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NAME OF STUDENT: Robert Patrick McCarthy

TITLE OF THESIS: CHEMICAL ANALYSIS OF
ATMOSPHERIC DUST

APPROVED BY READING COMMITTEE COMPOSED OF
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DATE: February 27, 1951

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UNIVERSITY OF LOUISVILLE

CHEMICAL ANALYSIS OF
" ATMOSPHERIC DUST

A Dissertation
Submitted to the Faculty
Of the Graduate School of the University of Louisville
In Partial Fulfillment of the
Requirements for the Degree
Of Master of Science

Department of Chemistry

By

Robert Patrick McCarthy

Year

1951

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I INTRODUCTION

The chemical analysis of atmospheric dust is of interest to two major groups, namely--the workers in industrial hygiene and the workers in the air cleaning and ventilating industries. The industrial hygienists, who are concerned with the prevention of occupational diseases and the maintenance of the health of industrial workers on a high level, are mainly interested in the concentration of irritating dusts, toxic dusts, fibrous-producing dusts, inert dusts and allergy-producing dusts that would obviously affect the health or comfort of industrial workers. Their interest, as one would expect, is in atmospheric dust of small particle sizes (10 microns and smaller), and in gaseous substances which they believe to be the most important from a health standpoint.²

The air cleaning and ventilating industries face an additional aspect of the problem of air pollution. Their problem is to devise instruments for capturing and removing solid matter from a stream of air. This solid matter includes fibrous material, such as lint, particles of earth, carbon, sand, ash, pollen, etc. Probably the most abundant of these solid particles is

carbon, which is the chief offender in soiling.⁹ The removing of this very undesirable property of soiling from the atmosphere is equally as important as removing materials that are harmful to health. The problem of control of soiling is unique with the air cleaning and ventilating industries and has led to the development of considerable testing technology for its evaluation. Experience in these industries has shown that it is not only necessary to know the type of dust, its concentration and its chemical composition but also the percentage of soiling material present in the atmosphere, if a synthetic testing material is to be created which will give a true efficiency rating for a filter in the laboratory. Studies indicate that there are variations in opinions as to what per cent carbon black (Free Carbon) a synthetic testing material of this nature should contain. The results of the analysis presented in this paper should help to clarify this problem of testing filters under conditions similar to those of actual field operations.

The chemical analysis of atmospheric dust is a complex problem. The complexity arises not only from the diversity of elements and compounds present in each local section of the earth's crust but also from the various local artificial dust produced by man.

Perhaps just as important as the concentration of these elements or compounds is the variety of physical forms these materials may take. The methods applied to the analysis of a dust sample depends primarily upon its physical form, and how much of a sample has been collected, and how much contaminant is present in the sample. These variations in the collected samples have led to the development of various methods of analysis.⁷ A preliminary survey of this analytical problem revealed that the gravimetric method was most suitable for these analyses.

This research program has been devoted to (1) developing a suitable analytical method for the determination of free carbon in atmospheric dust (2) analyzing thirty-seven samples of atmospheric dirt, collected in various United States cities by sales representatives of the American Air Filter Company, during the first four or five months of 1949, for free carbon, ash, mixed oxides, and silica, (3) adapting the developed analytical method for the determination of free carbon in atmospheric dust to a semimicro scale, (4) analyzing daily and weekly samples collected with electrostatic dust samplers in order to determine what the soiling conditions are in a given location at a given time.

For clearness to all readers, the term free carbon is uncombined carbon in any of its various forms and term ash refers to the product left after a sample has been burned in the laboratory under controlled conditions. This latter term should not be confused with fly ash.

II DEVELOPMENT OF ANALYTICAL METHOD FOR THE DETERMINATION OF FREE CARBON

Although the literature of the analytical chemistry of carbon is very voluminous, a literature search did not reveal definite evidence of a previous determination of free carbon in atmospheric dust samples. There are numerous instances in the literature where carbon determinations have been reported, but apparently they are total carbon rather than free carbon. The determination of free carbon in atmospheric dust is a problem of determining free carbon in a mixture of carbonaceous materials as well as inorganic substances. Since there was no method for the determination of free carbon available, it was necessary to develop an analytical method for this purpose.

A consideration of the possible avenues of attack on this problem led to the investigation of the work on gray solutions by the German workers. Preliminary investigations ruled out this possibility because of rapid sedimentation of the suspended dirt, since the method of collection had caused agglomeration of particles to greater than colloidal dimensions. A second and more promising approach was the application of wet oxidation methods to destroy the organic com-

pounds, the free carbon being very resistant to oxidation. Wet oxidations of this type are well established, with superoxol being widely used in biochemical research for destroying tissues, but here superoxol did not completely destroy the liny materials of atmospheric dirt.⁵

Although nitric acid is a standard analytical reagent for wet oxidation, there is evidence that it will attack free carbon on prolonged hot digestion. However, it seems to be the most suitable oxidizing agent available. The experiences in research by the rubber industry⁸ and by the Bureau of Standards⁴ substantiate this view since its use as a reagent for determining carbon black in rubber has become a widely accepted analytical procedure. This free carbon determination is based on the fact that the rubber polymer is soluble in hot nitric acid, leaving degradation products which are soluble in water and various organic solvents. This fact permits the transfer of the insoluble materials to a Gooch crucible, where they may be collected, dried, and weighed. The crucible is then ignited and the loss in weight calculated as free carbon. The determination developed for the analysis of free carbon in atmospheric dirt does not require the use of organic solvents to wash out the

degradation products and in general produces a method of greater simplicity.

In order to determine the effectiveness of wet oxidation on carbon black and the efficiency of the wet oxidation technique in determining carbon black in atmospheric dirt, a series of experiments were carried out using as test dirt substances already in use as standard test materials in the air cleaning field. To test the effect of nitric acid on pure carbon black, samples of 0.1 to 0.6 grams of carbon black were weighed into 250 ml. beakers and 25 ml. of 70% nitric acid added. The mixture was covered with a watch glass and boiled for various lengths of time as shown in Table I. The sample was diluted with 125 ml. 6N nitric acid and allowed to stand overnight. The supernatant liquid was decanted through tared Selas crucibles and the insoluble material collected and washed with water. The crucibles and contents were dried for two hours at 140°C., cooled, weighed, and recorded. Then they were ignited for two hours at 700°C., cooled, and weighed; the loss in weight being free carbon. The value of the mean is 100.5 ± 0.2% carbon recovered. This positive error is in agreement with results obtained at the Bureau of Standards⁴ but is less in magnitude probably because of wide differences in technique employ-

ed. The magnitude of the error is well within the limits normally expected for this type method.

Then to further test the wet oxidation technique, mixtures simulating atmospheric dirt were prepared from carbon black, wood flour, and finely powdered white sand. These mixtures were prepared in four approximate compositions--10% carbon black, 20% silica, 70% wood flour; 20% carbon black, 70% silica, 10% wood flour; 50% carbon black, 25% silica, 25% wood flour; 80% carbon black, 10% silica, 10% wood flour--in order to cover all probable carbon compositions. These samples were digested with 70% nitric acid until the wood flour had lost its gelatinous appearance. The digestion required from 20 minutes to an hour depending on the per cent wood flour present.

The amount of the various constituents recovered was determined by the following formulas:

Wood Flour--

$$(A+B+C+D)-(E) = \text{wood flour found.}$$

Carbon Black--

$$(E)-(F) = \text{carbon black found.}$$

Silica--

$$(F)-(D) = \text{silica found.}$$

where:

A = grams of wood flour taken.

B = grams of carbon black taken.

C = grams of mineral matter
(SiO_2) taken.

D = weight of Selas crucible.

E = weight of crucible and
contents after drying.

F = weight of crucible and
ash (SiO_2) after ashing.

The results of this series of tests are summarized in Tables II, III, IV, and V. The values for the free carbon found in the mixtures are no longer uniformly high, as in the case of the pure carbon, but deviate from the mean in a manner indicating accidental errors.

TABLE I
DIGESTION OF CARBON BLACK WITH 70% HNO₃

Grams Taken	Grams Found	Difference (mg)	Percent Carbon Black Recovered	Time Digested (minutes)
0.5897	0.5906	+ 0.9	100.2	15
0.3249	0.3253	+ 0.4	100.1	30
0.3186	0.3200	+ 1.4	100.4	45
0.3374	0.3381	+ 0.7	100.2	60
0.3405	0.3419	+ 1.4	100.4	75
0.3063	0.3080	+ 1.7	100.5	90
0.3487	0.3490	+ 0.3	100.1	30
0.3421	0.3422	+ 0.1	100.0	45
0.3513	0.3521	+ 0.8	100.2	90
0.1095	0.1104	+ 0.9	100.8	15
0.1105	0.1114	+ 0.9	100.8	30
0.1048	0.1053	+ 0.5	100.5	60
0.1010	0.1025	+ 1.5	101.3	90
0.1100	0.1108	+ 0.8	100.5	30
0.1049	0.1066	+ 1.7	101.6	45
0.1116	0.1129	+ 1.1	101.1	75
0.1149	0.1158	+ 0.9	100.8	90

Arithmetical mean --- 100.5%

Average deviation --- ± 0.2%

Average deviation of mean --- 0.01%

TABLE II

Digestion of Synthetic Samples with 70% HNO₃

(Approximate composition - 10% carbon black, 20% silica, 70% wood flour.)

Grams Taken	Grams Found	Difference (mg.)	Percentage Found
<u>Carbon Black</u>			
0.1077	0.1080	+ 0.3	100.2
0.1081	0.1067	- 1.4	98.71
0.1012	0.1001	- 1.1	98.93
0.1055	0.1047	- 0.8	99.22
0.1135	0.1133	- 0.2	99.82
<u>Silica</u>			
0.2034	0.2044	+ 1.0	100.3
0.2186	0.2183	- 0.3	99.86
0.2147	0.2151	+ 0.4	100.2
0.2413	0.2404	- 0.9	99.63
0.2029	0.2035	+ 0.6	100.3
<u>Wood Flour</u>			
0.8966	0.8953	- 1.3	99.83
0.8592	0.8609	+ 1.7	100.2
0.8883	0.8890	+ 0.7	100.1
0.8083	0.8100	+ 1.7	100.2
0.9292	0.9288	- 0.4	99.95

Values for Carbon Only

Arithmetical mean --- 99.34%
 Average deviation --- \pm 0.48%
 Average deviation of the mean --- 0.21%

TABLE III

Digestion of Synthetic Samples with 70% HNO₃

(Approximate composition - 20% carbon black, 70% silica, 10% wood flour.)

Grams Taken	Grams Found	Difference (mg.)	Percentage Found
<u>Carbon Black</u>			
0.2282	0.2276	- 0.6	99.74
0.2384	0.2386	+ 0.2	100.1
0.2048	0.2046	- 0.2	99.91
0.2041	0.2036	- 0.5	99.77
0.2099	0.2105	+ 0.6	100.2
<u>Silica</u>			
0.8576	0.8578	+ 0.2	100.0
0.8153	0.8154	+ 0.1	100.0
0.9922	0.9923	+ 0.1	100.0
0.8232	0.8246	+ 1.4	100.2
0.9511	0.9499	- 1.2	99.88
<u>Wood Flour</u>			
0.1219	0.1223	+ 0.4	100.3
0.1018	0.1015	- 0.3	99.63
0.1089	0.1090	+ 0.1	100.1
0.1096	0.1087	- 0.9	99.40
0.1036	0.1042	+ 0.6	100.7

Values for Carbon Only

Arithmetical mean --- 99.94%
 Average deviation --- \pm 0.16%
 Average deviation of mean --- 0.07%

TABLE IVDigestion of Synthetic Samples with 70% HNO₃

(Approximate composition - 50% carbon black, 25% silica, 25% wood flour.)

Grams Taken	Grams Found	Difference (mg.)	Percentage Found
<u>Carbon Black</u>			
0.5432	0.5435	+ 0.3	100.0
0.4339	0.4343	+ 0.4	100.1
0.4730	0.4745	+ 1.5	100.3
0.5358	0.5360	+ 0.2	100.0
0.4691	0.4692	+ 0.1	100.0
<u>Silica</u>			
0.2954	0.2944	- 1.0	99.77
0.2602	0.2594	- 0.8	99.48
0.2116	0.2108	- 0.8	99.62
0.2203	0.2203	± 0.0	100.0
0.2774	0.2782	+ 0.8	100.2
<u>Wood Flour</u>			
0.2287	0.2287	± 0.0	100.0
0.2306	0.2310	+ 0.4	100.2
0.2263	0.2256	- 0.7	99.93
0.2174	0.2172	- 0.2	99.91
0.2257	0.2248	- 0.9	99.55

Values for Carbon Only

Arithmetical mean --- 100.1%
 Average deviation --- ± 0.10%
 Average deviation of mean --- 0.04%

TABLE V

Digestion of Synthetic Samples with 70% HNO₃

(Approximate composition - 80% carbon black, 10% silica, 10% wood flour.)

Grams Taken	Grams Found	Difference (mg.)	Percentage Found
<u>Carbon Black</u>			
0.9051	0.9032	- 1.9	99.82
0.9016	0.9012	- 0.4	99.98
0.9127	0.9127	± 0.0	100.0
0.8400	0.8406	+ 0.6	100.1
0.8735	0.8744	+ 0.9	100.1
<u>Silica</u>			
0.1254	0.1257	- 0.3	100.2
0.1351	0.1353	- 0.2	100.2
0.1196	0.1196	± 0.0	100.0
0.1320	0.1316	+ 0.4	100.2
0.1155	0.1150	+ 0.5	99.30
<u>Wood Flour</u>			
0.1109	0.1115	+ 0.6	100.6
0.1095	0.1097	± 0.2	100.2
0.1086	0.1086	± 0.0	100.0
0.1122	0.1120	- 0.2	99.82
0.1075	0.1071	- 0.4	99.61

Values for Carbon Only

Arithmetical mean --- 100.0%

Average deviation --- ± 0.08%

Average deviation of the mean --- 0.04%

III SAMPLING

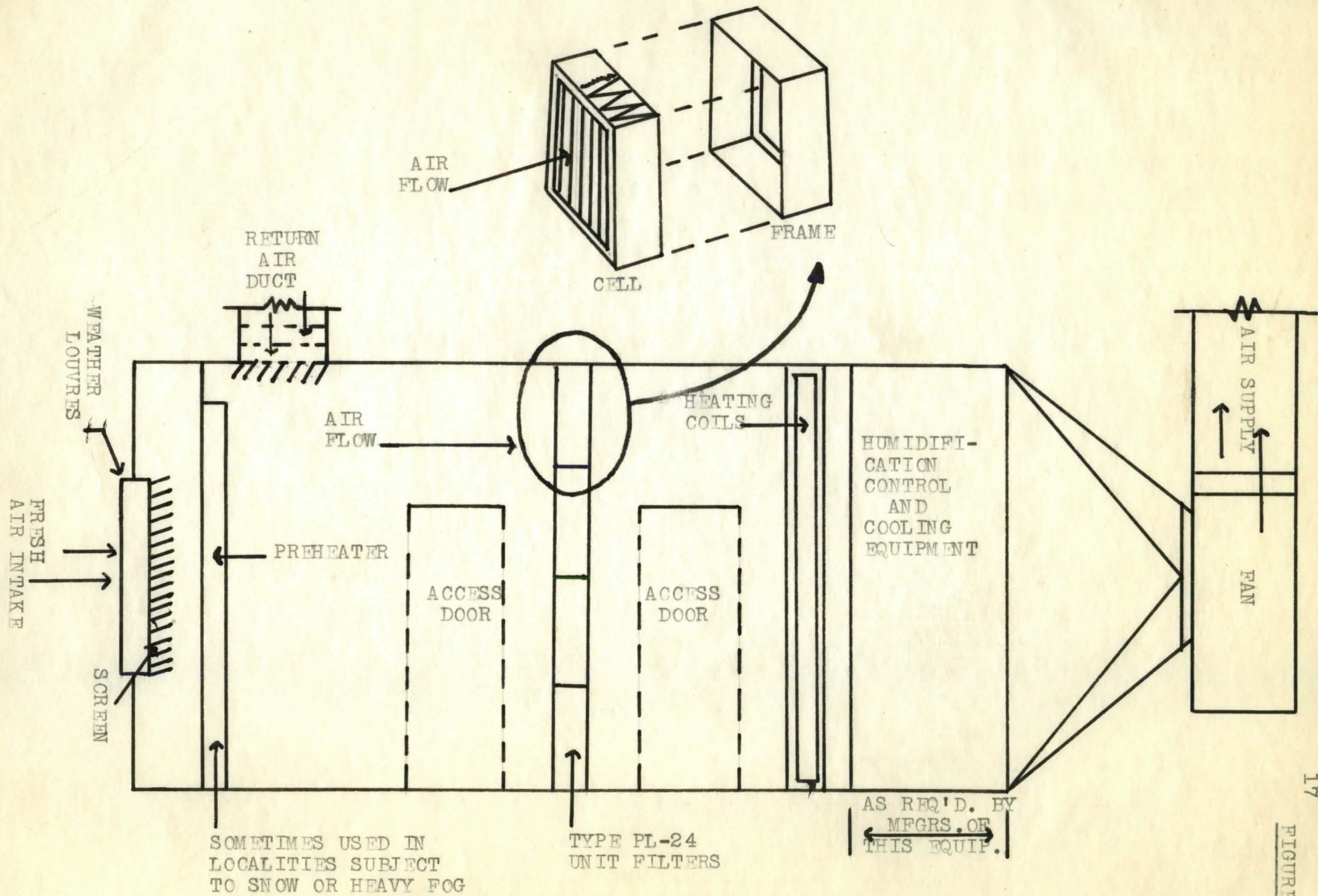
After considering the sampling problem from all its various aspects, it was decided that the best available source for a representative sample was from the PL-24 filter installations. The PL-24 is a mechanical filter constructed by folding sheets of six ply Airmat paper into a metal frame. The Airmat paper, which is a soft porous paper that has been previously treated with a high grade white petroleum oil, covers the 2' x 2' frame and constitutes a cell. Each cell has 29 square feet of exposed dust-collecting surface and is called an air filtering unit. The face velocity of the air stream for a unit of this type is 250 feet per minute and the velocity through the filtering medium is 35 feet per minute. A large industrial installation (Fig. 1) is composed of a number of these cells placed on a single layer across the air intake duct. This type arrangement has a collecting efficiency of about 85% - 95%.

The samples to be analyzed were collected from the PL-24 installations, during the first four or five months of 1949, by American Air Filter Company sales representatives in various cities. Care was exercised

during the collecting period to operate the PL-24 installations under as similar conditions as the units would permit. The sales representatives reported all factors that they considered important in the collecting process. Some of the factors that were considered of significance described the environment and location of the unit and the per cent fresh air used. This information, and samples, representing a dirt accumulation of from several days to several months, were packed in plastic bags and mailed to the laboratory.

This method of sampling has several undesirable factors:

1. The dirt concentration in the air being sampled cannot be determined.
2. This filter does not stop all the "fines"-particles below 2 to 3 microns.
3. Some of the particles first caught by the filter cannot be removed for analysis because they have embedded themselves in the filtering fiber.
4. The Airmat paper, even though wet with petroleum oil, contributes a small amount of lint to the sample.



TYPICAL VENTILATING SYSTEM WITH PL-24 FILTERS

IV PREPARATION OF SAMPLES FOR ANALYSIS

The Airmat paper containing the collected dirt was shaken over a piece of glazed wrapping paper and the oil-soaked dirt which fell off was retained for analysis. The sample was extracted with several small portions of ether to remove the oil, was oven-dried, and the sample then put through a 60 mesh screen to remove any particles of paper that may have come off the collecting medium. Each sample was dried for one hour at 100° C. before weighing.

V ANALYTICAL PROCEDURES

A. Determination of Free Carbon

Duplicate samples of 0.15 to 0.2 grams of the dust were weighed into 250ml. beakers and 25 ml. of 70% nitric acid added. The mixture was covered with a watch glass and boiled for twenty minutes, diluted with 125 ml. of 6N nitric acid and allowed to stand overnight. (It is necessary that the supernatant liquid be strongly acid or the carbon will become dispersed and incapable of being filtered.) The supernatant liquid was decanted through a tared Selas crucible and insoluble material collected. The crucibles and contents were dried for two hours at $140^{\circ}\text{C}.$, cooled, weighed, and recorded. Then they were ignited for two hours at $700^{\circ}\text{C}.$, cooled, and weighed, the loss in weight being free carbon.

B. Determination of Ash

Duplicate samples of 0.3 to 0.6 grams of the dust were weighed into platinum crucibles and ashed at 800°C in a muffle furnace. The gain in weight of the cooled crucible is the ash. The per cent combustibles can be

determined by subtracting the per cent ash from one hundred per cent.

C. Determination of Silica

The ash was fused with anhydrous sodium carbonate and silica determined by a standard analytical procedure.⁶

D. Determination of Mixed Oxides (R_2O_3)

The mixed oxides were determined by treating the filtrates resulting from the silica determination with a standard analytical procedure.³

E. Results of Analyses

The results of analyses of the thirty-seven atmospheric dust samples are given in Table VI. For convenience, the samples have been grouped by cities or geographical areas rather than consecutively by sample numbers.

TABLE VI
RESULTS OF ANALYSIS

Sample Number	Building or Installation and Location	Percent Fresh Air	Remarks	DATA: PER CENT BY WEIGHT			
				Free Carbon	Ash	Silica	Mixed Oxides
26	Commodore Perry Hotel, Toledo, Ohio	50	Intake second floor	36.52	36.23	42.32	16.29
11	Landers Corp., Toledo, Ohio	100	Company manufactures cotton fabrics - intake second floor	35.89	43.85	34.38	14.74
12	Collonnade Co., Bulkley Bldg., Cleveland, Ohio	100	Sample taken at 9th floor - roof	26.79	64.25	18.65	31.65
36	W. T. Grant Co., Cleveland, Ohio	100	Downtown area	17.49	64.56	26.04	20.40
30	Talbott Building Dayton, Ohio	?	From original installation, building-just opened in April	12.87	60.77	21.30	9.98
19	Allied Paper Mills, Kalamazoo, Michigan	?	Sample taken over 144-hour period, fans on, intake on ground level	14.52	69.22	34.08	30.33
10	Security National Bank, Battle Creek, Michigan	25	Intake located on fourth floor	35.45	68.42	21.28	18.52

TABLE VI (Con't.)
RESULTS OF ANALYSIS

Sample Number	Building or Installation and Location	Percent Fresh Air	Remarks	DATA: PER CENT BY WEIGHT			
				Free Carbon	Ash	Silica	Mixed Oxides
40	General Motors Research Bldg., Detroit, Mich.	100	Very satisfactory filtering results. Intake 75'-80' above street	36.13	62.30	30.51	19.70
29	Rockham Building, Detroit, Michigan	100	Filter in use 12 hours per day- Sat. & Sun. excluded	32.30	44.24	31.35	9.87
7	Nash Kelvinator Company, Milwaukee, Wisconsin	100	Semi-industrial area. Inlet over railroad yard, 5th floor level	20.04	65.52	30.40	19.70
24	U. S. Rubber Co., Mishawaka, Ind.	75	Intake on 4th floor	30.57	52.98	22.98	16.29
33	Miles Laboratories, Inc., Elkhart, Ind.	25	Intake on floor of warehouse. Lots of floor dust.	11.67	48.16	21.84	15.07
15	Joe Low Corporation, N. Elston., Chicago, Illinois	100	Industrial area. Intake on roof of 2nd floor.	27.05	52.51	21.46	21.26

TABLE VI (Con't)

RESULTS OF ANALYSIS

Sample Number	Building or Installation and Location	Percent Fresh Air	Remarks	DATA: PER CENT BY WEIGHT			
				Free Carbon	Ash	Silica	Mixed Oxides
16	Phoenix Metal Cap Co., 16th St., Chicago, Ill.	100	Near railroad switch yard. Intake on roof of 4th floor. Not a clean area, but fairly typical of industrial Chicago.	42.27	47.29	21.78	18.42
14	Mathieson Alkali, Niagara Falls, New York	100	Ground Floor Intake, near open area	28.39	51.33	24.38	18.70
13	N. Y. Telephone Company, Buffalo, New York	100	System runs 24 hours per day, 5th floor level	40.90	35.56	21.39	11.41
18	Chase National Bank, 15 Broad Street, New York City	?	Second floor intake	38.26	49.23	22.33	21.28
37	Walters Art Gallery, Baltimore, Maryland	100	Shopping district. Intake 18' above street level.	27.95	62.73	32.50	16.73

TABLE VI (Con't)
RESULTS OF ANALYSIS

Sample Number	Building or Installation and Location	Percent Fresh Air	Remarks	DATA: PER CENT BY WEIGHT			
				Free Carbon	Ash	Silica	Mixed Oxides
22	Julius Schmid, Inc., Little Falls, N.J.	100	Open country- 24 hour per day operation	23.13	62.53	36.98	19.38
39	Smith Kline & French Company, Philadelphia, Pennsylvania	100	Fresh air intake at 5th floor level on west side of building	32.78	58.84	27.63	18.35
17	Smith, Kline & French Company, Philadelphia, Pennsylvania	100	Above second floor	31.48	50.40	23.96	13.42
8	Shawinigan Resins, Indian Orchard, Mass.	100	600 hours continuous service. Intake 30' to 40' above ground.	55.82	9.43	5.85	3.23
9	Federal Land Bank, Springfield, Massachusetts	100	Intake at floor level adjacent to parking lot	43.25	55.51	32.93	11.88
31	Deerfoot Farms, Newton, Mass.	?	Intake on 2nd floor near smokestack and incinerator exhaust	21.71	64.10	32.53	22.67

TABLE VI (Con't)

RESULTS OF ANALYSIS

Sample Number	Building or Installation and Location	Percent Fresh Air	Remarks	DATA: PER CENT BY WEIGHT			
				Free Carbon	Ash	Silica	Mixed Oxides
32	Stone & Webster Building, Boston, Massachusetts	100	Intake on 3rd floor near center of Boston business district	46.47	45.45	16.74	7.81
2	Travelers' Insurance Company, Hartford, Conn.	100	Center of town. Fresh air taken in at the 10th floor.	7.70	74.60	40.40	15.80
23	South Vocational High School, Pittsburg, Penn.	50	Near industrial and business section. Intake 40' above street	36.03	45.08	20.07	18.81
21	Letsche Elementary School, Pittsburg, Pennsylvania	100	Poor residential area. Intake 40' above street	46.65	34.79	15.23	12.10
20	Whittier Elementary School, Pittsburg, Pennsylvania	70	Good residential area. Area intake on roof 50' above street.	33.96	50.75	24.60	12.73
29	Southwestern Bell Telephone Company, St. Louis, Missouri	?	Intake 2' above sidewalk.	23.15	65.53	33.22	20.58

TABLE VI (Con't)

RESULTS OF ANALYSIS

Sample Number	Building or Installation and Location	Percent Fresh Air	Remarks	DATA: PER CENT BY WEIGHT			
				Free Carbon	Ash	Silica	Mixed Oxides
1	S & W Cafeteria, Knoxville, Tenn.	25	PL-24's located on 3rd floor of building in downtown section	38.90	48.70	23.90	20.40
3	T.V.A. Power Building, Station O, Chattanooga, Tennessee	20	Weather mild. Intake 6 floors up	32.40	47.10	27.60	15.60
4	Federal Reserve Bank, Atlanta, Georgia	100	100% for 4 weeks. 75% recirculated for 1 week	27.60	51.60	32.20	16.80
5	Retail Credit Co., Atlanta, Georgia	90		26.20	58.40	32.90	18.70
28	A. Burglass Furniture Company, 1300 Canal St., New Orleans, La.	50		12.97	59.10	20.48	10.91
27	Kress Store, Tulsa, Okla.	75-100	Sample taken over 6 weeks' period	7.96	66.75	42.32.	9.36
6	U. S. Appraisers Building, San Francisco, California	100	Air intake at 18th floor	24.54	46.79	26.54	18.53

VI THE DETERMINATION OF FREE CARBON IN ATMOSPHERIC DUST BY A SEMIMICRO METHOD

A. INTRODUCTION

The soiling property of atmospheric dust is of major economic importance in heavily populated areas. Since this property is due chiefly to the amount of free carbon present in atmospheric dust, a convenient analytical method has been developed for evaluating its concentration. This method, although accurate, has two undesirable factors, namely--it requires a relatively large sample which in turn necessitates a long collecting period. In order to determine just what the soiling conditions are in a given location at a given time it was found necessary to eliminate these two undesirable factors. The eliminations were accomplished by adapting the free carbon determination to a semimicro scale and collecting daily* and weekly samples** with an electrostatic dust sampler.

* Daily Samples - Samples collected over a twenty-four period.

** Weekly Samples - Samples collected over a seven day period.

VII ADAPTATION PROCEDURE

In order to adapt the previously developed analytical procedure for the quantitative determination of free carbon in atmospheric dust to a semimicro scale the effect of nitric acid digestion on small pure carbon black samples had to be determined. The validity of this wet oxidation technique was tested by weighing samples ranging from 30 to 100 mgs. into 100 ml beakers and adding 10 ml of 70% nitric acid. The mixture was covered with a watch glass and boiled for fifteen minutes, diluted with 50 ml of 6N nitric acid and allowed to stand overnight. The supernatant liquid was decanted through a tared Selas crucible and the insoluble material collected and washed with water. The crucibles and contents were dried for two hours at 140°C., cooled, weighed, and recorded. Then they were ignited for two hours at 700°C., cooled, and weighed; the loss in weight being free carbon. The value of the arithmetical mean is 100.53% carbon recovered, which is in close agreement with the value obtained with larger samples in the previous section.

The wet oxidation technique was further tested for adaptation to a semimicro scale by preparing various mixtures of carbon black, wood flour, and powdered

white sand. These synthetic samples were prepared in 100 and 200 mg. portions, each portion having four different approximate compositions in order to cover all probable carbon compositions. The four 100 mg. portions had the following approximate compositions--

- 10% carbon black, 20% silica, and 70% wood flour;
- 20% carbon black, 70% silica, and 10% wood flour;
- 50% carbon black, 25% silica, and 25% wood flour;
- 80% carbon black, 10% silica, and 10% wood flour.

The approximate compositions of the four 200 mg. portions were--

- 15% carbon black, 75% silica, and 10% wood flour;
- 30% carbon black, 10% silica, and 60% wood flour;
- 50% carbon black, 25% silica, and 25% wood flour;
- 70% carbon black, 15% silica, and 15% wood flour.

Each mixture was digested with 10 ml. of 70% nitric acid for fifteen minutes and the free carbon was determined as described on the previous page.

The results of these tests are given in Tables VII through XV.

TABLE VIIDigestion of Carbon Black with 70% HNO₃

Digestion Time 15 Minutes

Mgs. Taken	Mgs. Found	Difference (mg.)	Percentage Found
65.82	66.23	+ 0.41	100.62
45.39	45.70	+ 0.31	100.69
98.22	98.62	+ 0.40	100.41
93.11	93.22	+ 0.11	100.12
50.69	51.00	+ 0.31	100.61
30.62	30.91	+ 0.29	100.94
80.41	80.70	+ 0.39	100.36
48.39	48.61	+ 0.22	100.45

Arithmetical mean --- 100.53%

Average deviation --- \pm 0.19%

Average deviation of mean --- 0.07%

TABLE VIIIDigestion of Synthetic Samples with 70% HNO₃

(Approximate weight - 100 milligrams)
 (Approximate composition - 10% carbon
 black, 20% silica, 70% wood flour.)

Mgs. Taken	Mgs. Found	Difference (mg.)	Percentage Found
9.11	9.91	+ 0.80	108.78
11.10	11.89	+ 0.79	107.11
11.49	12.03	+ 0.54	104.79
9.68	10.26	+ 0.58	105.99
10.71	11.00	+ 0.30	102.80
12.14	12.31	+ 0.17	101.40
8.89	9.60	+ 0.71	107.99
9.19	10.01	+ 0.82	108.92
12.70	13.48	+ 0.78	106.14
12.39	13.12	+ 0.73	105.89

Arithmetical mean --- 105.98%

Average deviation --- \pm 1.80%

Average deviation of mean --- 0.56%

TABLE IX

Digestion of Synthetic Samples with 70% HNO₃

(Approximate weight - 100 Milligrams)
 (Approximate composition - 20% carbon
 black, 70% silica, 10% wood flour.)

Mgs. Taken	Mgs. Found	Difference (mg.)	Percentage Found
19.40	19.98	+ 0.58	102.99
20.31	20.87	+ 0.56	102.75
24.69	25.48	+ 0.79	103.20
22.10	22.97	+ 0.87	103.93
18.80	19.19	+ 0.39	102.07
21.29	22.11	+ 0.82	103.85
24.31	24.70	+ 0.39	101.60
16.68	17.42	+ 0.74	104.43
19.62	20.01	+ 0.39	101.98
16.10	16.49	+ 0.39	102.42
15.91	16.22	+ 0.31	101.94
18.81	19.01	+ 0.20	101.06
19.19	19.80	+ 0.61	103.17
16.88	17.38	+ 0.50	102.96
18.11	18.71	+ 0.60	103.31

Arithmetical mean --- 102.77%
 Average deviation --- \pm 0.75%
 Average deviation of mean --- 0.19%

TABLE X

Digestion of Synthetic Samples with 70% HNO₃

(Approximate weight - 100 Milligrams)
 (Approximate composition - 50% carbon
 black, 25% silica, 25% wood flour.)

Mgs. Taken	Mgs. Found	Difference (mg.)	Percentage Found
44.11	44.91	+ 0.80	101.79
41.93	42.60	+ 0.67	101.59
48.89	49.69	+ 0.80	101.69
42.77	43.68	+ 0.91	102.10
45.23	45.77	+ 0.54	101.19

TABLE X (Con't.)

Mgs. Taken	Mgs. Found	Difference (mg.)	Percentage Found
41.89	42.40	+ 0.51	101.22
41.22	41.41	+ 0.19	100.46
45.31	45.59	+ 0.28	100.62
45.40	45.51	+ 0.11	100.24
47.72	47.95	+ 0.23	100.48
52.79	53.16	+ 0.37	100.68
50.41	51.10	+ 0.69	101.36
45.09	45.60	+ 0.51	101.13
49.11	49.24	+ 0.13	100.29
35.89	36.82	+ 0.93	102.59
50.01	50.60	+ 0.59	100.99
79.70	80.61	+ 0.91	101.14
47.90	48.35	+ 0.45	100.94
50.61	51.25	+ 0.64	101.26
44.80	45.67	+ 0.87	101.94
42.21	42.86	+ 0.65	101.54
44.00	44.57	+ 0.57	101.29

Arithmetical mean --- 101.21%

Average deviation --- \pm 0.46%

Average deviation of mean --- 0.10%

TABLE XI

Digestion of Synthetic Samples with 70% HNO_3

(Approximate weight - 100 milligrams)
 (Approximate composition - 80% carbon
 black, 10% silica, 10% wood flour.)

Mgs. Taken	Mgs. Found	Difference (mg.)	Percentage Found
74.49	75.13	+ 0.64	100.86
80.01	80.75	+ 0.74	100.92
77.60	78.39	+ 0.79	101.01
82.59	83.19	+ 0.60	100.72
80.12	80.52	+ 0.40	100.49

Arithmetical mean --- 100.80%

Average deviation --- \pm 0.16%

Average deviation of mean --- 0.07%

TABLE XIIDigestion of Synthetic Samples with 70% HNO₃

(Approximate weight - 200 Milligrams)
 (Approximate composition - 15% carbon
 black, 75% silica, 10% wood flour.)

Mgs. Taken	Mgs. Found	Difference (mg.)	Percentage Found
45.89	46.39	+ 0.50	101.08
36.58	37.30	+ 0.72	101.69
31.11	31.67	+ 0.56	101.83
32.50	33.09	+ 0.59	101.82
28.52	29.11	+ 0.59	101.72

Arithmetical mean --- 101.63%
 Average deviation --- \pm 0.22%
 Average deviation of mean --- 0.09%

TABLE XIIIDigestion of Synthetic Samples with 70% HNO₃

(Approximate weight - 200 Milligrams)
 (Approximate composition - 30% carbon
 black, 10% silica, 60% wood flour.)

Mgs. Taken	Mgs. Found	Difference (mg.)	Percentage Found
62.20	62.57	+ 0.37	100.59
52.51	53.41	+ 0.90	101.71
68.89	69.37	+ 0.48	100.69
71.28	72.28	+ 1.00	101.40
61.45	61.77	+ 0.32	100.42

Arithmetical mean --- 100.96%
 Average deviation --- \pm 0.47%
 Average deviation of mean --- 0.21%

TABLE XIV

Digestion of Synthetic Samples with 70% HNO_3

(Approximate weight - 200 Milligrams)
 (Approximate composition - 50% carbon
 black, 25% silica, 25% wood flour.)

Mgs. Taken	Mgs. Found	Difference (mg.)	Percentage Found
99.59	100.21	+ 0.62	100.64
108.84	109.82	+ 0.98	100.90
105.18	105.99	+ 0.81	100.70
102.67	103.60	+ 0.93	100.96
105.92	106.51	+ 0.59	100.56
Arithmetical mean --- 100.75%			
Average deviation --- \pm 0.14%			
Average deviation of mean --- 0.06%			

TABLE XV

Digestion of Synthetic Samples with 70% HNO_3

(Approximate weight - 200 Milligrams)
 (Approximate composition - 70% carbon,
 black, 15% silica, 15% wood flour.)

Mgs. Taken	Mgs. Found	Difference (mg.)	Percentage Found
166.12	166.80	+ 0.68	100.41
133.86	134.60	+ 0.74	100.55
125.20	126.19	+ 0.96	100.77
169.98	170.90	+ 0.92	100.54
117.71	118.51	+ 0.80	100.68
Arithmetical mean --- 100.59%			
Average deviation --- \pm 0.11%			
Average deviation of mean --- 0.05%			

VIII SAMPLING

The electrostatic precipitator offers a very accurate and convenient means of collecting atmospheric dust samples that are to be subjected to chemical analysis. Basically, the electrostatic sampler can be described as being an electrode-in-cylinder type of instrument that operates on the following principle. Dust-laden air is drawn through a strong electrostatic field by suction, where every particle of foreign matter, regardless of size or composition, receives a positive charge. The charged particles are then transported to the collecting electrode (cylinder) by the force exerted on them by the electric field.

Two different instruments, operating on the above principle, were used in collecting the daily and weekly samples. A commercial sampler,* whose precipitation unit is shown in (Fig. II), was employed to collect the daily samples, whereas the weekly samples were collected with a sampling instrument designed and constructed by the American Air Filter Company. Although unlike in appearance the only essential differences in these two units are slight variations in the precipitating and collecting electrodes. In the commercial

* The M.S.A. electrostatic sampler manufactured by the Mine Safety Appliances Company.

unit the central attachment, which supports the platinum precipitating electrode at one end only, is removable, whereas the constructed unit employed a removable tungsten wire electrode supported at both ends. The collecting electrodes differ only in that one is removable (commercial sampler) and the other is stationary (constructed sampler).

Collection was made directly upon the sides of the aluminum cylinder in the commercial unit but the constructed unit required a celluloid lining for collection because of its stationary collecting electrode. In both cases, the dust deposit, which is held in the form of a dry powder, is usually very dense at the entrance followed by a gradual tapering off. A small quantity of dust is also collected on the central attachment of the commercial unit; the constructed unit held this condition to a minimum. This deposit arises only when the dust does not stick well on the outer sampling tube and after a rather heavy deposit of such material has been made. The efficiency of the sampler, which is said to be 100% at 3 cu.ft. per minute, is not affected by this deposit, however it does necessitate weighing this attachment along with the outer tube in order to determine the total amount of dust collected.¹

A. Location and Environment of Samplers

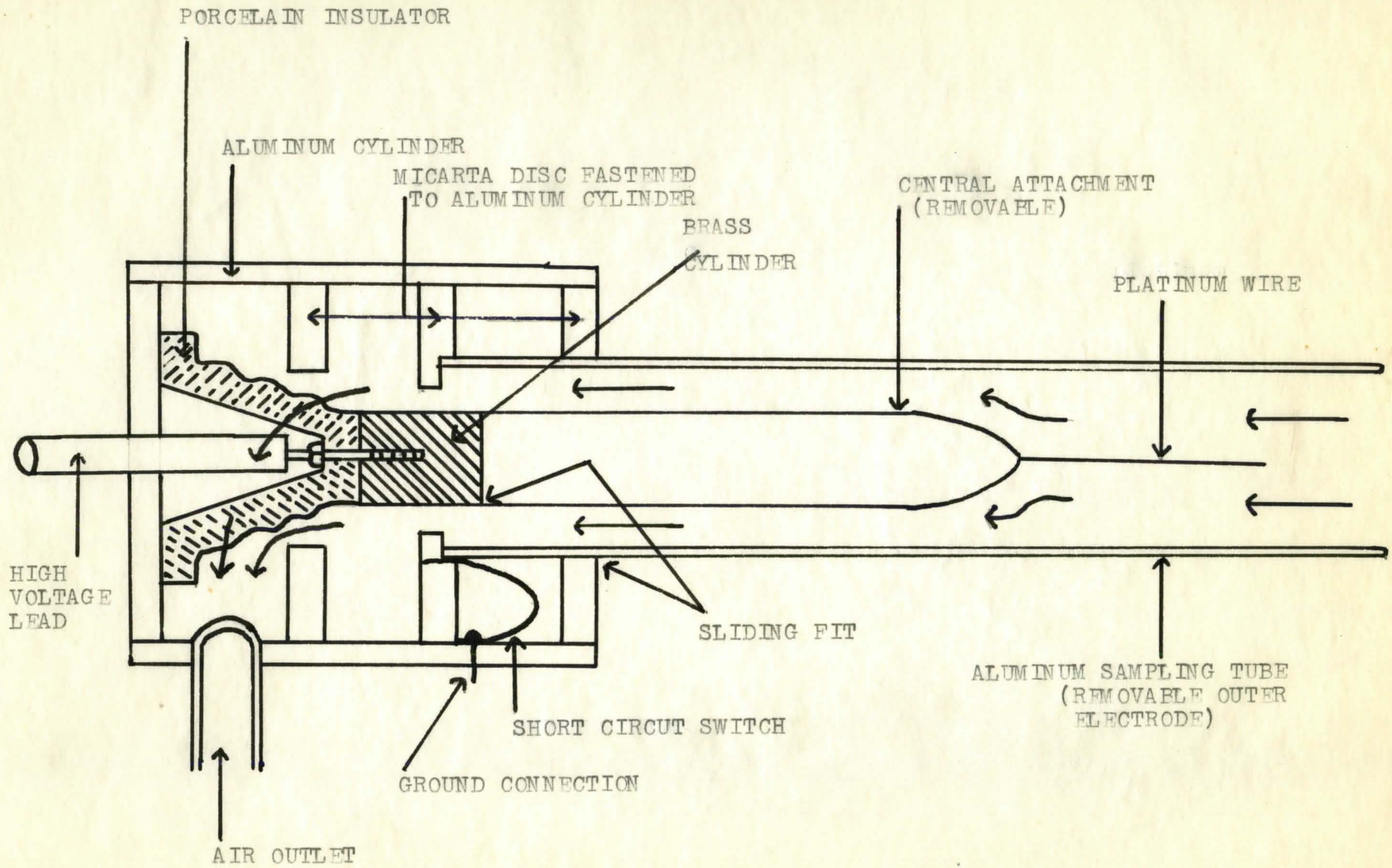
The electrostatic samplers used to collect the daily and weekly samples were situated so their sampling tubes extended out a second floor window (approximately 30 feet above ground level) of the American Air Filter Company's research laboratory. A number of small industries located near an average residential section constituted the outlying area; the immediate area consisted of a coal and a railroad switch yard.

B. Procedures

Daily Samples---The sampling tubes and central attachments are thoroughly washed, dried, cooled, and weighed. After washing and wiping, care must be exercised in handling. It was found convenient to wrap a small piece of paper around the tubes, and hold it in place with a rubber band after the first weights were taken. The tubes can then be handled and the samples taken without getting the tubes dirty on the outside. After the sample is collected, the tube and the central attachment are dried, cooled, and weighed. Then the dust sample is completely removed by washing into a 125 ml beaker with hot water. In order to determine the

weight of the sample recovered for analysis (which in most cases was 100%) the tube and central attachment were again dried, cooled, and weighed. Before proceeding with the free carbon determination the wash solution was evaporated just short of dryness.

Weekly Samples---A simpler procedure was used in collecting the weekly samples. The sample was collected on a piece of celluloid snugly fitted against the inside wall of the aluminum tube; then removed from the celluloid by scraping the dust loose with a metal spatula and brushing into a 100 ml beaker that had been previously washed, dried, cooled, and weighed. The weight of the sample recovered for analysis was obtained by subtracting the weight of the beaker from the weight recorded after drying, cooling, and weighing the beaker and sample.



PRECIPITATION UNIT¹

IX ANALYTICAL PROCEDURE

A. Determination of Free Carbon

The previously weighed sample is treated with 10 ml. of 70% nitric acid. The mixture is covered with a watch glass and boiled for 15 minutes, diluted with 50 ml. of 6N nitric acid and allowed to stand overnight. (It is necessary that the supernatant liquid be strongly acid or the carbon will become dispersed and incapable of being filtered.) The supernatant liquid is carefully decanted through a tared Selsas crucible and the insoluble material collected. The crucibles and contents are dried for two hours at $140^{\circ}\text{C}.$, cooled, weighed; then they are ignited for two hours at $700^{\circ}\text{C}.$, cooled, and weighed, the loss in weight being free carbon.

B. Results of Analyses

The results of the analyses of the daily and weekly dust samples are given in Tables XVI and XVII respectively.

TABLE XVI
DATA FOR DAILY SAMPLES

OPERATING TIME (IN MIN.)	CU.FT. OF AIR/MIN.	TOTAL VOLUME OF AIR (IN CU.FT.)	WT. OF SAMPLE (IN MGS.)	% FREE CARBON
1,535	2.5	3,838	21.40	40.19
1,350	2.5	3,375	34.51	42.90
1,440	2.5	3,600	21.19	30.16
1,305	2.5	3,262	28.45	45.77
1,440	2.5	3,600	42.31	44.28
2,880	2.5	7,200	41.29	40.19
1,470	2.0	2,940	16.48	48.18
1,410	2.3	3,243	31.21	44.12
1,440	2.3	3,312	32.44	42.04
1,290	2.0	2,580	22.99	45.06

Average % Free Carbon --- 42.29%

TABLE XVII
DATA FOR WEEKLY SAMPLES

DATE SAMPLE WAS COLLECTED	WT. OF SAMPLE REMOVED (MGS.)	% FREE CARBON
AUG. 8th TO AUG. 15th	130.31	58.86
AUG. 15th TO AUG. 22nd	77.03	38.83
AUG. 22nd TO AUG. 29th	112.53	57.68
AUG. 29th TO SEPT. 12th	219.23	39.32
SEPT. 12th TO SEPT. 19th	73.63	52.85
SEPT. 19th TO SEPT. 26th	38.32	39.86
SEPT. 26th TO OCT. 3rd	202.10	52.79
OCT. 3rd TO OCT. 10th	135.61	53.24
OCT. 10th TO OCT. 17th	104.70	43.84
OCT. 17th TO OCT. 24th	100.72	45.68
OCT. 24th TO NOV. 7th	271.61	53.60
NOV. 7th TO NOV. 14th	60.50	44.97

TABLE XVII (Con't.)
DATA FOR WEEKLY SAMPLES

DATE SAMPLE WAS COLLECTED	WT. OF SAMPLE REMOVED (MGS.)	% FREE CARBON
NOV. 14th TO NOV. 21st	71.22	42.99
NOV. 21st TO NOV. 28th	86.54	36.27
NOV. 28th TO DEC. 5th	90.00	49.30

Average % Free Carbon --- 47.34%

X SUMMARY AND CONCLUSIONS

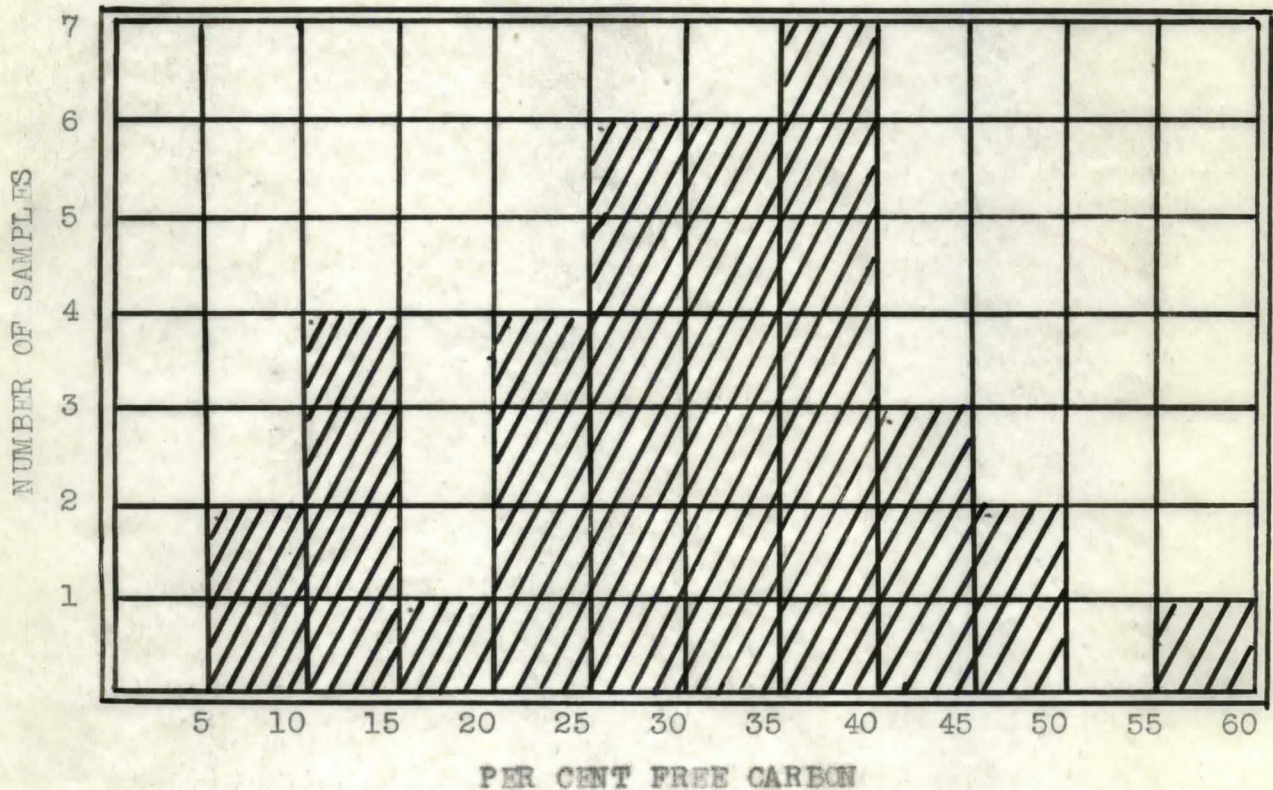
1. An analytical method, which has an absolute error of $\pm 0.5\%$, has been developed for determining free carbon in atmospheric dirt. The validity of this wet oxidation method was tested by determining the effect of nitric acid digestion on standard carbon black. Then the method was further checked against synthetic dust samples prepared from standard test materials used in the air cleaning field.

2. Thirty-seven samples that were collected with the PL-24 filters, during the first four or five months of 1949, in various urban areas, have been analyzed for free carbon, ash, mixed oxides, and silica. These samples varied widely in appearance and composition.

3. Results of the free carbon determinations, in atmospheric dirt collected by this method, varies from 7.70% (Hartford, Connecticut sample) to 55.82% (Indian Orchard, Massachusetts sample). This does not mean that Indian Orchard, Massachusetts, is the dirtiest city included in the survey. This view is taken because a dust sample represents only an area of a few blocks around the spot where it is taken.

Dust samples from industrial areas usually contained from 30 to 40 per cent free carbon.

The distribution of samples of various free carbon contents is shown in the chart below.



4. Samples taken from installations, which have the air intake on the upper floor levels, usually have a higher free carbon per cent than those taken from units having intakes at street level.

5. The developed analytical procedure for the determination of free carbon in atmospheric dust has been adapted to a semimicro scale, thereby making it pos-

sible to determine what soiling conditions are present in a given location at a given time. This adaption was accomplished by determining the effect of nitric acid digestion on small (30 to 100 mg.) pure carbon black samples and on various synthetic dust samples prepared from carbon black, silica, and wood flour. These synthetic dust samples, which were prepared in 100 and 200 mg. portions, had four different approximate compositions in order that all probable carbon compositions might be covered.

6. Daily and weekly samples were collected with electrostatic dust samplers and analyzed for free carbon content. The daily samples were collected during the month of May, whereas the weekly samples were collected from July through November of the same year (1950). The average per cent free carbon for the daily samples was 42.29%, as compared to the value of 47.34% obtained for the weekly samples. This variation is probably due to the different seasons of the year.

7. The results of these analyses show that the free carbon content of atmospheric dust varies considerably from city to city and somewhat less at different locations within a given city. It would be practically impossible to prepare dust mixtures

representative of each locality or community because of the difference of free carbon content found in atmospheric dust in various communities. These results indicate, however, that a test dust mixture should contain approximately 35% free carbon if it is to represent atmospheric dust of the majority of areas tested. Samples collected in the semi-industrial area by means of the electrostatic samplers indicate that a test dust mixture should contain 40 to 50% free carbon.

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