**CCQM-K \_\_\_\_\_**

**Measurement of Specific Adsorption A [mol/kg] of Ar on zeoliteat liquid argon temperature (to enable a traceable determination of the Specific Surface Area by following ISO 9277)**

# Technical protocol

**1. Introduction**

Specific argon adsorption to enablea traceable determination of specific surface area, specific pore volume and pore diameter in microporous solids are highly relevant parameters because they are often used for the specification of the vast majority of porous materials and substances (sorbents, catalytic agents, cross-linkers, zeolites, etc) used in advanced technology. To check the comparability of measurement protocols at NMIs and DIs adressing the porosity properties of technologically relevant microporous solids a Key comparison is launched by the Surface Analysis Working Group at CCQM/BIPM.

The comparison is being carried out for the purpose to enable participating NMIs and DIs to claim CMCs as detailed in table 1. **Only specific adsorption of gas and specific surface area potentially can be CMC claims. Specific pore volume and pore diameter are informative characteristics and using as an optional information.**

**Table 1** Layout of CMC claims to be underpinned by Key comparison CCQM-K\_\_\_

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| [**Meas. Serv. Category**](file:///C%3A%5CUsers%5C%D0%9F%D0%BE%D0%BB%D1%8C%D0%B7%D0%BE%D0%B2%D0%B0%D1%82%D0%B5%D0%BB%D1%8C%5CAppData%5CLocal%5CMicrosoft%5CWindows%5CTemporary%20Internet%20Files%5CContent.MSO%5C27FE4B13.xls#RANGE!C9) | [**Matrix**](file:///C%3A%5CUsers%5C%D0%9F%D0%BE%D0%BB%D1%8C%D0%B7%D0%BE%D0%B2%D0%B0%D1%82%D0%B5%D0%BB%D1%8C%5CAppData%5CLocal%5CMicrosoft%5CWindows%5CTemporary%20Internet%20Files%5CContent.MSO%5C27FE4B13.xls#RANGE!C10) | [**Measurand**](file:///C%3A%5CUsers%5C%D0%9F%D0%BE%D0%BB%D1%8C%D0%B7%D0%BE%D0%B2%D0%B0%D1%82%D0%B5%D0%BB%D1%8C%5CAppData%5CLocal%5CMicrosoft%5CWindows%5CTemporary%20Internet%20Files%5CContent.MSO%5C27FE4B13.xls#RANGE!A11) | [**Dissemination Range of Measurement Capability**](file:///C%3A%5CUsers%5C%D0%9F%D0%BE%D0%BB%D1%8C%D0%B7%D0%BE%D0%B2%D0%B0%D1%82%D0%B5%D0%BB%D1%8C%5CAppData%5CLocal%5CMicrosoft%5CWindows%5CTemporary%20Internet%20Files%5CContent.MSO%5C27FE4B13.xls#RANGE!A15) | **Range of Expanded Uncertainties as Disseminated** |
| [**Analyte or component**](file:///C%3A%5CUsers%5C%D0%9F%D0%BE%D0%BB%D1%8C%D0%B7%D0%BE%D0%B2%D0%B0%D1%82%D0%B5%D0%BB%D1%8C%5CAppData%5CLocal%5CMicrosoft%5CWindows%5CTemporary%20Internet%20Files%5CContent.MSO%5C27FE4B13.xls#RANGE!C12) | [**Quantity**](file:///C%3A%5CUsers%5C%D0%9F%D0%BE%D0%BB%D1%8C%D0%B7%D0%BE%D0%B2%D0%B0%D1%82%D0%B5%D0%BB%D1%8C%5CAppData%5CLocal%5CMicrosoft%5CWindows%5CTemporary%20Internet%20Files%5CContent.MSO%5C27FE4B13.xls#RANGE!C14) | [**From**](file:///C%3A%5CUsers%5C%D0%9F%D0%BE%D0%BB%D1%8C%D0%B7%D0%BE%D0%B2%D0%B0%D1%82%D0%B5%D0%BB%D1%8C%5CAppData%5CLocal%5CMicrosoft%5CWindows%5CTemporary%20Internet%20Files%5CContent.MSO%5C27FE4B13.xls#RANGE!C15) | [**To**](file:///C%3A%5CUsers%5C%D0%9F%D0%BE%D0%BB%D1%8C%D0%B7%D0%BE%D0%B2%D0%B0%D1%82%D0%B5%D0%BB%D1%8C%5CAppData%5CLocal%5CMicrosoft%5CWindows%5CTemporary%20Internet%20Files%5CContent.MSO%5C27FE4B13.xls#RANGE!C15) | [**Unit**](file:///C%3A%5CUsers%5C%D0%9F%D0%BE%D0%BB%D1%8C%D0%B7%D0%BE%D0%B2%D0%B0%D1%82%D0%B5%D0%BB%D1%8C%5CAppData%5CLocal%5CMicrosoft%5CWindows%5CTemporary%20Internet%20Files%5CContent.MSO%5C27FE4B13.xls#RANGE!C15) | [**From**](file:///C%3A%5CUsers%5C%D0%9F%D0%BE%D0%BB%D1%8C%D0%B7%D0%BE%D0%B2%D0%B0%D1%82%D0%B5%D0%BB%D1%8C%5CAppData%5CLocal%5CMicrosoft%5CWindows%5CTemporary%20Internet%20Files%5CContent.MSO%5C27FE4B13.xls#RANGE!C18) | [**To**](file:///C%3A%5CUsers%5C%D0%9F%D0%BE%D0%BB%D1%8C%D0%B7%D0%BE%D0%B2%D0%B0%D1%82%D0%B5%D0%BB%D1%8C%5CAppData%5CLocal%5CMicrosoft%5CWindows%5CTemporary%20Internet%20Files%5CContent.MSO%5C27FE4B13.xls#RANGE!C18) | [**Unit**](file:///C%3A%5CUsers%5C%D0%9F%D0%BE%D0%BB%D1%8C%D0%B7%D0%BE%D0%B2%D0%B0%D1%82%D0%B5%D0%BB%D1%8C%5CAppData%5CLocal%5CMicrosoft%5CWindows%5CTemporary%20Internet%20Files%5CContent.MSO%5C27FE4B13.xls#RANGE!C18) | [**Cov. factor**](file:///C%3A%5CUsers%5C%D0%9F%D0%BE%D0%BB%D1%8C%D0%B7%D0%BE%D0%B2%D0%B0%D1%82%D0%B5%D0%BB%D1%8C%5CAppData%5CLocal%5CMicrosoft%5CWindows%5CTemporary%20Internet%20Files%5CContent.MSO%5C27FE4B13.xls#RANGE!C18) |
| Advanced Materials | zeolite | zeolite | Specific adsorption of argon | 1 | 20 | mol/kg |  |  | mol/kg | 2 |
| Advanced Materials | zeolite | zeolite | Specific surface area | 500 | 1500 | m2/g |  |  | m2/g | 2 |

**2. Measurand and reporting**

The primary measurand values for CCQM-K\_\_\_ are specific adsorption of argon on zeolite at liquid argon temperature. Derived from that data the secondary measurand are specific surface area, specific pore volume and pore diameter of zeolite. **Only for specific adsorption of argon and specific surface area KCRV will be established. RV will be established for specific pore volume and pore diameter only for information.**

Each participant shall report the results for the values of specific adsorption argon, specific surface area, specific pore volume and pore diameter of zeolite. The results should be reported accompanied by a full uncertainty statement (including a combined standard uncertainty and an expanded uncertainty with a coverage factor applied).

For the estimation of the measurement uncertainty for specific adsorption of gases these issues have to be taken into account: mass of the analyzed sample, system volume, initial pressures, pressures after reaching equilibrium, gas temperatures, sample holder volume at cryogenic bath temperature, free space volume with sample holder immersed in cryogenic bath and uncertainty due to interpolation.

 In addition the report should include technical details on the measurement procedure, traceability links (as calibrations) and uncertainty contributions. Each of report should include tabular reports and graphs for the isotherm (dependence specific adsorption from relative pressure) and for the specific surface area

**3. Guidance values and target uncertainty**

Analyte/matrix: The test material used for the comparisons is zeolite. A range of measurands and target uncertainty are shown in table 2. A range of informative characteristic parameters and target uncertainty are shown in table 3. Points of relative pressure of argon for specific adsorption of Ar is presented in table 4.

**Table 2**

|  |  |  |  |
| --- | --- | --- | --- |
| [**Quantity**](file:///C%3A%5CUsers%5C%D0%9F%D0%BE%D0%BB%D1%8C%D0%B7%D0%BE%D0%B2%D0%B0%D1%82%D0%B5%D0%BB%D1%8C%5CAppData%5CLocal%5CMicrosoft%5CWindows%5CTemporary%20Internet%20Files%5CContent.MSO%5C27FE4B13.xls#RANGE!C14) | **Measurand** | [**Range**](file:///C%3A%5CUsers%5C%D0%9F%D0%BE%D0%BB%D1%8C%D0%B7%D0%BE%D0%B2%D0%B0%D1%82%D0%B5%D0%BB%D1%8C%5CAppData%5CLocal%5CMicrosoft%5CWindows%5CTemporary%20Internet%20Files%5CContent.MSO%5C27FE4B13.xls#RANGE!C15) | [**Target**](file:///C%3A%5CUsers%5C%D0%9F%D0%BE%D0%BB%D1%8C%D0%B7%D0%BE%D0%B2%D0%B0%D1%82%D0%B5%D0%BB%D1%8C%5CAppData%5CLocal%5CMicrosoft%5CWindows%5CTemporary%20Internet%20Files%5CContent.MSO%5C27FE4B13.xls#RANGE!C18) **relative expanded uncertainty** |
| Specific adsorption of argon at 1.0·10-4≤P/Po≤1.0·10-1 | Primary | (1-20) mol/kg | (1-10) % |
| Specific surface area | Secondary | (500-1500) m2/g |

**Table 3**

|  |  |  |  |
| --- | --- | --- | --- |
| [**Quantity**](file:///C%3A%5CUsers%5C%D0%9F%D0%BE%D0%BB%D1%8C%D0%B7%D0%BE%D0%B2%D0%B0%D1%82%D0%B5%D0%BB%D1%8C%5CAppData%5CLocal%5CMicrosoft%5CWindows%5CTemporary%20Internet%20Files%5CContent.MSO%5C27FE4B13.xls#RANGE!C14) | **Informative** **characteristic** | [**Range**](file:///C%3A%5CUsers%5C%D0%9F%D0%BE%D0%BB%D1%8C%D0%B7%D0%BE%D0%B2%D0%B0%D1%82%D0%B5%D0%BB%D1%8C%5CAppData%5CLocal%5CMicrosoft%5CWindows%5CTemporary%20Internet%20Files%5CContent.MSO%5C27FE4B13.xls#RANGE!C15) | [**Target**](file:///C%3A%5CUsers%5C%D0%9F%D0%BE%D0%BB%D1%8C%D0%B7%D0%BE%D0%B2%D0%B0%D1%82%D0%B5%D0%BB%D1%8C%5CAppData%5CLocal%5CMicrosoft%5CWindows%5CTemporary%20Internet%20Files%5CContent.MSO%5C27FE4B13.xls#RANGE!C18) **relative expanded uncertainty** |
| Specific pore volume | Secondary | (0.05-1.0) cm3/g | - |
| Most frequency pore diameter | Secondary | (0.4–2) nm |

**Table 4**

|  |  |  |  |
| --- | --- | --- | --- |
| № | P/Po\* | A, mol/kg | U(k=2), mol/kg |
| 1 | 1.0·10-4 |   |   |
| 2 | 1.0·10-3 |   |   |
| 3 | 1.0·10-2 |   |   |
| 4 | 1.0·10-1 |   |   |

*If relative pressure is not exactly equal to* ***P/Po=1,0·10-4; P/Po=1,0·10-3; P/Po=1,0·10-2; P/Po=1,0·10-1****, please calculate specific adsorption values using linear interpolation.*

**4. KCRVs**

* The processing of measurement results of specific adsorption nitrogen, specific surface area to the pilot lab will be carried out according to the following documents:CCQM Guidance note: Estimation of a consensus KCRV and associated Degrees of Equivalence (version: 6, Date 2010-03-01, Draft)
* Cox M.G. “The evaluation of key comparison data” [1]
* Jorg W.Muller. “Possible Advantages of a Robust Evaluation of Comparisons” [2].

**5. Methods of measurement**

Each participant should use the gas adsorption method for the measurement of the specific adsorption argon, specific surface area, specific pore volume and pore diameter of zeolite as defined in ISO 15901-3 [3] and ISO 9277 [4].

**Some details about measurement procedure of gas adsorption method are shown bellow**

Please perform at least 5 replicate measurements on separate aliquots of zeolite. The recommend minimum sample amount is about 0.3 gram for each run.

 **Sample pretreatment**

Heat the sample zeolite to 90 °С then the sample is vacuumed at a rate of 0.67 kPa/sec to a residual pressure of 10 Pa and vacuumed for 30 minutes. Then slom heating at a rate of not more than 10 °С/min to 350 °С. The hold temperature at 350 °С for at least 6 hour.

**Measurement of the complete Isotherm (adsorption branch) at 87 K and specific adsorption of argon at P/Po=1,0·10-5; P/Po=1,0·10-4; P/Po=1,0·10-3; P/Po=1,0·10-2; P/Po=1,0·10-1.**

First isotherm data point should be taken at P/Po=1,0·10-5, last adsorption isotherm data point should be taken at P/Po=1,0·10-1. Intermediate points are selected uniformly at the rate of (8-10) points for each order. The free volumes of the tube with the sample "warm" and "cold" should be measured after the measurements of specific adsorption of argon and then entered into the files in which the measurements are made for adjustment.

**Specific surface area S, m2/g**

For determination  must be measured at least five points in the P/Po Range from 0.001 to 0.015. Specific surface area must be calculated according to equation

 (1)

where  is Avogadro constant, mol-1;  is area occupied by one argon molecule 0.142·10-18 m2;  is specific monolayer capacity of adsorbate, mol·g-1.

Specific monolayer capacity of adsorbate must be calculated according to Langmuir equation:

 (2)

where  is specific adsorption of argon, mol·g-1; С is Langmuir constant;  - pressure of the adsorptive in equilibrium with the adsorbate, Pa.

**Specific pore volume (informative characteristic)**

Computed by the equation Dubinin-Radushkevich in the range P/Po from 0.005 to 0.10:

 , (2)

where  - specific volume adsorbed, cm3/g;

 - the sorption capacity of argon under normal conditions under filled micropores, calculated by regression analysis on the equation Dubinin, cm3/g.

The density of argon liquid =1.40 g/cm3 (87.29 K). The density of argon under normal conditions =1,7840 mg/cm3. The calculations used the ratio. Calculate the specific volume of pores according to the formula:

 (3)

where  - the sorption capacity of argon under normal conditions under filled micropores, calculated by regression analysis on the equation Dubinin, cm3/g.

**Most frequency pore diameter D, nm (informative characteristic)**

It is calculated as a mode of pore distribution over diameters with a modal interval equal to 0.01 nm (as a rule, it is calculated automatically using the software of gas adsorption analyzers). The pore diameter is calculated by the Horvath-Kawazoe and Saito-Foley method:

  (4)

The following parameters of the adsorbent and adsorbate given in tables 4, 5 are used to perform calculations by the Horvath -Kawazoe and Saito-Foley method.

**Table 4** — Parameters for zeolite adsorbent

|  |  |  |  |
| --- | --- | --- | --- |
| Physical quantity | Unit | Symbol | Zeolite |
| Polarizability | 10−24 cm3 |  | 2,50 |
| Magnetic susceptibility | 10−29 cm3 |  | 1,30 |
| Surface density (atoms per square metre of pore wall) | 1019 m−2 | *N*s | 1,31 |
| Diameter | nm | *d*s | 0,28 |

**Table 5** — Parameters of adsorbate - argon

|  |  |  |  |
| --- | --- | --- | --- |
| Physical quantity | Unit | Symbol | Argon |
| Polarizability | 10−24 cm3 |  | 1,63 |
| Magnetic susceptibility | 10−29 cm3 |  | 3,25 |
| Surface density (atoms per square metre of pore wall) | 1018 m−2 | *N*a | 8,85 |
| Diameter | nm | *d*s | 0,34 |

**6. Planned time schedule**

call for participants: by end of September 2020

latest registration of participant: by end of October 2020 (updated)

latest arrival of samples at participants: by end of December 2020

latest report of results: by end of February 2021

report A: by end of July 2021

report B: by end of September 2021

**7. Samples**

A bottle is planned to contain about 4 g of zeolite.

**8. Pilot laboratory**

Laboratory for metrological assurance of nanoindustrie, analysis of spectral methods and reference materials (251)

NMI’s name and abbreviation

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**9. References**

1. Cox M.G. The evaluation of key comparison data, Metrologia 39 (2002) 589-595.
2. Jorg W.Muller. Possible Advantages of a Robust Evaluation of Comparisons, Journal of Research of the National Institute of Standards and Technology Vol.105, No.4 (2000) 551-555.
3. ISO 15901-3 Pore size distribution and porosity of solid materials by mercury porosimetry and gas adsorption – Part 3: Analysis of micropores by gas adsorption. Geneva (2007).
4. ISO 9277 Determination of the specific surface area of solids by gas adsorption – BET method. International Organization for Standardization, Geneva (2010).
5. Gregg, S. J., Sing, K. S. W., Adsorption, Surface Area and Porosity. Academic Press, London 1982.