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CONSTRUCTION AND CALIBRATION OF AN APPARATUS FOR THE MEASUREMENT OF SURFACE AREAS OF POWDERED SAMPLES

(Report and 4 figures)

R. A. Washington

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ABSTRACT

An apparatus has been constructed for measurement of specific surface areas of powdered samples in the size range from 0.72 mm diameter (20 mesh) to 0.068 mm diameter (250 mesh). The method is rapid and easy to use. With a few simple precautions in the calibration an accuracy of about $\pm$ 5 per cent is possible. Following calibration with standard spherical glass beads the surface area of particles of any shape may be measured directly.

CONSTRUCTION AND CALIBRATION OF AN APPARATUS FOR THE MEASUREMENT OF SURFACE AREAS OF POWDERED SAMPLES

INTRODUCTION

In the course of experiments to measure the amount of trace elements adsorbed by silicate minerals, it has become necessary to determine the specific surface area of the adsorbents. Various techniques (Society for Analytical Chemistry, 1963)[1] for surface area measurement were considered. Some methods were rejected because an excessively complex apparatus is required (e.g. Connor and Hardwick, 1960; Lea and Nurse, 1939). Others, such as the well-known BET method (Brunauer, Emmett, and Teller, 1938; Harkins and Jura, 1944a, b; Jura and Harkins, 1944) are suitable only for much smaller particle sizes (and much larger specific surface areas) than are employed in the writer's experiments.

The most suitable method for the present work was one described by Payne (1953) and modified slightly by Ringqvist (1955), which was apparently based on the Carman method (Carman, 1937; 1938; 1939; 1948). The apparatus is simple to construct and operate, and the measurements can be made more rapidly than with other methods (e.g. the BET method). The surface area is measured by determining the work done in withdrawing a liquid from a bed of the powdered sample (which must be wetted by the liquid) against the surface tension forces. By using a series of standard samples of known specific surface area, a calibration curve can be obtained for the apparatus, which can then be applied to any sample in the appropriate size range.

One great advantage of the method lies in the fact that it is applicable to particles of any shape. It is therefore unnecessary to assume that the particles in the powdered sample are spherical, or to apply a 'shape factor' to allow for deviations from the assumed shape, as is required in some other suggested procedures (e.g. Harris, 1960; Shermway and Igelman, 1960). Moreover, the method is stated (Payne, 1953; Ringqvist, 1955) to be accurate to + 10% over the range of specific surface area from 25 cm^2/g to 3,000 cm^2/g, and can be used (with less accuracy) to 10,000 cm^2/g.

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[1] Names and/or dates in parentheses refer to publications listed in the References.

This paper reports on the construction of the apparatus, and outlines some calibration problems that were unexpectedly encountered. It is hoped that this will assist others employing the technique to avoid procedural difficulties that were not mentioned in the original papers.

The author wishes to thank T.R. Mason for his assistance in performing the laboratory work.

PROCEDURE

The apparatus is shown schematically in Figure 1. All parts were assembled from readily available apparatus. A water manometer was employed to measure pressures near atmospheric, where the mercury-filled manometer is difficult to read accurately.

Details of the experimental procedure have been given by Ringqvist (1955), and only a brief outline is presented here. Distilled water was used in all tests which were performed in an 'air-conditioned' room at about 25°C[1]. Samples of 8 to 10 grams were weighed to 0.01 gram, and were added slowly to the filtering funnel, which was tapped gently to induce the particles to settle uniformly. Distilled water was then added slowly down the side of the funnel, and the excess was allowed to drain, with the apparatus under atmospheric pressure. The burette volume was recorded, and a slight vacuum was applied. The pressure was observed on the appropriate manometer, and the new burette volume was recorded. The pressure was decreased, and the new pressure and volume were again recorded. This procedure was repeated until a further decrease of pressure caused no appreciable change in volume.

A curve was plotted of the volume increment (Δ v, cm^3) vs. applied pressure (p, cm H_2O). By graphical integration $\int p\,dv$ was determined, and this was plotted vs. the known surface area of the standard sample, mS (cm^2). The procedure was repeated for a series of samples of differing surface areas to provide a calibration curve.

The standard samples were Ballotini 'glass' beads (supplied by O.H. Johns Glass Co. Ltd.) of the following nominal diameters: 0.85 mm; 0.50 mm; 0.30 mm; 0.20 mm; and 0.10 mm. An additional sample of glass beads of stated diameter 0.068 mm was generously supplied by Dr. Hugh Dibbs of the Mines Branch, Department of Mines and Technical Surveys, Ottawa. Microscopic examination of these samples showed the beads to be

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[1] Although temperature records were not kept at the time of the experiments, subsequent observations indicate that the temperature variation was less than $\pm$ 2°C.

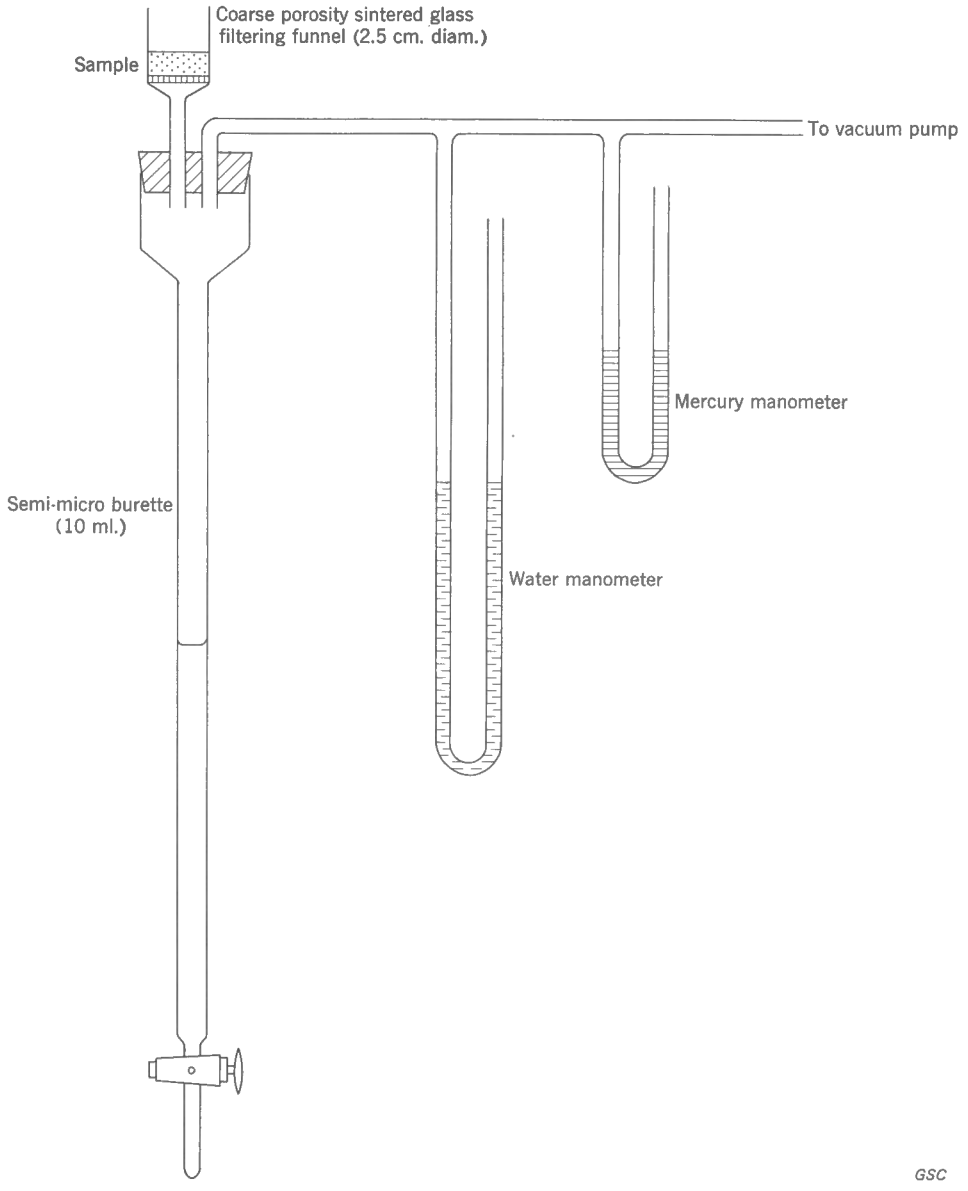

Figure 1. Apparatus for measurement of specific surface area

essentially spherical, but lack of a graticule prevented accurate measurement of the bead diameters. The nominal values were therefore accepted for the time being.

In order to plot the calibration curves, the total surface area of the standards must be known. For this purpose a counted number of beads of each size was weighed to the nearest microgram. The average weight and surface area of a single bead were calculated, and the total surface area, mS, of the sample could then be obtained, where m is the weight of sample in grams and S is the specific surface area in cm^2/g. Alternatively, m may represent the number of beads in the sample, and s the surface area of one bead.

Plotting mS vs. $\int p\, dv$ should give a curve of the general form

$$y = m x + b \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

where $y = mS$ and $x = \int p\, dv$ from which the slope (m) and intercept (b) can be calculated. These values can then be used to find mS for any other sample.

RESULTS AND DISCUSSION

Erratic results appeared in the earliest experimental tests, in which the expected linear relation between mS and $\int p\, dv$ was not observed. The results were therefore analyzed in some detail and additional tests were made in order to define the causes of the difficulty.

The following three factors apparently caused most of the error: (1) the stated diameter of beads was in error for some samples, and some samples contained beads of two or more different sizes; (2) the water used in the experiments sometimes failed to wet the sample; and (3) the weights of known numbers of beads were not reproducible, probably because of variable amounts of adsorbed water vapour on the surface of the beads.

The following steps were taken to eliminate these problems. First, the beads were screened using standard sieves. The results are shown in Table I. Mesh sizes refer to the Tyler numbers of the screens used. The nominal 0.10 mm diameter beads were not screened because suitable sieve sizes were not available. All samples were then thoroughly washed using, in order, $CC\ell_4$, ethyl alcohol, 6M. $HC\ell$, H_2O, 6M. HNO_3, and finally distilled and de-ionized H_2O. They were then covered to keep them dust-free, and carefully dried at 110°C. Finally, the total surface

Table I

Determination of Sizes of Standard Beads

Nominal Diameter (mm)	Mesh [1] Range	Size Range (mm)	Estimated [2] Average Size (mm)	Fraction [3] (%)
0.85	-20 +28	<0.84 >0.59	0.72	~50
	-28	<0.59		~50
0.50	-28 +35	<0.59 >0.42	0.50	~100
0.30	-48 +60	<0.295 >0.246	0.27	~50
	+48	>0.295	~0.30	~50
0.20	+80	>0.177	~0.20	~100
0.068	+250	>0.061	~0.068	~100

(1) Tyler numbers.
(2) Mean of limiting sizes, where applicable; estimated probable error ± 10 per cent.
(3) Estimated visually.

area of each sample was obtained by measuring the volume of a known weight of beads, and calculating the surface area from the relation

$$S_T = \frac{6\,V_T}{D} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

where S_T is the total surface area of the sample, V_T is the total volume, and D is the diameter of the beads. The volume, V_T, was measured by transferring about 5 grams of beads (weighed to the nearest centigram) to a graduated cylinder containing about 5 ml of water, taking care to avoid trapping air in the sample. The initial and final volumes were observed, and the difference was taken as the volume of the sample. The results are shown in Table II and Figure 2.

A weighed sample of beads was then transferred to the surface-area-measurement apparatus, and the graph of p vs. Δv was plotted according to the procedure described above. A typical curve is shown in Figure 3, for 0.72-mm beads. Graphical integration from Δv = 0 to Δv = 1.9 (dashed line) gave a value for $\int p\,dv$ of 22.5 cm^4. A similar procedure for other bead sizes gave the results in Table III. These data are also plotted in Figure 4, together with the line obtained by least squares analysis of the data.

The equation of the line is found to be $mS = (14.6 \pm 0.4) \int p\,dv - (112 \pm 21)$[1], if the data for 0.1 mm and 0.72 mm diameter beads are neglected. Visual observation indicated that the 0.1 mm diameter beads were not being properly wetted in the test, even after thorough cleaning, for the test results were erratic. It is suspected that the composition of these beads was different than the rest, or that they were coated with material that prevented wetting. The data for the 0.1 mm diameter beads were, therefore, rejected. All the other points, except that for the 0.72 mm diameter beads, fall on the line within experimental error. The deviation from a straight line for the 0.72 mm diameter beads indicates that the linear relationship does not hold for $\int p\,dv <$ ca. 30 cm^4. This may be caused in part by failure of capillarity when the beads, and the interstitial spaces between them, are too large.

By taking the precautions described above the estimated accuracy of the method has been reduced to about $\pm$ 5 per cent over the particle size range from 0.72 mm diameter to 0.068 mm diameter. This

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[1] Errors are statistical standard deviations, unless otherwise noted.

Table II

Specific Surface Areas of Standard Beads

Bead Diameter D (mm)	Weight of Sample, W (grams)	Volume of Sample, V_T (cm^3)	Surface Area of Sample, $S_T = \frac{6V_T}{D}$ (cm^2)	Specific Surface Area, $S = \frac{S_T}{W}$ (cm^2/g)
0.72	4.90	1.92	160	32.7
0.50	4.95	1.95	234	47.3
0.30	5.08	1.71	340	66.9
0.27	4.89	1.64	364	74.5
0.20	5.04	2.00	600	119.0
0.10	5.77	2.34	1,400	243.0
0.068	4.72	1.87	1,650	350.0

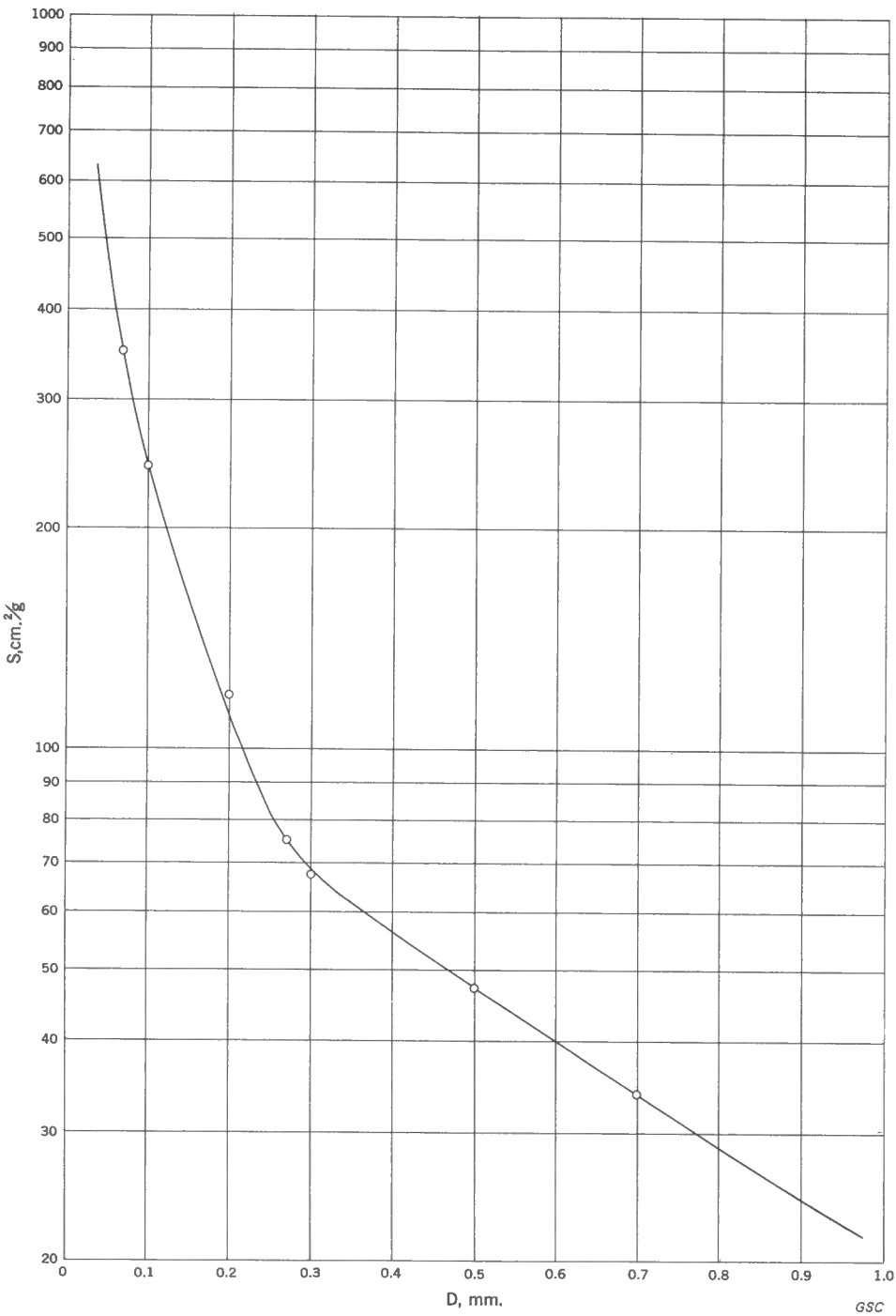

Figure 2. Measured specific surface area of standard Ballotini beads

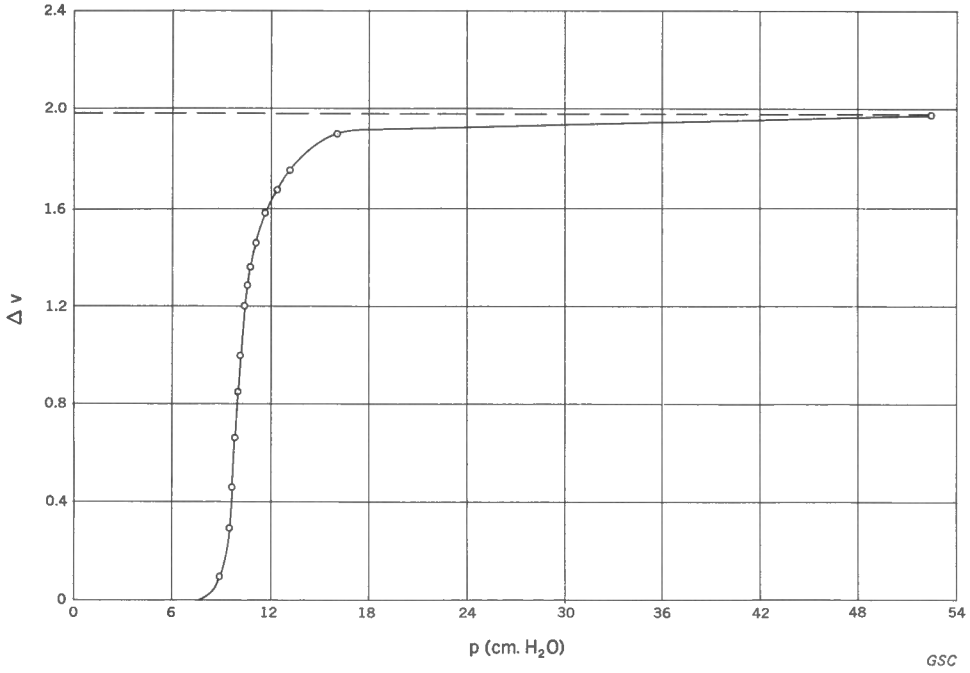

Figure 3. Plot of p vs. Δv for 0.72 mm. diameter beads

Table III

Total Surface Areas of Standard Beads

Bead Diameter (mm)	Sample Weight (m, g)	Total Surface Area, mS (cm^2)	$\int p\,dv$ (cm^4)
0.72	9.105	298	22.5
0.50	8.282	392	35.2
0.30	10.987	735	57.0
0.27	10.945	815	64.9
0.20	9.880	1,180	88.0
0.10	9.107	2,220	84.4
0.10	9.953	2,420	97
0.068	9.912	3,470	246

Mean $\frac{mS}{\int p\,dv} = 12.9 \pm 0.9$ (omitting values for 0.10-mm beads).

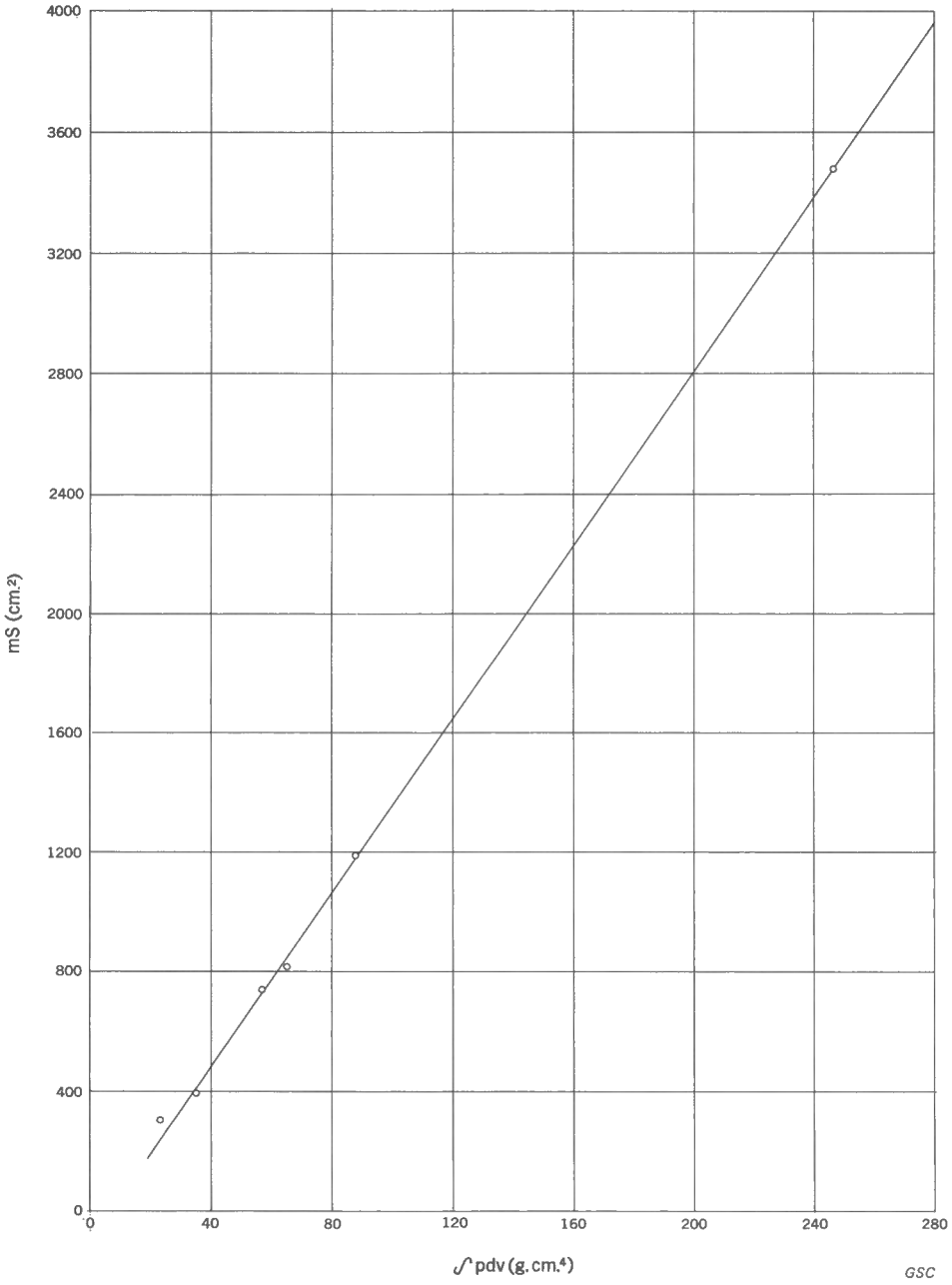

Figure 4. Calibration curve for surface area measurement

represents a significant improvement on the ± 10 per cent accuracy quoted by Ringqvist (1955). However, the present work covers a much smaller range of particle sizes, and it is possible that less accuracy might be obtained in tests on smaller particle sizes, which have larger specific surface areas. This interpretation is suggested by the fact that the tail of the curve of p vs. Δv rises more steeply for small-diameter beads than for the 0.72 mm beads (Fig. 3), leading to a larger error in the graphical estimate of $\int p\, dv$. However, the author's investigations do not require the use of very small particle sizes, and the accuracy of calibration is therefore very satisfactory.

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