



# Combining mercury thermoporometry with integrated gas sorption and mercury porosimetry to improve accuracy of pore-size distributions for disordered solids



Buhari Bafarawa<sup>a</sup>, Artjom Nepryahin<sup>a</sup>, Lu Ji<sup>b</sup>, Elizabeth M. Holt<sup>c</sup>, Jiawei Wang<sup>d</sup>, Sean P. Rigby<sup>a,\*</sup>

<sup>a</sup> Department of Chemical and Environmental Engineering, University of Nottingham, University Park, Nottingham NG7 2RD, United Kingdom

<sup>b</sup> Department of Chemical and Environmental Engineering, University of Nottingham, Ningbo, China

<sup>c</sup> Johnson Matthey, P.O. Box 1, Belasis Avenue, Billingham, Cleveland, United Kingdom

<sup>d</sup> School of Chemical Engineering and Analytical Science, University of Manchester, Manchester M13 9PL, United Kingdom

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## ABSTRACT

The typical approach to analysing raw data, from common pore characterization methods such as gas sorption and mercury porosimetry, to obtain pore size distributions for disordered porous solids generally makes several critical assumptions that impact the accuracy of the void space descriptors thereby obtained. These assumptions can lead to errors in pore size of as much as 500%. In this work, we eliminated these assumptions by employing novel experiments involving fully integrated gas sorption, mercury porosimetry and mercury thermoporometry techniques. The entrapment of mercury following porosimetry allowed the isolation (for study) of a particular subset of pores within a much larger interconnected network. Hence, a degree of specificity of findings to particular pores, more commonly associated with use of templated, model porous solids, can also be achieved for disordered materials. Gas sorption experiments were conducted in series, both before and after mercury porosimetry, on the same sample, and the mercury entrapped following porosimetry was used as the probe fluid for thermoporometry. Hence, even if one technique, on its own, is indirect, requiring unsubstantiated assumptions, the fully integrated combination of techniques described here permits the validation of assumptions used in one technique by another. Using controlled-pore glasses as model materials, mercury porosimetry scanning curves were used to establish the correct correspondence between the appropriate Gibbs–Thomson parameter, and the nature of the meniscus geometry in melting, for thermoporometry measurements on entrapped mercury. Mercury thermoporometry has been used to validate the pore sizes, for a series of sol–gel silica materials, obtained from mercury porosimetry data using the independently-calibrated Kloupek correlations. The pore sizes obtained for sol–gel silicas from porosimetry and thermoporometry have been shown to differ substantially from those obtained via gas sorption and NLDFT analysis. DRIFTS data for the samples studied has suggested that the cause of this discrepancy may arise from significant differences in the surface chemistries between the samples studied here and that used to calibrate the NLDFT potentials.

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## 1. Introduction

Disordered porous solids, such as sol–gel silicas, are used in many applications, including as catalyst supports or chromatographic media. The performance of these materials in these applications depends strongly upon the structural characteristics of the void space. Experimental methods such as gas sorption or mercury porosimetry are generally used to obtain the pore size

distributions (PSDs) for these materials. The most recent data analysis methods, to interpret raw gas sorption isotherm data for disordered materials, have been developed from studies using more ordered, model materials, such as MCM-41 and SBA-15 [1,2]. However, it is not clear that the theories and techniques developed for more regular structures, such as these, will give accurate PSDs for disordered materials with more complex and amorphous internal pore geometry, and more extensive void space interconnectivity. Previous work has suggested that conventional data analysis methods for gas sorption, such as the Barrett–Joyner–Halenda (BJH) algorithm and non-local density functional

\* Corresponding author.

E-mail address: [enzspr@exmail.nottingham.ac.uk](mailto:enzspr@exmail.nottingham.ac.uk) (S.P. Rigby).

theory (NLDFT) software, neglect effects such as variations in the causes of hysteresis around the boundary sorption curves, advanced condensation, and delayed adsorption [3–5]. These effects can result in errors of as much as 500% in a PSD [4]. It is thus necessary to both assess the level of systematic error introduced by these effects, and others, into the PSDs for disordered solids, and develop methods to remove this error.

Mercury porosimetry is still a frequently used characterisation method because it remains a rare technique that can provide data over the complete length-scale range from  $\sim 3$  nm to  $\sim 100$   $\mu$ m in a single experiment. Mercury porosimetry relies upon the principle that mercury is a non-wetting fluid for most surfaces, and, thence, ever increasing pressures are required to intrude it into ever smaller pores, according to the Washburn [6] equation. The constant of proportionality between imposed pressure and inverse pore size depends upon the contact angle and surface tension of mercury. The macroscopic contact angle can readily be measured using techniques such as the sessile drop experiment. However, there is often doubt as to whether the macroscopic measurement applies to mercury menisci with a small radius of curvature. Previous workers have attempted to calibrate the physical properties term in the Washburn equation using model materials with independently known pore sizes, such as controlled pore glass (CPG) [7,8].

Frequently, only the mercury porosimetry intrusion curve is used, for the purposes of obtaining a pore neck size distribution, and the extrusion curve is neglected. This is because, in general, the physical processes involved in retraction are more complex than those involved in intrusion. The variety of phenomena involved in retraction, such as contact angle hysteresis, snap-off, and entrapment, mean that interpretations of the retraction curve are often ambiguous, and highly model dependent. However, some workers have attempted to use mercury retraction data to determine pore network connectivity [9] or macroscopic heterogeneity in the spatial distribution of pore size [10]. These attempts at interpreting mercury retraction are often based upon results from glass, plastic or metal micromodels [11,12]. Partly as a means to improve the interpretation of retraction curves, Rigby and co-workers [13–15] introduced the integrated nitrogen sorption and mercury porosimetry technique. This method employs a series of alternating gas sorption and mercury porosimetry experiments carried out on the same single sample, with any mercury entrapped following a porosimetry experiment frozen in place before a subsequent gas sorption experiment is performed. The difference between the gas sorption isotherms before and after mercury entrapment can be used to infer information about the distribution of entrapped mercury, and thence, the retraction process.

In order to interpret properly the mercury porosimetry data from integrated experiments it is necessary to employ calibrated versions of the Washburn equation. Kloubek [8] obtained expressions for the variation of the surface tension and contact angle term with pore size, for both intrusion and extrusion, from the experimental data of Liabastre and Orr [7]. Liabastre and Orr [7] measured the pressures required for intrusion into, and extrusion from, controlled pore glasses (CPGs) for which the pore size could be obtained independently using electron microscopy. Rigby and co-workers [16,17] found that the Kloubek correlations could be used, with no amendments, to remove apparent contact angle hysteresis, and obtain superposition of the intrusion and extrusion curves, for some sol–gel silica materials with the same surface fractal dimension as the original CPG materials used by Liabastre and Orr [7]. Silica materials with different degrees of surface roughness required amendments to the Kloubek correlations to achieve a similar superposition [17]. These trends in the effects of surface roughness on hysteresis were also observed in results from mean-field density functional theory (MFDFT) simulations of mercury intrusion and extrusion on models with rough surfaces [17].

These findings suggested that mercury porosimetry hysteresis was a function of surface chemistry and roughness, and supported the use of the Kloubek [8] correlations to analyse porosimetry data for some sol–gel silicas. As will be seen below, analysing porosimetry data with the Kloubek correlations also allows an estimate to be made of the pore sizes that entrap mercury, but the method is indirect. The validity of the Kloubek correlations will be tested directly using mercury porosimetry scanning loops.

In the integrated method, the gas sorption isotherms can only probe the void space remaining externally accessible, and not the entrapped mercury itself. In this work, thermoporometry, using differential scanning calorimetry (DSC) will be used to probe the entrapped mercury directly. Thermoporometry is the determination of pore sizes from the melting or freezing point depression of fluids imbibed within pores. Previous work [18,19] on the freezing and melting of metals in porous solids has focused more on studying the internal structural changes in the metal, and the freezing and thawing mechanisms, rather than determining pore structural information. Further, where the DSC data was used to infer metal ganglia sizes the relevant Gibbs–Thomson parameter was determined from uncalibrated mercury porosimetry data.

In this work, the calibration of the constants of proportionality in the Washburn and Gibbs–Thomson equation will be given more attention, with a view to studying the consistency of the pore structural information obtained from the three methods, gas sorption, mercury porosimetry, and thermoporometry. The difference between the comparison of results for these different techniques presented here, and that made previously by others [20,21], is that exactly the same sample can be used to make a comparison, and, additionally, that comparison can be further narrowed to a particular sub-set of pores within a disordered material, rather than comparing overall PSDs. Hence, the integrated technique can approach the degree of definitive study permitted for templated model materials, via their high levels of order, but for amorphous, disordered materials. This work will also attempt to reduce the number of arbitrary assumptions that have been necessary for indirect characterisation methods in the past, such as the geometry of the meniscus at the phase transition and the applicability of physical parameters calibrated on model materials. Finally, this work will consider a potential explanation for the discrepancies observed between the different experimental techniques.

## 2. Experimental

The model material used in this work was the CPG PG24080-10CCM, (purchased from Sigma–Aldrich), denoted CPG1 here. The manufacturers report that the pore size is 24 nm. This has been confirmed by electron microscopy. The other samples used in this work were commercially available sol–gel silica spheres G2, S1 and S2. Details of these materials are given in earlier work [13–15,17].

### 2.1. Mercury porosimetry

The experiments were carried out using a Micromeritics Auto-pore IV 9500, which is capable of obtaining pressures of 414 MPa. Prior to any experiment, the samples were dried under vacuum to a temperature of 150 °C for 15 h. The purpose of the thermal treatment was to drive off any physisorbed water content on the sample but leave the morphology of the sample unchanged. Blank corrections were made before the experiments using the formula provided by the manufacturer. The sample, consisting of  $\sim 10$  pellets, was first evacuated to a pressure of 6.7 Pa under a low pressure analysis in order to remove physisorbed water from the interior of the pore sample. The standard equilibration times used in the experiments were 10 and 30 s, with the two different values

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