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REVIEW ON STANDARDISATION OF METHODS CHARACTERISING THE GEOMETRIC STRUCTURE OF DISPERSED OR POROUS SOLIDS

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Abstract

Short survey on the latest developments on standardisation and standard reference materials for particles, surfaces and pore size analysis.

Keywords: dispersed material, particle, pore, reference material, specific surface area, standardisation

Introduction

One prerequisite for the use of dispersed or porous material as adsorbents, carrier for catalyst or pharmaceuticals is the knowledge of the morphic structure of the surface. Most commonly it is characterised by the particle and pore size distribution, specific surface area, pore volume and density.

Many different measuring methods are available which are based on different principles and use probes which differ in size. All of these methods must be considered as indirect, comparative tests. The majority do not have the theoretical basis to allow quantitative calculation of results. In view of the complexity of dispersed solids, it is not surprising that the results obtained are not always in agreement and that no single technique can be relied upon to provide a complete picture. For comparison of materials it is therefore necessary to keep strictly to the measuring specifications and that's why standardisation is indispensable.

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Two approaches have been taken:

– standardisation of measuring methods and instruments, and
– certification of reference materials.

The vast majority of industrial nations have initiated standardisation associations and institutes for testing materials which also prepare reference materials. More and more standards are issued at the European Committee on Standardisation (CEN) based in Brussels (Belgium) [1] and the International Organisation for Standardisation (ISO) based in Geneva (Switzerland). The secretariat of ISO/TC 24, which is charged with the standardisation of particle, surface and pore characterisation is currently at the standards committee civil engineering (NABau) of the German Institute for Standardisation (DIN) [2], however a change just takes place. A comprehensive survey was published in Dąbrowski's book: Adsorption and its Application in Industry and Environmental Protection [3].

Standardisation

Sampling and sample preparation

Several standards, prepared by both national and ISO, exist for sampling and sample splitting. Advises for sampling and sample preparation are also included in the standards of the measuring methods. It should be emphasised that careless sampling or variations of the procedure of sample preparation may introduce significant measurement errors.

Density

Standardised density determinations concern the displacement of a liquid by the sample in a calibrated volume. Alternatively differences of the buoyancy of a sample in a liquid can be measured by means of a hydrostatic balance. Standards based on the measurement of gas displacement and of buoyancy in a gas are just prepared by the German standardisation group. The results of thermogravimetric or gravimetric sorption measurements must be corrected for buoyancy. Usually that corrections are used also for the determination of the density of the sample by comparison to a counterweight of known density.

Surface area, pore volume and pore size distribution

The surface area of dispersed material can be assessed from the flow resistance of air through the compressed sample (Blaine, Lee and Nurse). Similar results are obtained from the particle size distribution [4].

Widely used methods are based on the measurement of a gas adsorption isotherm at low temperature using N_2, Ar or Kr. They allow the determination of the pore size distribution in the meso- and micopore range [5]. Definitions and basic hints for the measurements are found in two IUPAC recommendations [6, 7]. Existing na-

tional standards will now be replaced by ISO standards. Standards concerning water sorption and chemisorption measurements have also been prepared.

An ISO draft concerns mercury porosimetry, a destructive method which covers a wide range from macro- to micropores. Several other impregnation methods for the determination of the total porosity using water are standardised at the national level for special requirements, e.g. for building materials.

Particle size distribution

A large variety of standardised methods concern the determination of the particle size distribution: sieve analysis, sedimentation in the gravitational field or in a centrifuge, optical and electrical sensing, laser diffraction, small X-ray scattering and image analysis. All these techniques are currently under discussion by ISO. Sample preparation for that purpose by dispersion of powders in liquids has also been comprehensively addressed.

Validation

Standards discussed so far do not meet the extraordinary requirements e.g. for pharmaceutical products. For such purposes measuring methods need to be validated. Validation is the process of determining the suitability of methods for providing useful analytical data with the required accuracy [8]. Guidelines for validation procedures are elaborated and standardised at international level in particular for pharmaceutical tests [9].

Reference materials

Approximately 70 certified reference materials for the comparison of particle size and surface area are offered from national testing institutes and industrial companies. Round robin tests concluded that the surface of highly dispersed materials could be substantially affected during storage and sample preparation. As a consequence only five materials are recommended as a reference for pore size. The development and handling of reference materials has also been recently discussed at an international conference [10]. On account of the high demand on standards of reasonable prize the instrument manufacturers offer (not certified) standards. Recently, from soda-lime glass microspheres at a mean size of about 50 μm a range of quality audit or transfer standards were developed [11].

High-performance column liquid chromatography (HPLC) is the most widely employed separation technique for the analysis of complex mixtures. The method is based on the adsorption on an adsorbent filled in a column as the stationary phase, when a sample solution flows through this column [12]. The method can also be applied to determine the pore size distribution of the column material by means of inverse size exclusion chromatography using macromolecular solutes of different but known size. Coordinated by the Institut für Anorganische Chemie und Analytische

Chemie der Johannes Gutenberg-Universität, a HPLC reference column was developed and is ready for certification [13].

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