SESSION X

TEST METHODS

Wednesday, August 9, 1978
CHAIRMEN: J. L. Kovach, J. W. Jacox

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THE NEW WASTE CALCINING FACILITY PROCESS OFF-GAS FILTRATION SYSTEM AND REMOTE IN-PLACE DOP TEST

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Abstract

The crabtrap, one component of a remotely-operable, experimental, in-place DOP test system for process off-gas HEPA filters being developed at Flanders Filters was tested with good results. The crabtrap is a device which is positioned downstream of a HEPA filter during in-place DOP testing to thoroughly mix and collect the air and DOP passing through the filter so the efficiency of the filter and the integrity of the supporting framework can be determined from outside the ventilating system. Concurrently, a test program was also initiated at the Remote Maintenance Development Facility located in the Idaho National Engineering Laboratory. The objective of the effort was to verify that a remotely operable and maintainable (by a single-arm manipulator) off-gas filtration system could be designed for use in the New Waste Calcining Facility being built at the Idaho Chemical Processing Plant. The capabilities demonstrated in the program included the remote replacement of filters, filter housing doors, seals, the filter support and elevating units, and remotely testing the filters using DOP aerosol within a space-limited plenum.

I. Introduction

The in-place dioctyl phthalate (DOP) test required by government regulations to determine the efficiency of High Efficiency Particulate Air (HEPA) filters is frequently incompatible with many other components in a ventilating system. Research and development has been performed at Flanders Filters, Inc. on various in-place test devices that could be incorporated in a filter housing in efforts to (a) reduce the space required to perform a successful in-place DOP test, (b) be able to accomplish the test (inject the DOP, operate the test equipment, etc.) from outside the plenum or filter housing, (c) independently test each filter in a multiple filter installation for efficiency, and (d) reduce the amount of DOP to be generated at a given time by testing the filters one at a time. Hopefully, the results of this program will have special significance in larger filter banks, installations where two or more filters in series must be tested, and in systems where the maintenance of the filters must be performed from a remote location.

The specific objectives of the program were directed towards (a) devising a method of achieving uniform dispersion of the DOP aerosol in the airstream immediately ahead of each HEPA filter and its supporting framework without the industry recommended seven to ten duct diameters and without using bypass ducting, and (b) providing a downstream device that would mix, collect and permit sampling for filter efficiency a short distance from the filter.

In early tests, dispersion was attained by electrically polarizing the DOP particles as the DOP was introduced into the airstream immediately ahead of the HEPA filter. A sheet metal partition was installed upstream of and between contiguous filters to isolate the DOP inlet and the dispersion apparatus which were installed ahead of each filter. However, because of potential maintenance problems and the fire hazard associated with the electro-static method, this method of dispersing DOP was abandoned and an effort began to develop a mechanical solution. However, capability of isolating filters to permit individual testing has been retained.

A device called a crabtrap (because of its unusual shape and the way that early versions opened and closed) has been used from the beginning of the program to sample the airstream a short distance downstream of a filter. One crabtrap device is installed downstream of each filter so that individual filters can be tested. Readings taken at the crabtrap have been found comparable to samples taken ten or more duct diameters downstream of the filter.

II. Description

Crabtrap

The crabtrap is shaped like a funnel, except that the "spout" (sample box) has been recessed into the body of the funnel, and the trap is square rather than round (Fig. 1 and 2) giving it the appearance of a pyramid with its top cut off. The base of the pyramid is 24 in. by 24 in. to correspond in size to the face area of the filters commonly used in larger ventilating systems. At the top where the sample box is recessed, the opening is 6 in. by 6 in. About a third of the way up from the base, the pyramid is broken on three sides and hinged on the fourth to permit it to be opened after testing. When in the test position, air leaving a filter is forced through the crabtrap, with a great deal of turbulence and mixing due to the sharply sloping interior walls of the pyramid and the sidewalls of the sample box. Air that has been diverted through the crabtrap is then sampled for an efficiency reading at a point 13 in. beyond the box. When the test is completed, the crabtrap is swung to the side leaving a 17 in. by 17 in. opening for the passage of air.

When more than one filter in parallel is being tested, all crabtraps are closed simultaneously so that the air through the system remains balanced.

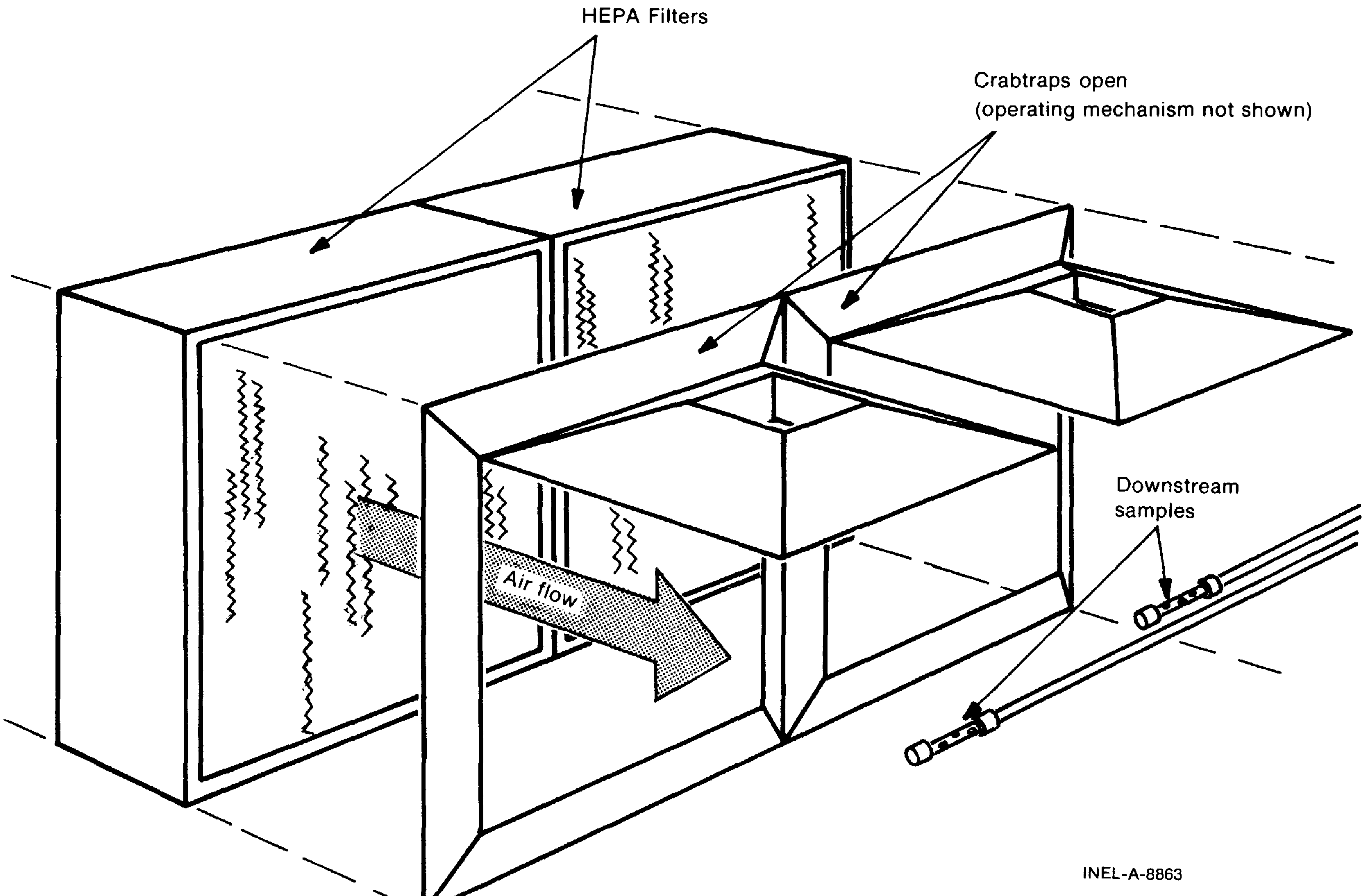


FIGURE 1

CRABTRAP - OPEN POSITION

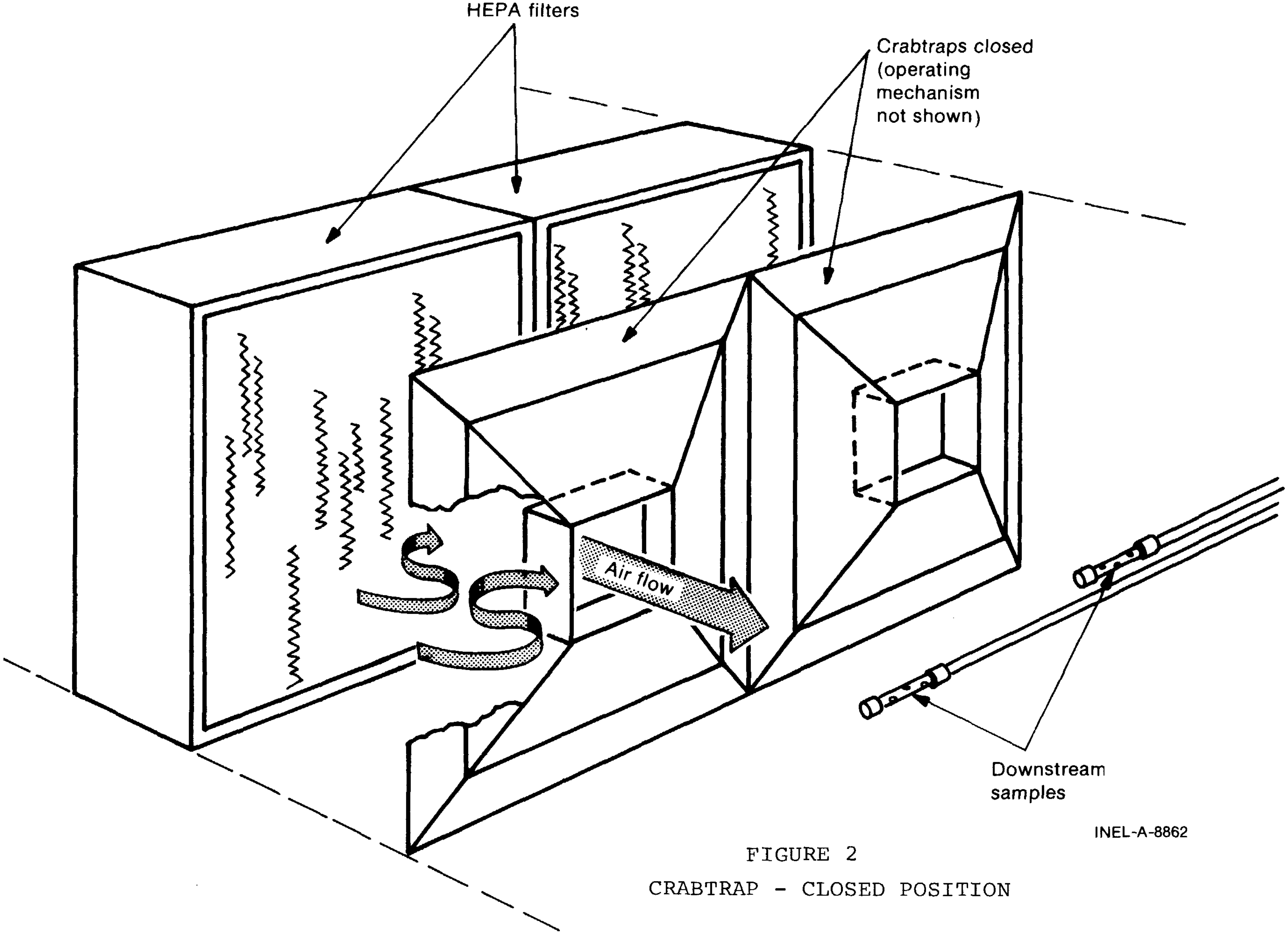


FIGURE 2

CRABTRAP - CLOSED POSITION

III. The New Waste Calcining Facility

Concurrent with Flanders Filters' remote DOP testing program, the New Waste Calcining Facility (NWCF) Project initiated a series of remote development programs. These programs were designed to confirm the remote replacement philosophy developed for high maintenance equipment within the NWCF. The specific objective of each program was to verify that all the remote operations designed for use in the NWCF could be accomplished. The remote design philosophy will contribute significantly to the control of problems such as lengthy facility downtime, costly decontamination efforts, and high personnel radiation exposures as compared with a nuclear facility with direct handling and replacement concepts.

As part of the remote development program, an off-gas filtration system incorporating the remote replacement philosophy was designed for use in the NWCF. To demonstrate the operability of the design, a full scale section of the remotely operable and maintainable filtration system was fabricated and tested at the Remote Maintenance Development Facility (RMDF) located at the Idaho National Engineering Laboratory (INEL). The design of this filtration system included positive positioning and sealing of the filters, remote filter replacement, remote in-place DOP filter testing, and remote replacement of selected filter plenum components which may require maintenance. To accomplish project objectives, the operability and compatibility of the filter system and the remote handling equipment was also developed and proven along with all the specific remote operating requirements.

As developed and designed, the NWCF process off-gas filtration system will contain four parallel filter plenums, each containing (in series) a prefilter plus two HEPA filters. The prefilter and HEPA filters will be 95% and 99.95% efficient, respectively, on 0.7 micron mean diameter DOP aerosols. Any three of the filter plenums are capable of accepting the total NWCF off-gas flow, thus permitting isolation of any single plenum for maintenance, filter replacement, or other remote operations. Overall, the system is designed to provide an off-gas decontamination factor for particulates of 8×10^7. Figure 3 shows the final design of the NWCF off-gas filtration system.

IV. Remote Testing

To simulate actual NWCF operating conditions, all remote handling operations in this test program were performed using a wall-mounted electro-mechanical, single-arm manipulator behind a simulated shielded viewing window. At the completion of the remote test program, the following remote operations had been successfully demonstrated with the aid of an impact wrench, special filter cover and handling tools:

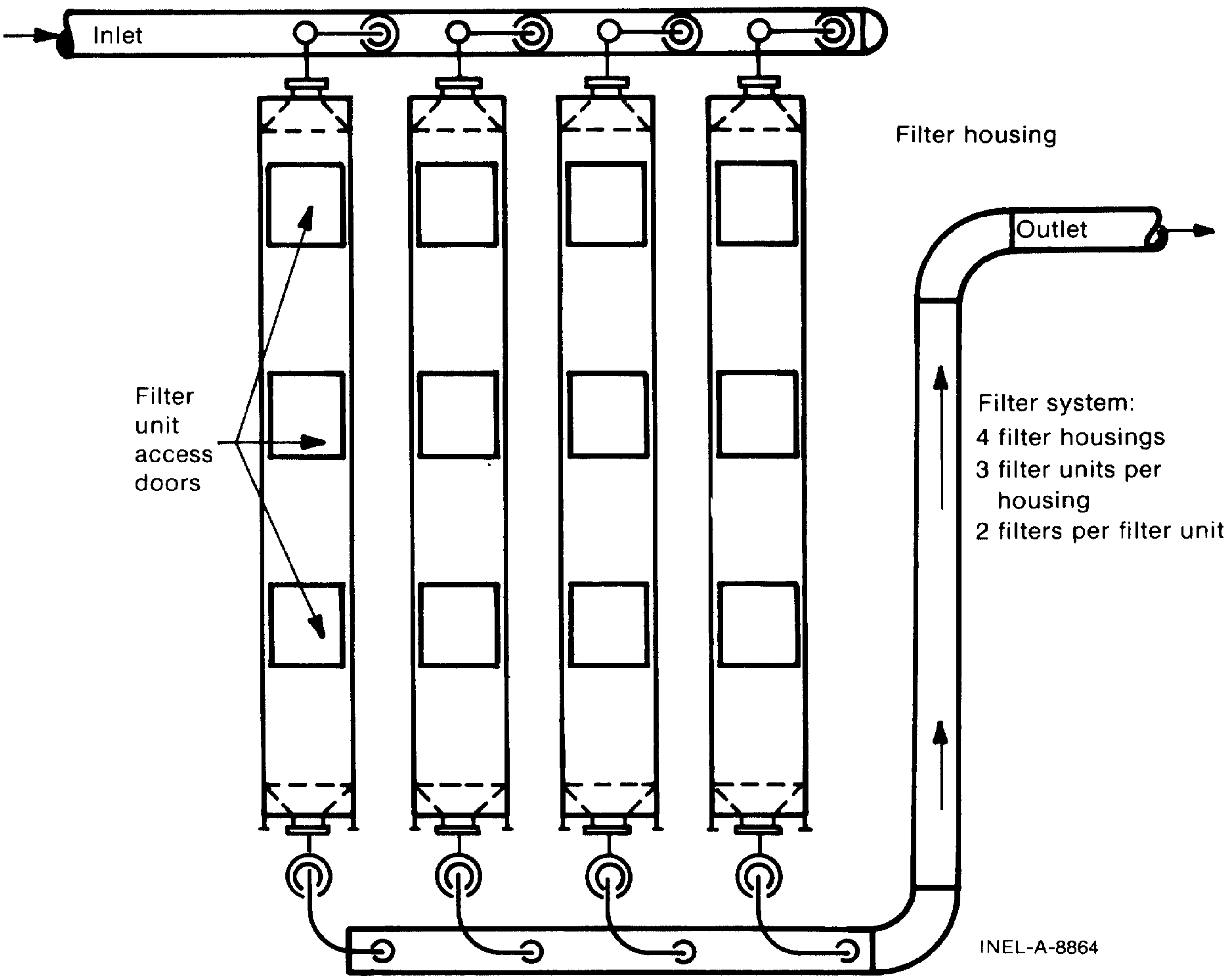


FIGURE 3

NWCF FILTER SYSTEM

1. disengaging the filter housing door bolts;
2. lowering and aligning the filter housing door;
3. operating the filter elevator mechanism for lowering or raising (sealing) the filters;
4. removing and replacing the filters;
5. transporting the filters from the filter cell;
6. removing the filter housing door for seal replacement;
7. removing the elevator assembly for repair.

Figures 4 through 9 show the auxiliary handling tools used and the remote operations verified in the test program.

V. DOP Testing

The NWCF design criteria requires that after replacement, each filter be tested in-place using 0.7 micron mean DOP aerosol, thus verifying that the filter will meet federal regulations. Unless such a test is conducted, the remote filter replacement procedure does not prove that the filter is in position and sealed, or that the filter has remained undamaged during replacement.

Due to the limited distance available between each filter unit (approximately 4 ft) in the NWCF filter plenums, conventional in-place DOP test methods (requiring approximately 10 duct diameters upstream for DOP injection and 15 duct diameters downstream prior to sampling) could not be utilized. Thus, another test method had to be developed to verify the integrity of the newly replaced filters. After several design iterations, a non-conventional DOP test system was finalized and tested. Two major problems, good upstream DOP distribution and good representative downstream samples, were finally solved through the use of a conical disperser, a crabtrap, and a multiple port sample line. With the aid of these special devices, the final DOP test system gives results comparable with conventional test methods.

The basic in-place DOP test set-up is illustrated in Figure 10. The conical disperser, crabtrap, and multiple port sample line are shown in Figures 11 and 12. In the test program, DOP aerosol was injected with approximately 200 scfm of clean air through the 5 in. DOP injection line and dispersed by the conical disperser upstream of the filter. DOP samples were collected upstream (10 in. in front of the filter face) at 12 different points on the same plane to determine the disperser's distribution characteristics. Samples were also collected downstream of the crabtrap and compared with samples collected by conventional methods.

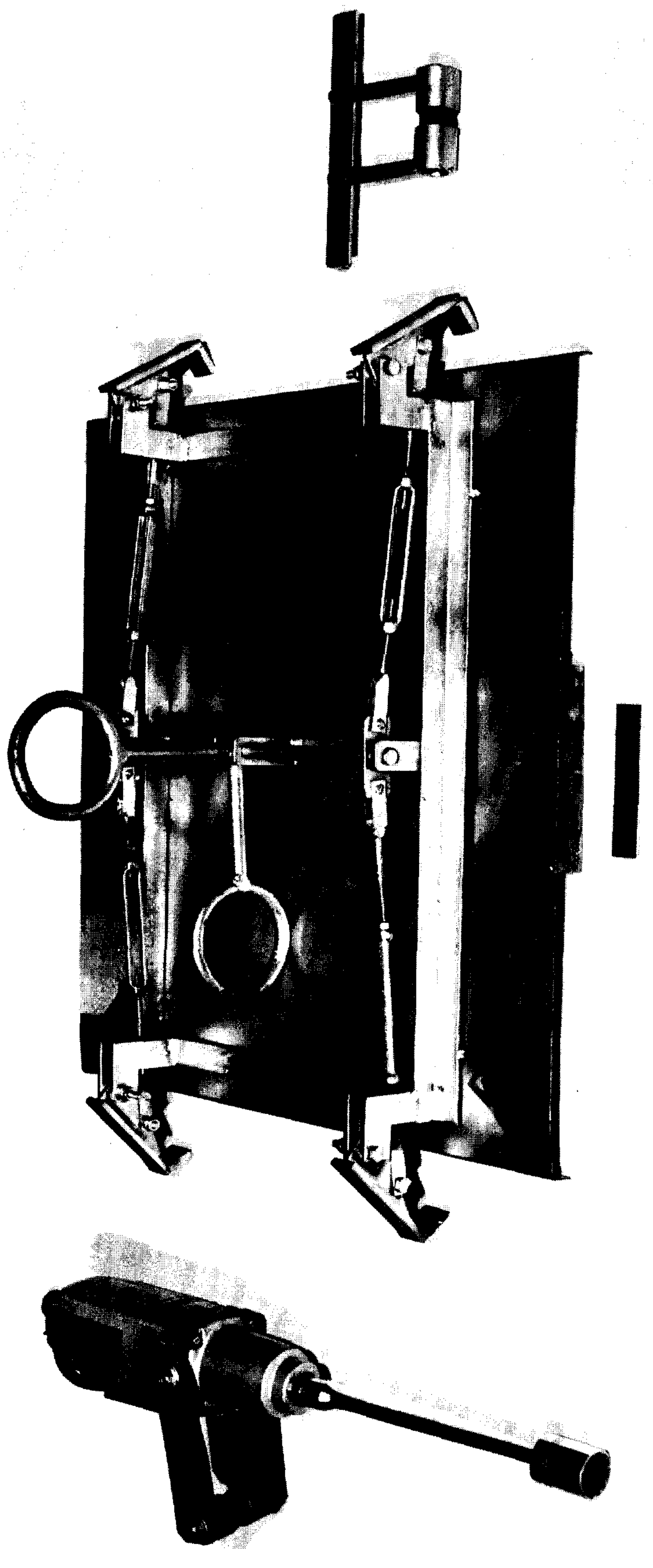


FIGURE 4
AUXILIARY TOOLS

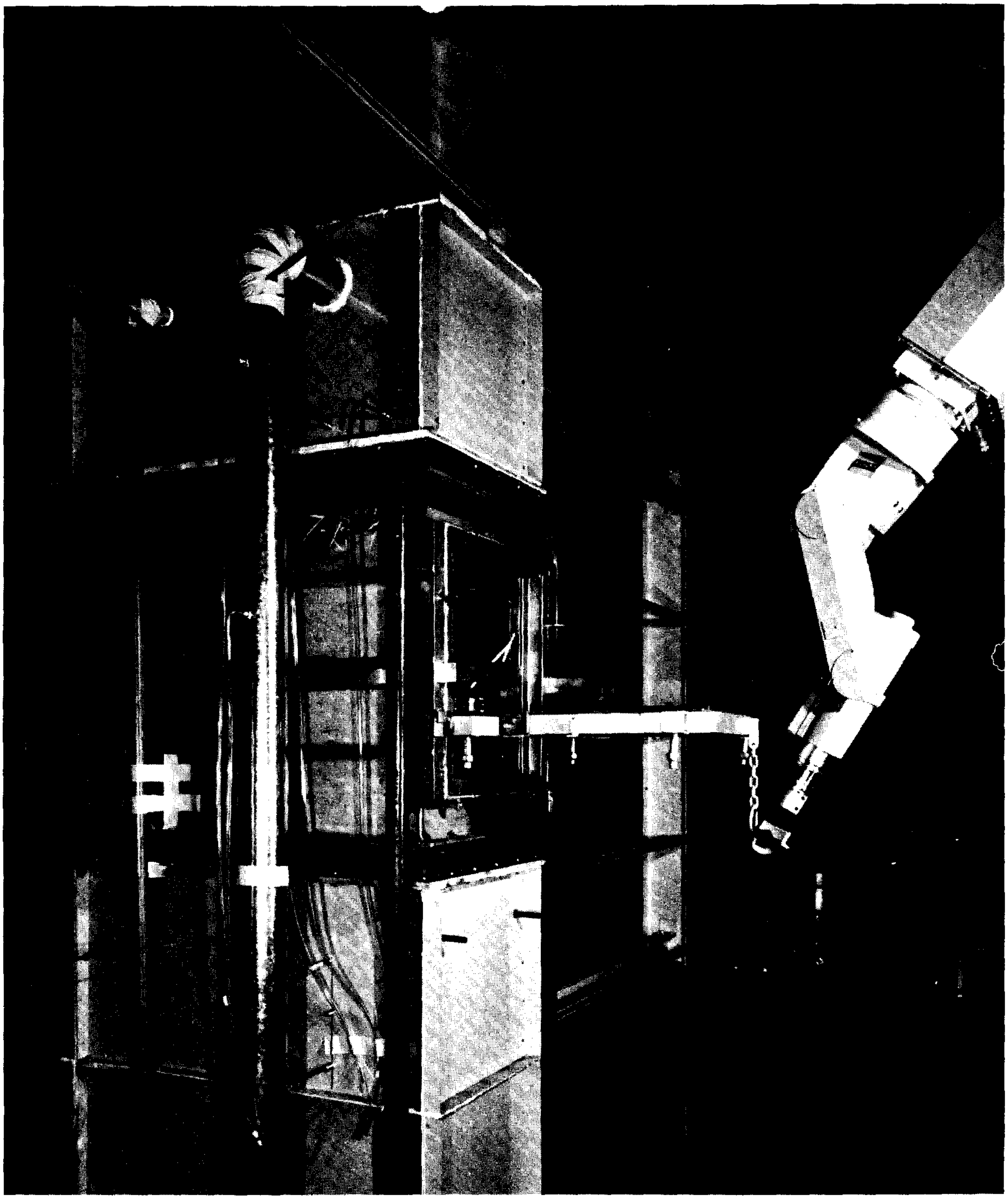


FIGURE 5

LOWERING AND ALIGNING FILTER PLENUM DOOR

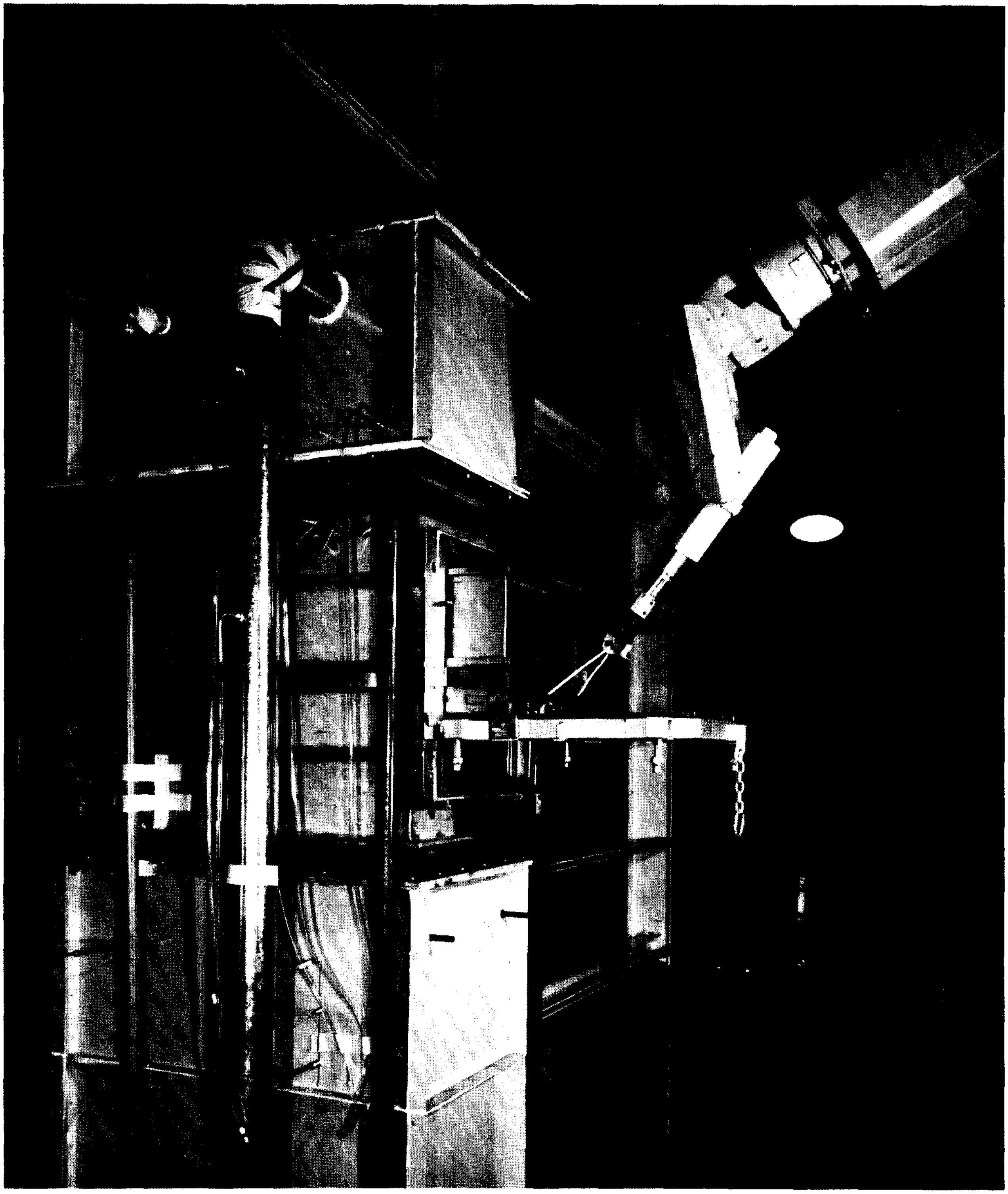


FIGURE 6

FILTER REMOVAL

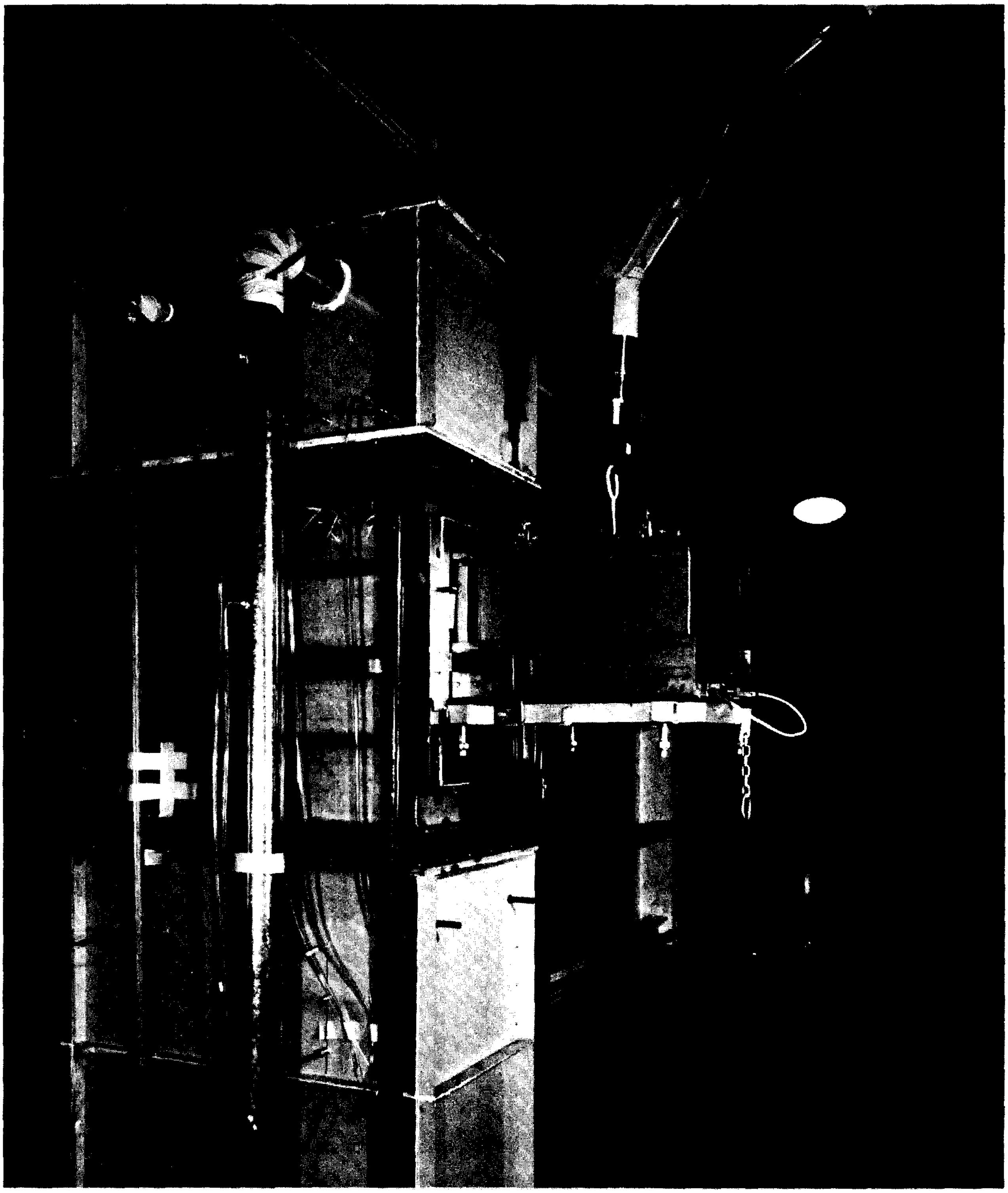


FIGURE 7

FILTER TRANSFER

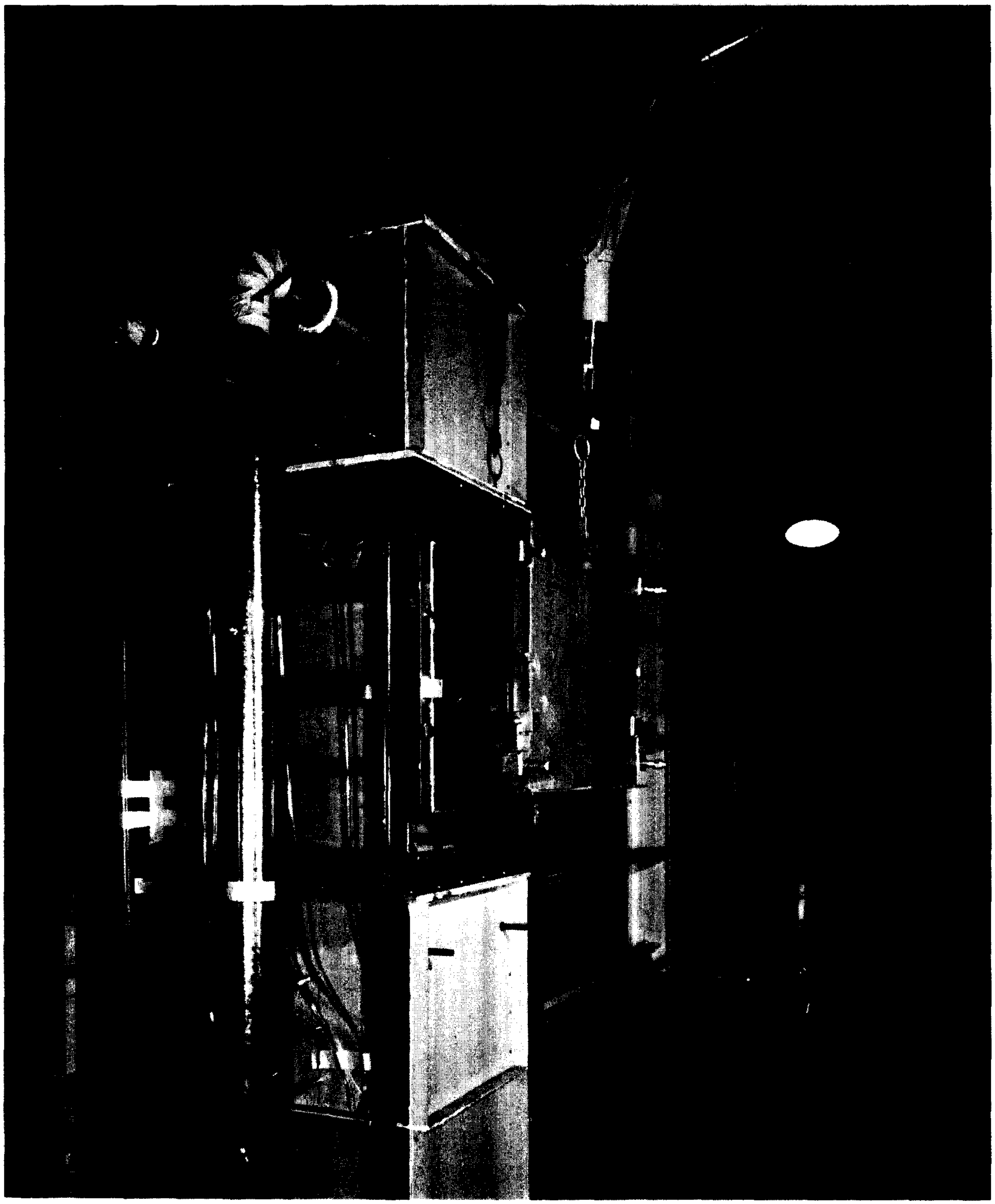


FIGURE 8

DOOR REMOVAL

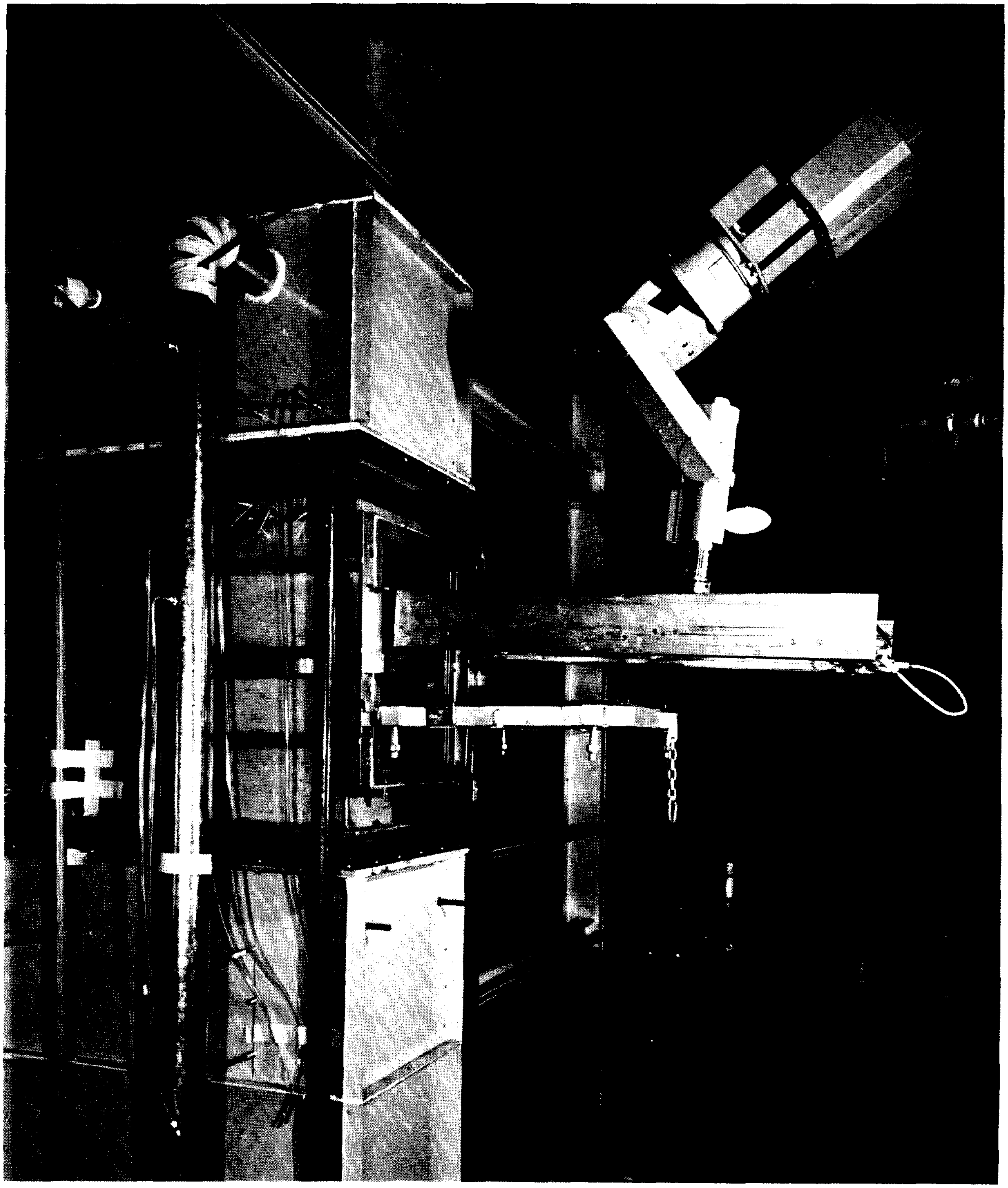
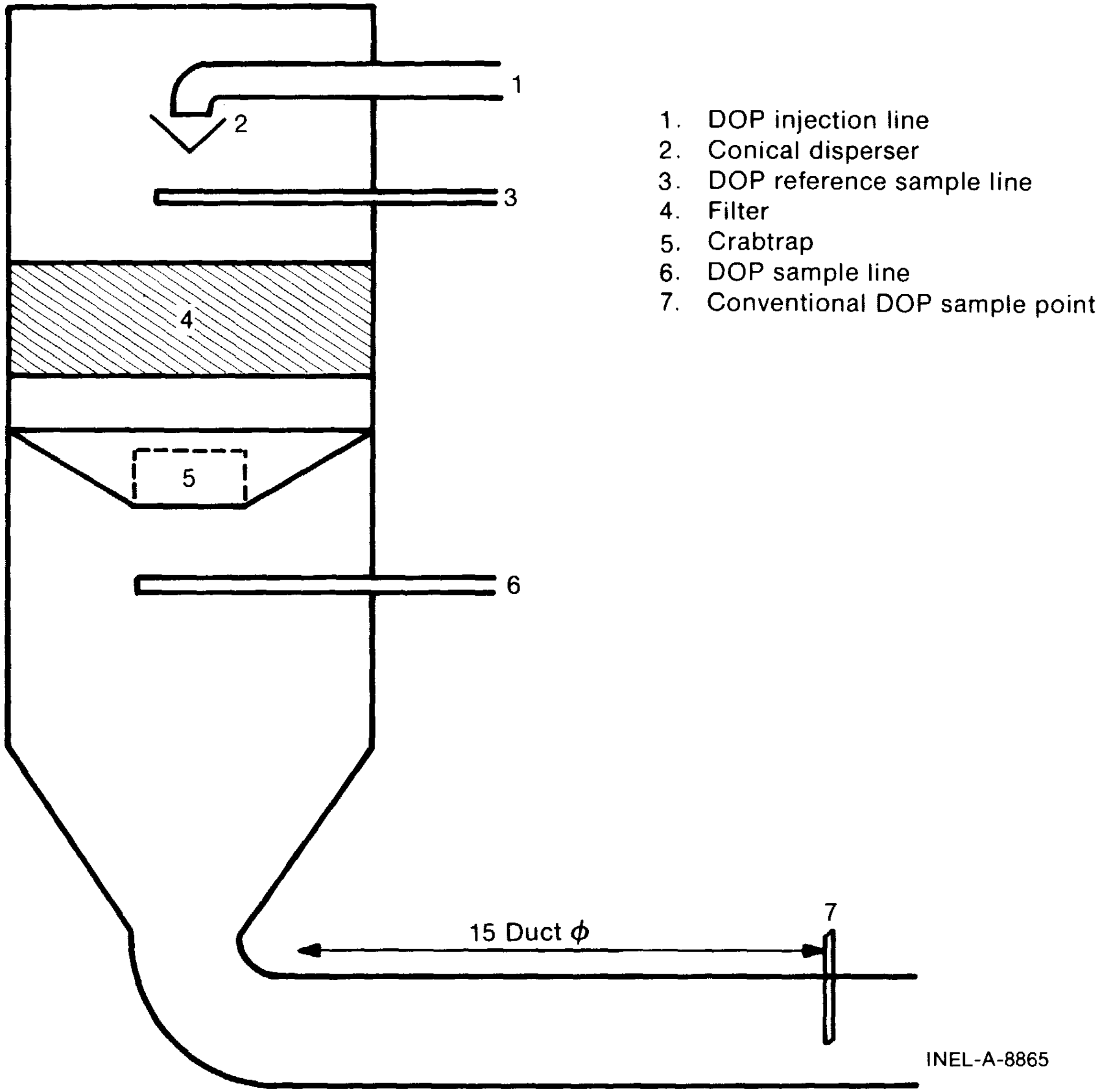


FIGURE 9

ELEVATOR REMOVAL



1. DOP injection line
2. Conical disperser
3. DOP reference sample line
4. Filter
5. Crabtrap
6. DOP sample line
7. Conventional DOP sample point

FIGURE 10
IN-PLACE DOP TEST SET-UP

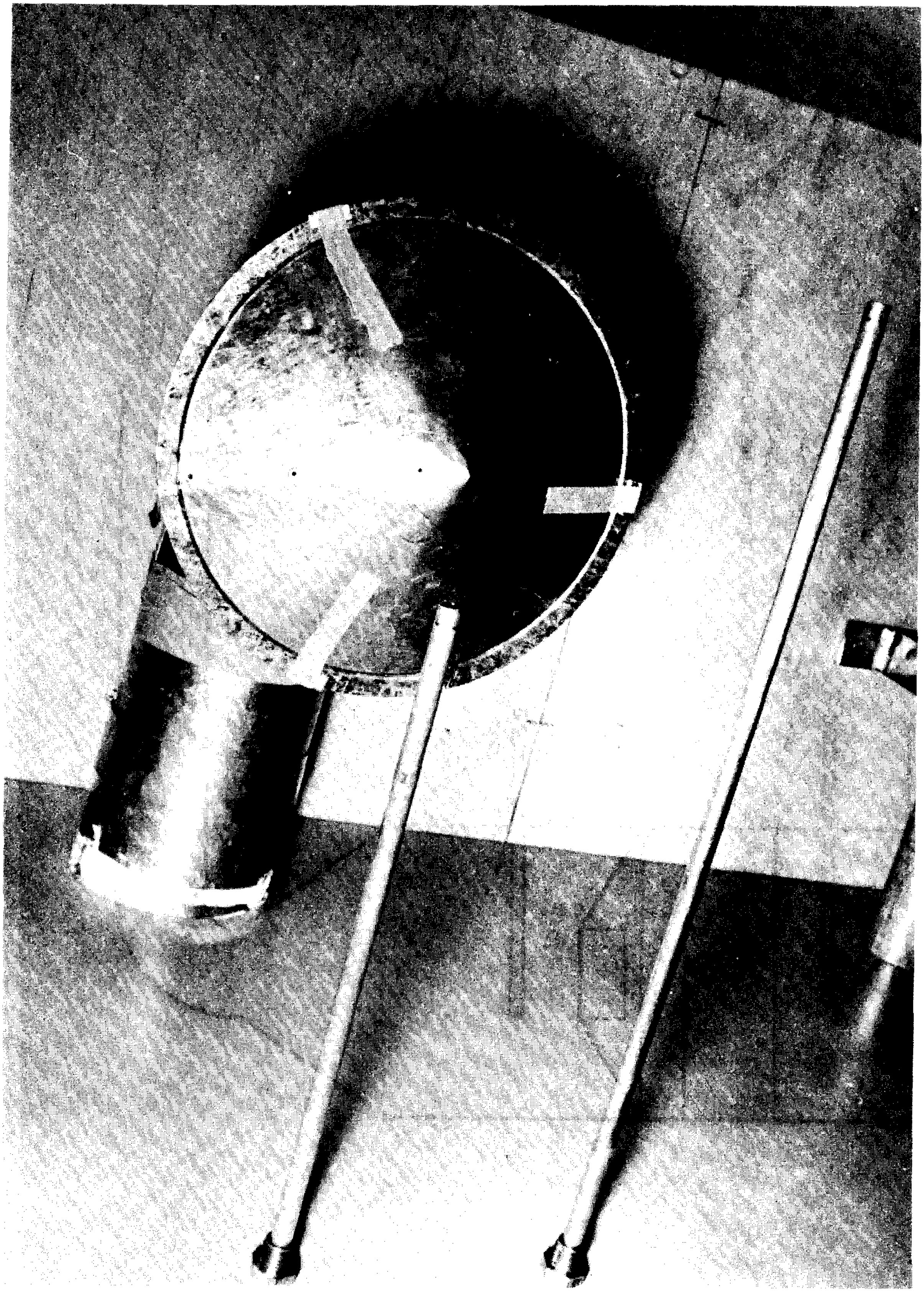


FIGURE 11
CONICAL DISPERSER

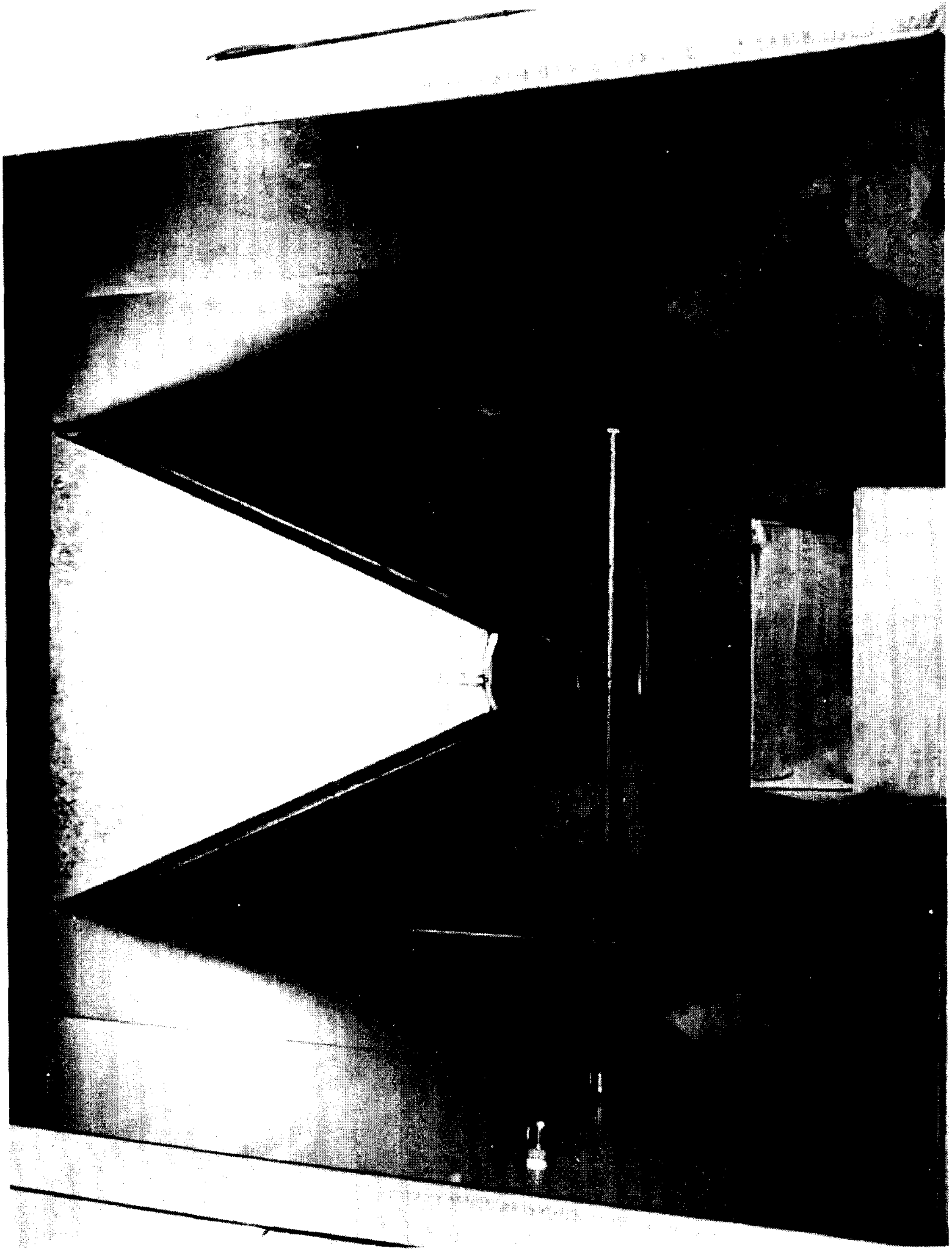


FIGURE 12

DOWNSTREAM SAMPLE LINE AND CRABTRAP-PARTIALLY OPEN

The sample data collected in this test program were in close agreement with sample data collected by conventional DOP test methods. In addition, typical sample readings collected upstream of the filter were within 1% of one another. The DOP sample collected downstream of the crabtrap was within 0.02% of the sample collected at the conventional DOP sample line which was more than 15 duct diameters downstream of the filter. These results indicate that the conical disperser has an almost perfect DOP distribution characteristic and that the crabtrap and multiple port sample probe will determine filter efficiency to within 0.02% of conventional sample methods.

Based on these preliminary test results, the final design of the in-place DOP test system to be used in the NWCF will essentially be identical to the test arrangement. However, the filter plenum manufacturer will be required to perform a final acceptance test to prove that the DOP test system to be used in the process is workable. Preliminary results, on a similar test set-up, (submitted by the plenum manufacturer) is given in Table I. The plenum manufacturer's set-up is identical to the one tested at the RMDF, other than the crabtrap was turned around.

Table I. In-place DOP test results

Filters Tested	Tested Air Flow (acfm)	DOP Upstream	Downstream Samples (crabtrap)	Downstream Samples 15 duct Ø
1A	193	100%	.015	.015
1B	223		.008	.015
2A	207		.012	.012
2B	204		.012	.018
3A	209		.070	.058
3B	209		.030	.039
4A	200		.017	.019
4B	193		.022	.026
5A	199		.025	.029
5B	186		.070	.038
6A	185		.022	.024
6B	219		.024	.024
7A	203		.140	.130
7B	212		.120	.065
8A	217		.065	.065
8B	206		.080	.039
9A	220		.055	.055
9B	221		.120	.055
10A	188		.027	.028
10B	195		.140	.110

VI. Summary

The test program conducted at the INEL's RMDF has proven to be extremely valuable in insuring a workable system prior to finalizing an equipment design. This program conducted at the RMDF has demonstrated that remote filter replacement, and filter housing preventive maintenance, and remote in-place DOP testing can be accomplished within a compact (space-limited) filter plenum. Development is continuing on other mechanical methods of introducing and dispersing the DOP ahead of the filters. One promising possibility of attaining dispersion is turning the crabtrap around so that the top of the pyramid points upstream and the sample box is recessed towards the filter. The DOP, introduced upstream of the reversed crabtrap, is forced to mix with the air being diverted through the sample box and is dispersed as it leaves the sample box prior to entering the filter. Further study is necessary in this area. The reversed crabtrap may also be used for sampling.

Presently, space is at a premium because of ever-increasing costs, yet ventilation systems are required to have an ever-increasing number of components in their make-up such as prefilters, entrainment separators, carbon adsorbers and HEPA's in series. Compact filter trains are less costly to build and easier to maintain, but are not always compatible with the requirements for an acceptable in-place DOP test. Also, at present, "hands on" maintenance of filters is under careful scrutiny for safety reasons. For the above reasons, remote testing of filters is certain to have increasing importance in years to come. Finally, the development of a workable in-place test requiring a minimum of space wherein individual filters can be tested is more stringent than challenging an entire filter bank. That is, when an entire bank of filters is challenged with DOP where only one filter might be leaking, the leak is diluted by the great volume of clean air passing through the rest of the filters (dilution effect), and the portion of the leaking filter that does not leak, thus perchance masking the leak. Testing filters individually will limit this effect.

DISCUSSION

FREEMAN: What costs are we looking at for this automated feature?

LOO: The total cost for fabricating the four filter housings to be used in the New Waste Calcinating Facility is $435,000. However, I would like to point out that these filter housings are designed and fabricated in accordance with the ASME code, Section VIII, Div. 1 to a design pressure of 10.0 psig positive and 8.5 psig vacuum, thus increasing the cost somewhat.

FREEMAN: What is the air volume?

LOO: Each filter housing contains two 24 x 24 x 11-inch filters. If you use the separatorless-type filters, there will be about 3,000 cfm of air through each filter housing.

T. T. ALLAN: I would like to comment further on Mr. Sam Freeman's question regarding the cost of the four housings because the response, $435,000, was not adequately qualified. The cost of all the internal components of the assembly (twelve sets in all) to operate, test and maintain the 24 HEPA filters and prefilters was 20% of the total cost and that included several years of development cost. The housings themselves, or vessels as they should have been called, are each 20 ft. high, 4 ft. deep, and 2 ft. wide and were designed to withstand operating pressures of ± 7 psi. They are to be constructed of 5/16 in. 304L stainless steel contained in reinforcing angles with 2 in. of insulation and a 304L stainless skin. The vessels were 80% of the cost.

If similar, remotely operable units were to be constructed of heavy gauge stainless without the operating pressures that were required for these units, they would cost 15-20% of the figure given by Henry Loo.

Finally, it should be pointed out that in the existing calciner hot cell, as in similar hot cells in other facilities, the procedure is to dispose of the entire housing or vessel with each filter change at a cost of several thousand dollars per housing. The ability to change just the filter remotely will be a considerable savings in maintenance costs on the NWCF.

WARNKE: Since these filters are remotely-operable and remotely maintained, have you done any time and motion studies with regard to remote change-out and in-place DOP testing? I would be interested in the time required for filter change-out, assuming the filter is already inside the cell and prepared for changeout.

LOO: Assuming the filter is completely prepared for change-out, the operation takes about 20 minutes per filter.

WARNKE: Also, how do you transfer the filter into the cell and what time frame are we looking at for this operation?

LOO: We have designed a parking area separation between the filter housing and the outside building corridor. We transfer the unused filters into this buffer zone and then into the hot filter area. Since the facility is not yet constructed, we have no exact idea of the time required.

WARNKE: What time frame are you looking at for DOP testing each filter bank? Again, assuming all DOP generating and testing equipment is ready to go and all that is required is the actual testing?

LOO: Assuming all equipment is ready, the DOP testing would take about 15 minutes per filter.

VAN BRUNT: Can you explain the much higher penetration of filter 7B and 9B? They appear to be much worse than any of the others.

LOO: The tests were conducted on two consecutive days, with tests 1-5 on the first, and 6-10 on the second. The much greater deviation noted on the second day is probably attributable to some inadvertent change in the set-up.

EVALUATION OF THE HEPA FILTER IN-PLACE TEST* METHOD IN A CORROSIVE OFF-GAS ENVIRONMENT

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Abstract

Experiments were performed to determine if the combined effects of temperature, humidity and oxides of nitrogen (NO_x) hinder the in-place testing of high-efficiency particulate air (HEPA) filters used for cleaning the off-gas from a nuclear waste solidification facility. The laboratory system that was designed to simulate the process off-gas contained two HEPA filters in series with sample ports before each filter and after the filter bank. The system also included a reaction bomb for partial conversion of NO to NO_2. Instrumentation measured stream flow, humidity, NO_x concentration, and temperature. Comparison measurements of the DOP concentrations were made by a forward light-scattering photometer and a single particle intra-cavity laser particle spectrometer. Experimental conditions could be varied, but maximum system capabilities were 95% relative humidity, 90°C, and 10,000 ppm of NO_x.

A 2^3 factorial experimental design was used for the test program. This design determined the main effects of each factor plus the interactions of the factors in combination.

The results indicated that water vapor and NO_x interfere with the conventional photometer measurements. Suggested modifications that include a unique sample dryer are described to correct the interferences. The laser particle spectrometer appears to be an acceptable instrument for measurements under adverse off-gas conditions.

I. Introduction

A nuclear waste solidification facility similar to the Waste Calcination Facility (WCF) at the Idaho Chemical Processing Plant (ICPP) produces an off-gas stream that has characteristics unique to the nuclear industry. The calcination process, the conversion of radioactive liquid wastes to solids, emits gases that are cleaned by cyclones, a scrubber, silica gel adsorbers, and HEPA filters (Figure 1). At the filters, the stream has a temperature of 90°C, a relative humidity of 95%, and an oxides of nitrogen concentration of 10,000 ppm. The filters are changed-out when radiation levels exceed a

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*Work performed under DOE Contract EY-76-C-07-1540

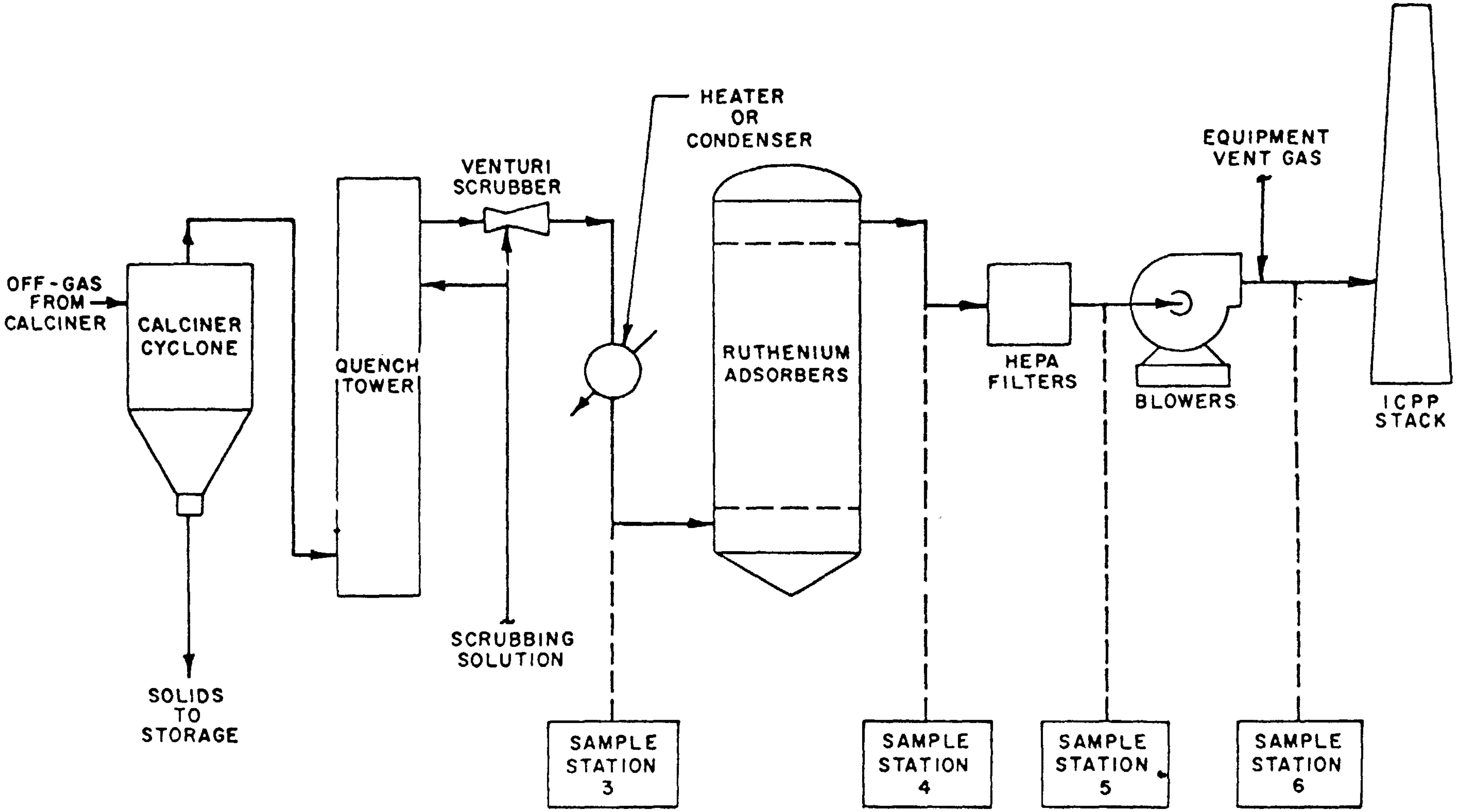

Figure 1. WCF OFF-GAS DECONTAMINATION SYSTEM

safe operating limit, when pressure drop is high, or when a filter breach is indicated. A breach can be detected by the continuous monitoring of radiation in the off-gas stream after the filters or by a "fail-test" of the DOP in-place test method.[1] However, the DOP test method has provided erratic and unreliable results and the need for filter changeouts is usually determined by the monitor.

The HEPA system in the WCF consists of three parallel banks of filters; each bank has two HEPAs in series. Each filter bank can be tested separately by closing the air flow valves. A sample port does not exist between the filters.

The objective of this HEPA filter testing program is to evaluate the combined effects of temperature, humidity, and oxides of nitrogen on the standard DOP test method, and to determine if the laser is an acceptable instrument for measuring filter efficiencies in series in this type of environment. The conventional forward light-scattering photometer (Air Techniques Model TDA-2DN with .01% scale) and a laser particle spectrometer (Particle Measuring Systems Model ASAS-300) are used as the aerosol measuring instruments. Because of the highly radioactive environment of the WCF off-gas, a laboratory experimental system was constructed to simulate the off-gas conditions excluding radioactivity.

Each of the three parallel HEPA filter banks in the WCF off-gas system can be opened and closed for testing of individual banks. Since the filters in each bank cannot be tested separately, possible test errors can occur due to agglomeration and evaporation between filters. Light-scattering photometers have an effective dynamic range of about 10^4 and, therefore, are not acceptable instruments for a two-stage system.[2] In the simulated system, the photometer and laser spectrometer are used as comparison instruments for testing of the single HEPA filter and the laser is used for testing the two HEPA filters in tandem. The laser is capable of measuring protection factors of 10^8, and it has the additional advantage of measuring various particle sizes in the 0.15 to 3.0 μm range. Protection factors as a function of particle size can be obtained.

The work that is reported in this paper is a part of the total program to evaluate in-place testing of HEPA filters in a corrosive environment. Work to date has involved the DOP test method. Future work will include comparison tests with the NaCl and uranine methods.

II. Experimental Procedure

The DOP studies were conducted with two 20-cm x 20-cm x 15-cm (8-in. x 8-in. x 5-7/8-in.) HEPA filters in tandem. Measurements of the DOP concentrations are taken upstream of both filters, between the filters, and after the final filter.

The apparatus shown in Figure 2 was used to conduct all testing. The system flow of 25 scfm was provided by a lubricated rotary vane vacuum pump. With a pressure drop of 5 inches of water, as in our

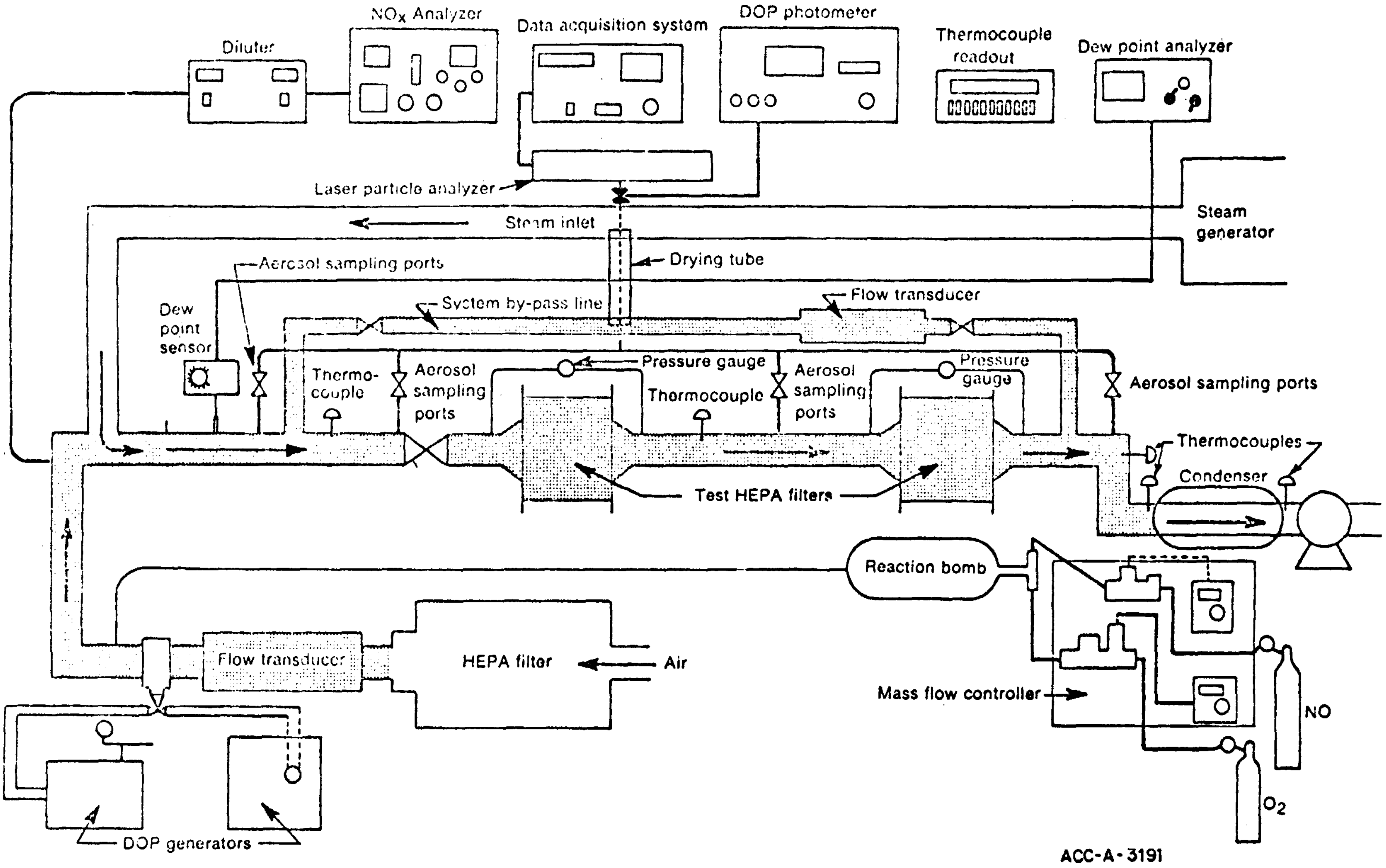

Figure 2. HEPA FILTER TEST SYSTEM

system, this pump has a flow capacity of 44 scfm. The inlet air is filtered through a 30-cm x 30-cm x 15-cm (12-in. x 12-in. x 5-7/8-in.) HEPA filter. The flow is measured after the inlet filter with a linear mass flow transducer.

Up to 10,000 parts per million (ppm) concentration of NO_x can be obtained downstream of the flow transducer by mixing measured amounts of NO and O_2 in a 7L reaction bomb. The gases are supplied from cylinders and their flow into the reaction bomb is controlled by mass flow controllers. The NO_x concentration is measured by a chemiluminescent analyzer. A blender is used to dilute the NO_x to a range within the measurement capabilities of the analyzer. Measurements of both NO and NO_2 can be obtained with the analyzer. A 50% NO - 50% NO_2 mixture was maintained during the tests.

Steam is injected into the system to furnish the moisture requirements of 50 to 95% relative humidity. The steam is supplied by an electric boiler. The moisture content can be controlled by boiler pressure and flow control valves. Moisture measurements are made by a dew point hygrometer. The operating temperature can be controlled to 0.5°C accuracy at any temperature between 66 and 93°C. The temperature is monitored by thermocouples at selected points along the system. Dioctylphthalate (DOP) is added downstream from the steam. The average DOP aerosol concentration was 102 µg/L ± 5 µg. Concentrations were determined by collection of the aerosol on a filter and by the photometer. A by-pass line in the system allows the filters to be avoided during startup and preliminary system checkouts. Another linear mass flow transducer in the by-pass line measures total flow. The system contains four sampling points. They are located before the by-pass, before Filter 1, and after Filter 2. All four points are connected to the light-scattering photometer or laser particle analyzer by a heat-traced and insulated line.

When conducting tests at dew points above 60°C, a drying tube was used to lower the sample dew point without removing aerosol. A sample from any point can be directed through the drying tube. The device operates by a process called permeation distillation.[3] In this procedure, a wet gas flows continuously into a bundle of tubes made of silicone polymer which is permeable to water vapor. Continuous drying is accomplished when the water vapor diffuses through the membrane and is swept by the dry gas flow in the reverse direction. The driving force of the process is the difference in relative humidities of the two streams. The dryer is designed in a shell and tube configuration, as shown in Figure 3. The wet sample passes through the tube side of the dryer and exits at the end of the bundle. The purge gas enters the unit on the shell side of the feed gas outlet and flows countercurrent to the wet feed gas. Drying efficiency and capacity are based on the dryer geometry (length and diameter) and the ratio of the purge-to-feed gas. The optimum purge-to-feed ratio is 1.5 to 1.

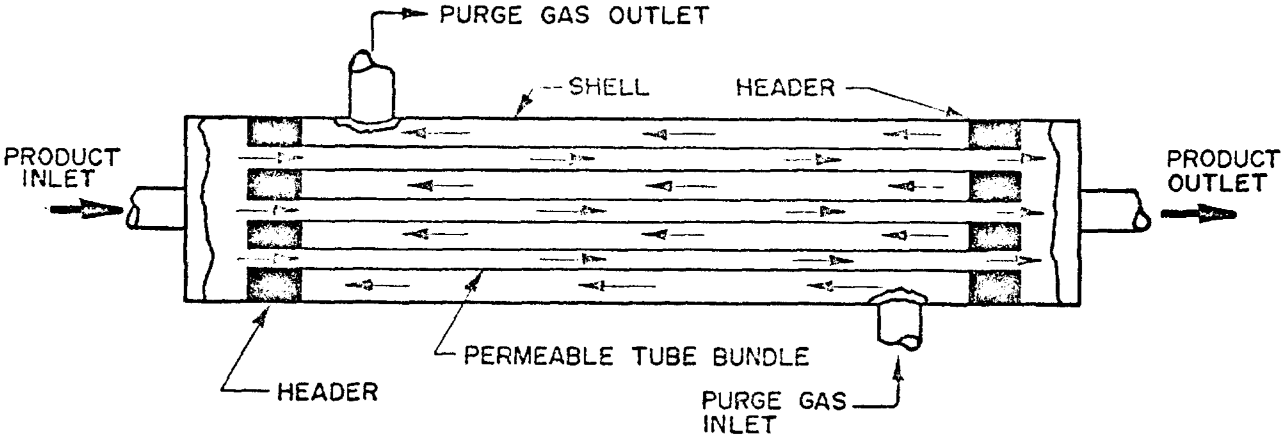

Figure 3. PERMEATION DISTILLATION DRYER

The HEPA test filters are sealed to the frame by a rubber base adhesive. These filters and the WCF process off-gas filters have identical specifications. Pressure drop is measured across each filter. After the test filters, the water is removed from the system by a condenser and a cryogenic probe. The dry stream then passes through the pump and is exhausted to the building ventilation system.

III. Experimental Results and Discussion

Baseline Measurements with Photometer and Laser

Preliminary tests were performed to establish a baseline for photometer and laser measurements of DOP in dry air. The tests were performed at a flow of 25 scfm and temperatures of 66 and 93°C. Each test period was two minutes, and 100 μg/L of DOP challenged the filters.

The results of the baseline tests are shown in Table I. These results were used as correction factors for all test measurements. Of particular interest is the great sensitivity of the laser measurements.

Photometer and Laser Measurements in Corrosive Environment

The effects of humidity, nitrogen oxides (NO_x) and temperature on the standard DOP test method were examined using a 2^3 factorial design. The design consists of eight tests, with three experimental variables (NO_x, temperature, relative humidity) that may be replicated as many times as desired. The important feature of this design is that it incorporates the extreme points of the factor space. The ranges of the variables were 500 to 10,000 ppm NO_x, 66 to 93°C, and 50 to 95% relative humidity.

The first DOP test was performed at 500 ppm NO_x and 50% relative humidity. The photometer gave a poor response. Additional tests were performed using room air (16% RH) and 10,000 ppm NO_x. The results are shown in Table II.

Table I. Baseline measurement with photometer and laser

Test Conditions			% Penetration			
			Photometer		Laser	
Relative Humidity %	NO_x ppm	Temperature °C	Filter 1	Filter 1&2[a]	Filter 1	Filter 1&2
*16	0	66	.002	--	.0001	.0001
16	0	66	.003	--	.0004	.0002
*16	0	66	.002	--	.0004	.0002
16	0	93	.002	--	.0002	.0002
*16	0	93	.002	--	.0002	.0001

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* Test performed using drying tube.

a Sensitivity of the photometer was not great enough to measure penetration of second filter in a series.

Test Conditions: flow, 25 scfm; challenge DOP concentration, ∿100 μg/L; test period, 2 min.; temperature, 66 and 93°C.

Table II. Water vapor and NO_x effects on measuring instrumentation

Test Conditions		% Apparent Penetration	
Relative Humidity %	NO_x Concentration ppm	Photometer	Laser
50	500	0-40% on 100% scale[a]	.0005
16	500	Negative Response[b]	.0002
50	0	0-40% on 100% scale	.0004
16	10,000	Negative Response	.0002
50	10,000	0-40% on 100% scale	.0001

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a The readings on the photometer were erratic varying from 0-40%; no readings were obtainable on the more sensitive scales of .01, .1, and 1% .

b The photometer reading was below zero on the .01 and .1% scales.

Note: All tests were conducted at 66°C and measurement made downstream of the first filter.

This difference in the performance of the photometer and the laser in humid atmospheres may be attributed to the difference in sampling areas of the two instruments as shown in Figure 4. In a forward light-scattering photometer, the sample is drawn through a solenoid valve and into the scattering chamber where the measurements are made. The stream exits the scattering chamber and is exhausted through a vacuum pump. The volume of the sample chamber of the photometer can cause a gas stream with a high dew point to be cooled followed by condensation. By contrast, the sampling area of the laser is extremely small. The sample is pulled through two small jets. This makes condensation an unlikely occurrence in the laser.

The response of the photometer when measuring a gas stream that contains NO_x appears to be caused by light absorption by NO_2. The standard DOP test method requires that "clean filtered air" be drawn through the scattering chamber while adjusting the stray light so that the photometer meter reads zero. After an adjustment is made in this manner and the gas stream containing NO_x is sampled, the light is not scattered forward but is absorbed by the NO_2 and the result is the negative response of the photometer's meter. The effect was eliminated by making the stray light adjustment while sampling a stream that contains NO_x. No NO_x interference was noticed with the laser.

The problem of condensation occurring in the photometer sample chamber was solved by installing the drying tube to remove water vapor. A comparison of data collected with the photometer and the laser is shown in Table III. The data indicate that the photometer performance improved greatly after the compensation for the NO_x and the removal of water vapor. However, the laser's sensitivity is still superior.

An analysis of the penetration data based on a two-level factorial design and the 95% confidence interval for an effect indicate:

Photometer

(1) H_2O effect = $15x10^{-3}\% \pm 2x10^{-3}\%$; adding water to the stream enhances the penetration of test filters.

(2) NO_x effect = $1x10^{-3}\% \pm 2x10^{-3}\%$; the effect of NO_x cannot be established within the confidence limits.

(3) Temperature = $-4x10^{-3}\% \pm 2x10^{-3}\%$; increasing the temperature lowers the penetrations.

(4) H_2O x NO_x interaction = $-4x10^{-3}\% \pm 2x10^{-3}\%$; the interaction between H_2O and NO_x lowers penetration.

(5) H_2O x temperature interaction = $3x10^{-3}\% \pm 2x10^{-3}\%$; the interaction between H_2O and temperature is very small as compared to experimental error, and may be questioned, but it also lowers penetration.

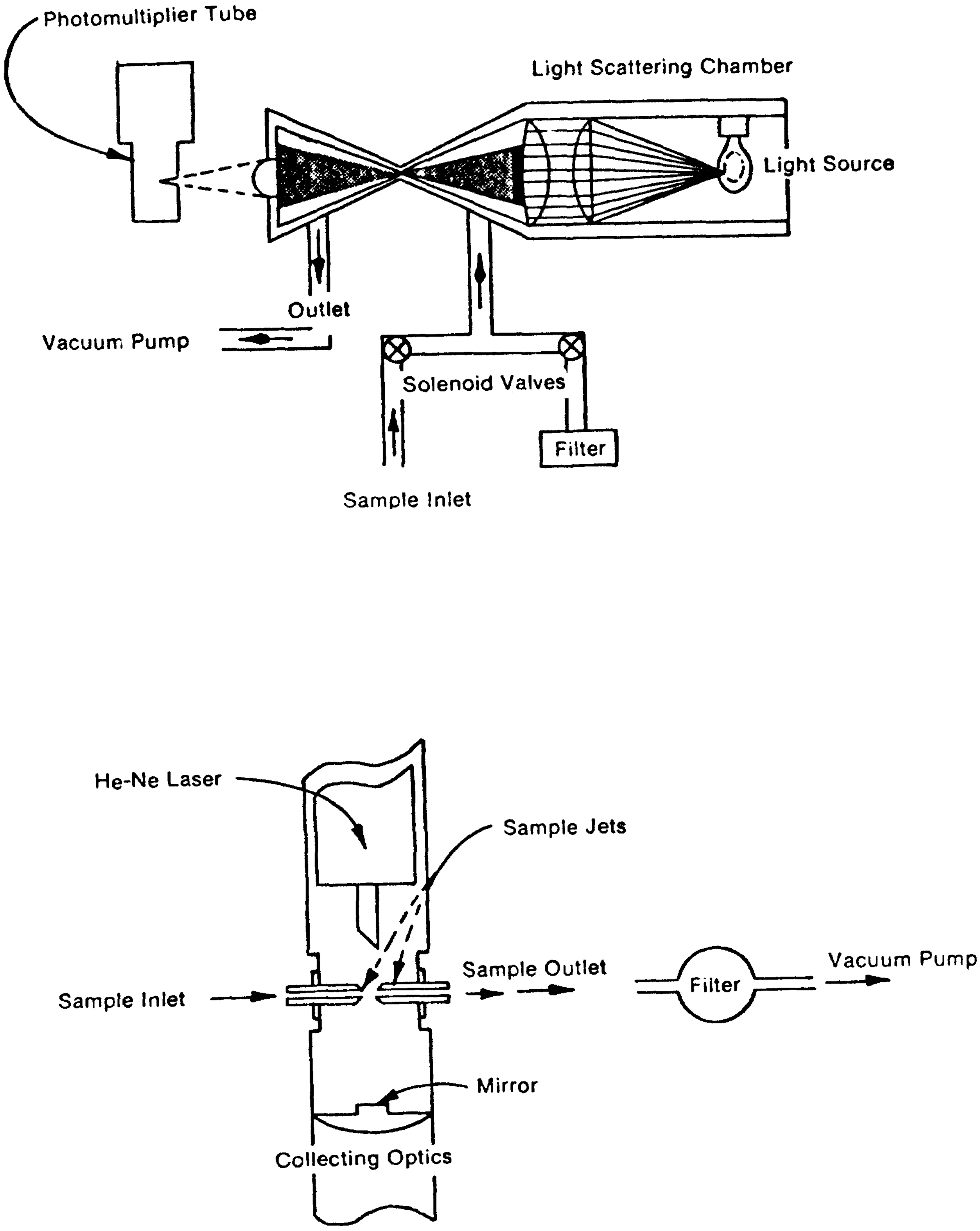

Figure 4. PHOTOMETER AND LASER SAMPLING SCHEMES

Table III. Measured HEPA filter efficiencies in corrosive environment

Test Conditions			% Penetration			
			Photometer		Laser	
Relative Humidity %	NO_x ppm	Temperature °C	Filter 1	Filter 1&2	Filter 1	Filter 1&2
50	550	66	.010	--	.0021	.0007
95	500	66	.030	--	.0025	.0016
50	10,000	66	.014	--	.0021	.0018
95	10,000	66	.030	--	.0048	.0007
50	500	93	.008	--	.0270	.0027
95	500	93	.025	--	.0420	.0021
50	10,000	93	.014	--	.0220	.0065
95	10,000	93	.020	--	.0310	.0058

Eight-test experimental design; design points were duplicated using both instruments for measurements.

Test period, 2 min.; DOP concentration, ∿100 μg/L (photometer), 10^6 counts (laser); the experimental uncertainty for laser measurements was ±.0008% .

Sensitivity of the photometer was not great enough to measure penetration of second filter in a series.

(6) NO_x x temperature and H_2O x NO_x x temperature = $1x10^{-3}\%$ ± $2x10^{-3}\%$, and $2x10^{-3}\%$ ± $2x10^{-3}\%$, respectively; the interactions between NO_x and temperature, and H_2O and NO_x and temperature are insignificant.

Laser

(1) H_2O effect = $6.0x10^{-4}\%$ ± $9.6x10^{-4}\%$; adding water vapor has no effect on DOP penetration of the filters.

(2) NO_x effect = $7x5x10^{-4}\%$ ± $9.6x10^{-4}\%$; the presence of NO_x in the test stream does not affect laser measurement.

(3) Temperature effect = $-2.6x10^{-3}\%$ ± $9.6x10^{-4}\%$; rises in temperature cause decreased filter penetration.

(4) H_2O x NO_x = $3.0x10^{-4}\%$ ± $9.6x10^{-4}\%$; the interaction between H_2O and NO_x is insignificant.

(5) H_2O x temperature = $-5x10^{-4}\%$ ± $9.6x10^{-4}\%$; the interaction between H_2O and temperature is also insignificant.

(6) NO_x and temperature = $8.5x10^{-4}\%$ ± $9x10^{-4}\%$; the interaction between NO_x and temperature cannot be established within the confidence limits.

(7) H_2O x NO_x x temperature $=3.0\times10^{-4}\%$ ± $9.6\times10^{-4}\%$; the interaction of all three variables is insignificant.

Computation of factor effect showed that water vapor was the only main effect when using the photometer as the measuring instrument. No main effect was indicated during use of the laser.

IV. Conclusion

Accurate results cannot be obtained when using the conventional forward light-scattering photometer in a corrosive off-gas environment to measure DOP concentrations by the ANSI N-101.1 method. The test data indicate interferences in the method due to water vapor and NO_x. However, by modification of the method to include a unique sample drying process before the sample enters the photometer, the water vapor interference can be eliminated. The NO_x effect on the photometer reading can also be corrected by a stray light adjustment. Temperatures used in these tests do not affect the conventional photometer.

The laser spectrometer appears to be a very capable instrument for filter test work. Its high sensitivity allows for the measurement of penetration factors in a corrosive off-gas environment when using two HEPA filters in series. It is not affected by water vapor, NO_x, or temperature under the described test conditions.

V. References

1. ANSI N-101.1-1972, "Efficiency testing of air-cleaning systems containing devices for removal of particles," New York (1972).
2. B. G. Schuster, D. J. Osetek, "The use of a single particle intracavity laser particle spectrometer for measurements of HEPA filters and filter systems," Proceedings of the 14th ERDA Air Cleaning Conference, CONF 760822.
3. Perma Pure Products, Inc., "Continuous drying of process sample streams," Manufacturer's Literature, Oceanport, NJ (1973).

DISCUSSION

STEINBERG: Did you take the scattering chamber apart after the test to see if there was any water in it?

MURPHY: Yes, we did. We ruined the photometer and had to buy another one.

STEINBERG: But, was there any water in the scattering chamber?

MURPHY: I assume that it had dried by the time we figured out what was going on and took it apart. We could see a white residue on the inside of the scattering chamber from dried water.

STEINBERG: We've run tests under high humidity conditions although not with

NO_x. Even when the scattering chamber was wet inside we have had pretty good results. Do you think it was the NO_x that might have been giving you the trouble?

MURPHY: No, I'm pretty sure it was condensation.

KOVACH: Have you made any runs with only high humidity and no NO_x?

MURPHY: Yes, with our standard room air (16% RH) and 500 ppm NO_x we got a negative response. When we increased water vapor to 50% RH and NO_x to 500 ppm or 10,000 ppm, the response of the photometer ranged from 0 to 40%, with no stability in the readings. This is shown in Table II of the paper.

STEINBERG: Usually, that sort of photometer response is indicative of something inside the scattering chamber that gives you extra stray light. This, in turn, gives you an erratic response. But, my curiosity is directed towards the water vapor because we have run under humidity conditions much higher than 50% with fairly good results. So, maybe you should try it again sometime.

MURPHY: OK, but I think that when the temperature drops below the dewpoint of your stream, you are going to get condensation inside the photometer. If you keep above the dewpoint, which we did not, you won't get condensation. Because our extreme condition was going to be 95% relative humidity, we decided to go to a drying tube. The dewpoint at 95% humidity is $90^{o}C$. I talked with several people who said that we shouldn't heat the stream up much more than $80^{o}C$ to make measurements with the photometer and with the laser. That's why we decided to dry the stream before we made our measurements.

STEINBERG: The next time you try it, you might also try putting heating tape around the scattering chamber.

MURPHY: That's what I'm saying. The reason we didn't do that is because of the extreme conditions of these tests. They require that our dewpoint be at $90^{o}C$ and we didn't want to heat the chamber up over $80^{o}C$. That's why we decided to use the drying tube; it would enable us to make measurements at 50 and 95% relative humidity without modifications to the system.

STEINBERG: What is the significance of the laser results? Were they able to tell you something about the condition of the HEPA filters, i.e., whether they were good or bad? Whether you had any leaks or not?

MURPHY: It told us that an increase in temperature caused increased penetration of the filters. That was the result of my tests with the laser.

ANDERSON: The data in Table III indicate that the second filter in a tandem filter combination is not as effective as the initial filter. I would suspect that the laser detection system is the explanation for the difference in the reported penetration results.

MURPHY: That's right.

ANDERSON: If both filters are in tandem, the number found should be anywhere from the sixth to the ninth decimal place to represent the combined efficiency.

MURPHY: I've had discussions with my section chief about this and he said the same thing. I'm not sure I understand what he's saying or what you're saying, but the way I took this measurement was probably contrary to what he recommended. This measurement is based on the upstream challenge aerosol concentration and the downstream aerosol concentration after the second filter. The numbers shown are what I got.

ANDERSON: By your data, you're indicating that the second filter was not effective inasmuch as it did not take very much more of the material out than one filter, alone. Take the case in Table III where you show .0021 for the first filter and .0007 for the second. If you assume that the effluent from the first filter is the input to the second, you divide 7 by 21 to find the second filter is only 30% effective.

MURPHY: That's exactly what it came out to be. We went through Dr. Schuster's paper on testing HEPA filters in series, and these are the results I got from my experimentation.

RIVERS: I believe you should indicate whether the percent penetrations were for individual filters or for two in series. Also, was the same pair of filters used for all experiments?

MURPHY: The same pair of filters was not used in all tests. I had trouble controlling the atmospheres in all the tests, but the design was sufficiently random that changing the filters didn't affect the test results.

IN SITU TESTING OF TANDEM HEPA FILTER INSTALLATIONS WITH A LASER SINGLE PARTICLE SPECTROMETER SYSTEM*

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Abstract

System components and methodology for in place testing of tandem HEPA filters are described. The system consists of a very high volume thermal DOP generator for producing sufficient challenge aerosol, a single particle intra-cavity laser particle spectrometer for high sensitivity detection, a forward light scattering photometer to measure challenge aerosol concentration, and a diluter to interface the spectrometer and photometer measurements. Results of the measurements on 11 tandem HEPA installations are presented along with problem areas and recommendations for future work.

I. Introduction

In order to implement the testing of tandem HEPA filter installations, a series of feasibility studies was initially performed on a small laboratory scale system. Using the concepts of measurement and digital counting obtained by implementing an intra-cavity single particle laser spectrometer rather than the conventional instantaneous analogue read-out of a forward light scattering photometer, tandem filter protection factors (PF) of 10^9 were readily measured. Challenge aerosols composed of solids (NaCl) and liquid (DOP) were employed. The size distributions of these two aerosols were essentially identical, as were the individual filter PF's, as a function of particle size. These measurements displayed a minimum PF at 0.19 μm with increasing protection on either side of this minimum. The fundamental difference in the use of liquid versus solid aerosols was in the rapid increase of pressure drop, i.e., filter plugging, that occurred with solid particulates, hence resulting in a semi-destructive test. The similarity of other results, however, suggests that DOP testing is a valid technique for exploring the critical behavior of filters.(1) The data also implies that since the size characteristics of a challenge aerosol are changed during the filter interaction, that the light scattering photometer PF's are really only a ratio of light scattering signals rather than a ratio of particle counts, masses, or areas. This follows from the very complex dependence on radius, wavelength, index of refraction, and concentration of the light scattering processes occurring within the photometer. In addition, the product of the PF's measured individually on a tandem system is likely to over estimate the system PF. This is a consequence of the first filter removing the most easily collected particles, hence effectively providing a

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challenge to the second filter of mostly difficult to collect particles. Only if the challenge aerosol were absolutely monodisperse would there be no measurement differences between the two detectors in the above situation, providing that the particle concentrations were kept low enough to avoid multiple scattering in the photometer and excessive coincidence errors in the spectrometer.

One additional advantage in the use of the spectrometer is its ability to integrate, i.e., store the particle count per size channel, over any required time period. This, coupled with the complete lack of instrument noise (a common feature of digital devices) enhances the detectivity for low particle concentration. In other words, it is not just an instantaneous rate, but the rate integrated over time that is measured. For extremely low concentrations, the measurement is facilitated by increasing the counting time.

In order to implement this technique for field test use, several new pieces of equipment had to be designed and built. Chief among these was a high volume thermal DOP generator(2) for producing the very large challenge aerosol concentrations required for tandem HEPA filter installation testing. This generator output is equivalent to 10 of the smaller commercially available units. A diluter for diluting the very high upstream challenge aerosol concentrations so that they are amenable to single particle measurement was also constructed.

The need for tandem HEPA filter testing was dictated by the desire to more accurately characterize system performance. Current test methods are limited to testing separate stages and may overestimate system performance. In addition to decreasing system downtime and worker exposure during testing, considerable dollar and space savings may be effected by designing tandem filter ventilation systems so they need not undergo stage-by-stage testing.

II. Test Apparatus

For tandem HEPA testing, protection factors of 10^7 to 10^8 are encountered, as opposed to 10^3 to 10^4 for single filter testing. It is obvious that much greater concentrations of challenge aerosol are required for the tandem test. Even though the detectivity of the laser spectrometer is considerably enhanced over that of the photometer, excessive integration times are undesirable. Additionally, the presence of downstream background aerosol, due usually to ductwork leaks, can mask the presence of very small concentrations of test aerosol. Typically, a challenge aerosol of 10 to 100 times the concentration normally used for single filter testing is required. The laboratory system of a six stem Laskin generator and associated compressed air supply, when considered in the multiplicity required for an industrial application, is far too cumbersome. In several tests, commercially manufactured thermal DOP generators were used, but their individually variable outputs and operating periods made multiple units awkward to work with. The DOP reservoirs in these devices were enlarged, which increased the operation time, but the combined output from the several generators did not behave in a temporally constant fashion and the tending of two to four separate generators proved unacceptable.

So that these difficulties could be overcome, an effort was directed at constructing a thermal DOP generator which would have an output several times that of the individual commercial generators and using the same basic principles of operation. The successful completion and splendid performance of this system provided confidence in the further scaling to a system providing ten times the output, i.e., 100 gms of DOP and 34 liters of CO_2, per minute, when operated at 30 psi.

The primary aerosol detector is a LAS-X single particle intracavity laser spectrometer specifically designed for this measurement. The instrument measures particles in a size range of 0.1 μm to 3.1 μm in 0.1 μm increments. The counts per size channel are stored and automatically printed out along with appropriate house keeping data such as time, date, and sample time. Graphical displays can be obtained with the use of an auxiliary oscilloscope or x-y recorder. Sample flow rate is 15 cm^3/s, considerably greater than previous designs of this instrument.

The advantages of such an instrument are manifold. The ability to measure a size spectrum obviates the problems associated with trying to generate a monodisperse aerosol and, in fact, characterizes a filter system's efficiency as a function of size. The digital technology associated with single particle counting insures against instrumental background. The counting feature enables a measurement to continue until a statistically significant sample of N counts has been registered, the percentage error then being proportional to $N^{-1/2}$. This is all in contradistinction to the instantaneous photometer type of readout which derives from a gross scattering of light from a population of particles, and is insensitive to single particles.

In the measurement of very high concentrations of upstream challenge aerosol, precautions must be taken to insure that any optical measuring system is not operated in a range for which it was not designed. In the case of the particle spectrometer, this limit is set by a maximum count rate, or electronically, by the frequency bandwidth of the instrument. For a photometer, the limitation is imposed by the onset of multiple scattering. This typically occurs when the optical depth reaches a value of 0.1 or greater. For the range of aerosol sizes normally encountered in filter test measurements, this corresponds to a concentration of order $10^7/cm^3$, which is reasonably below the concentrations used for the tandem testing procedure described in this paper. However, the upstream concentration will saturate the single particle detector.

In order to make use of the high saturation level of the photometer upstream and the great sensitivity of the single particle detector downstream, a diluter section is used in the measurement. This consists basically of a small wind tunnel into which HEPA filtered room air is drawn. A probe iso-kinetically samples the upstream challenge aerosol, introducing it into the diluter, where it is mixed with the much larger volume of clean air. Flow rate and pressure drop are controlled by varying blower power and throttling the air flow. Appropriate instrumentation is included to measure flow rate and pressure differentials. The dilution ratio, which is typically in the 10^{-3} range, can be computed and/or measured. Since the size distribution of the diluted sample should be unchanged from the original population, the photometer is used to determine this value. Measurement of the diluted sample with the spectrometer will then provide the upstream count rate, which is proportional to the challenge concentration.

The diluter also serves a second, very important purpose in that it is responsible for bridging three of the seven or eight orders of magnitude associated with the measurement of the protection factor. Although the spectrometer dynamic range is essentially unlimited, decreasing the challenge concentration to a point where it is directly measurable would result in enormously long downstream measurement times.

The photometer used for these measurements may be any one of the conventional forward scattering types now used for conventional HEPA filter testing. It should be of the linear read-out variety and be gain switchable over at least three noise-free orders of magnitude.

The two major systems of DOP generator and diluter are mounted on two-wheel hand carts. The two detection instruments are hand portable. The complete system is shown in Figure 1.

III. Procedure

The methodology associated with a tandem HEPA filter system test is not, with the exception of the dilution procedure, much different from conventional filter tests, but because of high protection factors usually involved, systems with flow rates greater than 20,000 CFM should usually not be attempted. The DOP generator is first emplaced as far upstream as is practicable. Appropriate iso-kinetic probes are installed and, if possible, centered immediately upstream and downstream of the tandem plenum. The upstream probe will usually consist of a probe pair so that the flows for both the diluter and photometer may be matched. The diluter has internal probes matched to the photometer and spectrometer flows. The generation of DOP is then initiated and monitored with the upstream sampling photometer until a steady state of generation obtains, at which time the photometer is switched to the diluter and a measurement made. Simultaneously, a diluter measurement is made with the spectrometer. Because of the still high concentration in the diluter, a spectrometer measurement for one minute will be quite sufficient. Over 10,000 counts will be registered in this interval, assuring an accuracy of better than 1%. The upstream concentration is now proportional to the product of the upstream photometer reading and the diluter spectrometer count rate divided by the diluter photometer reading. The downstream reading is made directly with the spectrometer. Ten minutes are typically required to obtain a count of 100, which will provide 10% accuracy.

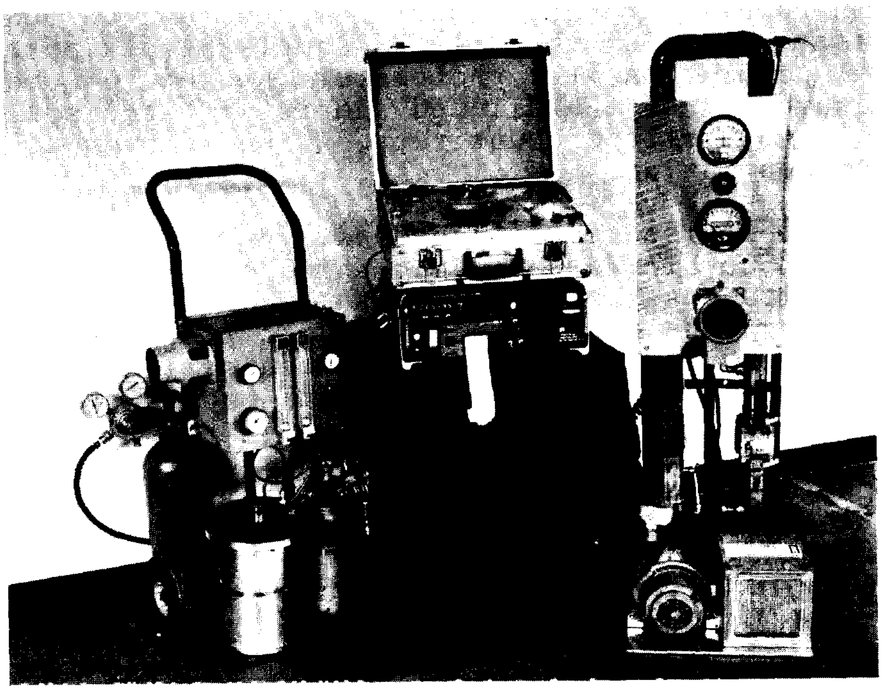

FIG. 1
FILTER TEST APPARATUS - GENERATOR, DILUTER, DETECTORS

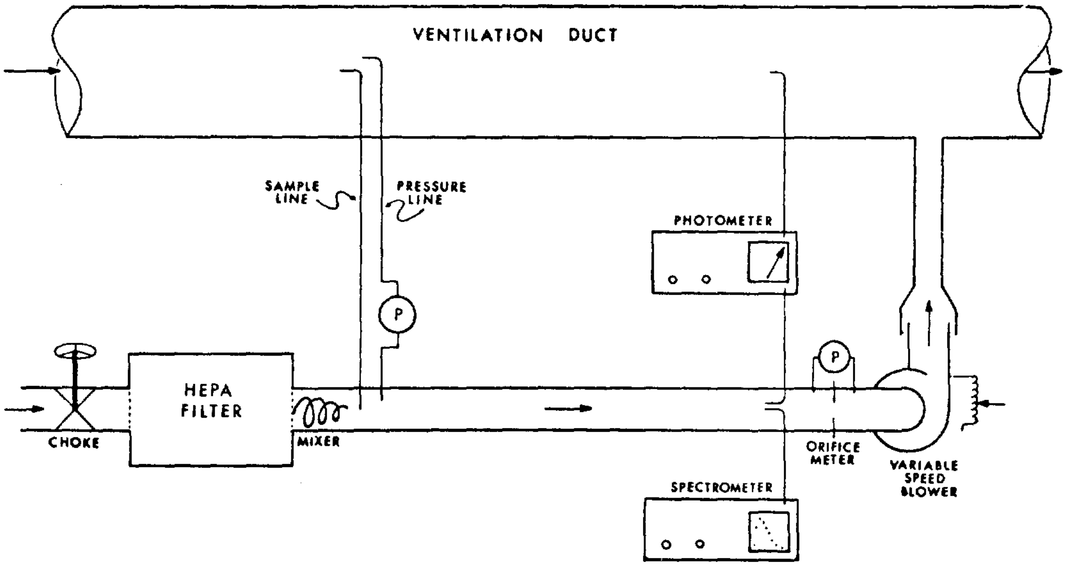

FIG. 2
TEST PROCEDURE SCHEMATIC

In a great many instances, a downstream background count will be present, due usually from in-leakage of ambient air into the downstream ducting, which is at a negative pressure with respect to the ambient air. In this case, background measurements should be made (with the aerosol generator turned off) before and after the system is challenged, so that they may be subtracted from the actual test measurement. Upstream background usually poses no problem because it is overwhelmed by the enormous challenge concentration. In some instances, the downstream background may be so high that it masks the test measurement. In this case, a lower limit on the system performance can still be obtained using the noncorrected downstream count. A schematic of the measurement procedure is shown in Figure 2.

IV. Results

Table I tabulates the results of nine systems measured during the acceptance testing phase at the new LASL Plutonium facility. These measurements were accomplished with an earlier model low flow rate spectrometer designed primarily for laboratory use. Conventional photometer data, for the acceptance tests, were acquired for individual banks. As anticipated, the tandem protection factors derived from these latter measurements usually overestimated the system performance by about a factor of two.

The data shown in Table II were acquired with the LAS-X spectrometer. Because of operational constraints associated with the test schedule for LASL filter systems, only these installations were able to be tested up to this point, but they are of particular interest. System 1 shows a typical downstream background count rate which is small enough so that it can be successfully subtracted from the test count rate to produce a reasonably accurate test. System 2 displays a very different sort of behavior in that the background count rate increases after the system has been challenged and in fact is greater than the count rate taken during the challenge. It appears that there is an interaction between the DOP and the material collected on the filter which creates the change. Simultaneously, there is an increase of pressure drop of 25 mm across the filter. This particular system has been measured several times with similar results. Laboratory tests on clean filters do exhibit an increase in P.F. immediately after and during the challenge, but no background due to DOP was ever observed. The P.F. for this system was computed by using the maximum downstream value observed, 1.13, and calling this the lower limit or minimum P.F. for the system.

V. Conclusions and Recommendations

The system that has been described can, of course, also be used for measuring single filter bank installations. One such system of 160,000 CFM flow rate was, in fact, successfully measured; a task virtually impossible with conventional test methods. The system has performed reliably and is readily portable. One problem area that has already been discussed is that of excessive downstream background. This situation is now under study using the

TABLE I

TA-55 FILTER TESTS

System	Tandem Test Protection Factor
C	7.2 ± 1.3 10^7
F	2.7 ± 0.3 10^7
A	1.3 ± 0.2 10^8
G	1.8 ± 0.4 10^7
B	9.8 ± 2.8 10^7
D	5.6 ± 1.6 10^7
E	5.5 ± 1.3 10^7
I	4.2 ± 0.4 10^5
H	6.2 ± 0.7 10^6

TABLE II

CMR FILTER TESTS

	System	
	CMR 1	CMR 2
Flow Rate	17500 CFM	16400 CFM
Upstream Count Rate	8.450 x 10^7	6.184 x 10^7
Downstream Count Rate		
Before Test	.30 ± .10	.29 ± .10
After Test	.30 ± .12	1.13 ± .20
During Test	2.20 ± .27	.30 ± .10
Downstream Net	1.90 ± .29	1.13 ± .20
P.F.	(4.4 ± .7) x 10^7	(5.5 ± 1.0) x 10^7

concept of a self-identifying challenge aerosol that can be distinguished from background particulates. The phenomenon of changed efficiency due to the interaction of the challenge aerosol medium and the filter is one which should be thoroughly studied in order to avoid falacious high efficiency measurements on older, partially loaded filters.

VI. Acknowledgements

The authors wish to express their gratitude to John Ortiz and Elmer Garcia for their aid in construction of the DOP generator and for participation in the field test program; and to Marvin Tillery for his helpful consultation.

References

1. B. G. Schuster and D. J. Osetek, "The use of a single particle intra-cavity laser particle spectrometer for measurements of HEPA filters and filter systems," Proceedings of the Fourteenth ERDA Air Clearing Conference, pp. 528-539.

2. B. G. Schuster and D. J. Osetek, "A new method for in-place testing of tandem HEPA filter installations," AIHA Conference, May, 1978, submitted for publication in AIHA Journal.

DISCUSSION

DUGAN: Do you know what percent of in-leakage there was downstream of the total design flow of the system?

SCHUSTER: I think it's very small, usually from pinhole leaks or welding leaks. From the point of view of contamination, one doesn't worry too much about it because the air is always going into the duct rather than coming out of it and it is also downstream of the filters. But it does mess up the measurements simply because one cannot distinguish between the challenge aerosol that has been introduced and whatever else leaks in by any method that relies on conventional electromagnetic scattering.

DUGGAN: Have you made an effort to pinpoint those leaks and reduce them to decrease your background?

SCHUSTER: We decorated lots of ducting with an awful lot of yellow tape.

CHEEVER: How long did the elevated background persist downstream from the HEPA filters after DOP testing the no. 2 system? Did it come back to the original background?

SCHUSTER: We monitored one system for about 36 hours and it took many hours to come back down. That was an unusual case. We think we were making smoke in that system. We don't know what was on the filter, but we suggested that when it was pulled that it ought to be analyzed chemically to determine what was on it.

MURROW: Can you explain the problem of anomalies with NO_x as expressed by the previous speaker?

SCHUSTER: I think I'm going to refer that to Tom Kyle because he's more of a spectroscopist than I and knows more about the adsorption of NO_x in the visible range.

MURROW: One more question, is your laser spectrometer available commercially?

SCHUSTER: Yes, it is.

McDONALD: Can you tell us the cost of the laser instrumentation relative to the cost of the forward scattering photometer system?

SCHUSTER: It's approximately two to two and a half times as much. The systems that we have are somewhat different because we usually provided specifications that make them essentially custom instruments. I think if other people would specify the same type of instrument, the price would go down. Ours have usually been prototype instruments.

WILHELM: Was there a large temperature effect due to the operation of the aerosol generators?

SCHUSTER: Typically, there isn't. As far as I know, nobody tampered with the blowers so, presumably, the flow was constant.

WILHELM: I am not asking about the flow, only the temperature, because you had a huge generator in front. Was there no increase in temperature during testing?

SCHUSTER: Yes, I believe that there was a slight increase in the temperature. After all, we were boiling off DOP and it is hot. But, by the time it got to the filters I doubt if there was very much of a temperature rise. I believe it was less than a degree centigrade.

STEINBERG: What was your upstream concentration of DOP?

SCHUSTER: The number I remember is 10^8 or 10^9 particles per liter. I can't give it to you in terms of mass per unit volume.

STEINBERG: I wonder if, with your generator, you were putting so much DOP on the filters that it was coming through and that was why you were getting penetration?

SCHUSTER: When we did the original tests, with clean filters, in the laboratory, we looked for that phenomenon. We put a lot of DOP on the filters, and turned off the generators, and then looked to see if anything was coming off. It wasn't.

STEINBERG: Did you notice any wetting by DOP on the upstream side of the filter?

SCHUSTER: In the laboratory, when we took the filters apart, we could see wetting, but we could not see any particles coming off downstream.

STEINBERG: How about in your test outside the laboratory; was there any wetting?

SCHUSTER: We did not go into the plenum to look at the filters.

STEINBERG: Usually, wetting is indicative of more DOP than you need to run a test.

SCHUSTER: Just remember that we were looking at two filters in tandem. In the laboratory we deliberately overloaded them to see if DOP would come off. I showed an anomalous example deliberately to indicate what might happen with a dirty filter, not a clean one.

MEASUREMENTS WITH SELF-IDENTIFYING AEROSOLS*

by

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ABSTRACT

The use of modern single particle detection of aerosols has made it possible to test multiple HEPA filter systems. Problems have been encountered in such tests with the background aerosol on the downstream side of the filters. Since the ducts are maintained at a negative pressure, ambient aerosols leak into the ducts and provide concentrations of particles which are comparable to the number of particles of the test aerosol passing through the filters. The background count creates an upper limit to the protection factor which can be measured.

This limitation can be overcome by the use of an identifiable aerosol. The most direct method of identifying an aerosol is to use fluorescent particles, which has been done in the past. In the present case, the fluorescence of the individual particle is used, rather than dissolving the particles in solution to develop the fluorescence. All the advantages of single particle detection are retained, such as orders of magnitude greater sensitivity, digital data techniques, and freedom from instrumentation drift. Possible new measurements include backfeed in air distribution systems, and the re-entrainment of particles from surfaces within air cleaning systems.

Two systems based upon fluorescent solid or liquid particles are being developed. Both involve single particle detection and excitation by a portable helium-cadmium laser.

The advantage of the solid particles system is the ability to capture the particles on a filter. The filter can then be dissolved and the number of particles counted and sized, since the particles do not dissolve. This also permits the use of greater sample flow rates than is possible with a real time system.

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I. Introduction

The testing procedures for HEPA filters involves introducing an aerosol upstream from the filter, then measuring the concentration of the aerosol previous to and after passing through the filter. In the past, the aerosol concentration was usually measured by means of the light scattered from a volume of air large enough to contain many particles. More modern equipment makes it possible to both count and determine the size of individual particles.

The capability of dealing with individual particles relieves some previous restrictions required to ensure valid testing. The ability to determine the size of the individual particles allows the test aerosol to have a wide range of sizes. By counting particles within a narrow size interval and neglecting all other sizes, the filtration efficiency can be described for the particle size range of interest. Although not required, considerations of efficient generation indicate that a reasonably narrow size distribution from the aerosol generator is desirable.

The most important improvement that single particle detection allows is in sensitivity. Use of light scattering from multiple particles requires a minimum concentration of particles per unit volume to provide a measurement. In the case of single particle detection, there is no lower limit of aerosol particle concentration that can be detected. The practical limit is in terms of time available to await the arrival of a particle in the measuring volume.

The increased sensitivity means that a single test can be used to determine the protection factor (PF) for multiple stages of HEPA filters. This has been tried and found to work. However, an unexpected problem was encountered that sometimes caused the technique to be unusable. The problem arises because the duct in which the filter is located is at a lower pressure than the surrounding room, and air from the room can leak into the duct. The aerosol particles in the room air are then counted because they cannot be distinguished from the aerosol particles introduced upstream from the filter. If the aerosol particles from the room air were only a small percentage of the total particles being counted, there would be no problem, but when the PF is high, the opposite case can occur. That is, only a small change in the number of particles is noted when the aerosol generator is turned on or off, because most of the generated particles are removed by the filter and leaked-in air is the primary source of particles.

The solution to the problem of aerosol particles leaking into the ducting and confusing the filter test is to generate an aerosol that is identifiable and to only count those particles that are identified as coming from the aerosol generator. All particles scatter light to some degree, and so some technique other than light scattering is required.

II. The Use of Fluorescent Particles

There is a method by which the particles can be identified and yet maintain the advantages of light scattering measurements. It is the use of fluorescent particles. When these particles are illuminated with light of one wavelength, they emit light at a longer wavelength. Thus, they can be distinguished because the emitted light is of a different wavelength than the illuminating light. The fluorescent nature of the particles causes them to emit light when illuminated by light of the proper wavelength, and this provides a signal akin to scattered light, but distinguishable from it by the shifted wavelength. Therefore, they can be measured by much the same techniques as light-scattering measurements.

In operation, one wavelength of light will illuminate the particle, and a longer wavelength will be emitted, and this longer wavelength is detected. This requires illumination by something other than white light. Otherwise, scattered and emitted light could not be distinguished, eliminating the unique identification of aerosol particles from the generator. Very small particles must be detected requiring a very intense source of illumination. These requirements are best satisfied by a laser, especially the need for high intensity light.

There are many naturally fluorescent materials, but few of these are highly fluorescent. Rather than search for naturally fluorescent materials from which an aerosol can be generated, it is usually more practical to determine the substance for the aerosol, then locate a fluorescent dye that can be used to make it highly fluorescent.

A dye for DOP is a desirable approach as it would allow all the DOP particle technology to be used, and thus reduce the complexity of the undertaking. The DOP technology includes answers to questions of the toxicity of the materials used for the testing of filters and the safety problems when introducing the test aerosol into the air cleaning system. These problems are more severe than it might appear, as can be illustrated by an example. The physical properties of glycerol made it attractive as an aerosol material, and an additive for making it fluorescent is known. However, this approach had to be dropped when it was pointed out that the nitric acid vapor in some air cleaning systems could react with the glycerol to form nitroglycerin.

A survey of 18 manufacturers and distributors of fluorescent materials resulted in no suggestions as to additives that would cause DOP to become fluorescent. Therefore, an experimental approach was used, during which 113 different dyes were added to DOP as a test of solubility. Those having a reasonable solubility were also analyzed in a fluorometer to determine the wavelength of maximum absorption of radiation and the emission spectra. The result was six materials that appear to satisfy the present requirements.

III. Particle Generation

Most fluorescent dyes would decompose at the temperatures encountered in thermal DOP generators. The use of a thermal generator is desirable because of the high output this type of generator provides. A method was sought to provide for dispersal of DOP in an aerosol with particle diameters of a few tenths of a micron, but with total throughput of up to a few liters per hour. It is not usually possible to generate droplets this small with a nebulizer or spray system, but at least one system has been found that satisfies the need for a high volume generator of submicron particles of DOP other than a thermal generator.

The unit is called a sonic atomizer and is commercially distributed by the Sonic Development Corporation, primarily as a spray for breaking fuel oil into very small droplets to promote better burning of the oil. The unit operates by using compressed air to create a standing sonic shock wave when the air flows through a convergent-divergent nozzle into a resonator chamber at supersonic velocity. This can be better visualized by reference to Fig. 1. As the air is reflected from the resonator, it creates a standing shock wave between the cavity and the body of the nozzle. Liquids pumped into the shock wave are vigorously sheared into fine droplets.

Tests were carried out on one of these units using DOP as the liquid and a compressed air pressure of 40 psi. Droplets having a mass median diameter of 0.35 microns were produced. The range of droplet sizes was too great to be considered monodisperse, but not unduely wide. It should be recalled that the particles are to be sized by the instrument so a monodisperse source of droplets is not required. The volume output of DOP in the form of the aerosol droplets was not determined, but on the basis of the manufacturer's specifications for water instead of DOP, a volume flow of 1 or 2 l/h seems reasonable.

The detection and sizing of the fluorescently dyed DOP can be carried out in much the same way as the presently used laser single particle measuring system. Two modifications are needed, but these are such that a new instrument would have to be purchased. The primary modification is the use of a helium-cadmium laser instead of a helium neon. The He-Cd laser provides a blue light output rather than red, which is required to induce the fluorescence in the dyes that are soluble in DOP. The second modification is the insertion of filters in front of the detector, which pass light of the wavelength where fluorescence occurs, yet blocks light at the wavelength of the laser. The blocking of the laser wavelength is necessary to avoid signals due to light scattering by aerosol particles that may or may not be fluorescent.

IV. Solid and Liquid Particles

It was originally felt that the most desirable system of identifiable particles would involve the use of DOP with fluorescent dyes. The advantage of using DOP was that it is accepted as producing no hazard by being introduced into an air cleaning system.

Some of this advantage is lost when dyes are introduced along with the DOP, because many, if not most, of them are suspected of having undesirable effects on health. A more significant advantage of DOP is the small but finite vapor pressure. This permits large quantities of DOP to be introduced upstream from the HEPA filter, so that a large burden is captured by the filter, with no long-term degradation of the filter, because the DOP will evaporate away rather than remain on the filter. Contrast this to the use of a solid nonevaporating particle. The large number of particles that must be introduced to allow a test of a filter system with a large protection factor could provide a permanent loading of the filter that would be a significant fraction of the total burden which the filter is capable of accepting. The implicit assumption in this reasoning is that the testing is the same for the solid as for the DOP aerosol.

Let a filter system have PF of P, which means that if N_1 particles are introduced before the filter, a number N_1/P will pass through the filter system. Let the flow of the air through the filter system be F_1 unit volumes per unit time, and let the sampling system extract air at a flow rate F_2. The number of particles collected by the sampling system will be N_2 and is given by:

$$N_2 = \frac{N_1}{P} \frac{F_2}{F_1} . \qquad (1)$$

If there is a background of particles that confuses the measurement, there is an advantage in supplying the N_1 particles in a very short time, but if the particles are to be identifiable, as in the present case, the rate of introduction is unimportant except for the time that the test requires. The number of particles that must be counted for the test is determined by statistical considerations and can be taken to be of the order of a thousand. The values of P and F_1 are determined by the system under test. The determining factor for the number of particles that must be introduced is F_2 alone. The larger F_2 is, the smaller the quantity of aerosol that must be generated in order to test the system.

The limitation on F_2 is the time that must be allowed to detect and size each particle. Most of the time there is no particle within the sensitive volume of the instrument, but when one does enter, it must remain in the volume for a minimum length of time to allow the signal-to-noise ratio to be large enough to provide a valid measurement. With the single particle laser spectrometer, the flow rates cannot exceed a few milliliters per second.

It is the limited flow rate that the measuring system requires that makes solid particles rather than DOP particles of interest. The DOP particles are liquid and must be measured in the air itself, as they would be absorbed or altered if collected on a filter, but solid particles do not have this shortcoming. By using solid particles, a large flow rate can be used for the sampling system, which will capture the particles on a membrane filter. The filter can then be dissolved in a proper solvent, and the liquid used to dissolve it will then contain the undissolved aerosol particles that were on the filter. Perhaps hundreds of liters of air were put through the filter to collect the particles, but they are now contained in a few milliliters of the liquid. The liquid can be put through the measuring system at a low flow rate and the individual particles sized and counted.

An example will illustrate the power of the collection of solid particles on a membrane filter in testing. Assume a standard (24-in. square) HEPA filter system is to be tested. The flow rate F_1, is 2.8×10^4 l/min and the PF is 10^8. The sample will be collected on a 47-mm filter using a flow rate, F_2, of 25 l/min and a total of 10^3 particles must be collected for a statistically valid test. Putting these values into (1) gives the result that a total of 4×10^{13} particles must be released upstream from the filter in order for the test to be statistically valid. If these particles are taken to have a specific gravity of 2, then only 1.14 g of material are required for the test. With this overall quantity of material, there is no significant problem with loading the filter.

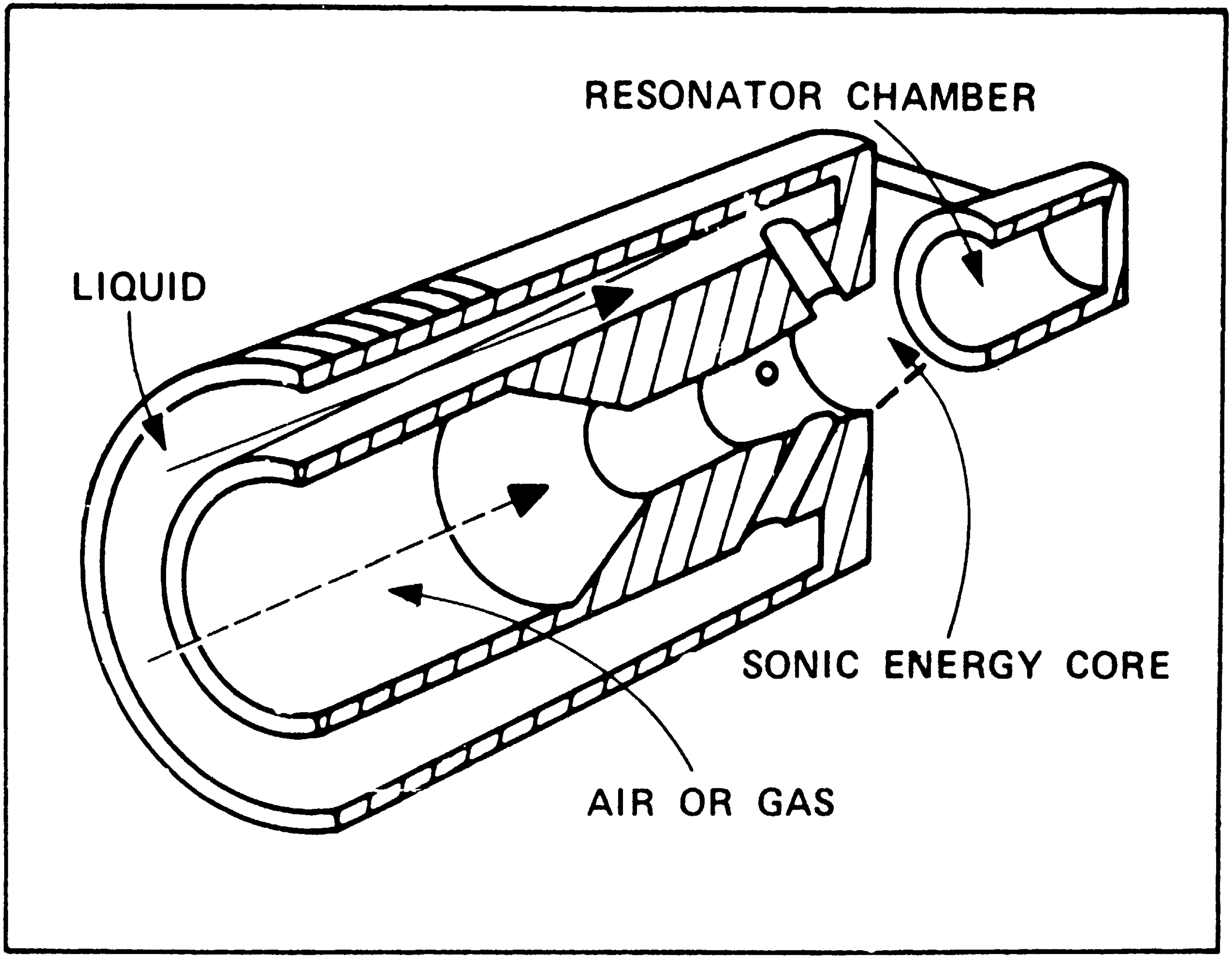
It is instructive to contrast the limitations of different approaches to filter testing. When filter systems are tested with light-scattering photometers, the particles must exceed a certain concentration, say 100 particles/cm^3, before they can be measured with an acceptable accuracy. In the case of multiple HEPA filters, the concentration of aerosol particles getting through the filter is too low for a measurement, and so the unit cannot be used for multiple HEPA filter tests. The single particle measuring systems have the sensitivity for measuring systems with high PFs, but leaks of room air into the system often contribute more particles than the aerosol generator, which prevents a valid test. This points out the need for an identifiable particle to use in the testing.

It might seem that an identifiable bulk material could serve the same purpose. For example, particles of sodium fluorescein could be generated, fed through the air cleaning system, and then captured on a membrane filter. The filter could then be dissolved along with the aerosol particles and the bulk fluorescence of the solution measured. In such a case, a concentration of the fluorescent material of one part in 10^8 would be needed. A simple calculation shows that in the case of multiple HEPA filters, the first filter would become overloaded before the required quantity of material was collected.

A single particle detection system using fluorescent particles can provide the desired measurement using either liquid or solid particles. There are advantages to either of these types of particles, but the solid particle approach is the one being followed at this time.

V. Fluorescent Plastic Particles

The solid aerosol particles being used have a number of desirable properties. The material is manufactured by Day-Glo Color Corporation for use as a fluorescent ink in the printing industry, and as a result of the large-scale production is reasonably priced.


RESONATOR CHAMBER
LIQUID
SONIC ENERGY CORE
AIR OR GAS

The particles are composed of a thermoplastic material with a fluorescent dye included within the plastic. This type of material is quite inert, and thus should retain the dye within it so that no hazard would be expected from breathing air containing the particles.

The particles are approximately spherical in shape and seem to have a smooth surface. Tests on the size spectra have been carried out. These tests give the mass median diameter of the particles in the range of 0.25 to 0.35 microns. The difference in the values determined is due to different experimental arrangements and different methods of measurements. The size spectrum is not wide, being a lognormal distribution with a dispersion of 1.35.

The operational use of the identifiable particle measuring system with solid fluorescent particles to test filter systems will proceed in somewhat the following manner. The particle dispersing unit will be an atomizer that disperses liquid droplets containing the solid particles. The liquid evaporates leaving only the fluorescent particle.

Air samples will be pulled immediately before and somewhat downstream from the filter system. Air from the system is simultaneously pulled through each of two membrane filters during the time the particles are being dispersed. These samples may be either returned to a central location, or they can be dissolved in a few milliliters of liquid and the particles counted immediately. That is, the system that sizes and counts the particles will be portable and capable of providing the test result in a few minutes; but if it is thought to be a better procedure, the filters can be brought back to a quality controlled situation for the quantification of the test results.

A system such as the one described here should be capable of providing more accurate tests of filter systems since it can test multiple stages of filters in a single test. The testing of multiple stages of filters in a single test should also provide economic savings in the cost of testing the filters.

DISCUSSION

McDONALD: We wish to point out that we have at NRL identified suitable fluorescent tags for DOP to use with a fluorescence detection. A 100 watt mercury lamp and 90° collection optics with photon counting gives a suitable dynamic range for single filter challenge. Toxicity and upstream filter wetting should not pose a problem. The dynamic range of the challenge technique, about 10^5, is straightforwardly extendable for challenge of tandem filters. This is more of a comment than a question.

KYLE: If your light scattering photometer has to have a minimum concentration of 10 particles per cubic centimeter downstream, you must have 10^9 particles per cc upstream if you require a protection factor of 10^8.

McDONALD: You can read in an analog mode if you want to. However, you can just as easily count photons and count as long as you wish. This is much the same way you do it by particle counting.

KYLE: I am concerned that when you wet the filter, you get an invalid test. I don't doubt you can read the signal; whether you've done a valid test is the question.

McDONALD: I see no reason why it should require wetting if you have a sufficient dynamic range to work with.

KYLE: Like 10^9 particles per cubic centimeter?

McDONALD: We are talking about developing a technique for testing one filter with 10^5 or 10^6 particles per cc. I don't know what this system will give in terms of discrimination against other particles.

KYLE: The need is to get by without upstream wetting. I have been looking at the numbers and it's doubtful that you get a valid test when you go to very high upstream concentrations.

SHAW: I have two questions. One, it seems to me that by using a sonic jet particle generator for the nebulization of fluorescent particles you make a lot of agglomerates. Have you checked to make certain you have monodisperse particles?

KYLE: You have to dilute down pretty thin in the solution.

SHAW: Because your concentrations are high, i.e., 10^9, you must have a lot of agglomerates.

KYLE: I don't recall using 10^9 particles. There isn't a minimum concentration we must reach upstream. Because we are counting individual particles, we don't need very high concentrations. We plan to select the dilution on the basis of (a) the particle sizes that can be detected with a single particle spectrometer and (b) avoidance of agglomerates.

SHAW: All I'm saying is that it should be checked to make sure what the amount is. Otherwise, by just measuring all the collected particles in the solution, you may filter large numbers of agglomerates and think you are doing a very good job.

KYLE: We will have to make sure they are not agglomerated. I certainly agree with you.

VAN BRUNT: When you dissolve the filter, aren't you worried about scattering and ghost effects on liquid fluorescence? Light measurements of particulate-liquid mixtures are extremely difficult unless you have taken the above mentioned effects into account.

KYLE: I have not taken them into account. I have looked in a cursory fashion and have not found any problems, but it is possible that problems will occur.

MUSEN: Did you check to see how the dye degraded the DOP?

KYLE: No, we did not.

A METHOD FOR COMPARING AIR VELOCITIES BETWEEN BULK CARBON AND ASSOCIATED TEST CANISTERS

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Abstract

An important design element to insure that a test canister will adequately represent the condition of the bulk adsorbent is to provide for a uniform face velocity between the bulk adsorbent and test canister.

This paper describes a suggested test method for comparing the air velocity through bulk carbon with that through associated test canisters. The rationale behind the test are discussed as are some advantages believed to be offered by this test method. The test method was applied to a full scale adsorber unit at CVI and the test and its results are described.

While this procedure has been developed specifically for activated carbon adsorbers, it is believed to be adaptable to others such as silver zeolite, although the use of a different test gas may be required. Also, the possible extension of this test method to more general applications is suggested.

Introduction

It is generally known that the impregnated carbons traditionally used in HVAC systems for I_2 and CH_3I removal are subject to weathering, a phenomenon that causes a progressive decrease in the adsorber performance. Test canisters subjected to service conditions comparable to those for the bulk carbon are periodically removed, laboratory tested and the performance level of the bulk carbon is extrapolated. It is apparent that this approach will provide meaningful results only if the carbon in the test canister is weathered to the same degree as the bulk carbon. This condition will not be met unless the flow through the test canister is representative of the flow through the bulk carbon. Primarily, this requires that the face velocity for the test canister be essentially the same as that for the bulk carbon.

If the test canister face velocity is much less than that for the bulk carbon, weathering of the bulk carbon will be more advanced than that of the test canister and the test results will over estimate the performance of the bulk carbon. On the other hand, if the face velocity for the test canister is too much greater than that for the bulk carbon, a severe economic penalty may result since the bulk carbon may be replaced pre-maturely.

Several factors may influence the velocity ratio between the test canister and the bulk carbon including the following:

a) Variation in average particle size

b) Variation in packing density (particularly probable if the method of filling is different)

c) Difference in static pressure drop across the test canister compared to that across the bulk carbon

d) Difference in bed depth between the test canister and the bulk carbon.

Some experimental and analytical data regarding the effect of the first two factors above are included in Reference 1 and 2. The effects of the last two factors are apparent. In view of the above, it was considered desirable that some means be established for measuring the relative face velocity (velocity ratio) between the bulk carbon and that in the test canister.

This paper describes a suggested test method that is considered to offer the following advantages:

a) It provides a unique capability for measuring velocity ratios at several discrete, local points as opposed to average values over larger areas.

b) It offers a means of direct measurement of the relative velocities without in anyway disturbing the system or the parameters being measured while the adsorber bed and test canister are operated simultaneously in the normal fashion.

c) It does not rely on measuring the low face velocities associated with this type of system.

d) It can be conducted utilizing equipment already required for filter testing.

Rationale Behind Test Method

The test method described herein uses a physical adsorption process to directly compare the velocities through the bulk carbon and the test canisters. For a physical adsorption process, the standard holdup equation relates the adsorbate breakthrough time to various system parameters. These parameters relate the delay time, τ, to the adsorbent mass, m, the dynamic adsorption coefficient, k, and the volumetric flow rate, V, as shown in Equation 1 below (see References 3 or 4 for one development of the delay equation).

$$\tau = \frac{mk}{V} \qquad \text{Equation 1}$$

where

τ = the mean breakthrough time (min)
m = the charcoal mass (g)
k = the dynamic adsorption coefficient (cm^3/g)
V = the actual volumetric flow rate (cm^3/min)

Equation 1 is generally valid for physical adsorption processes operating in the linear range of adsorption. By applying Equation 1 to both the bulk adsorbent and test canister and forming the ratio of the holdup times, a useful expression (see Equation 3A) is obtained from which the velocity ratios can be determined from known or measureable parameters. First, the mass "m" is expressed as density times volume.

$$m = \rho AL \qquad \text{Equation 2}$$

Where ρ = charcoal density (g/cm^3)
A = adsorbent cross section (cm^2)
L = depth of adsorbent (cm)

Define v = superficial face velocity
v = V/A (cm/min)

Subscript b — parameters relating to the bulk adsorbent

Subscript c — parameters relating to the canister

Substituting into Equation 1 and dividing the holdup time for the test canister by that for the bulk carbon

$$\frac{\tau_c}{\tau_b} = \frac{\rho_c L_c k_c v_b}{\rho_b L_b k_b v_c} \qquad \text{Equation 3}$$

It is expected that the test described herein would be performed on newly installed carbon and that the carbon used in the test canisters would be nominally the same as that used for the bulk carbon so that $k_c = k_b$.

Therefore, using $k_c = k_b$ and rearranging

$$\frac{v_c}{v_b} = \frac{\rho_c L_c \tau_b}{\rho_b L_b \tau_c} \qquad \text{Equation 3A}$$

Equation 3A provides the desired expression for velocity ratios as a function of known or measurable system parameters and was used for the analysis of the experimental results.

Equation 3A is a result of assuming that $k_c = k_b$. The effects of unaccounted for variations in the dynamic adsorption coefficients due to weathering are considered in the following. In a similar manner, the effects of unaccounted for variations in packing density were also examined.

Effect on Variations in "k" Values

If the test were to be performed on a system that has been weathered, it is believed that the test results would still be meaningful and that the net effect of weathering on the test results would be to make the test more sensitive to a poor flow distribution.

This can be illustrated by an example using a hypothetical system in which the face velocity through the bulk adsorber is somewhat higher than the test canister face velocity. It is assumed that the system is operated for a period of time prior to the test being performed so that the bulk carbon and the test canister are both weathered to some degree, which might result in a decrease in both k_c and k_b. However, since $v_b > v_c$, the bulk carbon would be weathered to a greater degree than the test canister carbon. It follows that when $v_b > v_c$ then $k_c \geqslant k_b$ and therefore from Equation 3 both act in the same direction to increase the breakthrough time ratio.

From the above, it is concluded that any foreseeable variation in the dynamic adsorption coefficient would tend to make the test results conservative by indicating a higher variation in velocity than is actually present. Furthermore, even this concern can be eliminated by testing the system when the adsorbent is installed. This is usually the appropriate time to conduct flow tests in any case.

Sensitivity of Results to Density Ratio

It is considered highly important that the packing density be uniform throughout the bulk carbon and consistent with the packing density in the test canister. However, it would be unrealistic to assume that this would always be the case.

The average packing density for both the bulk carbon and the test canister can be determined if the weight of adsorbent and the volume of the adsorbers are known. However, the accuracy of the estimated densities could be questioned. It is probably more instructive to consider the consequence of undetermined variations in the packing densities.

The most important consideration is in the limits of the variations. Granular carbon has been found to demonstrate a variation in packing density, for a given sample, of approximately ± 10%, depending on how well it is packed. However, given a ± 10% variation in packing density, the resultant variation in velocity would be expected to be the order of 300% from minimum to maximum velocity, other conditions being the same (see Reference 2). Therefore, there is a cause-effect relationship between density ratio and velocity ratio but the relative magnitudes make the density ratio a second order effect.

One other consideration is relevant: the direction of variation in packing density ratio and velocity ratio is such that both act to influence the holdup time ratio in the same direction. For example, if $\rho_c > \rho_b$ then, other conditions being equal, $v_b > v_c$ due to a higher flow resistance in the canister. From Equation 3, it follows that the two ratios supplement each other to increase the holdup time ratio τ_c/τ_b. Since τ_c/τ_b is measured and used in Equation 3A to estimate the velocity ratio, the test would be slightly more sensitive to variations in velocity due to non-uniform packing (considered to be the major cause of non-uniform flow).

Test Equipment

The test method incorporates a pulse injection technique in which the fluorocarbon refrigerant R-12 was injected upstream of the filter. R-12 was used in this test for convenience because it could be detected using equipment utilized for the standard in-place leak test for carbon adsorbers. Other adsorbates could undoubtedly be used. The mean breakthrough time for the bulk carbon and the canister were measured by sampling the air downstream of each component individually and recording concentration versus time.

The bulk adsorber/test canister physical configuration and general flow pattern are illustrated in the plan view in Figure 1. The adsorber/canister system was a full scale HECA® filter and CANSET™ canister manufactured by CVI.

The test apparatus is illustrated schematically in Figure 2 with a photograph of the inlet air duct, filter housing and gas chromatograph equipment included as Figure 3. The HECA® unit was designed for 42.5 m³/min flow. However, all testing was done with laboratory fans providing an aggregate flow of 38.2 m³/min.

A Valco Model 1200 Halocarbon Monitor gas chromatograph with a Varian A-5 strip chart recorder were used to monitor the R-12 breakthrough downstream of both the bulk adsorbent and the test canister

Air flow rates were measured with a pitot tube located upstream of the filter unit as illustrated in Figure 2. R-12 was injected upstream of the fan as also illustrated in Figure 2.

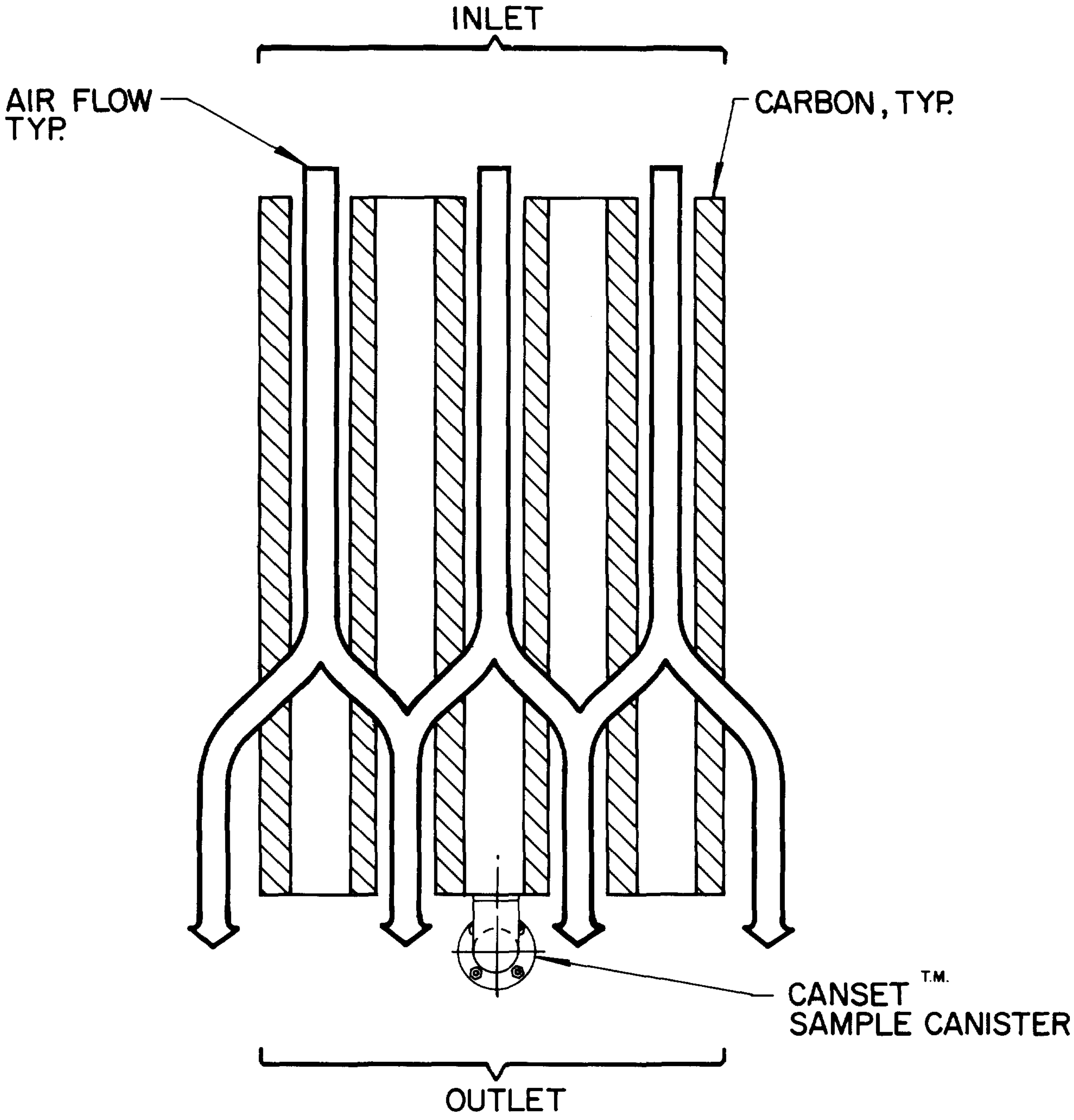

FIGURE 1. CROSS SECTION OF HECA® ASSEMBLY AS USED IN THE BREAKTHROUGH TEST

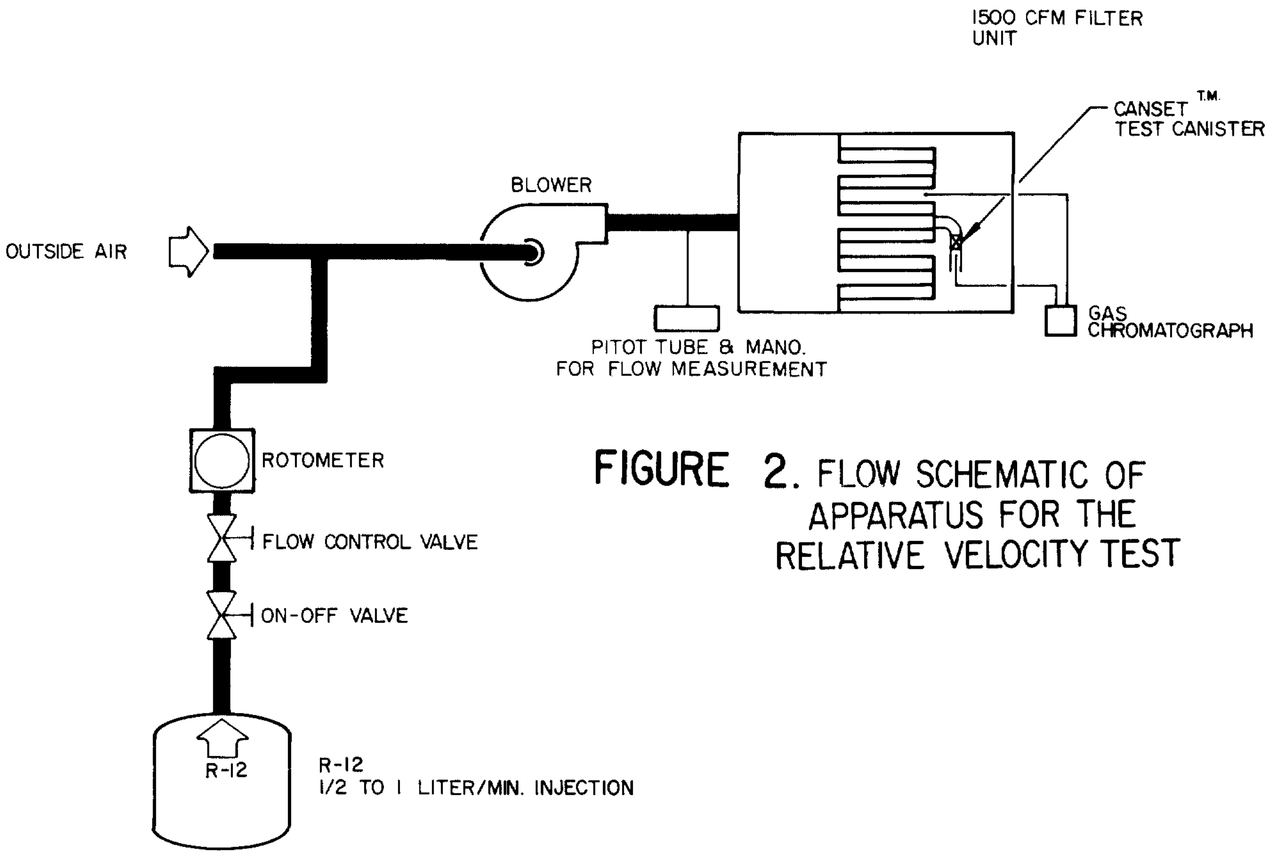

FIGURE 2. FLOW SCHEMATIC OF APPARATUS FOR THE RELATIVE VELOCITY TEST

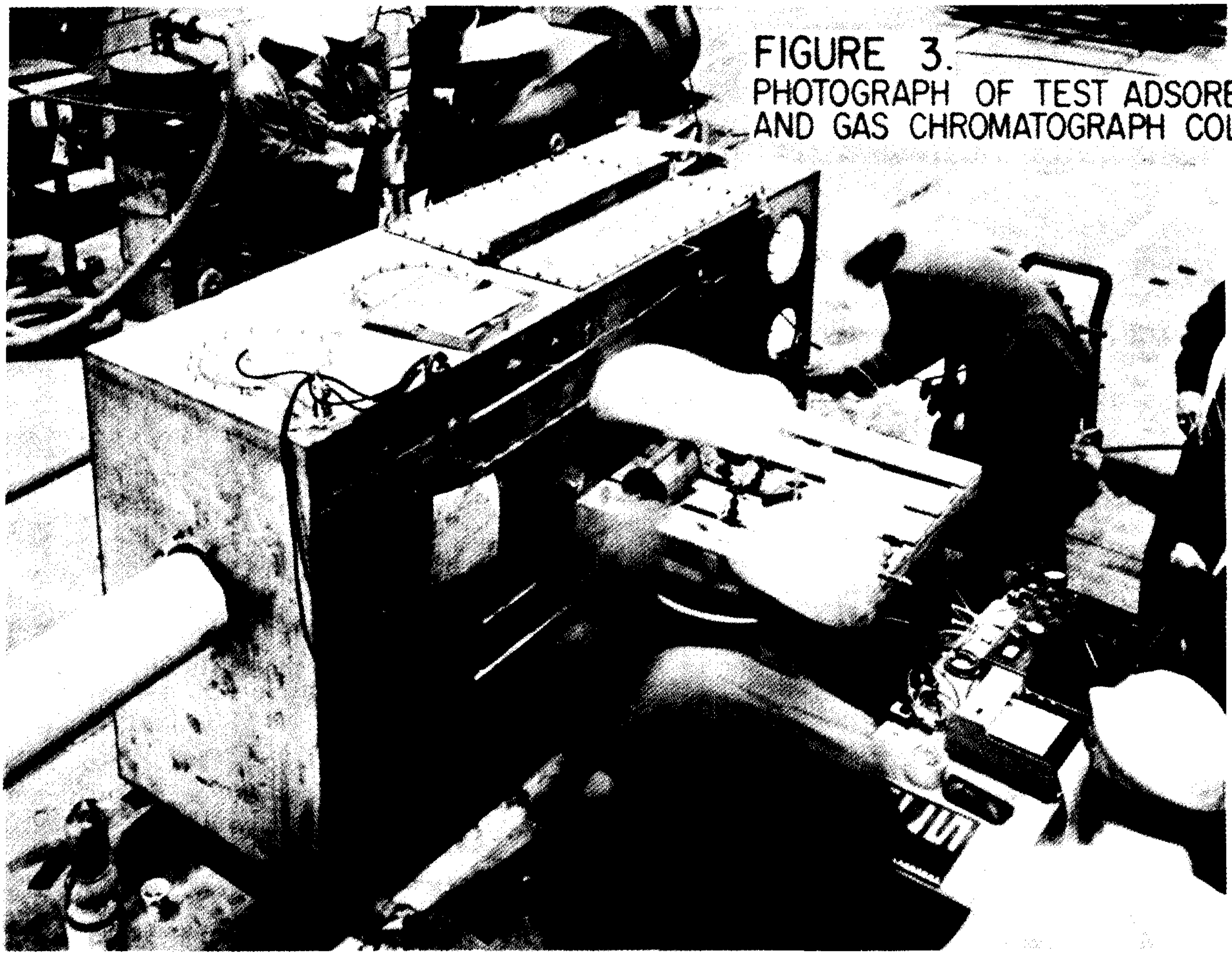

FIGURE 3. PHOTOGRAPH OF TEST ADSORBER AND GAS CHROMATOGRAPH COLUMN

Test Procedure

Prior to the first test, the bulk adsorber beds and the test canister were filled with carbon using a gravity packing method.

In subsequent testing, the system was purged and the effluent examined for R-12 periodically until it contained no detectable R-12. When the system was clean, the R-12 bottle was prepared for injection by adjusting a throttling valve to produce the desired flow rate of R-12. The R-12 was discharged to the atmosphere in such a manner that it would not be drawn back into the test system in subsequent runs. The R-12 flow rate was then terminated by means of an isolation valve until the beginning of the test.

A velocity traverse was performed for the inlet duct and the centerline velocity coefficient was determined. The G. C. was set up to draw a sample of gas and analyze it once every two minutes. A manual switching valve was provided so that the sample could be alternately drawn from downstream of the bulk carbon and downstream of the test canister. By using a single instrument to monitor the effluent from both the bulk carbon and the test canister, any instrument error would be common to both and the effect of any error would therefore be minimized. The characteristic breakthrough behavior of R-12 under test conditions resulted in pulses sufficiently broad that sampling each stream once every four minutes provided a very adequate description of the effluent pulse. These pulses generally took from 2 to 4 hours to elute, depending primarily on air temperature.

The G. C. was started approximately one hour prior to the test in order to allow the G.C. to stabilize. After the G. C. was stabilized the fans were started and the average duct velocity determined using the pitot tube to measure the centerline velocity and applying the centerline coefficient determined previously. The volumetric flow rate was calculated from the average duct velocity times the duct cross sectional area.

With the air flow established, the R-12 isolation valve is opened to initiate the R-12 flow, the strip chart recorder started and the start time indicated. As indicated previously, the sample lines were manually switched to provide alternate readings from downstream of the test canister and from downstream of the bulk carbon. The test was generally continued until most of the R-12 had been eluted.

Results and Discussion

The results of the R-12 breakthrough tests are illustrated in their most basic form in Figures 5, 6, 7 and 8 which show the G. C. output as a function of time for both the bulk carbon and the test canister effluents. The G. C. output is shown as peak height in percent of full scale.

Data from Test Number 2 are plotted in Figure 5. Generally, data in Test Number 2 were taken alternately from downstream of the bulk adsorber and the test canister. However, a few data points were taken in succession from the same sample line to confirm that switching from one sample line to the other did not introduce any unexpected effects on the results.

This was done, for example, at 154 minutes into the run when two measurements were taken in succession downstream of the canister followed by measurements taken in succession downstream of the bulk carbon bed. This procedure was repeated again at 200 and 222 minutes into the run. Whether or not the sample lines were switched made no observable difference in the results as evidenced by the continuity of the traces when consecutive readings were made.

From Figure 5 it can be seen that the elution curves from the bulk carbon and the test canister are very similar in shape and nearly simultaneous, indicating that the flow through each is very comparable. These results can be quantitavely evaluated from the mean breakthrough times from each. The mean breakthrough times were evaluated by graphically integrating the area under the curves as plotted in Figure 5. The resultant mean breakthrough times are also shown in Figure 5. For Test Number 2, the mean breakthrough time for the test canister preceded that for the bulk carbon by 3.6%, indicating the velocity through the test canister is higher than that through the bulk carbon. The analysis of the data is presented later. Results, including adjustment for path lengths, are tabulated in Table 1.

The results of Test Number 4 are illustrated in Figure 6. As in Test Number 2, the test canister was in normal operation with no artificial flow impediment. The mean breakthrough times were evaluated as for Test Number 2, from which it was determined that the mean breakthrough time for the test canister preceded that for the bulk carbon by 8.9% (see Table 1 for complete results).

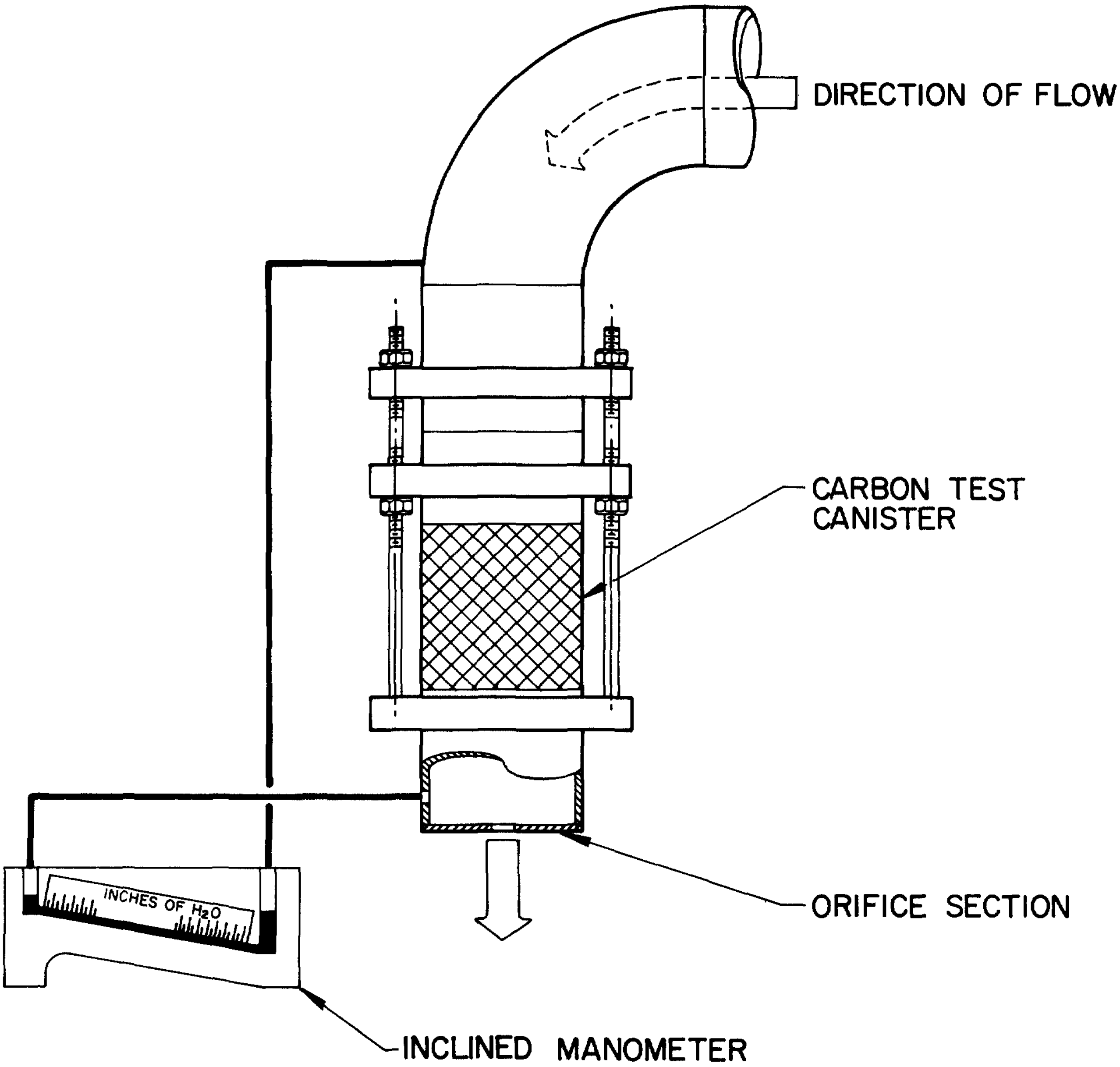

FIGURE 4. DIFFERENTIAL PRESSURE MEASUREMENT FOR CARBON TEST CANISTER

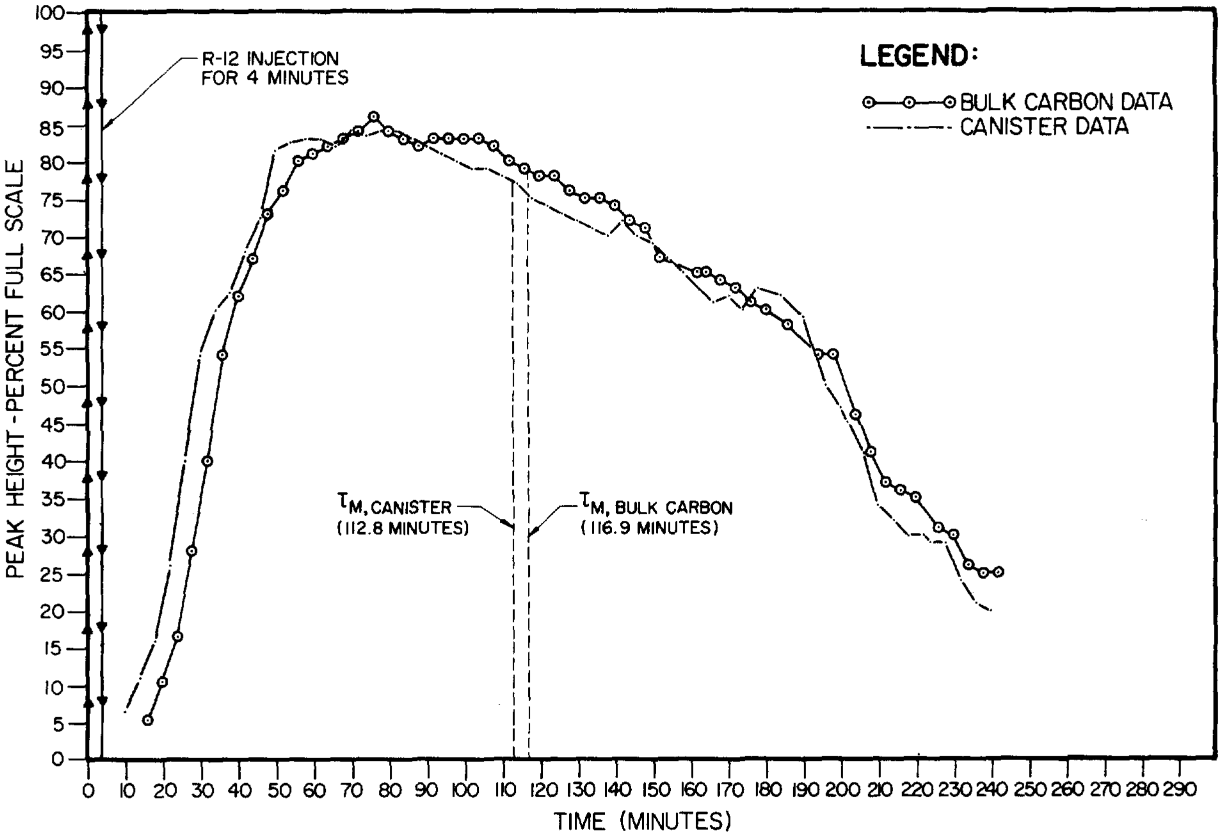

FIGURE 5. BREAKTHROUGH DATA FOR TEST NUMBER 2

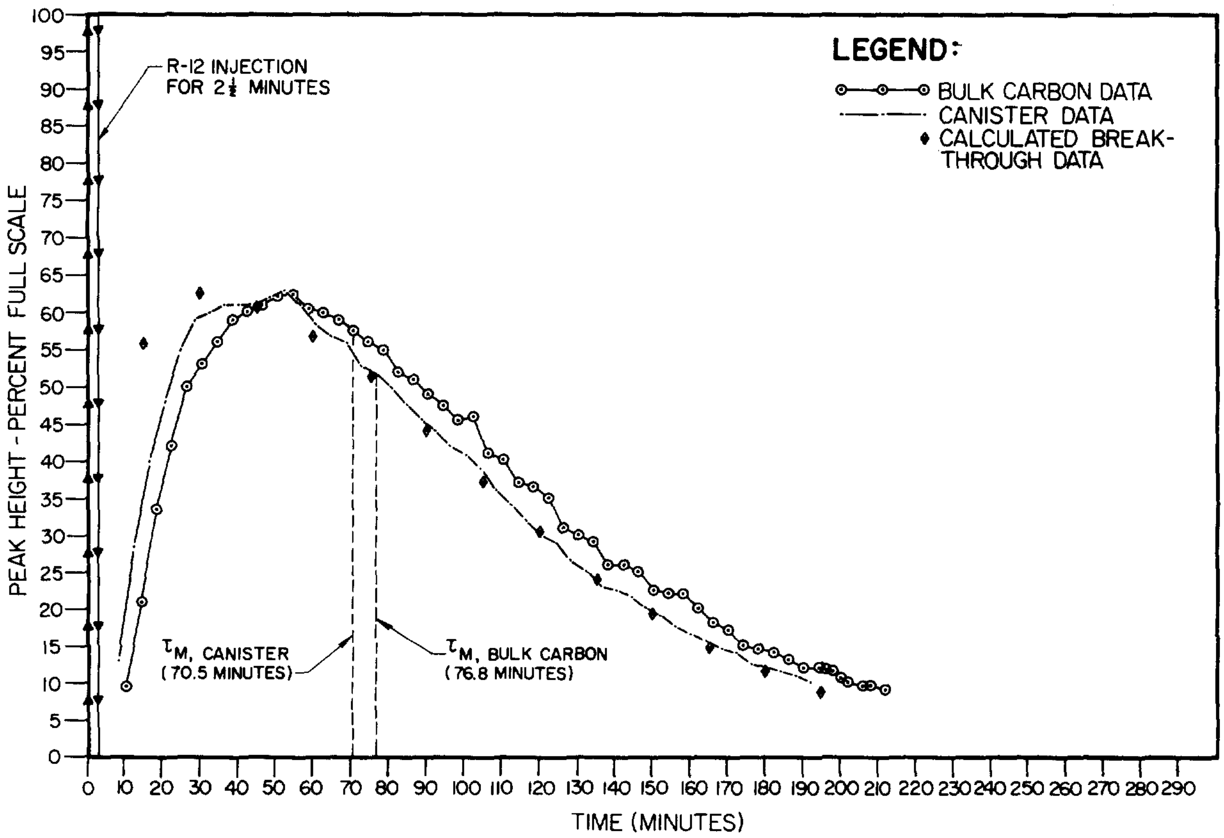

FIGURE 6. BREAKTHROUGH DATA FOR TEST NUMBER 4

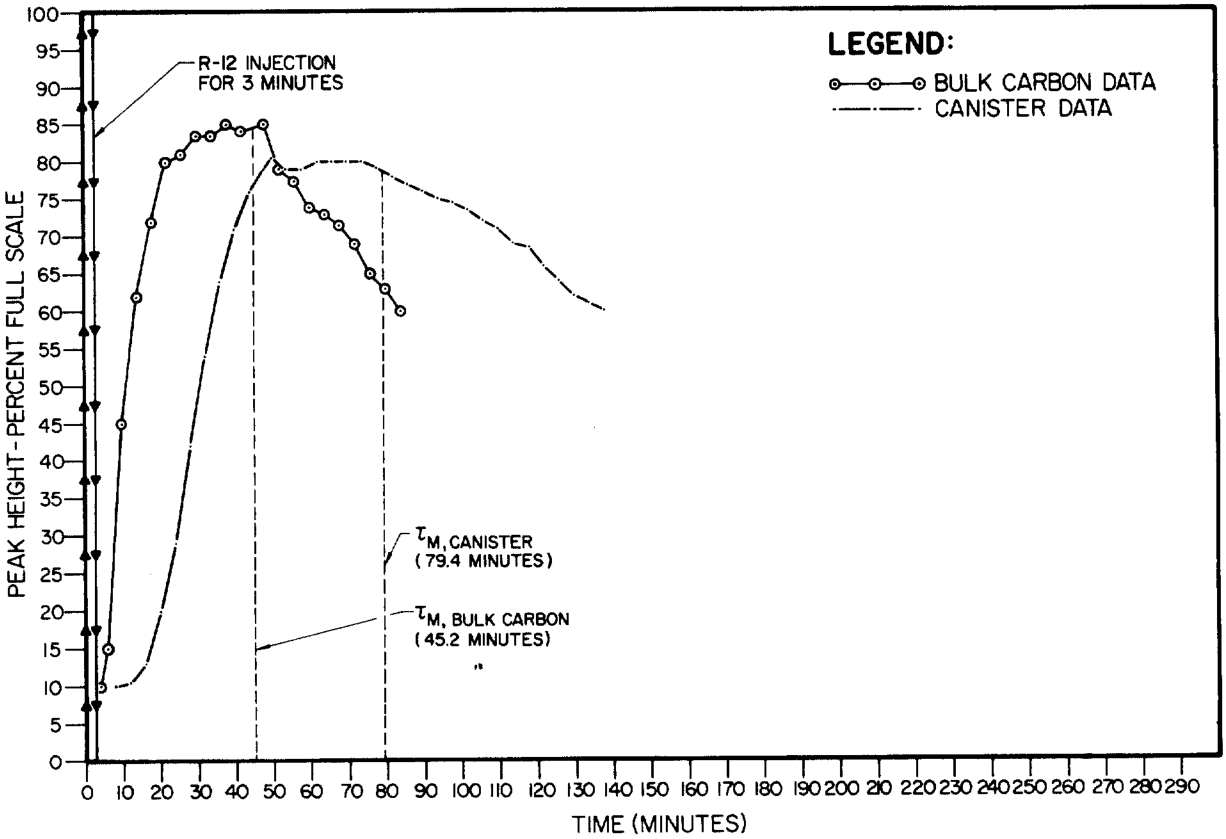

FIGURE 7. BREKTHROUGH DATA FOR TEST NUMBER 5

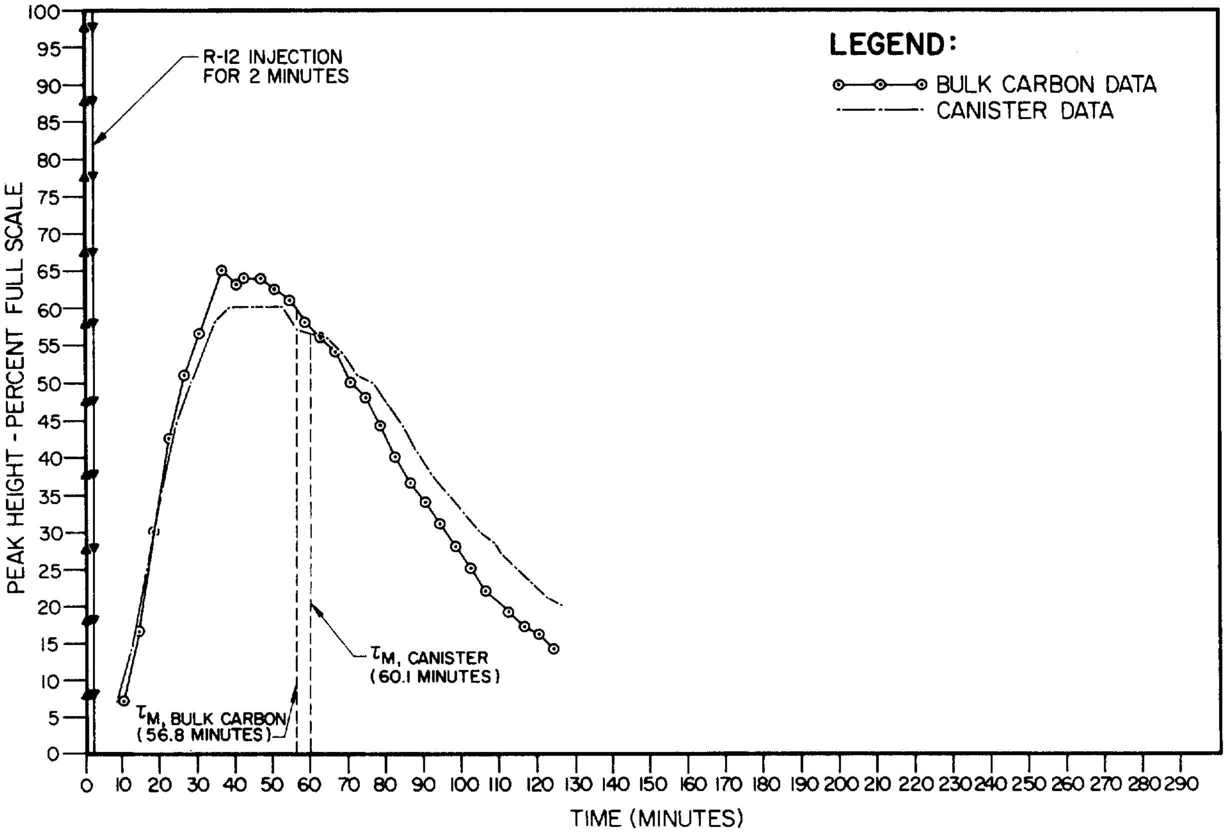

FIGURE 8. BREAKTHROUGH DATA FOR TEST NUMBER 7

The elution curves from Test Numbers 2 and 4 obviously do not exhibit the symmetrical pulse customarily observed for linear, physical adsorption systems. However, this was not too surprising because of the extremely small bed depth (nominally 2 inches). Nevertheless, it was decided to calculate the shape of the breakthrough curve, assuming a linear, physical adsorption process, and to compare the results with the observed breakthrough curve.

The calculations were performed using a physical adsorption model presented in Reference 5. The dynamic adsorption coefficient and height of transfer unit (HTU) were estimated from the test canister data of Test Number 4 to be 32,490 $\frac{cm^3}{g}$ and 1.65 cm., respectively. These empirically determined parameters were used to calculate the breakthrough curve. Therefore, the calculated breakthrough curve was forced to reproduce the mean breakthrough time and one point on increasing and one point on the decreasing curve. However, as seen in Figure 6, the shape of the entire calculated breakthrough curve agrees well with the experimental data, thereby increasing confidence in the assumption that the adsorption can be characterized as a linear, physical adsorption process.

To further evaluate the test method, the flow through the test canister was artificially decreased to see whether the breakthrough curve for the bulk adsorber preceded that for the test canister, as predicted by Equation 3A. In Test Number 5, the flow through the test canister was partially blocked by taping off its discharge nozzle and progressively enlarging an opening in the tape until the test canister flow was approximately ½ the normal flow. The relative flow was estimated by monitoring the pressure drop across the canister carbon bed only (see Figure 4) as the downstream flow resistance was developed. The flow was considered to vary as the ΔP to the 1.22 power (from carbon vendor data). The pressure differentials for the bulk carbon and the test canister carbon were not compared since it was considered that this could lead to substantial error. Instead, the pressure drop through the test canister carbon was measured both before and after adding the flow resistance, while the bulk carbon flow was maintained essentially constant. The velocity through the bulk carbon and the test canister are assumed to be approximately the same prior to throttling the test canister flow. Therefore, the ratio of the test canister velocity, after throttling, to that before throttling would be approximately the same as the ratio of the test canister velocity to bulk carbon velocity, after throttling. The results of the test, as can be seen in Figure 7, indicate that the bulk carbon eluted R-12 much more rapidly than the test canister, as it should. It will be noted that the test data were taken for a period of about 140 minutes and that neither bulk adsorber nor the test canister assembly had completely eluted the R-12 during this time interval. However, the data taken clearly demonstrates that the mean breakthrough time is closely related to the air velocity. The best estimates of the breakthrough times, shown in Figure 7, indicate the mean breakthrough time for the test canister to be 56.9% that of the bulk carbon (see Table 1 for complete results). Using the test canister carbon as a flow meter as described above, the canister velocity was estimated to be 51.8% that of the bulk carbon. This was considered to be satisfactory agreement, especially considering the approximate nature of the flow indication from the pressure differentials (considered to be probably less accurate than the relative breakthrough method).

Data from Test Number 7 are presented in Figure 8. This was another normal run in the sense that flow through the test canister was not artificially decreased as was done in Test Number 5. Again, the R-12 was eluted in very nearly the same time from both the bulk adsorber and the test canister. However, the mean breakthrough time for the canister lags that for the bulk carbon by about 5.5%.

Results for Test Numbers 1, 3 and 6 were not reported. Test Number 1 was a shakedown test to determine the appropriate quantity of R-12 to be injected, the approximate breakthrough time, etc. Test Numbers 3 and 6 were aborted due to an inadvertant change in total blower flow rate during the course of the test and due to an artificially induced flow imbalance, respectively.

Summary of Results

As indicated previously, the mean breakthrough times were evaluated by graphically integrating the area under the breakthrough curves. The resultant mean breakthrough times are shown in Figures 5 thru 8. The ratio of the mean breakthrough times are also included in Table 1. The density ratio, $\frac{\rho_c}{\rho_v}$, was taken to be unity. The ratio of the test canister bed depth to the bulk carbon bed depth was determined to be approximately 0.97. The mean breakthrough time ratios and the bed depth ratio were used in Equation 3A to calculate the relative velocities presented in Table 1.

From Table 1, the canister velocity was greater than the bulk carbon velocity in two out of three tests (not including Test Number 5). The maximum indicated difference was 8.3%.

The locations of the sample points downstream of the bulk carbon were not the same for all tests. The relatively minor variations in the measured velocity ratios probably reflect several factors as; 1) both the bulk adsorber and test canister were drained and refilled at least once during the test program, 2) possible variations in bulk carbon velocities as the sample point was moved from one point to another and 3) the reproducibility of the test (the latter was not directly determined).

Conclusions

The results and observations of this effort indicate that the test method can be used, as intended, to measure the ratio of the superficial face velocity for the test canister to the superficial face velocity for the bulk carbon. This velocity ratio may then provide valuable information to establish the relative effectiveness of the test canister.

A basis of the test was the assumption of a linear, physical adsorption system. The shape of the breakthrough curve, as calculated from an analytical model, closely reproduced the shape of the observed breakthrough curve. This increased confidence that the system satisfied the above assumption.

The test method was checked directly by artificially decreasing the superficial face velocity through the test canister to approximately 50% of full flow by means of an external flow resistance. The results (velocity ratios) from the breakthrough test method agreed with results obtained from measured pressure drops to within 3.4%.

Although it was beyond the scope of this effort to demonstrate, it is believed that this test could be extended to measure the flow uniformity through the bulk carbon. By placing two or more pickups at various locations on the outlet screen, this test method would offer a unique means for determining relative velocities at a number of discrete points, on a local basis, rather than less meaningful average velocities over a much larger area.

The above tests demonstrated the flow through the test canister, CANSET™, to be representative of the flow through the HECA® bulk carbon.

Acknowledgements

Our appreciation is expressed to Fred Leckie who provided and operated the G. C. and associated equipment. Fred's expertise in this area greatly facilitated the testing.

References

(1) Strauss, H. J., Winter, K., "Remarks on Testing the Reliability of Iodine Adsorption in Ion-Exchanging Charcoal-Filters with Respect to Solvent Loadings," Proceedings of the 14th ERDA Air Cleaning Conference.

(2) Parish, H. C., Muhlenhaupt, R. C., and Vogelhuber, W. W., "An Experimental Investigation of the Relationship Between Bed Packing and Flow Distribution," Proceedings of the 14th ERDA Air Cleaning Conference.

(3) Siegworth, D. P., Neulander, C. K., Pao, R. T., and Siegler, M., "Measurement of Dynamic Adsorption Coefficients for Noble Gases on Activated Carbon," Proceedings of the 12th AEC Air Cleaning Conference.

(4) Browning, W. E., and Bolta, C. C., "Measurement and Analysis of the Holdup of Gas Mixtures by Charcoal Adsorption Traps," ORNL-2116, 1956.

(5) Burnette, R. D., Graham III, W. W., and Morse, D. C., "The Removal of Radioactive Krypton and Xenon from a Flowing Helium Stream by Fixed-Bed Adsorption," Reactor Technology, TID-7622, July 1962.

Test Number	Ratio of mean breakthrough times $\frac{\tau_b}{\tau_c}$ (1)	Ratio of adsorber depths $\frac{L_c}{L_b}$	Ratio of flow velocities $\frac{v_c}{v_b} = \frac{L_c}{L_b} \times \frac{\tau_b}{\tau_b}$	Velocity ratio from canister ΔP $\frac{v_c}{v_b}$
2	1.036	0.97	1.005	—
4	1.089	0.97	1.057	—
5(2)	0.569	0.97	0.552	0.518
7	0.945	0.97	0.917	—

(1) Subscript b refers to bulk carbon, c refers to canister.

(2) Introduced artificial flow resistance downstream of canister and estimated velocity ratio both from R-12 breakthrough and from ΔP across canister.

TABLE 1 Summary of Breakthrough Tests

DISCUSSION

BELLAMY: Why is there a difference of 3% in the bed depths between the canister and the bulk bed?

PARISH: The bulk carbon was designed to be approximately 3% deeper to provide slightly more flow resistance through the bulk carbon relative to the flow canister as a conservative measure. The tests referred to were conducted in 1975. In recent years, we've gone to a little deeper bed relative to the canister as this helps to ensure that the flow resistance to the test canister, everything else being the same, will be less and therefore that there will be a slightly greater flow through the test canister.

BELLAMY: And your newer designs will have more conservatism?

PARISH: Yes.

BELLAMY: How much more?

PARISH: I'd say, on the average, an additional one or two percent.

DEMPSEY: Is the purpose of all this to be able to go back to the lab with the samples and analyze them for iodine sorption capability?

PARISH: Yes.

DEMPSEY: Our friends from other countries who have been attending these meetings for the last ten to twenty years have been telling us repeatedly that we should make iodine tests in the field because the moisture content of the carbon makes a drastic difference in the results, and we don't know what the moisture content is. It seems like such an easy step to go from what you're doing to making the iodine test in the field, perhaps on a limited fraction of the bed with a micromicromicrocurie of radioiodine, if you'd like, so that we could get some real field data. Is anyone considering that?

PARISH: I don't believe I am the proper one to answer that question. I would point out that although there is an interest in testing in the field in the manner you suggest, you still would want to assure yourself of an appropriate velocity distribution between various points in the adsorber bed. Perhaps you would not need a test canister if you were testing in the field. Nevertheless, I think you would still want to assure yourself that you had a proper flow distribution through the bed, at least within the ± 20% called for in Regulatory Guide 1.52. To that extent, this test, or some other type of flow distribution test, would still be needed.

DEMPSEY: Am I correct in assuming that the proportion of flow through the canister to that through the whole bed is one to a thousand?

PARISH: Something on that order, yes.

DEMPSEY: I am suggesting that by introducing the radioactivity into a very limited area of the bed, knowing exactly what the relative flow rate is, we could use extremely small amounts of radioiodine: one thousandth or a hundred thousandth less than what would have to be used for testing the entire bed.

PARISH: You mean, if you were injecting only upstream of the test canister?

DEMPSEY: Of that exact area. Perhaps there's an idea here that we could get the Nuclear Regulatory Commission to consider with us.

PARISH: I think that's an interesting concept; I hadn't heard it before.

RIVERS: You were speaking of ASTM D2804 which is in the process of establishing test conditions for the canisters after they are taken back to the laboratory as well as before they are installed. It is essential that we first have a baseline measurement of the carbon that is installed in the filter system by sampling and evaluating it in the same type of canister. Then, after service, the test canisters can be brought back to the laboratory and put through at least one of the test procedures that the original carbon batch was subjected to. At the moment, the feeling is that the appropriate test procedure should be one that couldn't possibly be done in the field because it is to be conducted at 80°C and 95% RH. Of course, that condition doesn't necessarily exist in the field system. Therefore, we have a problem in deciding what is to be the most desirable set of test conditions in the field or laboratory.

KOVACH: I have some questions and comments. I think just taking the mean breakthrough time is not really an accurate way of deciding how uniformly flow is distributed between the main bed and the test bed. Differences in the tail can be very important and the entire breakthrough curve is needed to show whether you have uniformity of flow or not. Although you didn't stress it, your curves match quite reasonably on most of the tests. I think that whoever is using this test procedure may be well warned to evaluate the exact differences when they develop the full breakthrough curve and to evaluate the entire region on a statistical basis. I don't think we always develop enough data to say that two samples are really identical. If we start using different canister bed depths to counteract potential differences in the adsorber when we run through the test conditions, we may be getting ultra-conservative and this can be just as bad from an economic standpoint when considering the frequency of changing out adsorber beds.

PARISH: I believe,when there is adequate flow distribution, that the mean breakthrough time is sufficient to establish the flow distribution and that is what it is that we are looking for. I will agree that differences in the tail of the curve or, for that matter, in the initial rise reflect changes in the height of a transfer unit which might be related to particle size or some other factor which has to do with the mass transfer in the adsorbent. But I stick to the claim that if you match the mean breakthrough times, based on the conditions that are outlined in the report, that you can establish whether or not you have uniform velocity through the adsorber. Other information can be obtained by examining the entire breakthrough curve.

KOVACH: The only comment I have is that Edgewood Arsenal uses the R-12 method to evaluate adsorber life. Identical mass-produced adsorbers are tested routinely with R-12 and measured for pressure drop. Their results show very limited, or no direct, correlation between pressure drop and R-12 values, both of which should relate to air velocity through the bed. Therefore, neither pressure drop nor R-12 mean number relates to flow rate through the bed. Do you have any comments on this observation?

PARISH: The reason we did not use ΔP measurement as the primary indication of flow distribution is because there are too many other variables such as packing density and particle size which affect the flow resistance and therefore ΔP. Thus I would not be surprised at the lack of correlation you noted.

PERFORMANCE EVALUATION OF AN 18,000 CFM FILL-IN-PLACE ADSORBER UNIT

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Abstract

Under a commercial contract MSA was required to assemble and factory test a complete 18,000 CFM air filtration train before shipment to the plant site. The filter train tested was approximately 14 ft. wide by 9 ft. high by 31 ft. long and weighed an estimated 33,500 pounds. It contained four stages of filtration — moisture separators (prefilters are substituted for this test), upstream and downstream HEPA filters and a Type III (Fill-In-Place) Sorber. Filter train design followed the guidelines set forth by ANSI N509-1976 and the tests were conducted under factory controlled conditions per ANSI N510-1975. (1),(2)

In addition to the ANSI N510 tests, an extensive program was conducted to determine "slot velocities", bed packing density, bed flow distribution, and effect of filling methods on particle size and sorber performance for the Type III High Efficiency Sorber.

The purpose of the testing was to demonstrate that after filling, the Type III sorber will function as designed for contaminant removal and thereby qualifying the fill method and Type III sorber design. Additional criteria were to develop and establish suitable testing procedures which can be implemented to demonstrate functional performance on any Type III sorber unit.

I. Introduction

In commercial power reactors, filtration units are used in various air-decontamination systems which prevent release of fission products to the atmosphere and/or cleanup for "in-house" environments. With heavy emphasis from the public, NRC* and other agencies the trend is to insure that these components are reliable and most of all that the units meet their design performance.

The purpose of this paper is twofold. The first is to demonstrate that a Type III sorber unit can meet all the applicable tests as outlined in ANSI N510 when the tests are conducted at the factory. The second purpose is to develop some tests which are not currently available to hopefully insure that the Type III sorber

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*Nuclear Regulatory Commission.

is reliable. It is erroneous to assume that these units when designed to current specifications and installed accordingly are adequate because manufacturing techniques, installation procedures, method of loading, size of unit and other factors can significantly affect the performance.

It should be realized that for most filtration systems the desired efficiency is 99.95% or higher. It appears paradoxical that when one reviews the requirements of HEPA filtration vs. gaseous filtration that the requirements put forth on HEPA filtration performance far exceed any performance tests conducted on the Type III sorber and still we see some significant HEPA filter rejection rates by ERDA* Q.A. stations. Furthermore, almost any person who deals with sorbent testing and bed filling techniques is aware of pitfalls in this area. It is not unusual to note significant flow variation and/or flow resistance because of bed packing density which, of course, would result in poor overall performance of the unit.

II. Test Facilities

A schematic of the test facility is shown in Figure 1. The air enters the filtration plenum through a rectangular inlet located in the top of the plenum approximately 13 feet by 1-1/3 foot. The air then travels through a mixing plenum approximately 14 feet wide by 8 feet high by 3 feet deep and continues through the prefilter, heater and HEPA filter sections of the plenum. The air then enters the Type III sorber and after-HEPA filter section and exits at the filtration plenum through an outlet duct approximately 13 feet by 1-1/3 foot at the top of the plenum. The duct transitions to a 45 inch diameter section where the static pressure taps are located. The 45 inch diameter duct is connected to a 40 horsepower centrifugal fan equipped with a flow control damper. Figure 2 depicts the test facility.

III. ANSI N510 Testing

Procedures

All testing was performed in accordance with procedures outlined in the ANSI N510 standard. Since these procedures are standard throughout the industry, they are not detailed herein.

Air Flow Capacity Test

An air flow capacity test was run in accordance with Section 8.3.1 of ANSI N510. The pitot tube traverse method was used to generate the necessary data for establishing the centerline velocity pressure vs. volume flow rate curve shown in Figure 3.** The manual damper was adjusted to give a centerline velocity pressure of .20, i.e. 18,000 CFM.

As an additional check to substantiate flow, the pressure drop of each HEPA filter in the upstream HEPA filter bank was determined after the unit test was completed. The resistance of

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*Energy Research & Development Administration.

**ANSI N510, Para. 11.4.

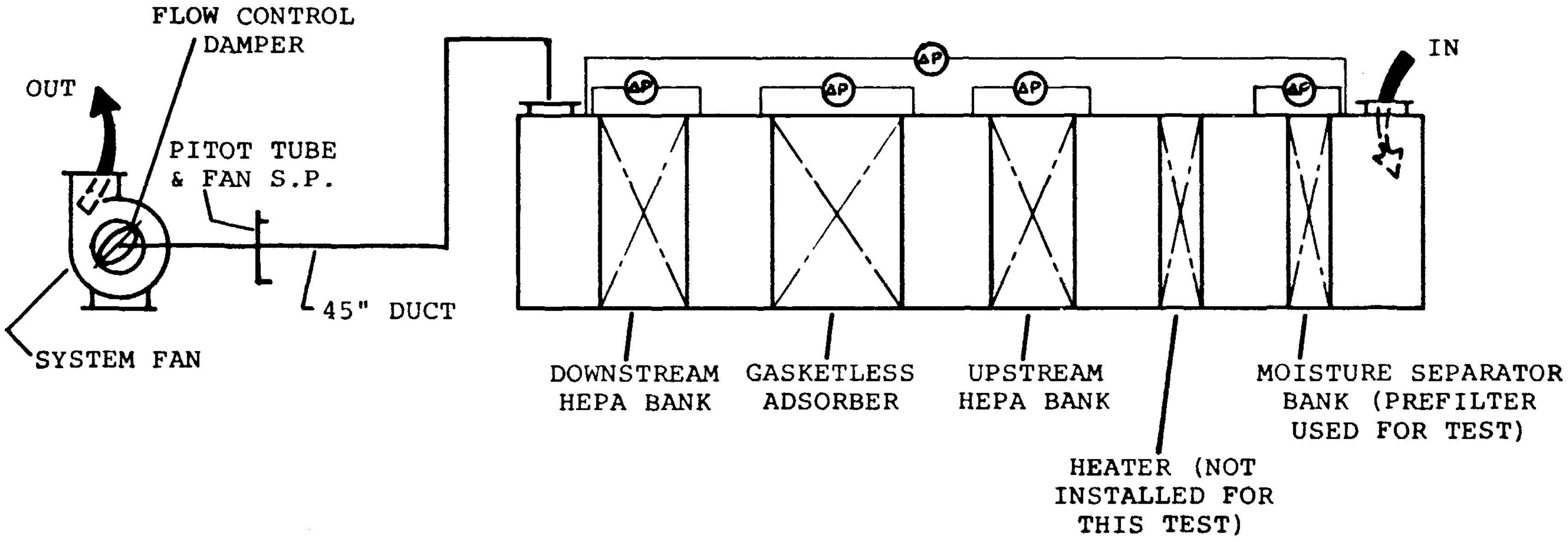

Figure 1. System flow schematic.

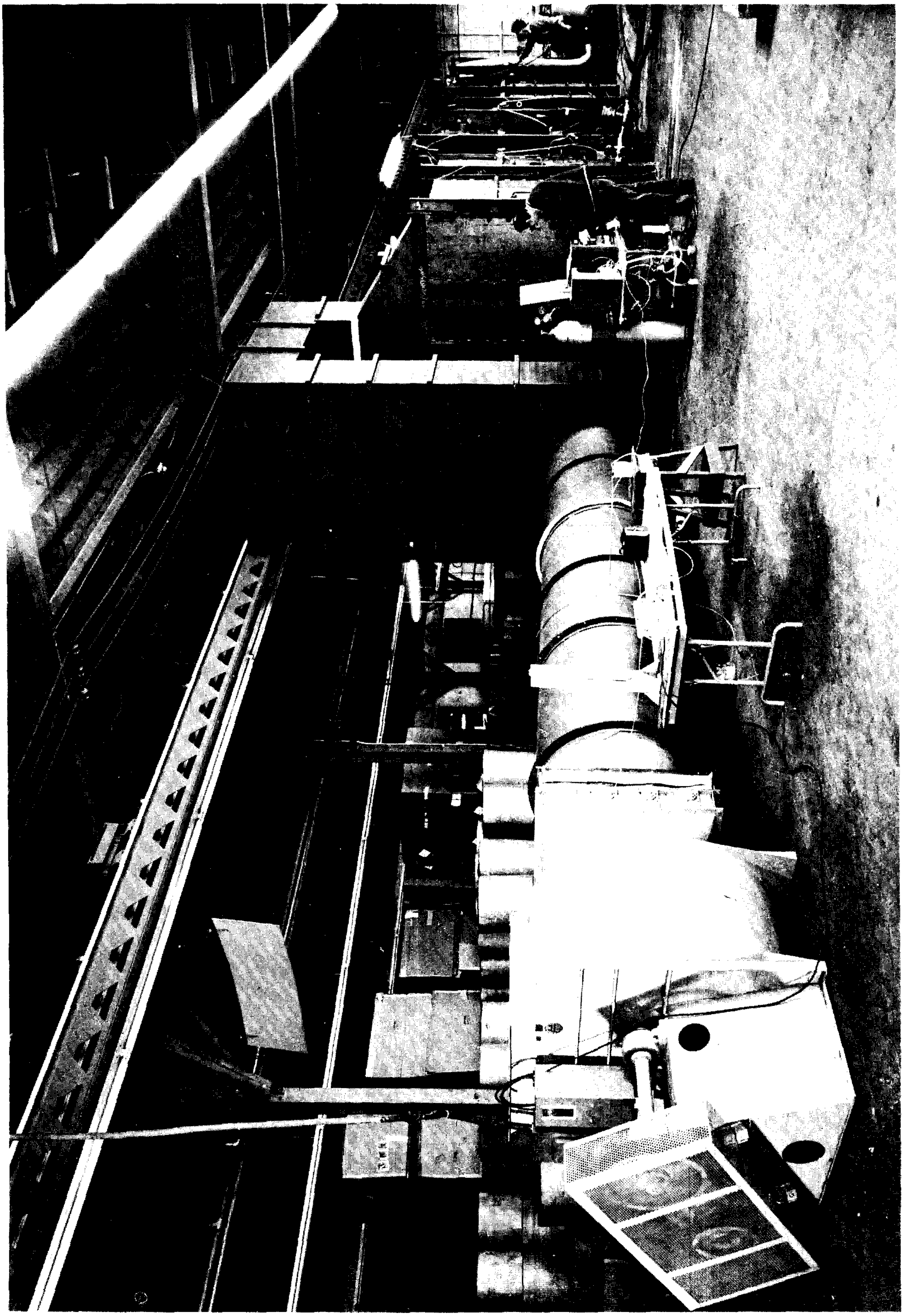

Figure 2. Test facility.

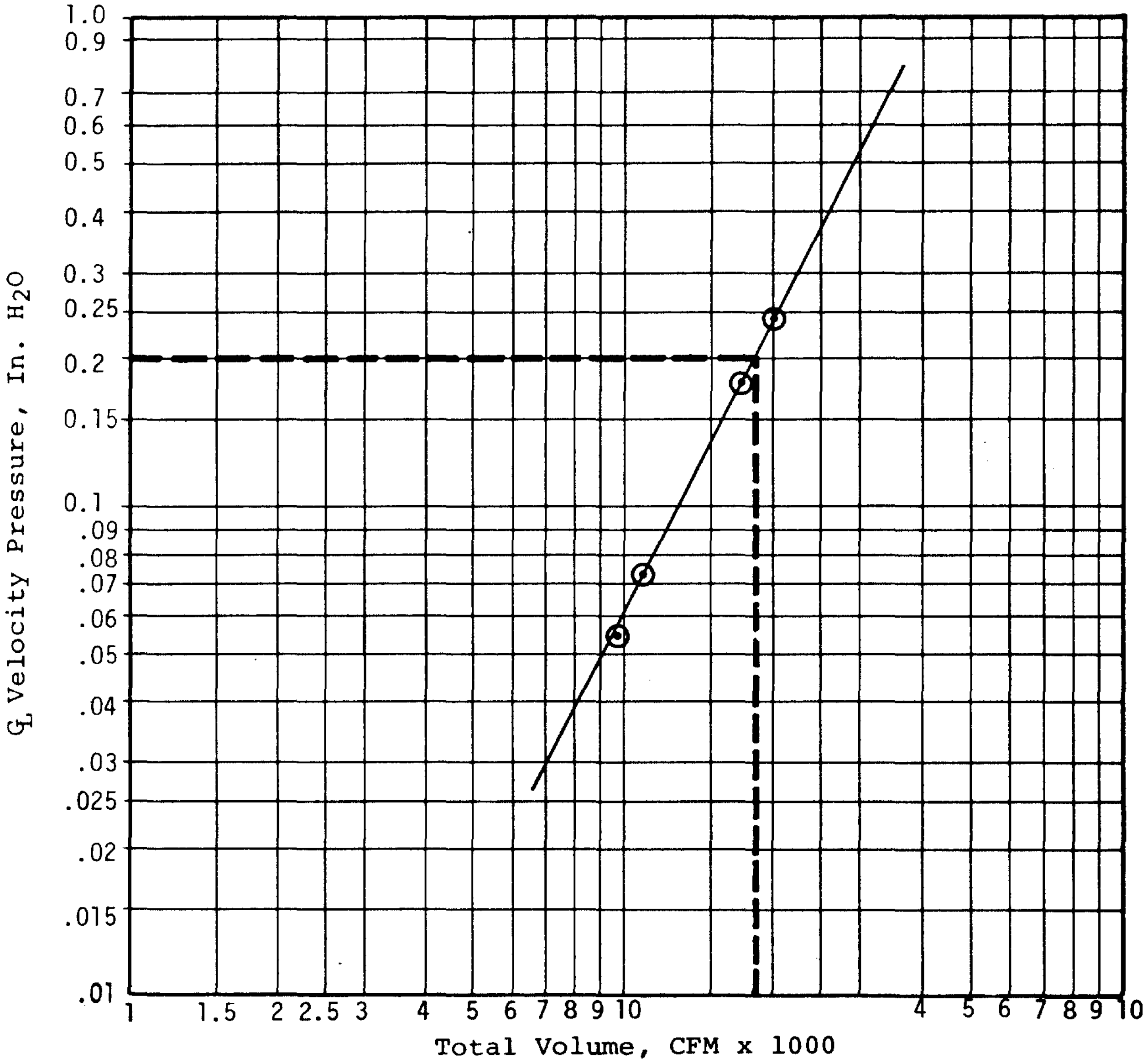

Figure 3. Volume flow calibration curve.

each filter was obtained on the production tester* (DOP machine) for each filter at 1000 CFM and averaged, see Table I. The average resistance was found to be 0.84 in. W.G. for 18 filters (18 filters x 1000 CFM/filter = 18,000 CFM). The average bank resistance obtained during unit testing was 0.83 in. W.G., a variance of 1.2% which indicated the volume flow as measured was correct.

Table I Upstream HEPA resistance — production tester at 1000 CFM. Resistance, inches W.G.

.88	.82	.84	.83	.82	.83
.87	.84	.81	.85	.90	.84
.82	.78	.88	.77	.86	.86

Note: Each block represents filter location in the bank.

Average = 0.84 in. W.G.

Air Flow Distribution

An air flow distribution test was performed across the upstream HEPA filter bank in accordance with ANSI N510, Paragraph 8.3.2. The data collected during this test is shown on Table II.

Table II Air flow distribution velocity.

Velocity, FPM

280	280	285	295	280	280
280	275	285	295	280	280
275	265	285	295	280	275

Note: Above readings corrected for anemometer calibration. Each block represents filter location in the bank.

Average velocity = 281 FPM
Allowable range - 225 to 337

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*Penetrometer, Filter Testing, DOP, Mil-Q107-Doc. No. 136-300-175A, U.S. Army, Edgewood Arsenal, Maryland. (3)

The velocities were taken upstream of the face at the center of each HEPA filter with an anemometer. The average velocity was calculated using the equation:

$$\bar{V} = \frac{\Sigma_i^n V_i}{n} \ * \qquad (1)$$

where $\bar{V}$ = average air flow velocity through the housing
V_i = individual anemometer readings
n = number of anemometer readings

The average velocity is 281 FPM. The allowable range of all readings per ANSI N510 is ±20% or 225 to 337 FPM. The actual readings are within ±6% of the average velocity.

An additional check of volume flow was performed by taking the superficial flow area of each HEPA filter times the number of HEPA filters times the average velocity.

$$C = A \times N \times \bar{V} \qquad (2)$$

where C = volume flow, $ft.^3/min.$
A = face area of a HEPA filter = 3.52 $ft.^2$
N = number of HEPA filters = 18
$\bar{V}$ = average velocity, ft./min.

$$C = 3.52 \times 18 \times 281$$

$$C = 17{,}804 \text{ CFM}$$

This volume flow is within 1.1% of actual.

Sorber Residence Time Calculation

The Type III sorber residence time was calculated from the equation:

$$T = \frac{nNt\ (A-b)^{**}}{28.8\ Qs} \qquad (3)$$

where T = residence time, sec.
n = number of cells in system = 1 for Type III sorber
N = number of sorbent beds per cell = 18
t = thickness of adsorbent beds = 4 in.
A = gross area of all sorbent-bed screens of one cell = 159,840 $in.^2$

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* Per ANSI N510-1975, Para. 8.3.2.

**Per ANSI N510-1975, Para. 8.3.3.

b = area of baffle, margin, and blank area of all sorbent-bed screens of one cell = 29,736 in.^2

Q = volumetric flow rate of system, from Para. 8.3.1 step 4 = 18,000 CFM

s = number of screens of one cell = 36

$$T = \frac{1 \times 18 \times 4\ (159{,}840 - 29{,}736)}{28.8\ (18{,}000)\ \ (36)}$$

$$T = 0.5 \text{ sec.}$$

Air Aerosol Mixing Uniformity Test

The air aerosol mixing uniformity test was performed in accordance with Para. 9 of ANSI N510. Aerosol is introduced into the air stream at a previously selected injection point. Aerosol concentration readings are taken across a plane parallel to, and a short distance upstream of the HEPA filter bank; the uniformity of these readings establishes the acceptability of the injection port location. Results are given in Table III. The results show uniform mixing within ± 10%.

Table III Aerosol uniformity.

Penetrometer Meter Reading

.65	.60	.65	.60	.65	.65
.55	.55	.60	.60	.60	.55
.55	.55	.55	.60	.55	.60

Note: Readings taken 6" in front of upstream HEPA. Each block represents the filter location in the bank.

Average = .592
Acceptable range - .533 to .651

In-Place Leak Tests of the Sorber

In-place leak test of the sorber stage will be described later in Section VII.

IV. Bed Pressure Drop Characteristics

Before filling the Type III sorber with carbon, differential pressure readings (ΔP_1) were taken at various flows to determine the "blank" pressure drop characteristics of the bed. These values are listed in Table IV. After filling the sorber, the tests were repeated and the total pressure drop (ΔP_2) of the sorber (unit + 4 inch depth of carbon) was recorded at the same flow rates as noted in Table IV. From these values, bed resistance was determined and correlated with the Reynolds Number through the bed. The correlation between sorber resistance (ΔP_3) and the Reynolds Number from Figure 4 is:

$$\Delta P_3 = .025\,(R_e)^{1.209} \qquad (4)$$

where ΔP_3 = differential pressure, inches H_2O
R_e = Reynolds Number

Table IV Sorber resistance data.

Flow CFM	ΔP_1 Empty In. H_2O	ΔP_2 Actual In. H_2O	Bed Resistance $\Delta P_3 = \Delta P_2 - \Delta P_1$ In. H_2O	R_e
21,800	0.13	1.29	1.16	24.61
19,300	0.11	1.15	1.04	21.79
18,000	0.10	1.13	1.03	20.32
17,000	0.10	0.995	0.90	19.19
16,200	0.095	0.93	0.83	18.29

The above test results showed close agreement (± 5%) with the pressure drop measured in the laboratory on a 3" dia. bed.

V. Effects of Filling Method on Particle Size and Sorbent Performance

To insure the functional performance of the Type III sorber, it is imperative that the method used to fill the gasketless sorber does not change the particle size distribution or bulk density of the charcoal beyond the acceptable range given in ANSI N509. As a result, any fill method used must be qualified.

MSA qualified two methods of filling. The methods were:

1) Sifter Fill Technique*- Method A
2) Pneumatic Fill with Vibration - Method B

The Sifter Fill Technique* combines pneumatic conveying of the sorbent from the shipping container to the fill hopper and sifter fill from the hopper to the Type III sorber (see Figure 5, Method A). The Pneumatic (low pressure) Fill Method (see Figure 5, Method B) conveys the sorbent from the shipping container to the

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*Sifter Fill Technique, "A Noiseless Method for Filling Packaging Containers", W. E. Gross, Army Chemical Center, Maryland. (4)

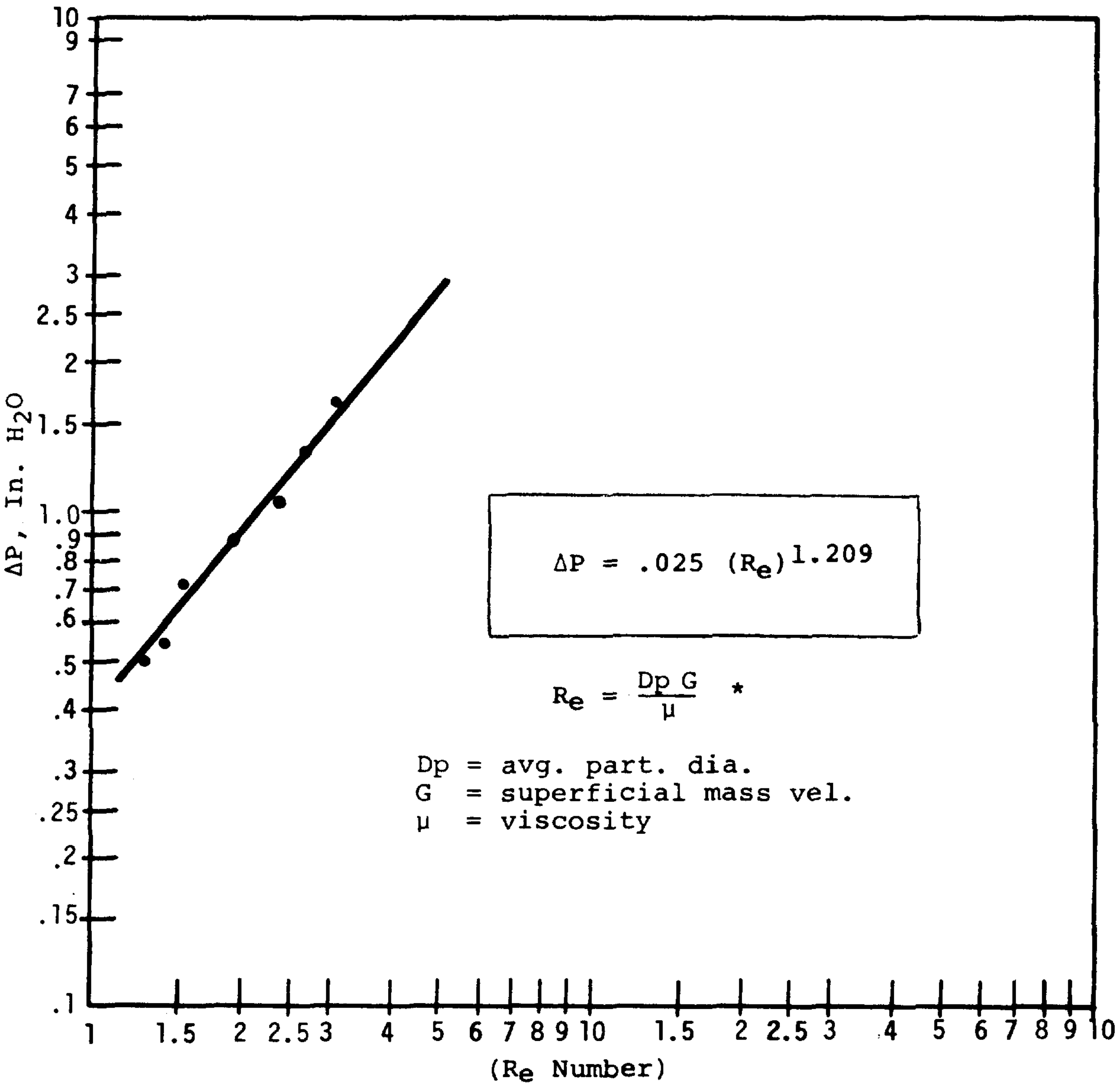

Figure 4. Sorber resistance vs. Reynolds number.

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*Perry, R. H., Chemical Engineer's Handbook, 4th Edition, p. 5-50, Equation 5-164. (12)

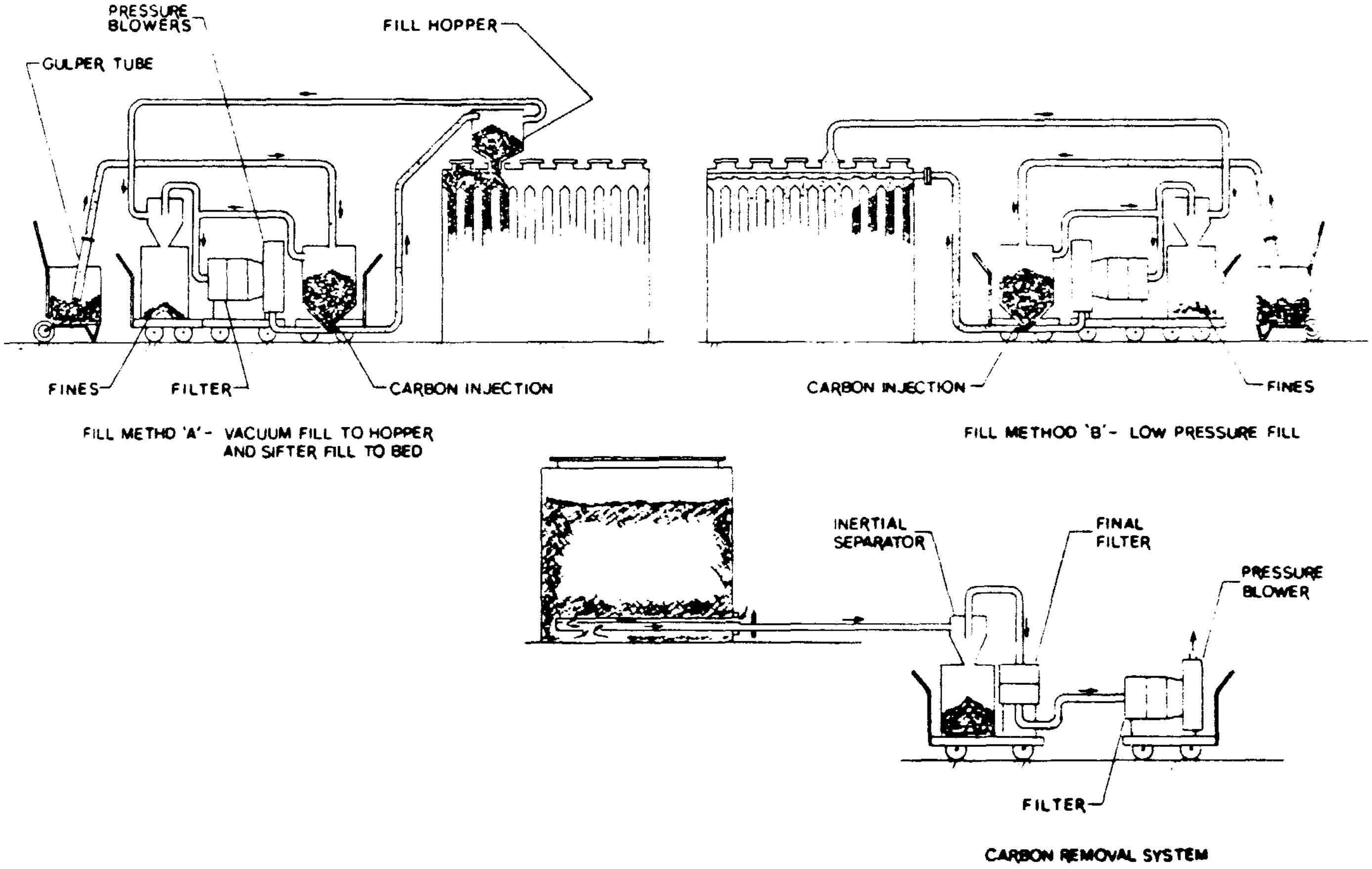

Figure 5. Gasketless adsorber fill and removal methods.

sorber unit. Vibration must be used with this method to insure uniform packing density. It should be noted that both of the above methods were achieved through research and development. Conventional conveying systems or simple dumping of sorbent into the Type III unit were proven unsatisfactory on early tests.

The 18,000 CFM unit was filled using Method A. During the filling stage, samples of charcoal were taken to determine what changes occurred in particle size during transfer. Samples were taken from the shipping drum and at the fill hopper prior to dropping the charcoal into the sorber.

Table V shows the particle size distribution on the charcoal sampled from the shipping drum and the system fill hopper. Average values in the drum and in the fill hopper can be listed as follows.

Table V Particle size distribution, sifter fill.

	Mesh Size **	Drum	Hopper	Allowable*
Through 6, retained on	8	1.5%	1.2%	5%
Through 8, retained on	12	45.4%	42.4%	40-60%
Through 12, retained on	16	51.5%	53.2%	40-60%
Through 16, retained on	18	1.6%	3.2%	5% max.

The above data shows that this method does not effect the particle size distribution of the carbon.

Fill Method B was qualified using the same methods. During the filling stage, samples of charcoal were taken to see if any changes occurred in particle size distribution during transfer. Samples were taken from each shipping drum and from the bed after each drum was transferred.

Table VI shows the particle size distribution of the charcoal sampled from the shipping drum and the adsorber bed. Average values were:

Table VI Particle size distribution, pneumatic fill with vibration.

	Mesh Size **	Drum	Sorber	Allowable*
Through 6, retained on	8	1.0%	1.3%	5%
Through 8, retained on	12	41.9%	42.8%	40-60%
Through 12, retained on	16	53.8%	53.4%	40-60%
Through 16, retained on	18	3.3%	2.5%	5% max.

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*Allowable values per Reg. Guide 1.52, July 1976. (5)

**Mesh size distribution tests were conducted per ASTM D2862-70. (6)

There was no significant change in the particle size distribution of the charcoal resulting from it's transfer from the shipping drum into the sorber.

Bed Packing Density

Bed packing density was determined by calculating the volume of the adsorber bed and measuring the weight of charcoal used to fill the bed.

$$\text{Bed density} = \frac{\text{wt. of sorbent}}{\text{volume of bed}} \qquad (5)$$

For Fill Method A and B, the calculated bed packing density was 31.52 lbs./ft.^{3} or 0.50 gms./ml. The average apparent density of the sorbent used was 31.92 lbs./ft.^{3} or 0.510 gms./ml. for Method A. The apparent density of the adsorbent used was 35.57 lbs./ft.^{3} or 0.569 gms./ml. for Method B.

The minimum packing density required by ANSI N510 is 0.38 gms./ml.

Apparent density tests were conducted per ASTM D2854-70.(7)

VI. Velocity Measurements

Velocity Profile Across the Sorber Slots

Procedure. The sorber air slot velocities were determined by taking velocity measurements 10 inches downstream of each slot. Ten inch long rectangular ducts, having the same cross-sectional area of the air slots were attached to the exit slots of the sorber unit, as depicted in Figure 6. A hot wire anemometer probe was placed at seven locations in each slot as indicated in Figure 6. The probe tip was located at the center line of each slot. Readings were recorded for each of the seven locations of each slot.

Results. The results of the test are summarized in Table VII.

The acceptable range is considered ±20% of the average velocity of 1145 FPM or 916 to 1374 FPM. Ninety-five (95) percent of the readings were within this range.

Theoretical average slot velocity is 867 FPM. This is calculated as follows:

$$SV = \frac{C}{SA} \qquad (6)$$

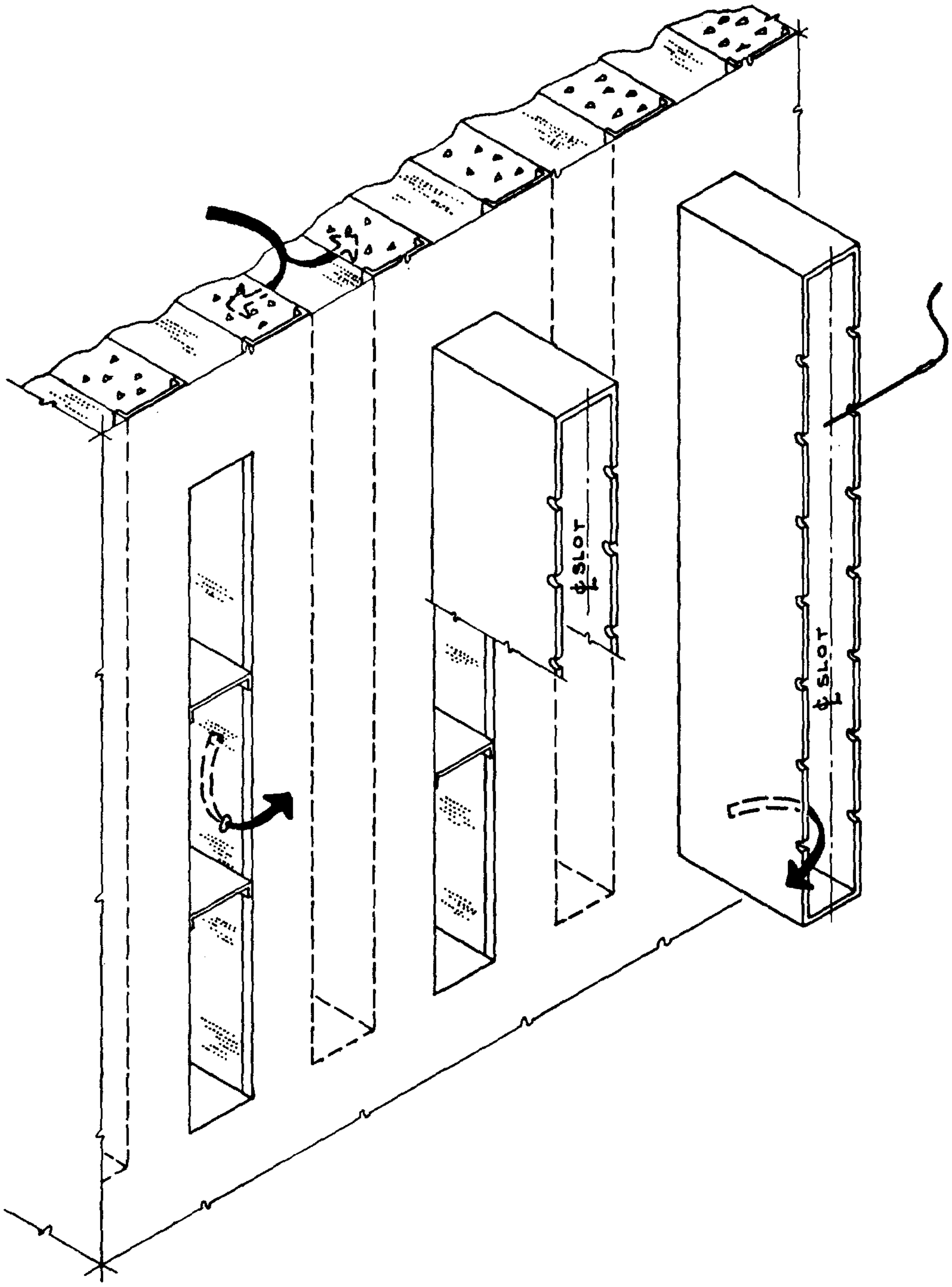

Figure 6. Sorber velocity profile.

Table VII Slot Velocities, fpm - center line velocities vs. probe location.

Location	Slot 1	Slot 2	Slot 3	Slot 4	Slot 5	Slot 6	Slot 7	Slot 8	Slot 9
1	1300	1325	1280	1290	1230	1250	1380	1370	1175
2	1050	1100	1000	1060	1025	1110	1140	1100	1100
3	1040	1050	1090	1125	1010	1140	1170	1160	1070
4	1040	1060	1040	1400	1100	1140	1125	1200	1060
5	1050	1060	1100	1400	1090	1200	1360	1060	1050
6	940	1125	1150	1210	1040	1075	1360	950	940
7	960	1130	1025	1210	980	1070	1360	960	925

Note: Readings are corrected for temperature and pressure.

where SV = slot velocity, FPM
C = volumetric flow, CFM = 18,000 CFM
SA = total slot area, ft.^{2}

Total slot area is calculated by:

$$S.A. = \text{No. Slots} \times \text{Slot Height} \times \text{Slot Width} \qquad (7)$$

where No. Slots = 9
Height Slot = 78.1 in.
Width Slot = 4.254 in.

$$S.A. = \frac{9 \times 78.1 \times 4.254}{144} = 20.76 \text{ ft.}^2$$

$$\text{Slot Velocity} = \frac{18{,}000}{20.76} = 867.05 \text{ FPM}$$

The reason for the disparity between the average slot velocity reading of 1145 FPM and the theoretical slot velocity of 867 FPM is most likely a combination of testing technique, bed packing and that the flow is in the transition zone between laminar and turbulent flow.

Velocity Through Test Canisters

Since the **sorbent** test canisters are a vital part of the Type III sorber unit, the velocity across each test canister was checked.

Procedure. A 15 inch long tube of the same diameter as the test canister was installed on the outlet of the test canister. A hot wire anemometer probe was placed at the open end of the tube with the probe tip located at the center of the tube. With the flow rate through the sorber at 18,000 CFM, readings were recorded.

Results. The average velocity through the test canisters was 39.9 FPM. The allowable range of velocities through the test canisters is 32 to 48 FPM. The actual range was 37.5 to 43 FPM. The test canister design was therefore determined satisfactory.

VII. Sorber Efficiency Tests

In-Place Leak Tests

The Type III sorber was leak tested with Freon-11 at a concentration of 20 PPM at an air flow rate of 18,000 CFM in accordance with ANSI N510, Section 12. The efficiencies determined exceeded the acceptance criteria. Efficiency is determined by the equation:

$$\text{Eff.} = 1 - \frac{R_{DS}}{500\ R_{US}}\ * \qquad (8)$$

where R_{DS} = Recorder units downstream
R_{US} = Recorder units upstream

	Time	Reading
R_{DS}	60 sec.	2
R_{US}	150 sec.	36

$$\text{Eff.} = 1 - \frac{2}{500 \times 36} = .9999 \text{ or } 99.99\%$$

Therefore the Type III sorber unit meets the leak test requirement of ANSI N510.

Freon Breakthrough Test with Time

The primary purpose of this test was to check the Freon adsorption on the charcoal beds throughout the adsorber. To accomplish this the Type III unit was challenged with 20 PPM of Freon-11 at rated flow (18,000 CFM). Gas samples were withdrawn at various predetermined points with time directly downstream of each slot. The efficiencies were measured and calculated per the method outlined in DP-1082. Figure 7 depicts the data collected in this test.

The curve shows the adsorption history for the various carbon beds at different stations until breakthrough occurred. This is the point where the exit concentration begins to rise rapidly with time. It should be noted that the breakthrough uniformity for the various slots and not the time the bed lasts is the important factor of this test. That is, all slots as monitored show approximately the same concentration gradient with time. This is indicative of a uniformly packed bed.

Quantitative Determination of Freon-11 (Trichlorofluoromethane) Sorbed on Charcoal

During removal of the charcoal from the bed, fifty-four (54) samples were taken to determine the amount of Freon sorbed on the charcoal.

The quantitative determination of Freon-11 sorbed on carbon was accomplished by a procedure utilizing solvent desorption and gas chromatography. The procedure was adapted from the method used for the determination of organic vapors in industrial atmospheres. (9),(10)

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*Per Savannah River Report DP-1082. (8)

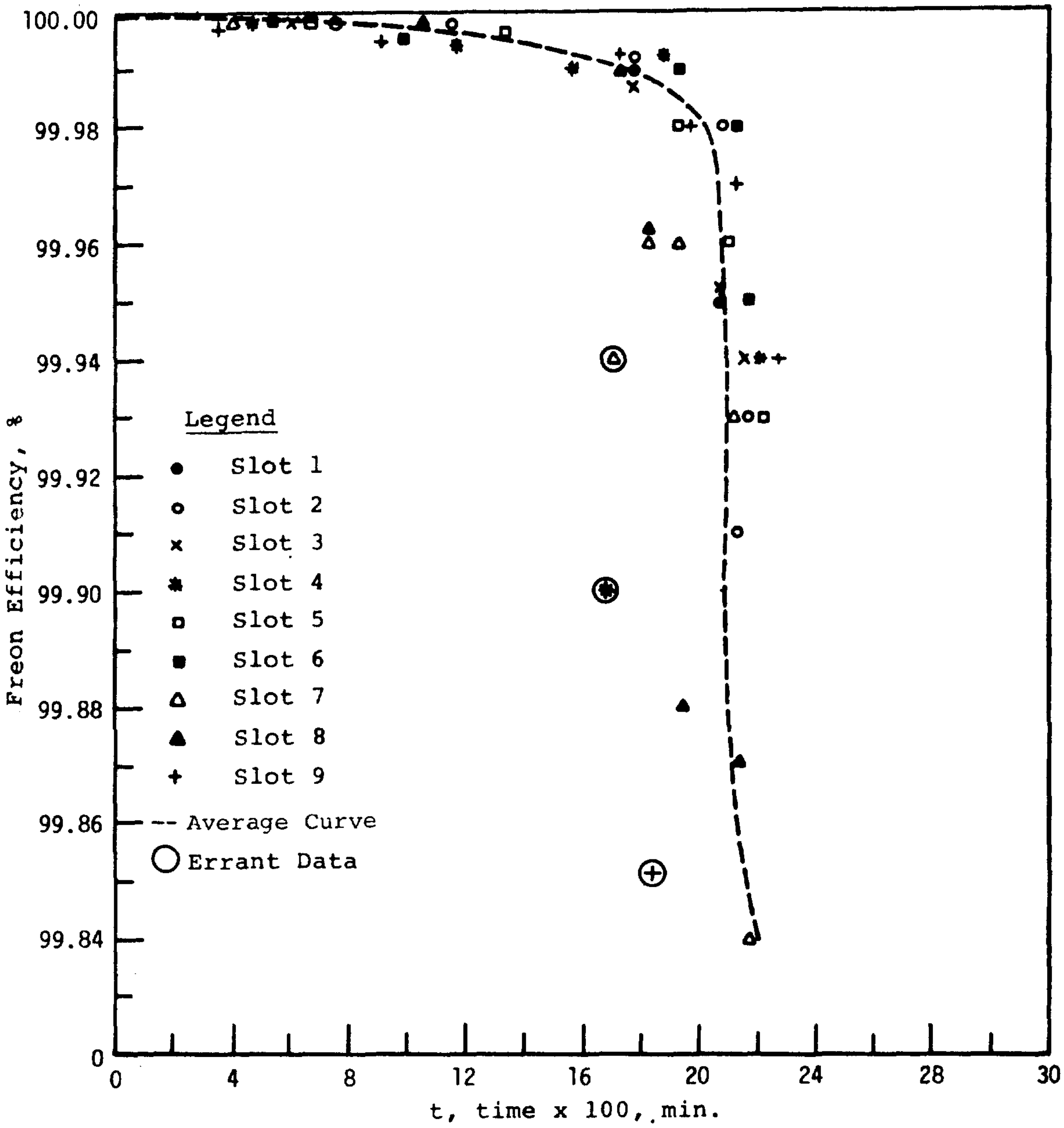

Figure 7. Freon breakthrough curve.

	Bed Number																	
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Top	58.8	51.3	51.2	51.4	67.1	54.1	68.9	40.3	57.3	48.3	68.3	44.6	72.7	51.8	47.1	56.0	75.6	63.5
Middle	55.3	50.4	79.0	69.0	74.5	51.6	66.7	48.1	44.7	67.9	43.8	63.6	70.9	82.4	68.8	51.4	53.1	57.9
Bottom	42.3	43.2	53.2	48.4	61.0	45.5	53.5	78.5	44.5	75.3	86.9	75.2	55.6	58.9	59.8	44.4	54.4	59.4

Average = 58.7

high 86.9 + 48%
low 40.3 - 31%

Expected error ± 35%

± 20% Air Dist.
± 10% Freon Mixing
± 5% Testing Error
35%

Expected Range
38 ⟷ 79

95% of Readings in Expected Range

Table VIII Freon-11 adsorbed on carbon, mg/g.

Results. Ninety-five percent of the samples were within the expected range of ± 35%. The results are shown in Table VIII. The average amount of sorption was 58.7 mg. Freon-11/gram of charcoal.

VIII. Inherent Problems with the Type III Sorber

The basic problem with the Type III sorber unit is that there is no test method currently available to assure functional performance in the field. The conventional Type I and Type II cells per AACC Standard* CS-8T are filled and tested at the factory prior to installation and again after installation.(11) Furthermore, these sorber cells have undergone extensive testing and each manufacturer's cell must meet the strict requirements put forth in AACC Std. CS-8T. Therefore, there is a strong need for a standard method for qualification testing of a Type III unit. Furthermore, field personnel should be trained and certified in this area.

Another potential problem is field repair. The most common repair necessary would be to the perforated portion of the sorber bed. In addition to accidental tearing or cutting of the screen, a not uncommon occurrence is accidental release of the water spray system. If the wet charcoal is allowed to remain in the sorber unit for a few days, corrosion damage could result to the perforated area due to the corrosive nature of the charcoal. It is very difficult to effect screen repair in the field.

IX. Conclusions

A deep bed Type III sorber unit is shown to meet current applicable test standard ANSI N510 when tested at the factory under controlled test conditions. Furthermore, test methods were developed to demonstrate flow distribution through the bed. The results of this program indicated that the Type III sorber unit when filled and tested by factory trained personnel can exhibit reasonable flow distribution through the bed; however, extreme care and extensive testing is necessary to prove or verify the efficacy of an on-line unit.

X. References

1. American National Standards Institute N509-1976, "Requirements for Nuclear Air Cleaning Units and Components", (1976).

2. American National Standards Institute N510-1975, "Testing of Nuclear Air Cleaning Systems", (1975).

3. U. S. Army, Edgewood Arsenal, Maryland, MIL-Q107-DOC136-300-175A, "Penetrometer Filter Testing".

4. W. E. Cross, Army Chemical Center, Maryland, "Sifter Fill Technique - A Noiseless Method for Filling Packaging Containers".

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*American Association of Contamination Control

5. U. S. Nuclear Regulatory Commission Regulatory Guide 1.52, "Design, Testing, and Maintenance Criteria for Post Accident Engineered-Safety-Feature Atmospheric Cleanup System Air, Filtration and Adsorption Units of Light-Water-Cooled Nuclear Power Plants", Rev. 2, (March 1978).

6. American Society for Testing and Materials D2862-70N, "Test for Particle Size Distribution of Granulated Activated Carbon", (1970).

7. American Society for Testing and Materials D2854-70, "Test for Apparent Density of Activated Carbon", (1970).

8. Muhlbaier, D. R., Savannah River Laboratory Report DP-1082, "Standardized Non-destructive Test of Carbon Beds for Reactor Confinement Applications", (1967).

9. White, L. D., Taylor, D. A., Mauer, P. A., and Kupel, R. E., U. Amer. Ind. Hyg. Assoc., 31 225, (1971).

10. NIOSH Manual of Analytical Methods, HEW Publication No. (NIOSH) 75-121, Superintendent of Documents, U. S. Government Printing Office, Washington, DC 20402 (GPO 1733-0041).

11. American Association for Contamination Control, AACC CS-8T, "Tentative Standard for High Efficiency Gas-Phase Adsorber Cells".

12. Perry, R. H., Chemical Engineer's Handbook, 4th Edition, 5-50 Equation 5-164, (1963).

DISCUSSION

KOVACH: I'm always glad to see the test procedures developed in the last few years being used and found applicable to our newer systems.

HALLIGAN: What is the MSA recommendation for the first step to deal with the problem of an initial field test failure on your carbon bank? The choice is either to remove the carbon (to eliminate possible voids) or to perform a shroud test. Both require a substantial amount of effort. Have you considered the approach you would recommend?

PORCO: We have considered it. One would want to check quality assurance documents to begin with and, also, to check that the units were properly filled. You can try a shroud method but I would have a tendency to withdraw the charcoal, recheck it, and then follow the recommended fill technique once again.

HALLIGAN: Both are fairly difficult and require a lot of effort in the field. It is a decision that people who perform the work have to make. Shroud tests on the designs are very difficult. You didn't mention how you would test the HEPA filter banks. Did you give any thought to test ports and DOP distribution upstream of the last HEPA filter bank?

PORCO: The unit I discussed was designed to ANSI 509. Test ports and injection ports are all there for testing per ANSI 510.

HALLIGAN: I am glad it has been worked out because achieving satisfactory DOP distribution on the downstream side, in accordance with ANSI 510, is difficult. Systems that big, employing HEPA filter-carbon-HEPA filter, pose some serious testing problems in the field.

PORCO: These units are tested every day and I know ours pass. I can't speak for everybody.

EXPERIMENTAL DETERMINATION OF FISSION GAS ADSORPTION COEFFICIENTS*

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Abstract

Large charcoal beds have been used for a number of years for the holdup and decay of radioactive isotopes of krypton and xenon. Reliable design of these beds depends on an accurate knowledge of the adsorption coefficient of krypton and xenon on the adsorbents used in these beds. It is somewhat surprising that there is no standard procedure of determining the adsorption coefficient for krypton and xenon. This paper gives fundamental information needed to establish a standardized reproducible test procedure.

Particular points examined in this paper include:

1) The breakthrough curves commonly used to analyze dynamic adsorption data can lead to serious systematic errors.

2) The adsorption coefficient, if calculated from the arithmetic holding time, is independent of geometric factors such as the shape of the adsorption bed and the irregular shape of the adsorbent.

I. Introduction

Precise, reproducible measurements are crucial to the nuclear industry. It is ironic that activated charcoal, one of the most useful materials in the nuclear industry, is also one of the most difficult materials to characterize. For example, what does it mean when we say that a certain sample of activated charcoal has a surface area of 1,500 square meters per gram? There are many assumptions behind the values stated for surface area and the consumer in the nuclear industry may not be aware of all of these assumptions. Is the user of this charcoal aware that the value for the surface area will depend on:

1) the selection of the vapor used to obtain an isotherm?

2) the temperature at which the isotherm is run?

3) the range of pressures over which the data is considered to be useful?

4) the choice of an equation to fit the data?

5) the area assumed to be taken up by a single adsorbed molecule?

The assumptions made in this measurement are important to the reported

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*This study was supported in part through Training Grant T900681-01 provided to the Harvard School of Public Health by the U.S. Environmental Protection Agency.

value. To illustrate this point a specific incident can be cited. Several years ago a study at the Harvard Air Cleaning Laboratory involved testing charcoals from various sources as adsorbants for noble gases. One of the parameters that we wished to determine was the relationship between the surface area and the ability of the charcoals to adsorb noble gases. It turned out that the surface areas, as reported by the manufacturers, were obtained by a variety of methods and that as the adsorbed molecule for these determinations we had results from nitrogen, propane, and iodine adsorption. Are these data equivalent? Probably not, but we did not realize it at that time.

Since this experience it has been useful to us to try to characterize the types of measurements that can be made on charcoal according to the reproducibility of these tests. Table I below shows how we have tried to rank the various types of analyses.

Table I. Precision of selected tests

Measurement	Degree of Precision	Reason
Temperature) Pressure)	High	These are thermodynamic properties which can be measured at equilibrium.
Bulk Density	Moderately Good	Depends on force by which charcoal is packed. Also influenced by adsorbed air, which can be about 1% of measured value.
Surface Area	Fair	Assumptions as noted above.
Removal of Methyl Iodine	Poor	Depends on rate of chemical reactions. Kinetic data are always difficult to reproduce even under the best of conditions.

The purpose of this paper is to evaluate the underlining accuracy of dynamic procedures for determining the adsorption coefficients of charcoals for noble gases. As will be seen, a strong argument can be made that the measurement of the adsorption coefficient, like the measurement of surface area, depends on many assumptions, some of which may be valid and others not. However, the conclusion in this paper will be that a dynamic adsorption coefficient can be determined precisely and given an exact physical meaning. It is our hope that this paper will contribute to the development of standardized procedures for the measurement of noble gas adsorption coefficients.

II. Use of Breakthrough Curves

Dynamic adsorption data are usually obtained by injecting a pulse of noble gas into a gas stream passing through a charcoal bed and then measuring the effluent noble gas concentration. The dynamic adsorption coefficient can then be determined from these data. The usual procedure for the analysis of these data has been to fit the data to a two-parameter curve in which one of these parameters is the adsorption coefficient. In this manner, a "best" value for the adsorption coefficient can be found. As shown in Table II, there are a number of theoretical curves that have been used for this purpose.

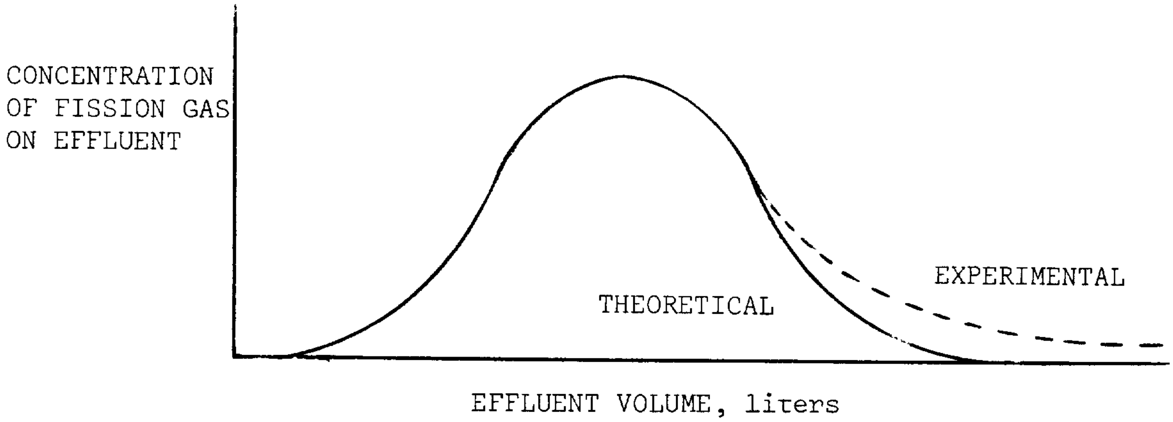
Table II. Common breakthrough equations

Author of Equation	Second Adjustable Parameter	Comments
Browning(1)	Number of subdivisions in bed in which mixing occurs	Doubtful that such subdivisions (called theoretical Chambers by Browning) exist.
Burnette(2)	Mass transfer rate across air film surrounding each particle	In general, air film does not control mass transfer in adsorption
Madey(3)	Gas phase diffusion	Valid only at low carrier gas velocities
Rosen(4)	Diffusion in adsorbent	Assumes adsorbent consists of internally homogeneous spheres of equal diameter

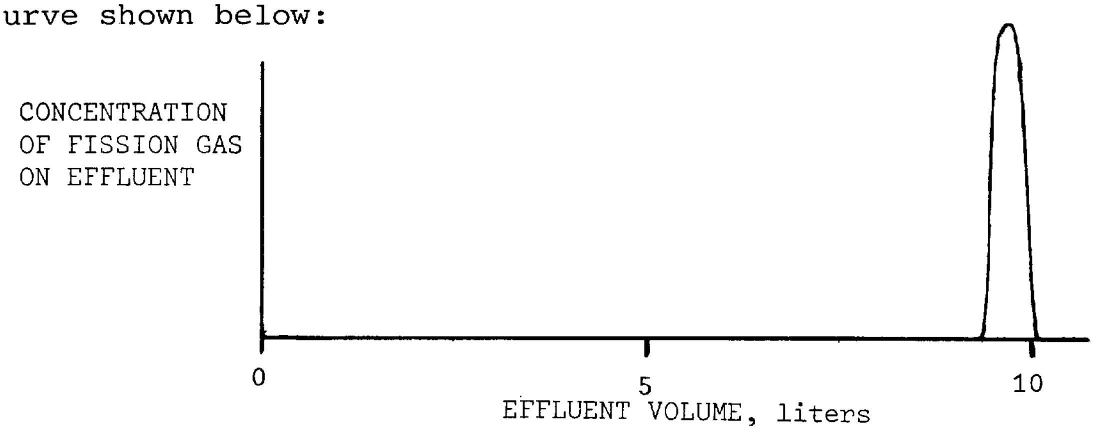
The basic difficulty is that these equations, although they can in themselves appear complex, represent fairly simple models of fission gas behavior, and each can account individually for only one mechanism of mass transfer. Therefore, these equations are not strictly applicable to normally operating fission gas adsorption beds, in which a number of mass transfer mechanisms are important. There is no guarantee that the use of any one of these equations will be appropriate and lead to results of a specified accuracy. In fact, it has been our experience that in general, fission gas breakthrough curves exhibit a tailing which is greater than that predicted by any one of the above equations. The reason for the presence of this excessive tailing, we have believed, is the presence in the charcoal adsorbent of pores or pore areas, where the diffusion of fission gases is highly restricted. Only a small fraction of the input fission gas may reach such areas, but once this occurs these gases find it equally difficult to diffuse out of these areas. Hence, as the sketch below shows, generally, the breakthrough curve has an excessive tailing. Until recently we were not certain how to handle this effect in calculating the adsorption coefficient.

III. Direct Calculation of the Adsorption Coefficient

It is our belief that the adsorption coefficient is best calculated directly from the experimental data without use of a theoretical



breakthrough curve. To show in a simplified manner how this is done, suppose that we inject a pulse into a bed and obtain the breakthrough curve shown below:



It is apparent from this curve that the bed retarded the release of the input fission gas over a period of time in which 10 liters passed through the beds. The adsorption coefficient is then calculated as

$$k = \overline{V}/m , \qquad (1)$$

where $\overline{V}$ = the retention volume,

and m = the mass of charcoal.

In any real bed the effluent output appears as a skewed Gaussian curve, and the arithmetic average retention volume can be calculated as

$$\overline{V} = \int_0^\infty c\,V\,dV \Big/ \int_0^\infty c\,dV \qquad (2)$$

The use of the arithmetic average retention volume to calculate the adsorption coefficient has the following advantages:

1. The result is consistent with all the breakthrough curves cited above. For example, we used a computer to generate the breakthrough curve predicted by the Madey equation, and then applied this method of analysis to that curve. In this test of this procedure the actual error was less than one part in a thousand, and the error could have been further reduced by increasing the precision of the

integration procedure used for this analysis. On the other hand, if we take the same breakthrough curve and try to fit it by a least squares procedure to the curve predicted by one of the other theories, e.g., Browning's theoretical chamber model, a finite error will be found that cannot be reduced by taking more data points. In other words, the procedure of taking the arithmetic average is such a general procedure that it can be used to analyze data from each of the popular models for breakthrough curves, even though these models themselves cannot be used interchangeably between themselves.

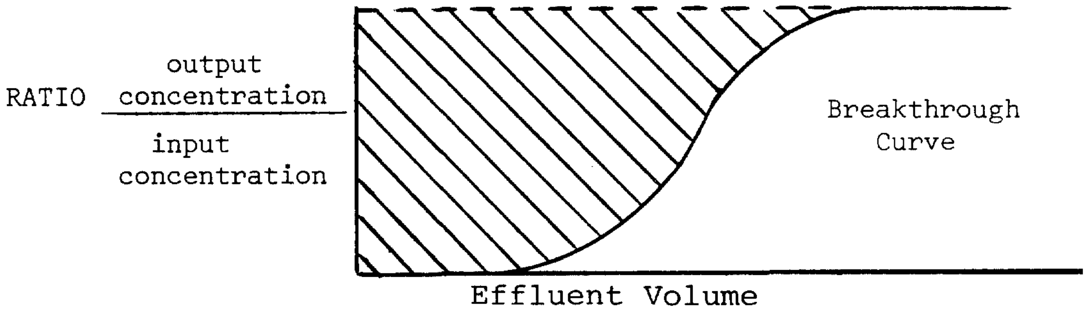
2. This procedure is sufficiently simple as to be carried out using a desk calculator. In contrast, some of the breakthrough curves mentioned above involve Bessel functions, and least squares fitting to these curves requires a computer.

3. As long as the effect of the pressure drop can be ignored, the results obtained from this type of analysis are independent of either the shape of the bed or the flow velocity of the carrier gas. If corrections must be made for the effect of pressure drop, they are extremely difficult to incorporate into any of the breakthrough curves cited above.

4. The "tail" of the breakthrough curve is included in the analysis by the arithmetic mean holdup time. In contrast, other methods of analysis are not able to account for the tailing, which results, we think, from ill-defined pore restrictions in the charcoal granules.

5. The results have a precise physical meaning: The adsorption coefficient obtained in this manner is identical to the static adsorption coefficient obtained if the charcoal is allowed to come into equilibrium with a constant concentration of fission gas.

The proof of this latter assertion is as follows: If a bed is exposed to a constant concentration of fission gas, as it approaches equilibrium saturation with the fission gas, the breakthrough curve will have the following shape:



The hatched area above the breakthrough curve is proportional to the amount of material removed by the bed from the air stream and therefore can be used to determine the quantity of material adsorbed by the bed at equilibrium saturation. If certain rather general assumptions are made, such as a constant carrier gas velocity, constant diffusion coefficients, and a linear isotherm (all these factors were assumed in the derivations of the breakthrough curves which were cited in the previous section), then the hatched area will be identical with the arithmetic average holdup volume determined from a pulse input.

In order to make this paper as readable as possible, we have left out as much mathematics as possible. This includes the mathematics involved in proving the above statement. However, the more adventuresome of the readers may be interested in a paper which appeared in Nature last year.(5) The central theorem, as stated in this paper, is that for simple flow systems "the mean residence time of material is independent of internal characteristics and always equal to the ratio of total holdup of material to its overall flow rate through the system." It is also stated that this theory has been "central to the development of a model independent theory of chromatography which supersedes previous treatment, based on specific models of the chromatographic process by obviating the restrictive assumptions on which these are founded." It is our belief that the best procedure for determining fission gas adsorption coefficients is based on the same powerful mathematical technique.

IV. Summary

The use of the mean retention volume to calculate the adsorption coefficient is both a simple method of analysis and probably the most precise procedure currently available.

V. References

1. Browning, W. E. and Bolta, C. C., "Measurement and analysis of the holdup of gas mixtures by charcoal adsorption traps," ORNL-2116, Third Issue, Oak Ridge National Laboratory (1959).

2. Burnette, R. D., Graham, W. W. III, and Morse, D. C., "The Removal of radioactive krypton and xenon from a flowing helium stream by fixed-bed adsorption," TID-7622, pp. 218-35, Oak Ridge National Laboratory (1962).

3. Madey, R., Fiore, R. A., Pflumm, E., and Stephenson, T. E., "Transmission of a pulse of gas through an adsorber bed," Trans. Am. Nucl. Soc., 5, 465 (1962).

4. Rosen, J. B., "General numerical solution for solid diffusion in fixed beds," Ind. Eng. Chem., 46, 1590 (1964).

5. Gibilaro, L. G., "Mean residence times in continuous flow systems," Nature, 270, 47-48 (1977).

DISCUSSION

WOOD: The pulse technique is advantageous only with a relatively inefficient bed. With sorbent beds highly efficient for a test adsorbate (such as charcoal and iodine) no pulse would come through unless the challenge pulse overloads the bed.

UNDERHILL: For the study of noble gas adsorption, it is possible to use pulses of ^{85}Kr or ^{133}Xe. These radionuclides can be detected at very low concentrations. The equations given here are too simple to account for removal by chemical reactions. However, this can be done and the appropriate equations were given at a previous Air Cleaning Conference.

WOOD: These are inert gases. I'm thinking in terms of radioiodine.

UNDERHILL: I mentioned radioactive krypton and xenon. I didn't include iodine because iodine reacts chemically in the bed. The technique described here would not apply to radioiodine unless you had a form that wasn't reactive, and that's not in the cards.

WOOD: A second question. Did you say that the top, or the median, of the pulse curve was the only important thing?

UNDERHILL: No, I didn't. What I'm really trying to say is that the entire breakthrough curve is important.

DEITZ: Does not a pulse technique that you advocate introduce both adsorption and desorption coefficients displaced in the time interval of the pulse?

KOVACH: In reference to Dr. Deitz's question, in all dynamic adsorption processes, whether pulsed or continuous, both adsorption and desorption rates influence the process.

UNDERHILL: Kovach's explanation is absolutely correct. This has been looked at. If you have a very constricted pore system, very few atoms will diffuse in. Most of the adsorbate may simply bypass the constricted pore area and produce tremendous tailing. This results in slow adsorption which can't be detected when looking at only one part of the curve. But the long tail represents the small amount that did get in. I am trying to use a classical mathematical proof to point out that if the pores are wide open, you can diffuse in and diffuse out very rapidly and the K value determined from this type of analysis is identical. It doesn't make any difference how constricted the pore area is; you will get the same K value. It is independent of the diffusion coefficient. That is really remarkable

LEVINS: While I agree, in principle, with the methods you advocate, practical problems can arise in some circumstances using the method of moments when applied to pulse data. These arise because integrations must be taken to infinity. In the presence of severe tailing or base-line drift, a practical decision must be taken as to when to terminate the integration. Some work with which I am familiar found that experiments were apparently non-reproducible when processed by the method of moments because the tail made a significant, but not experimentally reproducible, contribution to the total area. When, however, the curves were fitted in the region near the peak, which is known with greater precision, the agreement was excellent.

UNDERHILL: We had no difficulty applying the technique to the adsorption of krypton. With a higher concentration of radon you may have been able to analyze accurately the tailing section of your breakthrough curves. We found with krypton that if too little is injected, the tail becomes difficult to analyze.

PARISH: It seems to me that this tailing effect may be a practical consideration in regeneration. Have you taken a look at that?

UNDERHILL: Spreading mechanisms, including those that cause tailing, are central to calculations of regeneration efficiency. There have been a number of theoretical calculations of the effect of tailing on regeneration, but to my knowledge, the actual measurements of this effect in regard to fission gas adsorption and desorption are not sufficiently accurate to permit accurate application of these theories.

PARISH: I would just like to clarify a point. This analysis would not apply to delay beds but only to batch type systems?

UNDERHILL: To regeneration systems, where you are heating and cooling.

JONAS: The methods of Rosen, Masamune and Smith, and Schneider and Smith, using statistical moments, are based on the inlet gas concentration being on the linear portion of the isotherm. However, we are sometimes concerned with challenge concentrations of nerve gas which are on the plateau of the isotherm. For these cases, the Wheeler type kinetic equation holds very well since it can pinpoint the time at which a very small concentration exits the bed. The generic type of sigmoidal curves obtained from complete breakthrough may not be able to accomplish this time pinpointing as well as the kinetic breakthrough equations.

UNDERHILL: Let me add one additional comment about the appropriateness of this type of analysis to the particular problem that it was assigned to. When you're dealing with offgases from a nuclear reactor, it can be shown that the releases are in the range of parts per million. There are, already, part per million concentrations in the air. Therefore, there will be isotopic exchange and the assumption of linearity works beautifully. There is no question about it for this particular case. For the case that you're dealing with, it sounds like the type of work that a mathematician would love to do. It's a very interesting problem.

A RADIOIODINE DETECTOR BASED ON LASER INDUCED FLUORESCENCE

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Abstract

A technique is described to measure airborne concentrations of $^{129}I_2$ in nuclear power generation and reprocessing plants. Due to its low specific activity, long half-life, and low energy decay products, radio-counting techniques for ^{129}I are not practical. A laser fluorescence technique based on coincidences between a $^3He-^{22}Ne$ laser and $^{129}I_2$ absorption lines is used and is shown to be sensitive to near 10^{-12} g/cm^3 of $^{129}I_2$ in a scrubbed system; at 1 atm of argon and 1 atm air the sensitivities are reduced by factors of 86 and 131.7 respectively. Possible interferences, measurements under flowing conditions, and ultimate sensitivities are discussed. An evaluation of the technique and extension to a portable, real time monitoring instrument for use in the field is given.

I. Introduction

Needs and Applications for Radioiodine Monitoring

Of the six major iodine isotopes produced in nuclear reactors, ^{129}I represents only about 1% of the main fission product iodine isotope yield.[1] Although this isotope has the lowest specific activity and the lowest energy decay products, after a few days of cooling outside the reactor the major iodine isotope present is ^{129}I, because the next longest-lived isotope ^{131}I has a decay half-life of 8.0 days. In view of the very long ^{129}I half-life of about 17 million years, new attention has been directed to its cumulative effects.[2,3] In spent fuel processing ^{129}I will have to be recovered and stored indefinitely because of its longevity. Because of the low specific activity, low energy decay products, and because ^{129}I is a minor iodine isotopic constituent in an active core, its detection by counting techniques is often slow and impractical.

Activated charcoal is the most widely used material employed for iodine removal, and it is also used as a means for decay storage. Because organic compounds of iodine are adsorbed less well than I_2 on activated charcoal substrates, in some applications charcoals are used which have been impregnated with substances which react chemically with I_2 and compounds of iodine or which undergo an isotopic exchange.[1] Among examples currently used are charcoals impregnated with KI (or other inorganic iodine compounds) in which the stable isotope of the impregnant iodine can undergo an exchange (or reaction) with the radioiodine. Note that such an exchange can release a stable iodine into the effluent.[1] The efficiency of charcoal filters is strongly dependent upon their environmental history, (particularly extended exposure to very high relative humidity)[4] and the desorption rate of iodine from the filters is strongly dependent upon temperature.[5] It appears that there exists a need to monitor and measure quantitatively in real time, iodine concentrations in several areas:

(a) as a continuous monitor to observe breakthrough behind critical filter facilities;

(b) as a testing and trouble shooting field measuring tool to test the integrity of in place filters;

(c) as a monitor of fairly high ^{129}I ambient concentrations in spent fuel reprocessing; and

(d) as a monitor to observe accidental large releases of radioiodine in the spent fuel reprocessing cycle.

Proposed Research

For the reasons outlined above, NRL in cooperation with DOE (Oak Ridge Operations Office) has contracted to design and laboratory test an instrument for the detection of low concentrations of $^{129}I_2$ in ambient atmospheres. The proposed instrument is to be based upon a laser induced fluorescence technique. In the design and evaluation of the proposed instrument the following characteristics were to be stressed:

(a) the specified final instrument must be easily portable and capable of use under field conditions;

(b) the instrument should be specific for ^{129}I;

(c) the specified instrument should be capable of making real time measures - preferably on flowing gas samples;

(d) the final field hardened instrument should be capable of continuous operation over extended periods of operation; and

(e) the instrument should be as sensitive as possible consistent with an economic appeal which would allow widespread use in the industry of the field instrument.

II. Experimental

Approach to Experimental Problem

A laser induced fluorescence technique was chosen for application to monitoring of I_2 concentrations. In this technique a laser photon of appropriate frequency impinging upon the sample is selectively absorbed by the iodine molecule placing it in a metastable excited electronic state. The excited iodine molecule can relax by collisional processes back to the ground state in which case it will not be detected, or it may relax by reemitting a photon (of longer wavelength) by a fluorescence mechanism. This fluorescence emission may be detected by a photoelectric detector. The resulting fluorescence signal, after appropriate corrections are made for competing collisional relaxation processes, collector efficiency, detector response characteristics, and other emissive interferences, can be used to determine the I_2 concentrations in a gas sample. Several problems which must be considered in the application of this technique to quantitative measurements are enumerated below:

(a) a laser excitation frequency must be chosen which corresponds to an optical resonance of the specific molecule to be detected;

(b) excitation frequencies must be selected which do not correspond to resonances of other species in the sample (i.e., other I_2 isotopes);

(c) evaluation must be made of all non-fluorescing deactivation pathways which the selected molecule may undergo;

(d) possible fluorescing interferences from other species must be accounted for; and

(e) allowance must be made for all possible molecular forms in which the atom to be detected may occur and appropriate corrections be made.

Spectroscopic Considerations

The I_2 molecule has a very characteristic absorption in the visible region of the spectrum. The major absorption features and the electronic transition assignment have been known for many years[6,7] for the red band system. The transition is a spin forbidden process $\tilde{B}\ (^3\Pi_{ou+} \leftarrow \tilde{X}\ (^1\Sigma_g^+)$ which is made relatively allowed by the heavy atom nature of the atoms involved. The visible band fluorescence of this system was first critically evaluated over 70 years ago.[8] Scores of studies of both absorption and emission have been carried out in the intervening years. Recently the absorption lines in this transition have been chosen to use as a new secondary wavelength standard by workers at the National Bureau of Standards. For this application it has been necessary to catalogue very precisely many of the absorption features of this spectrum. Hanes and Dahlstrom,[9] Wallard[10] and Hanes et al.,[11] have frequency stabilized a ^3He-^{20}Ne laser to hyperfine components in the absorption spectrum of $^{127}I_2$ at 633 nm and Knox and Pao[12] have frequency stabilized a ^3He-^{20}Ne laser to hyperfine components in the $^{129}I_2$ spectrum near 633 nm. More recently Schweitzer,[13] et al. have carried out similar work using a ^3He-^{22}Ne laser monitoring reasonances of $^{129}I_2$. It was shown in the latter work that the gain curve of the ^3He-^{22}Ne laser overlaps ∿20 hyperfine components in the $^{129}I_2$ spectrum, but does not have any interferences from absorption features of the more common isotope $^{127}I_2$.

For the above reasons the ^{2}He-^{22}Ne laser was chosen as the preferred excitation source for the laser induced fluorescence experiments on I_2.

Equipment Design

$^{129}I_2$ and ^{22}Ne Spectral Characteristics

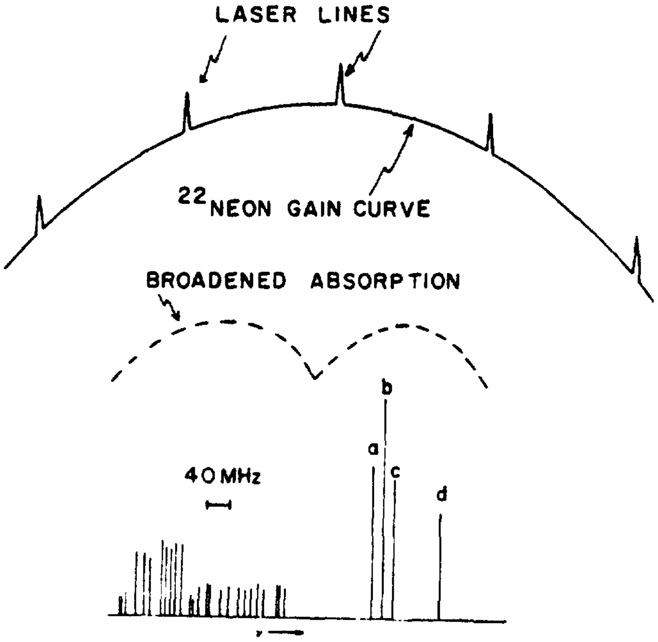

Fig. 1 — Spectroscopic characteristics of the $^{129}I_2$ spectrum and the ^{3}He-^{22}Ne laser. The line spectrum at the bottom is the hyperfine absorption spectrum of $^{129}I_2$ measured by Lamb Dip spectroscopy from Ref. 13. The dashed curve above this represents the Doppler and pressure broadened absorption of $^{129}I_2$ characteristic of ambient temperature and pressure conditions. The solid curve at the top schematically represents the ^{3}He-^{22}Ne laser gain curve while the spikes on this curve schematically represent five oscillating modes characteristic of the laser employed in this work.

In Figure 1 a portion of the spectrum of $^{129}I_2$ in the region of the ^{22}Ne gain curve is shown. These spectral lines are shown as measured by Lamb Dip spectroscopy and are not pressure or Doppler Broadened. The wavelength of the B feature is 6329.90Å. The B feature is separated from the A feature by ∿0.003Å. In experiments such as those conducted in this work the Doppler and pressure broadening of the features shown in Figure 1 will merge all these hyperfine components into an apparent continum absorption as represented schematically by the dashed curve immediately above the stick spectrum. A schematic of the gain curve of ^{22}Ne laser is shown immediately above the dashed curve as a solid line. A ^{22}Ne laser oscillating between two cavity mirrors can lase upon a selected frequency or frequencies anywhere on this gain curve. The actual operating characteristics (bandwidth, number of cavity modes operating and mode spacing) of an individual He-Ne laser will depend upon gas mix, discharge current and cavity length of the laser employed.

Specifications of ^{3}He-^{22}Ne Laser

The laser purchased for this is a basic Jodon Model HN-7 configured for TEM_{00} operation at 6328Å. A special fill of ^{22}Ne was specified for the laser. The power output of the laser upon arrival was 16.0 mwatt, a value which has held constant over several months of operation. The spectral characteristics of the laser were measured with a Coherent Optics Model 380 Interferometer. We find that there are five to six cavity modes oscillating at all times. The oscillation of these cavity modes with their characteristic 260 MHz cavity spacing is indicated schematically superimposed upon the laser gain curve shown in Figure 1. Since the Doppler width of the I_2 resonances is $\sim$200 MHz, any frequency jitter in the ^{22}Ne laser frequencies is not reflected in the absorption efficiency of the pseudo continuous absorption of $^{129}I_2$ across the whole ^{22}Ne laser gain curve.

Fluorescence Cells and Photomultiplier Detection

The fluorescence cells used for static measurements are constructed of quartz and are 1 inch cubes. The scattered laser light is rejected by combinations of corning glass long wavelength pass sharp cut filters and specially constructed dielectric blocking filters. The 6328Å laser light is rejected, and all fluorescence of $\lambda \gtrsim$ 6600Å is detected. The detector is an RCA 31000A 2" photocathode extended S-20 response photomultiplier. A block diagram of the breadboard detector is shown in Figure 2.

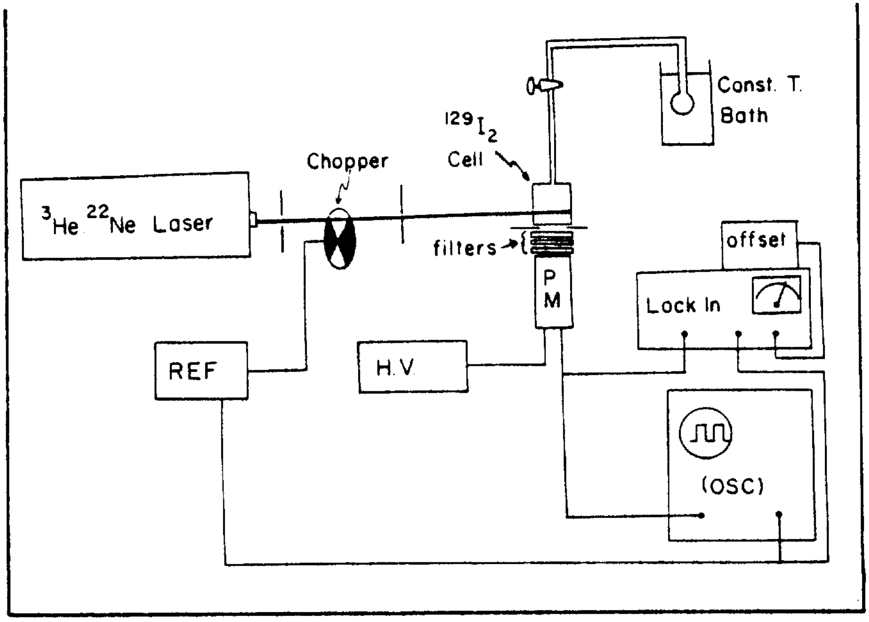

Fig. 2 — Schematic representation of the breadboard detector employed in this work

$^{129}I_2$ Samples and Pressure Control

In order to generate a set of working curves, it is necessary to make static measurements on known pressures of $^{129}I_2$. The $^{129}I_2$ samples were obtained commercially from ICN, Inc. in sealed ampules each containing 3 mg of $^{129}I_2$. The samples were introduced into the fluorescence cells on a vacuum line and then sealed off. The $^{129}I_2$ pressure is controlled in the static cells by means of constant temperature slush baths. I_2 vapor pressure curves as a function of temperature were taken from the International Critical Tables. Various constant temperature slush baths were employed to control the temperature between -55 and 0°C. In addition, various measured temperature baths were produced with ice-NaCl-H_2O mixtures. A Table of convenient slush baths with corresponding temperatures and I_2 pressures is shown in Table I.

Table I

Compounds	Slush Temperature	I_2 Pressure (mtorr)
H_2O (ice)	0°C	31
H_2O (ice) + NaCl	0°, -14°C	31 - 7.0
CCl_4	-22.5°C	2.6
Chlorobenzene	-47°C(-45.2°C)	0.13
Chloroform ($CHCl_3$)	-53°C	.035
N_2 (liquid)	-196°C	0

Fluorescence Signal Detection and Processing

Because of the ease of operation and availability of equipment, it was decided to measure fluorescence signals by means of lock-in amplifier detection. It should be possible to obtain equivalent results by photon counting techniques. The lock-in amplifier employed is a PAR Model HR-8 used with the appropriate chopper and chopper reference. Because of small, but finite, scattered laser light signals, we have found it convenient to employ a PAR Model 123 A.C. zero offset to null out the scattered laser light signal when measuring low level signals. Using this nulling device, one can easily zero out scattered laser light down to < 10 volts full scale thus extending the sensitivity by ∿ a factor of a hundred.

The photomultiplier signal is also monitored by an oscilloscope which is convenient for monitoring the signal level at relatively high I_2 pressures for purposes of monitoring photomultiplier dark current levels and for aligning the laser and fluorescence cells, etc.

Notes on Handling $^{129}I_2$ in Static Cells

During the course of this work we have noted a deterioration of fluorescence signals from our $^{129}I_2$ reference cells on several occasions. These problems were tracked down to a H_2O contamination problem. I_2 reference samples which have been exposed to a trace contamination of H_2O have much different vapor pressure characteristics than when completely dry. The introduction of one atmosphere of moist laboratory air is sufficient to form a surface layer coating over the I_2 samples which is visible to the eye. Resublimation of these samples does not allow one to recover the samples effectively. In all cases, contaminated samples of I_2 give significantly lower equilibrium vapor pressure of I_2 than do the pure samples. We have been able to introduce dry air into the fluorescence cells and subsequently reclaim the I_2 reference samples if one uses clean vacuum techniques and carefully handles the samples. I_2 samples for reference cell purposes are best prepared under dry high vacuum techniques and should be permanently sealed off.

III. RESULTS

Static Measurement

Single Component Gases

Using the detector design shown in Figure 2, $^{129}I_2$ fluorescence signals were measured from two different fluorescence cells for two separate samples of $^{129}I_2$ over many repetitions at various temperatures in cells containing only $^{129}I_2$. Apparent pressure equilibrium is obtained after ten minutes with a new temperature slush bath. Before and after each series of measurements the sample is frozen out at 77°K to check the background correction factor. The upper curve in Figure 3 shows a plot of fluorescence signal intensity as a function of $^{129}I_2$ pressure (and concentration). Measurements have been made over iodine concentrations between 5×10^{-7} and 4×10^{-10} g/cm^3. A good straight line signal response is obtained over this range. For the lower concentration measurements the ability to measure signals is not limited by fluorescence signal, but by the uncertainty in the known vapor pressure curves of I_2 as a function of temperature. The practical limits of sensitivity for fluorescence measurements are indicated by the dotted line extension of this curve. Since the signals follow a linear response curve, it is possible to measure in evacuated systems I_2 concentrations to near one picogram per cm^3. The working curve so obtained is in no way dependent upon a need to independently measure the absolute I_2 concentration by vapor pressure curves or other techniques below the 10^{-10} g/cm^3 level.

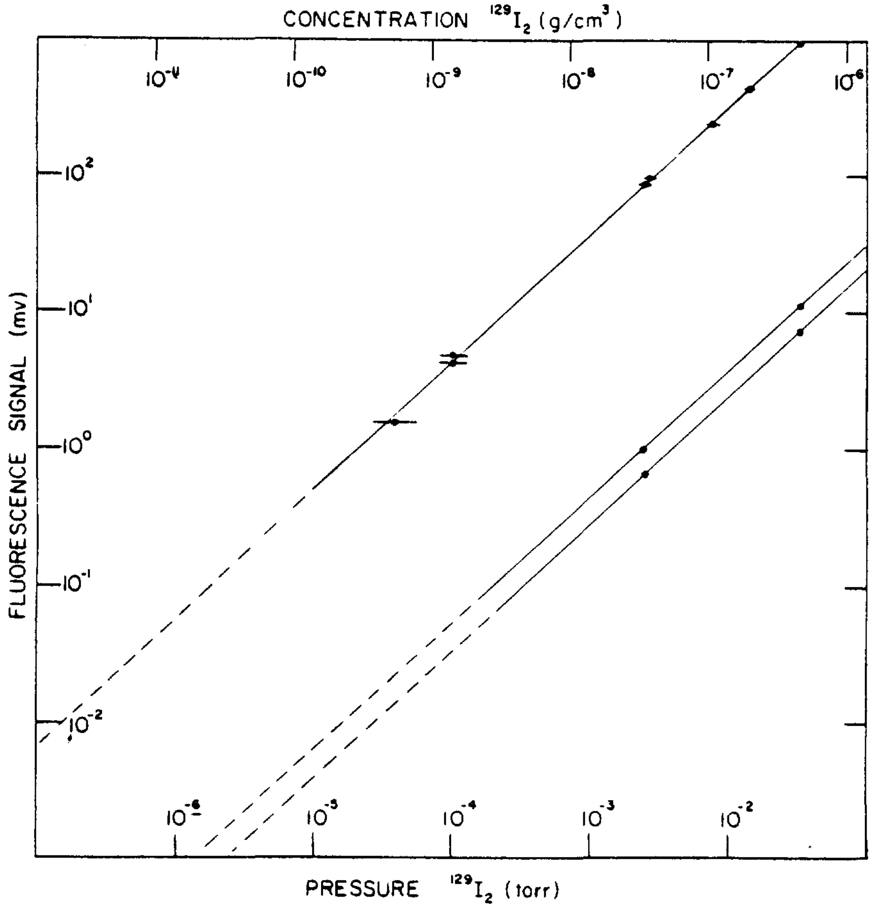

Fig. 3 — Working curves for $^{129}I_2$ fluorescence intensity as a function of pressure or concentration. The upper curve is measured for $^{129}I_2$ in evacuated static cells. The horizontal error bars represent the uncertainty in the I_2 pressure resulting from uncertainty in the absolute temperature-vapor pressure measurements for I_2. The vertical error bars are smaller than the size of the dots in the figure, i.e. ~±10μvolts. The center and lower curves are fluorescence signal response for $^{129}I_2$ in a static cell in the presence of 1 atm of argon and 1 atm of air respectively.

Multicomponent Gas Mixtures

Working fluorescence signal curves were also obtained for $^{129}I_2$ in the presence of a rare gas buffer and in the presence of air. Since bimolecular quenching of I_2 fluorescence is a well documented process, the loss of fluorescence signal in the presence of other gases is predictable.[14] However, since the quenching process is dependent upon the pressure, the collision partner, and the excitation wavelength, independent measurements are required for this new experimental setup. As it is anticipated that measurements will be made with this detection system only under either evacuated conditions or in the presence of one atmosphere of air or some other buffer gas, multicomponent gas mixtures were measured only at one atmosphere total pressure. The middle curve in Figure 3 shows a plot of I_2 fluorescence signal as a function of I_2 concentration in the presence of one atmosphere of Argon while the lower curve is in the presence of one atmosphere of air. In the presence of Argon the fluorescence signals are decreased by a factor of 86.0 while in air the signals are decreased by a factor of 131.7 over the respective values under evacuated conditions. The quenching cross sections for He, Ar, N_2, O_2 and CO_2 from Capelle and Broida[14] are given in Table II for excitation at 6234Å. The relative fluorescence efficiencies observed in this work are in essential agreement with what is expected based upon the relative quenching efficiencies of the gases in Table II. It is apparent that there is little advantage to be gained from scrubbing I_2 from the air and rediluting it in an Argon carrier gas. On the other hand, the data in Table II indicate that one might gain a factor of ten to twenty in increased sensitivity if one were to make measurements in one atmosphere of He gas as opposed to air.

Table II

Quenching Gas	Cross Sections (in 10^{-16} cm^2)
He	0.44 ± 0.26
Ar	5.62 ± 0.24
N_2	5.0 ± 0.6
O_2	7.8 ± 0.3
CO_2	22.1 ± 0.9

With the equipment as presently set up, it is feasible to measure $^{129}I_2$ concentrations at atmospheric pressure (air) to concentration levels at or below 10^{-10} g/cm^3. As this limit of sensitivity appears to be in the range required for applications of the proposed instrument, the specified equipment design will be built around measurements to be made in ambient air. This will simplify the design of the final instrument and will avoid the requirement for scrubbing I_2 and rediluting it into inert carrier gases. It will also avoid the possible pitfalls resulting from the tendency of I_2 to plate out and hang up on otherwise clean surfaces.

Measurements Under Flowing Conditions

At the present time we have not extended our measurements to flowing cells. To make laboratory measurements under these conditions will require:

(a) A much larger inventory of radioactive $^{129}I_2$ than used in the static experiments.

(b) glassware, gas metering, and flow measuring equipment;

(c) construction of flowing gas cells; and

(d) an independent means of measuring the $^{129}I_2$ effluent from our experiments.

Such measurements are to be desired for several reasons:

(a) the measurements will demonstrate that the technique can be transferred from measurements under static conditions to a performance level which will be required in the field;

(b) an independent crosscheck can be made between this technique and a wet chemical analysis technique currently used in our laboratories[5];

(c) the proposed monitor can be evaluated against radiocounting analysis; and

(d) laboratory procedures need to be developed for use in evaluating prototype fluorescence detection instruments to be acquired.

IV. EVALUATION OF THE LASER FLUORESCENCE TECHNIQUE

Applications and Limits of Sensitivity

Laboratory measurements with the breadboard detector clearly demonstrated that an $^{129}I_2$ monitor based upon the laser fluorescence technique will be a sensitive, practical and relatively inexpensive field monitoring instrument for $^{129}I_2$ measurements down to or below the one hundred picogram/cm^3 level. Such an instrument will be capable of real time instantaneous measurements or capable of operating in an integrating mode to give accumulation loads over a period of time. The components of the prototype instruments should be capable of continuous operation over many thousands of hours for use as a monitoring device. The field and prototype models will be essentially self-contained and readily portable for use in the field checking the integrity of power plant charcoal filters. The dynamic concentration range of the prototype and field instruments should be in excess of 10^5 and if required and specified will be capable of measurements over a range of 10^8, i.e., up to $\sim 10^{-2}$ g/cm^3 of $^{129}I_2$.

Interferences and Isotopic Scrambling

Measurements have been made with the breadboard detector for sensitivity using samples of $^{127}I_2$. The signals measured indicate that $^{127}I_2$ is detected with a sensitivity of less than 1% that of $^{129}I_2$. It is unclear at this point whether fluorescence signals from $^{127}I_2$ result from excitation by the plasma discharge light in the He-Ne laser or whether there exist very weak unmeasured $^{127}I_2$

resonances in the region of the laser gain curve. These determinations can be made if the need warrants it.

If a very large excess of $^{127}I_2$ over $^{129}I_2$ is present in the effluent gas to be measured, a significant portion of the ^{129}I present will be tied up in the mixed isomer molecule ^{127}I - ^{129}I. Our detection sensitivity for this molecule and other mixed isomer molecules is undetermined.

We are presently setting up the experimental apparatus to determine the effect of such isotopic scrambling. The tests will be conducted with known concentrations of the mixed isotopic species, and the importance of this scrambling will be assessed.

We are also concerned with interferences from other gaseous products of the fuel reprocessing cycle. At the present time, the only apparent interferent may be NO_2. NO_2 is known to absorb over the entire visible region and fluoresces strongly. However, if NO_2 fluorescence is determined to be a strong interferent, several steps may be taken to minimize its effect on $^{129}I_2$ measurements:

(a) the fluorescence may be blocked by a suitable combination of bandpass filters;

(b) the NO_2 may be scrubbed before $^{129}I_2$ measurements are taken;

(c) at pressures of ∿1 atmosphere the quenching of NO_2 fluorescence results in a reduction of the fluorescence quantum yield by $\sim 10^5$ and so may pose no problem.

In any case, we are currently investigating the effect of NO_2 on the measurement of $^{129}I_2$ concentration.

It has been pointed out that a portion of the iodine present, particularly downstream from charcoal filter beds, is in the form of alkyl iodides (CH_3I, C_2H_5I, etc.). The laser fluorescence technique developed herein is completely insensitive to ^{129}I in any organic form. Work underway at NRL[15] on a catalytic pyrolizer has shown the capability of conversion of organic iodides to molecular iodide. If such a device is required, its inclusion immediately prior to the gas intake of the laser fluorescence detector can be provided for. This instrument should also serve to strip I_2 adsorbed on the surface of any particulate matter in gas stream to be detected.

Specification of Prototype Instrument

At this point laboratory studies have made it possible to specify many of the desirable design features which should go into the construction of the prototypes for $^{129}I_2$ field monitors. A contract has been let for the procurement of a prototype instrument.

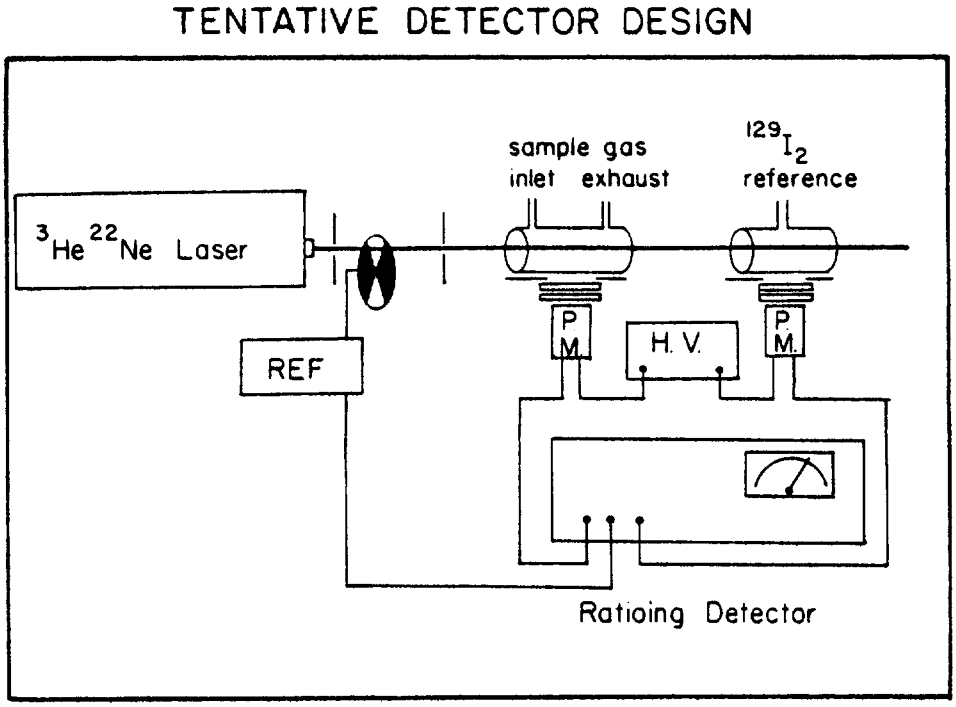

Fig. 4 — Schematic diagram of a proposed prototype iodine monitoring device. Explanations and possible changes are noted in the text.

A schematic block diagram of the proposed prototype detector is shown in Figure 4. The prototype instrument contains a reference sample of $^{129}I_2$ which will be used to ratio against the unknown samples to be measured. In this way, small variations in the laser power or alignment of components will not effect the accuracy of measurements. The fluorescence is monitored by lock-in detection, and the mechanical chopper has been replaced by a "Tuning Fork" chopper due to space limitations. The final design instrument contains microprocessing circuitry to allow automatic sensitivity changes to be made and to supply digital readout and integrated sample loadings. The prototype instrument also allows for some internal reference measurements (i.e., laser power, absolute reference signal intensity, background signal nulling, etc.) to aid in field adjustment and trouble shooting. The prototype system is of a ruggedized and modular design which will allow for ease of portability and operation. The only external connection which is required is a standard 110V ac power outlet.

Other Design Options

It should be noted that several options are feasible for incorporation into a laser fluorescence iodine monitor. The present studies have been built around an assumed need to specifically measure $^{129}I_2$. By changing the specifications of the excitation laser it is possible to build a detector which will detect essentially the sum of all isotopic I_2 species. Such a detector would not be specific for $^{129}I_2$, but if used in conjunction with the detector specified in this work, it would be possible to detect both $^{129}I_2$ and total I_2.

If a requirement becomes apparent to measure much lower concentrations of $^{129}I_2$ than is feasible with the present detector, it should be possible to extend the limits of sensitivity of the proposed instrument by using I_2 scrubbing techniques for larger samples of air followed by measurement of $^{129}I_2$ in a carrier flow of helium. It would likely be possible to extend the sensitivity limits by several factors of 10 for the proposed instrument.

REFERENCES

1. "Environmental Aspects of Nuclear Power"
   G. G. Eicholz
   Ann Arbor Science, Inc., 1976.

2. "Control of Iodine in the Nuclear Industry"
   Technical Reports, Series No. 148 (Vienna: International Atomic Energy Agency, 1973).

3. "Environmental Radiation Dose Commitment: An Application to the Nuclear Power Industry"
   Report EPA-520/4-73-002, U. S. Environmental Protection Agency, Washington, DC, 1974.

4. "The Effect of Exposure Times in the Prehumidification of Impregnated Charcoals"
   V. R. Deitz and C. H. Blachly
   Proceedings of the 14 ERDA Air Cleaning Conference.

5. "Iodine Emission During a Programmed Heating of Impregnated Charcoals in Carrier Air"
   V. R. Deitz and J. B. Romans
   Proc. of the 14th ERDA Air Cleaning Conference.

6. "Spectra of Diatomic Molecules"
   G. Herzberg
   Van Nostrand Reinhold Company, New York, 1950.

7. "Photochemistry"
   J. G. Calvert and J. N. Pitts
   Wiley, New York, 1966.

8. R. W. Wood
   Phil. Mag., <u>12</u>, 499 (1906).

9. "Iodine Hyperfine Structure Observed in Saturated Absorption at 633 nm"
   G. R. Hanes and C. E. Dahlstrom
   Appl. Phys. Lett. <u>14</u>, 362 (1969).

REFERENCES (Continued)

10. "Frequency Stabilization of the Helium-neon Laser by Saturated Absorption in Iodine Vapor"
A. J. Wallard
J. Phys. E-5, 926 (1972).

11. "Stability, Reproducibility and Absolute Wavelength of a 633 nm He-Ne Laser Stabilized to an Iodine Hyperfine Component"
G. R. Hanes, K. M. Baird, and J. DeRemigis
Appl. Opt. 12, 1600 (1973).

12. "Absorption Profiles and Inverted Lamb Dips of I_2 Vapor at 633 nm as Studied with a He-Ne Laser"
J. D. Knox and Y. H. Pao
Appl. Phys. Lett. 18, 360 (1971).

13. "Description, Performance, and Wavelengths of Iodine Stabilized Lasers"
W. G. Schweitzer, Jr., E. G. Kessler, Jr., D. R. Deslatts, H. P. Layer, and J. R. Whetstone
Appl. Optics 12, 2927 (1973).

14. For instance, see
J. I. Steinfeld
J. Chem. Phys. 44, 2740 (1966) and
G. A. Capelle and H. P. Broida
J. Chem. Phys. 58, 4212 (1973).

15. V. R. Deitz
Unpublished results.

DISCUSSION

DUGGAN: Two questions: can you give us an idea of the approximate cost of this instrument, and also what specific applications do you see for it?

McDONALD: With respect to cost, the components for the instrument are under $3,000 off the shelf. The prototypes cost about $40,000. We have a guarantee from the supplier to make more for under $20,000. I don't know what they will finally cost if they are produced in bulk. Initially, it will be tested in the field stack to measure effluent wastes.

PARKER: There's a possibility this instrument could be recommended for use in reprocessing offgas streams for measurement of iodine. Have you taken a look at all the possible constituents that might be in dissolver offgas that could interfere? I am specifically thinking of chlorine compounds.

McDONALD: I have talked to many people about what substances might be present in offgas effluents. The only molecule I can identify that absorbs at 6328 Ångstroms is NO_2. There are no chlorides or other halogens that are close to that absorption region. Molecular bromine might be present, but it will be several orders of magnitude below iodine.

HULL: This is a comment, rather than a question. This is a very elegant paper; I am very impressed with what you have done. But it seems to me, as the previous questioner has suggested, that if the device described has any application, it is to reprocessing facilities. Your paper mentions power reactors, for which, it seems to me, the cost would be all out of proportion to the value of the measurements. It seems to me that the driving force for this, as well as for the removal of ^{129}I from offgas streams, which was described yesterday, is EPA's release standard in 40CFR190. I suggest that even if one is a devout believer in the linear hypothesis, that the cost per health effect averted from the application of this standard is preposterous, especially when the cost of the development and application of your instrument is added to the costs EPA identified in their cost-benefit analysis. I feel that we should try to keep in mind the reasonableness of what we are trying to accomplish, as well as the challenge to our technical abilities.

McDONALD: The use of detectors such as I have described by the nuclear power industry involves economic, political, and emotional decisions in which I am not, and do not wish to be, involved. Our task was to develop this detector because DOE believed that it was in their best interests to determine its feasibility. The modest detector which we have designed is likely not nearly sensitive enough to measure ^{129}I concentrations at power facilities at the present time. I do feel, however, that DOE and other facilities are correct in being far-sighted enough to invest in R & D for instrumentation not required by current effluent standards but which may be vitally needed in 5-10 years. The development time for such diagnostics strongly mitigates against their development after the fact.

GIBSON: In the figure with the schematic diagram, you show the laser beam first absorbed by the sample cell and then passing on to the reference cell. Could you explain why this is done instead of having the beam split for the sample and reference cells?

McDONALD: Any conceivable $^{129}I_2$ concentration in the sample cell will absorb only a negligible fraction of the HeNe laser light. More important, if there were a high concentration of noniodine absorbing species such as NO_2, or scatters, the light subsequently impinging on the reference cell will be reduced in intensity as it was in the sample cell, thus giving a ratio signal which is representative of the light available to each cell.

AN INORGANIC RADIOIODINE ADSORBER WITH LOW NOBLE GAS RETENTION*

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Abstract

A silver loaded silica gel was developed as an adsorber for air monitoring subsequent to a release from containment power reactor accident. Requirements of high efficiency for known radioiodine species under wide ambient conditions of humidity and temperature and low noble gas adsorption efficiency are satisfied by the material.

Silver loadings from 2 to 24% by adsorber weight have been tested against organic radioiodine, hypoiodous acid, elemental radioiodine, and noble fission gases. Relative humidity was varied between 5 and 99%, and stay times of .11, .073, and .055 seconds were used.

Silver loading requirements depend on sampling duration and relative humidity. Environmental monitoring, to define safe living areas, requires about 25 ft^3 of air be sampled and analyzed by the proposed system of an air mover, an adsorber, and a civil defense readout instrument. A silica gel adsorber can be used with a 4% silver loading for an efficiency of better than 93% with a .11 second stay time, and for all ambient conditions tested. Similar tests using 4% silver loaded 13X molecular sieve or about 60% silver zeolite yielded lower efficiencies.

Xenon adsorption was $<5 \times 10^{-3}\%$ at $55^{\circ}C$ with no post-release flushing. This value was about 1/20 of the value for charcoal under the same conditions.

A silver loading apparatus was developed to easily process ∿5 Kg of silica gel per day. The method involves prehumidification, boiling under high vacuum, oven drying, sieving, and finally packaging.

I. Introduction

Radioactivity releases from power reactor containments under accident conditions are expected to be extensive and will spread over a large geographic area. Concentrations of pertinent radioisotopes can be predicted mathematically, but with an uncertainty that will increase with distance from the reactor. Inhalation exposure will depend significantly on atmospheric stability and vertical cloud dispersion. Evacuation of personnel will be governed by thyroid dose commitments and whole body exposures. The lack of reliable air concentration predictions and the need to define evacuation boundaries combine to require air concentration measurements be made in the environment.

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* Research performed at Brookhaven National Laboratory under contract with the U.S. Nuclear Regulatory Commission.

The probability of a reactor accident was estimated(1) to range from 1×10^{-4} to 5×10^{-7} per reactor year. The less probable, and more damaging, accidents would have U.S. probability of about 2×10^{-3} per hundred power reactors life times of 20 years assumed per reactor. The small aggregate accident probability and large geographic area potentially envolved lead to a desirable solution of a significant number of inexpensive air sampling apparatus which can be stored indefinitely.

Costly measurement methods using gamma analysis can be avoided by developing a sample specifically for iodine, thereby permitting any beta or gamma detector to be used for measurement. Particulate fission products include dozens of noniodine radionuclides. Use of a prefilter(2) before the adsorber bed separates the activity into gaseous and particulate fractions, and allows a determination of gaseous radioiodine.

Adsorption of fission gases relative to iodine can be reduced by using an appropriate inorganic adsorber. Several commercial inorganic adsorbers were tested, but were too expensive or inefficient for the organic or hypoiodous acid forms of iodine. A silver impregnated silica gel adsorber was developed that had over 90% efficiency for collection of radioiodine for sampling times of several minutes. The material provided corresponding Xenon efficiencies of less than .04% at temperatures above 7°C.

The properties of the silver loaded silica gel adsorber were used in conjunction with vacuum cleaner air movers and Civil Defense GM survey meters to make possible economical air sampling and assessment following release from containment accidents.

Adsorber Loading Method

Solutions of silver nitrate were used to impregnate molecular sieve and silica gel. Since cost is an important factor, silver loadings of less than 8% by weight were extensively studied. Loadings of >20% by weight were easily accomplished with about the same loading efficiency.

The loading method(3) started with prehumidification of factory dry silica gel(4) material. Keller(5) found that dry zeolite pore structures would fracture with addition of liquid water. Prehumidification with moist air allowed the heat of adsorption to be controlled to prevent fracturing.

Kilogram quantities of dry silica gel sieved to >30 mesh were prehumidified by 4 liters per minute of lab air bubbled through distilled water maintained at 60°C. The process required about 18 hours, overnight, for complete saturation. The wet gel was slurried with an aqueous solution of the silver salt, and boiled under vacuum for about 2.5 hours. After boiling, the material was transferred to drying trays and heated in an air-circulated oven at 105°C for 24 hours. The dried adsorber was resieved and the >30 mesh fraction was stored in clean gallon sized metal paint cans ready for use.

Loading efficiency was studied(6) by measuring the quantity of silver on the absorber surface. This was accomplished by tumbling the silica gel pellets for 4 to 76 hours to allow self abrasion to remove the surface layer. Three fractions, which proved to be time independent, were developed by sieving, using 30, and 80 mesh screens. Nearly all of the material was retained on the 30 mesh screen, and broken pellets, corners and sharp edges were trapped on the 80 mesh screen. Particles smaller than 80 mesh were assumed to represent the silica gel pellet surface and constituted less than 0.2 by weight of the total. Analysis for silver indicated that about .2 to .4% of the silver was on the <80 mesh fraction for 4 to 24% silver loaded silica gel stock. Clearly the pore loading efficiency was better than 99.6% since some part of the <80 mesh fraction consisted of pellet fragments.

A water leaching experiment(6) was conducted with prehumidified 4% silver loaded silica gel. A silver recovery efficiency of 88% ± 3 indicated that the impregnated silver was in the nitrate form since the oxides and nearly all silver salts are not very soluble. Further, the silver nitrate appeared to be weakly held by the silica gel.

CH_3I Generator

A fission iodine generator was constructed(7) using <3 micron thick ^{235}U alloy foil positioned around a 10^8 neutron/sec AmBe source. Approximately $3m^2$ of foil, containing 16.2 gm of ^{235}U, was assembled in a 12 cm wide strip. The foil was positioned on a continuous strip of .15 cm thick by 12 cm wide open mesh polyethylene-polypropylene and wound on a form around the neutron source. The resulting 22 cm spool was placed in an aluminum pressure tank and all voids, except in the mesh, were filled with paraffin. The assembly provided an average thermal neutron fluence of about 7×10^4 cm^{-2} sec^{-1} along the outer end of the spool.

The pressure chamber, filled with argon gas, 180 psig, containing .3% CH_4, was used for iodine exchange reactions. Approximately 5.4% of the ^{135}I theoretical yield was measured, corresponding to a $CH_3{}^{135}I$ activity of 0.16 microcuries. A method outlined by Keller(8) was used to test and confirm the chemical species. The species differentiator indicated the discharged mixture consisted of 95 to 99% organic iodine and 1 to 5% HOI. Since both oxygen and water are absent in the generator, the HOI indication was probably due to HI.

The generating method used had the advantage of also producing all of the fission gases; so that tests were made with noble gases as well as organic radioiodine.

HOI Generator

The HOI generator was patterned after Kabet(9,10,11). Carrier free ^{131}I was added to a 3×10^{-5} M KIO_3 water solution. The pH was adjusted to 2.0 with H_2SO_4, and the mix was placed in a fritted bubbler. Helium gas was used to strip HOI from the solution. Demisting was accomplished with a Gelman glass fiber filter. A second helium stream of about the same flow rate, .04 CFH, was used to dry the combined stream prior to passing through a stack of six 40 mesh copper screens described by Barry(12). The screens were routinely pickled in HI, washed in distilled water, and air dried immediately before use.

The Keller species differentiator indicated that about 95% of the iodine was adsorbed on the p-iodaphenol impregnated alumina adsorber. The remaining 5% was trapped on the TEDA impregnated charcoal backup filters.

I_2 Generator

Convenience and economy of multiple use prompted the conversion of the easily generated and controlled HOI into I_2. This required the reduction of I^+ by oxidation of Cr_2O_3 at 510°C.

The HOI - He generator stream was passed through a 1 cm diameter quartz tube mounted in a tube furnace. Glass wool was used to center the C_2O_3 in the furnace. Nichrome heating wire was wound around the discharge end of the quartz tube and the teflon tubing used to transfer the I_2 to the air stream leading to the test adsorber

Table I. CH_3I Adsorption Tests

Material	Impregnant W/O	Mesh U.S.	Relative Humidity %	Temp. °C	Pre-Run Minutes	Run Minutes	Stay Time Seconds	Flush Minutes	Efficiency
Silica Gel	0	6x16	45	41	-	23	.11	-	.01
Silica Gel	0		84	40	-	25	.11	-	.003
Silica Gel	2% Ag	6x16	17	66	-	23	.11	-	.99+
Silica Gel	2% Ag		80	41	-	26.5	.11	-	.75
Silica Gel	3.5% Ag	6x16	17	66	-	23	.11	-	.99+
Silica Gel	4% Ag	6x16	6	47	-	8	.08	-	.99+
Silica Gel	4% Ag		7	49	-	8	.05	-	.98
	4% Ag		36	44	-	8	.08	-	.93
	4% Ag		35	45	-	8	.05	-	.89
	4% Ag		67	42	-	8	.11	-	.98
	4% Ag		67	42	-	8	.08	-	.94
	4% Ag		86	40	-	13	.11	2	.79
	4% Ag		88	40	-	24	.11	-	.94
	4% Ag		90	40	-	24	.11	-	.85
	4% Ag		97	42	-	8	.11	-	.93
	4% Ag		96	42	-	8	.05	-	.92

(cont'd)

Table I. continued

Material	Impregnant W/O	Mesh U.S.	Relative Humidity %	Temp. ^{o}C	Pre-Run Minutes	Run Minutes	Stay Time Seconds	Flush Minutes	Efficiency
Silica Gel	4% Ag		98.5	34	-	8	.05	-	.81
Silica Gel	6% Ag	6x16	98	34	-	8	.05	-	.96
Silica Gel	8% Ag	6x16	1	110	2	22	.11	-	.99+
	8% Ag		8	28	-	8	.05	-	.99+
	8% Ag		17	71	-	27	.11	-	.99+
	8% Ag		22	35	-	25	.11	-	.99+
	8% Ag		36	48	-	8	.11	-	.99+
	8% Ag		36	48	-	8	.08	-	.98
	8% Ag		35	48	-	8	.05	-	.97
	8% Ag		72	45	-	8	.08	-	.96
	8% Ag		62	48	-	8	.05	-	.93
	8% Ag		85	37	-	23	.11	-	.97
	8% Ag		85	38	-	13	.11	2	.94
	8% Ag		92	37	40	24	.11	-	.37
	8% Ag		97.5	40	-	8	.11	-	.97
	8% Ag	6x16	96	39	-	8	.08	-	.98

(cont'd)

Table I. continued

Material	Impregnant W/O	Mesh U.S.	Relative Humidity %	Temp. °C	Pre-Run Minutes	Run Minutes	Stay Time Seconds	Flush Minutes	Efficiency
Zeolite	~60% Ag	20x40	98	34	-	8	.05	-	.81
Zeolite	~60% Ag		98	34	~40	27	.08	-	.82
Zeolite	~60% Ag		98	35	~40	28	.034	-	.48
13X Mole Sieve	4% Ag	8x12	99	32	-	8	.05	-	.06
Char. G215	(R-51)AO		88	36	-	9	.04	-	.75
Char. G618	TEDA	18x30	91	32	~ 1	8	.113	11@110°C	.95
	TEDA		95	33	~ 1	8	.106	11@110°C	.96
	TEDA		75	35	~ 1	6	.06	11@110°C	.87
Char. W-337	None	8x16	67	45	24	8	.44	8	.99
	None		95	33	120	8	.44	10	.97
	None		96	34	70	8	.05	10	.26
Char. BC845	TEDA	14x30	97	33	-	8	.05	-	.99+
Char. BC540	KI_3	14x30	97	40	-	8	.05	-	.88
MSA #2133	Char.	Cloth	44	35	-	8	.8CFM	-	~.01

Table II. $HO^{131}I$ Adsorption Tests

Material	Impregnant W/O	Mesh U.S.	Relative Humidity %	Temp. °C	Pre-Run Minutes	Run Minutes	Stay Time Seconds	Flush Minutes	Efficiency
Silica Gel	0	6x16	<10	31	-	28	.11	-	.82
	0		85	42	-	26	.11	-	.51
	0		88	40	-	26	.11	-	.31
Silica Gel	4% Ag	6x16	<10	33	-	26	.11	-	.93
	3.7% Ag	6x16	13	41	-	8	.11	-	.99+
	3.7% Ag		12	43	-	8	.08	-	.99+
	3.7% Ag		13	43	-	8	.05	-	.99
	4.0% Ag		35	35	-	8	.05	-	.99+
	4.0% Ag		45	36	-	8	.11	-	.97
	4.0% Ag		65	40	-	8	.05	-	.97
	4.0% Ag		75	41	-	8	.11	-	.99+
	4.0% Ag		85	40	-	26	.11	-	.71
	4.0% Ag		86	42	-	28	.11	-	.81
	4.0% Ag		95	41	-	30	.11	-	.76
	4.0% Ag		97	42	-	8	.11	-	.99+
	4.0% Ag		97	42	-	8	.08	-	.98
	4.0% Ag		97	43	-	8	.05	-	.74

(cont'd)

Table II. continued

Material	Impregnant W/O	Mesh U.S.	Relative Humidity %	Temp. °C	Pre-Run Minutes	Run Minutes	Stay Time Seconds	Flush Minutes	Efficiency
Silica Gel	4.0% Ag		~100	40	-	16	.11	14	.63
Silica Gel	8.0% Ag	6x16	5	51	-	8	.08	-	.99
	8.0% Ag		5	52	-	8	.05	-	.98
	8.0% Ag		40	37	-	8	.11	-	.99+
	8.0% Ag		50	38	-	8	.05	-	.79
	8.0% Ag		63	40	-	8	.11	-	.99+
	8.0% Ag		68	37	-	8	.05	-	.98
	8.0% Ag		86	37	-	28	.11	-	.71
	8.0% Ag		96	40	-	8	.11	-	.99+
	8.0% Ag		96	40	-	8	.08	-	.99
	8.0% Ag		98	39	-	8	.05	-	.92
Zeolite	~60% Ag	~20x40	~100	39	-	30	.11	-	.26
13X Mole Sieve	4% Ag		75	40	-	26	.11	-	.18
Char. W-337	0	8x16	71	45	15	8	.44	8	.99+
	0		96	39	15	8	.44	8	.99+
	0		98	35	40	8	.05	10	.66

(cont'd)

Table II. continued

Material	Impregnant W/O	Mesh U.S.	Relative Humidity %	Temp. °C	Pre-Run Minutes	Run Minutes	Stay Time Seconds	Flush Minutes	Efficiency
BC-845	TEDA	14x30	7	52	-	8	.05	-	.99
	TEDA		96	42	-	8	.11	-	.99+
	TEDA		95	43	-	8	.08	-	.99+
	TEDA		95	42	-	8	.05	-	.99
Char. BS-540	KI_3	14x30	9	49	-	8	.05	-	.99
	KI_3		97	40	-	8	.11	-	.99+
	KI_3		97	40	-	8	.08	-	.99+
	KI_3		96	40	-	8	.05	-	.99+
MSA-2133	Char.	Cloth	~100	38	-	15	3.8CFM	-	<.01

chamber. A minimum transfer line temperature of 100°C was maintained with an average temperature of >160°C.

A modified Keller species differentiator was used to analyze the I_2 discharge stream. The elemental iodine fraction was measured with a bank of 6 Barry(12) screens replacing the standard cadmium iodide loaded chromasorb. Results indicated that 18% of the iodine was on the Gelman glass filter, followed by 73% on the screens, 2% on the HOI adsorber, and finally by 7% on the TEDA impregnated charcoal. The 18% trapped by the glass filter was probably due to adsorption rather than particulate filtration. In any event, at least 91% of the total was elemental iodine.

Results

Attempts were made to summarize the results graphically. However, the number of parameters were too extensive requiring a tabulation of important variables. Some of the parameters may require specification. Pre-run, run and flush times refers to the number of minutes that the temperature and humidity controlled air passes through the trial adsorber. Test CH_3I, HOI, I_2, or Xe were released during the run stage. Flow conditions were set by the stay time defined as the quotient of adsorber bed volume and volume flow rate.

In general the data follow increasing silver impregnation from 0 to 8%, decreasing stay time, and increasing relative humidity. Certain other inorganic adsorbers results are next with charcoal and a cloth filter material completing the list.

Adsorber criteria(7) dominated the testing scheme. In general the adsorber material had to be highly efficient, better than 90%, for any known species of iodine under all expected conditions of temperature and humidity. Sampling time was changed in mid-experiment from a maximum of 15 minutes to 5; so that two sampling times appear in the data. Finally the adsorber must be at least 2 orders of magnitude less efficient for noble gases than iodine.

Table I summarizes the CH_3I results. The unimpregnated silica gel is inefficient for CH_3I adsorption. For high humidity and a stay time of 0.11 seconds, 4% silver loaded silica gel had an adsorption efficiency of 93% for an 8 minutes sampling time. Increasing the silver content increased the efficiency; but was not considered to be cost effective.

The commercial silver zeolite had a surprisingly low efficiency considering the >60% silver loading and small particle size.

Charcoal impregnated with TEDA is more efficient than 4% Ag - silica gel. However, high noble gas adsorption effiency of several percent, Table IV, precluded its use.

HOI results are presented on Table II. It is interesting to note that HOH and HOI have one polar end in common. Hydrophilic adsorbers, such as silica gel, should be efficient for HOI, and this was confirmed with silica gel. Increasing silver impregnation tends to increase adsorption efficiency, but again 4% Ag - silica gel is adequate.

Silver zeolite had a poor efficiency of 26%. Addition of a 30 minute equilibration run under test conditions of temperature, humidity, and flow rate apparently saturated the zeolite with water thereby reducing efficiency. The same effect was expected and noticed during the longer runs with silica gel.

The charcoal HOI results were similar to the organic iodine test. All of the charcoals were highly efficient. Impregnation doesn't appear to be as important for HOI as for CH_3I.

As expected the elemental iodine results, Table III, are uniformly good. The highly reactive atomic and molecular iodine is attracted by any surface cooler than the sublimation temperature such as the unimpregnated silica gel.

The tests reflecting the Xenon results were more involved. A mixture of noble gases and organic iodines from the fission generator was split into two flow rate monitored and controlled streams. Room temperature, silver zeolite filters were used in each leg to quantatatively trap the iodines. One of the streams was sent to an air duct leading to the test chamber, and the other to two sequential charcoal adsorbers maintained at dry ice temperatures.

Ge(Li) analysis of the 250 keV ^{135}Xe line indicated that all of the cold leg Xenon, >99%, was trapped on the zeolite and first cold charcoal adsorber. Analysis of the radioiodine activities in both legs provided reliable flow fractions between the two legs to supplement flow meter results.

Xenon results, Table IV, indicate that silica gel is about .09 ÷ .0004 ~200 less efficient than TEDA loaded charcoal at about 10°C. The charcoal results are comparable to earlier work shown in Figure 1. The two BC 845 charcoal results fall slightly below the results obtained independently by Seigworth(13) and Collins(14).

Ratios of Xe to I counting rates expected for perfect adsorbers were calculated(2) for the nine pressurized water and boiling water reactor accidents postulated in WASH 1400(1). Selection of 4% Ag - silica gel would allow clear iodine detection in all but the BWR 5 case. At 7°C ambient air temperature, the iodine concentration would be overestimated by a factor of 2.7 for 2 hours total decay and 7.5 for 24 hours. Since the average temperature is >7°C and the adsorber bed temperature is normally appreciable due to water adsorption the overestimation will be largely reduced. For typical conditions of 20°C and 50% RH the air leaving the bed was measured to 20°C higher than the entering air. This would reduce the overestimate by a factor of 3 to 5. Further the magnitude of the radioactive release for the BWR 5 case is the smallest of the cases considered, and would result in a total iodine release of only about 2 curies. This would lead to a very small iodine exposure problem.

The ideal adsorber for radioiodine monitoring subsequent to a release from containment accident should have the following properties:

a. The adsorber should be highly efficient for all species of iodine expected in the environment.

b. Noble gas adsorption efficiency must be at least two orders of magnitude smaller than the iodine.

c. Long term storage should not degrade the adsorber.

d. The adsorber must be economical as hundreds of kilograms are required.

All of criteria are satisfied by 4% silver loaded silica gel in a system requiring a sampling time of several minutes and a .11 stay time.

Table III. $^{131}I_2$ Adsorption Tests

Material	Impregnant W/O	Mesh U.S.	Relative Humidity %	Temp °C	Pre-Run Minutes	Run Minutes	Stay Time Seconds	Flush Minutes	Efficiency
Silica Gel	0	6x16	97	37	0	8	.05	-	.92
Silica Gel	4% Ag	6x16	8	46	-	8	.06	-	.99+
			37	36	-	8	.06	-	.99+
			66	36	-	8	.06	-	.99+
			95	34	-	8	.06	-	.99+
			98	36	-	8	.05	-	.98
Silica Gel	8% Ag	6x16	98	35	30	10	.05	-	.94

Table IV. ^{135}Xe Adsorption Tests

Material	Impregnant W/O	Mesh U.S.	Relative Humidity %	Inlet Temp. °C	Outlet Temp. °C	Run Time Minutes	Stay Time Seconds	Efficiency
Silica Gel	None	6x16	45	39	45	23	.11	$3x10^{-5}$
Silica Gel	4% Ag	6x16	75	39	59	25	.11	$5x10^{-5}$
Silica Gel	0	6x16	84	40	61	25	.11	$4x10^{-5}$
Silica Gel	4% Ag	6x16	34	7	12	10.5	.11	$4x10^{-4}$
Char. G618	TEDA	18x30		125	119	18	.11	$1x10^{-3}$
Char. BC845	TEDA	14x30	34	12	12	10.5	.006	$5x10^{-3}$
						Normal to	.11	$9x10^{-2}$

Table V. Xenon to Iodine Shielded DCV 700 Response for Various WASH 1400 Containment Releases

	Xe/I Decay Time	
	2 hours	24 hours
PWR 1	.04	.10
2	.04	.10
3	.11	.30
4	.18	.51
5	.25	.71
6	2.97	8.38
7	4.17	11.70
8	.53	1.50
9	.78	2.20
BWR 1	.07	.19
2	.03	.09
3	.26	.74
4	11.10	31.20
5	6700.00	18900.00

Xe includes 133, 135, 138

I includes 131, 132, 133, 134, 135

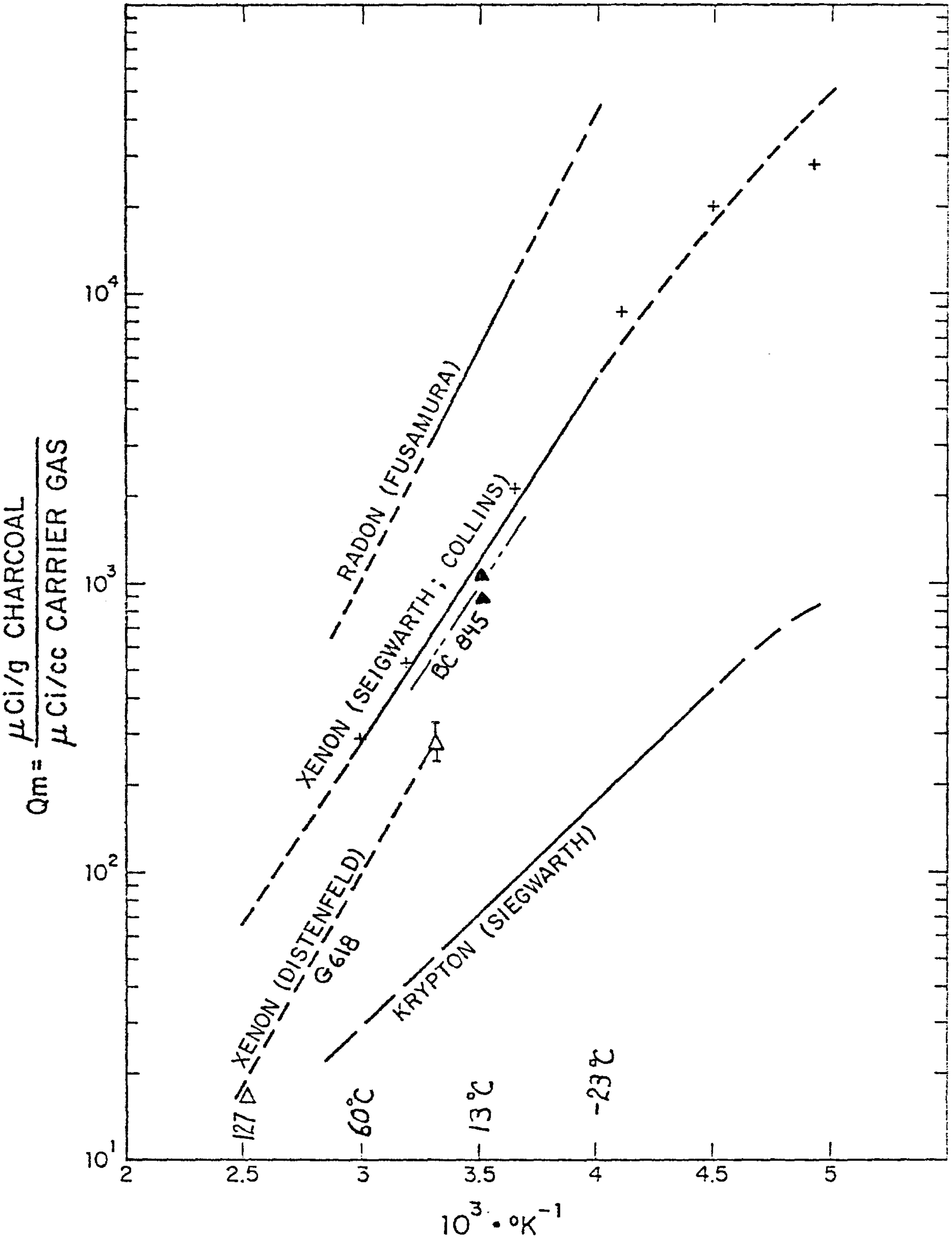

Figure 1. Temperature dependence on noble gas adsorption on charcoal.

References

1. U. S. Nuclear Regulatory Commission, "Reactor safety study" WASH 1400, App. VI, October 1975.
2. Distenfeld, C. H., Klemish, J. R., "Monitoring of radioiodine from containment accidents", BNL 23112, July 1977.
3. Distenfeld, C. H., Klemish, J. R., "Composition and method of collecting radioiodine", BNL Patent Application, S-47, 491, 1978.
4. Davidson Chemical Division, W. R., Grace Company, Charles & Baltimore Streets, Baltimore, Maryland 21202.
5. Keller, J., Private Communication, Allied Chemical Corporation, Idaho Falls, Idaho Falls 83401.
6. Agnew, B., "Analysis of silver on the surface of silver impregnated silica gel", Results from the BNL Semester Program, Spring 1978.
7. Distenfeld, C. H., Klemish, J. R., "High efficiency mixed species radioiodine air sampling, readout and dose assessment system", BNL 21541, May 1976.
8. Keller, J. H., et.al., "An evaluation of materials and techniques used for monitoring airborne radioiodine species", 12th Air Cleaning Conf., p. 322.
9. Kabet, M. J., "Testing and evaluation of absorbers for gaseous penetrative forms of radioiodine", 13th Air Cleaning Conf., p. 765.
10. Kabot, M. J., "Selective sampling of hypoiodous acid", 14th Air Cleaning Conf., p. 1.
11. Kabot, M. J., Private Communication, Ontario Hydro, Pickering Generating Station, Box 160, Pickering, Ontario, Canada.
12. Barry, P. J., "Sampling for airborne radioiodine by copper screens", H.P. 15, p. 243, 1968.
13. Seigwarth, D. P., et.al., "Measurement of dynamic adsorption coefficients for noble gases on activated carbon", 12th Air Cleaning Conf., p. 28.
14. Collins, D. A., et.al., "Adsorption of krypton and xenon from argon by activated charcoal", TRG Report 1578 (W), 1967.
15. Fusamura, N., et.al., "On the study of radon removal with active carbon", Sands Translation SC-T-64-904, August 1963.

DISCUSSION

DEUBER: In many of your experiments you had no preconditioning. Do you expect reasonable results without preconditioning?

DISTENFELD: The adsorber is used in the field without preconditioning of any sort. In fact, the adsorber must be stored away from moisture prior to use. This is done so that the laboratory tests reflect field conditions and are not conservative.

DEUBER: Can you really expect a reasonable retention efficiency if you do no preconditioning?

DISTENFELD: Yes, I have demonstrated that in my paper.

DEUBER: What will be the sampling time for measurements in the field?

DISTENFELD: The collecting cycle will be five minutes and all tests were run at eight minutes, so that the adsorber was still unsaturated, with respect to water, at the end of the collection cycle. Therefore, I expect better results in the field than in the laboratory, i.e., 95 to 99% efficiency for all species of iodine.

DEUBER: Other iodine species than those examined in your tests, such as organic iodides, might occur in the case of an accident. These might be retained to a lesser extent by your material. Shouldn't it, therefore, be more reasonable to sample with impregnated carbon and flush off the rare gases if necessary? We have made measurements with other species than those mentioned by you, and when we find good retention with charcoal, the retention is always very poor with inorganic adsorbers impregnated with silver nitrate.

DISTENFELD: We considered doing that very thing; in fact, the original work was a heating operation while sampling. Alternately, a heating operation afterwards in clean air. But, a containment loss accident will cause contaminated areas that may extend for several tens of kilometers. A flushing operation would have to be done at high temperature, $110^{\circ}C$ or more, for 10 to 15 minutes, and in uncontaminated air according to studies reported in BNL 23112 and BNL 21541. Because of these restrictions, and the power needed for hot flushing, we developed the silver loaded silica-gel as the alternative and better solution. I understand that higher polymers or higher organics are even more efficiently absorbed.

DEUBER: Just to give you one example, we made measurements with iodine benzene and we found that retention with inorganic absorbers was very poor compared to charcoal.

DISTENFELD: I am not arguing that our material has a better absorption efficiency. I am saying that, under the conditions of the test, the absorption efficiency was fully adequate, i.e., in excess of 90%.

HULL: Dr. Deuber's paper yesterday, on species identification in nuclear power plants and your paper today indicate that there is some question about the presence of hypoiodous acid and, particularly how much hypoiodous acid there might be in an accident situation. If there are any questions about the ability of charcoal systems to retain HOI, even if impregnated, as compared to silica gel, perhaps we should be looking at correctly employed strategies--particularly for incident situation--if a large amount of HOI is anticipated in them. At Brookhaven we have a system for the production of ^{124}I and ^{126}I by the irradiation of CsCl targets by protons underwater in a tank, in which there was a recent minor incident producing an air release of the ^{124}I and ^{126}I. This was completely undetected by conventional (unimpregnated) charcoal samples both in the stack and in the field. However, silica gel samples for tritium showed unusual counts in the high energy region in liquid scintillation counting. When run on a Ge-Li detector, the ^{124}I and ^{126}I were readily apparent. This is a form of iodine that was completely undetected by the conventional charcoal systems for detecting iodine and there was so little of it that it was called undetectable but it was quite obvious on the silica gel system. Seriously, it is hypoiodous acid and, if this is so, we had better start taking a look at what we expect from this situation, particularly in an incident.

KOVACH: Before we go further, I would like to mention that I certainly would not call an unimpregnated carbon sampler a "conventional system." I don't think any power reactor would have anything to do with an unimpregnated charcoal sampler for iodine.

HULL: I was talking about using them for field sampling, particularly if you are not looking for organic compounds in the field.

DISTENFELD: Impregnated charcoals should always be used because of much better weathering resistance and efficiency for other than I_2 iodine species. Stay time should be maintained at a reasonable level: approximately $\geq$ 0.1 seconds.

DEUBER: After five years of operating iodine monitors in German reactor stations with silicic acid impregnated silver (published in 1974 in the 13th Air Cleaning Conference), we found that there are still problems. Figures for xenon retention and a description of the instrument used are given in this reference. We found that one of the problems is that in betweem the granules of the sorption material there is a gas volume containing rare gas. You can't avoid it. The only way to get rid of it is to flush it with fresh air. This is important if you measure the offgas of boiling water reactors, as we do continuously, because sometimes the level of rare gas is so much higher than the level of iodine. We tested the instrument and found it can be flushed out in five minutes with fresh air from pressurized tanks. But this is not the only problem. Cesium and rubidium, the daughter products of xenon and krypton, pass through the aerosol filter in the form of gas and stick partly to the sorption material. We are not through with that problem, at the moment. I only wanted to point out that the measurement of very small amounts of iodine in the environment, at the level of rare gases, is still a problem.

DISTENFELD: The retention data that I showed did not include flushing. The efficiency cited was for a non-flush system.

WILHELM: Radioactive particles of the daughter products Rb and Cs from Kr and Xe may influence the measurements, as we learned from iodine monitoring in the exhaust air of a BWR. They may be generated after the air has passed the aerosol filter. Those measurements were performed with AC 6120, a silver nitrate impregnated silic acid, which is regularly used as an iodine sorption material in the exhaust air of German LWRs for monitoring with a continuously working iodine monitor.

SIPP: We also measure iodine in the environment with cartridges to determine iodine species. It started four years ago when we had leaky fuel. Sampling showed about a 33% split between methyl iodide, hypoiodous acid, and elemental iodide. So, we've had no problems with halogens or inert gases in environmental monitoring. It looks like such sampling would be useful during an accident situation where there would be a larger amount of xenon, and I think it's very worthwhile.

CLOSING REMARKS OF SESSION CHAIRMAN:

KOVACH:

I always feel at these conferences that I should remind people that there were other air cleaning conferences before this one and that it would be very helpful if they would all go through the Proceedings that have been published from the Second Air Cleaning Conference on. We can learn a lot of things from what was done before. Inevitably, by attending the Conferences, you see a certain cycling. Some of the problems come up and some of the same solutions also come up. So, I think it would be very beneficial for all of us if we would go back and see what was done in the early days. Some of that work isn't so bad.