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A NOTE ON SORPTION MEASURING INSTRUMENTS

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Abstract

Gas sorption phenomena can be used to characterise porous solids and dispersed materials. Usually isotherms of nitrogen and noble gases like He, Ar, Kr are measured at low temperatures (77–90 K). Other gases and vapours like water, CO_2 and benzene are used at near ambient conditions of pressure and temperature. From the amount of gas adsorbed on the (external or internal) surface characteristic quantities like the specific surface area, specific pore volume and pore spectrum of the material are derived by standardised methods. Experimental techniques most often used are the carrier gas, the volumetric/manometric and the gravimetric method. A comprehensible overview of today's available instruments, their advantages and drawbacks is given.

Keywords: adsorption, gravimetry, pore size, specific surface area, volumetry

Introduction

Most important applications of dispersed and porous materials include adsorption of gases or solutes [1]. Also when such materials are processed as a starting material, chemical reactions begin often with adsorption of reactive species. To understand such processes knowledge of the surface parameters is required. Besides the chemical composition of the surface, its geometry needs to be characterised, usually by the following parameters:

- specific surface area
- pore size distribution
- specific pore volume
- particle size distribution
- density

A variety of methods is available for the investigation of the surface but not any provide absolute values for that parameters. On account of the fractality of the surface structure the results depend on the size of the yardstick or unit-measure used. Furthermore, in the range of nanostructures we find no reliable edges at which the yardstick

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could be placed. In this case, it is advisable to apply a measuring method which corresponds to the application in mind. Adsorption measurements using chemical inert gases can give the required information of the surface structure, though not absolute values either. In adsorption measurements the yardstick is the area required by one adsorbed molecule or its volume, respectively. Furthermore, sorption measurements are always accompanied by other interfering physical phenomena. Therefore, measurements using model gases need to be supplemented by investigations using the reactive species itself.

Usually nitrogen or noble gases like He, Ar, Kr at low temperatures (77–90 K) are used. Other gases and vapours like water, CO_2 and benzene are used for measurements at near ambient conditions of pressure and temperature. This provides experimental advantages, however the molecular area of these gases varies with the chemical nature of the solid.

To measure the adsorbed amount as a function of pressure and temperature several effects can be applied:

- measurement of the adsorbed mass by means of a balance
- measurement of consumption of the sorptive gas by means of calibrated volumes
- measurement of concentration changes in a carrier gas by means of gas chromatography
- measurement of changes of the dielectric constant
- measurement of the heat of adsorption
- measurement of nuclear magnetic resonance of special adsorptives
- measurement of radiation dose of radioactive labelled gas.

The following survey is confined to instruments specialised for the measurement of the specific surface area, specific pore volume and pore size distribution. In addition the sorption kinetics can be observed and from multiple measurements changing the measuring condition (pressure, temperature) thermodynamic data may be derived. The same or modified instruments may be used to study the reaction of gases at technical conditions and its reaction kinetics. If designed suitably also density determinations are possible. Preferably sorption isotherms are measured, sometimes isobares. General literature is summarised in the references [2–9].

Sorption measuring instruments

Four types of sorption measuring instruments are on the market: volumetric/manometric, gravimetric, carrier gas and calorimetric. With respect to dangers in handling of radioactive material the determination of the adsorbed amount by measuring the dose of radioactive radiation from radioactive isotopes of xenon or krypton is out of practice. We abstain also from discussing the calorimetric method. This method provides in addition thermodynamic data. However, measurement of differential heats requires highly sensitive calorimeters and sophisticated measuring techniques. Specialised instruments are not on the market and thus calorimetric measurements of adsorption are restricted to special cases.

Sorption measuring methods are standardised in many countries and on the international level. For the calibration and checking of instruments reference materials are offered [10].

Carrier gas method

The carrier gas method according to Nelsen and Eggertsen [11] is a variant of gas-chromatography and an available gas-chromatograph may be supplemented by a sorption measuring cell. Degassing of the sample is performed by flushing with the non-adsorbing carrier gas helium at elevated temperature. The apparatus (Fig. 1) consists of a device in which the adsorptive gas is added in a pre-determined concentration to the carrier gas. The gas stream is fed through the sample tube which is cooled with liquid nitrogen. Some nitrogen is adsorbed and for a short time the concentration in the carrier gas decreases. After removal of the cooling bath the gas is desorbed. Both effects are registered in comparison to a reference gas stream as voltage peaks by a gas detector, usually a heat conductivity cell. In general, the desorption peak is integrated and compared with a calibration peak of reference material. Adsorption isotherms up to near saturation may be obtained by a series of measurements using increasing concentrations of nitrogen. With a pulsed gas stream micropore filling can be distinguished from surface covering [12].

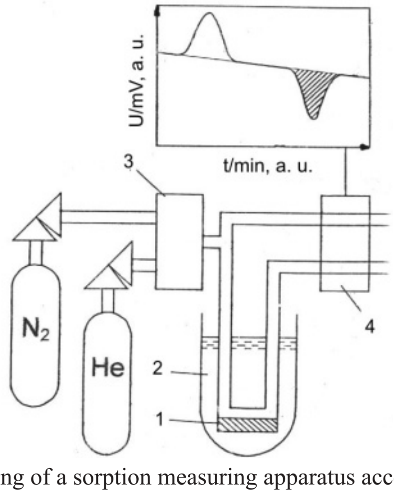

Fig. 1 Schematic drawing of a sorption measuring apparatus according to the carrier gas method. 1 – sample, 2 – Dewar vessel with liquid nitrogen (or heater for degassing the sample), 3 – gas mixer, 4 – heat conductivity gas detector. The measuring result are peaks of the voltage *U vs.* time *t*

Volumetric/manometric method

A volumetric/manometric sorption measuring apparatus consists of a calibrated and thermostatted sample bulb, a burette or a metering valve for controlled admission of the sorptive gas and some manometers (Fig. 2). Besides the measuring gas for calibration helium is required in addition. The sample is dried mostly in a separate degassing station in vacuum at elevated temperature. Preferably optimum degassing conditions are found out thermogravimetrically. To measure nitrogen isotherms the sample bulb is cooled down in a Dewar vessel filled with liquid nitrogen and certain quantities of nitrogen are admitted stepwise. At each step the pressure in the confined sample volume decreases until constant gas pressure is attained. From pressure and volume the gas volume consumed by adsorption is calculated using the general gas equation and taking into account the gas remaining in the dead space of the sample bulb. This is the volume not required by the sample and which is calibrated in advance using helium.

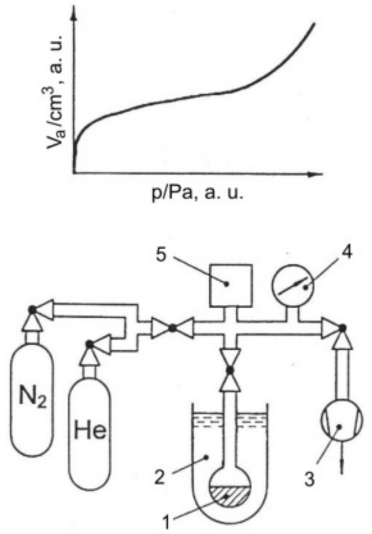

Fig. 2 Volumetric/manometric apparatus, V_a – normal volume of gas adsorbed per unit mass of sorbent, p – pressure of sorptive gas; 1 – sample, 2 – Dewar vessel with liquid nitrogen, 3 – vacuum aggregate, 4 – manometer, 5 – calibrated volume

Gravimetric method

In gravimetry the adsorbed amount is measured by a vacuum microbalance (Fig. 3). For the measurement of adsorption isotherms the pressure is stepwise changed and then kept constant, measured by an electronic manometer and controlled by means of solenoid valves. Sample degassing is performed at the balance in vacuum at elevated temperature. Prior to the measurement buoyancy must be determined.

Comparison of sorption measuring methods

Carrier gas apparatus are simple, cheap and easy in handling. Vacuum is not required. The measurement of the adsorbed amount is indirect and the method does not claim

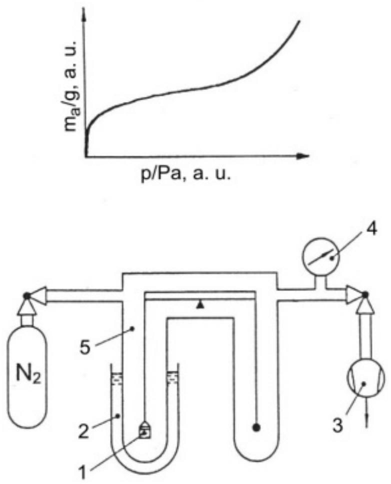

Fig. 3 Gravimetric apparatus; V_a – specific volume adsorbed, p – pressure of sorptive gas, m_a – specific mass adsorbed; 1 – sample, 2 – Dewar vessel with liquid nitrogen, 3 – vacuum aggregate, 4 – manometer, 5 – balance

for high accuracy. The method is usually applied for fast single point determinations of the specific surface area. Multipoint measurements of isotherms are complicated.

In comparison to gravimetric apparatus the volumetric are simpler in design and easier to operate. Because samples of any size can be investigated using suitable sample bulbs a high sensitivity can be achieved but unfortunately not a higher accuracy. Indeed, the relative sensitivity of both methods is equivalent. The most serious error in volumetry is the error in calibration of the dead space; in gravimetry it is the error in the determination of buoyancy. Indeed with gravimetry not the adsorbed mass but the difference between mass and buoyancy is measured and in volumetry the difference between the volume of sorptive gas consumed and the gas remaining in the dead space. Both erroneous influences are equal because both are based on the sample volume [13]. Therefore that influence cannot be cancelled out by simultaneous measurements using these both methods. The two variables: pressure and adsorbed amount are determined by only one instrument: the manometer and by calibrated volumes and this may result in a slightly larger measuring error which is added up at each step of the adsorption isotherm. At low pressures a pressure difference due to the Knudsen effect should be taken into account. Results of dead space calibration may be used to calculate the sample density.

Favourably with the gravimetric method all variables: adsorbed mass, gas pressure and temperature are measured independently. The sorptive pressure is controlled at each step. Sample preparation is registered and thus optimum degassing conditions (temperature, pressure and time) can be found out and the mass of the dry sample can be determined. By buoyancy measurements at different pressures the sample density can be determined. The gravimetric apparatus is more complicated and more expensive on account of the additional vacuum microbalance. Balance operating requires some skills. The sample is not in direct contact with the thermostat and must be shielded against false heat radiation. Measures to avoid the influence of eddy gas flow are required. At low pressure the Knudsen pressure difference causes thermal gas flow which seriously interferes in measurements in the Henry region.

Stepwise measurements using any of both methods can be remarkably shortened by extrapolation of the equilibrium values according to a procedure introduced by Jäntti [14, 15]. It is possible to draw conclusion from the kinetic curves on the mechanism of adsorption [16]. Combining the results of volumetric and gravimetric measurements enables to determine the adsorbed masses of single components from two-component gas mixtures [17]. Hardly investigated is concurrent adsorption from multinary gas mixtures [18]. For that purpose measurements are necessary using at least two independent methods, e.g. the volumetric and the gravimetric one [19], or additional head space gas analysis.

Table 1 Manufacturer of volumetric and carrier gas sorption measuring instruments and of gas pycnometers

Manufacturer	A	P	C	D
Beckman Coulter UK Ltd., Oakley Court, Kingsmead Business Park, London Rd. High Wycombe Bucks. HP11 1JU, UK (including Omicron), Tel.: +44-149444-1181, Fax: -7558, beckmancoulter_uk@beckman.com, www.beckmancoulter.com	●	●	●	●
Thermo Finnigan, Thermoquest Italia, Strada Rivoltana, s.n., I-20090 Rodano, Milano, Italy, Tel.: +39-02950592-66, Fax: -56, woodwardc@finnigan.co.uk, www.thermo.com, www.porotec.de, info@porotec.de	●	●	●	●
Jouan Robotics - Gira, Rue des Bruyères, Z.I. Berlanne, F – 64160 Morlaas, France, Tel: +33-559-308-38-3, Fax: -4, g.chancel@gira-france.com, www.gira.fr	●	●	●	
Micromeritics, 1 Micromeritics Drive, Norcoss, GA 30093-1877, USA, Tel.: +1-770-662-36-60, Fax: -96 , international@micromeritics.com, www.micromeritics.com	●	●	●	●
Porous Materials, Inc., Cornell University Research and Technology Park, 83 Brown Road, Bldg. 4, Ithaca, NY 14850, USA, Tel.: +1-607-257-554, Fax: -5639, www.pmiapp.com, info@pmiapp.com	●	●	●	●
Quantachrome Corp., 1900 Corporate Drive, Boynton Beach, Florida 33426 USA, Tel.: +1-561-731-4999 Fax: -732-9888, www.quantachrome.com, webmaster@quantachrome.com	●	●	●	●
Zeton Altamira, 149 Delta drive, Suite 200 Pittsburgh, PA 15238, USA, Tel: +1-412-9636-385, Fax: -485, www.zetonaltamira.com, altamira@compuserve.com	●			

A – Specific surface area, *P* – Pore size distribution, *C* – Chemisorption, *D* – Density

Commercial instruments

In Table 1 manufacturers of carrier gas and volumetric adsorption measuring instruments are compiled. Most of these companies offer also mercury porosimeter and gas pycnometer. Mercury porosimetry extends the measuring range of the sorption method towards larger pores.

For pressure measurements electronic diaphragm manometers are especially suitable. Also instruments with piezo-quartz, spring-tube or vibrating tube are used for that purpose.

Table 2 Manufacturer of gravimetric gas sorption measuring instruments

Manufacturer	Balance	A	P	C	W	D
Thermo Cahn, 5225 Verona Road, Madison, WI 53711 USA, Tel.: +1-608-276-633, Fax –273-6827, www.cahn.com, www.thermocahn.com, www.theromhaake.com	Cahn	●	●	●	●	
CI Electronics Ltd., Brunel Rd. Churchfields, Salisbury, Wiltshire SP2 7PX, U.K., Tel.: +44-1722-424100, Fax: 323222, admin@cielec.com, www.cielec.com	CI			●	●	
Hiden Isochema Ltd., 420 Europa Bd., Gemini Business Park, Warrington WA5 7UN, England, Tel: +44–1925-445225, Fax: -416518, info@hiden.demon.co.uk, www.hidenanalytical.com	Cahn	●	●	●	●	
Rubotherm, Universitätsstr. 142, D-44799 Bochum, Germany Tel.: +234-70996-0, Fax: -22, www.rubotherm.com, info@rubotherm.de	Rubotherm			●	●	●
Surface Measurement Systems, 3 Warple Mews, Warple Way, London W3 0RF, UK Tel.: +44-20 8749 4900, Fax: -6749, www.smsuk.co.uk, info@smsuk.co.uk	Cahn	●	●	●	●	
VTI Corp. 7650 W. 26th Ave., Hialeah, FL 33016-5704, USA, Tel.: +1-305-828-4700, Fax –0299, www.vticorp.com, vti@vticorp	Cahn or CI	●	●	●	●	

For gravimetric sorption apparatus generally electronic beam microbalances are used with relative sensitivity up to 10^{-7} which can be operated in vacuum (Table 2). For investigations in corrosive gases and in ultrahigh vacuum the magnetic suspension balance is favourable but expensive. A cheap alternative are helical quartz spring balances which, however, are not commercially manufactured. Recently, gravimetric apparatus for routine measurements of the nitrogen isotherm are available. Other gravimetric apparatus are designed for the measurement of water vapour isotherms (Table 3).

Table 3 Manufacturer of vacuum balances

Manufacturer	V	T	S	M
Beckman Instruments Inc., Fullerton, CA 82834, USA / 90 Boroline Rd., Allendale, NJ 07401-1613, USA (including Stanton-Redcroft), Tel.: +1-201-818-8900, Fax: -9740, www.beckmancoulter.com		●		
Thermo Cahn, 5225 Verona Road, Madison, WI 53711 USA, Tel.: +1-608-276-633, Fax –273-6827, www.cahn.com, www.thermocahn.com	●	●		
CI Electronics Ltd., Brunel Rd. Churchfields, Salisbury, Wiltshire SP2 7PX, U.K., Tel.: +44-1722-424100, Fax: -323222, admin@cielec.com, www.cielec.com	●	●		
Linseis Meßgeräte GmbH, Viellitzer Str. 43, D-95100 Selb, Germany, Tel.: +49-9287-880-0, Fax: -70867, linseis@t-online.de, www.linseis.com		●	●	
Mettler-Toledo AG, Im Langacher, P.O. Box, CH-8606 Greifensee, Switzerland Tel.: +41-1-944-45-45, Fax: -10, info.ch@mt.com, www.mt.com		●		●
Perkin-Elmer Instruments, 710 Bridgeport Ave, Shelton CT 06484-4794, USA, Tel.: +1-203-925-4600, Fax: -4654, www.perkinelmer.com, info@perkinelmer.com	●	●		
Rheometric Scientific, Inc. One Possumtown Road, Piscataway NJ 08854, USA, Tel.: +1-732-560-8550, Fax: 7451, www.rheosci.com, marketing@rheosci.com (formerly Omnitherm & PL)		●		
Rubotherm, Universitätsstr. 142, D-44799 Bochum, Germany, Tel.: +49-234-70996-0, Fax: -22, , www.rubotherm.com, info@rubotherm.de			●	
SETARAM, 7 rue de l'Oratoire, F-69300 Caluire, France, Tel.: +33-47-2102525, Fax: -8286355, sales@setaram.com, www.setaram.com	●	●		
Sartorius AG, 37070 Göttingen, Tel.: +551-308-0, Fax: -289, www.sartorius.com, webmaster.go.de@sartorius.com				●
TA Instruments, 109 Lukens Drive, New Castle, DE 19720-2795, USA, Tel. : +1-302-427-400-0, Fax: -1, www.tainst.com, info@tainst.com (formerly DuPont)		●		

V – vacuum balance, *T* – thermobalance, *S* – suspension balance, *M* – microbalance

References

1 A. Dąbrowski (Ed.), Adsorption and its Application in Industry and Environmental Protection. 2 Vols. Surface Science and Catalysis, vol 120 A/B. Elsevier, Amsterdam 1999.

2 F. Rouquerol, J. Rouquerol and K. Sing, Adsorption by Powders & Porous Solids. Academic Press, San Diego 1999.

3 R. Sh. Mikhail and E. Robens, Microstructure and Thermal Analysis of Solid Surfaces. Wiley, Chichester 1983.

4 S. Lowell and J. P. Shields, Powder Surface Area and Porosity, 3. Ed., Chapman & Hall/Kluwer, Dordrecht 1991.

5 IUPAC Recommendations 1984: K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouquérol and T. Siemieniewska, Pure & Appl. Chem., 57 (1985) 603.

6 IUPAC Recommendations 1994: J. Rouquérol, D. Avnir, C. W. Fairbridge, D. H. Everett, J. H. Haynes, N. Pernicone, J. D. F. Ramsay, K. S. W. Sing and K. K. Unger, Pure & Appl. Chem., 66 (1994) 1739.

7 J. Rouquérol, D. Avnir, D. H. Everett, C. W. Fairbridge, M. Haynes, N. Pernicone, J. D. F. Ramsay, K. S. W. Sing and K. K. Unger, Guidelines for the Characterization of Porous Solids. In: J. Rouquerol, F. Rodriguez-Reinoso, K. S. W. Sing and K. K. Unger (Eds), Characterization of Porous Solids III. Elsevier, Amsterdam 1994.

8 J. P. Baselt, H. Kral, G. Kreysa, J. Rouquérol, K. S. W. Sing and K. K. Unger (Eds), Characterization of Porous Solids I-III, V. Studies in Surface Science and Catalysis. Elsevier, Amsterdam 1988-2000.

9 B. McEnaney, T. J. Mays, J. Rouquérol, F. Rodriguez-Reinoso, K. S. W. Sing and K. K. Unger (Eds), Characterization of Porous Solids IV. Royal Society of Chemistry, Cambridge 1997.

10 E. Robens, K.-F. Krebs, K. Meyer and K. K. Unger, Standardization of sorption measurements and reference materials for dispersed and porous solids. Chapter 3 of: A. Dąbrowski (Ed.): Adsorption and its Application in Industry and Environmental Protection. Vol. 1: Application in Industry. Studies in surface science and catalysis, Vol. 120 A. Elsevier, Amsterdam 1999, pp. 95–116.

11 F. M. Nelsen and F. T. Eggertsen, Improvements in or relating to method and apparatus for the Estimation of Surface Areas of Solids. British Patent 831639, 30.4.1958.

12 E. Baumgarten and F. Thielmann, Chemie Technik, 27 (1998) 38.

13 C. H. Massen, E. Robens, J. A. Poulis and Th. Gast, Thermochim. Acta, 82 (1984) 43.

14 O. Jäntti, J. Junttila and E. Yrjänheikki, Suomen Kemistilehti, A 43 (1970) 214.

15 E. Robens, C. H. Massen, J. A. Poulis and P. Staszczuk, Adsorption Sci. and Tech., 17 (1999) 801.

16 C. H. Massen, J. A. Poulis and E. Robens, Adsorption, 6 (2000) 229.

17 R. Staudt, G. Saller, F. Dreisbach, M. Tomalla and J. U. Keller, Determination of gas adsorption equilibria by volume-gravimetric measurements. In: J. U. Keller and E. Robens (Eds): Microbalance Techniques, Proceedings of the 25th Conference on Vacuum Microbalance Techniques 1993 Siegen, Multi-Science Publishing, Brentwood 1994, S. 205–210.

18 J. U. Keller, F. Dreisbach, H. Rave, R. Staudt and M. Tomalla, Adsorption (1999) 199.

19 M. Tomalla, R. Staudt and J. U. Keller, In: J. U. Keller and E. Robens (Eds): Microbalance Techniques, Proceedings of the 25th Conference on Vacuum Microbalance Techniques 1993 Siegen, Multi-Science Publishing, Brentwood 1994, pp. 193–204.