How reproducible are surface areas calculated from the BET equation?

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123 **To the editor:**

124 The Brunauer-Emmett-Teller (BET) equation is arguably one of the most used equations in physical
125 chemistry and porosimetry. Since its conception in the 1930s¹ to estimate open surfaces whilst
126 working with adsorbents of the time such as Fe/Cu catalysts, silica gel, and charcoal, it has found
127 widespread use in the characterisation of synthetic zeolites.² Furthermore, it gained considerable
128 momentum following the discovery of more complex porous materials such as mesoporous silicas,³
129 porous coordination polymers (PCPs),⁴ metal-organic frameworks (MOFs),⁵ and covalent organic
130 frameworks (COFs).⁶ Novel porous materials are of significant academic and industrial interest due
131 to their applications in gas storage and separation,^{7–10} catalysis,¹¹ and drug delivery,¹² and the BET
132 area is their *de facto* standard for the characterisation. It has been recognized by the International
133 Union of Pure and Applied Chemistry (IUPAC) as “the most widely used procedure for evaluating
134 the surface area of porous and finely-divided materials”,^{13,14} and it has been an International
135 Organization for Standardization (ISO) standard for surface area determination since 1995.¹⁵ Whilst
136 concerns over the applicability of the BET theory for microporous materials are important, it remains,
137 arguably, the most important figure of merit for porous materials. Given the broad use of the BET
138 equation, it is not surprising to see that much has been written on the *applicability* and the *accuracy*
139 of the BET theory – that is, its model of the adsorption process – and on the reproducibility of the
140 raw data, *i.e.* the adsorption isotherm.^{16–19}

141 The advent of materials with more complex pore networks and dynamic frameworks through
142 material design strategies such as reticular chemistry has boosted interest in BET theory (**Figure**
143 **S1**) and given rise to reported BET areas in excess of 8,000 m² g⁻¹.^{8,20,21} Often, these modern
144 materials have complex adsorption isotherms that are more problematic or ambiguous to fit to the
145 BET model, *e.g.* several steps can occur due to different pore types and/or flexibility being present
146 in the material.²² Whilst adsorption rigs capable of ultra-low pressure (<10⁻⁵ mbar) recordings have
147 been developed, reliance on manual calculations of BET areas remains commonplace. In this
148 context, ‘manual’ refers to the judicious selection of the *optimal pressure range* by a scientist, be it
149 through a self-developed spreadsheet or commercial software. This raises the question of the
150 *reproducibility* of BET calculations *from the same measured isotherm* but from different assessors.

151 The eponymously named Rouquerol criteria (**Section S2**, Supplementary Information) aim to
152 ensure good practice in identifying a valid fitting range, and, as such, they have found widespread
153 acceptance in the literature and have been adopted in both IUPAC and ISO standards.^{13–15,17,18,23,24}
154 Despite this safeguard, we herein propose that current BET area calculations are many times
155 irreproducible for two reasons: first, the Rouquerol criteria are indeterminate in identifying the correct
156 fitting region, as they apply to multiple regions simultaneously. Second, even if they were
157 determinate, they are too cumbersome and lengthy to be systematically implemented and are
158 therefore often neglected in practice.

159 To prove our hypothesis and to assess the current spread of BET calculation results, we have
160 shared a set of 18 experimental isotherms representing four classes of porous materials (zeolites,
161 mesoporous silicas, MOFs, and COFs) with 60 laboratories with expertise in adsorption science and
162 synthesis of porous materials. In this round-robin exercise, we asked the researchers to calculate
163 the BET areas in the way they saw most fit. More details about the specific materials and the
164 adsorption isotherms, sampled both from our laboratory and from the NIST/ARPA-E database,²⁵ are
165 included in the Supplementary Information, **Section S12**. To avoid any recognition bias, all
166 isotherms were anonymised and scaled off arbitrarily.

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

178 **Figure 1** shows the comparison between BET areas calculated by researchers in the round-
179 robin evaluation and using BETSI. Bar a few exceptions, virtually no two groups of experts reported
180 identical BET areas for any given isotherm. The results are fully tabulated and graphically
181 represented in **Section S4** and **Section S5** respectively. We observed a spread of at least 300 m²
182 g⁻¹ for each isotherm; however, that number was significantly higher for some individual isotherms.
183 For NU-1104, a modern MOF with substantial porosity²¹ the highest estimate of 9,341 m² g⁻¹ and the
184 lowest estimate of 1,757 m² g⁻¹ differed by an astonishing 7,584 m² g⁻¹, making the highest estimate
185 more than five times higher than the lowest one. Most groups (90%) reported using the Rouquerol
186 criteria in their manual calculation, 23% used a commercial software package, and 6% used a self-
187 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 m² g⁻¹ in the social study to 235 m² 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

211 exercise that lie within the BETSI range. **Figure 2** demonstrates the correlation between the *Pass*
212 *Rate*, the *BETSI Variation Coefficient*, and the *Hit Rate*. Simply put, the more BET fits are valid, the
213 greater the spread of possible BET areas is, and the more likely researchers are to satisfy the
214 Rouquerol criteria in manual calculations; an alternative representation can be found in **Section S10**.
215 From **Figure 2**, we classify adsorption isotherms into three broad categories, types A, B and C.
216 Whilst it is difficult to generalise about the shape of these isotherms, we offer some discussion about
217 common features in **Section S11**. Type A isotherms fit the BET model ‘best’. Under BETSI, they
218 have a relatively high Pass Rate and return a fairly narrow spread of results. Examples include
219 materials such as Al fumarate, NU-1000, Zeolite-13X and MCM-41. Hit Rates greater than 70% are
220 generally observed for these materials, suggesting that the majority of researchers did not struggle
221 with the fittings. Type B isotherms only fit the BET model over a very limited range. These have
222 extremely low Pass Rates, meaning that only a few BET fits are valid, which in turn will be spread
223 narrowly. Examples include MOF-5, DMOF-1, NU-1104, HKUST-1, and NU-1105. For the latter, out
224 of 9,409 hypothetical 10-point fits (the minimum point requirement for BET fits), only one is
225 permissible under the Rouquerol criteria. Such prohibitively low Pass Rates make the correct BET
226 assignment by hand virtually impossible and demonstrate the need for computational support. Type
227 C isotherm fittings are arguably the most problematic. They have high Pass Rates and,
228 concomitantly, they return large spreads of BET results. Typical materials that fit into this category
229 are MIL-101, MIL-100, TPB-DMTP-COF and PCN-777. It is for these materials that the necessity to
230 extend the Rouquerol criteria is demonstrated and the BETSI algorithm makes an unambiguous BET
231 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

254 BETSI to eliminate doubt and treat a particular BET area as ‘true’. Researchers should remain aware
255 of the limitations of BET theory when applied to microporous adsorbents in general and when BET
256 areas are reported, the pressure range and number of points used should always be stated. We
257 further recommend here that isotherms must be reported transparently and in detail, *i.e.* semi-log
258 representation to show the low-pressure regions. The ‘experiment’ is the adsorption isotherm – not
259 the BET area.

260

261 Online Content

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

265 Isotherm data reported with this paper are included in the NIST/ARPA-E Database of Novel and
266 Emerging Adsorbent Materials, <https://adsorption.nist.gov>, and may be accessed directly at
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