Final Report July 1971

DEVELOPMENT OF PARTICULATE EMISSION CONTROL TECHNIQUES FOR SPARK-IGNITION ENGINES

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Prepared for: Office of Air Programs
Environmental Protection Agency
2565 Plymouth Road
Ann Arbor, Michigan 48105

Attention: Mr. Charles L. Gray, Jr.
Project Officer

Contract EHS 70-101

EHS 70-101 | APTD-0949

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FOREWORD

This report was prepared by the Transportation Research Group, Organic Chemicals Department, The Dow Chemical Company, Midland, Michigan, under Contract EHS 70-101. The work reported herein was administered under the direction of the Office of Air Programs, Environmental Protection Agency, with Mr. Charles L. Gray, Jr., as Project Officer.

The report covers work performed from May 1, 1970, to July 1, 1971.

The authors of this report are John B. Moran, Otto J. Manary, Dr. Russell H. Fay, and Dr. Michael J. Baldwin.

The authors wish to acknowledge the significant contributions of the following individuals:

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This report was submitted by the authors on August 5, 1971.

ABSTRACT

This report describes work carried out on a research program to characterize and trap particulate emissions from automotive power plants. The work is presented in two separate phases necessitated by a Governmental initiated change in the scope of the work made in mid-contract year.

Phase I describes the characterization of particulate matter emitted from automotive power plants operating on leaded gasoline. These were sampled at four locations in the exhaust system ranging from near the exhaust manifold to the tail pipe, and after air dilution. Particle characterization was carried out with a dynamometer controlled engine operating at the equivalent of 60 mph cruise, 30 mph cruise, and under mild cycling conditions. The development of an exhaust particle-trap device is also described. This device was found to be effective at 60 mph cruise conditions but performed poorly at 30 mph cruise and under mild cyclic conditions. Loss of the trapping medium, a molten salt mix, was also evident under cycling conditions. Optimization of the trap was not achieved because of a change in the contract scope.

Phase II describes the characterization of particulate emissions from automotive power plants operating on non-leaded fuels. Changes in the particulate emissions were determined at a rich and lean air/fuel ratio and in the presence of two catalytic convertors using the same engine operating conditions as in Phase I. Particulate sampling was conducted after air dilution. Particle mass emission rates, particle mass-size distributions, and total aldehyde emissions were measured.

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I. INTRODUCTION

Increased public concern over pollution of the atmosphere has resulted in the identification of exhaust emissions from the internal combustion engine as a major contributor to this problem. Although a significant amount of work has been directed towards achieving reductions in the levels of emitted carbon monoxide, unburnt hydrocarbons, and oxides of nitrogen from this source, a lesser effort has been expended on the identification and removal of those potentially toxic combustion products which are present at lower concentrations in the exhaust stream. These include particulate matter.

Although considerable technology has been developed for the removal of suspended particulate matter from gas streams, the exhaust effluent of the internal combustion engine poses special problems. Large variations in both temperature and gas velocity can occur within the exhaust system depending on engine operating conditions. In addition, particle size varies between wide limits from those visible to the naked eye to those approaching molecular dimensions. Particles in the 1 to 0.1μ range can be retained in the lungs upon inhalation and pose the most significant threat to human health. Because of their small size, these are among the most difficult to remove from the exhaust stream. The limited space and power available in the automobile also place constraints on the design of a practical particle trapping device.

This report describes two pieces of work, subsequently referred to as Phase I and Phase II, directed towards the characterization and potential removal of particulate emissions.

Phase I of the program was directed towards the design and construction of a trapping device to remove particulate matter from the exhaust stream of an automobile engine operating on leaded gasoline. The following sequence of tasks was defined as necessary to the attainment of this objective.

1. The temperature profile along the exhaust system of a vehicle operating at a variety of highway cruise conditions should be determined.
2. Correlation of this profile to that of a similar engine operating on a laboratory dynamometer test stand should be made.
3. Characterization of the emitted particulate matter as it traverses the engine exhaust system should be made. This would involve the sampling of particulates at several points along such a system and their subsequent analysis to determine particle mass size, concentration, and chemical composition.
4. Based on the data generated above, selection of a suitable trapping medium would be made and the design of a trapping device undertaken.
5. Construction, evaluation of the device under a variety of engine operating conditions and subsequent optimization would be performed.

The purpose of Tasks 1 and 2 was to ascertain the degree of correlation between the temperature profile of a vehicle exhaust system operating under roadway driving conditions and that of a similar exhaust system fitted to an engine operating on a laboratory dynamometer. A close correlation would assure that subsequent laboratory studies of exhaust particulate matter within the exhaust system would relate directly to vehicles driven on the roadway.

The objective of Task 3 was to define a profile for emitted particulate matter within the exhaust system so that the most appropriate design of a trapping device could be made in Task 4.

In Task 5 this device would be constructed and evaluated to determine its efficiency and the need for further optimization.

A Government-initiated change in the scope of work mid-way through the program permitted the successful completion of Tasks 1-4. However, only limited testing of a prototype device in Task 5 was possible.

Phase II of the program was directed towards characterization of the particulate matter emitted from an internal combustion engine operating on non-leaded gasoline. In particular, it was necessary to determine the effects of the following variables on such emissions.

1. Air/fuel ratio - one rich and one lean.
2. The presence in the system of catalytic reactors designed to reduce regulated automotive emissions. Two such reactors were evaluated.

In addition, aldehyde emissions from the engine were monitored. Throughout this phase of the work, particulate sampling was made after air dilution of the exhaust stream under controlled conditions using the system reported by Moran and Manary[1] and described in detail on page 22 of this report.

PHASE I

II. CONCLUSIONS

Phase I of this report covers a study of the chemical and physical nature of particulate emissions as they traversed the exhaust system of a 350 CID Chevrolet V8 engine. A particulate trapping device was constructed and tested to determine its effect on particulate emissions at 1200 rpm, 2250 rpm, and under mild cycling conditions. The following conclusions were reached:

1. The temperature profile for the exhaust system of the Chevrolet test vehicle was nearly linear from the manifold to the end of the tail pipe; the temperature profile for different engine speeds forms a family of essentially parallel curves. Temperatures varied between 900-1375°F at the exhaust manifold to 325-810°F at the tail pipe (30-80 mph).

2. The temperature profile for the exhaust system of the same type engine on a dynamometer stand forms a similar family of parallel curves at different speeds. The rate at which the temperature drops is less than in the moving vehicle. Temperatures varied between 890-1130°F at the exhaust manifold to 430-750°F at the tail pipe (30-60 mph).

3. Collection of particulate matter directly from the exhaust system on heated Andersen Samplers identified that the bulk of the particulate matter was formed in the muffler. Prior to the muffler (∿900°F) the exhaust effluent was mainly gaseous in nature. This conclusion is supported by the identification of crystal growth on non-heated filters located ahead of the muffler. Subsequent to the muffler, there was little precipitation or growth of particulate matter, but considerable shattering and disintegration. The D_{70} value of particles collected

at the tail pipe was 1 micron while that of particles collected immediately after the muffler under identical conditions was 8.8 microns.

4. The larger particles (>1μ) (hence, more easily trapped) were shown to be primarily lead halides. Particles smaller than 1μ were again mainly inorganic but their major components were lead sulfates and chlorophosphates. No discreet particles of organic matter were observed. However, many of the smaller (<1μ) particles examined were identified as a nucleus of inorganic matter in a matrix of organic matter.

5. In the sampling of air diluted exhaust effluent, the grams/mile of particulate matter collected was shown to be a function of the sampling flow rate used. In general more particulate matter was collected when sampling at 1 cfm than at 4 cfm.

6. A 70 percent KNO_3-30 percent $LiNO_3$ mixture proved to be a promising trapping medium for lead particulate. However, the design of the trapping device itself needs to be optimized since severe loss of the trapping medium occurred under non-steady state conditions.

7. For the leaded fuel evaluated, the bulk of particle precipitation occurs within the exhaust system itself. Any further precipitation which may occur after air dilution is small. Thus the level of condensable organics in the exhaust effluent must be low.

III. EXPERIMENTAL PROCEDURE

A. DETERMINATION OF EXHAUST SYSTEM TEMPERATURE PROFILE ON THE VEHICLE

A 1970 Chevrolet Impala equipped with a 350 CID, 2-barrel carburetor, V8 engine was procured and instrumented to allow the determination of the temperature profile of the exhaust system. Selection of the Chevrolet car was based on its extensive field usage. Chromel-alumel thermocouples were brazed to standard hose clamps and inserted into the exhaust system at the locations shown in Figure 1. The thermocouple locations were identified as follows:

Position I - immediately after the junction of the two sides of the exhaust manifold.

Position II - immediately ahead of the muffler.

Position III - immediately after the muffler.

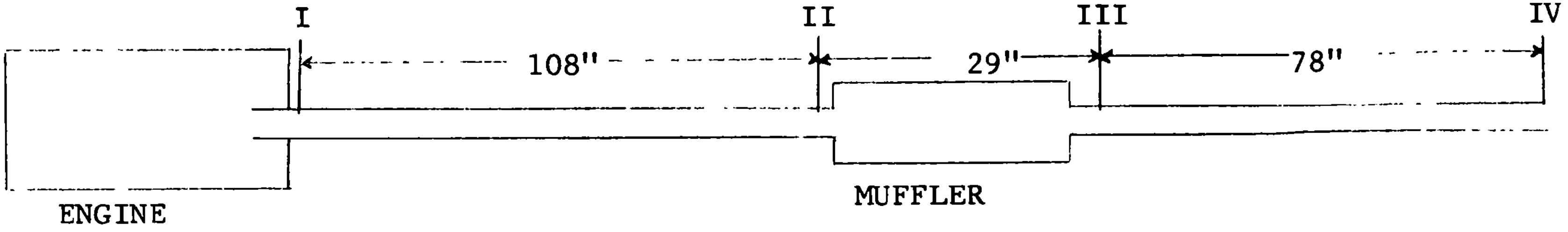
Position IV - near the end of the tail pipe.

The output of each thermocouple was determined via a Thermo Electric Minimite Potentiometer - Model 80200. The engine revolutions per minute (rpm) was measured with a Sun Tachometer - Model PT-4, the intake manifold vacuum by a Sun Electric Model No. FPT-1 vacuum gauge connected into the distributor vacuum line, and the vehicle road speed via the car speedometer.

Data was collected by having a driver keep the car a constant speed on a nearly level stretch of expressway while an assistant recorded the various instrument readings. Tests were made over a variety of road speeds and during several days so that the effect of changes in ambient air temperature could be assessed. On each day of testing runs were made in both directions on the expressway to compensate for wind effects.

FIGURE 1

EXHAUST THERMOCOUPLE LOCATIONS - VEHICLE TESTS



B. DETERMINATION OF EXHAUST TEMPERATURE PROFILE IN LABORATORY

A new 1970 Chevrolet V8, 2-barrel carburetor, 350 CID engine was obtained and mounted on a General Electric - Model 1G614 dynamometer test stand. The engine had the following specifications:

Displacement	350 cubic inches
Horsepower	255 at 4800 rpm
Carburetor	2-barrel Rochester
Compression ratio	9.0:1
Bore	4.0 inches
Stroke	3.48 inches
Spark plugs	AC R45S
Plug gap	0.035 inches
Point dwell	28-32°
Timing	4° B.T.C.

A Meriam Laminar Flow Element- Model 50MC-2-45F Air Flow Measurement unit was attached to the carburetor via a flexible rubber hose to monitor air flow rate. An AC paper filter element was attached to the Meriam unit to filter incoming air.

The engine dynamometer was completely instrumented to monitor and/or control coolant temperature, oil temperature, manifold vacuum, fuel flow rate, air flow rate, engine rpm, load, etc.

Indolene HO 30 fuel was used throughout the experimental work. A physical and chemical analysis of the fuel is shown in Table I. Amoco 200, SAE 30 lubricating engine oil was used in all laboratory runs. This oil was chosen as minimum acceptable oil with a low additive package content so that any contribution of the oil to the emitted particulate matter would be minimized. The physical properties of the oil are shown in Table II and its trace metal analysis in Table III.

TABLE I
ANALYSIS OF TEST FUEL

PHYSICAL

		Indolene HO 30
Distillation ASTM D86		
(°F)	IBP	90
	5	118
	10	133
	20	162
	30	188
	40	208
	50	222
	60	234
	70	249
	80	273
	90	320
	95	368
	EP	394
% Recovery		96.5
% Residue		0.5
% Loss		3.0
Octanes: D		
MON		95.9
RON		102.9
FIA: D		
% Saturates		68.1
% Olefins		3.0
% Aromatics		28.9
cc/gal TEL		3.0

TRACE METAL ANALYSIS

Lead	----	Aluminum	<1.0 ppm
Iron	<1.0 ppm	Calcium	<1.0 ppm
Nickel	<0.5 ppm	Manganese	<1.0 ppm
Copper	<0.2 ppm	Tin	<1.0 ppm
Magnesium	<0.5 ppm	Titanium	<1.0 ppm
Zinc	<3.0 ppm		

TABLE II
PHYSICAL PROPERTIES OF LUBRICATING OIL

Gravity	26.4
Flash, °F	450
Pour, °F	0
Viscosity 100°F	555 SUS
210°F	66 SUS
V.I.	95
Color, ASTM	5
Sulfated Ash, % wt.	1.0
Carbon Residue, % wt.	1.3

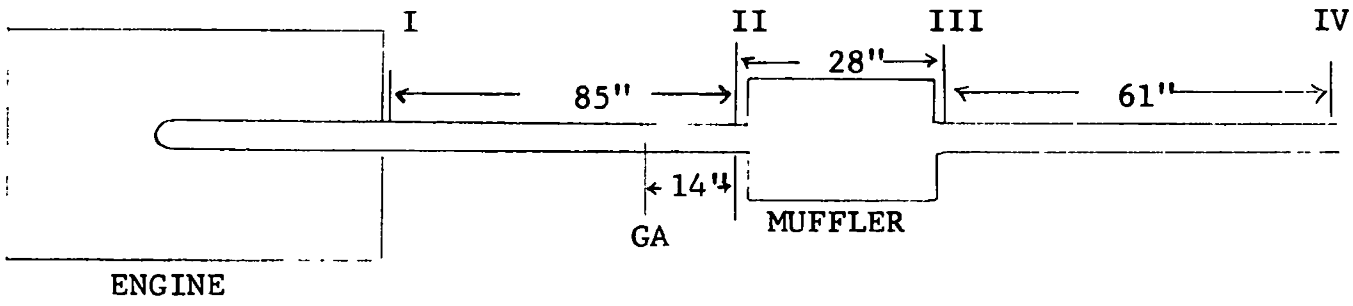
TABLE III
TRACE METAL ANALYSIS OF LUBRICATING OIL
(Weight %)

Fe	<.0005	Mn	.0004
Ni	<.0005	Pb	<.0005
Cu	<.0001	Cr	<.0005
Al	<.0005	Sn	<.0005
Ca	.0017	Zn	.092
Si	.0021	Ti	<.0005
Mg	.13		

The engine exhaust system consisted of a 2-1/2 inch ID exhaust pipe from the manifold to the muffler. The muffler was a Walker Model No. 21530, W-5798 and was 21 inches long. The tail pipe was 1-3/4 inches ID. A schematic of this system is shown in Figure 2. Thermocouples were introduced into the exhaust system through 1/4 inch pipe nipples welded into the piping and positioned in such a way as to be equivalent to those used in the vehicle road tests. Because of differences in the configuration of the exhaust systems

FIGURE 2

EXHAUST THERMOCOUPLE LOCATIONS - DYNAMOMETER TESTS



GA - sample probe for exhaust gas analysis used on the vehicle and in the laboratory work, the distances between successive thermocouples were slightly different. However, the same relative positioning was maintained. At points 2 inches ahead of each thermocouple, a second 1/4-inch nipple was welded to the system to accommodate sampling probes to be used in the later stages of the project. A final nipple was located 12 inches ahead of Position II (Figure 2) so that a probe could be introduced to obtain samples for exhaust gas analysis.

Temperature profiles of the exhaust system were thus generated in several engine dynamometer runs. These runs are outlined in Table IV.

C. PARTICLE GENERATION

Exhaust particulate matter was generated by running the Chevrolet engine on the dynamometer test stand under a variety of controlled road load operating conditions. The engine was first run on a conditioning cycle for 75 hours to stabilize engine deposits, emission levels, and engine condition. This cycle is shown in Table V.

TABLE V
ENGINE CONDITIONING CYCLE

Cycle	RPM	Observed H.P.	Time (min)	Vacuum (in. Hg)	Equivalent Cruise Speed (mph)	Decay (min)
1	800	1.8	2.0	18.8	-	-
2	1070	15.0	13.0	16.4	27	0.5
3	1615	21.5	20.0	17.2	45	0.5
4	2125	42.3	13.0	14.3	57.5	0.5
5	1070	15.0	12.0	16.4	27	0.5

The sequence repeats after cycle 5. Previous work reported by Moran and Manary[1] has shown that repetition of such a cycle over the 75-hour period is satisfactory for the engine to reach quasi-stabilized operation.

TABLE IV

EXHAUST STREAM SAMPLING

PARTICULATE SAMPLING DEVICE LOCATION BY TEST SERIES NUMBER

Test No.	RPM	Andersen Stack Sampler (Position)	Gelman Filter (Glass Fiber) (Position)	Cold Trap (Ice/Water) (Position)	Sampling Time	
I	870	No	I, II, III, IV	I, II, III, IV	30 minutes	
	1070	No	I, II, III, IV	I, II, III, IV	30 minutes	
	1615	No	I, II, III, IV	I, II, III, IV	30 minutes	
	2125	No	I, II, III, IV	I, II, III, IV	30 minutes	
II	2250	IV	IV (2)*	IV (3)*	5 hours	
III	2250	IV	I, II, III, IV	I, II, III, IV	5 hours	
IV	2250	III	I, II, III, IV	I, II, III, IV	5 hours	Dry ice/ acetone cold trap @ ice/ water trap @ Position IV
V	2250	II	I, II, III, IV	I, II, III, IV	5 hours	

Note: See Figure 2 for sampling position location.

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*Numbers in parentheses indicate the number of sampling devices of the type indicated placed in series at the positions shown.

The complete set of test runs performed is outlined in Tables IV and VI.

The first series of tests (Numbers I-V, Table IV) was designed to allow for characterization of particles along the length of the exhaust system.

During Test I, steady state sampling of particle was conducted at four different engine operating conditions. The engine was first allowed to equilibrate at 870 rpm for 1 hour. Particulate sampling was then initiated for a 30-minute period after which time the various sampling devices, described later, were cleaned, and the engine speed was increased to 1070 rpm. A second set of samples was collected for 30 minutes under these conditions. This procedure was repeated at 1615 and 2125 rpm.

At the start of Tests II through V, the engine was held at steady state operation identical to that under which subsequent sampling was performed for a period of at least one hour. Sampling of particulate matter was then made over a period of five hours. This time period allowed sufficient matter to be collected at each of the particulate sampling devices for comprehensive analytical evaluations to be made (see page 26).

In the second series of dynamometer test runs (VI-XI, Table VI), the exhaust system effluent was fed into an air dilution tube, which is described later. In order to perform this set of tests, it was necessary to relocate the Chevrolet engine on a Dynamatic Model 1014DG dynamometer test stand, again instrumented to control and/or monitor relevant engine variables.

Of the six tests made (Tests VI-XI, Table VI), Tests VI-VIII utilized the same muffler as in the previous runs (Tests I-V) in an exhaust system of similar overall length. However, a change in exhaust system configuration was necessary to provide for convenient hook-up to the dilution tube. The experimental set-up is shown in Figure 3. Tests VI-VIII were thus used to establish base-line particulate characterization for the dilution tube work at 60 mph cruise, 30 mph cruise, and under mild cycling conditions.

In order to maintain temperatures at the sampling zone of the dilution tube at 75-80°F, only one-half of the engine exhaust (left bank of cylinders) was fed to the tube. The validity of this approach was established by Moran and Manary[1].

Prior to Test VI, the engine was conditioned in the Dow 5 mode cycle for a period of 26 hours. The exhaust system was then connected to the dilution tube and particulate matter sampled over a 6-hour period. For Tests VII and VIII, the engine was allowed to warm up for at least 1 hour under the conditions specified (Table VI) and the diluted exhaust stream again sampled for 6-hour periods.

In Tests IX-XI, the conventional exhaust muffler was replaced by the prototype lead trap muffler described in Section E.

D. SAMPLE COLLECTION

1. Particulate Matter

For clarity of presentation, two distinct sets of particulate sampling procedures will be discussed: those utilized for sampling direct from the exhaust stream and those for sampling from air-diluted exhaust.

Direct Exhaust Sampling - In the first set of runs (Tests I-V, Table IV), particle collection was effected via sampling probes located in the exhaust system at various points along its length. Their position has

TABLE VI

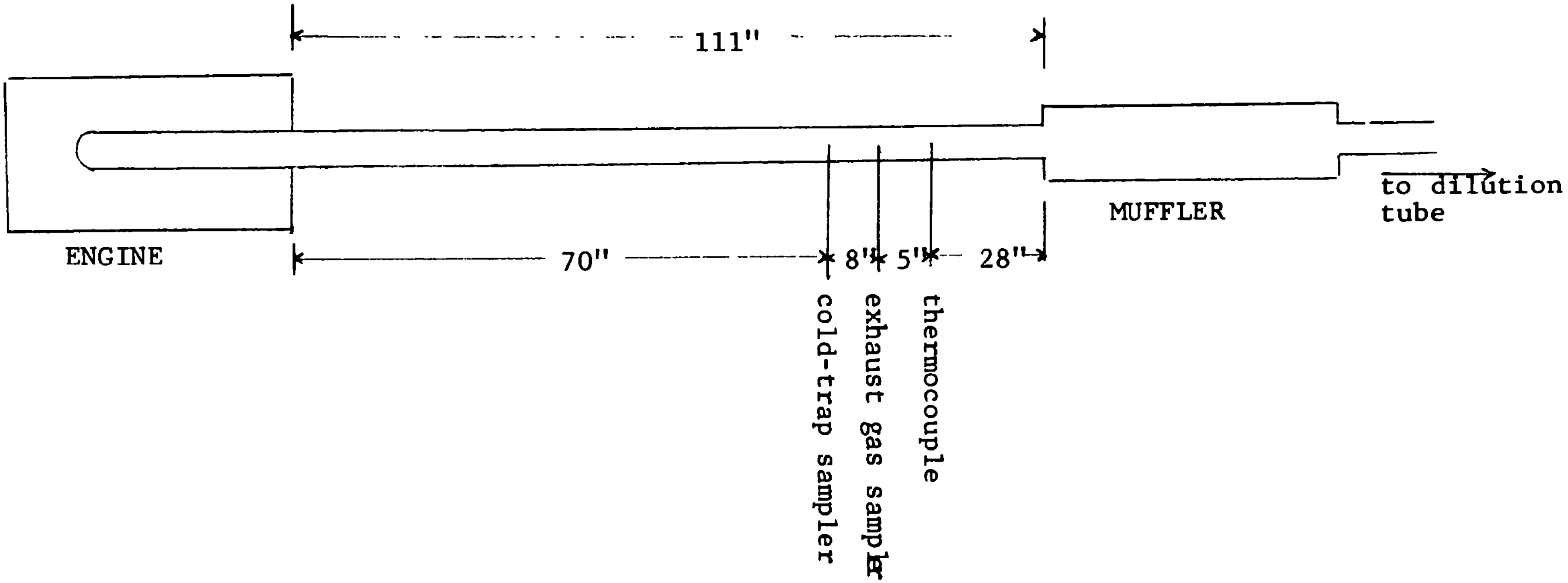
AIR DILUTION TUBE SAMPLING

PARTICULATE SAMPLING DEVICE LOCATION BY TEST SERIES NUMBER

		Exhaust System Before Muffler			After Muffler Cold Trap	Dilution Tube				
			Cold Trap			1 cfm		4 cfm		
Test	RPM	Gelman Glass Fiber Filter	Ice/Water	Dry Ice/Acetone		Andersen Sampler	Millipore Filter	Glass Fiber	Glass Fiber	Glass Fiber
VI	2250	Yes	Yes	Yes	-	Yes	Yes	Yes	Yes	Yes
VII	Cycle	Yes	Yes	Yes	-	Yes	Yes	Yes	Yes	Yes
VIII	1200	Yes	Yes	Yes	-	Yes	Yes	Yes	Yes	Yes
IX	1200	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
X	2250	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
XI	Cycle	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes

FIGURE 3

EXHAUST SYSTEM FOR LEAD TRAP EVALUATION



already been described (page 11 and Figure 2). Each probe was constructed of stainless steel tubing and sized to assure isokinetic sampling. Such sizing was based on calculated exhaust gas flow rates at various sampling points along the length of the system when sampling at 1 cubic foot per minute (cfm). The probes were introduced into the system in such a way that their inlet axes lay parallel to and facing the exhaust gas stream and mid-way across the cross-section of the exhaust piping (see Figure 4).

A variety of devices were used to collect particulate samples from these probes. Exhaust effluent was drawn through these devices by means of vacuum pumps. The devices are outlined below:

a. Andersen Stack Sampler

Particle fractionation by aerodynamic size was achieved by the use of an Andersen[2] eight-stage stack sampler operated at a flow rate of 1 cfm. This was designed to function at temperatures up to 1500°F. The sampler was heated by a 230-volt band-electric heater controlled by a Variac so that the temperature of the sampling device could be maintained at that of the exhaust gas stream at the sampling point. This technique was aimed at avoiding precipitation of particulate matter due to thermal quenching. In the Andersen Sampler the incoming gas stream is forced through successive plates, each having a number of jet orifices of the same size. The size of the orifices decreased on each successive plate and particle aerodynamic separation is thus achieved. The Andersen unit used allowed separation of particles into the aerodynamic size fractions shown in Table VII.

FIGURE 4

INSTALLATION OF EXHAUST PARTICULATE SAMPLING PROBE AND THERMOCOUPLE

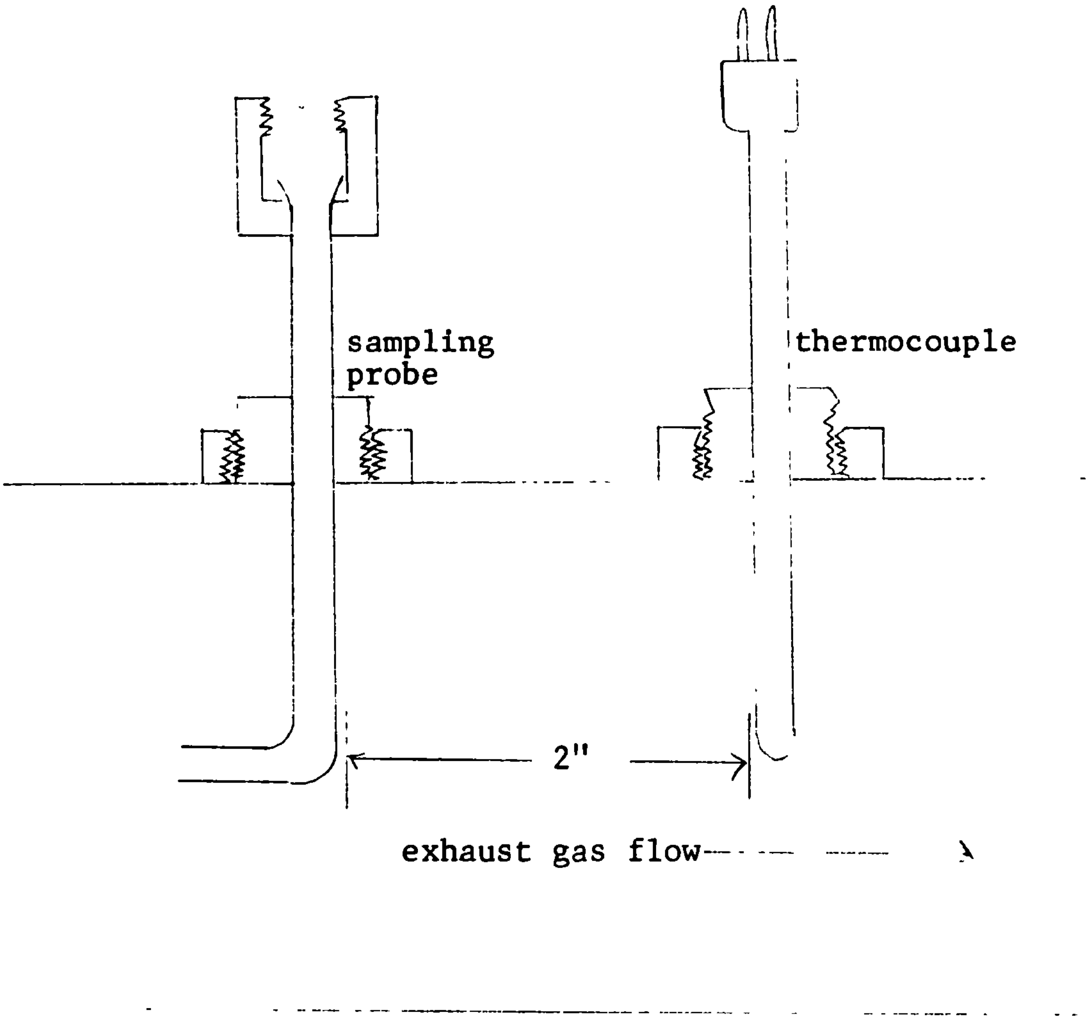


TABLE VII
CUT-OFF VALUES FOR ANDERSEN STACK SAMPLER

Stage	D_{50} Value* (microns)
0	9.5
1	6.1
2	4.0
3	2.8
4	1.75
5	0.9
6	0.54
7	0.36

*D_{50} = mass median equivalent diameter

b. Gelman Filter

Gelman filters were used for sampling both directly from the exhaust stream and as a back-up to the Andersen unit. This filter unit consisted of a 2-5/16 inch diameter stainless steel filter holder (Model 2220) containing a Gelman Glass Fiber Filter Pad, Type A of 2-inch diameter. This filter system has an efficiency rating of greater than 98 percent for particles as small as 0.05 microns. These filters were not heated as was the Andersen unit.

The glass fiber filter pads were held in a dessicator and weighed to the nearest 0.1 milligram (mg) immediately prior to use. After sampling they were returned to the dessicator and weighed periodically until two successive weighings showed no change. This technique assured that the sample was free from moisture and that a reliable determination of the mass of collected particulate matter could be made.

Since the Gelman filters were not heated in use, there exists the real possibility that condensation of volatile organic matter from the exhaust effluent could occur at the Gelman filter pads. Therefore, the only true indication of the presence of actual organic particulate matter within the exhaust system would result from analysis of those particulate samples collected at the heated Andersen stack sampler.

c. Cold Traps

As a final back-up for the Andersen and Gelman filters, the exhaust effluent sample was drawn through one or more cold traps. The cold traps were immersed in an ice/water cooling mixture although the effect of using a dry-ice/acetone cooling medium was also evaluated.

In some instances, samples were also obtained from the surfaces of the sampling probes by sweeping the latter with a pipe cleaner.

The dispostion of the various sampling devices described above is outlined for Tests I-V in Table IV.

The major objective of the sampling work undertaken in Tests I-V was to establish a reliable profile and analysis for particulate matter along the length of the exhaust system. This profile was then used as a basis for selection of a suitable trapping medium for removal of particulate products in the exhaust system.

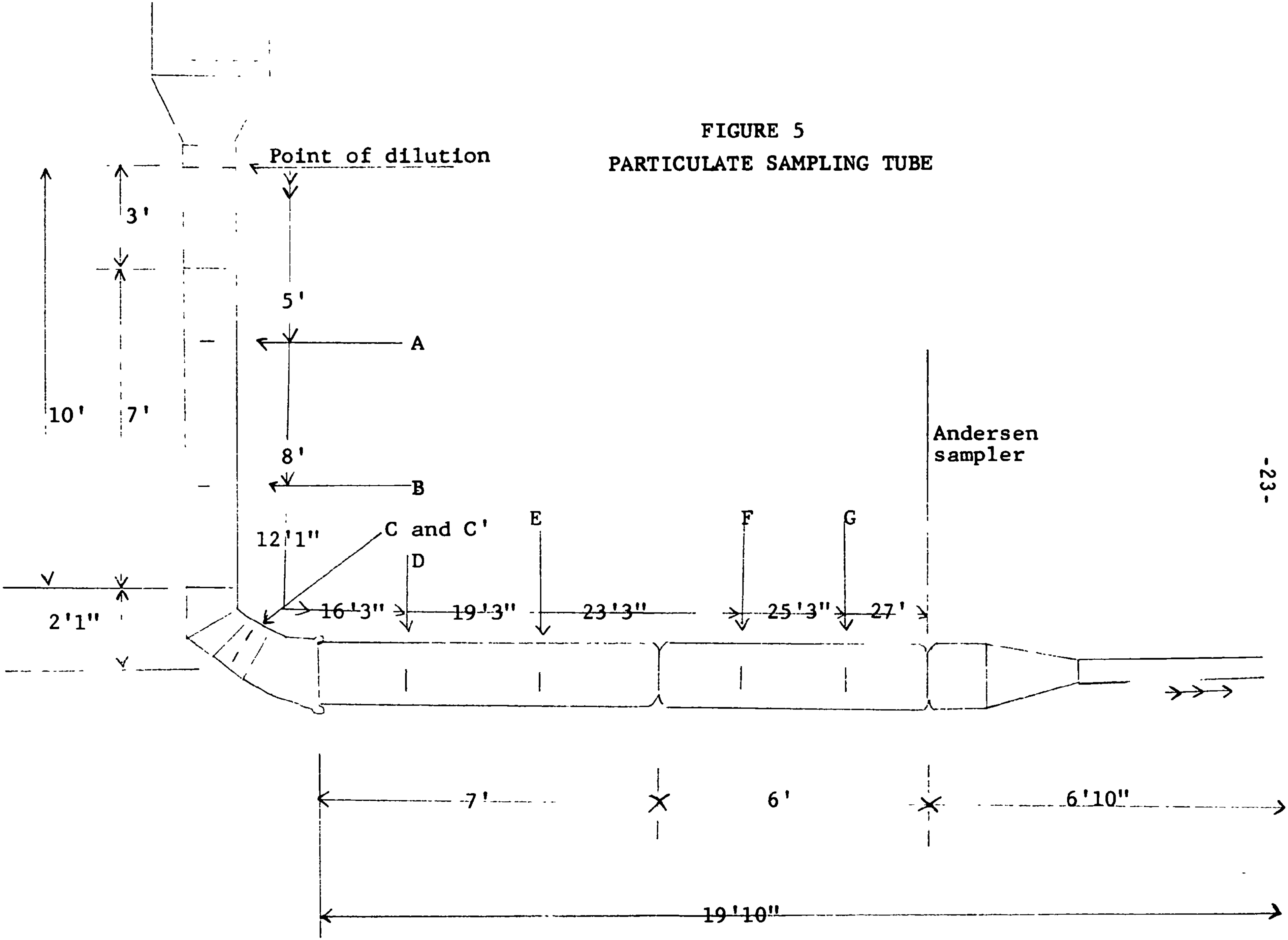
In order to evaluate the effect of a candidate trapping medium on the nature of the residual particles emitted from the exhaust into ambient air, it was necessary in subsequent testing to subject the exhaust system effluent to air dilution as described in the subsequent section and in Reference 1.

Sampling of Air-Diluted Exhaust Effluent - In the second set of tests (VI-XI, Table VI), the effluent from the engine exhaust system was passed into an air dilution tube prior to sampling. The dilution tube is an extruded pipe made of polyvinyl chloride. It is 16 inches in diameter with a 1/4 inch wall thickness. In total it is 27 feet long which includes a 90° bend section, as shown in Figure 5. A 7-foot air induction head which houses the air filter assembly, exhaust inlet elbow, and mixing baffle is mounted in the wall between the instrument room and the engine test cell. The mixing baffle consists of a sheet metal donut attached to the inside wall of the air induction head which acts to force the incoming diluent air through the hole in the baffle at the center of the tube. The exhaust inlet elbow enters at 90° to the tube axis and is bent 90° so that the flow axis of the exhaust gas parallels the axis of the dilution tube. The exit end of the exhaust elbow is in the same plane as the baffle. A schematic diagram of this apparatus is shown in Figure 6.

An exhaust fan is located at the exit end of the dilution tube. A throttle plate is located in the dilution tube exit assembly just following the fan in order to allow control of air flow volumes through the tube. The dilution tube is of several sections with butt joints which are taped during assembly. This construction allows for easy removal, cleaning, and inspection of the complete dilution tube after each run.

Several small slits have been cut in the bottom of the tube along its length. Special glass collecting plates were fabricated which are attached to the outside of the tube under each slit to collect particulate samples. Such samples are referred to herein as "slit samples." Slit locations are shown as short, dashed lines perpendicular to the tube axis in Figure 6.

FIGURE 5
PARTICULATE SAMPLING TUBE



A through G indicate positions of slit samplers

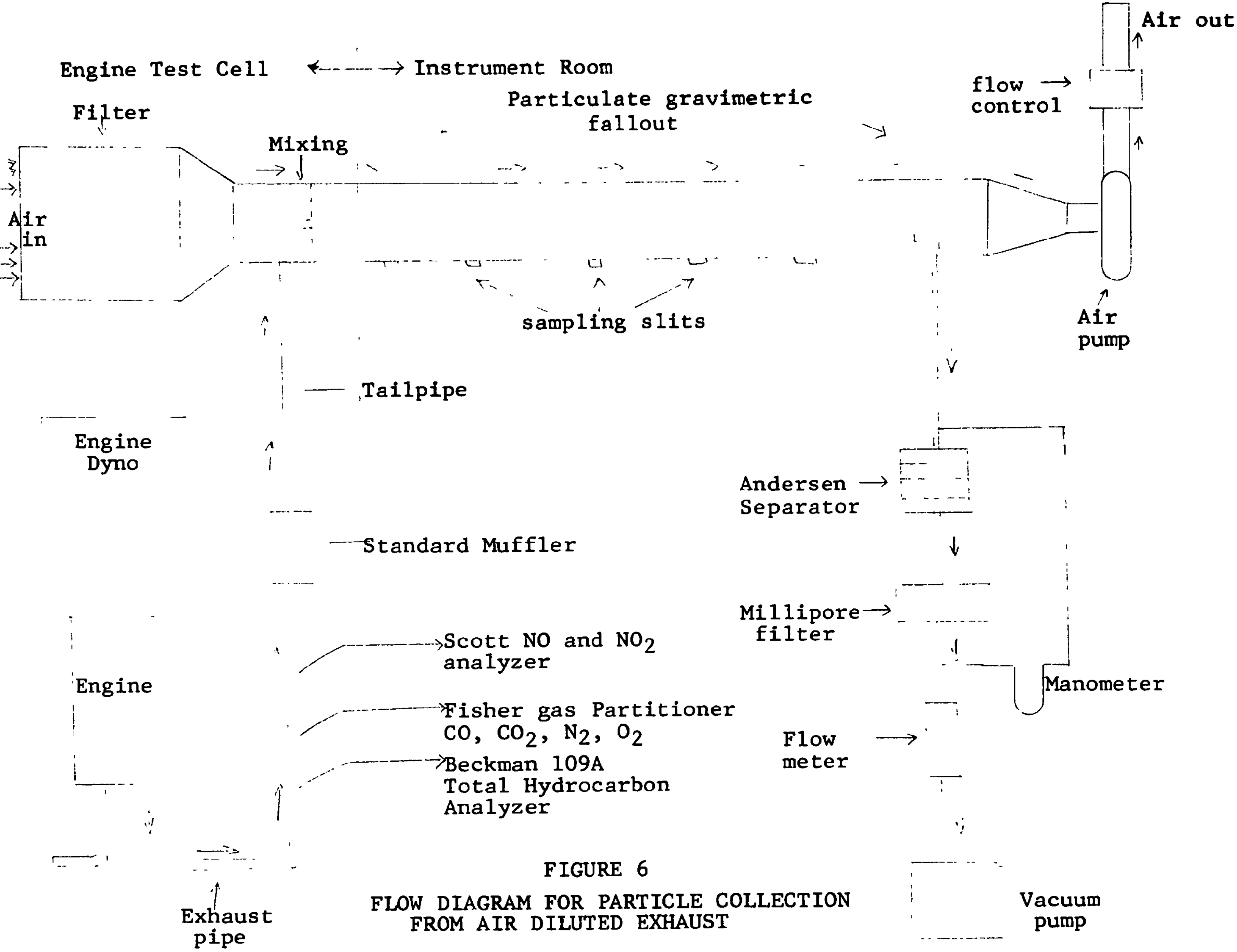


FIGURE 6

FLOW DIAGRAM FOR PARTICLE COLLECTION FROM AIR DILUTED EXHAUST

The diluent air coming into the tube is filtered by means of a Dri-Pak Series 1100 Class II PIN 114-110-020 untreated cotton filter assembly. This filter assembly is 24" x 24" and has 36 filter socks which extend to 36 inches in length. This filter will pass particles 0.3μ in size and smaller. Pressure drop at 600 cfm flow rate is minimal.

The particulate sampling zone for particles smaller than 15μ is located at the exhaust end of the dilution tube. Three sample probe elbows are located in the exhaust-air stream. One probe is connected to an Andersen Impact Sampler Model 0203, a filter assembly, and a vacuum pump, in that sequence. The probes are 0.754 inch ID aluminum tubes. These sample tubes are located as shown in Figure 6. A mercury manometer is connected between the dilution tube probe and the exhaust side of the filter assembly, and was used to monitor and regulate the flow through the Andersen Sampler during the course of each run. The remaining sample probes were both connected to 4 cfm Millipore filter holders (142 mm) fitted with Gelman Type A fiberglass filter pads and vacuum pumps. The Andersen Sampler collection plates were weighed before and after the run, the difference being sample weight.

Prior to use, the fiberglass filters were stored in the instrument room which is temperature and humidity controlled. The filters were placed on the tray in a Mettler Analytical balance, allowed to reach equilibrium, and then weighed out to 0.1 milligram.

After the test, the filters were removed from the holders and again allowed to reach equilibrium, noted by no further change in weight, and then weighed to 0.1 milligram. This was done in the same room in which the papers are stored. The Millipore filter pads used were 142 mm Type AAWP 0.8μ. The fiberglass filter pads used were Gelman 0.3μ Type A.

2. Exhaust Gas Sampling

Throughout Tests I-V (Table IV), samples for gaseous analysis were collected through the stainless steel sampling probe described earlier (page 16 and Figure 2) into a 2 cu ft saran bag via a Neptune dyna-pump. The bag was filled with exhaust effluent and evacuated three times prior to a sample being collected for analysis. A water-cooled copper condenser fitted with a trap was introduced between the exhaust sample port of the dyna-pump to remove water from the gas stream.

In Tests VI-XI (Table VI), stainless steel sample probes were also introduced into the exhaust system both ahead of and after the muffler (Figure 3). Gas samples were drawn from these ports through a cooled copper condenser by a dyna-pump and fed directly to the gas analysis equipment. A Gelman glass fiber filter fitted with a back-up cold trap was also periodically connected to the system via these same probes. This permitted aldehyde analysis to be performed on the condensates collected.

E. SAMPLE ANALYSIS

1. Particulate Matter Analysis

In order to characterize and define the various samples of particulate matter collected throughout the course of this investigation, a wide variety of analytical procedures was employed.

One of the principal approaches used was that of microscopic examination. This included the use of optical, scanning electron, and transmission electron microscopy. The application of these techniques to the characterization of particulate emissions from the internal combustion engine has been previously described by Moran and Manary[1].

Optical microscopy was used at magnifications from 3X to 400X. Lower magnifications were used to determine particle distribution and impingement points on the plates of the Andersen Sampler. The higher magnification served to determine particle size ranges and to study the birefringent properties of the particulate matter under polarized light. Particle samples examined by these techniques were also submitted for X-ray diffraction analysis.

Use of the scanning electron microscope at magnifications of 1000X to 10,000X allowed examination of individual particles. This instrument was also fitted with an X-ray fluorescence spectrometer probe which afforded elemental analysis of both single particles and particle aggregates. Single element scans were also made to determine the concentration profile of specific elements within a single particle.

Particles of less than 1μ size were examined under the transmission electron microscope at magnifications of 10,000X and 60,000X. The opacity of the particle image on a photomicrograph affords a measure of the electron density within the particle. The darker images indicate high electron density resulting from the presence of inorganic elements such as the heavy metals. The less opaque images result from particles having a high content of organics.

X-ray diffraction afforded a powerful tool for the identification of specific crystalline species present at greater than 5 percent concentration in the particulate samplers. The resulting X-ray diffraction patterns could be compared to those of over 10,000 known compounds. The quantitative accuracy of this procedure is about ±10 percent based on the amount of a specific moiety present.

Samples of cold-trap condensate obtained in Test I-V were analyzed by emission spectroscopy to afford a qualitative and quantitative determination of the various cations present.

A limited number of particulate samples were analyzed by atomic absorption spectroscopy to determine the relative amounts of lead and other inorganics present.

Detailed accounts of the above analytical procedures can be found in Appendix A.

2. Gas Analysis

The engine exhaust gas was analyzed for oxygen, nitrogen, carbon monoxide, carbon dioxide, total and unsaturated volatile hydrocarbons. The analysis is done by gas chromatography, chemical absorption, and a total hydrocarbon analyzer. Data reduction is by an IBM 1800 computer through a Bell Telephone ASR 33 Teletype interface.

Analytical Equipment

A Fisher Gas Partitioner is used for the analysis of oxygen, nitrogen, carbon monoxide, and carbon dioxide. The column system consists of a 6-foot hexamethyl phosphoramide and a 6-1/2 foot, 13x molecular sieve in series.

Total hydrocarbons are obtained from a Beckman Model 109A Total Hydrocarbon Analyzer. The concentration of unsaturated hydrocarbons is determined by passing the sample through an absorption tube 8" x 12" filled with 30-60 mesh pink Chromosorb® impregnated with 50 percent mercuric perchlorate.

Standardization

A gas mixture containing known concentrations of oxygen, nitrogen, argon, carbon monoxide, carbon dioxide, and n-hexane is used as a reference standard for the total hydrocarbon analyzer and the Fisher Gas Partitioner.

Component identification is done by peak retention time. Shifts in retention time and changes in detector response are compensated for by standardization preceding each series of samples.

Operation

The operator types the proper computer code and program number on the teletypewriter, injects the reference standard, and presses the integrator start button. As the peaks emerge, the time and area information is encoded and stored on punched paper tape. Each succeeding exhaust gas is identified along with the total hydrocarbon level, and run in the same manner as the standard. When the series is finished, the punched tape is sent to the computer by teletype over regular telephone lines.

Data Reduction

A typical output format for the gas analysis is shown in Figure 7. Identification of the components in the standard is based upon each peak size in descending order. Estimated retention time is the up-dated time of each peak in the standard. Retention time windows are 4 seconds plus 2 percent of the retention time. Actual percent is a direct ratio of the area counts in the unknown sample to the area counts in the standard times the volume percent in the standard. The total percent actual will normally be 97-98 percent since water is removed from the saturated sample after the sampling valve.

FIGURE 7

```
G. C. ANALYSIS - TECHNICAL DATA -                    10-20-70
GOV RUN # 1778-3 OCT 20 1970
TIME 8.0 HRS
HC 670. PPM

 PEAK      TIME          PCT. VOL.         COMPOUND
  NO.  ACT.    EST.   ACTUAL    NORM.    IDENTIFICATION


   1    22.     22.    0.000     0.000   COMPOSITE
   2    58.     58.   10.302    10.661   CARBON DIOXIDE
   3    82.     82.    2.723     2.817   OXYGEN
                       0.900     0.931   ARGON
   4   103.    103.   79.210    81.973   NITROGEN
   5   182.    182.    3.494     3.615   CARBON MONOXIDE
                     -------   -------
                      96.628   100.000   TOTALS
                       3.371             BALANCE BY DIFFERENCE
                       3.371             TOTAL CONTAMINATION LEVEL

---------------------------------------------------------------
---------------------------------------------------------------

          EXHAUST GAS ANALYSIS            10-20-70

GOV RUN # 1778-3 OCT 20 1970
TIME 8.0 HRS
HC 670. PPM

 TIME  PERCENT  IDENTIFICATION

  82.      0.9  ARGON
 103.     82.0  NITROGEN
  82.      2.8  OXYGEN
 182.     3.62  CARBON MONOXIDE
  58.     10.7  CARBON DIOXIDE
         -----
         100.0  TOTAL

FRACTION CARBON IN FUEL 0.8625

TOTAL HYDROCARBON CONTENT  670. PPM.

AIR FUEL RATIO 14.8
```

A correction for the unresolved argon in oxygen is made based upon response factors and the amount of argon found in a number of exhaust gas samples by mass spectroscopy.

The actual percent is normalized to 100 percent in the next column on a moisture-free basis, and an Exhaust Gas analysis report is issued as shown in Figure 7. The air-to-fuel ratio is calculated from this analysis, the total hydrocarbon content, and the percent carbon in the fuel.

Oxides of Nitrogen

Equipment: Beckman Ultraviolet Analyzer
Beckman Infrared Analyzer
Recorder - Texas Instrument Company

The above pieces of equipment are in a single, self-contained unit built by Scotts Research Labs, Inc., San Bernadino, California.

Calibrating Gases:
Nitric oxide (3545 ppm in nitrogen)
Nitrogen dioxide (862 ppm in nitrogen)
These standard gases are furnished by Scotts Research Labs, Inc. Nitrogen is used as zero calibrating gas.

Procedure:
Before making NO, NO_2 measurements, the paper filters (Whatman #3) to each analyzer are changed and the Drierite dryer in the exhaust sample line is replaced.

Both analyzers are standardized using the appropriate calibrating gas at a constant flow by use of a flow meter. The zero standardizing is done using nitrogen as the calibrating gas using the same flow rate.

As the instrument is standardized, the exhaust gas is then passed through the analyzer using the same constant flow rate as in the standardization step. The NO, NO_2 values are recorded by the dual pen Servo-riter recorder.

3. Aldehyde Determination

Samples of cold trap condensate collected both ahead of and behind the muffler in Tests VI-XI were analyzed for their aldehyde content by the polarographic procedure described in Appendix A.

IV. EXPERIMENTAL RESULTS

A. DETERMINATION OF EXHAUST SYSTEM TEMPERATURE PROFILE - VEHICLE TESTS

Temperatures measured for the Chevrolet exhaust system during the period of ten days of road testing are presented in Tables VIII-XII. This data is summarized in Figure 8 which shows a plot of the exhaust system temperature profile as a function of road speed. Figure 9 shows a plot of vehicle road speed against engine rpm's.

TABLE VIII

EXHAUST TEMPERATURE PROFILE - ROAD TEST CAR

				Temperature Profile (°F)			
Road Speed	Engine RPM	Intake Manifold Vacuum	**	Manifold Outlet	Ahead of Muffler	After Muffler	End of Tail Pipe
30 mph	1200	19"	E	943	529	406	328
			W	988	575	461	367
40 mph	1575	19"	E	1047	623	470	373
			W	1057	652	515	392
50 mph	1860	-	E	1180	772	618	501
			W	1165	726	605	508
70 mph	2250	14"	E	1321	968	802	*
		15	W	1321	942	802	*

Weather Conditions:
Temp - 75°F
Wind - SW 7 mph
Humidity - 37%
Clear
Barometer - 30.18" steady

*Thermocouple malfunctioning
**Car direction

TABLE IX

EXHAUST TEMPERATURE PROFILE - ROAD TEST CAR

Road Speed	Engine RPM	Intake Manifold Vacuum	**	Temperature Profile (°F) Manifold Outlet	Ahead of Muffler	After Muffler	End of Tail Pipe
50 mph	1875	17.5	E	1150	755	610	480
60	2150	16.25	W	1235	880	690	558
	2150	16.5	E	1240	850	705	560
70	2525	15.0	W	1315	955	818	680
	2525	14.5	E	1285	920	780	645
80	2875	12.5	W	1380	1070	900	760
	2850	13.75	E	1375	1060	910	760
70	2500	15.5	W	1310	930	790	655
	2500	15.5	E	1315	945	790	640

Weather Conditions:

Temp - 77°F

Wind - 5-10 mph

Humidity - Intermittent drizzle

Barometer - 30.11" steady

**Car direction

TABLE X

EXHAUST TEMPERATURE PROFILE - ROAD TEST CAR

Road Speed	Engine RPM	Intake Manifold Vacuum	**	Temperature Profile (°F) Manifold Outlet	Ahead of Muffler	After Muffler	End of Tail Pipe
Warm up				206	166	154	132
30 mph	1200	-	E	900	576	-	325
	1200		W	985	564	-	348
40 mph	1475	-	E	1086	623	-	382
	1550	-	W	1107	720	-	440
50 mph	1900	-	E	1187	799	-	454
	1900	-	W	1210	782	-	472

Weather Conditions:

Temp - 58°F

Winds - Variable

Humidity - 87%

Cloudy

Barometer - 30.22" decreasing

**Car direction

TABLE XI

EXHAUST TEMPERATURE PROFILE - ROAD TEST CAR

Road Speed	Engine RPM	Intake Manifold Vacuum	**	Temperature Profile (°F) Manifold Outlet	Ahead of Muffler	After Muffler	End of Tail Pipe
60 mph	2150	17.75	E	1230	745	680	540
70	2500	19.00	W	1320	800	670	650
80	2900	10.00	E	-	970	930	800
Idle	800	19.5		880	500	460	360
50	1850	18.25	W	980	580	570	400
60	2200	16.5	E	1160	780	640	560
70	2550	14.5	W	1160	880	640	510

Weather Conditions:

Temp - 69°F

Winds - Westerly at 5 mph

Humidity - 65%

Cloudy

Barometer - 30.07"

**Car direction

TABLE XII

EXHAUST TEMPERATURE PROFILE - ROAD TEST CAR

Road Speed	Engine RPM	Intake Manifold Vacuum	**	Temperature Profile (°F) Manifold Outlet	Ahead of Muffler	After Muffler	End of Tail Pipe
50 mph	1875	17.5	E	1150	755	610	480
60	2200	15.0	W	1235	880	690	558
	2150	16.5	E	1240	850	705	560
70	2550	12.5	W	1315	955	818	680
	2525	15.0	E	1285	920	780	645
80	2875	12.5	W	1380	1070	900	760
	2850	13.75	E	1375	1060	910	760
70	2500	15.5	W	1310	930	790	655
	2500	15.5	E	1315	945	790	640

Weather Conditions:

Temp - 90°F

Winds - SSW at 11 mph

Humidity - 76%

Partly cloudy

Barometer - 29.80" steady

**Car direction

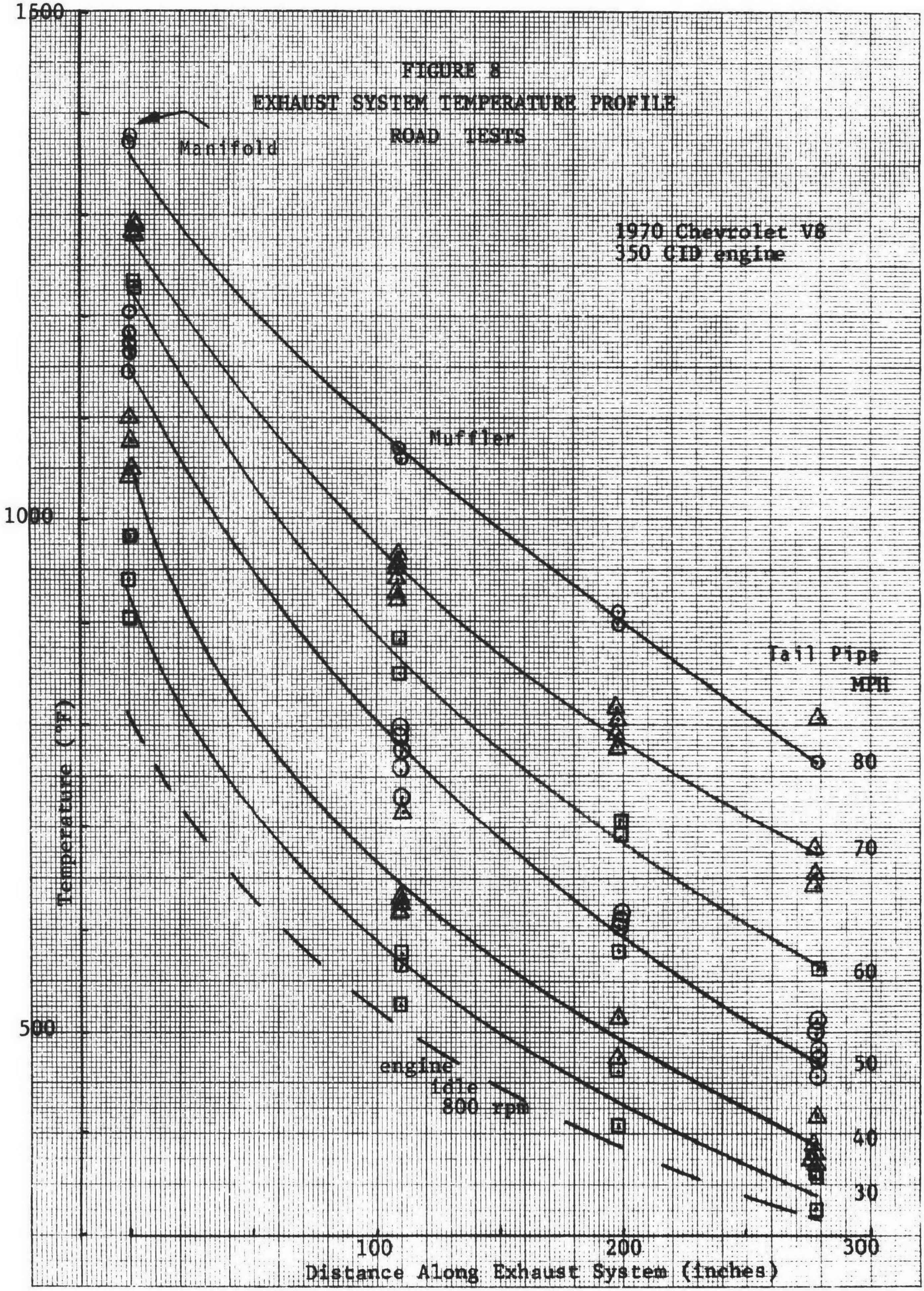


FIGURE 8
EXHAUST SYSTEM TEMPERATURE PROFILE
ROAD TESTS

FIGURE 9

ENGINE SPEED vs ROAD SPEED

(1970 Chevrolet Car)

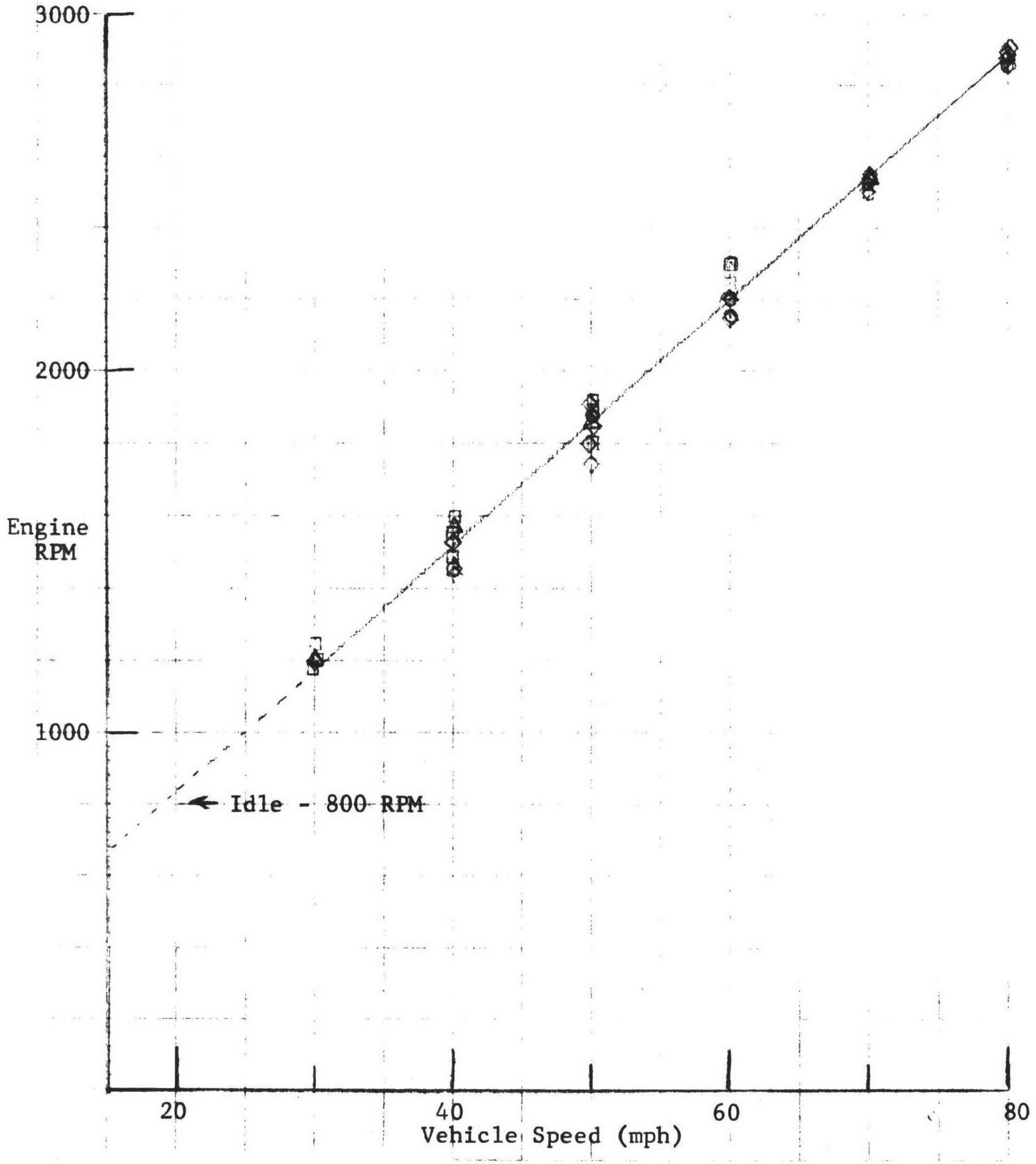
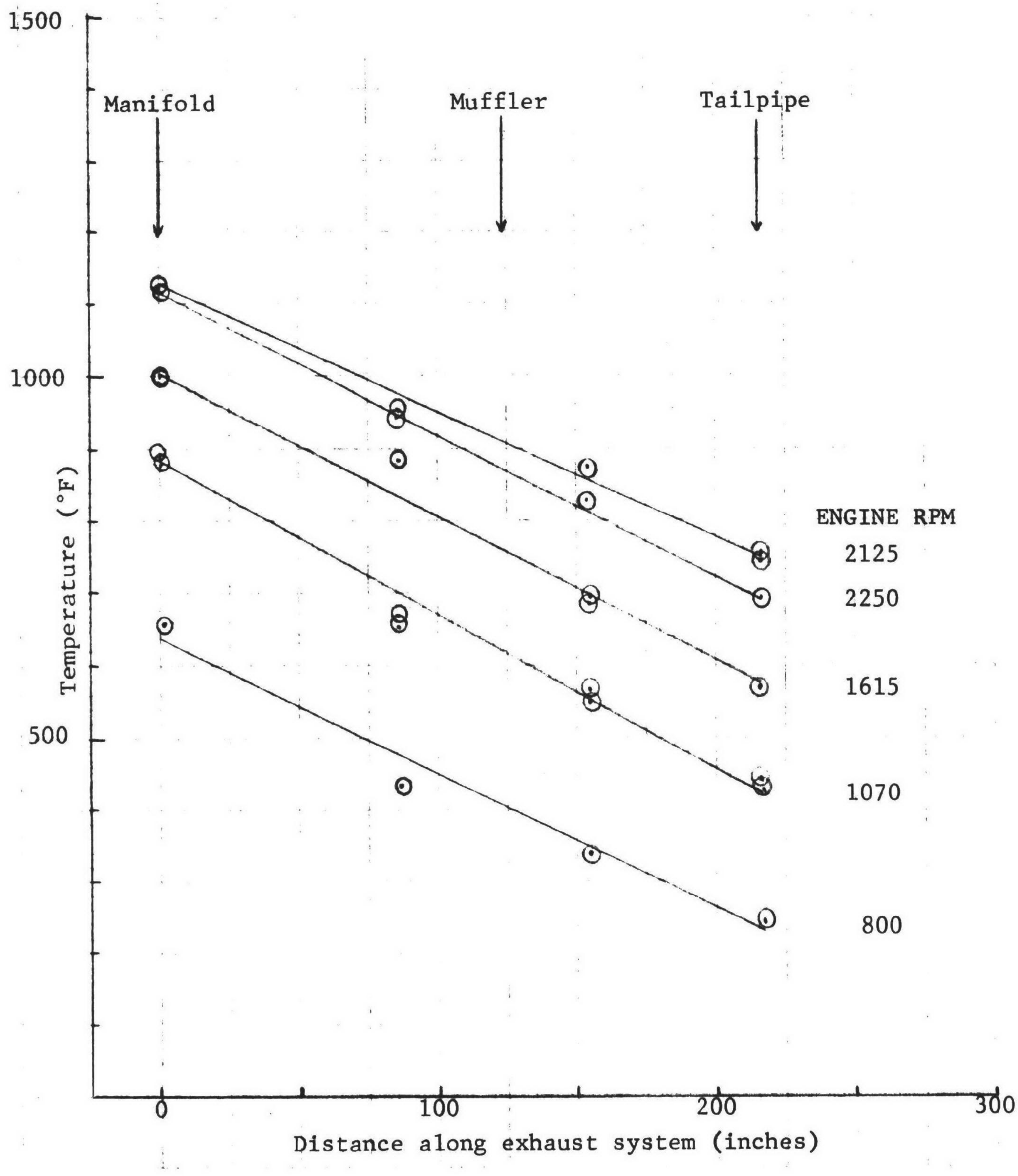


FIGURE 10

EXHAUST SYSTEM TEMPERATURE PROFILE
DYNAMOMETER TESTS
(1970 Chevrolet V8-350 CID)



B. DETERMINATION OF EXHAUST SYSTEM TEMPERATURE PROFILE - DYNAMOMETER TESTS

Data generated in laboratory Tests I and II at five different engine operating speeds is presented in Table XIII and graphically in Figure 10.

TABLE XIII

CHEVROLET EXHAUST SYSTEM TEMPERATURE PROFILE
DYNAMOMETER TESTS

RPM	Observed H.P.	Fuel Lbs/hr	Vacuum Inches Hg	Temperature by Thermocouple Position (°F) I	II	III	IV
800	1.8	8.4	20.3	855	430	325	234
1070	15.0	11.3	16.2	883	657	552	426
1615	21.5	18.0	17.2	996	780	685	560
2125	42.3	31.0	14.4	1120	950	870	740
2250	27.5	29.2	17.2	1109	921	826	690

C. EXHAUST STREAM ANALYSIS

For clarity of presentation the data generated from exhaust stream sampling will be described in two sections. The first deals with those samples collected directly from the exhaust system in Test I-V. The second presents similar data for the analysis of air diluted exhaust stream samples (Tests VI-XI). Data is presented on a run by run basis.

1. Direct Exhaust Stream Analysis

a. Particulate Mass - Weights of particulate matter collected via the four exhaust system sampling probes are shown for a variety of engine operating conditions in Table XIV. These are discussed in the "Discussion of Results" section.

b. Particulate Analysis

Test I - The objective of Test I was to evaluate the sampling procedures chosen and to determine the effect of variations in engine operating conditions on the exhaust system particulate profile.

TABLE XIV

SAMPLING TEMPERATURE AND PARTICULATE SAMPLE WEIGHTS

Test	RPM	Position	Temperature (°F)	Andersen Sampler and/or Gelman Filter (gm/mile)	Cold Trap Condensate (gm)
I	870	I	655	0.0394	21.02
		II	430	.0403	26.55
		III	325	.0357	17.38
		IV	234	.0475	37.46
	1070	I	883	.0727	19.80
		II	657	.0342	29.07
		III	552	.0161	24.78
		IV	426	.0346	38.72
	1615	I	996	.0976	19.18
		II	780	.0709	28.50
		III	685	.0601	23.38
		IV	560	.0565	27.12
	2125	I	1120	.245	24.12
		II	950	.316	34.19
		III	870	.477	27.37
		IV	740	.513	24.02
II	2250	I	1109		
		II	921		
		III	826		
		IV	690	.0298*	242 30.6899 4.0762 (b)
III	2250	I	1125	.0765	66.63
		II	925	.0448	89.73
		III	825	.00474	13.16
		IV	690	.0720*	111.45
IV	2250	I	1125	.0859	94.35
		II	945	.0590	205.54
		III	850	.0737*	1.13
		IV	725	.0059	31.48
V	2250	I	1100	.165(a)	63.27
		II	905	.0155*	11.91
		III	810	.00916	1.82
		IV	675	.0155	13.54

(a) Sample contaminated by metal from back-up plate

*Andersen and Gelman (b) Three cold traps in series

FIGURE 11

PARTICULATE SAMPLING DEVICES - TEST I

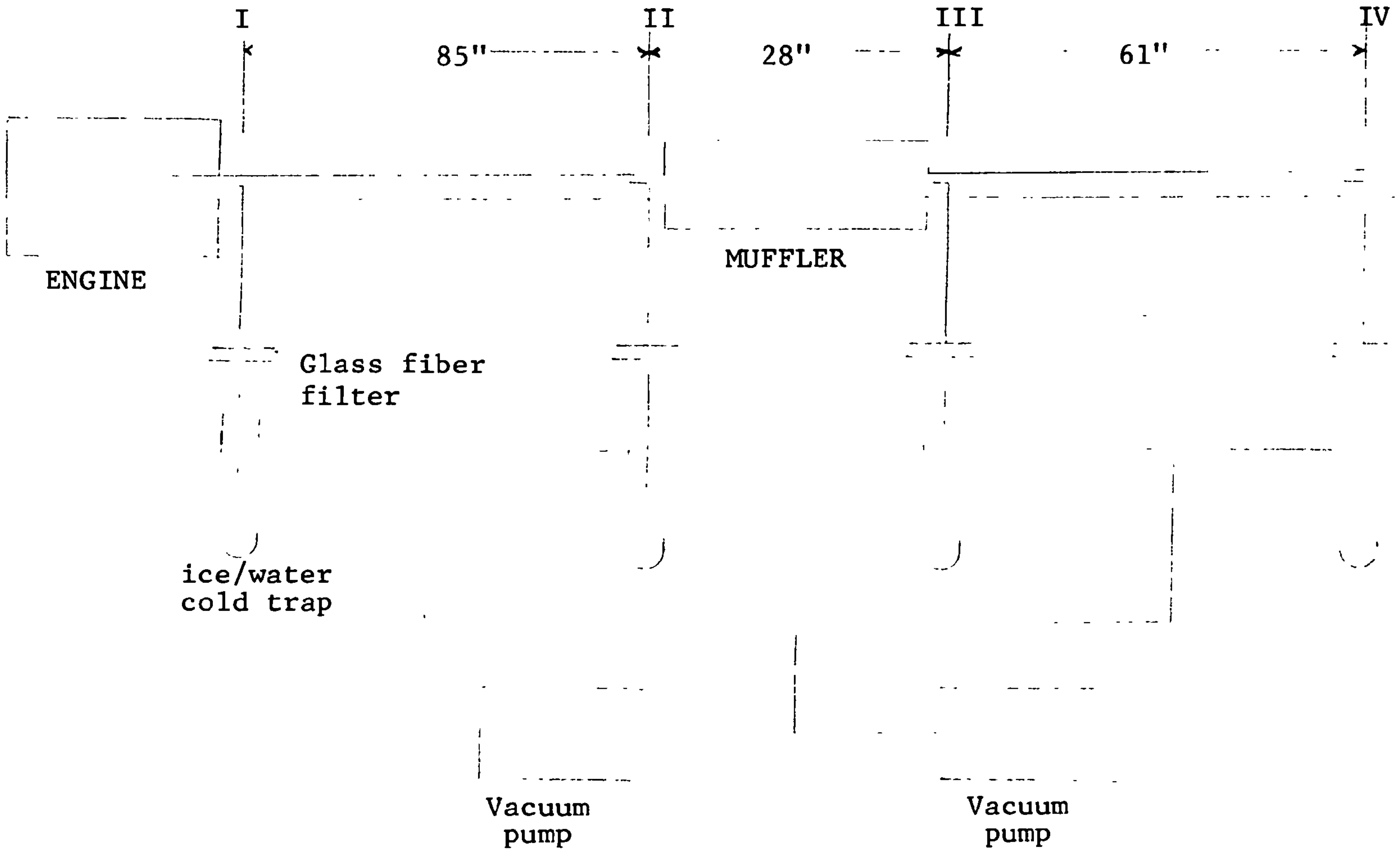


TABLE XV

SUMMARY OF OBSERVATIONS ON PARTICULATES COLLECTED AT POSITION I
(Exhaust Manifold Outlet)

	870 RPM	1070 RPM	1615 RPM	2125 RPM
Distribution on filter	Uniform	Heaviest at center and outer edge with sparse concentration in between.	Heaviest at center and outer edge with sparse concentration in between.	Heaviest at center and outer edge with sparse concentration in between.
Overall appearance	Fine, light colored particles only.	Fine, light colored particles plus a few larger dark particles.	Fine, light colored particles plus a few larger dark particles.	Fine, light colored particles plus a few larger dark particles.
Crystal growth on glass fibers	Very evident	Very evident	Very evident (some of growth is abnormally dark up where the deposit is light.	Very evident (some of growth is abnormally dark up where the deposit is light.
Appearance with polarized light	Supports above conclusions.	Shows the presence of some dark, opaque non-birefringent particles in addition to the transparent birefringent crystals.	Shows the presence of some dark, opaque non-birefringent particles in addition to the transparent birefringent crystals.	Shows the presence of some dark, opaque non-birefringent particles plus some dark red birefringent particles (probably Fe_2O_3) as is the transparent birefringent crystals.
Particle size	<1-20μ	<1-10μ	<1-10μ	<1-6μ
X-ray diffraction identification	$Pb(Br,Cl)_2$ Br:Cl ∿1:1	$Pb(Br,Cl)_2$ Br: Cl ∿1:1 with lesser amount of unidentified phase and 5% metallic lead. (This is the first time that metallic lead has been detected as such.	$Pb(Br,Cl)_2$ Br:Cl ∿1:1	$Pb(Br,Cl)_2$ Br:Cl ∿1:1 with lesser amount of unidentified phase and 5% metallic lead.

TABLE XVI

SUMMARY OF OBSERVATIONS ON PARTICULATES COLLECTED AT POSITION II
(Muffler Inlet)

	870 RPM	1070 RPM	1615 RPM	2125 RPM
Distribution on filter	Uniform, appears to be continuous fused deposits.	Uniform and does not have fused appearance.	Uniform, does not have fused appearance, but is a heavier deposit than found for 1070 rpm.	Uniform, does not have fused appearance, but is a heavier deposit than found for 1615 rpm.
Overall appearance	Only a few foreign particles observed.	Only a few foreign particles observed.	Only a few large dark particles observed.	Only a few large dark particles observed.
Crystal growth on glass fibers	Evident but not as evident as at manifold outlet.	Relatively small.	Moderate on exposed fibers.	Heavy on exposed fibers, but most fibers are covered by deposit.
Appearance with polarized light	Lower birefringent than observed on Series I and only a trace of foreign particles.	Similar to 870 rpm but shows occasional highly birefringent particle.	Similar to that at 870 and 1615 rpm.	5-10% of highly birefringent particles as well as occasional red particle.
Particle size	<1-20μ	<1-5μ except for occasional particle as large as 10-20.	<1-5μ	<1-10μ
X-ray diffraction identification	$Pb(Br,Cl)_2$ Br:Cl ∿1:1	$Pb(Br,Cl)_2$ Br:Cl ∿1:1	$Pb(Br,Cl)_2$ Br:Cl ∿1:1	$Pb(Br,Cl)_2$ Br:Cl ∿15:1

TABLE XVII

SUMMARY OF OBSERVATIONS ON PARTICULATES COLLECTED AT POSITION III (Muffler Outlet)

	870 RPM	1070 RPM	1615 RPM	2125 RPM
Distribution on filter	Non-uniform with certain small areas having no deposit.	Non-uniform with certain small isolated areas having almost no deposit. Lesser deposit than at 870 rpm.	Uniform deposit except for several isolated points which have no deposit. Heavier deposit similar to that at 870 rpm.	Uniform deposit except for several isolated points which have no deposit Heaviest deposit of the III series.
Overall appearance	Matted appearance moderate number of larger dark particles found only in certain areas.	A few larger dark particles are present.	Closely matted deposit. A few larger dark particles are present.	Matted appearance Surface pitted due to presence of many larger particles - some light and some large dark particles.
Crystal growth on glass fibers	Crystal growth on glass fibers varied from light to moderate depending upon area observed.	Light crystal growth on glass fibers.	Minor crystal growth on fibers.	Most of the glass fibers are covered by the deposit, but a few exposed fibers do show crystal growth.
Appearance	Low birefringence.	Low birefringence.	Low birefringence.	In addition to the low birefringent particles ∿5% of high birefringent and 5-10% black and white particles were observed. Reddish particles, probably Fe_2O_3.
Particle size	<1-5μ	<1-7μ	<1-10μ	<1-8μ
X-ray diffraction identification	$Pb(Br,Cl)_2$ Br:Cl ∿1:1 Unidentified phase which is different than found in 1070 rpm and 2125 rpm.	$Pb(Br,Cl)_2$ Br:Cl ∿1:1	$Pb(Br,Cl)_2$ Br:Cl ∿1.5:1	$Pb(Br,Cl)_2$ Br:Cl ∿1.5:1 Dark particles; equal parts Fe_2O_3 and $Pb(Br,Cl)_2$- Br:Cl ∿1.5:1.

TABLE XVIII

SUMMARY OF OBSERVATIONS ON PARTICULATES COLLECTED AT POSITION IV
(End of Tail Pipe)

	870 RPM	1070 RPM	1615 RPM	2125 RPM
Distribution on filter	Fairly uniform deposit except for a few irregular, nearly void spots.	Fairly uniform deposit but less than at 870 rpm.	Fairly uniform deposit similar to that at 1070 rpm.	Heaviest deposit of the series.
Overall appearance	Matted surface with numerous larger light particles as well as larger dark particles embedded in the matted surface.	Not sufficient deposit to have matted appearance. Dark particles are smaller than on other filters but they are numerous.	Dark particles and other larger agglomerates are larger than found after the muffler at 1070 rpm.	Matter surface with a heavy deposit of large dark particles as well as a moderate amount of medium sized light particles.
Crystal growth on glass fibers	Most glass fibers are covered by deposit but a few exposed fibers do show light crystal growth.	Slight crystal growth on fibers.	More extensive than observed at 1070 rpm.	Moderate crystal growth on exposed fibers.
Appearance with polarized light	In addition to low birefringent particles, there is a trace of high birefringent particles and up to 5% of reddish or blackish particles.	In addition to low birefringent particles, there is a trace of high birefringent particles and up to 5% of reddish or blackish particles.	In addition to low birefringent particles, there are 1-5% highly birefringent particles and about 5% of reddish and blackish particles.	In addition to low birefringent particles, there are 1-5% highly birefringent particles and up to 5% of reddish and blackish particles.
Particle size	<1-8μ	<1-12μ	<1-8μ	<1-8μ
X-ray diffraction identification	$Pb(Br,Cl)_2$ Br:Cl $\sim$1:1 plus 5-10% of some unidentified phase as found after the muffler at 870 rpm.	$Pb(Br,Cl)_2$ Br:Cl $\sim$1:1 plus 10-15% of some unidentified phase as found after the muffler at 870 rpm.	$Pb(Br,Cl)_2$ Br:Cl $\sim$1:1	$Pb(Br,Cl)_2$ Br:Cl $\sim$1.5:1 Dark particles: Fe_2O_3 plus 10-20% $Pb(Br,Cl)_2$ - Br:Cl $\sim$1:1

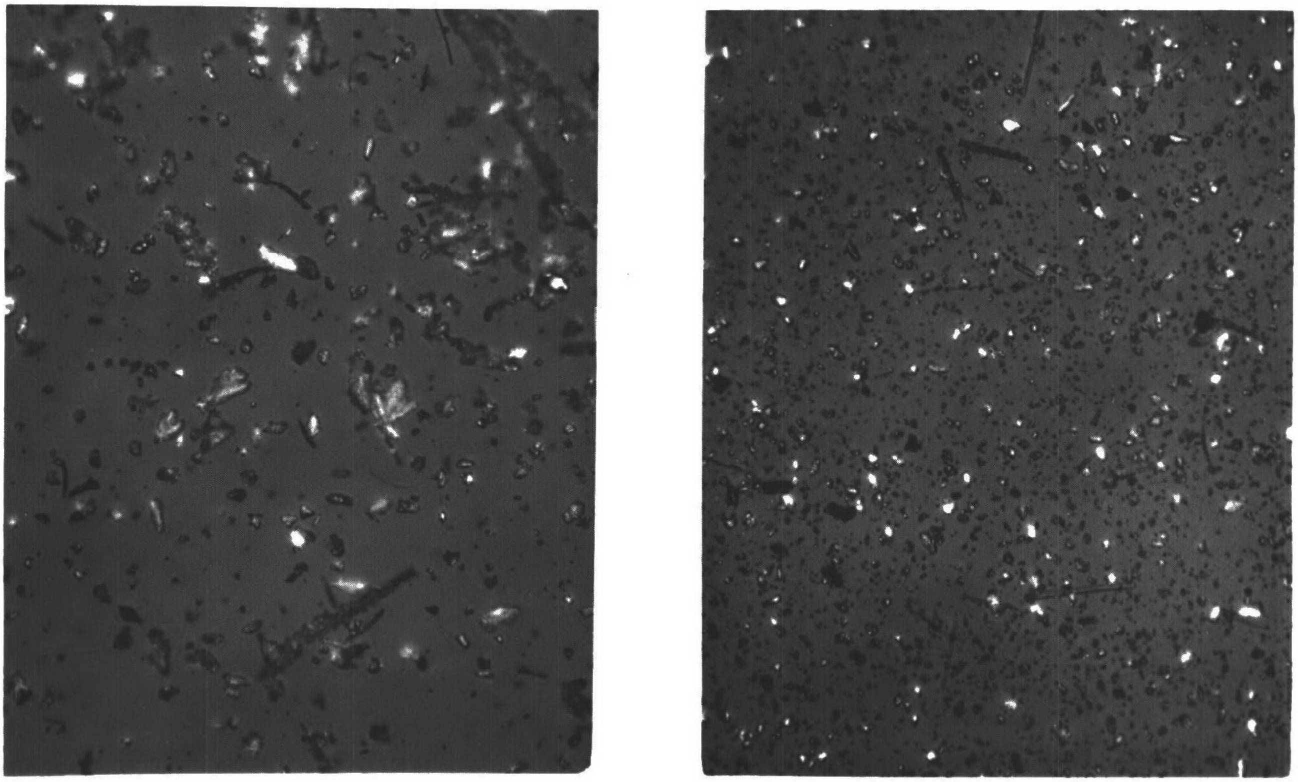
TABLE XIX

OBSERVATIONS OF CRYSTAL GROWTH AGAINST DECREASING EXHAUST GAS STREAM TEMPERATURES

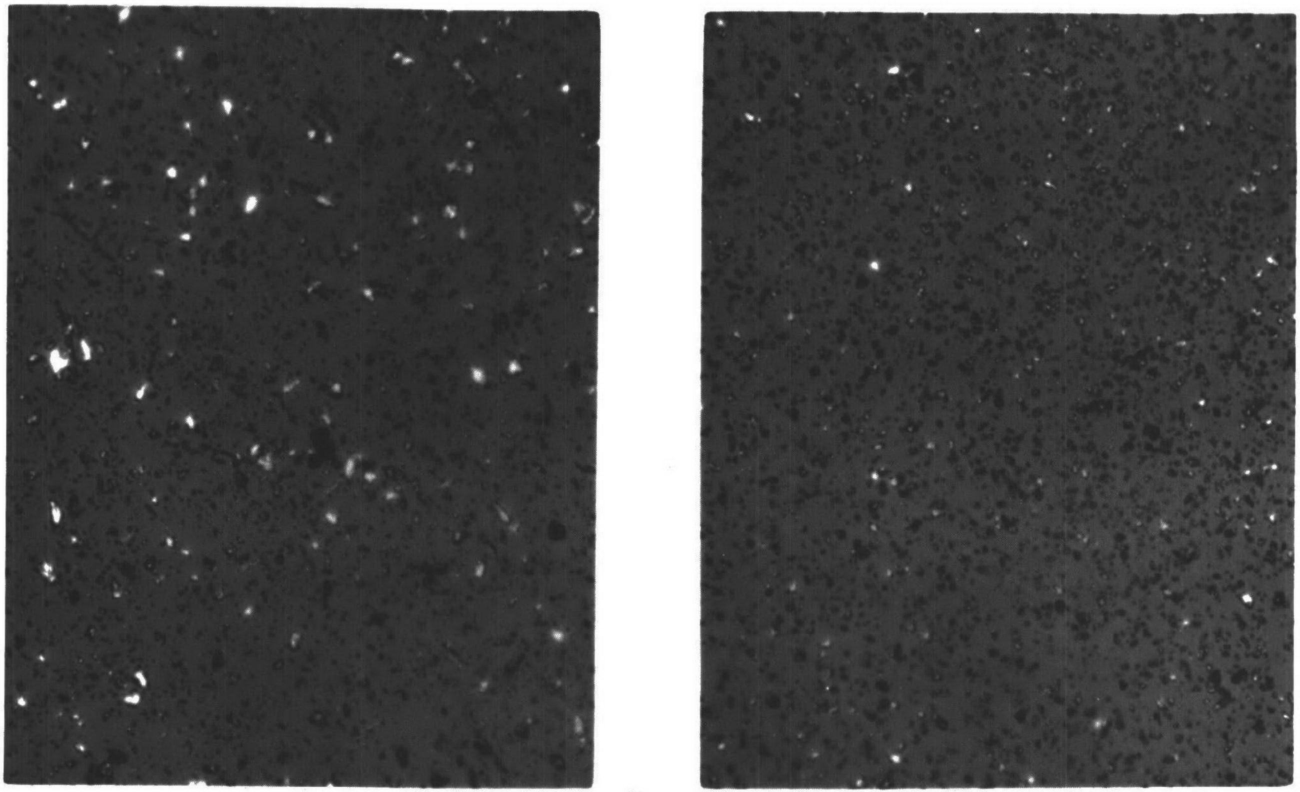
Position	RPM	Temp. (°F)	X-ray Diffraction Species	Dendritic Crystal Growth
I	2125	1120	$Pb(Br,Cl)_2$ ∿1:1 <5% Pb, 5-10% unknown (Compound "A")	Very evident
I	1615	995	$Pb(Br,Cl)_2$ ∿1:1	Very evident
II	2125	952 934	$Pb(Br,Cl)_2$ ∿1.5:1 (M. Pt. $PbCl_2$)	Heavy on exposed fibers
I	1070	880	$Pb(Br,Cl)_2$ ∿1:1	Very evident
III	2125	870	$Pb(Br,Cl)_2$ ∿1.5:1 Fe_2O_3	Very evident on exposed fibers
II	1615	780	$Pb(Br,Cl)_2$ ∿1:1	Moderate
IV	2125	740 702	$Pb(Br,Cl)_2$ ∿1:1 (M. Pt. $PbBr_2$)	Moderate
III	1615	685	$Pb(Br,Cl)_2$ ∿1.5:1	Minor
II	1070	660	$Pb(Br,Cl)_2$ ∿1:1	Relatively small
I	870	655	$Pb(Br,Cl)_2$ ∿1:1	Very evident
IV	1615	560	$Pb(Br,Cl)_2$ ∿1:1	Moderate
III	1070	555	$Pb(Br,Cl)_2$ ∿1:1	Light
IV	1070	430	$Pb(Br,Cl)_2$ ∿1:1 10-15% unknown (Compound "B")	Slight
II	870	430	$Pb(Br,Cl)_2$ ∿1:1	Evident
III	870	325	$Pb(Br,Cl)_2$ ∿1:1 10-15% unknown (Compound "B")	Light to moderate
IV	870	234	$Pb(Br,Cl)_2$ ∿1:1 5-10% unknown (Compound "B")	Light

Figure 12

THE EFFECT OF ENGINE SPEED ON THE PARTICULATE MATTER COLLECTED AT POSITION I (NEAR EXHAUST MANIFOLD)



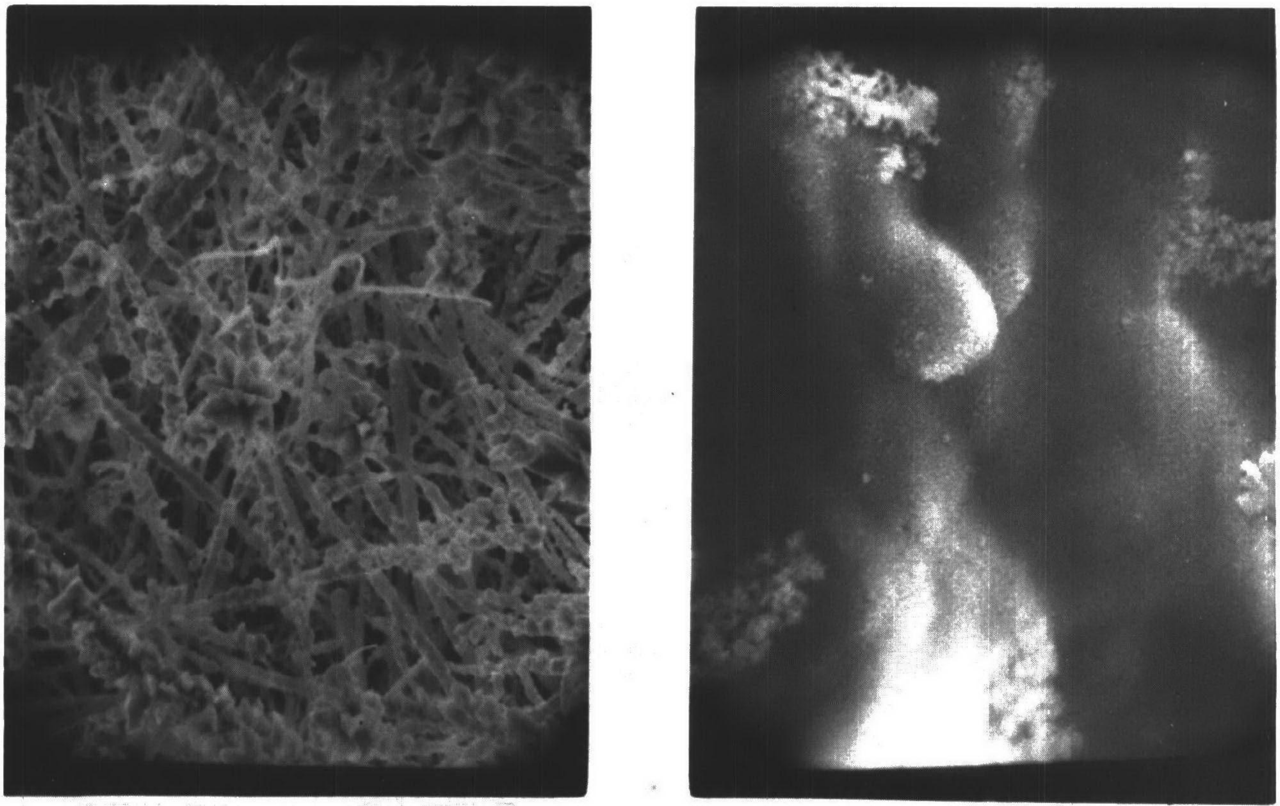
870 RPM 400X 1070 RPM



1615 RPM 2125 RPM

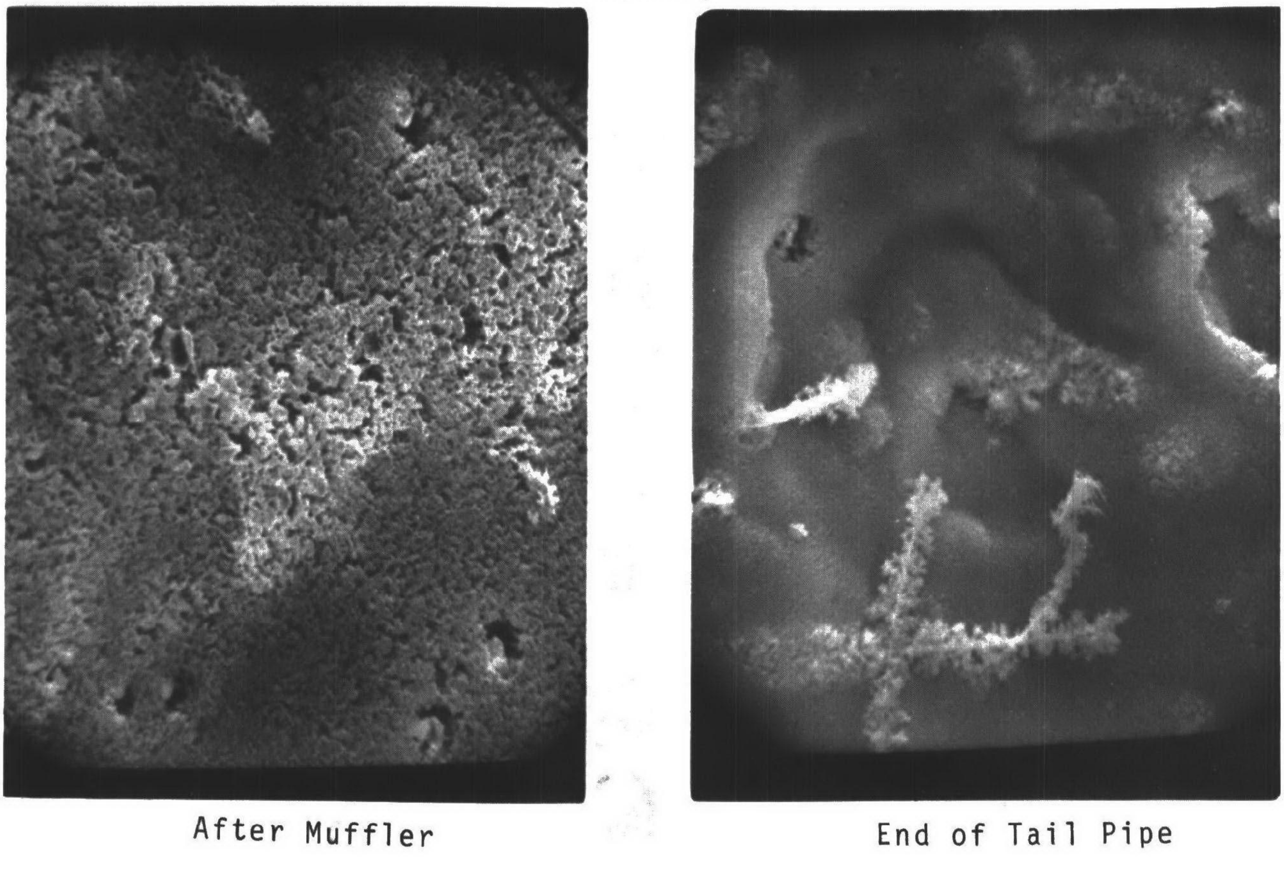
Figure 13

SEM STUDY OF PARTICULATE MATTER COLLECTED
AT FOUR LOCATIONS IN THE EXHAUST SYSTEM AT
870 RPM



Near Exhaust Manifold 1,000x Ahead of Muffler

A-series



After Muffler End of Tail Pipe

Figure 14

SEM STUDY OF PARTICULATE MATERIAL COLLECTED
AT POSITION I AT 870 RPM

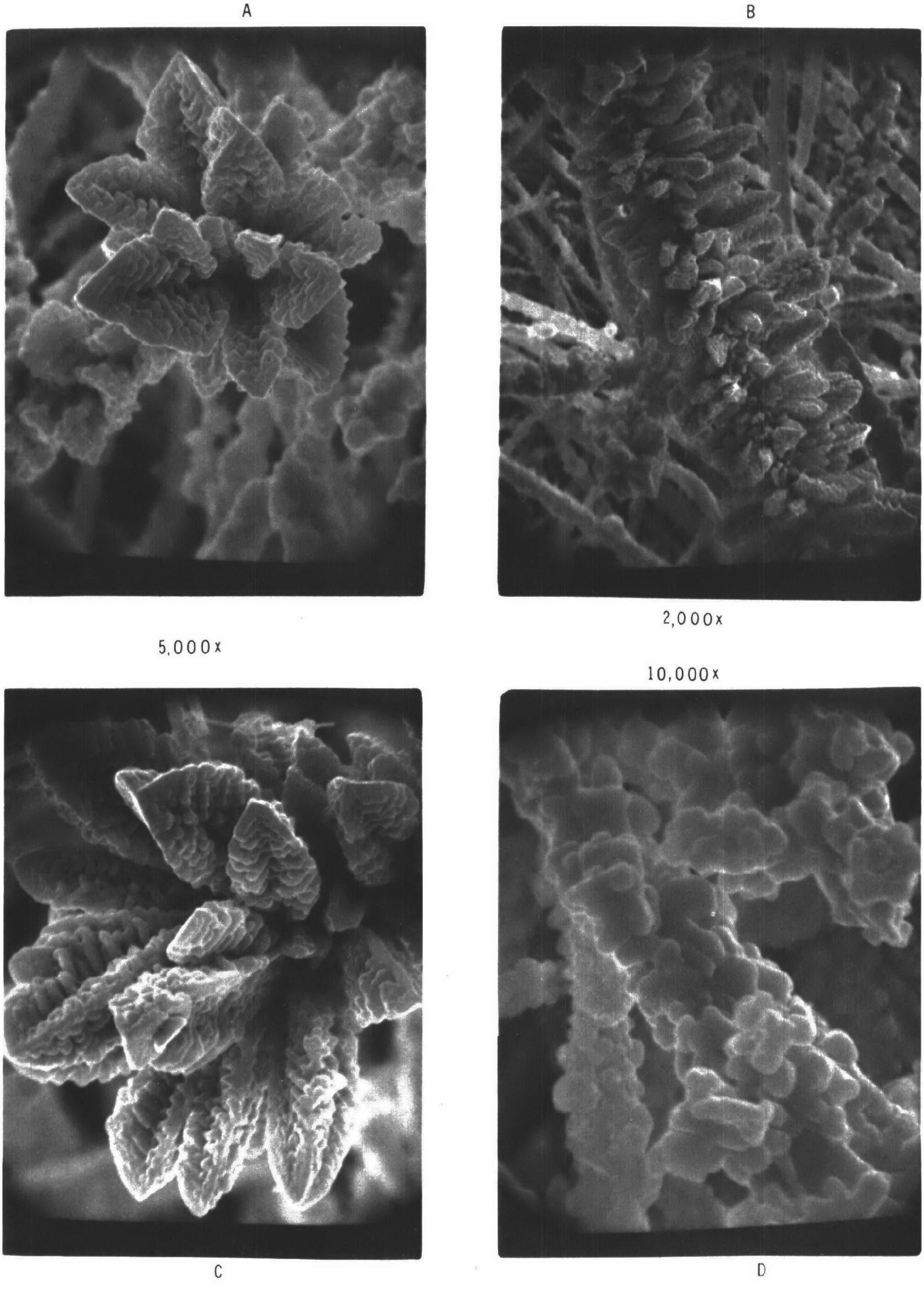
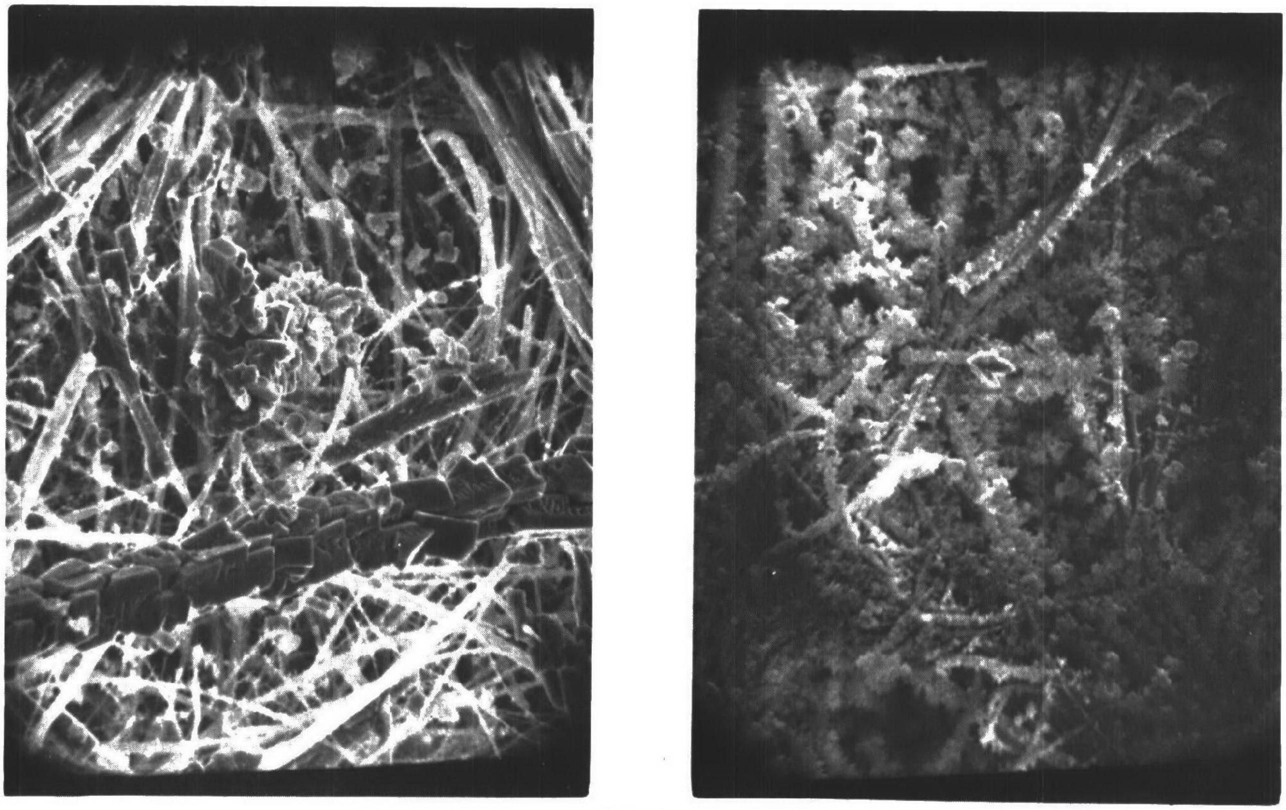


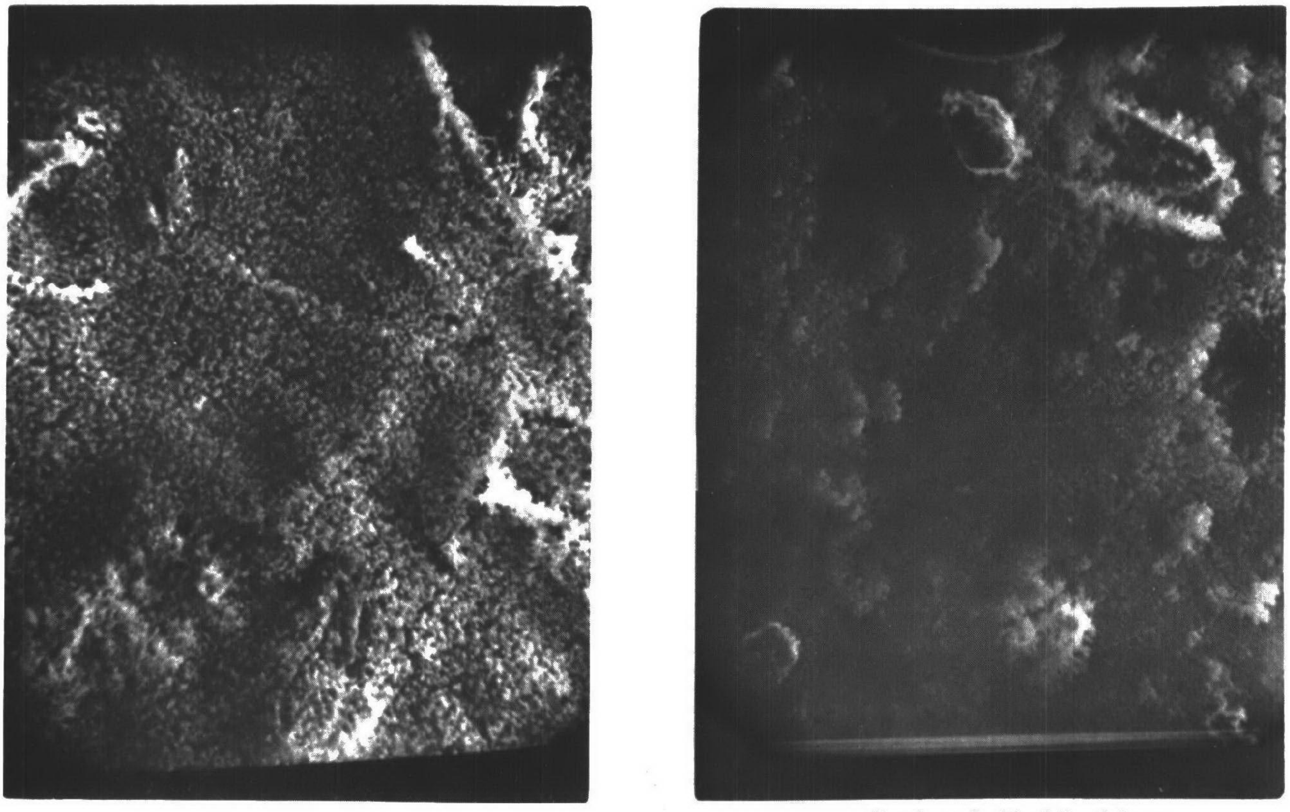
Figure 15

SEM STUDY OF PARTICULATE MATERIAL COLLECTED AT FOUR LOCATIONS IN THE EXHAUST SYSTEM AT 1070 RPM



Near Exhaust Manifold 1,000x Ahead of Muffler

B-series



After Muffler End of Tail Pipe

Figure 16

SEM STUDY OF PARTICULATE MATERIAL COLLECTED
AT POSITION I AT 1070 RPM

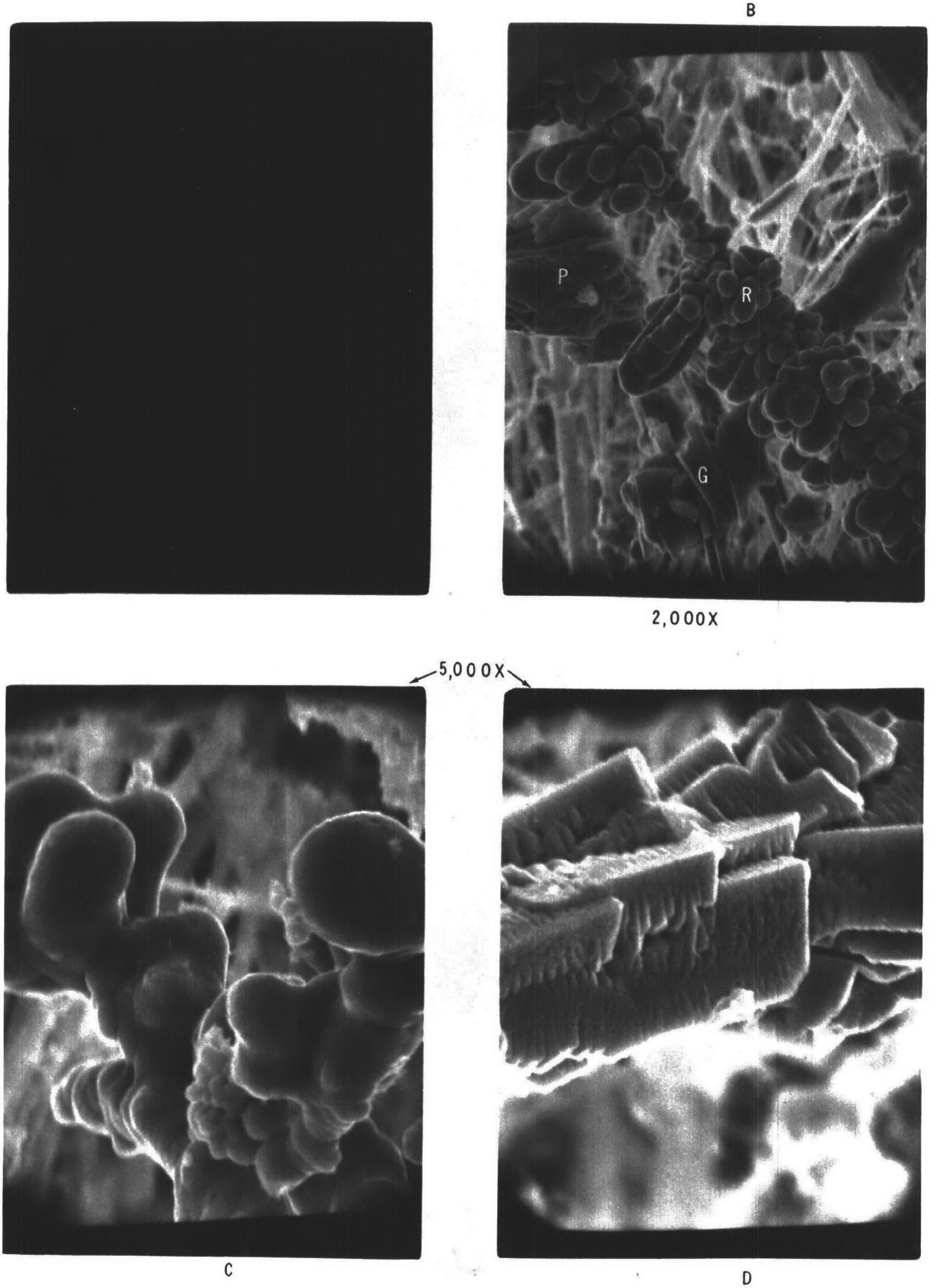
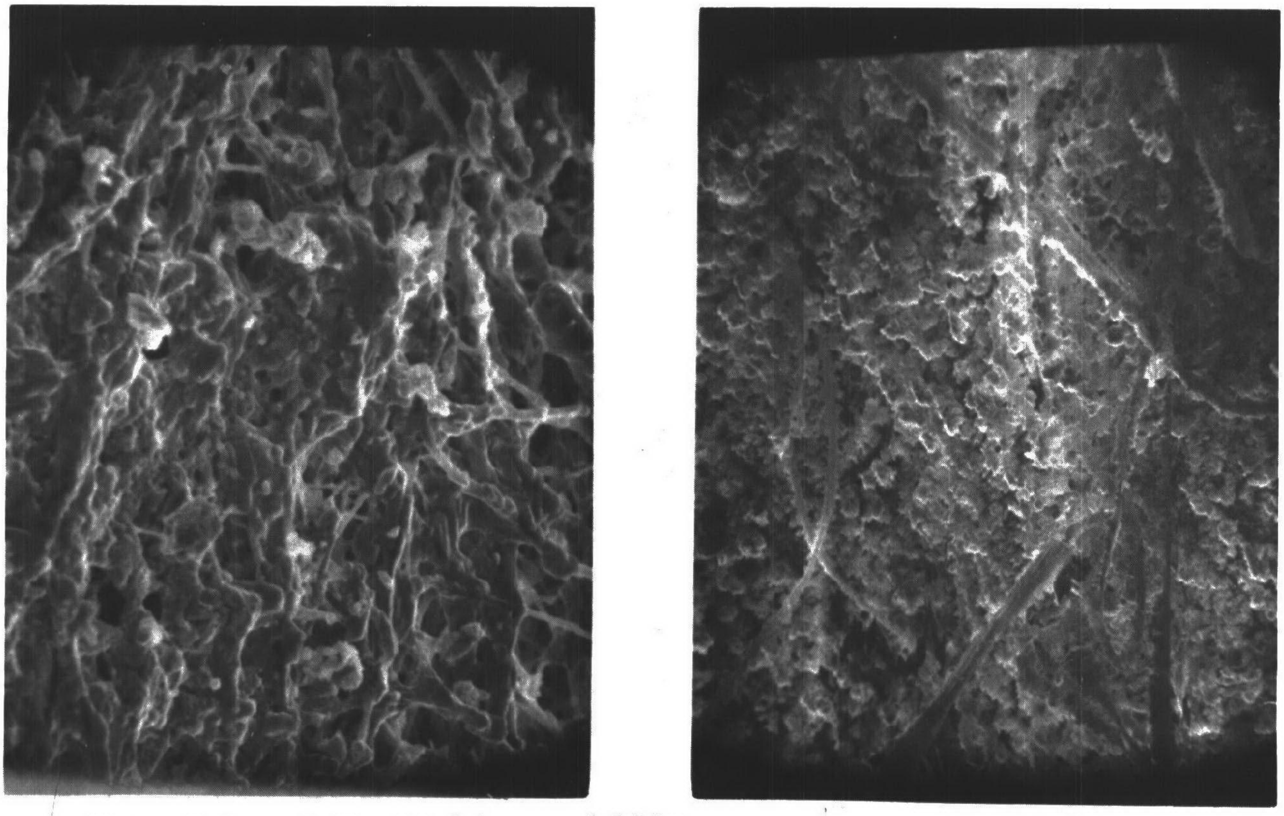


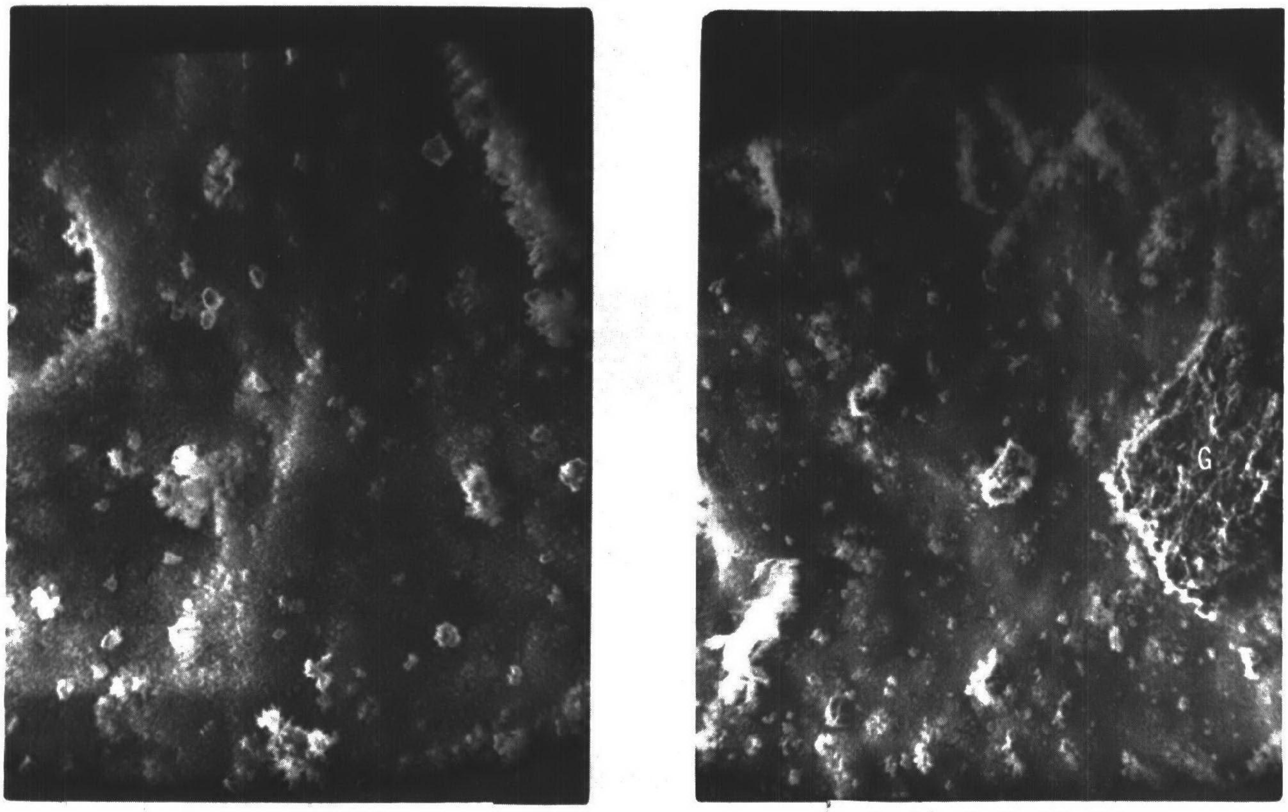
Figure 17

SEM STUDY OF PARTICULATE MATERIAL COLLECTED
AT FOUR LOCATIONS IN THE EXHAUST SYSTEM AT
1615 RPM



Near Exhaust Manifold 1,000x Ahead of Muffler

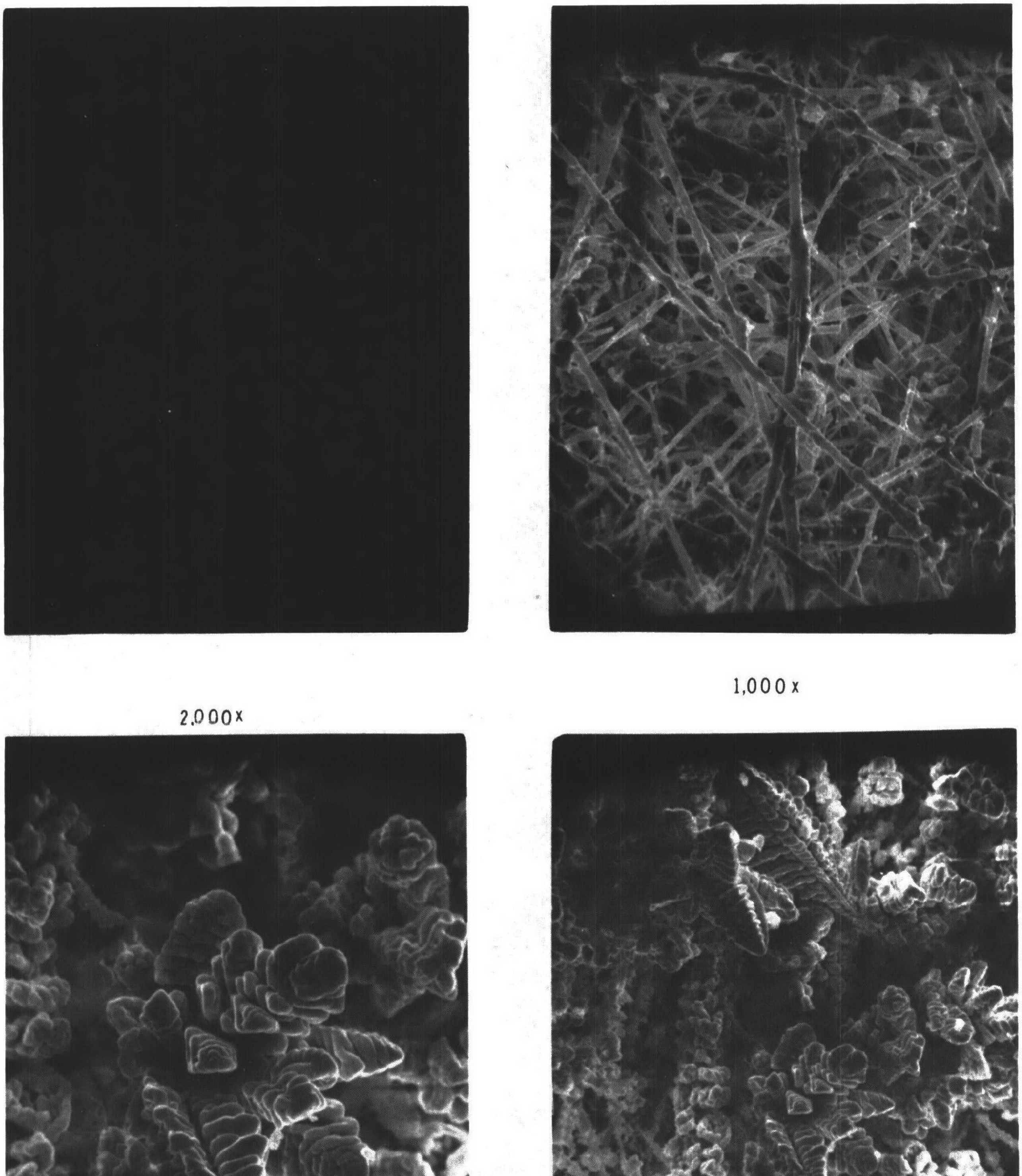
C-series



After Muffler End of Tail Pipe

Figure 18

SEM STUDY OF PARTICULATE MATERIAL COLLECTED AT POSITION I AT 1615 RPM

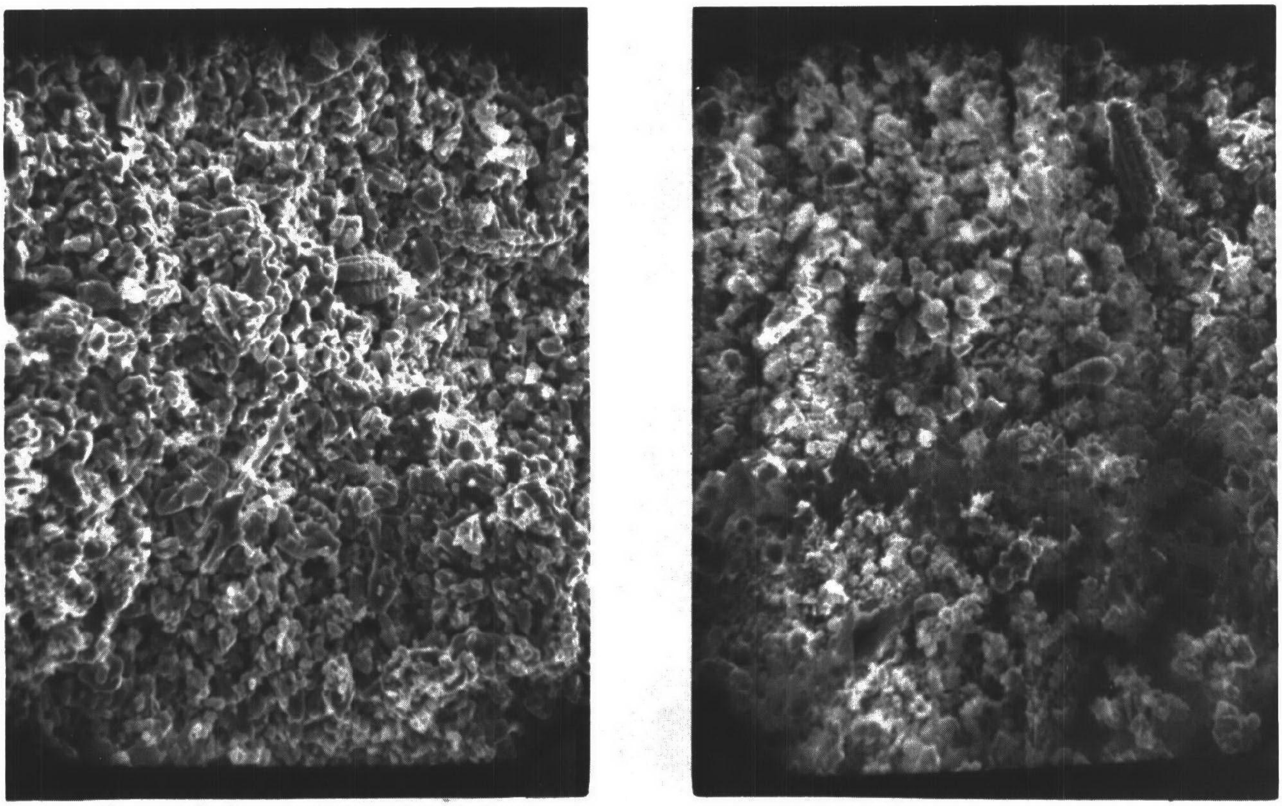


2,000x

1,000x

Figure 19

SEM STUDY OF PARTICULATE MATERIAL COLLECTED
AT FOUR LOCATIONS IN THE EXHAUST SYSTEM AT
2125 RPM

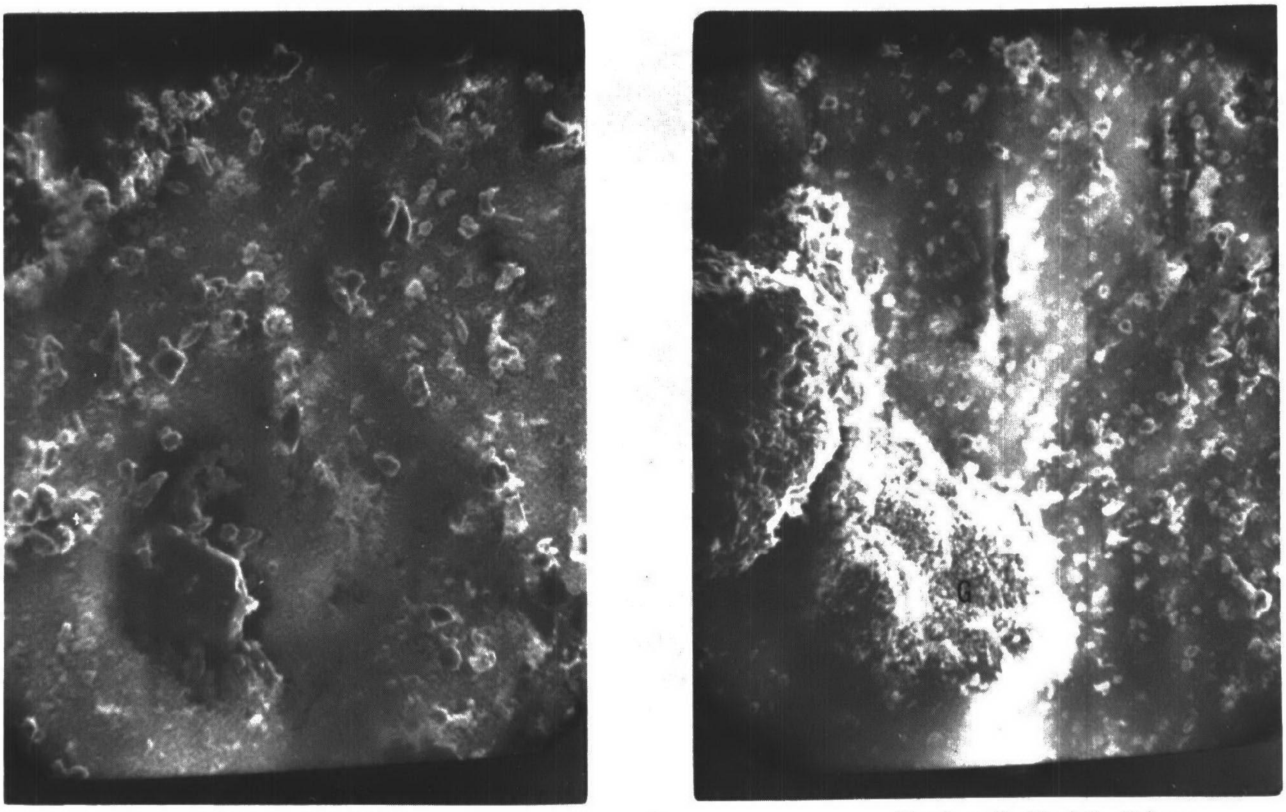


Near Exhaust Manifold

1,000x

Ahead of Muffler

D-series

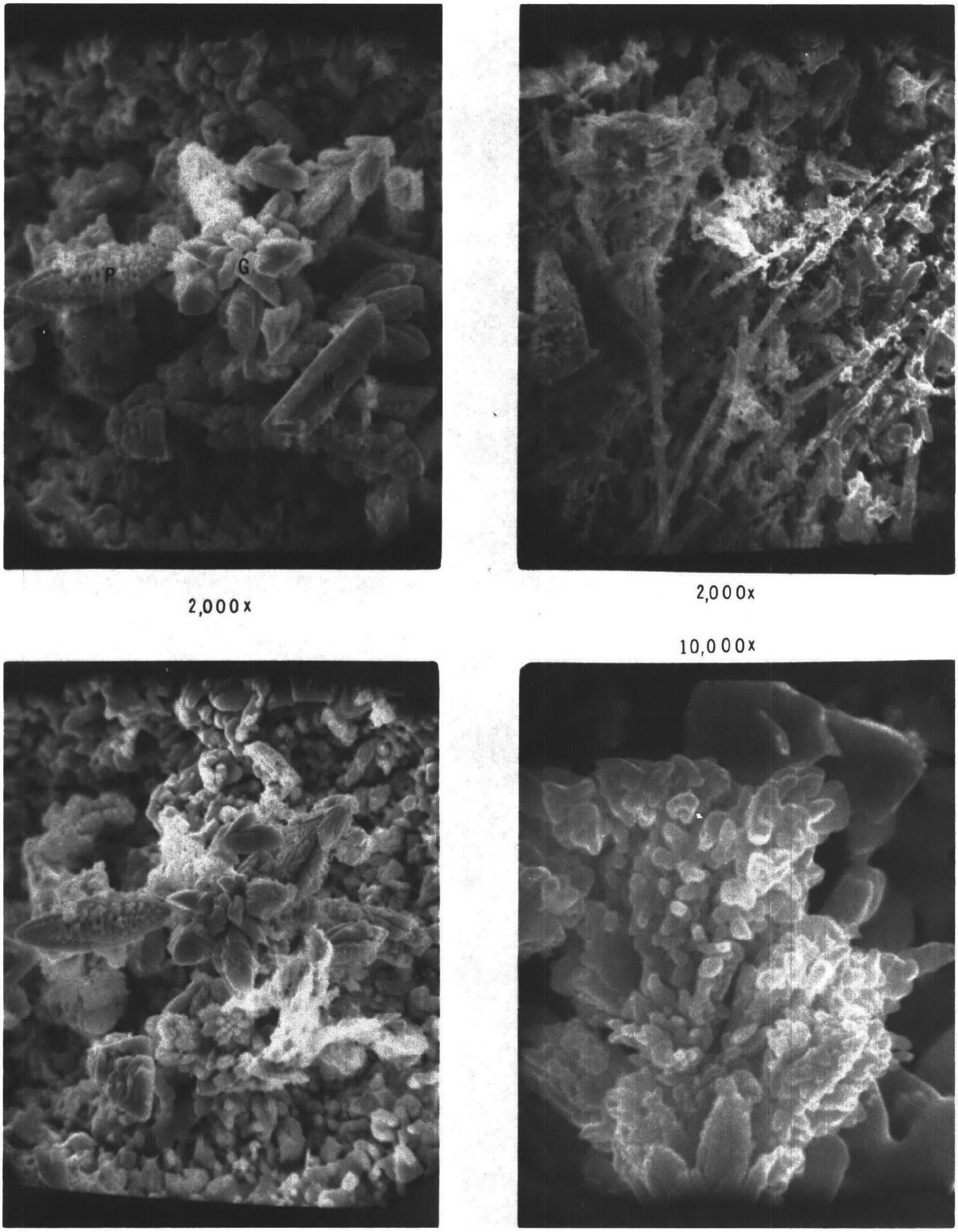


After Muffler

End of Tail Pipe

Figure 20

SEM STUDY OF PARTICULATE MATERIAL COLLECTED AT POSITION I AT 2125 RPM



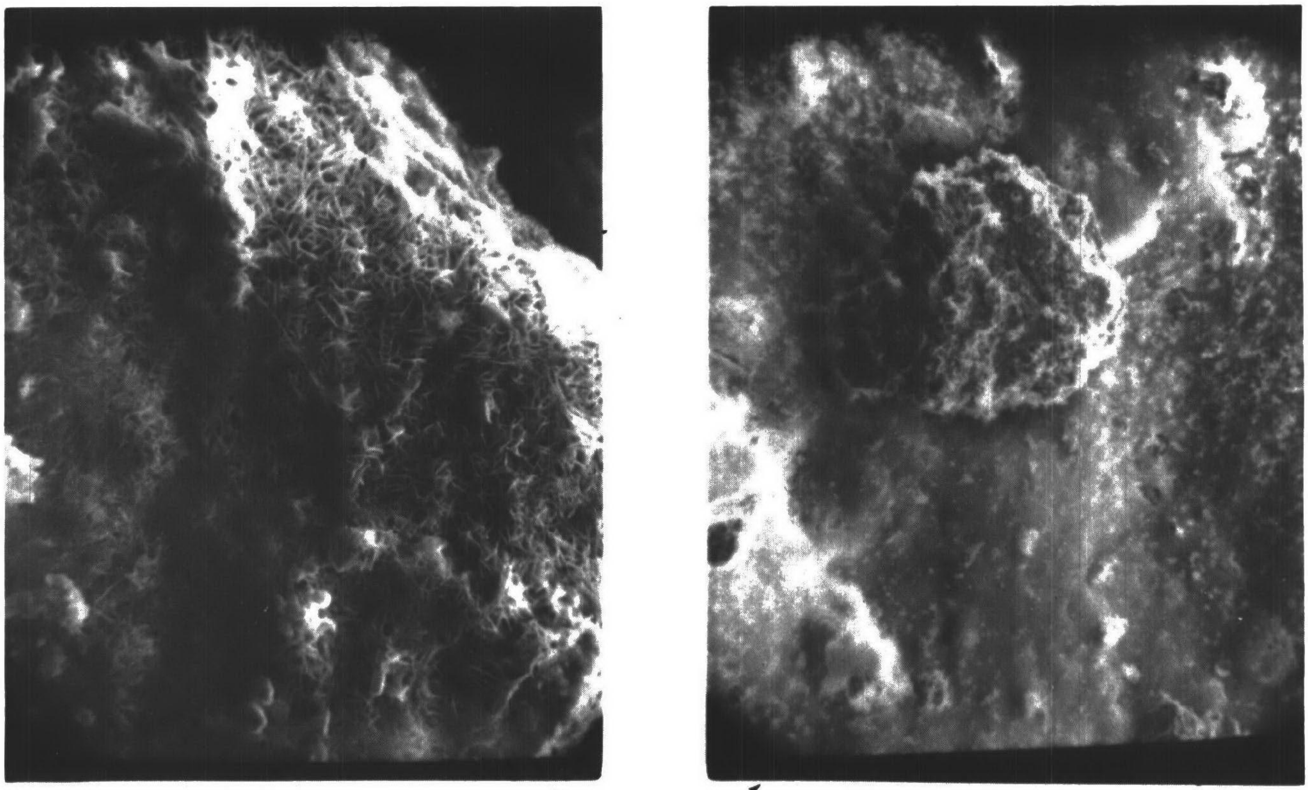
2,000x

2,000x

10,000x

Figure 21

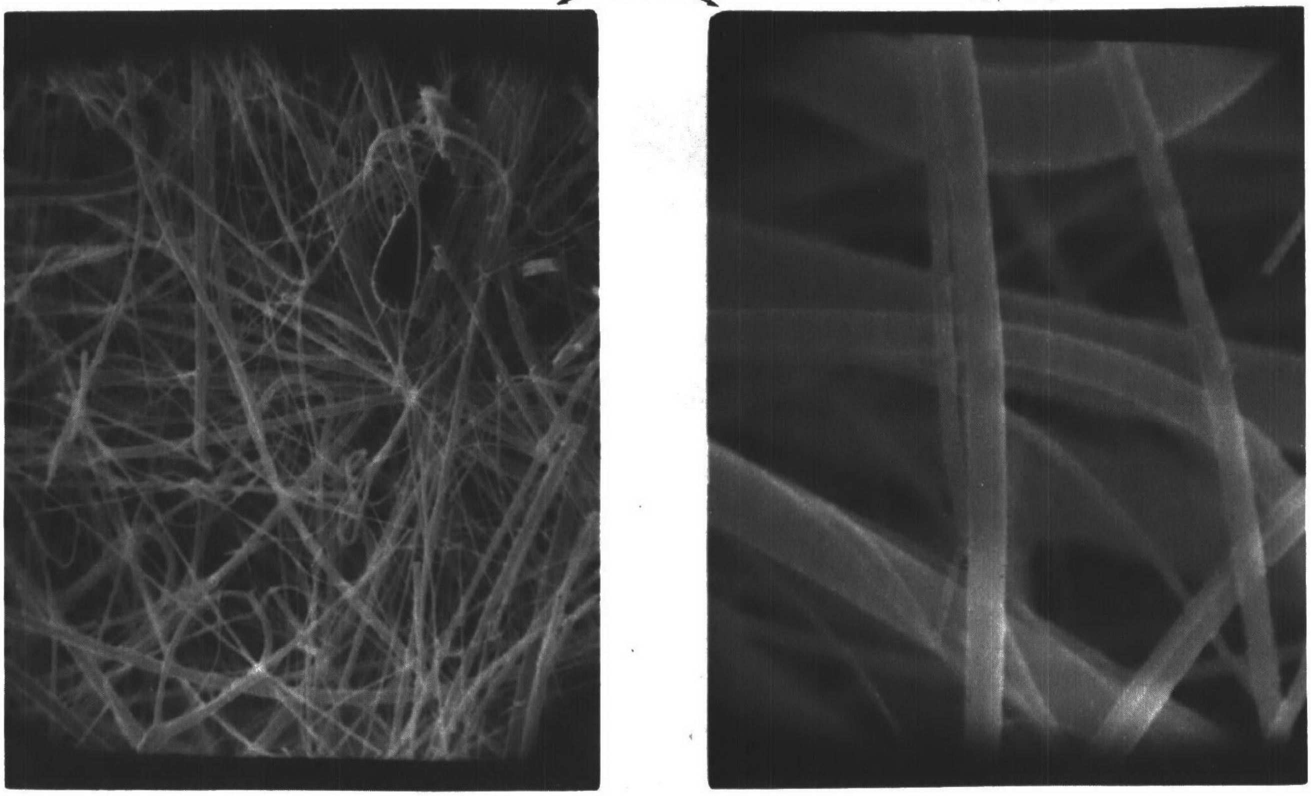
SEM STUDY OF PARTICULATE MATERIAL COLLECTED AT POSITION IV AT 2125 RPM



1,000x ← filter IV-D → 200x

SEM STUDY OF UNUSED GLASS FIBER FILTER

← blank → 10,000x



1,000x

Figure 22

TRANSMISSION ELECTRON MICROSCOPY STUDY OF PARTICULATE MATERIAL COLLECTED AT POSITION I

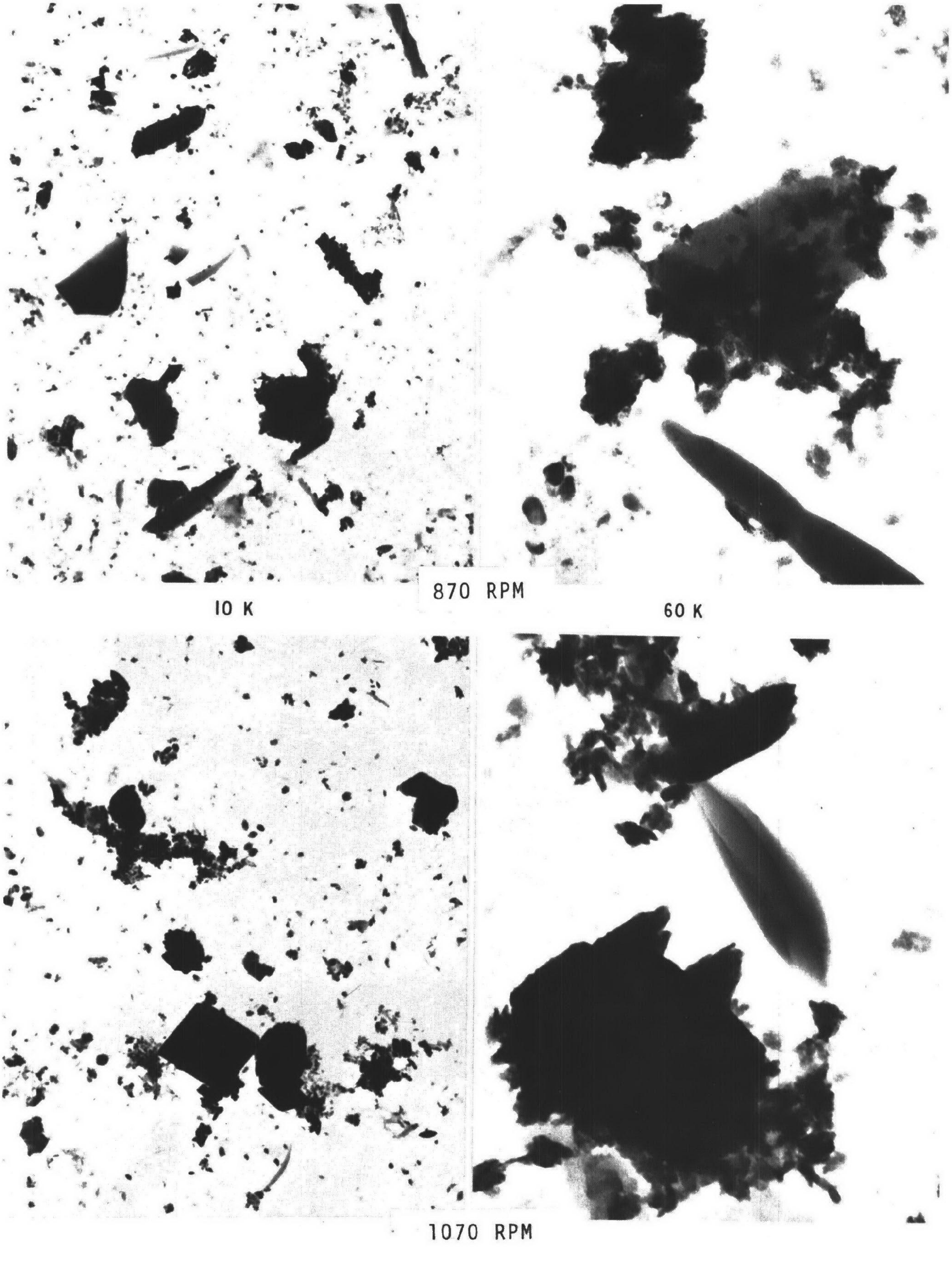


Figure 23

TRANSMISSION ELECTRON MICROSCOPY STUDY OF PARTICULATE MATERIAL COLLECTED AT POSITION I

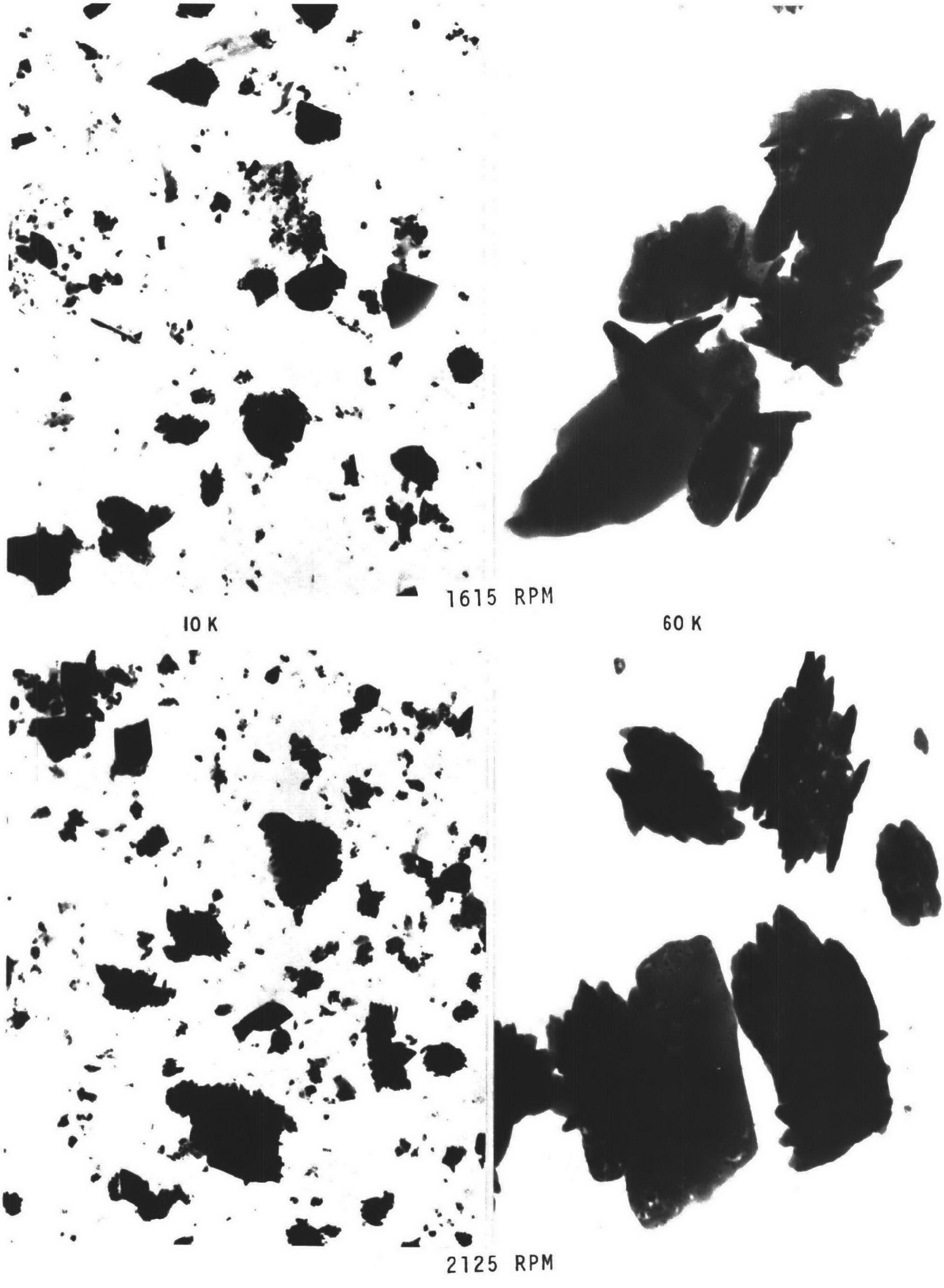
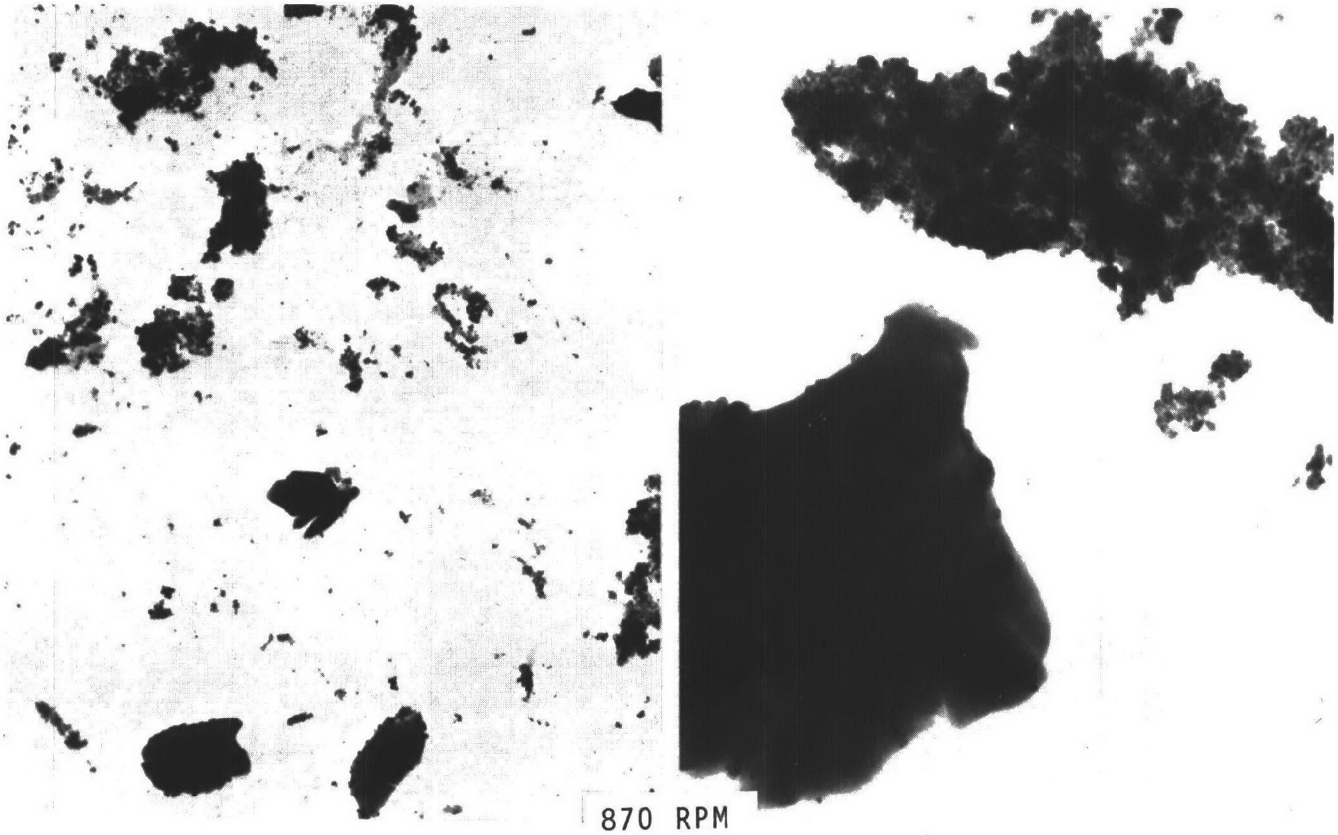


Figure 24

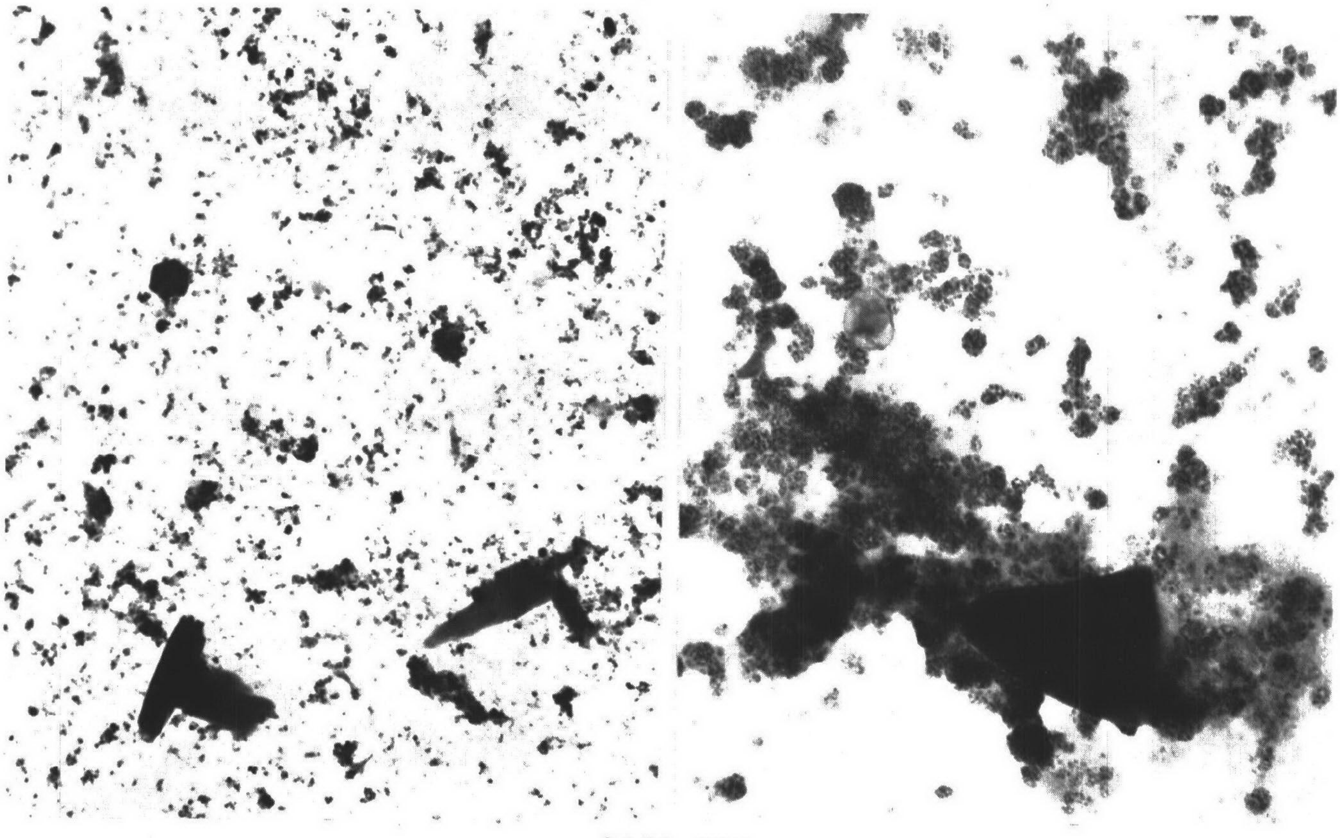
TRANSMISSION ELECTRON MICROSCOPY STUDY OF PARTICULATE MATERIAL COLLECTED AT POSITION II



870 RPM

10 K

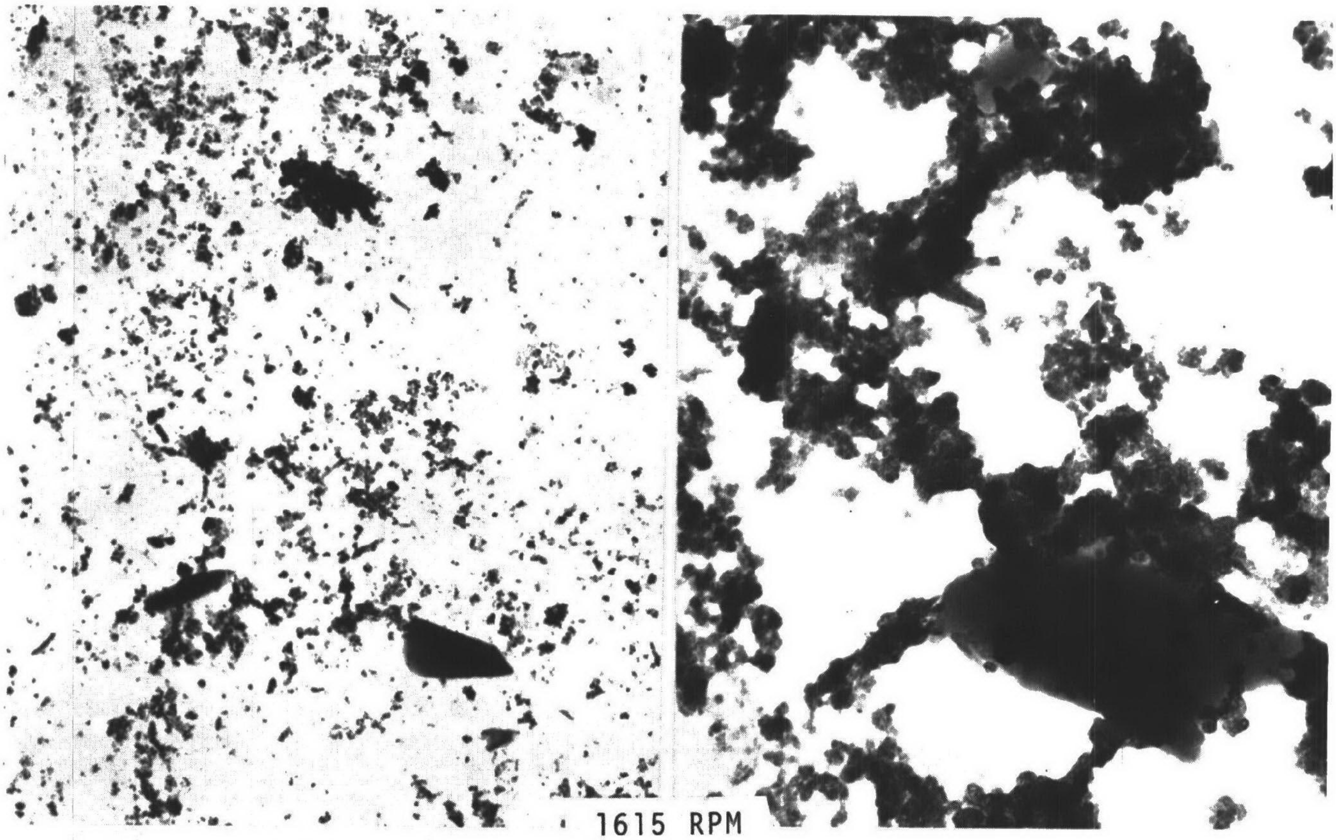
60 K



1070 RPM

Figure 25

TRANSMISSION ELECTRON MICROSCOPY STUDY OF PARTICULATE MATERIAL COLLECTED AT POSITION II



1615 RPM

10 K

60 K

2125 RPM

Figure 26

TRANSMISSION ELECTRON MICROSCOPY STUDY OF PARTICULATE MATERIAL COLLECTED AT POSITION III

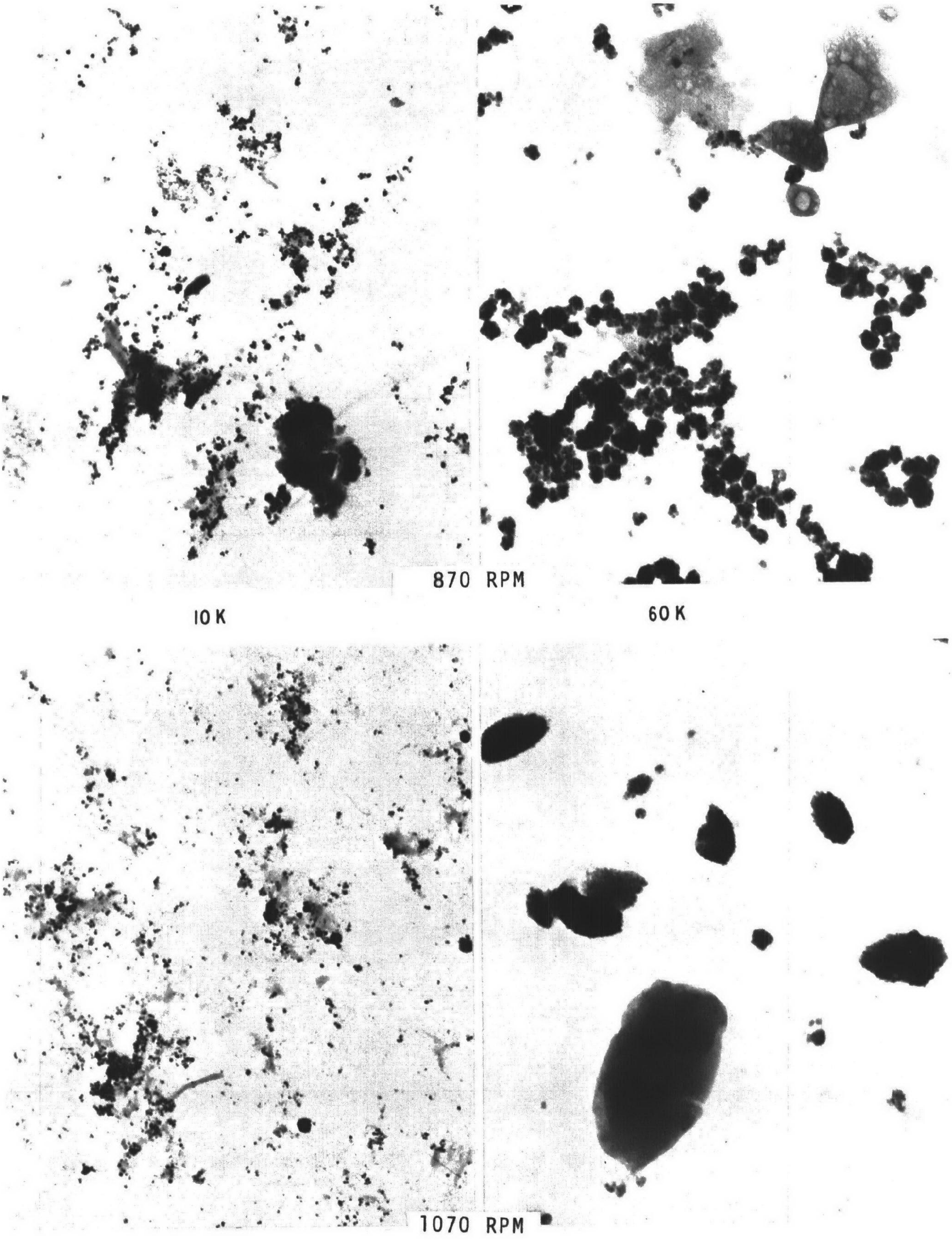
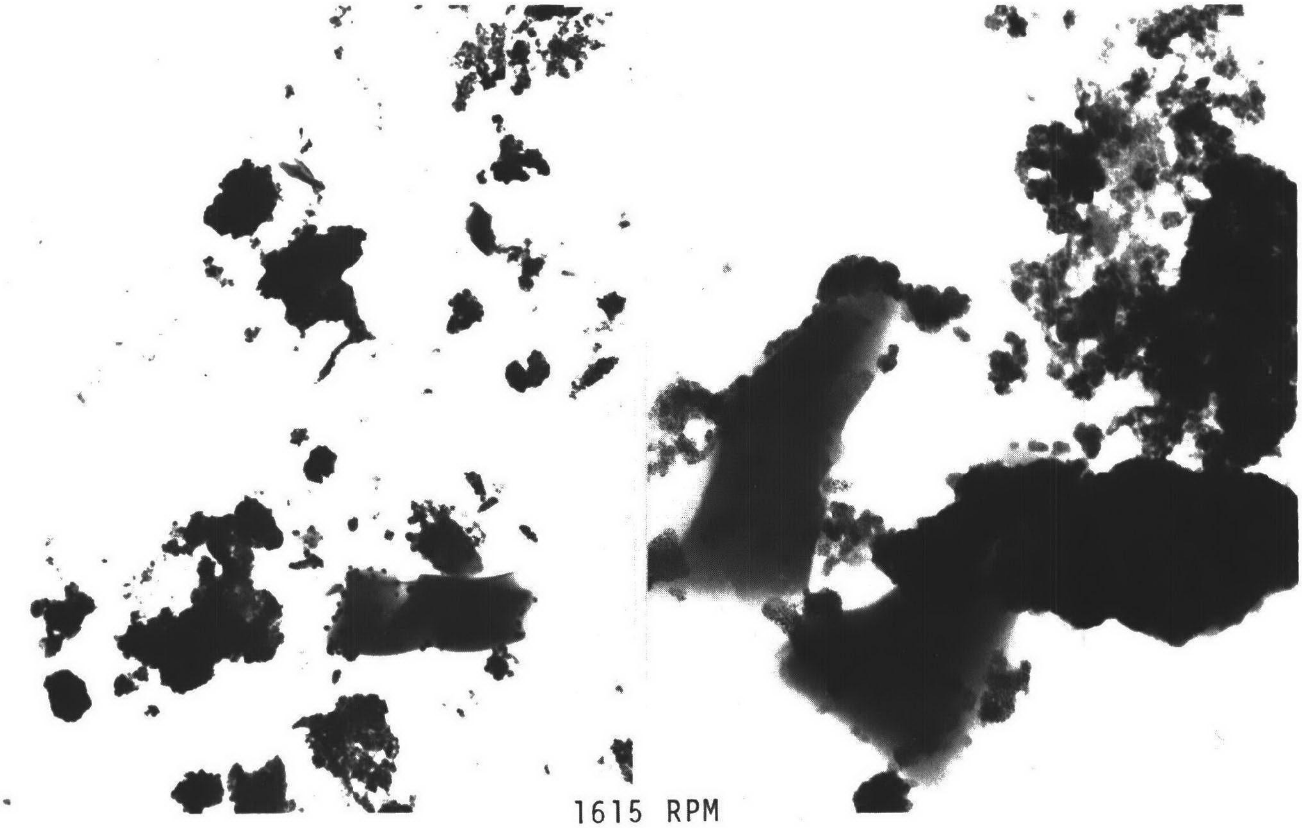


Figure 27

TRANSMISSION ELECTRON MICROSCOPY STUDY OF PARTICULATE MATERIAL COLLECTED AT POSITION III



1615 RPM

10K

60K

2125 RPM

Figure 28

TEM STUDY OF PARTICULATE MATERIAL COLLECTED AT POSITION IV - TEST I

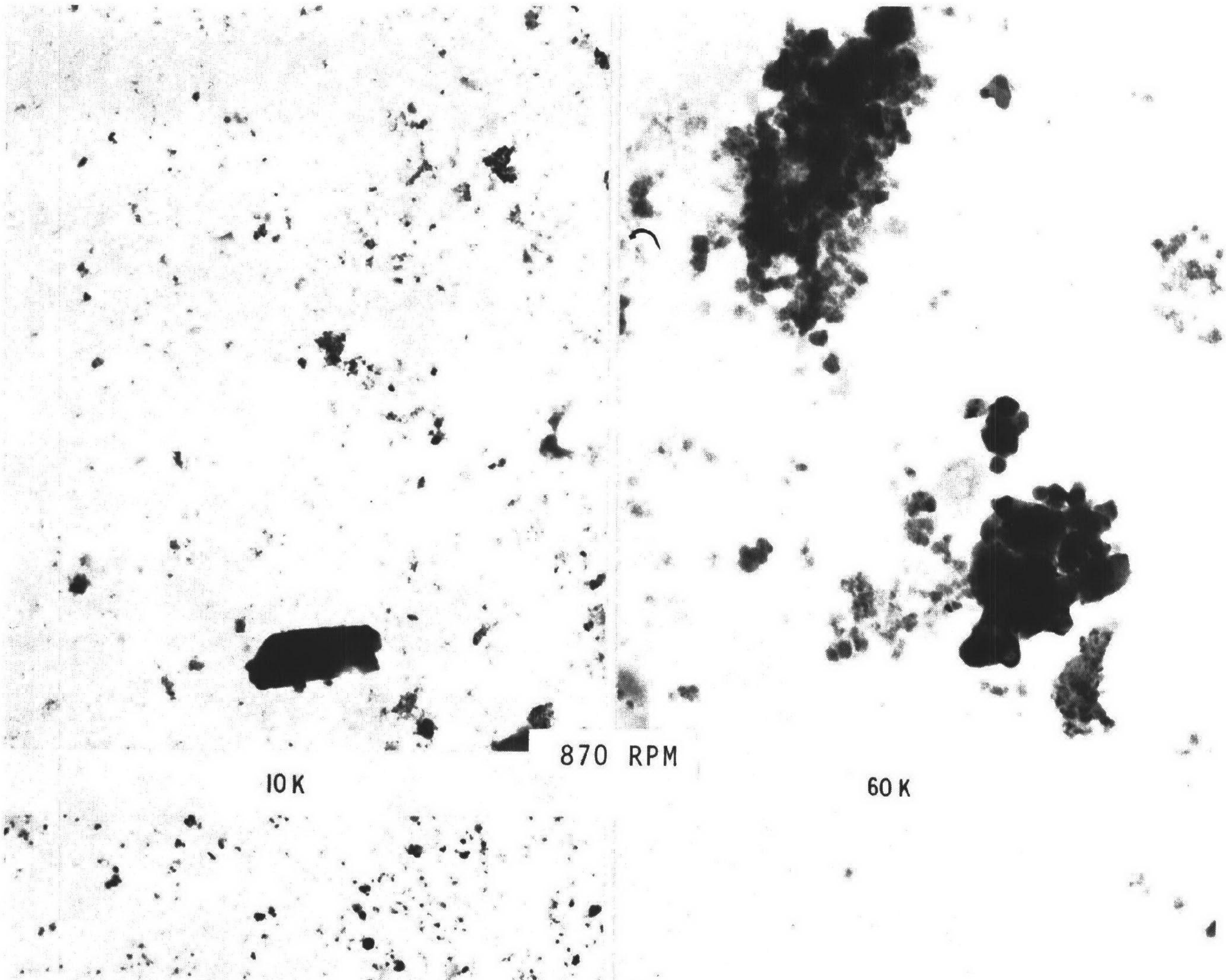
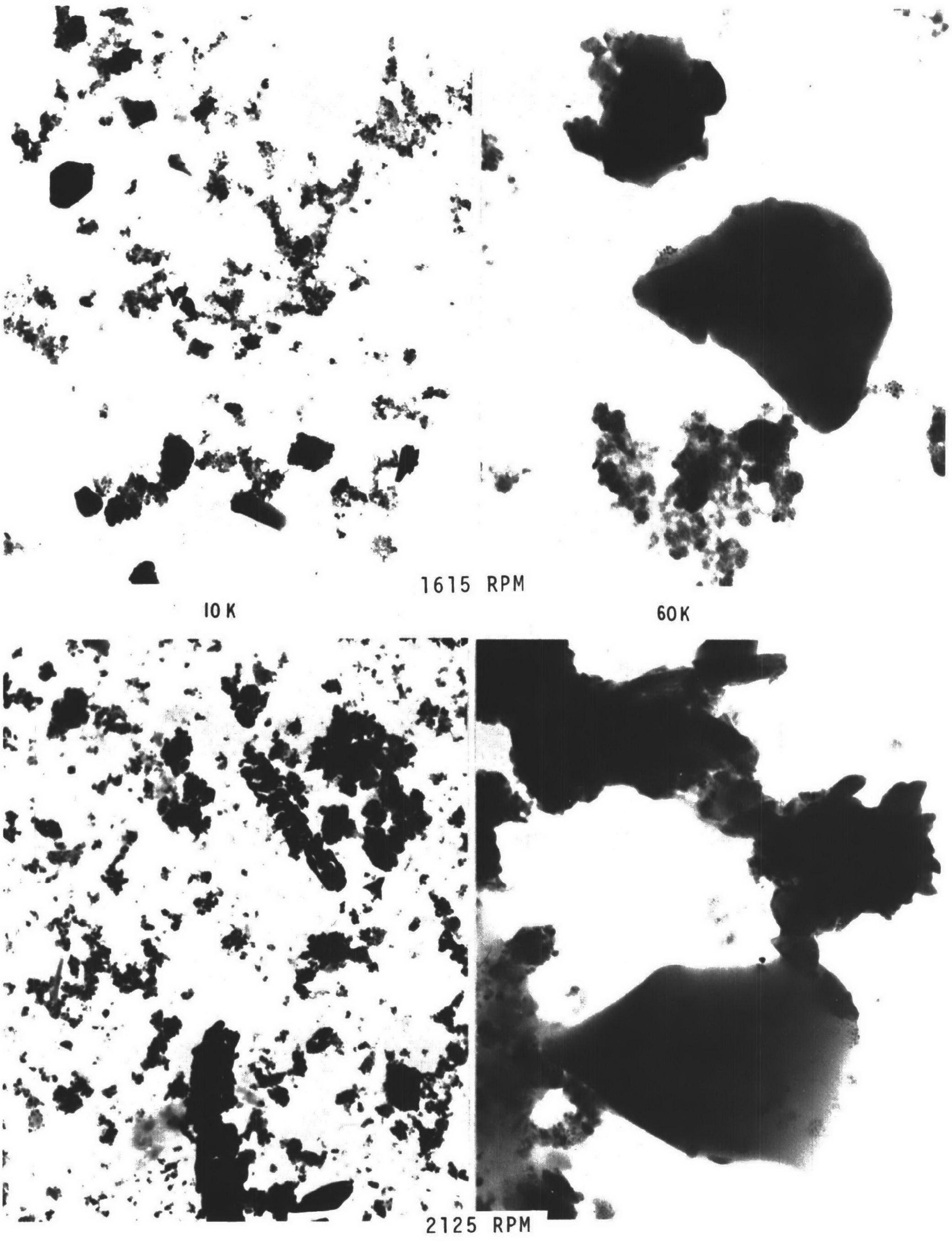


Figure 29

TEM STUDY OF PARTICULATE MATERIAL COLLECTED AT POSITION IV - TEST I



Samples collected at the four glass fiber filters (see Figure 11) were examined by several analytical techniques. Tables XV through XVIII summarize the results of studies on these samples by low power microscopy and X-ray diffraction. The bulk of the crystalline material present was found to be lead halides. Figure 12 shows typical photomicrographs (400x magnification) of the Gelman filter pads after exposure at sampling Position I for 30 minutes. At the four different engine speeds the presence of uncombined lead in low concentrations at the exhaust manifold outlet during operation at 1070 and 2125 engine rpm should be noted (Table XV). In Table XIX the crystalline species observed are tabulated against decreasing exhaust gas stream temperatures.

The collected particulate matter was next examined by Scanning Electron Microscopy. Figures 13 through 21 show photomicrographs of selected samples at magnifications from 1000x to 10,000x. In general those samples collected at sample Position I, immediately after the exhaust manifold, show crystal growth from nuclei on the glass fiber filters. Samples taken at Positions II, III, and IV along the exhaust system appear more matted and in some instances, particle fusion can be observed (see Figure 13). Use of the X-ray fluorescence probe confirmed the previous X-ray diffraction studies and indicated lead chlorobromides as the major particulate components. At 2125 engine rpm, several particles of high iron content were observed. These probably originated from the exhaust system itself rather than from the engine since they were detected mainly on the tail pipe side of the muffler.

Transmission electron photomicrographs of the particulate samples were obtained at 10,000x and 60,000x magnification. These are shown in Figures 22 through 29. The particles were dispersed in ethylene glycol prior to examination to eliminate matting. Many of the larger particles appear to be composed of very fine inorganic matter of high electron density in an organic matrix of low electron density (see Figures 22 and 28).

The cold trap condensates collected at all four sampling locations were examined by emission spectroscopy. The data is summarized in Table XX. A large proportion of the mass of condensed particles in these traps is associated with lead and iron. The actual weight of these elements present in the condensates in shown in Table XXI. A profile for the mass of condensed lead collected along the exhaust system under the different engine operating conditions is shown in Figure 30. This data illustrates the high level of lead compounds present in the vapor state immediately after the exhaust manifold. A surprising result is the relatively higher vapor phase concentration of lead compounds at engine idling speed (870 rpm) compared to those at 1070, 1615, and 2125 rpm.

<u>Test II</u> - Test II was designed to evaluate the efficiency of the Andersen Stack Sampler for determining the particle mass-size profile at sampling Position IV of the exhaust system. Position IV is located close to the end of the tail pipe and is thus subjected to temperatures lower than those encountered in the remainder of the exhaust system. Isokinetic (1 cfm), isothermal sampling was conducted at an engine speed of 2250 rpm. This speed was selected so the data generated could be compared to that of similar tests performed under Government Contract CPA-22-69-145[1].

Samples of particulate matter were examined from the sampling probe, from Stages 0, 2, 5, 7, and 8 of the Andersen sampler, and from the back-up Gelman filter (Figure 31).

TABLE XX

EMISSION SPECTROSCOPIC ANALYSIS OF COLD TRAP CONDENSATE - TEST SERIES

Position	RPM	ppm: Fe	Ni	Cu	Al	Ca	Si	Mg	Mn	Pb	Cr	Sn	Zn	Ti
I	870	5	4	1	0.5	3	0.3	0.9	0.4	257	0.4	<0.2	2	<0.2
I	1070	3	5	0.9	<0.2	3	<0.2	0.3	0.2	113	0.2	<0.2	3	<0.2
I	1615	3	0.7	0.6	<0.2	4	<0.2	<0.2	0.07	77	<0.2	<0.2	0.5	<0.2
I	2125	1	<0.2	0.2	<0.2	3	<0.2	<0.2	<0.05	88	<0.2	<0.2	<0.5	<0.2
II	870	18	10	0.05	<0.2	4	<0.2	0.8	0.5	29	1	<0.2	7	<0.2
II	1070	2	0.7	0.08	<0.2	3	<0.2	0.3	<0.05	10	0.2	<0.2	4	<0.2
II	1615	2	0.2	0.4	<0.2	4	<0.2	0.4	<0.05	11	0.4	<0.2	12	<0.2
II	2125	3	<0.2	0.5	<0.2	5	<0.2	4	<0.05	7	0.5	<0.2	18	<0.2
III	870	0.3	0.2	<0.05	<0.2	5	<0.2	<0.2	<0.05	3	<0.2	<0.2	0.5	<0.2
III	1070	<0.2	0.2	<0.05	<0.2	4	<0.2	<0.2	<0.05	0.6	<0.2	<0.2	0.7	<0.2
III	1615	0.2	0.2	<0.05	<0.2	4	<0.2	0.5	<0.05	3	<0.2	<0.2	16	<0.2
III	2125	<0.2	0.2	<0.05	<0.2	3	<0.2	<0.2	<0.05	3	<0.2	<0.2	3	<0.2
IV	870	0.2	0.2	<0.05	<0.2	5	0.2	0.5	<0.05	5	<0.2	<0.2	<0.5	<0.2
IV	1070	0.2	0.2	<0.05	<0.2	3	<0.2	0.2	<0.05	8	<0.2	<0.2	0.5	<0.2
IV	1615	0.7	0.2	<0.05	<0.2	4	0.3	<0.2	<0.05	10	<0.2	<0.2	0.7	<0.2
IV	2125	0.5	0.2	<0.05	<0.2	3	0.5	0.2	<0.05	4	<0.2	<0.2	<0.5	<0.2

TABLE XXI
IRON AND LEAD CONTENT OF COLD TRAP CONDENSATE - TEST I

		Sampling Position			
RPM		I	II	III	IV
870	Iron (ppm)	5	18	0.3	0.2
	Condensate (g)	21.02	26.55	17.38	37.46
	Iron (mg)	0.105	0.4779	0.0052	0.00749
1070	Iron (ppm)	3	2	<0.2	0.2
	Condensate (g)	19.80	29.07	24.78	38.72
	Iron (mg)	0.0594	0.0581	<0.004956	0.00774
1615	Iron (ppm)	3	2	0.2	0.7
	Condensate (g)	19.18	28.05	23.38	27.12
	Iron (mg)	0.0575	0.0561	0.00468	0.01898
2125	Iron (ppm)	1	3	<0.2	0.5
	Condensate (g)	24.12	34.19	27.37	24.02
	Iron (mg)	0.0241	0.1026	<0.0055	0.0120
870	Lead (ppm)	257	29	3	5
	Condensate (g)	21.02	26.55	17.38	37.46
	Lead (mg)	5.702	0.76995	0.052	0.187
1070	Lead (ppm)	113	10	0.6	8
	Condensate (g)	19.80	29.07	24.78	38.72
	Lead (mg)	2.237	0.2907	0.01487	0.3098
1615	Lead (ppm)	77	11	3	10
	Condensate (g)	19.18	28.05	23.38	27.12
	Lead (mg)	1.477	0.3086	0.0701	0.271
2125	Lead (ppm)	88	7	3	4
	Condensate (g)	27.12	34.19	27.37	24.80
	Lead (mg)	2.12	0.239	0.082	0.096

FIGURE 30

LEAD CONTENT OF COLD TRAP CONDENSATES
(TEST I)

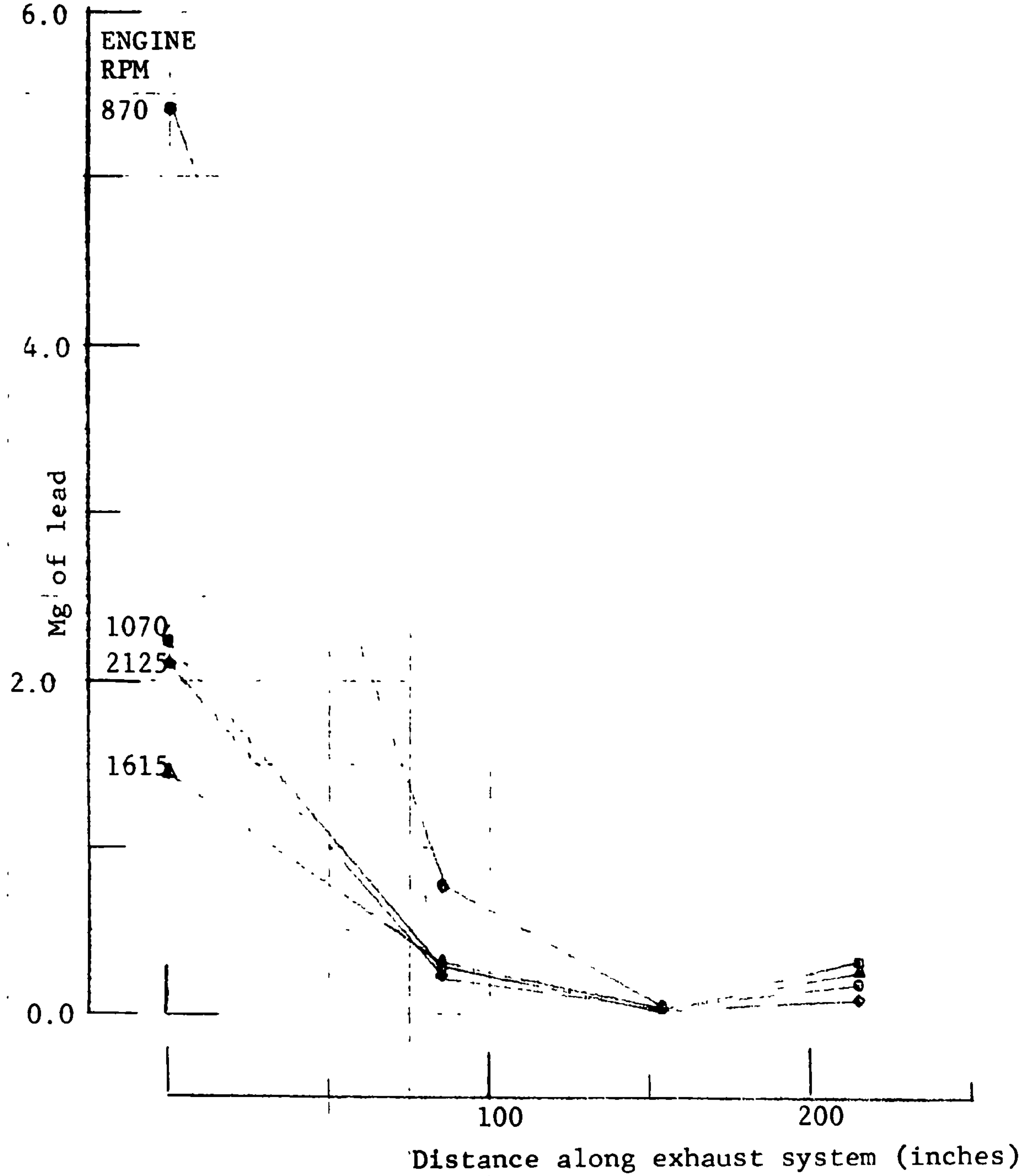
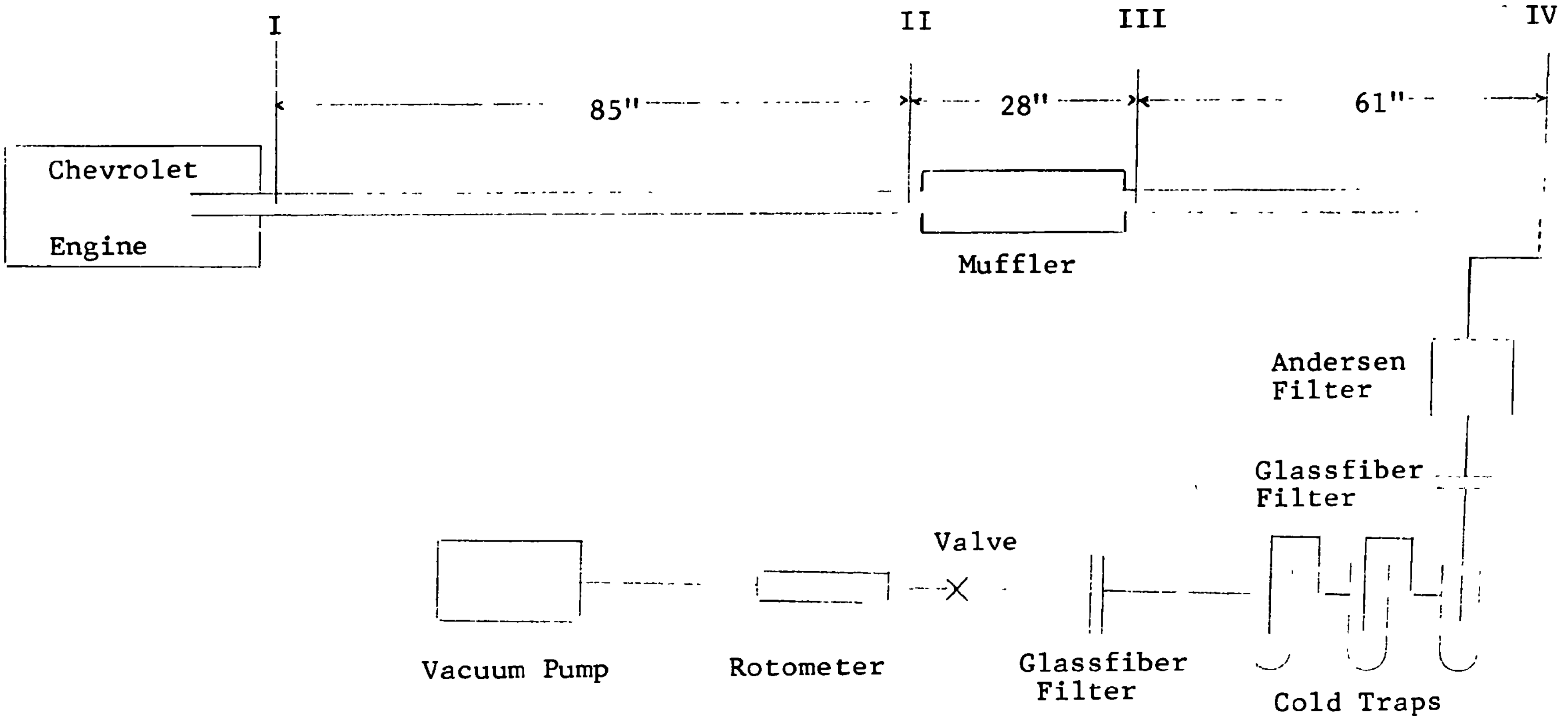


FIGURE 31

PARTICULATE SAMPLING DEVICES-TEST II



The results of an examination of these samples by optical microscopy and X-ray diffraction are summarized in Table XXII. Figure 32 shows photomicrographs at 15x magnification of particulate matter collected on the Andersen plates. The above analyses indicated that in general, as particle size decreased through the Andersen, the concentration of lead halide and particle birefringence decreased. Optical microscopy indicated that particle size varied from <1 to 20 microns on Plate 0 of the Andersen to $\sim 1\mu$ on the glass fiber filter.

The same samples were also examined by scanning electron microscopy. Figure 33 shows photomicrographs at 1000x and 2000x magnification of particles collected from the surface of the sampling probe. A single element X-ray fluorescent scan for iron on Particle D shows clearly that the distribution of this metal is non-uniform (photomicrograph C). Multi-element scans indicated the presence of lead, chlorine, bromine, and iron in all the particles shown.

Figures 34-37 show Scanning Electron Microscopy (SEM) photomicrographs of particles collected on Plate 0 of the Andersen sampler.

Figure 34 is representative of the hard black deposits encountered at Plate 0 of the Andersen. Multi-element X-ray scans of the particle shown in "B" indicated high concentrations of lead, chlorine and bromine at Position R. Position G had low concentrations of these elements but was high in iron. Zinc was also detected. These same two types of elemental composition were observed in particles scraped from Andersen Plate 0 (Figure 35). Pictures B and D show particles which on X-ray scan proved to be composed mainly of lead chlorobromide.

TABLE XXII

EXAMINATION OF PARTICULATES FROM TEST II

Sample Location	Birefringence	Size	X-ray Diffraction
Sampling probe	75 wt. % highly birefrigence 1-15μ size; 10-20% black opaque 5-20μ	<1% below 1	$Pb(Br,Cl)_2$ - Br:Cl ∿1:1
Andersen Sampler Plate 0 Lighter portion	25-50% highly birefringence 1-20μ size	<1% below 1μ	$Pb(Br,Cl)_2$ - Br:Cl ∿1:1 "R" form and $PbO \cdot Pb(Br,Cl)_2$
Darker portion	25-50% black opaque 5-20μ size fused, very hard, impossible to be representative; high in dark reddish particles of low transparency (possibly iron compound).		Same except higher in $Pb(Br,Cl)_2$; no crystalline iron compound.
Plate 2	<5% highly birefringent 1-10μ size ∿50% black opaque 5-20 size ∿5% dark reddish, transparent probably iron containing		Major - $PbSO_4$ Medium - NiO
	Remaining irregular agglomerates of low birefringence	<10μ	
Plate 5	Majority of sample agglomerates of low birefringence. 10% transparent and red Trace highly birefringent	99% 1-10μ	Major components: $PbSO_4$, NiO Minor: $Pb_5Cl(PO_4)_3$, NH_4Br, ZnO
Plate 8	Majority of sample single particles of low birefringence plus few agglomerates.	0.5 to 5μ Avg. ∿1-2μ	Major component: $Pb_5Cl(PO_4)_3$ Medium: $PbSO_4$, NiO
Glass fiber filter	Most particles single crystals. Majority are low birefringence <5% highly birefringence reddish (iron?) particles rare.	Very uniform ∿1μ	Unidentified patterns. U.P. 1876 plus second unknown.

Figure 32

DISTRIBUTION OF PARTICULATE MATERIAL ON ANDERSEN SAMPLER PLATES AT POSITION IV - TEST II

B Plate 0

D_{50} >9.5μ

15X

D Plate 2

D_{50} 6.1μ

G Plate 5

D_{50} 1.75μ

J Plate 8

D_{50} 0.36μ

Figure 33

SEM STUDY OF PARTICULATE MATERIAL FROM SAMPLING PROBE AT POSITION IV - TEST II

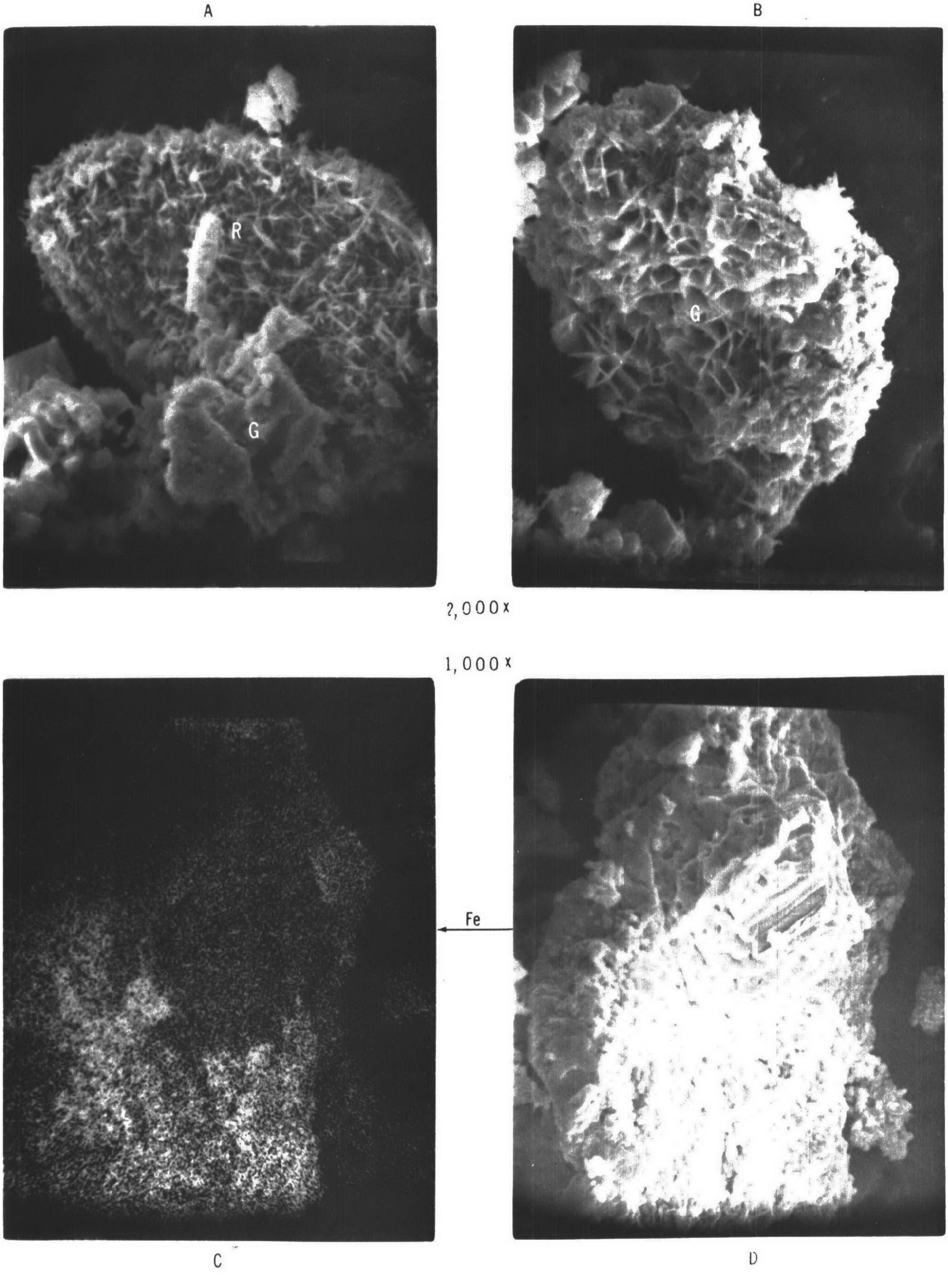


Figure 34

SEM STUDY OF PARTICULATE MATERIAL FROM PLATE 0
OF THE ANDERSEN SAMPLER AT POSITION IV - TEST II

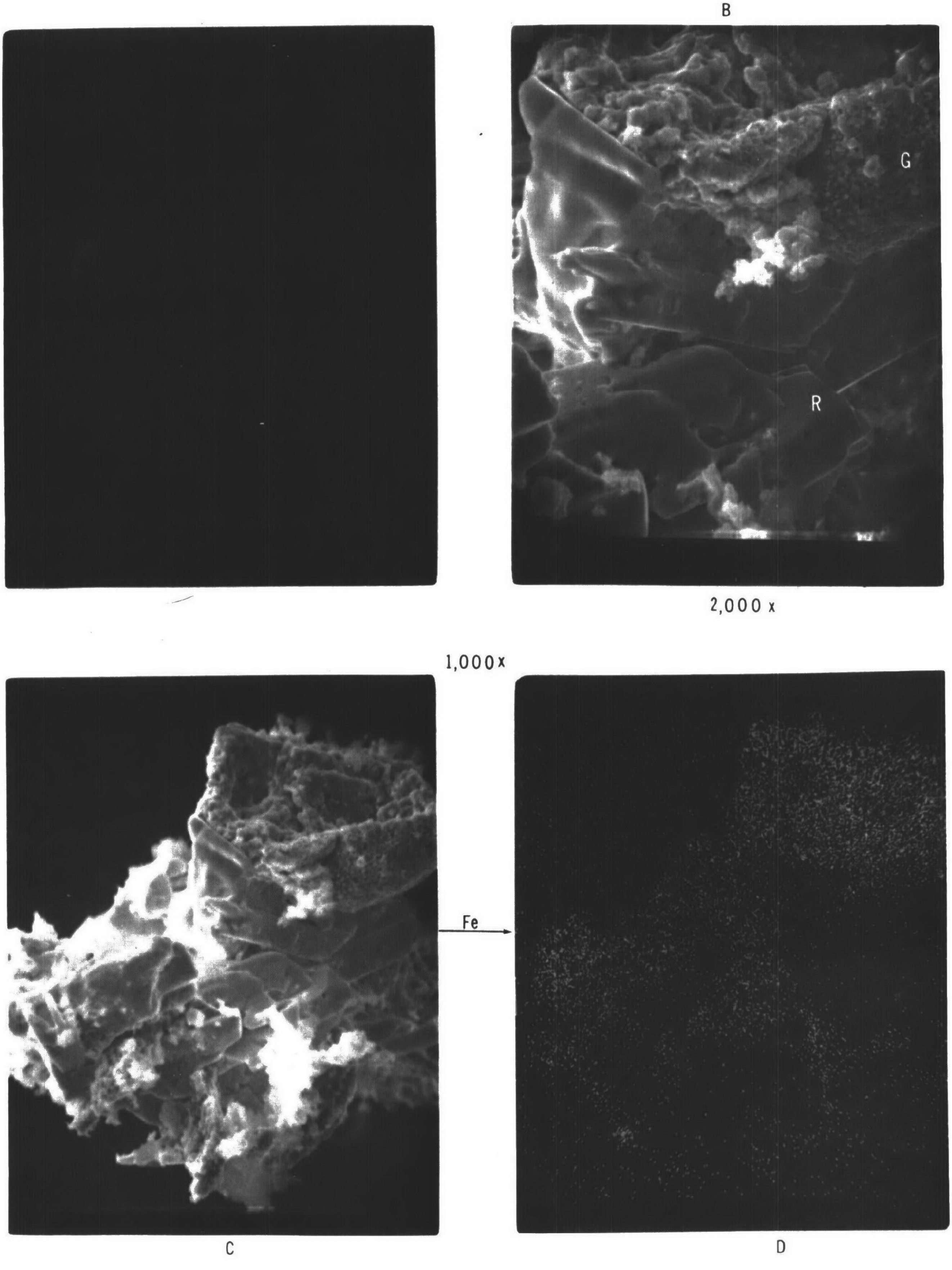


Figure 35

SEM STUDY OF PARTICULATE MATERIAL FROM PLATE 0
OF THE ANDERSEN SAMPLER AT POSITION IV - TEST II

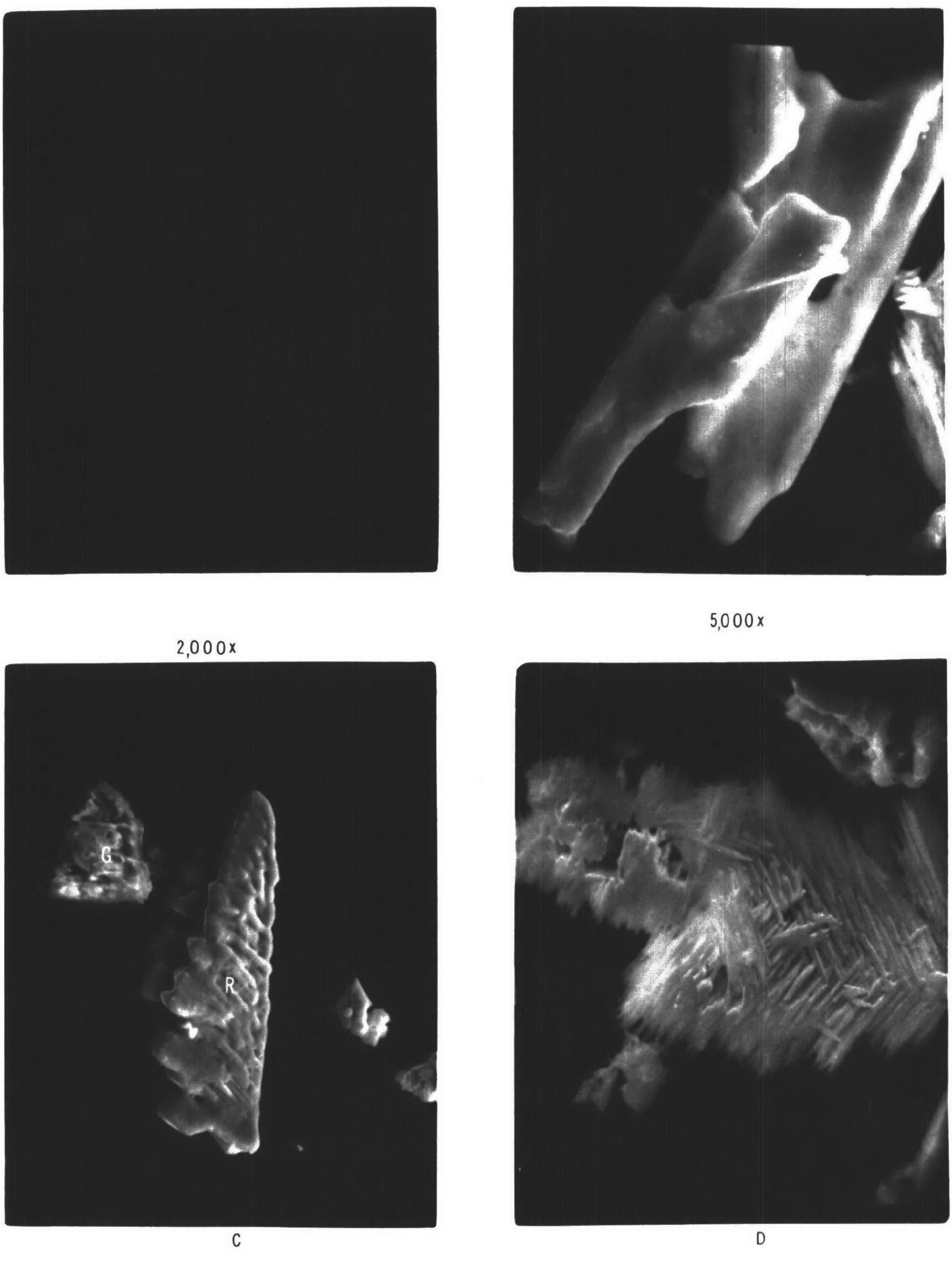


Figure 36

SEM STUDY OF PARTICULATE MATERIAL FROM PLATE 0
OF THE ANDERSEN SAMPLER AT POSITION IV - TEST II

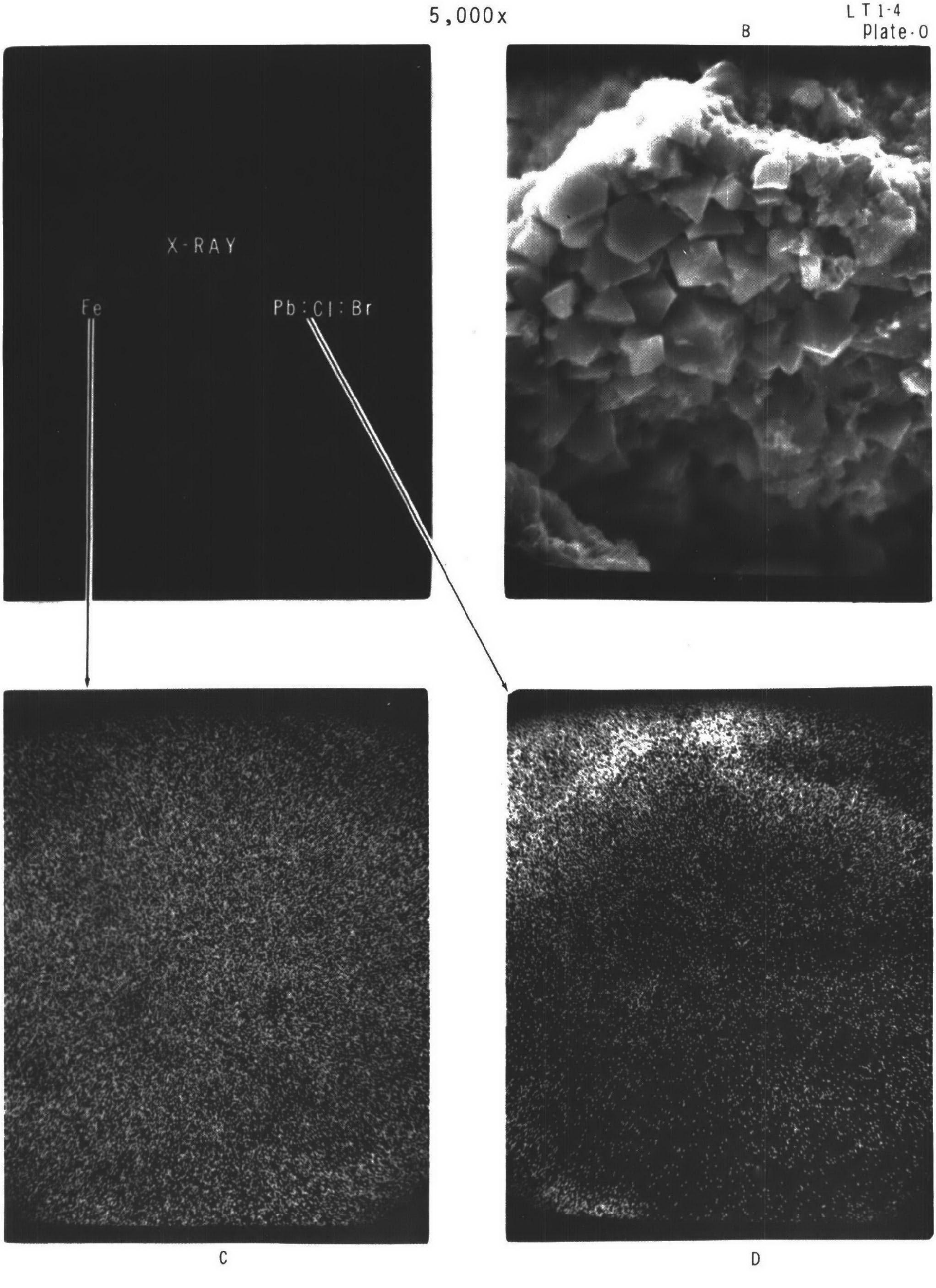
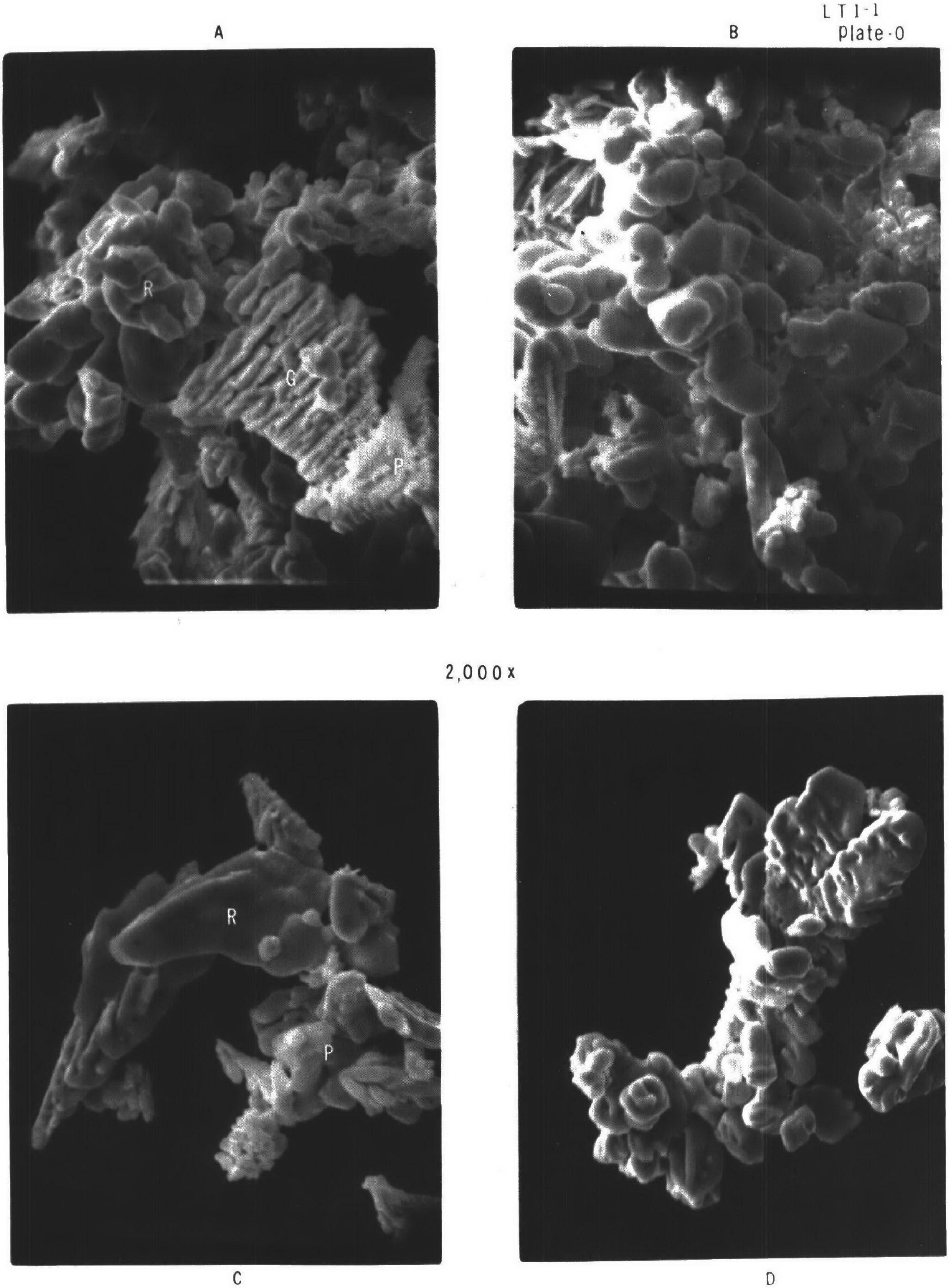


Figure 37

SEM STUDY OF PARTICULATE MATERIAL FROM PLATE 0
OF THE ANDERSEN SAMPLER AT POSITION IV - TEST II



Particle R in Picture C was also lead chlorobromide. Particle G in the same picture shows much lesser amounts of this compound but showed a high concentration of iron with smaller levels of nickel, copper, and zinc.

Figure 37 shows more examples of particles collected at Plate 0. Of special interest are the particles shown in Pictures B and D. Picture B is again representative of the hard black deposits which accumulated. Analysis proved this material to contain lead, chlorine, and bromine. Picture D is representative of the most commonly observed particle type. An X-ray scan showed the presence of lead, chlorine, and bromine.

Multi-element X-ray scans of the particle shown in Figure 36-B indicate a non-uniform distribution of lead, chlorine, bromine, and iron throughout the particle (see Figure 36-C and D).

SEM analysis of the material collected on Plate 2 of the Andersen separator again indicated the presence of lead halides in combination with nickel and lower concentrations of iron and zinc. Again single element scans indicated a non-uniform distribution. No photomicrographs were made for particles collected on Plates 5 and 8 because of their small size and mass. X-ray fluorescence analysis, however, indicated high concentrations of lead, nickel, and iron with lesser amounts of copper and zinc. Halide concentration was low.

Particulate matter smaller than 1 micron was studied by Transmission Electron Microscopy (TEM). Samples were obtained from the Gelman filters following both the Andersen and the cold trap (Figure 31) and from the sample probe. Under 60,000x magnification these particles appeared as an organic matrix with inorganic matter embedded on their surface. Typical photomicrographs are shown in Figures 38-40. Some of the same types of particle structure were observed as in previous studies under Contract CPA-22-45-145[1]. These include the "log-shaped" particle shown in Figure 38.

No particulate mass-size distribution was obtained in this test since thermal decomposition of the asbestos O-rings in the Andersen sampler led to erroneous weights of the various Andersen plates.

Test III - This test was performed in an indentical manner to Test II to establish a particle mass-size distribution from the heated Andersen separator located at Position IV of the exhaust system. However, in order to avoid thermal decomposition of the asbestos plate separators used in the Andersen, these were preheated to a temperature some 50°F above that encountered at this sampling location for a period of 3 hours before sampling. The equivalent mean mass diameter for particles collected on the Andersen is plotted in Figure 41.

Test IV - The major objectives of this test were to establish a mass-size distribution and characterization for particles collected on the Andersen Impactor at Position III of the exhaust system. Samples were also obtained at the three remaining sample ports both on Gelman filters fitted with back-up cold traps and by sweeping the probes at the end of the test (Figure 42). X-ray diffraction and X-ray fluorescent analyses of the probe sweepings are shown in Table XXIII. X-ray diffraction analysis of the material collected on the Gelman filters and on Plates 0, 5, and 8 of the Andersen is presented

Figure 38

TEM STUDY OF PARTICULATE MATERIAL COLLECTED AT SAMPLING POSITION IV

Glass Fiber Filter

10K 60K

Sampling Probe

Figure 39

TEM STUDY OF PARTICULATE MATERIAL COLLECTED
ON ANDERSEN SAMPLER AT POSITION IV

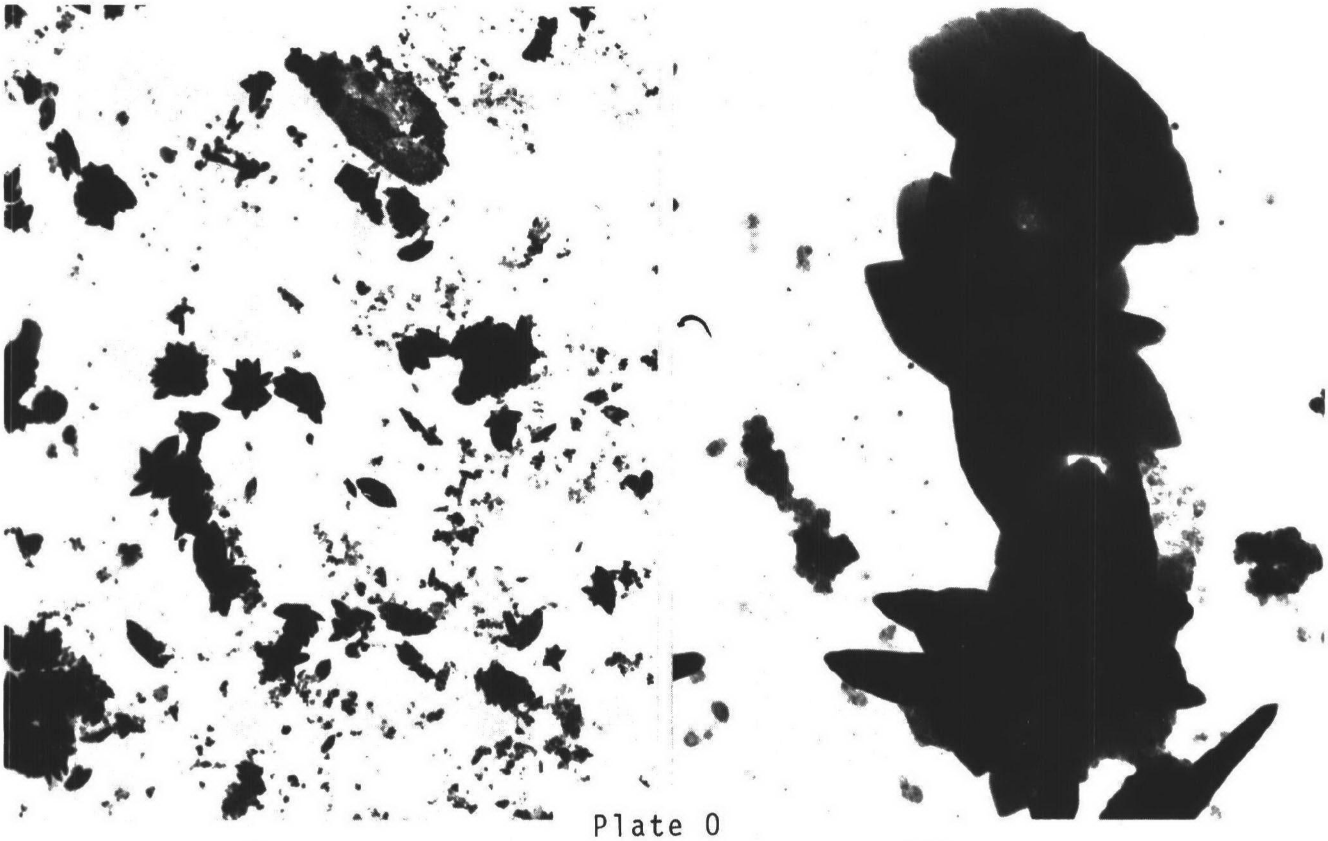


Plate 0

10 K

60 K

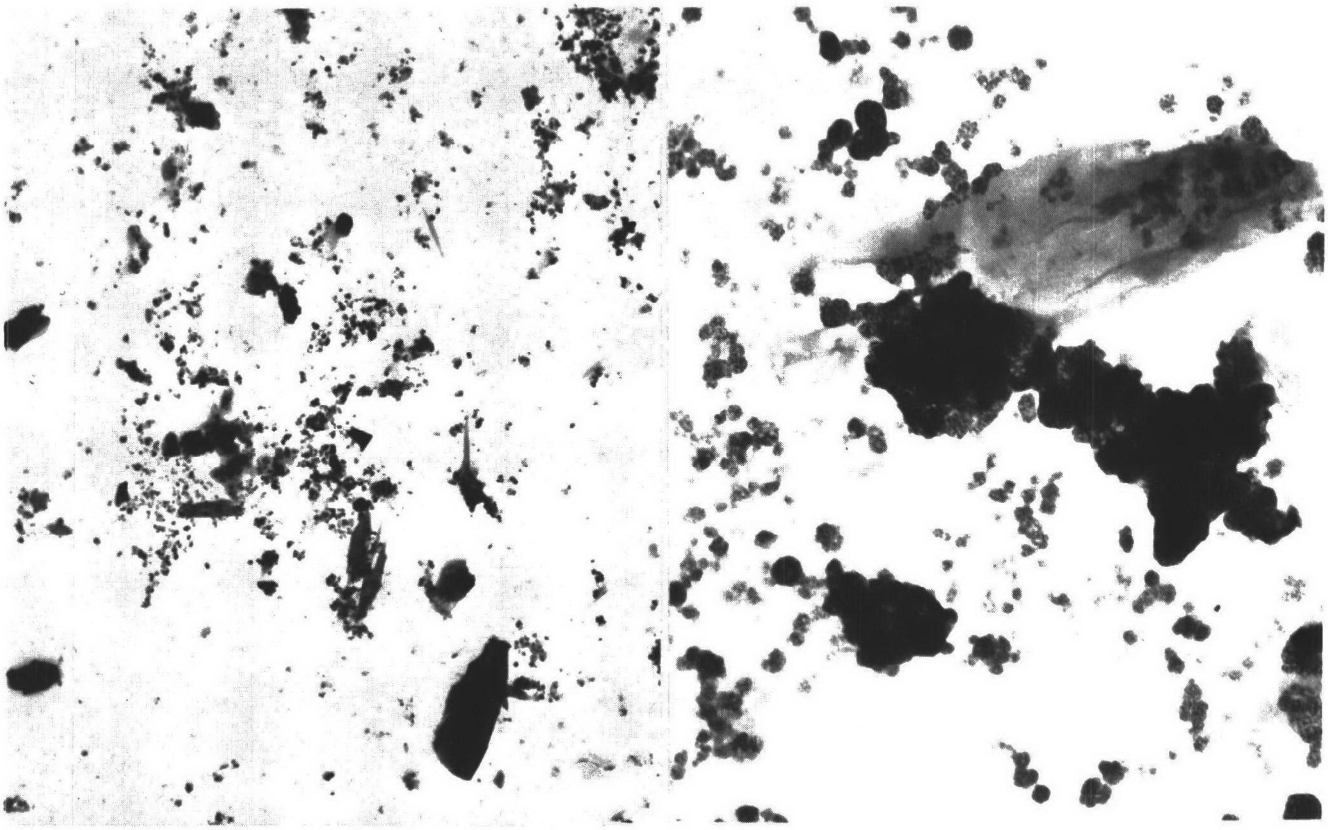


Plate 2

Figure 40

TEM STUDY OF PARTICULATE MATERIAL COLLECTED
ON ANDERSEN SAMPLER AT POSITION IV

Plate 5

10 K

60 K

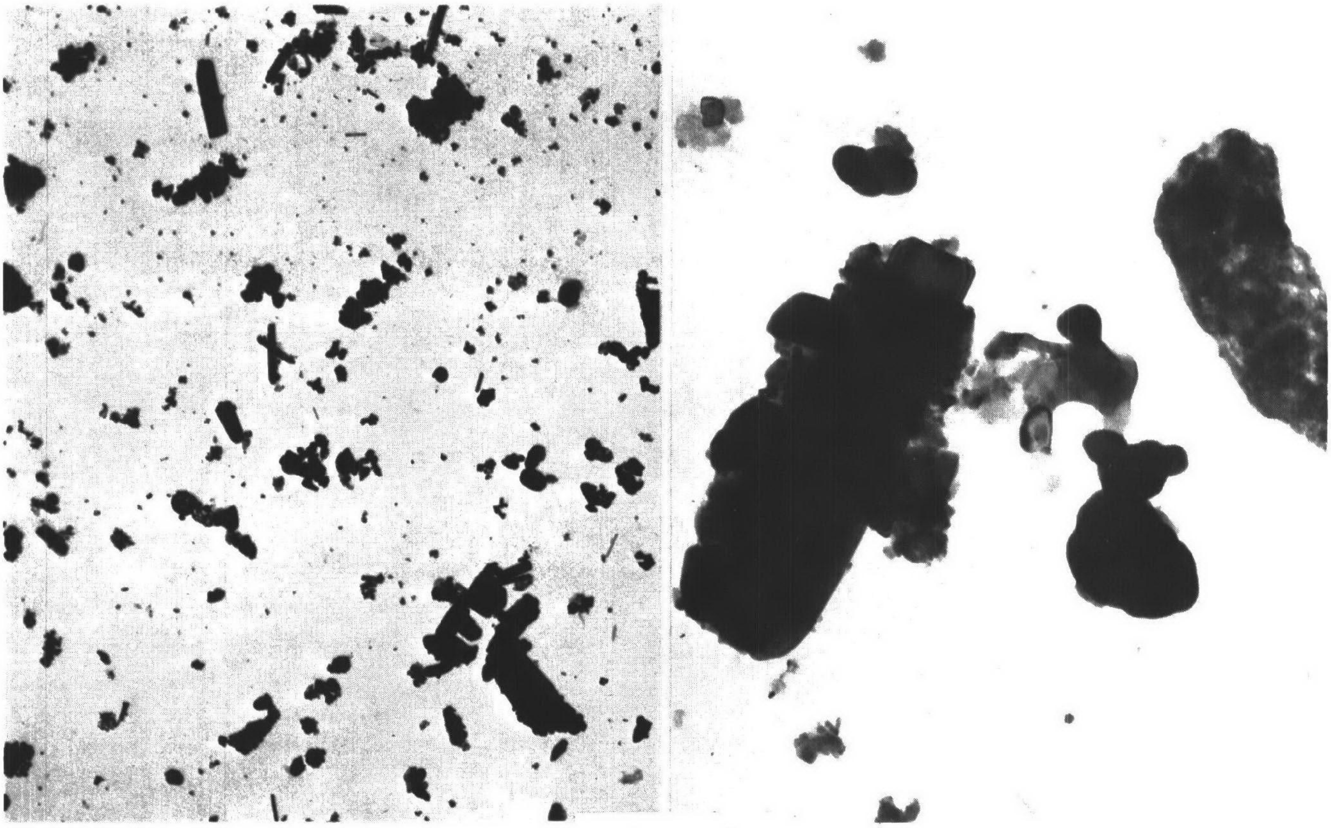


Plate 8

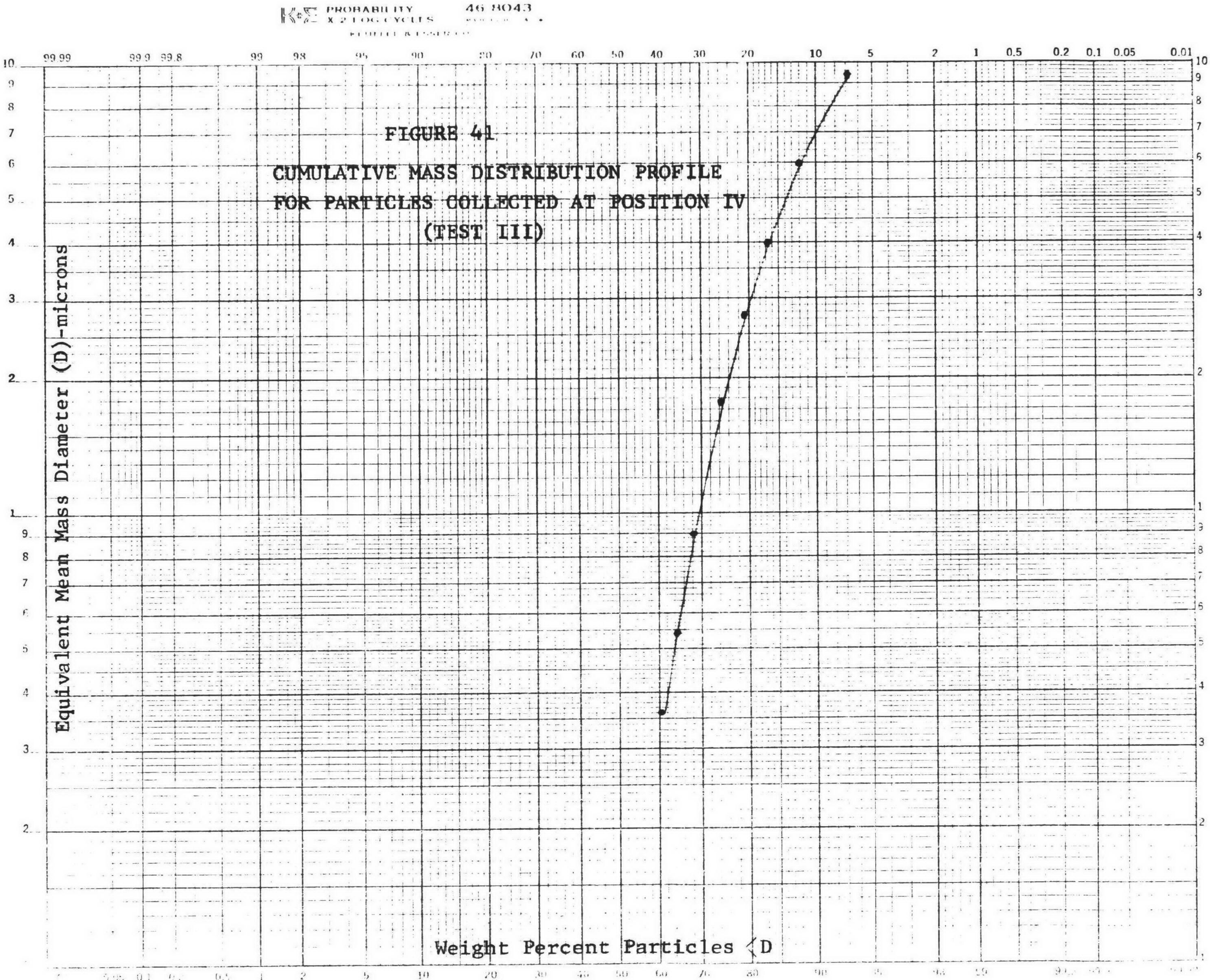
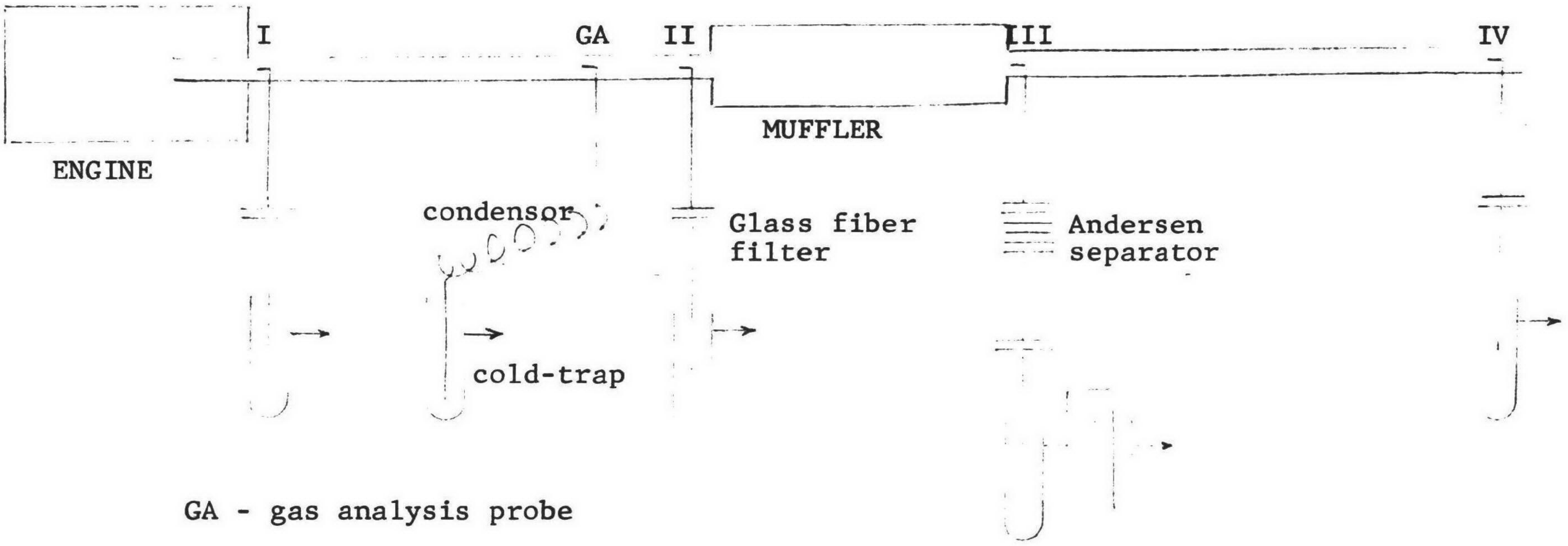


FIGURE 41

CUMULATIVE MASS DISTRIBUTION PROFILE FOR PARTICLES COLLECTED AT POSITION IV (TEST III)

FIGURE 42

PARTICULATE SAMPLING DEVICES - TEST IV



GA - gas analysis probe

TABLE XXIII
PARTICULATES ON PROBES IN TEST IV

Position	X-ray Diffraction		X-ray Fluorescence (Ratios only)	
			Br/Cl	Zn/Fe/Pb
I	$Pb(Br,Cl)_2$	Br:Cl ∿1:1	0.9	1:9.8:92
Residual Hydrocarbon Analysis Probe	$Pb(Br,Cl)_2$	Br:Cl ∿1.5:1	0.6	1:2:3
II	$Pb(Br,Cl)_2$	Br:Cl ∿1:1	1.1	1:14:147
III	$Pb(Br,Cl)_2$	Br:Cl ∿1.5:1 Fe_2O_3 5% or less ZnO 5% or less	0.86	1:3.3:2.9
IV	$Pb(Br,Cl)_2$ $PbSO_4$ Fe_2O_3		Sample too small	

in Table XXIV. Similar data is also included for particles collected on the glass fiber filter used as a back-up to the Andersen.

Transmission Electron Microscopy (TEM) of these samples revealed the same type of crystal structure reported in Tests I and II.

The cumulative mass distribution for particles collected on the Andersen is shown in Figure 43. Comparison of Figure 43 to Figure 41 (Andersen at sampling Position IV) shows a shift in the size of particulate matter to a smaller equivalent mass median diameter for Position IV.

Test V - In Test V an attempt was made to establish a particle mass-size profile for position II in the exhaust system by means of the Andersen Sampler. However, on examining the unit at the end of the test it was found that not only had the sampler plates collected negligible amounts of particulate matter, but they all had also lost weight. In this test the Andersen was heated to 905°F, equivalent to the temperature at exhaust Probe II. Passage of exhaust effluent through the sampler at this temperature resulted in extensive damage to the sampling stages. Figure 44 illustrates the destruction which took place at Plate 0 of this device. In view of these findings, no attempt was made to locate the Andersen unit at sampling Position I (near the exhaust manifold) where the exhaust stream temperature was even higher.

c. Gaseous Analysis

Analysis of exhaust stream gases in Tests IV and V was used for the calculation of engine air/fuel ratios. This data is presented in Table XXV.

TABLE XXIV

CRYSTALLINE PARTICULATE SAMPLES COLLECTED FROM TEST IV

Position		Crystalline Particulates		
I		$Pb(Br,Cl)_2$	Br:Cl ∿1:1	
II		$Pb(Br,Cl)_2$	Br:Cl ∿1:1	
III (Andersen Sampler)				
Plate 0 (light particulates)		$Pb(Br,Cl)_2$	Br:Cl ∿1:2	
		Pb	∿5%	
		Possibly $Fe_2(SO_4)_3$	5-10%	
(dark particulates)		$Pb(Br,Cl)_2$	Br:Cl ∿1:1	40-50%
		ZnO		40-50%
	possibly	$ZnCl \cdot 4Zn(OH)_2 \cdot 1H_2O$		5-10%
Plate 5		$PbSO_4$	40-50%	
		ZnO	20-30%	
		Fe_2O_3	10-15%	
	possibly	NiO	5-10%	
	possibly	Fe_3O_4	5-10%	
Plate 8		$PbSO_4$	30-40%	
		ZnO	30-40%	
		$PbCl(PO_4)_3$	10-15%	
		Fe_2O_3	10-15%	
	possibly	NiO	<5	
	possibly	Fe_3O_4	5-10%	
Plate 8 (fused)		$PbSO_4$		
		ZnO		
Glass fiber filter		Fe_2O_3	40-60%	
		$PbSO_4$	20-30%	
		PbS	20-30%	
IV		$PbSO_4$		
		Fe_2O_3		

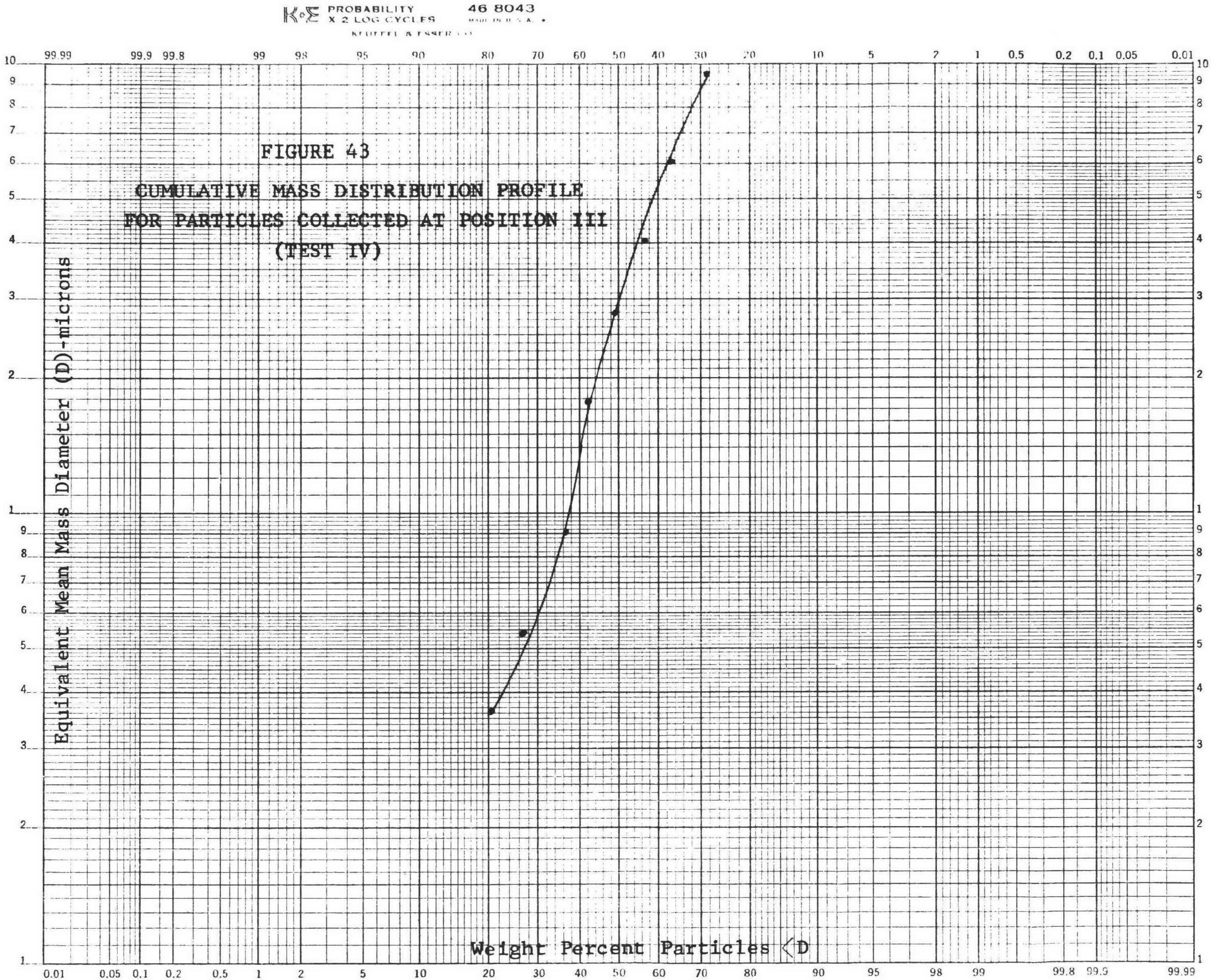


FIGURE 43

CUMULATIVE MASS DISTRIBUTION PROFILE FOR PARTICLES COLLECTED AT POSITION III (TEST IV)

Figure 44

DEGRADATION OF ANDERSEN SAMPLER PLATE AT POSITION II (AHEAD OF MUFFLER)

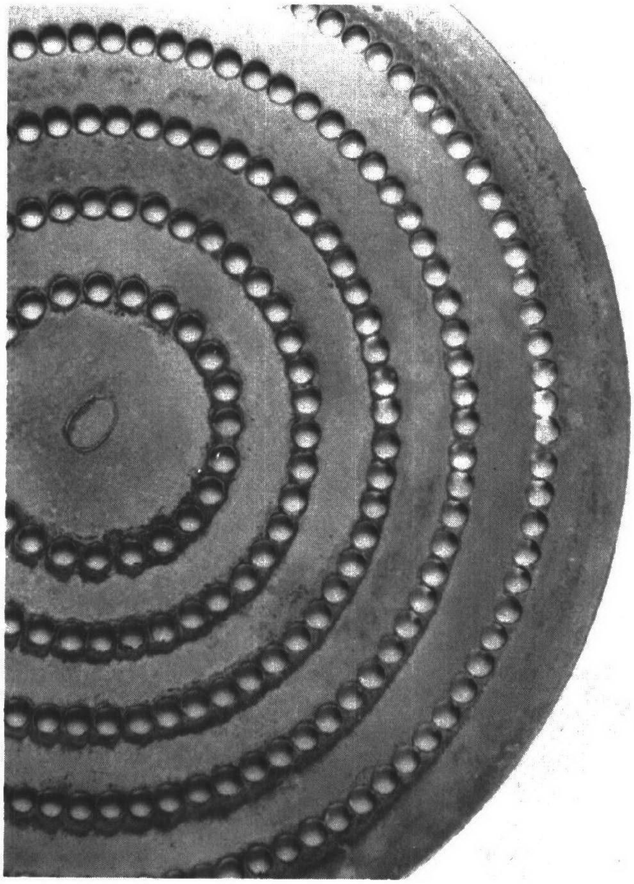


TABLE XXV

AIR/FUEL RATIOS BY EXHAUST ANALYSIS

Test IV	Residual HC	Air/Fuel
8 hours	670 ppm	13.4
	670	14.8
Test V		
3 hours	555	15.0
	555	14.4
4.75	575	15.0
	575	15.0
	575	15.0

2. Diluted Exhaust Stream Analysis

a. Particulate Mass

Throughout Tests VI-XI particulate matter in the air diluted exhaust stream was collected on one or more 4 cfm filters and at 1 cfm on an Andersen Impactor fitted with a back-up Millipore filter. This sampling procedure has been described earlier. Particulate mass measurements were made from both sampling devices and the data is presented in Table XXVI. A discussion of the disparity of results obtained at the 1 cfm and 4 cfm filters is presented on page 110.

TABLE XXVI

EFFECT OF LEAD TRAP ON MASS OF PARTICULATE MATTER EMITTED IN AIR DILUTED EXHAUST

Test No.	Engine Condition	Muffler	4 cfm Filter (gm/mile)	Andersen and 1 cfm Filter (gm/mile)
VIII	1200	Conventional	0.096	0.125
VI	2250	Conventional	0.104	0.117
VII	Cycle	Conventional	0.140	0.150
IX	1200	Lead trap	0.109	0.143
X	2250	Lead trap	0.122	0.118
XI	Cycle	Lead trap	0.125	0.135

At the start of Tests IX-XI, the lead trap was allowed to warm up by operating the engine for 30 minutes under the specific test conditions prior to connecting the tail pipe to the dilution tube. This insured that the contents of the trap were molten.

b. Particle Analysis

Samples of particulate matter collected on the stages of the Andersen Impactor were analyzed by atomic absorption spectroscopy for their lead content. This allowed mass-distribution profiles to be calculated for both the total particulate matter collected in this way and for the leaded particulates. The data are plotted in Figures 45 through 50.

Material collected on the 4 cfm Millipore filter was also analyzed by atomic absorption spectroscopy for its lead, potassium, and lithium content. The results of these determinations are presented in Table XXVII on a gm/mile basis.

No analyses were performed on particulate matter which accumulated within the dilution tube as a result of gravitational fallout although the tube was cleaned between runs.

TABLE XXVII

PARTICLE MASS EMISSIONS (4 CFM FILTER)

Test	Engine RPM	Muffler	Particle Mass (gm/mile) Total	K	Li	Pb
VIII	1200	Conventional	0.096	0.0004	<0.00002	0.038
VI	2250	Conventional	0.104	0.00021	<0.00002	0.035
VII	Cycle	Conventional	0.140	0.00029	<0.00003	0.055
IX	1200	Trap	0.109	0.0016	0.00014	0.038
X	2250	Trap	0.122	0.0032	0.00045	0.019
XI	Cycle	Trap	0.122	0.0026	0.00058	0.043

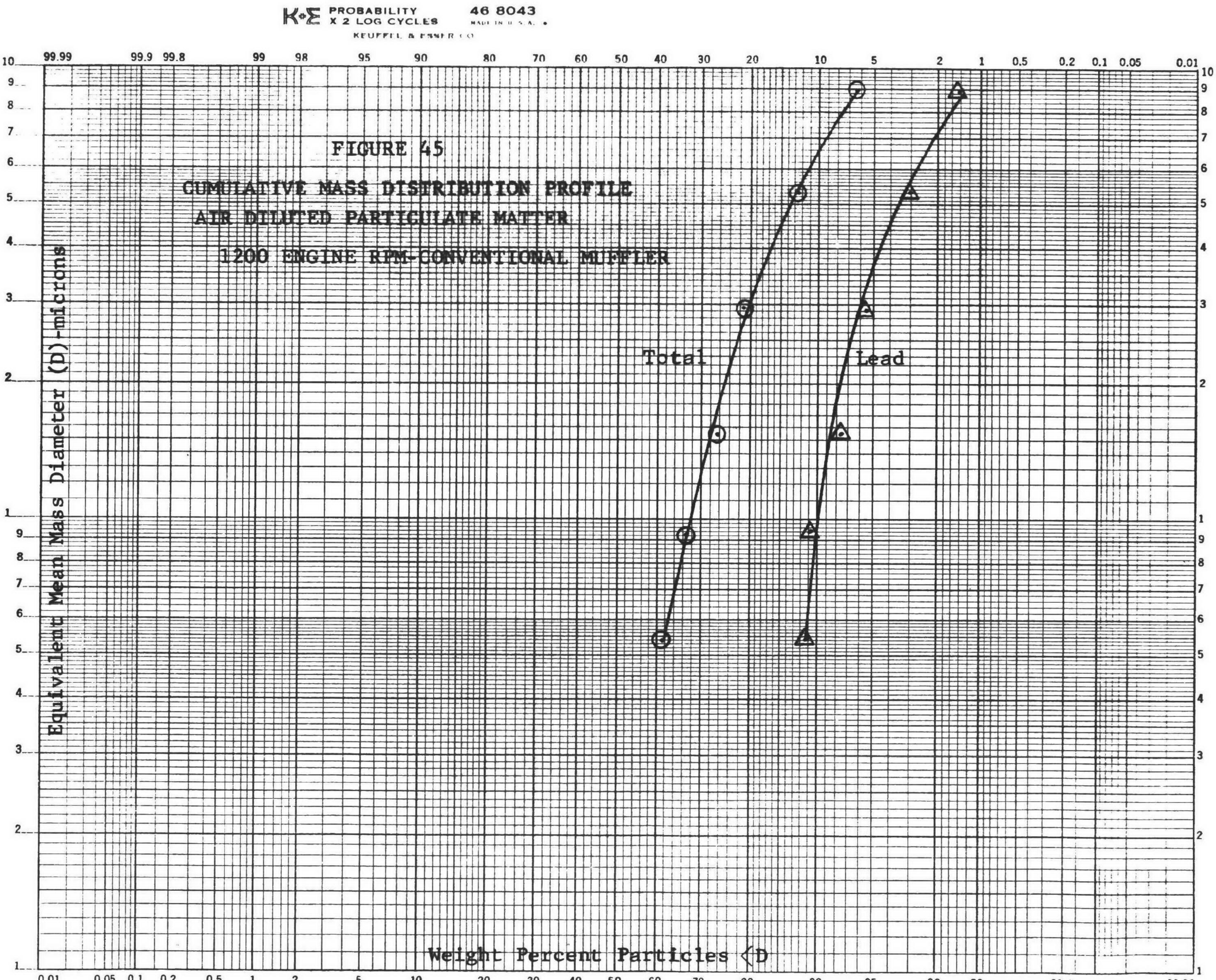
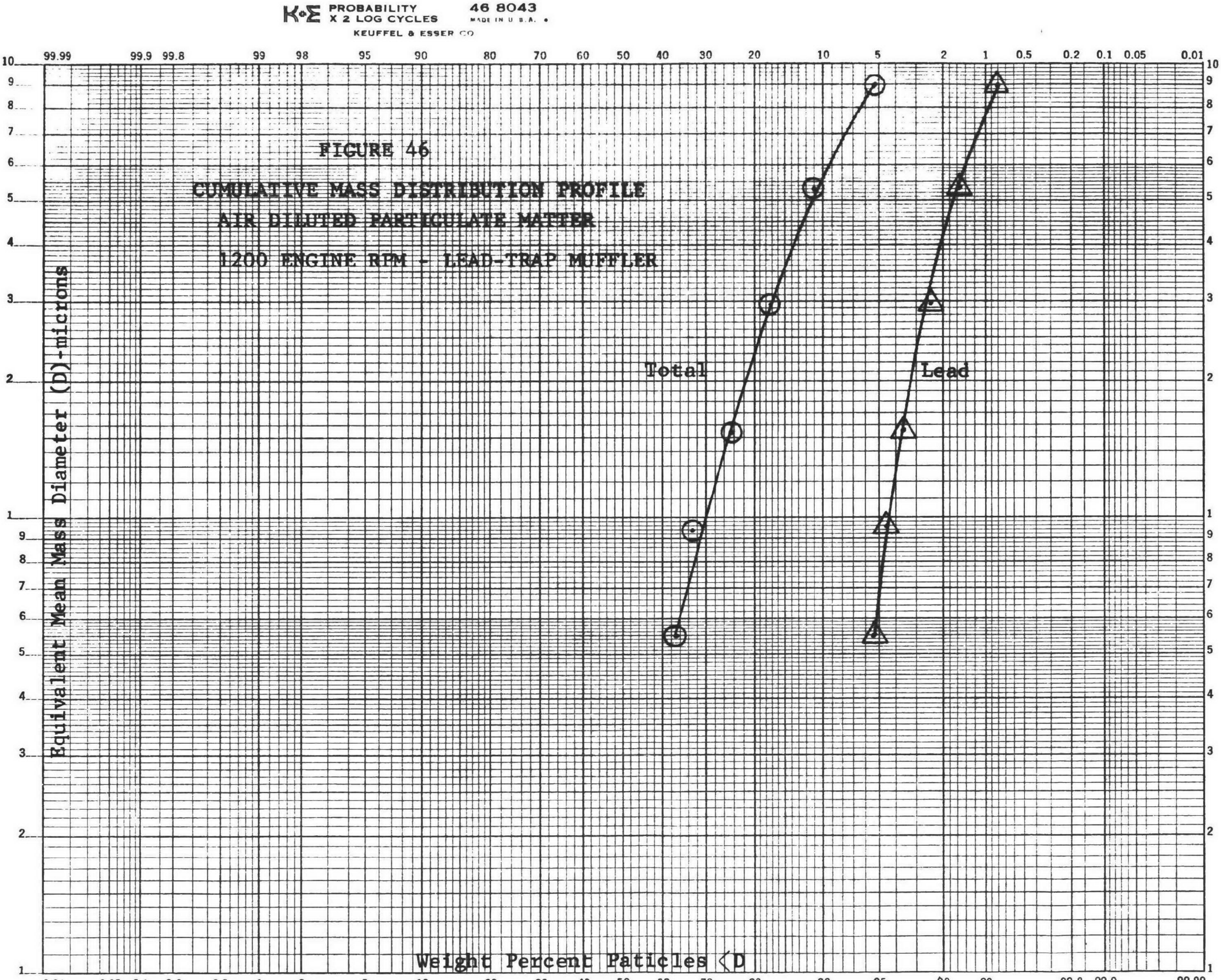


FIGURE 45

CUMULATIVE MASS DISTRIBUTION PROFILE AIR DILUTED PARTICULATE MATTER 1200 ENGINE RPM-CONVENTIONAL MUFFLER

FIGURE 46

CUMULATIVE MASS DISTRIBUTION PROFILE
AIR DILUTED PARTICULATE MATTER
1200 ENGINE RPM - LEAD-TRAP MUFFLER



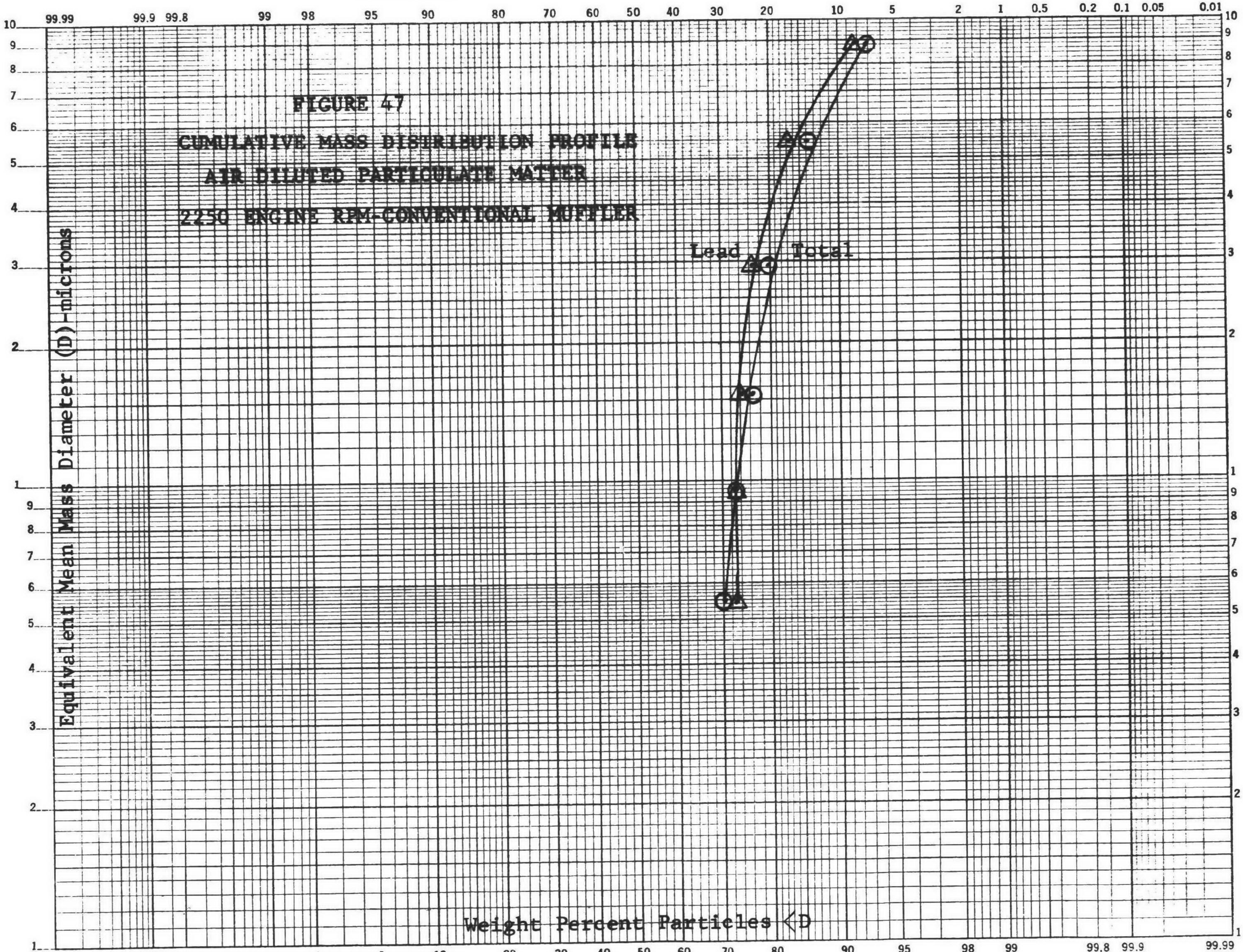


FIGURE 47

CUMULATIVE MASS DISTRIBUTION PROFILE
AIR DILUTED PARTICULATE MATTER
2250 ENGINE RPM-CONVENTIONAL MUFFLER

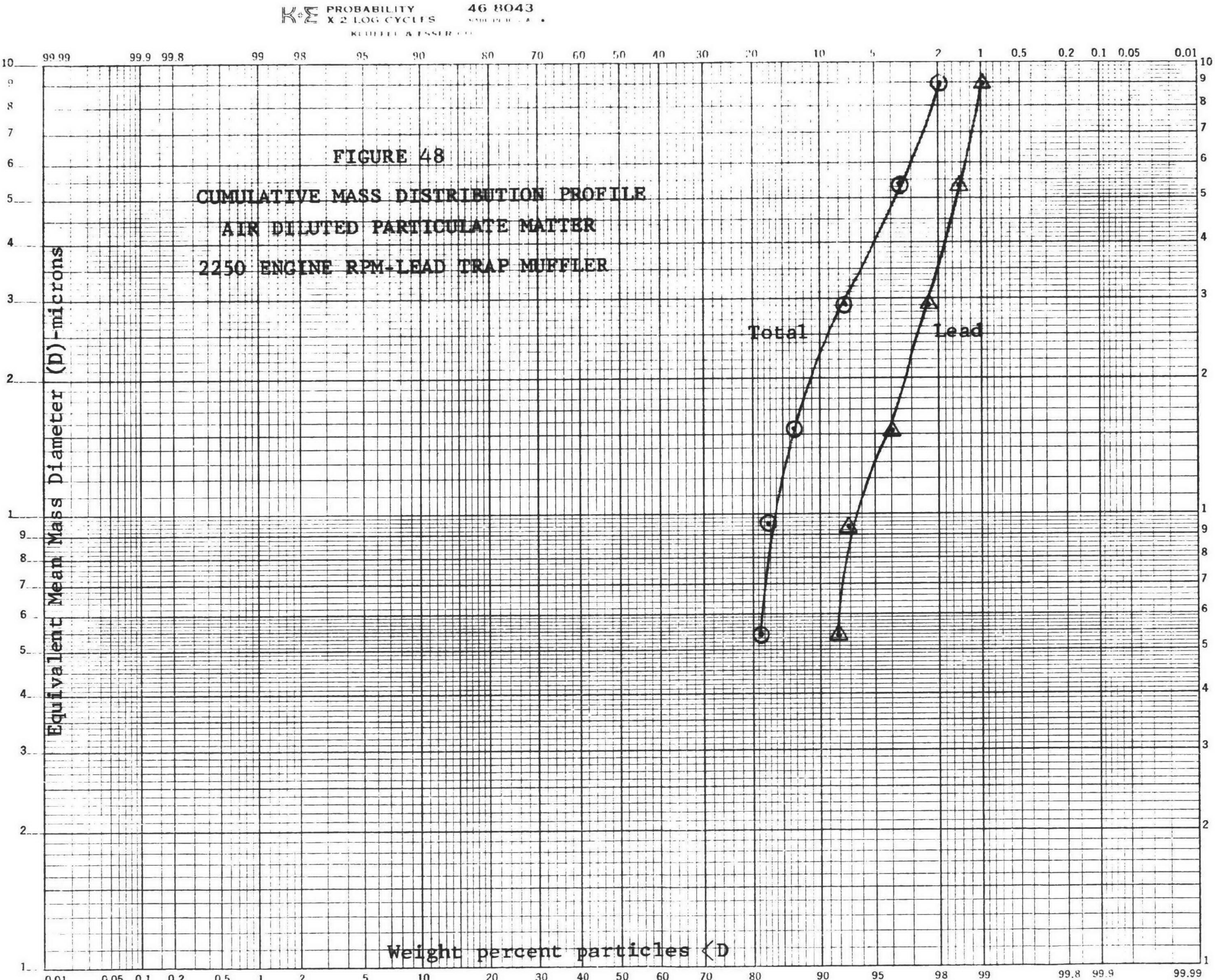


FIGURE 48

CUMULATIVE MASS DISTRIBUTION PROFILE

AIR DILUTED PARTICULATE MATTER

2250 ENGINE RPM-LEAD TRAP MUFFLER

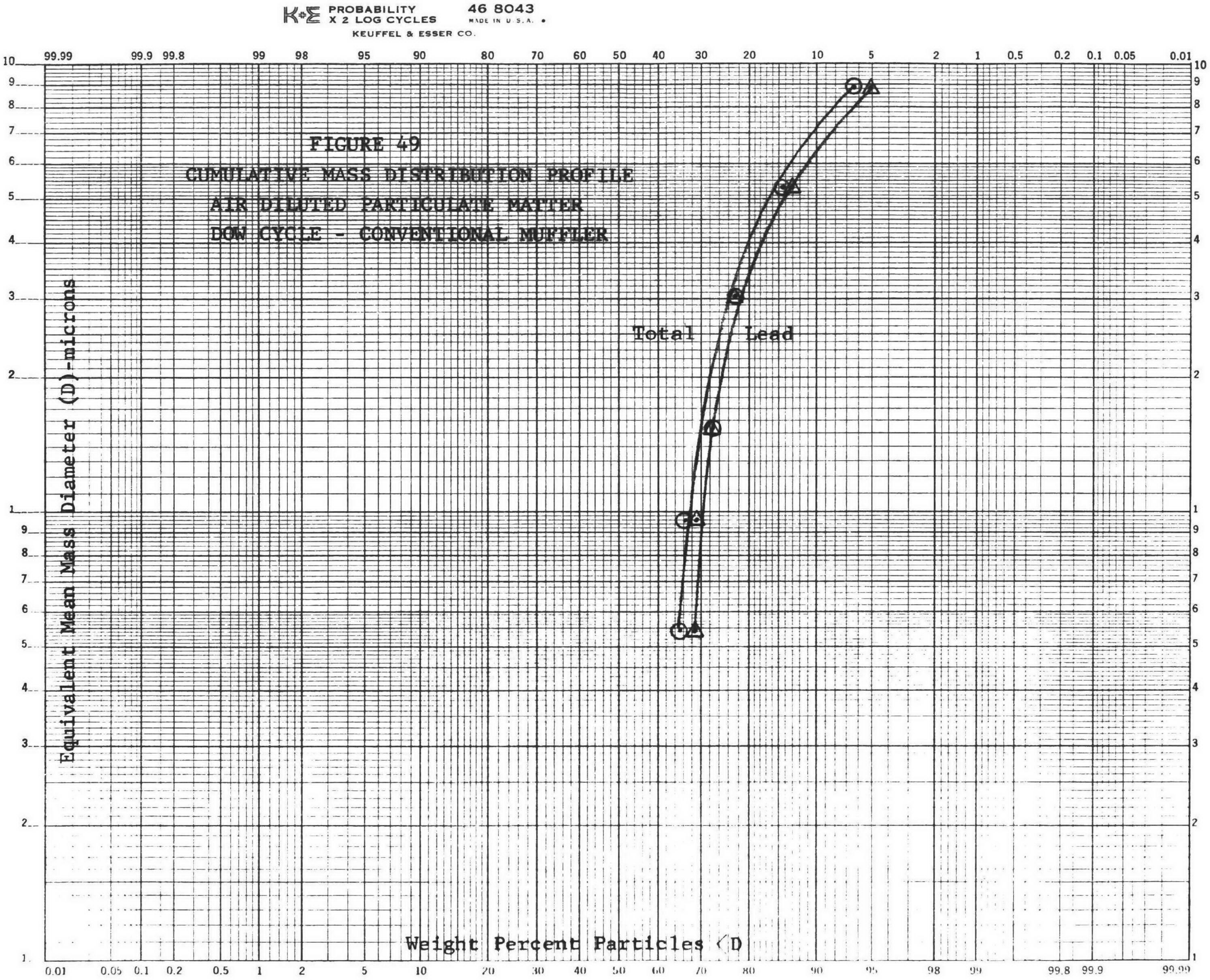


FIGURE 49

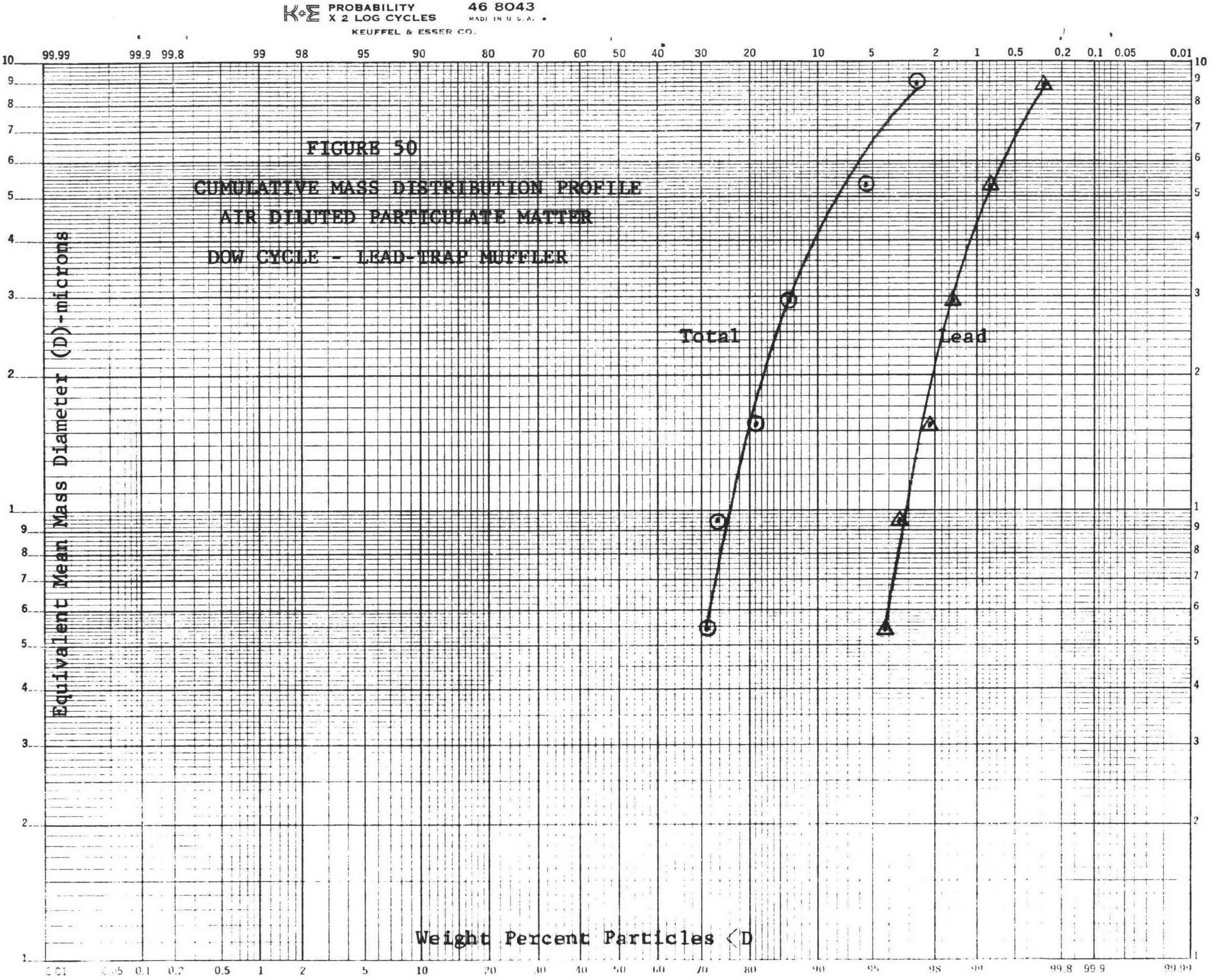
CUMULATIVE MASS DISTRIBUTION PROFILE

AIR DILUTED PARTICULATE MATTER

DOW CYCLE - CONVENTIONAL MUFFLER

FIGURE 50

CUMULATIVE MASS DISTRIBUTION PROFILE
AIR DILUTED PARTICULATE MATTER
DOW CYCLE - LEAD-TRAP MUFFLER



Analysis of the salt trapping medium was made at the completion of Tests IX and X, and again after Test XI. In the latter case analyses were performed on salt from both the exhaust inlet and outlet halves of the muffler. Data are shown in Table XXVIII.

TABLE XXVIII

ANALYSIS OF SALT FROM LEAD TRAP AFTER DYNAMOMETER TESTING

	Weight %		
	Potassium	Lithium	Lead
After Tests IX and X	24.0	3.12	1.80
After Test XI (Inlet half)	22.6	3.10	0.45
After Test XI (Outlet half)	24.6	2.77	0.71

At the completion of Tests IX and X, the salt trap was examined visually to determine if substantial quantities of the molten salt trapping medium were being lost. At the completion of Test XI, the trap was weighed to determine salt loss. The data are shown in Table XXIX. No attempt was made to add salt to the trap between runs.

TABLE XXIX

WEIGHT OF SALT IN LEAD TRAP MUFFLER

Initial - 6089 gm
After Tests IX and X - Little visual change
After Test XI - 1476 gm

The bulk of the salt lost from the trap in Tests IX-XI accumulated within the tail pipe section of the exhaust system. The pressure drop across the lead trap was found to be ∿1 cm of mercury in Tests XI and X, and between 0.5 and 5.0 cm of mercury under the cycling conditions of Test XI.

c. Aldehyde Analysis

Data from the polarographic determination of aldehydes for the cold trap condensates collected both ahead of and behind the lead trap muffler in Tests IX-XI is presented in Table XXX. For comparison purposes, similar analyses are reported for runs VI-VIII in the presence of the conventional muffler. In these runs only a single analysis was obtained ahead of the muffler.

These analyses cannot be related directly to the concentration of aldehyde in the exhaust stream since, as has been discussed earlier, the sample probes feeding the cold traps were not used exclusively for this purpose but were also used for obtaining exhaust gas analyses. Nevertheless, the relative orders of magnitude of the numbers are significant.

TABLE XXX

ALDEHYDE ANALYSIS OF COLD TRAP CONDENSATES

Test	Sampling Location*	Engine RPM	Aldehyde (ppm HCHO)
VIII	1	1200	950
VI	1	2250	1100
VII	1	Cycle	2000 (30 benzylphenone
IX	1	1200	910
	2		660
X	1	2250	420
	2		1.3 (2.9 CH_3CHO)
XI	1	Cycle	1500

*1 - ahead of muffler
2 - behind muffler

D. TRAPPING MEDIUM SELECTION

Considerable technology has been developed for the removal of particles from gas streams; however, few systems afford the diversity of conditions that are encountered in the exhaust system of an internal combustion engine. Temperatures may range from over 1500°F in the combustion zone to those of ambient air (e.g., -30°F or lower). The volume of gas within the system varies from very low values at engine idle to several hundred SCFM at accelerated vehicle speeds. The exhaust gas stream velocity has been calculated to be of the order of 15,000 fpm at about 60 mph. Particle size distribution is known to vary over wide limits, from the visible corrosion products of the exhaust system to the products of the combustion process that could approach molecular dimensions[1]. The smallest particles (e.g. <5 microns) represent the greatest inhalation hazard (hence potentially the most dangerous to health) and are the most difficult to remove. In designing a device to remove particulate matter from automotive exhaust, there are additional constraints due to the space and power available in the vehicle.

In considering the design of a device to remove particulate matter from automobile exhaust, one would expect that a gravitational separator would be impractical because of the space it would occupy and its increasing inefficiency in removing the smaller particles. Inertial devices would amplify the inherent separating tendencies of the particulates by increasing gas velocities and provide rapid changes in direction. However, these devices can only be designed for narrow ranges of gas flow rates and may introduce considerable pressure drops in the system.

Electrostatic precipitators are very effective for removing particles from gas streams but must be designed for the maximum use condition; hence, in the automobile they would have very large power requirements.

The approach chosen for design of a trapping device was to contact the particles with a suitable liquid medium so that they would be removed by chemical reaction or inertial separation. The liquid medium would facilitate inertial separation by increasing the mass of the particles by wetting.

The primary criterion in the selection of the trapping medium was its fluid vs. temperature range. A literature survey was made to determine compositions of matter which had melting points in a range that appeared comparable to that expected in the vehicle exhaust stream. It was anticipated that a liquid would be more efficient than a solid as a trapping medium; therefore, it would be desirable to have the melting point as low as practical. An arbitrary maximum melting point of 1000°F was selected as the cut-off point for the purposes of the literature search.

Once a tabulation had been made (Appendix B) based on melting point, other characteristics were considered. Obviously the vapor pressure would have to be negligible at the temperature of operation to prevent excessive loss of the trapping medium during use. In addition, a practical medium would have to be sufficiently non-corrosive so it could be contained for the useful life of the device, e.g., halides are known to be very corrosive. The medium must not present a toxic hazard to the atmosphere, e.g., cyanides or chromates would be undesirable. The possibility of detonation or explosion was also considered, e.g., ammonium nitrite would be undesirable from this standpoint.

Once a selection had been made, based on these criteria, other characteristics of the medium could be considered. For example, an economical, readily available medium would be preferable. Chemical reaction with the exhaust emissions would be desirable if it improved the efficiency of the device. However, reaction might lead to decreased efficiency such as the formation of carbonates in an alkaline trapping medium from reaction with the carbon dioxide in the exhaust stream. Carbonates have greatly increased melting points which are less desirable.

The trapping medium of choice was a 70 percent potassium nitrate-30 percent lithium nitrate mixture. It was selected on the basis of:

1) A relatively low melting point (284°F).
2) Low corrosivity and high thermal stability - Nitrate salts are used in the metal treating industry at temperatures over 900°F and are contained in mild steel.
3) Potential for acting as an oxidizing agent - In addition to the mechanical entrapment of particulates, oxidation of the organic fraction of the exhaust stream can be postulated.

A potential disadvantage was the resultant emission of reduced nitrogen oxide.

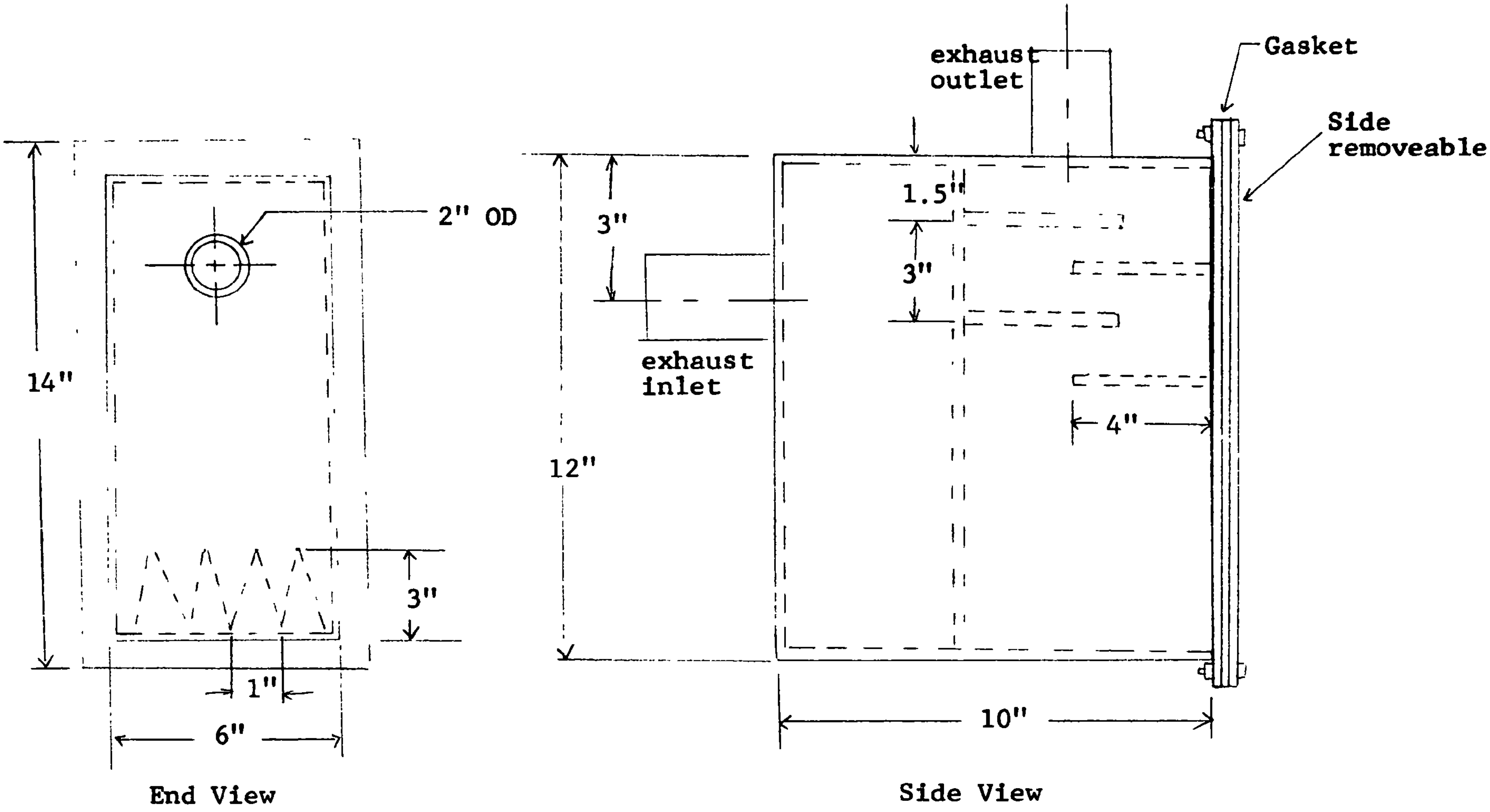
E. DESIGN OF TRAP

The effective trapping of exhaust particles depends on wetting them so that they become aerodynamically unstable. This is a function of proper trap design. The particles must first be contacted with the trapping medium and the wetted particles then removed from the exhaust stream. To better study this process and the effect of trapping medium viscosity on trap efficiency, two prototype mufflers were constructed of transparent methyl methacrylate. An exhaust stream was simulated with compressed air and exhaust particles by expanded polymeric microspheres.

Initially particles were introduced with a syringe but this caused them to pass through the muffler in "spurts" which could not be witnessed or photographed. Subsequently an aspirator was used which permitted control of flow through the muffler so that photographs could be taken. Due to the contractor requesting a change in the emphasis of the contract, the effect of trapping medium viscosity was not investigated. The muffler design selected was based on a device previously used in a proprietary research program. The device is shown schematically in Figure 51.

FIGURE 51

PROTOTYPE LEAD-TRAP



V. DISCUSSION OF RESULTS

The data from the road tests show that the temperature profile of the exhaust system forms a family of essentially parallel curves at different speeds from 30 to 80 mph. If allowance is made for the increased path of travel of the gas through the muffler, the temperature drop of the gas is essentially linear throughout the exhaust system. The temperature drop tends to be greater from the exhaust manifold to the muffler than in the remainder of the system and proportionately this initial drop is greater at the lower speeds. Temperatures ranged from 900-1400°F at the exhaust manifold to 300-800°F at the end of the tail pipe.

The temperature profiles generated in laboratory Tests I and II again show that the temperature drop along the exhaust system is linearly related to distance from the exhaust manifold. However, the temperature drop along the system is somewhat less than was experienced in the road tests. This is undoubtedly due to the fact that in the laboratory tests the exhaust system is not exposed to the same air cooling which is encountered in the moving vehicle. Nevertheless, these temperature profiles were considered close enough to those experienced in the road tests to allow meaningful data on particulate matter to be developed in the dynamometer tests.

The mass data generated on particulate matter collected at the heated Andersen Sampler in Tests II-V allows the determination of a particle mass profile for the exhaust system at 2250 engine rpm.

In Test I the Gelman filters used at sampling Positions I-IV were not maintained under isothermal conditions or at temperatures equivalent to those of the exhaust system at their respective locations, thus there exists the possibility of condensation of organic matter which may in fact be volatile at the various sampling point temperatures of the exhaust system. Particulate matter collected on these filters and their back-up cold traps was nevertheless of real value in defining the nature of the exhaust particles present along the length of the exhaust system as will be shown later in the discussion.

In Tests II-V, an effort was made to define a mass distribution profile for the exhaust system under 60 mph steady state engine operation by locating the heated Andersen stack sampler at successively different sampling positions along this system. This approach was successful at sampling Positions III and IV (immediately after the muffler and close to the end of the tail pipe) but failed at sampling Position II (ahead of the muffler) due to degradation of the Andersen plates. It is nevertheless significant that at this sampling position, virtually no particulate matter was detected in the Andersen unit, suggesting that at this point in the system the exhaust effluent is almost exclusively gaseous in nature.

It is again significant that the weights of particulate matter collected at the various unheated Gelman filters used in Tests II-V does not necessarily relate to the actual concentration of particulate matter present within the exhaust system since thermal quenching at these filters undoubtedly occurred.

Comparison of the particle mass-size distribution profiles for Positions III and IV of the exhaust system shows that there is a shift in the size of the particulate matter to a smaller equivalent mass median diameter as the exhaust effluent moves towards the end of the tail pipe. This indicates that particle shattering, rather than agglomeration, is occurring in this section of the exhaust system. Such a phenomenon must result from the highly turbulent motion of the exhaust effluent within the tail pipe.

Analysis of particulate matter collected on the plates of the Andersen sampler in sampling Positions III and IV of the exhaust system confirmed that lead halides were the major components of the larger particles collected. As particle size decreased, however, the concentration of halide diminished and the levels of lead sulfate and lead chlorophosphate increased. Iron, zinc, and nickel were also detected. Salts of the first two of these elements probably result from degradation of the exhaust system itself. Nickel compounds could be a result of reaction of the exhaust effluent with the nickel-plated stages of the Andersen unit. In general, all the particulate matter analyzed by scanning electron microscopy showed non-homogeneity, especially toward the tail pipe end of the exhaust system.

Transmission electron photomicrographs of the smaller particles collected ($<1\mu$) indicated these to be made up of inorganic matter embedded in an organic matrix. No discreet particles of purely organic matter could be identified. A limited amount of mass spectrographic analysis of cold trap condensates collected from the exhaust system in an engine run which was not performed as a formal part of the test sequence described in this report indicated that the organic matter present in the condensate was very similar to that previously reported by Moran and Manary[1] in a similar study on leaded gasoline. The relative quantities of organic material present were very small.

Microscopic examination and related analysis of particulate matter collected on the Gelman filters and associated cold traps at different positions in the exhaust system is particularly useful in determining the changing character of particulate matter along the exhaust system. Particles collected on the Gelman located close to the exhaust manifold (Position I) were highly birefringent, suggesting highly ordered crystalline structure. This was confirmed by SEM analysis. It is suggested that this is a result of particle nucleation actually occurring at the fiber glass filter with resultant dendritic crystal growth. This type of crystal growth and particle birefringence decreases considerably as one moves towards the tail pipe. This is interpreted to mean that the exhaust effluent is essentially gaseous in nature between the exhaust manifold and the muffler. The bulk of particle precipitation and agglomeration occurs within the muffler to afford particulate matter having random orientation and thus low birefringence.

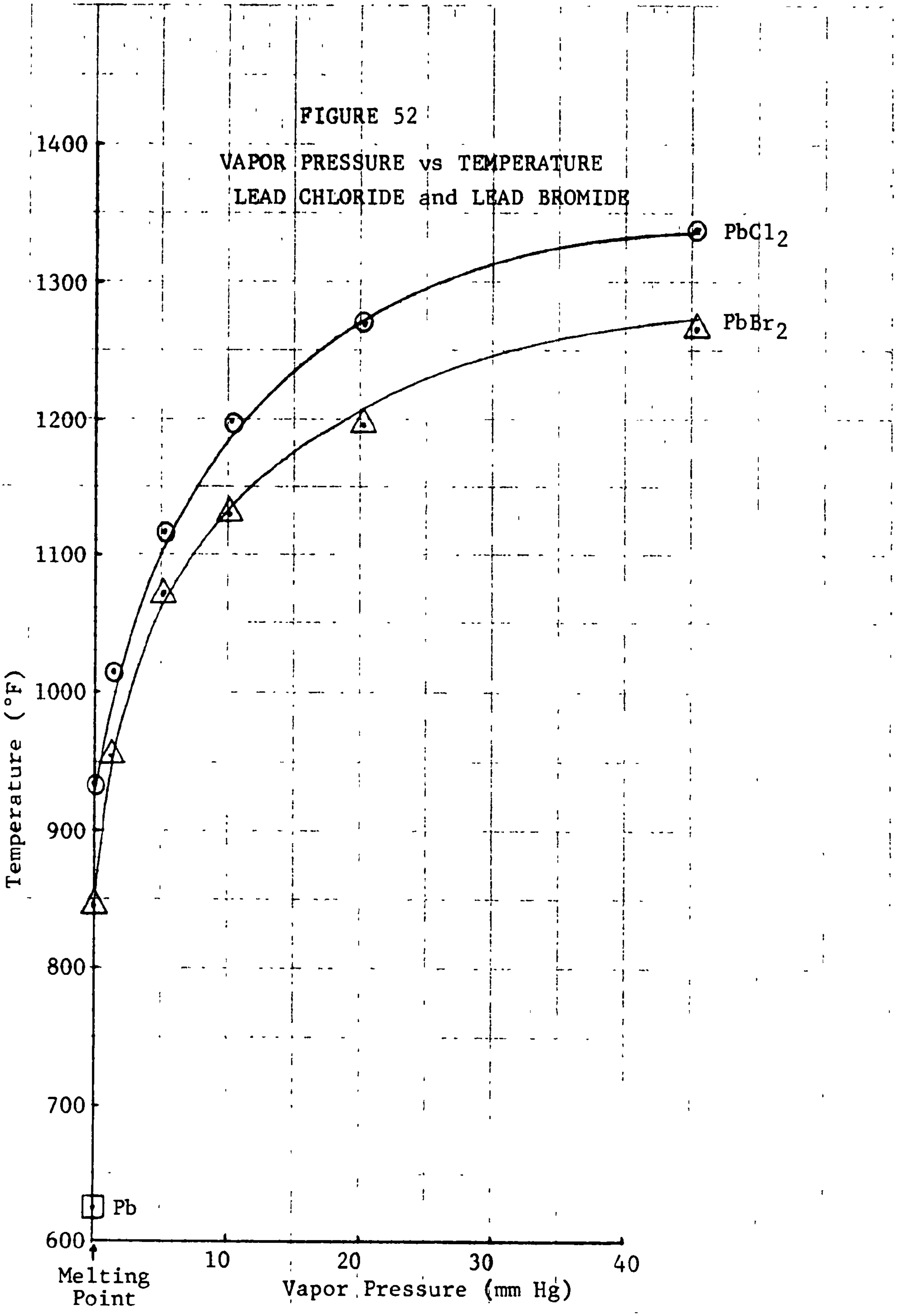
The principal component of the particulate matter collected during direct sampling of the exhaust system was found to be lead halide, specifically lead chlorobromide. Examination of the vapor pressure curves for lead chloride and lead bromide shown in Figure 52 suggests that these salts would not be expected to precipitate from the exhaust stream prior to the muffler because of the high temperatures which exist in this section of the exhaust system. Also, since lead bromide has a higher vapor pressure than lead chloride at any given temperature, one would expect lower concentrations of the latter salt nearer the manifold end of the exhaust. This was found to be the case. It should also be noted, however, that the concentration of ethylene dichloride scavenger in the fuel is twice that of ethylene dibromide. This fact would account for the relatively higher concentrations of chloride at the end of the tail pipe.

Lead determinations on the cold trap condensates sampled from the exhaust system substantiated the hypothesis that the exhaust stream is essentially gaseous in nature prior to the muffler. The concentration of lead in these condensates dropped substantially from exhaust manifold to tail pipe.

The identification of uncombined lead during Test I is interesting. Its presence, especially at engine idling conditions (870 rpm), must result from incomplete fuel combustion.

FIGURE 52

VAPOR PRESSURE vs TEMPERATURE
LEAD CHLORIDE and LEAD BROMIDE



The mass distribution profiles plotted for the total air diluted particulate matter collected in Tests VI, VII, and VIII (conventional muffler) were very similar and in close agreement with that for particles collected at the end of the tail pipe under 2250 engine rpm. Comparison of the masses of air diluted particulate matter collected in Tests VIII and VI (1200 and 2250 engine rpm) shows them to be 0.096 gm/mile and 0.104 gm/mile, respectively, very similar to that obtained at 2250 rpm from the Andersen unit positioned close to the end of the tail pipe (0.072 gm/mile) (Test III).

From this data one would conclude that for the leaded fuel tested and under steady state conditions employed, the bulk of particle precipitation occurs within the exhaust system and that any further precipitation which does take place in the dilution tube results in very little change in particle mass median equivalent diameter. The data also substantiates the fact that the bulk of particulate matter present in both the exhaust system and the air diluted exhaust effluent is associated with lead salts.

The difference in the gram/mile of particulate matter collected in Tests VI-IX on the 4 cfm filter compared to that collected on the Andersen sampler and back-up 1 cfm filter is significant and merits discussion. In all cases except Test X, the data obtained at the 1 cfm filtering system is higher than that obtained at the 4 cfm filter (Table XXVI). This is believed to result from the longer residence time of particulate matter in the 1 cfm sampling system caused by the lower pumping rate. Also the adiabactic expansion of the diluted exhaust effluent as it passes through the Andersen unit could result in thermal quenching and the condensation of volatiles within the unit.

Before any further work is undertaken in this area it is imperative that the above sampling anomolies be resolved.

At 2250 engine rpm and under mild cycling conditions, the mass-distribution profiles for total air diluted particulate matter and lead associated particles are almost identical. At 1200 engine rpm, however, the lead associated particles are smaller than the total particulate matter collected.

Introduction of the prototype lead trap muffler into the exhaust system showed little effect on either the total mass of air diluted particulate matter collected or on its mass median equivalent diameter at 1200 rpm. The amount of lead detected was unchanged. There is, however, a decrease in the mass median equivalent diameter for lead particulates.

The lead trap muffler was most effective at 2250 engine rpm when the total mass of lead in the particles collected dropped by over 50 percent. The mass of total filtered particulate matter, however, increased slightly, undoubtedly a result of nitrate salts being carried over from the trap itself. In this instance the mass median equivalent diameter for both total and lead associated particles decreased. Under these conditions, the trap appears to be most efficient for the removal of the large lead particles.

Particle data generated from the lead trap test under cycling conditions is considered to be unrealistic because of the massive amount of salt lost from the trapping device.

A Government-initiated change in the scope of the work precluded further optimization of the lead trap unit. However, based on the performance of this device at 2250 engine rpm, it is felt that such a unit would form a good base for further activity in this area.

PHASE II

VI. CONCLUSIONS

Phase II of this study covers an investigation of the particulate emissions from an automotive engine operating on non-leaded fuel. The effect on such emissions of changes in air-to-fuel ratio, and of two emission control devices were evaluated.

The tests on the effect of the air/fuel ratio lead to the following conclusions:

1. Over the range tested (13.3-17.1), the air/fuel ratio had little effect on the mass of particles emitted per mile. At 1200 rpm the ratio of lean/rich emissions was 1.3 by the 4 cfm filter, 1.1 by the 1 cfm filter. At 2250 rpm the ratio was 1.0 by the 4 cfm and 1.1 by the 1 cfm. The cumulative mass distribution profiles are very similar at a given speed.

2. The mass of particles/mile were smaller at 2250 rpm than at 1200 rpm; the ratio was about 0.5 with the 4 cfm filter, 0.7 with the 1 cfm filter.

3. The 1 cfm filter collected a proportionately greater mass of material than the 4 cfm filter due to the greater residence time in the filter system and lower temperature at the filter interface.

   The test of the noble metal catalytic device led to the following conclusions.

   a. The emissions of an engine fitted with the catalytic device as compared to the same engine without the device
      1) had lower residual hydrocarbons (about one-half at 2250 rpm, one-quarter at 1200 rpm).
      2) had lower aldehydes (about one-third at 2250 rpm).

3) had increased mass of particles per mile, using the 4 cfm filter 6.5x at 1200 rpm, 22x at 2250 rpm; using the 1 cfm filter 1.3x at 1200 rpm, 4x at 2250 rpm.
4) had decreased particle size, from 20 percent less than 1μ to 85 percent at 1200 rpm, from about 50 percent less than 1μ to 90 percent at 2250 rpm.

b. Considering the Pontiac engine outfitted with a noble metal catalyst device, the mass of particle per mile increased 60 percent (with 4 cfm filter) and 140 percent (with 1 cfm filter) when the speed was increased from 1200 to 2250 rpm.

The test of the packed bed catalytic muffler led to the following conclusions:

a. The emissions of an engine fitted with the catalytic device as compared to the same engine without the device
   1) had lower residual hydrocarbons (about 45 percent at 1200 rpm, 75 percent at 2250 rpm).
   2) had about one-half reduction in aldehydes.
   3) had about 156 percent increase in the mass of emissions (at 2250 rpm - 1 cfm filter).
   4) had decreased particle size (from 68 percent less than 1 micron to 82 percent less than 1 micron).

b. Considering the Chevrolet engine outfitted with the packed bed catalyst device, the mass of particles per mile increased 461 percent (with 4 cfm filter) or 535 percent (with 1 cfm filter) when the speed was increased from 1200 to 2250 rpm.

VII. EXPERIMENTAL PROCEDURE

Studies under Phase II of the program were aimed at establishing baseline exhaust emission data for an engine operating on Amoco 91 octane non-leaded gasoline and subsequently evaluating the effect on such emissions of two different catalytic reactors. A fuel analysis is shown in Table XXXI. No analyses of the particulate matter collected were made.

In order to perform these tasks, a 1971 Pontiac V8, 400 CID engine was set up on the Dynamatic dynamometer test stand. The exhaust stream from the left bank of cylinders after passage through a conventional exhaust system was fed to the air dilution tube described under Phase I of this report.

The series of tests performed are outlined in Table XXXII. In Tests 2 and 3, the engine was operated at 1200 rpm at two different air/fuel ratios - lean and rich. Tests 1 and 4 were conducted at 2250 engine rpm with the same two air/fuel ratios.

Particulate matter and condensate was collected through a Gelman glass fiber filter with a backup cold trap via a sample probe located immediately ahead of the muffler. Additional particulate samples were collected from the various sections of the dilution tube by sweeping at the end of the test, and at an Andersen Model 0203 impactor located at the end of the tube, sampled isokinetically at 1 cfm and fitted with a backup Millipore filter (142 mm Type AAWP 0.8μ). Other samples of particulate matter were collected isokinetically (4 cfm) through two separate Millipore filter holders fitted with fiberglass filter pads via probes located at the end of the dilution tube. This sampling system has been previously described in detail by Moran and Manary[1]. In Runs 5-10, an additional Gelman filter and back-up cold trap were introduced immediately after the catalytic units tested. Because of the limited amount of time available to complete Phase II of the research

TABLE XXXI
ANALYSIS OF FUEL FOR PHASE II

Physical Analysis

ASTM D		American Unleaded
Boiling Range:	IBP	93
	5	119
	10	129
	20	150
	30	169
	40	188
	50	204
	60	219
	70	234
	80	258
	90	294
	95	329
	EP	372
% Recovery		98.5
% Residue		0.2
% Loss		1.3
Research octane no.		91.0
Motor octane no.		82.7
Reid Vapor Pressure, psi		8.8
API Gravity		61.9
FIA:	% Saturates	73.0
	% Olefins	5.4
	% Aromatics	21.6

Trace Metal Analysis

	%		%
Fe	0.00005	Pb	<0.0001
Ni	<.00005	Cr	<.00005
Cu	<.00003	Sn	<.00005
Al	<.00005	Zn	<.0001
Ca	<.0001	Ti	<.00005
Si	<.0001	Sb	<.00005
Mg	<.00005	P	<.0005
Mn	<.00003		

TABLE XXXII

PONTIAC ENGINE SAMPLING DEVICES FOR PHASE II
91 RON - 0 TEL FUEL

	EXHAUST SYSTEM SAMPLES						DILUTION TUBE SAMPLES					
	Ahead of Muffler			After Catalytic Muffler					1 cfm		4 cfm	
	Glass Fiber Filter	Cold Trap		Glass Fiber Filter	Cold Trap							
Test		Ice/Water	Dry Ice/ Acetone		Ice/Water	Dry Ice/ Acetone	Slit	Tube Sweepings	Andersen Sampler	Millipore Filter	Glass Fiber	Glass Fiber
1. 2250 rpm A/F 15.5-16.0	Yes	Yes	Yes				Yes	Yes	Yes	Yes	Yes	Yes
2. 1200 rpm A/F 15.5-16.0	Yes	Yes	Yes				Combined		Yes	Yes	Yes	Yes
3. 1200 rpm A/F 13.5-14.0	Yes	Yes	Yes				Yes	Yes	Yes	Yes	Yes	Yes
4. 2250 rpm A/F 13.5-14.0	Yes	Yes	Yes				Yes	Yes	Yes	Yes	Yes	Yes
Noble Metal Catalytic Muffler												
5. 2250 rpm	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
6. 1200 rpm	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
7. Dow cycle	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Proprietary Catalytic Muffler												
8. Dow cycle	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	No	Yes	Yes	Yes
9. 1200 rpm	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
10. 2250 rpm	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes

program, no analytical work was conducted on the particulate samples obtained at the Gelman filters located ahead of and after the muffler. Since such samples were not collected isothermally, the determination of gram/mile particulate matter from these filters was not considered to be of value.

At the start of the test series, the Pontiac engine, which had been operated only on non-leaded gasoline, was checked and conditioned for 48 hours on the Dow cycle. At the beginning of each of the tests in this phase of the program, the engine was held under the desired test condition for 1 hour prior to introduction of the exhaust effluent to the dilution tube. Sampling was then conducted over a six hour period.

An unsuccessful attempt was made to get baseline data for the engine operating in the Dow cycling mode with rich and lean air/fuel ratios. However, it proved impossible to maintain this variable within the prescribed limits over the various modes of the cycle. This was not unexpected due to the idle and low rpm conditions involved. Air/fuel ratios were calculated from analysis of exhaust gases as described in Phase I of this program. No data was collected on this run.

Tests 5-7 were conducted to evaluate the effect of a noble metal catalyst on particulate emissions, residual hydrocarbons, and aldehyde concentrations, under three different engine operating conditions: 2250 rpm cruise, 1200 rpm cruise, and the Dow cycle. The catalyst unit was introduced into the exhaust system in place of the conventional muffler (and located 14 inches after the Y junction normally present below the mainfold). During the above test sequences, it operated at from 680 to 870°F. The proper operation of this device required the introduction of air into the exhaust system ahead of the unit. This was accomplished by means of pumping air into the exhaust stream in such a way that the exhaust effluent entering the catalyst unit contained 1.5 percent of the oxygen by analysis. Thus, calculation of engine air/fuel ratio by exhaust gas analysis was not possible. Data obtained in Runs 1-4, however, indicated that variations in this parameter had little effect on the mass-size profile of emitted particles. Air/fuel ratios were calculated from air and fuel flow measurements.

A similar series of tests (8-10, Table XXXII) were conducted in the presence of a third party proprietary catalytic device designed to reduce emissions of residual hydrocarbons and carbon monoxide. Tests 8-10 were again run on a 350 CID Chevrolet V8 engine. The change in engine was necessitated by the fact that the required air injection system for the second catalytic device studied could not be readily adapted to the Pontiac exhaust manifold. The 350 CID Chevrolet engine was cleaned, checked, and conditioned for 24 hours on the Dow cycle using Amoco 91 gasoline (non-leaded) prior to starting these tests. This catalytic unit was physically located 14 inches from the normal Y junction below the exhaust manifold to insure adequate heating. Again, to insure effective operation of the device, air was pumped into the exhaust system ahead of the catalyst so as to maintain a free oxygen content of 2.1 percent by analysis.

The exhaust stream was sampled before and after the catalytic device at 1 cfm. The exhaust gas sampled at each position was passed through a Gelman filter fitted with a glass fiber filter pad, an ice/water cold trap, and a dry-ice/acetone cold trap. The ice/water cold trap condensate was analyzed for carbonyl content. The dilution tube was sampled as before. The grams per mile and the mass distribution profile for the particular emissions were calculated from the dilution chamber data.

VIII. EXPERIMENTAL RESULTS

Air/fuel ratios calculated from exhaust gas analyses and air and fuel flow rates are shown in Table XXXIII.

TABLE XXXIII
AIR/FUEL RATIOS FOR PHASE II

Test 1	2250 rpm	15.2 - 15.3[1]
Test 2	1200 rpm	15.0 - 15.2[1]
Test 3	1200 rpm	13.8 - 14.6[1]
Test 4	2250 rpm	13.3 - 15.0[1]
Test 5	2250 rpm	16.4 - 17.1[2]
Test 6	1200 rpm	15.7 - 15.8[2]
Test 7	1070 rpm	14.7[2]
	1615 rpm	16.0[2]
	2125 rpm	16.9[2]
Test 8	1070 rpm	14.3[2]
	1615 rpm	15.0[2]
	2125 rpm	14.0[2]
Test 9	1200 rpm	14.2[2]
Test 10	2250 rpm	13.8[2]

1 Determined by exhaust analysis
2 Determined by air/fuel measurement

Particle mass data for Tests 1-4 is shown in Table XXXIV. One one-half of the total exhaust was fed into the dilution tube (left bank of cylinders) and only a limited volume of the diluted exhaust was passed through the filters (1 cfm or 4 cfm). This data has, therefore, been corrected to the equivalent mass for the total engine exhaust flow.

TABLE XXXIV

PARTICULATE SAMPLES FOR PHASE II
TESTS 1, 2, 3, 4,
(Dilution Tube Samples)

			1 cfm		4 cfm	
	Slit	Tube Sweepings	Andersen Sampler	Millipore Filter	Glass Fiber	Glass Fiber
2250 rpm Lean A/F	0.0102g	0.1748 g	5.50 g	5.6 g	2.08 g	1.55 g
1200 rpm Lean A/F	Combined	0.0204	7.3	0.2	2.3	2.32
1200 rpm Rich A/F	0.0020	0.0236	6.2	0.30	1.95	1.68
2250 rpm Rich A/F	0.0144	0.1824	6.7	3.0	1.98	1.9

Test Period - 6 Hours

The resultant calculated values for the particulate emissions in grams per mile are listed in Table XXXV.

TABLE XXXV

EFFECT OF AIR/FUEL RATIO ON PARTICULATE EMISSIONS

	4 cfm Filter* (gm/mile)	Filter Temp. (°C)	1 cfm Andersen and Filter (gm/mile)	Filter Temp. (°C)
Lean Mixtures:				
1200 rpm	0.0128	23	0.0406	23
2250	.00555	45	.0308	30
Rich Mixtures:				
1200 rpm	.00972	23	.0361	23
2250	.00538	41	.0269	29

*Average of two filters

The differences in data obtained at the 1 cfm and 4 cfm filter systems are discussed on page 134.

The mass distribution profiles for these particulate emissions are illustrated in Figure 53 for the lean and rich air/fuel mixture at 1200 rpm, and in Figure 54 for the two air/fuel ratios at 2250 rpm.

The next series of tests employed the same Pontiac 400 CID engine with the standard muffler replaced by a noble metal catalytic device. The data, again corrected for the total exhaust gas flow, is shown in Table XXXVI, with the calculated grams/mile particulate emissions in Table XXXVII.

TABLE XXXVI

PARTICULATE SAMPLES FOR PHASE II
TESTS 5, 6, 7
NOBLE METAL CATALYST
(Dilution Tube Samples)

			1 cfm		4 cfm	
	Slit	Tube Sweepings	Andersen Sampler	Millipore Filter	Glass Fiber	Glass Fiber
2250 rpm	0.0118g	0.1118 g	4.6 g	37.4 g	46 g	48 g
1200 rpm	.0016	.0254	1.9	6.9	12.46	14.08
Dow cycle	.0172	.1736	3.8	18.5	23.5	24.0

Test Period - 6 Hours

TABLE XXXVII

EFFECT OF NOBLE METAL CATALYTIC DEVICE ON PARTICULATE EMISSIONS

	4 cfm Filter* (gm/mile)	Filter Temp. (°C)	1 cfm Andersen and Filter (gm/mile)	Filter Temp. (°C)
1200 rpm	0.0737	26	0.0489	23
2250	.120	29	.117	42
Dow cycle	.0978	24-44	.0918	24-26

*Average of two filters

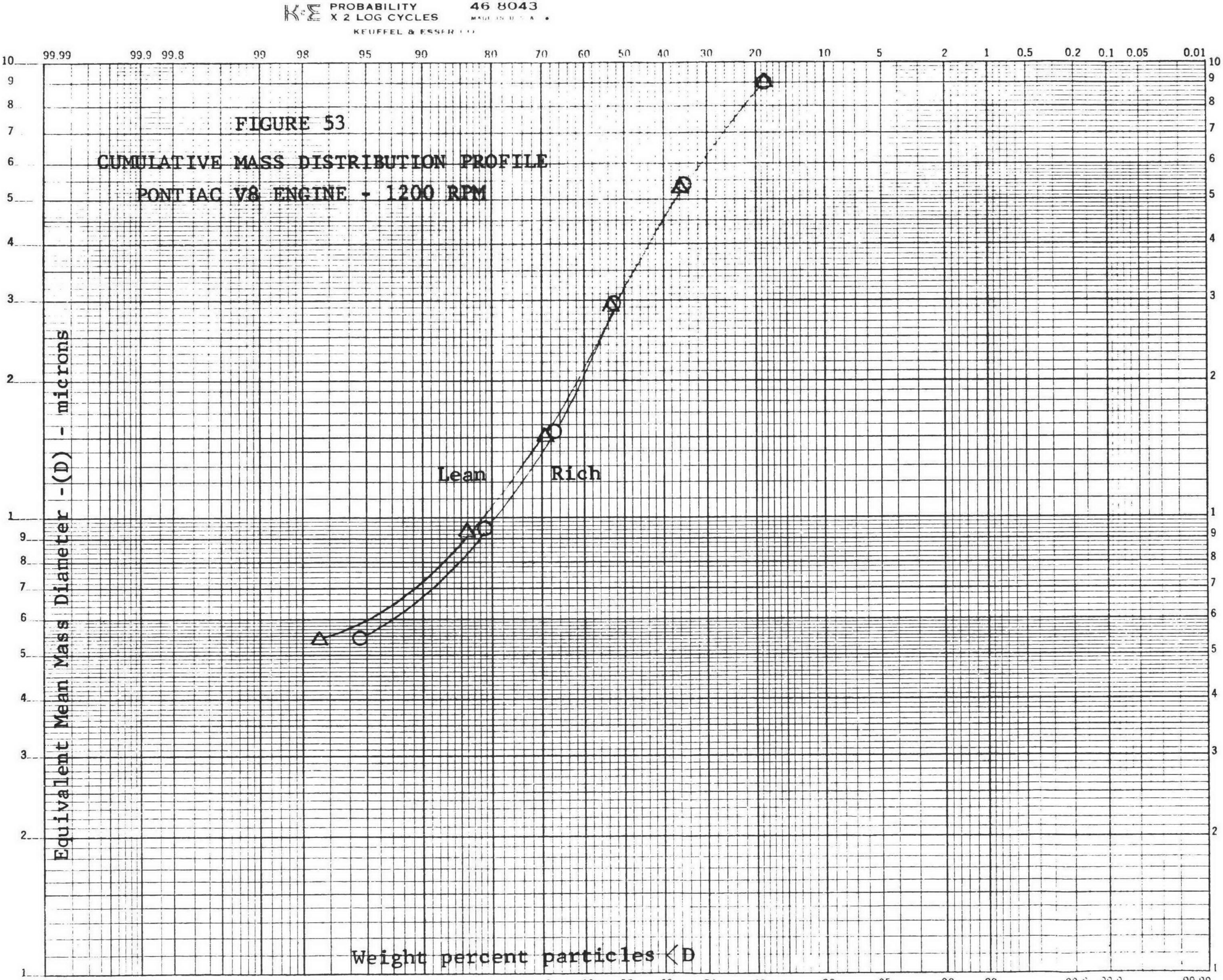


FIGURE 53

CUMULATIVE MASS DISTRIBUTION PROFILE

PONTIAC V8 ENGINE - 1200 RPM

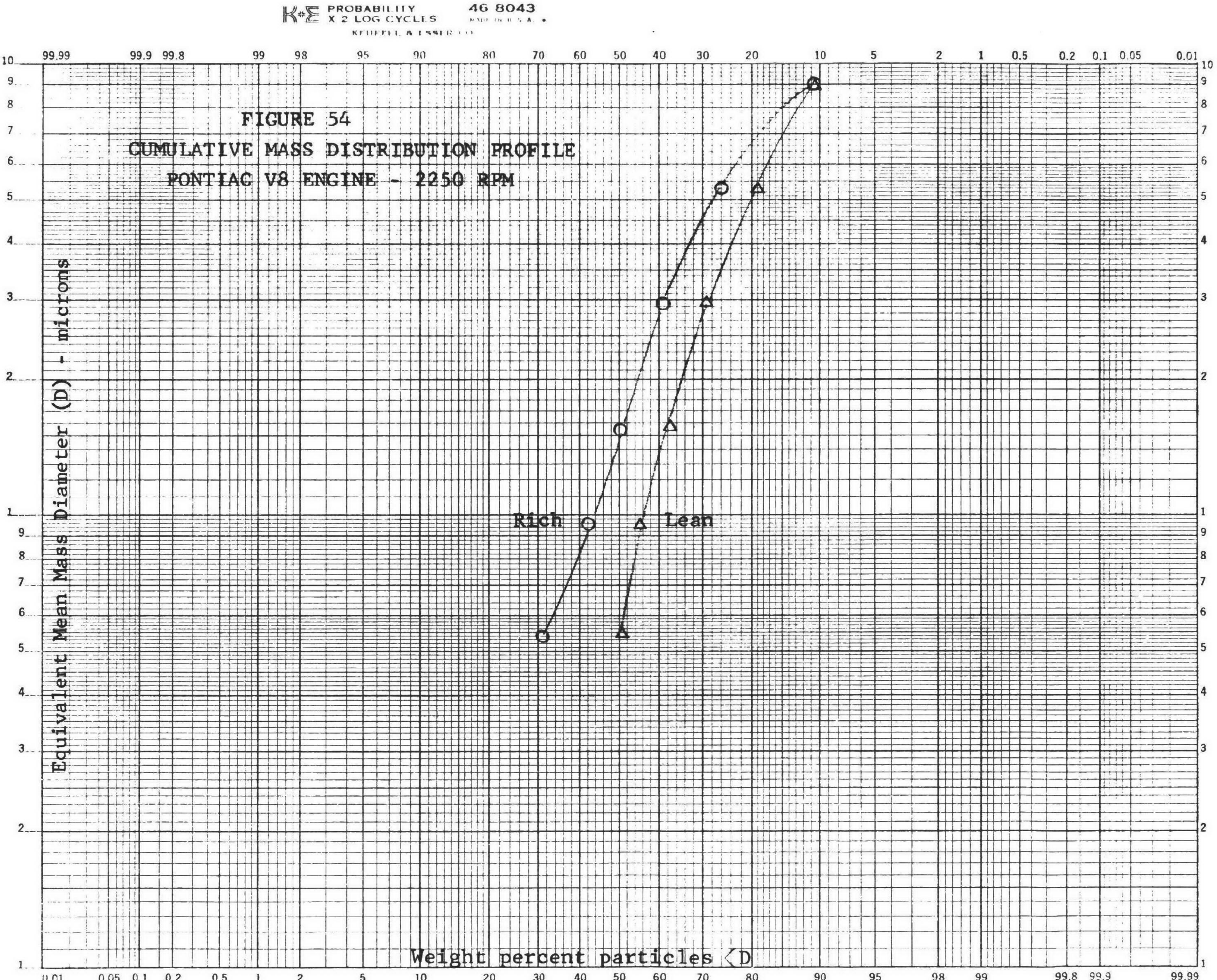


FIGURE 54
CUMULATIVE MASS DISTRIBUTION PROFILE
PONTIAC V8 ENGINE - 2250 RPM

The effect of this noble metal catalytic device on the residual hydrocarbons in the exhaust gas stream is presented in Table XXXVIII. The mass distribution profiles for 1200 rpm, 2250 rpm, and the Dow cycle follow in Figures 55, 56, and 57.

TABLE XXXVIII
EFFECT OF NOBLE METAL CATALYTIC MUFFLER ON HYDROCARBON EMISSIONS

		Ahead of Muffler (ppm)	After Muffler (ppm)
2250 rpm		130	30
		250	135
		80	45
		125	30
1200		130	25
		170	45
Dow cycle Mode	#2	195	Not available
	#3	50, 50	
	#4	160, 135, 135	
	#5	180, 190, 190	

The cold trap condensates collected before and after the noble metal catalytic device at 2250 rpm were analyzed for their aldehyde content. The aldehyde content decreased from 330 ppm formaldehyde in the condensate ahead of the device to 99 ppm after the device.

The final series of tests (8-10) necessitated the use of the Chevrolet 350 CID engine to accommodate the auxiliary air injection equipment for the proprietary catalytic device. The particulate sample weights from the dilution tube corrected for the complete exhaust gas flow are given in Table XXXIX. The particulate emissions, calculated in grams per mile, are shown in Table XL. The corresponding

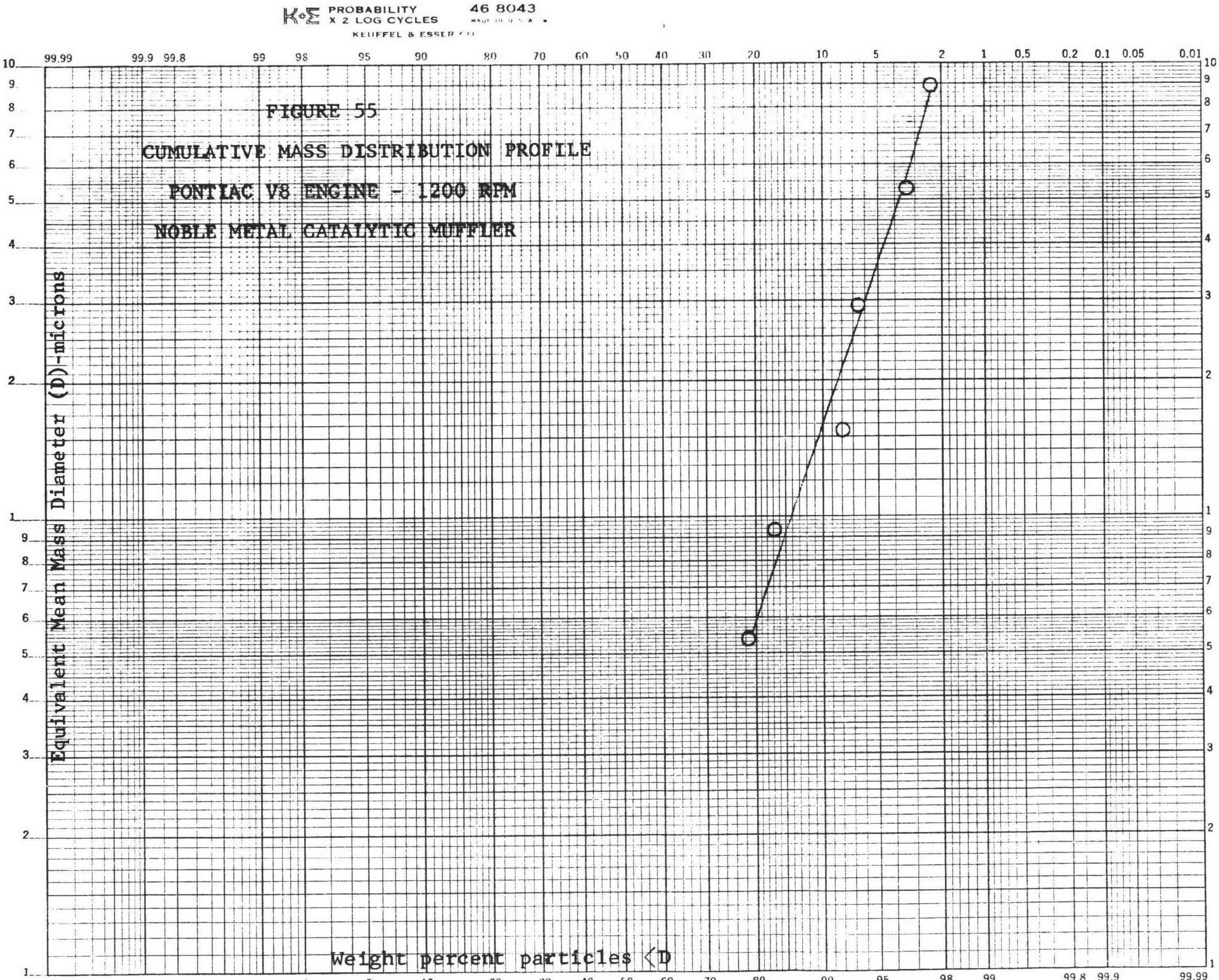


FIGURE 55

CUMULATIVE MASS DISTRIBUTION PROFILE

PONTIAC V8 ENGINE - 1200 RPM

NOBLE METAL CATALYTIC MUFFLER

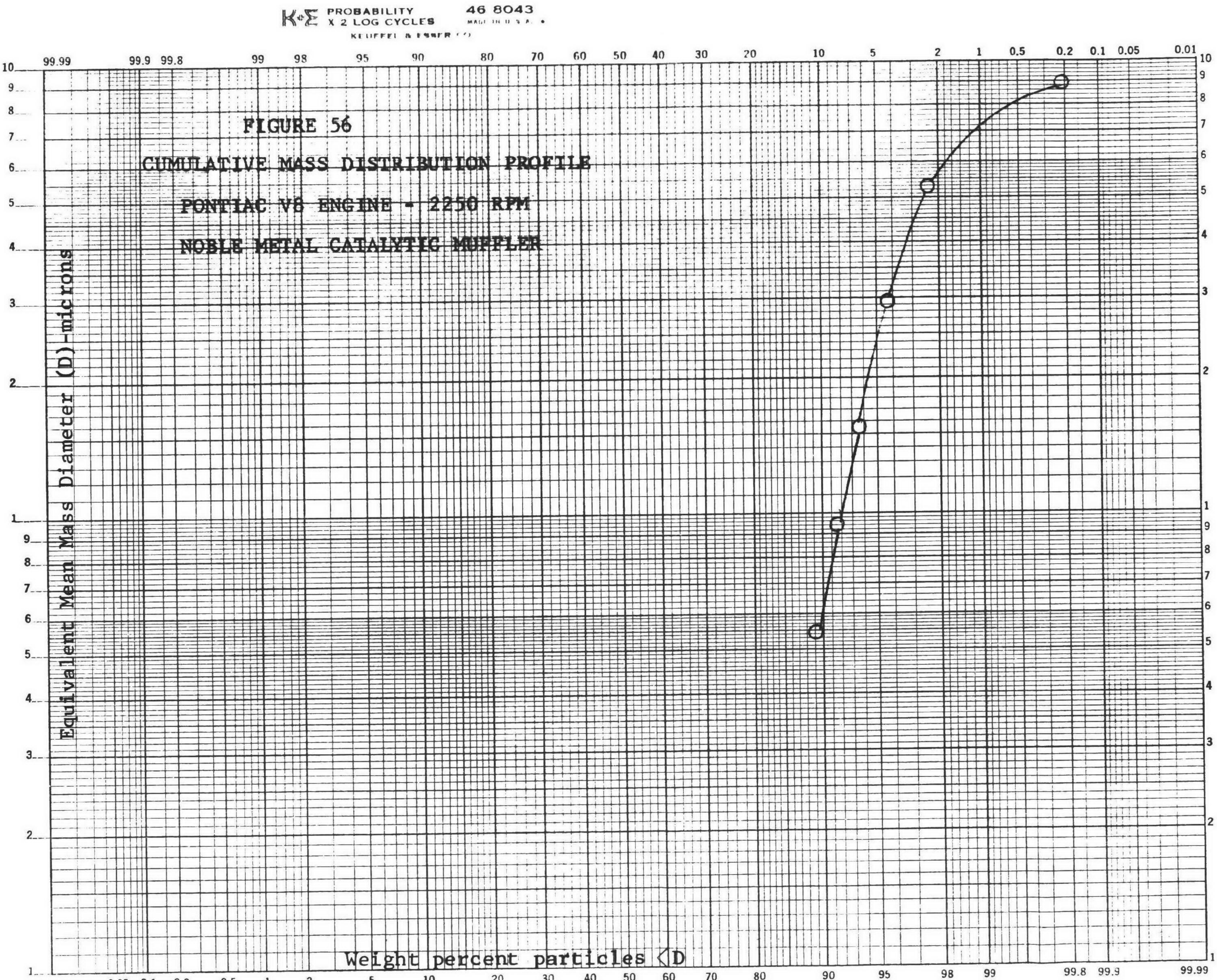


FIGURE 56

CUMULATIVE MASS DISTRIBUTION PROFILE

PONTIAC V8 ENGINE - 2250 RPM

NOBLE METAL CATALYTIC MUFFLER

FIGURE 57

CUMULATIVE MASS DISTRIBUTION PROFILE
PONTIAC V8 ENGINE - DOW CYCLE
NOBLE METAL CATALYTIC MUFFLER

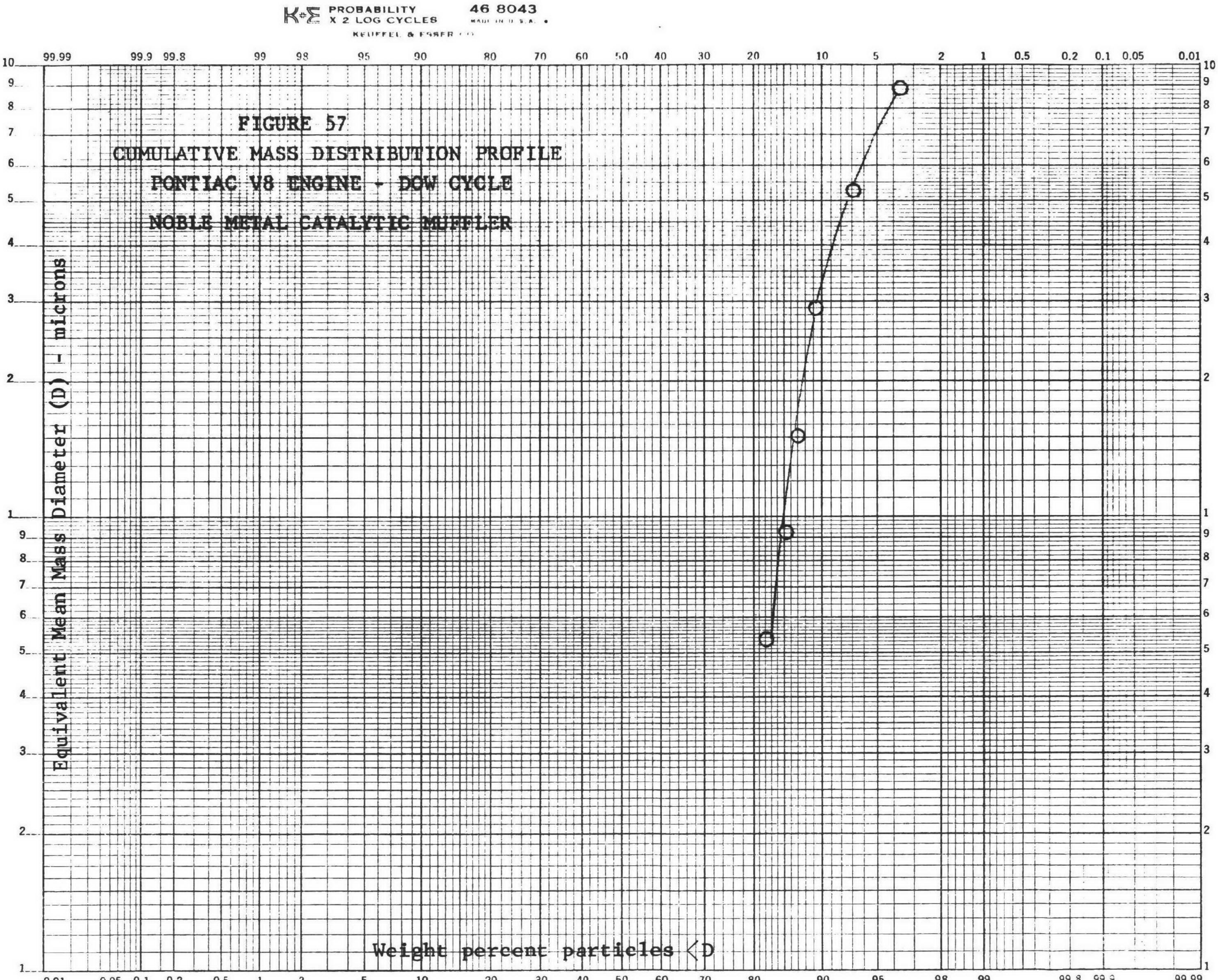


TABLE XXXIX

PARTICULATE SAMPLES FOR PHASE II, TESTS 8, 9, 10 (Dilution Tube Samples)

	Slit	Tube Sweepings	1 cfm Andersen Sampler	1 cfm Millipore Filter	4 cfm Glass Fiber	4 cfm Glass Fiber
Dow cycle						
3.3 hrs				0.000 g	1.11 g	1.05 g
7				1.55	2.40	3.54
7				2.1	3.45	3.19
Total 17.7	0.1922 g	2.8136 g	-	3.65	6.96	7.78
1200 rpm						
24 hrs	0.0471	0.8261	3.35	4.20	4.18	4.14
2250 rpm						
24 hrs	0.0515	2.1551	4.7	37.3	46.6	46.7

TABLE XL

EFFECT OF PROPRIETARY PACKED BED CATALYTIC DEVICE ON PARTICULATE EMISSIONS

	4 cfm Filter (gm/mile)	Filter Temp. (°C)	1 cfm Andersen and Filter (gm/mile)	Filter Temp. (°C)
Dow cycle				
3.3 hrs	0.0089	37-46	0.0084	Thermocouple failed
7	.0094	52-74	.0338	
7	.0117	40-72	.0074	
1200 rpm	.00578	35	.0046	28
2250 rpm	.0324	68-73 (70)	.0292	38-42 (40)

mass distribution profile curves are shown in Figure 58. A curve for the same engine and fuel without the proprietary catalytic device is shown in Figure 59. The mass of emission amounted to 0.0114 gm/mile for the Andersen sampler and Millipore filter (1 cfm filter); no 4 cfm filters were used in this baseline test. This baseline data was developed under Contract CPA-22-69-145[1].

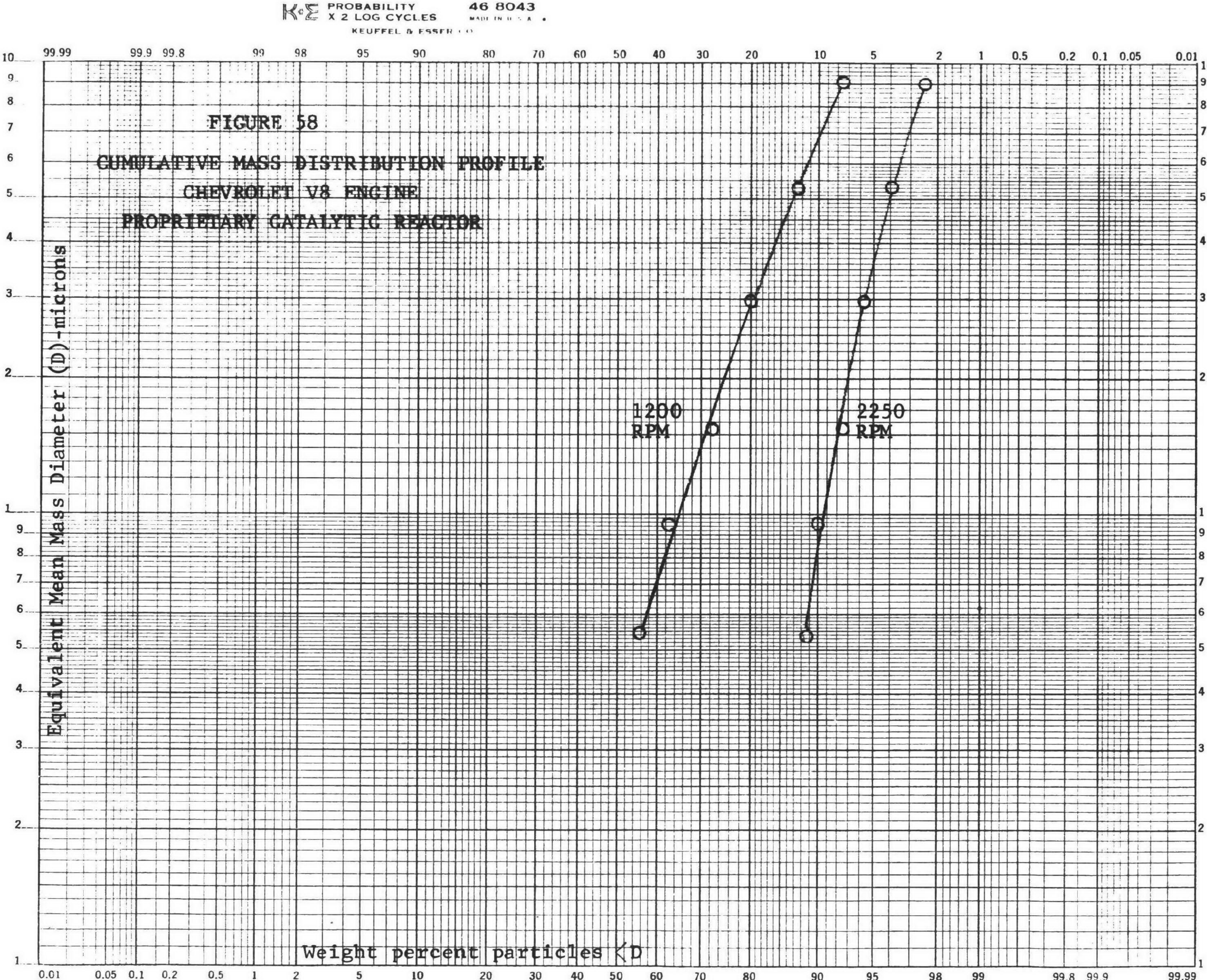


FIGURE 58

CUMULATIVE MASS DISTRIBUTION PROFILE
CHEVROLET V8 ENGINE
PROPRIETARY CATALYTIC REACTOR

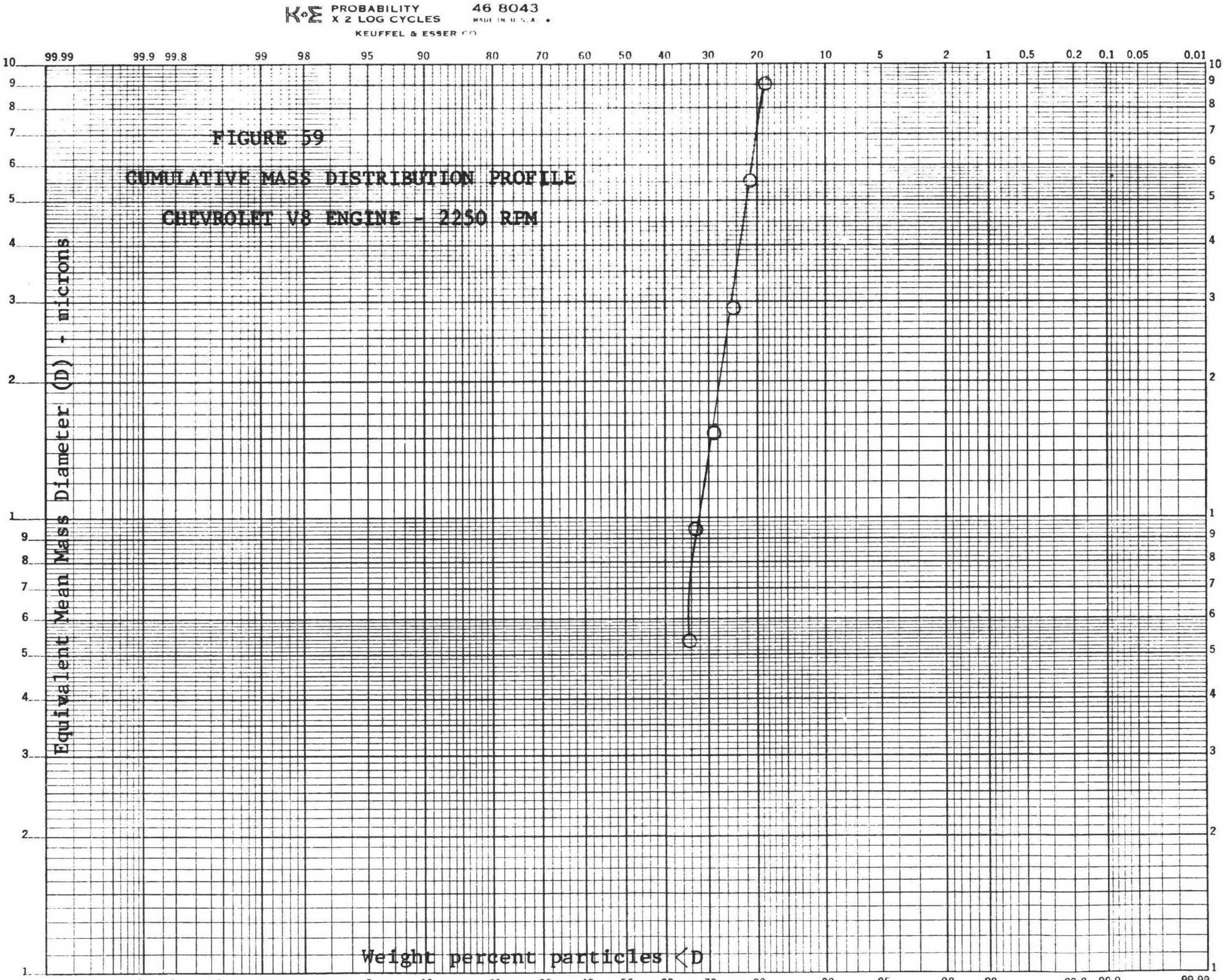


FIGURE 59

CUMULATIVE MASS DISTRIBUTION PROFILE

CHEVROLET V8 ENGINE - 2250 RPM

IX. DISCUSSION OF RESULTS

A comparison of the particle mass data generated in Tests 1-4 indicates that variations in air/fuel ratio had little effect on the grams/mile of particulate matter collected at 1200 or 2250 engine rpm. This engine variable had a similarly small effect on the particle cumulative mass distribution profile.

At each engine speed, there was a slightly higher mass of particulates from the lean air/fuel mixture and the mass of particulates was greater (3 to 5 times) with the 1 cfm than with the 4 cfm filter.

The cumulative mass distribution profiles for the 1200 rpm tests had a D_{50} value of 3.2μ. The curves were identical for particles larger than this median value. However, for smaller particles the particulate matter from the lean mixture was slightly larger than those from the rich air/fuel (A/F) mixture. At 2250 rpm the cumulative mass distribution profiles were again similar but not as nearly identical as in the 1200 rpm run. For the 2250 rpm run, the median particle size (D_{50}) was 1.5μ for the rich fuel mixture and 0.5μ for the lean fuel mixture; the particles from the latter run averaged a smaller equivalent mass over the entire profile.

Engine speed had a significant influence on both the total grams/mile of particulate matter collected and on the particle cumulative mass distribution profile. At 2250 rpm there was a significant decrease in the grams/mile, compared to 1200 rpm, particularly with the 4 cfm filter where the decrease was about one-half. The marked difference in the mass of particulate matter (grams/mile) collected on the 4 cfm filter compared to that collected on the Andersen sampler and back-up 1 cfm filter is believed to result from the longer residence time of particles in the 1 cfm sampling system caused by the lower pumping rate. Another contributing factor could be the cooling effect of the expanding gases after being forced through the Andersen sampler resulting in lower filtering temperature. The latter factor is more noticeable at higher engine speeds. The subject is discussed further in papers by Moran, Manary, Herling, Karches, and Wagman[3,4].

Introduction of the noble metal catalyst into the exhaust system resulted in the emission of up to 22 times greater grams/mile of particulate matter than in the baseline series of tests. At the same time a sharp decrease in the mass median equivalent diameter occurred at both 1200 and 2250 rpm. During this series of tests, the mass of particles increased with increasing engine rpm. At both 2250 rpm and under Dow cycling conditions, there was good agreement in the mass of particles per mile as measured by the 1 cfm and 4 cfm filters. The data on residual hydrocarbons measured ahead of and after the device indicates that the catalyst was 50-75 percent efficient in their removal. The concentration of formaldehyde was also reduced by 67 percent over the catalyst.

The implication of this data is that the particulate material collected in this latter series of tests is of a different nature than that which was observed in the baseline tests (1-4). Since there is a very significant decrease in the hydrocarbon content of the exhaust stream, one would suspect that the increase in grams/mile of particulate matter must be due to inorganic material. This hypothesis is supported by the close correlation of 1 cfm and 4 cfm filter data in the tests with this catalytic reactor.

With the second catalytic device there was again better agreement between the 1 cfm system and the 4 cfm system than was observed without the catalytic device. There was also an increase in the mass of emissions (grams/mile) when the engine speed was increased from 1200 to 2250 rpm. A direct comparison of the two devices would not be appropriate because of the difference in engines.

A basis for the comparison of the Chevrolet engine at 2250 rpm without the catalytic device is available from Contract CPA-22-69-145. There was nearly a threefold increase in grams/mile of emissions with the catalytic device in place. In contrast, there was a decrease of the particle size in the cumulative mass distribution profile when the engine speed increased from 1200 to 2250 rpm. A comparison with the cumulative mass profile from the engine operating with a conventional muffler indicates that the equivalent mass of the particles is larger without the device. The effect of this device was again to (1) decrease the average particle size, (2) decrease the residual hydrocarbons and aldehydes, and (3) increase the mass of particles per mile.

X. FUTURE

Under the Clean Air Act Amendments of 1970, stringent regulation of hydrocarbons, carbon monoxide, and nitrogen oxide emissions from automotive exhaust systems is prescribed. Consequently, an intensive program is underway to develop devices and procedures to accomplish the required reduction of these emissions, and also to develop rapid and reliable measuring devices for monitoring compliance with the regulations.

While it is of major importance to the public health and welfare that these regulated emissions be substantially reduced, it is recognized that there are also other constituents of automotive exhaust gases which may adversely affect health and welfare, and further that the nature and quantity of these constituents may be substantially and perhaps adversely affected by the control devices or procedures which are proposed. Typical of the constituents which are being identified are polynuclear aromatic compounds (other than the oxides) and metallic compounds with hazard potential.

During the course of the work described in this report, procedures for quantitative sampling and for physical and chemical characterization have been developed and successfully applied to the characterization of exhaust particulates, aldehydes and other non-regulated emissions from internal combustion engines operating under a number of selected conditions and in several configurations. This program should be extended to provide information on the character and quantities of the non-regulated constituents in exhausts over a wider representation of operating conditions as well as a wider range of emissions control systems and of light-duty vehicle power plants.

In order to properly assess the performance of proposed emission control devices and technology, it is essential to have information concerning the potential hazard of the emissions from the controlled systems. Potentially hazardous constituents have already been identified in some of these emissions, and the quantities of these materials emitted by the proposed systems under a variety of operating conditions need to be determined in order that their true (quantitative) hazard potential can be judged. Concurrently, there is also a need for refinement of the techniques of identification and measurement both to provide more complete characterization of the constituents, and to identify other constituents which may be present.

To be properly effective, such information must be developed concurrent with the development of the control technology for the regulated emissions.

XI. REFERENCES

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2. "New Sampler for the Collection, Sizing, and Enumeration of Viable Airborne Particles," A. A. Andersen, J. Bacteriol. 76, 471 (1958).

3. "A Comparison of Automotive Particle Mass Emission Measurement Techniques," O. J. Manary, J. B. Moran, R. H. Herling, W. E. Karches, and J. Wagman, presented at Combustion Institute 1971 Technical Session, Ann Arbor, Mich., March 23-24, 1971.

4. "The Nature of Automotive Aerosols," J. B. Moran, O. J. Manary, R. J. Herling, W. E. Karches, and J. Wagman, presented at the 45th National Colloid Symposium, ACS Division of Colloid and Surface Chemistry, Atlanta, Georgia, June 21-23, 1971.

APPENDIX A

ATOMIC ABSORPTION METHODS FOR ENGINE PARTICULATES AND DEPOSITS

Method for Lead Determination

Following nitric acid digestion, the samples are washed into 50-ml volumetric flasks and diluted to mark. This normally puts the concentration of lead in the flasks between 20 and 200 μg Pb/ml. If the concentration is higher than 200 μg Pb/ml, redilute the sample. The samples are analyzed on an atomic absorption spectrophotometer (Perkin-Elmer Model 303) using a hollow cathode lamp with a lead cathode filament. Operating conditions are as follows: 10 milliamps tube current, light path slit opening - 4, ultraviolet light range, acetylene-air oxidizing flame, one-slot burner head, wavelength - 2170 angstroms. The sample solution is aspirated into the flame where lead atoms present absorb the light from the lead cathode filament. The amount of absorbed light is proportional to the concentration of lead. The samples are analyzed in conjunction with the following series of lead standards: 10, 20, 40, 60, 80, 100, 150, and 200 μg Pb/ml. The concentration of the standards is plotted versus their absorbance values giving a standard curve. With the absorbance values for the samples and the standard curve, we can determine the concentration of lead in the samples. The sensitivity for the lead determination in an air-acetylene flame is about 0.25 μg Pb/ml at 1 percent absorption. The detection limit is about 0.1 μg Pb/ml.

Determination of Lead and Other Metals in Fibergass Filters

The fiberglass filters cannot be digested completely with nitric acid. They are cooked with concentrated nitric acid for two hours to leach out the metals. The pulp is filtered and washed and the filtrate analyzed by atomic absorption for lead, and by emission spectroscopy for other metals.

Determination of Lithium and Potassium

Lithium and potassium were determined for some $LiNO_3/KNO_3$ catalysts and some fiberglass filters. This procedure consists of dissolving or leaching the sample and then analyzing by atomic absorption (similar to lead method).

MICROSCOPY

The responsibility of the Microscopy Laboratory is to apply light, transmission, and scanning electron microscopes in characterization of the automotive exhaust particulates relative to:

1. Color
2. Size
3. Shape, form
4. Fusion characteristics
    a. Melting point
    b. Sublimation
    c. Crystallinity
5. Electron diffraction
6. Solubility
7. Organic-inorganic composition
8. Elemental analysis of X-ray fluorescence while in the scanning electron microscope.

The work on the exhaust particle was divided into four parts. Submitted here are summary reports of what has been accomplished.

SCANNING ELECTRON MICROSCOPY AND X-RAY FLUORESCENCE ANALYSIS

A. Purpose

To characterize (SEM) and identify (X-ray spectrometer) the particulates in exhaust emission collected by the Andersen sampler or collected on the Millipore filter following the sampler.

B. Instrumentation

Cambridge Stereoscan Mark 2A
Ortec Non-dispersive X-ray Detector
Nuclear Data Analyzer
Varian Vacuum Evaporator
Kinney Vacuum Evaporator

C. Work Outline

1. Particle characterization (SEM) on plates of the Andersen sampler.
2. Particle identification (X-ray).
3. Single element X-ray scan.
4. X-ray spectra on impingement area of plates and spectra on final filter.

D. Techniques and Methods

1. Substrates for sample collection. Most satisfactory for photomicrography were micro cover glasses, while where X-ray analysis was to be done ultra pure carbon strips proved best. Silica interference from the micro cover slips, halogens in epoxy, and thermal instability in mylar film reduced the desirability for using these materials as substrates where X-ray analysis was to be done.

2. Storage and sample preparation. All samples were maintained in a dry atmosphere from collection to examination. Both the glass cover slip and the carbon strip substratum were attached to SEM sample stubs with conducting silver paint. Samples for SEM characterization were made conductive with a thin layer ($\sim$200 Å) of gold or gold-palladium evaporated onto under vacuum (5×10^{-4} Torr). Graphite carbon was sputtered on the samples used for X-ray diffraction.

3. Normal operation for the Stereoscan.

(a) Gun potential - 20 to 30 kV (depending on degrading of sample and resolution needed).

(b) Vacuum - ∿10^{-4} Torr maintained.

(c) Sample angle - 20°.

(d) Working distance - 11 mm

(e) Polaroid P/N Type 55 film with 100 sec exposure.

4. Normal operations for X-ray Spectrometer (warranted 215 ev FWHM resolution)

(a) Gun potential - 30 kV.

(b) 1024 channel - Series 2100 Nuclear Data Multichannel Analyzer.

(c) Collection time - 200 sec.

(d) Count rate - ∿600 c.p.s.

(e) Spectra recorded on Moseley 7035B X-Y Recorder.

(f) Single channel recording
Polaroid P/N Type 55 film
400 sec or 800 sec exposure depending on concentration.

E. Analysis

1. Particle characterization and photomicrographical documentation was done with the scanning electron microscope employing standard operational procedures.

2. Particle identification involved elemental analysis using the X-ray spectrometer on the scanning electron microscope. This included, for multiple particles, full spectrum elemental scan, and single element scan. Spot scans were carried out on single particles or in specific regions of particles.

APPLICATION OF LIGHT MICROSCOPY TO AUTO EXHAUST ANALYSIS

1. Low Power Photomacrography (15x)

This documentation is done with oblique reflected light showing the sample as received against a black background.

2. Polarized Light Photomicrography (400x) and X-ray Diffraction

The particles are scraped from the glass plate using a disecting knife and transferred to a clean microscope slide and covered with a clean cover slip. The slide is then placed on a hot plate (∿140°C) and a drop of Arochlor 5442 (also heated to ∿140°C) is applied at one edge of the cover slip. Capillarity draws the Arochlor across the preparation. The particles are dispersed by using the eraser end of a pencil to move the cover glass around a little. The excess Arochlor is removed with absorbent paper tissue. When the slide is removed from the hot plate, a permanent mount is obtained.

A like sample to that used for polarized light microscopy was impregnated into a small amount of rubber cement and worked into a ball and then mounted on the end of a 500μ diameter glass rod. Such samples were taken for an X-ray diffraction identification.

TRANSMISSION ELECTRON MICROSCOPY OF AUTO PARTICULATES

The purpose of this work of using the transmission electron microscope (TEM) was to characterize and photographically document those particles which are smaller than one micron and to obtain crystallographic analysis of them by means of electron diffraction.

The sampling for this work was done by attaching transmission electron microscope grids, which had been previously given a carbon reinforced collodion substrate, directly onto the Andersen sample collection plates and on the Millipore filter after the sampler. After the sampling, the grids were removed and stored in a desiccator to await analysis.

The TEM used was the Philips EM300 where standard instrumental operating conditions were employed including a 100 kV operating potential to give the best penetration of the electron dense particles.

The particles under consideration here were those ranging in size from 100 to 1000 Å. Photomicrographic documentation was carried out recording similarities and differences as these were observed.

POLAROGRAPHIC ANALYSIS

The analytical method for the determination of carbonyl compounds in automotive exhaust emissions employed polarographic techniques. A Princeton Applied Research Model 170 Electrochemistry System was used as the monitoring device. The derivative pulse polarographic mode yielded the best combination of resolution and sensitivity for the classification of carbonyl compounds. A dropping mercury electrode with a Princeton Model 172 Drop Timer was employed as the working electrode.

Hydrazine derivatives (hydrazones) were employed for the determination of the carbonyl compounds, since hydrazones are easier to reduce than the free compounds, thus eliminating many possible interferences.

An acetate buffer of approximately pH 4 (an equimolar mixture of acetic acid and sodium acetate, 0.1M in water) was used to control pH for hydrazone formation and also acted as supporting electrolyte. Hydrazine was added as a 2 percent aqueous solution. In this system formaldehyde gave a peak potential (half-wave potential) of -0.92v vs. a saturated calomel reference electrode. A platinum wire was employed as the auxiliary electrode.

With the above system, it is possible to distinguish between and simultaneously determine aromatic aldehydes, formaldehyde, higher aliphatic aldehydes, and aliphatic ketones as shown in Figure A.

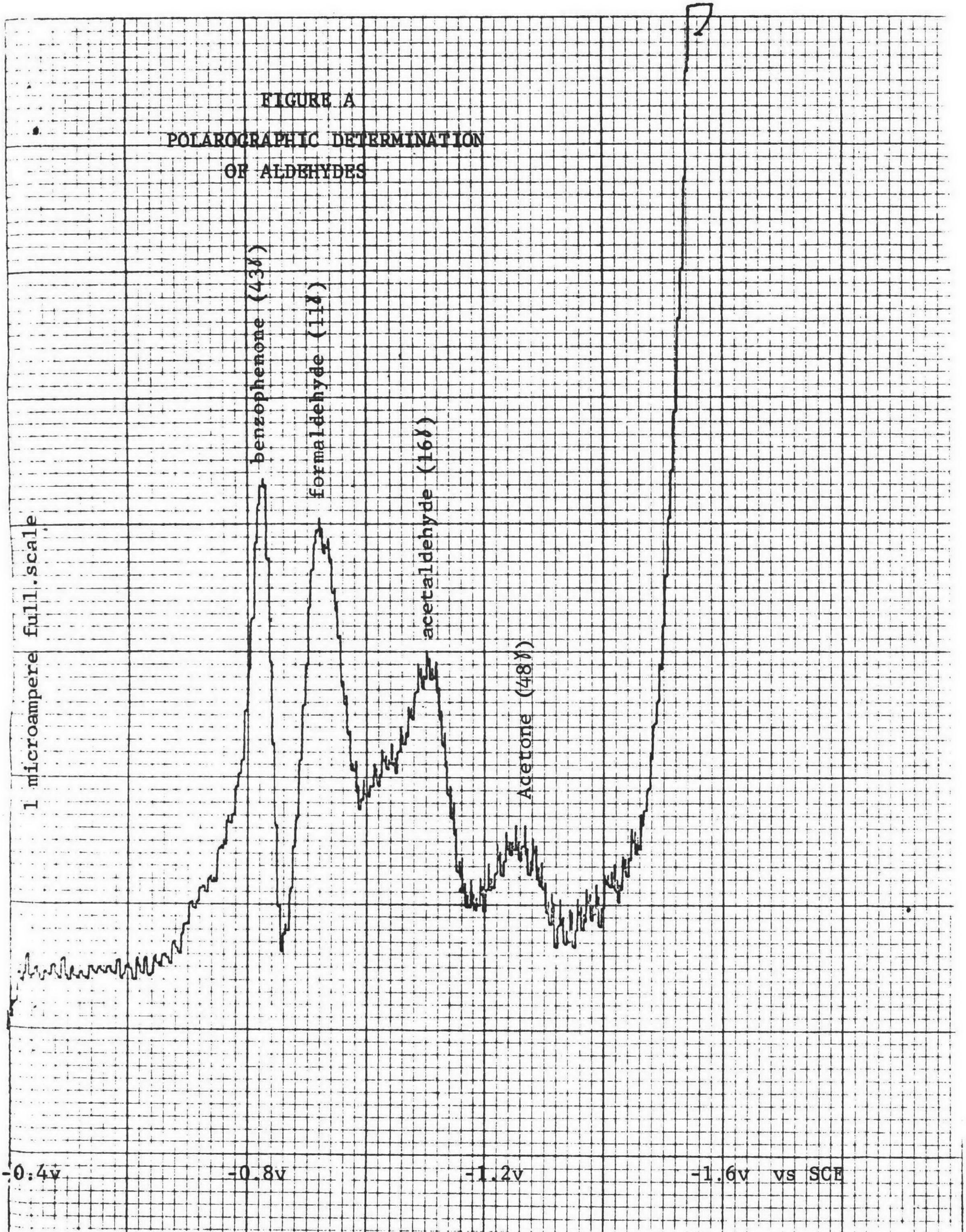


FIGURE A

POLAROGRAPHIC DETERMINATION OF ALDEHYDES

Since aromatic ketones, e.g. benzophenone, give polarographic response in pH 4 buffer without hydrazine, it is also possible to detect aromatic ketones. Lead and zinc could also be determined from the samples under these conditions.

Since formaldehyde was the main carbonyl component of the condensate samples, all results were calibrated against and reported as formaldehyde. The upper curve in Figure B shows an actual sample without hydrazine present and demonstrates the lack of interference in the carbonyl region. The lower curve shows the same sample after the addition of hydrazine. Figure C shows the same solution after the addition of a formaldehyde standard. These two figures clearly establish the presence of formaldehyde in the exhaust samples.

SPECTROSCOPIC DETERMINATION OF METALLIC IMPURITIES IN ORGANIC COMPOUNDS

1. Scope

This method provides for the determination of ten elements in the range of 0.00001 to 0.01% in organic compounds. Although the method specifically describes the analysis of organic materials, the same method can be applied to the analysis of many inorganic samples. Nor is the technique limited to the ten elements listed, but it may be extended to cover practically all of the metallic elements.

2. Principle

The organic matter is destroyed by wet ashing in sulfuric, nitric and perchloric acids. The resulting solution is taken to dryness and the residue is taken up in a spectroscopic buffer solution containing the internal reference element, palladium. A portion of the solution is dried on pure graphite electrodes. The electrodes thus prepared are excited in an a.c. arc discharge and the spectrum is photographed. The intensity ratios of selected lines are

FIGURE B
POLAROGRAPHIC DETERMINATION
OF ALDEHYDES

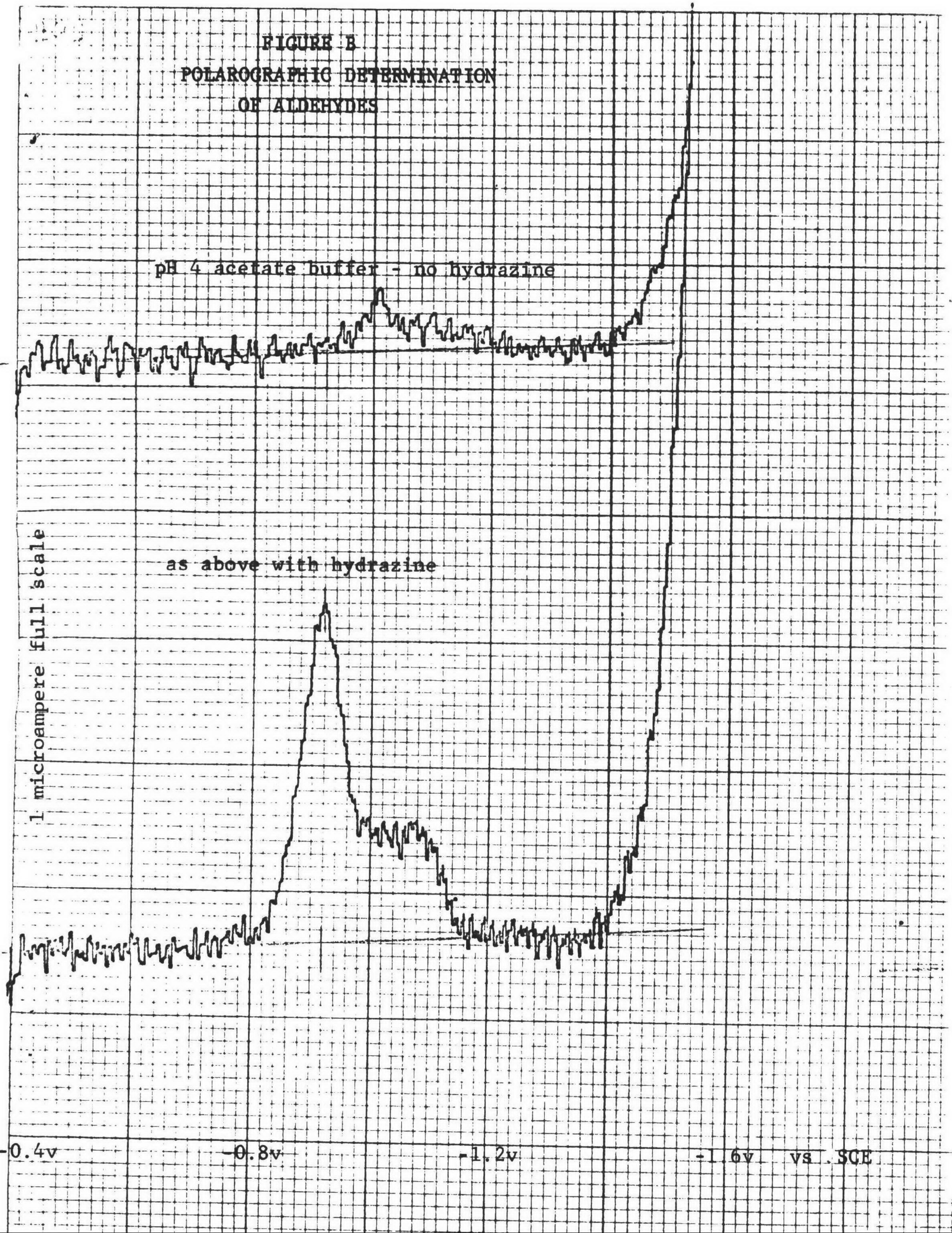
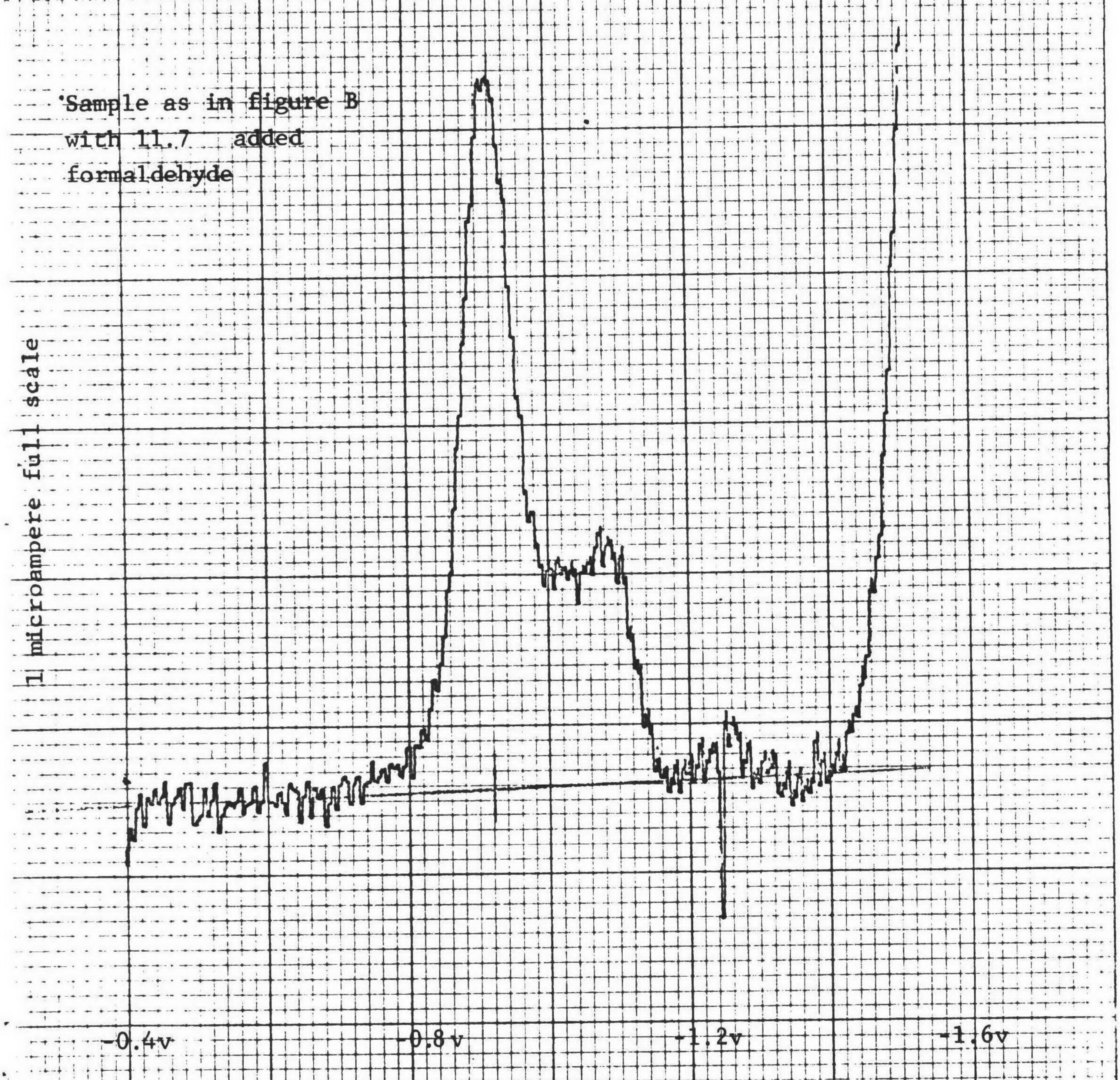


FIGURE C

POLAROGRAPHIC DETERMINATION
OF ALDEHYDES



determined photometrically and the concentration of each element is read from an analytical curve relating intensity ratio to concentration.

3. Apparatus

(a) Excitation. Excitation is obtained by the use of a 2400 volt a.c. arc discharge. Jarrel-Ash Custom Varisource, Jarrel-Ash Co., 26 Farwell St., Newtonville 60, Mass., or equivalent.

(b) Spectrograph. The instrument used is a Baird 3 meter grating spectrograph. Reciprocal dispersion is 5.55 A/mm in the first order.

(c) Developing equipment. Jarrel-Ash Company. Plates are developed in a thermostatically controlled developing machine, washed and dried over heat in a stream of air.

(d) Densitometer. Spectral lines are measured with a non-recording projection type densitometer. Densitometer Comparator, Baird Associates Inc., Cambridge, Mass., or equivalent.

(e) Calculating equipment. A calculating board is employed to covert densitometer readings to log intensity ratios. Jarrel-Ash Co.

(f) Wet ashing equipment. A micro Kjeldahl digestion rack is used for wet ashing the organic solvents.

4. Reagents and Materials

(a) Distilled nitric and perchloric acids. CAUTION! Perchloric acid is an intense oxidizing agent. Do not permit organic matter to be heated in perchloric acid unless in the presence of sulfuric or nitric acid.

(b) Sodium nitrate, reagent grade ($NaNO_3$).

(c) Palladium diamine nitrite, $Pd(NH_3)_2(NO_2)_2$.

(d) Water soluble salts of the elements Al, Ca, Cu, Fe, Mg, Mn, Ni, Pb, Sn, and Zn.

(e) Electrodes, high purity graphite, 1/4" diameter by 3/4" length. Ultra Carbon Corporation, Bay City, Michigan.

(f) Photographic plates, Eastman Spectrum Analysis No. 3.

(g) Kjeldahl flasks, 10 ml.

5. Calibration

(a) Dissolve 0.2182 gm of palladium diammine nitrite, $Pd(NH_3)_2(NO_2)_2$, in water, add 10 ml of concentrated reagent grade nitric acid, and dilute to volume with water in a 100 ml volumetric flask. This solution contains 1 mg Pd per ml.

(b) Prepare the following buffer solution. Dissolve 20 gm of sodium nitrate in water, add 5.0 ml of the palladium solution (5a), 7.5 ml of concentrated reagent grade nitric acid, and dilute to 100 ml. Multiples of these numbers can be used to provide larger amounts.

(c) Prepare a stock solution containing 0.01% (0.1 mg/ml) each of the elements Al, Ca, Cu, Fe, Mg, Mn, Ni, Pb, Sn, and Zn. Dilute two aliquots of this solution ten-fold and one hundred-fold to provide 0.001% and 0.0001% solutions.

(d) Make standard additions of the impurity elements to Kjeldahl flasks as shown in Table I.

(e) Add 0.5 ml of concentrated reagent grade sulfuric acid to the Kjeldahl flask and evaporate to dryness. Allow the flask to cool, add 1 ml of concentrated nitric acid and evaporate to dryness again. The residue is taken up in 5 ml of buffer solution, warming, if necessary, to put the salts into solution.

(f) Polish the ends of the 3/4" graphite electrodes on filter paper and place in a stainless steel drying tray. Place a drop of kerosene on the top of each electrode to seal the porosity and allow to dry. Prepare one pair of electrodes for each of the standard addition solutions by pipetting 0.03 ml of the solution onto the end of each electrode. Dry the electrodes slowly over micro burners in a gas drying oven and store in a desiccator until run.

(g) Excite the samples in water cooled electrode holders using the following conditions:

(1) Current, 4.0 amps, a.c. arc.
(2) Spectral region, 2150-3550 A.
(3) Slit width, 50μ.
(4) Electrode gap, 2 mm.
(5) Pre-burn period, 10 seconds.
(6) Exposure period, 90 seconds.

(h) Calibrate the emulsion by use of a stepped filter or by other recommended methods described in the "Recommended Practice of Photographic Photometry in Spectrochemical Analysis" A.S.T.M. Designation: E116, Methods for Emission Spectrochemical Analysis, (1964).

(i) Process the emulsion according to the following conditions:

(1) Developer (D19, 20.5°C), 3 1/2 minutes.
(2) Stop bath (SB-4), 1 minute.
(3) Fixing bath (Kodak Rapid Fixer), 2 minutes.
(4) Washing, 3 minutes.
(5) Drying, in a stream of warm air.

(j) Select the analytical line pairs from Table II. Measure the relative transmittances of the internal standard line and each analytical line with a densitometer. Convert the transmittance measurements of the analytical line pairs to intensity ratios by the use of an emulsion calibration curve and a calculating board.

(k) Construct analytical curves by plotting concentration as a function of intensity ratio on log-log graph paper. For best results, plot the average of at least four determinations recorded on two plates.

6. Procedure

(a) Weigh a 0.4 gm or available sample directly into a Kjeldahl flask. A 0.4 gm sample size is seldom ever used because the amount of material available is much less than this. A fraction of a milligram may at times be the entire sample. Sulfuric acid is not used in the wet ash procedure because the sample usually contains a large amount of lead which would form the insoluble sulfate. Wet oxidation is carried out with nitric and perchloric acid only. Extreme caution should be exercised in the use of this technique. Add concentrated nitric acid dropwise, a few tenths ml at a time, to the hot mixture to aid in oxidation. A few drops of concentrated perchloric acid may be added to the hot solution after most of the free carbon has been destroyed, to hasten complete oxidation. When the solution becomes water clear, evaporate to dryness. Allow the tube to cool, add 0.5 ml of nitric acid and evaporate the solution to dryness. Repeat the addition of 0.5 ml of nitric acid and evaporate the solution to dryness again. The inorganic residue is dissolved in dilute nitric acid and the volume is adjusted to a known concentration, usually 10 mg/ml. If the original sample size is below 30 mg, a less concentrated solution is usually made up. Aliquots of this solution are taken to dryness and then the buffer solution (5b) is added in an amount to give a dilution factor of 100x. One sample is analyzed by the direct reader while another one is examined photographically. A sample may have to be run at factors larger than 100x in order to get the concentration for some elements to fall within the range of the analytical curves. By varying the sample to buffer ratio any number of concentration or dilution factors can be achieved. Carry through a blank of the acids used in the same manner as the sample.

(b) Proceed as in 5(f), (g), (h), (i), and (j) of the calibration procedure. Duplicate spectra are recorded for each sample.

7. Calculations

Convert the intensity ratios to concentration by use of the analytical curves.

8. Precision and Accuracy

Representative precision and accuracy of the method are given in Table III. Each of the twelve samples A_1, A_2, A_3, B_1, B_2, B_3, C_1, C_2, C_3, D_1, D_2, D_3, was analyzed by means of duplicate excitation.

9. Literature References

(a) Hess, T. M., Owens, J. S. and Reinhardt, L. G., - Ind. Eng. Chem. Anal. Ed., 11, 646 (1939).

(b) American Society for Testing Materials, 1916 Race St., Philadelphia 3, Pa., "Recommended Practice of Photographic Photometry in Spectrochemical Analysis," ASTM Designation E116 (1964).

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The analytical procedures given herein have been adapted from literature sources or developed upon the basis of experimental data which are believed to be reliable. In the hands of a qualified analyst they are expected to yield results of sufficient accuracy for their intended purposes. However, The Dow Chemical Company makes no representation or warranty whatsoever concerning the procedures or results to be obtained and assumes no liability in connection with their use. Users are cautioned to confirm the suitability of the methods by appropriate tests.

TABLE I

Concentration	ml. of standard addition impurity solution		
Blank			
0.00001%	0.5 ml.	0.0001%	solution
0.000025%	1.25 ml.	"	"
0.00005%	0.25 ml.	0.001%	"
0.0001%	0.5 ml.	"	"
0.00025%	1.25 ml.	"	"
0.0005%	2.5 ml.	"	"
0.00075%	0.375 ml.	0.01%	"
0.001%	0.5 ml.	"	"
0.0025%	1.25 ml.	"	"
0.005%	2.5 ml.	"	"
0.01 %	5.0	"	"

TABLE II

Analytical Line Pairs

Element	Analytical Line A	Internal Standard Line A	Concentration Range %
Al	3092.71	3027.91 Pd	0.000025-0.0010
Ca	3179.33	"	0.00025-0.010
Cu	3273.96	"	0.00001-0.00025
Fe	3021.07	"	0.0001-0.010
Fe	3020.64	"	0.000025-0.0050
Mg	2802.69	"	0.000025-0.0010
Mg	2779.83	"	0.0005-0.010
Mn	2933.06	"	0.0005-0.010
Mn	2794.82	"	0.00001-0.0010
Ni	3414.77	"	0.000025-0.0010
Ni	3037.94	"	0.0005-0.010
Pb	2873.32	"	0.0010-0.010
Pb	2833.07	"	0.00005-0.0050
Sn	3175.02	"	0.00005-0.0050
Sn	2863.33	"	0.00075-0.010
Zn	3345.02	Background	0.0001-0.010

TABLE III

Representative Precision and Accuracy

Sample	% Al	% Ca	% Cu	% Fe	% Mg	% Mn	% Ni	% Pb	% Sn	%Zn
A_1	0.000044	0.00043	0.000048	0.00043	0.00049	0.00046	0.00047	0.00056	0.00052	0.00040
	0.000052	0.00050	0.000054	0.00055	0.00052	0.00057	0.00055	0.00059	0.00059	0.00045
A_2	0.000045	0.00043	0.000046	0.00044	0.00047	0.00051	0.00045	0.00050	0.00053	0.00054
	0.000052	0.00037	0.000047	0.00043	0.00050	0.00050	0.00051	0.00051	0.00050	0.00040
A_3	0.00004	0.00043	0.000050	0.00046	0.00053	0.00049	0.00047	0.00052	0.00050	0.00052
	0.000052	0.00050	0.000048	0.00046	0.00049	0.00046	0.00048	0.00053	0.00046	0.00042
B_1	0.00012	0.00105	0.00012	0.0010	0.00105	0.0010	0.0010	0.00105	0.0011	0.00094
	0.000097	0.00093	0.00010	0.00094	0.00095	0.0012	0.00096	0.00098	0.00094	0.0012
B_2	0.000097	0.00096	0.000099	0.00090	0.00092	0.0011	0.0010	0.0010	0.00105	0.00125
	0.000094	0.00068	0.000095	0.00105	0.00091	0.00066	0.00105	0.00105	0.00105	0.0010
B_3	0.000082	0.00085	0.000095	0.0010	0.0010	0.00086	0.0010	0.0010	0.00099	0.00096
	0.00011	0.00074	0.000096	0.0010	0.00090	0.00092	0.00105	0.0010	0.0010	0.00115
C_1	0.00028	0.0023	0.00023	0.0025	0.0023	0.00265	0.00245	0.00235	0.00255	0.0014
	0.00030	0.0018	0.00028	0.0030	0.0023	0.00195	0.00265	0.00255	0.0027	0.00215
C_2	0.00020	0.00225	0.00023	0.0023	0.0023	0.00265	0.0023	0.00245	0.00215	0.00225
	0.00023	0.00265	0.00025	0.00235	0.0024	0.00275	0.00245	0.0026	0.0023	0.0030
C_3	0 00024	0.0025	0.00026	0.00275	0.0023	0.00245	0.0026	0.0025	0.0025	0.0030
	0.00028	0.00275	0.00028	0.00285	0 0024	0.0025	0.00255	0.00245	0.00265	0.0020
D_1	0.00074	0.0070	--	0.0065	0.0057	0.0059	0.0065	0.0056	0.0064	0.0058
	0.00064	0.0064	--	0.0063	0.0051	0.0058	0.0058	0.0045	0.0059	0.0050
D_2	0 00059	0.0049	--	0.0057	0.0048	0.0045	0.0056	0.0045	0.0053	0.0050
	0 00063	0.0057	--	0.0059	0.0047	0.0048	0.0057	0.0048	0.0057	0.0060
D_3	0.00059	0.0048	--	0.0050	0.0045	0.0047	0.0050	0.0043	0.0054	0.0037
	0.00053	0.0060	--	0.0055	0.0055	0.0054	0.0055	0.0049	0.0049	0.0041

A_1, A_2, and A_3 contain 0.00005% of Al and Cu, and 0.0005% of each other element. B_1, B_2, and B_3 contain 0.0001% of Al and Cu, and 0.0010% of each other element. C_1, C_2, and C_3 contain 0.00025% of Al and Cu and 0.0025% of each other element. D_1, D_2 and D_3 contain 0.0005% of Al and Cu and 0.0050% of each other element.

APPENDIX B

TABULATION OF CANDIDATE TRAPPING MEDIUM BY INCREASING MELTING POINT

Temperature		
°C	°F	
-14	7	7% KNO_3 - 93% HCN
1	34	YF_3
17	63	MOF_6
30	77	Ga
36	97	NH_4CN
57	135	9% KCl - 91% $SbCl_3$
70	158	2% KBr - 98% $SbCl_3$
73	163	$SbCl_3$
77	171	$GaCl_3$
86	187	24% $LiNO_3$ - 5% NH_4Cl - 71% NH_4NO_3
87	188	$SbBr_3$
89	192	13% KBr - 87% $AlBr_3$
90	194	8% NaBr - 92% $AlBr_3$
92	198	41% KNH_2 - 59% $NaNH_2$
97	207	0.7% $MgBr_2$ - 99.3% $AlBr_3$
98	208	$AlBr_3$
100	212	56% NH_4CNS - 44% $(NH_2)_2CS_3$
113	235	9% NaCl - 8% $NaNO_3$ - 83% NH_4NO_3
		18% $NaNO_3$ - 5% NH_4Cl - 77% NH_4NO_3
114	237	17% LiCl - 83% $AlCl_3$
118	244	20% $NaNO_3$ - 2% Na_2SO_4 - 78% NH_4NO_3
119	246	23% $NaNO_3$ - 71% NH_4NO_3 - 6% $(NH_4)_2SO_4$
121	250	21% $NaNO_3$ - 79% NH_4NO_3
124	255	74% KCNS - 26% NaCNS
		28% NaCl - 72% $AlCl_3$
		8% NaCl - 92% NH_4NO_3
131	268	27% KNO_3 - 73% $AgNO_3$
135	275	23% $AlCl_3$ - 77% $SnCl_3$
		11% KCl - 1% NH_4Cl - 88% NH_4NO_3
		13% KNO_3 - 9% NH_4Cl - 78% NH_4NO_3

Temperature		
°C	°F	
136	277	26% KCl - 74% CaCl
137	279	12% KCl - 88% NH_4NO_3
		2% NaCl - 89% $NaNO_3$ - 9% NH_4Cl
139	282	70% KNO_3 - 30% $LiNO_3$
142	288	$(NH_2)_2CS$
		9% KBr - 91% $AgNO_3$
143	289	10% KCl - 4% KNO_3 - 86% NH_4NO_3
148	298	36% RbCl - 64% CaCl
150	302	NH_4CNS
157	315	14% KNO_3 - 86% NH_4NO_3
158	316	23% KCl - 77% $AlCl_3$
159	318	5% KCl - 95% $AgNO_3$
160	320	17% KNO_3 - 81% NH_4NO_3 - 2% $(NH_4)_2SO_4$
162	324	7% $NaNO_3$ - 93% $TlNO_3$
165	329	50% KCNS - 50% RbCNS
170	338	NH_4NO_3
172	342	33% Cu_2Cl_2 - 67% $SnCl_2$
173	343	KCNS
175	347	80% KHF_2 - 20% $NaHF_2$
176	349	12% K_2SO_4 - 88% NH_4NO_3
178	352	76% $SnCl_2$ - 24% TeCl
180	356	20% KCl - 80% $SnCl_2$
		66% $SnCl_2$ - 34% $ZnCl_2$
182	360	28% KBr - 72% CuBr
		14% KNO_3 - 86% $TlNO_3$
183	361	13% NaCl - 87% $SnCl_2$
		95% $Na_2H_2S_2O_8$ - 5% $Na_2S_2O_7$
185	365	58% KOH - 42% NaOH
186	367	$NaH_2S_2O_8$
		11% $MgCl_2$ - 89% $AlCl_3$
		38% KNO_3 - 19% $NaNO_3$ - 43% $Pb(NO_3)_2$
190	374	$AlCl_3$

Temperature		
°C	°F	
195	383	RbCNS
		12% $CaBr_2$ - 88% AlBr
		30% KCl - 9% NaCl - 61% $ZnCl_2$
201	394	88% $K_2H_2S_2O_8$ - 12% $K_2S_2O_7$
206	403	$NaNH_2$
		$TlNO_3$
		49% $LiNO_3$ - 51% $NaNO_3$
207	405	41% KNO_3 - 59% $Pb(NO_3)_2$
208	406	53% KNO_3 - 37% $NaNO_3$ - 10% $Sr(NO_3)_2$
210	410	$KHSO_4$
211	412	68% KNO_3 - 32% $Ca(NO_3)_2$
212	414	$AgNO_3$
214	417	$K_2H_2S_2O_8$
		27% $FeCl_3$ - 73% $ZnCl_2$
215	419	9% KBr - 8% NaBr - 83% $ZnBr_2$
216	421	33% CsCl - 67% CuCl
		96% $NaNO_2$ - 4% $Ba(NO_3)_2$
218	424	11% $NaNO_3$ - 89% $AgNO_3$
219	426	40% KNO_2 - 60% $NaNO_2$
221	430	45% $NaNO_2$ - 55% $NaNO_3$
227	440	KHF_2
228	442	3% KBr - 97% $HgBr_2$
		29% RbBr - 71% AgBr
230	446	$AgClO_3$
		5% $MnCl_2$ - 95% $SnCl_2$
232	450	27% KCl - 73% $ZnCl_2$
233	451	10% $CdCl_2$ - 90% $SnCl_2$
236	457	$HgBr_2$
		$K_2Cr_2O_7$
237	458	59% $NaNO_3$ - 41% $Ca(NO_3)_2$
241	466	50% NaOH - 50% RbOH
242	468	18% Cu_2Cl_2 - 82% $ZnCl_2$
245	473	0.5% $MgCl_2$ - 99.5% $SnCl_2$
246	475	$SnCl_2$
248	478	$NaClO_3$

Temperature		
°C	°F	
250	482	2% Li_2CO_3 - 98% $LiNO_3$
		16% $NaCl$ - 84% $ZnCl_2$
251	484	4% $KClO_3$ - 96% $NaClO_3$
		8% $NaClO_3$ - 92% $AgClO_3$
		92% $NaClO_3$ - 8% $BaClO_3$
252	486	1% KCl - 99% $NaClO_3$
		1% KNO_3 - 99% $NaClO_3$
		97% $LiNO_3$ - 3% Li_2SO_4
		4% $NaBr$ - 96% $NaClO_3$
		96% $NaClO_3$ - 4% Na_2CrO_4
		98% $NaClO_3$ - 2% $NaNO_2$
253	487	1% $NaCl$ - 99% $NaClO_3$
		98% $NaClO_3$ - 2% Na_2CO_3
		36% $RbCl$ - 64% $AgCl$
254	489	0.2% $CsClO_3$ - 99.8% $NaClO_3$
		99% $NaClO_3$ - 1% NaF
255	491	$LiNO_3$
258	496	31% $CsCl$ - 69% $AgCl$
		67% KNO_3 - 33% $Sr(NO_3)_2$
		6% KCl - 5% $NaCl$ - 89% $ZnCl_2$
260	500	39% $NaBr$ - 61% $NaOH$
261	502	$ZnCl_3$
262	504	$ZnCl_2$
		1% $CdCl_2$ - 99% $ZnCl_2$
		1% $RbCl$ - 99% $HgCl_2$
263	505	1% $CsCl$ - 99% $HgCl_2$
264	507	0.3% KCl - 99.7% $HgCl_2$
		0.2% $NaCl$ - 99.8% $HgCl_2$
265	509	21% $LiCl$ - 79% NH_4Cl
266	511	14% K_2CO_3 - 13% Na_2CO_3 - 73% $NaOH$
268	514	57% $NaNO_3$ - 43% $Pb(NO_3)_2$
271	520	$NaNO_2$
		0.7% $MgCl_2$ - 99.3% $ZnCl_2$

Temperature		
°C	°F	
275	527	$HgCl_2$
		82% LiBr - 18% LiOH
		1% $MnCl_2$ - 99% $ZnCl_2$
277	531	62% KCN - 38% $Cu(CN)_2$
278	532	6% KCl - 94% $ZnCl_2$
280	536	12% Na_2CO_3 - 88% NaOH
282	540	$FeCl_3$
		9% KCN - 91% KCNO
285	545	21% KBr - 39% CdBr-NaBr - 30% $FeCl_3$
288	550	31% KBr - 14% NaBr - 55% $CdBr_2$
290	554	34% KBr - 66% AgBr
		51% LiCl - 49% LiOH
291	556	49% KCN - 51% AgCN
295	563	4% K_2CrO_4 - 96% KNO_3
297	567	KNO_2
		86% $NaNO_3$ - 14% $Ba(NO_3)_2$
299	570	14% KNO_3 - 70% $LiNO_3$ - 16% $Ba(NO_3)_2$
300	572	RbOH
		0.4% $BaCl_2$ - 99.6% $SbCl_3$
		53% KBr - 47% KOH
		0.3% LiCl - 99.7% SbCl
		92% $NaNO_3$ - 8% Na_2SO_4
304	579	42% KBr - 58% $CdBr_2$
		5% NaCl - 95% $NaNO_3$
		4% Na_2CO_3 - 96% $NaNO_3$
306	583	43% KCl - 57% AgCl
		50% KOH - 50% RbOH
307	584	4% NaBr - 96% $NaNO_2$
308	586	$NaNO_3$
312	594	76% KNO_3 - 24% $Ba(NO_3)_2$
		30% LiCl - 70% RbCl
316	601	17% NaCl - 83% CuCl
318	604	NaOH
		32% LiCl - 2% NaCl - 66% RbCl

Temperature		
°C	°F	
320	608	AgCN
		17% KNO_2 - 83% KNO_3
		32% LiCl - 2% NaCl - 66% CsCl
323	613	$BaClO_3$
		NaCNS
326	619	5% K_2CO_3 - 95% KNO_3
329	624	KNH_2
332	628	97% CsCl - 3% LiCl
		6% KCl - 94% KNO_3
		95% KNO_3 - 5% K_2SO_4
334	633	KNO_3
		55% KBr - 45% $MgBr_2$
335	637	9% NaCl - 91% NO_2
342	648	10% LiCl - 90% TlCl
343	649	10% $BaCl_2$ - 90% $ZnBr_2$
345	653	HgBr
		17% NaCN - 83% $Cu_2(CN)_2$
348	658	48% KBr - 52% LiBr
350	662	NH_4Cl
351	664	46% KCl - 5% KF - 49% LiCl
352	666	55% KCl - 45% LiCl
354	669	10% $BaBr_2$ - 90% $ZnBr_2$
357	675	$Pb(NO_3)_2$
360	680	29% NaCl - 71% NaOH
361	682	12% $MgCl_2$ - 88% TlCl
362	684	72% KCl - 19% LiCl - 9% NaCl
363	685	51% LiCl - 49% NaCl
364	687	56% KCl - 44% LiCl
366	691	9% KCl - 91% $K_2Cr_2O_7$
367	693	31% NaBr - 69% $CdBr_2$
368	694	$KClO_3$
374	705	31% KCl - 13% NaCl - 56% $CdCl_2$
		34% KCl - 5% KF - 50% LiCl - 11% NaCl

Temperature		
°C	°F	
380	716	KOH
383	721	17% KCl - 83% $CdCl_2$
385	725	76% $K_2Cr_2O_7$ - 24% $K_2W_2O_7$
		53% KCl - 12% $BaCl_2$ - 1% CaF_2 - 34% $MgCl_2$
390	734	2% CsCl - 98% TlCl
392	738	21% NaCl - 79% $CdCl_2$
394	741	$ZnBr_2$
396	745	11% KCl - 9% NaCl - 80% $MgCl_2$
		15% KCl - 26% NaCl - 16% $MgCl_2$ - 43% $ZnCl_2$
397	746	17% KCl - 23% NaCl - 60% $MnCl_2$
400	752	11% $CaCl_2$ - 89% CuCl
401	754	$Na_2S_2O_7$
406	763	21% KCl - 79% $PbCl_2$
407	765	22% RbCl - 78% $PbCl_2$
		58% KCl - 1% NaF - 1% CaF_2 - 18% $MgCl_2$ - 22% $MnCl_2$
408	766	10% LiCl - 90% CuCl
		1% $MgCl_2$ - 99% CuCl
409	768	18% KCl - 24% NaCl - 58% $MgCl_2$
410	770	13% $CdCl_2$ - 87% Cu_2Cl_2
		11% LiCl - 89% $PbCl_2$
		8% NaCl - 92% $PbCl_2$
		17% KCl - 22% NaCl - 7% $BaCl_2$ - 54% $MgCl_2$
412	774	4% NaCl - 96% TlCl
414	777	$K_2S_2O_7$
416	781	8% $SrCl_2$ - 92% TlCl
419	786	3% $CaCl_2$ - 97% TlCl
		56% KCl - 6% $BaCl_2$ - 1% CaF_2 - 37% $MgCl_2$
422	792	CuCl
		57% KCl - 3% $BaCl_2$ - 1% CaF_2 - 39% $MgCl_2$
		41% KCl - 14% NaCl - 3% $BaCl_2$ - 1% $CaCl_2$ - 41% $MgCl_2$
424	795	Cu_2Cl_2
		47% NaCN - 53% AgCN

Temperature		
°C	°F	
425	797	32% NaCl - 68% $MnCl_2$
426	799	62% KCl - 38% $MgCl_2$
428	802	52% KCl - 48% $MnCl_2$
430	806	TlCl
		1% $BaCl_2$ - 99% TlCl
		41% KCl - 59% KOH
		21% LiF - 79% LiOH
		44% NaCl - 56% $MgCl_2$
431	808	45% NaBr - 55% $MgBr_2$
432	810	51% KCl - 8% NaCl - 1% $CaCl_2$ - 40% $MgCl_2$
433	811	45% KCl - 12% NaCl - 5% $BaCl_2$ - 1% CaF_2 - 35% $MgCl_2$ - 2% MgO
434	813	AgBr
		48% KCl - 6% NaCl - 14% $BaCl_2$ - 32% $MgCl_2$
437	819	45% $LiNO_3$ - 55% $Ba(NO_3)_2$
		59% KCl - 5% CaF_2 - 36% $MgCl_2$
440	824	$BaCl_2$
		38% KCl - 15% $BaCl_2$ - 47% $MgCl_2$
441	826	62% KCl - 38% $MgCl_2$
446	835	LiI
448	838	43% NaCl - 3% CaF_2 - 54% MgF_2
450	842	LiOH
		45% $BaCl_2$ - 55% $CdCl_2$
		15% $CaCl_2$ - 85% AgCl
452	846	8% $MgCl_2$ - 92% AgCl
		53% KF - 25% LiF - 12% NaF - 7% BaF_2 - 1% CaF_2 - 2% MgF_2
453	847	97% LiBr - 3% LiF
		42% LiBr - 58% $SrBr_2$
		54% KCl - 13% $BaCl_2$ - 33% $MgCl_2$
454	849	58% KCl - 4% NaCl - 3% $CaCl_2$ - 35% $MgCl_2$
455	851	AgCl
		75% KF - 16% LiF - 9% NaF

Temperature		
°C	°F	
457	855	55% KCl - 4% NaCl - 3% $BaCl_2$ - 4% $CaCl_2$ - 34% $MgCl_2$
458	856	59% KF - 28% LiF - 13% NaF
		25% KCl - 4% NaCl - 3% CaF_2 - 68% $MgCl_2$
459	858	7% $MgCl_2$ - 93% $PbCl_2$
460	860	10% KCl - 90% KNO_2
		38% NaCl - 5% $BaCl_2$ - 57% $MgCl_2$
466	871	50% KCl - 12% $BaCl_2$ - 38% $MgCl_2$
		35% NaCl - 4% $BaCl_2$ - 9% CaF_2 - 52% $MgCl_2$
467	873	8% $CaCl_2$ - 92% $PbCl_2$
468	874	9% LiCl - 91% AgCl
472	882	9% KCl - 25% NaCl - 4% $BaCl_2$ - 62% $MgCl_2$
473	883	$Cu(CN)_2$
		23% LiCl - 77% $SrCl_2$
		9% KCl - 26% NaCl - 65% $MgCl_2$
		29% KCl - 2% $BaCl_2$ - 2% CaF_2 - 67% $MgCl_2$
		38% KCl - 3% NaCl - 3% $BaCl_2$ - 1% $CaCl_2$ - 55% $MgCl_2$
475	887	$Cu_2(CN)_2$
		90% $Na_2B_4O_7$ - 10% $Ca_3(PO_4)_2$
482	900	68% KF - 32% LiF
484	903	47% LiBr - 53% $BaBr_2$
485	905	87% LiCl - 13% LiF
486	907	21% NaBr - 79% $SrBr_2$
487	909	69% KCN - 31% $ZN(CN)_2$
488	910	6% KCl - 32% $BaCl_2$ - 58% $CaCl_2$ - 4% CaF_2
		37% KCl - 12% $BaCl_2$ - 4% CaF_2 - 47% $MgCl_2$
		8% KBr - 11% KCl - 81% KI
490	914	$BeBr_2$
		5% KCl - 95% KI
		52% Li_2WO_4 - 48% Na_2WO_4
		12% NaCl - 88% $SrBr_2$
		40% KCl - 40% Na_2CO_3 - 20% NaOH
		10% KF - 64% LiCl - 26% NaCl
491	916	6% KCl - 31% $BaCl_2$ - 59% $CaCl_2$ - 4% CaF_2
492	918	79% $K2CO_3$ - 21% $LiCO_3$
493	919	85% CoCl - 15% NaCl

Temperature		
°C	°F	
495	923	81% Na_2MoO_4 - 19% MoO_3
496	925	7% $KAsO_3$ - 93% $NaAsO_3$
		38% LiCl - 62% $CaCl_2$
499	930	61% $SrCl_2$ - 39% $MnCl_2$
501	934	$PbCl_2$
		25% NaCl - 5_1 $BaCl_2$ - 65% $CaCl_2$ - 5% CaF_2
502	936	47% KCN - 53% NaCN
		81% KI - 19% NaCl
		16% KBr - 5% KCl - 79% KI
		4% KCl - 6% NaCl - 90% $MnCl_2$
503	937	37% $SrCl_2$ - 63% $CdCl_2$
		33% KCl - 14% KI - 53% NaI
504	939	CuBr
		49% $BaCl_2$ - 51% $MnCl_2$
		5% KCl - 28% NaCl - 67% $CaCl_2$
		23% KCl - 22% NaCl - 55% SrCl
505	941	33% NaCl - 67% $CaCl_2$
		48% Na_2S - 52% Cu_2S
		9% KCl - 5% NaCl - 71% KF - 15% LiF
508	946	32% LiF - 68% NaF
510	950	27% LiCl - 73% $BaCl_2$
512	954	16% KCl - 84% KI
		52% LiBr - 48% $MgBr_2$
513	955	$(NH_4)_2SO_4$
		14% KCl - 64% KI - 22% NaCl
514	957	26% NaBr - 74% $CaBr_2$
		10% KBr - 18% KCl 0 72% NaI
		30% KCl - 19% KI - 4% NaBr - 47% NaI
		26% KCl - 24% KI - 8% NaBr - 42% NaI
515	960	2% KCl - 81% KI - 17% NaCl
		69% KI - 19% NaCl - 12% NaI
516	961	6% KBr - 11% KCl - 32% KI - 8% NaCl - 43% NaI
517	962	4% KCl 0 27% NaCl - 69% $CaCl_2$
521	970	23% NaCl - 5% $BaCl_2$ - 68% $CaCl_2$ - 4% CaF_2

Temperature		
°C	°F	
522	972	89% LiBr - 11% LiCl
		3% CaF_2 - 36% $MgCl_2$ - 61% $SrCl_2$
		20% K_2CrO_4 - 4% KF - 76% NaI
523	974	56% KBr - 8% NaBr - 36% NaI
524	976	5% KCl - 57% $BaCl_2$ - 38% $CaCl_2$
		18% KCl - 82% NaI
		81% KI - 19% NaCl
		6% KCl - 34% KI - 9% NaCl - 51% NaI
525	977	77% LiBr - 23% NaBr
528	982	72% KCl - 19% LiCl - 9% NaCl
		53% KCl - 5% KF - 12% NaCl - 30% $CaCl_2$
		47% KCl - 20% LiCl - 2% LiF - 31% NaCl (Dow 45-B)
		47% KCl - 23% LiCl - 26% NaCl - 4% NaF (Dow 45-C)
		61% KCl - 10% LiCl - 3% $BaCl_2$ - 24% $CaCl_2$ - 2% CaF_2
530	986	40% Li_2CO_3 - 60% $LiSO_4$
		9% KBr - 18% KCl - 8% KI - 65% NaI
531	988	40% KCl - 24% LiCl - 31% NaCl - 5% CaF_2
		31% KCl - 7% $BaCl_2$ - 24% $LiCl_3$ - 31% NaCl - 7% $CaCl_2$
		40% KCl - 18% LiCl - 3% LiF - 32% NaCl - 7% $CaCl_2$
		40% KCl - 24% LiCl - 24% NaCl - 5% NaF - 7% $CaCl_2$
532	990	66% KI - 25% NaBr - 9% NaCl
533	992	37% KBr - 5% NaCl - 58% NaI
534	993	32% KBr - 68% $SrBr_2$
535	997	61% K_2SO_4 - 39% $CoSO_4$
		28% K_2SO_4 - 72% Li_2SO_4
		37% KBr - 6% KCl - 57% NaI

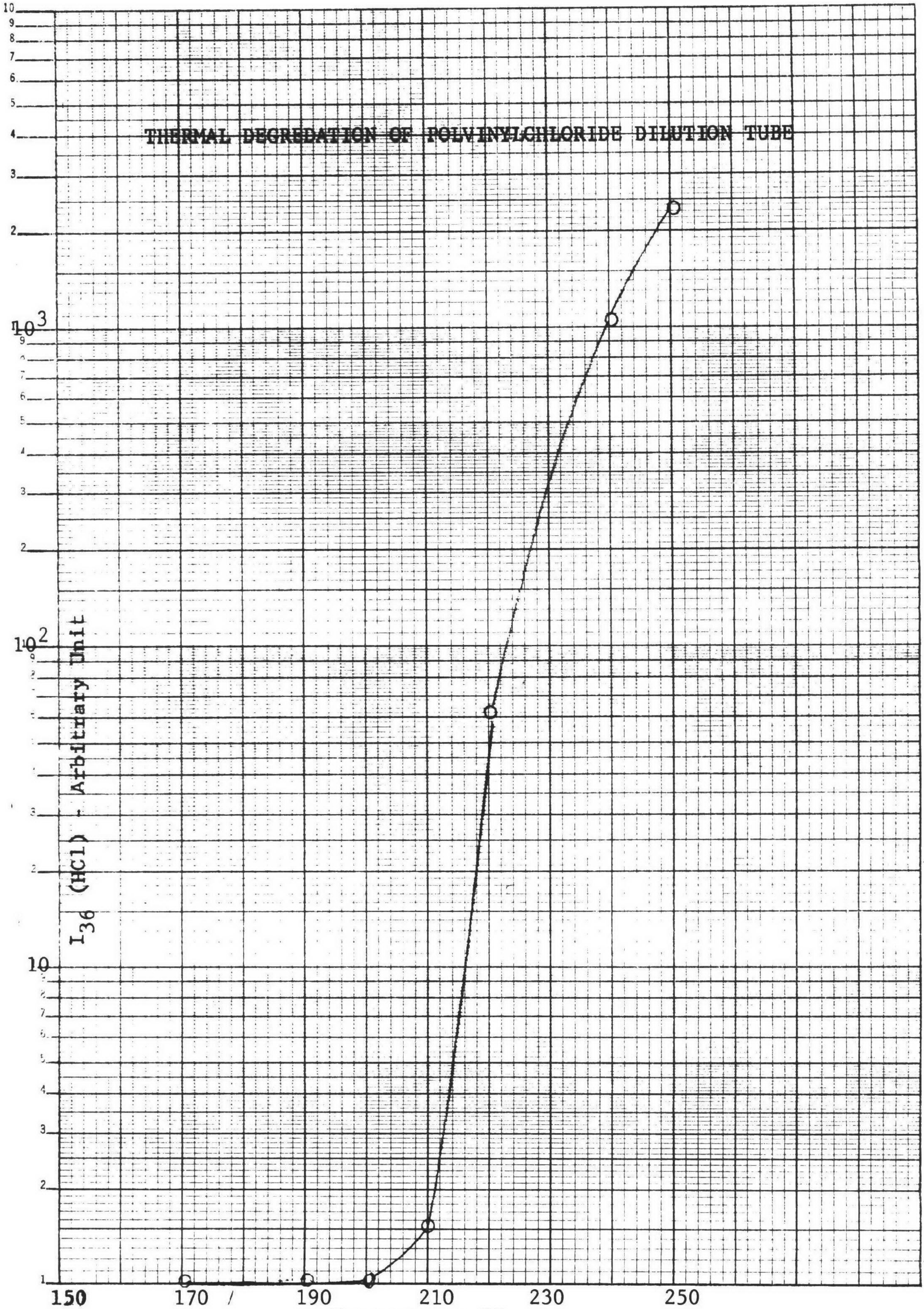
APPENDIX C

THERMAL DECOMPOSITION OF PVC DILUTION TUBE

Tests were run to determine if thermal decomposition of the polyvinyl chloride (PVC) dilution tube was contributing in any way to the halide analysis of particulate emissions collected in the samplers. Shavings were taken from samples of the tube. These were gradually heated (about 10°C per 7 minutes) to 250°C. Decomposition of the material was measured by mass spectroscopic monitoring of the peaks at $m/e = 36$ and 38 which would indicate the presence of HCl. As can be seen in the following graph, decomposition did not occur at temperatures below 200°C.

A second test was made to determine the effect of prolonged heating at lower temperatures. PVC shavings were heated at 150°C for 100 minutes. No significant evolution of HCl was detected.

Since the dilution tube cannot be practically used at temperatures over 50°C because of excessive softening and loss of rigidity, it could not impart any significant quantity of halides to the particulate emissions analyzed.


THERMAL DEGREDATION OF POLVINYLCHLORIDE DILUTION TUBE
I_{36} (HCl) - Arbitrary Unit
10^3
10^2
10
1
150
170
190
210
230
250
Temperature °C