Equilibration Time: 5 s
Sat. Pressure: 103.3533 kPa
Sample Mass: 1.0016 g
Sample Density: 1.000 g/cm³

Comments: 610155 <2MM

BET Surface Area Report

BET Surface Area: 16.5310 ± 0.1458 m²/g
Slope: 5.879506 ± 0.051200 g/mmol
Y-Intercept: 0.022932 ± 0.009420 g/mmol
C: 257.392157
Qm: 0.16942 mmol/g
Correlation Coefficient: 0.9998105
Molecular Cross-Sectional Area: 0.1620 nm²

Relative Pressure (p/p°)	Quantity Adsorbed (mmol/g)	1/[Q(p°/p - 1)]
0.074866061	0.17153	0.47178
0.107341166	0.18329	0.65605
0.139739436	0.19343	0.83976
0.172134854	0.20257	1.02643
0.204584839	0.21118	1.21797
0.237090173	0.21958	1.41528
0.269411707	0.22776	1.61905

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Gemini V2.00 Unit 1 Serial #: 144 Page 4

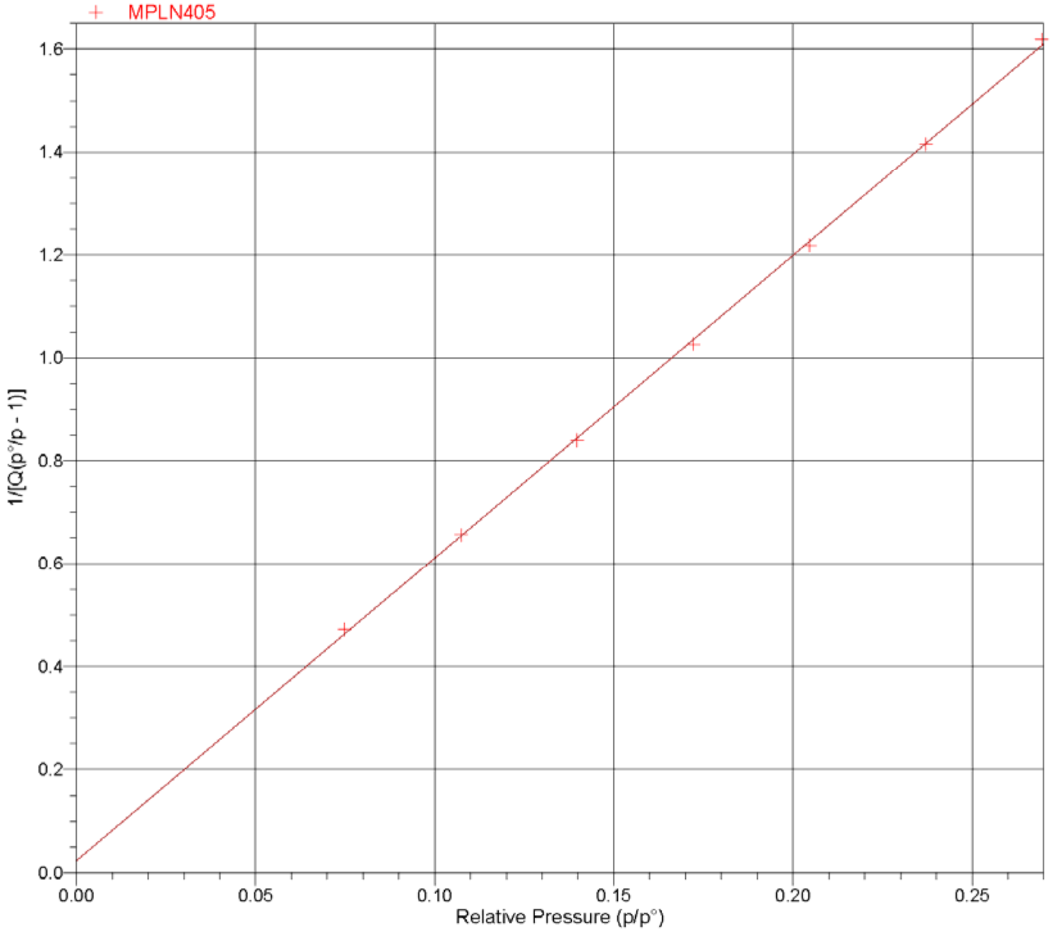
MPL sample: MPLN405
Operator:
Submitter:
File: C:\GEMINI\DATA\051.SMP

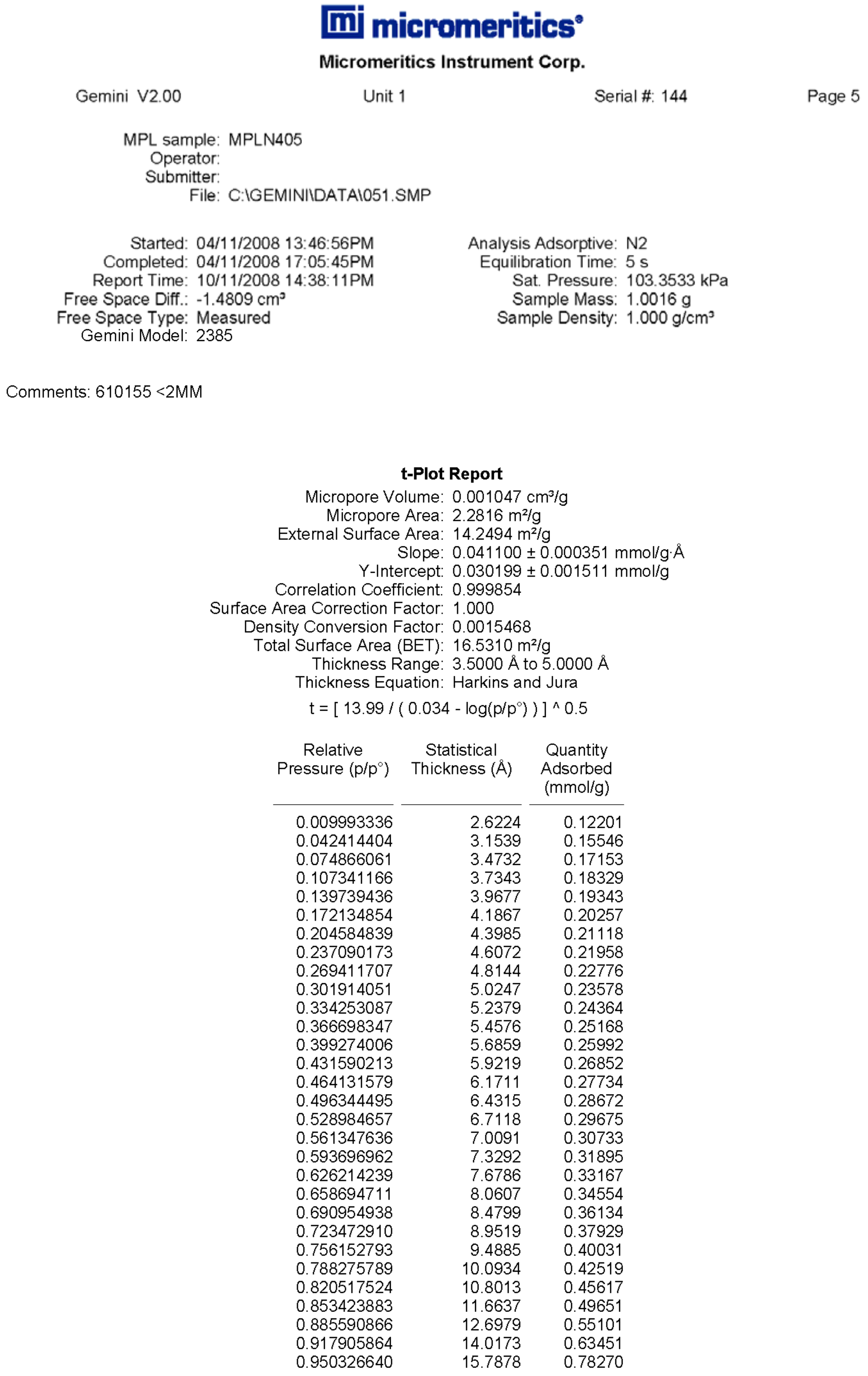
Started: 04/11/2008 13:46:56PM
Completed: 04/11/2008 17:05:45PM
Report Time: 10/11/2008 14:38:11PM
Free Space Diff.: -1.4809 cm^3
Free Space Type: Measured
Gemini Model: 2385

Analysis Adsorptive: N2
Equilibration Time: 5 s
Sat. Pressure: 103.3533 kPa
Sample Mass: 1.0016 g
Sample Density: 1.000 g/cm^3

Comments: 610155 <2MM

BET Surface Area Plot





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Micromeritics Instrument Corp.

Gemini V2.00 Unit 1 Serial #: 144 Page 5

MPL sample: MPLN405
Operator:
Submitter:
File: C:\GEMINI\DATA\051.SMP

Started: 04/11/2008 13:46:56PM
Completed: 04/11/2008 17:05:45PM
Report Time: 10/11/2008 14:38:11PM
Free Space Diff.: -1.4809 cm³
Free Space Type: Measured
Gemini Model: 2385

Analysis Adsorptive: N2
Equilibration Time: 5 s
Sat. Pressure: 103.3533 kPa
Sample Mass: 1.0016 g
Sample Density: 1.000 g/cm³

Comments: 610155 <2MM

t-Plot Report

Micropore Volume: 0.001047 cm³/g
Micropore Area: 2.2816 m²/g
External Surface Area: 14.2494 m²/g
Slope: 0.041100 ± 0.000351 mmol/g·Å
Y-Intercept: 0.030199 ± 0.001511 mmol/g
Correlation Coefficient: 0.999854
Surface Area Correction Factor: 1.000
Density Conversion Factor: 0.0015468
Total Surface Area (BET): 16.5310 m²/g
Thickness Range: 3.5000 Å to 5.0000 Å
Thickness Equation: Harkins and Jura

t = [13.99 / (0.034 - log(p/p°))] ^ 0.5

Relative Pressure (p/p°)	Statistical Thickness (Å)	Quantity Adsorbed (mmol/g)
0.009993336	2.6224	0.12201
0.042414404	3.1539	0.15546
0.074866061	3.4732	0.17153
0.107341166	3.7343	0.18329
0.139739436	3.9677	0.19343
0.172134854	4.1867	0.20257
0.204584839	4.3985	0.21118
0.237090173	4.6072	0.21958
0.269411707	4.8144	0.22776
0.301914051	5.0247	0.23578
0.334253087	5.2379	0.24364
0.366698347	5.4576	0.25168
0.399274006	5.6859	0.25992
0.431590213	5.9219	0.26852
0.464131579	6.1711	0.27734
0.496344495	6.4315	0.28672
0.528984657	6.7118	0.29675
0.561347636	7.0091	0.30733
0.593696962	7.3292	0.31895
0.626214239	7.6786	0.33167
0.658694711	8.0607	0.34554
0.690954938	8.4799	0.36134
0.723472910	8.9519	0.37929
0.756152793	9.4885	0.40031
0.788275789	10.0934	0.42519
0.820517524	10.8013	0.45617
0.853423883	11.6637	0.49651
0.885590866	12.6979	0.55101
0.917905864	14.0173	0.63451
0.950326640	15.7878	0.78270

Gemini V2.00 Unit 1 Serial #: 144 Page 6

MPL sample: MPLN405
Operator:
Submitter:
File: C:\GEMINI\DATA\051.SMP

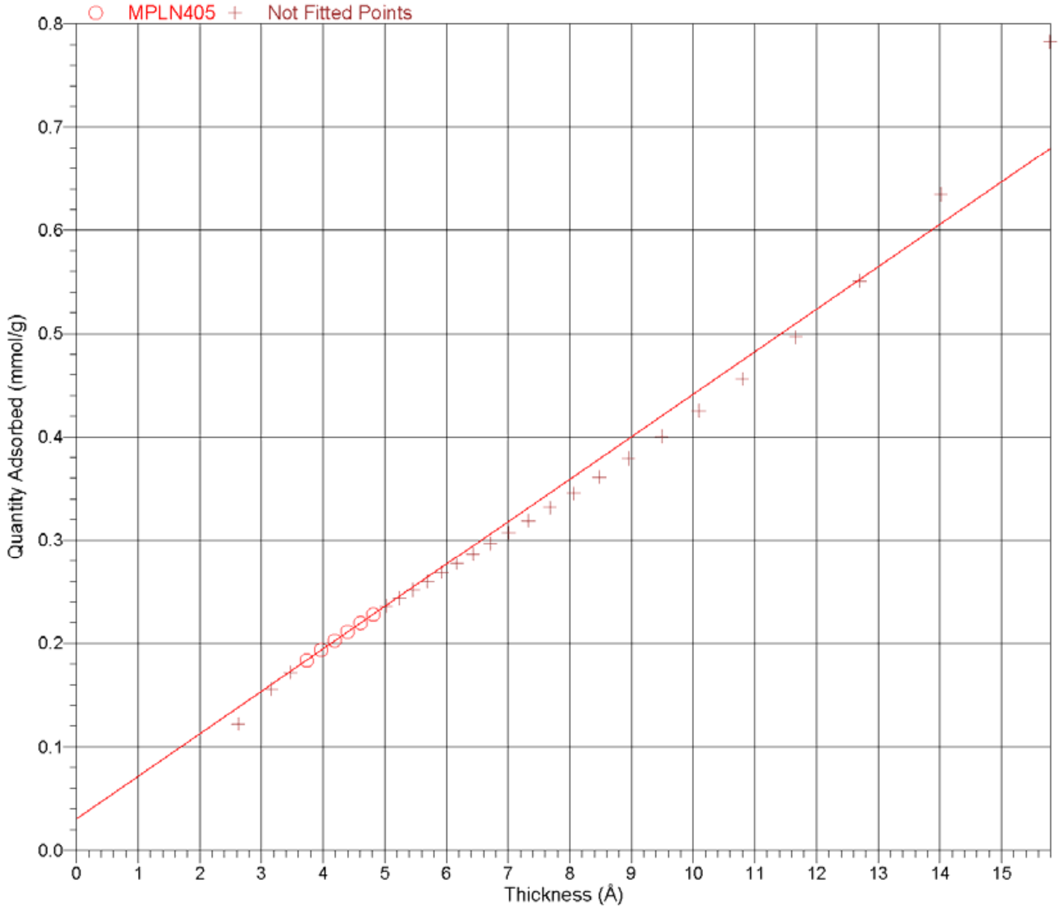
Started: 04/11/2008 13:46:56PM
Completed: 04/11/2008 17:05:45PM
Report Time: 10/11/2008 14:38:11PM
Free Space Diff.: -1.4809 cm³
Free Space Type: Measured
Gemini Model: 2385

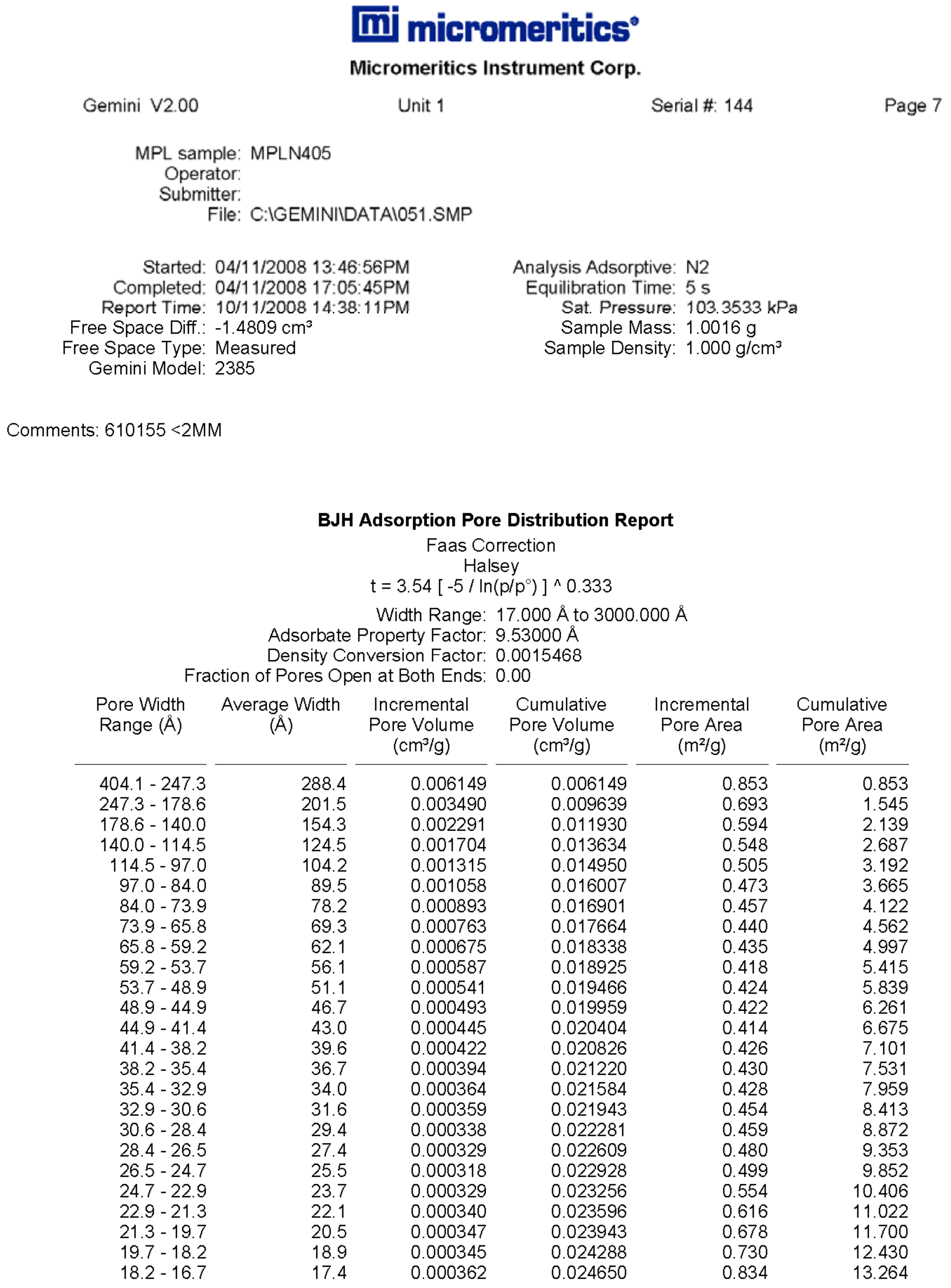
Analysis Adsorptive: N2
Equilibration Time: 5 s
Sat. Pressure: 103.3533 kPa
Sample Mass: 1.0016 g
Sample Density: 1.000 g/cm³

Comments: 610155 <2MM

t-Plot

Harkins and Jura





Micromeritics Instrument Corp.

Gemini V2.00 Unit 1 Serial #: 144 Page 7

MPL sample: MPLN405
Operator:
Submitter:
File: C:\GEMINI\DATA\051.SMP

Started: 04/11/2008 13:46:56PM
Completed: 04/11/2008 17:05:45PM
Report Time: 10/11/2008 14:38:11PM
Free Space Diff.: -1.4809 cm^3
Free Space Type: Measured
Gemini Model: 2385

Analysis Adsorptive: N2
Equilibration Time: 5 s
Sat. Pressure: 103.3533 kPa
Sample Mass: 1.0016 g
Sample Density: 1.000 g/cm^3

Comments: 610155 <2MM

BJH Adsorption Pore Distribution Report

Faas Correction
Halsey
$t = 3.54 [-5 / \ln(p/p^\circ)] ^ 0.333$

Width Range: 17.000 Å to 3000.000 Å
Adsorbate Property Factor: 9.53000 Å
Density Conversion Factor: 0.0015468
Fraction of Pores Open at Both Ends: 0.00

Pore Width Range (Å)	Average Width (Å)	Incremental Pore Volume (cm^3/g)	Cumulative Pore Volume (cm^3/g)	Incremental Pore Area (m^2/g)	Cumulative Pore Area (m^2/g)
404.1 - 247.3	288.4	0.006149	0.006149	0.853	0.853
247.3 - 178.6	201.5	0.003490	0.009639	0.693	1.545
178.6 - 140.0	154.3	0.002291	0.011930	0.594	2.139
140.0 - 114.5	124.5	0.001704	0.013634	0.548	2.687
114.5 - 97.0	104.2	0.001315	0.014950	0.505	3.192
97.0 - 84.0	89.5	0.001058	0.016007	0.473	3.665
84.0 - 73.9	78.2	0.000893	0.016901	0.457	4.122
73.9 - 65.8	69.3	0.000763	0.017664	0.440	4.562
65.8 - 59.2	62.1	0.000675	0.018338	0.435	4.997
59.2 - 53.7	56.1	0.000587	0.018925	0.418	5.415
53.7 - 48.9	51.1	0.000541	0.019466	0.424	5.839
48.9 - 44.9	46.7	0.000493	0.019959	0.422	6.261
44.9 - 41.4	43.0	0.000445	0.020404	0.414	6.675
41.4 - 38.2	39.6	0.000422	0.020826	0.426	7.101
38.2 - 35.4	36.7	0.000394	0.021220	0.430	7.531
35.4 - 32.9	34.0	0.000364	0.021584	0.428	7.959
32.9 - 30.6	31.6	0.000359	0.021943	0.454	8.413
30.6 - 28.4	29.4	0.000338	0.022281	0.459	8.872
28.4 - 26.5	27.4	0.000329	0.022609	0.480	9.353
26.5 - 24.7	25.5	0.000318	0.022928	0.499	9.852
24.7 - 22.9	23.7	0.000329	0.023256	0.554	10.406
22.9 - 21.3	22.1	0.000340	0.023596	0.616	11.022
21.3 - 19.7	20.5	0.000347	0.023943	0.678	11.700
19.7 - 18.2	18.9	0.000345	0.024288	0.730	12.430
18.2 - 16.7	17.4	0.000362	0.024650	0.834	13.264

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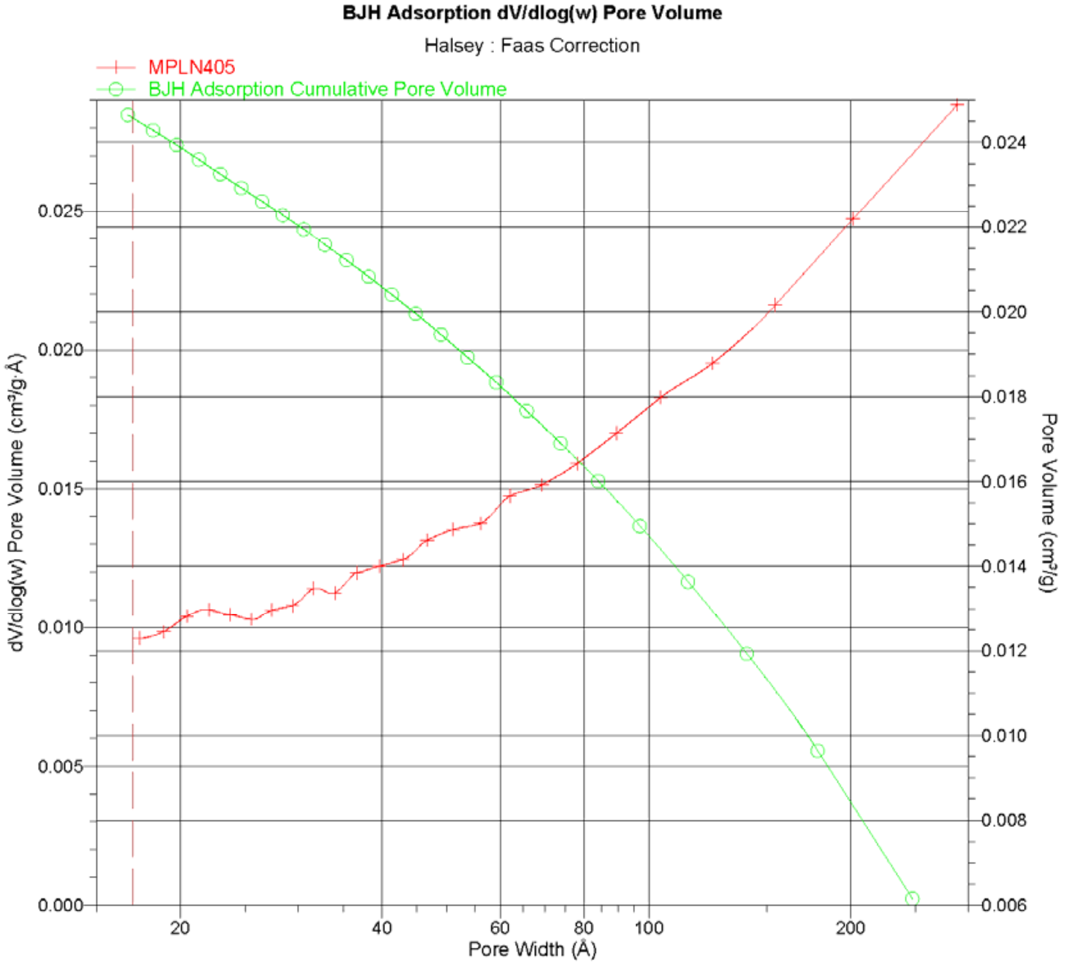
Gemini V2.00 Unit 1 Serial #: 144 Page 8

MPL sample: MPLN405
Operator:
Submitter:
File: C:\GEMINI\DATA\051.SMP

Started: 04/11/2008 13:46:56PM
Completed: 04/11/2008 17:05:45PM
Report Time: 10/11/2008 14:38:11PM
Free Space Diff.: -1.4809 cm³
Free Space Type: Measured
Gemini Model: 2385

Analysis Adsorptive: N2
Equilibration Time: 5 s
Sat. Pressure: 103.3533 kPa
Sample Mass: 1.0016 g
Sample Density: 1.000 g/cm³

Comments: 610155 <2MM



BJH Adsorption dV/dlog(w) Pore Volume

Halsey : Faas Correction

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Gemini V2.00 Unit 1 Serial #: 144 Page 9

MPL sample: MPLN405
Operator:
Submitter:
File: C:\GEMINI\DATA\051.SMP

Started:	04/11/2008 13:46:56PM	Analysis Adsorptive:	N2
Completed:	04/11/2008 17:05:45PM	Equilibration Time:	5 s
Report Time:	10/11/2008 14:38:11PM	Sat. Pressure:	103.3533 kPa
Free Space Diff.:	-1.4809 cm³	Sample Mass:	1.0016 g
Free Space Type:	Measured	Sample Density:	1.000 g/cm³
Gemini Model:	2385		

Comments: 610155 <2MM