

CHROM. 10,520

## DIRECT DETERMINATION OF SPECIFIC SURFACE AREAS AND ROUGHENING FACTORS OF GLASS CAPILLARIES

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### SUMMARY

In order to promote the spreading of stationary phases, the inside surface of glass open-tubular columns can be modified chemically or physically (surface roughening). The measure of surface roughening after an etching process is the Wenzel coefficient, defined as the ratio of the cosines of the contact angles or the specific surface areas after and before etching.

A method for the direct determination of the specific surface areas of glass capillaries is described. The method is based on the thermal desorption of nitrogen with the use of a microcatharometer. The results of measurements of specific surface areas of glass open-tubular columns etched with "etching ether" are presented.

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### INTRODUCTION

The presence of a thin, homogeneous layer of stationary phase is necessary for satisfactory operation and high efficiencies of glass open-tubular columns. Many methods for the preparation of high-efficiency open-tubular columns with up to 8000 theoretical plates per metre have been described<sup>1-5</sup>. However, the preparation of a reproducible glass surface is not easy in view of its good wettability by polar stationary phases. This is connected with the poor wettability of high-energy surfaces by most organic liquids<sup>6</sup>. High-energy surfaces undergo ready adsorption and hydration, which change their properties to those of low-energy surfaces (autophobic effect)<sup>7</sup>. Using the so-called critical surface tension (CST) as a measure of the wettability of a solid surface, it was shown that CST for smooth, clean glass surfaces is  $\leq 30$  dyne/cm and the surface tensions of typical stationary phases are in the range 30-50 dyne/cm. According to the definition of CST these values lead to non-wettability of the glass surfaces<sup>2</sup>. For these reasons, the inside surfaces of glass open-tubular columns have to be modified physically<sup>1-5</sup> and/or chemically<sup>8,9</sup> (surface roughening).

The chemical modification involves changing the chemical character of the glass surface by adsorption or chemical binding with active hydroxyl groups, followed by increasing or decreasing the CST of a given surface to the surface tension of the particular stationary phase concerned. On this basis, the concept of the chemical compatibility of solid surfaces and stationary phases has been proposed<sup>8,9</sup>.

Physical modifications include all processes for increasing the specific surface area, *e.g.*, etching with inorganic acids and bases, or gases such as hydrogen chloride and hydrogen fluoride. Contact with water or aqueous solutions leads to irreversible changes of the glass surface that are difficult to control and that can be explained in terms of hydration and ageing processes<sup>7,8</sup>. Gaseous hydrogen chloride or hydrogen fluoride, the latter commonly evolved from the so-called "etching ether", are usually used<sup>1-5,8</sup>.

The possibilities of directly coating the inside surface of capillaries with fine salt particles (analogous to preparing procedures for PLOT columns) such as sodium chloride<sup>3</sup> or crystallisation of insoluble salts (barium carbonate)<sup>10</sup> have been reported. Such modified glass surfaces were shown according to Wenzel<sup>11</sup> to have decreased contact angles and are able to create thin, homogeneous liquid films. The Wenzel coefficient (*r*), defined as the ratio of cosines of the contact angles ( $\cos \theta' / \cos \theta$ ) or the specific surface areas ( $A'/A$ ) after and before etching was used as the measure of surface roughening:

$$r = \frac{\cos \theta'}{\cos \theta} = \frac{A'}{A} \quad (1)$$

Nečasová and Tesařík<sup>12</sup> introduced another measure of the wettability of a glass surface, the so-called "wettability coefficient", defined as the ratio of the interfacial tensions after ( $\gamma_e$ ) and before ( $\gamma'$ ) the modification process:

$$k_w = \frac{\gamma_e}{\gamma'} \quad (2)$$

Both interfacial tensions can be calculated from the Young equation, using the surface tensions measured by the capillary rise method for a liquid with a zero contact angle (methanol)<sup>12</sup>. The wettability coefficient seems to be a very characteristic value but its usefulness has not yet been fully verified. Actual contact angle measurements can be carried out for a flat surface<sup>2</sup>, which is not a convenient choice and may give results that are not equivalent to the contact angles that exist in capillaries.

The measurement of specific surface area seems to be a simple method for the determination of the surface roughening and Wenzel's coefficient. The most popular method for this measurement is the classical B.E.T. method, with static weight or volumetric pressure measurement<sup>13</sup>. Faster and better characterization of adsorption under dynamic conditions can be achieved by the Nelson and Eggersten method<sup>14</sup>, based on the low-temperature thermal desorption of nitrogen or argon. A modification of the last method, proposed by Engelhard and Engelbrecht<sup>15</sup>, permitted the measurement, by changing the measurement temperature range ( $-190^\circ$  to  $-70^\circ$ ), of the specific "effective" surface area; the surface can be covered with an adsorption or a liquid layer.

The measurement of specific surface area is a non-destructive method and can be carried out so as to give an average value for the full length of a capillary or for any part of it. The adsorbate pressure gradient and the very small volume in which adsorption takes place complicate the determination of the specific surface area of a capillary by the thermal desorption method, which may explain the lack of suitable apparatus in the literature.

In this work, investigations of the low-temperature processes of nitrogen and argon adsorption-desorption in thin capillaries were carried out.

## EXPERIMENTAL

A simple apparatus for the measurement of specific surface areas and determination of surface roughening factors was constructed (Fig. 1). The apparatus consists of a pressurised adsorbate gas mixture supply (1), two flow restrictors (2), a measured capillary (3) in a cooling bath (4), a calibration injector (7), measurement (5) and reference (6) cells of the microcatharometric detector (6- $\mu$ l cell volume), a retarding tube (8) and two damping (buffer) capillaries (9). A Model 21 S recorder (Laboratorní Přístroje, Prague, Czechoslovakia) was used.

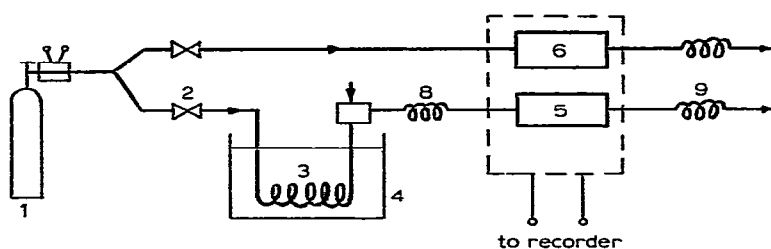


Fig. 1. Schematic diagram of the apparatus for specific surface area measurements: 1, Nitrogen-hydrogen mixture supply; 2, flow regulators; 3, capillary; 4, low-temperature bath (liquid nitrogen); 5, measurement cell of the detector; 6, reference cell of the detector; 7, calibration injector; 8, retarding tube; 9, damping (buffer) capillaries.

The measurements are based on a Wheatstone bridge; through the measurement and reference cells flow two independent streams of a 10% (v/v) nitrogen-hydrogen mixture. The adsorption process takes place at the temperature of liquid nitrogen and the desorption process at room temperature. Both processes change the balance of the Wheatstone bridge, which causes a detector signal that is proportional to the surface area.

The retarding glass tube (8, Fig. 1), with an inside diameter a few times larger than that of the capillary, is connected in the measurement stream between the capillary and detector in order to eliminate the irregular peak shape of the desorption curve.

Fig. 2 shows three typical examples of desorption curves, which were obtained with different lengths (volumes) of the retarding tube. For the determination of specific surface area the desorption curves were used. The microcatharometer was of the flow-through type and consisted of two tungsten wires, each 20  $\mu$ m in diameter and of 30  $\Omega$  resistance.

The surface under the desorption curve in each instance was directly proportional to the specific surface area of the capillary. The regular shape (Fig. 2c) is suitable for integration purposes and can be achieved by an appropriate choice of the dimensions of the retarding tube. However, this causes a longer measurement time.

The total volume of the measurement stream is very small, both in itself and relative to the volume of the cooled capillary. This difference influences the shape of

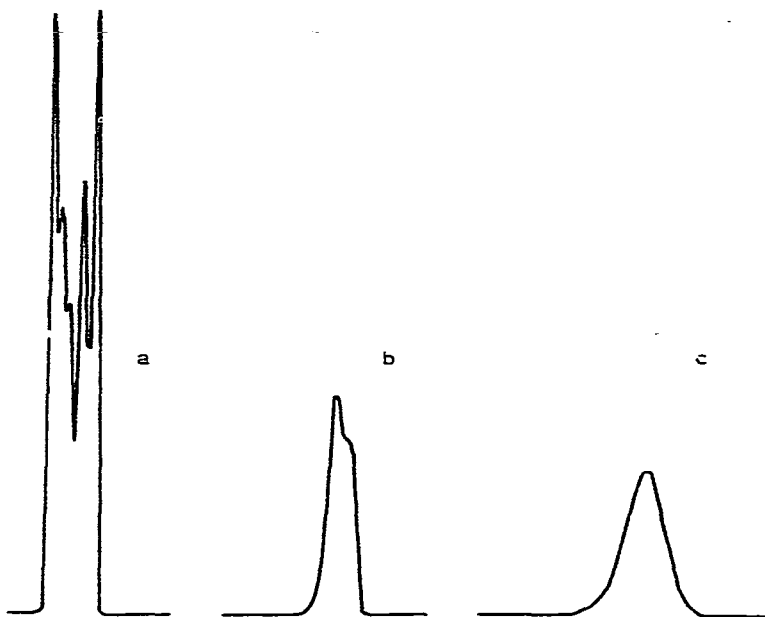


Fig. 2. Typical examples of desorption curves obtained with different lengths (volumes) of retarding tube of I.D. 1.0 mm: a, 15 m; b, 25 m; c, 35 m.

the desorption peak and results in baseline noise. To eliminate this noise, damping capillaries (9, Fig. 1) were used.

Connections with low temperature gradients were used to connect the capillaries into the measurement stream. The measurement parameters were as follows: flow-rate of adsorbate mixture, 3 ml/min, which corresponds to a linear velocity of *ca.* 100 cm/sec for a 0.25-mm I.D. capillary; detector sensitivity, 1500 mV/ml·mg, achieved at a current of 340 mA; limit of detection, 30 ppm of nitrogen, for a 10% (v/v) nitrogen-hydrogen mixture. The maximal adsorbate concentration during the measurements on hydrogen fluoride etched capillaries was *ca.* 1000 ppm.

## RESULTS AND DISCUSSION

To estimate the usefulness of the apparatus, simple measurements using smooth-walled capillaries of different lengths were carried out.

Fig. 3 (Table I) shows the linear relationship between the specific surface area and capillary length. Line 1 represents the geometrical surface area of the inside capillary walls, calculated from its dimensions, and line 2 the results calculated from the desorption peaks using the Temkin<sup>16</sup> equation (eqn. 3) and the B.E.T. adsorption isotherm:

$$a_m = a \left( 1 - \frac{p}{p_s} \right) \left[ 1 + \frac{\left( \frac{p_s}{p} \right) - 1}{C} \right] \quad (3)$$

$$A = a_m N_A w_m \quad (3a)$$

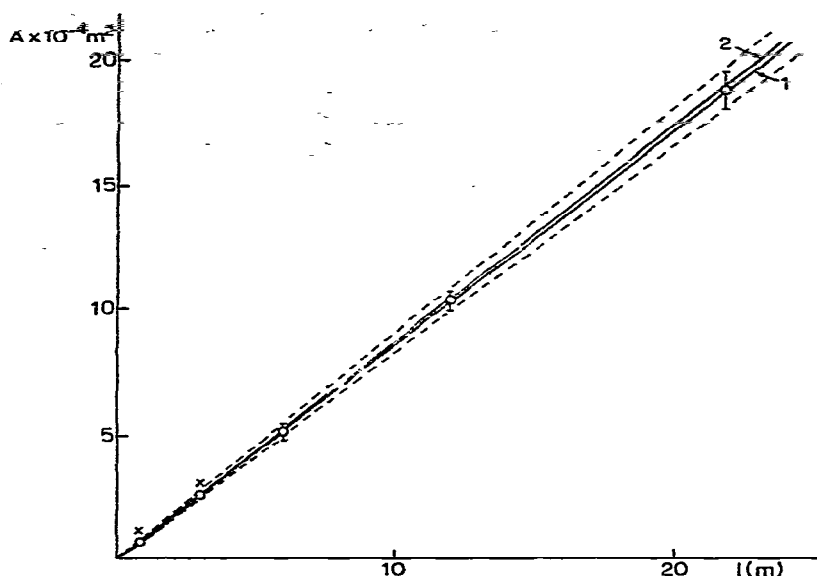


Fig. 3. Relationship between specific surface area and smooth-wall capillary length (numerical data from the Table I).

TABLE I

COMPARISON OF SPECIFIC SURFACE AREAS CALCULATED FROM GEOMETRICAL CAPILLARY DIMENSIONS AND DETERMINED BY MEANS OF THE THERMAL DESORPTION METHOD

Measured capillary length (m)	Geometrical surface area, $A_g$ ( $m^2 \times 10^4$ )	Measured surface area, $A_m$ ( $m^2 \times 10^4$ )	$A_m/A_g$
0.82	0.71	0.81	1.17
3	2.58	2.98	1.15
6	5.16	5.26	1.019
12	10.3	10.35	1.005
21.9	18.8	18.9	1.005

where

$a$  = amount of nitrogen adsorbed (mole/m);

$a_m$  = amount adsorbed in monolayer (monolayer capacity) (mole/m);

$C$  = constant in the B.E.T. equation;

$p$  = actual nitrogen pressure in the mixture ( $N/m^2$ );

$p_s$  = pressure of nitrogen-saturated vapour at the temperature of adsorption ( $n/m^2$ );

$A$  = specific surface area ( $m^2/m$ );

$N_A$  = Avogadro constant (molecules/mole);

$w_m$  = settling surface area of one adsorbate molecule ( $m^2/molecule$ ).

The Tomkin equation (the use of the coordinates of a single adsorption point) introduces a systematic error of ca. 5%, due to the simplifications involved. The error

in calculations of geometrical surface areas due to inaccuracies in the measurement of the inside diameter of a capillary and the variation in the inside diameter along the length of a capillary is  $\pm 4\%$  (see the area between the broken lines in Fig. 3).

It can be seen that the geometrical and measured specific surface areas agree within the limits of experimental error (Fig. 3). As one of the calculation parameters is the ratio of adsorbate pressures,  $p/p_s$ , the pressure gradient for a long capillary should be taken into account. For this purpose, the original B.E.T. equation (eqn. 4) has been modified, assuming that the inlet pressure is higher than the outlet pressure and that the whole adsorption process is a sum of many individual processes without a pressure gradient ( $p = \text{constant}$ , eqn. 5):

$$\frac{\frac{p}{p_s}}{a \left(1 - \frac{p}{p_s}\right)} = \frac{1}{a_m C} + \frac{C-1}{a_m C} \cdot \frac{p}{p_s} \quad (4)$$

$$a = \frac{a'_m p_s}{(p_{\text{in}} - p_0)} \left[ \frac{1}{C-1} \cdot \ln \frac{1 + (C-1) \frac{p_0}{p_s}}{1 + (C-1) \frac{p_{\text{in}}}{p_s}} + \ln \frac{1 - \frac{p_0}{p_s}}{1 - \frac{p_{\text{in}}}{p_s}} \right] \quad (5)$$

where  $a'_m$  is the monolayer capacity with pressure gradient correction,  $p_{\text{in}}$  is the nitrogen inlet pressure and  $p_0$  is the nitrogen outlet pressure.

Comparison of eqns. 4 and 5 shows that the error due to neglecting the pressure gradient is significant only for long capillaries. For example, it is ca. 7% for a capillary of length 60 m and I.D. 0.33 mm. The calculations for short capillaries up to 20 m long can be performed without a pressure gradient correction (eqns. 3 or 4). Eqns. 4 and 5 allow the adsorption isotherm to be determined and permit a more precise determination of the specific surface area, for which two or three measurements at different concentrations of the nitrogen-hydrogen mixture are necessary.

The Wenzel coefficient can be determined as the ratio of two specific surface areas, after and before the glass capillary modification process (eqn. 1).

The use of the method described may give interesting information about the "effective" specific surface area, after coating the inside capillary wall with a thin film of a stationary liquid or another liquid, such as water; the determination can be carried out by changing the desorption temperature from room temperature to  $-70^\circ$ .

The method and the apparatus described can be used generally for the determination of specific surface areas, roughening factors and "effective" specific surface areas in very thin capillaries, or in open-tubular columns, including PLOT (SCOT) columns, without their destruction. The homogeneity of surface roughening along the length of a capillary can also be tested. Measurements of specific surface areas and determinations of roughening factors for some capillaries of different lengths and made of different types of glasses etched by the same method were carried out. For the same capillaries the wettability coefficients were determined by means of Nečasová and Tesařík's method<sup>12</sup>. The results are given in Table II.

Three types of glass (two soda-lime and one borosilicate glass) were etched

TABLE II

SPECIFIC SURFACE AREAS, ROUGHENING FACTORS, ROUGHENING HOMOGENEITY FACTORS AND WETTABILITY COEFFICIENTS FOR DIFFERENT TYPES OF GLASS CAPILLARIES ETCHED WITH "ETCHING ETHER" AT 380°

Type of glass	$A' (m^2 \times 10^4/m)$		$A (m^2 \times 10^4/m)$ , geometrical surface area	$r$	Roughening homogeneity coefficient, $r_h$	$\gamma'_s$ (dyne/cm)	$\gamma'$ (dyne/cm)	$k_w$
	Measured							
	Full length of capillary	1-m section						
Soda-lime, type I	56.7	54.4	10.68	5.3	1.04	20.46	19.85	1.031
Soda-lime, type II	81.09	79.0	10.36	7.8	1.03	20.08	19.63	1.023
Borosilicate (Sovirel)	32.14	32.9	7.85	4.1	0.98	20.83	21.33	0.977

with "etching ether" at 380°. The capillaries were subsequently flushed with oxygen at 380° in order to remove carbon residues. The specific surface areas of the etched capillaries were measured on the apparatus described and specific surface areas of smooth-walled capillaries were calculated from their geometrical dimensions. It can be seen from Table II that there is a close correlation between the roughening factors and wettability coefficients. Because a roughening factor of about 4 corresponds to a wettability coefficient of about 1, this value seems to be the most suitable for promoting the spreading of stationary liquids. The roughening homogeneity factor ( $r_h$ ) is the ratio of the specific surface area per metre calculated from the measurement for the full capillary length to the specific surface area measured for a 1-m section of the same capillary. The closer to unity this roughening homogeneity factor is, the better is the homogeneity of roughening (Table II).

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