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► **To cite this version:**

Johannes Osterrieth, James Rampersad, David Madden, Nakul Rampal, Luka Skoric, et al.. How Reproducible Are Surface Areas Calculated from the BET Equation?. 2021. hal-03453291

HAL Id: hal-03453291

<https://hal.science/hal-03453291>

Preprint submitted on 28 Nov 2021

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1 How reproducible are surface areas calculated from the BET 2 equation?

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128 **To the editor:**

129 The Brunauer-Emmett-Teller (BET) equation is arguably one of the most used equations in physical
130 chemistry and porosimetry. Since its conception in the 1930s¹ to estimate open surfaces whilst
131 working with adsorbents of the time such as Fe/Cu catalysts, silica gel, and charcoal, it has found
132 widespread use in the characterisation of synthetic zeolites.² Furthermore, it gained considerable
133 momentum following the discovery of more complex porous materials such as mesoporous silicas,³
134 porous coordination polymers (PCPs),⁴ metal-organic frameworks (MOFs),⁵ and covalent organic
135 frameworks (COFs).⁶ Novel porous materials are of significant academic and industrial interest due
136 to their applications in gas storage and separation,^{7–10} catalysis,¹¹ and drug delivery,¹² and the BET
137 area is their *de facto* standard for the characterisation. It has been recognized by the International
138 Union of Pure and Applied Chemistry (IUPAC) as “the most widely used procedure for evaluating
139 the surface area of porous and finely-divided materials”,^{13,14} and it has been an International
140 Organization for Standardization (ISO) standard for surface area determination since 1995.¹⁵ Whilst
141 concerns over the applicability of the BET theory for microporous materials are important, it remains,
142 arguably, the most important figure of merit for porous materials. Given the broad use of the BET
143 equation, it is not surprising to see that much has been written on the *applicability* and the *accuracy*
144 of the BET theory – that is, its model of the adsorption process – and on the reproducibility of the
145 raw data, *i.e.* the adsorption isotherm.^{16–20}

146 The advent of materials with more complex pore networks and dynamic frameworks through
147 material design strategies such as reticular chemistry has boosted interest in BET theory (**Figure**
148 **S1**) and given rise to reported BET areas in excess of 8,000 m² g⁻¹.^{8,21,22} Often, these modern
149 materials have complex adsorption isotherms that are more problematic or ambiguous to fit to the
150 BET model, *e.g.* several steps can occur due to different pore types and/or flexibility being present
151 in the material.²³ Whilst adsorption rigs capable of ultra-low pressure (<10⁻⁵ mbar) recordings have
152 been developed, reliance on manual calculations of BET areas remains commonplace. In this
153 context, ‘manual’ refers to the judicious selection of the *optimal pressure range* by a scientist, be it
154 through a self-developed spreadsheet or commercial software. This raises the question of the
155 *reproducibility* of BET calculations *from the same measured isotherm* but from different assessors.

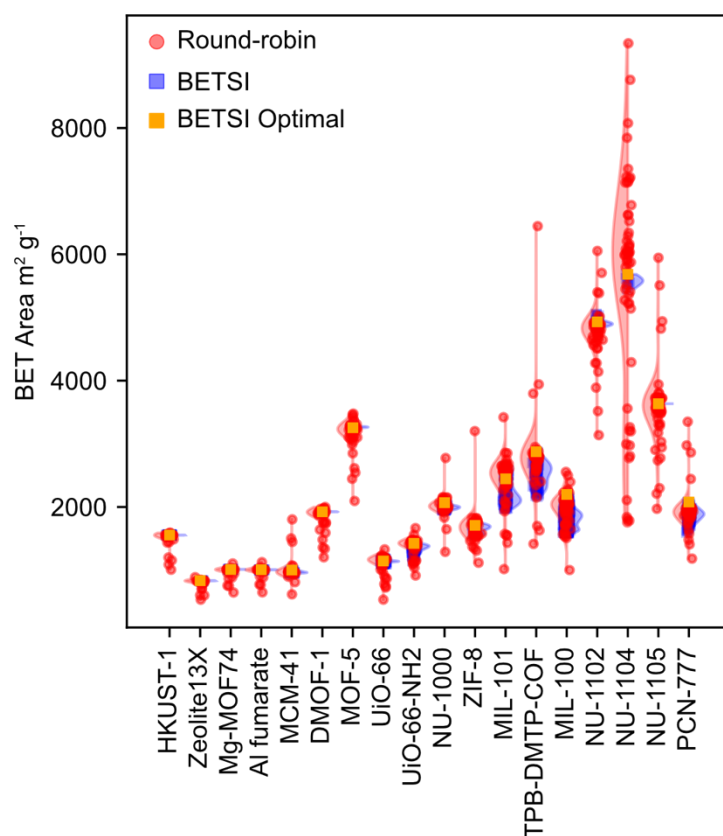
156 The eponymously named Rouquerol criteria (**Section S2**, Supplementary Information) aim to
157 ensure good practice in identifying a valid fitting range, and, as such, they have found widespread
158 acceptance in the literature and have been adopted in both IUPAC and ISO standards.^{13–15,17,18,24,25}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

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

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

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

183 **Figure 1** shows the comparison between BET areas calculated by researchers in the round-
184 robin evaluation and using BETSI. Bar a few exceptions, virtually no two groups of experts reported
185 identical BET areas for any given isotherm. The results are fully tabulated and graphically
186 represented in **Section S4** and **Section S5** respectively. We observed a spread of at least 300 m²
187 g⁻¹ for each isotherm; however, that number was significantly higher for some individual isotherms.
188 For NU-1104, a modern MOF with substantial porosity²² the highest estimate of 9,341 m² g⁻¹ and the
189 lowest estimate of 1,757 m² g⁻¹ differed by an astonishing 7,584 m² g⁻¹, making the highest estimate
190 more than five times higher than the lowest one. Most groups (90%) reported using the Rouquerol
191 criteria in their manual calculation, 23% used a commercial software package, and 6% used a self-
192 developed code. Full details on each individual group's methods can be found in **Section S13**.



193

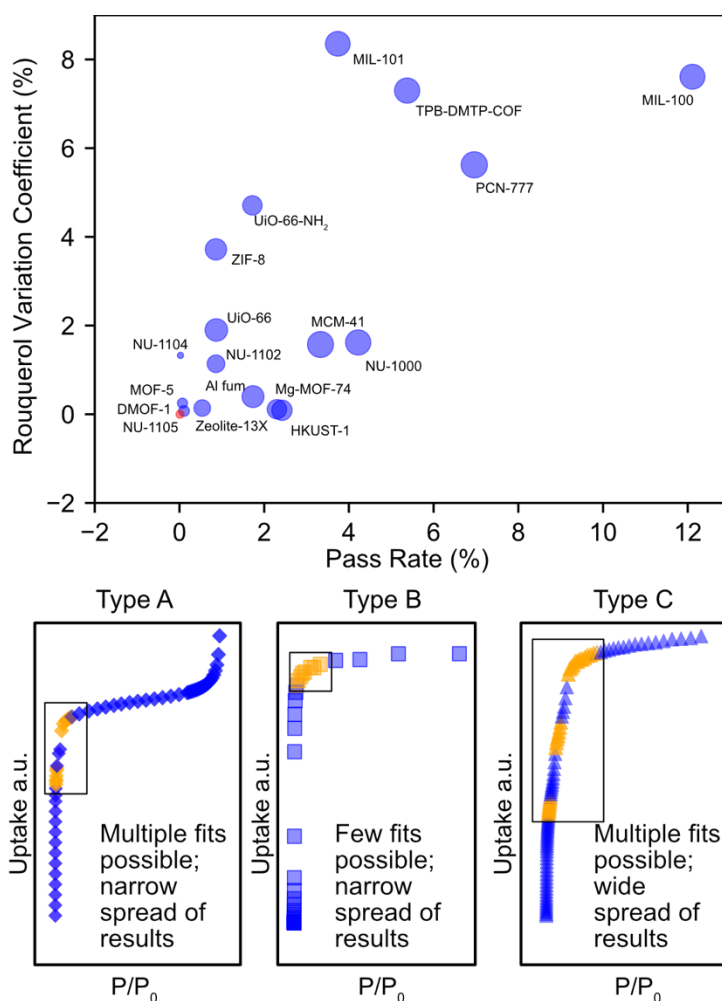
194 **Figure 1 | Round-robin results and BETSI results.** Distribution of BET areas from identical isotherms as
 195 calculated by 60 laboratories with expertise in adsorption science and synthesis of porous materials in red.
 196 Superimposed are normalised probability distribution functions obtained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

198

199 Under BETSI, on the other hand, whilst multiple BET areas are passed as valid, the spread of
 200 values was considerably narrower than that obtained by manual calculation (**Figure 1**; for full BETSI
 201 results, see **Section S6** and further comparative data **Section S7**, **Section S8**, and **Section S9**).
 202 From this, both our first and second hypotheses are substantiated: since BETSI calculates *all* valid
 203 BET areas, it proves that the Rouquerol criteria by themselves are indeterminate and that even full
 204 compliance does not guarantee an unambiguous answer. Besides, since the spread of all valid BET
 205 areas is narrower than that obtained in the round-robin exercise, it demonstrates how the manual
 206 and systematic implementation of the Rouquerol criteria is difficult and often neglected in practice.
 207 For instance, in the case of NU-1104, the range of estimates decreases from 7,500 m² g⁻¹ in the
 208 social study to 235 m² g⁻¹ under BETSI.

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

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



237

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

246

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

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

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

265

266 **Online Content**

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

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

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337 **Acknowledgements**

338 This project has received funding from the European Research Council (ERC) under the European
339 Union’s Horizon 2020 research and innovation programme (NanoMOFdeli), ERC-2016-COG
340 726380. D.F.-J. thanks the Royal Society for funding through a University Research Fellowship.
341 Mark Carrington is acknowledged for his contribution to the COF isotherm.

342 O.K.F. and R.Q.S. acknowledge funding from the U.S. Department of Energy (DE-FG02-
343 08ER15967).

344 R.S.F. and D.B. acknowledge funding from the European Research Council (ERC) under the
345 European Union’s Horizon 2020 research and innovation programme (SCoTMOF), ERC-2015-StG
346 677289.

347 Sandia National Laboratories is a multimission laboratory managed and operated by National
348 Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell
349 International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration
350 under contract DE-NA-0003525. The authors gratefully acknowledge funding from the U.S.
351 Department of Energy, Office of Energy Efficiency and Renewable Energy, Hydrogen and Fuel Cell
352 Technologies Office, through the Hydrogen Storage Materials Advanced Research Consortium
353 (HyMARC). This paper describes objective technical results and analysis. Any subjective views or
354 opinions that might be expressed in the paper do not necessarily represent the views of the U.S.
355 Department of Energy or the United States Government.

356 J.D.E acknowledges the support of the Alexander von Humboldt Foundation and the Center for
357 Information Services and High-Performance Computing (ZIH) at TU Dresden.

358 S.K.G. and S.M. acknowledge SERB (Project No. CRG/2019/000906), India for financial support.

359 K.K. and R.K. acknowledge Active Co. Research Grant for funding.

360 S.K. acknowledge funding from the European Research Council (ERC) under the European Union's
361 Horizon 2020 research and innovation programme (COSMOS), ERC-2017-StG 756489.

362 N.L. and J.G.M acknowledge funding from the European Commission through the H2020-MSCA-
363 RISE-2019 program (ZEOBIOCHEM – 872102) and the Spanish MICINN and AEI/FEDER
364 (RTI2018-099504-B-C21). N.L. thanks the University of Alicante for funding (UATALENTO17-05).

365 ICN2 is supported by the Severo Ochoa program from the Spanish MINECO (Grant No. SEV-2017-
366 0706)

367 S.M.J.R. and A.L wish to thank the Fund for Scientific Research Flanders (FWO), under grant nos.
368 12T3519N and 11D2220N. V.V.S. acknowledges the Research Board of the Ghent University and
369 funding from the European Union's Horizon 2020 research and innovation programme (consolidator
370 ERC grant agreement No. 647755 – DYNPOR (2015-2020)).

371 L.S. was supported by the EPSRC Cambridge NanoDTC EP/L015978/1

372 C.T.Y. and T.S.N. acknowledge funds from the National Research Foundation of Korea, NRF-
373 2017M3A7B4042140 and NRF-2017M3A7B4042235

374 P.F. and H. Y. acknowledge US Department of Energy, Office of Basic Energy Sciences, Materials
375 Sciences and Engineering Division under Award No. DE-SC0010596 (P.F.).

376 R.O would like to acknowledge funding support during his Ph.D study from Indonesian Endowment
377 Fund for Education-LPDP with the contract No. 202002220216006

378 S.W. and J.A. acknowledge funding from the Basque Government Industry Department under the
379 ELKARTEK and HAZITEK programs.

380 B.V.L, S.T.E and A.M.P acknowledge funding from the European Research Council (ERC) under
381 the European Union's Horizon 2020 Research and Innovation Program (Grant agreement no.

382 639233, COFLeaf), and the Deutsche Forschungsgemeinschaft (DFG) via the cluster of excellence
383 e-conversion (project number EXC2089/1-390776260).

384 VPT and JLR would like to acknowledge funding from the EPSRC (EP/R01650X/1).

385 M.A.v.d.V and D.R. are grateful for funding from the European Research Council (ERC) under the
386 European Union's Horizon 2020 research and innovation programme (grant agreement n° 759212)

387