①

National Defence
Défense nationale

CHEMICAL EFFECTS IN PARTICULATE FILTRATION

I. THE SIZE RANGE 0.1 - 0.3 μm (U)

by

J.R. Coleman

DEFENCE RESEARCH ESTABLISHMENT OTTAWA
TECHNICAL NOTE 87-16

Canada

July 1987
Ottawa

88 1 20 048

National Défense
Defence nationale

CHEMICAL EFFECTS IN PARTICULATE FILTRATION
I. THE SIZE RANGE 0.1 - 0.3 μm (U)

by

J.R. Coleman
Chemical Protection Section
Protective Sciences Division

DEFENCE RESEARCH ESTABLISHMENT OTTAWA
TECHNICAL NOTE 87-16

PCN
051LB13

July 1987
Ottawa

ABSTRACT

micrometers

Aerosols were prepared from sixteen materials, liquid and solid. These were used, over the size range 0.01-0.30 µm, to challenge a standard filter paper. Penetration was nearly independent of the chemical nature of the aerosol in the size range 0.10-0.30 µm. Below 0.10 µm, penetration varied widely from challenge to challenge.

RÉSUMÉ

Des aérosols ont été préparés à partir de seize substances, liquides et solides, dans la plague de diamètres de o,01 à 0,30 µm, pour éprouver un papier-filtre standard. Le pénétration est presque indépendante de la composition chimique des aérosols dans cette plage. En deçà de 0,10 µm, la pénétration varie beaucoup d'une épreuve à l'autre.

TABLE OF CONTENTS

1.0 INTRODUCTION

Present-day theories of particulate filter action attribute capture to mechanisms of interception and impaction, and to settling under gravity at larger size, with diffusion (Brownian motion) becoming an important factor in the submicron range. Additionally, electrostatic modes of capture operate when either the particle or the filter medium is charged. For a given filter and air flow rate, only geometric factors (particle size and shape) are considered, it being assumed that the chemical nature of the medium or aerosol does not enter into account.

With instrumentation developed in recent years one can survey aerosols from different materials to test the correctness of this assumption. The electrostatic classifier (1) can select from a heterogeneous aerosol particles or droplets of narrowly defined size, to challenge the filter. Any sufficiently involatile liquid or solid for which a compatible volatile solvent can be found, can be used as a source of aerosol. The resulting concentrations upstream and downstream of the filter can be measured by the condensation nucleus counter (CNC) (2).

In the present work sixteen substances were employed. The test medium was a filter paper available in quantity, whose characteristics were found to be uniform from sample to sample.

In summary, it was found that, between a particle/droplet size of 0.10 and 0.30 µm, filter penetration was nearly independent of material, in accordance with expectations. A plot of per cent penetration vs diameter results lay for the most part in a narrow band with only a few outliers. However at sizes ≤ 0.05 µm penetration varied markedly on passing from one challenge material to another. This phenomenon, and other observations made with small particle sizes are the subject of a separate note.

2.0 EXPERIMENTAL

2.1 Apparatus

The filter test system FTS 400[1] has been described (3). In addition to the classifier-CNC combination for use in the submicron region, it incorporates a method, not used here, for generating aerosols in the size range 0.5 - 10 μm.

Aerosol is generated in one of several atomizers which are supplied from stock bottles containing solutions of the involatile challenge. The atomizer spray dries to leave a heterodisperse aerosol of droplets or particles. In the classifier a single narrowly defined size is selected on the basis of the electrical mobility of singly charged particles. The monodisperse aerosol after introduction of dilution air passes to the test chamber containing the filter under examination, and thence by separate upstream and downstream sampling paths to the CNC.

The system was originally designed to produce two standard challenges - sodium chloride (NaCl) from water, and dioctyl phthalate (DOP) from isopropanol (IPA). Three aqueous solutions of NaCl (0.01, 0.1, 1.0% w/v) were used with three atomizers, to match concentration to the required particle size, in the ranges < 0.02 μm, 0.02 to < 0.10 μm, and 0.10-0.31 μm. A computer program activates the correct atomizer. Excess NaCl is returned from the atomizer to the stock bottle in a recirculating system. With DOP in isopropanol, the solvent evaporated too rapidly in the atomizer, leading to excessive concentration of DOP in the stock; therefore solutions were discarded after one passage through the atomizer. Two concentrations (0.05% w/v and 0.2% w/v) were employed, covering the size domain up to 0.05 μm, and above this size. A second program is provided for testing with DOP.

In the work described here the same arrangement is used, with three solution concentrations and the original FTS program for water-soluble materials; and for non-aqueous solvents the DOP program, and two concentrations, the solutions again being discarded after one passage through the atomizers. Some preliminary trial and error was necessary in arriving at suitable stock solution concentrations. Earlier observations

---

[1] A product of TSI Inc, St. Paul, Minnesota, USA

have shown however that results, as judged by measured per cent penetration of a standard filter, were not very sensitive to concentrations, unless these were grossly out of line. As per cent penetration is a ratio of two measurements on downstream and upstream aerosol, perturbing factors largely cancel out.

In this work a radioactive neutralizer (TSI 3077) is installed in the line downstream from the classifier, to reduce measurement errors at small particle size, as described in earlier work (4).

2.2 Challenge Materials

These are listed below, grouped under their solvents used to prepare solutions for atomization. A few notes on chemical/physical properties are added. The two (or three) numbers following each entry are the concentrations in g/1000 ml of the stock solutions.

TABLE I

Material	m.p.	b.p.	Mol weight	Remarks
-- WATER --				
NaCl (0.1, 1.0, 10.0)	801	-	58	
Glycerol		290	92	polyalcohol
Dextrose	148-150		180	monosaccharide
Glycine	232-6		75	amino acid
Urea	133		60	
Sodium potassium tartrate	~100		282	tetrahydrate
Citric acid	153		210	monohydrate
Polyethylene[1] glycol			~400	
Triethylene glycol (0.2, 2.0, 12.0)			150	liquid dialcohol
Oxamide[2] (0.095, 0.142, 0.190)	417-419		88	diamide; highly insoluble

---

[1] Aldrich Chemical Co 20,239-8, PEG 400, average molecular weight 400 (i.e. nine ethylene glycol units on average)

[2] The extremely low solubility of this compound necessitated using slightly undersaturated solutions. Saturation at 20°C is about 0.25 g/1000 ml H_2O. Complete saturation was avoided, since evaporation might lead to clogging of the atomizer nozzles.

TABLE I (cont'd)

Material	m.p.	b.p.	Mol weight	Remarks
-- ISOPROPANOL --				
Dioctyl phthalate (0.5, 2.0)			358	aromatic diester
-- ETHANOL --				
Silicone oil[3]				of general form: CH_3 $[(CH_3)_2 SiO_2]_n Si(CH_3)_3$
Oleic acid (0.5, 2.0)	16	285-6/ 100 mm	282	long chain unsaturated fatty acid
Phthalic anhydride (0.5, 5.0)	131		148	
-- ISOOCTANE --				
Paraffin oil[4] (0.5, 2.0)				comparable to light machine oil
-- TOLUENE - XYLENE (3:1) --				
Anthracene (0.5, 2.0)	217	340	178	polynuclear aromatic

---

[3] Aldrich Chemical Co, 17,563-3 silicone oil, high temperature.

[4] Fisher Scientific Co, 0-119, paraffin oil, light, white, domestic.

This range of compounds was chosen so as to include liquid and solid, organic and inorganic, ionic and covalent, and polar and non-polar materials. Solvents and their solutes had to be non-corrosive and compatible with components that they could encounter in the FTS 400. When changing from one material to the next the system was purged with mutually compatible solvents to avoid precipitating materials that might block nozzles or lines.

2.3 Filter Paper

A high efficiency filter paper produced by Hollingsworth and Vose, (East Walpole, Mass. U.S.A.), was used. The DREO designation for the paper was HV4A.

2.4 Procedure

Sheets of HV4A were run in quadruplicate. The flow rate was 16 LPM, which for the 4" diameter circular test area corresponds to the 32 LPM in certain standard tests used at DREO. Using the FTS or FTS DOP program as appropriate, penetration was measured at seven sizes between 0.01 and 0.30 µm.

3.0 RESULTS AND DISCUSSION

Experimental results are collected in Table II, as percent penetration with standard deviation. To facilitate comparison, from the sixteen materials eight were selected whose penetrations in the size interval 0.10 to 0.30 µm were judged to lie in the mainstream or "normal" range. Their average penetrations and standard deviation are plotted in Figure 1. The remaining eight, deemed somewhat arbitrarily to be "high" or "low" are plotted individually. To avoid complicating the figure these latter results are plotted only down to 0.05 µm.

It is evident that above 0.1 µm the assumption that filter behaviour is not dependent on the chemical nature of the particle is supported. Three materials, DOP, silicone oil and oleic acid were placed in the high penetration category, but all penetration results were less than twice the average for the normal materials, most of them considerably less. These three might indeed plausibly have been included among the normal materials. Five materials were classed as having low penetration, one of these (phthalic anhydride) rather dubiously so. Deviations in the negative are greater than those in the positive direction. Results for one of these materials, oxamide, were considered questionable because of the low concentrations of its stock solutions (Table I). However, per cent

TABLE II

PER CENT PENETRATION OF HV4A PAPER BY VARIOUS MATERIALS

Material	Diameter (μm)						
	0.01	0.02	0.05	0.10	0.15	0.20	0.30
NaCl	.0068 ±.0045	.00016 ±.00007	.0043 ±.0008	.030 ±.003	.035 ±.006	.029 ±.004	.0075 ±.0006
Glycerol	.0059 ±.0033	.00038 ±.00017	.0016 ±.0002	.012 ±.001	.020 ±.005	.029 ±.003	.023 ±.003
Dextrose	.011 ±.0006	.0075 ±.011	.012 ±.002	.032 ±.002	.035 ±.006	.031 ±.004	.010 ±.002
Glycine	.011 ±.001	.0076 ±.001	.011 ±.002	.025 ±.002	.028 ±.001	.026 ±.003	.011 ±.005
NaK Tartrate	.0097 ±.0016	.00074 ±.00006	.0043 ±.0006	.029 ±.004	.033 ±.004	.032 ±.004	.012 ±.003
Citric Acid	.010 ±.002	.00091 ±.00022	.0061 ±.0014	.029 ±.004	.033 ±.004	.032 ±.002	.010 ±.0003
Phthalic Anhydride	.00094 ±.00054	.00010 ±.00005	.0018 ±.0002	.019 ±.003	.024 ±.003	.025 ±.004	.012 ±.001
Dioctyl Phthalate	.048 ±.015	.010 ±.002	.0029 ±.0006	.035 ±.002	.045 ±.004	.038 ±.005	.0106 ±.0009
Oleic Acid	.047 ±.018	.00044 ±.00013	.0041 ±.0004	.025 ±.003	.038 ±.004	.043 ±.003	.0133 ±.0003
PEG 400	.024 ±.015	.0047 ±.0003	.013 ±.002	.024 ±.001	.030 ±.003	.023 ±.004	.0087 ±.0003
Paraffin Oil	.045 ±.010	.00027 ±.00013	.0016 ±.0003	.024 ±.002	.0311 ±.0002	.0313 ±.0008	.015 ±.003
Anthracene	.0014 ±.0008	.000036 ±.000024	.00047 ±.00019	.0067 ±.0010	.012 ±.001	.012 ±.001	.0048 ±.0015
Silicone Oil	.051 ±.009	.00029 ±.00009	.0026 ±.0007	.030 ±.003	.045 ±.004	.050 ±.006	.018 ±.001
Urea	.0018 ±.0004	.0022 ±.0012	.0068 ±.0010	.017 ±.001	.029 ±.002	.031 ±.004	.011 ±.002
Oxamide	.057 ±.026	.0014 ±.0005	.0021 ±.0005	.0141 ±.0007	.0113 ±.0009	.0066 ±.0006	.0039 ±.0026
Triethylene Glycol	.0079 ±.0022	.000068 ±.000027	.00050 ±.00002	.0031 ±.0003	.0052 ±.0006	.0082 ±.0004	.0131 ±.0009

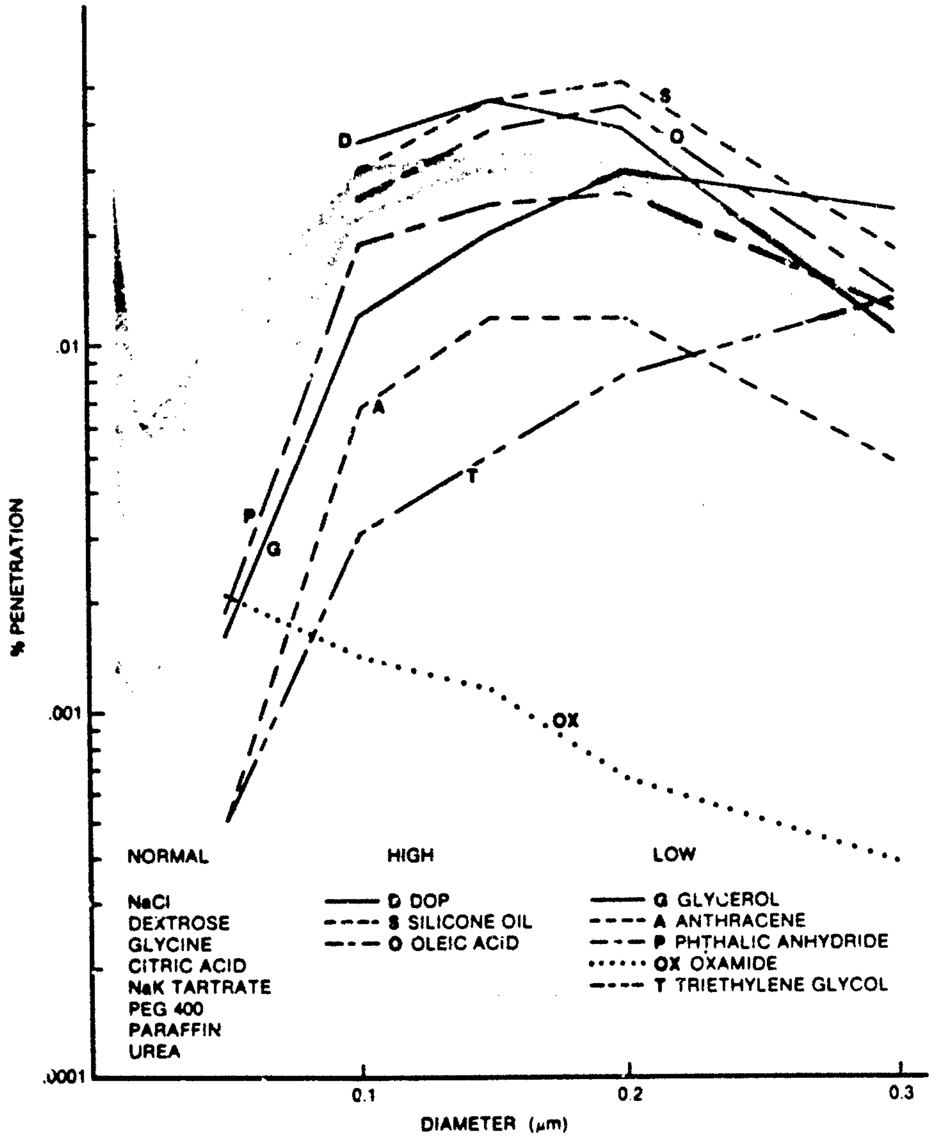

Figure 1 Penetration of HV4A paper by sixteen aerosol challenges.

penetration results on HV4A using NaCl solutions of the same concentration lay again in the normal range, so that this appears to be an intrinsic property of oxamide.

DOP, silicone and oleic acid, the high penetrants are all liquids; however glycerol and triethylene glycol, also liquids, are in the low category, while paraffin oil and PEG 400 are normal. Considering materials of closely related chemical nature, triethylene glycol (three glycol units) is low, PEG 400 (with approximately nine glycol units) is normal; urea, a diamide, is normal, oxamide, also a diamide, is low. Citric acid is normal, phthalic anhydride low. No distinction based on presence or absence of polar, or ionizable groups is discernible. In short these relatively small differences in penetration are not relatable to any chemical property of the materials.

One factor not considered is particle shape. In the operation of the classifier it is assumed that spherical, singly charged aerosol particles had been formed, whose motion in an electric field is governed by Stokes law with corrections appropriate to the submicron size range. Particles result in fact from forced evaporation of small droplets produced in the atomizers, and their shape cannot be predicted. Deviation from sphericity can have two effects a) a slight displacement in the size selected by the classifier b) particle shape could directly affect efficiency of capture in the filter. To clarify this point direct examination by electron microscopy is required. This has not yet been possible. Particle shape, if it is a factor, is not the only one; there is considerable variation in penetration among liquid penetrants which are all spherical.

At small particle size the minimum in penetration near 0.02 µm is again noted (4), urea being the only material that did not display it. Penetration-size relationships vary greatly in detail from one material to another, and no correlation could be found between behaviour in this size region, and the division into low, normal and high penetrants at larger sizes. The point is illustrated in Figure 2, using data from Table II. The extreme broadening of the hatched area, representing the standard deviation, at sizes less than 0.1 µm, in Figure 1, is another indication of variability of results even among substances that behave very similarly at larger size.

3.1 Modification of Filter Paper

In the previous work the challenge was varied but the same HV4A paper was used. In a few miscellaneous experiments the procedure was reversed; the effect of chemical modification of the paper surface was determined, using the same challenge.

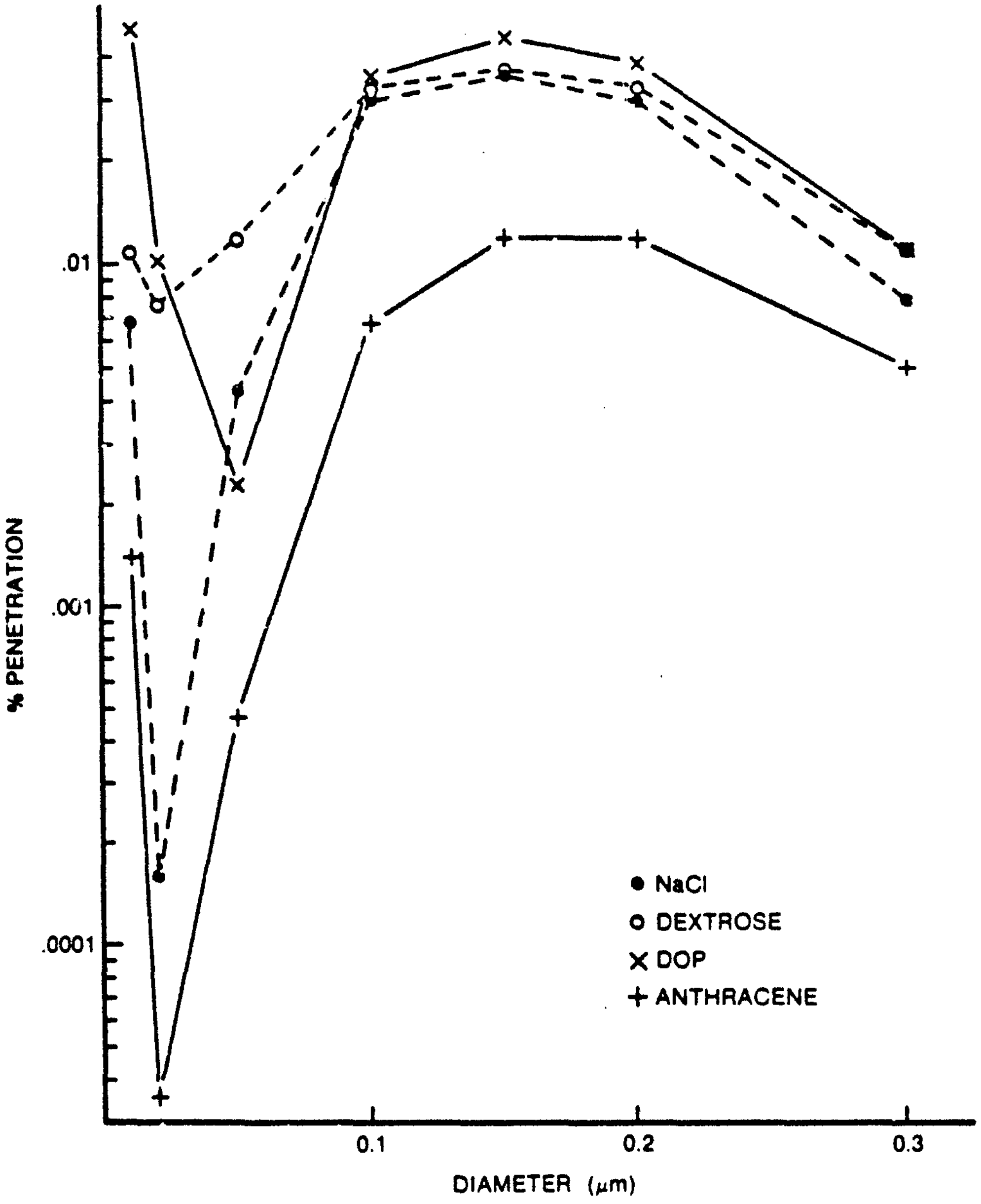

Figure 2 Detail of HV4A penetration, four cases showing extremes in behaviour.

HV4A paper was soaked in silicone oil dissolved in alcohol, or paraffin in isooctane (0.5 g/60 ml) and after drying tested for penetration with NaCl. Several obvious interferences must be considered:

a) Physical blockage of the filter by the impregnant. At the dilutions employed, the volume fraction of silicone or paraffin deposited in the filter paper should not be significant. The only information on this subject comes from pressure drops measured during the testing. These are unchanged: 14.0 ± 0.7 mm H_2O for the original HV4A, 14.4 ± 0.3 for paraffin-treated and 13.9 ± 0.5 for silicone-treated HV4A.

b) Swelling or shrinking of the filter-paper by the solvent (ethanol or isooctane) not reversed on subsequent drying. NaCl penetration tests were conducted on HV4A paper soaked in the solvents above and then dried. These gave results closely similar to those for NaCl penetration of the original HV4A (Table II, first entry). All the results, including the check for solvent swelling, are listed in Table III. It cannot be claimed with certainty that all sources of error (physical modification of filter paper) are eliminated from consideration by the checks described above; yet there is a strong indication that surface modification of the filter fibres by deposition of a deposit has increased penetration by, in some cases, a factor of two or three.

4.0 CONCLUSIONS

1. Chemical effects play only a second-order role in the filtering of particles in the submicron range down to about 0.10 µm.

2. Surface modification of the filter paper by soaking treatments in various chemicals either had no effect or increased the NaCl penetration.

TABLE III

PER CENT PENETRATION OF HV4A PAPER BY NaCl AS FUNCTION OF PRE-TREATMENT

Treatment	Diameter (μm)						
	0.01	0.02	0.05	0.10	0.15	0.20	0.30
None	.0068 ±.0045	.00016 ±.000072	.0043 ±.00082	.030 ±.0034	.035 ±.0061	.029 ±.0037	.0075 ±.0006
Isooctane Washed	.0098	.00019	.0037	.027	.031	.028	.0083
Paraffin Treated	.00018 ±.000089	.00028 ±.00017	.0088 ±.0013	.055 ±.005	.068 ±.014	.069 ±.014	.0215 ±.0003
EtOH Washed	.0070	.00017	.0050	.034	.038	.033	.013
Silicone Treated	.00023 ±.00011	.00019 ±.00006	.0070 ±.0012	.042 ±.005	.051 ±.008	.046 ±.005	.017 ±.002

5.0 BIBLIOGRAPHY

1. B.Y.H. Liu and D.Y.H. Pui, J. Colloid. Interfac Sci. 47 155 (1974).
2. J.K. Agarwal and G.J. Sem, J. Aerosol Sci. 11 343 (1979).
3. J.R. Coleman, Observations on the Use of the FTS 400 (U), DREO Technical Note in preparation.
4. J.R. Coleman, Observations on Electrostatic Effects in a Filter Test System, DREO Technical Note in preparation.

DOCUMENT CONTROL DATA

(Security classification of title, body of abstract and indexing annotation must be entered when the overall document is classified)

1. ORIGINATOR (the name and address of the organization preparing the document. Organizations for whom the document was prepared, e.g. Establishment sponsoring a contractor's report, or tasking agency, are entered in section 8.)

DEFENCE RESEARCH ESTABLISHMENT OTTAWA
Department of National Defence
Ottawa, Ontario K1A 0Z4

2. SECURITY CLASSIFICATION (overall security classification of the document, including special warning terms if applicable)

UNCLASSIFIED

3. TITLE (the complete document title as indicated on the title page. Its classification should be indicated by the appropriate abbreviation (S,C,R or U) in parentheses after the title.)

CHEMICAL EFFECTS IN PARTICULATE FILTRATION. I: THE SIZE RANGE 0.1 - 0.3 μm (U)

4. AUTHORS (Last name, first name, middle initial. If military, show rank, e.g. Doe, Maj. John E.)

COLEMAN, John R.

5. DATE OF PUBLICATION (month and year of publication of document)

JULY 1987

6a. NO. OF PAGES (total containing information. Include Annexes, Appendices, etc.)

15

6b. NO. OF REFS (total cited in document)

4

7. DESCRIPTIVE NOTES (the category of the document, e.g. technical report, technical note or memorandum. If appropriate, enter the type of report, e.g. interim, progress, summary, annual or final. Give the inclusive dates when a specific reporting period is covered.)

TECHNICAL NOTE

8. SPONSORING ACTIVITY (the name of the department project office or laboratory sponsoring the research and development. Include the address.)

DREO

9a. PROJECT OR GRANT NO. (if appropriate, the applicable research and development project or grant number under which the document was written. Please specify whether project or grant)

051LB13

9b. CONTRACT NO. (if appropriate, the applicable number under which the document was written)

10a. ORIGINATOR'S DOCUMENT NUMBER (the official document number by which the document is identified by the originating activity. This number must be unique to this document.)

DREO TECHNICAL NOTE NO.

10b. OTHER DOCUMENT NOS. (Any other numbers which may be assigned this document either by the originator or by the sponsor)

11. DOCUMENT AVAILABILITY (any limitations on further dissemination of the document, other than those imposed by security classification)

(xx) Unlimited distribution
( ) Distribution limited to defence departments and defence contractors; further distribution only as approved
( ) Distribution limited to defence departments and Canadian defence contractors; further distribution only as approved
( ) Distribution limited to government departments and agencies; further distribution only as approved
( ) Distribution limited to defence departments; further distribution only as approved
( ) Other (please specify):

12. DOCUMENT ANNOUNCEMENT (any limitation to the bibliographic announcement of this document. This will normally correspond to the Document Availability (11). However, where further distribution (beyond the audience specified in 11) is possible, a wider announcement audience may be selected.)

13. ABSTRACT (a brief and factual summary of the document. It may also appear elsewhere in the body of the document itself. It is highly desirable that the abstract of classified documents be unclassified. Each paragraph of the abstract shall begin with an indication of the security classification of the information in the paragraph (unless the document itself is unclassified) represented as (S), (C), (R), or (U). It is not necessary to include here abstracts in both official languages unless the text is bilingual).

Aerosols were prepared from sixteen materials, liquid and solid. These were used, over the size range 0.01-0.30 um, to challenge a standard filter paper. Penetration was nearly independent of the chemical nature of the aerosol in the size range 0.10-0.30 μm. Below 0.10 μm, penetration varied widely from challenge to challenge.

14. KEYWORDS, DESCRIPTORS or IDENTIFIERS (technically meaningful terms or short phrases that characterize a document and could be helpful in cataloguing the document. They should be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location may also be included. If possible, keywords should be selected from a published thesaurus. e.g. Thesaurus of Engineering and Scientific Terms (TEST) and that thesaurus identified. If it is not possible to select indexing terms which are Unclassified, the classification of each should be indicated as with the title.)

FILTER TEST SYSTEM
AEROSOLS
FIBROUS FILTERS
PENETRATION
SIZE EFFECTS
SODIUM CHLORIDE
DIOCTYL PHTHALATE
ORGANIC COMPOUNDS
INORGANIC COMPOUNDS