Separation and Purification Technology 199 (2018) 198–205

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

On the accuracy of capillary flow porometry for fibrous filter media

H.E. Kolb*, R. Schmitt, A. Dittler, G. Kasper

Institut für Mechan. Verfahrenstechnik und Mechanik, Karlsruhe Institute of Technology, Germany

ARTICLE INFO

Keywords:
Fibrous media
Characterization
Porometry
Volatility
Wetting liquid

ABSTRACT

The application of capillary flow porometry by gas-liquid displacement to the measurement of the pore size distribution in identical glass microfiber filter media can lead to surprisingly divergent results. The causes for these differences as well as the factors that influence the over-all reliability of data obtained by this widely used technique are investigated. Among the key factors studied were the volatility and viscosity of four common wetting liquids, the scan rate (i.e. the holding time between increments of differential pressure Δp or volumetric flowrate $\dot{V}$), and the scan sequence (i.e. dry before wet, or wet before dry scan). Most measurements were made with a porometer designed in house, in order to have complete control over all aspects of operation. Data obtained with commercial porometers are also reported. For best comparability, all measurements were made with the same batch of standard glass microfiber media.

The largest error source by far was the volatility of fluorinated compounds commonly used as wetting liquids. While the vapor pressures of such compounds may be relatively low, their use in combination with a flow of air through the porous matrix can have an enormous effect on the evaporation rate during a scan. Neglecting this effect (which obviously depends on the scan rate) may ultimately result in an error of almost arbitrary magnitude in the pore size distribution. Silicone oil on the other hand has a negligible volatility and provides reliable results for a wide range of operating conditions. The liquid viscosity in the tested range of 5–100 mm^2/s played a comparatively insignificant role. These and other factors of uncertainty are discussed on the basis of experimental data.

1. Introduction

Capillary flow porometry is a well-established technique for measuring pore size distributions in polymer membranes and fibrous media, with a useful range of typically about 1–50 μm for the latter. Its operating principle, as suggested by Erbe [1], is based on saturating small samples of the media completely with a wetting liquid, and then progressively "discharging" pores with a second fluid by increasing the differential pressure Δp across the sample. From the attendant increase in volumetric flow rate (or flow velocity) through the sample one can then derive a cumulative pore size distribution. The displacing fluid can be either air, as in most commercial porometers, or another liquid [2].

Assuming the pores have an ideally circular cross-section, the relationship between the differential pressure Δp and the smallest empty pore d_{pore} is given by classical capillary theory, as

$$d_{pore} = 4\frac{\gamma\cos(\Theta)}{\Delta p} \tag{1}$$

with corrections required for a non-ideal pore morphology [3,4]. Assuming further that the surface tension γ and the wetting angle Θ are constant for the entire internal surface of the media, the pore size distribution can be calculated from the ratio of the respective volumetric air flow rates through the dry and the wet media, obtained at the same Δp:

$$Q(\Delta p) = 1-\frac{\dot{V}_{wet}}{\dot{V}_{dry}} \tag{2}$$

Q(Δp) is the cumulative number distribution of (equivalent) pore diameters d_{pore} as given by Eq. (1). The largest pore diameter (i.e. at Q = 1) corresponds to the bubble point (as defined e.g. by ASTM F316 [5]) and is relatively easy to establish. On the other hand, the smallest pore diameter (at Q = 0) depends on the maximum Δp sustainable by the media and possibly other external factors. A method of extending the lower limit of detectable pores is discussed by Hernandez et al. [6]. This technique will not be used here, however.

Capillary flow porometry is quite attractive to characterize porous media for applications such as filtration [7–9], catalysis [10] or chromatography [11]. Being a flow-based method, it is often preferable to purely geometric or tomographic techniques such as described by Lehmann et al. [12] or Hoferer et al. [13], and also less cumbersome. Porometers are thus available commercially, and ASTM F316 describes their use for "non-fibrous membranes". Despite such widespread use,

* Corresponding author.
E-mail address: eckhard.kolb@kit.edu (H.E. Kolb).

https://doi.org/10.1016/j.seppur.2018.01.024
Received 4 October 2017; Received in revised form 5 January 2018; Accepted 13 January 2018
Available online 31 January 2018
1383-5866/

the scientific literature contains few critical analyses of the method's fundamental reliability. The ASTM guideline F316 is vague with regard to details of applying the method.

Yunoki et al. [14] investigated the influence of three wetting fluids (alcohol, Porofil™ and ethylene glycol) on the pore size distribution of fibrous media. The authors observed a tendency of the distribution to become narrower and shift towards larger pores, which they correlated with the viscosity of the fluid and attributed to kinetic effects during the blow-out of wetting liquid. The same paper also shows the effect of scanning rate, as will be discussed later.

Dixon [15] also discusses the impact of a broad range of wetting fluids on capillary flow porometry as applied to filter media. This hard-to-access conference paper also describes a "scatter" among the wet curves for more volatile liquids such as alcohol, and a relative independence of the bubble point. On the other hand, a "reduced effect of volatility for smaller pores" was observed.

Due to our interest in obtaining reliable pore size data for glass fiber filter media, we have in the past conducted comparative tests with several commercial porometers. The results (presented in the next section of this paper) showed very good reproducibility when repeated on the same machine and with the same sample material, but varied considerably between porometers. The reasons for these variances were not immediately clear, but may have been due to a number of reasons, including differences in the properties of the wetting liquids recommended by the respective porometer manufacturers, in scanning times of Δp or $\dot{V}$, in sample area, and perhaps also unknown details of the proprietary software routines to convert raw data into pore size distributions.

Consequently, we conducted a more thorough study on the reliability and comparability of this important technique, focusing on the influence of wetting fluids and the way a porometer is operated. In order to make the influence of these parameters fully transparent and independent of any specific commercial device, the measurements reported here are based on a laboratory prototype device designed specifically for that purpose. On the other hand, the experiments reported hereunder were limited to a single type of glass microfiber media, which can be considered representative of an entire class of such media.

2. Preliminary comparison tests with commercial porometers

The evaluation included three porometers, a *CFP-1500-AFX* (PMI Inc.), a *3GzH* (Quantachrome GmbH), and a *PSM 165* (Topas GmbH). Of these, the PMI device is available in house, the other measurements are courtesy of the respective instrument manufacturers with samples of glass microfiber of the same media investigated later in this paper.

Sample results for one typical filter medium are shown in Fig. 1 to characterize the differences in resulting pore size distribution. Evidently, the differences are substantial in various aspects of the distribution. Values for the largest pore corresponding to the "bubble point" – normally very easy and reliable to determine – range from 16 μm (Topas) to 20 μm (PMI), with the value for Quantachrome (red curve) in between. The d_{50} values agree for two of the three instruments (around 7 μm), while the third instrument gives a larger value of about 10 μm. Both the upper and the lower ranges of the respective distributions differ substantially with regard to shape and contribution to the distribution. Especially the red curve (labeled Quantachrome) appears to be multimodal on the upper end, while the others are mono-modal. In fact, the only thing all three porometers seem to agree on is the minimal pore size around 5 μm.

Data for other tested media show a similar spread of values, but are not presented here, because more data would add nothing further to the description of the problem. Despite the observed deviations *between* instruments, repeated measurements on the *same* device produced nearly identical pore size distributions. (To some extent, this eliminates differences in sample size from the list of candidate causes.)

In sum, the differences between the respective curves are substantial and far too big to make these data useful for inter-comparisons of media, or the interpretation of filter behavior. Considering furthermore

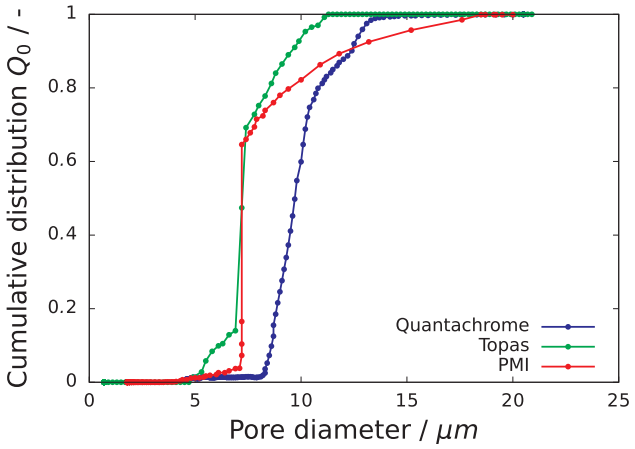

Fig. 1. Pore size distributions obtained by 3 different porometers for the identical type of glass fiber filter media. Working fluids used and scan procedures are those recommended/implemented by the instrument manufacturers.

that the operation of a porometer involves only standard measurements of flow and pressure, these results are hard to explain. They cannot simply result from a translational shift due to some kind of calibration offset. Even though some deviations may be due to differences in instrument design and/or operation (e.g. sample area or scan time), other, major questions remain regarding the influence of the wetting fluids, the scan mode (Δp-scan vs. $\dot{V}$-scan), or the software.

3. Experimental set-up and methods

A porometer consists of only three essential components, an open-face sample holder, a differential pressure gauge, and a device (such as a mass flow controller) to measure and control the airflow, as shown in Fig. 2. We therefore chose to build our own, in order to have all factors under our control.

The circular filter sample had an effective diameter of 14 mm, which constituted a compromise between mechanical strength and a representative sample area with sufficient pores. Also, the area was large enough compared to the clamped fringes. The sample holder was checked for leak-tightness.

For the sake of better comparison, all measurements reported hereunder were performed on the same type and batch of glass microfiber filter media, a standard commercial product (Hollingsworth & Vose) with a mean fiber diameter of 1.6 μm, a porosity of 95%, and a thickness of about 0.5 mm. These media show spontaneous liquid wicking and may be considered fully wettable to all the liquids used in this work. The filter material was chosen because of its relatively good uniformity, which eliminates one potential error source from the measurements.

A flow of clean and dry compressed air was fed to the sample holder

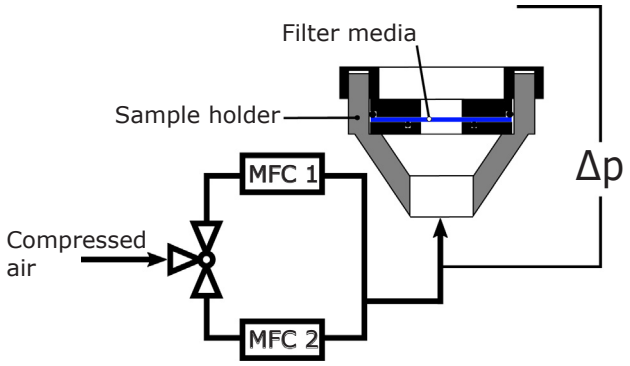

Fig. 2. Schematic diagram of the prototype porometer operating at differential pressures of 0–1000 mbar and volume flows of 0–200 L/min (by one of two mass flow controllers, MFC).