

Application of nitrogen gas-adsorption technique for characterization of pore structure of mudrocks

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Subcritical N_2 gas-adsorption techniques are used more frequently now for characterizing the pore structure of mudrocks. This article discusses some application challenges associated with mudrocks: sample preparation, choice of inversion techniques of the raw isotherm data, representation of pore-size distribution (PSD) data, and reproducibility of measurement data. Gas-adsorption analysis on hand-ground <40-mesh powder samples is recommended over using intact rock samples because of the slow diffusion process. Crushing the sample to <40-mesh powder has no significant effect on any of the measured pore-structure attributes. The $dV/d(\log D)$ representation is recommended for graphical PSD results because log-scale pore-size abscissa are used most commonly for geologic materials. Pore-size distribution inversion using the Barrett-Joyner-Halenda (BJH) method should be preferred over the density-functional-theory (DFT) method because it yields more consistent and less noisy inverted data. The Harkins-Jura thickness equation is recommended as the choice of thickness equation. The Brunauer-Emmett-Teller (BET) theory specific surface area, total pore-volume, and PSD are reproducible within a variation range of 10% to 20%.

Introduction

Quantitative characterization of different pore-structure attributes (e.g., total porosity, pore-size distribution, specific surface area, and so forth) is crucial in modeling geophysical and petrophysical behavior of any porous media (e.g., elastic and mechanical behavior, movement, and flow of fluids). Porosity is the most commonly used pore-structure parameter; however, this single-value volumetric quantification does not provide specific information on the geometric details of the pore structure. Pore-size distribution (PSD) of a porous media quantifies the relative pore volumes associated with different pore sizes.

Such information can provide the missing link to relate the elastic moduli and permeability of porous media, as demonstrated by Prasad (2003). Mbia et al. (2013) show good correlation between equivalent pore radius and elastic moduli of clays and shales. Kuila and Prasad (2013) show that fine-scale pore structure in mudrocks is controlled by the intrinsic PSD of clay aggregates, unaffected by compaction, and has implications in building clay-water composite end-members for rock-physics modeling of shale.

Pressure-dependent acoustic velocity data are often correlated with pore compressibility (e.g., Zimmerman et al., 1986). PSD data can allow us to create improved pore-compressibility models in separating the total pore volume in small incompressible pores and larger, potentially compressible pores. In addition to that, PSD is the basic input in pore-network models to understand and predict

multiscale gas-transport mechanisms in unconventional gas-shale reservoirs (e.g., Mehmani et al., 2013).

Most recent studies of pore-structure characterization in mudrocks are based on advanced imaging techniques, which reveal a nanometer-scale pore structure within their inorganic and organic components (e.g., Chalmers et al., 2012; Curtis et al., 2012; Milliken et al., 2013). Such analyses provide visual qualitative image of mudrock porosity; however, quantitative pore-structure attributes cannot be obtained directly, and additional effort is required (e.g., Curtis et al., 2012; Milliken et al., 2013). These imaging techniques cannot resolve pores smaller than 5 nm and thus cannot see a significant portion of the pore structure (Chalmers et al., 2012). The scale of observation is generally limited to about $1500 \mu\text{m}^2$, and thus the imaged pore structure might not be representative of the rock because of millimeter-scale stratigraphic heterogeneities observed in these formations (Chalmers et al., 2012).

Subcritical nitrogen gas adsorption (at 77 K) is used widely in the chemical, ceramic, and pharmaceutical industries and is useful in characterizing materials with fine pores (< 200-nm diameter). The dominance of nanometer-scale pores in mudrocks makes this technique useful for characterization of unconventional reservoirs. Application of such methods is becoming more widespread in the hydrocarbon industry

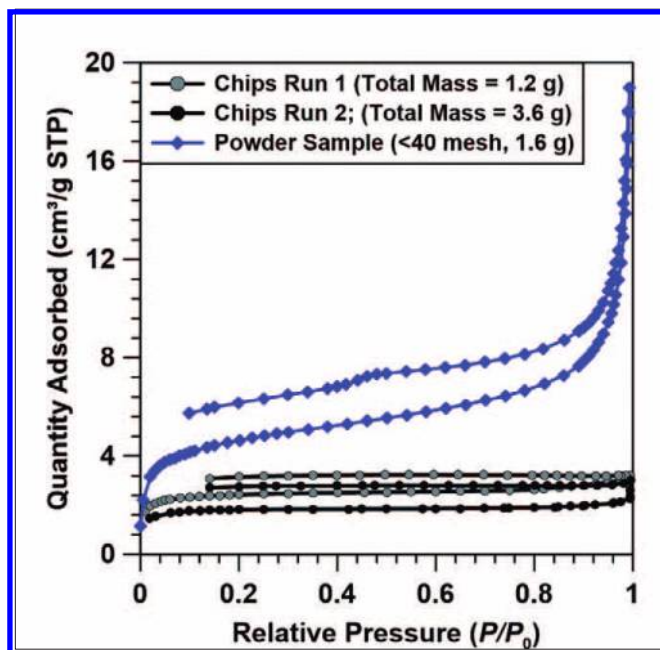


Figure 1. Comparison of N_2 adsorption isotherms of the same sample but with different sample preparation. The intact sample showed limited adsorbed amounts compared with the hand-ground <40-mesh samples with unusual flat adsorption and desorption branches. The isotherm indicates a significant diffusion problem of N_2 into the sample (Jeff Kenvin, personal communication, 2012).

because of the focus on unconventional plays (e.g., Adesida, 2011; Chalmers et al., 2012; Clarkson et al., 2012; Clarkson et al., 2013; Kuila and Prasad, 2013).

However, researchers have used different protocols for measurement of the gas-adsorption isotherm and different inversion schemes to invert the isotherm data for pore-structure attributes. As a consequence, several considerations are necessary to obtain useful results from the technique and to avoid inconsistent comparison and interpretation. In this article, we will discuss the following questions concerning the application of nitrogen gas-adsorption techniques for characterization of the pore structure of mudrocks:

- Should the analysis be done in intact core samples or on crushed powders?
- What is the best way to represent data about pore-size distribution?
- How do different inversion schemes of the raw adsorption data affect PSD data?
- How reproducible and repeatable are the measurements?

The answers to these questions are important for standardization of the technique for mudrock application. Any interpretation and model building using the gas-adsorption data will depend critically on reliable data acquired at standardized conditions and on the understanding of the limitations of the technique.

Preparation of samples: Intact or crushed?

The low permeability (in nanodarcy range) of mudrocks makes the diffusion and/or penetration and equilibration of the N_2 molecules impossible or impractical for intact samples. Most core-measurement analyses of mudrocks are done on crushed rock samples and follow the procedure established by the Gas Research Institute (Luffel and Guidry, 1989). This decreases the path length for the gas to access the entire pore structure and achieves equilibrium within a reasonable time. This is particularly important for N_2 gas adsorption because the low temperature (77 K) used significantly decreases the gas-diffusion rate through pores.

Previous studies have used different sample-preparation techniques for such experiments. Clarkson et al. (2012) used intact core plugs; however, proper equilibration of N_2 molecules in these remains a point of concern. On the other hand, the concerns on using crushed-sample preparation are potential damaging

of the rock structure and sampling bias using different sieve fractions. The different mechanical properties of the constituent mineral grains of mudrocks result in differential tendency to grind into smaller sizes and can result in a bias in the composition and mineralogy of each sieved fraction.

Adesida (2011) report the sampling bias in measured pore structure by using different sieved fractions of the same crushed samples. The total specific pore volume and the specific surface area (SSA) measured increase with decreasing sample particle size.

N_2 gas-adsorption isotherm results on the intact rectangular chip samples (-2 to 3 cm in width and each weighing

| Equilibration Interval | SS2-1 | SS2-5 |
|------------------------|-------|-------|
| 10 s | 22.85 | 4.11 |
| 20 s | 23.29 | 4.24 |
| 20 s (Run II) | ---- | 4.19 |
| 30 s | 23.01 | 4.25 |
| 45 s | 23.11 | 4.36 |
| 100 s | ---- | 4.32 |

Table 1. BET SSA with different equilibration criteria. The equilibration criteria used in these experiments are less than 0.01% pressure change evaluated by an 11-point Savitzky-Golay algorithm over user-defined time intervals or the "equilibration interval" (see Micromeritics MicroActive DataMaster v5.00 software manual, 2011).

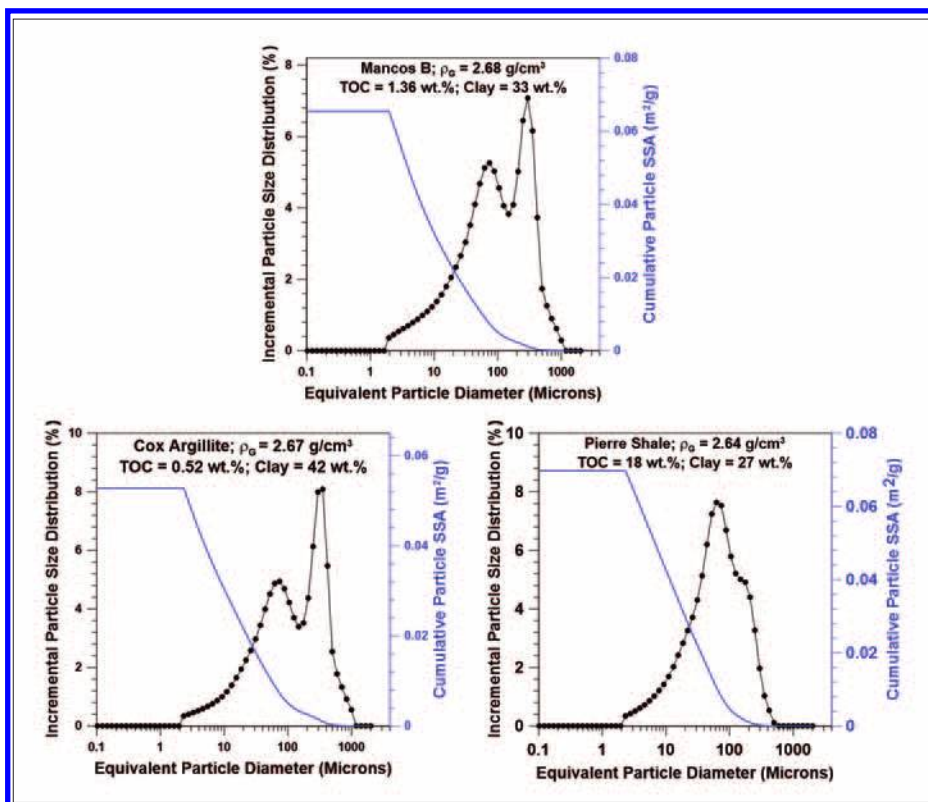


Figure 2. Incremental volume percent particle-size distribution of as-received SWy-2 and hand-ground mudrock <40-mesh powders measured by laser profile-size analysis in suspension in isopropyl alcohol (black curve with filled circles). The cumulative external specific surface area (blue line) of the powder is calculated assuming spherical grains. Note that the reported particle-size distribution is that of a crushed powder and not the actual grain-size distribution of the sample.

0.5 – 1 g) from a mudrock show significantly reduced adsorption over the entire relative pressure range compared with the isotherm obtained from powder samples from the same material. The middle part of the adsorption branch and the entire desorption branch are too flat, indicating a severe diffusion problem. This experimental result suggests that reliable data for gas adsorption cannot be obtained using intact chips for mudrock samples.

Crushing the sample is a practical necessity, but the use of any particular sieve fraction must be avoided. We recommend using crushed hand-ground <40-mesh powder, in which the entire sample is crushed using minimal energy to pass through a 40-mesh sieve instead of using a sieve fraction. This is based on the methodology proposed by McCarty (2002) because it is effective in producing mineralogically and chemically homogenous splits. Repeatability tests on two mudrocks (SS2-1 and SS2-5) using different equilibration times showed a minimal variation in SSA within 2% (relative percent) for SS2-1 and 6% for SS2-5 (Table 1). The measured SSA did not show any systematic variation with equilibration time, suggesting that complete equilibration is achieved when hand-ground < 40-mesh powder is used.

One potential drawback of using crushed samples is that crushing will damage the pore structure of the equivalent intact material and artificially create excess external surface area. The median particle size of three mudrock powders, obtained by the recommended procedure, is more than 200 times greater than the upper limit on pore size (~200 nm, or 0.02 μm) measurable by the N_2 gas-adsorption technique. The calculated external SSA of the hand-ground powders, based on their particle-size distribution (Figure 2), are 0.053 to 0.070 m^2/g , which is an order of magnitude lower than the precision limit of such techniques.

It can be concluded that creation of new surfaces during crushing will not significantly affect measured SSA. Hence, it can be assumed safely that grinding and crushing do not affect the pore-structure data within the range of investigation.

Graphical representation of PSD data

The gas-adsorption inversion techniques use a stepwise calculation of the incremental specific pore volume (i.e., normalized per unit weight) ΔV at each pressure interval, which

is then related to the particular pore-size interval. Different ways are used in the literature to represent PSD data; the most common are (1) dV/dD (derivative pore volume normalized to the pore-diameter interval) and (2) $dV/d(\log D)$ (derivative pore volume normalized to natural logarithm of pore-diameter interval). Such differential distributions normalize the effect of irregular experimental point spacing (Meyer and Klobes, 1999).

The log-differential distribution uses the difference in log of the upper and lower pore sizes of the interval ($\Delta \log D$). Both these distributions are plotted with the differential value along the y -axis versus the midpoint of the related pore-size interval. For bimodal or multimodal pore-size distribution, these two distributions have a different shape and give a different interpretation of the pore system of the investigated sample (e.g., Clarkson et al., 2013). Figure 3 suggests that the shape of the dV/dD distribution function visually overemphasizes the presence of smaller pores. A direct comparison

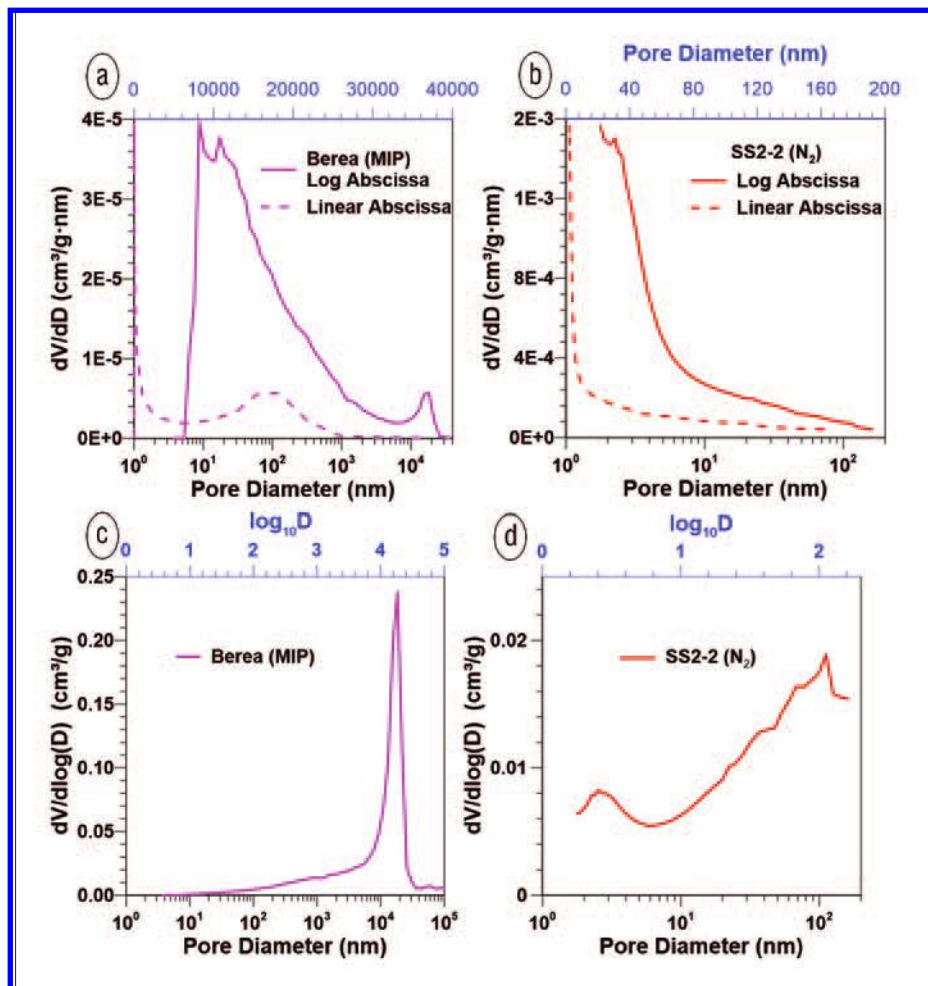


Figure 3. Comparison of two presentations of PSD. (a) and (b) dV/dD representation of PSD for two samples: Berea Sandstone obtained by MIP (magenta) and mudrock SS2-2 obtained by N_2 gas adsorption (red). Bold lines are dV/dD functions with logarithmically compressed pore-size abscissa; dotted lines are dV/dD function with linear pore-size abscissa (on top, blue). (c) and (d) $dV/d(\log D)$ representations of PSD for two samples: Berea Sandstone obtained by MIP (magenta) and mudrock SS2-2 obtained by N_2 gas adsorption (red). The $dV/d(\log D)$ is related to linear $\log_{10} D$ values scale (abscissa at the top of the plots).

of these two distributions is not allowed because the units of these two distribution functions are different (Meyer and Klobes, 1999).

The dV/dD values are proportional to the relative number between different pore-size intervals. The $dV/d(\log D)$ function is mathematically equivalent to a weighted dV/dD multiplied by a factor 2.303 times D , and therefore it is proportional to the relative volume of the different pore sizes. Understanding the difference between these two PSD representations should be considered during data interpretation and application in mathematical modeling.

It should be noted that the partial porosity for each pore-size bin (interval) should be obtained by numerical integration of the functions (peak area under the curve with related abscissa). The distribution dV/dD should be represented with a linear abscissa (linear D scale), as shown by the dashed line in Figure 3b. The plot of this function with a logarithmic abscissa (Figures 3a and 3b, bold lines) is visually misleading because the area under the curve is not proportional to the partial volumes (Meyer and Klobes, 1999).

For geologic materials, because a logarithmically compressed D -axis is preferred to represent the pore-size axis, the $dV/d(\log D)$ distribution should be plotted versus $\log D$. However, it should be noted that the parameter $dV/d(\log D)$ is related to a linear abscissa of “ $\log D$ ” values (blue abscissa in Figures 3c and 3d). The absolute values of $dV/d(\log D)$ should not be confused with partial pore volumes, even though they have the same units (cubic centimeters per gram) (Meyer and Klobes, 1999).

How do different inversion schemes affect pore-structure attribute data?

There are several methods to transform raw adsorption isotherm data into pore-size distributions; the most commonly used are the BJH and DFT techniques. The BJH technique (named after the initials of the proponents of the theory, Barrett, Joyner, and Halenda) is based on classical thermodynamic theory using simplified assumptions. The density functional theory (DFT) uses statistical thermodynamics to construct model isotherms that account for gas-solid and gas-gas interactions along with the geometric configuration of pore walls during adsorption. The experimental isotherm can be thought of as a “kernel” or collection of several modeled individual pore-model isotherms. The PSD is solved numerically using a deconvolution algorithm.

Details of these techniques and the mathematical formalism are

presented in Webb and Orr (1997). However, several such models account for interactions for a particular pair of solid-gas in a particular finite pore geometry (e.g., N_2 on carbon surface with cylindrical pores, N_2 on oxide surface with cylindrical pores, N_2 on pillared clays, N_2 on carbon slit pore, and so forth). Overfitting the experimental data by the deconvolution process in case of noisy data or a wrong model is generally controlled by the “regularization” parameter (or the smoothing parameter).

DFT has been used recently for characterization of the pore structure of mudrock. However, the DFT model type is based on a particular pair of solid-gas interactions, and it is especially sensitive to surface composition and different pore geometries. Adesida (2011) and Clarkson et al. (2012) used a DFT model of N_2 adsorption on a carbon slit model (at 770 K) as the “kernel” for PSD inversion. There are other DFT models for N_2 adsorption on other surface types and different pore geometries. The different model pore types used in Figure 4a resulted in noisy and inconsistent PSD data, although each produced a good fit for the experimental isotherm data points (Figure 4b). Thus, a good fit of the model and experimental isotherm data is not an indicator of the correct choice of model and PSD of the sample (e.g., Clarkson et al., 2012).

Current DFT models are not adequate to model the solid-gas interaction in real mudrocks, mainly because of the compositional heterogeneity and difference in surface energies of their constituent inorganic minerals and porous organic matter. Although the DFT method is sophisticated

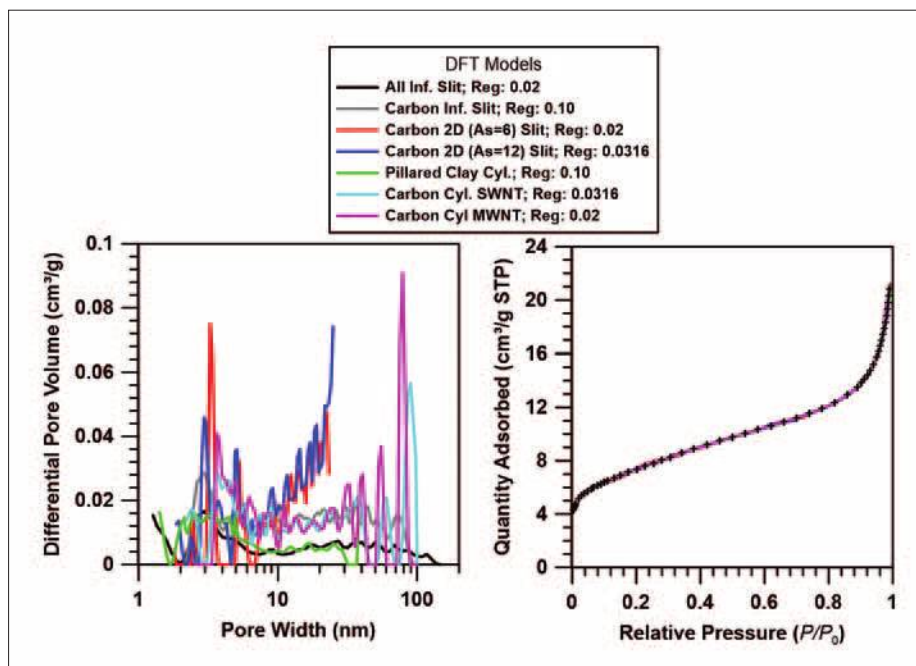


Figure 4. (a) Comparison of PSD results obtained by using different DFT models with N_2 as adsorptive for inversion of the adsorption data for sample SS2-1. The regularization parameter (Reg) is optimized with the rms error fit and is reported in the legend. The inverted results are highly sensitive to the choice of methods. (b) Model fit to the experimental adsorption data (plus symbols). The models show a reasonable match with the experimental data, but the inverted PSD results are noisy and inconsistent with respect to each other. Inf. = infinite; As = aspect ratio; Cyl = cylindrical pore; SWNT = single-wall nanotube; MWNT = multiwall nanotube.

and has potential for mudrock applications in the future, the BJH method based on the Kelvin model is suggested for the mesopore PSD inversion of isotherm data for mudrock applications at present.

Another important key assumption, used for inverting the isotherm data to obtain micropore volume (pore size < 2 nm, IUPAC classification) and PSD by t -plot and BJH theory, respectively, is the thickness (t) curve equation. It quantifies the thickness of the adsorbed layer on the pore surface as a function of relative pressure (P/P_0).

Ideally, the thickness curve should be obtained from an isotherm on a reference nonporous solid with the same chemical and surface properties; this is difficult to obtain for mudrocks because of compositional heterogeneity. Several thickness equations have been proposed as a representative “universal thickness curve,” of which the most generally applicable and most frequently employed are those of Harkins-Jura, Halsey, and Broekhoff-de Boer. Each was developed for a specific type of material using N_2 as the adsorbate. The other commonly used thickness equations are those of Kruk-Jaroniec-Sayari and the Carbon STSA equation. These thickness equations are all empirical. In this section, we will investigate the effect of the choice of “thickness” equation on the inverted results of t -plot micropore volume and BJH pore-size distribution.

| Thickness equation | Micropore volume (cm^3/g) | |
|-----------------------|---|------------|
| | SS2-1 | SS2-5 |
| Kruk- Jaroniec-Sayari | 0.008 | -0.000 (1) |
| Halsey | 0.009 | -0.000 (3) |
| Harkins-Jura | 0.010 | 0.000 (4) |
| Broekhoff-de Boer | 0.012 | 0.000 (3) |
| Carbon STSA | 0.006 | 0.000 (3) |

Table 2. Inverted micropore volumes for samples SS2-1 and SS2-5 using t -plot method with different thickness curve equations.

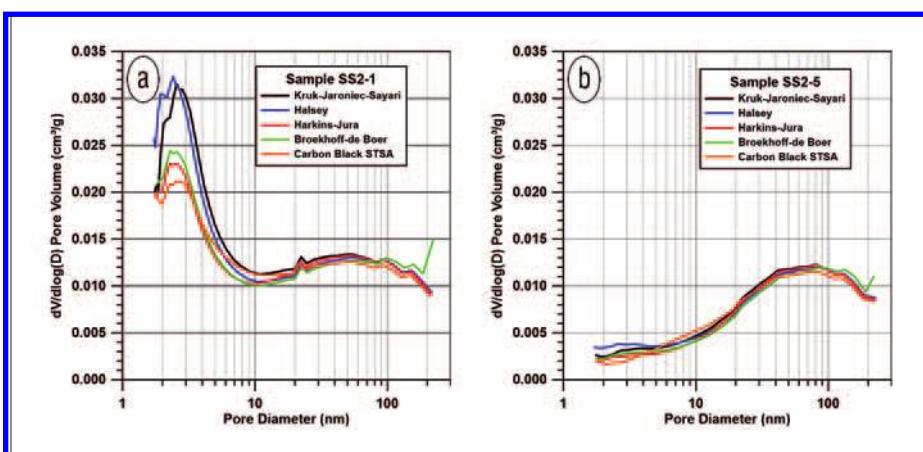


Figure 5. PSD obtained from inversion of N_2 gas-adsorption data for two samples, (a) SS2-1 and (b) SS2-5, using different thickness equations in the BJH method. The pore-size distribution data show the similar peaks, but the absolute partial volume differs depending on the thickness equation used.

Two examples are shown for t -plot and BJH inversion of adsorption isotherm data using different thickness equations, keeping all other parameters constant: one with a large volume of fine pores of 2–5 nm (SS2-1) and one with an abundant volume of pores > 10 nm (SS2-5). The inverted micropore volume for SS2-1 varied from 0.006 to 0.012 cm^3/g , depending on the choice of thickness equation, with a coefficient of variability of 0.249. The inverted micropore volume for SS2-5 has variation beyond three significant digits (Table 2).

Significant differences in the inverted PSD using the BJH technique were present, depending on which thickness equation was used (Figure 5). In each case, the dominant pore modes remain the same regardless of the thickness equation used, but the differential pore volume for each pore size differs by as much as 30%, particularly in the smaller size range. The mismatch in the differential pore volume is not significant for pore diameters > 10 nm.

The BJH computation method starts from higher pressures, hence larger pore sizes, with lower pressures (smaller pore sizes) in the later steps. Because of the method of calculation, errors become cumulative toward the smaller pore sizes, and the difference is more pronounced. Note that in Figure 5, the distribution of pore sizes for the two kinds of materials (one contains smaller mesopores than the other) is consistent regardless of the thickness equation used. Only the pore-volume values differ.

Because the physical measurement of the true t -curves is difficult to obtain experimentally for heterogeneous geologic samples such as mudrocks, for comparative study on similar samples, the choice of any given thickness equation is immaterial as long as it is consistent across a sample set. In this study, we found that the Harkins-Jura thickness equation works best for mudrocks. It provides the most consistent t -plot transform curve shapes and the closest (0, 0) intercept in t -plots for the majority of low-SSA mudrock samples that were analyzed.

It should be noted that the reality of pore structure is much more complex than models can account for, and inversion of data based on theoretical grounds includes simplifying assumptions (Rouquerol et al., 1994). The absolute, or “true,” value of any pore attribute cannot be measured, and each experimental technique and theoretical inversion gives a unique value (Rouquerol et al., 1994). The results should be used in a semi-quantitative way to understand the difference in pore structure among samples of interest. The reported pore sizes should be interpreted as an “equivalent cylindrical pore-size distribution” and should not be considered “absolute.”

Reproducibility of N₂ gas-adsorption experimental data

Reproducibility tests were performed on five samples (SS2-1 through SS2-5) using the Micromeritics ASAP 2020 in two laboratories, one in Golden, Colorado, USA, and one in Houston, Texas, USA. Both instruments were calibrated by certified standards, and the reported values were within the range of uncertainty. The atmospheric pressure of these two places is different, which resulted in the saturation pressure of nitrogen, and measured saturation pressure under experimental conditions was 603 to 626 torr in Golden and 757 to 766 torr in Houston. Different masses of hand-ground < 40-mesh powder splits were used (~ 3 g in Houston and ~5 g in Golden).

The comparison of raw adsorption data suggests that measurements in the Golden laboratory reported systematically higher amounts of adsorbed gas compared with the Houston laboratory for all samples. The inversion methodology and parameters of the experimental data were consistent for all samples. The inverted SSA (using the BET method), total specific pore volume (using the Gurevich rule), and PSD (using the BJH method with Harkins-Jura curve) are systematically higher when measured in Golden compared with Houston (Table 3; Figure 6).

The average relative variation in measured BET SSA for the five samples is about 10.5% (1.4% to 17.9%), and the average relative variation in the measured total specific pore volume is 7.2% (5.4% to 9.1%). The PSD shows similarly consistent profiles and shapes with similar modes; however, the partial volumes varied within 10% to 20% (Figure 6). This uncertainty in the inverted pore-structure attributes is caused by uncontrolled experimental variations. A reproducibility study (Klobes et al., 2006) on a certified mesoporous material CRM BAM-PM-103 which involved 25 laboratories reported a variation of 9.2% in SSA using the BET method (mean of 156.0 m²/g) and variation of 6.4% in specific pore volume using the BJH method (mean 0.250 cm³/g).

Summary

Our conclusions are:

- 1) An intact shale sample might have slow diffusivity and incomplete equilibrium during nitrogen gas-adsorption analysis (at 77°K). Crushed hand-ground < 40-mesh powder is recommended for such

analysis in mudrocks. Crushing to < 40 mesh does not potentially damage the pore structure in the range of investigation of as much as 200 nm.

- 2) Linear dV/d(logD) ordinate versus logarithmic pore-size abscissa plots are recommended for PSD data representation.
- 3) BJH inversion is preferred over DFT inversion.
- 4) The *t*-plot and BJH inverted results depend on the choice of thickness equation. It follows that any thickness equation can be used as long as it is consistent across a sample set or comparison. The Harkins-Jura thickness curve is preferred for mudrock application. Furthermore, the results should be used in a semiquantitative way to understand the difference in pore structure among samples of interest.
- 5) The average experimental uncertainty of measured specific surface area and total specific pore volume is 10.5 relative percent and 7.2 relative percent. The pore-size distribution shows similar modes; however, the partial volumes varied between 10 and 20 relative percent. **TLE**

| Sample | BET SSA (m ² /g) | | Total specific pore volume* (cm ³ /g) | |
|--------|-----------------------------|---------|--|---------|
| | Golden | Houston | Golden | Houston |
| SS2-1 | 26.28 | 23.29 | 0.0309 | 0.0287 |
| SS2-2 | 9.73 | 9.26 | 0.0208 | 0.0197 |
| SS2-3 | 8.99 | 8.87 | 0.0273 | 0.0257 |
| SS2-4 | 18.65 | 15.59 | 0.0333 | 0.0304 |
| SS2-5 | 4.41 | 3.87 | 0.0140 | 0.0131 |

*Single-point adsorption-specific pore volume of pores with less than 149.1-nm diameter, calculated by the Gurevich rule. Quantity adsorbed interpolated at P/P₀ = 0.987.

Table 3. Results of reproducibility test for laboratories in Golden and in Houston.

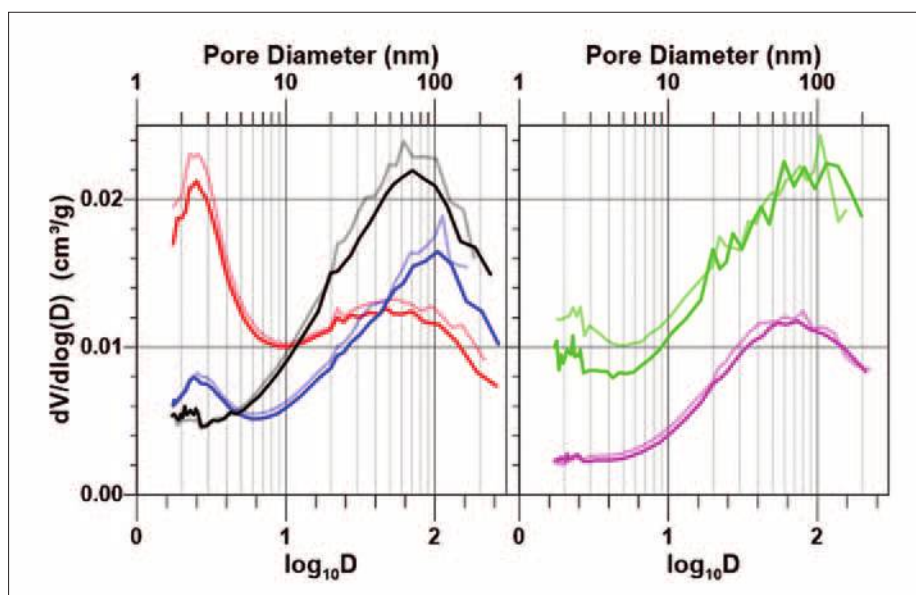


Figure 6. Comparison of PSD for different samples measured in Golden (lighter shade) and in Houston (darker shade). (a) Red = SS2-1, blue = SS2-2, black = SS2-3. (b) Green = SS2-4, magenta = SS2-5.

References

- Adesida, A., 2011, Pore size distribution of Barnett Shale using nitrogen adsorption data: M.S. thesis, University of Oklahoma.
- Chalmers, G. R., R. M. Bustin, and I. M. Power, 2012, Characterization of gas shale pore systems by porosimetry, pycnometry, surface area, and field emission scanning electron microscopy/transmission electron microscopy image analyses: Examples from the Barnett, Woodford, Haynesville, Marcellus, and Doig units: AAPG Bulletin, **96**, no. 6, 1099–1119, <http://dx.doi.org/10.1306/10171111052>.
- Clarkson, C. R., J. Wood, S. E. Burgis, S. D. Aquino, and M. Freeman, 2012, Nanopore-structure analysis and permeability predictions for a tight gas siltstone reservoir by use of low-pressure adsorption and mercury-intrusion techniques: SPE Reservoir Evaluation & Engineering, **15**, no. 6, 648–661, <http://dx.doi.org/10.2118/155537-PA>.
- Clarkson, C. R., N. Solano, R. M. Bustin, A. M. M. Bustin, G. R. L. Chalmers, L. He, Y. B. Melnichenko, A. P. Radlinski, and T. P. Blach, 2013, Pore structure characterization of North American shale gas reservoirs using USANS/SANS, gas adsorption, and mercury intrusion: Fuel, **103**, 606–616, <http://dx.doi.org/10.1016/j.fuel.2012.06.119>.
- Curtis, M. E., B. J. Cardott, C. H. Sondergeld, and C. S. Rai, 2012, Development of organic porosity in the Woodford Shale with increasing thermal maturity: International Journal of Coal Geology, **103**, 26–31, <http://dx.doi.org/10.1016/j.coal.2012.08.004>.
- Klobes, P., K. Meyer, and R. G. Munro, 2006, Porosity and specific surface area measurements for solid materials: U. S. Department of Commerce, Technology Administration, National Institute of Standards and Technology.
- Kuila, U., and M. Prasad, 2013, Specific surface area and pore-size distribution in clays and shales: Geophysical Prospecting, **61**, no. 2, 341–362, <http://dx.doi.org/10.1111/1365-2478.12028>.
- Luffel, D. L., and F. K. Guidry, 1989, Core analysis results, comprehensive study wells, Devonian shale: Topical Report GRI-89-0151: Gas Research Institute; Restech.
- Mbia, E. N., I. L. Fabricius, and C. O. Oji, 2013, Equivalent pore radius and velocity of elastic waves in shale: Skjold Flank-1 Well, Danish North Sea: Journal of Petroleum Science Engineering, **109**, 280–290, <http://dx.doi.org/10.1016/j.petrol.2013.08.026>.
- McCarty, D. K., 2002, Quantitative mineral analysis of clay-bearing mixtures: The “Reynolds Cup” Contest: IUCr CPD Newsletter, **27**, 12–16.
- Mehmani, A., M. Prodanović, and F. Javadpour, 2013, Multiscale, multiphysics network modeling of shale matrix gas flows: Transport in Porous Media, 1–14.
- Meyer, K., and P. Klobes, 1999, Comparison between different presentations of pore size distribution in porous materials: Fresenius' Journal of Analytical Chemistry, **363**, no. 2, 174–178, <http://dx.doi.org/10.1007/s002160051166>.
- Milliken, K. L., M. Rudnicki, D. N. Awwiller, and T. Zhang, 2013, Organic matter-hosted pore system, Marcellus Formation (Devonian), Pennsylvania: AAPG Bulletin, **97**, no. 2, 177–200, <http://dx.doi.org/10.1306/07231212048>.
- Prasad, M., 2003, Velocity-permeability relations within hydraulic units: Geophysics, **68**, no. 1, 108–117, <http://dx.doi.org/10.1190/1.1543198>.
- Rouquerol, J., D. Avnir, C. W. Fairbridge, D. H. Everett, J. H. Haynes, N. Pernicone, J. D. F. Ramsay, K. S. W. Sing, and K. K. Unger, 1994, Recommendations for the characterization of porous solids (Technical Report): Pure and Applied Chemistry, **66**, no. 8, 1739–1758, <http://dx.doi.org/10.1351/pac199466081739>.
- Webb, P. A., and C. Orr, 1997, Analytical methods in fine particle technology: Micromeritics.
- Zimmerman, R. W., W. H. Somerton, and M. S. King, 1986, Compressibility of porous rocks: Journal of Geophysical Research: Solid Earth, **91**, no. B12, 12765–12777, <http://dx.doi.org/10.1029/JB091iB12p12765>.

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