

THE IMPORTANCE OF OPTICAL REFRACTION IN CONNECTION WITH THE SURFACE AREA MEASUREMENT OF POWDERS BY SOME PHOTOMETRIC APPARATUS

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SUMMARY

The surface areas of 3 powders with widely differing transparencies were measured in 4 liquids with refractive indices varying from 1.33 to 1.50 on both a wide angle photometer (WASP) and a narrow angle photometer (EEL). The results indicate that the wide angle photometer is greatly influenced by the transparency of the particle and by the refractive index of the suspending liquid whereas the narrow angle photometer shows a lesser degree of dependence upon these factors. The surface area data obtained are compared to those of two standard permeameters.

INTRODUCTION

There are a number of possible interactions between a light beam and a particle dispersed in a liquid. The most important are absorption, reflection, refraction, transmission and diffraction. The extent of each of these interactions is dependent upon particle size, particle transparency, particle surface texture and the respective refractive indices of the particle and the dispersing liquid, and is also dependent upon the optical design of the receiver in the apparatus used.

When using instruments based on the light blocking principle, the interactions required between the particle and the incident light are theoretically, absorption, reflection and refraction, i.e. none of the light that impinges directly upon the particle should be picked up by a receiver, for instance a photocell placed behind the particle. Receivers can be classified according to the angle of acceptance that they utilize, which is mainly dependent upon the size of the mechanical aperture placed in front of a photocell. Rose and Lloyd (1946) and Allen (1969a and b) have both described apparatus that employ narrow

and wide angle of acceptance respectively. In practice, problems are encountered with the refracted light, because if the angle of refraction is low and the angle of acceptance of the receiver is wide, this light portion will be detected by the receiver. Furthermore, transmission of light through, and diffraction from particles will interfere when applying the principle of light blocking. Transmission will decrease the measured surface area, while diffraction will increase it, compared to the 'true' surface area of a particle.

To compensate for the deviation from the laws of classical optics, the so-called extinction coefficient is used. For a specific apparatus, this ratio expresses the amount of light picked up by the receiver, divided by the amount of light that would have been picked up if the laws of classical optics had been valid. The change of the extinction coefficient, with changing particle size, has been investigated for light blocking instruments having receivers of different optical design, but only for opaque particles, where transmission and refraction are avoided (Rose, 1950; Allen, 1969a and b). In such cases the extinction coefficient is a correction term that compensates only for the effect of diffraction. However, in the case of transparent or partly transparent particles, the interference of transmission and refraction must also be considered.

The effect of transmission is probably less important, because it demands both a smooth flat surface on the particle and an incident light beam, normal to that surface, if the particle and the liquid do not have the same index of refraction. The effect of transmission will influence the measurement of surface area to the same extent, irrespective of the angle of acceptance of the receiver. However, the influence of the effect of refraction is to a large extent dependent upon the design of the receiver. It seems reasonable to assume that the wider the angle of acceptance, the more important is the demand for a correction. If not corrected, the refraction will decrease the measured surface area, compared to the 'true' surface area, giving an apparent extinction coefficient below unity. It may be assumed that the smaller the difference in refractive index between the particle and the liquid, the more significant the correction will be.

For a number of pharmaceutical substances Nyström et al. (1977) have shown that a photometer using a wide angle of acceptance, gave lower values of surface area than a photometer using a narrow angle of acceptance. The intention of the present investigation was therefore to test more specifically the influence of transmission and refraction on the measurement of the surface area of powders, using narrow and wide angle photometry.

MATERIALS AND METHODS

Powders

Microcrystalline cellulose (Avicel pH 101, FMC Corporation) was classified in an Alpine 100 MZR air classifier to obtain particles less than 10 μm .

Calcium carbonate (Kebo-Grave) was classified in an Alpine 100 MZR air classifier to obtain particles less than 10 μm .

Nickel spheres, (Goodfellow Metals, U.K.) having a weight mean diameter of 8 μm according to the manufacturers specification.

Liquids

Demineralized water, with the addition of 0.1% w/w of Calgon, refractive index, 1.33.

Isopropanol, (Analytical grade, Kebo-Grave), refractive index, 1.38.

Cyclohexane, (Analytical grade, Kebo-Grave), refractive index 1.43.

Benzene, (Laboratory grade, Kebo-Grave), refractive index 1.50.

The 3 powders having different degrees of transparency were each dispersed and measured in 4 different liquids, of different refractive indices.

The densities of the 3 powders were measured with a Beckman Air Comparison Pycnometer (Model 930), and the mean values of 3 determinations were, microcrystalline cellulose 1540 kg^{-3} , calcium carbonate 265 kg^{-3} , and nickel spheres 880 kg^{-3} .

Wide angle photometry

Three samples of each suspension were measured with the Wide Angle Scanning photo-sedimentometer (WASP, Microscal, U.K.). The volume specific concentration (C_v) was in the range between 1.4×10^{-5} to 7.8×10^{-4} . All powders were dispersed in an ultrasonic bath for one minute (240 W and 35 kHz), after which time no further increase in specific surface area was obtained. The volume specific surface areas (S_v) were calculated assuming that the extinction coefficient (K) remains equal to unity down to a particle size of $1 \mu\text{m}$ (Allen, 1969a):

$$S_v = \frac{4 \cdot \ln(I_0/I)}{K \cdot L \cdot C_v} \quad (1)$$

where S_v is the volume specific surface area; I_0 is the light transmission through the dispersing liquid; I is the light transmission through the suspension; L is the length of the light path in the suspension; and C_v is the volume specific concentration. No corrections were made for the effects of transmission and refraction.

Narrow angle photometry

Three samples of each suspension were measured with a EEL photosedimentometer (Evans Electro Selenium, U.K.). All powders were dispersed as described above and the volume specific concentration was kept between 3.3×10^{-5} and 6.1×10^{-4} . The surface areas were calculated by applying the correction for the extinction coefficient proposed by Rose and Sullivan (1959):

$$S_v = 4.5 \frac{4 \cdot \ln(I_0/I)^{0.77}}{L \cdot C_v} \quad (2)$$

Permeametry

As a reference, all powders were measured both in a fixed pressure permeameter (Sub-sieve, Fisher Scientific) and in a variable pressure permeameter (Blaine Fineness Tester, Tonindustrie). Three samples of each powder were compressed to standard fixed porosities, being in the middle of the porosity range possible, giving porosities of 0.66, 0.50 and 0.60 for microcrystalline cellulose, calcium carbonate and nickel spheres respectively. The specific surface areas were then calculated on the Fisher apparatus using a calibration capillary tube and on the Blaine apparatus by using an aspect factor of 5. The surface

areas were not corrected for slip or molecular flow, because most particles were around 5–10 μm , where the importance of any correction is small (Nyström et al., 1977).

RESULTS AND DISCUSSION

The results of specific surface areas as measured by wide and narrow angle photometry are compared with the results from permeametry in Figs. 1–3.

Surface area of microcrystalline cellulose

This powder, representing the most transparent substance, shows the greatest differences in surface area for different combinations of dispersing liquid and degree of angle of acceptance (Fig. 1).

The measurement of surface area with the WASP is highly influenced by the differences in refractive index of the liquids used. When the refractive index of the liquid approached the refractive index of microcrystalline cellulose, as in the case of benzene, the measured surface area approached zero.

The measurements with the EEL apparatus are also influenced by the differences in refractive index, although these values of surface area are higher and much closer to the values obtained by permeametry.

The differences obtained between the two permeametry techniques may be explained by the different procedures used for calibration.

Surface area of calcium carbonate

These results (Fig. 2) show the same pattern as for microcrystalline cellulose, although the influence of the dispersing liquid is not as pronounced.

In this case, the WASP still produces results that are highly influenced by the refractive index of the liquid, but for this substance it is possible to approach the permeametry

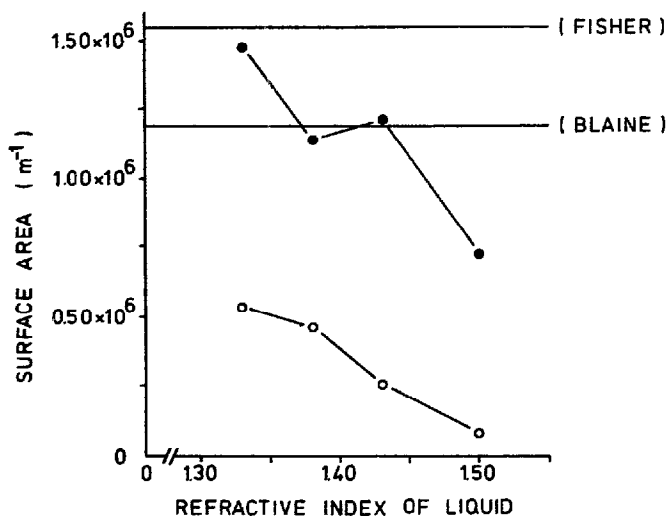


Fig. 1. Surface area of microcrystalline cellulose obtained: ●, the EEL photosedimentometer; ○, the WASP.

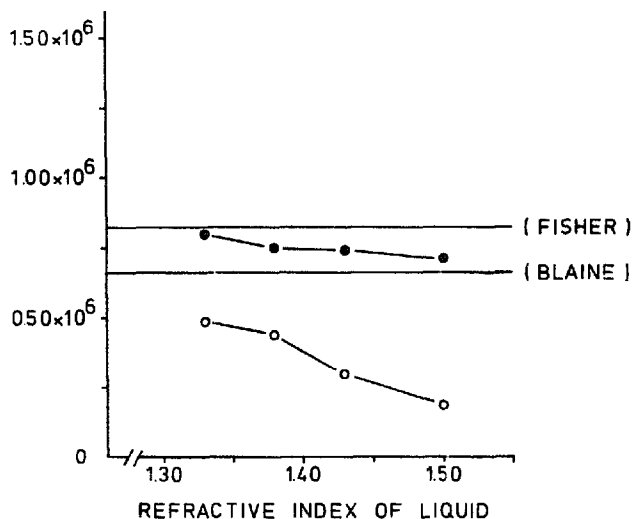


Fig. 2. Surface area of calcium carbonate obtained by: ●, the EEL photosedimentometer; ○, the WASP.

values by using a liquid with a low index of refraction, e.g. water.

Although there are slight decreases in the surface areas with increasing refractive index of the liquids, the results obtained by the EEL photometer are all in agreement with the results obtained by permeametry.

Surface area of nickel spheres

With this opaque powder, the result showed for all liquids a fairly good agreement with the permeametry results, independent of the photometer and angle of acceptance used (Fig. 3).

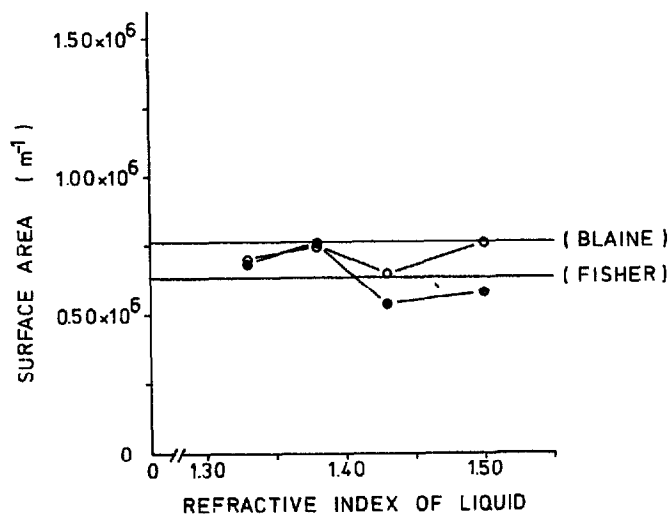


Fig. 3. Surface area of nickel spheres obtained by: ●, the EEL photosedimentometer; ○, the WASP.

The slight variation in surface areas obtained for the different liquids could probably be explained by the different tendencies toward settling during measurement and by the low repeatability of the results obtained by photometry, being about 6%, expressed as the coefficient of variation (Nyström et al., 1977).

It can be concluded that the results obtained by a narrow angle photometer are fairly constant and independent of the physical character of the system measured, whilst a wide angle photometer gives results which are highly dependent upon the particle transparency and the differences in the refractive indices of the powder and the liquid. Consequently for transparent particles, a greater difference in refractive indices between powder and liquid will increase the value of the measured surface area. It seems reasonable therefore that the effect of refraction is of great importance compared to the effect of refraction in the calculation of surface area when measuring transparent or partly transparent particles with a wide angle photometer.

REFERENCES

- Allen, T., Theoretical estimate of variation in extinction coefficient with particle size using a white light source. *Powder Technol.*, 2 (1969a and b) 133–140.
- Allen, T., Comparison between wide-angle and narrow-angle photosedimentometers and experimental determination of extinction coefficients. *Powder Technol.*, 2 (1969a and b) 141–153.
- Nyström, C., Malmqvist, K. and Alex, W., Comparison of permeametry and photometry for the measurement of surface area of powders. *Acta Pharm. Suec.*, 14 (1977) 497–504.
- Rose, H.E., The design and use of photo-extinction sedimentometers. *Engineering (London)*, 169 (1950) 350–351, 405–408.
- Rose, H.E. and Lloyd, H.B., On the measurement of the size characteristics of powders by photo-extinction methods. I. Theoretical considerations. *J. Soc. Chem. Ind.*, 65 (1949) 52–58.
- Rose, H.E. and Sullivan, R.M., Rapid estimation of the specific surface of a powder. *Nature (London)*, 184 (1959) 46–47.