Graphical Representation Reliability of Experimental Data Concerning to Structural and Surface Properties of Substances

D V Mayorov¹, T T Gorbacheva² and Yu O Velyaev³

¹Tananayev Institute of Chemistry and Technology of Rare Elements and Minerals Tananaeva, Kola Science Center Russian Academy of Sciences (ICTREM KSC RAS), 26a, Akademgorodok, Apatity, Murmansk Region, 184209, Russia
²Institute of Industrial Ecology of the North, Kola Science Center Russian Academy of Sciences (INEP KSC RAS), 14a, Akademgorodok, Apatity, Murmansk Region, 184209, Russia
³Polytechnical Institute, Sevastopol State University, 33, Universitetskaya, Sevastopol, 299053, Russia

E-mail: d.maiorov@ksc.ru

Abstract. Using experimental data on the pore distribution of a sample of magnesium-aluminum layered double hydroxide, various variants of their graphical representation are analyzed. It is shown that graphical interpretation of the obtained data in the coordinates \(dV/dD\) – \(D\) or \(dV/d\log(D)\) – \(D\) is not of practical (scientific) interest and may lead to incorrect conclusions about the predominance of pores of a certain diameter in the sample and other errors. It is concluded that to avoid possible errors and provide the most complete information about the pore distribution of the studied samples, the presented graphic materials should be supplemented with histograms of the pore distribution.

1. Introduction

In scientific and engineering literature, there are two approaches to presenting experimental porosimetry data. The first one is \(dV/dD\) – \(D\) or \(dV/d\log(D)\) – \(D\) [1–15] graphs, where the values of \(dV/dD\) (\(dV/d\log(D)\)) plotted along the Y axis are in \(\text{cm}^3/(g\cdot\text{nm})\) (or \(\text{cm}^3/(g\cdot\text{Å})\)). Here, \(V\) means pore volume (usually in \(\text{cm}^3/g\)) in a certain range of diameters \(D_{pore}\) (\(a < D_{pore} < b\), usually in nm or Å), while \(D\) means average pore diameter \(\langle D_{av}\rangle\) in this range, because it’s almost impossible to measure the pore volume for a predefined diameter value (for example, \(D = 5.629... \text{ nm}\)).

In the second approach, the particle volume distribution is also presented as \(dV/dD\) – \(D\), but the \(dV/dD\) values are expressed in \(\text{cm}^3/g\) [3, 6, 9, 16, 17]. This implies that there is a \(V – d\) relationship, which is explicitly indicated in [18].

However, we believe that both of these presentations are of little practical (scientific) interest and may lead to incorrect conclusions about the predominance of a certain pore diameter or total pore volume in a specimen.

This paper aims to show the incorrectness of such representations of experimental data and the resulting potentially erroneous conclusions, as well as the incompleteness of the information presented.
2. Experimental procedure and discussion

Table shows the experimental data on the pore diameter distribution in a specimen of magnesium-aluminum layered double hydroxide (Mg-Al LDH). The product was obtained by solid-phase synthesis by mixing crystalline magnesium and aluminum chlorides with ammonium carbonate and its composition can be described by the formula of Mg₄Al₂(OH)₁₂CO₃·3H₂O [19]. The pore distribution data for the specimen was collected using a TriStar 302 specific surface area and porosity analyzer based on nitrogen desorption isotherm using the BJH (Barret-Joyner-Halenda) method. Classification into pore size intervals (1÷10) and column names (a÷d) were added by us, as described below.

Table 1. Experimental data on specific volume and pore area distribution in the synthesized Mg-Al LDH specimen by pore diameter.

| Pore Diameter Range (nm) | Average Diameter (nm) | Incremental Pore Volume (cm³/g) | Cumulative Pore Volume (cm³/g) |
|-------------------------|-----------------------|---------------------------------|-------------------------------|
| No 10 214.9 ÷ 48.3      | 55.9                  | 0.022561                        | 0.022561                      |
| No 9 48.3 ÷ 24.9        | 29.6                  | 0.016884                        | 0.039445                      |
| No 8 24.9 ÷ 15.1        | 17.7                  | 0.014623                        | 0.054068                      |
| No 7 15.1 ÷ 12.1        | 13.3                  | 0.007331                        | 0.061400                      |
| No 6 12.1 ÷ 9.7         | 10.6                  | 0.007419                        | 0.068818                      |
|                          | 9.7 ÷ 8.1             | 0.005555                        | 0.074374                      |
| No 5 8.1 ÷ 6.9          | 7.4                   | 0.005206                        | 0.079580                      |
|                          | 6.9 ÷ 6.0             | 6.4                              | 0.084241                      |
|                          | 6.0 ÷ 5.2             | 5.5                              | 0.088448                      |
| No 4 5.2 ÷ 4.6          | 4.9                   | 0.003797                        | 0.092244                      |
|                          | 4.6 ÷ 4.1             | 4.3                              | 0.095744                      |
|                          | 4.1 ÷ 3.7             | 3.9                              | 0.099070                      |
| No 3 3.7 ÷ 3.3          | 3.5                   | 0.013257                        | 0.112327                      |
|                          | 3.3 ÷ 3.0             | 3.2                              | 0.117967                      |
|                          | 3.0 ÷ 2.8             | 2.9                              | 0.119446                      |
| No 2 2.8 ÷ 2.4          | 2.6                   | 0.000979                        | 0.120424                      |
|                          | 2.4 ÷ 2.3             | 2.3                              | 0.120756                      |
| No 1 2.3 ÷ 2.0          | 2.1                   | 0.000294                        | 0.121050                      |
|                          | 2.0 ÷ 1.8             | 2.9                              | 0.121157                      |

Based on the representation of the collected data in the form of a differential dV/dD – D distribution (Figure 1a), it can be concluded that pores with an average diameter of 3.5 nm predominate in the specimen, i.e. the distribution is monomodal. And that is the only conclusion that can be made. But the average value of a parameter (in this case, pore diameter) characterizes a given value range of the parameter (between a and b). Based on Figure 2a, this range remains unknown for both $D_{av} = 3.5$ nm and other values of $D_{av}$.

As can be seen from Table, for pores in the diameter interval 10 (48.3÷214.9 nm), the average diameter is 55.9 nm, which is not even the arithmetic mean value $D_{ar.mean} = (48.3 + 214.9) / 2 = 131.6$ nm and can probably be interpreted as a weighted average. Same applies to the interval 7-9 and, given a more precise calculation of $av$, is likely to be true for the other intervals. In addition, if the available hardware (or software) could produce data with a greater resolution (narrower pore diameter
ranges), one would probably see a slightly different distribution pattern and, accordingly, could draw completely different conclusions.

Some additional information can be obtained from the integral pore distribution by diameter (Figure 1b). Specifically, pores with an average diameter of 3.2 to 3.5 nm have a volume of 0.018897 cm$^3$/g, which is $\approx 15.6\%$ of the total pore volume (0.121157 cm$^3$/g (Table, column d)). This distribution pattern is detected without micropores, whose volume in this case is extremely small (less than 1%). This is insufficient for a prevailing value found on the basis of differential distribution data (Figure 1a). In addition, integral distribution gives only the average pore diameter value in a given interval, which does not answer the question about the actual pore diameter intervals.

Figure 1. Differential ($dV/dD - D$) (a) and integral (b; 1 – in cm$^3$/g; 2 – in %) pore distribution in the synthesized Mg-Al LDH specimen (desorption branch).

Visualizing porosimetry data (in this case, Table) as a histogram (Figure 2), which is identical to the data in Table, but easier to interpret, has no such drawbacks. Using such a histogram, it is possible to find the exact volume of the pores in a given pore diameter range. For example, Figure 2a shows detailed histograms for each of the pore volume ranges in Table, while Figure 2b (for convenience of interpretation) shows these for the combined intervals 1÷10 defined by us. In addition, it can be seen that the volume of macropores ($D_{\text{pore}} > 50$ nm) equal to 0.022561 cm$^3$/g is comparable with the volume of pores with $D_{\text{av}} = 3.5$ nm and amounts to $\approx 18.6\%$ of the total pore volume of the specimen. Thus, based on the data in Table or Figure 2, completely different conclusions can be drawn and more complete information about the porosity of the specimen can be obtained:

1. The Mg-Al LDH specimen is mesoporous (mesopore volume $\approx 80\%$ of the total pore volume).
2. Mesopore distribution ($2 < D_{\text{pore}} < 50$ nm) is polymodal dominated by pores with $D_{\text{av}} = 3.5$, 17.7, and 29.6 nm in the diameter ranges 3.3÷3.7, 15.1÷24.9, and 24.9÷48.3 nm, respectively.

Conclusion 2 indicates that the conclusion about the monomodality of the pore distribution and the predominance of pores with an average diameter of 3.5 nm, drawn from the data in Figure 1a, is erroneous.

The second approach to presenting the particle volume distribution ($V - D$) is also not without flaws and leads (upon detailed examination) to unexpected results. Figure 3 shows the pore volume distribution in a $V - d$ space (according to Table). In Figure 3a, the pore distribution is given with the preservation of experimental data points (which somewhat improves the situation), while in Figure 3b, the experimental data points are excluded (which is more common in the literature). By processing the data in Figure 3b (Figure 3c), we find the total (combined) pore volume of the specimen (Figure 3c), which is 0.121157 cm$^3$/g. The obtained value matches the experimental data, which is not surprising, since we know the position of the experimental data points and the curves were plotted using these. What if experimental data points are missing?
In Figure 3d, the total pore volume is found using additional data points ($D$ values) (dashed curves) while keeping the data points from Figure 3c. Here we see a total pore volume larger than the actual one (0.121157 cm$^3$/g) and, accordingly, higher than 100%. What if we find the total pore volume, not knowing the data in Table, based on other values of $D$? It is extremely unlikely that we will succeed and choose (i.e. guess) the actual values of $D$, based on which the curve is plotted, and accordingly, the actual pore volume value (0.121157 cm$^3$/g). Most likely, the values of $D$ will be different, and we will get a total pore volume value that is either lower or higher than the actual one.
In addition, such a distribution does not answer the question raised earlier concerning $D_{av}$ and the pore range corresponding to this value.

3. Conclusion

Thus, we believe that presenting pore diameter distribution in a $dV/dD$ or $dV/d\log(D)$ – $D$ and $V$ – $D$ space is not justified and may lead to erroneous conclusions. Most appropriate is presenting porosimetry data either in the form of Table or in the form of histograms (Figure 2 and [20–23]). If presenting the pore diameter distribution in a $dV/dD$ – $D$, $dV/d\log(D)$ – $D$, or $V$ – $D$ space conveys any additional information unknown to us, for the sake of clarity and completeness, the respective findings should be presented together with histograms.

References

[1] Schmitt M S, Fernandes C P, Fabiano G W, Bellini da Cunha Neto J A, Rahner C P and Santiago dos Santos V S 2015 Characterization of Brazilian tight gas sandstones relating permeability and Angstrom-to micron-scale pore structures Journal of Natural Gas Science and Engineering 27 785–807 Online. Available: https://doi.org/10.1016/j.jngse.2015.09.027

[2] Cervantes-Martinez C V, Emo M, Lebeau B, Garcia-Celmad M-J, Stébé M-J and Blin J-L 2019 Insights of the kolliphor/water system for the design of mesostructured silica materials Microporous and Mesoporous Materials 285 231–240 Online. Available: https://doi.org/10.1016/j.micromeso.2019.05.019

[3] Xiao D, Lu Z, Jiang S and Lu S 2016 Comparison and integration of experimental methods to characterize the full-range pore features of tight gas sandstoned. A case study in Songliao Basin of China Journal of Natural Gas Science and Engineering 34 1412–1421 Online. Available: http://dx.doi.org/10.1016/j.jngse.2016.08.029

[4] Trublet M, Maslova M V, Rusanova D and Antzutkin O N 2016 Mild syntheses and surface characterization of amorphous TiO(OH)(H$_2$PO$_4$)·H$_2$O ion-exchanger Materials Chemistry and Physics 183 467–475 Online. Available: http://dx.doi.org/10.1016/j.matchemphys.2016.09.002

[5] Maslova M V, Rusanova D, Naydenov V, Antzutkin O N and Gerasimova L G 2012 Extended study on the synthesis of amorphous titanium phosphates with tailored sorption properties Journal of Non-Crystalline Solids 358 2943–2950 Online. Available: https://doi.org/10.1016/j.jnoncrysol.2012.06.033

[6] Zhang L, Lu S, Xiao D and Gu M 2017 Characterization of full pore size distribution and its significance to macroscopic physical parameters in tight glutenites Journal of Natural Gas Science and Engineering 38 434–449 Online. Available: http://dx.doi.org/10.1016/j.jngse.2016.12.026

[7] Assaker K, Lebeau B, Michelin L, Gaudin P, Carteret C, Vidal L, Bonne M 2015 Blin J L 2015 Zn-TiO$_2$ mesoporous oxides prepared by mechanical milling Journal of Alloys and Compounds 649 1–10 Online. Available: http://dx.doi.org/10.1016/j.jallcom.2015.07.085

[8] Naboulsi I, Lebeau B, Michelin L, Carteret C, Bonne M and Blin J-L 2018 Influence of crystallization conditions and of gaseous ammonia treatment on mesoporous TiO$_2$ properties Microporous and Mesoporous Materials 262 1–12 Online. Available: https://doi.org/10.1016/j.micromeso.2017.11.025

[9] Cervantes-Martinez C V, Emo M, Garcia-Celma M-J, Stébé M-J and Blin J-L 2019Morphosynthesis of porous silica from biocompatible templates Chemical Engineering Research and Design 151 179–189 Online. Available: https://doi.org/10.1016/j.cherd.2019.09.006

[10] Kuznetsova T F and Eremenko S I 2014 Synthesis of aerogel-type mesoporous silica Colloid Journal 76 3 327-333 Online. Available: https://doi.org/10.1134/S1061933X14030089
[11] Julve D, Ramos J, Pérez J and Menéndez M 2011 Analysis of mercury porosimetry curves of precipitated silica, as an example of compressible porous solids Journal of Non-Crystalline Solids 357 1319-1327 Online. Available: https://doi.org/10.1016/j.jnoncrysol.2010.12.042

[12] Kuznetsova T F and Eremenko S I 2013 Properties of sol-gel derived silica membranes Inorganic Materials 49 159–164 Online. Available: https://doi.org/10.1134/S002016851302012X

[13] Kuznetsova T F, Rat'ko A I and Eremenko S I 2012 Textural and adsorption properties of mesoporous silicophosphate Colloid Journal 74 1 78-84 Online. Available: https://doi.org/10.1134/S1061933X11060111

[14] Vorontsova O A, Lebedeva O E and Roessner F 2009 Synthesis of layered hydroxides stable in redox media Kinetics and Catalysis 50 6 863-866 Online. Available: https://doi.org/10.1134/S002315840906010X

[15] Zima T M, Bkalanova N I and Lyakhov N Z 2012 Composites of mesoporous Al2O3 and Fe- or Co-containing nanoparticles Inorganic Materials 46 8 852-857 Online. Available: https://doi.org/10.1134/S0020168512080091

[16] Hua J 2015 Synthesis and characterization of bentonite based inorgano–organo-composites and their performances for removing arsenic from water Applied Clay Science 114 239-246 Online. Available: http://dx.doi.org/10.1016/j.clay.2015.06.005

[17] Maslova M V and Gerasimova L G 2011 The Influence of Chemical Modification on Structure and Sorption Properties of Titanium Phosphates Russian Journal of Applied Chemistry 84 1 1-8 DOI 10.1134/S1070427211010010

[18] Matveev V A and Majorov D V Method of obtaining layered hydroxide of madnesium and aluminium RU Patent 2678007

[19] Zhang Z and Yang Z 2013 Theoretical and practical discussion of measurement accuracy for physisorption with micro- and mesoporous materials Chinese Journal of Catalysis 34 1797–1810 Online. Available: https://doi.org/10.1016/S1872-2067(12)60601-9

[20] Fedoročková A, Plešingerová B, Sučik G, Raschman P and Doráková A 2014 Characteristics of amorphous silica prepared from serpentinite using various acidifying agents International Journal of Mineral Processing 130 42–47 Online. Available: http://dx.doi.org/10.1016/j.minpro.2014.05.005

[21] Gerasimova L G, Shechkina E S, Maslova M V, Gladkikh S N, Garayev G R and Kolobkova V M 2017 Synthesis of Rutile Titanium Dioxide from Russian Raw Materials Polymer Science, Series D 10 1 23–27 Online. Available: https://doi.org/10.1134/S1995421217010099