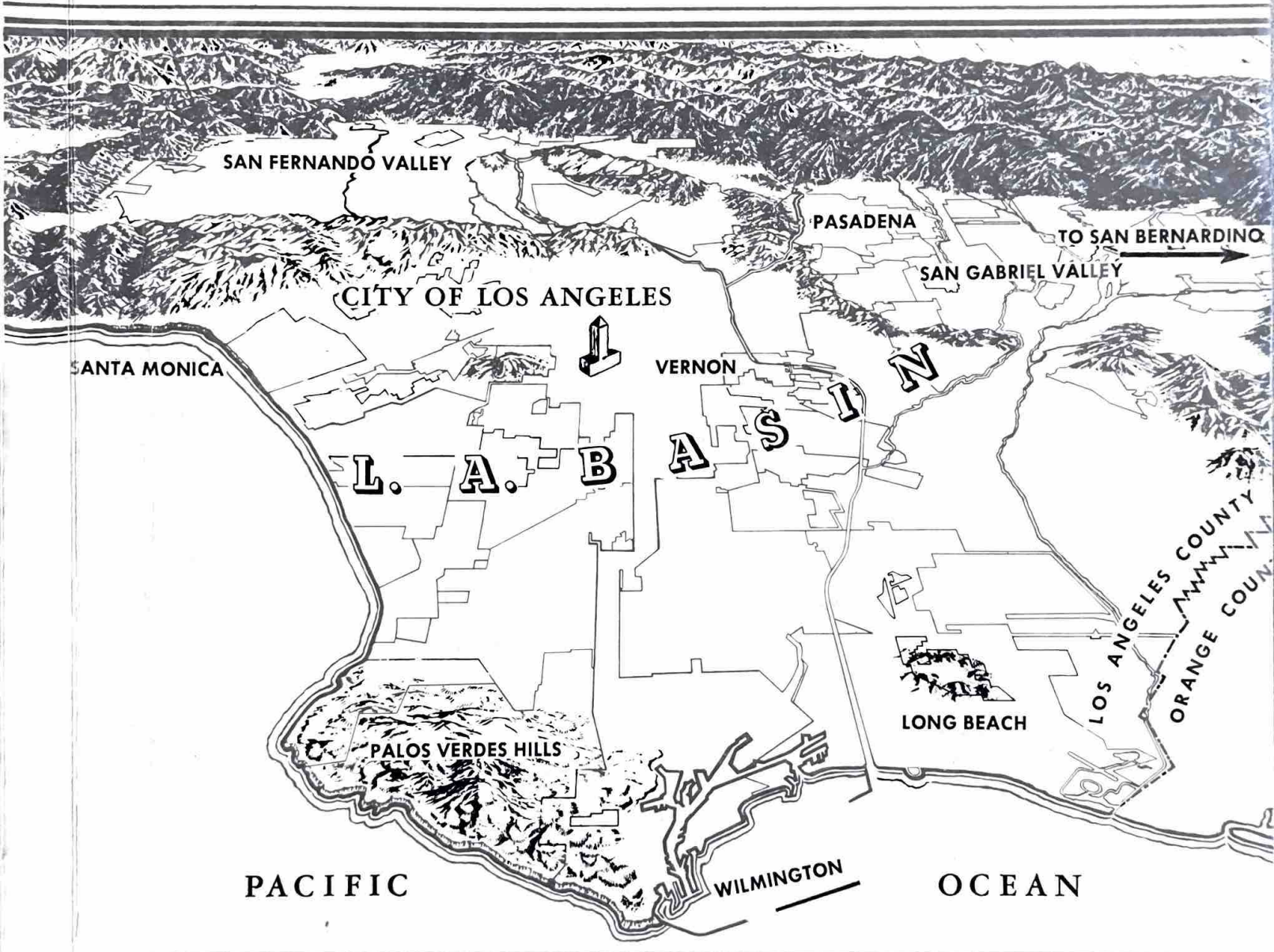


Report No. 4

FIRST TECHNICAL PROGRESS REPORT



Volume 1
Number 4

AIR POLLUTION FOUNDATION

Los Angeles, California

"Dedicated to the solution of the smog problem" REFERENCE ROOM COPY

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W. M. Keck Engineering Laboratories
California Institute of Technology

THE AIR POLLUTION FOUNDATION BELIEVES

That the answers to the smog problem will be found; that eye irritation and air pollution can be conquered; that it will take time.

That the evaluation of existing research and the conduct of new research projects will make possible the control of smog and shorten the time required for its elimination.

That impartial fact-finding, without fear or favor, is now, and will continue to be, the object of our Scientific Team.

The Foundation's Scientific Team

DR. LAUREN B. HITCHCOCK, *president and managing director*

DR. W. L. FAITH, *vice president and chief engineer*

DR. MORRIS NEIBURGER, *senior meteorologist*

DR. NICHOLAS A. RENZETTI, *senior physicist*

DR. LEWIS H. ROGERS, *senior chemist*

PROJECT APF 80-55-4

JAN 20 1969

FIRST TECHNICAL PROGRESS REPORT

Covering Work Done in 1954

Prepared by the
Scientific Staff of the

AIR POLLUTION FOUNDATION

W. L. Faith, L. B. Hitchcock, M. Neiburger,
N. A. Renzetti, L. H. Rogers

Helen G. Marcus
Editorial Assistant

March, 1955

FOREWORD

A PROGRESS report is a link in a chain of knowledge—a link between the known past and future hope. This report is based on what I believe to be a very painstaking and conscientious digest of all information available to us bearing on the Los Angeles air pollution problem as of late 1954. All of this was the work of others, which we began to collect and evaluate in February, 1954.

In addition, this report describes our own research and field work, which got underway in July and was steadily increasing through the following months. Only preliminary results from this initial, brief period are available as this is written. Even so, in conjunction with the summary of the findings of others, this report helps to bring the whole complex problem into a little better focus, to establish a better (though still inadequate) definition. When a problem can be clearly defined, it has been said that it is half solved. We are still far short of that.

Acknowledgment of the contributions of others to this report and to our first year's indoctrination here is our first duty and one we undertake with pleasure, though so many have helped directly and indirectly that it is impossible to mention them all or to attempt any fair measure of their assistance. We came here in 1954 not only as strangers to the community, but as newcomers to the field of air pollution.

The Los Angeles County Air Pollution Control District headed by Gordon P. Larson; Professor A. J. Haagen-Smit of the California Institute of Technology; Stanford Research Institute represented by Dr. Fred E. Littman, Dr. L. M. Richards, D. H. Hutchison, and Dr. A. M. Zarem; Professor Francis E. Blacet of the University of California at Los Angeles; Professor John T. Middleton of the University of California at Riverside; and Vance N. Jenkins for the Smoke and Fumes Committee of the American Petroleum Institute have given unsparingly of their time and knowledge. Dr. Arnold O. Beckman as an individual leader in air pollution work, and Dr. Ulrich B. Bray are representative of many public-spirited citizens who have assisted our Foundation group generously. The Board of Supervisors of Los Angeles County and Chief Administrative Officer Arthur J. Will have shown unfailing interest in our work and participated importantly in our program, as have A M Rawn and Francis R. Bowerman of the Sanitation Districts.

Our own Board of Trustees under the leadership of Dr. Fred D. Fagg, Jr., President of the University of Southern California, did everything conceivable during this first year to get us off to a flying start. This is not the appropriate place to recognize their individual contributions in overcoming the problems of establishing this

unique Foundation, but the Research Committee of the Board of Trustees under the chairmanship of Dr. Lee A. DuBridge, President of the California Institute of Technology, has the basic responsibility for the approval of our research projects and the appropriation of funds. Their counsel, and understanding of the uncertainties which surround the plotting of research into new territory, have been most helpful and reassuring. Their names are listed elsewhere in this report.

Between one hundred and two hundred other scientists and engineers from this country and abroad have given us freely many days of their time, individually and in conferences; they have come from the Bureau of Standards, the Bell Telephone Laboratories, The Kettering Laboratory of the University of Cincinnati, the Taft Laboratory of the U. S. Public Health Service, the Coordinating Research Council, and many others for conferences on ozone chemistry, photochemistry, hydrocarbons, motor vehicle combustion products, meteorology, and incineration and other methods of rubbish disposal. Their cooperation with us in the common cause of public

March 1, 1955

service is deeply appreciated.

The U. S. Navy is part of this community too; they converted one of their blimps from the Santa Ana base into a flying laboratory to help us collect several hundred samples of Los Angeles polluted air and meteorological data under, in, and above the inversion layer over the Basin during the 1954 Aerometric Survey. Our thanks to Commanders Peeler and McCartney and the men of the Naval Reserve!

To my associates who have done most of the work of evaluation, followed by the planning, placing, and supervising of the research projects, I can only say it has never been my good fortune to work with a finer group of scientists, nor one more devoted to the cause. Their names appear with their respective chapters. The rest of our staff, unnamed here, have done all those countless tasks well, without which these results could never have reached you.

By the end of 1955, we may not have "cracked" the problem, but I am sure we will have still more interesting results to report.

LAUREN B. HITCHCOCK

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I. INTRODUCTION

THIS Foundation exists primarily to find the facts. It believes that the evaluation of existing research and conduct of new research will make possible the control of smog and shorten the time required for its elimination. It is committed to the prompt publication of its findings and recommendations, so that the efforts of all groups and individuals may be coordinated properly, so that the public may be informed, so that government may in its discretion implement such findings and recommendations through enforcement and control measures.

The organization, purposes, and general operation of the Foundation have recently been described in the President's Report.¹

In submitting this First Technical Progress Report, an attempt is made to evaluate and summarize pertinent information collected from many sources, to describe our own projects started in 1954, and to give such preliminary findings as are possible at this time. Since the scientific staff was not completed until June, 1954, the period covered by this technical report is essentially July 1—December 31, 1954. Most of the projects are continuing actively and will eventuate in a series of more complete individual reports during 1955. The final report of the Aerometric Survey, with interpretation of results and conclusions, is due in April. In the near future, reports will appear on the Air Tracer Survey, Trends in Visibility 1930 - 1954, and Statistical Studies of the Los Angeles Basin with reference to sources of air pollution.

¹Presented November 16, 1954; copies available on request.

The principal contributions which we think the present report makes are (1) to define the Los Angeles air pollution problem so far as it is possible in our present state of knowledge; (2) to critically examine the status of our knowledge and research programs; and (3) to indicate what seem to us the most immediate goals.

The Los Angeles Air Pollution Problem in February, 1954

In early 1954 there was general scientific agreement that:

(1) Air pollution is one of the problems resulting from the growth of population and industry, whose combined miscellaneous emissions began during World War II to exceed the variable capacity of our natural ventilation, peculiarly limited in this area by local topographical and meteorological conditions, and which now exceed this capacity more and more frequently.

(2) The production of pollution is more or less constant, if not from hour to hour, at least from day to day or week to week, and growing from year to year in proportion to the expansion of the metropolitan area.

(3) The pollution acquires obnoxious characteristics called "smog" in proportion to its confinement by low temperature inversions, lack of wind, and exposure to sunlight.

(4) Smog cannot yet be identified as to its chemical or physical composition, but may be defined generally by its "fingerprints" which include at times one or more of these manifestations:

- (a) eye irritation
- (b) reduced visibility
- (c) odor
- (d) high "oxidant" value
- (e) plant damage

(5) No specific gaseous pollutant nor mixture of gaseous pollutants *in the concentrations found in our atmosphere* has been proved to be responsible for eye irritation or reduced visibility; however, typical high oxidant values have been produced in the laboratory by:

(a) irradiation of hydrocarbons when NO_2 was added, both being at experienced concentrations,

(b) irradiation of auto exhaust (which contains NO_2) at experienced concentrations and plant damage has been obtained in the laboratory by fumigating with auto exhaust and added ozone, but not with hydrocarbons and ozone, at experienced concentrations. The fact that plant damage has been obtained with hydrocarbons at concentrations as low as a few parts per million (though several times experienced concentrations), plus ozone at experienced concentrations, implicates hydrocarbons with respect to this one smog effect. Qualitative effects of eye irritation and reduced visibility have been noted, again at higher concentrations. In brief, the evidence, though circumstantial, justifies intensive studies of means for the material reduction of both hydrocarbons and auto exhaust.

(6) Smog, thus characterized, does not appear to originate *as such* from any known source.²

(7) Smog forms *from* man-made pollutants, but how may be explained so far, if at all, only in vague generalities. Thus:

Its occurrence is quite variable;

It is only roughly predictable at short range (24 to 48 hours);

²except for the synthetic rubber plant in Los Angeles operated during World War II and shut down in 1947; and except for very limited, highly localized brief emissions from some motor vehicles presumably in improper operating condition, and then only in high concentrations found close to such vehicles or in very confined spaces or tunnels.

From *which* pollutants it is formed, singly or in combination, is unknown (though partly suggested with respect to certain hydrocarbons, as will be described);

Its intensity is indicated largely by the subjective effects listed above, varying according to place, time, and pollution levels in ways understood not at all;

Eye irritation and high oxidant values are rarely, if ever, found at night.

(8) The great bulk of our air pollution consists of combustion products, including motor vehicle exhausts, stack gases from the burning of natural gas and fuel oil for heat, light, and power, and burning of rubbish; it consists of industrial emissions including hydrocarbons from the production, refining, and distribution of petroleum products, and miscellaneous dusts, gases, solvent vapors, and smokes associated primarily with manufacturing processes other than combustion.

(9) The chemical composition of these sources is at worst not known at all, and at best not reliably or fully known.

(10) The gross daily quantities of gas, oil, gasoline, and rubbish consumed have been estimated, and the daily production of pollutants therefrom calculated on the basis of available knowledge concerning the composition of specific sources. (See Tables I, II, and Fig. 1)

(11) Gross tonnages of pollutants are only a measure of contribution to air pollution; until we know which pollutants produce which smog effects, we cannot directly relate sources and tonnages to smog; it is entirely possible that certain pollutants have importance as smog-formers out of all proportion to the quantity of the sources in which they occur, or to their concentrations.

(12) The information on the concentrations of specific pollutants in the Los Angeles atmosphere, especially during periods of low temperature inversion, is generally spotty and inadequate; such data as exist for carbon monoxide, hydrocarbons, and oxides of nitrogen and sulfur agree qualitatively with values calculated from

CHAPTER I — TABLE I
DAILY EMISSIONS, COMBUSTION AND EVAPORATION — 1953*

Not including Particulates, Metallurgical Operations, CO, and Miscellaneous,
for Los Angeles County in Tons per Day

Material Burned	Tons/Day	<u>COMBUSTION</u>						Tons/Day Total Pollutants
		Ald.	NH ₃	NO ₂	SO ₂	Acids	Orgs.	
General Public:								
Gas**	8640	8.5	—	60	—	11	12	
Oil	2370	3	—	32	71	32	11	
Gasoline	14380	40	5	177	40	4	1016	
Trash	5060	9	4	1	2	2	414	
Total	30450	60.5	9	270	113	49	1453	1955
Petroleum Industry:								
Gas**	9890	11	5	75	103	13	16	
Oil	2820	3	—	38	84	38	12	
Total	12710	14	5	113	187	51	28	398
Other Industries:								
Gas**	12873	12	—	88	—	17	20	
Oil	3640	4	—	49	111	50	17	
Refuse	2500	3	0.1	2	0.2	0.6	29	
Total	19013	19	0.1	139	111.2	67.6	66	402.9
Grand Totals	62173	93.5	14.1	522	411.2	167.6	1547	2756
<u>EVAPORATION</u>								
General Public (Autos and Service Stations)						Hydrocarbons		216
Petroleum Industry						"		251***
Total, Combustion and Evaporation						"		3223

TOTAL FUELS BURNED DAILY, TONS

Gas	31403
Oil	8830
Gasoline	14380
Refuse	7560
<u>Grand Total</u>	<u>62173</u>

* *The Smog Problem in Los Angeles County*, Stanford Research Institute (January, 1954); Tables XLIV and XLVI; these figures are the best available as of April 1, 1955, but the Air Pollution Foundation has not as yet measured the composition or amounts of combustion effluents and cannot vouch for the accuracy of these data.

** Revision by Air Pollution Foundation as of December, 1954 based on data from the Southern California Gas Company for 1954.

*** Air Pollution Foundation audit as of March, 1954.

the estimated quantities emitted, assuming reasonable dispersion over the metropolitan area under the inversion height existing at the time of the measurements. However, monitoring of presumably significant pollutants has not been done in a consistent and continuous manner. There are just enough data accumulated irregularly over recent years to permit differing interpretations of the origins and movement of polluted air masses, as well as the chemical and physical reactions taking place which cause observable smog manifestations. Concentrations of aldehydes, low as they are, appear to be significantly higher than can be accounted for from all known sources. The same is true of oxidants, especially ozone.

(13) Methods of analysis and instrumentation essential to reliable measurement of small frac-

tions of a part per million of various gases, liquids, and solids are for the most part inadequate. No systematic, statistically significant techniques exist for the measurement of eye irritation or plant damage.

Scientific Conferences

That the foregoing general outline approximates the status of scientific opinion at this time is indicated not only by the consensus of published reports, but is more specifically evidenced by the minutes of conferences held in early 1954 (see Appendix). One of the first activities of the Foundation was to invite representatives of the principal scientific laboratories and agencies that had been working on the problem to meet in round-table sessions and exchange views. Participants included:

CHAPTER I — TABLE II

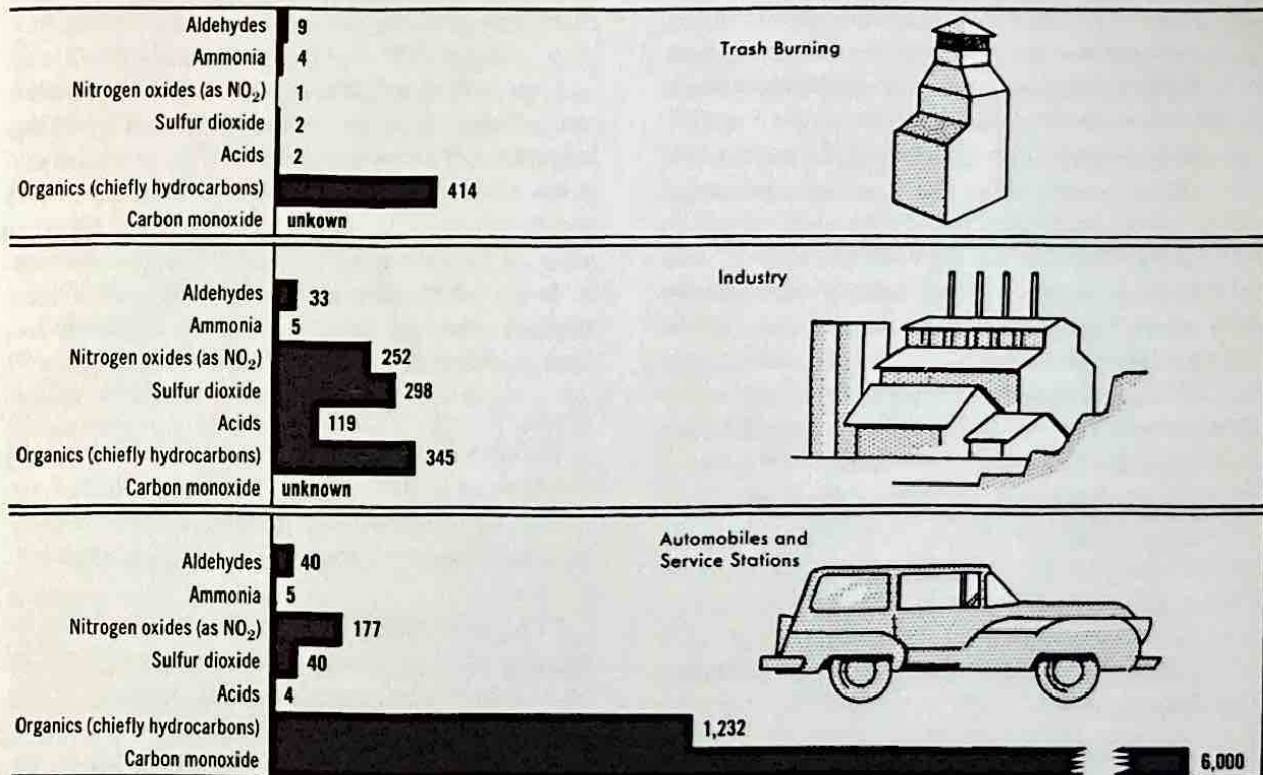
SUMMARY OF "IMPORTANT" POLLUTANTS, LOS ANGELES COUNTY — 1954*

Combustion and Evaporation Processes Only in Tons per Day

	General Public Auto & Service Stations	Other	Petroleum Industry	Other Industries	Total
Acids	4	45	51	67.6	167.6
Aldehydes	40	20	14	19	93
Olefins	26 (E)	—	16 (E)	—	42
	292	—	—	—	292
Other Organics	190 (E)	—	28	—	218
	724	437	235 (E)	66	1462
Nitrogen Oxides	177	93	113	139	522
	1453	595			
Total	2048		457	291.6	2797
E—Evaporation					

*Derived from Table I

DAILY GASEOUS EMISSIONS FROM SELECTED SOURCES
Los Angeles County—1954 (Tons per day)



Los Angeles County Air Pollution Control District: G. P. Larson, W. J. Hamming; Consultants to Air Pollution Control District: A. O. Beckman, U. B. Bray; Air Pollution Foundation: L. B. Hitchcock, L. H. Rogers; American Petroleum Institute: V. Jenkins; California Institute of Technology: A. J. Haagen-Smit; Stanford Research Institute: L. M. Richards, F. E. Littman; University of California, Los Angeles: F. E. Blacet.

Through conferences and correspondence over a period of about 60 days, the following conclusions were unanimously agreed to:

1. Hydrocarbons are present in the Los Angeles atmosphere.
2. Auto exhaust gases plus ozone, at realistic

concentrations, give plant damage.

3. Auto exhaust gases alone are not damaging, nor do they of themselves cause eye irritation at realistic concentration.
4. Petroleum hydrocarbons (whether coming directly from refineries or gasoline, or coming from auto exhaust pipes) plus reaction products of the internal-combustion engine, of themselves will not cause smog; some further oxidative process must take place.
5. Hydrocarbons, etc., in auto exhaust fumes plus NO₂ plus ozone give plant damage.
6. Some petroleum hydrocarbon unsaturates may cause eye irritation when irradiated with some oxidant.

7. We believe that at least some petroleum hydrocarbons may enter into reactions in a significant way to produce what we call "smog." There are some hydrocarbons emitted into the atmosphere along the line from the oil well up to the input of the automobile which may enter into smog-producing reactions; more specifically, certain olefins which may react with ozone.
8. Petroleum hydrocarbons and/or their derivatives produced in the internal-combustion engine may be a significant contributor to smog, but we cannot yet completely and satisfactorily establish this significance; we agree that some of the more reactive hydrocarbons and/or their derivatives may contribute to smog by a mechanism or mechanisms not yet fully understood, although much progress has been made.
9. Ozone formation appears to be sufficiently significant in the conversion of certain hydrocarbons to smog to warrant further study.
10. Some petroleum hydrocarbons may contribute to smog through some oxidative process.
11. Ozone may participate in some way not yet fully understood in the oxidative process but the evidence is still inconclusive as to whether ozone is itself a reactant or a reaction product.
12. A photochemical reaction or reactions seem to be involved in the formation of ozone and in the reaction of NO_2 and some organic materials.
13. Ozone may also be produced by a separate reaction at the same time that smog is being formed.

In addition to these conferences many others were held with scientists invited from all over the country. The extent of their agreement turned out to be much more substantial than was generally anticipated. But since the scientific workers in general had not correlated their findings to any appreciable extent and indeed seemed to have been emphasizing their points of disagree-

ment, it is not surprising that the general public had no perspective on the problem.

Actually, this scientific disagreement was typical of pioneering in a new field which we know now to be one of great complexity. The analogy was made to the three blind men who for the first time grasped different parts of an elephant, and each described a different animal. But the man in the street, at times severely annoyed by smog, was inclined to attribute the inability of the scientist to stop smog to stupidity, bias, or worse, and found little satisfaction or hope of relief in what he heard or read. Under these conditions it is not surprising that it was difficult to distinguish between fact and fancy, between numerous theories and speculative remedies.

Areas of Disagreement

Definite disagreement existed as to the extent to which available data proved that certain smog effects were caused by specific sources of specific pollutants in those sources. For example, whether:

(1) Hydrocarbons reacted photochemically in the presence of oxides of nitrogen and air to form both oxygen complexes and ozone.

(2) These oxygen complexes caused eye irritation as well as plant damage, the latter distinguishable from damage caused by ozone, or sulfur dioxide and other pollutants.

(3) Cracking of rubber by ozone and by organic peroxides or free radicals was distinguishable.

(4) Concentrations at which some smog effects were simulated in the laboratory were "realistic," or produced effects equivalent to those experienced in the Los Angeles atmosphere.

(5) Fumigations with mixtures of selected pollutants (such as selected hydrocarbons or auto exhaust) and ozone, or oxides of nitrogen and sunlight or artificial radiation, were significant. Wall effects, residence time, wave length and intensity of light source, and other experimental difficulties were typical of pioneering scientific research.

There was disagreement, consequently, not only as to the approximate magnitudes of our

principal sources of pollution, but as to their relative importance smog-wise. For example, total emissions of incinerators in the Basin were estimated variously from 90 tons per day of "harmless smoke" to 500 tons per day of ash, smoke, and largely invisible organic compounds. Particulate matter and ordinary smoke were described by some as remarkably low in Los Angeles, while others claimed it was one of the dirtier cities in the country. Again, this disagreement was due largely to the great variability in such pollutants as to time and place, and the lack of adequate data.

Dual Approach to the Air Pollution Problem

In these chapters prepared by our scientists the situation will be described substantially as it existed at the end of 1954. We approached the air pollution problem with two dominant philosophies:

(1) that certain pollutants may be largely responsible for smog effects and these substances can be identified and means found for their elimination;

(2) that all pollution is undesirable, and means must be found for reducing the amount to tolerable levels and maintaining these in a growing metropolitan area. We assume polluted air is unhealthy.

We do not know yet which approach will bring relief sooner. We doubt if anyone else does. Both are quite likely to be productive. Both require research, based on continuous study and review of all available information from all quarters. Both require development of new or greatly improved methods of analysis and control.

Identification of principal sources of pollution does not tell us how to abate them. The magnitude of motor vehicle exhaust as a contributor to modern urban air pollution has only lately begun to be appreciated. No workable control remedy has been devised so far, although the automobile manufacturers, the Coordinating Research Council, the Foundation, and others are doing everything they know to find practicable remedies at the earliest possible date.

An independent audit of hydrocarbon losses from the production and refining of petroleum

products was conducted by the Foundation, indicating as of March 1, 1954, a total of about 250 tons per day, a substantial reduction from the losses estimated two years ago. The oil industry in the Basin anticipates further significant reduction upon the completion of controls under Rule 56 by May 1, 1955. They are also working on devices for collecting vapors presently lost in filling tank trucks and controlling other emissions even though no control regulations have been issued.

But we do not have to wait until all information is in on all sources before acting. We, like others, are reporting our findings as rapidly as possible. For example, there seems to be adequate evidence that incineration of rubbish in the Los Angeles Basin creates a serious nuisance, and consensus of authorities over the country recommends discontinuance of all present-day incinerators, domestic or municipal, in view of the local conditions. But prohibition by edict must, at the same time, offer a workable alternative, so the "bury-and-cover" method is recommended in a thorough technical report just published by the Foundation.³ Copies are being furnished to all Los Angeles County and municipal officials, as well as to our contributors and others to whom it may be helpful.

Duplication of the work of either our contemporaries or our predecessors is something for which we have neither time nor money. We have too many urgent new projects waiting for manpower. *Additional* work is often necessary on an important subject which has only been opened up by prior workers.

How long it will take to find the causes and subsequent controls for our air pollution problem, and when the remedies for the principal sources will be developed, are, of course, of the greatest concern to all of us. The impatience of the public is equalled only by the impatience of the workers on the problem, whose whole satisfaction and fulfillment in life can come in no other way than by finding the solution at the earliest possible time.

³Report No. 3, "Incineration, Rubbish Disposal, and Air Pollution," January, 1955.

II. METEOROLOGICAL ASPECTS

DEFICIENCIES IN DATA AVAILABLE AS OF APRIL 1, 1954

IN order to make readily accessible existing knowledge on the meteorological conditions in the Los Angeles area as they affect the occurrence of atmospheric pollution, the Foundation commissioned the writer to prepare a summary. In collaboration with Dr. James G. Edinger the material was published as Report No. 1, "Meteorology of the Los Angeles Basin."¹

This report pointed to the need for certain types of additional meteorological investigations. In the first place, the representativeness of the wind observations was questioned. Surface wind observations were available from an extensive network of stations, but the exposure of the instruments and, in many cases, the quality of the instruments and observers were of doubtful reliability. In the case of upper air winds, measurements were made at only two points and additional stations were essential in order to complete the picture of the air flow over the Basin. It was suggested that tracer studies be carried out to check how accurately the air trajectories, i.e. the paths of polluted air, could be determined from surface wind observations.

The use of meteorological data in evaluating improvement due to control measures was discussed in the report. An example was given in which the Air Pollution Control District showed

¹M. Neiburger and J. G. Edinger, "Summary Report on Meteorology of the Los Angeles Basin With Particular Respect to the 'Smog' Problem." Air Pollution Foundation, April, 1954.

that the monthly average visibility for a given wind speed has had some tendency to increase in downtown Los Angeles since control of the emission of particulate matter was put into effect, even though the average heights of the inversion for corresponding months were stated to be approximately the same. A need was indicated for further studies of the trend in visibility during periods of increasing pollution, while testing the effectiveness of control measures.

It was pointed out that systematic measurements of pollution concentrations and effects were sorely lacking in correlating meteorological conditions and smog. In particular, the lack of controlled reports of eye irritation and plant damage prevented a quantitative estimate of smog intensity to which meteorological variables as well as chemical analyses might be related.

Based on this report and on additional discussions and conferences, the decision was made to undertake two meteorological investigations during 1954: (1) an air tracer study to test the reliability of trajectories computed from surface wind reports, and (2) an analysis of past visibility records to see how much visibility had been reduced by pollution, as well as to examine any evidence of improvement due to control measures. The decision to conduct the air tracer study and various points about the way to conduct it were greatly influenced by a conference with leading meteorologists, including among others Dr. O. G. Sutton, director of the Meteorological Service of the British Air Ministry, Dr. Harry Wexler, chief of the Scientific Services Division of the U. S. Weather Bureau, and Dr. E. Wendell Hewson, professor of meteorology at the University of Michigan.

AIR TRACER STUDY²

The design of the air tracer experiment had as its principal purpose a test of the accuracy of trajectories computed from surface winds. A secondary purpose was to see whether discrepancies, if they occurred, could be accounted for adequately on the basis of winds at upper levels, and for this purpose special upper wind stations were established at four points in addition to the regular stations at Long Beach and Burbank. The four special stations and the Air Force Station at Long Beach took winds-aloft observations every two hours during the tracer tests.

As a tracer material a fluorescent pigment, zinc-cadmium sulfide powder, was selected. This powder consists of fairly uniform-sized particles

²This work was supported by the Los Angeles County Air Pollution Control District through a research contract with the Air Pollution Foundation.

having a mean "diameter" of less than two microns, so that once dispersed into the air, they fall very slowly and move with the air currents almost as gaseous molecules (Fig. 1). They are collected on millipore filters through which the air is passed. The retained pigment particles glow under ultraviolet light with a characteristic yellow-gold color quite different from naturally occurring dust and haze particles, so that they may be distinguished and counted easily.

Wind observations appeared more likely to give a good indication of the movement of pollutants during the afternoon sea breeze than during the light, variable land breezes at night and in the early morning. It was decided, therefore, to make the tests in such a fashion as to release the tracer material early in the morning and to have the sampling network far enough away so that the tracer cloud would reach the sampling stations only after the sea breeze



CHAPTER II - FIG. 1

Courtesy of The Ralph M. Parsons Co.

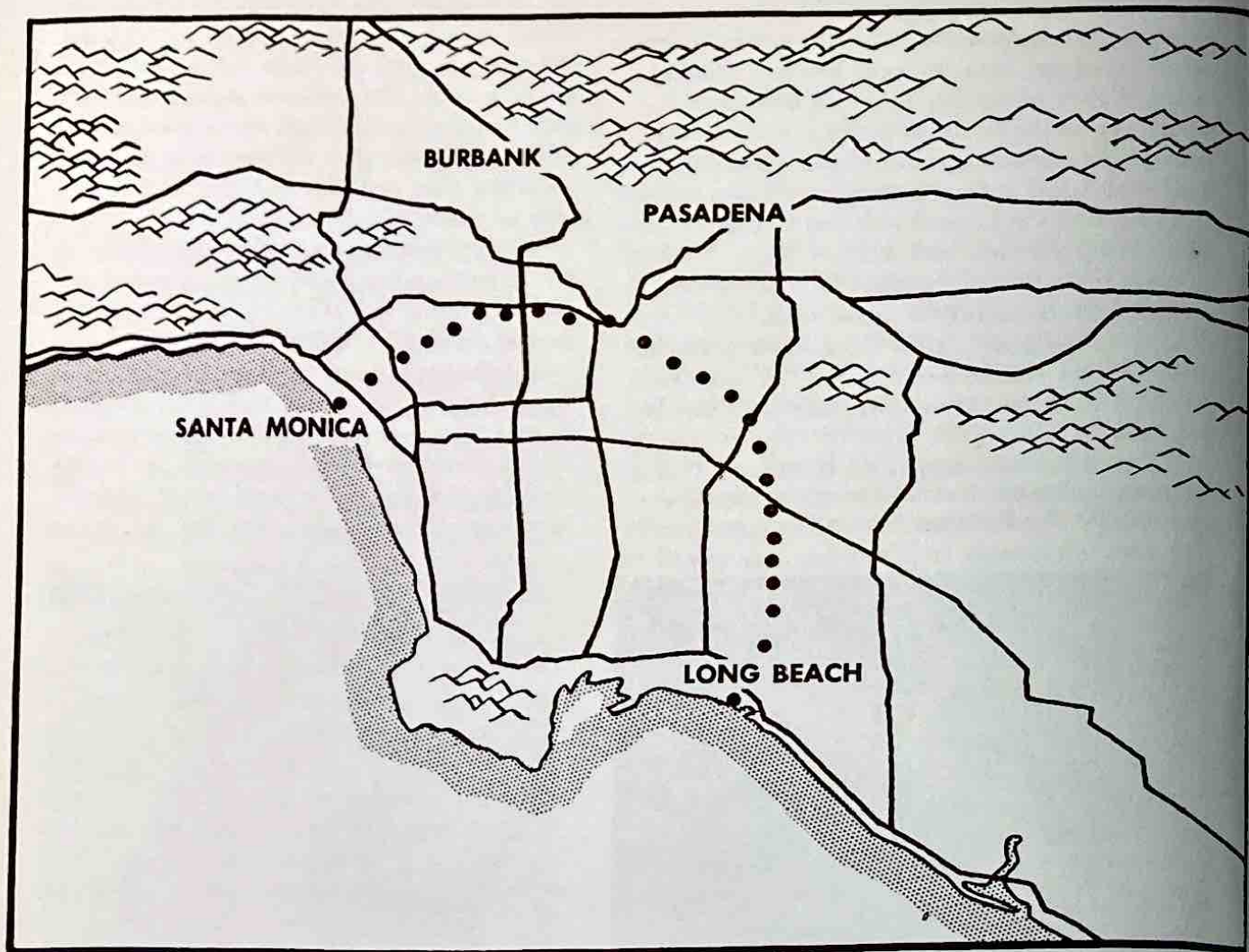
Dispersal of fluorescent particles for tracer tests



CHAPTER II - FIG. 2

Changing filter in air sampler for sampling fluorescent particles in tracer tests

CHAPTER II - FIG. 3
Air tracer sampling stations



started up. In laying out the sampling network, advantage was taken also of the normal wind pattern, with light movement from the north and east at night and moderate to fresh south to west winds during the day. The sampling stations were located on an arc extending eastward and southward from Venice through downtown Los Angeles to Seal Beach (see Fig. 2), and the dispersing station (Fig. 3) was located in Torrance near the center of the arc.

The dispersal and sampling was carried out by The Ralph M. Parsons Co., with personnel provided by the Los Angeles County Air Pol-

lution Control District to man the sampling stations.

The dispersal took place during one hour, and it was computed that the cloud would spread during the movement to the sampling network into a volume about six miles in diameter extending from the ground to the inversion base.

It was decided that five or six tests should provide a sample of enough meteorologically different situations for an adequate indication of the extent to which the trajectories computed from wind observations represent the path traveled by pollutants.

As is the case in many such experiments, the behavior of the experiment varied considerably from expectations. Modifications were made in an effort to improve the results as the series of

trials progressed, and whether or not it was due to these changes, the last two tests resulted in particle counts of the order anticipated, whereas in the first four the counts were very much smaller.

CHAPTER II - TABLE I

Operational Conditions during Tracer Tests

Test No.	1	2	3	4	5	6
Date	8/4	8/18	8/31	9/3	9/21	10/15
Inversion Base Heights (ft.) 1900 PST Prev. Day					280	
" 0100 PST	2550	80	Sfc	Sfc		Sfc
" 0700 PST	4200	1850	600	1600	950	390
" 1300 PST	2650	1450	1100	920		950
" 1900 PST	2800	1100	340	885	Sfc	Sfc
Place of Dispersal	Shell Chem. Co.	Shell Chem. Co.	Shell Chem. Co.	Shell Chem. Co.	Compton Airport	Compton Airport
Height of Dispersal above Ground, ft.	15	45	45	45	25	25
Time of Dispersal	0300-0400	0300-0400	0300-0400	0415-0515	0500-0600	0500-0600
Weather at Dispersal	Cloudy	Clear	Clear	Dense Fog	Moderately Dense fog	
Visibility at Dispersal	Good					
Wind at Dispersal	SE		ESE-E 3-6 NE-N 2-1	E-N 1.5-2.5 mph	NNW-N 1-2 mph	WNW-NW 2-4 mph
Amt. of F.P. Dispersed (grams)	1200	2400	2400	3000	2400	2400

Summary of Sampling Results in Tracer Tests

Test No.	1	2	3	4	5	6	
	Outer	Outer	Outer	Outer	Outer	Inner	Outer*
Sampling Network	Outer	Outer	Outer	Outer	Outer	Inner	Outer*
Period of Sampling PST	06-16	06-16	06-16	06-16	06-16	05-13	06-16
Sampling Rate (liters/hr)	600	600	600	600	600	600	600
Maximum Particle Count	10	11	104	7	2848	70512	315
Stations with Significant Counts (5 particles or more)	1+2	1-5	1	12+13	16-23	33-36+38	15-25
Stations Expected from Surface Trajectories computed by Vance	1+2	1-11	1-3	23-25	14-18	34-38	17
Above Computed by Graham		1-12	1-3	14-16	23-25	35-38	17-21
Above Computed by Neiburger						32-36	15-17
Stations Expected from Trajectories Surface and Aloft with Mixing between Levels	1+2	1-15	1-3	5-25	13-25	34-38	17-25
Observed Time of Significant Counts (PST)	07-08	08-12	07-08	12-13	09-12	05-11	07-13
Time Computed from Surface Trajectories by Vance	08-09	11-13	09-12	11	13-14	07-12	13-14
Time Computed from Surface Trajectories by Graham	08-09	11-14	08-11	13-14	09-10	06-12	12-13
Time Computed from Surface Trajectories by Neiburger						07-12	13
Time Computed from Mixed Trajectories	06-09	08-14	09-12	10-14	10-14		11-15

*Odd numbered stations only.

In the sixth test, in addition to the outer sampling net, an inner circle of sampling stations with a radius of four miles was established.

Table I gives a summary of the operational conditions during the tests, and Table II gives the sampling results, comparing them with the results expected from the trajectory computations. Table III gives more details concerning the stations and hours at which the highest numbers of particles were found in each test. In the case of Test No. 6, there was double maximum at both the inner and outer sampling station circles.

Surface wind trajectories were computed for all the tests independently by William Vance, a UCLA meteorology student with considerable experience in the Air Force weather service, and by Roderick D. Graham, research forecaster for the United States Weather Bureau. In addition, for Test No. 6, the writer computed a surface trajectory. Besides the surface trajectories, Mr. Vance computed the trajectories of the air moving at 500 ft., 1000 ft., etc., up to the base of the inversion in each case, and also the development of the cloud on the assumption that at each point the air was mixed vertically from the ground to the inversion base. All trajectories were com-

puted with no knowledge of the sampling results. As an example, the surface trajectories for Tests 2 and 5 are shown in Fig. 4. Sampling stations which had filter counts greater than four particles in any hour are enclosed in shaded areas.

It will be seen from Table II and Fig. 4 that the surface wind trajectories are generally consistent with each other and give a reasonable approximation of the region where the fluorescent particles were found, but in some cases (Tests 4 and 5) the trajectories computed by the two analysts were rather far apart, and in almost every case the times at which the particles were observed were earlier than the computed times. In general, the computation assuming mixing at all levels resulted in movement which carried the fluorescent cloud to all stations where they were actually observed, but in addition to many other stations where no particle count was observed. The hypothesis of this mode of development and movement of the cloud of tracer material predicted times of cloud arrival at the stations closer to those observed than the trajectories using surface winds alone.

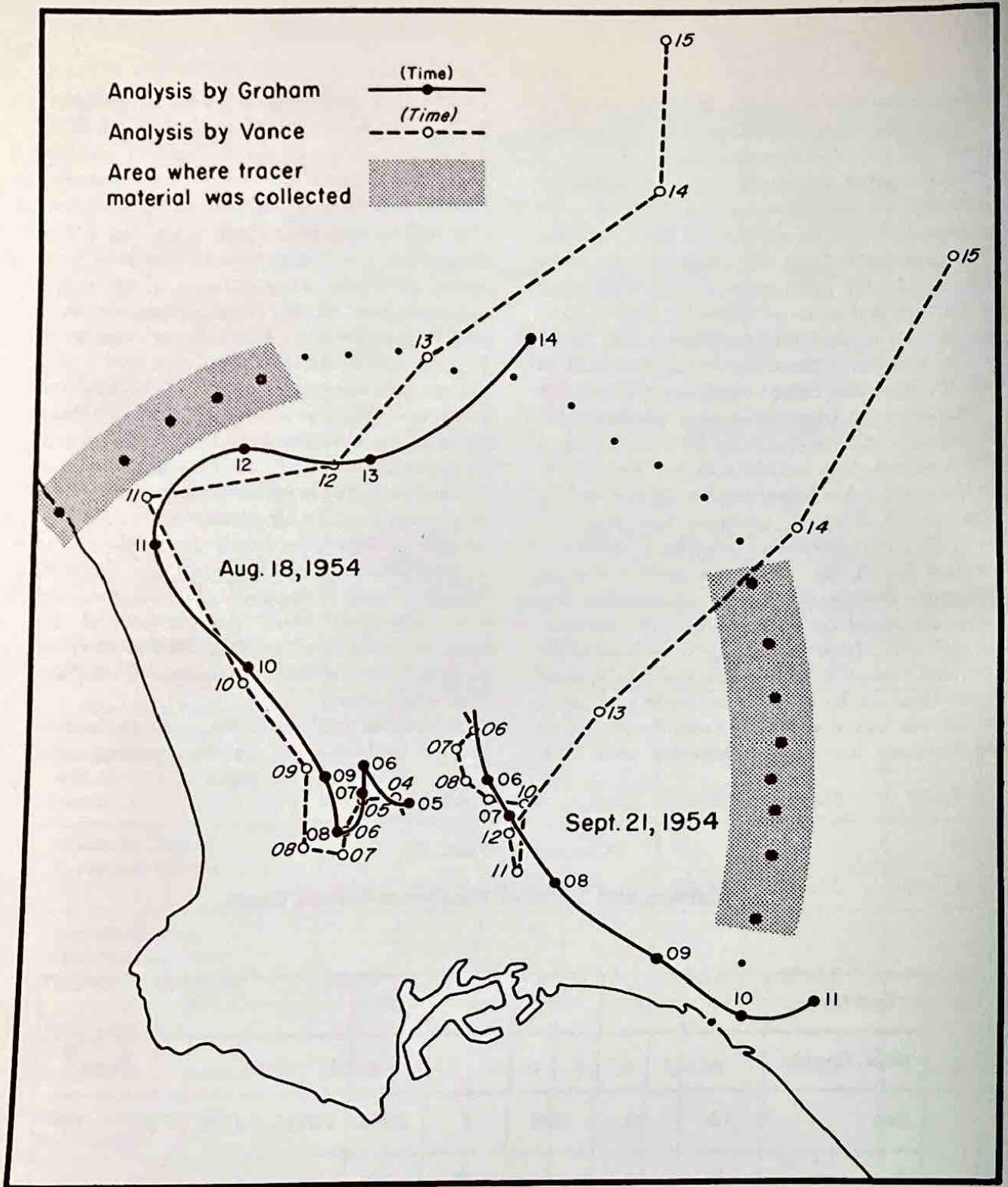
A detailed analysis of the results is reserved for the final report of the tracer project, which

CHAPTER II - TABLE III

Stations and Times of Maximum Particle Count

Test No.	1	2	3	4	5	6			
Max. Count.						Inner		Outer *	
No.	10	11	104	7	2848	70512	4773	315	157
Sta.	1	4	1	12	18	36	36	23	15
Time	07-08	10-11	07-08	12-13	10-11	06-07	08-09	07-08	11-12

*Odd numbered stations only.



CHAPTER II — FIG. 4
 Computed trajectories in tracer tests 2 and 5

is now being prepared. For the present, the following tentative conclusions may be put forward:

(1) Trajectories from the surface winds computed independently by different analysts are usually nearly the same, but may differ markedly. This difference appears due to the existence of gaps in the wind station network, which permit varying interpolations of the wind pattern, particularly during a period of light winds.

(2) The trajectories computed from the surface winds are usually good indications of the general area of movement of the air, but may in some cases be fairly far from the real movement shown by the tracer material.

(3) The surface trajectories almost invariably indicate slower movement of the air than shown by the tracer material.

(4) The combination of surface and upper winds leads to an improvement in the areal designation, but also indicates too great a dispersion of the cloud; it leads to improvement of the speed of movement of the forward edge of the cloud, but also to too great a duration of cloud passage.

In summary, the tracer tests indicate that a fair amount of reliance may be placed on the surface wind trajectories, but that allowance must be made for errors with respect to timing. Since the errors appear to be present even when the inversion is low, it seems that variation of wind with height is not the only factor. Two measures seem desirable in seeking improvement: (1) certain large gaps in the surface wind station network should be filled by establishing new stations; and (2) the whole network should be calibrated by exposing standard wind instruments for a period of about one week at each of the stations, and a routine for checking and servicing the stations should be established. In addition, there is enough indication of the influence of upper winds to call for the establishment of additional upper wind stations for the purpose of micrometeorological and pollution studies.

STUDY OF VISIBILITY TREND

Systematic observations of visibility began only with the development of commercial aviation about 1930 and until very recently depended entirely on subjective estimates. The observer ascends to a place with a relatively unobstructed horizon and attempts to determine visually which of several pre-selected conspicuous structures he can just see well enough to recognize. This type of measurement varies somewhat from observer to observer, but the main differences in external conditions will be evident. Thus, if the statement were true that years ago Catalina Island was visible from Los Angeles every day both summer and winter, the early visibility records would show this fact.

In addition to the influence different observers might have on the records, conclusions from comparison of the visibility records from year to year are rendered difficult because visibility is influenced by many meteorological factors in addition to the increase in sources of pollution. Among them are inversion height and wind speed, which reflect the volume of air into which the pollution is diluted; wind direction, which indicates what pollution sources may have contributed to reducing the visibility; the general weather pattern which prevails; and the relative humidity, which indicates to what extent liquid water may have condensed on the particles present. In addition to these factors, there are the general flow pattern and the air mass structure, reflecting the source region and history of modification of the air as it has approached the area from long distances. In general, Los Angeles visibility is better in polar than in tropical air, in continental than in maritime air masses.

Measurements of the inversion height and other aspects of the upper air structure have been made for only a relatively small part of the period of visibility records. Correlation or sorting by general flow pattern would require development of typing procedures and the examination of the daily weather maps for the more than twenty years of record. It was decided there-

fore to attempt only to separate the observations according to locally measured factors, with the expectation or hope that the effects of the others would average out.

Of the factors which influence visibility, relative humidity and wind direction were selected as the two which might be most influential.

The stations in the Los Angeles Basin at which long visibility records are available are Burbank, International Airport, and downtown Los Angeles. Of these, the downtown station provides both the longest homogeneous record and the

one most likely to reflect the effect of pollution. It suffers from the fact that the measurements were made on top of high office buildings, and thus do not give a good indication of the variations at street level.

The procedure used in the visibility study consisted of tabulating the observations at 4:30 a.m., 12 noon and 4:30 p.m. PST, and turning them over to the service department of International Business Machines, Inc., where they were punched on cards, sorted, and tabulated according to humidity and wind direction groups.

CHAPTER II — TABLE IV

Noon

Relative Humidity 41% - 70%

Percentage of Observations with Visibility less than 3 Miles						
Years	Wind Direction Group 2 ESE - S			Wind Direction Group 3 SSW - W		
	Jan-Feb Nov-Dec	March- June	July- Oct	Jan-Feb Nov-Dec	March- June	July- Oct
1933-1935	33	24	43	25	13	27
1936-1939	24	26	22	34	11	15
1940-1943	26	28	39	6	20	31
1944-1947	22	37	65	40	22	43
1948-1951	30	25	36	57	17	28
1952-1954	21*	25	49	20*	20	36

Percentage of Observations with Visibility more than 12 Miles						
Years	Wind Direction Group 2 ESE - S			Wind Direction Group 3 SSW - W		
	Jan-Feb Nov-Dec	March- June	July- Oct	Jan-Feb Nov-Dec	March- June	July- Oct
1933-1935	21	18	11	19	35	8
1936-1939	24	14	11	37	29	12
1940-1943	30	20	10	62	22	9
1944-1947	12	10	2	26	18	7
1948-1951	23	13	4	26	22	5
1952-1954	20*	21	3	44*	22	1

*Excluding December, 1954

The relative humidity groups used were (1) 1%-40%, (2) 41%-70%, (3) 71%-90%, (4) 91%-100%. The wind direction groups were (1) north-northeast to east, (2) east-southeast to south, (3) south-southwest to west, (4) west-northwest to north, (5) calm (speed less than 1.5 miles an hour). Observations with current precipitation were eliminated. In order to have a sufficient number of observations for a particular humidity and wind direction group, the data for groups of three or four years were lumped together. Altogether six such groups were used, covering the period 1933 to 1954.

Table IV gives an example of the type of results which can be obtained—the percentage of noon observations with visibility less than three miles and more than twelve miles, for relative humidity group 2 and wind direction groups 2 and 3.

It will be seen in the Table that, except for the winter season, the period 1944-1947 had a larger percentage of days with noon visibility less than three miles than any other period, as seen particularly in the July-October columns. This may be due to the fact that these months are the ones when the subsidence inversion is almost always present and is lowest, so that the influence of pollution is felt the most. The larger percentage of low visibilities for wind direction group 2 than for wind direction group 3 may reflect the distribution of heavy industry to the southeast of downtown Los Angeles.

The decrease in percentage of days with visibility less than three miles after 1947 suggests that the measures adopted to control the emission of particulates were effective.

Failure of the winter data for wind direction group 2 to show the same pattern as for the other seasons may indicate that in the unstable air masses of that season pollution is so rapidly diffused upward that it is not a major factor in the visibility variation.

In summer, noon visibilities greater than twelve miles occurred less than 12% of the time with these humidities and wind directions, even

in the early 1930's when smog and its eye-irritating and plant-damaging effects were unheard of. At least for the summer period, and to some extent in other months, there has been a fairly consistent decrease through the years. In the case of high visibilities, the introduction of control measures in 1947 seems to have had no effect in stemming the decrease in the frequency of their occurrence.

As in the case of the tracer study, full presentation of these data and their discussion must be reserved for the separate report on the visibility study, now being prepared.

EVALUATION OF SPECULATIONS TO ELIMINATE SMOG BY METEOROLOGICAL EFFECTS

The meteorological staff of the Foundation has examined several proposals for the removal of smog by altering the temperature structure or flow pattern of the air over the Basin. In general, although several ingenious proposals have been put forward, we found that such proposals invariably ignore the vast amount of energy required to accomplish these purposes. There have also been suggestions that a search be made for some effect which will trigger natural forces adequate to achieve them. Until there is some indication that natural forces exist in latently unstable equilibrium, it remains the impression of the Foundation staff that such a search is not deserving of the investment of time and money. All the presently available meteorological information emphasizes the great stability of the situation.

As an example of the tremendous amounts of energy involved, the following computation may be of interest. It has been frequently suggested that a line of giant windmills be installed to blow the smog away. Neglecting the effect of the confining mountains, the opposing pressure forces which would be set up the moment the air began to move, or the turbulence which would be

created, we computed the amount of energy required to maintain a wind against ground friction over the area (4000 km²) of the Los Angeles Basin.

The energy required is proportional to the cube of the velocity, the constant of proportionality depending on the roughness of the terrain. If the entire Los Angeles area were as smooth as a golf green, it would require about 400,000 kilowatts or 535,000 horse power to maintain a wind of 4½ miles per hour, and 3,200,000 kilowatts or 4,300,000 horse power to maintain a wind of nine miles per hour against surface friction. For the actual character of the terrain it seems reasonable to assume a roughness factor at least five times that for a close-cropped lawn. Thus, we have for the minimum likely values 2,000,000 kw (2,700,000 HP) for the 4½ mile-per-hour wind, and 16,000,000 kw (21,500,000 HP) for the 9 mile-per-hour wind.

Interpreted in terms of 5,000 HP engines operating fans at 100% efficiency in producing translational motion, at least 540 fans would be required to maintain a 4½ mile-per-hour wind, or 4,300 fans for a 9 mile-per-hour wind. An appreciation of the amount of energy involved can be had by comparison with the total installed capacity of electric generating plants in the United States, which was 82,000,000 kw at the end of 1952. Thus a minimum of 2½% of the total capacity of the U. S. would be required for maintaining a 4½ mile-per-hour wind, and 20% of it would be needed for maintaining a 9 mile-per-hour wind.

As stated earlier, this computation ignores the effects of confining mountains, opposing pressure forces, and turbulence generated by the fans. Since the energy requirement is prohibitively great even when these effects are neglected, no computation was undertaken with them taken into account.

FUTURE RESEARCH

(1) Of top priority in future meteorological investigations is the calibration of the existing

network of wind stations, which was discussed briefly in the section on the tracer study. The tracer study indicated that the movement of air pollution over the Basin is faster than that indicated by the surface winds. While this may be to some extent due to its being carried at higher levels and mixed downward, there is evidence that in large part it is due to deficiencies of the wind speed measurements, particularly for low speeds.

It was learned that the Los Angeles County Air Pollution Control District, under whose efforts the network was established, has no program of checking or servicing the instruments. The monitoring is done only to call attention of the cooperating agency to any indication in the data that the equipment is not functioning properly. Since the plotting and analysis of the data by the APCD usually takes several months, these obvious defects can pass unnoticed for long periods. The Foundation will propose that the APCD establish a program of routine maintenance and service.

The Foundation intends to propose that four standard sensitive anemometers be purchased and operated for a week at each of the existing wind stations. In the course of a week, the variations of wind will enable comparison of the station observations with accurate wind measurements. The speeds at which the station anemometer and wind vane first begin to respond and a correction for all normally occurring wind speeds will be established. In the course of three or four months such comparisons can be made at all stations in the network.

(2) A second meteorological project which has been proposed, and may be carried out in the Department of Meteorology at the University of California at Los Angeles, is a study of the feasibility of computing wind trajectories on high-speed digital computing machines. For the interpretation of the measurements made in the Aerometric Survey (see Chapter V), it is desirable to compute thousands of trajectories. Computation of these by traditional methods would involve a tremendous expenditure of time

by skilled personnel. It is hoped that methods can be devised which will enable their computation by machine in much less time and with much less expense.

(3) Another meteorological project, which has been proposed for the Department of Meteorology at the University of California at Los Angeles, is entitled "Pollution Concentrations from Area Sources in the Los Angeles Basin." It is planned to assume reasonable models for the distribution of pollution source intensity as a function of space and time and to compute the resulting concentrations as a function of space and time, using observed patterns of wind and other meteorological data.

Both the above projects are dependent on ap-

propriation of funds to the University by the State Legislature, or alternately on equivalent support from the National Science Foundation or other federal agencies.

(4) As part of the Aerometric Survey for 1955, it is planned to take temperature soundings by captive balloon at stations near downtown Los Angeles and in Pasadena. These, together with the regular radiosonde observations taken four times a day at Long Beach, will give information concerning the variation in height of the inversion over the Basin. This information will be valuable in interpreting the chemical, plant damage, and eye irritation data, as well as giving additional valuable meteorological statistics.

III. CHEMICAL ASPECTS

INTRODUCTION

THERE is reasonable agreement among workers on the air pollution problem in Los Angeles that a photochemical oxidation process is responsible for the plant-damaging and eye-irritating characteristics of Los Angeles smog. However, because of the extremely low concentration of most of the substances involved and the complex mixture of pollutants that arise from a rapidly growing industrialized area, the experimental problem of duplicating these reactions in the laboratory is quite formidable.

The reactants, with the possible exception of oxygen, are present in amounts no larger than

one part per million parts of air. This has a profound effect on reaction rates.

There is uncertainty as to the starting compounds, intermediate and end products, mechanism and rates of reactions, and the intensity and wave lengths of light which produce the reactions.

Further study of these problems is imperative. Any solution to the smog problem should have as its goal a maximum allowable concentration of the reacting substances. Furthermore, the evaluation of possible control measures such as a "blocking" reaction, or increasing the rate of degradation of the smog-causing intermediates, or including a harmless side reaction, can only be carried out after the nature of the reactions is understood.

The work being carried on in this program includes a critical review of the literature of atmospheric chemistry, studies of smog-forming reactions using the Los Angeles atmosphere, and studies of photochemical reactions in the laboratory using synthetic gas mixtures.

REVIEW OF LITERATURE

A critical examination of the literature of atmospheric chemistry has been undertaken by Professor Philip A. Leighton and Professor William A. Perkins, both of the Chemistry Department at Stanford University. It is planned not only to evaluate critically the available published reports but also to discuss with the research workers their latest and unpublished findings.

At present, all available reports are being collected and digested. A compilation has been made of several dozen possible reactions of oxides of nitrogen, and the most probable reactions are being determined. This project is expected to take an additional six months or more.

SMOG-FORMING REACTIONS SCRUBBING EXPERIMENTS

This project is concerned with the mechanism of formation of smog utilizing the Los Angeles atmosphere directly, subjecting it to various treatments including the addition of ozone, irradiation with controlled intensity and wave lengths, and the subtraction of materials by scrubbing the air with various reagents. The contractor on this project is Stanford Research Institute.

From an experimental point of view, the problem resolves itself into the controlled formation of smog by reacting polluted but non-smoggy air with oxidizing agents such as ozone or the oxides of nitrogen under conditions comparable in time and concentration to those encountered in the atmosphere. There are two possible sources of polluted, non-smoggy air: (1) night air, or (2) daytime air treated to remove the plant-damag-

ing agents without altering its composition otherwise. It has been shown previously that this may be possible by filtration of the air through a bed of crumbled foam rubber which removes ozone and the phytotoxic agents but not the organics. Ozone may then be added to polluted air in concentrations comparable to those found in the atmosphere, permitted to react for a period of time ranging from a few minutes to several hours, and the air can then be examined for smog. Ozone will also be formed *in situ* by irradiation of polluted air to determine if smog develops. Once the techniques of controlled formation of smog are available, constituents can be removed selectively to determine their effect on smog formation.

From this account some fundamental experimental problems become evident. The first is an analytical one, for it will be necessary to know when smog has been formed and to get a measure of its activity. Since smog is defined by its plant-damaging, eye-irritating, and visibility-reducing properties, these criteria will have to be applied. Of these, plant damage is experimentally the most easily accessible one, and indicator plants will be used as a criterion of smog formation. Once the experimental conditions are sufficiently narrowed, eye irritation studies will be incorporated. Measurements of visibility will supplement the other techniques.

The use of indicator plants for the detection of smog has been described previously.¹ As always, when dealing with biological assays, elaborate precautions have to be taken in order to obtain meaningful and reproducible results. As many variables as possible have to be controlled in the growing of plants to assure uniform material: temperature, relative humidity, light, composition of the nutrient solution, age of the test plants, and the particular variety of plants used.

Two rooms for the growing of plants under carefully controlled conditions have been con-

¹Haagen-Smit, A. J., Darley, E. F., Zaitlin, M., Hull, H., and Noble, W. "Investigation on Injury to Plants from Air Pollution in the Los Angeles Area." *Plant Physiology* 27, 18-34 (Jan., 1952).

structed. These rooms provide control of light, temperature, moisture, filtration of outside air through charcoal filters, and careful control of the plant nutrient solution. In addition, a reaction chamber has been constructed of glass-lined steel of 500-cubic-foot capacity together with the necessary blowers, ducts, flow meters, and other control devices. Also two smaller exposure chambers of about ten cubic feet have been constructed from plate glass. These chambers are provided with adequate light, so that plants which are being exposed to various atmospheres will be growing under conditions which approximate daylight.

Several different varieties of the plants are being grown: pinto beans, *Poa annua*, spinach, and romaine lettuce. The results of a typical experiment, using statistical test planning, appear in Table I. In this experiment ozone was added to carbon-filtered night air to give an oxidant concentration of 25 pphm. Three species of plants of identical age were fumigated; plant damage was experienced by all three.

CHAPTER III — TABLE I

PLANT FUMIGATION WITH OZONE AND CARBON-FILTERED AIR

Time of fumigation:	5:00 P.M.—8:00 A.M.
Oxidant level in fumigation chamber:	25 pphm
Residence time of ozone and carbon-filtered air mixture before entering fumigation chamber:	1 min.

Species fumigated	Total No. of plants fumigated	Total No. of leaves on fumigated plants	Mean % of leaf area damage
Romaine lettuce	38	228	8
Spinach	12	72	47
<i>Poa annua</i>	62	312	12

Eight mercury arc lights have been installed on the outside of the 500-cubic-foot reaction chamber. With these eight lamps in operation, intensity of illumination at the center of the

chamber was approximately one-third the intensity of noon illumination from the sun. With this intensity, oxidant values of 5 to 7 parts per hundred million were obtained using night air. Simultaneously, using outside air and a different experimental setup in which the intensity of artificial irradiation was approximately ten times that of noon sun, oxidant values of approximately 20 parts per hundred million were produced. Plants exposed to the air, which had been irradiated, showed no smog damage, even though it was known that the intensity of irradiation was not adequate to produce the maximum oxidant value of which it was capable. Additional mercury arc lights are now being installed.

Future Work

Irradiation of night air with appropriate intensity of light and exposure of plants will be undertaken, together with eye irritation studies and measurements of visibility. If the results from these studies indicate that smog manifestations are produced, the next phase of the program, selective removal of various constituents, will be undertaken.

PHOTOCHEMICAL REACTIONS

This project studies the mechanism of reaction between synthetic atmosphere under the influence of controlled radiation both as to intensity and wave length. The contractor is Armour Research Foundation, Chicago, Illinois.

It has been determined by a number of workers that the principal chemical characteristics of Los Angeles smog is the presence of extremely high oxidant concentrations during periods of high pollutant intensity. In an attempt both to duplicate the lachrymatory effects of smog and to identify a possible source of the oxidant, Haagen-Smit and his co-workers² investigated the photochemical reactions of a series of synthetic mixtures of nitrogen dioxide and hydrocarbons in both air and oxygen car-

²Haagen-Smit, A. J., and Fox, M. M., "Photochemical Ozone Formation with Hydrocarbons and Automobile Exhaust," *Air Repair*, 4, No. 3 (November, 1954).

riers. In these systems, the oxidant was produced photochemically; the yield was extremely dependent on the hydrocarbon-nitrogen dioxide concentrations. Hydrocarbons containing four or more carbon atoms per molecule were found to have oxidant-forming tendencies when irradiated in the presence of nitrogen dioxide.

The most complete study made by Haagen-Smit was on the nitrogen dioxide-3-methyl-heptane system, with the resultant preparation of a three dimensional curve showing the interrelations between the reactant concentrations and resultant oxidant level. In this latter system, for example, the choice of 0.4 ppm nitrogen dioxide with 10 ppm 3-methyl heptane resulted in appreciable rubber cracking under the selected experimental conditions. However, if the hydrocarbon concentration chosen was zero or greater than one hundred ppm, no rubber cracking was observed under his experimental conditions. Other workers (unpublished work) repeated some of Haagen-Smit's work with respect to reactant concentrations but with different irradiation conditions and found that cracking occurred at 1170 ppm 3-methyl heptane in filtered air in the pres-

ence of 0.4 ppm nitrogen dioxide and also that cracking occurred in nitrogen dioxide alone.

It is important to resolve these and other discrepancies. The differences in the results mentioned may be due to the differences in wavelength distribution and intensity used in the radiation.

This project is in its construction phases. The ozone generator and the associated analytical gas train have been fabricated and are in operation. The photolysis system is nearly complete. The reactant chambers, dilution bulbs, gas inlet system, and the photolysis bulb are assembled. Other items, including a long absorption cell for observing ozone formation *in situ*, using its ultraviolet absorption band, the light system for the photolysis source, and electronic equipment are being assembled.

Future Work

When construction is complete, the nitrogen dioxide-hydrocarbon-irradiation system will be investigated under carefully fixed conditions of wave length, light intensity, and irradiation time to determine the important reaction parameters.

IV. STUDY OF COMBUSTION PRODUCTS

THE various gaseous pollutants entering the Los Angeles atmosphere result primarily from the combustion of organic material, e.g. gasoline, fuel oil, natural gas, and refuse. A great deal of the particulate matter (smoke) arises from the same sources. The other source of gaseous pollutants is evaporation of volatile solvents such as gasoline, paint solvents, and dry-cleaning fluids.

The exact contribution of the different pollutants to smog manifestations is not known. The Foundation has therefore initiated several research projects directed toward determining the relative importance of various components of combustion effluents in the formation of smog. Such information will be invaluable in the development of adequate control methods.

Data available at the time of the formation of the Foundation have been assembled and analyzed in Report No. 2¹ of the Foundation. On the basis of the report, further work was planned to reconcile differences among various investigators and to extend our knowledge of the field.

COMPOSITION OF AUTO EXHAUST MIDWEST RESEARCH INSTITUTE KANSAS CITY, MISSOURI

Background

Investigators have been able to produce smog damage to plants by subjecting them to the re-

¹Faith, W. L., "Combustion and Smog," *Air Pollution Foundation, Report No. 2*, September, 1954.

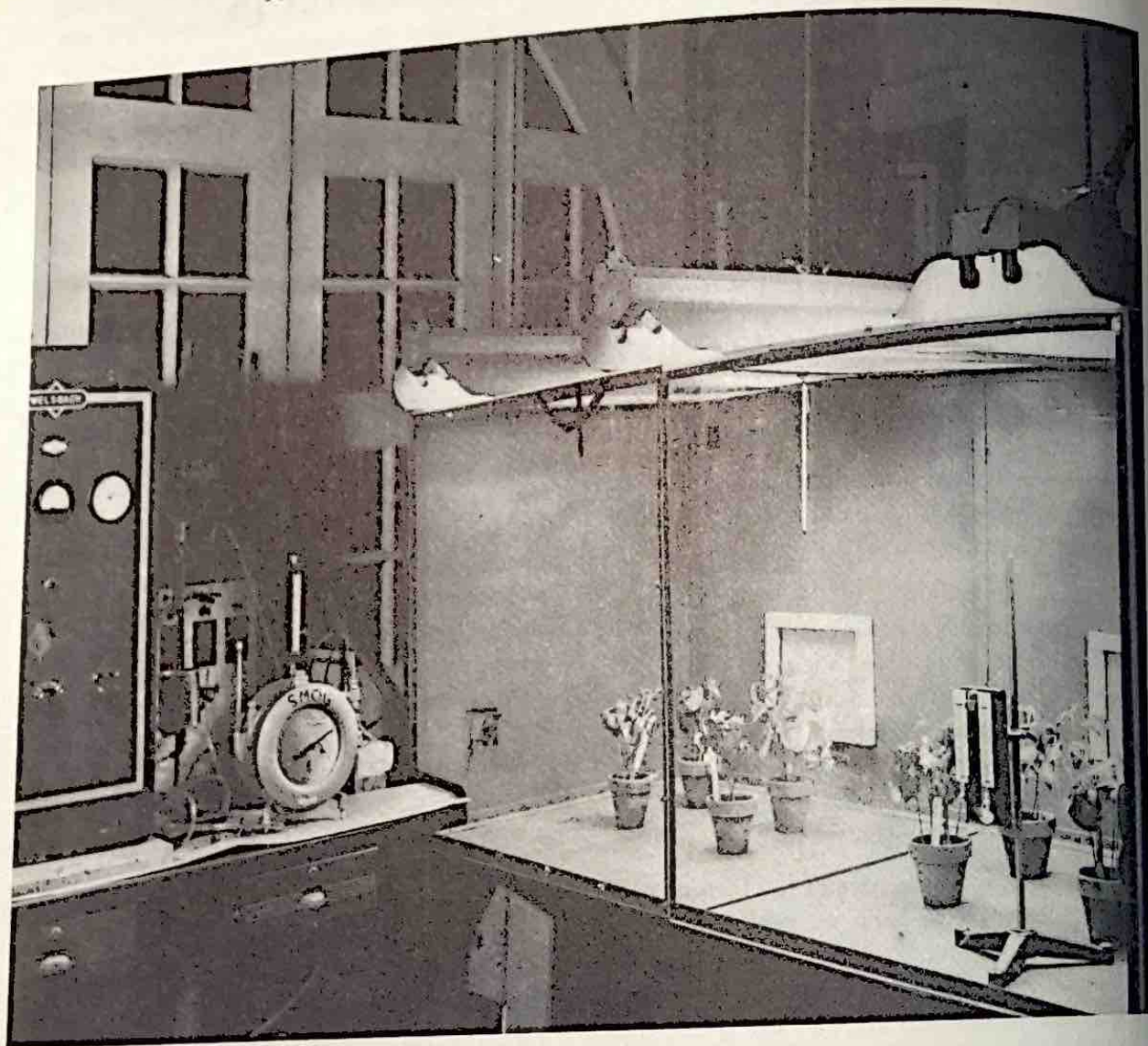
action products of ozone and various hydrocarbons, and also ozone and automobile exhaust. In all cases, the amount of hydrocarbons necessary has been higher than concentrations experienced in the Los Angeles atmosphere. On the other hand, damage has been produced with ozone and automobile exhaust in concentrations even lower than those often experienced in Los Angeles. This anomaly leads one to wonder if plant damage is a function of gross hydrocarbon concentration or if some individual constituent is responsible for the ease with which auto exhaust-ozone mixtures produce typical smog damage on plants.

General Plan

Equipment has been devised at Midwest Research Institute to freeze out the liquefiable portions of auto exhaust under various conditions of engine operation and use of fuels of different composition. These liquefiable products will then be separated into various fractions by both chemical and physical means, and the effect of each fraction on producing plant damage after being mixed with ozone will be tested. It is possible that one or more of the various fractions will produce plant damage much more readily than the others. In this event, further study will be directed toward the composition of the reactive fractions for the purpose of determining more exactly the material responsible for plant damage and, later, eye irritation.

Status

Facilities for testing the effect of mixtures of exhaust gases and ozone on pinto beans (the test



plant) have been built (Fig. 1). Source of exhaust gas is a 1941 Cadillac which during idling emits an exhaust gas containing 0.15% hydrocarbons. The test chamber and the bean plants are currently being calibrated. Initial results indicate that considerable difficulty may be expected in using the pinto bean for more than a qualitative estimation of plant damage.

Concurrently with the above work, tests are also under way to determine the effect of addition of various amounts of ethyl alcohol to gasoline on the composition of exhaust gases. A 1952 Ford V-8 station wagon is being used for these tests which are just getting under way (Fig. 2). Initial analyses will be made with the Beckman IR-2 spectrophotometer.

**COMPOSITION OF
INCINERATOR GASES
BATTELLE MEMORIAL INSTITUTE
COLUMBUS, OHIO**

Background

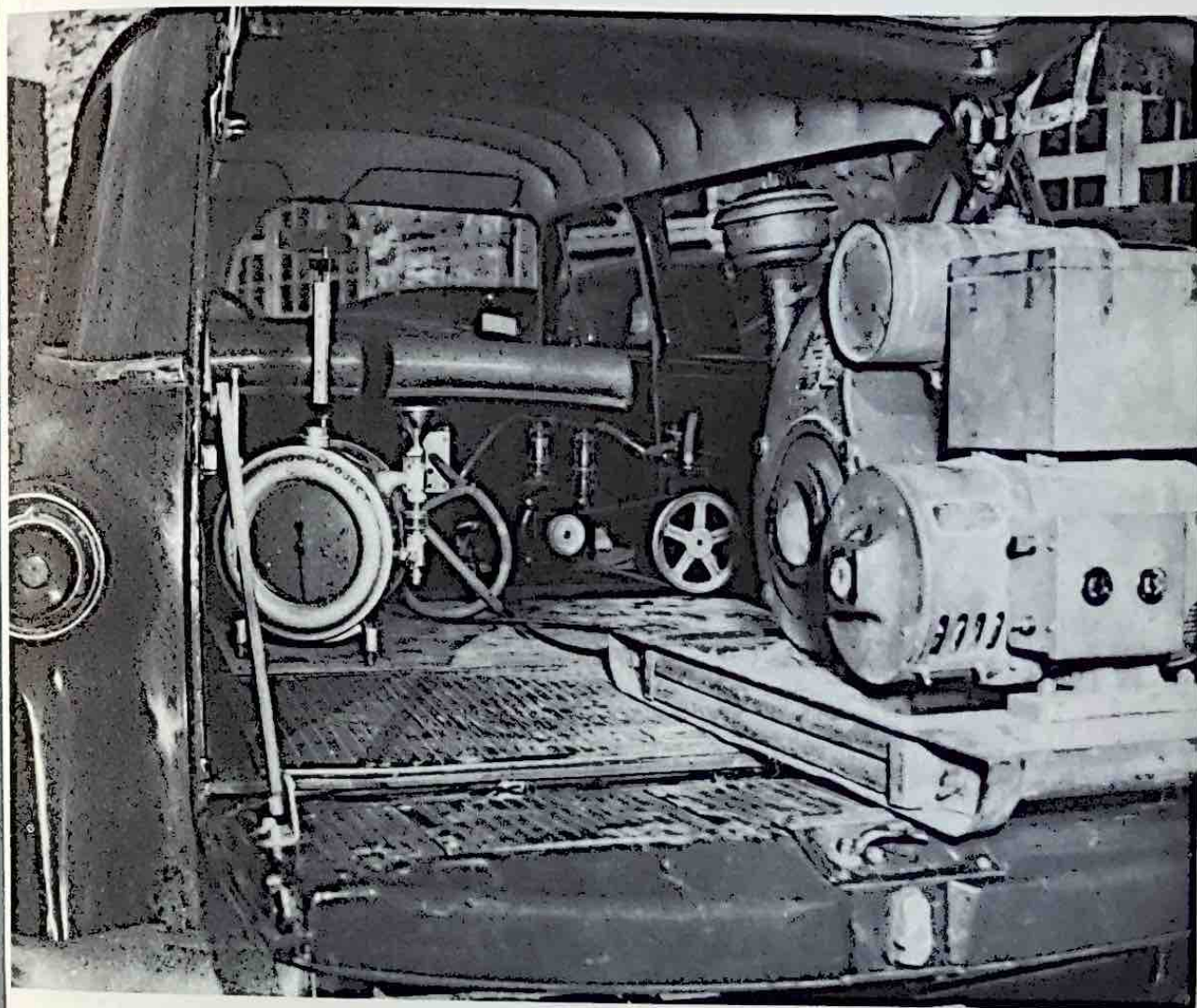
Work by different investigators leading to information on the composition of effluent gases from backyard incinerators is fragmentary and conflicting. The Los Angeles County Air Pollution Control District² holds that the primary con-

²"Smog—What Has Been Done—What Must Be Done." *Los Angeles County Air Pollution Control District*, April, 1954.

tribution of incinerator effluents to smog is the 100 tons of smoke which decreases visibility and adds to the haze. No effect on vegetation damage and eye irritation has been found.

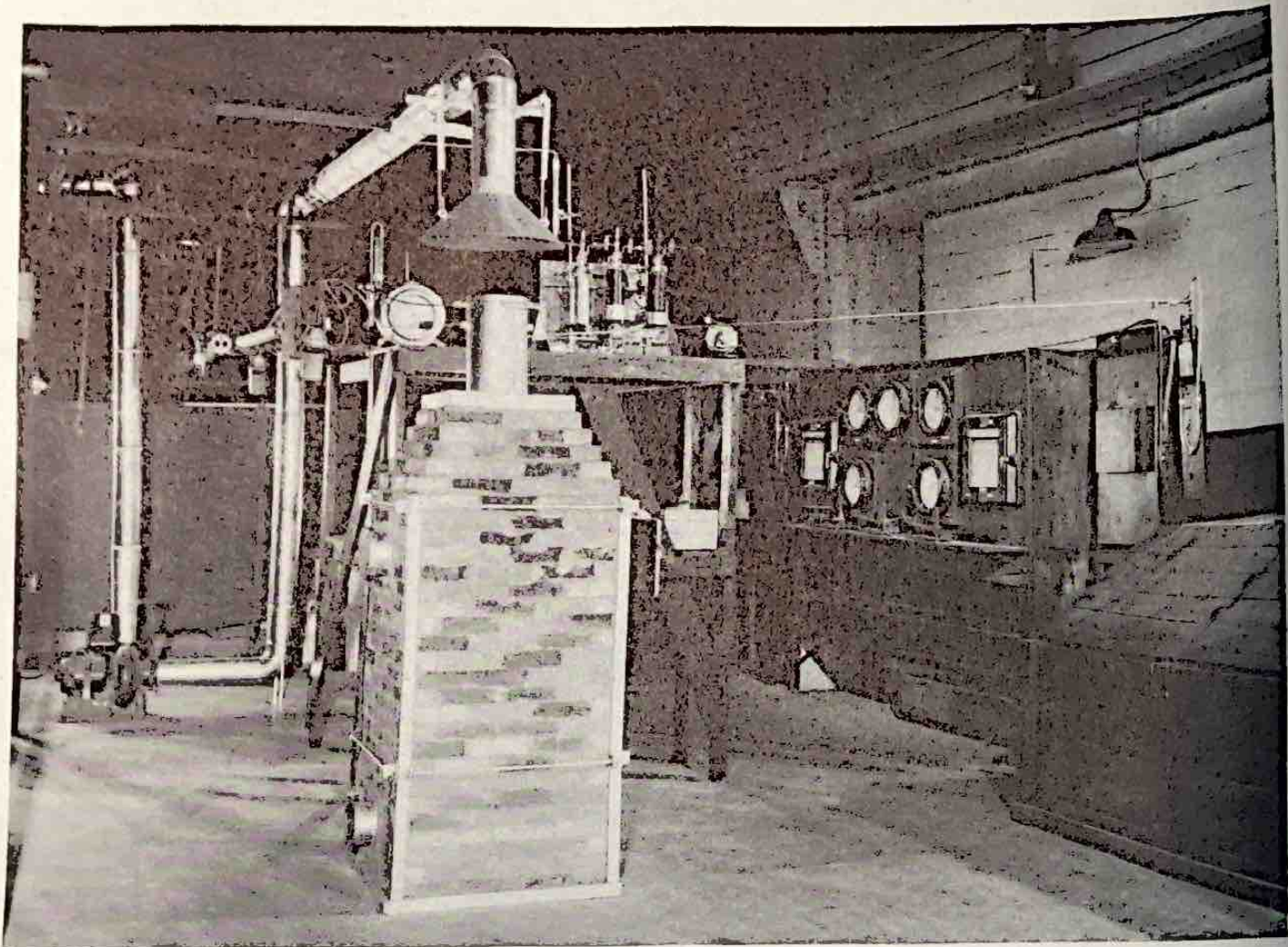
On the other hand, Stanford Research Institute reports³ that backyard incinerators in the Los Angeles Basin produce over 500 tons of invisible "organics" of undetermined nature. These materials could well be effective in damaging plants and causing eye irritation.

³"The Smog Problem in Los Angeles County," *Stanford Research Institute*, January, 1954.



CHAPTER IV - FIG. 2
Exhaust sampling equipment in Ford station wagon—Midwest Research Institute

CHAPTER IV - FIG. 3
"Backyard" incinerator and auxiliary equipment—Battelle Memorial Institute



General Plan

A typical backyard incinerator will be operated with the various types and ratios of refuse usually burned in the Los Angeles area. Under a variety of operating conditions, the effluent gases will be analyzed for types of gaseous materials in the effluent, using infrared, ultra-violet, and mass spectrometers as well as gas chromatography. Aerosols evolved will also be collected

on a weight as well as a size and count basis, and analyzed.

Status

This project got under way on November 15, 1954. A backyard incinerator of six-cubic-foot capacity has been built and the necessary control and analytical equipment procured and assembled (Fig. 3). Tests started about January 20, 1955.

SMOG-FORMING POTENTIAL OF VARIOUS COMBUSTION EFFLUENTS

We propose to carry out large test chamber experiments, working with actual pollutants instead of synthetic mixtures, to study Los Angeles smog under conditions which can be controlled in this chamber. We should prefer to experiment with the entire Los Angeles Basin. This is impossible, as we cannot control the weather. In Operation Pilot Plant, we could control the temperature, wind, humidity, concentration of pollutants, the amount of light, etc. In a large chamber of special construction, perhaps as big as an airplane hangar, we could supply straight auto exhaust at one time, backyard incinerator smoke at another, hydrocarbons at another; then mixtures of two or more of these pollutants. We could find accurate answers to such questions as "does auto exhaust actually form smog?" or "what would be the effect of closing down the refineries, stopping all incinerators, or keeping all cars off the roads?" Two years with this operation, whatever the cost, would be time and money saved in trying futile experiments on the whole Basin itself. Operation Pilot Plant is a natural for the University of California; the main installation would probably be built at Riverside; experts from other faculties would be called in and perhaps some of the work might be assigned to other sections of the University of California. Because this work would increase understanding of air pollution problems in the San Francisco Bay Area, in San Diego, and other cities, it is a good state project. The University of California is interested in carrying out a project of this nature and is currently seeking funds from the state legislature to underwrite the project.

CONTROL OF AUTO EXHAUST

Even though the Foundation believes further information is necessary to pinpoint the actual constituents of combustion effluents responsible for various manifestations of smog, it would be remiss if some activity were not directed toward

controlling the emission of auto exhaust. Two projects have accordingly been initiated in this area.

Evaluation of Control Devices for Automobile Exhaust Southwest Research Institute, San Antonio, Texas

Background

Of the many proposed devices for controlling hydrocarbon emissions from automobile tailpipes, three general types are attractive: (1) exhaust oxidation devices, (2) fuel feed cutoff devices operating during deceleration, and (3) fuel injection devices.

The automobile industry is greatly interested in the fuel cutoff valves because they show promise of not only reducing hydrocarbon emissions but also of adding to fuel mileage. Several companies are working on the development of such devices, and the Foundation is keeping informed of progress. A device of this sort may be expected to reduce hydrocarbon emissions by 30% to 50%. Proposed fuel injection devices would involve major changes in engine design and, hence, many years of development. This approach does not appear to be sufficiently promising at an early enough date to warrant study at this time. The third possibility, the oxidation of exhaust hydrocarbons to carbon dioxide and water in a specially designed muffler, gives promise of application to both new and old cars, and possibly a 99% reduction in exhaust hydrocarbons.

The most promising device in this field is the Houdry catalytic muffler for use with leaded gasoline. Preliminary tests made by both Oxy-Catalyst, Inc. and the Los Angeles County Air Pollution Control District showed that the device has merit. It therefore appeared necessary to submit the muffler to road tests under various conditions of operation, terrain, weather, etc. A contract was therefore made with Southwest Research Institute to carry out these tests in its laboratory in San Antonio, Texas, under the supervision of its Department of Engines, Fuels and Lubricants Research.



CHAPTER IV - FIG. 4
Houdry catalytic muffler being installed on automobile—Southwest Research Institute

General Plan

The plan is to carry out life tests of catalytic converters installed on several makes of automobiles. Four converters for use with leaded gasoline will be installed on a 1954 Ford V-8, 1954 DeSoto V-8, 1953 Buick V-8, and a 1953 Cadillac (Fig. 4). The individual cars will be run on a proposed 20,000-mile road test, during which time the operators will determine the effect of these converters on the operating characteristics of the automobile. At the end of each 1,000 miles, the car will be returned to the laboratory for an inspection and also for an analysis of the hydrocarbon content of the exhaust gases under different conditions of operation. At the end of the test, exhaust gas analyses will be checked by the Los Angeles County Air Pollution Control District. If the converters fail during the 20,000 mile road test, the catalyst will be reconditioned in the presence of a representative of Southwest Research Institute or the Air Pollution Foundation, and the converter put back on the car. It is possible that when these tests are completed other types of devices may also be subjected to life tests.

Status

Tests started on February 15, 1955. In addition to the tests using leaded gasoline, two converters designed for use with white (nonleaded) gasoline will be installed on 1954 Chevrolet Powerglides and evaluated in the same way as the leaded gasoline mufflers. Thus, if the latter type fails and the former does not, a stopgap method may be available to the area, provided sufficient white gasoline can be made available.

Economic Feasibility of Stopgap Methods Southwest Research Institute, San Antonio, Texas

Background

It is becoming apparent that the ultimate solution to the Los Angeles smog problem may require automotive or fuel changes which will not be effective in the Los Angeles area for perhaps ten years. As the population of the Los Angeles

Basin increases, smog frequency may be expected to increase. To obtain relief at an early date, we may have to resort to stopgap procedures which are not economic in the long run. Many such stopgap procedures have been proposed, not only by the uninformed, but also by men of considerable stature in scientific, civic, and political affairs of Southern California. The facts concerning the technical and economic feasibility of these proposals have not been available either to community leaders or to the public.

Proposals for stopgap procedures include the following:

(a) The use of nonleaded gasoline and the OCM catalytic muffler. This proposal is based on the generally accepted supposition that the catalytic converter for nonleaded gasoline has been successfully developed.

(b) The use of the Houdry catalytic converter, which is supposedly effective in oxidizing the hydrocarbon constituents of leaded gasoline.

(c) The use of liquefied petroleum gases in place of gasoline in internal-combustion engines. This proposal is based on the theory that only hydrocarbons of four carbon atoms per molecule or above contribute to smog.

(d) Alcohol blends as automotive fuel. This is based on claims that alcohol improves the combustion of hydrocarbons in the cylinder.

(e) Fuel rationing. The supposed advantages of this proposal are obvious.

(f) Control of excessive fumes from "smokers." There is considerable opinion that automobiles which emit a blue trail of unburned lubricating oil droplets from the exhaust pipe not only contribute greatly to reduced visibility, but that they also emit much larger quantities of unburned gasoline than properly maintained and operated cars.

(g) Further control of hydrocarbon losses which accompany the distribution of automotive fuels. After present control methods are adopted by the petroleum refining industry, the largest contributions to hydrocarbon emissions as such

will be from filling tanks at bulk storage terminals, tank trucks, filling station delivery tanks, and automobile fuel tanks. The costs involved in further control of these emissions must be determined.

General Plan

It is proposed to study *all* of the factors involved in making any of the above changes, either in whole, or in part, or in combination one with another. Most of the data will be secured by conversations with experts in the petroleum and automotive fields. In a few cases, some preliminary test work may have to be carried out; but in general, the proposals will be evaluated both on the basis of current knowledge of the effectiveness of the method under consideration and also on the assumption that partially developed methods may be made 100% effective. It is obvious to many technical men that many of these proposals will require such far-reaching expenditure of funds and changes in our way of life that it might be easier to move the city than to impose the suggested remedies on the Los Angeles public. It is important, however, that these facts be clearly pointed out and made available to the public.

Status

Studies are in progress and only partial answers are therefore available. However, one design of an afterburner has been unearthed which shows considerable promise in the bus

field. Arrangements are being made to test the device. Preliminary results also indicate that up to 50% elimination of hydrocarbon emissions would result from proper maintenance of automobiles, and particularly, proper adjustment of air/fuel ratios. A further dividend from the latter adjustment would be improved gasoline mileage.

FUTURE RESEARCH

Basic Design Data for Exhaust Converters

Background

Many attempts have been made to design a device in which the hydrocarbon content of auto exhaust gases could be oxidized completely to carbon dioxide and water. It is obvious, however, that one cannot design a piece of equipment until the process requirements are known.

General Plan

It is proposed to initiate a laboratory study to determine the effects of time, temperature, pressure, catalyst, and concentration variables on the oxidation of the hydrocarbons present in exhaust gases. This information will then be made available to any and all persons interested in the design of equipment to carry out this reaction.

Status

A proposal is being prepared by a well-known research laboratory.

V. AEROMETRIC SURVEY¹

INTRODUCTION

A REVIEW of reports and data available to anyone concerned with the smog problem in February, 1954 revealed the following questions and gaps in the status of knowledge:

1. Sufficient data had not been obtained to permit any sound conclusion to be drawn with respect to the possible movement of smog or smog-producing substances.

2. What was the relationship between oxidant value and manifestations of smog, namely eye irritation, plant damage, and reduced visibility?

3. How were the manifestations of smog distributed in severity and time throughout the entire Basin?

With the above factors in mind it was reasoned that a continuous monitoring of the Los Angeles atmosphere during the period of highest incidence of smog was appropriate. Accordingly, with the best meteorological data available, a network of ten sampling stations was established (Fig. 1) and one monitoring station outside the Los Angeles Basin was also set up. The stations were chosen to lie along typical surface wind trajectories for the period in question, namely: August 1 to December 1, 1954. One series of trajectories involved stations in Venice, Wilshire

District, downtown Los Angeles, Pasadena, Azusa; another involved Venice, Wilshire District, downtown Los Angeles, and Burbank; another involved Dominguez, downtown Los Angeles and either Pasadena, Azusa or Burbank; another series extended from Artesia, Rivera to Bassett and Azusa. Finally, it was decided that data should be obtained on a continuous basis when at all feasible, twenty-four hours a day throughout the period.

DESCRIPTION OF STATIONS

With the cooperative support of the Los Angeles County Air Pollution Control District, Los Angeles County Department of Charities, California Institute of Technology, American Cyanamid Company in Azusa, and various Los Angeles City and County departments, sites were inspected during June and July, 1954. Final selections were made in the middle of July as follows:

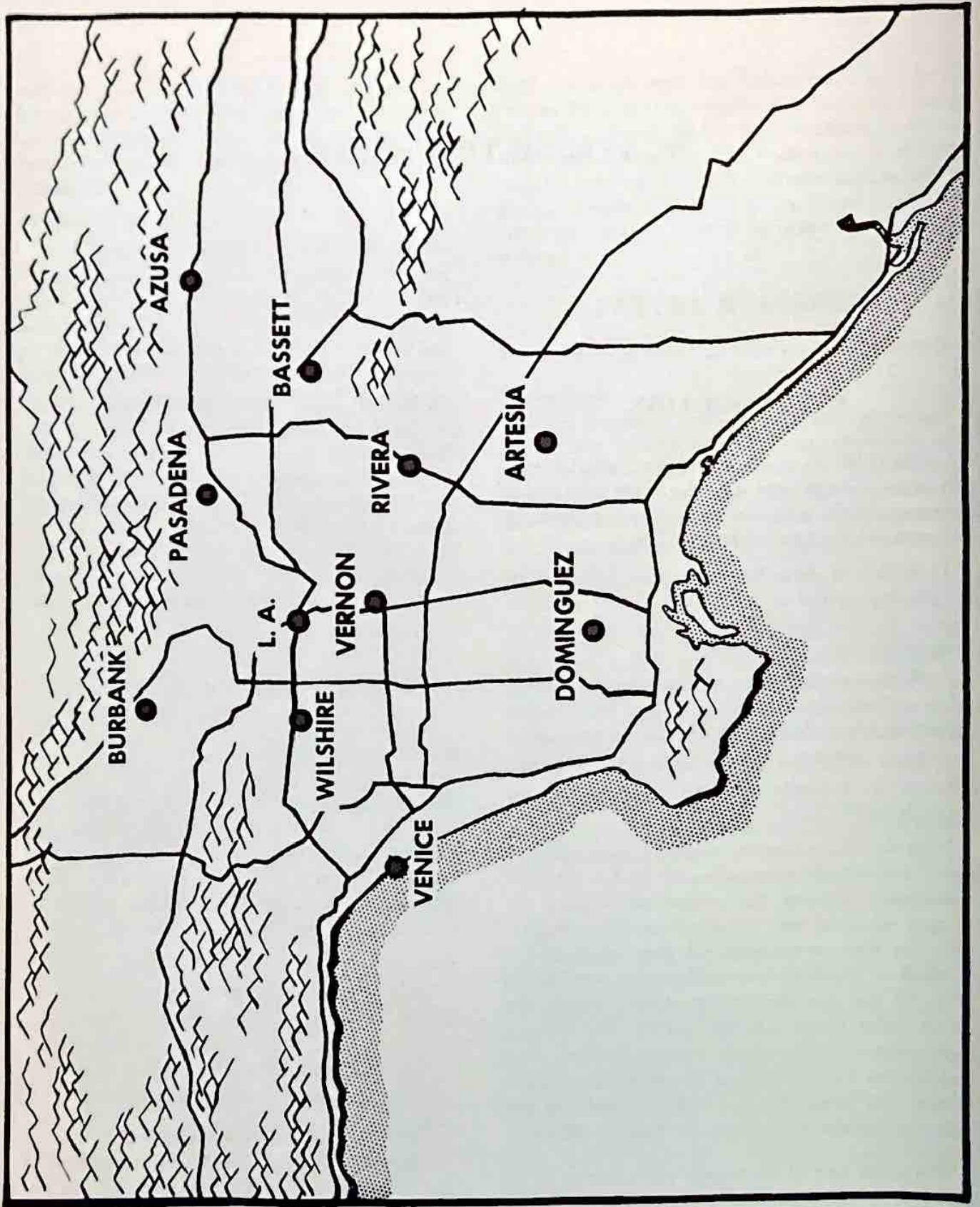
Station 1—Venice

This sampling site was at the shore of the Pacific Ocean in a recreational, residential-type area with some commercial activity. Here were installed an oxidant recorder; oxides of nitrogen sampler, and surface wind anemometer.

Station 2—Wilshire District

This sampling site was on the third floor of the Los Angeles High School; the area is primarily residential. The site was used both by the Air Pollution Control District and the Foun-

¹The major part of this survey was supported by the Los Angeles County Air Pollution Control District through a research contract with the Air Pollution Foundation.





CHAPTER V - FIG. 2
View from Fidelity Building

dation. Equipment was installed in a room 9' x 12' whose windows overlooked an inside court large enough to be considered in equilibrium with the general atmosphere of the area. The Foundation installed an oxidant recorder; a plant damage test chamber; a hygromograph, and a transmissometer on the roof of the main building. The District operated a sulfur dioxide recorder and sampled for hydrocarbons, carbon monoxide, aldehydes, and oxides of nitrogen.

Station 3—Downtown Los Angeles

This station (Fig. 2) was in an office on the fourth floor of the Fidelity Building at Sixth and Spring Streets, overlooking a clear expanse immediately below which is a parking lot to the north; this sampling site is obviously in the heavy commercial and industrial area. The Foundation installed here an oxidant recorder; sulfur dioxide recorder; oxides of nitrogen sampler; plant test chamber; hygromograph; equipment for sampling hydrocarbons, aldehydes, carbon monoxide; AISI hourly particulate sampler, and a high volume particulate sampler.

Station 4—Pasadena

This sampling site (Fig. 3) was located on the fourth-floor roof of a California Institute of Technology building in a residential area. The

CHAPTER V - FIG. 3
California Institute of Technology
View from roof of physics building



Foundation installed an oxidant recorder; oxides of nitrogen sampler; plant test chamber; hygromograph; equipment for sampling hydrocarbons, aldehydes, and carbon monoxide; AISI hourly particulate sampler; high volume twenty-four (24) hourly particulate sampler, and a transmissometer.

Station 5—Burbank

This sampling site was located on a ground floor room of a school building overlooking a recreational area in a commercial district. The Foundation installed an oxidant recorder and an oxides of nitrogen sampler in an unused ante-room, with sampling tubes from the equipment through a window to the outside.

Station 6—Dominguez

This station located in the oil refinery area was in the backyard of a fire station alongside the parked mobile laboratory of the Los Angeles County Air Pollution Control District. It consisted of two plywood shacks, one to house the oxidant recorder and recorder for the transmissometer, the other to house the plant test chamber and hygromograph. The transmissometer transmitter was located on the roof of a cafe approximately 500 feet east of the receiver which was on the fire station roof proper.

Station 7—Artesia

This sampling site was in a commercial area on the ground floor of the school district office building. The Foundation installed an oxidant recorder in this room and ran a sampling tube out the window.

Station 8—Rivera

This station was on the ground floor of the Insectary of the County Agricultural Commission Building, which for practical purposes was open to the atmosphere. The Foundation installed here an oxidant recorder and plant test chamber with hygromograph. The station was in an open space between light industrial areas.

Station 9—Bassett

This sampling site was located in the recreation building of a park. The Foundation installed an oxidant recorder with sampling tube out

through a window and the plant test chamber with hygromograph outside the building near some bushes. This station was in an agricultural area.

Station 10—Azusa

This station was in a little used building on the grounds of the American Cyanamid Company, an industrial area. The Foundation installed an oxidant recorder on the ground floor with sampling tube through the window.

Station 12—Santa Barbara

This station was near the Santa Barbara Airport, about 100 miles northwest of Los Angeles. The Foundation installed an oxidant recorder. Station 12 was considered a monitoring point for the Los Angeles Basin, remote from human activity, but under similar meteorological influences and conditions.

In addition to the above stations, oxidant recorder data were available from the District headquarters in Vernon, a heavy industrial area, and from the Riverside Campus of the University of California. In the downtown Los Angeles area, Hall of Records ninth floor, the Los Angeles County Air Pollution Control District had equipment for sampling hydrocarbon, aldehydes, carbon monoxide, and oxides of nitrogen; across the street, data from a particulate sampler and sulfur dioxide recorder on the roof (18th floor) of the Federal Building were available, as well as transmissometer data on the sixth floor level. The latter sites were labelled Stations 13 and 13a.

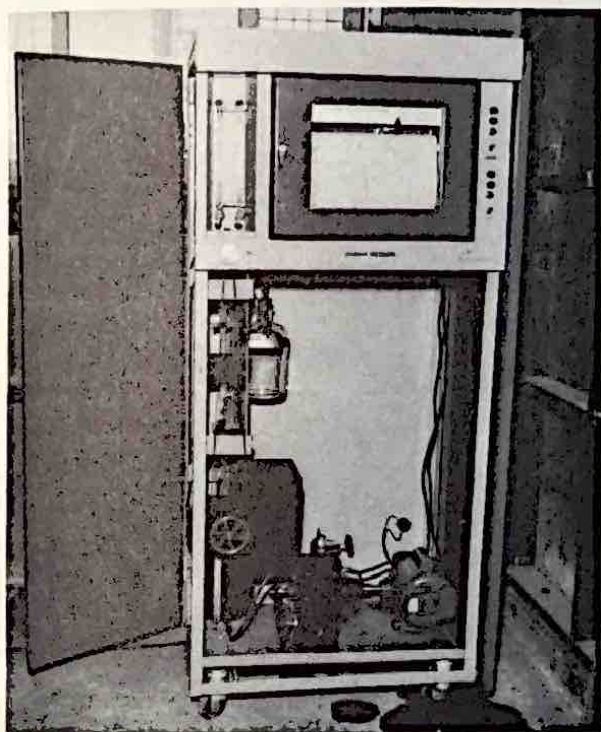
Instrumentation

(1) Oxidant Recorder

Twelve recording instruments for this survey based on the design of Littman and Benoiel² were constructed by Beckman Instruments, Inc. at Fullerton, California. These recorders (Fig. 4) consist of two functional parts: a recording colorimeter and a continuous counter current gas scrubber. A glass column packed with single turn

²Littman, F. E. and Benoiel, R. W., "Continuous Oxidant Recorder." *Analytical Chem.*, 25, 1480-1483 (1953).

CHAPTER V - FIG. 4
Oxidant recorder



glass helices was used as the absorbing device and neutral potassium iodide solution as the reactant. The output of the colorimeter was recorded on a Brown recorder calibrated in parts per hundred million expressed as ozone.

Ten of these recorders were located at Stations 1 to 10 described previously; an eleventh instrument was located at Santa Barbara, and a twelfth instrument was located at the Los Angeles County Air Pollution Control District headquarters at 5201 South Santa Fe Avenue. The instruments at Stations 1 to 10 were operated from early August, 1954 to November 30, 1954.

The instruments required frequent servicing in the early phases of the operation. Several of the instruments required daily service, others were serviced every other day. After September 15, 1954 servicing had become routine, the instruments then requiring attention every second or third day. Various minor instrumental difficulties were gradually discovered and eliminated.

(2) Oxides of Nitrogen Sampler

Four special oxides of nitrogen samplers were designed and constructed for use in this survey by A. L. Chaney and Kenneth Johnson (Fig. 5). These samplers consisted of a turntable holding eight 500 ml. evacuated sample bottles. This turntable was designed to rotate either at the rate of one revolution in twenty-four hours or one revolution in eight hours, depending upon the gear train used.

Each sample bottle was closed with a serum stopper and evacuated through a side arm which could be sealed off either with a stopcock or with a piece of plastic tubing and a short piece of glass rod. The eight bottles were held firmly on the rotating turntable.

As each bottle passed a fixed point, a pin actuated a microswitch. This operated a solenoid which forced a hypodermic needle on a lever arm down through the serum stopper. After a



CHAPTER V - FIG. 5
Chaney-Johnson nitrogen oxide sampler

period of approximately two minutes, during which time a sample of air was drawn into the evacuated bottle, the solenoid was switched off and the hypodermic needle was withdrawn by a spring. The four samplers were located at Stations 1, 3, 4, and 5.

The procedure for analysis was modified from that of B. F. Rider and M. G. Mellon.³ The sample flasks were prepared in the laboratory by stoppering each bottle with the serum stopper and evacuated to twenty-five inches of mercury. A measured quantity of 0.05 normal sodium hydroxide was added with a hypodermic needle pushed through the serum stopper. Eight sample bottles and two blank bottles were prepared for each sampling machine. These bottles were placed in the sampler each day and replaced the following day with another set.

After the samples were collected, 0.5 ml. of reagent solution containing sulfanilic acid and hydrochloric acid were added to each sample for diazotization of sulfanilic acid by any nitrous acid absorbed in the sodium hydroxide. After standing five minutes, 0.5 ml. of a coupling reagent containing N-(1-naphthyl)-ethylenediamine dihydrochloride was added. This was allowed to stand for five minutes; then a measured quantity was placed in a spectrophotometer cell, and the color was read at 540 millimicrons. The results were reported as oxides of nitrogen calculated as nitrogen dioxide.

(3) Hydrocarbon Sampler

Air samples for hydrocarbon analyses were collected by a freeze-out technique and determined by infrared absorption.⁴ The freeze-out assembly consisted of a flow meter, an ascarite trap, a Shepherd trap immersed in a Dewar flask

³Rider, B. F. and Mellon, M. G. "Colorimetric Determination of Nitrites," *Ind. & Eng. Chem.*, 18, 96 (1946).

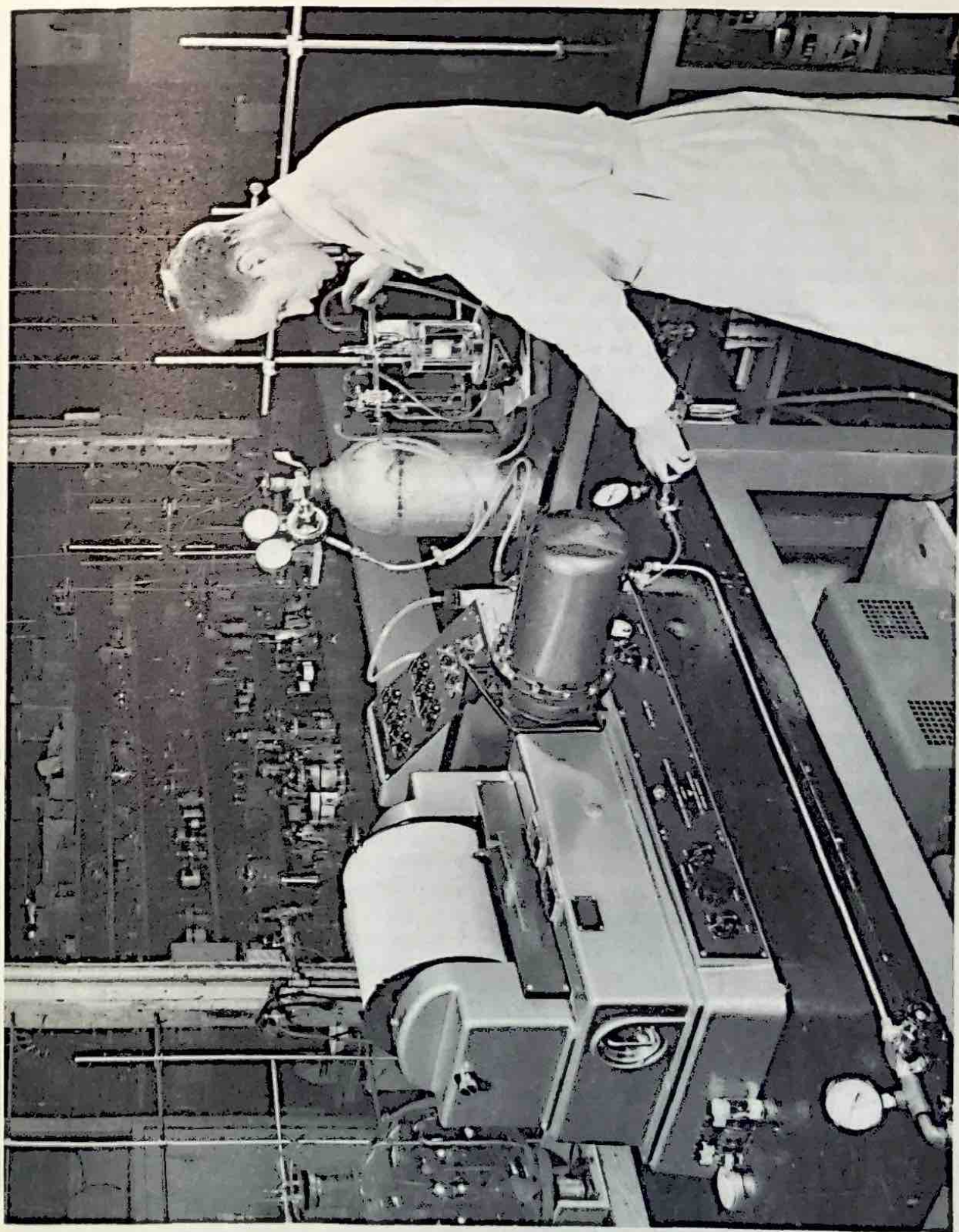
⁴Mader, Paul, Heddon, M. W., Lofberg, R. T., Koehler, R., "Determination of Small Amounts of Hydrocarbons in the Atmosphere," *Analytical Chem.*, 24, 1899 (1952).

containing liquid oxygen, a vacuum gauge, and a vacuum pump. A flow rate of one liter of air per minute was used and samples were taken for a one-hour period. At the end of this time, the Shepherd trap was disconnected, stored in a Dewar flask filled with crushed ice, and returned to the laboratory. The use of crushed ice for storage of Shepherd traps containing freeze-out samples was discontinued on October 18, 1954. Instead, the traps were evacuated to 50 mm. of Hg absolute pressure while still at liquid oxygen temperature, then closed off and stored at room temperature until the time of analysis.

A Perkin-Elmer model 21 infrared spectrophotometer equipped with sodium chloride optics and a ten-meter multiple reflection gas cell was used for the analysis. The instrument was calibrated against hexane as a standard using the carbon-hydrogen absorption band at 3.45 microns. The trap containing a sample was connected to the gas cell by heating and flushing the trap with dry nitrogen gas. Dry nitrogen was used to bring the pressure in the gas cell to approximately one atmosphere absolute. A photograph of the Perkin-Elmer spectrophotometer and ten-meter gas cell appears as Fig. 6.

(4) Carbon Monoxide Indicator

Carbon monoxide was determined at Stations 3 and 4 on an hourly basis corresponding to the schedule for hydrocarbon samples. The Mine Safety Appliance carbon monoxide indicator tube was used for this determination. The squeeze bulb was replaced by a system consisting of a one-gallon bottle containing water which was siphoned out at a measured rate into a graduated cylinder. The indicator tube was connected to the air intake line to the bottle. Water was siphoned from the bottle into the graduate at a rate of approximately 65 ml. per minute until the color change in the indicator tube was very pronounced. The color thus produced was compared against the color scale provided by the Mine Safety Appliance Company. This value was recorded together with the volume of air sampled as measured by the water in the gradu-



CHAPTER V - FIG. 6
Perkin-Elmer spectro-photometer and ten meter gas cell

ate cylinder, and the carbon monoxide concentration was calculated in parts per million.

(5) Aldehyde Sampler

The method for determination of aldehyde was based on the addition reaction of bisulfite to aldehydes, liberation of the bisulfite and its estimation by iodometric titration.^{5,6} Ten ml. of a one per cent sodium bisulfite solution was placed in each of three midjet impingers placed in series. Air was drawn through these impingers at the rate of one-tenth cubic foot per minute for one hour. At the end of this time, the contents of the impingers were transferred to a flask. After various manipulations, the bisulfite which had been released was titrated with dilute iodine solution.

(6) AISI Particulate Sampler

Two of these instruments developed by Hemeon, Haines, and Ide⁷ were used, one at Station 3 and the other at Station 4. This unit used filter paper tape, through which outside air was pumped at the rate of approximately 0.25 cubic feet per minute. These instruments were set to sample for a one-hour period, at the end of which time the filter paper tape was advanced and another sample of one-hour duration was taken. The spots thus obtained on the filter paper tape were approximately one inch in diameter. These filter paper samples were evaluated by measuring the transmission of light through them with a special densitometer. Hemeon has defined a special unit called a Coh unit as being equivalent to an optical density of 0.01. Thus a spot giving a light transmission value of 50% corresponds to an optical density of 0.301 or 30.1 Coh units.

⁵"Los Angeles Air Pollution Control District Test Procedure and Methods in Air Pollution Control," page 35.

⁶Goldman, F. H. and Yagoda, Herman, "Collection and Estimation of Traces of Formaldehyde in the Air," *Industrial and Engineering Chem., Analytical Edition*, 15, 377 (1943).

⁷Hemeon, W. C. L., Haines, George F. Jr., and Ide, Harold M., "Determination of Haze and Smoke Concentrations by Filter Paper Samplers," *Air Repair*, 3, No. 1, 22-28 (August, 1953).

In addition to the measurement of the light transmission of the spots, a total of approximately 1200 of the individual spots were cut from the paper tapes and their lead content determined by the dithizone method, as described by Cholak.⁸

(7) High Volume Sampler

Two Staplex high volume air samplers were used, one at Station 3 and the other at Station 4. These units consist of an air pump for sampling large volumes of air for particulate matter by means of filter media. These samplers were modified by constructing two aluminum filter heads to permit the use of a specially fired glass-fibre filter web. A rectangular filter, 8" x 10", was used, the filtering area being 63 square inches (7" x 9").

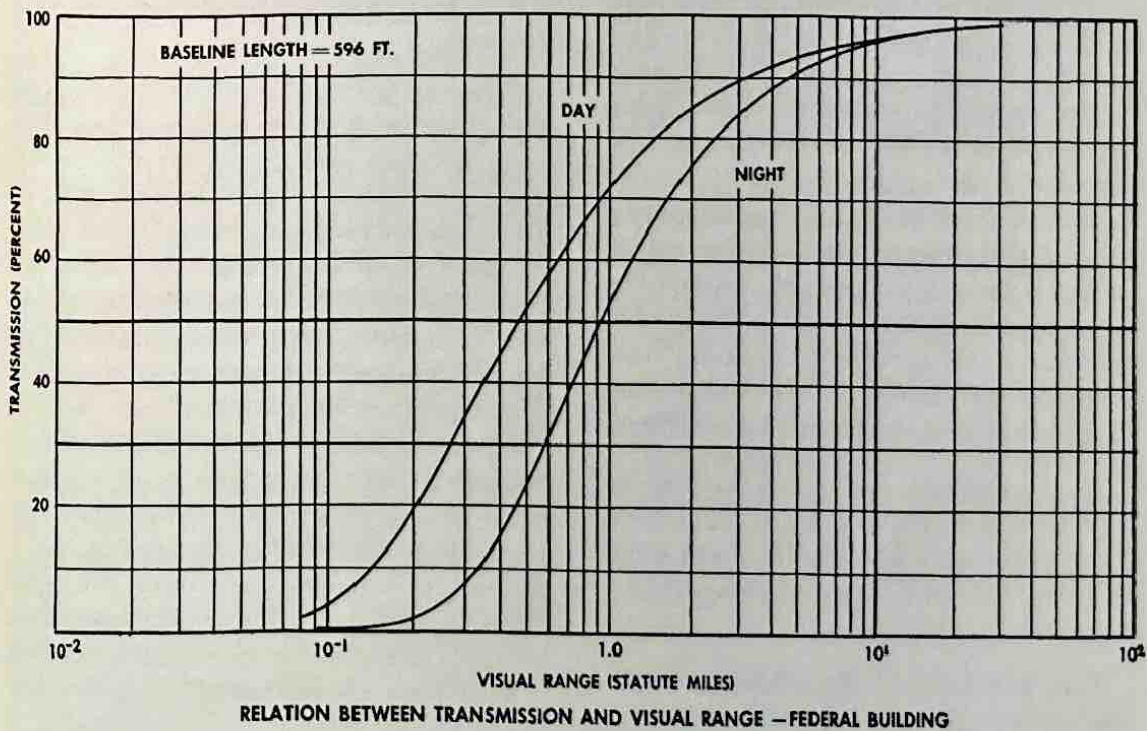
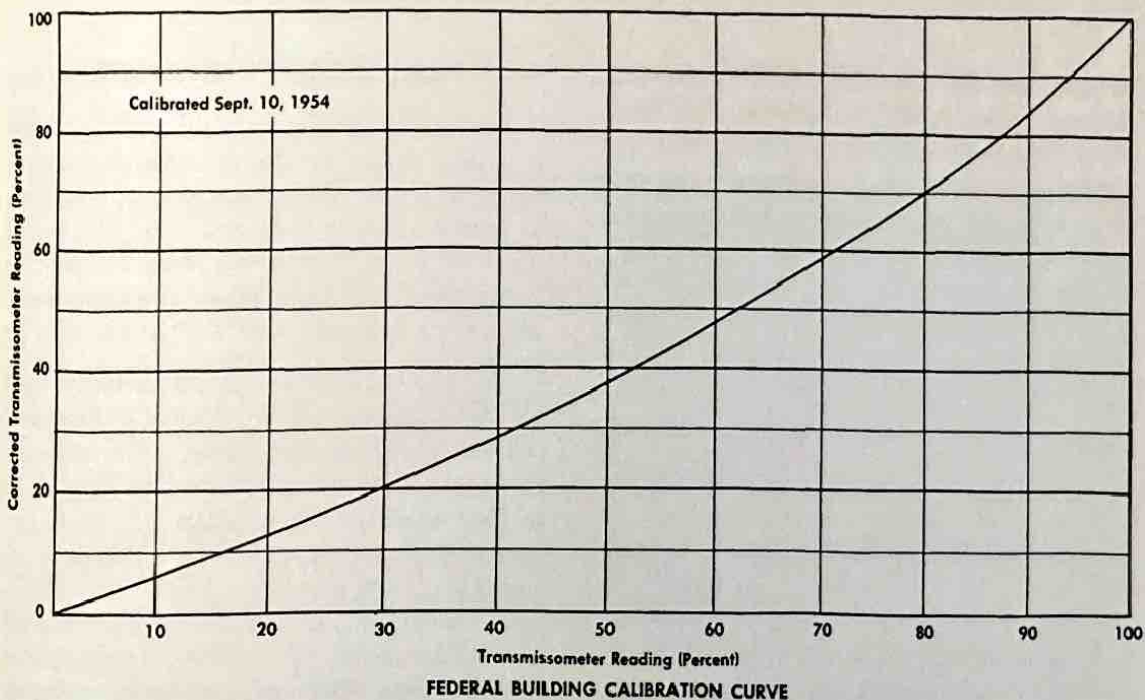
Air was pumped through these units at the rate of approximately 60 cubic feet per minute, so that a total of about 85,000 cubic feet of air was pumped in each twenty-four hour period. The total sample weight was determined and the weight of the particulate matter in micrograms per cubic meter was calculated. In addition, organic matter, polycyclic hydrocarbons and anions were determined chemically. Spectrochemical analyses were carried out for fourteen cations.

(8) Sulfur Dioxide Recorder

A single instrument for recording the sulfur dioxide content of the air was borrowed from the Kaiser Steel Corporation and operated at Station 3. This instrument is described by Thomas, Ivie, and Fitt,⁹ and consists of a scrubbing device in which air and liquid move counter-currently. Air at the rate of 12 to 15 liters per minute is pumped up through the absorbing

⁸Cholak, J., Hubbard, D. M., and Burkey, R. E., "Micro-determination of Lead in Biological Material with Dithizone Extraction at High pH," *Analytical Chem.*, 20, 671 (1948).

⁹Thomas, Moyer D., Ivie, James O., and Fitt, T. Cleon, "Automatic Apparatus for Determination of Small Concentrations of Sulphur Dioxide in Air," *Industrial and Engineering Chem., Analytical Edition*, 18, 383-387 (1946).



CHAPTER V - FIG. 7

column, and the absorbing solution containing hydrogen peroxide and dilute sulfuric acid flows down through the column. The solution with absorbed gases flows into a conductivity cell and the conductivity of the solution is automatically measured and recorded on a strip chart recorder.

Considerable difficulty was experienced with this unit when it was placed in operation; hence records were obtained only for a portion of the period from August 1 to November 30, 1954.

(9) *Visual Range*

It was considered necessary to the survey that not only eye irritation and plant damage be measured at certain stations but data be obtained on reduction of visibility as an important manifestation of smog. There are unfortunately few continuous recording-type instruments for getting such information. The only such instruments available to the Foundation for day and night readings were four Douglas (Bureau of Standards) transmissometers. These had been used by the Los Angeles International Airport in their studies on fog dispersal systems. They were *not* ideally suited for the survey but nevertheless they were put into service. The instrument is described in the reference below;¹⁰ it consists basically of a light projector having an intensity of about 10^5 candles mounted solidly on a stand or post. A photocell receiving unit is mounted on a post and placed 500-1000 ft. away. Essentially, transmission readings were obtainable as a function of time and these were transformed to visual range determinations by curves shown in Fig. 7.

Considerable work was involved in getting the instruments in shape and calibrated. Particularly the projector lamps were short-lived and prone to drift in intensity despite good voltage regulation.

Data were presented on an Esterline Angus line recorder and each fifteen minutes the light was automatically turned off and a reading on background illumination was obtained.

¹⁰U. S. Dept. of Commerce, Civil Aeronautics Administration, Techn. Dev. Rep. No. 47.

PLANT TEST CHAMBER¹¹

The two primary leaves of the pinto bean plant were used as the basis for assessing air pollution injury to plants. Pinto bean seed of a uniform lot was planted in four-inch clay pots, so that when the plants reached the proper maturity for testing there were three plants of a uniform size and age in each pot.

The plants reach the proper maturity when grown in a glasshouse from 10 to 15 days after seeding. Thus, from the time of initial seeding to exposure to the atmosphere, a time lapse of 10 to 15 days occurs. These plants were grown and protected from air pollution exposure in an especially built glasshouse located in West Covina. The glasshouse was of aluminum construction and measured 14' x 18'10". It was provided with a carbon filter and evaporative cooler, so that all of the air introduced into the house was cooled as well as passed through the activated charcoal to remove the naturally occurring phytotoxicants.

When the plants attained the proper age for their exposure, five pots containing three plants each, and each plant having two uniform, primary leaves, were set aside for each of the six aerometric sampling stations used in this survey. A station wagon was provided for the transport of these plants to the six stations. The rear portion of the station wagon was sealed and the only air inlet was passed through activated charcoal. A small, six volt, squirrel-cage fan provided the necessary air flow through the activated charcoal and into the body of the truck. Since it required about four hours to completely cover the survey route, the possibility of plants being exposed to natural air pollution while being transported about Los Angeles County was eliminated. Each group of plants at the individual stations was exposed for a 24-hour period.

The man in charge of changing the plants in the exposure boxes started his route about 3:30

¹¹by John T. Middleton, Citrus Experiment Station, University of California, Riverside, California.

p.m. Pacific Standard Time. The first change was made at Station 6 in Dominguez.

At each of these stations the plants were placed in a plywood box measuring two feet on the base, three feet in height, and four feet in length. A transparent covering was provided on three sides of each box so that sufficient light was transmitted into the box. The rear end was enclosed with a plywood covering except for the opening where a small squirrel-cage fan with an operating capacity of about 146 cu. ft. per minute was placed in order to provide a constant air flow through each of the boxes. The front end of each box was covered with an open-mesh screen. One box was placed at each station, so that it did not receive direct sunlight. The five pots of plants were placed in each box at a predetermined location. Thus, pots numbered 1, 2, 3, 4, and 5 were placed at the same location in the box at each of the six stations. The plants were watered amply after placing them in the exposure boxes. A recording hygrothermograph was also present in each of the six plant exposure boxes (Fig. 8). The plants exposed the previous 24 hours to the change were placed in the air-filtered station wagon for transport back to the glasshouse at West Covina.

The second change was made at Station 2, Los Angeles High School; the third change at the Fidelity Building, Station 3; the fourth change at the California Institute of Technology, Station 4; the fifth change at the Los Angeles Insectary at Rivera, Station 8; the last change was made at Bassett Park, Station 9. This circuit was completed about 9:30 p.m. PST.

The exposed plants were allowed to remain in the glasshouse at West Covina for approximately 48 hours before they were assessed for plant damage. At the end of this time each individual



leaf was examined and rated for the extent of tissue collapse on the lower side of the leaf. Ten classes of damage were provided in the rating. A leaf with no damage received a rating of 0; one in which there was a trace to 10% of the leaf area involved received a rating of 1; from 11% to 20% received a rating of 2; 21% to 30% received a rating of 3, etc., until the maximum was reached where 100% of the leaf area was involved in tissue collapse, and that received a rating of 10. A sum was taken of all the leaf ratings within a pot, and an average leaf damage rating was obtained by dividing by the number of leaves involved in this sum. If a mean value for leaf damage was desired for the station for a particular day, the five pot averages were summed and this sum was divided by five.

EYE IRRITATION MEASURE¹²

Part of the Aerometric Survey called for a measure of eye irritation, which would be as nearly correct as possible, and which could be used in computing correlations with atmospheric variables. Eye-irritating elements in smog had to be evaluated in their effects on people. Since individuals vary greatly in their sensitivity to smog, it was decided to determine measures of eye irritation for groups rather than for individuals. It was presupposed that the sources of variability in individuals could be made equivalent for a group from one situation to the next and that the composite effect of the sources of individual variability would be essentially the same on all situations.

The minimum size of the panel was ten individuals, drawn from office and/or factory workers near all ten of the station sites used for the survey. Investigators visited the site from which the panel was drawn, made sure that the office was not air conditioned, that ventilation was at least average, and that employee turnover was not too high. All individuals cooperating did so voluntarily; they were chosen on a basis of conscientiousness, good attendance records, and interest; high sensitivity to smog was not required.

Eye Irritation Scale

It was decided to use a form of graphic rating scale as shown in Fig. 9. The scale is a line 5½ inches long, on which the rater places a mark to show the degree of the factor being rated. The graphic rating is analyzed by measuring the linear distance from a reference point on the line to the rater's mark. The reference point is the left-hand end of the line, the unit of measurement is one-tenth of an inch.

Individual irritation amounts were averaged arithmetically to obtain the mean irritation for the entire panel, and the group value is referred

to as the "station-day-mean." The standard deviation and standard error of the mean were then computed.

The standard deviation is a measure of the variability between the individuals composing the panel; the standard error of the mean is a measure of the variability of the mean value for the panel. A sample computation is given in Table I. Values of smog sensitivity as represented in numbers are shown in Table II.

SOUTHERN CALIFORNIA AIR POLLUTION FOUNDATION
"SMOG" SENSITIVITY SCALE

Name _____ Organization _____
Date _____ Time of Day _____ Hours since eating _____

Instructions: Please make a mark across each of the three lines below to show the amount of irritation from smog you feel today.

Amount of Irritation Today

None Some Moderate Severe Worst

EYES: _____
NOSE: _____
THROAT: _____

* * *

Instructions: Please make a mark across each of the three lines below to show how the amount of irritation today compares with the amount you felt yesterday.

Today Compared To Yesterday

More Today About the Same Less Today

EYES: _____
NOSE: _____
THROAT: _____

Please submit this form as arranged for your organization.

THANK YOU

¹²by Philip R. Merrifield and Floyd L. Ruch, Department of Psychology, University of Southern California.

CHAPTER V - FIG. 9
Eye irritation scale

A COMPUTATIONAL EXAMPLE

Assume that the scales for the twenty individuals composing this panel have been measured, and that the values listed below represent the distance, in tenths of inches, from the reference point to the observer's marks.

Obs.	E	PST	()	Obs.	E	PST	()
01	03	()	11	21	1300	(5)
02	14	1600	(17)	12	25	1245	(4)
03	33	1400	(8)	13	26	1400	(9)
04	33	1530	(16)	14	34	1400	(10)
05	34	1230	(2)	15	15	1400	(11)
06	34	1655	(18)	16	25	1500	(15)
07	36	1230	(3)	17	28	1300	(6)
08	05	()	18	35	1200	(1)
09	34	1500	(14)	19	26	1300	(7)
10	38	1425	(13)	20	14	1400	(12)

Notes: E refers in this example to reports of maximum irritation at the time specified in the next column, PST.

The numbers in () to the right of certain of the times is the rank order from earliest to latest of the given times. There were 18 time values reported, so the median will divide these into two groups of nine time values each. The median value is taken as the arithmetic mean of the 9th and 19th values, in this example. It turns out that both of these are the same, 1400 PST, so this value is the median time.

The 95% confidence interval, for a set of this size, will be bounded by the 5th and 14th cases in serial order. These values are 1300 and 1500 PST. The 95% confidence interval is thus two hours, specifically, 1300-1500 PST.

$$\Sigma E = 531$$

$$\Sigma E^2 = 15245$$

$$N = 20$$

$$\text{MEAN} = 25.65$$

$$\sigma_M^2 = 5.4909$$

STANDARD ERROR
OF THE MEAN, $\sigma_M = 2.35$

FORMULAS FOR COMPUTATION:

$$\text{MEAN } M = \frac{\Sigma E}{N}$$

$$\sigma_M^2 = \frac{N \Sigma E^2 - (\Sigma E)^2}{N^2 - (N-1)}$$

$$\sigma_M = \sqrt{\sigma_M^2}$$

MEAN VALUE = 25.65

CHAPTER V—TABLE II

Number	Cue word	Comment
05	None	A mean value, or an individual value of 20.5 may be interpreted as indicating an amount of irritation that is greater than "some" but less than "moderate."
15	Some	
25	Moderate	
35	Severe	
45	Worst	

Table III displays results obtained downtown Los Angeles for the month of August.

Two Methods of Reporting Eye Irritation

Eye irritation data were collected in *two phases*: one, a random sampling of days and a predetermined time of reporting, and the second, a selected sample of days with individuals reporting the maximum irritation experienced during the day and the time at which the maximum irritation occurred.

Phase I: Early in the survey investigators decided to sample smoggy as well as non-smoggy days. Routine reports were made on Tuesday and Friday of each week, and as conditions warranted, additional reports were requested. Each panel was assigned a time of day to observe and report irritation. Several panels were employed at each station and soon comments were received from individuals on different panels to the effect that irritation had been bad the previous day when no report was made. Therefore, Phase II was inaugurated.

Phase II: In this stage more emphasis was placed on investigating days with apparent irritation and some method was devised to measure the irritation at its peak. Observers were asked to report the greatest amount of irritation experienced and the time of day at which this maximum was noticed, and also whether they were indoors or outdoors. The selection of days for which to request reports depended on the

CHAPTER V—TABLE III

EYE IRRITATION SURVEY Downtown Los Angeles, August 1954

Date	Mean Eye Irritation (01-55)	Median Time PST	Number in Panel	Standard Error of Mean
8/11	17.0	1025	19	2.37
8/17	22.0	1000	20	1.97
8/18	14.9	1030	17	2.17
8/20	14.9	1000	16	2.03
8/24	10.2	1000	21	1.44
8/27	16.6	1000	22	1.83
8/31	15.3	1000	23	1.68

irritation forecasts by the Air Pollution Control District. Instructions included specifically reporting maximum irritation "inside and outside." A statistical investigation was made to show the validity of the hypothesis that there is "no difference between inside and outside maximum irritation reports." Accordingly, "inside" and "outside" maximum values were pooled without correction. Maximum irritation is computed in the same way as "station-day-mean" and is called "mean-maximum." In order to determine the time of maximum irritation, a median of the reported times was decided on as furnishing the best estimate of the true time of occurrence of maximum irritation.

Expert Panel

As a contrast with the regular panels composed of people at random, one expert panel was selected at California Institute of Technology composed of Dr. A. J. Haagen-Smit and his co-workers. A comparison of mean values reported by this panel with those reported by a lay panel on the campus of California Institute of Technology shows that the expert panel reported means of about 5 units less. This is possibly due to the fact that the experts had a higher criterion for eye irritation since they were familiar with odors and irritants. Variability of the expert panel was comparable to the other panels, and reliability was estimated as 0.66 during a period when the variability of the daily means was relatively low.

Using Eye Irritation Measures

It was presupposed that each panel represented a random sample of the same people-in-general population, that one panel was equivalent to the next panel in reporting mean values of irritation, and that therefore it was possible to infer a different level of stimulus from different mean values of irritation thus reported. However, this presupposition seems somewhat questionable and can be tested in order to obtain a correction factor. Until this is done, the data from different panels should not be pooled.

Relationships developed within each panel may be compared to similar relationships developed by another panel at another station. Correlations between eye irritation and atmospheric variables, for instance, can be proved or disproved in this fashion. At this stage of the survey, the comparison between panels of obtained relationships was preferred to the pooling of basic data in an effort to find relationships applicable to all stations.

SUPPORTING METEOROLOGICAL OBSERVATIONS

Inversion Height

Inversion height data were determined from radiosonde observations taken at the Long Beach Municipal Airport by the Air Force Air Weather Service detachment. Observations were made four times daily: 1:00 a.m., 7:00 a.m., 1:00 p.m., 7:00 p.m., PST. The radiosonde consists essentially of an aneroid barometer, a resistance thermometer, and a hygrometer controlling the audio signal sent out by a radio transmitter. The radiosonde is carried aloft by means of a free balloon. The ground station receives radio signals representing the temperature, humidity, and pressure at the various levels of the atmosphere through which the radiosonde passes.

Radiation

Continuous radiation records were obtained using Eppley pyrhemometers at the U.S. Weather Bureau—Los Angeles City Office, U.S. Weather Bureau—Airport Station, University of California at Riverside, University of California at Los Angeles, and Mt. Wilson.

Total direct solar radiation and "sky" radiation, i.e. the short-wave radiation scattered toward the ground by the atmosphere, were recorded continuously by the Eppley pyrhemometer. The radiation falls on two concentric silver rings, of which one is painted with lamp black to absorb most of the radiation and the other (outer

cold ring) is coated with magnesium oxide to form a reflecting surface. The difference in temperature between these two surfaces is measured by thermocouples which are in thermal contact alternately with the blackened and the whitened rings but are electrically insulated from the silver. Either 10 or 50 thermocouple junctions form the thermopile. The whole thermopile is mounted at the center of a three-inch glass bulb filled with dry air and sealed. Only radiation shorter than about 2.5 microns is transmitted by the glass. The 10 junction-type pyrhelimeter has a sensitivity of about 2 millivolts per gram calorie per minute per centimeter squared and records on a millivolt recorder.

Wind Velocity

Surface wind speed and directions were observed hourly at about fifty-five stations throughout the Basin and surrounding hills. Various types of anemometers and wind vanes were used in making these measurements. The stations included the Weather Bureau, Air Force, Navy, and Marine stations, as well as equipment operated by public and private utility companies and various industrial concerns. These data were obtained and coordinated by the Los Angeles County Air Pollution Control District and made available to the Foundation.

Temperature and Relative Humidity

At six of the Aerometric Survey stations, temperature and relative humidity were recorded continuously by means of a hygrothermograph in the plant test chamber. A hair-type hygroelement and a Bourdon-type thermo-element actuated pens which plotted the relative humidity and temperature traces on a chart. The chart was mounted on a cylinder which revolved once a week. In addition, temperature and humidity records were available from the three Weather Bureau stations in the Basin and several other stations including those of the military.

OPERATIONS

Measurement Schedule

1. The survey got underway on July 30 when an oxidant recorder was put into operation at Station 3. As instruments became available and stations were readied, the recorders were put into operation so that all were going by August 6, except at Azusa where work started on August 16. Except for occasional breakdowns and troubles, the oxidant recorders were operating continuously until the end of the survey November 30, 1954. The Ralph M. Parsons Company, Research and Development Division, Pasadena, California, was given a contract to operate these recorders.

2. The sampling program for oxides of nitrogen got under way on a seven-day week as follows:

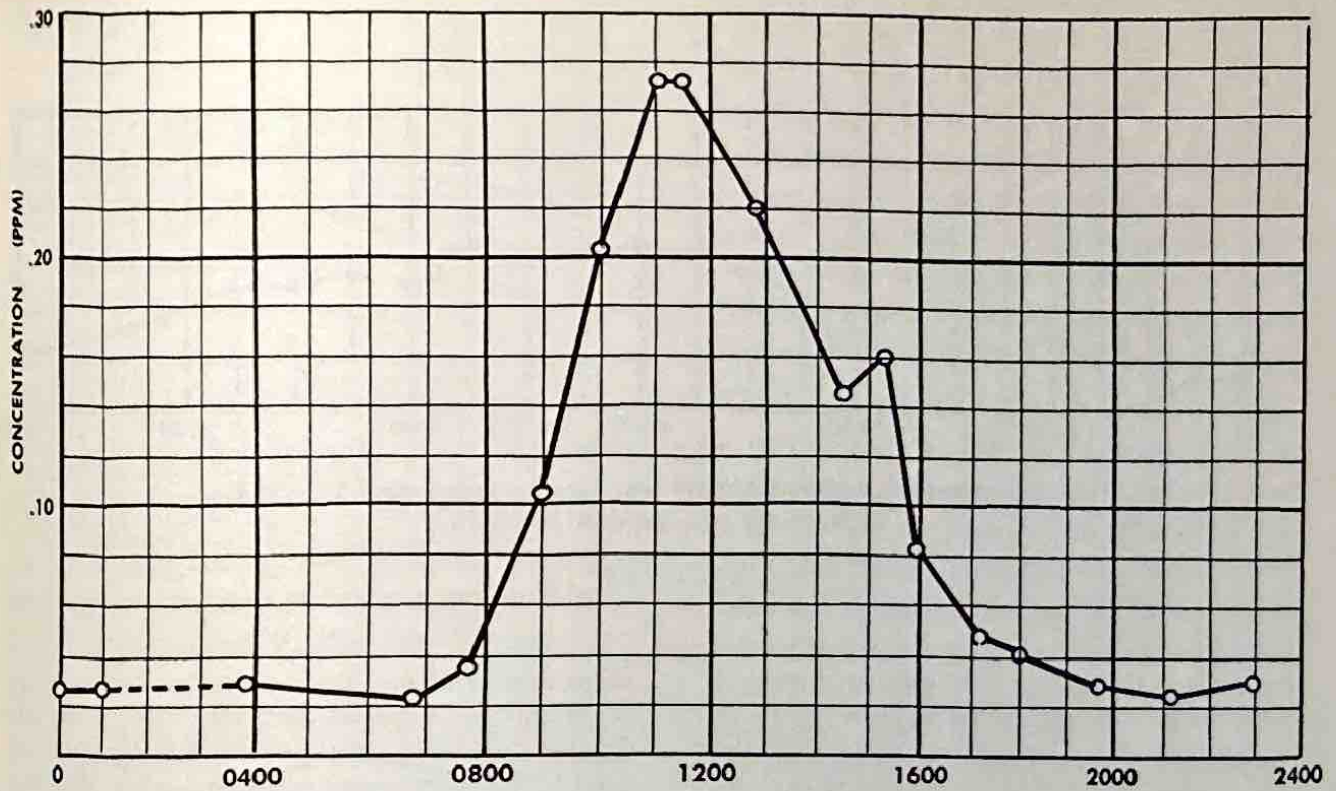
Station 3	8:00 a.m.	August 7
" 4	8:00 a.m.	August 8
" 5	8:00 a.m.	August 9
" 1	8:00 a.m.	August 9

Samples of air were obtained every three hours around the clock for each station until about September 30. Starting about October 1, hourly samples were obtained as follows:

Station	Time of Samples	Dates
1	6:00 a.m.-1:00 p.m.	10/1/54-11/30/54
3	6:00 a.m.-1:00 p.m.	10/4/54-11/30/54
4	6:00 a.m.-1:00 p.m.	10/2/54-11/30/54
5	6:00 a.m.-1:00 p.m.	10/4/54-11/30/54

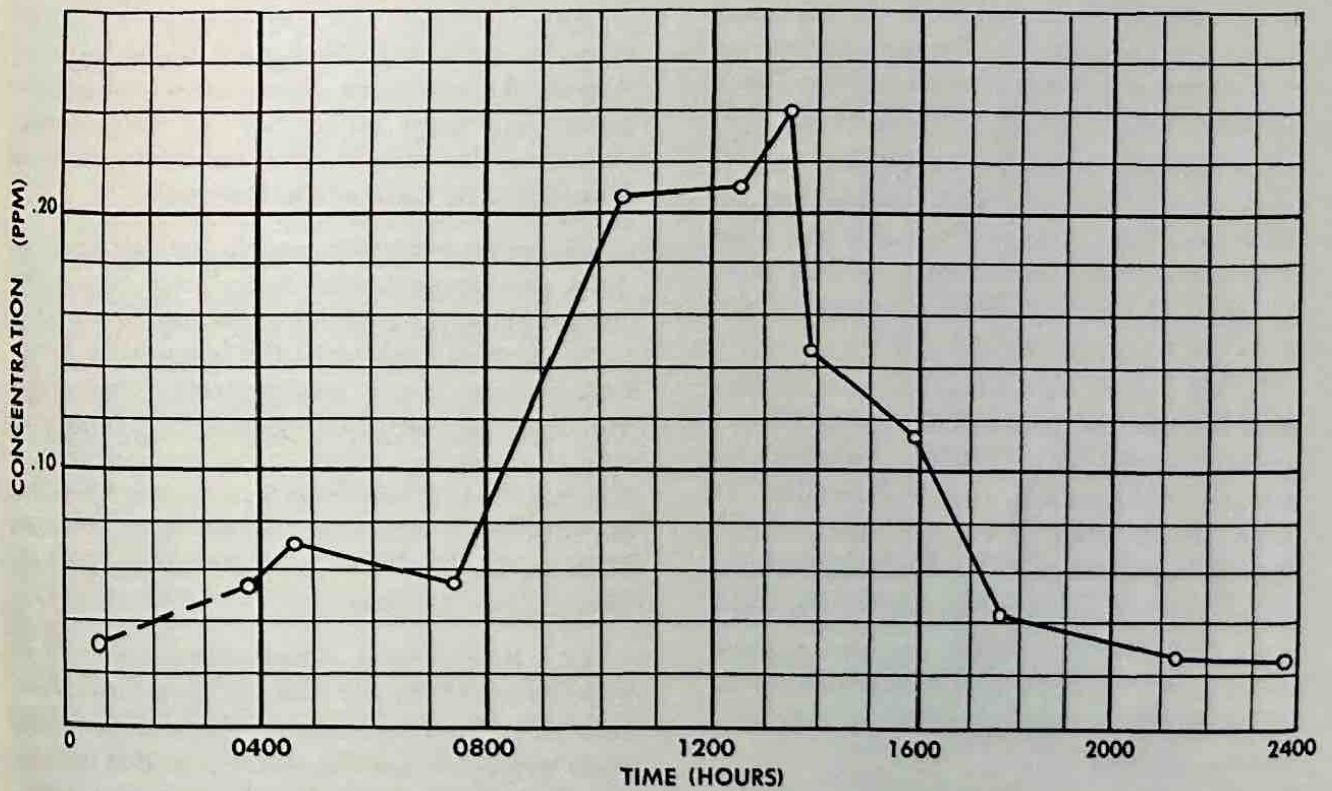
The operation and laboratory analyses were done under contract with the A. L. Chaney Laboratories, Glendale, California.

3. and 4. Hydrocarbon and carbon monoxide measurements were started on August 2 at Stations 3 and 4. Samples of freeze-out hydrocarbons were obtained on an hourly basis at Station 3 and Station 4, five days a week. On October 21, sampling was initiated for six days a week, Thursday through Tuesday, omitting Wednesday. At each station six samples were collected



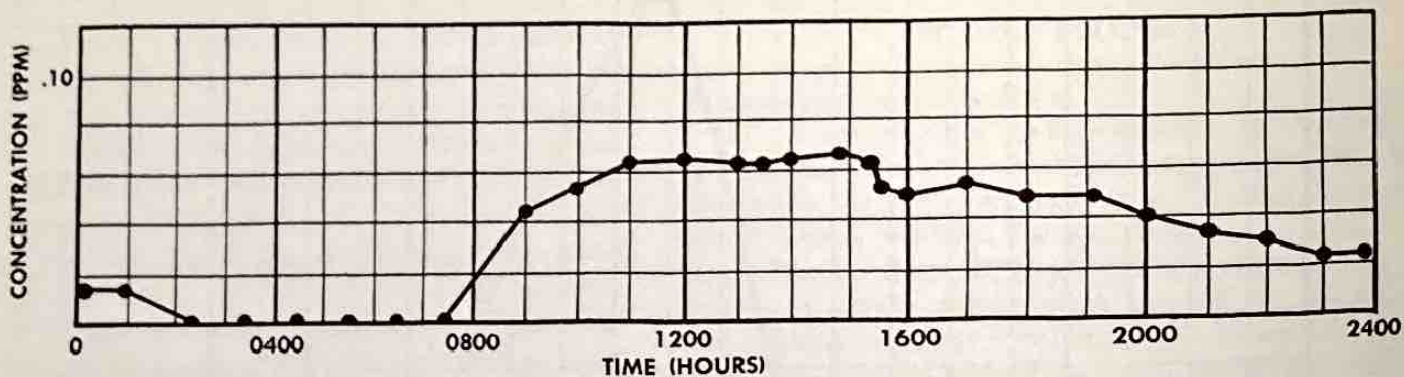
OXIDANT CONCENTRATION VS. TIME—October 8, 1954 STATION 4—PASADENA

CHAPTER V—FIG. 10a



OXIDANT CONCENTRATION VS. TIME—November 15, 1954 STATION 2—WILSHIRE DISTRICT

CHAPTER V—FIG. 10b



OXIDANT CONCENTRATION VS. TIME — September 14, 1954
STATION 12 — SANTA BARBARA

CHAPTER V — FIG. 10c

on an hourly basis from 6:30 a.m. at Station 3, and at Station 4 from 10:30 a.m. until 4:30 p.m. As for oxides of nitrogen additional samples were obtained at selected low inversion periods.

5. Sampling for aldehyde analyses was not started until September 21 at Stations 3 and 4. Hourly samples were obtained on the same schedule as hydrocarbons. The above three operations were done under contract with the Truesdail Laboratories, Los Angeles, California.

6. The AISI automatic smoke filter equipment for particulate sampling was put into operation at Station 3, August 9, and hourly samples were obtained continuously to November 30, 1954. This was also done at Station 4, August 12 to November 30, 1954.

7. The Staplex high volume particulate samplers were put into operation at Stations 3 and 4 on August 9 and 10, and 24-hour samples were obtained seven days a week until November 30, 1954. The operation of the AISI and Staplex were under contract with The Kettering Laboratory, University of Cincinnati, Cincinnati, Ohio.

8. The sulfur dioxide recorder was operated continuously from September 4 to November 30 at Station 3, under contract with The Ralph M. Parsons Company.

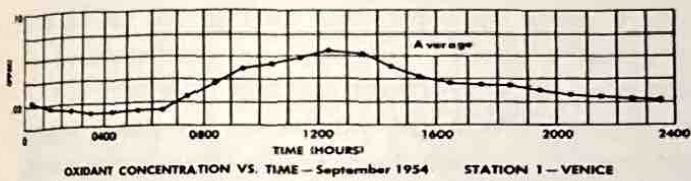
9. The transmissometers were set in place during August, but because of difficulties of

alignment and calibration, useful data were not obtained until September 10, 1954. From that date on, all four stations were operating continuously 24 hours a day until November 30, 1954, under contract with The Ralph M. Parsons Company.

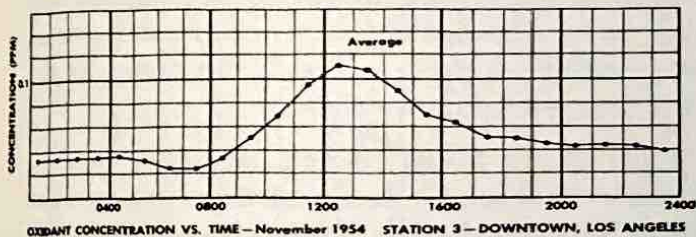
10. The plant test chambers were put at Stations 2, 3, 4, 6, 8, 9, August 4 and starting on August 5 pinto bean plants were put out almost every day until November 30. This operation was done by means of a research grant to the University of California, Riverside.

11. Eye irritation panels were set up during July and August, and initial reports were submitted from August 10 to August 31 for two or three days a week until the last week of November. During August and September surveys were run Tuesdays and Fridays plus usually one other day if smog was forecast; no data are available for Saturdays and Sundays. During November surveys were run only on the basis of a smog forecast by the Los Angeles County Air Pollution Control District.

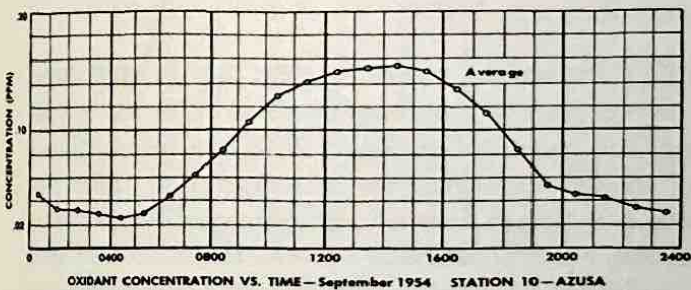
12. Radiosonde observations are made all year by the U. S. Air Force at Long Beach; therefore data for obtaining inversion characteristics were available for the entire period of the Aerometric Survey except for a few days late in September when helium supply was exhausted.



CHAPTER V - FIG. 11a



CHAPTER V - FIG. 11b



CHAPTER V - FIG. 11c

13. Solar radiation measurements are made all year at the Weather Bureau City Office and Airport Stations, and at the University of California at Riverside. The UCLA station was under way before August 1 on an all-year operation. The Mt. Wilson station was put into operation November 5 and was discontinued November 30.

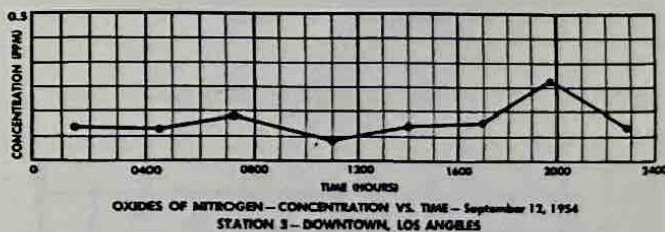
14. Wind velocity and direction data are obtained all year and therefore were available to the Foundation for the period of the survey through the Los Angeles County Air Pollution Control District.

15. Temperature and relative humidity measurements taken by hygrothermographs were put into operation in the plant test chambers on August 5 as part of the plant study with the University of California, Riverside.

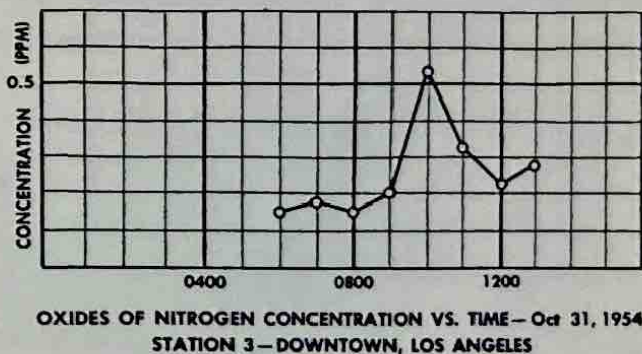
Preliminary Data

Information which has been compiled on this project is still being processed to determine averages, correlations of various measurements, maxima and minima, and other manipulations. To indicate the type of data assembled, examples of some of the measurements are described below.

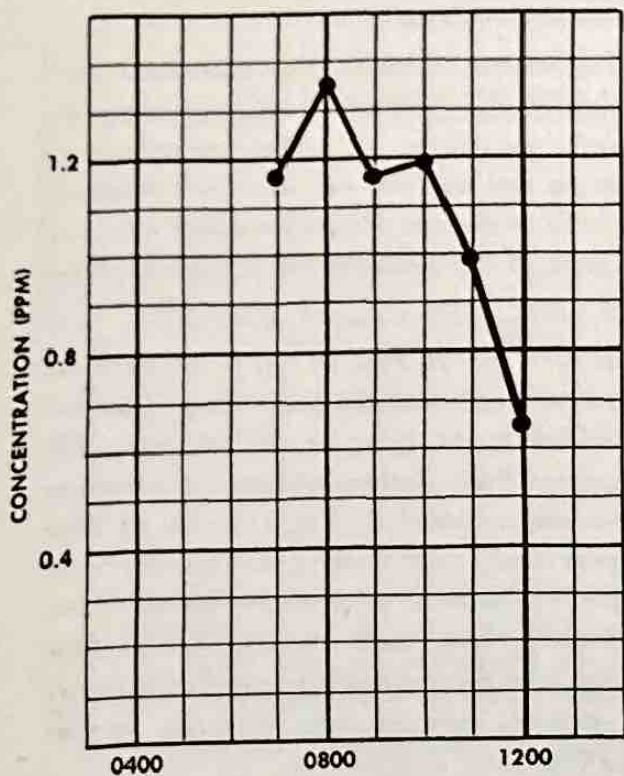
1. *Oxidant*. In Fig. 10 (a, b, c) there are three curves showing the daily values of oxidant concentration vs. time for the Pasadena, Wilshire, and Santa Barbara stations. The particular dates are indicated. In Fig. 11 (a, b, c) there appear three curves showing the average oxidant value for the month of September for the Venice, downtown, and Azusa stations. All of these curves show the previously reported daily change in oxidant, with maxima appearing between 11:00 a.m. and 1:00 p.m.



CHAPTER V - FIG. 12a

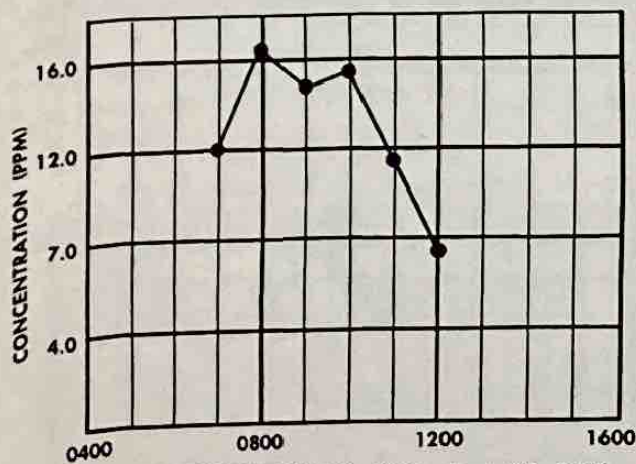


CHAPTER V - FIG. 12b



HC CONCENTRATION VS. TIME—Sept 24, 1954
STATION 3—DOWNTOWN, LOS ANGELES

CHAPTER V - FIG. 13a



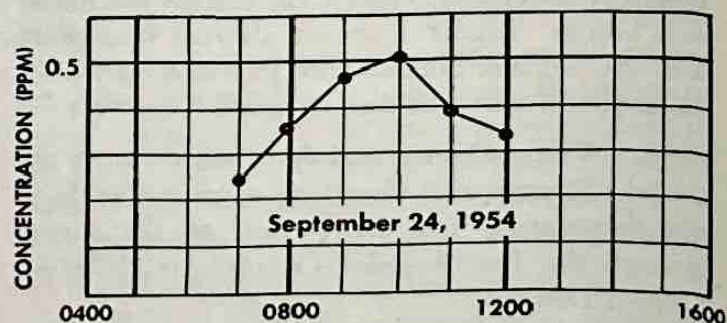
CO CONCENTRATION VS. TIME—Sept 24, 1954
STATION 3—DOWNTOWN, LOS ANGELES

CHAPTER V - FIG. 13b

2. *Oxides of nitrogen.* In Fig. 12 (a, b) two curves are shown, giving the concentration of oxides of nitrogen against time. In part (a) of this figure, the eight points on the curve represent samples which were taken three hours apart. In part (b) of the figure, the eight points shown were taken at hourly intervals. This change from three hour sampling to one hour sampling was made in an attempt to find whether a daily variation existed which was not being shown by the three hour sampling period.

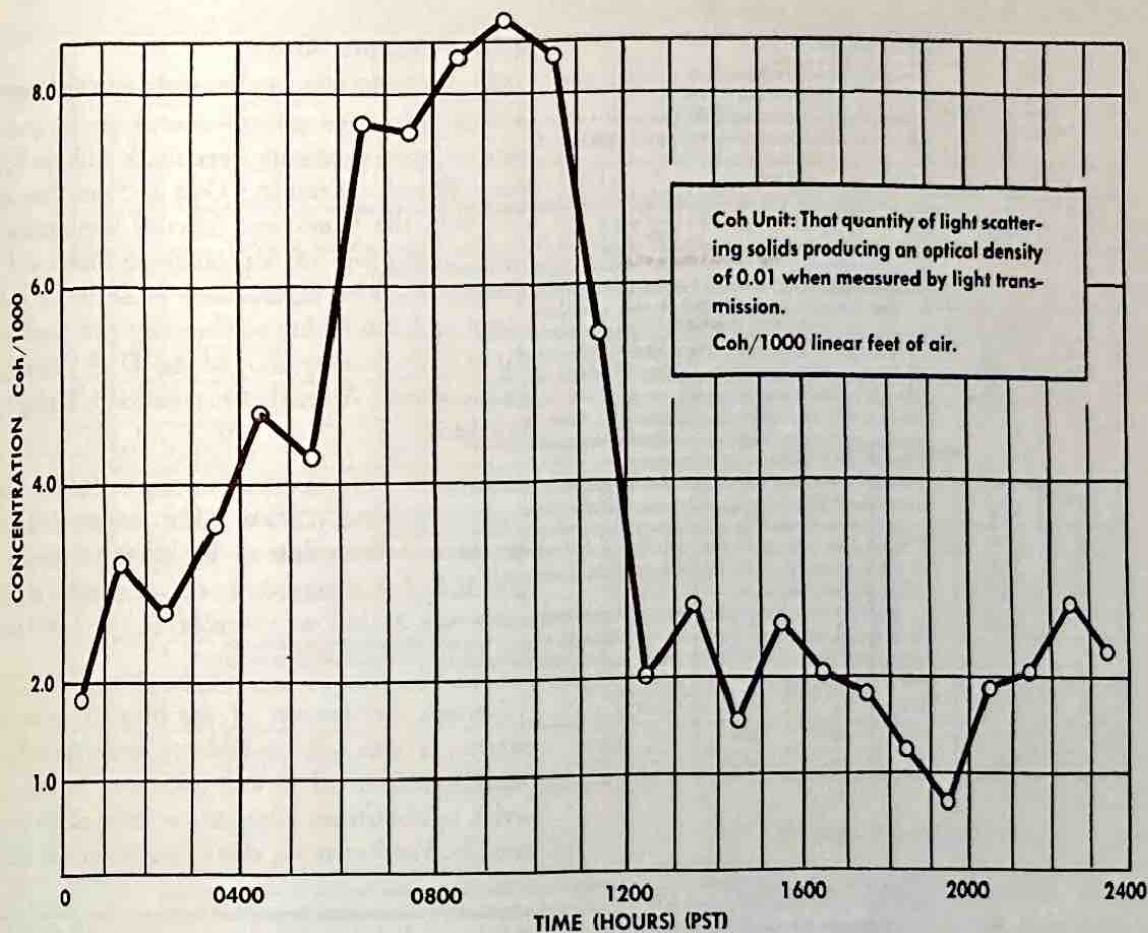
3. *Hydrocarbons, carbon monoxide, and aldehydes.* In Fig. 13 (a, b, c) there appear three curves showing hydrocarbon concentration, carbon monoxide concentration, and aldehyde concentration measured at the downtown station on September 24, 1954.

4. *Particulate matter.* Fig. 14 (a, b) shows a curve giving the variation in Coh units with time for September 24, 1954 and in addition a bar chart showing the average Coh units per thousand lineal feet of air averaged for each day for the month of September, 1954. A Coh unit is defined as that quantity of light scattering solids which produce an optical density of 0.01 when measured by light transmission of a circular spot on a filter paper through which has been drawn a measured quantity of air.

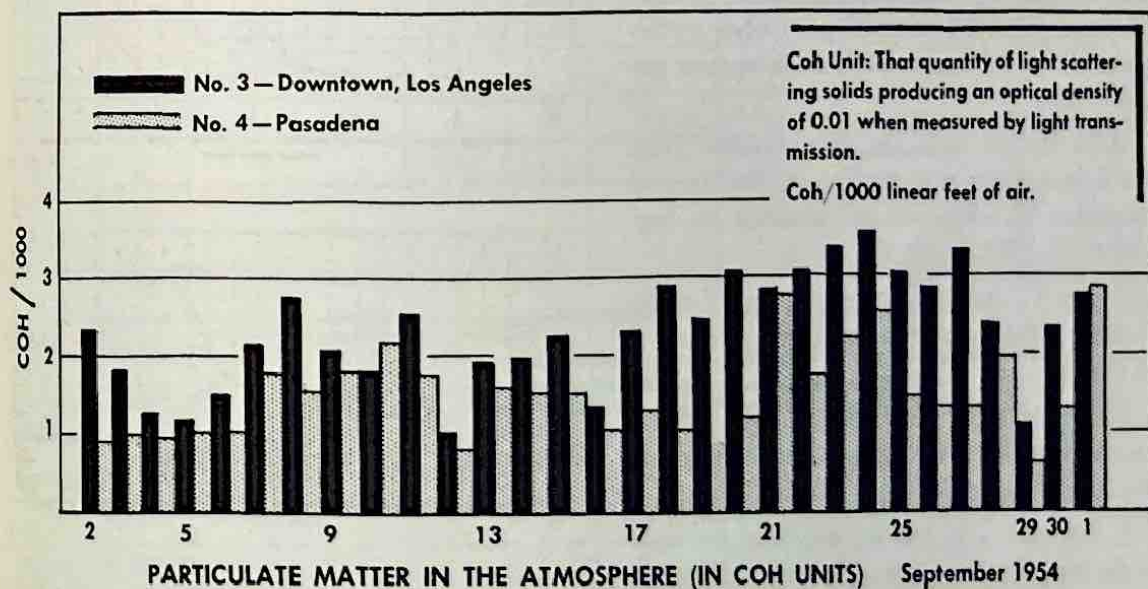


ALDEHYDES CONCENTRATION VS. TIME
STATION 3—DOWNTOWN LOS ANGELES

CHAPTER V - FIG. 13c



COH CONCENTRATION VS. TIME—September 24, 1954 STATION 3—DOWNTOWN, LOS ANGELES
CHAPTER V - FIG. 14a



PARTICULATE MATTER IN THE ATMOSPHERE (IN COH UNITS) September 1954

CHAPTER V - FIG. 14b

AIR POLLUTION SURVEY

Sampling Station: No. 3
(Downtown, Los Angeles)
Sampling Date: 9/23-24/54
2:00 P.M.
Sampling Time: 23 hrs. 55 min.

AIR VOLUME		SAMPLE WEIGHT			
Cu. ft.	Cu. M.	Final	Initial	Wt. mg.	$\mu\text{g}/\text{cu. m}$
60,300	1700	4.152	3.245	907	534

ANALYTICAL DATA

ORGANIC MATTER			POLYCYCLIC HYDROCARBONS		
mg. Extracted	$\mu\text{g}/\text{cu. m}$	% of Sample	mg.	$\mu\text{g}/\text{cu. m}$	% of Sample
179.6	105.6	19.8	10.4	6.1	1.15

INORGANIC ANALYTICAL RESULTS

Metal, etc.	$\mu\text{g}/\text{M}^3$	%	Metal, etc.	$\mu\text{g}/\text{M}^3$	%
Mn	0.26	0.05	Mg	4.7	0.9
Pb	11.7	2.2	Na	7.3	1.4
Sn	0.01	0.01	K	5.0	0.9
Fe	7.4	1.4	Sr	0.18	0.03
Al	---	---	Be	0.0001	0.0001
Cu	0.21	0.04	As	nil	nil
Ag	0.0012	0.0002	F-	1.07	0.20
Ti	0.57	0.11	SO ₄ ⁻²	41.2	7.7
V	0.029	0.006	NO ₃	22.5	4.2

CHAPTER V - FIG. 15

5. *Analysis of particulate matter.* Fig. 15 gives data for the analysis of the particulate matter collected on the high volume Staplex sampler for September 24, 1954. A total of 60,300 cubic feet of air was sampled on this particular day, and the total particulate matter collected was 4.15 grams or 534 micrograms per cubic meter.

6. In Fig. 16 there are data obtained from the *transmissometers* at the Federal Building on November 15, 1954 and at Pasadena on September 10, 1954.

7. Fig. 17 shows *plant damage data* for the months of August and September at Station 9 in Bassett.

8. Fig. 18 gives *eye irritation data* for the month of October for Station 6, Dominguez, and Station 4, Pasadena.

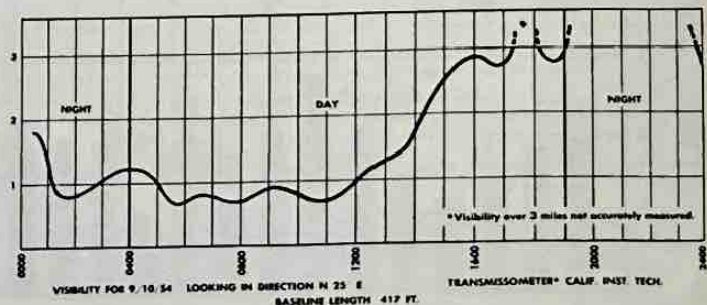
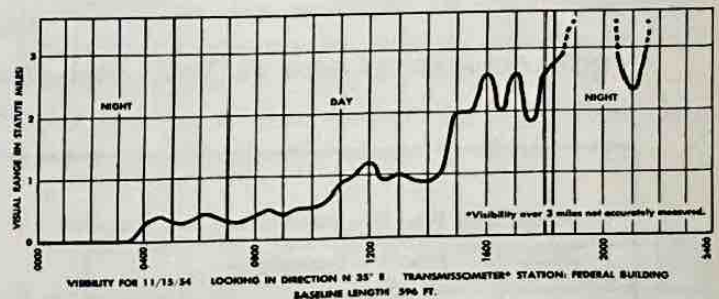
9. Fig. 19 is a plot of the height of the base of the inversion layer as measured by *radiosonde* at Long Beach for each day of October, 1954.

Measurements Aloft

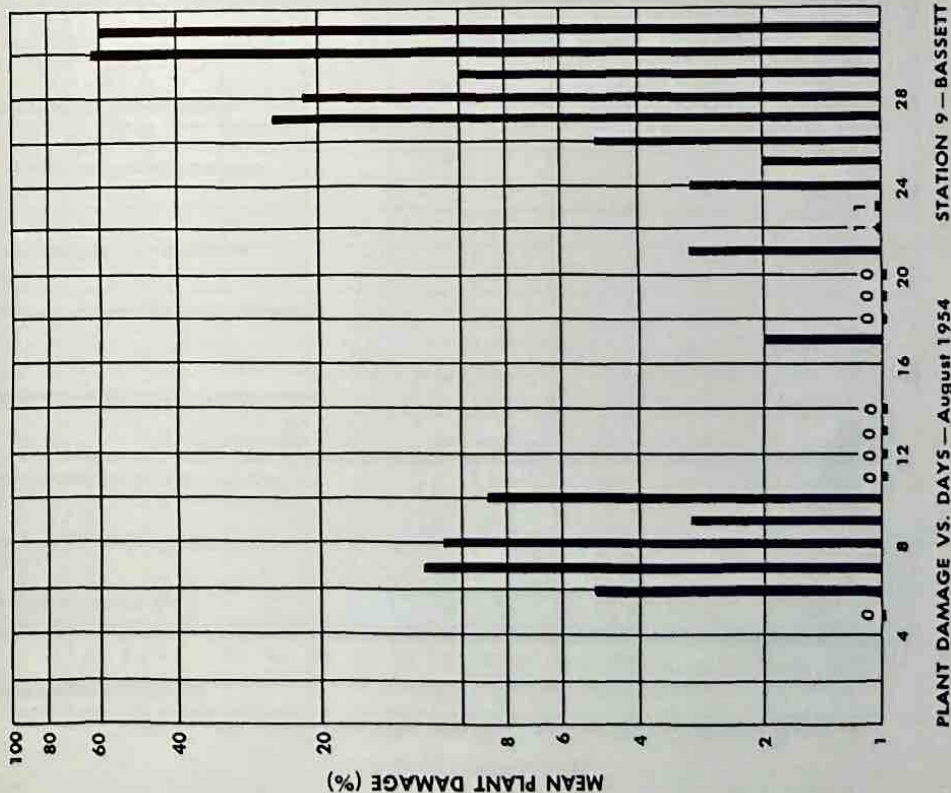
To study the dispersion of the contaminants at various altitudes above several of the ground stations, arrangements were made with the U. S. Navy Reserve Training Unit at Santa Ana and also with the Goodyear Aircraft Corporation to make a number of air sampling flights with a blimp. Thirteen flights were made in the Navy blimp and two flights were made in the Goodyear blimp. The cooperation of the U. S. Navy and the Goodyear Aircraft Corporation is highly appreciated.

Samples were taken as nearly as possible over existing ground stations. The pattern followed was to ask the pilot of the blimp to execute a tight turn for a period of several minutes at altitudes (a) as low as possible, (b) at 1,000 feet, and (c) as high as possible.

Certain limitations of the blimp became apparent. It was not possible to hover at a fixed point, but instead it was necessary to circle in order to obtain an adequate volume of air for a sample. Furthermore, due to the manner in which

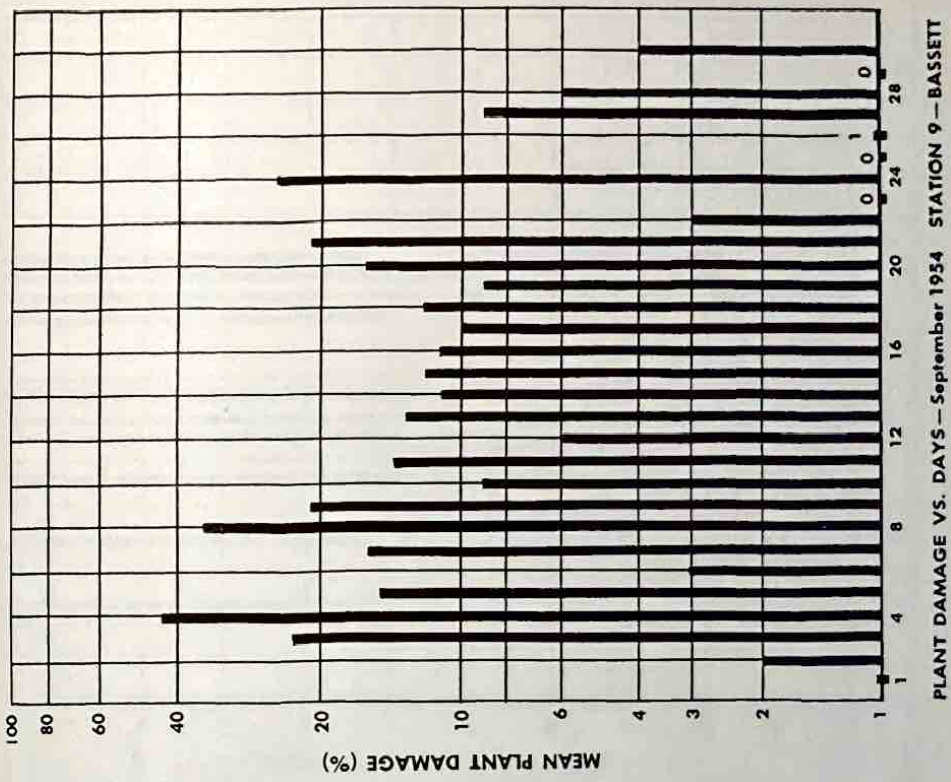


CHAPTER V - FIG. 16



PLANT DAMAGE VS. DAYS—August 1954

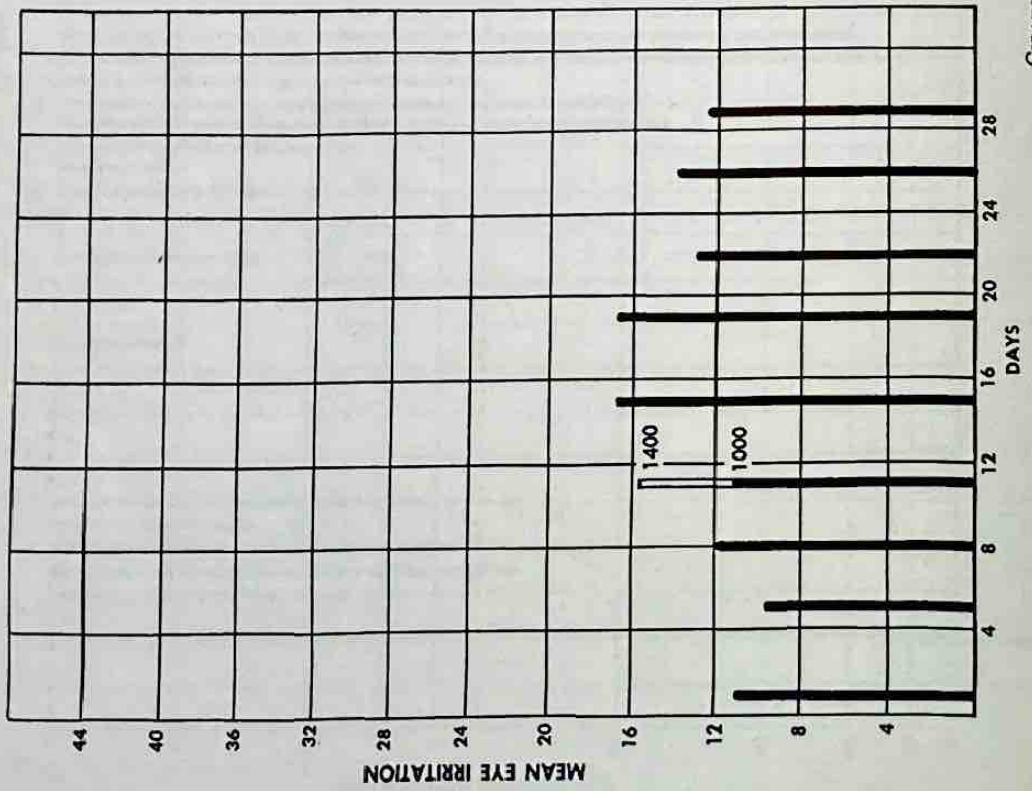
STATION 9—BASSETT



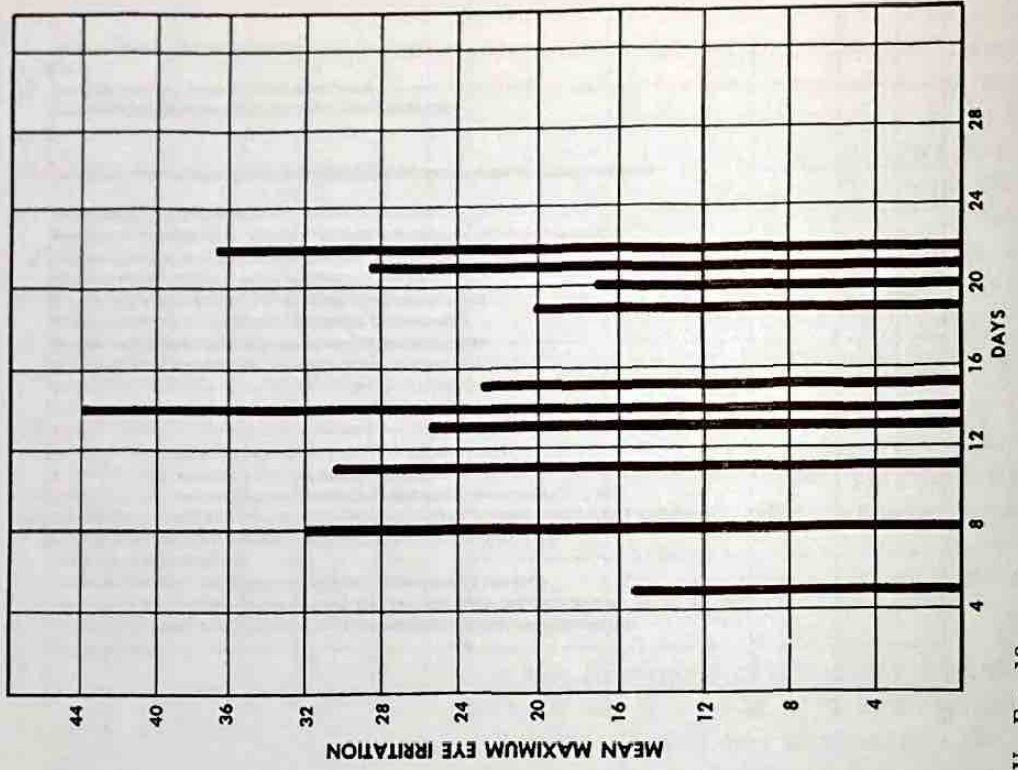
PLANT DAMAGE VS. DAYS—September 1954

STATION 9—BASSETT

CHAPTER V—FIG. 17



EYE IRRITATION VS. DAYS - October 1954
STATION 6 - DOMINGUEZ

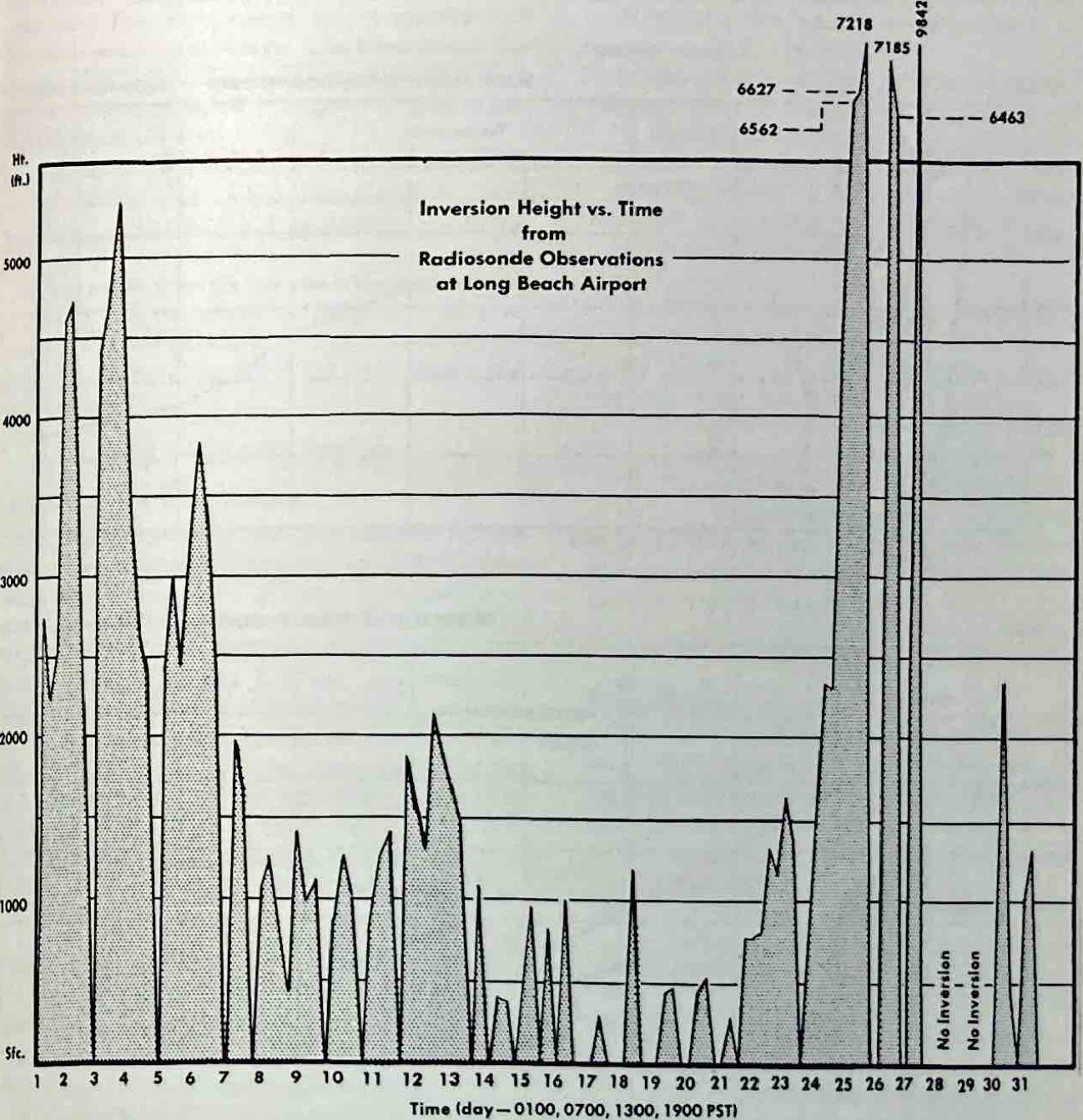


EYE IRRITATION VS. DAYS - October 1954
STATION 4 (LAY PANEL) - PASADENA

the blimp was ballasted, it was usually not possible to attain altitudes very much above 3,000 feet without valving helium.

Oxidant determinations were made by sampling air over a period of six minutes while the blimp was circling. A special 24-volt motor at-

tached to the blimp electrical system was used to drive an air pump which drew air through an A.S.T.M. sulfur absorber. This absorber contained a measured quantity of potassium iodide solution, which was placed in the scrubber just before sampling. Air was drawn through a dry



INVERSION HEIGHT VS. TIME—October 1954

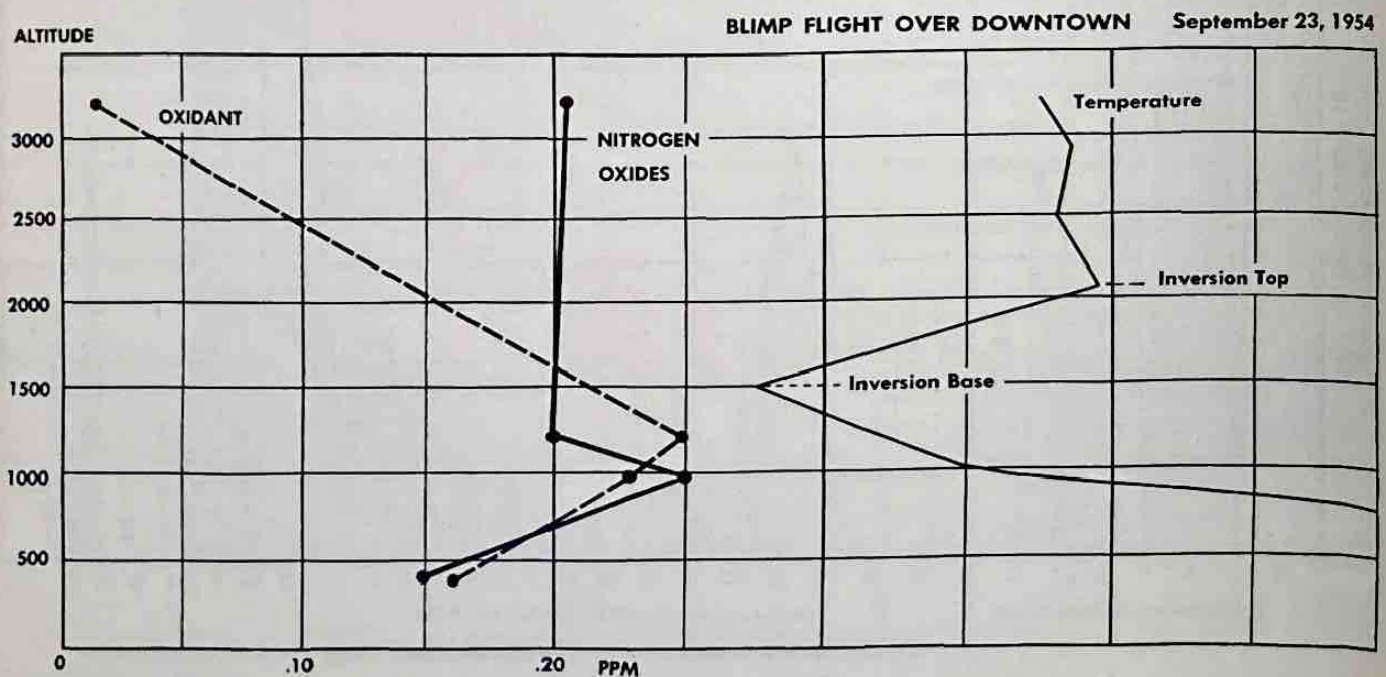
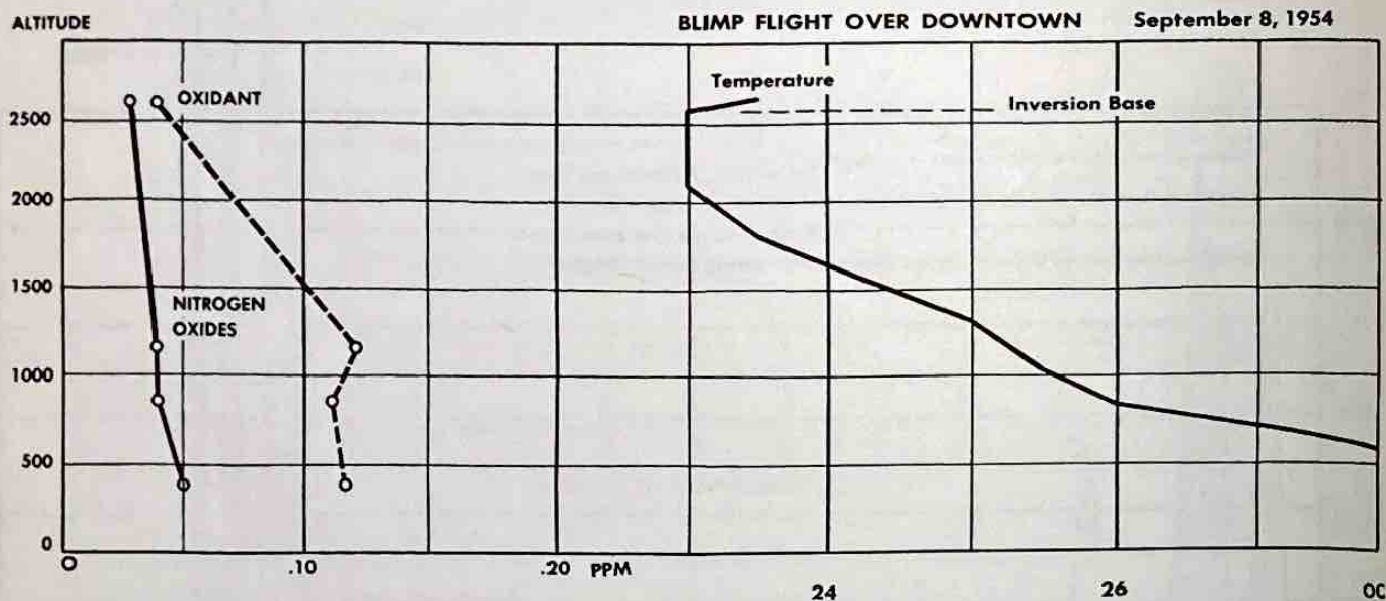
CHAPTER V—FIG. 19

test meter at the rate of five liters per minute for about six minutes.

Immediately following sampling, the solution was removed from the scrubbers and placed in small bottles which were shielded from light. As soon as possible, the iodine concentration in the

sample was measured colorimetrically, using the reagent from a second scrubber as a blank. Results were calculated in parts per hundred million of ozone.

Oxides of nitrogen samples were taken at the same time as the oxidant samples with an evacu-



CHAPTER V - FIG. 20

ated flask fitted with a serum stopper. In the flask was placed a measured amount of 0.05 normal sodium hydroxide solution. The flask was held out of the window of the blimp gondola while a hypodermic needle was plunged through the stopper. After one minute the needle was withdrawn. This experiment was repeated and the flasks were returned to the laboratory for analysis. The Griess-Ilosvay procedure was used for the determination of nitrogen dioxide essentially as described above.

Temperature and humidity determinations were also made with an aerometerograph at the same time as the chemical samples were being taken.

Plots are being made for each flight, showing variation in concentration of oxidant, oxides of nitrogen, and temperature with altitude. An example of the data obtained for two flights appears in Fig. 20.

DATA REDUCTION

IBM Setup and Tabulations

Early in the setup of the Aerometric Survey it was realized that an enormous amount of data would be developed in the measurement program. Therefore, it was necessary to use modern methods of data handling in order to cope with manipulations required for the projected analyses and correlations of these data. A contract was made with Stanford Research Institute, Palo Alto, to handle not only the data reduction but also the processing of the information on IBM cards. Stanford Research Institute, in turn, sub-contracted for the use of IBM equipment with the Department of Mathematics at Stanford University.

Plots and Graphs

Most of the data for the four-months survey were processed as follows:

1. Daily curves of oxidant concentration vs. time of day for each station for each day.
2. Twenty-four (24) hour integration of oxidant concentration for each day for each station.
3. Monthly curves for each station of oxidant

concentration, showing hourly average vs. time of day, together with range of maximum values for each hour.

4. Daily curves of oxides of nitrogen (as NO_2) concentration vs. time of day for each station.

5. Monthly average curves for oxides of nitrogen (as NO_2) concentration.

6. Daily curves of hydrocarbon (as hexane) concentration vs. time of day for each station.

7. Monthly average curves for hydrocarbon (as hexane) concentration.

8. Daily curves of carbon monoxide concentration vs. time of day for each station.

9. Monthly average curves for carbon monoxide concentration.

10. Monthly bar graphs of mean severity of injury to test plants vs. day of the month.

11. Monthly bar graphs of mean or maximum eye irritation vs. day of the month.

12. Daily curves of Coh units vs. time of day for each station.

13. Daily curves of ratio of carbon monoxide to hydrocarbon concentration vs. time of day.

In addition to these plots, Stanford Research Institute completed tables of all data which were printed directly from the IBM cards.

ANALYSES

Hypotheses

The following hypotheses were set up in October and forwarded to Stanford Research Institute for formulating the corresponding statistical hypotheses and pertinent tests:

1. Plant damage increases as 24-hour integrated oxidant increases.
2. Plant damage increases as 24-hour integrated oxidant increases where these integrations are performed above each of the levels 5, 10, 15, and 20 pphm oxidant.
3. Plant damage increases as 24-hour integrated oxidant increases for each of two groups of data; these groups being defined as (a) those with high value of the product of temperature and relative humidity, and (b) those with low value.

4. Plant damage increases as average value of NO₂ concentrations for the day increases.
5. Plant damage increases as average value of aldehyde concentrations for the day increases.
6. Plant damage increases as eye irritation increases.
7. Plant damage increases as average visibility (6:00 a.m. to 6:00 p.m.) decreases.
8. Twenty-four hour integrated oxidant at Stations 3 and 4 increases as total solar radiation increases (pyrheliometer data taken at U. S. Weather Bureau City Office).
9. Twenty-four hour integrated oxidant increases as inversion height at 7:00 a.m. decreases.
10. Same as (9) except inversion height at 1:00 p.m.
11. Eye irritation increases as oxidant value at time of irritation increases.
12. Eye irritation increases as oxidant value increases above a certain value (try 10, 20 ppm).
13. Eye irritation increases as average value of aldehyde concentration increases.
14. Eye irritation increases as average value of hydrocarbon concentration increases.
15. Eye irritation increases as average value of nitrogen oxide concentration increases.
16. Eye irritation increases as Coh value increases.
17. Eye irritation increases as visibility decreases.
18. Eye irritation increases as total organics concentration increases.
19. Eye irritation increases as total mass concentration of particulates increases.

Correlations

During November, Stanford Research Institute proposed the following method to determine the degree of correlation between the various pairs of variables:

1. Breakdown by Groups.

Variable A will be sorted by value and

then broken down into six (6) equal groups. Thus there will be six groups of equal size, each containing all the values of A in a certain range.

The average value of A and the $\Sigma\Delta^2$ (Δ being the difference between A and the average value of A) will be computed for each group. The average value of the variable B and the $\Sigma\Delta^2$ will be likewise computed for each group.

2. Least Squares Fit.

Variable A will be expressed as a function of B in the form:

$$A = a + bB + cB_2$$

The coefficients will be computed so as to give the least squares fit with the experimental data.

The $\Sigma\Delta^2$ will be computed where Δ is the difference between the experimental A and the corresponding A on the least squares curve. Intermedial results such as ΣB , ΣB_2 , ΣB_3 , ΣAB , etc., will also be listed.

3. Analysis:

The results of A and B will be analyzed for possible correlations. Where significant correlation is found, scatter diagrams will be drawn and the correlation will be expressed in its most meaningful form.

Pairs of Variables

Below is a list of the pairs of variables to be correlated:

Variable A	Variable B
Plant Damage	24-hr. Oxidant Integration
Plant Damage	“ (above 5 pphm)
Plant Damage	“ (above 10 pphm)
Plant Damage	“ (above 15 pphm)
Plant Damage	“ (above 20 pphm)
Plant Damage	NO ₂ (daily average)
Plant Damage	HC (daily average)
Plant Damage	Aldehyde (daily average)
Plant Damage	Eye Irritation
Plant Damage	Visibility (6:00 a.m. to 6:00 p.m. average)

Eye Irritation	Oxidant
Eye Irritation	Oxidant (above 10 pphm)
Eye Irritation	Oxidant (above 20 pphm)
Eye Irritation	NO ₂ (daily average)
Eye Irritation	HC (daily average)
Eye Irritation	COH value
Eye Irritation	Visibility
Eye Irritation	Total organics (24-hr. sample)
Eye Irritation	Total mass (24-hr. sample)

All of the above pairs are to be studied using:

1. Total data.
2. Data corresponding to a product of temperature and relative humidity greater than the median value.
3. Data corresponding to a product of temperature and relative humidity less than the median value.

Other pairs to be correlated are:

<u>Variable A</u>	<u>Variable B</u>
Visibility	Oxidant
Oxidant (24-hr. Intgr.)	Solar Radiation
Oxidant (24-hr. Intgr.)	Inversion Height 7:00 a.m.
Oxidant (24-hr. Intgr.)	Inversion Height 1:00 p.m.

During December Stanford Research Institute analyzed data for August and September to test the hypotheses outlined above. Some of the results can be summarized as follows:

1. Plant damage shows no significant correlation with concentrations of hydrocarbons and oxides of nitrogen; integrated oxidant; maximum oxidant; nor with concentrations of hydrocarbons, oxides of nitrogen, nor aldehydes at time of maximum oxidant; nor with average visibility (6:00 a.m.-6:00 p.m.); nor with visibility at time of maximum oxidant; but a possible correlation with average aldehyde concentration during daylight hours.
2. Mean eye irritation shows no correlation with concentration of average or instantaneous oxides of nitrogen; aldehydes; total

organics from particulate sampler; nor with average or instantaneous visibility; but a possible correlation with instantaneous oxidant, and a stronger correlation with hourly particulate in Coh units and 24-hour integrated oxidants when integrated above 10, 15, and 20 pphm.

3. Plant damage shows no correlation with eye irritation.

Trajectories

For the interpretation of the chemical analyses and the measurements of eye irritation and plant damage, it is desirable to be able to tell where the air sampled at the various stations came from. For this purpose, we have undertaken to compute the trajectories of the air reaching the various Aerometric Survey stations for certain hours of interest. A total of 1,000 trajectories were planned, of which only about 3% could be computed for the explanation of the data at the various stations throughout the survey. However, the amount of work involved precluded the computation of a larger number of trajectories.

The basis for selection of the trajectories to be computed was principally the paths of the air for which the highest values of pollution were measured. The 1,000 trajectories were distributed throughout the four months of the Aerometric Survey roughly in proportion to the amount of pollution which was recorded.

The procedure of computing trajectories consists of plotting the wind observations for the approximately fifty wind stations in the area on hourly maps, drawing lines of constant speed on these maps and streamlines or lines representing the direction of flow over the area, and finally computing from these hourly maps the motion which an air parcel reaching a station would have traveled each hour previous to arrival at the station.

At the time of this writing, approximately half of the necessary maps have been plotted, and about one-fourth of them have been analyzed.

VI. GENERAL STATISTICAL DATA OF THE LOS ANGELES BASIN¹

INTRODUCTION

THIS study of statistical data of the Los Angeles Basin in relation to the smog problem was made for the Air Pollution Foundation by Mr. Neil Goedhard while associated with the School of Public Administration of the University of Southern California. Mr. Neil Goedhard is now City Manager of Covina, California. A summary of this report follows.

AREA

Early in its work on statistical data of the Los Angeles Basin, the Foundation decided upon the meteorological approach as the most logical and scientific premise upon which to build a definition of the area of the Basin. The natural boundaries, such as the ocean and mountain ranges which hinder the unobstructed dispersal of elements in the air, were used to define the area; this area was then further broken down following statistical and/or political boundaries. Thus three basic regions were defined as shown in Fig. 1:

- 1a. Los Angeles Region
- 1b. Orange County Region
2. San Fernando Valley Region
3. San Gabriel Valley Region

The portions of Los Angeles and Orange Counties included in this definition of the Basin repre-

¹in preparation as Report No. 6 of the Air Pollution Foundation.

sent an area of 1,629.7 square miles or 33.4% of the total area (4,870.5 square miles) of Los Angeles and Orange Counties.

POPULATION 1930 - 1960

The increase in population in the Los Angeles Basin is of primary importance in understanding the development of air pollution in southern California. This research has shown that the Basin's population is essentially that of Los Angeles and Orange Counties combined. Only 33.4% of the area of these two Counties is situated in the Basin, yet 97.6% of the people in these two Counties live in the Basin. The percentage increase of population in the Basin between 1930 and 1954 shows a startling picture:

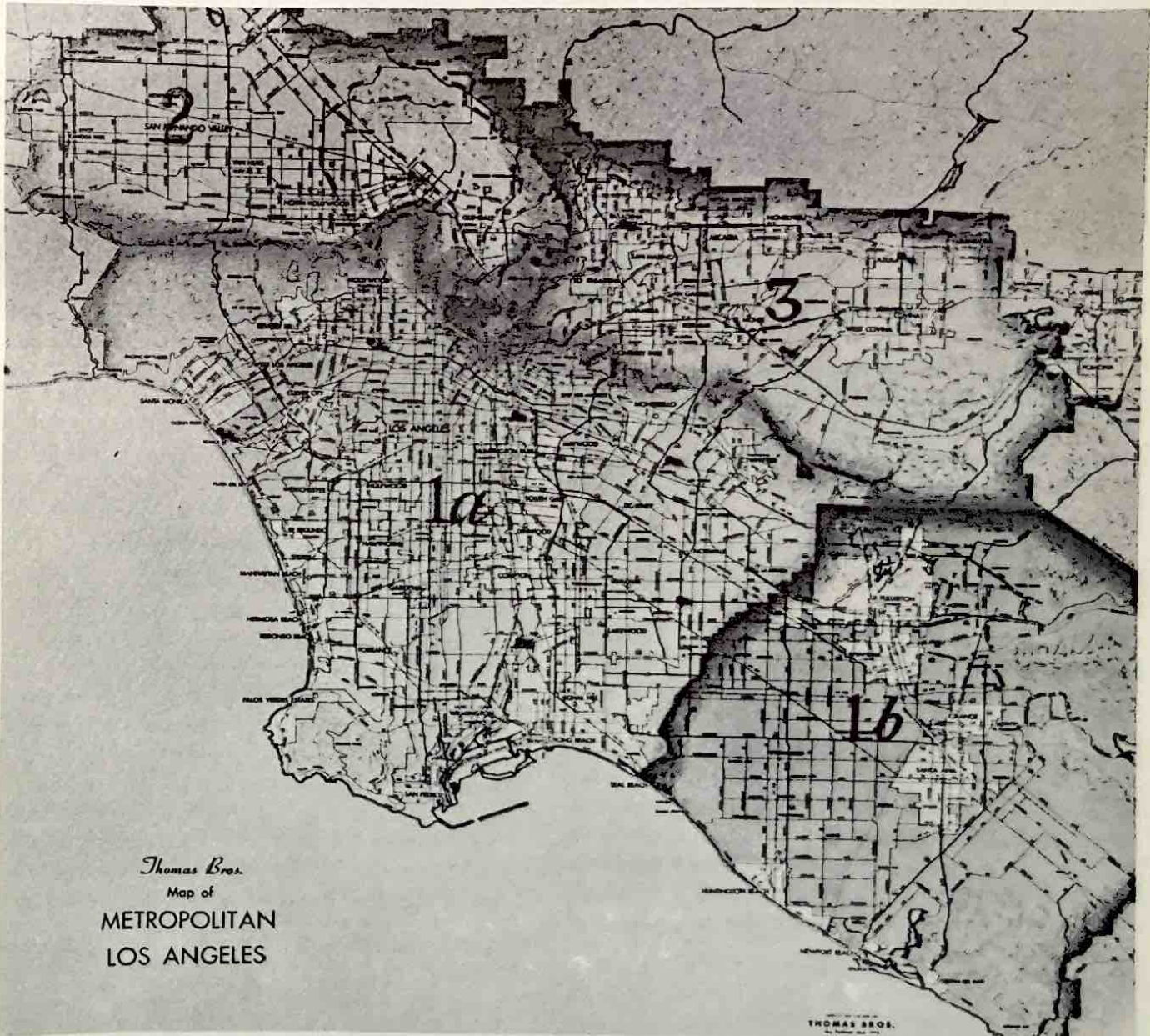
Year	Population	Increase
1930	2,280,630	
1940	2,859,258	25%
1950	4,275,395	49% since 1940
1954	5,028,367	76% since 1940

Based on these figures, a 1960 population estimate was developed showing a low figure of 5,791,000 and a high figure of 6,191,000 for the parts of Los Angeles and Orange Counties situated in the Los Angeles Basin. This study is widely documented and includes detailed statistics such as per cent increase and numerical increase of the population in the Basin, in each county, and further in each statistical area or township.

MOTOR VEHICLE REGISTRATION GASOLINE & DIESEL FUEL CONSUMPTION

The concentration of motor vehicles in the Los Angeles Basin and the consumption of gasoline

and diesel fuel have increased in proportion to the growth of population. Based upon the figure of 97.6% for all the people of Los Angeles and Orange Counties living in the Basin, prorated statistics for motor vehicles registered in the Basin are given in the table below:



CHAPTER VI - FIG. 1
Regions of the Los Angeles Basin
Black dots represent sampling stations used in Aerometric Survey

Motor Vehicle Registration in Los Angeles Basin

Year	All Vehicles	A u t o m o b i l e s % of Total
1930	878,000	836,000 95.2
1954	2,361,000	2,115,000 89.7
1960*	2,980,000	2,657,000 85.8

*Estimated from 1950-1954 increase.

In developing figures for the consumption of automotive fuel, certain difficulties were encountered. Records of actual consumption are maintained by the California State Board of Equalization only on a state level. Therefore, a different approach had to be devised. In order to arrive at a figure for gasoline consumption in the Basin, three separate computations were made, based upon (a) the population of Los Angeles and Orange Counties proportional to that of California, (b) weighing the number of motor vehicle registrations in the counties proportional to that of California, and (c) total number of vehicle registrations in the two Counties proportional to that of California. In addition, certain figures for gallons of gasoline sold subject to retail sales tax were used for 1950 and 1954. Here then are the figures for estimated gasoline consumption in gallons in the Los Angeles Basin:

Year	Low	High	Daily Estimate
1936	665,991,000	686,703,000	1,825,000
1954	1,708,127,000	1,789,895,000	4,758,000
1960*	1,900,000,000	2,300,000,000	6,200,000

*Estimated from 1950-1954 increase.

The same problems were encountered in estimating gallons of diesel fuel consumed. Two computations were made: one, by population of the two Counties proportional to California, and two, by truck registrations in the two Counties proportional to California.

Year	By Population	By Truck Registration	Daily Estimate
1938	4,257,000	3,571,000	11,000
1954	73,965,000	57,802,000	202,000
1960*	115,000,000	89,000,000	315,000

*Estimated from 1950-1954 increase.

The above statistics show an upward surge in the use of diesel fuel far greater percentage-wise than the increase in gasoline consumption; but it is nevertheless quite apparent that in terms of total fuel used, the amount of diesel fuel consumed by motor vehicles is small compared to the tremendous consumption of gasoline in the Los Angeles Basin.

VEHICLE COUNTS IN THE CENTRAL BUSINESS DISTRICT, 1929 - 1950

In spite of the marked increase in population and motor vehicle registration in the Los Angeles Basin, the daily number of vehicles entering and leaving the Los Angeles Central Business District has been decreasing gradually since 1948. Likewise, the number of buses and streetcars entering and leaving the Los Angeles Central Business District between 8:00 a.m. and 11:00 a.m. and between 3:00 p.m. and 6:00 p.m. has been decreasing in the same period. This trend would conform to the economic decentralization of the Central Business District area as shown in a decrease of retail sales downtown and the increase of retail sales in outlying areas.

The downtown area, or Los Angeles Central Business District, is the area bounded by Sunset Boulevard on the north, Pico Boulevard on the south, Figueroa Street on the west, and Los Angeles Street on the east. This study analyzed seven 16-hour cordon counts made between 6:00 a.m. and 10:00 p.m. by the Automobile Club of Southern California, the County of Los Angeles Regional Planning Commission, and the City of Los Angeles Street Traffic Engineering Department, between 1929 and 1950 prior to the opening of the Hollywood and Harbor Freeways.

Year	Total Number Vehicles Entering or leaving Downtown Los Angeles	Automobile Registration Los Angeles County	Population Increase Los Angeles County
	% Variation	% Variation	% Variation
1941	625,513	1,176,174	
1947	800,274 +27.9	1,320,911 +12.3	+26.7
1950	770,933 -3.7	1,719,900 +30.2	+14.3

Starting in 1948 the California State Highway Commission undertook annual traffic counts at two intersections in the Central Business District. The following conclusions can be made from these recent counts: the total flow of traffic has stabilized itself at a level comparable to that of 1948-1950, although decreasing at a slow rate. Estimates of traffic flowing along the freeways show an unparalleled increase in the total number of vehicles passing through the business district, thereby contributing to air pollution in this area. Due to the progress of freeway construction around the Central Business District, no 16-hour cordon counts were taken by the City of Los Angeles after 1950. However, a count has been scheduled for 1955.

INCINERATORS AND RUBBISH DISPOSAL

Very few accurate facts and records were available to determine (1) the number of residential and commercial incinerators, (2) the amount of open burning, and (3) the extent to which combustible rubbish is collected and disposed in the Los Angeles Basin.

(1) The following numbers of dwelling units are indicated for Los Angeles and Orange Counties.

1940.....	1,010,550	(1950 Census Count)
1950.....	1,521,849	(1950 Census Count)
1954.....	1,830,000	(estimated by Los Angeles Chamber of Commerce)
1960.....	2,292,000	(based on 1950-1954 increase)

Assuming one incinerator per dwelling unit, the above figures would establish a maximum number of backyard incinerators in the Basin. The Los Angeles County Air Pollution Control District estimates one incinerator for 1.3 dwelling units, or 1,500,000 backyard incinerators in 1953 for Los Angeles County.

(2) There are no burning dumps in the Los Angeles County portion of the Basin. In the Orange County portion, however, there are eleven burning dumps. No statistics are available on the tonnage of combustibles burned, but it has

been observed that since the ban on open-dump burning has become effective in Los Angeles County, the Orange County dumps located near the Los Angeles County boundary have experienced a noticeable increase in daily volume of combustibles.

(3) Our study of combustible rubbish disposal in the Los Angeles Basin indicates that various types of collection service are provided for residential and commercial establishments in most of the 46 cities in Los Angeles County, the City of Los Angeles being one of the few exceptions. In Orange County, at least 8 of the 13 cities provide collection service. In the unincorporated areas of Los Angeles County combustible refuse is collected from all residential and most commercial establishments; no such service is provided in the unincorporated areas of Orange County, other than by private arrangement. Frequency and scope of collection are subject to the desire of the citizens. Concerning the quantity of refuse thus collected, three different reports² were studied, all of which arrive at a fairly close per capita figure of 1.10 lbs., 1.54 lbs., and 1.16 lbs. of combustible refuse collected per day from residential and commercial establishments. It should be remembered here that these figures do not represent all combustible refuse produced; if no backyard burning were to take place, the Rawn report² estimates that per capita production of combustible refuse would be 2 lbs. At present, it is estimated that the daily minimum of combustible refuse burned in the Los Angeles Basin amounts to 4,224,000 lbs. out of an estimated minimum of 10,057,000 lbs. produced. The difference of 6,000,000 lbs. of combustible refuse produced but not burned in commercial or domestic incinerators is collected; an unknown quantity of this amount is burned

²Arnold, C. E., "Report on Rubbish and Refuse Disposal for Los Angeles County," April, 1949.

Schneider, W. A., "Report on Proposed Plan for Collection and Disposal of Combustible Rubbish in the City of Los Angeles," April, 1948.

Rawn, A M, "Report upon the Collection and Disposal of Refuse in the County Sanitation Districts of Los Angeles County, California," October, 1950.

in municipal incinerators and in open burning dumps.

In general the rubbish disposal study showed a dire lack of reliable information and suggests additional study of the entire combustible refuse program in the Basin.

REFINERY EMISSIONS³

In order to obtain an independent audit of the daily hydrocarbon losses from refinery operations, the Foundation commissioned Southwest Research Institute to make the necessary investigations. As of March, 1954 total hydrocarbon emission to the atmosphere in Los Angeles County was found to be 251 tons per day; this compares with the figure of 224 tons per day reported by the Western Oil and Gas Association. Similarly, olefin losses of amylenes and heavier were audited to be 16.4 tons per day, which compares with the 12.2 tons per day reported by the Association (Table I).

CHAPTER VI — TABLE I
 COMPARED HYDROCARBON VAPOR LOSSES
 RESULTING FROM THE PRODUCTION,
 REFINING, AND BULK MARKETING
 OF PETROLEUM PRODUCTS IN
 LOS ANGELES COUNTY
 AS OF MARCH, 1954

Source of Hydrocarbon Loss	Olefin Loss Amylenes and Heavier tons/day	Total Hydrocarbon Loss tons/day
Production	0	28
Refining	11.3	179.3
Marketing	5.1	43.8
Total	16.4	251

For the purpose of this investigation the industry was divided into three functions: production, refining, and marketing. Field trips were made wherever possible and supporting data

³in preparation as Report No. 5 of the Air Pollution Foundation.

from the literature were used to round out the information gathered.

Production Losses

A total of 359,409 barrels per day are produced from over forty oil fields in the Los Angeles Basin. Production losses occur during field storage, including breathing and filling losses, casinghead gas, and such other losses as occur during separation of bottom sediment and water.

Refining Losses

In Los Angeles County there are ten major oil refineries representing 93.6% of the total of 748,770 barrels per day capacity, and eleven smaller refineries, representing the other 6.4%. Refinery losses consist of evaporation losses from gasoline and crude oil storage; from separators; from pump gland leakages; from vapor and liquid blowdown; losses from discharge gases in catalytic regeneration units; and miscellaneous losses resulting from leakages from valves and fittings, batch treating, sewer manholes, etc. In addition, there are losses due to fires and resulting non-normal operation, involving above average amounts of crude or gasoline in storage.

To obtain information on losses from storage, a detailed inventory was compiled describing the type of tank and the materials handled in all storage tanks at all refineries. The calculation methods used were those contained in a report by the American Petroleum Institute, published in November, 1952 and titled "Evaporation Loss of Petroleum from Storage Tanks."

Separator losses come mostly from uncovered separators, but there is some loss from covered ones through breathing and venting. Influent and effluent stream samples were specified and witnessed, and suitable analyses were performed.

Over 500 pumps, representing about 75% of the gasoline and lighter pump capacity of the refineries, were checked during this audit. The rate of pump leakage was determined either by

actual timed measurements or visual observation.

Losses from vapor and liquid blowdown were checked by inspecting flares to see whether pilot burners were in operation. Also a check was made of units operating under vacuum and of blowdown facilities to handle emergency vapor discharges from relief valves.

The amount of hydrocarbons discharged from regeneration units of catalytic crackers was determined by mass spectrographic analyses of the flue gases.

Miscellaneous losses, such as leakage from valves and fittings, spills during blind changing, etc., were estimated by observation of actual losses during visits and discussions with operating personnel.

Marketing Losses

These include filling losses from tank cars, tank trucks, ships and barges, and filling and breathing losses from storage at bulk terminals and marine terminals. These losses were estimated according to correlations made by the American Petroleum Institute from reported vapor pressure, type and dimensions of tank, and volume throughput.

Olefin Losses

The percentage of olefins in the hydrocarbons going to the atmosphere was estimated by the Scientific Subcommittee of the Committee on Smoke and Fumes of the Western Oil and Gas Association on the basis of an average gasoline composition for 1953 for the Los Angeles area. The result is believed to be close to that obtainable from a compilation prepared from detailed hydrocarbon analyses of each individual source of olefin loss.

Status

Much effort has been made by the petroleum companies to reduce hydrocarbon vapor losses. The single largest item at present is the loss from gasoline stored in floating roof tanks, which are acceptable under Rule 56. The next largest item is the vapor loss from crude oil stored in cone roof tanks.

The refineries are installing mechanical seals on pumps, which will further reduce pump gland losses; separator losses are being reduced by further improvements in installations. Beyond this, the next significant improvement would result from the installation of expensive protection equipment, which would not be self-amortizing.

VII. PHYSICAL MEASUREMENTS

INTRODUCTION

THE physical measurement program has three major objectives: (1) exploring of various techniques of detection, identification and concentration measurement of the various contaminants in smog based on the physical characteristics of these constituents; (2) obtaining physical descriptions of the reactions which take place in the atmosphere by suitable laboratory and field experiments correlated with appropriate theories; (3) determining the physical and chemical characteristics of the aerosols in smog.

As of the date of this report, only objective (1) has received attention, although literature surveys were conducted with the entire program in mind. Our review indicated the strong desirability of exploiting spectroscopic techniques to a much higher degree than had been attempted in the past on smog studies. These techniques cover not only those involving the ultraviolet into the far infrared absorption, i.e. 250 millimicrons to 15 microns, but also into the microwave region. In the microwave spectrum there are three possible methods of analysis.

- (a) Absorption spectra
- (b) Paramagnetic resonance spectra
- (c) Nuclear magnetic resonance spectra

Mass spectrometry was also considered an important method to be explored further in this problem. Finally, modern electronics provides techniques for studying physical properties of aerosols. Physical methods of the above are considered appropriate not only because they potentially are capable of higher sensitivity and

greater specificity, but by their nature they do not affect the chemistry of the constituent reactions, nor the constituents themselves, except possibly in the use of the mass spectrometer. Furthermore, they are more likely to lend themselves to direct measurements in smog.

OZONE

Background

According to the previous investigations of Dr. Haagen-Smit¹ for the Los Angeles County Air Pollution Control District, and Stanford Research Institute¹ for the Western Oil and Gas Association, ozone is one of the more important constituents of Los Angeles smog. It has been detected, identified, and its concentration measured by various techniques, namely:

(1) The release of iodine in a buffered potassium iodide solution. A continuous recording instrument based on this principle is discussed in Chapter V of this report;

(2) The oxidation of phenolphthalin ($C_{20}H_{16}O_4$) to phenolphthalein ($C_{20}H_{14}O_4$) and the measurement of color development using hydrogen peroxide H_2O_2 to develop a standard curve for the colorimeter;

(3) The cracking of bent or stretched rubber measuring either depth of crack or time of initial cracking to give ozone concentration;

(4) The absorption in the ultraviolet by spectroscopic means;

(5) The response of certain plants to ozone resulting in characteristic damage to upper leaf.

¹see bibliography at end of chapter.

As a result of the use of these techniques, the status on the ozone identification and concentration in the summer of 1954 can be summarized as follows:

The potassium iodide and phenolphthalin methods gave different readings; when sampling the same atmosphere the latter method gave higher concentrations. Neither method is specific to ozone and both will respond to other "oxidants." Rubber cracking is not specific to ozone since free radicals give similar behavior and free radicals are possible constituents of smog. The spectroscopic evidence is based on eight readings in the atmosphere taken in July, 1952². Of the eight, four agreed to about 10%, two agreed to about 30%, one agreed to 40%, and one to zero per cent when compared to the potassium iodide method where nighttime values were assumed to be 0 to 3 parts per hundred million. All of these values were for 16 pphm or less total oxidant. The difference between the average values by the two methods was 15%.

An additional bit of spectrographic evidence was obtained by Stanford Research Institute³. However, their method involved concentrating ozone on silica gel and desorbing into an optical cell with only 45% recovery.

The plants exposed to Los Angeles smog did *not* show characteristic ozone damage, although the oxidant values to which they were exposed, if they represented mainly ozone, should have caused it.

General Plan

With this background, the Foundation decided to obtain more definitive data on the presence and amount of ozone in the Los Angeles atmosphere. After reviewing the work of Regener, Stair, W. A. Baum, and O. R. Wulf⁴, the Foundation decided to build an ozone spectrometer to be used directly on the atmosphere. This in-

strument is under contract with the Borman Engineering Company, North Hollywood, Calif.

The instrument will consist of a projector having a 6-inch aperture and using a type CH3 85-watt high pressure mercury lamp; the radiation will be pulsed at 90 cycles per second by a three-bladed shutter; it will have a prism radiometer with an exit collimator 5½ inches in diameter and 20 inches focal length. The prism is a Fresnel type assembly of four 60° fused quartz prism elements. The slit subtends 7½ millimicrons at 300 millimicrons. A synchronous motor will drive the wavelength and program cam. The radiation will be measured by means of a photo multiplier tube and is modified by transmission through two similar Corning glass filters.

Significant data for obtaining ozone concentration appear below:

Wavelength Millimicron	Relative Energy	Ozone Coeff.*
265	8.14	123
295	33.85	10
315	75.9	0.6

*Decadic absorption coefficient per cm. of ozone gas at STP (Standard Temperature and Pressure).

Initial experiments will be conducted at 675 ft. of optical path from projector to receiver. In order to establish energy at the source, auxiliary measurements will be made at about 60 ft. from the receiver and the projector aperture reduced by a diaphragm to simulate the long-range geometry. The attenuation of the diaphragm will be measured separately by means of an ultraviolet photoelectric photometer which evaluates energy at 365 millimicrons. Measurements of transmitted energy through smog will be repeated at 15-minute intervals, day and night.

Status

During this reporting period the manufacture and assembly of this instrument reached 75% completion. Also, the Foundation made a contract with the Ordnance Department of the U. S.

²see ref. (7) in bibliography.

³see ref. (11) in bibliography.

⁴see bibliography at end of chapter.

Army, Rock Island Arsenal, to provide them ozone data in exchange for the loan of equipment built for Ordnance by the Bureau of Standards (ref. 8).

Future Plans

It is planned to complete the instrument and give it an extensive field trial. It will then be put into service during the 1955 smog season and results will be compared with other measurements, particularly oxidant, as recorded by the potassium iodide and phenolphthalin methods.

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EXPLORATORY STUDIES

Solar Spectrometer Analysis of Smog

Background

Classically, astrophysicists have used spectrometry to detect and identify the gaseous constituents of the earth's atmosphere as well as solar and planetary atmospheres. Grating spectrometers, particularly, are capable of resolving the absorption lines of the various constituents, thereby identifying them. In recent years such compounds as methane and nitrous oxide have been found in the earth's atmosphere.

General Plan

The Foundation's approach to the use of this analytical technique consisted first of trying readily available prism spectrometers with the powerful light source, namely the sun, throughout the spectrum of available energy, 290 millimicrons in the ultraviolet to 15 microns in the infrared. It was necessary to do this in two parts because of equipment differences and availability. The first survey was conducted by Ralph Stair⁵ on leave from the National Bureau of Standards. During the literature search and as a result of discussions with the Bureau, it was as-

⁵see bibliography at end of chapter.

certained that they had available a Carl Zeiss double-prism or mirror monochromator mounted on a polar axis and capable of automatically following the sun for field measurements of solar radiant energy. Stair, who designed the equipment and had previously made spectral distribution studies of energy from the sun, was available to carry out a similar study in Pasadena. The equipment was set up on top (fourth floor) of the roof of the West Bridge Laboratory of Physics of the California Institute of Technology by October 1, 1954, and runs were made every day for about a month. Figs. 1 and 2 show the equipment in operation at Pasadena.

The second survey was conducted by Professor D. M. Gates of the University of Denver. The equipment used for this purpose was a Perkin-Elmer model 12C spectrometer equipped with rocksalt and also with lithium fluoride optics. In addition, a heliostat was borrowed from the National Bureau of Standards to direct the sun's radiation on the slit of the spectrometer. A photograph of this equipment appears in Fig. 3. Observations of the solar spectrum were made in the infrared region, 2 to 15 microns, on all days during November, 1954 when the sun was not obscured by clouds. A number of measurements could be made each day, as only thirty minutes were required in order to scan from 2 to 15 microns.

Status

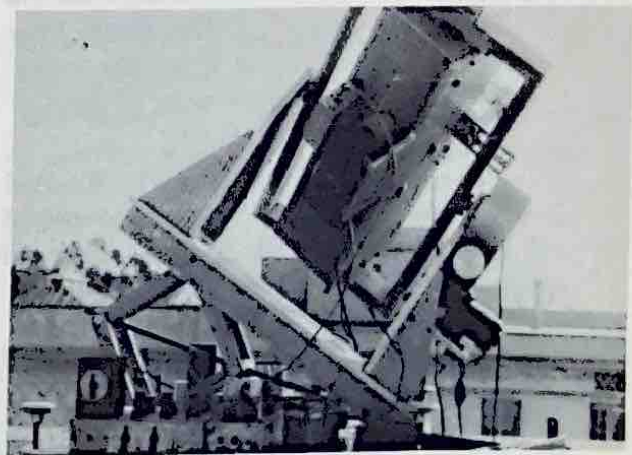
Reduction of the original data is in process and daily curves are being constructed for analyses at the National Bureau of Standards, at the University of Denver, and at the Foundation. The spectra will be compared with similar data obtained at Sacramento; Peak, New Mexico; Denver, Colorado, and possibly Washington, D. C. The following questions will be asked of the data from these experiments:

- (1) Do any new absorption bands show up in the spectral region covered, namely 290 millimicrons to 15 microns, due to presence of gases or compounds in the lower atmosphere?
- (2) Is there any evidence of the absorption of

solar radiant energy which leads to photochemical reactions in the polluted atmosphere?

(3) What can be said about the attenuation in relation to aerosol scattering?

(4) What mechanisms, or the presence of what compounds or types of compounds, are necessary to explain the actual spectral data?



CHAPTER VII - FIGS. 1 AND 2
Solar radiometer at
California Institute of Technology



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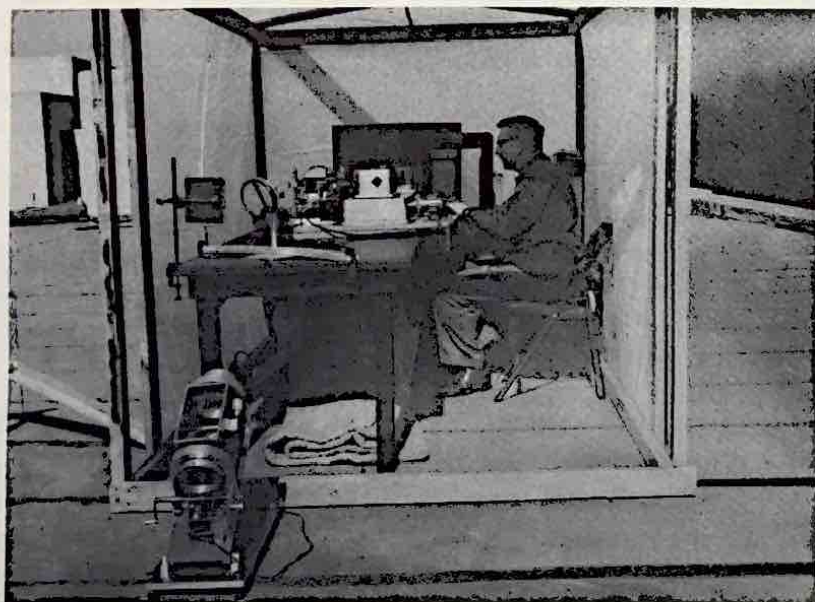
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Carbon Isotopes in the Los Angeles Atmosphere⁶

Background

The earth's carbon cycle has attracted interest to many branches of science and a variety of techniques have been brought to bear on its study. These investigations involve photosynthesis and respiration by plants, the decay of organic matter, the preservation of carbon in the form of coal and oil, and the concentration of CO₂ in the atmosphere among other matters

⁶by Samuel Epstein, Ph.D., Professor of Geochemistry, California Institute of Technology.



CHAPTER V - FIG. 3

D.M. Gates at the spectrometer

which are of well-recognized importance to our civilization. In recent years a new tool, the mass spectrometer, has been successfully adapted to the study of carbon in nature with significant and relevant results.

Understanding the significance of isotope measurements is due primarily to the early work of Urey and his colleagues⁷, who showed that the thermodynamic properties of chemical compounds are dependent to a slight degree upon the isotopic composition of the atomic constituents. This leads to the expectation that processes involved in the carbon cycle fractionate the isotopes, so that carbon from different components of the cycle should be isotopically dissimilar.

About fifteen years ago Nier and his co-workers made the first precise measurements on the isotopic composition of carbon from a number of different natural sources. They found the C^{12}/C^{13} ratio in these materials varied by as much as 5%. For example, the C^{12}/C^{13} ratio of carbon in oil, coal, and terrestrial plants, although different, averaged approximately 92.5%, whereas the ratio in carbonates was about 89.2%. The C^{12}/C^{13} ratio in carbon from meteorites, certain graphites, and carbon dioxide of the atmosphere was of intermediate values⁷.

Recently, interest in carbon isotope research has increased. Craig⁷, using a modified Nier-type mass spectrometer with a precision $\pm 0.01\%$ of the C^{12}/C^{13} ratio, made a more complete survey on the variations of the isotopic composition of carbon in nature. He substantially verified and extended Nier's general finding, but in addition made an attempt to point out possible causes for C^{12}/C^{13} variations, including those found in a single chemical group. For example, he analyzed samples of wood from twenty-two modern trees grown in widely separated areas geographically and found a range in C^{12}/C^{13} ratio of 0.45% (over 20 times the experimental error). A similar range in ratio values was obtained from a series of tree rings in a single sequoia. Clearly,

a better understanding of these variations with respect to the biology and ecology of tree growth and their possible correlation with variation in atmospheric CO_2 would be of utmost interest from a biological and climatological point of view. Craig's measurements of the C^{12}/C^{13} ratio of six samples of CO_2 in Chicago air showed a range of 0.25%. In this case the samples were collected within a week and could be markedly affected by the activity of surrounding steel mills and direction of wind.

Recent Work on Carbon Isotopes at California Institute of Technology

During the past year, the Division of Geological Sciences has pursued a limited study on the variation of the isotopic composition of carbon in nature. To date, principal investigations have been concerned with samples of wood. In collaboration with Professor Edmund Schulman of the University of Arizona, Tree Ring Laboratory, the C^{12}/C^{13} ratio has been determined for some 250 wood samples from two Douglas firs of the Mesa Verde region of Colorado and from a California sequoia. A mass spectrometer capable of a precision of better than .01% has been used in this work, and the results are summarized briefly below.

Upon dividing a single tree ring into 60 samples by means of a biological microtome, each sample representing about a week's growth, and analyzing the C^{12}/C^{13} ratio of each sample, a progressive and continuous change in the ratio with the growing season was found. The C^{12}/C^{13} ratio is highest in the first wood deposited in spring and tends to decrease progressively through the rest of the ring. The late wood has a C^{12}/C^{13} ratio about 0.1% less than the first grown wood. In addition, we have found that within a given year the carbon-isotope ratio changes slightly with the position around the circumference of the tree trunk. It is clear that several factors contribute to the variations in the isotopic composition of carbon in trees. Among these factors are probably the various aspects of ecological conditions under which the tree grew, including the isotopic composition of the carbon

⁷see bibliography at end of chapter.

in the atmosphere. Investigations of these factors are feasible, and it is hoped that they will be pursued in the near future.

One of the more interesting results obtained is a consistent increase of the C^{12} content in recent years. Since 1840, the carbon-isotope ratio (C^{12}/C^{13}) has increased in the trees so far investigated. This can be explained on the basis of a change in carbon ratio in carbon dioxide atmosphere resulting from the burning of the C^{12} -enriched coal and petroleum. The possible consequences of a changing concentration of the CO_2 in the atmosphere with reference to climate, rates of photosynthesis, and rates of equilibration with carbonate of the oceans may ultimately prove of considerable significance to civilization.

General Plan

From the above it is clear that a thorough investigation of the distribution of the isotopes of carbon in the atmosphere is desirable and of particular importance in connection with isotope studies pertaining to marine and terrestrial photosynthesis, to studies of carbonates, and with respect to changes in the atmosphere. Comparison of atmospheric samples gathered over the ocean, over mountainous areas, and from industrial localities similar to the Los Angeles Basin is desirable. The relationship between the C^{12}/C^{13} ratio in atmospheric carbon dioxide and in the air pollutant, the effect of industrial activity, elevation, geographic location, and fluctuations in weather and air currents on these ratios, and the isotopic composition of petroleum and plant materials would be important to geochemistry and should be relevant to the smog problem of the Los Angeles Basin.

The major aspects of the investigation are (1) collection of suitable samples, (2) preparation and isotope analyses of the samples.

(1) Collection of Samples: for collection of samples existing agencies already engaged in sampling the air for the pollution research program will be used. In addition, apparatus will have to be prepared for use in locations not dealt with by agencies already in existence.

(2) Preparation of Samples: this would be done entirely at California Institute of Technology by means of existing facilities and additional ones to be built.

Facilities

The operating equipment and materials necessary for this research are listed below:

(1) A mass spectrometer which is now functioning satisfactorily and can detect changes of 0.01 per cent in the C^{12}/C^{13} ratio. The analyses can be done by a technician in a routine manner. The use of this instrument is contingent upon the official approval of the AEC which provided the funds for its construction. Such approval is expected with considerable certainty.

(2) At least two high vacuum lines, one for the combustion of the carbon samples to carbon dioxide, the gas used in the mass spectrometer, and the other for separation of carbon dioxide from the air samples. The technique for these procedures is known and has in part been used in our previous work.

(3) Chemicals, glassware, liquid nitrogen, and dry ice constitute the principal expendable items used for this work.

(4) In addition, equipped chemical and instrumental laboratories are available at the Institute.

Status

A research grant was made to the California Institute of Technology, Department of Geological Sciences, by the Air Pollution Foundation on December 1, 1954. Training of a laboratory assistant and recruitment of a post-doctoral fellow were involved in getting started; permission for the use of the currently operating mass spectrometer was obtained from the Atomic Energy Commission.

Future Plans

It is planned to obtain samples of CO_2 as well as other carbon-bearing compounds and analyze them in the mass spectrometer. By the analysis of about one thousand samples definite information might be obtained on the feasibility of the

following applications for this technique:

- (1) A method for determining the sources of the carbonaceous material in samples of the atmosphere.
- (2) A method for tracing the flow of air masses over the Basin using CO₂ as the tracer gas.
- (3) A method for arriving at an index of pollution by studying the change in isotopic composition of CO₂.
- (4) A method for studying mixing rates of gaseous pollutants in the atmosphere by measuring the isotopic composition of CO₂ throughout the mixing volume and as a function of time.

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Nuclear Magnetic Resonance (n-m-r) Spectrometer

Background

Nuclear magnetic resonance spectroscopy is based on the fact that the various nuclei of the elements can be separately identified according to their differing nuclear gyromagnetic constants. Just as there is a certain mass and electric charge associated with each nucleus, so there is a spin, or angular momentum, associated with each nucleus. It has been found that all those nuclei whose spins do not have the value zero also possess a magnetic moment—that is, each behaves as though it were a tiny magnet with a

well-defined, unique magnetic strength. The ratio of the magnetic moment value to the spin value, which is a constant for a given atomic nucleus, is called the gyromagnetic ratio for that particular nucleus. The fact that these ratios differ from isotope to isotope permits separation and identification according to the scheme of n-m-r spectroscopy.

It has been demonstrated that a special version of this new kind of spectroscopy, "High Resolution," represents a penetrating new method for determining molecular structure and identifying and measuring components in a mixture.

The method is completely nondestructive. Radio frequency energy of a particular frequency is applied to the sample, and the atomic nuclei in that sample respond with a signal of their own. It has been shown that the character of the responding signal can be profoundly affected by the chemical environment in which the atomic nuclei producing the signal find themselves. In this way valuable information concerning that chemical environment can be obtained without disturbing the molecular structure in any way.

General Plan

The first application of this technique was made on a freeze-out sample of the Los Angeles atmosphere as follows:

Date of sampling: November 24, 1954.

Location: downtown Los Angeles, Hall of Records, fourth floor.

Amount of air sampled: 28,000 liters.

Approximate volume of condensate in capillary tube: 0.030 ml.

Duplicate sets of ten Shepherd traps, immersed in liquid oxygen, were connected in parallel to a common manifold air intake and a manifold outlet. The outlet connections on the manifold were made with Tycon tubing to 5/12 socket joints which could be connected to the traps. The outlet manifold was connected first to a dry test meter and then to a rotary vacuum pump. A bleeding device between the pump and the meter served to regulate the rate of flow.

At the end of the sampling period, all traps were evacuated to 50 mm. while still at liquid oxygen temperature and returned to the laboratory.

The capillary sample cell, submitted by Varian Associates, was sealed to the bottom of a Shepherd trap. This trap was then immersed in liquid oxygen. The outlet was connected to a regular trap also immersed in liquid oxygen. The purpose of this second trap was to collect vapors which might not be condensed in the trap with the capillary.

Each of the twenty traps was then connected over an ascarite bridge to the inlet connection of the capillary trap. While flushing nitrogen gas through the complete assembly, the trap was warmed up to 80°C to insure complete evaporation.

Five liters of nitrogen were used on each trap over a period of ten minutes. After the contents of all twenty traps were transferred, the trap at the outlet connection was removed from the liquid oxygen and its content was also transferred to the capillary trap in the same manner.

The capillary trap was then evacuated to 50 mm., while still immersed in the liquid oxygen, and the stopcocks closed off. The trap was removed from the liquid oxygen and slowly brought back to room temperature. At this stage, no liquid was down in the capillary tube; however, a few droplets were hanging on the inside wall of the Shepherd trap. To condense the vapors into the capillary, the trap was warmed while the capillary itself was cooled with a dry ice bath. This procedure was repeated several times until no more liquid condensed out.

While still immersed in the dry ice, the capillary was then sealed off about one centimeter below the trap and removed. This sample was then mailed to Varian Associates, Palo Alto, California.

Status

Varian Associates analyses of the above sample were as follows:

Fig. 4 is the record of the spectrum as obtained from the high resolution n-m-r spectrometer.

The present interpretation of the various regions in the spectrum follows (Fig. 5).

Region (1)—Protons on aromatic rings.

Region (2)—Protons in olefinic parts of hydrocarbon—actually attached to doubly bonded carbon atom.

Region (3)—Protons on first carbon atom in side chains attached to aromatic rings.

Region (4)—Cyclo paraffins.

Region (5)—CH₂ groups in saturated hydrocarbons.

Region (6)—CH₃ groups in saturated hydrocarbons.

Fig. 6, made up from known compounds, verifies some of these assignments. All of these groups appear to be present in gasolines, although in different blends, except the cyclo paraffin peak, which may be present in a small enough quantity to be masked by the large CH₂ and CH₃ background from the saturated hydrocarbons.

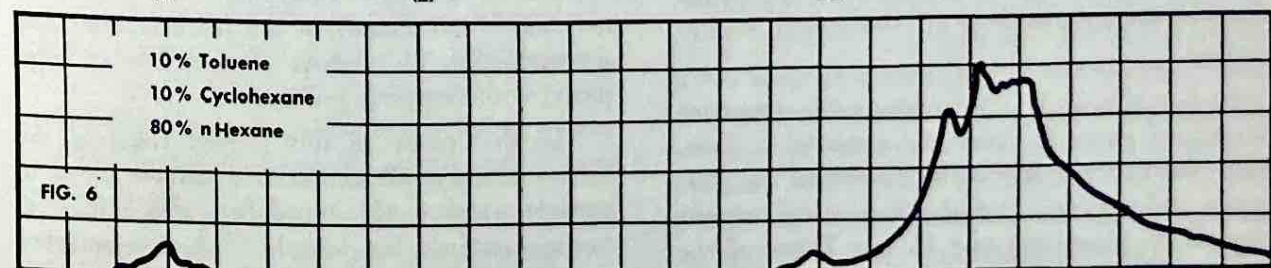
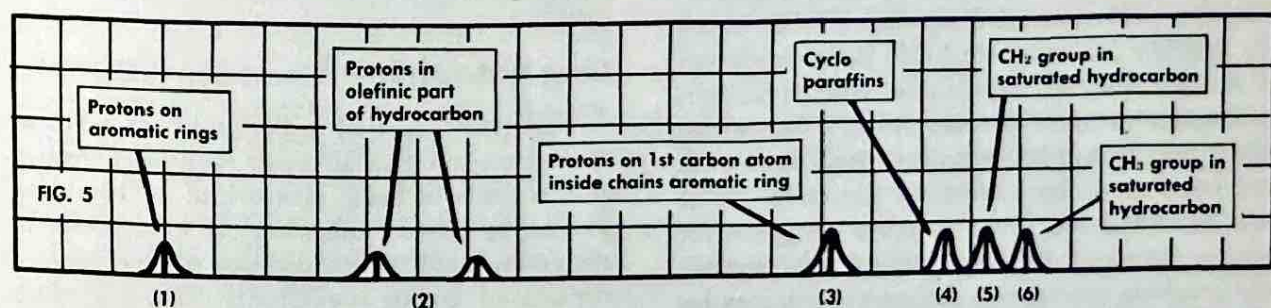
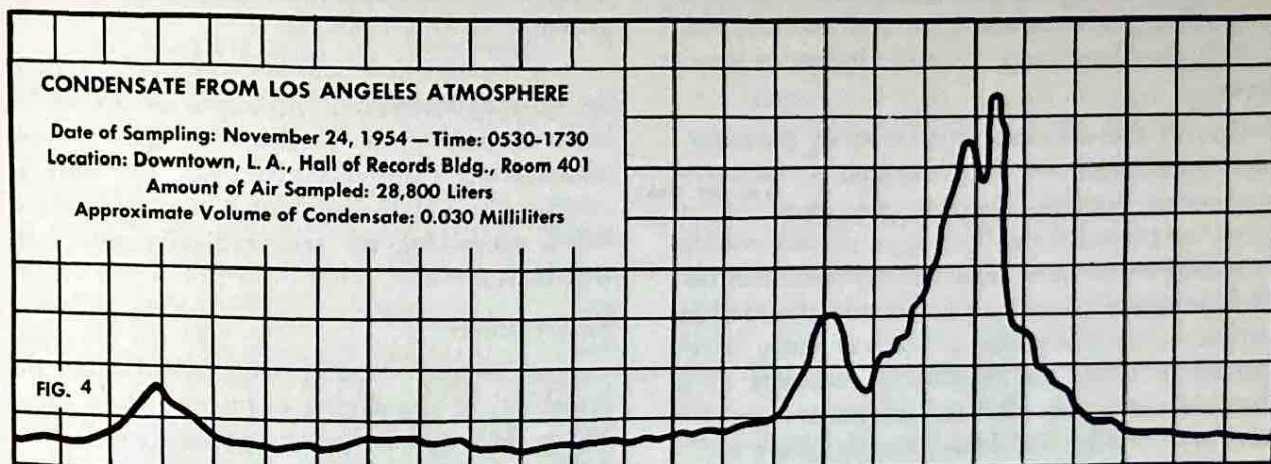
The condensate appears to contain the major chemically identifiable groups in proportions which probably approximate the average of most of the major gasoline blends sold in the area. It might be an interesting experiment to make up such a blend with liquid gasolines and compare spectra again.

It certainly seems that the percentage of unsaturated hydrocarbons in the condensate represents a very small fraction of the total hydrocarbon in the atmosphere, assuming that the unsaturates get through the ascarite drying agent.

We believe that the n-m-r determination represents a strong piece of evidence verifying the suspected existence of unmodified, unburned gasoline in the Los Angeles atmosphere.

Future Plans

It is planned to collect samples during the next smog season (1955) under different conditions, i.e. night time sample vs. day (irradiated)



NUCLEAR MAGNETIC RESONANCE SPECTRA

sample; eye irritation vs. no eye irritation, etc., and subject them to n-m-r analyses in order to identify the hydrocarbon components responsible for manifestations of smog, if any. It may be interesting to see if this technique is useful in analyzing hydrocarbons from auto exhaust. Ideally, of course, it would be preferable to analyze the gaseous smog directly by this method in order to get indications of the various hydrogen-bearing intermediate reaction and oxidation products.

Paramagnetic Resonance Spectrometer

Background⁸

A few gaseous substances, the most familiar of which are O₂, NO, NO₂, Cl₂O, and F₂O, have unpaired electrons in the ground state and hence have large magnetic moments as compared with

⁸Gordy, W., Smith, W. V., Trambarulo, W. F., *Microwave Spectroscopy*, John Wiley & Sons, Inc., N.Y. (1954).

those of most molecules which have a $^1\Sigma$ ground state. These paramagnetic gases have large Zeeman effects; also, when there is a nucleus with $I \neq 0$, they have large magnetic hyperfine structures.

One of the simplest ways to study paramagnetic gases in the microwave region is to observe transitions between Zeeman components of a given rotational state. This type of observation is analogous to paramagnetic resonance and nuclear magnetic resonance commonly observed in solids. A field of only a few kilogauss is required to bring the resonance frequency of a free-electron spin into the microwave region. One can conveniently leave the microwave oscillator frequency fixed and "sweep" the absorption line to the desired frequency of observation by varying the magnetic field. Hyperfine structure and other effects can be studied as perturbations of the "Zeeman lines." The strong fields, which must be employed, break down weak magnetic couplings so that the simple theory of the Paschen-Back effect is often adequate for interpretation of the perturbations. Nevertheless, the resulting spectrum is frequently complex because of the large number of interactions usually present.

So far, the study of paramagnetic resonance spectra of gases has been concentrated at Yale, with the experimental side developed by Beringer and Castle⁹, and the theoretical aspects treated by Margenau and Henry. Three of the more common paramagnetic gases, O_2 , NO , and NO_2 , have been investigated. Although there are only a few more substances of this type to be studied, the possible application of the experimental method and the theory to gaseous free radicals or ions makes the subject potentially of wide interest.

Status

An attempt will be made to detect and subsequently identify free radicals formed in an irradiated mixture of hydrocarbon and air. Stanford Research Institute at Palo Alto will provide

⁹Beringer and Castle, *Phys., Rev.*, 78, 581 (1950).

the chemistry of the experiment and Varian Associates will analyze the gas mixture for the presence of free radicals.

A paramagnetic resonance spectrograph along the lines of the general principle described⁹ has been assembled at Varian. Preliminary runs using strongly paramagnetic gas NO_2 will be run to test out the apparatus and procedure. When successful, the free radical experiments will be run.

Future Plans

It is planned to give some attention to the feasibility of developing an instrument for measuring NO_2 and NO concentrations in air mixtures using a paramagnetic resonance spectrometer.

Long Path Infrared Absorption Cell

This study applied a Perkin-Elmer infrared spectrometer with a 10-meter multiple reflection cell, capable of being pressurized to 10 atmospheres, to direct studies on the atmosphere to determine unusual components for the concentrations of known components. This procedure may offer advantages in the identification and determination of gaseous components as compared with trapping procedures.

The first phase of this project required the selection and modification of a suitable air compressor which could introduce a minimum contamination into the sample. The unit selected was a three-stage Cornelius compressor which was modified to operation at 1/10 its designed speed and was lubricated with silicone oil instead of hydrocarbon oil. When a silicone is used for lubrication, it is preferable that either or both surfaces be of nonferrous material. Accordingly, brass liners were introduced in the cylinders, and the cylinders rebored and polished to take these liners. This compressor is now operating satisfactorily.

The second phase of this project will be the development of a means for removal of excess carbon dioxide and water from atmospheric samples with the least amount of change in the

original composition of the sample. This phase of the project is now in progress.

COLLABORATIVE STUDIES

Microwave Absorption Spectroscopy¹⁰

Background

The normal atmosphere is transparent to radio waves from the longest waves of about 15,000 meters down to waves approximately 3 cm. in length (corresponding to a frequency of 10,000 megacycles). Nitrogen, hydrogen, and carbon dioxide do not absorb any radio frequency waves. However, if one goes to shorter wave lengths (higher frequencies) the atmosphere becomes highly absorbing, water vapor absorbing at 1.37 cm. (22,235 mc.) and oxygen absorbing at 6 mm. (50,000 mc.). Radar equipment works successfully for long-range purposes at 3.2 cm. (9400 mc.), while components exist for work at 8 mm. (38,000 mc.). At this latter wave length, transmission is accomplished between the water vapor and oxygen absorption bands. In addition, more than 100 gases such as formaldehyde, the alcohols, sulfur dioxide, and others absorb microwaves, particularly in the wave length region below 1.0 cm. Microwave propagation, as contrasted to propagation of visible light, is not greatly affected by particles in the atmosphere such as smoke or haze.

During World War II, radar equipment developed at 1.25 cm. was found to be useless owing to the short range of the waves in an atmosphere with high water vapor content. In an atmosphere of pure water vapor, the signal strength would drop to half its initial value in one mile of travel, and the absorption in moist gases is proportional to the partial pressure of the water. Thus, signal strength at 1.25 cm. falls to one-half the initial value after 100 miles of travel when one per cent of the atmosphere is water vapor by volume.

¹⁰by W. D. Hershberger, Department of Engineering, University of California at Los Angeles.

General Plan

In the microwave spectroscope, the gas under study is confined in a section of wave guide or in a resonant cavity at reduced pressure, and microwave power is passed through the gas sample to determine its propagation characteristics. Tools used are klystrons, crystal detectors, cavities, etc. The gases of interest in a smog study would be studied in the microwave spectroscope. Resolution in the spectroscope is better than in the optical region by a factor of 10,000. Ozone, the aldehydes, and oxides of nitrogen may be of particular interest in the present study. Whether it would be desirable to irradiate a sample of gas with ultraviolet light is open to question, but the method of handling a sample would permit such techniques to be employed, if field studies indicate that the incidence of sunlight on gases in the inversion layer has a measurable effect on microwave propagation through the layer. In this portion of the study samples would be collected from the atmosphere when smog occurs and the microwave spectroscope would be used in analysis.

The value of microwaves in a field study of smog arises in part from the fact that by their use a large area may be surveyed for gases, particularly those not visible to the eye in the presence of smoke or other particles. In the preliminary study of the instrumentation it is proposed that a long-distance transmission path be set up in Los Angeles in sunlight and the usual weather conditions. A transmitter working at two wave lengths, say 1.25 cm. and 8 mm., could, for example, be set up on the roof area at City Hall and a narrow beam or pencil of radiation transmitted to receivers located at UCLA, where automatic records of the received signal strength at both operating frequencies would be obtained. Only one absorption line occurs for water, that at 22,235 mc., while 30 lines have been observed for methyl alcohol and 8 lines for formaldehyde, scattered over the band. Multiple line absorption is common, and single lines are exceptions. The differential absorption at the two wave lengths is the criterion to be used in studying

smog. Water vapor mainly determines absorption at 1.25 cm., the wave length to be used as a monitor, and the other gases are mainly responsible for absorption at 6 mm. or 8 mm. A beam width of 3° is reasonable and beam formation will be accomplished by a parabolic reflector or horn, such as is used in radar. One aspect of the proposed study is the development of the instrumentation needed for study of smog *along a single path*, as for example, between City Hall and UCLA. The problem requiring an experimental solution is the one that arises because the water vapor content of the atmosphere is variable and because the magnitude of absorption by contaminants peculiar to the Los Angeles area is not known.

If the results under the above are sufficiently precise and revealing, it would be possible in a future program to employ a receiver with a slowly rotating microwave antenna at City Hall; a complete rotation could be made once every twenty minutes or so. Transmitters now could be placed at outlying points so that City Hall would be visible from the outlying stations. Such stations could be located at UCLA, International Airport, Palos Verdes, Long Beach, Burbank, Pasadena, San Gabriel, etc., and information would become available as to absorption along each of the named paths. Automatic records of atmospheric absorption would be kept for each path and, from records obtained after a clearing rain or wind, one could evaluate smog sources as regards to their location and importance. Heavy industrial areas and oil refineries have been

blamed as well as exhaust gases from automobiles. The purpose of the study would be to localize the sources of smog, if local sources are responsible. If local sources are not responsible, this fact needs to be known. The merit of this method is that it would permit the rapid collection of data simultaneously over an extended area during the critical time when smog is in the process of formation. Once smog is present in large quantities over the whole area, general observations probably would not be particularly revealing.

One could refine the method to determine direction of arrival of the microwave beam and thus the height of the inversion layer responsible for trapping the gases known as smog. This is accomplished by "nodding" as well as rotating the parabolic reflectors or horns which are used to focus microwave beams. Also, in the Los Angeles area, transmissions may be effected through the inversion layer itself by placement of a transmitter on Mount Wilson to make direction-of-arrival studies.

Status

The University of California at Los Angeles has initiated support of this research under the general supervision of Dean L. M. K. Boelter and the technical direction of the writer. Equipment is being purchased and assembled for the gas absorption spectrometer.

Future Plans

The Foundation will work closely with this investigation and maintain itself in a position to take advantage of the results obtained.

VIII. DISPOSAL OF REFUSE

CONFERENCE ON INCINERATION, REFUSE DISPOSAL, AND AIR POLLUTION

ON December 2 and 3, 1954, a Conference on Incineration, Rubbish Disposal, and Air Pollution¹ was held for the purpose of orienting all interested parties as to available information on incinerator emissions, types of equipment currently available and their merits, methods of "cut and fill," composting, and any other disposal means, complete with cost data. Participants of the Conference included sanitation engineers, government administrators in the field of sewage and sanitation on the municipal, state and federal levels, academic personnel, and various other specialists in the field of air pollution control.

These engineers, scientists, and administrators agreed upon specific recommendations and conclusions, which were adopted as representing the soundest advice that could be offered to Los Angeles communities:

RECOMMENDATIONS AND CONCLUSIONS

1. The combustion of rubbish in household and backyard incinerators has the twofold detrimental effect of distillation of a large proportion of the material, and the production and discharge to the air of particulate materials capable of forming extensive and persistent aerosols which aggravate air pollution. Household and back-

yard-type incinerators and open rubbish fires should be recognized as unsatisfactory solutions of the community refuse disposal problem in the Los Angeles metropolitan area.

2. Combustion of rubbish in the municipal or industrial incinerator, which leads to the discharge into the atmosphere of an unsatisfactory stack effluent, is indefensible.

3. Since the sanitary landfill method of refuse disposal has been shown to be economical and acceptable from the standpoint of public health, and since it creates no air pollution problems, this method should be given immediate consideration for the disposal of rubbish in the Los Angeles metropolitan area.

4. In the economic appraisal of the proposed solutions to the community refuse disposal problems, assuming there is some profit to be gained, the criterion of appraisal should be the least net cost of the total operation, particularly where some means of conservation is involved such as land reclamation by sanitary landfill, garbage feeding to hogs, composting, or transportation and treatment of garbage with sewage in a water-carriage system.

5. Engineering studies should be instituted immediately to determine not just the most economical but the most satisfactory pattern of storage, collection, transportation, and disposal of solid refuse, with particular reference to air pollution.

6. By the application of these measures, the total interests of the citizens in this area will be served and a great step will be taken with respect to the air pollution aspects of community waste disposal problems.

¹The Proceedings of this Conference are published as Report No. 3 of the Air Pollution Foundation.

APPENDIX

REPORTS ISSUED IN 1954

Report No. 1, Neiburger, M. and Edinger, J. G., "Meteorology of the Los Angeles Basin," April, 1954

"Proceedings of the Conference on Vehicle Combustion Products and Other Emissions," August, 1954
(Note: This report was distributed to conferees only.)

Report No. 2, Faith, W. L., "Combustion and Smog," September, 1954

President's Report, Hitchcock, L. B., Address given before Annual Meeting of Air Pollution Foundation, Hotel Ambassador, November 16, 1954

Report No. 3, "Proceedings of the Conference on Incineration, Rubbish Disposal, and Air Pollution," December, 1954

REPORTS SCHEDULED FOR PUBLICATION IN 1955

Report No. 5, Hydrocarbon Losses from the Petroleum Industry in Los Angeles County

Report No. 6, Statistical Data of the Los Angeles Basin

Report No. 7, Air Tracer Surveys

Report No. 8, Visibility Study

Report No. 9, Aerometric Survey, 1954

TECHNICAL CONFERENCES HELD IN 1954

SUBJECT	LOCATION	DATE
Reactions of Hydrocarbons and Other Organic Compounds in the Los Angeles Atmosphere	California Club	February 26 and March 5
Rubber Cracking, Ozone Formation and Detection	Foundation Office	May 13-14
Meteorology of the Los Angeles Basin	Foundation Office University of California, Los Angeles	May 17 May 18
Vehicle Combustion Products and Other Emissions	The Huntington-Sheraton Hotel	August 19-20-21
Incineration, Rubbish Disposal, and Air Pollution	The Huntington-Sheraton Hotel	December 2-3

PRINCIPAL LECTURES BY FOUNDATION STAFF 1954

DATE	STAFF MEMBER	LOCATION	SUBJECT
4/13	Hitchcock	Los Angeles County Council of Real Estate Boards	"The Foundation's Program Against Smog"
5/12	Hitchcock	APF Luncheon at Ambassador Hotel	"President's Report— First Progress Report Review"
6/15	Rogers	Property Owners Division of Pasadena Realty Board	"The New Air Pollution Foundation— Who, Why, and How"
6/23	Hitchcock	Los Angeles Breakfast Club, Radio KPOL	"Free As Air?"
6/27	Hitchcock	KNBH—NBC (TV)	"Get the Facts" (L. A. EXAMINER) with Mr. Fred Ortman as panel guest
7/2	Faith	San Bernardino County Air Pollution Study Committee	
7/14	Hitchcock	Rotary Club, Pasadena	"Scientific Approach to Direct Action"
7/30	Hitchcock	KFI Radio Station	"Town Hall of the Air" W. B. Miller, Moderator; with A. M. Zarem and Gordon Larson
8/17	Hitchcock	American Institute of Chemical Engineers	"Scientific Approach to Direct Action"
8/25	Leiper ²	Rotary Club, Culver City	
9/23	Hitchcock	Western Governmental Research Association, 14th Annual Conference, Claremont Hotel, Berkeley	"The Scientific Approach to Control of Urban Air Pollution" ¹
10/13	Faith	American Society of Civil Engineers, Southern California Section	"Atmospheric Waste Pollution"
10/14	Faith	American Society of Civil Engineers, Riverside-San Bernardino Branch	"Atmospheric Waste Pollution"
11/1	Hitchcock	University of California, Riverside, Synapsis Club	"Air Pollution Research Challenges the Scientist"
11/4	Leiper	Sigma Delta Chi Forum, Roger Young Auditorium	
11/16	Hitchcock	APF Annual Meeting, Hotel Ambassador	"President's Report" ¹
12/7	Renzetti	Scientific Research Society of America, China Lake Chapter	"Some Technical Aspects of Air Pollution"
12/30	Hitchcock	American Association for the Advancement of Science, Symposium on Air Pollution, Berkeley, California	"Definition of Air Pollution Today in American Cities"
12/30	Faith	American Association for the Advancement of Science, Symposium on Air Pollution, Berkeley, California	"Vehicle Combustion Products and Possible Remedies" ¹

¹Reprints available.

²Public Information Officer, Air Pollution Foundation

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