How reproducible are surface areas calculated from the BET equation?

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To the editor:

The Brunauer-Emmett-Teller (BET) equation is arguably one of the most used equations in physical chemistry and porosimetry. Since its conception in the 1930s[1] to estimate open surfaces whilst working with adsorbents of the time such as Fe/Cu catalysts, silica gel, and charcoal, it has found widespread use in the characterisation of synthetic zeolites.[2] Furthermore, it gained considerable momentum following the discovery of more complex porous materials such as mesoporous silicas,[3] porous coordination polymers (PCPs),[4] metal-organic frameworks (MOFs),[5] and covalent organic frameworks (COFs).[6] Novel porous materials are of significant academic and industrial interest due to their applications in gas storage and separation,[7–10] catalysis,[11] and drug delivery,[12] and the BET area is their *de facto* standard for the characterisation. It has been recognized by the International Union of Pure and Applied Chemistry (IUPAC) as "the most widely used procedure for evaluating the surface area of porous and finely-divided materials",[13,14] and it has been an International Organization for Standardization (ISO) standard for surface area determination since 1995.[15] Whilst concerns over the applicability of the BET theory for microporous materials are important, it remains, arguably, the most important figure of merit for porous materials. Given the broad use of the BET equation, it is not surprising to see that much has been written on the *applicability* and the *accuracy* of the BET theory – that is, its model of the adsorption process – and on the reproducibility of the raw data, *i.e.* the adsorption isotherm.[16–20]

The advent of materials with more complex pore networks and dynamic frameworks through material design strategies such as reticular chemistry has boosted interest in BET theory (**Figure S1**) and given rise to reported BET areas in excess of 8,000 m^2 g^{-1}.[8,21,22] Often, these modern materials have complex adsorption isotherms that are more problematic or ambiguous to fit to the BET model, *e.g.* several steps can occur due to different pore types and/or flexibility being present in the material.[23] Whilst adsorption rigs capable of ultra-low pressure (<10^{-5} mbar) recordings have been developed, reliance on manual calculations of BET areas remains commonplace. In this context, 'manual' refers to the judicious selection of the *optimal pressure range* by a scientist, be it through a self-developed spreadsheet or commercial software. This raises the question of the *reproducibility* of BET calculations *from the same measured isotherm* but from different assessors.

The eponymously named Rouquerol criteria (**Section S2**, Supplementary Information) aim to ensure good practice in identifying a valid fitting range, and, as such, they have found widespread acceptance in the literature and have been adopted in both IUPAC and ISO standards.[13–15,17,18,24,25] Despite this safeguard, we herein propose that current BET area calculations are many times irreproducible for two reasons: first, the Rouquerol criteria are indeterminate in identifying the correct

fitting region, as they apply to multiple regions simultaneously. Second, even if they were determinate, they are too cumbersome and lengthy to be systematically implemented and are therefore often neglected in practice.

To prove our hypothesis and to assess the current spread of BET calculation results, we have shared a set of 18 experimental isotherms representing four classes of porous materials (zeolites, mesoporous silicas, MOFs, and COFs) with 60 laboratories with expertise in adsorption science and synthesis of porous materials. In this round-robin exercise, we asked the researchers to calculate the BET areas in the way they saw most fit. More details about the specific materials and the adsorption isotherms, sampled both from our laboratory and from the NIST/ARPA-E database,[26] are included in the Supplementary Information, **Section S12**. To avoid any recognition bias, all isotherms were anonymised and scaled off arbitrarily.

In parallel, we have developed a computational approach to calculating BET areas that only requires the adsorption isotherm as input data. The BET Surface Identification (BETSI) algorithm, steps through *all* possible fitting regions and outputs a full distribution of BET areas that are consistent under the Rouquerol criteria. We further propose an addition to the criteria that makes, for the first time, an unambiguous assignment of BET areas from an adsorption isotherm possible: the ideal fitting range ends on the highest permissible pressure point under all criteria, representing the end of the bulk adsorptive activity of the material, *i.e.* the isotherm knee. Further, it is chosen as having the lowest percentage error under the last Rouquerol criterion. Further details on the BETSI algorithm and the extension of the Rouquerol criteria can be found in **Section S3**, and a more detailed description in **Section S14**. The source code is fully published under GitHub https://github.com/fairen-group/betsi-gui.

Figure 1 shows the comparison between BET areas calculated by researchers in the round-robin evaluation and using BETSI. Bar a few exceptions, virtually no two groups of experts reported identical BET areas for any given isotherm. The results are fully tabulated and graphically represented in **Section S4** and **Section S5** respectively. We observed a spread of at least 300 m^2 g^{-1} for each isotherm; however, that number was significantly higher for some individual isotherms. For NU-1104, a modern MOF with substantial porosity[22] the highest estimate of 9,341 m^2 g^{-1} and the lowest estimate of 1,757 m^2 g^{-1} differed by an astonishing 7,584 m^2 g^{-1}, making the highest estimate more than five times higher than the lowest one. Most groups (90%) reported using the Rouquerol criteria in their manual calculation, 23% used a commercial software package, and 6% used a self-developed code. Full details on each individual group's methods can be found in **Section S13**.

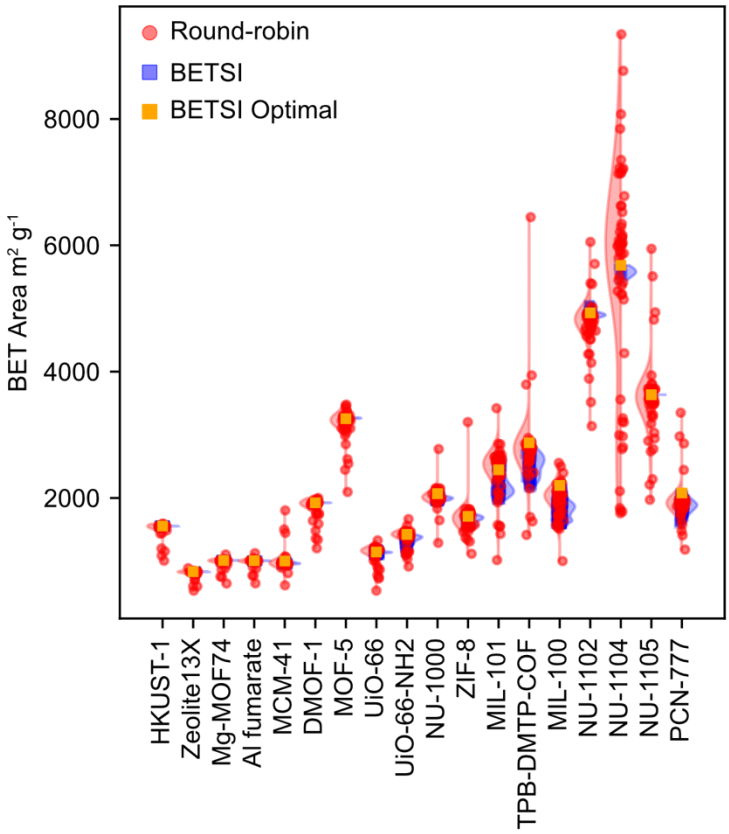

Figure 1 | Round-robin results and BETSI results. Distribution of BET areas from identical isotherms as calculated by 60 laboratories with expertise in adsorption science and synthesis of porous materials in red. Superimposed are normalised probability distribution functions obtained by kernel density estimation. Predictions under BETSI are shown in blue alongside, and the 'optimal' BET area in yellow.

Under BETSI, on the other hand, whilst multiple BET areas are passed as valid, the spread of values was considerably narrower than that obtained by manual calculation (**Figure 1**; for full BETSI results, see **Section S6** and further comparative data **Section S7**, **Section S8, and Section S9**). From this, both our first and second hypotheses are substantiated: since BETSI calculates *all* valid BET areas, it proves that the Rouquerol criteria by themselves are indeterminate and that even full compliance does not guarantee an unambiguous answer. Besides, since the spread of all valid BET areas is narrower than that obtained in the round-robin exercise, it demonstrates how the manual and systematic implementation of the Rouquerol criteria is difficult and often neglected in practice. For instance, in the case of NU-1104, the range of estimates decreases from 7,500 $m^2\ g^{-1}$ in the social study to 235 $m^2\ g^{-1}$ under BETSI.

Interestingly, some isotherms returned under BETSI much larger spreads of results than others, suggesting that they BET model does not describe them as naturally and thus they were more susceptible to problems associated with the Rouquerol criteria; a trend that was mirrored in the round-robin evaluation. To further investigate the goodness of the isotherm fittings, we define the *BETSI Variation Coefficient* as the relative standard deviation of BETSI results, and the *Pass Rate* as the number of BET fits that pass under the Rouquerol criteria as a fraction of all potential fits.

Further, the *Hit Rate* expresses the fractional number of BET areas calculated in the round-robin exercise that lie within the BETSI range. **Figure 2** demonstrates the correlation between the *Pass Rate*, the *BETSI Variation Coefficient*, and the *Hit Rate*. Simply put, the more BET fits are valid, the greater the spread of possible BET areas is, and the more likely researchers are to satisfy the Rouquerol criteria in manual calculations; an alternative representation can be found in **Section S10**. From **Figure 2**, we classify adsorption isotherms into three broad categories, types A, B and C. Whilst it is difficult to generalise about the shape of these isotherms, we offer some discussion about common features in **Section S11**. Type A isotherms fit the BET model 'best'. Under BETSI, they have a relatively high Pass Rate and return a fairly narrow spread of results. Examples include materials such as Al fumarate, NU-1000, Zeolite-13X and MCM-41. Hit Rates greater than 70% are generally observed for these materials, suggesting that the majority of researchers did not struggle with the fittings. Type B isotherms only fit the BET model over a very limited range. These have extremely low Pass Rates, meaning that only a few BET fits are valid, which in turn will be spread narrowly. Examples include MOF-5, DMOF-1, NU-1104, HKUST-1, and NU-1105. For the latter, out of 9,409 hypothetical 10-point fits (the minimum point requirement for BET fits), only one is permissible under the Rouquerol criteria. Such prohibitively low Pass Rates make the correct BET assignment by hand virtually impossible and demonstrate the need for computational support. Type C isotherm fittings are arguably the most problematic. They have high Pass Rates and, concomitantly, they return large spreads of BET results. Typical materials that fit into this category are MIL-101, MIL-100, TPB-DMTP-COF and PCN-777. It is for these materials that the necessity to extend the Rouquerol criteria is demonstrated and the BETSI algorithm makes an unambiguous BET assignment possible.

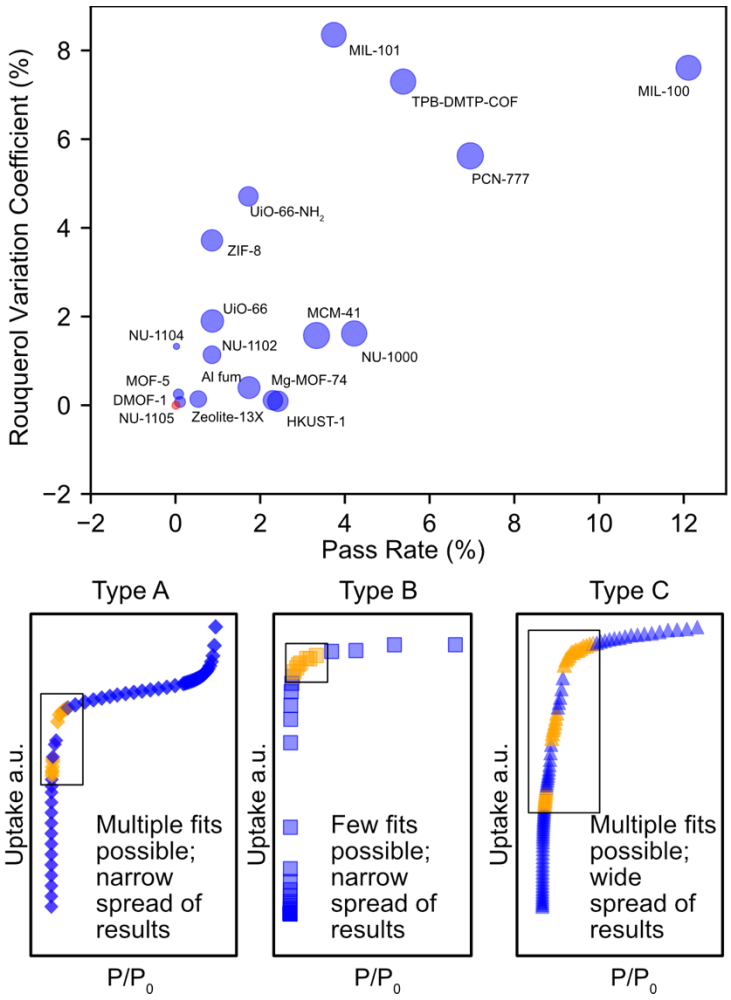

Figure 2 | Isotherm classifications. Plot of the BETSI Variation Coefficient (relative standard deviation of BETSI results) against the Pass Rate (fraction of valid fits against all hypothetical ones). Bubble size scales with the Hit Rate, the fraction of results from the social study that lie within the BETSI range. Red symbols have a Hit Rate of zero. Note the positive correlation between all three parameters. Isotherm fit classifications. Type A fits have a relatively wide fitting window, within which multiple fits are possible, but return a relatively narrow spread of BET results. Type B fits have a narrow fitting window and concomitantly return a narrow set of spread of results. Type C fits have wide fitting windows, which translates to multiple passable fits and a wide spread of permissible BET areas.

In conclusion, BET theory is a great success story. Developed in the 1930s for open surfaces, it continues to be applied to modern adsorbents with complex porosities. Despite the advances from classical density functional theory (DFT) methods, the BET area will likely continue playing a crucial role in porosimetry for decades to come, with impacts in energy research, transport, medical applications and climate-change mitigation. In light of these future developments, it will become increasingly important to share critical scientific metrics reliably to find a common language to report both academic and industrial progress.

Here, we have demonstrated the difficulties in unambiguously determining BET areas from adsorption isotherms, which in turn affect the assessment of material quality and reproducibility. These problems arise from imperfect and insufficient manual calculations and can only be met using modern computational methods. BETSI is a step towards greater transparency and critical

assessment in reporting BET areas. We stress here that it is neither the function nor the purpose of BETSI to eliminate doubt and treat a particular BET area as 'true'. Researchers should remain aware of the limitations of BET theory when applied to microporous adsorbents in general and when BET areas are reported, the pressure range and number of points used should always be stated. We further recommend here that isotherms must be reported transparently and in detail, *i.e*. semi-log representation to show the low-pressure regions. The 'experiment' is the adsorption isotherm – not the BET area.

Online Content

Any methods, additional references, source data, extended data, supplementary information, acknowledgements, peer review information; details of author contributions and competing interests are available at request.

Isotherm data reported with this paper are included in the NIST/ARPA-E Database of Novel and Emerging Adsorbent Materials, https://adsorption.nist.gov, and may be accessed directly at https://adsorption.nist.gov/isodb/index.php?DOI=10.XXXX/YYYYY#biblio.

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