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The Permeability and Elutriation Methods for Determining the Specific Surface of Dry Chemical Fire-Extinguishing Powders

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ABSTRACT

Two methods of measuring the specific surface of powders were examined for their suitability in characterizing dry chemical fire extinguishing powders. The air permeability (Blaine) method gives a direct measure of the total surface of a powder sample. The air elutriation (Roller) method gives the distribution of particle diameters in a sample, from which the surface can be found by numerical or graphical integration.

Measurements of the specific surface by the permeability method of powders ranging from approximately 2600 to 5900 cm^2/g were reproducible to within ±1.5% when the test was carried out in a preferred manner. Samples which were frequently exposed to the atmosphere by repeated opening of their containers over a period of a few months suffered an apparent loss of specific surface which could be only partially restored by agitation. Samples which were stored in continuously closed containers showed no change over the same period of time. Mixtures of equal weights of two powders of different composition and different grain shapes gave experimentally determined values of specific surface in good agreement with the average calculated from the specific surfaces of the individual powders.

The air elutriation method proved to be very sensitive to the relative humidity of the operating air when used with the same powder as used in the permeability method. In some instances, separating with dry air gave values of specific surface nearly double those obtained using moist air. In view of this sensitivity to operating conditions, as well as the much greater time required for each determination, the elutriation method appeared to be unsuitable for characterizing dry chemical powder extinguishants.

PROBLEM STATUS

This is a final report on one phase of the problem; work on the problem is continuing.

AUTHORIZATION

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THE PERMEABILITY AND ELUTRIATION METHODS FOR DETERMINING THE SPECIFIC SURFACE OF DRY CHEMICAL FIRE-EXTINGUISHING POWDERS

INTRODUCTION

Various investigations have shown a relationship between the specific surface (surface area per unit weight) of fire extinguishing chemical powders and their effectiveness. The exact relationship has been difficult to establish because of the lack of a reliable, reproducible method of measurement. Numerous schemes have been suggested for specific surface determination [1,2], and two of these, the air permeability (Blaine) method and the air elutriation (Roller) method, were selected for further study, with special reference to the determination of the specific surface of potassium bicarbonate-base, dry chemical powder fire extinguishants. The permeability method requires relatively inexpensive, commercially available apparatus, and several determinations can be run in a working day. The data obtained with this apparatus give a measure of the specific surface, which can be converted by simple arithmetic to mass mean diameter of the powder sample. No information, however, is obtained on the particle size distribution in the sample. The Roller particle size analyzer, also commercially available, permits the determination of the fraction of a powder sample lying within rather narrow size ranges so that a size distribution curve can be established. This data also permits calculation of the specific surface and mass mean diameter of the powder sample. Unfortunately, part of the sample is invariably lost, due in part to adherence to the walls of the apparatus. The difference in weight of the sample introduced into the apparatus and the sum of the separate size fractions collected is customarily assigned in linear proportion to each size range, although there is no real basis for assuming that the lost material has the same particle size distribution as in the original sample. The following investigation was carried out to determine the optimum procedure for carrying out each method of particle size determination, and, if possible, to find a correlation between the results obtained by the two methods.

A large sample was drawn from each of three commercial lots of dry powder extinguishing agent. Two of these samples were "Purple-K Powder" (PKP) made by different manufacturers, and the third sample was protein foam compatible (FCK) powder made by one of these two manufacturers. In addition, three small samples of experimental batches of PKP and one sample of potassium chloride-base experimental extinguishant powder were used, these also being supplied by the manufacturer of the FCK used.

PERMEABILITY METHOD

Earlier work in this and other laboratories showed considerable spread in the determinations [3] of specific surface (S_w, cm^2/g) made with the Blaine permeability apparatus. Such spread of results was seen in repeated determinations made in individual laboratories, as well as in the comparison of average S_w obtained by different laboratories. However, one laboratory showed a much smaller spread of results than any of the others, and this suggested that variations in operator technique are responsible for the inconsistencies. All tests presumably were made in accordance with specifications for testing "Purple-K" dry powder fire extinguishant [4]. The procedure given also cites ASTM method C-204 [5]. In view of the simplicity of the apparatus used, it seemed obvious that the source of the variations lay in the technique used in charging the powder holding cell. The following experiments were made to find a technique for packing powder in the sample holder to give the most reproducible results.

Since the S_w is an additive property of powders, the selected technique was further tested by determining the S_w of mixtures of equal weights of two powders having substantially different S_w with the expectation that the mixture would have an S_w midway between that of the individual powders. Some of the tests were made on powders prepared by the same manufacturer and presumably identical except for particle size distribution. In another test two powders of different S_w and from different manufacturers were mixed. Since the coating and free-flowing additives used by the two manufacturers are different, concordance of the experimentally determined S_w with the calculated S_w for the mixture would demonstrate the independence of the method in regard to chemical composition or any other property unique to each brand of powder.

The effect of variations in packing density on the S_w determined experimentally was explored, this exploration being possible since it was found that the void fraction (e), which is the complement of the packing density, of the powder bed prepared for successive tests of the same powder could be varied over a substantial range.

Finally, the effects of aging and storage conditions were examined by redetermining the S_w of two of the samples after the sample jars had been frequently opened over a period of several weeks. These results were compared with those obtained at the start, and with the S_w measured on powder from freshly opened shipping containers of the same lots of powder.

Fig. 1 - Permeability apparatus for determining the specific surface of S_w of powders

Apparatus

The apparatus used was the "Blaine air permeability fineness tester" made by the Precision Scientific Company* in accordance with method C 204-55 of the American Society for Testing Materials [5]. Briefly, the apparatus (Fig. 1) consists of a powder holder having a perforated bottom attached to the top of one arm of a U-tube containing a low vapor pressure oil. In operation, a powder bed of the specified depth is prepared in the powder holder and the weight of powder is determined on an analytical balance. The powder holder is attached to one arm of the U-tube and the oil is raised in that arm by means of an auxiliary suction bulb. The oil is then allowed to fall, drawing air through the powder bed. The time required for the oil to fall between two fixed points is noted. The S_w is then computed using Carman's relationship between S_w and permeability. The calculations used [5] involve the rate of flow (time T for the oil to pass between the fixed points), density of the powder, void fraction e, viscosity of air η, and various constants of the apparatus. For the apparatus used in these tests, the relationship reduces to

$$S_w = \frac{15.54}{(1-e)} \sqrt{\frac{e^3 T}{\eta}}$$

*The use of the manufacturer's name is only for convenience in describing the apparatus and is not necessarily an endorsement of this particular source.

where

S_w = specific surface, cm^2/g

ρ = density of the powder particles, g/cm^3

T = time for the meniscus of the oil to pass between two fixed points, sec

η = viscosity of air at the temperature of the test, poise

e = void fraction = 1 - (density of the bed/ρ), where the density of the bed is the weight of the bed material divided by the volume calculated from the inside diameter of the powder holder and the depth of the powder bed.

The ASTM method C 204-55 is intended primarily for testing Portland cement and specifies an empirical correction to compensate for variations of e in repeated tests on the same powder namely, replacing the $1 - e$ term by $1 - (e/0.850)$. This correction was found to be inappropriate for dry chemical powder extinguishant and was not used in calculating the specific surface.

Sources of the Powder Samples

The samples from commercial lots of powder have been designated powders I and III and are "Purple-K Powder" (PKP) supplied in accordance with specification MIL-F-22287A(Wep) [4]. Powder II was a large experimental lot of potassium bicarbonate-based extinguishant designated FCK; it was intended to meet the same specifications as PKP [4] and yet be compatible with mechanical foam. This powder reportedly uses a heavy metal organic salt as a coating and flowing agent for the bicarbonate grains, whereas PKP produced by the same manufacturer (powder III) uses other, proprietary, flowing agents. Samples designated a, b, and d are similar to PKP, but they were taken from special laboratory batches by this same manufacturer. Near the end of the investigation a new powder, based on potassium chloride, became available from the manufacturer of powders II, III, a, b, and d, and this is designated as powder IV. The age and past handling of this powder are uncertain. However, it is known that the sample was at least one month old and that the sample container had been opened several times after it was received by this Laboratory.

Preparation of the Powder Bed

The technique finally adopted for building up a powder bed consisted of adding increments of powder of not more than 1/2 g and rapping the powder holder on the bench after each addition. The rapping consisted of dropping the powder holder on the bench top from a height of 1 or 2 mm at first, and finally from about 1 cm, until air pockets in the bed were removed. The release of air trapped in pockets was evidenced by vigorous spurting of material from the top surface of the powder bed. Usually, ten drops of the holder was enough to compact each increment. When a dense bed was desired, the 1-cm drop was repeated 25 to 50 times. The bed was built up in this manner until it was high enough to support the packing plunger just above its closed position; i.e., the collar of the plunger, without any force applied, was within 1/2 mm of the rim of the powder holder. Finally, a disk of filter paper was placed over the powder bed, and the plunger was seated by gently placing a 1, 2, or 3 kg weight on it. The powder holder was then attached to the rest of the apparatus and the S_w determined immediately. In a few instances where the plunger could not be fully seated by a 3-kg force, the plunger was seated by as much additional force as necessary and the test continued. This procedure gave substantially lower results than when the packing force was limited to 3 kg.

Pretreatment of the Powder Sample

It has been suggested [5] that powder samples may require fluffing up by mechanical agitation. Such agitation was provided in some of the tests by rotating the sample jar end-over-end 25 times immediately before preparing the powder bed. No other pretreatment of the sample was performed. One of the samples which had been agitated before determining its S_w was allowed to stand overnight and its S_w redetermined without further agitation.

Results

The results of the S_w determinations are given in Tables 1 through 7. The range of void fraction e shown for each powder covers the maximum and minimum that could be obtained while using the packing technique previously described. As a measure of precision of the method, the deviations of individual determinations from the average is shown. In addition, the standard deviations and coefficients of variation (C.V.) were calculated using standard statistical methods [6]. The results of all test runs are included in Tables 1 through 7; i.e., none were dropped because of apparent conflict with the average of other tests in the same group.

As shown in the data for powder I, agitation of the powder produced approximately a 3% increase in the measured S_w (162 cm^2/g). A repeat determination on the same sample made after a lapse of about 5 months showed a decrease of 4% (173 cm^2/g) in comparison with the fresh, agitated sample. A second sample taken from an unopened can of the same lot of powder approximately 6 months later and analyzed immediately showed essentially the same S_w as the unaged first sample. There was little effect of agitation on the average and standard deviations of the repeat determinations of the S_w of fresh samples. The aged sample showed a much greater spread of results than did the fresh samples.

Powder II reputedly has a different type of flowing agent added to the potassium bicarbonate crystals, probably a heavy metal pelargonate. This powder showed a similar effect of agitation on the apparent S_w and a much greater effect resulting from aging and handling of the sample. Failure to agitate the sample immediately before preparing the powder bed resulted in an approximately 4% (204 cm^2/g) drop in S_w. Aging with repeated exposure to the ambient atmosphere over a period of 4 months resulted in a 14% (649 cm^2/g) drop in S_w. As before, a fresh sample of the same batch of dry chemical powder obtained from a previously unopened container showed an S_w almost identical with the earlier value obtained for the first sample.

Some particles 20 μ and smaller of powder II which had been separated by air elutriation (Roller analyzer), and which had been stored for about the same length of time, were on hand. Microscopic examination showed that the particles had agglomerated to form nearly regular structures. Four or five particles had joined to form rods, generally 75 to 105 μ long, whose ends were joined to form an open, cubic lattice. These agglomerates were sufficiently strong that vigorous rapping on the microscope slide caused them to move around without breaking up their structure. Similar lattices were observed in the complete first sample after the aging period. An attempt was made to restore the original S_w by vigorous shaking. The sample jar was placed on a laboratory shaking machine (one which moved in a horizontal, orbital motion) for 10 minutes. The shaking machine produced strong turbulence in the sample. However, the S_w determined after shaking was only slightly higher than without shaking as shown in Table 3a. The sample was returned to the shaking machine for an additional 20 minutes. Again, the S_w found was only slightly higher than that of the unshaken sample (Table 3b), although the spread (and standard deviation) of S_w was much smaller after the more extensive shaking.

Table 1
Specific Surface of Powder I as Determined
by the Permeability Method

Void Fraction e	S_w (cm²/g)	Dev. From Average (cm²/g)
First sample; not aged; not agitated		
0.380	4954	76
0.397	4886	8
0.414	4840	-38
0.426	4831	-47
	av = 4878	av = 42
		std. dev. = 5624
		c.v. = 1.15%
First sample; not aged; agitated		
0.382	5040	0
0.414	5008	-32
0.415	4982	-58
0.422	5133	93
0.423	5038	-2
	av = 5040	av = 37
		std. dev. = 57.10
		c.v. = 1.13

Void Fraction e	S_w (cm²/g)	Dev. From Average (cm²/g)
First sample; aged; agitated		
0.390	5079	212
0.390	4897	30
0.401	4785	-82
0.402	4678	-189
0.414	4898	31
	av = 4867	av = 108
		std. dev. = 149.37
		c.v. = 3.07
Second sample; agitated (obtained from previously unopened container)		
0.383	5130	74
0.392	5053	-3
0.394	4984	-72
	av = 5056	av = 50
		std. dev. = 73.03
		c.v. = 1.44

Powder III, although manufactured to meet the same specifications as Powder I, was obtained from a different manufacturer, and undoubtedly had different flowing agents. Since this sample was obtained late in the test program, no tests were run on aged samples. The specific surface of the fresh sample was measured to show the precision of the method when applied to powders from this source. As indicated in Table 4 the standard deviation of five repeat determinations was 42 cm²/g. This value has about the same magnitude as the deviations found for powders I and II using the same measuring technique.

Powder IV was an experimental batch of dry chemical extinguishing agent based on potassium chloride in place of potassium bicarbonate. Microscopic examination of the powder at 100 × magnification showed that many of the powder grains had sharp edges and corners. In contrast, the grains in powders I, II, and III were generally rounded. As indicated in Table 5, the standard deviation of repeated determinations of S_w was improved by agitation of the powder before preparing the test bed.

Specific Surface of Mixtures of Powders — Three samples of experimental batches of potassium bicarbonate-base dry powder extinguishant were available whose S_w values together with those of powders I through IV, covered a fairly wide range. Determining S_w on mixtures of the powders provided an opportunity to study whether the permeability method is independent of variations in the composition and the physical form of the powders. If the method is valid, the indicated S_w would be expected to be proportional to the amount and S_w of the individual powders in each mixture.

Table 2
Specific Surface of Powder II

Void Fraction e	S_w (cm^2/g)	Dev. From Average (cm^2/g)
First sample; not aged; not agitated		
0.429	4333	-126
0.429	4606	147
0.441	4379	-80
0.443	4624	165
0.453	4431	-28
0.454	4383	-76
	av = 4459	av = 104
		std. dev. = 124.64
		c.v. = 2.80%
First sample; not aged; agitated		
0.429	4598	-65
0.430	4620	-43
0.441	4736	73
0.454	4661	-2
0.455	4699	36
	av = 4663	av = 44
		std. dev. = 56.35
		c.v. = 1.21
First sample; not aged; agitated and allowed to stand overnight		
0.429	4606	95
0.443	4624	113
0.453	4431	-80
0.454	4383	-128
	av = 4511	av = 104
		std. dev. = 121.90
		c.v. = 2.84

Void Fraction e	S_w (cm^2/g)	Dev. From Average (cm^2/g)
First sample; aged; agitated		
0.499	4210	196
0.507	4231	217
0.520	3887	-127
0.535	3917	-97
0.552	3824	-190
	av = 4014	av = 165
		std. dev. = 191.79
		c.v. = 4.78
Second sample, agitated (obtained from previously unopened container)		
0.437	4615	-36
0.447	4666	15
0.458	4720	69
0.463	4657	6
0.466	4595	-56
	av = 4651	av = 37
		std. dev. = 48.62
		c.v. = 1.05

The S_w of the individual samples of powders a, b, and d were determined using the same sample agitation and bed compaction technique used for powders I, II, III, and IV. Unfortunately, too little sample powder was available to permit more than two or three repeat determinations for some of the powders. The results for powders a, b and d are given in Table 6.

Table 3
Specific Surface of Powder II After Aging Followed by Shaking on Shaking Machine

Void Fraction e	S_w (cm²/g)	Dev. From Average (cm²/g)
a. 10 minutes of shaking		
0.423	4293	39
0.430	4112	-142
0.434	4282	28
0.461	4463	209
0.493	4122	-132
	av = 4254	av = 110
		std. dev = 144.55
		c.v. = 3.40%
b. 30 minutes of shaking		
0.407	4153	-10
0.425	4153	-10
0.431	4208	45
0.465	4137	-26
	av = 4163	av = 23
		std. dev. = 31.10
		c.v. = 0.75

Table 5
Specific Surface of Powder IV

Void Fraction e	S_w (cm²/g)	Dev. From Average (cm²/g)
Sample not agitated		
0.382	2596	16
0.387	2664	84
0.396	2537	-43
0.406	2596	16
0.410	2507	-73
	av = 2580	av = 47
		std. dev. = 60.72
		c.v. = 2.35%
Sample agitated		
0.374	2595	-7
0.380	2665	63
0.390	2601	-1
0.401	2546	-56
0.410	2602	0
	av = 2602	av = 25
		std. dev. = 42.30
		c.v. = 1.63

Table 4
Specific Surface of Powder III; Sample Not Aged; Agitated

Void Fraction e	S_w (cm²/g)	Dev. From Average (cm²/g)
0.386	4050	10
0.395	4065	25
0.400	3977	-63
0.400	4024	-16
0.401	4085	45
	av = 4040	av = 32
		std. dev. = 41.76
		c.v. = 1.03%

Table 6
Specific Surface of Powders a, b, and d

Void Fraction e	S_w (cm²/g)	Dev. From Average (cm²/g)
Powder a		
0.368	3225	34
0.413	3157	-34
	av = 3191	av = 34
		std. dev. = 48.08
		c.v. = 1.51%
Powder b		
0.387	3039	-14
0.402	2997	-56
0.415	3122	69
	av = 3053	av = 46
		std. dev. = 63.61
		c.v. = 2.08
Powder d		
0.420	5922	27
0.437	5869	-26
	av = 5895	av = 27
		std. dev. = 37.48
		c.v. = 0.64

Table 7
Specific Surface of Mixtures of Powders

Void Fraction e	S_w (cm^2/g) Found	Calculated	Difference	Percent Difference
Powders a and d				
0.399 0.409	4544 4593 av = 4569	4543	26	+0.57
Powders b and d				
0.402 0.413	4459 4465 av = 4462	4474	-12	-0.27
Powders I and III				
0.391 0.399 0.405 0.407 0.415	4598 4670 4564 4568 4436 av = 4567 std. dev. = 84.76 c.v. = 1.86%	4540	27	0.50
Powders I and IV				
0.365 0.372 0.383 0.384 0.392	3676 3837 3643 3711 3601 av = 3694 std. dev. = 89.88) c.v. = 2.43%	3821	-127	-3.32

Mixtures were prepared from equal weights of a and d, b and d, I and III, and I and IV. These were thoroughly mixed by rotation of the containers and then allowed to stand at least overnight before proceeding with the test. Powder beds were then prepared using the usual agitation by 25 rotations of the sample jar, packing by rapping, and compression with the plunger, using not over 3 kg force. The results of these tests are given in Table 7. The calculated value of S_w is obviously the average S_w of the two components. The difference is given both as cm^2/g and as percentage based on the assumption that the calculated value is the true value.

The agreement between the measured and calculated values of the S_w of the first three mixtures, ranging from -0.3% to +0.6%, is remarkably good, especially since in some mixtures one component had about twice the S_w as the other. In addition, different flowing agents were present in the mixture of the powders I and III. The agreement between the measured and calculated value (-3.3%) for the mixture of powders I and IV appears reasonable. In this case, not only was there a 2:1 ratio of the S_w values of the powders and a difference in flowing agents, but the component powders differed chemically and in the shape of the grains.

Effect of Varying the Void Space in the Powder Bed — As noted earlier, the packing of the powder bed, and consequently the void fraction e, could be controlled to some extent by varying the amount of rapping of the powder holder after adding each increment of powder. Thus, the void space of powder packed just firm enough to avoid further settling during handling could be as much as 10% higher than in a bed which required much rapping to permit seating the loading plunger by a 3 kg or less force, although an increase of about 6% was more general.

To determine the effect of different degrees of packing of the powder bed on the apparent specific surface, a straight line relationship was calculated for each group of replicate determinations, using the method of least squares. The void fraction e was used to express the degree of packing, so that the relationship was in the form

$$S_w = b_0 + b_1 e .$$

A positive coefficient b_1 indicates an apparent S_w increasing with increasing e, while a negative b_1 indicates an apparent S_w decreasing with increasing e. The resulting coefficients are given in Table 8, grouped according to the method of preparing the powder bed and the age of the powder sample. The S_w at the minimum and maximum value of e actually used was calculated for each set of replicate data, and the differences are shown in the table. Fresh powder samples, agitated immediately before preparing the powder test bed, generally showed an increase in specific surface with increasing void fraction e ranging from 0.5 to 1.7%. Tests made without agitation of the sample, or made on aged samples generally showed an apparent S_w decreasing with increasing void fraction. For these tests, the ranges of the apparent S_w were higher; many were more than 3% of the average value, and one reached nearly 9%.

Summary and Discussion

Samples of two commercial lots of potassium bicarbonate-based dry chemical powder fire extinguishant (PKP) and several samples of experimental batches of similar composition were subjected to the air permeability test for S_w determination. In addition to these samples, one sample of an experimental batch of powder having potassium chloride substituted for the bicarbonate was used, and samples from a rather large lot of "foam compatible" potassium bicarbonate-base powder were included. The latter was distinguished from the others by the use of a heavy metal salt of pelargonic acid as a grain coating and flowing agent.

Careful preparation of the powder bed using somewhat more stringent techniques than those previously specified resulted in less scatter of the data obtained on repeated determinations of S_w. It was found generally desirable to agitate or fluff up the powder samples immediately before preparing the powder bed. By using the technique described for preparing the powder bed, repeated determinations of S_w showed a standard deviation of approximately 50 cm^2/g, or less than 1.5% of the area measured. Aging of some of the samples for several weeks, during which time the sample containers were frequently opened, considerably reduced the measured S_w and increased the spread of results of repeated determinations. Manifestly, proper sample handling and storage is required to obtain meaningful measurements of S_w.

Mixtures of powders whose components had substantially different S_w values were prepared, and the S_w values of the mixtures were determined using the preferred technique. When the basic powders were rounded grains of potassium bicarbonate, the agreement between the measured S_w of the mixture and that calculated from the S_w values of the individual components was excellent, even though the grains were coated with different protective or flowing agents. Of the three mixtures tested, the difference between the measured and calculated S_w ranged only between 0.3 and 0.6%. Finally, when sharp

Table 8
Coefficients of the Equation $S_w = b_0 + b_1 e$, Representing the Relationship Between the Apparent Specific Surface Determined by the Permeability Method and the Void Space in a Powder Bed

Powder	b_0, (cm^2/g)	b_1, (cm^2/g)	Range of e		S_w (max e) − S_w (min e)	
			Min.	Max.	cm^2/g	% of S_w
Not aged; agitated before preparing the powder bed						
I (1st sample)	4800	584	0.382	0.423	24	0.5
I (2nd sample)	3077	5024	0.377	0.394	85	1.7
II (1st sample)	3429	2794	0.429	0.455	73	1.6
II (2nd sample)	4313	744	0.437	0.466	29	0.6
III	4625	-1477	0.386	0.401	-22	-0.5
Not aged; not agitated before preparing the powder bed						
I	6000	-2771	0.380	0.426	-127	-2.5
II	1724	+6195	0.429	0.454	+155	+3.3
I & III mixed	7143	-6385	0.391	0.415	-153	-3.4
Aged; agitated before preparing the powder bed						
I (1st sample)	7200	-5840	0.390	0.414	-140	-2.8
II (1st sample)	8088	-7796	0.499	0.552	-413	-8.9
Not aged; agitated and then allowed to stand overnight before preparing the powder bed						
II	8095	-8059	0.429	0.454	-201	-4.3
Aged 4 months; shaken 10 minutes on the mechanical shaker						
II	4491	-523	0.423	0.493	-37	-0.8
Aged 4 months; shaken 30 minutes on the mechanical shaker						
II	4316	-354	0.407	0.465	-21	-0.5
Potassium chloride-base dry-chemical extinguishant whose age and past history were unknown; agitated before preparing the powder bed						
IV	3103	-1283	0.374	0.410	-46	-1.8
Potassium chloride-base dry-chemical extinguishant whose age and past history were unknown; not agitated before preparing the powder bed						
IV	3939	-3431	0.382	0.410	-96	-3.7

cornered grains of a potassium chloride-based powder were mixed with one of the rounded bicarbonate-based powders, the difference between the measured and calculated S_w was only slightly over 3%. Since these S_w values were calculated from the data using the basic Carman equation without empirical corrections to bring the test results into line, the method appears to be one capable of measuring a specific physical parameter of the powders, presumably S_w.

The effect of varying packing density, or void space, in the powder test bed was explored by intentionally varying the packing density over the widest practical range. For fresh samples, the widest spread of results was 1.7% of the average of four or five repeat determinations, and for several powders the spread was considerably less. Tests made on aged samples showed a substantially greater effect of varying the void fraction.

AIR ELUTRIATION METHOD

Air elutriation has been used to separate powders into fractions encompassing relatively narrow ranges of particle diameters. One common apparatus is the Roller particle separator described, for example, in ASTM test method B 293-60 [7]. In this method, the powder sample is dispersed by a jet of air and carried into a vertical column in which the air flow velocity can be set to a predetermined value. Particles up to a certain size are carried from the column to a filter paper collection thimble for weighing, while coarser particles remain in the column. The maximum size carried over is calculated from Stoke's law, assuming the particles to be spherical. Thus,

$$D = \sqrt{\frac{18\,\eta\,u}{g\,(\rho_1 - \rho_2)}}$$

where D is the diameter in cm, η is the viscosity of air in poise, u is the air velocity in cm/sec, g is the gravitational constant (980 cm/sec^2), and ρ_1 and ρ_2 are, respectively, the particle density (g/cm^3) and air density. (The term ρ_2 is generally ignored since it is negligible in comparison to ρ_1.) In carrying out a particle size analysis, the air velocity is increased stepwise, and the powder collected at each velocity is weighed. The data are plotted to give a curve of cumulative fraction of the total sample weight vs particle diameter in microns. The data are also used to compute S_w.

While the elutriation method appears simple in theory, several phenomena contribute to inaccurate results in its application. Among these, sticking of the powder to the walls of the separation column results in loss of some of the sample, and there is no known way of attributing this lost powder to particular size ranges. In addition, some of the columns required in a practical apparatus are quite large in diameter (up to 9 inches), and there is no assurance that the air flow velocity is the same throughout the cylindrical portion of the column as the velocity calculated from flow meter readings. In fact, it seems highly probable that air near the walls of the column will be slowed down by viscous drag force, so that air near the axis will move faster than the caculated velocity. Hence, particles larger than calculated may be included in a given size range. Finally, there is a tendency for particles of dry chemical extinguishants to agglomerate, with several small particles acting as a single large particle. Claims have been made, for example in the apparatus manufacturer's operating instructions and in the ASTM method B 293-60 [7], that many of the problems of agglomeration and of powder sticking in the separating chamber can be ameliorated by humidification of the air stream.

The experimental work reported here was done to assess the reproducibility of the method when repeated determinations of S_w were made under the same operating conditions, and to determine the effects of humidification of the air stream on the separation of the dry chemical extinguishant powders.

Apparatus

The separator used was identified as the "Roller Particle Size Analyzer," catalog number 5-445, American Instrument Company.* Basically, the apparatus (Fig. 2) comprises four vertical columns, with inside diameters of 9, 4-1/2, 2-1/4, and 1-1/4 inches, any one of which may be placed in the operating position. A gooseneck of glass tubing is attached to the bottom, or inlet, end of the cylinder to hold the powder sample, while another gooseneck is attached to the top to hold a filter paper powder collection thimble. A nozzle is affixed to the entrance end of the lower gooseneck to introduce air to disperse the sample and supply the separating air flow in the column. Auxiliary equipment consists of motor driven rappers arranged to strike the column and to jar the powder-holding gooseneck and of an externally mounted capillary air flow meter and control valve. In some tests, the air supply was arranged to bubble through aqueous solutions immediately preceding the flow meter, to raise the relative humidity (R.H.) to various levels.

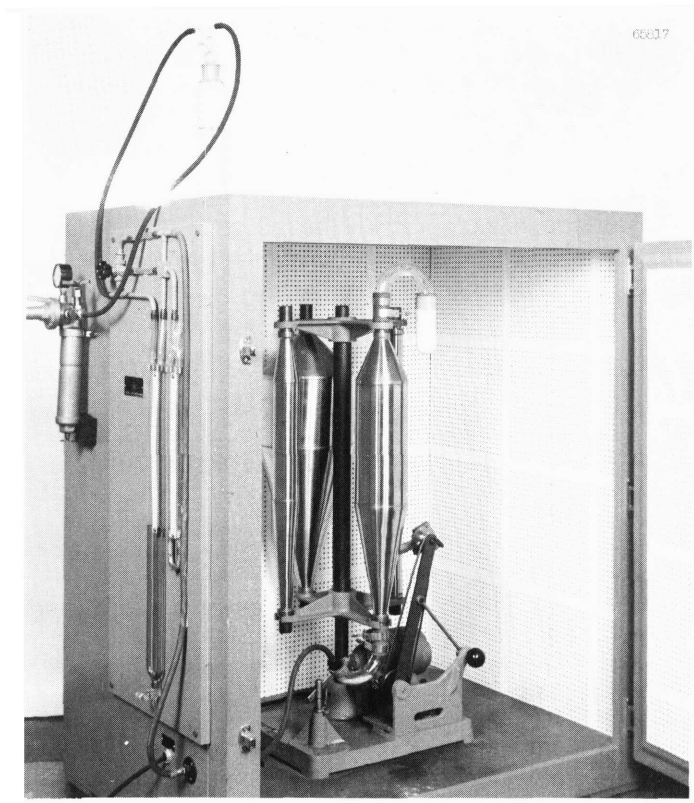

Fig. 2 - Roller apparatus for determining the particle size distribution by air elutriation

Sources of the Powder Samples

The dry chemical powder extinguishants used in these tests were taken from the same gross samples that were described in the section on the permeability method.

*The use of the manufacturer's name is only for convenience in describing the apparatus and is not necessarily an endorsement of this particular source.

Preparation of the Samples

Since the apparatus is limited to particles with maximum diameters of about 74 μ, substantial quantities of the powders were first separated on a series of 149, 105, and 74 μ (100, 140, and 200 mesh) sieves. The portion passing through the 74-μ (200-mesh) sieve was used for separation in the Roller apparatus. About 90% of the powders passed through the 74-μ screen.

Operation of the Particle Separator

In general, the apparatus was operated in accordance with the manufacturer's instructions. The principal exception made to these instructions was in the R.H. of the operating air. Briefly, about 15 g of -200-mesh powder was weighed to the nearest milligram, placed in the sample gooseneck, and the air nozzle was then installed. A filter paper collection thimble was weighed to the nearest milligram and fastened to the outlet gooseneck. Air flow was started at the velocity calculated to carry over the maximum particle size desired and allowed to run for 2 minutes. The collection thimble was weighed and immediately returned to the apparatus, and the same air flow was again started. The thimble was then weighed at approximately 15-minute intervals until the rate of powder transfer to the thimble was less than 1/10 the rate during the first 2 minutes. At this point the air flow was increased to the next selected rate, and the process was repeated. In the first few runs, air flows were selected to provide data at 10-μ-diameter intervals up to 70 μ, and any residue in the sample gooseneck was assigned to the 70 to 74 μ range. However, in the first few runs, large portions of the powders were found in the smallest diameter range (0 to 10 μ), where the relationship between S_w and diameter changes rapidly with changing particle size. Subsequent runs were made with the first two steps being 0-5 and 5-10 μ, followed by 10-μ intervals.

Repeated determinations of the size distribution of the same powder were made, using air with the R.H. varied. Air having zero R.H. was obtained by passing the air through a Drierite column. Air having 19% R.H. was obtained directly from the compressed air line, using only a porous ceramic separator to remove entrained water droplets; air having 24% R.H. was obtained by passing the air through a bubbler containing a solution of two parts by volume of reagent grade sulfuric acid and one part of water; air having 45% R.H. was obtained by bubbling the air through a saturated calcium nitrate solution; and air having 75% R.H. was obtained by bubbling the air through saturated ammonium chloride. The various solutions used were not thermostatted, and changes in flow rate had some effect; hence, the indicated values of R.H. are nominal and in practice varied slightly. The values given were measured by the wet and dry bulb thermometer technique at approximately 25°C ambient temperature.

Calculations

As noted earlier, the combined weights of the powder collected in the successive size ranges always was less than the weight of the initial sample, mainly because of powder sticking to the apparatus walls. This loss was distributed proportionally over the entire group of sizes by using the total weight of powder collected, rather than the starting weight, as the basis of calculation. Thus, the weight fraction of a particular size range in the -200-mesh sample is calculated as the weight of powder collected in that size range divided by the total weight of powder collected. A further calculation was made to allow for the particles larger than 74 μ (200 mesh) which were previously removed by sieving, generally about 10% of the original powder. The fraction in each size range found by the Roller method was multiplied by the factor 1 - weight fraction of powder retained on the 200-mesh and coarser sieves. The combined data obtained by the Roller apparatus and by sieving was plotted as the cumulative weight fraction vs the

logarithim of the particle diameter. The data obtained from determinations repeated under the same conditions were quite reproducible, so that the data points from two or more runs were plotted on the same semilog chart paper and a single curve was drawn for the best fit with the combined data.

In calculating the S_w of the powders, the curves were extrapolated toward the smaller diameters where small changes in diameter make relatively large changes in specific surface. The size fractions lying in the intervals 0 to 2.5, 2.5 to 5, 5 to 10, 10 to 15, ..., 45 to 50, 50 to 60, 60 to 70, 70 to 74, 74 to 105, and 105 to 149 μ were scaled from the curves. (The S_w of the powder larger than 149 μ (100 mesh) was ignored, since there was very little of it, and the contributions of large particles to the total S_w is negligible.) The ratio of surface area to volume was calculated for each size range according to

$$\frac{S}{V} = \frac{6}{d_i}$$

where

S = surface area, cm^2

V = volume, cm^3

d_i = arithmetic mean diameter of the size range, cm.

The specific surface of the whole powder is

$$S_w = \frac{6}{\rho} \sum \frac{n_i}{d_i} \ cm^2/g$$

where n_i is the weight fraction of powder having an average diameter of d_i, and ρ is the density of the powder, g/cm^3.

Results

The apparent particle size distributions of powder I, using elutriating air of different R.H. are given in Figs. 3 through 6. Individual data points are shown to illustrate the reproducibility of the procedure when replicate determinations are made under the same conditions. These curves were redrawn on a single graph sheet in Fig. 7 to illustrate the effects of changing the R.H. of the air. Similar curves are given for powder II in Figs. 8 through 12, except that the maximum R.H. shown is 45% rather than 75%. Air at 75% R.H. was tried, but the powder rapidly formed a pasty, wet mass, and little if any of the powder was carried out of the gooseneck of the apparatus. A separation with air at 55% R.H. also was tried, but there was some agglomeration of the powder. A 45% R.H. appeared to be the highest the powder could tolerate. Sufficient amounts of powders a, b, and d were available to permit one or two determinations of particle size distributions at only one value of R.H. (37%). The results of these determinations are shown in Figs. 13 through 15. Table 9 shows the apparent S_w of these powders, calculated by the method described in the preceding subsection.

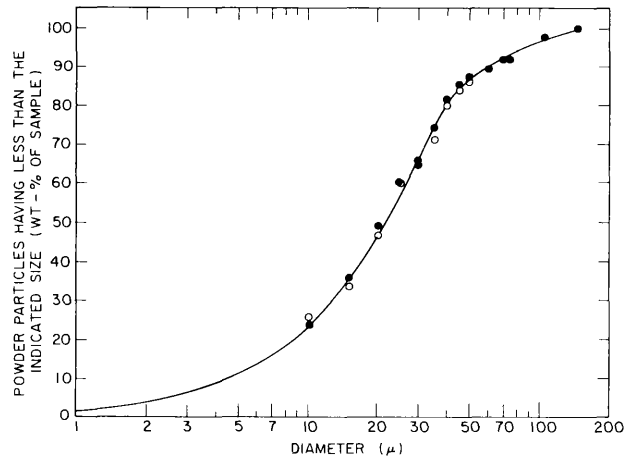

Fig. 3 - Particle size distribution of powder I, using air having 75% R.H.

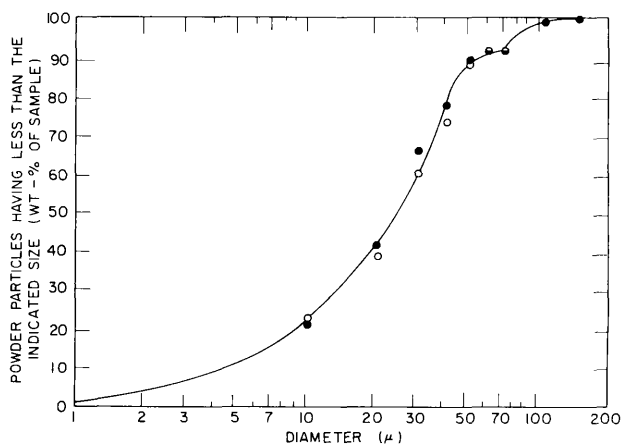

Fig. 4 - Particle size distribution of powder I, using air having 24% R.H.

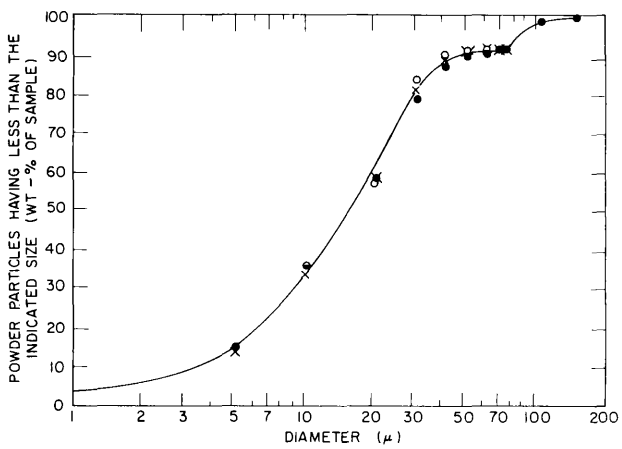

Fig. 5 - Particle size distribution of powder I, using air having 19% R.H.

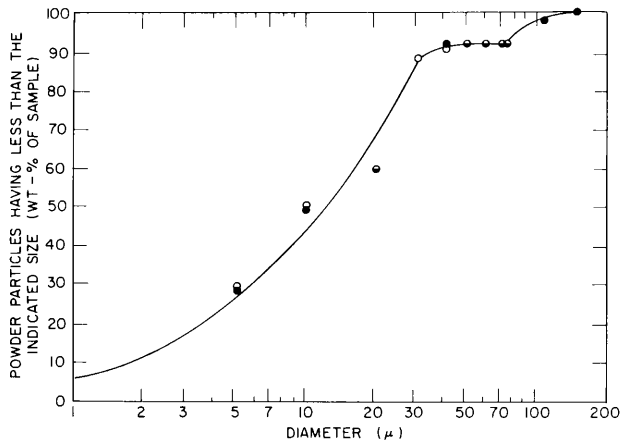

Fig. 6. - Particle size distribution of powder I, using dry air

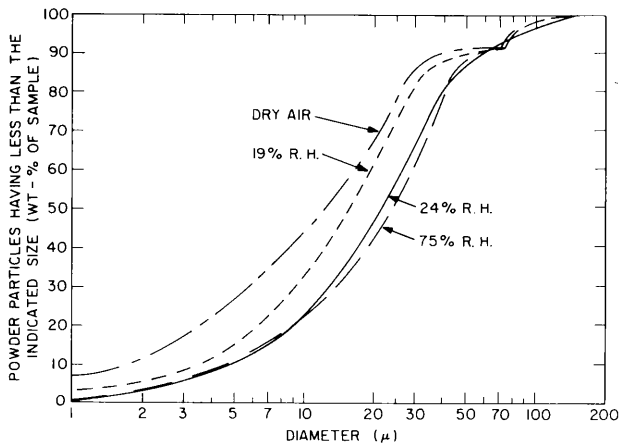

Fig. 7 - Curves for powder I from Figs. 3 through 7

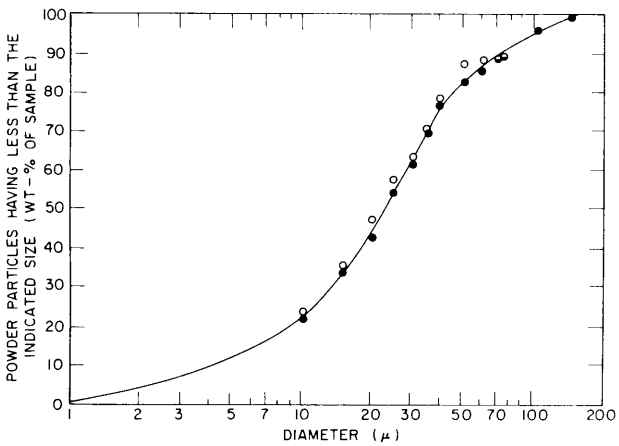

Fig. 8 - Particle size distribution of powder II, using air having 45% R.H.

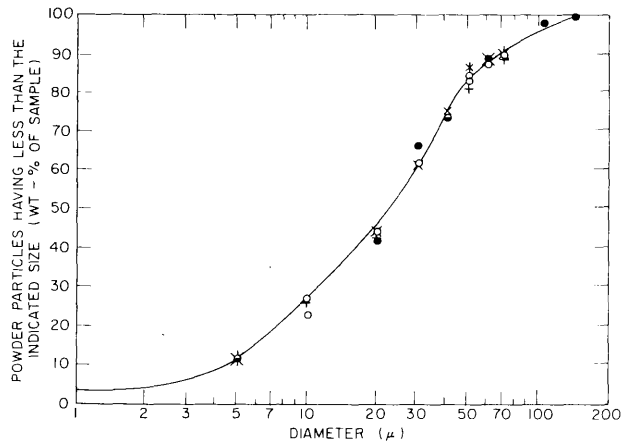

Fig. 9 - Particle size distribution of powder II, using air having 24% R.H.

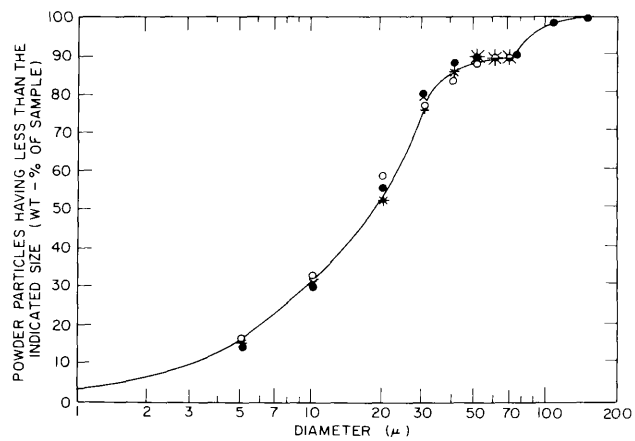

Fig. 10 - Particle size distribution of powder II, using air having 19% R.H.

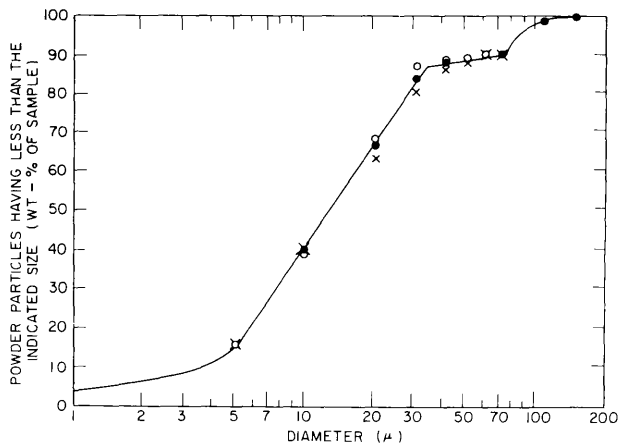

Fig. 11 - Particle size distribution of powder II, using dry air

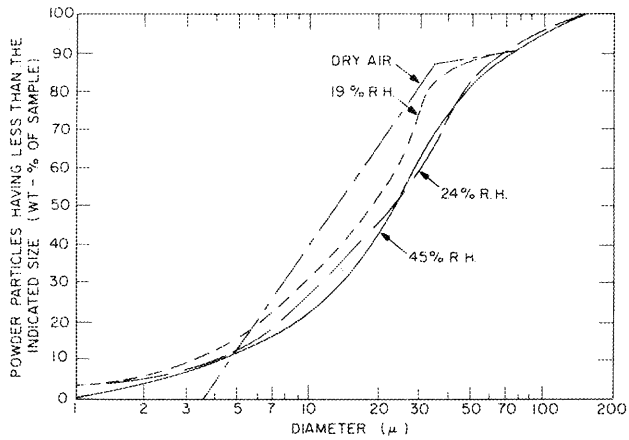

Fig. 12 - Curves for powder II from Figs. 8 through 11

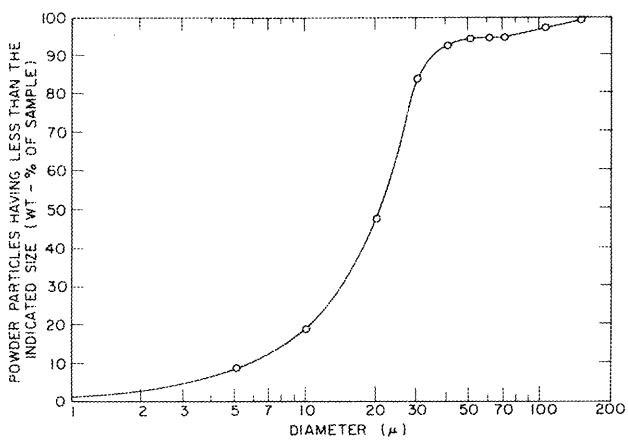

Fig. 13 - Particle size distribution of powder a, using air at 37% R.H.

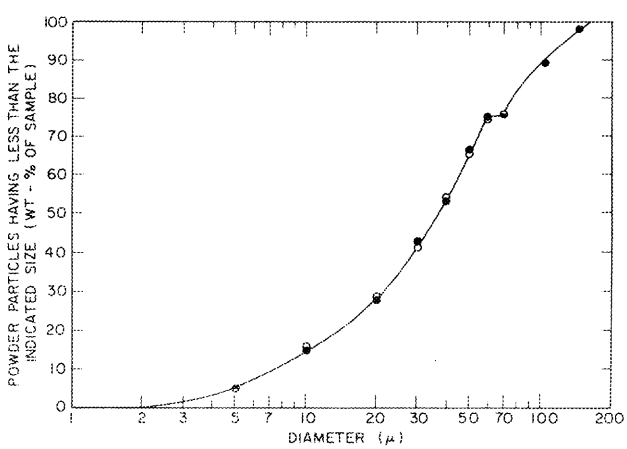

Fig. 14 - Particle size distribution of powder b, using air at 37% R.H.

Table 10
Standard Deviations and Coefficients of Variation for Replicate Determinations of the Specific Surface Using the Roller Apparatus

R.H. of Air (%)	Number of Determinations	Std. Dev. (cm^2/g)	C.V. (%)
Powder I			
75	2	43.8	1.7
24	2	48.8	2.0
19	3	126.2	4.0
0	2	43.8	1.0
Powder II			
45	2	130.1	5.2
24	4	81.6	3.2
19	4	97.9	3.2
0	3	66.2	2.0
Powder b			
37	2	4.2	0.3

Table 11
Proportion of Powder Charges Recovered in the Collecting Thimble of the Roller Apparatus

R.H. of Air (%)	Powder Recovered (wt-% of initial sample)
Powder I	
75	90.3, 79
24	84.7, 87.3
19	88.8, 98.9, 89.6
0	78.4, 77.7
Powder II	
45	94.9, 91.5
24	90.5, 92.6, 90.9
19	85.0, 93.6, 96.4, 90.4
0	86.0, 84.0, 89.8

R.H. of Air (%)	Powder Recovered (wt-% of initial sample)
Powder a	
37	92.6
Powder b	
37	93.5, 92.3
Powder d	
37	97.2

maximum R.H. In any event, the Roller method of particle size analysis of dry chemical fire extinguishing powders was shown to be very sensitive to changes in R.H. of the operating air. For example, changing from air at 75% R.H. to dry air nearly doubled the S_w found for powder I.

GENERAL DISCUSSION

Two methods for measuring the S_w of powders were examined for their suitability in characterizing dry chemical powder fire extinguishants. All of the powders, except one, were of the potassium bicarbonate base. One powder contained potassium chloride as its major constituent.

It was found that the permeability (Blaine) method gave results that were reproducible to within ±1.5%. To obtain this precision, it was necessary to pay attention to the preparation of the powder bed in the apparatus and to the handling of samples prior to the area determination. Preparation of the powder bed was best carried out by adding small increments of powder to the holder and compacting the powder by rapping the holder on a solid surface. Final compaction was done by a plunger to ascertain that the powder space was completely filled, but this part of the compaction was held to a minimum, otherwise, excessive ramming with the plunger resulted in erratic results, usually in the direction of a lower apparent S_w.

Repeated opening of the sample containers over a period of several weeks, with its consequent exposure of the sample to the atmosphere, resulted in a decrease in the measured S_w. This is presumably due to agglomeration of some of the particles when exposed to moist air. The original S_w of the powders could be only partly restored by extensive agitation of the sample. The determinations were made without special consideration of the ambient atmospheric conditions other than a small correction for the change of air viscosity with temperature. The independence of the permeability method of the physical and chemical composition of the powders was demonstrated by comparing experimentally determined S_w values of mixtures of powders with S_w values calculated from the ratios of the component powders and their individually determined S_w values. Like powders of widely differing S_w, and powders having different coatings, or different basic constituents, were mixed. The experimental values were in very good agreement with the calculated values.

The elutriation (Roller) method of particle size analysis proved to be very sensitive to the R.H. of the operating air. Changing from moist to dry air resulted in nearly doubling the apparent S_w of some powders. As shown in Figs. 7 and 12, larger particles disappear and consequently the proportion of fine particles increases as the operating air becomes drier. This, of course, leads to large increases in the S_w calculated from the data. There is no way to ascertain which distribution curve is correct, although it seems unlikely that there would be a substantial quantity of particles missing in the size range between the relatively sharp break in the Roller curve and the smallest sieve size used in the preliminary screening.

An attempt was made to find a correlation between the S_w of a powder found by the permeability method and that found by the elutriation method. Table 12 shows the ratios of S_w found by the two methods. For powders I and II, two ratios are given for each powder: one is for elutriations made with dry air, and the other is for elutriations made with air having the highest moisture content used. As shown in the table, there was no satisfactory correlation.

The permeability method was shown to be capable of precise determinations of S_w when carried out with reasonable care. Each determination requires approximately 30 minutes. The elutriation method gave ambiguous results with the powders used. In addition, the method requires from 8 to 24 hours of the analyst's time for each determination.

Table 12
Ratios of the Specific Surface Determined by the Permeability Method to those Determined by the Elutriation Method Using Dry Air and Moist Air

Powder	Ratio	
	Dry Air	Moist Air
I	1.73	0.919
II	1.61	1.07
a	-	1.26
b	-	1.93
d	-	1.95

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13. ABSTRACT

Two methods of measuring the specific surface of powders were examined for their suitability in characterizing dry chemical fire extinguishing powders. The air permeability (Blaine) method gives a direct measure of the total surface of a powder sample. The air elutriation (Roller) method gives the distribution of particle diameters in a sample, from which the surface can be found by numerical or graphical integration.

Measurements of the specific surface by the permeability method of powders ranging from approximately 2600 to 5900 cm^2/g were reproducible to within ±1.5% when the test was carried out in a preferred manner. Samples which were frequently exposed to the atmosphere by repeated opening of their containers over a period of a few months suffered an apparent loss of specific surface which could be only partially restored by agitation. Samples which were stored in continuously closed containers showed no change over the same period of time. Mixtures of equal weights of two powders of different composition and different grain shapes gave experimentally determined values of specific surface in good agreement with the average calculated from the specific surfaces of the individual powders.

The air elutriation method proved to be very sensitive to the relative humidity of the operating air when used with the same powder as used in the permeability

(continued)

14 KEY WORDS	LINK A ROLE	LINK A WT	LINK B ROLE	LINK B WT	LINK C ROLE	LINK C WT
Powders						
Surface area						
Specific surface						
Measurement						
Air permeability method						
Permeability						
Air elutriation method						
Dry chemical fire extinguishing powders						
Effectiveness						
Extinguishant						
Fire Extinguishers						

ABSTRACT (Continued)

method. In some instances, separating with dry air gave values of specific surface nearly double those obtained using moist air. In view of this sensitivity to operating conditions, as well as the much greater time required for each determination, the elutriation method appeared to be unsuitable for characterizing dry chemical powder extinguishants.