

# The Smog problem in Los Angeles County : second interim report on studies to determine the nature and sources of the smog.

Los Angeles : Committee on Smoke and Fumes, Western Oil and Gas Association, c1949.

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Second Interim Report on  
**THE SMOG PROBLEM**  
**IN LOS ANGELES COUNTY**

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Stanford Research Institute  
1949

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UNIVERSITY OF CALIFORNIA  
INSTITUTE OF TRANSPORTATION  
AND TRAFFIC ENGINEERING

COMMITTEE ON SMOKE AND FUMES  
WESTERN OIL AND GAS ASSOCIATION



# THE SMOG PROBLEM IN LOS ANGELES COUNTY

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**Second Interim Report by Stanford Research Institute on  
Studies to Determine the Nature and Sources of the Smog**

*August 1949*

**This Research Program Has Been Sponsored by the  
COMMITTEE ON SMOKE AND FUMES OF THE  
WESTERN OIL AND GAS ASSOCIATION**

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**COMMITTEE ON SMOKE AND FUMES  
WESTERN OIL AND GAS ASSOCIATION**

**510 West Sixth Street  
Los Angeles 14, California**

## FOREWORD

**T**HE COMMITTEE on Smoke and Fumes of the Western Oil and Gas Association is pleased to submit to the public the Second Interim Report of the Stanford Research Institute, covering the Institute's work in the investigation of what smog is and where it comes from.

The petroleum industry has been interested in the problem of smog since before the war. After considerable study it became evident that the problem is highly complex and requires the use of scientific personnel and approaches not normally available in the laboratories of industry. Accordingly, the services of the Stanford Research Institute, an independent research organization serving the West, were engaged to make this investigation.

The complexity of the problem is amply illustrated by the research reported herewith. The investigation has progressed on scientific lines and is now well on the way toward a full understanding of the smog problem. The work is being continued, and the results will be made available to the public.

Reports on this research are being published for the information of interested individuals and authorities. The First Interim Report on the smog research by Stanford Research Institute appeared in 1948. This Second Interim Report presents the principal results of the research to date, covering two years of work. Copies may be obtained by writing to the Committee on Smoke and Fumes, 510 West Sixth Street, Los Angeles 14, California.

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# THE SMOG PROBLEM IN LOS ANGELES COUNTY

STANFORD RESEARCH INSTITUTE—SECOND INTERIM REPORT

## CONTENTS

<b>I. INTRODUCTION AND SUMMARY</b>	<b>5</b>
<b>II. ANALYSIS OF THE AIR—GASES</b>	<b>11</b>
<b>III. ANALYSIS OF THE AIR—PARTICULATE MATTER</b>	<b>22</b>
<b>IV. FACTORS AFFECTING VISIBILITY</b>	<b>30</b>
<b>V. FACTORS AFFECTING EYE IRRITATION</b>	<b>37</b>
<b>VI. THE METEOROLOGICAL MECHANISM OF THE SMOG</b>	<b>46</b>
<b>VII. THE SMOG INDEX AND SMOG FORECASTING</b>	<b>52</b>
<b>VIII. APPENDICES</b>	<b>53</b>



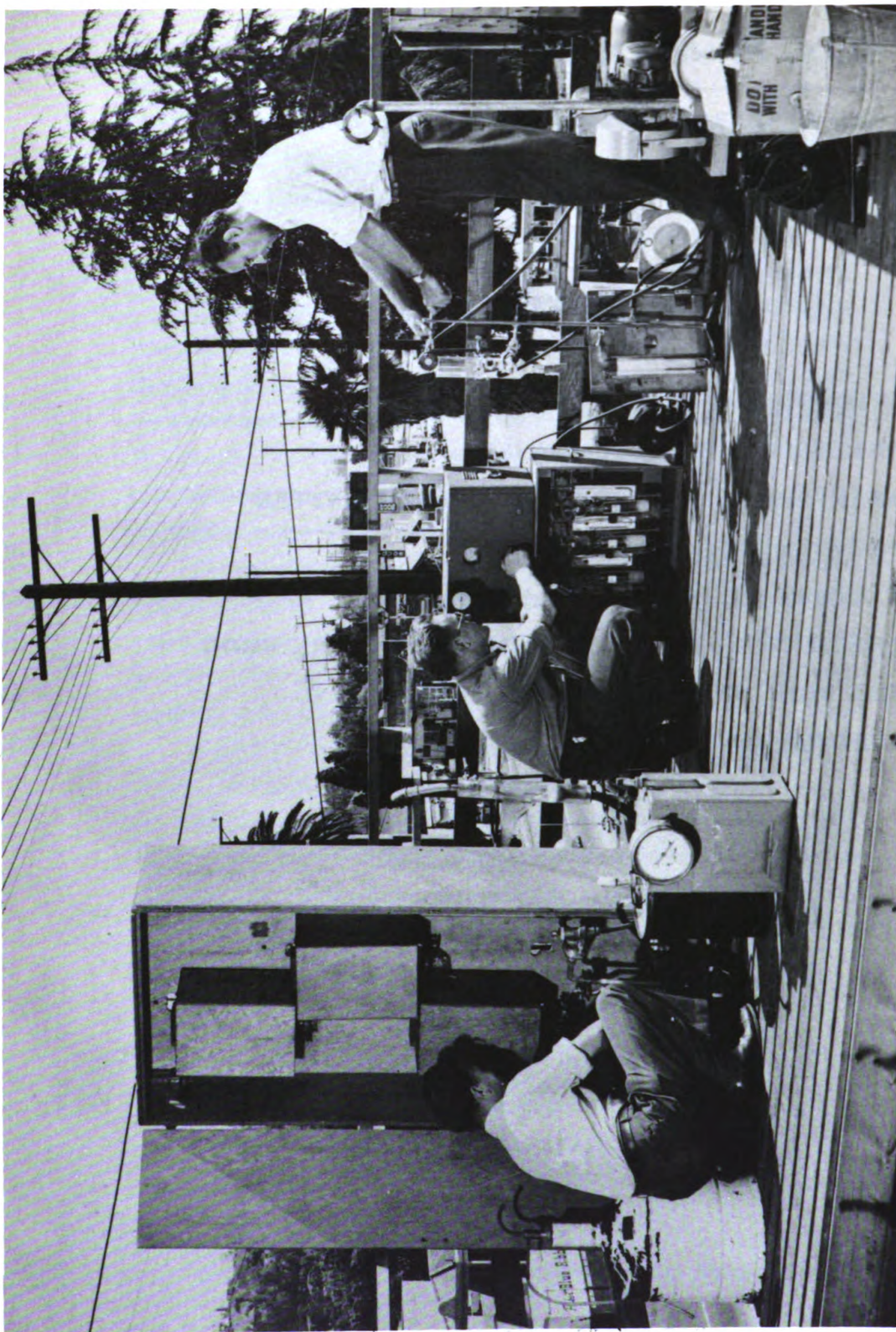


PLATE 1

Chemists analyzing air at sampling platform on roof of 4105 North Figueroa Street, Los Angeles, showing (left to right) freeze-out trap, electrostatic precipitator, and equipment for oil aerosol analysis

# THE SMOG PROBLEM IN LOS ANGELES COUNTY

Stanford Research Institute  
Second Interim Report—1949

## I

### INTRODUCTION AND SUMMARY

LOS ANGELES has long been noted for pleasant climate, clear skies, and unparalleled recreational facilities. These have brought millions of visitors and many new residents to the region, with the result that in recent years the area has enjoyed remarkable growth in population and industry. This growth has been accompanied by problems associated with large and closely settled populations, one of the most troublesome being the increase in intensity and unpleasant effects of the periodic phenomenon known as smog.

As originally used in other cities, the word "smog" describes a combination of smoke and fog. In Los Angeles the smog is never associated with fog in the usual sense. It is produced by a complex mixture of gases and fine particles, including dust, metals, crystals, and liquid droplets. It imparts a general murkiness to the air, reduces visibility, and frequently irritates the eyes. These effects may be present at times in other cities, but in Los Angeles eye irritation is more severe.

Since the smog's intensity has increased as a result of human activities, an apparently simple solution would be to control the activities that are principal contributors to the smog, in such a manner as to eliminate or diminish the harmful substances now liberated into the air.

But this proposal is not as simple as it may seem. It raises a host of questions for which accurate scientific answers are required. Selective control can be successful only if specific information exists as to the origins of the contamination, the mechanisms through which

it produces the smog, and the economic effects of controlling, modifying, or eliminating the sources.

The petroleum industry, as one of the major industrial activities of the Los Angeles basin, became interested more than a decade ago in the problem of smog and has made numerous studies of its causes and possible means of control. It became evident in the course of this work that the complexity of the problem was even greater than had been supposed, and that its solution requires personnel and techniques not usually found in industrial laboratories.

The industry accordingly sought independent outside research help. In 1947 it engaged the services of Stanford Research Institute to undertake an investigation directed toward answering the question: What is smog and where does it come from?

The work has been carried on intensively since that time by the Institute, under the sponsorship of the Committee on Smoke and Fumes of the Western Oil and Gas Association. It is probably the most extensive research program so far undertaken anywhere to learn the sources and nature of air pollution. It has drawn upon the technical resources of Stanford Research Institute, the cooperative contributions of major research organizations in the Los Angeles area, and the talents of nationally-known consultants and authorities.

It was agreed between the Institute and the sponsors that the technical results would be made public at intervals during the course of the work,

for the information of other industries; city, county, and other authorities engaged in the study of smog; and the general public.

Pursuant to that arrangement, the First Interim Report on smog research by Stanford Research Institute was published in 1948. This is the Second Interim Report; it brings together the main findings of the two-year investigation to date.

### Lines of Inquiry

The basic assignment of the Institute—determination of what smog is and where it comes from—involves finding the answers to six broad questions:

1. What contaminants in the Los Angeles air produce smog?
2. What is the meteorological mechanism of the smog?
3. What causes reduction in visibility?
4. What causes eye irritation?
5. What is the chemical and physical nature of the contaminants?
6. Where do the contaminants come from?

The smog research program follows these lines of inquiry. It is now approximately 80 per cent complete. Important data have been obtained on all of the questions, and work is progressing on the final phases of the program.

### What Contaminants in the Los Angeles Air Produce Smog?

The Los Angeles smog is produced by a complex mixture of more than forty contaminants found regularly or periodically in the air, and at least seven others which have been found occasionally.

The contaminants include gases such as ammonia, aldehydes, sulfur dioxide, sulfur trioxide, oxides of nitrogen, gaseous hydrocarbons, and ozone; liquids such as oil droplets, nitric acid droplets, and sulfuric acid droplets; and solid materials (present as fine particles) including calcium, sodium, aluminum, and silicon compounds; magnesium, titanium, lead, iron, potassium, and barium compounds; traces of copper, manganese, nickel, zinc, lithium, bari-

um, strontium, silver, boron, vanadium, tin, chromium, zirconium, bismuth, and cobalt compounds; also various fibers, pollen, carbon particles, and tarry organic material.

Table I provides a list of the contaminants

TABLE I.—CONTAMINANTS FOUND IN LOS ANGELES ATMOSPHERE

<i>A. Contaminants Accurately Measured</i>		
CONTAMINANT	APPROXIMATE CONCENTRATION FOUND ON SMOGGY DAYS	MAXIMUM CONCENTRATION FOUND
Sulfur dioxide	0.1 ppm by vol.	0.6 ppm
Ammonia	0.1 ppm by vol.	0.15 ppm
Oxides of nitrogen (probably mainly nitric acid)	Little correlation with smog	0.4 ppm by wt.
Sulfur trioxide (probably exists as sulfuric acid and inorganic sulfates)	0.05 ppm by wt.	0.2 ppm by wt.
Aldehydes (including formaldehyde and acetaldehyde)	0.15 ppm by wt.	0.2 ppm by wt.
Filterable oil (mainly hydrocarbon)	Insufficient data as yet	0.3 ppm by wt.
<i>B. Other Contaminants Known with Certainty to Exist in Los Angeles Atmosphere</i>		
Soluble chlorides		
Carbon		
Ozone		
Hydrogen sulfide		
Fibers		
Pollen		
Tarry organic material		
Calcium, sodium, aluminum, and silicon compounds, probably from minerals		
Small amounts of magnesium, titanium, lead, iron, potassium, and barium compounds		
Traces of compounds of copper, manganese, nickel, zinc, lithium, barium, strontium, silver, boron, vanadium, tin, chromium, zirconium, bismuth, and cobalt		
<i>C. Contaminants Found Occasionally</i>		
Organic peroxides		
Acrolein		
Fluorides		
Methyl chloride		
Formic acid		
Sodium chloride		
Gaseous hydrocarbons		

found frequently or occasionally in the Los Angeles air. Traces of others may also be present, but these are the principal substances that cause the smog.

### **The Meteorological Mechanism of the Smog**

Though contaminants are always in the air, smog occurs only periodically. It is more frequent and more intense in the late summer and early autumn than in winter or spring. It almost never occurs at night or in cloudy weather.

The conditions necessary to the formation of smog are now understood. It does not occur until atmospheric conditions are such as to favor it. Three sets of air phenomena work together to produce it.

The first is the frequent presence over Los Angeles of a warm stratum of air known as the Pacific inversion layer, which is part of a gigantic atmospheric swirl extending westward as far as the Hawaiian Islands. It acts as a huge, invisible lid over the Los Angeles area. Smoke, fumes, dust, and gases originating anywhere in the basin are carried upward by surface air currents to the base of the inversion layer, where they accumulate, building up a reservoir of materials that can later produce smog. The Pacific inversion layer rises and lowers like a huge deck in response to meteorological conditions affecting it. Smog is more likely to be noticed when the layer is low.

The second set of air phenomena is turbulent up-and-down currents of air occurring as the ground is heated during the morning hours by sunlight. When the sun's rays heat the earth, the adjacent layers of air become warm and rise. Cooler air from above comes down to take its place, bringing smog materials with it. This vertical turbulence increases as the sun's intensity grows during the morning. Contaminants that have accumulated at the base of the inversion layer during the preceding hours or days are transported down to street level, and widely mixed through the air.

Surface breezes, the third factor, move the newly-formed smog clouds across the area.

Breezes in the Los Angeles basin normally blow toward the ocean at night and toward the land in the daytime, reversing shortly after sunrise. On smog days the reversal at first may add to the turbulence caused by the vertical thermal currents. Then, as it grows stronger, the landward breeze pushes the intensifying smog clouds across Los Angeles County, picking up those in downtown Los Angeles, where smog is usually first observed, and carrying them toward Pasadena, Glendale, and the mountain canyons in the east.

These atmospheric activities follow known meteorological laws. As a result it has been possible to develop an objective measure of each day's smog intensity (the Smog Index), which has proved highly valuable in the smog research program, and an accurate forecasting method which can predict smog as much as three days in advance.

### **What Causes Reduction in Visibility?**

The haziness produced by the smog has been proved to result from small solid particles and liquid droplets—particulate matter—in the air. In the size range from 0.2 micron to 10 microns, the atmosphere in Los Angeles may contain from 30 million to 600 million particles per square foot. Gases have been shown to have little or nothing to do with reduction in visibility.

Los Angeles would have many days of haze even if there were no people living in the area. The natural occurrence of so-called tropical haze is a well-known fact, substantiated by old photographs, the recollections of long-time residents, and observations of its occurrence elsewhere along the Pacific Coast in regions where there are no industrial sources of air contamination. The natural haze is believed to be caused by dust, pollen, fibers, salt, and other materials of earth, ocean, plant, and animal origin.

In Los Angeles the natural haziness is considerably increased by particles and droplets of industrial, vehicular, combustion, and other human origin.

In all, five types of particulate matter have been found, the amounts of which vary markedly

from time to time, producing a corresponding variation in their effects on visibility:

1. *Carbon and metal particles.* These are black, opaque particles occurring in clumps or aggregates. They are responsible for from 10 to 50 per cent of the decrease in visibility.
2. *Transparent, light-scattering crystals.* These water-insoluble particles, including aluminum oxides and silica, account for from 10 to 30 per cent of the decrease in visibility.
3. *Small, water-soluble and oil-soluble particles and oil droplets.* Effect on visibility is not known, but believed to be small.
4. *Substances capable of forming moisture droplets in the air.* The principal one is sulfur trioxide, which forms droplets of sulfuric acid on contact with atmospheric moisture. This group of substances accounts for from 5 to 20 per cent of the decrease in visibility.
5. *Large soluble crystals.* Sulfates, nitrates, and chlorides. They account for from zero to 80 per cent of the decrease in visibility.

It has been demonstrated that the effect of these particles on visibility depends on the size of the particles as well as on the materials of which they are composed. Particles with diameters approximating 0.3 to 0.4 micron have the maximum light-scattering power and produce the largest effect on visibility. On days when visibility is especially low, a large percentage of the particles are of this size range. Such particles are small enough to remain in the air for long periods.

### What Causes Eye Irritation?

It has long been thought that the eye irritation from smog was produced by some one substance; and from time to time various atmospheric constituents have been singled out and given the blame for it. The best evidence now is that no single material produces the eye irritation; it results from a number of contaminants working together.

At least nine substances capable of causing

eye irritation have been identified in the Los Angeles air. Although no one of them is present in sufficient quantity to produce eye irritation of itself, all nine substances in combination have been shown by Smog Chamber tests to cause definite eye irritation, even when present in the quantities found in the Los Angeles atmosphere.

Among the substances in the Los Angeles air which—either singly or in combination with others—may cause eye irritation when present in sufficient amounts, are formaldehyde, ammonia, sulfur dioxide, sulfur trioxide, nitrogen oxides, acrolein, ozone, carbon particles, and oil.

The possibility must not be ruled out that other substances as yet undiscovered in the air, may also contribute to the eye irritation. Various mechanical and physical effects, such as motion of the air or the intensity of sunlight, may also be as yet undetermined factors.

### What Is the Chemical and Physical Nature of the Contaminants?

Progress is now being made in determining the chemical and physical identities and states of the principal contaminants of the air, through the use of standard methods including the spectroscope, the electron microscope and the mass spectrograph, and by employing the newest method: proton bombardment.

### Where Do the Contaminants Come From?

Evidence obtained so far suggests that the contaminants have their origin in a wide variety of sources. Silicates, fibers, salt, pollen, and some others are of natural origin, though possibly present in greater quantity because of artificial stirring by traffic. Contaminants such as carbon, oil, lead, zinc, copper, sulfates, and metal particles result from industrial processes, automobile and truck exhausts, and combustion.

Research is in progress to determine the principal processes and activities that are producing contaminating materials, and to gain an idea of their approximate contributions to the smog.

### The Instruments and Methods

The smog research has required development or adaptation of many new instruments and methods for the precise and delicate task of extracting, measuring, counting, and identifying the smog contaminants, producing objective measurements of smog effects, and artificially creating smog conditions in the laboratory to permit controlled experiments.

Before measurements of the fine particles in the air could be made, it was necessary to devise, build, or adapt several items of equipment especially for this purpose. A large electrostatic precipitator was used to collect enough particles for chemical analysis. A collecting device was constructed that hurls fine particles at a glass plate with the speed of sound, so that the particles adhere to the plate and can be examined. A thermal precipitator was used which collects particles more gently by repelling them from a hot wire and causing them to adhere to a glass disc. The hot-wire collector gathers the particles in such a manner that they can be viewed, counted, and measured by optical and electron microscopes.

To be sure that the number of particles collected by these various means is a correct number, not increased by fracturing the particles, or decreased in the case of droplets by evaporation, a special camera was constructed that photographs individual fine particles as they float in a measured volume of space.

An instrumental method for measuring visibility was developed which avoids the errors present when only the human eye is used. The method employs black targets, which are photographed from a distance through color filters. This method not only provides an exact way to measure visibility, but also gives an additional means of determining the size of particles.

The reduction in visibility calculated from data provided by the collecting devices and the dust camera previously mentioned is in good agreement with that observed photographically, establishing that the particles which have been collected and examined can account for the reduction in visibility.

In the detection and measurement of gases, a similarly complex array of new or adapted instruments is used, including two types of continuous analyzers that give a record of some of the gases in the atmosphere not only hour by hour but minute by minute. With the help of these instruments it has been possible to determine to what extent the gaseous contaminants of the air increase during smog and to correlate the presence of contamination with meteorological data and the physical effects of smog. One such correlation is shown in Plate 5.

Because smog occurs only infrequently during most of the year, it has been necessary to devise equipment making possible production and investigation of artificial smog at will, permitting continuous research and controlled experiments. One of these devices, located at the laboratories of Stanford Research Institute, is a transmissometer—a long tube through which light can be passed one or more times with the aid of mirrors. When a known amount of contaminant is introduced into this tube, its effect on visibility can be determined by comparing the amount of light that gets through the contaminated air with that transmitted through the same distance in clean air. This instrument has made it possible to learn how various materials act in reducing visibility in smog.

Another piece of equipment of great usefulness in this investigation is the Smog Chamber—a large box equipped with means of introducing and mixing into the air inside it small measured quantities of various contaminants. Human or animal test subjects inside the box provide data on their physical reactions to the contaminants. This device has yielded a major part of the new information on the effects of various eye irritants.

### Future of the Work

The smog research program is continuing. Some of the principal points now under investigation are these:

1. Are there still-undiscovered materials present in the atmosphere that may account for some of the physical effects of smog, such as eye irritation and the characteristic odor which some

people detect? Or can all the effects of smog be accounted for by the action of contaminants already known?

2. Ozone, or some similar powerful oxidizing agent, has been detected in the atmosphere in unexpectedly large concentrations, coinciding with the appearance of smog. What is the relationship, if any, between this material and the eye irritation or other effects of smog?

3. Characteristically-shaped small crystals have recently been found to occur in the liquid mists that are extracted from apparently dry atmosphere by instruments used for collecting particulate matter. What are these crystals, and what effect do they have on smog?

4. Are the contaminants in the same chemical and physical states in the air as when they left their sources of contamination? Or do they react with each other or their environment in such a way as to acquire properties they did not originally have? If so, what are these reactions, and their effects on smog formation? What part do they play in causing eye irritation?

5. What are the contributions of specific industries, vehicles, incineration processes, combustion processes, and other human activities to the effects of smog?

6. Since it is probably impractical to prevent all contaminants from reaching the air, elimination of what materials will produce the greatest results in alleviating smog? For example, can the eye irritation be substantially reduced by eliminating one or two key substances from the air? If so, which substances?

### Acknowledgments

Many organizations and research institutions have worked with Stanford Research Institute on

the smog investigation or have given valuable assistance and suggestions. A complete list would be voluminous. Particular mention, however, is made of the following:

A. L. Chaney Chemical Laboratory  
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 California State Department of Public Health  
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 General Petroleum Corporation  
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 Los Angeles County Air Pollution Control District  
 National Technical Laboratories  
 Shell Development Company  
 Stanford University  
 Truesdail Laboratories  
 Union Oil Company  
 United States Chemical Warfare Service  
 United States Public Health Service  
 United States Weather Bureau  
 University of California  
 University of California at Los Angeles  
 University of Illinois  
 University of Southern California  
 University of Virginia

### This Interim Report

Highlights of the technical data on the various phases of the investigation to date are presented in the subsequent sections of this report and in the Appendix. Additional information on the research program and the instrumentation developed for it is being published in appropriate scientific journals.

## II ANALYSIS OF THE AIR—GASES

**A**NALYSIS of the air, fundamental to the smog investigation, has as its object discovery of what substances are in the Los Angeles atmosphere at all times of the day, in various localities, during all kinds of weather. This work is intended to yield both qualitative and quantitative values for various contaminants from day to day and, where possible, from minute to minute.

The analysis has been directed toward determination of the nature and quantities of two kinds of contaminants: gaseous and particulate. In this section are reported the results of the work on gases. The work on analysis for particulate matter is reported in Section III.

### ROUTINE ANALYTICAL METHODS

A daily routine analysis for gaseous materials considered to be important pollutants in the atmosphere was started in November 1948 at 4105 North Figueroa Street, Los Angeles. This location was selected because it is in a direct air path between Los Angeles and Pasadena and is one of the main channels through which smog flows out of Los Angeles.

Among the materials tested for were ammonia, the aldehydes, sulfur dioxide, the nitrogen oxides, and sulfur trioxide.

*Ammonia* was collected by passing 50 cubic feet of the atmosphere through a single scrubber (Plate 2). The scrubber contained known volumes of 0.1 normal sulfuric acid. The ammonia content was determined colorimetrically with Nessler's reagent, using a Lumetron colorimeter equipped with an M-440 color filter.

*Aldehydes* were collected by scrubbing 50 cubic feet of the atmosphere with a scrubber (Plate 2) containing 50 ml. of 1 per cent sodium bisulfite. The amount of aldehyde in the solution was determined by a double titration with iodine solution: one titration for a blank before absorption and one after absorption and decom-

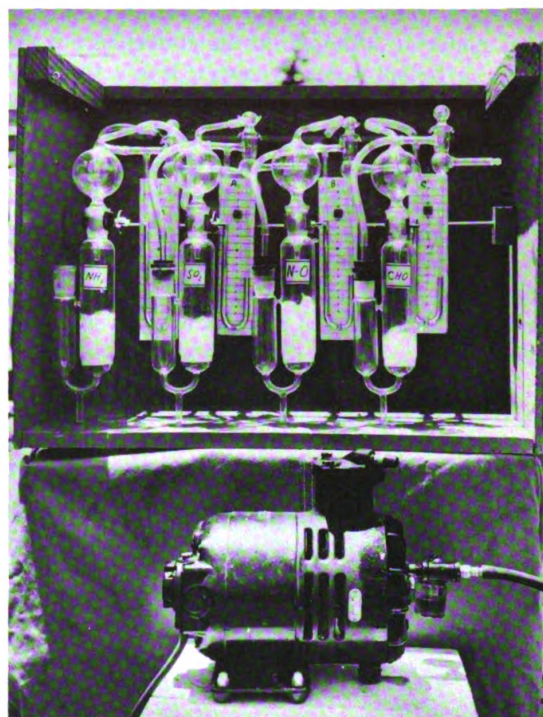


PLATE 2  
Gas scrubber assembly

position of the bisulfite-aldehyde complex by means of a buffer solution.

*Sulfur dioxide* was collected by scrubbing 50 cubic feet of air in an absorber containing 50 ml. of 0.1 normal sodium hydroxide. The solution was cooled and four volume per cent of benzyl alcohol added to minimize oxidation of sulfur dioxide. The concentration of sulfur dioxide was found by use of the sensitive chromogenic reaction of sulfur dioxide, fuchsin, and formaldehyde in acid, described by Grant (Ref. 1). Color intensity was measured using a Cenco Photometer equipped with a green filter.

*Nitrogen oxides* were collected by scrubbing 50 cubic feet of air in a scrubber (Plate 2) containing 50 ml. of a 5 per cent sodium hydroxide solution. The nitrogen oxides in a solution were



oxidized to nitric acid with hydrogen peroxide. The amount of nitric acid was then estimated colorimetrically by using phenoldisulfonic acid reagent.

*Sulfur trioxide* is usually considered a gaseous material, although in the atmosphere it absorbs sufficient water to convert it to a fine mist of sulfuric acid. This mist is exceedingly difficult to collect by using packed columns or other types of laboratory absorption devices. To overcome this difficulty, a laboratory model venturi scrubber was devised (Plate 3) which is based in principle on the larger industrial models described by A. W. Anthony, Jr. (Ref. 2). A more detailed description of this model is given in Appendix 1.

The venturi scrubber removes all types of particulate matter from the atmosphere, includ-

ing water-soluble and insoluble materials. The insoluble portions are removed by filtering and measured by weighing. The sulfuric acid from sulfur trioxide and the soluble sulfates are determined turbidimetrically. All soluble sulfates are reported as sulfur trioxide.

## Results

The results of these analyses are shown in Figure 1. Plotted in Figure 2 are some of the more important meteorological data. There is a correlation in some instances between occurrence of increased quantities of pollutants and weather conditions.

*Ammonia.* The days of high ammonia concentrations in the air usually occur when the Smog Index (Section VII) is high and visibility low, indicating that the ammonia content may in some way be related to the materials that cause murkiness in the atmosphere.

*Aldehydes.* Concentrations of aldehydes have rarely exceeded 0.2 part per million by weight, and the high concentrations did not coincide with periods of eye irritation. This lack of correlation tends to indicate that aldehydes alone are not responsible for eye irritation.

*Sulfur Dioxide.* This material was below 0.01 part per million during 1949 to date, although it reached a concentration as high as 0.4 part per million in November 1948. In terms of the sulfur dioxide content in other cities, this is quite low.

*Nitrogen Oxides.* The concentration of nitrogen oxides was much lower at the end of the period of testing than at the beginning.

*Sulfur Trioxide.* The concentration of this material in the atmosphere has been quite low throughout the period of test. There was a slight tendency to increase in April 1949.

## Tests for Fluoride Content

The fluoride content was measured in three cold trap samples, taken on March 11, March 27, and April 6, 1949. The analyzing procedure involved distillation and colorimetric thorium-alizarin titration for fluoride. Amounts of fluoride, possibly hydrogen fluoride, were found,

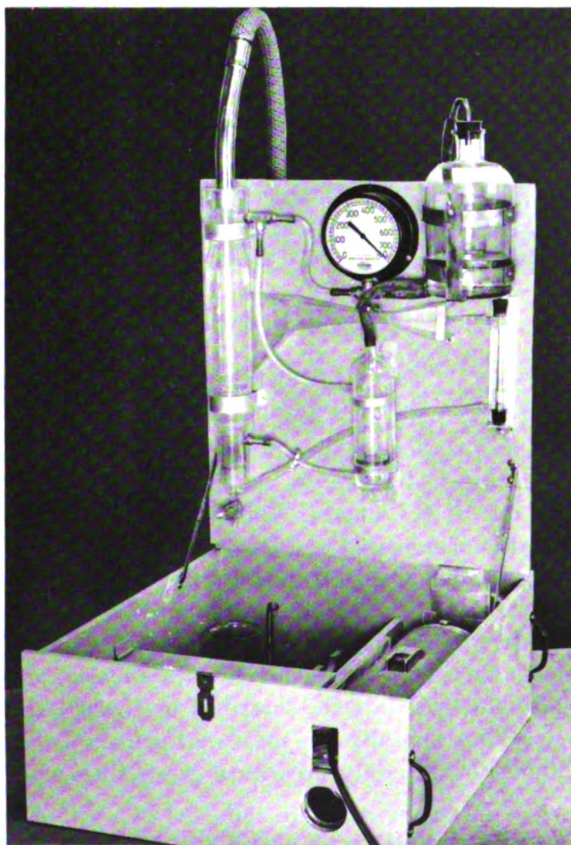


PLATE 3  
Portable venturi scrubber

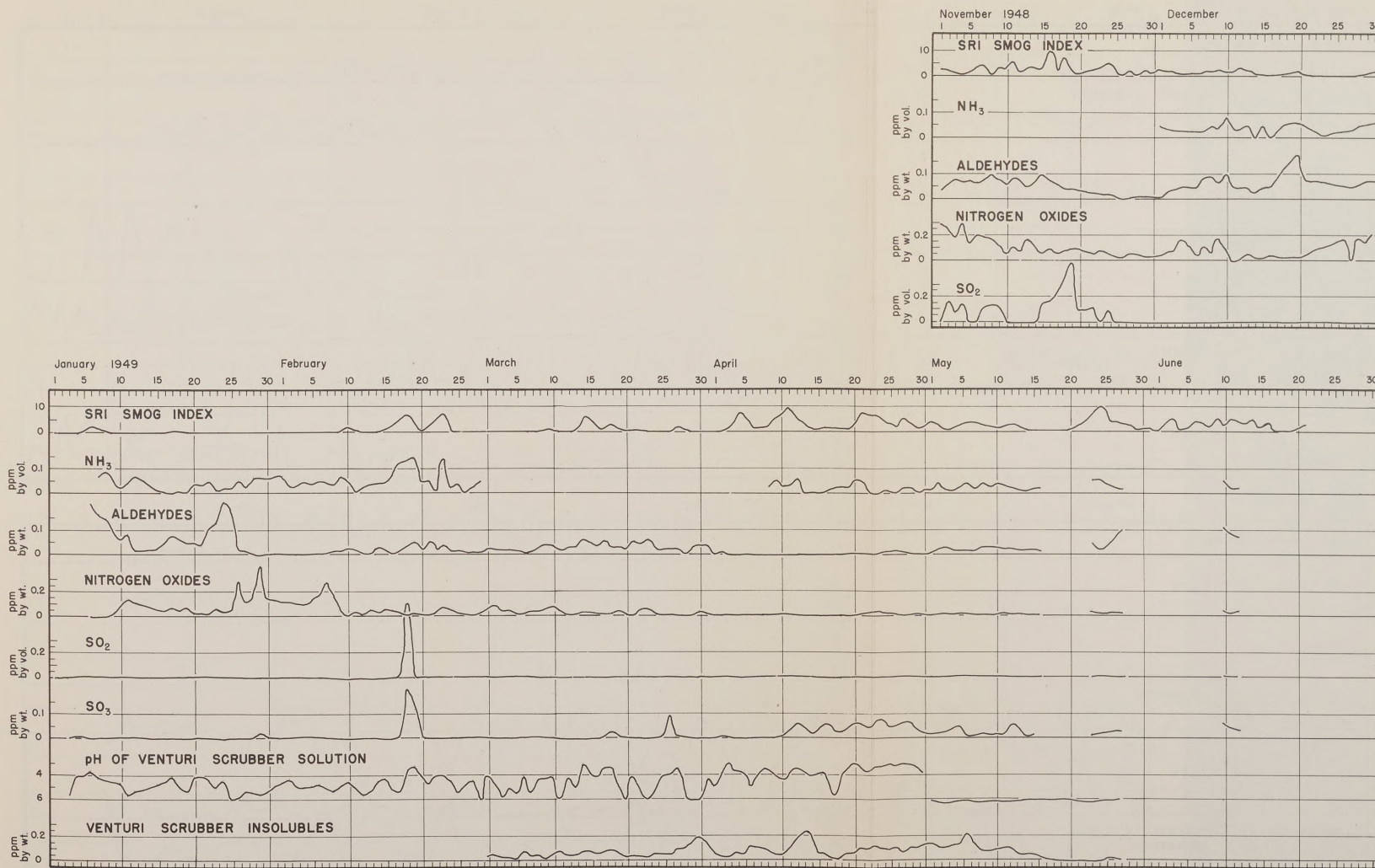


FIG. 1

Analysis of Los Angeles atmosphere

A daily routine analysis of gaseous materials in the atmosphere made at 4105 North Figueroa Street, Los Angeles. Results from November 1948 to June 30, 1949 are shown.

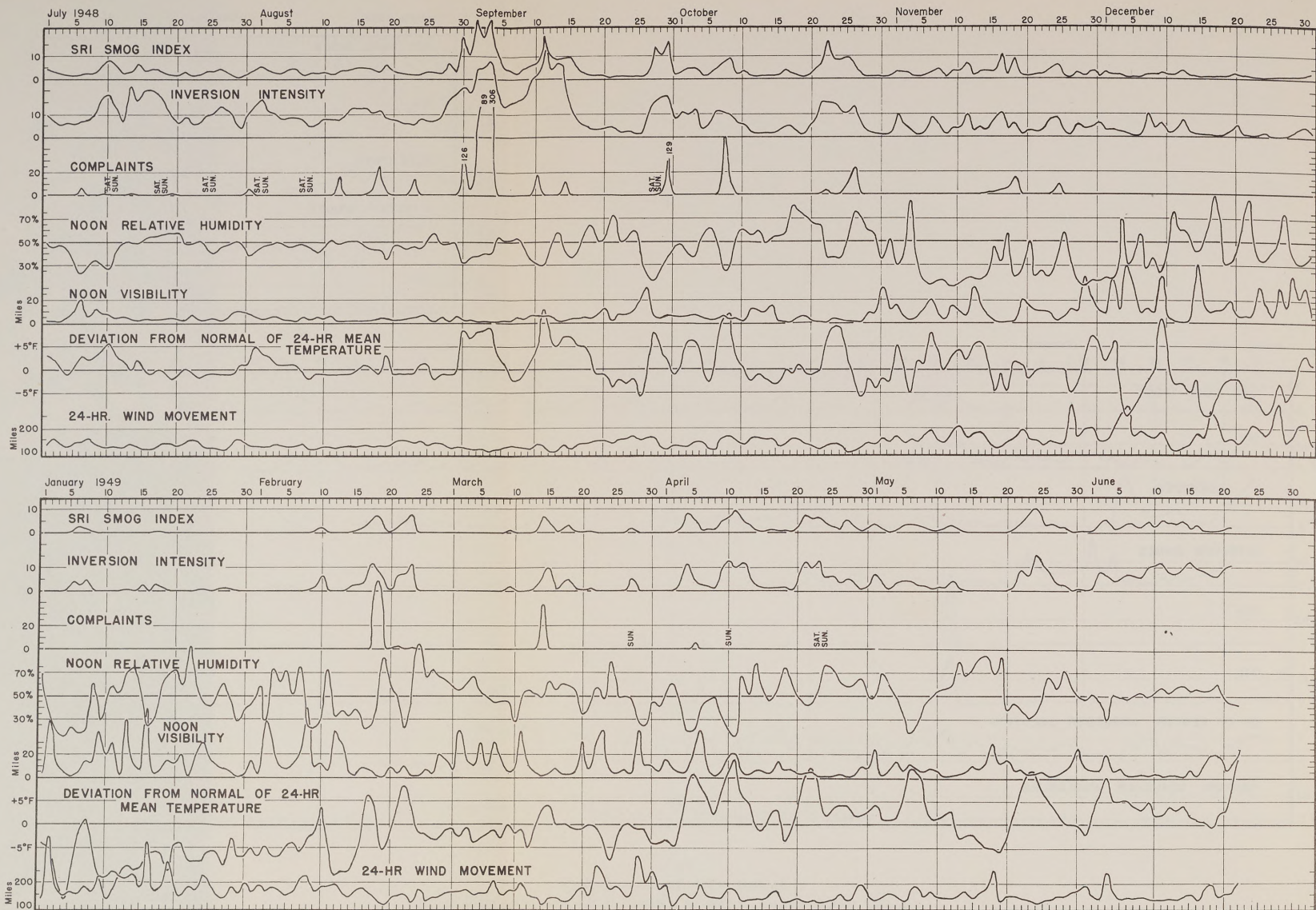


FIG. 2  
 Meteorology of Los Angeles

corresponding to 0.076, 0.0054, and 0.0052 part per million by weight in the atmosphere.

Twenty venturi scrubber samples were also subjected to this analysis. This method of sampling is more effective than the cold trap for collecting particulate matter (solid fluorine salts) but may be less efficient in removing gaseous fluorine compounds from the air. These samples, taken April 21-30, averaged 0.0051 part per million fluoride by weight in the air, with maximum and minimum values of 0.0178 and 0.0005.

### CONTINUOUS ANALYZERS

For more detailed analysis of the sulfur dioxide content of the air, automatic analyzers provide useful data that cannot be obtained by manual methods. Those used in this work operate continuously and have quick response to small changes in concentration.

#### Testing Procedures

Five continuous, automatic analyzers, primarily designed to measure the sulfur dioxide

content of the atmosphere, were installed in the Los Angeles area at the four positions shown in Figure 3. Four of these analyzers were of the design described by Thomas (Ref. 3). The fifth was a Titrilog manufactured by the Consolidated Engineering Company, Pasadena, California. A Thomas analyzer, constructed at Stanford Research Institute, is shown in Plate 4.

*The Thomas instrument* was designed for the measurement of sulfur dioxide, which is absorbed from the atmosphere in a hydrogen peroxide solution, where it is oxidized to sulfuric acid. The measurement of the sulfur dioxide concentration is then made by recording the electrical conductivity of the sulfuric acid solution.

Obviously this record would be affected by atmospheric impurities other than sulfur dioxide, if they were absorbed and were electrically conducting in solution. For the purposes of the smog investigation, however, even in the absence of identification it is helpful to measure and record the quantitative effect of such materials as a measure of contaminant concentration.

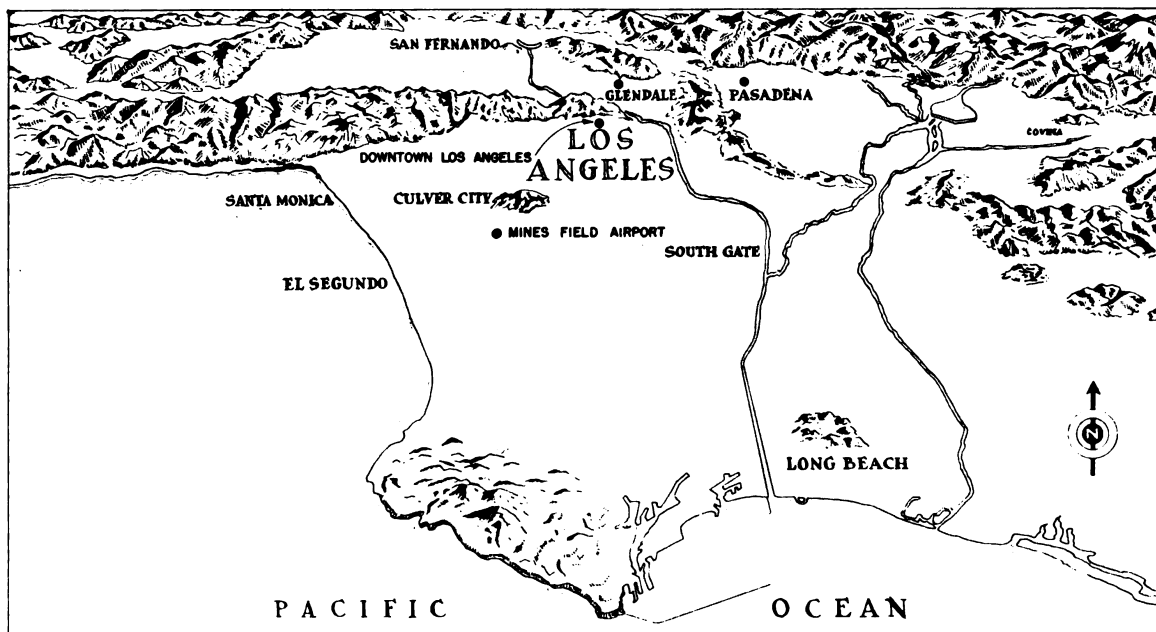


FIG. 3

Location of Thomas continuous analyzers

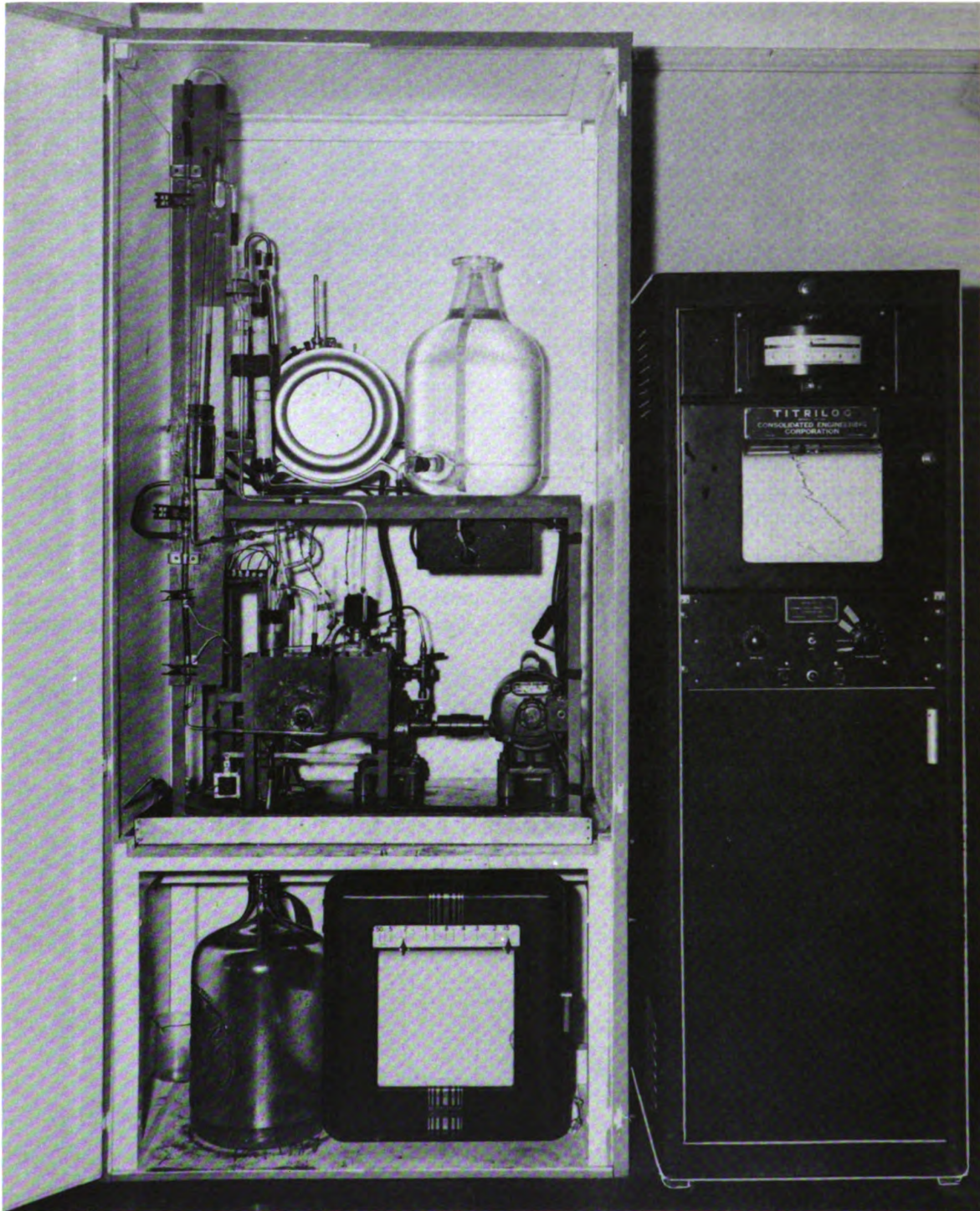


PLATE 4  
Thomas continuous conductivity recorder (left) and Consolidated  
Engineering Corporation Titrilog in use in Los Angeles

The *Titri-log* operates on a somewhat different principle from the Thomas instrument in that, instead of measuring the electrical conductivity of a solution, it provides a measure of materials that exert a reducing action on an acid solution of bromine. One Thomas analyzer and the *Titri-log* were installed side by side in downtown Los Angeles and were arranged to operate on a common sampling duct. The purpose of this was to take advantage of the difference in method of measurement. It was reasoned that, when a difference in concentration of contaminants was recorded, some information could be gained concerning the properties of the materials producing the difference. The *Titri-log* is especially effective for measuring hydrogen sulfide, sulfur dioxide, mercaptans, and organic sulfides. Before installation, both types of instruments were carefully calibrated by operating them with known mixtures of sulfur dioxide in air and were found to record the same values.

## Results

Figure 4 shows typical analyses by the five continuous analyzers at the four stations.

It will be observed that the total equivalent sulfur dioxide content of the atmosphere did not exceed 0.32 part per million and that in some cases the *Titri-log* records a somewhat higher equivalent sulfur dioxide content than the Thomas instrument. This difference might be due to the presence of trace quantities of hydrogen sulfide or other organic sulfur compounds.

The concentration of impurities, as recorded by these automatic analyzers, is usually greater in downtown Los Angeles than at any of the other stations. Further, the peak concentration in downtown Los Angeles usually occurs later than the peak concentration at the airport at Mines Field, and earlier than in the cities of Pasadena and Glendale. This corresponds with the general time pattern of subjective human perception of smog.

The automatic analyzers appear to provide an objective measure of the smog conditions illustrated in the sequence of photographs in Plate 5. These photographs were taken from a

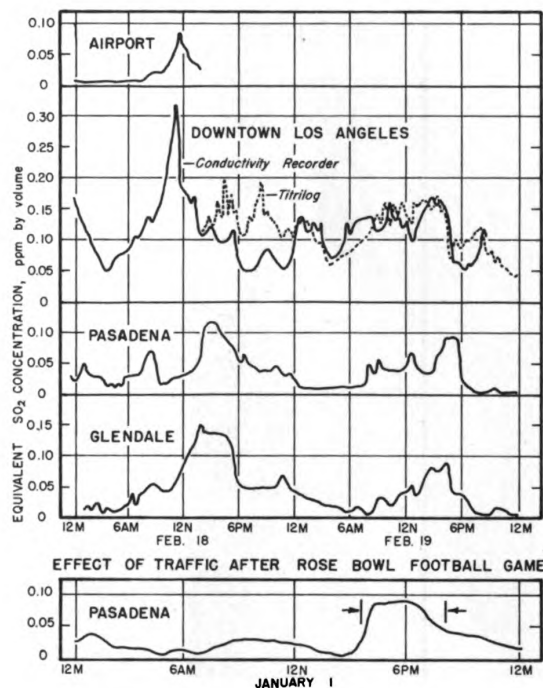


FIG. 4

Continuous instrumental analysis of Los Angeles atmosphere. Dates refer to 1949.

position opposite 4105 North Figueroa Street, Los Angeles, on May 23, 1949, during smoggy conditions when some eye irritation existed and when there was present in the atmosphere what some individuals described as a typical smog odor.

At 9 A.M. a row of eucalyptus trees on the crest of a hill was fairly distinct, and an automatic recorder showed a sulfur dioxide equivalent concentration (arbitrary smog units) of 0.01 part per million. By 10 A.M. the recorder indicated 0.02 part per million, and the photographs show that the haze had increased in density so that the row of eucalyptus trees was much less distinct than an hour earlier.

The maximum odor and minimum visibility occurred at about 10:45 A.M., at which time the chart reading had increased to 0.04 part per million.

By 11:30 A.M., the visibility was slightly improved. The chart reading was still about

THE SMOG PROBLEM

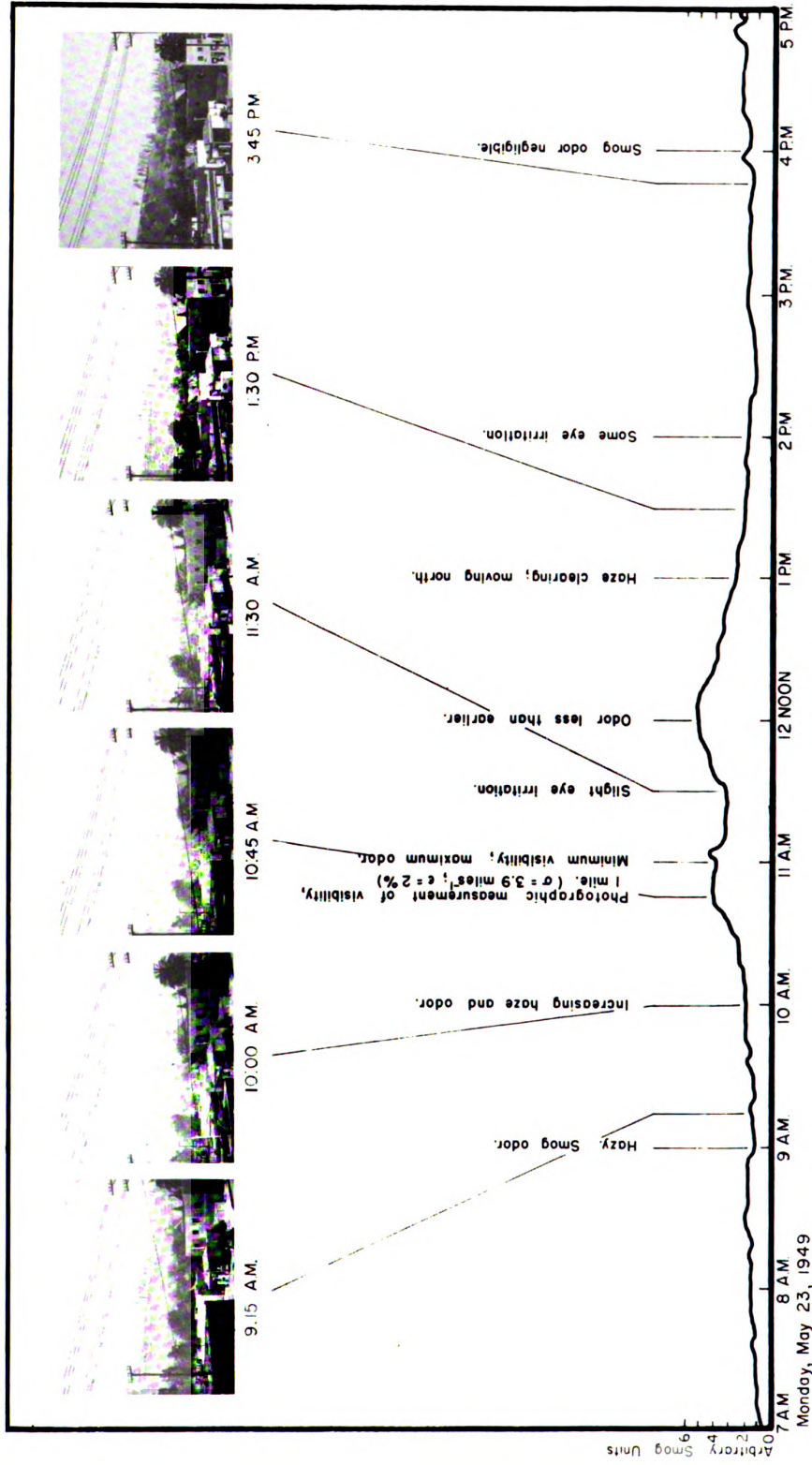


PLATE 5

Subjective reactions of people on the streets can be paralleled by photographic data and by analysis of the atmosphere. This composite brings together a series of photographs of the same scene taken at different hours of a smog day, air pollution data obtained at the same site by a continuous conductivity recorder, and the reactions of observers.

0.04 part per million, and the first slight indication of eye irritation was noticed.

The maximum recorded reading occurred at about 12 noon and started to decline shortly thereafter, reaching 0.02 part per million by 1:30 P.M. The atmosphere was clearing by this time, and by 3:45 P.M. the haze had nearly vanished and the odor decreased considerably.

The haze layer appeared to arrive from the south and move to the north. Table II gives the visibilities recorded by the weather station at downtown Los Angeles, and the relative humidities at the point where the photographs were taken and in downtown Los Angeles. It will be noted that the relative humidity did not exceed 40 per cent during the day and that the recorded visibility, as estimated by the Weather Bureau, was one mile, which is the same value as that obtained by the photographic method (described in Section IV) at 10:45 A.M., at the 4105 North Figueroa Street location.

TABLE II.—RELATIVE HUMIDITY AND VISIBILITY IN DOWNTOWN LOS ANGELES, MAY 23, 1949

TIME	RELATIVE HUMIDITY		VISIBILITY
	4105 NORTH FIGUEROA STREET PER CENT	DOWNTOWN LOS ANGELES PER CENT	DOWNTOWN LOS ANGELES MILES
8:00 A.M.			6
8:30 A.M.		37	
8:40 A.M.	28		
9:00 A.M.			4
10:00 A.M.			2
10:30 A.M.		30	
10:45 A.M.	40		
11:00 A.M.	32		1
12:00 NOON			5
12:30 P.M.		27	
1:00 P.M.			7
1:30 P.M.	23		
2:00 P.M.			8
2:30 P.M.		20	
3:00 P.M.			10
4:00 P.M.			20
4:30 P.M.		28	

Thus it appears that the subjective reactions of people on the streets can be paralleled by photographic data and by instrumental analysis of the atmosphere. The faint, not unpleasant odors reported resemble ozone or bleaching solution and are not those of sulfur dioxide. The

concentrations of pollutants recorded are far below concentrations at which sulfur dioxide can be sensed as an odor.

### FREEZE-OUT TESTS

Components of the atmosphere have been concentrated by freezing them out of the air, using liquid nitrogen at  $-195^{\circ}$  C. The apparatus, shown diagrammatically in Figure 5, is portrayed in Plate 6.

In the freeze-out train the air is passed successively through three traps, the first and second kept at  $-80^{\circ}$  C, and the third at  $-195^{\circ}$  C. Gaseous impurities are condensed on the walls of these flasks. In most operations some of the oxygen of the air is also liquefied. After a quantity of the atmosphere—usually about 300 cubic feet—has passed through the apparatus, the flasks are removed and allowed to warm slowly. The characteristics of the residue are carefully noted.

In some cases the material has an odor similar to that associated by some persons with smog, though it is much stronger and more concentrated. Although the odor has been variously described as resembling that of ozone or "bleach solution," in the freeze-out samples it apparently was not due to either of these materials. Reagents such as potassium iodide or sodium thio-sulfate, which destroy bleach and ozone, had no effect on the odor. Neither did the odor appear to be caused by organic peroxides, since it persisted even after the usual reactions had occurred which are used to destroy the peroxides.

The same material was collected from the atmosphere at the top of Mt. Wilson, but little if any was collected at Santa Barbara. The identity of the substance giving off this characteristic odor has not been established.

### Organic Peroxides

Organic peroxides are oxidation products of many types of organic materials.

Their presence in the atmosphere may arise from oxidation and the effect of sunlight on almost any oily matter suspended in the air. Some organic materials are known to form per-



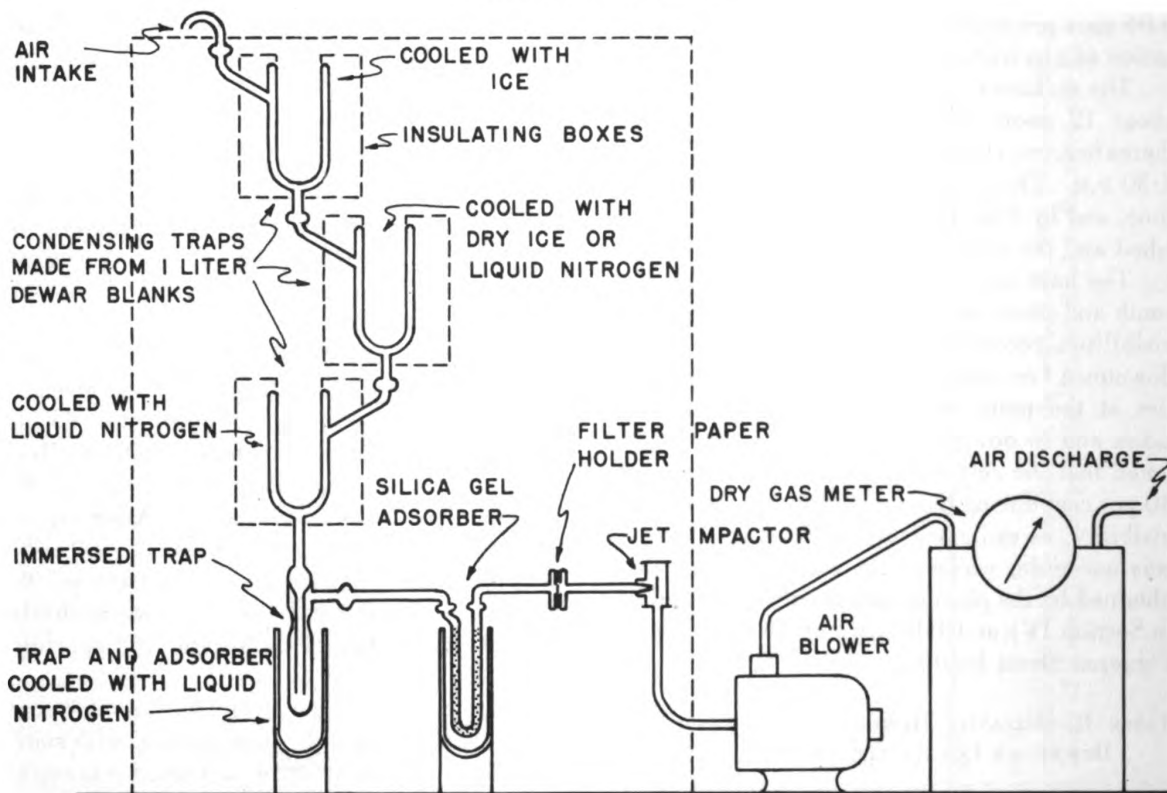


FIG. 5  
Freeze-out train and auxiliary equipment

oxides in the dark, when in the presence of air. Chlorophyll in the leaves of plants is known to be a powerful catalyst in the formation of peroxides from fatty oils. Some of the lower molecular weight organic peroxides, such as ethyl hydroperoxide, are reported to have strong suffocating odors and to be irritating to the nose and throat. Further, they are also reported to have a bleach (calcium hyperchlorite) odor (Ref. 4).

The presence of organic peroxides in the Los Angeles atmosphere was first reported by the Los Angeles County Air Pollution Control District. Since that time numerous analyses have been made to determine their concentration. The freeze-out method and the venturi scrubber previously referred to have been used for the collection of material that is analyzed for organic peroxides. It is quite probable that neither method collects all of such materials from the atmo-

sphere. In the laboratory the venturi scrubber was demonstrated to collect approximately 50 per cent of various organic peroxides that were introduced into the atmosphere in known small concentrations. The absolute efficiency of the collection methods was not considered to be important until further information had been obtained on the identification of the organic peroxides.

So far, well over 100 analyses have been made for organic peroxides. The maximum concentration has been of the order of 0.02 part per million by weight in the atmosphere. It would appear from these tests that organic peroxides are not present in Los Angeles air in significant quantities. Moreover, their occurrence does not coincide with occasions of eye irritation. Further tests (Section V) on the effect of organic peroxides as eye irritants tend to confirm this viewpoint.

The method of measuring the amount of organic peroxides used in obtaining the results given above is based on their ability to oxidize iodide ion to iodine. In all such measurements of this nature it is obviously significant that only the net effect of the oxidizing over the reducing action of the various materials in the atmosphere is measured. Thus, if there exists in the atmosphere a mixture of, for example, an

organic peroxide and a reducing substance such as sulfur dioxide, the concentration of both substances may bring about a mutual alteration that would result in a lower measurement for peroxide than exists in the open air. There also exist in the atmosphere other oxidizing agents which may give a reaction similar to organic peroxides, such as oxides of nitrogen and ozone.

The various organic peroxides, depending on

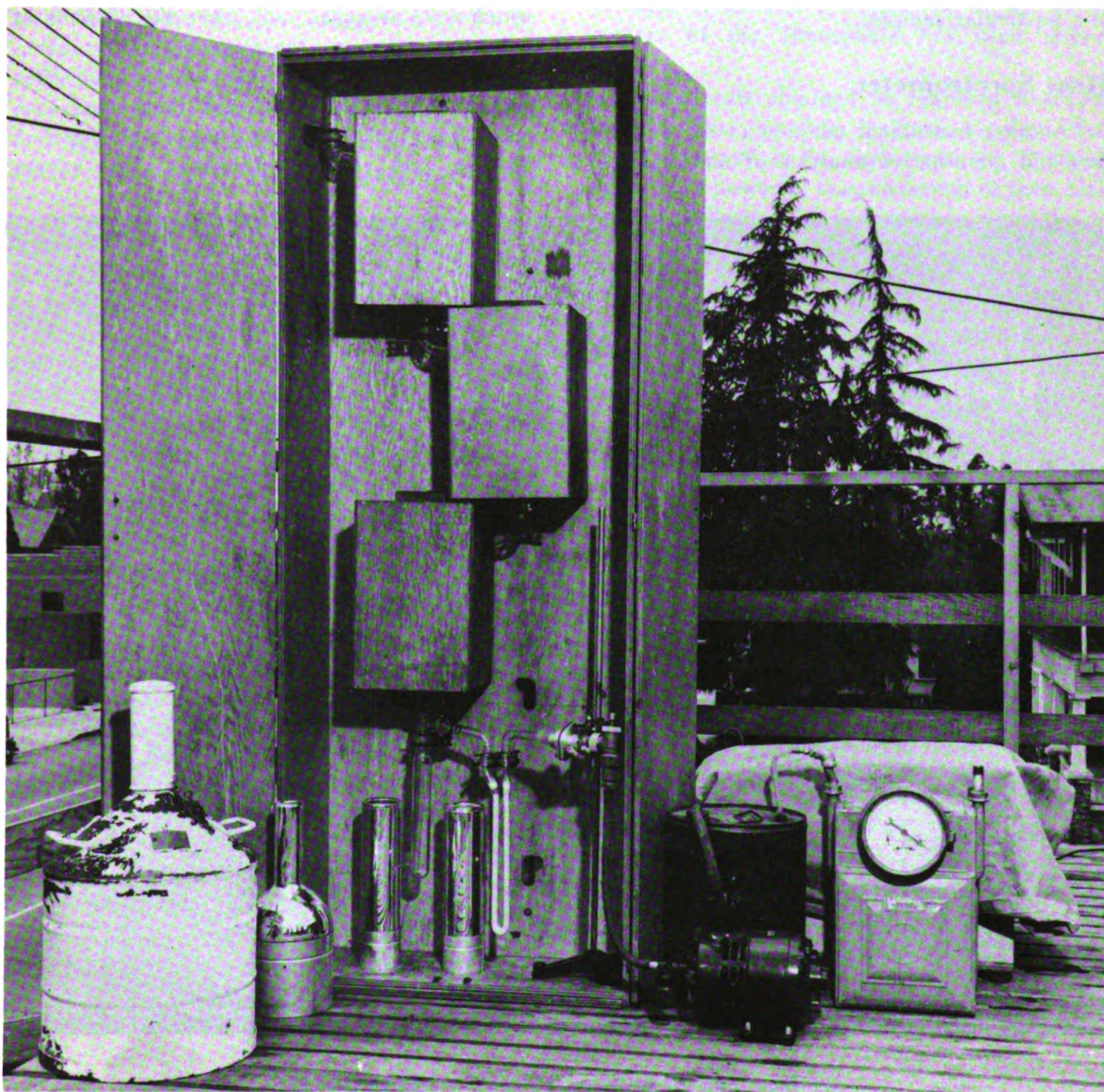


PLATE 6

Freeze-out train for collecting atmospheric contaminants

their molecular structure, differ widely in their ability to oxidize iodide ion to iodine. For example, the hydroperoxides liberate iodine rapidly from sodium iodide dissolved in acetic acid, whereas the dialkyl peroxides liberate iodine only slowly over a period of many hours in strong acetic acid. By means of these reactions it is possible to obtain an approximate measure of the relative proportions of the oxides of nitrogen, the alkyl peroxides, and the hydroperoxides in a particular sample.

### Mass Spectrometer

Another instrument adapted to the qualitative and quantitative analysis of material col-

lected by the freeze-out method is the mass spectrometer. This instrument has shown great utility in other analytical applications where minute quantities of volatile materials must be measured and identified. The transfer of the trace quantities of materials from the freeze-out train to the mass spectrometer was accomplished as follows:

To the freeze-out train (Figure 5) there is connected a chilled tube containing silica gel which is so arranged that, when the contents of the traps warm up, the more volatile constituents are driven off and are adsorbed on the silica gel. As the sample is collected, there are frozen out of the atmosphere quantities of water, carbon dioxide, and various impurities. The vapors

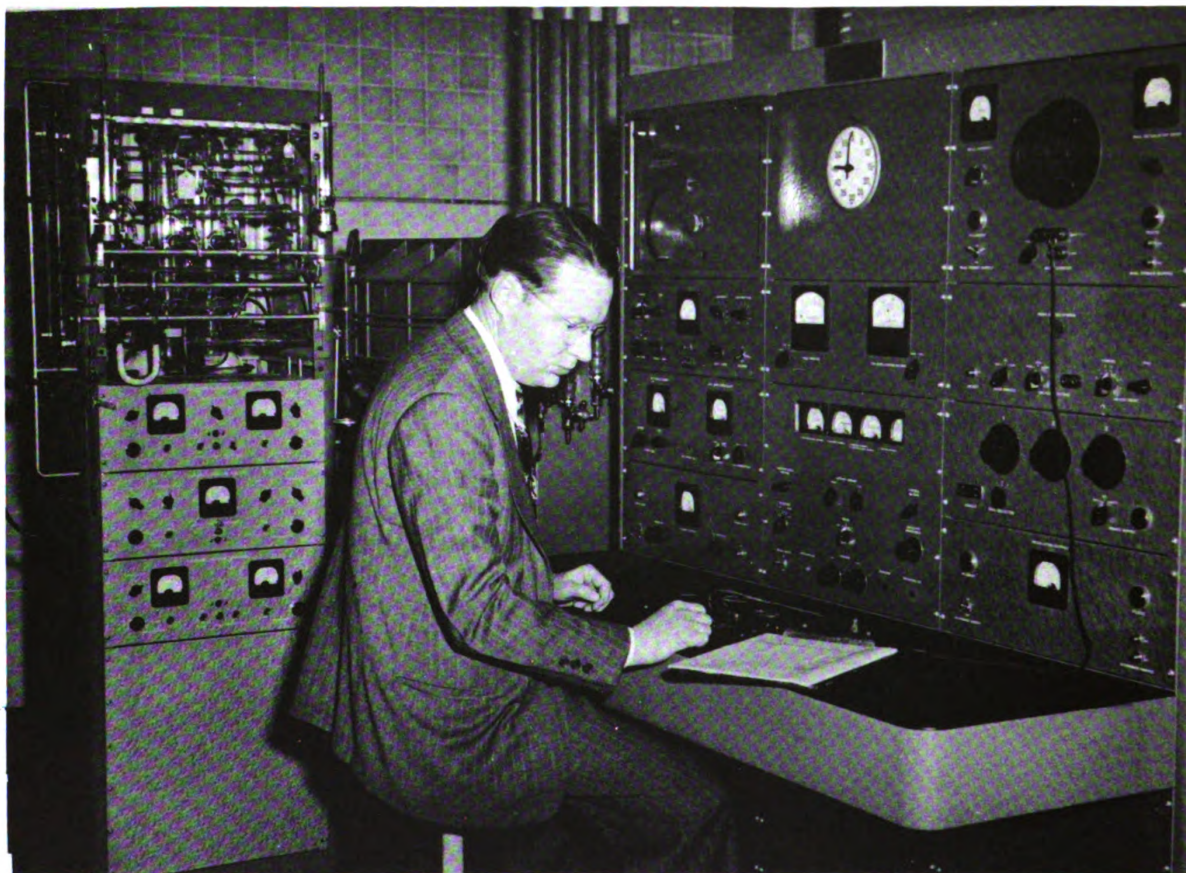


PLATE 7

Analyzing with the mass spectrometer some of the materials removed from the atmosphere by the freeze-out method

from the evaporating carbon dioxide carry with them some of the more volatile impurities frozen out in the absorption train, and these are retained by the silica gel. By carefully warming the silica gel containing the adsorbed materials, it is possible to drive these impurities off and release them into a mass spectrometer for analysis.

The mass spectrometer used was provided by the laboratories of the Union Oil Company of California. The sample analyzed was collected on June 7, 1949, between the hours of 9:15 A.M. and 3 P.M., from approximately 100 cubic feet of air. The mass peaks detected by the spectrometer and possible materials that will produce these peaks are tabulated in Table III. Thus far, results qualitatively confirm the analyses made by other methods.

TABLE III.—MASS SPECTROMETER ANALYSIS OF SILICA GEL FROM FREEZE-OUT TRAIN

MASS AT WHICH PEAK INDICATED	POSSIBLE MATERIAL
84	
71	
70	
69	
64	sulfur dioxide or ? <sup>1</sup>
58	} hydrocarbon <sup>2</sup>
57	
56	
55	
48	sulfur dioxide <sup>1</sup> , mercaptan or ?
46	nitrogen oxide <sup>1, 3</sup> , alcohol
45	
44	CO <sub>2</sub> , N <sub>2</sub> O, aldehyde <sup>1, 2, 3</sup>
43	} hydrocarbon <sup>2</sup>
42	
40	
39	
31	} alcohol, aldehyde <sup>1, 2, 3</sup>
30	
24	? (perhaps doubly charged mass 48)

<sup>1</sup>Also identified in Los Angeles atmosphere by scrubbing.

<sup>2</sup>Also found in samples collected with electrostatic precipitator.

<sup>3</sup>Found in liquids condensed directly from the Los Angeles atmosphere.

## OZONE

It has been believed for some time that ozone or some material resembling it is present in Los Angeles in greater quantities than in many other cities. This was first indicated by the more rapid deterioration of rubber goods in the Los Angeles area. When smog is present in heavy concentrations, an odor resembling ozone is frequently detected. Because ozone is known to be a powerful irritant, systematic investigation of the ozone content of the atmosphere has been undertaken.

The results obtained by Stanford Research Institute thus far show beyond question that there is present in the atmosphere an oxidizing agent more powerful than elemental oxygen. Calculated as "ozone," it is present in quantities as high as 50 parts per hundred million. Rubber bands placed on the roof of the laboratory in Los Angeles exposed to the atmosphere show rapid deterioration, while those not exposed to the atmosphere but exposed to the sunlight show no similar effect.

Analyses conducted throughout the day have shown what is believed to be significant: namely, the "ozone" content of the atmosphere drops immediately upon the setting of the sun. It also appears to be much lower inside of buildings than outside, during the daylight. The parallelism between these observations and the occurrence of smog is believed to be too important not to investigate thoroughly.

The Thomas analyzers are being refitted to make a continuous recording of the "ozone" content of the atmosphere. Potassium iodide does not conduct electric current between two platinum electrodes because of polarization in the absence of iodine or some similar de-polarizing substance. The iodine liberated by the "ozone" increases the flow of current and the increase in flow is a direct measure of the "ozone" content.

### III

## ANALYSIS OF THE AIR—PARTICULATE MATTER

**T**HE PARTICULATE matter of the atmosphere, such as crystals, aggregates, mists, and dusts, including fine particles of carbon and metal compounds, affects visibility and either by itself or in combination with gaseous materials may produce eye irritation.

Particulate matter presents a quite different problem in analysis from that presented by gaseous materials. Complete analysis of the particulate matter requires a measurement of the number and sizes of particles in a known volume of air, as well as determination of their chemical composition.

### COLLECTING EQUIPMENT

No single method for collecting particulate matter permits all the desirable information to be obtained. A combination of several methods is therefore used. A description of these methods follows:

*Westinghouse Precipitron.* To conduct an adequate chemical analysis, several grams of sample are desirable. To obtain this amount of material, a Westinghouse Precipitron was employed. This instrument is a household-type unit that electrostatically collects the dust from a 1200-cubic-foot-per-minute air stream which is drawn through the equipment by means of a blower. The dust is collected on dry aluminum plates and may be removed either by brush (the technique used in these studies) or by flushing with water or a solvent.

*Laboratory Model Electrostatic Precipitator.* A portable laboratory model electrostatic precipitator was also designed and constructed. This device has the advantage of collecting the samples on an easily removed, flat collector plate from a carefully metered quantity of air. The equipment is shown diagrammatically in Figure 6. A collection head, which is of special construction, is illustrated in some detail. The power supply can be regulated to provide a known corona discharge of direct current across the electrodes. The air is metered by means of

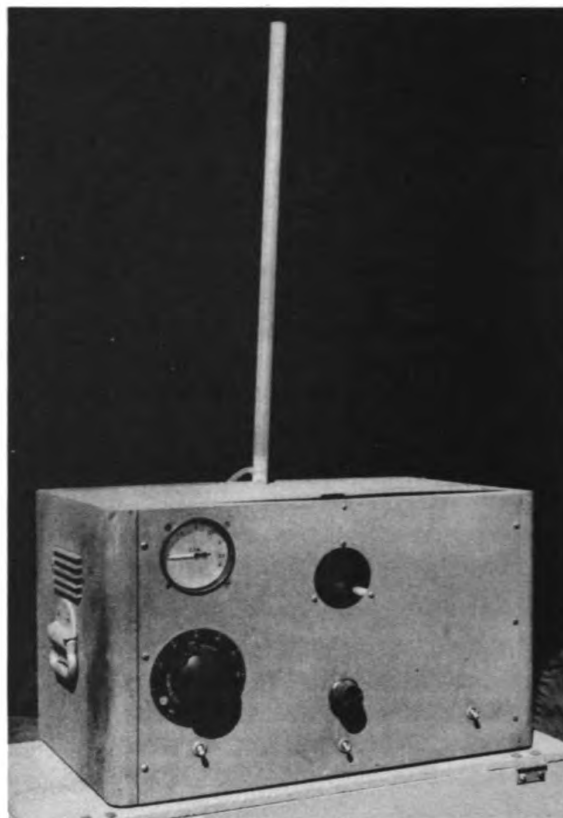


PLATE 8

Electrostatic precipitator used for collecting samples of airborne particulate matter

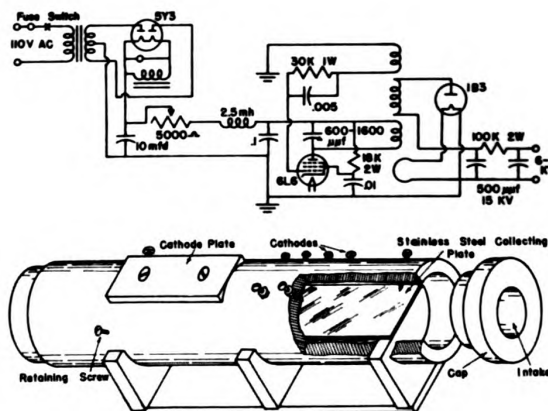


FIG. 6

Electrostatic precipitator head and wiring diagram

a venturi flowmeter, using a modified airplane type rate-of-climb meter to measure the pressure drop in the flowmeter. This instrument has proved most useful for the collection of sulfur trioxide mists in the laboratory.

*Venturi Scrubber.* The venturi scrubber has been referred to previously (Section II and Appendix 1). It is useful for particulate matter as well as gases.

*Sonkin Impactor.* The collection of fine particles by causing the air stream in which they are contained to impinge sharply upon a solid surface is a common technique. The use of air velocities approaching the speed of sound was first described by Sonkin (Ref. 5), who showed that high efficiency could be attained by this method for the collection of particles less than one micron in diameter.

Figure 7 shows a diagram of the impactor

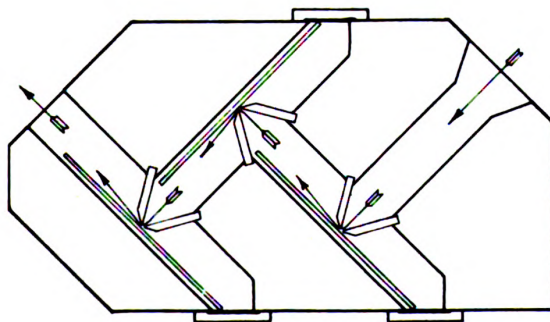
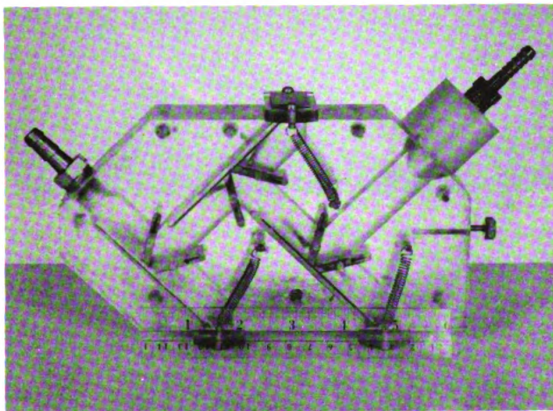


FIG. 7  
Photograph of modified Sonkin impactor and  
diagram of path of air through it

used. In the operation of this instrument it is necessary to have a pressure drop across the last jet of at least one-half atmosphere in order that the critical velocity approaching the speed of sound is reached in the jet. The use of three or more jets of different sizes in series, and an equivalent number of collection plates, permits a rough segregation of the particles according to size range, with the larger particles being collected at the outlet to the largest jet.

For the collection of particles as large as 10 microns, it was found necessary to coat the first plate with an adhesive material, such as glycerine jelly; otherwise, the high velocity of the jet caused these particles to be swept off the first plate and onto the second or even the third. The smaller particles have naturally adhesive properties.

The Sonkin impactor has the advantage that only a small volume of air need be used, and the particles may be collected on a microscope slide where they can be readily examined. It has the disadvantage that the expansion of the air through the jets causes condensation of moisture; and this sometimes results in agglomeration of the particles on the slide. Hygroscopic particles tend to agglomerate, and soluble crystals may lose their original form.

*Thermal Precipitator.* The thermal precipitator was first described by Aitken (Ref. 6) and later developed by Green *et al.* (Ref. 7). A commercial model was obtained from C. F. Casseis, Ltd., London, England. Its construction is illustrated in Figure 8.

The thermal precipitator removes dust by causing the air to flow around a fine, heated wire that is placed between two cooled surfaces. The dust is repelled by the heated wire and forced against cooled surfaces, where it is collected. By using microscope cover glasses for the cooled surfaces, it is possible to obtain samples that may be readily examined and counted.

The thermal precipitator has the advantage of high efficiency of collection for very small particles. It has the disadvantage that only very small flow rates of air can be used, and therefore the size of the sample is limited.

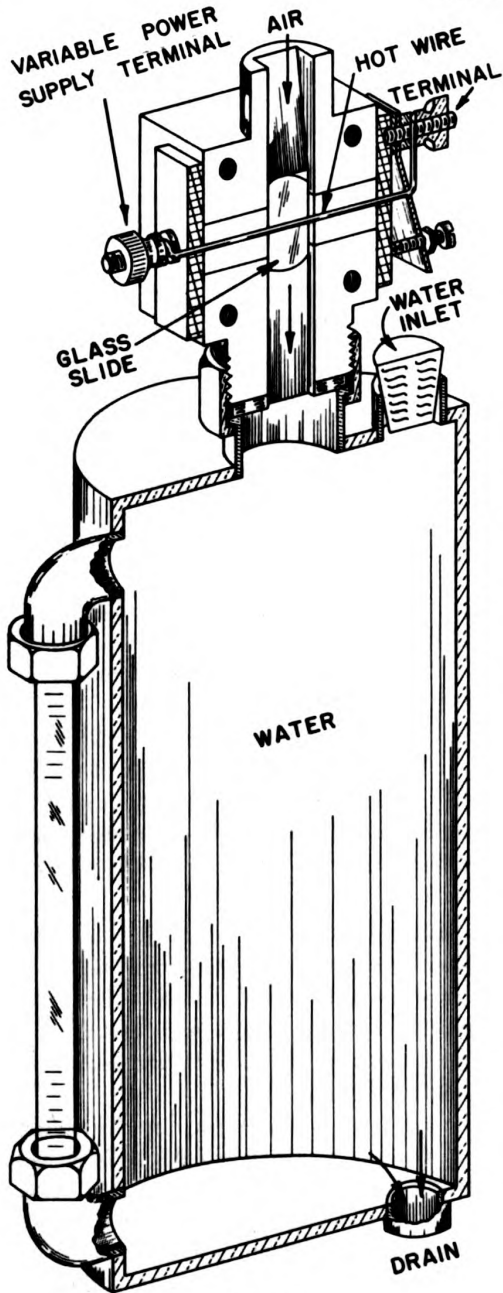
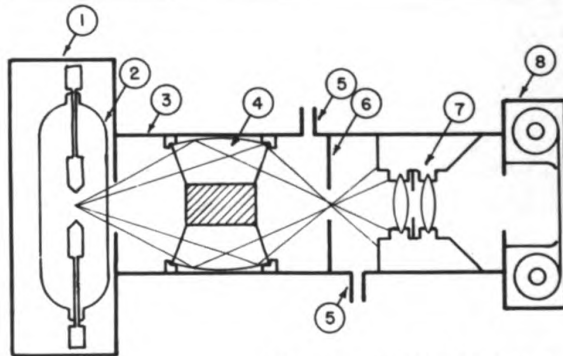
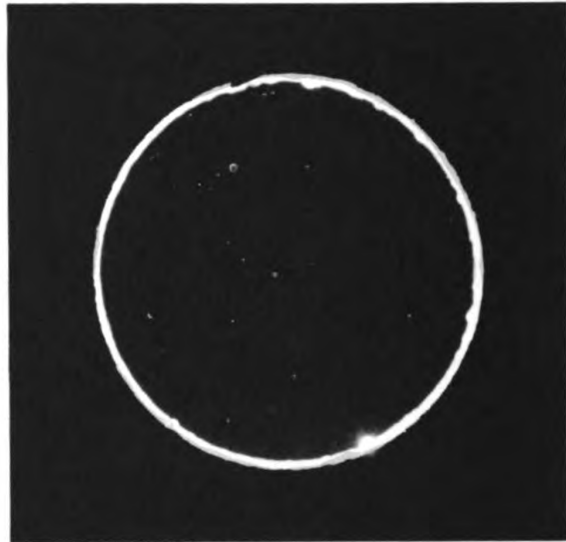


FIG. 8  
Thermal precipitator

**Dust Camera.** All the methods previously described for the collection of particulate matter tend to modify in some manner the dust or mist being collected. Fine dust is sometimes agglomerated, and mists are caused to lose or gain water

content, thereby changing the size of the particles.

To count the particles, it is desirable to view them just as they exist in the atmosphere. A dust camera that photographs particles suspended in air in their natural state was devised by the Chaney Laboratories in Los Angeles and has been modified for use in the investigation of smog. Plate 9 illustrates the design of the camera and



Notes: (a) Image of flash discharge is focussed on defining baffle by annular lucite condenser in conical beam which does not enter objective lens.

1. Flash tube and trigger circuit box.
2. GE. FT-230 flash tube.
3. Tubular body.
4. Lucite elliptical reflecting condenser.
5. Air flow inlet and outlet.
6. Field defining baffle.
7. 25mm. photographic objective.
8. 35mm. camera box.

(b) Defining baffle and film are at conjugate foci of 25mm. objective, imaging scattered light from particles within depth of focus of lens.

PLATE 9

Design of the Chaney Dust Camera, and one of the dust photographs taken with it

the type of photograph of smog particles it yields.

The equipment consists of a tube containing a focussing, reflecting lens, a high-speed, high-intensity electric photoflash bulb, and a small aperture through which the light passes from the bulb through an optical lens system to a 35 mm. camera. The tube is provided with a means of introducing and withdrawing the atmosphere under investigation through the same aperture traversed by the light entering the camera. The reflecting lens is so arranged that light from the flash bulb cannot enter the camera directly, and the field of view of the camera is therefore black unless there are particles of dust in the atmosphere. In this manner each particle in the field of focus will show up as a dot of light on the film similar to the image on the human eye viewing a mote of dust lighted by a ray of sunlight in a darkened room.

By knowing the diameter of the aperture and the depth of focus of the camera, it is possible to calculate the volume of space that is in focus. The number of dots on the photographic film is a direct measure of the dust content of the air. This method has the great advantage of not requiring disturbance of the dust particles prior to or during their measurement. The high-speed flash bulb "stops" the dust, and thus permits accurate interpretations to be made.

## Results

The particulate matter in the air collected by the various means referred to in the preceding pages has been examined by electron and optical microscopic methods, emission spectroscopy, mass spectroscopy, and chemical analysis under the microscope. The method chosen in each case was selected as the most satisfactory for the particular materials at hand. Results of sampling by different methods are given below.

*Precipitron Samples.* Detailed chemical analyses of the particulate matter collected on the Westinghouse Precipitron plates have been made, and the results are shown in Tables IV and V. The precipitron is believed to collect

about 90 per cent of the particulate matter in the air.

From Table IV it can be seen that the suspended material in the air is made up of approximately 45 per cent minerals and other inorganic substances. Many of the metal compounds are apt to be of soil origin, whereas others, such as lead, zinc, and copper, are likely to be industrial and automotive emissions. Ammonia is also present and may exist in the air either as a sulfate or a nitrate, or both.

The remainder of the particles is a complex mixture of organic compounds, carbon, pollen, and volatile substances. A considerable portion is of an oily nature, accompanied by aldehydes and organic acids. The total quantity of such material collected from the atmosphere is estimated to be not more than 0.1 part per million by weight in the atmosphere.

*Sonkin Impactor Samples.* The samples of dusts collected by the impactor range in size from below 0.1 micron in diameter to about 10 microns in diameter. In the size range from 0.2 micron to 10 microns, the atmosphere in Los Angeles may contain from 30 million to 600 million particles per cubic foot. Many of the particles appear to have a refractive index of about 1.5. From 20 to 50 per cent of the particles are water soluble, depending upon the particular sample. Both optically isotropic and anisotropic crystals exist. Also, fine opaque material, sometimes in aggregates, is present, which appears to be carbon.

Ammonia was identified on a number of the slides by placing a coating of collodion over the strip of collected particles on the glass and then applying Nessler's reagent to the collodion. Ammonia proved to be associated with certain of the particles, which may have been crystals of ammonium salts. The presence of ammonia on the slides was confirmed by converting it to the characteristically shaped octahedra of ammonium chloroplatinate.

Sulfates were identified on the slides, although sulfate was not shown to be associated with any particular crystals. The reagents used were barium chloride, lead acetate, and potassium rhodizonate.



## THE SMOG PROBLEM

TABLE IV.—ANALYSIS OF SAMPLE COLLECTED FROM WESTINGHOUSE PRECIPITRON  
(Sample Collected February 16–February 23, 1949)

Minerals and other inorganic substances about 45 per cent of total	{ Water-soluble fraction about 15 per cent  Water-insoluble fraction about 30 per cent	Elements identified by emission spectrograph:	
		Large Amount 10 per cent +	Calcium* Aluminum* Silicon*
		Small Amount 1–9 per cent	Sodium Magnesium Titanium Lead Iron
		Very Small Amount 0.1–0.9 per cent	Copper Manganese Nickel Zinc
		Trace 0.001–0.1 per cent	Lithium Barium Strontium Silver Boron Vanadium Tin Chromium
		Substances identified by chemical analysis:	
		Sulfates as H <sub>2</sub> SO <sub>4</sub>	PER CENT 5.7
		Ammonia	1.5
Organic compounds, soluble in benzene or petroleum ether about 16 per cent		Mainly aliphatic hydrocarbons	
		Also small amounts of aldehydes and organic acids	
		Peroxides, 0.15 per cent calculated as hydrogen peroxide	
Fibers, pollen, carbon, and highly polymerized organic material about 15 per cent			
Water and volatile organic substances (by difference) about 24 per cent			

\* Probably from minerals

ANALYSIS OF THE AIR—PARTICULATE MATTER

TABLE V.—ANALYSIS OF SAMPLE COLLECTED FROM WESTINGHOUSE PRECIPITRON  
(Sample Collected March 24–April 19, 1949)

Minerals and other organic substances about 60 per cent of total	{ Water-soluble fraction about 15 per cent of total  Water-insoluble fraction about 45 per cent of total	Elements identified by emission spectrograph:	
		Large amount 10 per cent +	Silicon Aluminum Iron
		Small Amount 1–9 per cent 1 per cent	Titanium Calcium Magnesium Barium Sodium Potassium
		Very Small Amount 0.1–0.9 per cent 0.1 per cent	Lead Zinc Vanadium Manganese Nickel
		Trace 0.01–0.1 per cent	Tin Copper Zirconium Strontium
		0.001–0.01 per cent	Boron Chromium
		0.001 per cent	Bismuth Cobalt
		Substances identified by chemical means:	
			PER CENT
		SiO <sub>2</sub> Iron and aluminum as oxides Calcium (as Ca) Fluoride (as F) Sulfate (as H <sub>2</sub> SO <sub>4</sub> ) Ammonia Nitrate (as HNO <sub>3</sub> ) Chloride (as NaCl) Nitrite Sulfide Sodium (as NaCl)	14.3 7.8 5.2 0.05 2.5 0.70 4.8 0.26 0.00 0.00 4.6
Organic compounds soluble in organic solvents about 10 per cent	{ Mainly hydrocarbons  Also small amounts of organic acids (0.27 per cent), and aldehydes  Peroxides, 0.04 per cent, calculated as hydrogen peroxide		
Fibers, pollen, carbon and highly polymerized organic material about 15 per cent			
Water and volatile organic substances (by difference) about 15 per cent			

Positive tests were obtained with diphenylbenzidine reagent. This is usually considered to be a test for nitrates, although other oxidizing agents such as peroxides give a similar reaction—that is, the formation of a blue color.

In all the slides examined, only a very few cubical crystals were observed. There was never enough chloride in the impactor streaks to give positive tests for chloride with silver nitrate. Tests for calcium were negative, as were also tests for iron and copper.

As mentioned previously, the Sonkin impactor causes water to collect on the slides during collection of the particles. Mist and crystals tend to follow the tracks of the water droplets. Many of the crystals are strongly hygroscopic and appear to be immersed in a thin layer of syrupy or gummy fluid.

In one test, the particles collected by the Sonkin impactor from 40 cubic feet of air were carefully weighed, and the mean particle size was determined under a microscope to be approximately 0.3 micron in diameter. Assuming a mean specific gravity of 2, the total number of particles collected was calculated to be 100 million per cubic foot of air, which is somewhat larger than was counted optically but of the same order of magnitude. The difference may have been due to the hygroscopic nature of the particles.

*Thermal Precipitator Samples.* The thermal precipitator appears to be more efficient for collecting particles in the size range below one micron than the Sonkin impactor. A comparison between the two methods was made by collecting material from the atmosphere during a light smog haze. One hundred cc.'s of air were passed through the thermal precipitator and approximately 75 cc.'s of air through the impactor. A particle count gave 130 million particles per cubic foot for the thermal precipitator; the total count for the second and third slides of the impactor yielded 30 million particles per cubic foot.

*Dust Camera.* Only preliminary measurements have thus far been made with the dust camera. Early results show that the number of particles which can presently be photographed

suspended in the air is not as great as the number that are collected by the thermal precipitator. The number is gradually being increased by the use of improved photographic methods and more sensitive films.

### PROTON BOMBARDMENT

The chemical identification of the exceedingly small quantities of materials collected by the impactor method has been supplemented by the use of the proton bombardment analysis.

This method has not been used anywhere before for this purpose. It is a new tool that provides a semiquantitative analysis of samples that may be considerably less than 0.000001 grams in total quantity.

A short discussion of the instrument and the method is contained in Appendix 4, but in brief the method involves collecting a sample of particulate matter by either the thermal precipitator or the impactor method on a slide in such quantities that the sample is only a few molecules in thickness. The sample is placed in a vacuum and bombarded with positive hydrogen ions (protons). When these protons strike the sample of material to be analyzed, they are bounced off at various velocities, depending upon the weight of the individual atoms contained in the analyzed sample. By measuring the velocities of the protons that have rebounded, it is possible to determine the exact element they have struck.

The first sample analyzed in this manner was collected on August 7, 1949 from the roof of a building at the California Institute of Technology. The relative humidity was approximately 40 per cent. There was no odor in the atmosphere. The haze appeared to be dry, and the visibility on the order of 4 to 5 miles. The Sierra Madre Mountains were not visible at the time the sample was taken. The analysis showed only lead, sulfur, oxygen, and carbon to be present. The sulfur and oxygen were in the right ratio to correspond to the presence of sulfuric acid.

Two other samples have since been analyzed, obtained from the roof of 4105 North Figueroa Street, Los Angeles, one collected on Wednesday, August 17, 1949 and the other on Thursday,

August 18, 1949. The Wednesday sample also contained sulfur, lead, carbon, and oxygen, and in addition some copper or zinc and some cadmium or tin—with the setting of the apparatus it was not possible to distinguish which. The sample collected on Thursday showed the presence of lead, sulfur, oxygen, and zinc, but on this day there was a much larger quantity of lead than on previous days. Whereas in the sample collected on August 17 the lead was only about 0.004 the amount of sulfur, the sample collected on August 18 contained 0.08 as much lead as sulfur, or a twentyfold increase.

The above results are believed to be most significant. They show the variability of smog and confirm the presence of the elements responsible for its effect. The constant presence of lead points either to industrial sources or to automobile exhausts. Carbon and sulfur would be expected from the combustion of any sulfur-containing material.

The fact that some elements recorded by other methods were not recorded by proton bombardment, may arise from the use of a small cy-

clone separator attached to the impactor from which the analyzed samples were taken. The separator permitted the collection of the finer particles only. Work will be continued, using this instrument for as long as it is available.

### OTHER METHODS OF INSTRUMENTAL ANALYSIS

Still other specialized methods of instrumental analysis have been tried to discover what contaminants may be in the atmosphere. The methods used are x-ray diffraction and infrared and ultraviolet spectroscopy.

The results of the x-ray diffraction showed qualitatively the presence of silica (alpha quartz) and a number of halos at positions that would indicate the presence of long-chain alkyl-type organic liquids. Most of the material was noncrystalline.

The results from the spectrographic methods were, in general, nonspecific, but tentatively identified aromatic organic compounds.

## IV FACTORS AFFECTING VISIBILITY

**I**N ADDITION to chemical and physical analyses of the substances in the Los Angeles air, it has been necessary to investigate the optical properties of the atmosphere, in order to determine in what manner visibility is reduced by the substances that produce smog.

The first need was for an objective, instrumental method of measuring the haziness of the atmosphere. As a result, a photographic method of recording and measuring visibility has been developed.

This new method also provides an additional means of measuring the sizes of the particles responsible for the reduction in visibility, and thus serves as a valuable check on the other instruments used.

It is significant that the particles determined by the photographic method to be principally responsible for poor visibility are also the particles that are being collected and analyzed by the other means. This indicates that analytical results reported in the preceding Sections have provided the information needed to identify the air contaminants affecting visibility.

The particles collected, counted, and measured appear to account fully for the loss in visibility. Much of the particulate matter has been identified. Among the contributors to loss in visibility are the following: carbon particles, calcium salts or oxides, aluminum, silicon, sodium, titanium, lead, iron, oil droplets, and smaller quantities of manganese, nickel, and zinc.

The smog particles that have been collected and measured can be roughly classified into five groups, as follows:

1. *Carbon and metal particles.* Black, opaque particles which occur in aggregates. Responsible for from 10 to 50 per cent of the decrease in visibility.
2. *Transparent, light-scattering crystals,* water insoluble. Include iron and aluminum oxides and silica. Account for from 10 to 30 per cent of the decrease in visibility.

3. *Small, water- and oil-soluble particles and oil droplets.* Effect on visibility not known, but believed to be small.
4. *Substances capable of forming water droplets in air.* Principally sulfur trioxide. Account for 5 to 20 per cent of the decrease in visibility.
5. *Large soluble crystals.* Sulfates, nitrates, chlorides, and fluorides. Account for from zero to 80 per cent of the decrease in visibility.

### Photographic Measuring Method

As used in Los Angeles, the photographic method involves setting up two black targets at known distances from a camera, and photographing them. Because of the scattering of light by impurities in the atmosphere, the more distant target appears to have the lighter shade of the two. The reduction of visibility is determined by calculations based on the measured relative shade of darkness of the targets in the developed photographic negative (see Appendix 2).

Color filter photography provides a means of approximating the size of the particles. Fine particles in the atmosphere produce color effects without themselves having a color in the popular sense of the word. Particles below one micron in diameter, when suspended in the air, scatter blue light relatively more than red. This behavior provides valuable clues to the size range of particles that affect visibility (Ref. 8).

Plate 5 (p. 16) illustrates the correlation of the photographic observations with instrumental records from the continuous conductivity recorder, and with subjective human observation of smog.

Photographic measurement of visibility has been carried on routinely throughout most of 1949 to date. Measurements are omitted on days when the sky is not uniformly bright, or when an obvious fog is present.



PLATE 10

Black target used in photographic method of determination of visibility



PLATE 11

Long focal length camera used in photographic method of determination of visibility

**Effect of Particle Size on Visibility**

The mean effective size of the particles causing poor visibility in Los Angeles has proved to be approximately 0.3 micron. This range of particle size (from 0.2 to 0.6 $\mu$ ) produces the maximum obscuration of light. This means, of course, that the obscuration produced by particulate matter depends not so much on the substances of which it is composed, as upon the size of the particles. If the same weight of dust were composed of particles much smaller or much larger than 0.3 micron, visibility would not be affected to the same degree.

Photographic measurements of haze show a greater proportion of small particles on the average on days when a strong inversion is present than when the inversion is absent. This fact is shown in Figure 9, in which the ratio of the scattering of blue light relative to red light is plotted on the same graph with the inversion intensity.

An explanation of this phenomenon may be found in the mechanism by which smog is dispersed into the atmosphere (Section VI). It is

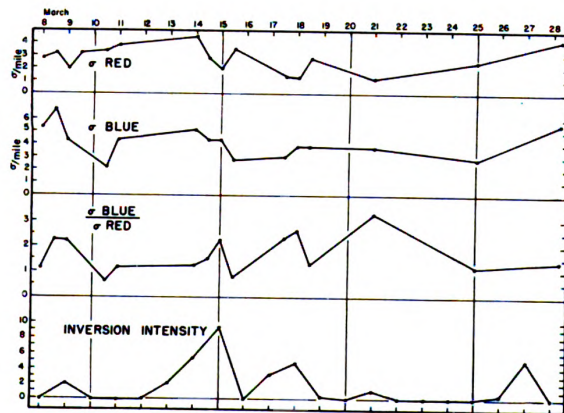


FIG. 9

Relationship of inversion intensity to the scattering of blue and red light

offered here as an hypothesis that the finer particles are more readily diffused upwards and vertically dispersed out of the area when an inversion is not present or is not intense. But when the inversion is strong and the warm air ceiling relatively impermeable, the finer particles are retained under the inversion deck in large quantities and thus make up a relatively high proportion of the particulate content of the air.

### Effect of Sulphur Trioxide on Visibility

Sulfur trioxide, as such, rarely exists in the atmosphere, since it attracts water to itself and forms a mist of sulfuric acid. This mist is known to have an effect in decreasing visibility.

Sulfur trioxide may arise from many sources, but in general it is introduced into the air as the result of combustion of any product containing sulfur. In the combustion of sulfur compounds

the bulk of the sulfur is converted to sulfur dioxide and a minor portion to sulfur trioxide (Ref. 9).

Sulfur dioxide dissolved in water in the presence of oxygen is quickly converted to sulfur trioxide. Sulfur dioxide irradiated with sunlight in the absence of water also appears to be converted to sulfur trioxide. Little is known with certainty concerning the conversion of sulfur dioxide to sulfur trioxide in the atmosphere. However, it is possible to measure directly the amount of sulfur trioxide present in the air (Section III), and to determine quantitatively what effect this concentration would have, under various conditions, in reducing visibility.

Figure 1 (facing p. 12) shows the sulfur trioxide content of the Los Angeles atmosphere, existing either as sulfuric acid mist or in combination with other substances. It should be noted

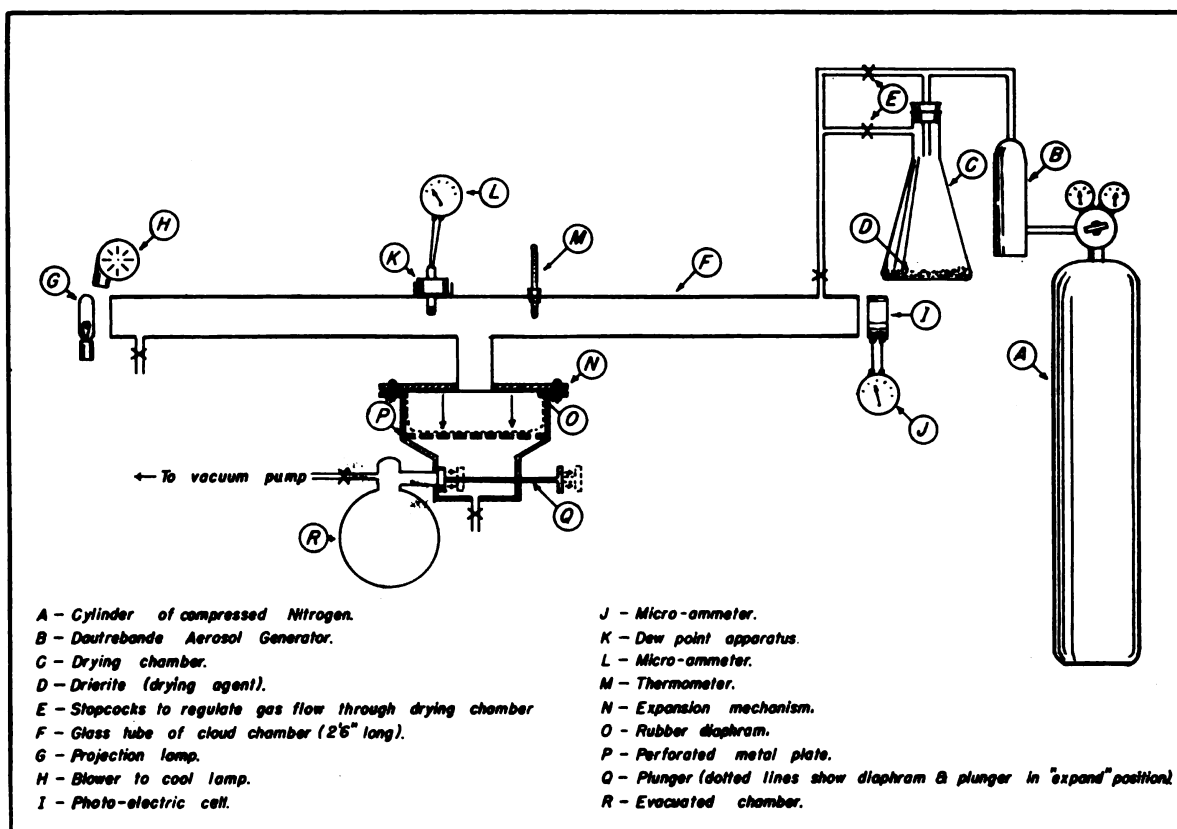


FIG. 10

Cloud chamber and aerosol generating equipment

that the values reported also include any solid soluble sulfates, such as ammonium sulfate, which could also reduce visibility, though to no greater extent than if the same amount of sulfate were present in the form of a sulfuric acid-water mist.

The effect of sulfur trioxide in decreasing visibility under various conditions has been measured through an adaptation of the Wilson cloud chamber (Ref. 10), and the use of a modified transmissometer. Both instruments are briefly described herewith.

*Wilson Cloud Chamber.* The Wilson cloud chamber (Figure 10) consists of a glass tube  $2\frac{1}{2}$  feet long and  $1\frac{1}{4}$  inches in diameter, to which is connected a small gas expansion mechanism. The chamber has flat glass windows at each end and stopcocks through which the gases or aerosol suspensions of salts under study may be introduced and entrapped. There are also provisions for inserting a thermometer and a small dew-point instrument for measuring the humidity of gases.

The density of the cloud in the chamber is determined by measuring the intensity of a beam of light which has passed through the tube. For this purpose a projection lamp is placed at one end of the tube and a photocell, to which is attached a micro-ammeter, is attached at the opposite end.

The expansion mechanism is adjusted so as to expand the gas within the chamber suddenly by increasing the volume in which it is contained by approximately 4 per cent. When this expansion occurs, a cloud is formed. The density of this cloud is recorded by the micro-ammeter.

When the expansion occurs, the relative humidity in the chamber is suddenly increased over its original value. By measuring the change in light intensity, it is possible to determine the effect of an increase in relative humidity on a gas or aerosol. Pure, clear air containing water vapor alone does not cause cloud formation under the conditions described.

*Transmissometer.* The modified transmissometer used was similar in principle to that de-

scribed in the First Interim Report (Ref. 11). This instrument is shown in Plate 12 and Figure 11.

The arrangement is such that, by means of reflecting mirrors, light can be passed through a forty-foot column of air one or more times. The opacity of the air in the column is measured by instrumental means. The scale reading of the instrument is directly proportional to the intensity of the light passing through the air column. Thus a comparison of scale readings with clear air and readings with air containing known concentrations of sulfuric acid mist permits a calculation of the approximate visibility that would exist in similar open-air conditions.

Results of measurements with these instruments were as follows:

*Wilson Cloud Chamber Tests.* Since smog occurs at low relative humidities, sulfur trioxide was studied with particular regard to its effectiveness as a fog former at various humidities.

In cloud chamber tests with sulfur trioxide, filtered air was passed through two parallel bubblers, one containing distilled water, and the other fuming sulfuric acid. In this manner the relative humidity of the sulfur trioxide-air mixture could be regulated.

The results of sulfur trioxide tests, shown in Figure 12, indicate that sulfur trioxide is effective as a cloud-forming agent at all humidities tested down to 34 per cent, but becomes much more effective as the humidity is increased from 75 to 80 per cent.

*Transmissometer Tests.* The results of the transmissometer measurements are shown in Figure 13. Data from transmissometer tests made with sulfur trioxide are extrapolated to compute the effect which would be produced on visibility by the concentrations existing in the Los Angeles area (as determined by the analyses of Figure 1).

Comparing these calculations with the observed visibilities in Figure 2 (facing p. 13), it can be seen that sulfur trioxide has only a minor effect on the over-all visibility in Los Angeles. Even this effect occurs but rarely.



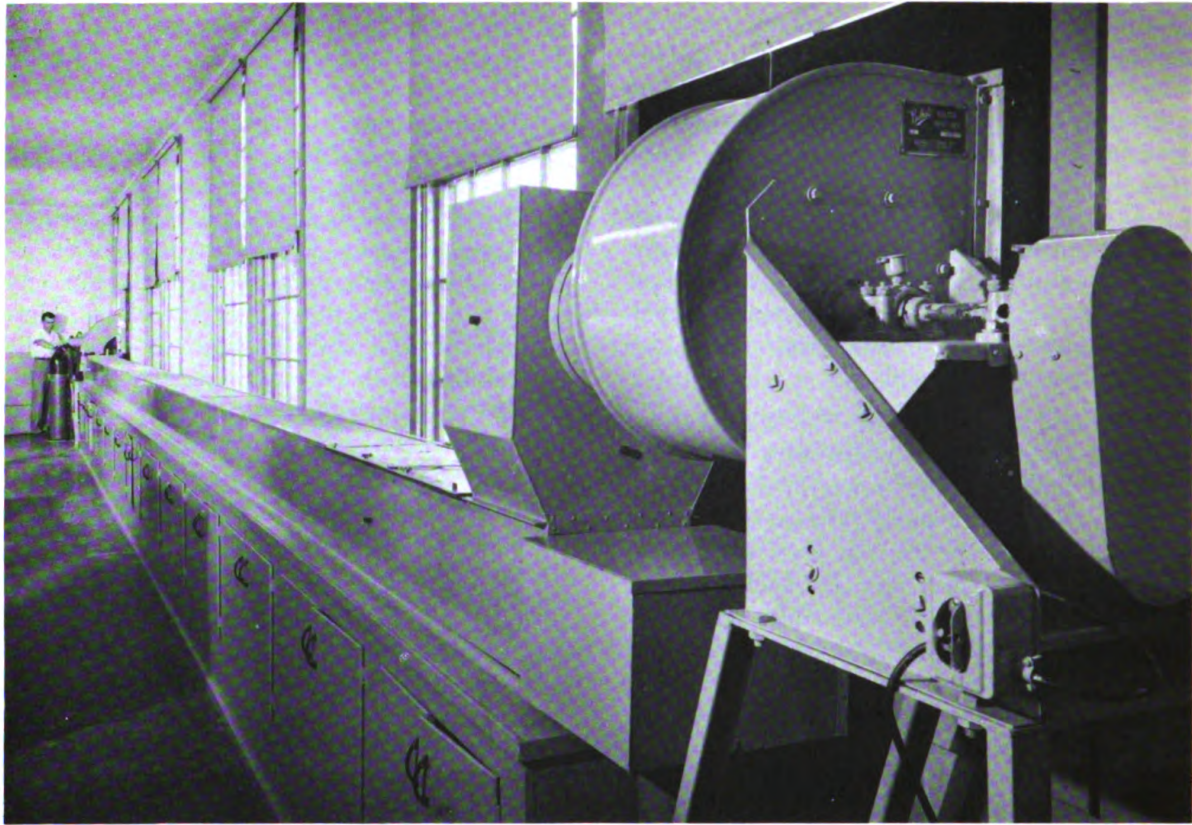


PLATE 12

Transmissometer at the laboratories of Stanford Research Institute used to measure the effect of various substances in decreasing visibility

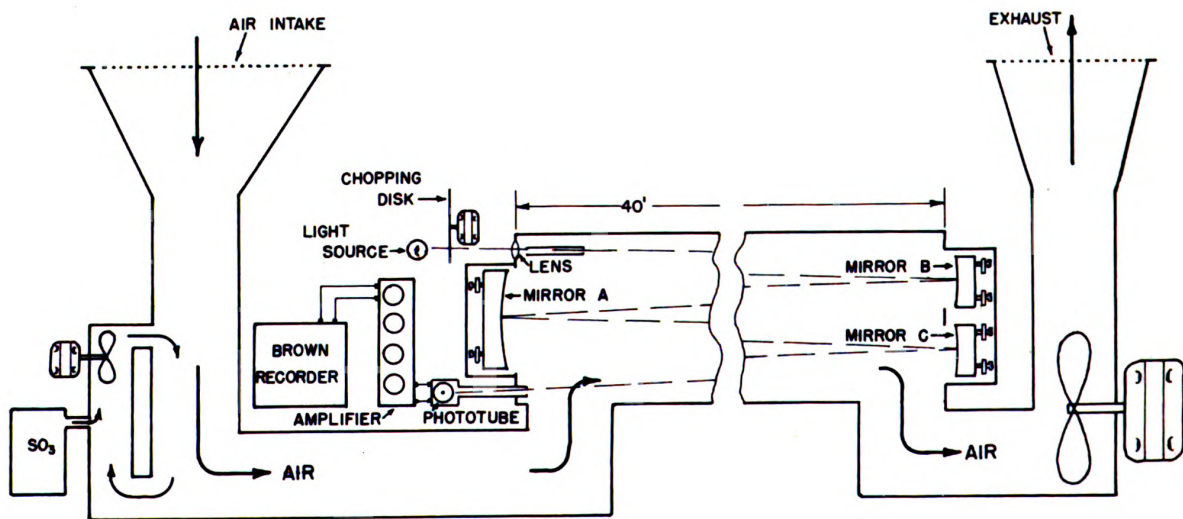


FIG. 11

Schematic arrangement of transmissometer

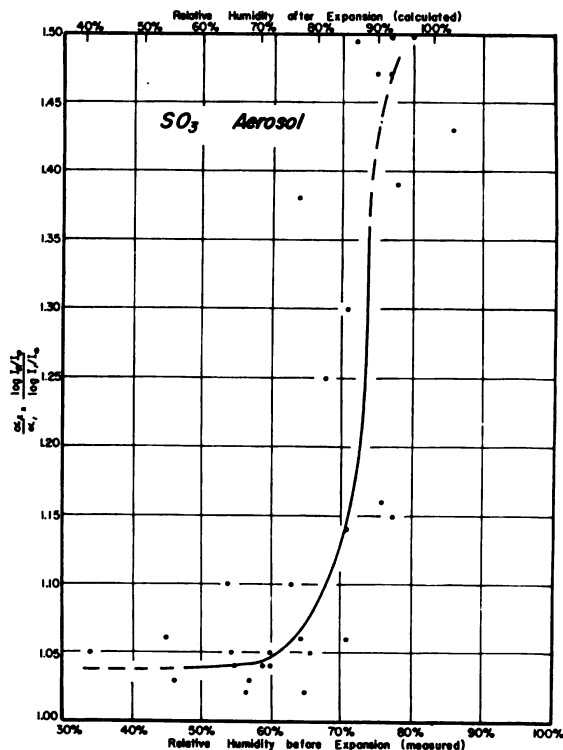


FIG. 12  
Results of Wilson cloud chamber tests on the fog-forming properties of sulfur trioxide

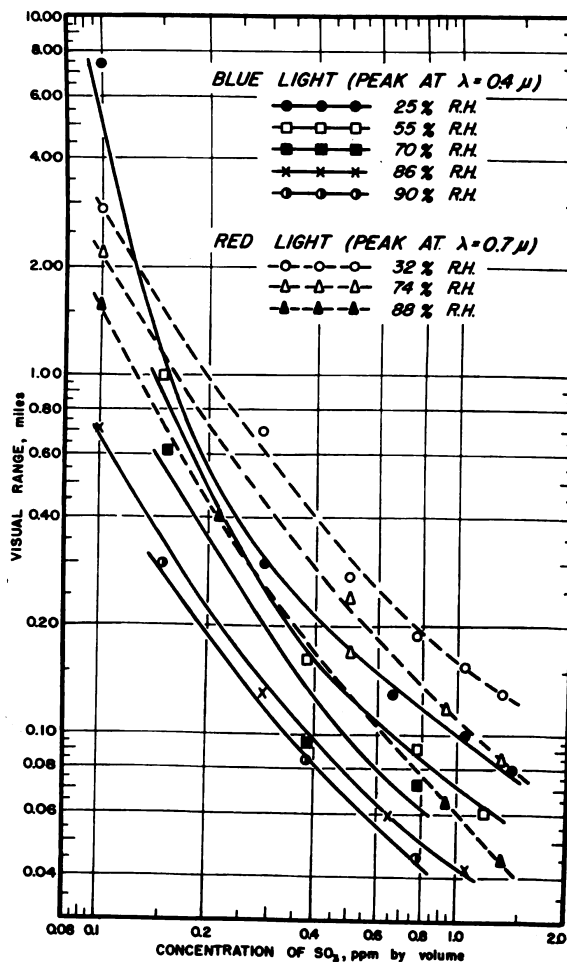


FIG. 13 (Right)  
Results of transmissometer tests on the effect of sulfur trioxide in decreasing visibility

**Effect of Other Condensation Nuclei on Visibility**

Other materials have been thought to behave like sulfur trioxide in collecting moisture from the air and forming mists that may reduce visibility. These materials, often referred to as condensation nuclei, include sea salt, sulfur dioxide, nitrous acid, and other gases. These substances have been submitted to cloud chamber tests to determine their behavior as fog formers.

**Salt.** Sodium chloride was introduced into the chamber as an aerosol produced by a Dautrebände aerosol generator (Refs. 12, 13), using a saturated salt solution. The humidity of the aerosol-bearing gas was reduced by passing a portion of it through a large side-arm flask con-

taining a small amount of Drierite. Any desired fraction of the gas could by-pass this flask so that any humidity from about 30 per cent to 100 per cent was obtainable. The dew point was measured with the apparatus indicated. The manner in which the data are interpreted is outlined in Appendix 3.

Results of the tests with sodium chloride are shown in Figure 14. They indicate that salt is inactive as a fog-forming substance below a relative humidity of 66 per cent but is quite active at higher humidities. Since smog occurs at relative humidities lower than 66 per cent, salt is ruled out as a contributor to loss in visibility by the formation of fog. As particulate matter, however, it can still reduce visibility.

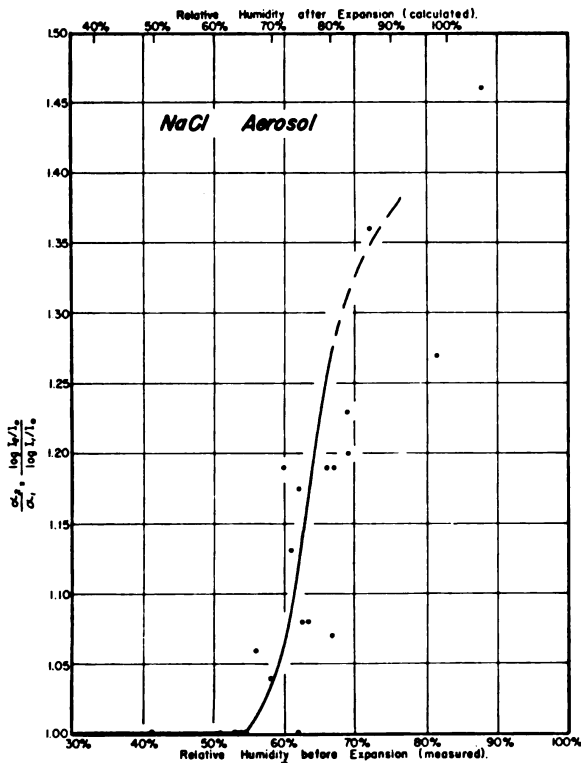


FIG. 14

Results of Wilson cloud chamber tests on the fog-forming properties of salt solution

*Sulfur Dioxide.* Small amounts of sulfur dioxide in moist, filtered air caused no fog to be

formed, thus substantiating similar results obtained with the transmissometer (reported in the First Interim Report).

*Nitrogen Oxides.* Nitrogen oxides were introduced into the chamber by passing moist, filtered air over fuming nitric acid. The gases thus produced formed no cloud upon expansion of the gas.

Although frequent references are made in the literature to the oxides of nitrogen as condensation nuclei (Ref. 14), little actual experimental data have been presented. The Stanford Research Institute experiments to date do not indicate that they act in this manner.

### Significance of Ammonia

During the last six months a high ammonia content has been found to parallel the Smog Index. Days of high ammonia were also days of poor visibility. The presence of ammonia in solid, combined form has been verified by samples from the electrostatic precipitator and the Sonkin impactor.

In addition to the effect the combined ammonia may have on visibility, it is possible that the ammonia may serve as a tracer for other materials which affect visibility, if it emanates from the same source or results from the same process in the air. This is being investigated.

V

FACTORS AFFECTING EYE IRRITATION

**E**YE IRRITATION is unquestionably the most disagreeable aspect of the Los Angeles smog. Study of the factors affecting eye irritation and a search for the substance or substances causing it have been carried on since the beginning of the investigation.

In the past two and one-half years eye discomfort has occurred in Los Angeles with sufficient intensity to evoke spontaneous complaints on 82 occasions. Haziness in the atmosphere is present much more frequently.

The eye irritation associated with smog occurs when the moisture content of the air is low.

The relative humidity is often as little as 25 to 30 per cent.

The records show that eye irritation rarely occurs on humid days, rainy days, or during the hours of darkness. In downtown Los Angeles it takes place chiefly between the hours of 9 A.M. and 12 noon, although it may occur earlier in the day at locations nearer the coast and later in the day at locations inland toward the mountains (Figure 15). The sun is frequently bright, the sky cloudless (although a haze is usually present), and the wind velocity may be between three and five miles per hour.

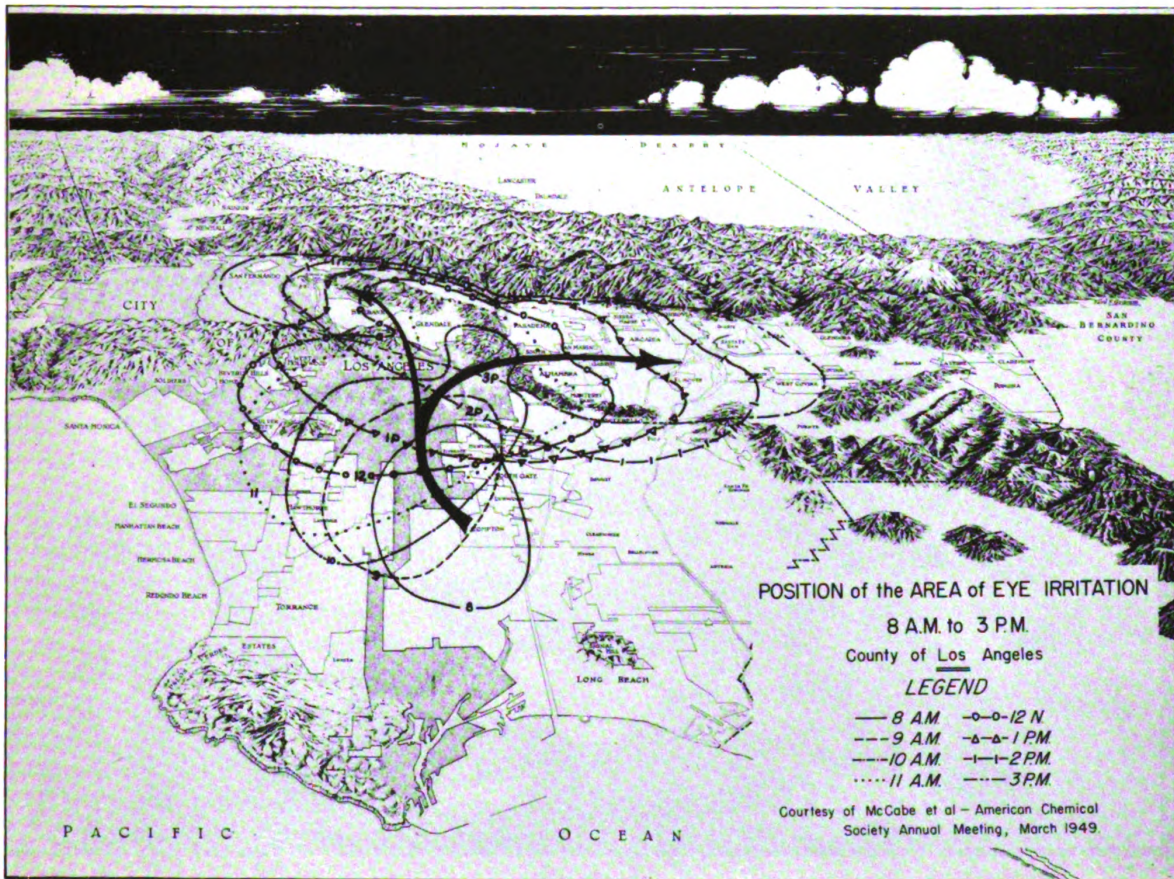


FIG. 15

### Number of People Affected

On threshold days and severe smog days alike the eye-irritating effects are likely to be fairly local. To obtain information concerning the number of people affected by eye irritation during smog and to determine the time of its occurrence, the location, and the over-all severity of its effects, a survey was made to secure facts concerning the opinion of the man on the street. Trained survey personnel presented verbally a carefully prepared questionnaire to over 28,000 people in the cities of Los Angeles, Pasadena, and Glendale.

In Figure 16, some of the results are shown in graphic form. On the worst days recorded, 85 per cent of the people interviewed noticed smog effects.

### Blink-Rate Studies

At the beginning of the survey question period, the time interval between the blinks of the

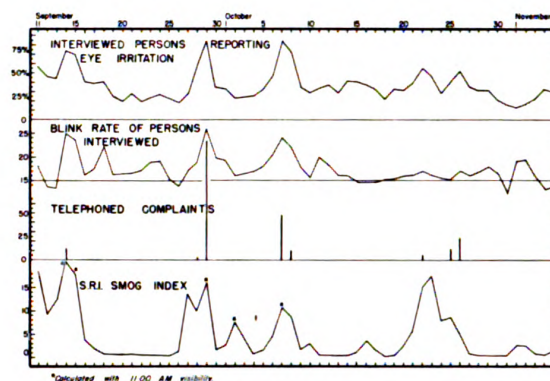


FIG. 16

Public reaction to smog, September–November 1948. The two upper curves present results of a public opinion survey, measuring smog both by subjective human perception of it and by an involuntary increase in the rate at which the eyes of persons interviewed blinked. Note the correspondence between these curves and those representing telephoned complaints and the Stanford Research Institute Smog Index — different methods of measuring smog.



PLATE 13

Photoelectric apparatus for measuring blink rate. A photoelectric cell notes the interruption of light reflected from the eyeballs when the lids are closed.

eyes of the people questioned was recorded. The purpose was to correlate the blink rate with the degree of irritation, if possible.

To further verify the value of the use of the blink rate as an evaluation of the severity of eye irritation, a photoelectric device (Plate 13) was employed to make an automatic record of the number of times the eye blinks. This is done by a photoelectric cell which notes the interruption of light reflected from a subject's eyeballs when the lids are closed. By exposing individuals to low and nontoxic concentrations of formaldehyde, it was verified that low concentrations of irritants caused an involuntary increase in the blink rate.

### SEARCH FOR MATERIALS CAUSING EYE IRRITATION

Identification of the materials in the atmosphere that produce smog eye irritation requires information as to what irritating substances may be present, the amounts of such substances required to produce irritation, and determination whether they are present in the Los Angeles air in these amounts.

The investigation accordingly requires not only analyses of contaminants in the air, but also means of determining the characteristics of suspected eye irritants by testing them on human and animal subjects.

Equipment to accomplish this has been developed at the Stanford Research Institute and used to test substances definitely found in the Los Angeles air which were thought to be possible irritants. Many other substances of an irritating nature, which might conceivably be in the Los Angeles air, were also tested. If found effective as irritants, methods were then developed to search for them in the atmosphere.

### The Smog Chamber

The principal item of equipment used in the eye-irritation tests is a special test chamber, generally referred to as the Smog Chamber, located in the laboratories of Stanford Research Institute.

The Smog Chamber, shown in Figure 17, is a galvanized metal room of 353 cubic foot capacity, with an airtight door in front and a large observation window in one wall. Leading to the rear of the chamber is a five-inch i.d. galvanized sheet-metal duct connected to a one-tenth horsepower blower that delivers 208 cubic feet of air per minute at a quarter-inch water static pressure. The blower is the central unit of the chamber's circulation duct system. Air from the blower enters the chamber through the vaporizing box, where it picks up any vapors or aerosols generated. The air may then either be disposed of through a vent in the ceiling or recirculated through the chamber.

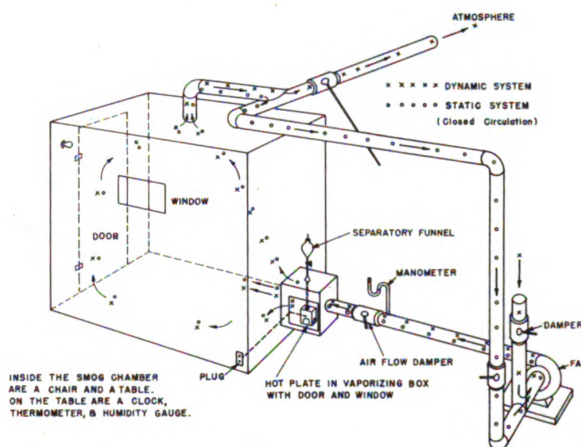


FIG. 17  
The Smog Chamber

Mounted on a panel board attached to the table in the chamber are a thermometer, a humidity indicator, and an electric clock. Changes in humidity during tests may be noted on the humidity indicator. Accurate humidity readings are taken during the test by means of a hand-operated Friez psychrometer.

The Smog Chamber has been accurately calibrated. (A more detailed description may be found in the First Interim Report.)

*Testing Procedures.* The observer in the chamber sits on a chair facing the table. He makes minute-by-minute notations of his sensory responses throughout the test. Sensations especially noted are odor, nose irritation, throat ir-

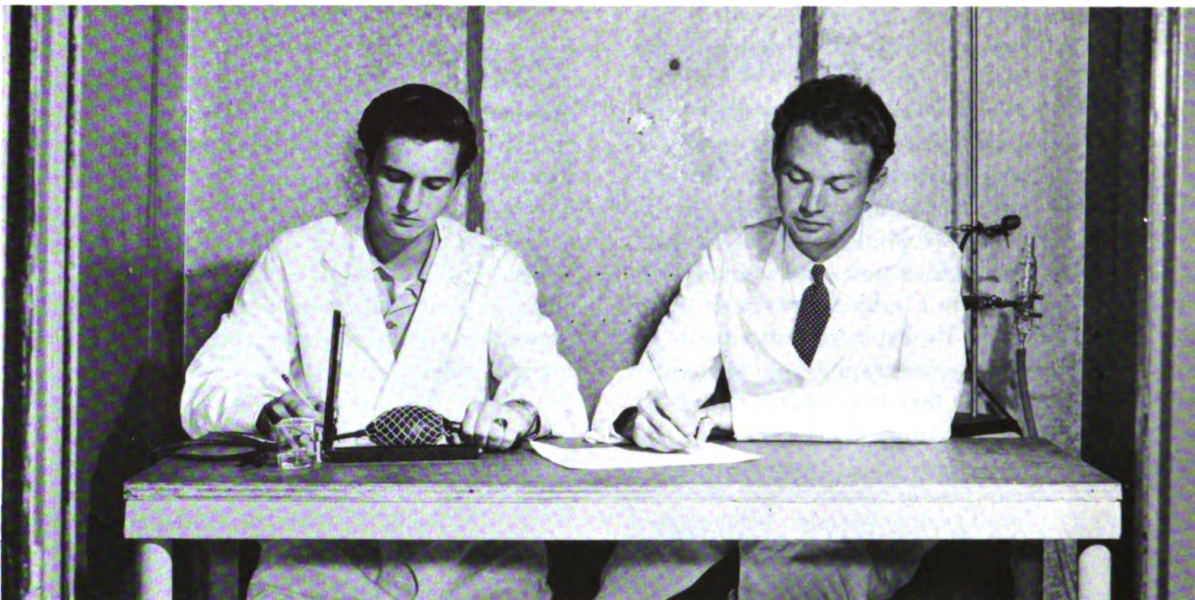


PLATE 14

Test in progress in the Smog Chamber. Test subjects record their sensory impressions on uniform test forms developed for the purpose. See Figure 26.



PLATE 15

View of part of the Stanford Research Institute Air Pollution Laboratory. The Smog Chamber is in the far right background, the transmissometer is along the wall at the left.

ritation, eye irritation, and lachrymation. These are all recorded on a standard data sheet (Appendix 5, Figure 26). A method for assigning a numerical value to subjective reactions, described by Roth and Swenson (Ref. 15), is employed (Appendix 5).

For practical reasons tests are limited to ten minutes. It is possible that reactions would be more pronounced if subjects were exposed for longer periods of time, as are people in the Los Angeles area on smoggy days, but so far no such lengthy tests have been made.

Two types of tests are carried out. *Dynamic* tests are those in which the irritant under investigation is mixed with air and blown, in the form of vapor, smoke, dust, or fog, through the sealed chamber at a constant rate.

*Static* tests are those in which the contaminants are added to the chamber atmosphere and allowed to mix thoroughly for from five to sixty minutes before the observer enters. Static tests are used primarily when it is desirable to determine the possible absorption of gases in liquid or solid aerosols, after they have been permitted to mix in the air.

### Preparation of Test Materials

A problem always encountered in preparing known small concentrations of irritant gases in air is the accurate measurement of these materials. Not only must they be measured, but in many cases they must also be finely subdivided to form aerosols. Numerous attempts were made before an apparently satisfactory method was developed for subdividing and measuring substances to be tested.

*Rerosols.* A Dautrebande (Refs. 12, 13) aerosol generator is used to prepare aerosols of oils or aqueous solutions containing salts. These aerosol generators can be constructed of glass or metal. The inside of the generator is equipped with a fine atomizing spray device. Above the atomizer are a series of baffles so arranged that the liquid being atomized is refluxed counter-current to the outward flow of gas. This reflux is so arranged that the fine spray is, in effect, scrubbed by passing through five separate layers

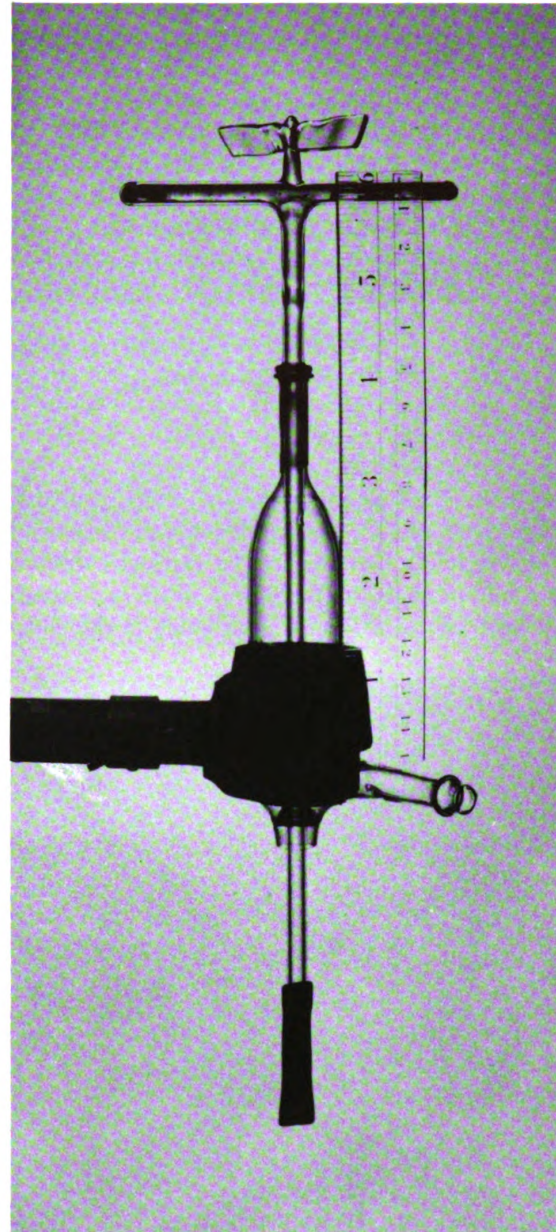


PLATE 16

Dust disperser used in Smog Chamber to achieve a uniform distribution of dust. Flowing of air through disperser makes the crossbar spin.

of liquid. Operating in this manner, only those particles escape that avoid being collected by the scrubbing action.

Calibration of these instruments has shown



that they produce particles of a mean size of 0.4 micron and range from somewhat less than 0.2 micron to roughly 1.0 micron in diameter. These aerosol generators can be made in small sizes, so that they may be placed on a balance and weighed before and after the experiment. In this fashion the amount of material introduced can be measured. In the case of volatile solutions, correction must be made for vaporization loss.

*Dispersion of Dusts.* The dispersion of dusts is accomplished by the device shown in Plate 16. This mechanism is located adjacent to a flowmeter used for measuring the air used in its operation (see Plate 17).

The dust is contained in a cylinder approximately two centimeters in diameter and five centimeters long. Centered in the vertical cylinder is a hollow shaft, on the top of which is located a crosspiece so arranged with holes in the ends

that a flow of air through the apparatus causes it to spin as a reaction turbine. Small holes are located near the top of the glass shaft inside the cylinder containing the dust.

Air flows out of the cylinder through these holes in the shaft and also from the holes in the tips of the crosspiece at the top. The air enters tangentially into the cylinder, and the combined action of the air stream and the spinning of the shaft keeps the dust agitated. The high velocity at the tips of the spinner creates a uniform distribution of the dust in the atmosphere. The amount of dust dispersed is controlled by measuring the flow of air through the apparatus. Carbon black containing 9 per cent added oil can be dispersed at reproducible rates by this method to produce dust concentrations as low as 0.1 part per million.

*Aqueous Solutions.* A glass hypodermic syringe with a plunger moved by a clock motor (Plate 17, left) is used to meter small quantities of aqueous solutions such as sulfuric acid, formaldehyde, etc.

The dispersion of these materials may be accomplished by dropping them on a hot plate. If heat is not desirable, the apparatus shown at left of the photograph may be used. This consists of a vertically mounted, high-speed motor (15,000 rpm) on the top of which is located a cup-shaped spinner with a toothed periphery. Around the center of the shaft and concentric with it is a small tube through which an air stream may be blown vertically upward under the cup to assist in the dispersion. The assembly at the left of the photograph shows the outlet of the Dautrebande aerosol generator connected to the motor-driven spinner toward which the hypodermic needle tip of the syringe feeding device is directed.

This arrangement has been used when it has been desirable to bring into intimate contact such materials as an oil aerosol and formaldehyde vapors. The whole assembly is small enough to place in one corner of the Smog Chamber. When it is set, it produces a constant and controlled feed of irritant impurities for the purposes of the test.

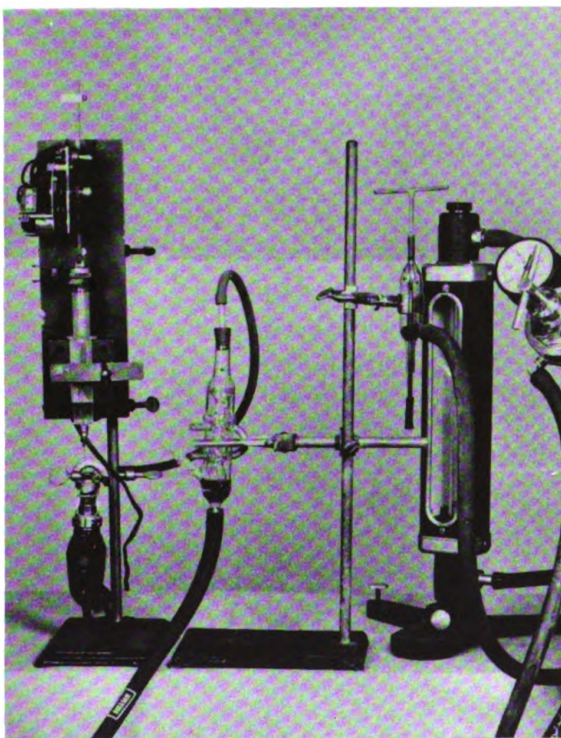


PLATE 17

Syringe feeding device, aerosol generator, dust disperser, and flowmeter used in connection with Smog Chamber tests

**Results of Smog Chamber Tests**

In the period since the First Interim Report was published many new substances have been tested in the Smog Chamber. Recent results are based upon approximately 190 tests involving 350 exposures of individuals.

Three important values are sought in relation to each substance tested. These are:

*Threshold concentration*, or the lowest concentration at which irritation occurs. In Figures 18 and 19, where some of the results are presented graphically, this value is represented by  $C_0$ , the point where the concentration curve crosses the axis.

*Constant for the substance*, or the rate at which an increase in concentration causes an increase in irritation. This value (R) represents the slope of the line and is characteristic of the substance.

*Concentration for mild irritation*, or the concentration which causes a mild sensory reaction for a full ten-minute period. This is the concentration at which the sensory effect is unity.

Results for some of the more important substances tested are given in Table VI.

TABLE VI.—EYE-IRRITATING EFFECTS OF SUBSTANCES TESTED  
(All values in parts per million)

CONTAMINANT	THRESHOLD CONCENTRATION	CONSTANT FOR THE SUBSTANCE	CONCENTRATION FOR MILD IRRITATION
Benzyl chloride	0.41	0.64	1.94
Acrolein	0.12	0.34	2.4
Formaldehyde	0.44	0.21	48.0
Ethyl hydroperoxide	0.67	0.23	48.0
Sulfur suspension	0.17	0.146	167.
T-butyl hydroperoxide	0.45	0.15	355.
Hydrogen peroxide	0.82	0.16	425.

*Aldehydes.* It will be noted from Table VI that the threshold value of acrolein is 0.12 part per million, but that it would require 2.4 parts per million to cause a mild, continuous irritation. As shown in Figure 1 (facing p. 12), these substances are not present in the Los Angeles atmosphere in sufficient quantities to be major irritants.



PLATE 18

Testing a new model electrostatic precipitator designed to extract sulfur trioxide from the air (as acid droplets)

*Organic Peroxides.* Ethyl hydroperoxide is roughly comparable in irritant properties to formaldehyde. T-butyl hydroperoxide has approximately the same threshold concentration as formaldehyde but requires a much larger quantity in the atmosphere to produce a mild, constant irritation.

It has not been conclusively established that organic peroxides can be accepted as existing in measurable concentrations in the Los Angeles atmosphere. Present methods of collecting and analyzing the atmosphere for peroxides are being refined and developed, in order to arrive at a method mutually satisfactory to all researchers engaged in this investigation.

Current indications are that organic peroxides do not exist in the atmosphere in sufficient concentrations to cause irritation.

*Elemental Sulfur Suspension.* Colloidal sulfur is an active irritant, as judged by the concentration required for threshold sensory effects. However, it requires relatively large quantities for constant irritation. The substance has not been found in the atmosphere of Los Angeles in quantities sufficient to cause irritation.

THE SMOG PROBLEM

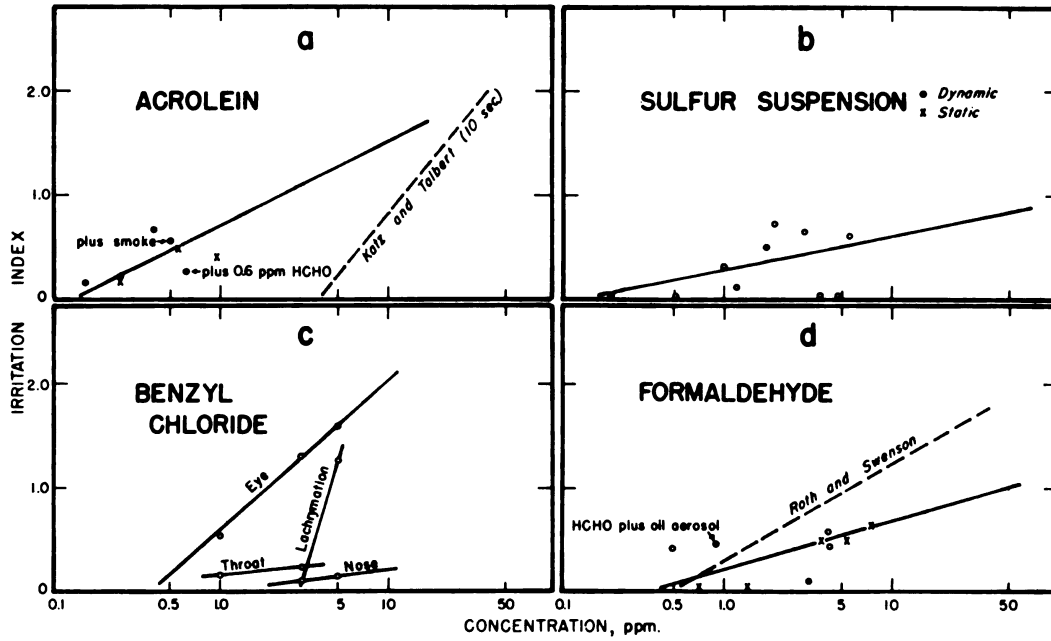


FIG. 18

Results of Smog Chamber tests with acrolein, sulfur suspension, benzyl chloride, and formaldehyde. The solid lines represent the concentration curve. The threshold value is represented by  $C_0$ , the point where the concentration curve crosses the axis.

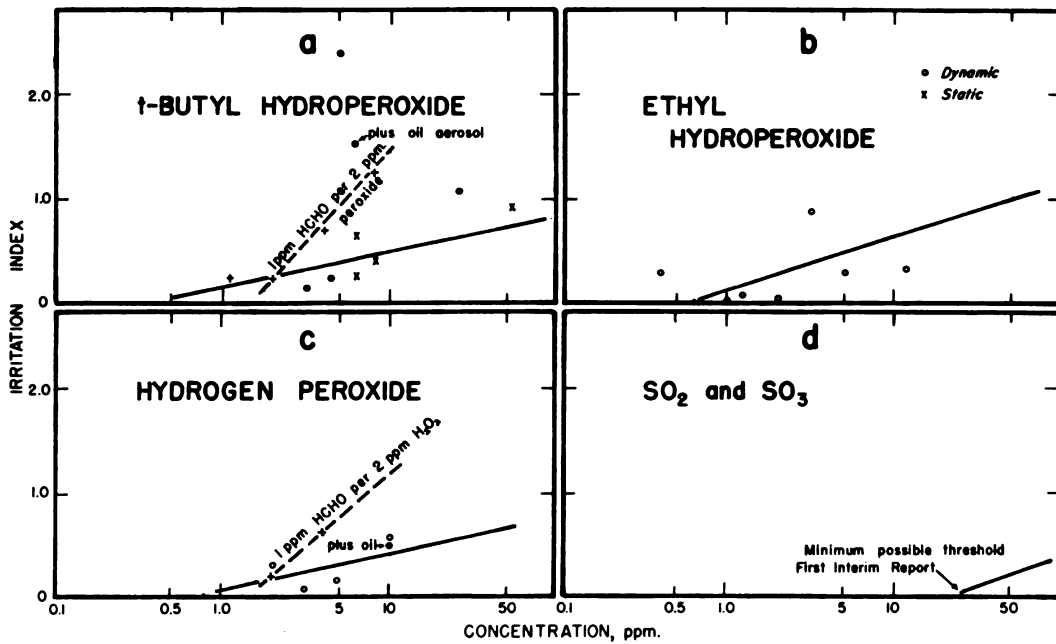


FIG. 19

Results of Smog Chamber tests with t-butyl hydroperoxide, ethyl hydroperoxide, hydrogen peroxide, sulfur dioxide, and sulfur trioxide. The constant for the substance, or the rate at which an increase in concentration causes an increase in irritation, is represented by the slope of the curve and is characteristic of the substance.

*Oil Aerosol.* Used oil aerosols have proved to have some irritating effects. Moreover, when combined with another irritant, they exhibit an enhancing effect—that is, the combination has irritant powers greater than could be expected from the sum of the irritant properties of the two substances individually.

There is evidence that oil is present in the Los Angeles atmosphere. It has not yet been established whether the droplets are of the kind that can produce irritation or that can combine with other substances to produce an enhanced effect.

### Reconstituted Smog

A new approach to eye-irritation investigation, now under development, is through the production of a "synthetic smog," in which various contaminants known to be present in the Los Angeles area are all introduced together into the Smog Chamber, in the approximate concentrations found in Los Angeles.

Since the concentrations of the components of actual smog vary not only from day to day but from hour to hour, the synthetic smog used for test purposes is necessarily based on one simulated set of conditions. It is probable that a large variety of combinations may have to be tried before the effect of background contamination on the eye irritation is adequately known.

The composition of the reconstituted smog used in tests so far is based upon the maximum values obtained by analysis for each component during the period from November 1948 to April 1949 (Figure 1). On this basis, the components and their concentrations are:

Ammonia	0.14 ppm by volume
Formaldehyde	0.22 ppm by weight
Sulfur dioxide	0.55 ppm by volume
Sulfur trioxide	0.20 ppm by weight
Nitrogen oxides (nitric acid)	0.40 ppm by weight

In addition, the following are incorporated into the reconstituted smogs so far tested: 0.01 ppm acrolein, 0.01 ppm hydrogen peroxide, 0.50 ppm oil aerosol, and 1.00 ppm particulate matter (91 per cent carbon black and 9 per cent oil). Artificial lighting conditions designed to simulate sunlight were also employed.

While concentrations of the components of the reconstituted smog are as high as any that have ever been detected in the Los Angeles atmosphere, they are considerably lower than would be required to cause irritation individually. The results indicate that such reconstituted smog has a higher eye-irritation index than could be anticipated from the additive eye-irritation indices of the separate components at the concentrations involved.

This provides strong evidence that the eye irritation of the smog is not the product of any one substance but is an enhancing effect.

This phase of the research is still in preliminary form. A systematic program is under way to study, singly and in combination, the eye-irritating effect of a large number of impurities found in the Los Angeles atmosphere. It will include a thorough investigation of the indicated enhancing action, including study as to how it might be alleviated, as for example by elimination from the atmosphere of one or more contaminants that may play a key role in producing it.

## VI

### THE METEOROLOGICAL MECHANISM OF THE SMOG

**I**N DEALING with the smog problem it is essential to understand the peculiarities of the California region in which smog occurs and the way in which meteorological and topographical factors combine to prevent normal dispersal of polluting substances resulting from human activity.

Los Angeles County is located in a basin bounded on three sides by high mountains and on the fourth by the Pacific Ocean. Over the entire area, during a large part of the year, extends a warm stratum of air, or "inversion layer," resulting from the presence of a high-pressure area over the North Pacific. The region is also subject to ocean fogs and to alternating land-and-sea breezes. All these circumstances contribute to the formation of the smog. As a result of the Stanford Research Institute investigation, the meteorological mechanism of the smog now seems to be adequately explained.

The inversion layer acts as a canopy over the Los Angeles basin, preventing contaminated air from escaping either vertically or toward the east. A natural haze composed of oceanic salt, dust particles, and plant pollen combines with man-made pollution and collects at its base. Owing to the isolating action of the layer, it is possible for the smoke and fumes of several days to build up and remain trapped in the Los Angeles area.

Beneath the canopy of the inversion layer, a daily reversal of wind direction forms a part of the normal weather pattern. From midmorning until late afternoon or evening the prevailing winds blow in from the sea. At night they change direction and blow outward from the land.

As a result, during periods of low wind velocity masses of polluted air accumulated during the day are sometimes blown a short distance out to sea at night, only to be returned the next day by winds blowing toward the land. Such a contaminated air mass may pass over the city a number of times before it is finally carried completely away from the area by strong winds.

At night and during foggy weather the con-



PLATE 19

Assembling apparatus for ozone measurement,  
Stanford Research Institute laboratories

taminated stratum of air remains at its own level, in a compact mass. On sunny days, however, the earth, as it warms, sets up vertical thermal currents somewhat resembling those in a room over a hot stove. These currents create air turbulence. They swirl higher and higher into the atmosphere, catch the polluted layer, and bring the contaminated air down to street level in a widespread, uneven, mixing action. The contaminating substances are then dispersed by the morning landward breeze throughout the total volume of air below the inversion layer. Unless the wind below the inversion is strong enough to carry them away, they produce the phenomenon of smog.

#### Wind Movements

As has been pointed out, the Los Angeles basin is usually under a land-and-sea breeze re-

gime. Sometime during the midmorning hours the wind starts blowing in from the sea, reaching a maximum velocity in the middle of the afternoon. In late afternoon and evening the sea breeze diminishes; and during the night the wind blows from the land toward the sea. This change in flow of the breezes occurs almost simultaneously at points on the shore line and farther inland.

The exact time when the movement switches direction from land to sea and back again is dependent upon the temperature and pressure conditions existing on the particular day. While the strength of the wind depends on the time of the change and on the weather pattern, the wind usually blows more strongly inward from the ocean during the day than it blows outward toward the ocean at night. This results in a net transport of air out of the Los Angeles basin through the mountain passes to the east and north.

In addition, the direction of the land breeze is much more variable than the direction of the sea breeze. The average seasonal conditions can be seen from the accompanying charts (Figure 20).

Because of the change in the direction of wind movement from day to night and because of low wind velocity on some days, it is possible for a mass of air from the ocean to arrive over the Los Angeles area and either stagnate there during the night or move toward the sea, only to retrace a part of its path the next day—while, on the average, gradually moving farther north or east.

### Diffusion of Pollutants

The diffusion of substances in the air is highly dependent upon the temperature of the ground and the lower layers of the air. The sun's rays do not warm the air directly, but for the most part merely pass through it. The source of heat for the lower layers of the atmosphere is the earth, which is warmed by the sun and in turn warms the air. This effect brings about a sequence of air movements in Los Angeles that helps explain the dispersion of pollutants.

During the night, when the air is relatively

calm and clear, the earth becomes colder than the lower layers of the atmosphere. The cooling of the lower air continues during the night and the cool layer reaches higher and higher levels. The final condition is one in which the air—cool at the surface of the earth—becomes progressively warmer above the surface, up to some distance. After this, it again starts to cool as higher elevations are reached.

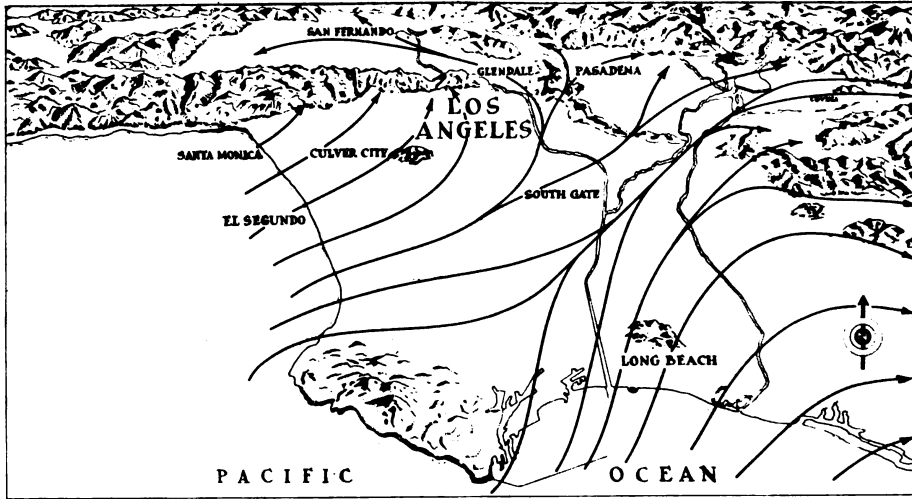
This condition is described as a *radiation inversion* and differs from the Pacific high-pressure-area inversion, in which the warm layer of air is usually found at some distance above the ground surface.

When the inversion induced by the Pacific high-pressure area is forced low enough, the two inversion phenomena may coexist, resulting in a layer of air considerably warmer than the air layer near the surface. Any vertical currents that are mechanically induced, such as those caused by the flow of air over buildings or other obstacles, are rapidly eliminated. Fumes dispersed into the atmosphere under these conditions will remain in a relatively compact mass which may be moved horizontal to the earth by any slight breeze that may exist. This meteorological condition is described as *stable*, and there is no vertical transport of heat due to air motion.

Shortly after sunrise, the earth begins to warm and vertical air currents arise as a result of this heating. As the day progresses, the circulation swirls higher into the atmosphere and continues to do so until the earth begins to cool again in the afternoon. For each rising current there is a compensating descending current. These conditions are called *unstable*, and the air is in motion, carrying heat energy from the earth's surface to the upper layers of air.

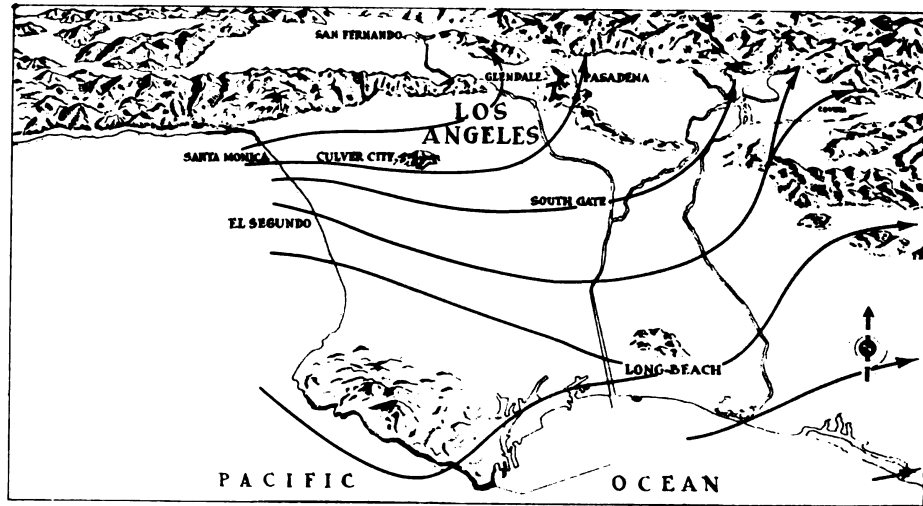
By means of these thermal currents, substances are dispersed vertically in the atmosphere. The thermal currents catch the polluted air suspended at the base of the combined inversion layers and mix it through the total volume of air below the inversion.

To this may be added a third condition which occurs frequently. When a horizontal wind is blowing strongly, it stretches the flow lines of air



Arrows show typical wind directions for 9 A.M.-noon during summer months. Wind speed averages 3 to 9 m.p.h.

Wind directions for noon-midnight in the summer, and noon - 4 P.M. in the winter. Speed averages 7 to 12 m.p.h.



Wind directions for midnight-7 A.M. in summer and 7 P.M.-10 A.M. in winter. Speed averages 1 to 3 m.p.h.

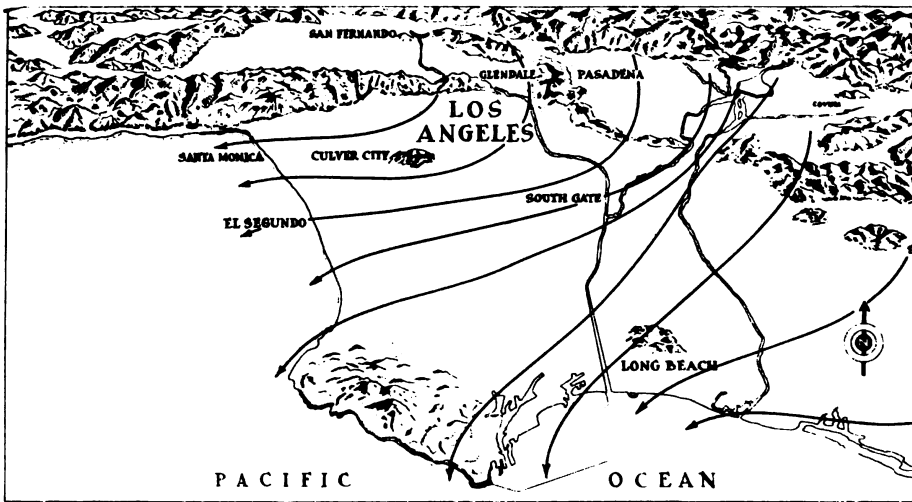


FIG. 20

Alternating land-and-sea breezes are part of the normal weather pattern in the Los Angeles County area

transport horizontally and overcomes the effect of the vertical mixing caused by hot air currents.

**The Formation of Smog**

A typical pattern in Los Angeles at the beginning of a smog day would show a stable condition in the atmosphere in the early morning hours before sunrise, with smoke from various sources drifting off lazily in rather compact streamers. One or two hours after sunrise the air begins to stir vertically and unstable conditions develop, with the smoke streamers being stirred into a turbulent mass of air (Plate 20).

The distance above the earth's surface of the Pacific temperature inversion is an important factor in determining whether or not smog will occur under these conditions. When the base of the inversion is no more than 600 to 1000 feet above the surface, the situation is conducive to smog.

During the time the air is stable in the morning preceding a smog period, the pollutants col-

lect beneath the base of this inversion. They cannot penetrate it and are thus held at low altitudes.

So long as the air beneath the contaminated layer remains in a nonturbulent or stable condition, the contamination will tend to remain at the same level and will not settle to the earth, even after being carried long distances. Careful observations have shown that smoke streamers can drift in compact columns as far as 15 miles (Ref. 16).

The manner in which pollutants are believed first to accumulate, then disperse, in the Los Angeles atmosphere can best be described by reference to the sketches in Figure 21, which illustrates the development of the smog cycle.

The cycle starts with the presence of a Pacific high-pressure inversion, whose base is usually some distance above the ground, as shown in Figure 21a. Coexistent with the Pacific inversion may or may not be a radiational inversion, whose base, as shown in Figure 21b, is normally at ground level during the pre-dawn hours.



PLATE 20

Two views looking southward across Hollywood on November 24, 1948—a day classified as moderately smoggy. The left-hand photograph, taken at 6:30 A.M. (sunrise at 6:35 A.M.), shows pre-dawn pollution trailing off in horizontal streamers. Turbulence has not yet set in. The photograph at the right, taken at 8:20 A.M., shows the start of turbulent mixing of pollution from surface sources with pollution from aloft. Diffusion of the pollutants is not yet uniform, since the top of the building at the left can be seen more clearly than its base.



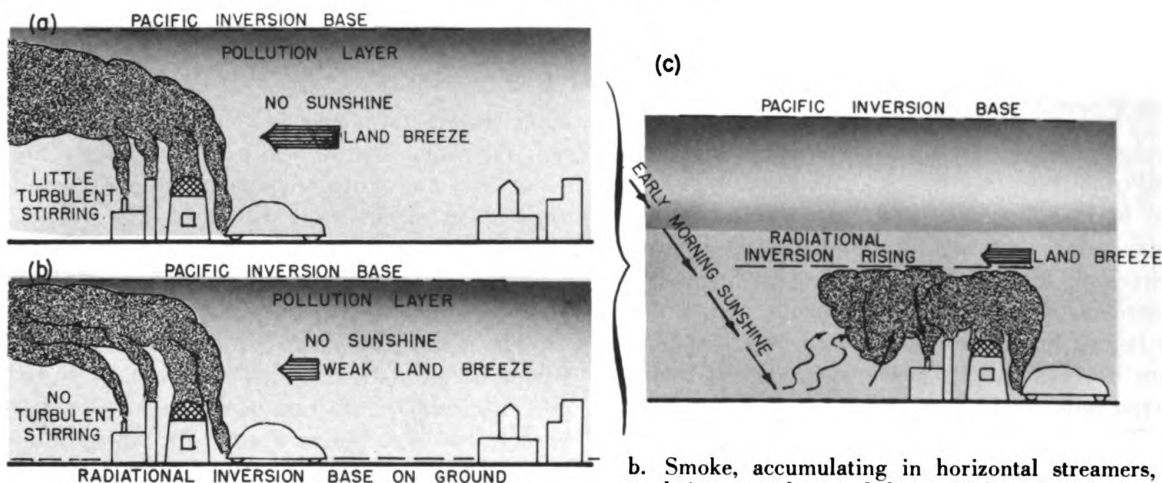


FIG. 21

### Meteorological Mechanism of the Smog

In these sketches the vertical scale of air movements and inversion height has been exaggerated for clarity.

- a. Smoke is trapped beneath the inversion base while being moved horizontally by a breeze from the mountains toward the ocean. No source of heat is present, and the inversion base is above ground. Pollution from previous days has collected beneath the inversion base.

In Figure 21a, the smoke can be seen rising to become trapped beneath the inversion base, while being moved horizontally by a breeze from the mountains to the ocean. This occurs when the ground is receiving no heat from the sun, and an inversion base is above the ground.

In Figure 21b, the smoke is accumulating in horizontal streamers and also is being moved toward the ocean by the land breezes. A radiational cooling of the earth's surface has been marked enough to establish an inversion base resting on the ground.

In Figure 21c, the accumulation of the pollutants is altered with the rising of the sun and the beginning of vertical stirring of the air. The contaminants are caught in the descending currents and are carried down to the surface from their layered position, to be diffused through the whole volume of air below the original pollution layers. This action usually begins within an hour or two after sunrise; but the time may vary, depending upon such factors as type of terrain, intensity of sunlight, and intensity of in-

- b. Smoke, accumulating in horizontal streamers, is being moved toward the ocean by a land breeze. A radiational inversion exists along the ground. The Pacific inversion is also present.

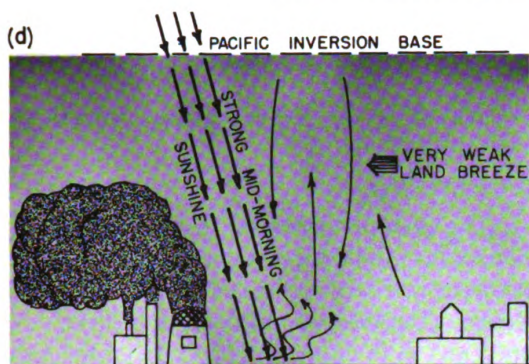
- c. From either of these pre-dawn conditions the situation shown in (c) can develop. With the rising of the sun, vertical stirring of the air begins. In the case of (a), contaminants caught in the descending currents are carried toward the ground from their layered position. In the case of (b), the onset of turbulence causes the radiational inversion base to rise and become established at the top of the turbulent layer.

version. During this period of shallow stirring the base of the radiational inversion rises and is established at the top of the turbulent layer.

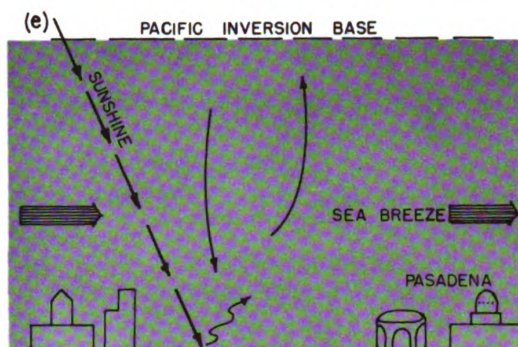
Figure 21d shows the period of maximum (rolling) turbulence which occurs as the wind ceases blowing toward the sea and begins blowing toward the land. This is the period of maximum pollution, since contaminants from all layers beneath a low inversion are carried to ground level. During the summer and fall months this occurs in Los Angeles at about 10 A.M. It is significant that the minimum visibility in Los Angeles usually occurs just prior to or simultaneously with the change in wind direction.

Figure 21e shows the final sequence of the movement. The vertically distributed pollution cloud is moving as a mass from Los Angeles toward Pasadena and Glendale and will finally be dissipated upward and through mountain gaps.

The phenomena described in connection with Figure 21 help to explain why, on a typical smog day, the visibility in Los Angeles is relatively



- d. As solar heat increases, the radiational inversion is destroyed, and the turbulent currents reach higher altitudes. The base of the Pacific inversion effectively limits the vertical extent of the turbulence. Maximum turbulence occurs as the wind direction tends to change. At this time pollution from all levels below the Pacific inversion is carried downward, thus creating smog at ground level.



- e. The polluted air beneath the inversion is carried away from the downtown Los Angeles area. Turbulent mixing is still in progress as sea breeze carries polluted air toward Pasadena and Glendale. Sources of pollution in relation to fuel consumed are as follows: Gasoline (automobile), 1,000,000,000 gallons a year; fuel oil (industry), 275,000,000 gallons a year; and rubbish, 1,750,000 tons a year.

good before sunrise, but decreases sharply thereafter. The horizontal air motion of the night breezes carries the contaminated air masses toward the ocean, and they are not returned to Los Angeles and brought down from aloft by vertical turbulence until after the sun has risen.

This concept of the smog mechanism also accounts for the movement and spread of eye-irritation areas during a smog day. The pollution moves horizontally in a northeasterly direction but continues to expand in area as it is brought to the surface of the earth more and more by vertical mixing.

It also helps to explain why irritation is rarely found at night or at times when a heavy fog

is reported in downtown Los Angeles. Under such conditions the sun does not warm the earth enough to set up vertical currents to stir the air. The pollutants consequently are not brought down to street level.

It is interesting to note from the table of smog meteorological data in Appendix 6 that fog was observed at Long Beach at some time during the nights previous to 68 of 81 days on which eye-irritating smog was reported in downtown Los Angeles. Fog indicates stable conditions in the lowest layers of the atmosphere, and the presence of liquid water in the fog may facilitate some of the chemical processes needed for the formation of the eye-irritating smog substance.

## VII THE SMOG INDEX AND SMOG FORECASTING

**F**ROM THE BEGINNING of this investigation it has been evident that some method of predicting smog would be needed, as well as some objective means of measuring the intensity of smog conditions.

The first step was to establish a mathematical relation between meteorological conditions that must exist for smog to occur and smog as indicated by subjective human experience. This effort resulted in the Stanford Research Institute Smog Index—a formula that tells with a high degree of certainty whether smog is, or is not, present in some part of the Los Angeles basin at the moment for which the Index is calculated (see Appendix 7).

The success of the Smog Index in correlating the presence of smog with weather characteristics gave rise to a reasonably accurate method of forecasting days when smog *was not likely* to occur. Over the past year a more reliable method of forecasting has been developed, which makes possible the prediction of days on which smog *will* occur. Using data collected over a two-year period, the new method has correctly predicted the occurrence of smog 84 per cent of the time.

### The Smog Index

The Smog Index (described in the First Interim Report) is based on five separate aspects of meteorological conditions, including:

1. Wind movements for 24 hours.
2. Noon visibility in miles.
3. Relative humidity at noon.
4. The difference between the daily mean temperature and the normal mean temperature.
5. The height of the Pacific temperature inversion layer.

In Figure 16 (p. 38) the Stanford Research Institute Smog Index is plotted for comparison with the results of the popular survey described in Section V, and the incidence of spontaneous complaints to the County bureau. It will be noticed that there is good correspondence between the curves—all three of which represent different means of measuring smog. Other examples

are shown in the meteorological summary in Figure 2 (facing p. 13).

### Forecasting

The Stanford Research Institute forecasting method for predicting days on which smog would not occur was fully described in the First Interim Report. The method which has now been developed and is in current use to predict the occurrence of smoggy days involves several new equations expressing meteorological conditions.

The first equation predicts, two or three days in advance, a tendency for smog to develop when there are rapid changes in the height of the 700-millibar surface, simultaneously with marked deviation from the 10,200-foot level.

The second equation states that there is a tendency for smog to develop two or three days in the future when the inversion is strong and there is a south wind at the 10,200-foot level.

The third equation takes into account the degree of cloudiness and shows that there is a tendency for smog to be formed two or three days in the future when the skies are cloudless and there is no wind.

The inclusion of the daily maximum and minimum temperatures at the surface level completes the forecasting data required.

A detailed description of the method and its use is contained in Appendix 7.

The method has been tested with data compiled from 1946 through 1948. Over this period 84 per cent of the reported smog days fell on days when smog was forecast. Smog was reported by the residents of the area on 40 per cent of the days for which it was predicted. This is a favorable record, since telephoned complaints of smog can be expected to identify only a portion of the actual smog days.

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## VIII APPENDICES

1. Laboratory Model Venturi Scrubber	54
2. Photographic Measurement of Visibility	54
3. Interpretation of Data Obtained in Wilson Cloud Chamber Tests with Sodium Chloride	55
4. Proton Scattering Analysis of Smog	56
5. Interpreting Smog Chamber Test Results	58
6. Summary of Weather Conditions for All Reported Smog Days, 1949—May 31, 1949	60
7. Forecasting of Smog	60
8. References	64

## 1. LABORATORY MODEL VENTURI SCRUBBER

THE LABORATORY model venturi scrubber (Figure 22) was made of lucite plastic, which has the advantages of not reacting with the materials with which it is used and of permitting observation of the spray and separator action. The model was sized to operate with a tank-type vacuum cleaner, which draws air through at a rate of about 35 cubic feet per minute. The venturi, made square for ease of construction, has a 2 x 2 inch entrance and a 0.5 x 0.5 inch throat to obtain a gas velocity of 250 to 300 feet per second. The cy-

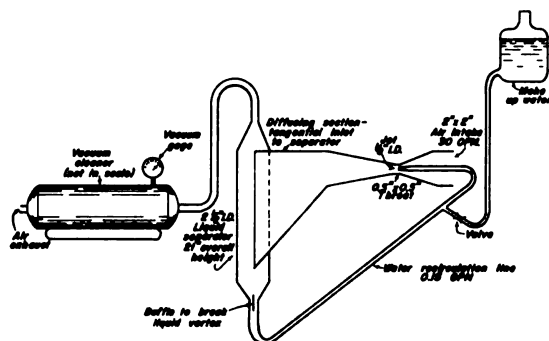


FIG. 22  
Venturi scrubber

clonic separator is 2 $\frac{3}{4}$  inches in diameter and 21 inches over-all height.

In order to concentrate the particulate matter in a minimum volume of water, the scrubbing water is recirculated from the bottom of the separator back through the spray jet in the venturi throat. A flowmeter in the water circulation line permits regulation of the flow rate, and it was found that 10 to 15 gallons of water per 1000 cubic feet of air scrubbed gives optimum results. The total liquid in the venturi scrubber is about 150 cc. A connection, through a constant level device, is provided to a reservoir in order to maintain a constant quantity of water in circulation and make up for evaporation losses. The flow rate of air through the system is held constant by adjusting controls to maintain a constant reading on a vacuum gage.

With this equipment it is possible to scrub 10,000 cubic feet of air in a period of five to six hours and retain the removed impurities in a volume of water no larger than 100 cc. Laboratory tests on known mixtures of sulfuric acid mist in the air showed that the venturi scrubber can recover at least 80 per cent of the sulfuric acid in the air at concentrations below one part per million by weight, and with particle sizes of the mist of the order of 0.5 to 0.7 micron in diameter.

## 2. PHOTOGRAPHIC MEASUREMENT OF VISIBILITY

IN TABLE VII are shown the results of measurements made during the months of March and April. These measurements are expressed in terms of an extinction coefficient called  $\sigma$ . The visibility in miles can be obtained by finding the value of  $\sigma$  in the Table and substituting it in the equation:

$$\text{Visibility} = \frac{3.91}{\sigma} \quad (\text{Ref. 17})$$

Satisfactory correlation has been achieved between results from the photographic method and those obtained with the unaided human eye. Because it is difficult for observers to agree on the visual range in the absence of instrumental methods, the method as developed has proved very practical.

One application of the photographic technique is illustrated by a series of measurements made on the morning of June 6, 1949. Particles were collected from a 100 cc. sample of air by means of a thermal precipitator and simultaneous photographic measurements were made of the haze. The number of particles in the atmosphere, estimated by counting particles on a

section across a slide, was found to be 600 million per cubic foot. Microscopic observation of the particles indicated that they were approximately 0.2 to 0.3 micron in diameter.

The photographic measurement of the haze gave the following results:

Filter	Red	Yellow	Blue
$\sigma$ (mi. $^{-1}$ )	2.2	1.7	4.3

These measurements show that the ratio of the extinction ( $\sigma$ ) of the blue to the red light is close to 2.0. Chemical and microscopic analyses, results of which have been previously described, showed that most of the particles collected had a refractive index of 1.5. Using data from the photographic measurement and this refractive index, the mean effective diameter of the particles in the atmosphere at the time of photographing was calculated as 0.3 micron. This corresponds closely with that observed under the microscope.

A further verification was also made. By using the number of particles observed (600 million per cubic

foot) and assuming the refractive index to be 1.5 and the visual light to have a wave length of 5.240 Å, the extinction coefficient (a measure of the limit of visual range) was calculated as follows, assuming different sized particles:

Diameter (micron)	0.2	0.3	0.4
σ(mi. <sup>-1</sup> )	0.4	3.4	10.

The calculated extinction coefficient for particles 0.2 micron in diameter was smaller than that measured photographically and that calculated for 0.4 micron was larger than that observed. Thus it again appears that the mean effective size of the particles causing the poor visibility in Los Angeles is approximately 0.3 micron.

TABLE VII.—EXTINCTION COEFFICIENT AS MEASURED PHOTOGRAPHICALLY

1949 Date	Hour	σ (miles <sup>-1</sup> )					Ratio B/R	Weather
		No Filter	Red A	Yellow K-2	Green B	Blue C-5		
3-8	10 A.M.	1.66	2.90	4.35	3.62	3.40	1.17	Clear
	3 P.M.	2.49	3.08	5.50	6.86	6.86	2.23	Partly cloudy
3-9	11 A.M.	1.31	1.96	3.91	3.55	4.35	2.22	Partly cloudy
	2:30 P.M.	3.12	3.13	3.72	.....	.....	.....	Clear
3-10	3 P.M.	1.86	3.40	0.98	2.37	2.24	0.66	Cloudy
3-11	11 A.M.	2.06	3.72	3.40	3.91	4.35	1.17	Clear
3-14	10:30 A.M.	.....	4.25	.....	4.90	5.15	1.22	Smoggy
	1:45 P.M.	3.00	2.90	1.96	2.37	4.35	1.50	Smoggy
3-15	10:30 A.M.	3.91	1.96	2.60	3.91	4.35	2.22	Smoggy & foggy
	2:00 P.M.	2.00	3.56	4.35	3.12	2.80	0.79	Slight smog
3-17	2 P.M.	1.95	1.31	2.80	1.96	3.00	2.29	Slight haze
3-18	10 A.M.	5.08	1.51	2.11	4.25	3.91	2.59	Smoggy & foggy
	2 P.M.	2.70	2.90	1.96	3.26	3.91	1.35	Smoggy & foggy
3-21	10 A.M.	1.12	1.12	2.36	4.11	3.72	3.32	Slight haze
3-25	11:15 A.M.	0.80	2.45	2.80	2.30	2.80	1.14	Slight haze
3-28	2:15 P.M.	2.60	4.05	4.05	5.20	5.60	1.38	Slight haze
		.....	.....	.....	.....	.....	.....	(windy)
4-20	P.M.	0.70	2.00	2.45	2.45	2.95	1.46	Windy, haze
4-21	A.M.	.....	2.60	2.75	3.55	3.31	1.26	Smog
	P.M.	1.10	3.95	3.00	3.40	4.50	1.14	Slight smog
4-22	A.M.	2.70	1.80	1.80	2.10	2.70	1.50	Slight smog
	A.M.	1.30	1.00	1.75	2.60	3.50	3.45	Fog - smog
4-25	P.M.	2.05	2.60	2.35	2.35	3.75	1.44	Slight smog
	P.M.	1.80	1.60	1.80	2.45	3.60	2.25	Slight haze
4-28	A.M.	.....	2.35	.....	2.85	4.30	1.83	Fog

3. INTERPRETATION OF DATA OBTAINED IN WILSON CLOUD CHAMBER TESTS WITH SODIUM CHLORIDE

THE DATA obtained in Wilson cloud chamber tests with saturated salt solution are interpreted by using the following mathematical formula (Ref. 17). The equation for the passage of light through a medium is:

$$I = I_0 e^{-\sigma d}$$

or

$$\sigma = d \ln \frac{I}{I_0}$$

where

- I = resultant intensity
- I<sub>0</sub> = incident intensity
- σ = extinction coefficient
- d = length of path

If the measure of efficiency as condensation nuclei is taken to be the ratio of the extinction coefficient

after expansion (σ<sub>2</sub>) to the extinction coefficient before expansion (σ<sub>1</sub>), it is found

$$\frac{\sigma_2}{\sigma_1} = \frac{\ln \frac{I_2}{I_0}}{\ln \frac{I_1}{I_0}}$$

where

- I<sub>1</sub> = intensity of transmitted light before expansion
- I<sub>2</sub> = intensity of transmitted light after expansion
- I<sub>0</sub> = intensity of transmitted light through the empty tube

## 4. PROTON SCATTERING ANALYSIS OF SMOG

THE ACCOMPANYING curves show the results of a proton scattering analysis of a smog sample taken with the impactor. The results definitely show the presence of lead, sulfur, oxygen, carbon, and little or none of any other elements of atomic number greater than 4.

The sample was taken in Pasadena on August 7, 1949, during a warm, dry day, with a haze of such intensity that the mountains five miles away were completely invisible. There was no indication of odor or eye irritation, the smog being apparently entirely limited to the bright haze which commonly affects visibility in Los Angeles during summer days.

The smog was sampled with a single-stage impactor with a 0.003-inch jet, preceded by a glass cyclone to remove large particles (over five microns). The air jet was directed against a clean piece of beryllium metal, cemented to the glass slide in the impactor. A large number of streaks were deposited side by side, distributed over a 2-mm.-wide area to provide a target for the proton bombardment.

The sample was bombarded by protons from the electrostatic accelerator in the Kellogg Laboratory at California Institute of Technology. The arrangement

of the apparatus is shown schematically in the simplified accompanying diagram (Figure 23). The protons are produced in the ion source at the top of the accelerator and accelerated by the high potential difference maintained between the top and bottom of the accelerating column, in a collimated beam. The beam passes between the two curved condenser plates in the electrostatic analyzer, which bends the beam through 90°, and is used to measure and control the proton energy. The protons strike a target which is insulated, so that the total electric charge of incident protons can be measured. A very small fraction of the protons are scattered, of which a portion enters the 180° magnetic spectrograph, which focuses them on the fluorescent screen of a scintillation counter.

By adjusting the magnetic field of the spectrograph, only those protons of selected energy can be made to impinge on the counter, so that one can count the number of scattered protons of each energy from some target, relative to a fixed number of protons incident on the target. Since the energy of a proton scattered elastically by an atom depends on the atomic weight, the atomic weights of the elements causing the scattering can be determined and the elements thereby identified. By considering the relative number of scattered protons of different energies, the relative abundance of the elements in the sample can be determined. The samples required for this purpose need only be a very thin film, weighing less than a microgram, if necessary.

In order to estimate the relative abundance of the elements in the sample, it is necessary to take into account the fact that the scattering cross section of each element, in accordance with the theory of Coulomb scattering, is proportional to the square of its atomic number (the number of protons in the nucleus of the atom). For example, sulfur has an atomic number of 16, and oxygen, 8. If sulfur and oxygen are present in equal abundance, the sulfur would scatter four times as many protons as oxygen.

The curves (Figures 24 and 25) shown are plotted as observed scattered proton counts against an abscissa scale of direct readings of the fluxmeter potentiometer of the magnetic spectrograph. These potentiometer readings are inversely proportional to the field strength in the spectrograph and therefore inversely proportional to the square root of the energy of the scattered protons.

The bombarding energy used for these experiments was 744 kilovolts (chosen arbitrarily), which corre-

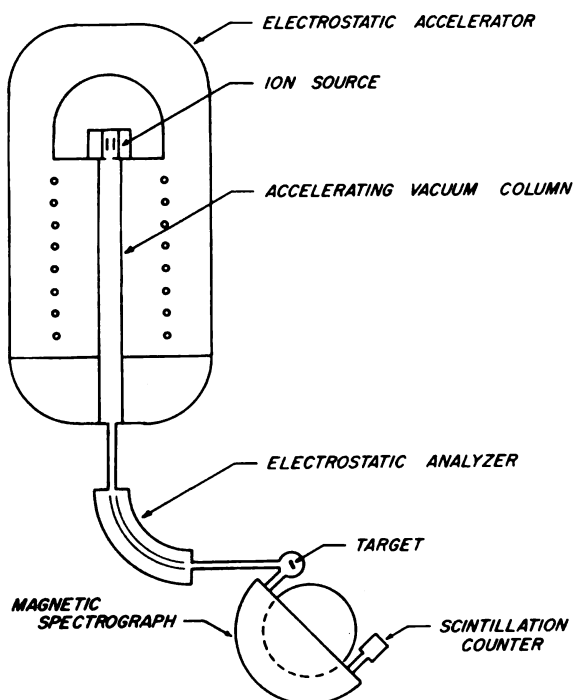


FIG. 23

Diagram of proton scattering apparatus

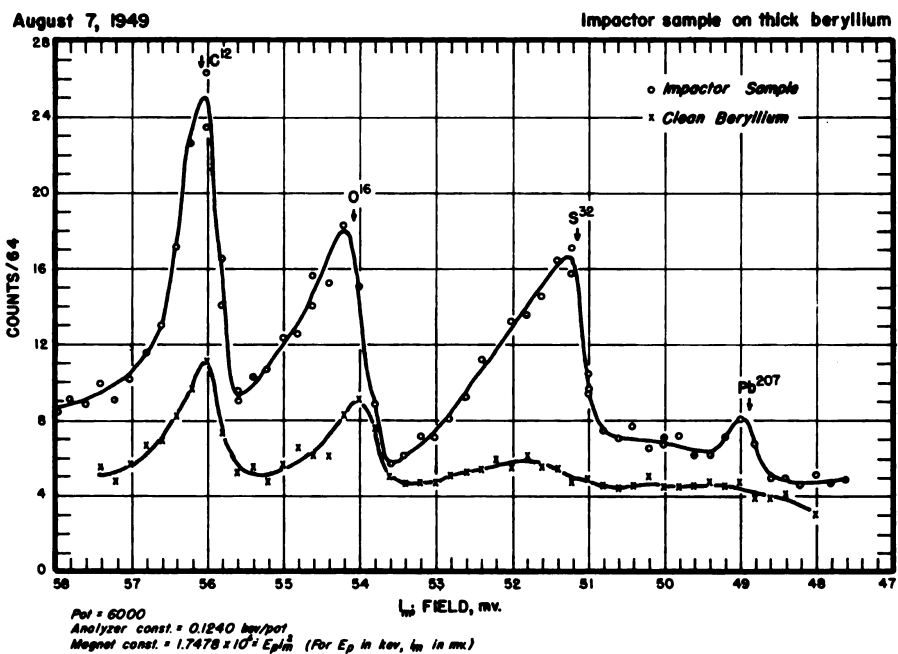


FIG. 24  
Proton bombardment analysis of smog sample

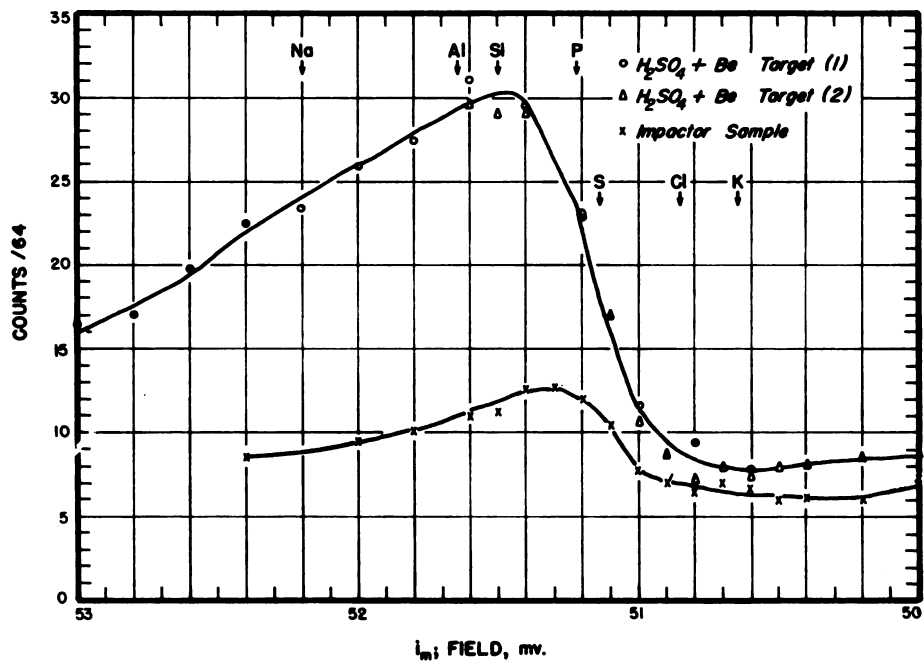


FIG. 25  
Sulfur comparison—proton bombardment



sponds to a magnet setting of 48.5 mv. Since all the elastically scattered protons are scattered by atoms of finite mass, they will all have less energy than this. The energy of protons scattered from the beryllium target corresponds to a magnet setting of 59.0 mv., so the entire atomic scale heavier than beryllium will lie between 48.5 and 59.0 mv. The heavy elements will be crowded into one end of this scale, but since there are not very many heavy elements likely to be found in significant concentration in the open atmosphere, a single peak at this end of the scale, such as was found, is not too difficult to assign.

Figure 24 shows the full scale, run both on the smog sample and on a clean area of the same piece of beryllium, away from the impactor sample. The four peaks are labeled with the element to which they are assigned. The identification of the carbon and oxygen peaks is absolutely certain, since the separation between elements of such low atomic weight is quite large. The sulfur peak was confirmed by a comparison run with a target made by treating beryllium metal with  $H_2SO_4$ , and the two curves are shown in Figure 25. A scale at the top shows where all the adjacent elements would fall compared with the standard sulfur peak at 51.12 mv., and even the closest element, phosphorus, is distinctly off the smog curve. The identification of the lead peak is less certain; however the arrow is located at the calculated position of a lead peak, and the agreement is excellent. Only the elements heavier than the rare earths would give a peak in essentially the same place as lead, within the reproducibility and resolution of these curves, and of these only lead seems to have much probability of occurrence.

It should be pointed out that the oxygen and sulfur peaks appear to correspond to "thick targets," and the carbon and lead correspond to "thin targets." Thin targets are thin in energy spread compared to the spectrograph resolution and are located by the center of the peak; thick targets have a large energy spread compared to the resolution and are located by the half-rise point of the front edge to correspond to the thin target scale. This has to do with the theory of experi-

mental "window curves" and will not be explained here in detail.

Both the relative magnitude and the similarity in shapes of the sulfur and oxygen peaks suggest that they are probably combined as  $SO_4$ , and since they appear thick compared with both carbon and lead, this probably means that they have penetrated into the beryllium, just as the  $H_2SO_4$  of the comparison target evidently did. Since no other elements heavier than beryllium were found in significant quantity and since hydrogen would not be shown, it seems most likely that the sulfur was chiefly in the form of sulfuric acid in the atmosphere sampled. Since the integral under the lead peak is only about one-tenth that under sulfur, and lead has 26 times the scattering cross section of sulfur, its atomic concentration was approximately 0.004 times that of sulfur.

Part of the background shown on the comparison curve for clean Be is due to contaminants in the Be and to reaction products, such as deuterons and alpha-particles produced in nuclear reactions between the bombarding protons and the beryllium. Some experiments on carbon and aluminum targets show them to be much cleaner than beryllium, and also it appears practical to observe carbon and oxygen on aluminum, even though the aluminum has greater atomic weight, since the curve runs quite flat on the aluminum plateau, above 51.5 mv.

Some targets with coatings of Aquadag on aluminum foil have been prepared for the impactor, to use as soon as some smog occurs. The impactor is being modified to provide means for moving the slide back and forth continuously during the run to make a uniformly thin target to obtain improved resolution of the peaks. By shortening the jet opening, the impactor can conveniently be used with existing pumps (or with an automobile windshield wiper connection) with the 0.018-inch jet.

The very helpful cooperation of Dr. C. C. Lauritsen at California Institute of Technology in providing the use of the facilities of Kellogg Laboratory and his own time in running these experiments is gratefully acknowledged.

## 5. INTERPRETING SMOG CHAMBER TEST RESULTS

FOR PURPOSES of comparison it is highly desirable that results of subjective tests be capable of being assigned a numerical value. For this purpose a method described by Roth and Swenson (Ref. 15) was employed. In this method the individual subjected to the test is requested to score his response each minute. If

the response is mild, one check is made; two checks are made for a moderate response, and three checks for severe reactions. At the completion of the test, the total number of checks in a column is added and divided by the total number of minutes the test lasted.

Thus a value of one indicates mild irritation for

the duration of the test (usually 10 minutes). This index gives a relative measure of the amount of irritation, and for any given series of tests may be averaged. The relative usefulness of this average is, of course, increased as the number of individuals in the test group is increased. A sample calculation is shown on the test sheet (Figure 26).

In order to show the data obtained in these tests in graphical form, the results were plotted on a graph in accordance with Weber's law (Ref. 18). This law states that the relative degree of irritation of a substance at two different concentrations can be represented as a constant multiplied by the logarithm of the two concentrations.

Expressed mathematically:

$$I = R \ln \frac{C}{C_0}$$

where

I=the irritation index or lachrymation index, as the case may be

R=constant for the substance employed

C=concentration under consideration

C<sub>0</sub>=the threshold value at which irritation may first be noticed.

In plotting the data the best straight line through these points was obtained by the method of averages; that is, the positive and negative deviations along the ordinant axis have been balanced to zero.

TEST SHEET						
Subjects: <i>Jana Doe</i>			Age: <i>26</i>		Test Number: <i>56</i>	
Date: <i>May 20, 1949</i>			Sex: <i>Female</i>		Wet Bulb Temperature: <i>65</i>	
					Dry Bulb Temperature: <i>77</i>	
OBSERVATIONS						
Time	Nose		Eye		Throat Irritation	Remarks
	Smell	Irritation	Irritation	Lach.(tears)		
9:03	✓					
4	✓					
5	✓			✓		
6	✓			✓✓		
7	✓			✓✓		
8	✓			✓✓✓		
9	✓			✓✓✓		
10	✓			✓✓✓	✓	
11	✓			✓✓✓	✓	
12	✓			✓✓✓	✓	
	<u>10/10</u>	<u>10/3</u>	<u>10/20</u>	<u>10/3</u>		
	1.0	0.3	2.0	0.3		
INSTRUCTIONS FOR FILLING OUT THIS SHEET						
1. Please fill out heading for name, date, age, sex, and wet and dry bulb temperature. Temperature can be obtained as follows:						
Open metal cover of the Fries psychrometer and put the sock on the wet-bulb thermometer. Close metal cover and pump air by the bulbe, until the thermometers reach a steady state.						
2. Record your observations once a minute, according to the electric clock in the chamber. The test will last ten minutes unless stated otherwise.						
Under each heading record your sensations with the following marks:						
✓ mild,			✓✓ moderate,		✓✓✓ severe.	
Remarks will include coughs, sneezes, yawns, bloodshots, or any special physiological reaction or condition.						
Thank you for your cooperation.						

FIG. 26

Sample data sheet—test sheet used in Smog Chamber tests

## 6. SUMMARY OF WEATHER CONDITIONS FOR ALL REPORTED SMOG DAYS, 1946-MAY 31, 1949

TABLE VIII gives a summary of weather conditions as observed on all the days in the period 1946 through May 31, 1949 when smog was reported. In all cases the data have been taken from the records of the U.S. Weather Bureau. The Smog Index and the Inversion Intensity have been calculated (App. 7).

The values of the inversion intensity and the inversion height are based either upon the actual Long Beach radiosonde or upon an average of the San Diego and Santa Maria radiosondes when the Long

Beach sounding was not taken. Checks made when the three soundings were taken have shown this method to give reasonable accuracy under normal conditions. The height of the 700-millibar pressure surface and the value of the 10,000-foot wind were interpolated from the analyzed 700-millibar map. In estimating the probable time of the start of the sea breeze, the shift in the direction of the wind to a direction from south to west, inclusive, was used. Minimum visibility data cover the period 0700-1400 inclusive.

## 7. FORECASTING OF SMOG

IN THE DEVELOPMENT of a smog forecasting system a smog day was considered as a day when people within the Los Angeles area complained of eye irritation. These smog complaints, in order to be recorded as such, had to be reported to the Los Angeles County Air Pollution Board, where records were kept concerning the location of the complainant and the date of the complaint. By using these records as a basis and calling a day "smoggy" when more than a minimum of three complaints were recorded, certain characteristic weather conditions were seen to be typical of a smog day.

While the visibility on a smog day was usually quite low, a smog day was not a foggy day. This was shown rather conclusively by the observations of temperature and relative humidity on the days of reported eye irritation. The temperatures recorded on smog days were usually high, with the daily mean temperature usually above the daily normal temperature. The relative humidity observations on smog days indicated that irritation was accompanied by low relative humidity. The average noon relative humidity in downtown Los Angeles for all the reported smog days was 40 per cent, with only a few values as high as 60 per cent. In addition to high temperature and low humidity, a smog day also showed a low and usually strong inversion with weak surface wind flow. These variables—deviation of mean temperature from normal, noon relative humidity, daily surface wind movement, inversion intensity, and noon visibility—were combined into the SRI Smog Index, which was quite useful in estimating the probability that smog occurred on any certain day.

A further refinement is provided through a close inspection of the recorded hourly visibility observations

taken in downtown Los Angeles. A typical irritation day is characterized by a distinctive pattern of visibility during the morning hours. In the early morning, usually before 8 or 9 o'clock, the visibility begins to improve but then decreases to a very low value between 1000 and 1200, with improving visibility in the afternoon. During this period of decreasing visibility the relative humidity decreases, so that the lowered visibility must be the result of increased pollution and not of the presence of fog. This characteristic pattern of visibility can often be used to distinguish days when there is obvious pollution present from days when all other factors indicate a high probability of smog even though no reports of irritation are recorded.

In addition to the weather conditions on the actual smog day, the complaint data indicated that certain conditions should prevail at least 48 hours prior to the reporting of the actual irritation. These relations have been used in developing an objective smog forecasting method, the details of which follow.

### METHOD FOR FORECASTING SMOG

The objective forecasting of smog involves the problem of forecasting the days when the inversion will be low and relatively strong, the relative humidity low, wind movements small, and the temperature warm. The time interval between the forecast and the predicted occurrence for best utility should be at least 36 to 48 hours. For example, Monday's forecast should be able to predict smog for Wednesday. The method is completely objective in character, so that it may be used with accuracy by personnel untrained in meteorological techniques. All the data which are required for the several calculations are readily available from the local stations of the U.S. Weather Bu-





reau. If the method given here were used by a trained meteorological staff and in conjunction with standard synoptic forecasting procedures, it should be possible to apply the method with increased accuracy over the 48-hour range and possibly extend the range of the forecast to more than 48 hours with no loss in accuracy.

The several parts which make up the forecasting method are logically divided into those based on upper air observations (10,000-foot level, which also include temperature sounding for inversion data) and those based upon surface observations. The following discussion pertains to a description and use of the newly developed forecasting method, together with the results that have been obtained. The method is not in its finished form and is still being refined, but it is believed to represent considerable improvement over methods used in the past.

1. Upper Air Forecasting Rules

As a first consideration it is desirable to have a measure of the strength of the Pacific high-pressure area and of its changing intensity. This is useful because of the area's connection with the inversion in the lower layers in the atmosphere. Conditions at the 700-millibar pressure level (approximately 10,000 feet) have been chosen to represent changes which will be later reflected at the surface level. These conditions are represented by the following equation:

$$Z_1 = (25 + \Delta H) (H - 1000)$$

where

$\Delta H$  = change in height of 700-mb. surface over 48 hr. in units of 10's of feet

H = height of 700-mb. surface in 10's of feet

This expression states in mathematical terms that there is a tendency for smog to develop when there are rapid positive changes in the height of the 700-millibar surface simultaneously with marked deviations from the 10,000-foot level. These same conditions should contribute to the development of the inversion by increasing subsidence<sup>1</sup> in the layers above the inversion. Because of the weak wind pattern usually associated with the high-pressure cell, the weak surface winds needed for smog are a likely result. Figure 27 presents this equation in graphical form. The isopleths of  $Z_1$  on the graph correspond to the critical values of  $Z_1$  which separate "smog" and "no smog" conditions for the indicated months of the year.

The second expression based on upper air observations is:

$$Z_2 = (I - 2) (V_y + 25)$$

<sup>1</sup>The slow settling or sinking of a mass of air.

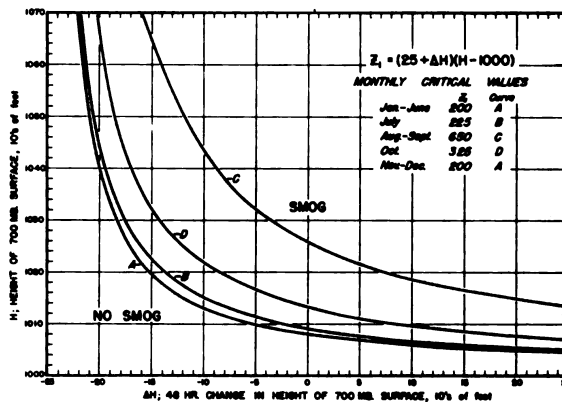


FIG. 27

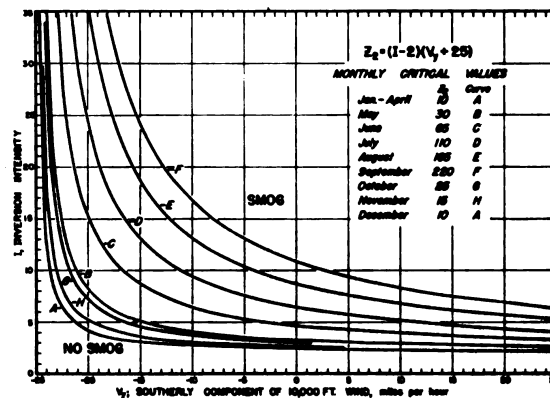


FIG. 28

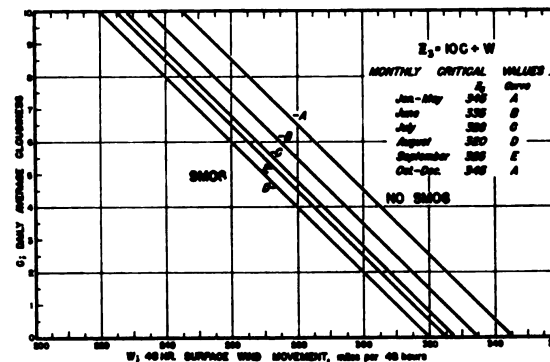


FIG. 29

where  $I$  = inversion intensity (see Section 5 below)

$V_y$  = southerly component of the 700-mb. wind in miles per hour.

This expression indicates that there is a tendency toward smog when the inversion is strong and there is southerly wind at the 10,000-foot level. Thus, an inversion at the surface above which southerly air flow is normally producing convergence<sup>2</sup> will result in a high value for  $Z_2$ . Convergence and southerly flow at this upper level can be expected by considering the vorticity theorem and assuming conservation of vorticity in the flow pattern.<sup>3</sup> Unless this resulting convergence is completely balanced by divergence<sup>4</sup> in layers other than the surface layer beneath the inversion, the inversion can be expected to become considerably more intense. Some of the most intense inversions and the more serious smog days have occurred under conditions of strong southerly winds aloft producing strong convergence above the inversion. Should the convergent flow reach the surface, the inversion itself would be destroyed, giving smog-free conditions and a negative, nonsignificant value for  $Z_2$ . Figure 28 gives this relationship in the form of a graph indicating the critical isopleths of  $Z_2$  for the various months.

### 2. Forecasting Rules Based on Surface Observations

Experience with reported smog days has shown the existence of a period of accumulation before the actual day of occurrence. During this accumulation period the inversion must be present to limit upward diffusion and the winds must be low enough to limit the pollution to the Los Angeles basin area. It has been observed that the action of the surface temperatures and sunshine seems to contribute to the formation, or at least the activity, of the irritants. Whether this is due to photochemical action or flow effects in the atmosphere is not known at this time and is outside the scope of this particular discussion. It is sufficient to note that an improvement in forecasting is possible when the factors in the following equation are taken into account:

$$Z_3 = 10 \text{ (average daily cloudiness) } + 48\text{-hr. surface wind movement}$$

(Average daily cloudiness is taken from the U.S. Weather Bureau observations using a scale of 0-10,

<sup>2</sup>The increase of mass within a given layer of the atmosphere when the winds are such that there is net horizontal inflow of air into the layer.

<sup>3</sup>*Dynamic Meteorology*, Holmboe, Forsythe, Gustin, Chap. XII.

<sup>4</sup>A net outflow of mass across a closed surface bounding a limited volume of the air.

where 0 represents a clear day and 10 is completely overcast.) This formula shows that there is a tendency for smog to be formed when the skies are clear and there is no wind.

The formula serves to separate the days on which either the wind movement was too great to allow the accumulation of the pollution or when the cloud cover was sufficient to reduce the sunshine to a minimum value. This expression resulted from a graphical combination of the variables. Better results were obtained by using data based on cloudiness rather than data representing direct sunshine measurements.

Figure 29 indicates the seasonal changes in critical values of  $Z_3$ .

The inclusion of the values of the daily maximum and minimum temperatures completes the set of forecasting rules. These are given in Table IX.

### 3. Use of Forecasting Rules

There is considerable seasonal variation in the frequency of smog days, but smog days have been recorded in every month of the year. The most favorable season as well as the season of highest frequency for smog is found in the months of August and September.

The expressions given above have been used to make smog forecasts two days in advance by applying the critical values given in Table IX and shown graphically in Figures 27, 28, and 29. The seasonal variations were determined by an examination of the complete list of reported smog days. In addition, where the number of cases warranted it, confidence limits were applied using standard statistical procedures.

The conditions for occurrence of a smog day seem to be critical enough so that should any of the considerations not be satisfied, a no-smog forecast can safely be made. The time interval between the forecast and the occurrence or nonoccurrence of smog is two days in all cases. Thus, the observations taken on a Monday will determine whether a smog will be forecast for the following Wednesday.

A no-smog forecast is made whenever any of the terms except  $Z_3$  are equal to or less than the given value. In the case of  $Z_3$  the value for a nonsmog forecast is equal to or greater than the given value.

### 4. Results of the Forecasting Method

Test forecasting by this method has been made on the period from July 1946 through December 1948. It was necessary to use this period because it is the time during which records have been kept concerning

APPENDICES

TABLE IX.—CRITICAL VALUES FOR SMOG FORECASTS

	$Z_1$ ( $25+\Delta H$ ) ( $H-1000$ )	$Z_2$ ( $I-2$ ) ( $V_y+25$ )	$Z_3$ 10 (av. cloud) + 48 hr. wind	T Max.	T Min.
January .....	200	10	345	60° F.	40° F.
February .....	200	10	345	61	41
March .....	200	10	345	63	42
April .....	200	10	345	65	44
May .....	200	30	345	69	49
June .....	200	65	335	75	55
July .....	225	110	328	77	56
August .....	650	165	320	78	55
September .....	650	220	325	78	54
October .....	325	25	345	69	48
November .....	200	15	345	64	44
December .....	200	10	345	60	42

the irritation effects of smog. Over this length of time 84 per cent of the reported smog days fell on days when smog was forecast. Of the days for which a forecast of smog was made, 53 per cent of the days could be classified as smog days by the method given in the discussion of what constitutes a smog day. This is not a poor record in view of the fact that identifying a day as a smog day by this method is quite restricted in the type of days which may be classed as probable smog days, other than the actual reported irritation days. As even more information is gained about the mechanics of smog, the forecasts and their verifications can become more restrictive and, until it is possible to give a more complete definition of actual smog days, it will be necessary to tolerate a relatively large proportion of no-smog days on the days when smog is forecast.

The accuracy of no-smog forecasts is 96 per cent and the over-all accuracy of the forecasting method including both smog and no-smog forecasts is 85 per cent.

5. Calculation of Inversion Intensity and the Stanford Research Institute Smog Index

The measure of the temperature inversion as it pertains to the smog problem is obtained by calculating the inversion intensity, I. The formula for inversion intensity is

$$I = \frac{(\Delta\theta)^2}{3 + Z\Delta Z}$$

where

$\Delta\theta$  = change in potential temperature through the inversion layer in degrees Kelvin (Potential temperature is defined by Poisson's equation:

$$\theta = T \left( \frac{100}{P} \right)^{0.286}$$

T = degrees K

P = pressure in centibars)

Z = height of inversion base in 100's of meters

$\Delta Z$  = thickness of inversion layer in 100's of meters

When Z is less than 150 meters (1.50 in formula) it is arbitrarily set equal to 150 meters and then both  $\Delta\theta$  and  $\Delta Z$  are measured from the point Z=150 meters.

The calculation of the Smog Index is given by the formula

$$S = \frac{10(T+10)}{R W} \sqrt{\frac{I}{V}}$$

where

T = deviation in degrees F of daily mean temperature from normal mean temperature for that particular date

R = noon relative humidity

W = total 24-hour wind movement in miles

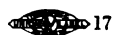
I = inversion intensity (see above)

V = noon visibility in miles



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## VII THE SMOG INDEX AND SMOG FORECASTING

**F**ROM THE BEGINNING of this investigation it has been evident that some method of predicting smog would be needed, as well as some objective means of measuring the intensity of smog conditions.

The first step was to establish a mathematical relation between meteorological conditions that must exist for smog to occur and smog as indicated by subjective human experience. This effort resulted in the Stanford Research Institute Smog Index—a formula that tells with a high degree of certainty whether smog is, or is not, present in some part of the Los Angeles basin at the moment for which the Index is calculated (see Appendix 7).

The success of the Smog Index in correlating the presence of smog with weather characteristics gave rise to a reasonably accurate method of forecasting days when smog *was not likely* to occur. Over the past year a more reliable method of forecasting has been developed, which makes possible the prediction of days on which smog *will* occur. Using data collected over a two-year period, the new method has correctly predicted the occurrence of smog 84 per cent of the time.

### The Smog Index

The Smog Index (described in the First Interim Report) is based on five separate aspects of meteorological conditions, including:

1. Wind movements for 24 hours.
2. Noon visibility in miles.
3. Relative humidity at noon.
4. The difference between the daily mean temperature and the normal mean temperature.
5. The height of the Pacific temperature inversion layer.

In Figure 16 (p. 38) the Stanford Research Institute Smog Index is plotted for comparison with the results of the popular survey described in Section V, and the incidence of spontaneous complaints to the County bureau. It will be noticed that there is good correspondence between the curves—all three of which represent different means of measuring smog. Other examples

are shown in the meteorological summary in Figure 2 (facing p. 13).

### Forecasting

The Stanford Research Institute forecasting method for predicting days on which smog would not occur was fully described in the First Interim Report. The method which has now been developed and is in current use to predict the occurrence of smoggy days involves several new equations expressing meteorological conditions.

The first equation predicts, two or three days in advance, a tendency for smog to develop when there are rapid changes in the height of the 700-millibar surface, simultaneously with marked deviation from the 10,200-foot level.

The second equation states that there is a tendency for smog to develop two or three days in the future when the inversion is strong and there is a south wind at the 10,200-foot level.

The third equation takes into account the degree of cloudiness and shows that there is a tendency for smog to be formed two or three days in the future when the skies are cloudless and there is no wind.

The inclusion of the daily maximum and minimum temperatures at the surface level completes the forecasting data required.

A detailed description of the method and its use is contained in Appendix 7.

The method has been tested with data compiled from 1946 through 1948. Over this period 84 per cent of the reported smog days fell on days when smog was forecast. Smog was reported by the residents of the area on 40 per cent of the days for which it was predicted. This is a favorable record, since telephoned complaints of smog can be expected to identify only a portion of the actual smog days.

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## VIII APPENDICES

1. Laboratory Model Venturi Scrubber	54
2. Photographic Measurement of Visibility	54
3. Interpretation of Data Obtained in Wilson Cloud Chamber Tests with Sodium Chloride	55
4. Proton Scattering Analysis of Smog	56
5. Interpreting Smog Chamber Test Results	58
6. Summary of Weather Conditions for All Reported Smog Days, 1949—May 31, 1949	60
7. Forecasting of Smog	60
8. References	64

## 1. LABORATORY MODEL VENTURI SCRUBBER

THE LABORATORY model venturi scrubber (Figure 22) was made of lucite plastic, which has the advantages of not reacting with the materials with which it is used and of permitting observation of the spray and separator action. The model was sized to operate with a tank-type vacuum cleaner, which draws air through at a rate of about 35 cubic feet per minute. The venturi, made square for ease of construction, has a 2 x 2 inch entrance and a 0.5 x 0.5 inch throat to obtain a gas velocity of 250 to 300 feet per second. The cy-

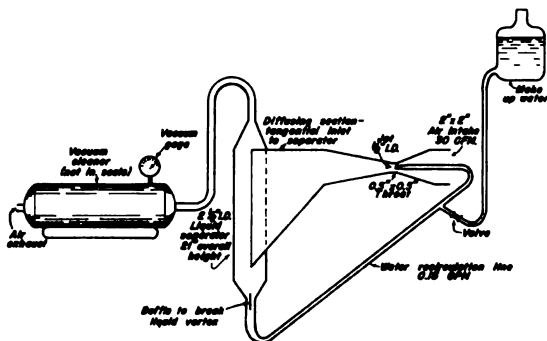


FIG. 22  
Venturi scrubber

clonic separator is 2 $\frac{3}{4}$  inches in diameter and 21 inches over-all height.

In order to concentrate the particulate matter in a minimum volume of water, the scrubbing water is recirculated from the bottom of the separator back through the spray jet in the venturi throat. A flowmeter in the water circulation line permits regulation of the flow rate, and it was found that 10 to 15 gallons of water per 1000 cubic feet of air scrubbed gives optimum results. The total liquid in the venturi scrubber is about 150 cc. A connection, through a constant level device, is provided to a reservoir in order to maintain a constant quantity of water in circulation and make up for evaporation losses. The flow rate of air through the system is held constant by adjusting controls to maintain a constant reading on a vacuum gage.

With this equipment it is possible to scrub 10,000 cubic feet of air in a period of five to six hours and retain the removed impurities in a volume of water no larger than 100 cc. Laboratory tests on known mixtures of sulfuric acid mist in the air showed that the venturi scrubber can recover at least 80 per cent of the sulfuric acid in the air at concentrations below one part per million by weight, and with particle sizes of the mist of the order of 0.5 to 0.7 micron in diameter.

## 2. PHOTOGRAPHIC MEASUREMENT OF VISIBILITY

IN TABLE VII are shown the results of measurements made during the months of March and April. These measurements are expressed in terms of an extinction coefficient called  $\sigma$ . The visibility in miles can be obtained by finding the value of  $\sigma$  in the Table and substituting it in the equation:

$$\text{Visibility} = \frac{3.91}{\sigma} \quad (\text{Ref. 17})$$

Satisfactory correlation has been achieved between results from the photographic method and those obtained with the unaided human eye. Because it is difficult for observers to agree on the visual range in the absence of instrumental methods, the method as developed has proved very practical.

One application of the photographic technique is illustrated by a series of measurements made on the morning of June 6, 1949. Particles were collected from a 100 cc. sample of air by means of a thermal precipitator and simultaneous photographic measurements were made of the haze. The number of particles in the atmosphere, estimated by counting particles on a

section across a slide, was found to be 600 million per cubic foot. Microscopic observation of the particles indicated that they were approximately 0.2 to 0.3 micron in diameter.

The photographic measurement of the haze gave the following results:

Filter	Red	Yellow	Blue
$\sigma$ (mi. <sup>-1</sup> )	2.2	1.7	4.3

These measurements show that the ratio of the extinction ( $\sigma$ ) of the blue to the red light is close to 2.0. Chemical and microscopic analyses, results of which have been previously described, showed that most of the particles collected had a refractive index of 1.5. Using data from the photographic measurement and this refractive index, the mean effective diameter of the particles in the atmosphere at the time of photographing was calculated as 0.3 micron. This corresponds closely with that observed under the microscope.

A further verification was also made. By using the number of particles observed (600 million per cubic

foot) and assuming the refractive index to be 1.5 and the visual light to have a wave length of 5.240 Å, the extinction coefficient (a measure of the limit of visual range) was calculated as follows, assuming different sized particles:

Diameter (micron)	0.2	0.3	0.4
$\sigma$ (mi. <sup>-1</sup> )	0.4	3.4	10.

The calculated extinction coefficient for particles 0.2 micron in diameter was smaller than that measured photographically and that calculated for 0.4 micron was larger than that observed. Thus it again appears that the mean effective size of the particles causing the poor visibility in Los Angeles is approximately 0.3 micron.

TABLE VII.—EXTINCTION COEFFICIENT AS MEASURED PHOTOGRAPHICALLY

1949 Date	Hour	$\sigma$ (miles <sup>-1</sup> )					Ratio B/R	Weather
		No Filter	Red A	Yellow K-2	Green B	Blue C-5		
3-8	10 A.M.	1.66	2.90	4.35	3.62	3.40	1.17	Clear
	3 P.M.	2.49	3.08	5.50	6.86	6.86	2.23	Partly cloudy
3-9	11 A.M.	1.31	1.96	3.91	3.55	4.35	2.22	Partly cloudy
	2:30 P.M.	3.12	3.13	3.72	.....	.....	.....	Clear
3-10	3 P.M.	1.86	3.40	0.98	2.37	2.24	0.66	Cloudy
3-11	11 A.M.	2.06	3.72	3.40	3.91	4.35	1.17	Clear
3-14	10:30 A.M.	.....	4.25	.....	4.90	5.15	1.22	Smoggy
	1:45 P.M.	3.00	2.90	1.96	2.37	4.35	1.50	Smoggy
3-15	10:30 A.M.	3.91	1.96	2.60	3.91	4.35	2.22	Smoggy & foggy
	2:00 P.M.	2.00	3.56	4.35	3.12	2.80	0.79	Slight smog
3-17	2 P.M.	1.95	1.31	2.80	1.96	3.00	2.29	Slight haze
3-18	10 A.M.	5.08	1.51	2.11	4.25	3.91	2.59	Smoggy & foggy
	2 P.M.	2.70	2.90	1.96	3.26	3.91	1.35	Smoggy & foggy
3-21	10 A.M.	1.12	1.12	2.36	4.11	3.72	3.32	Slight haze
3-25	11:15 A.M.	0.80	2.45	2.80	2.30	2.80	1.14	Slight haze
3-28	2:15 P.M.	2.60	4.05	4.05	5.20	5.60	1.38	Slight haze
		.....	.....	.....	.....	.....	.....	(windy)
4-20	P.M.	0.70	2.00	2.45	2.45	2.95	1.46	Windy, haze
4-21	A.M.	.....	2.60	2.75	3.55	3.31	1.26	Smog
	P.M.	1.10	3.95	3.00	3.40	4.50	1.14	Slight smog
4-22	A.M.	2.70	1.80	1.80	2.10	2.70	1.50	Slight smog
4-25	A.M.	1.30	1.00	1.75	2.60	3.50	3.45	Fog - smog
	P.M.	2.05	2.60	2.35	2.35	3.75	1.44	Slight smog
4-27	P.M.	1.80	1.60	1.80	2.45	3.60	2.25	Slight haze
4-28	A.M.	.....	2.35	.....	2.85	4.30	1.83	Fog

3. INTERPRETATION OF DATA OBTAINED IN WILSON CLOUD CHAMBER TESTS WITH SODIUM CHLORIDE

THE DATA obtained in Wilson cloud chamber tests with saturated salt solution are interpreted by using the following mathematical formula (Ref. 17). The equation for the passage of light through a medium is:

$$I = I_0 e^{-\sigma d}$$

or

$$\sigma = d \ln \frac{I}{I_0}$$

where

- I = resultant intensity
- I<sub>0</sub> = incident intensity
- $\sigma$  = extinction coefficient
- d = length of path

If the measure of efficiency as condensation nuclei is taken to be the ratio of the extinction coefficient

after expansion ( $\sigma_2$ ) to the extinction coefficient before expansion ( $\sigma_1$ ), it is found

$$\frac{\sigma_2}{\sigma_1} = \frac{\ln \frac{I_2}{I_0}}{\ln \frac{I_1}{I_0}}$$

where

- I<sub>1</sub> = intensity of transmitted light before expansion
- I<sub>2</sub> = intensity of transmitted light after expansion
- I<sub>0</sub> = intensity of transmitted light through the empty tube



## 4. PROTON SCATTERING ANALYSIS OF SMOG

THE ACCOMPANYING curves show the results of a proton scattering analysis of a smog sample taken with the impactor. The results definitely show the presence of lead, sulfur, oxygen, carbon, and little or none of any other elements of atomic number greater than 4.

The sample was taken in Pasadena on August 7, 1949, during a warm, dry day, with a haze of such intensity that the mountains five miles away were completely invisible. There was no indication of odor or eye irritation, the smog being apparently entirely limited to the bright haze which commonly affects visibility in Los Angeles during summer days.

The smog was sampled with a single-stage impactor with a 0.003-inch jet, preceded by a glass cyclone to remove large particles (over five microns). The air jet was directed against a clean piece of beryllium metal, cemented to the glass slide in the impactor. A large number of streaks were deposited side by side, distributed over a 2-mm.-wide area to provide a target for the proton bombardment.

The sample was bombarded by protons from the electrostatic accelerator in the Kellogg Laboratory at California Institute of Technology. The arrangement

of the apparatus is shown schematically in the simplified accompanying diagram (Figure 23). The protons are produced in the ion source at the top of the accelerator and accelerated by the high potential difference maintained between the top and bottom of the accelerating column, in a collimated beam. The beam passes between the two curved condenser plates in the electrostatic analyzer, which bends the beam through  $90^\circ$ , and is used to measure and control the proton energy. The protons strike a target which is insulated, so that the total electric charge of incident protons can be measured. A very small fraction of the protons are scattered, of which a portion enters the  $180^\circ$  magnetic spectrograph, which focuses them on the fluorescent screen of a scintillation counter.

By adjusting the magnetic field of the spectrograph, only those protons of selected energy can be made to impinge on the counter, so that one can count the number of scattered protons of each energy from some target, relative to a fixed number of protons incident on the target. Since the energy of a proton scattered elastically by an atom depends on the atomic weight, the atomic weights of the elements causing the scattering can be determined and the elements thereby identified. By considering the relative number of scattered protons of different energies, the relative abundance of the elements in the sample can be determined. The samples required for this purpose need only be a very thin film, weighing less than a microgram, if necessary.

In order to estimate the relative abundance of the elements in the sample, it is necessary to take into account the fact that the scattering cross section of each element, in accordance with the theory of Coulomb scattering, is proportional to the square of its atomic number (the number of protons in the nucleus of the atom). For example, sulfur has an atomic number of 16, and oxygen, 8. If sulfur and oxygen are present in equal abundance, the sulfur would scatter four times as many protons as oxygen.

The curves (Figures 24 and 25) shown are plotted as observed scattered proton counts against an abscissa scale of direct readings of the fluxmeter potentiometer of the magnetic spectrograph. These potentiometer readings are inversely proportional to the field strength in the spectrograph and therefore inversely proportional to the square root of the energy of the scattered protons.

The bombarding energy used for these experiments was 744 kilovolts (chosen arbitrarily), which corre-

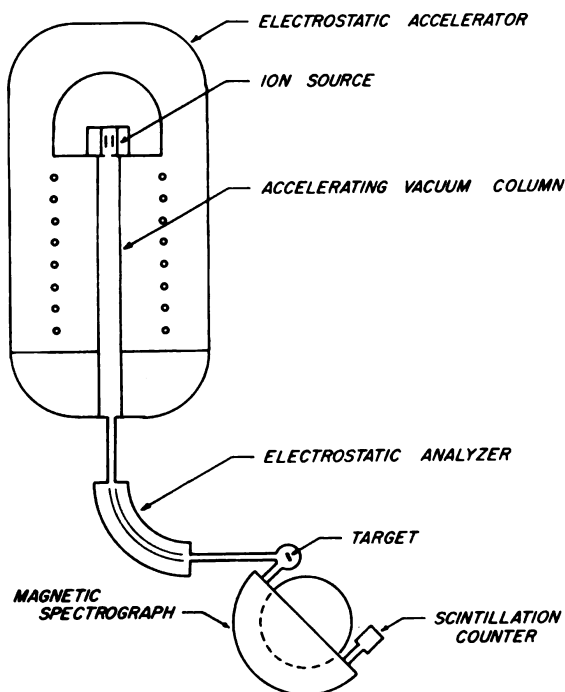


FIG. 23

Diagram of proton scattering apparatus

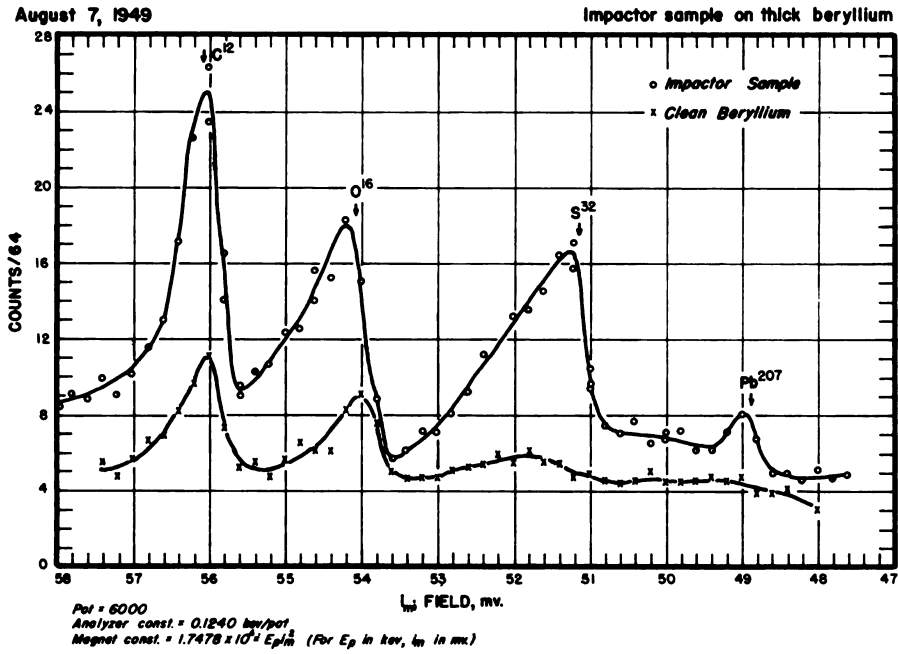


FIG. 24  
Proton bombardment analysis of smog sample

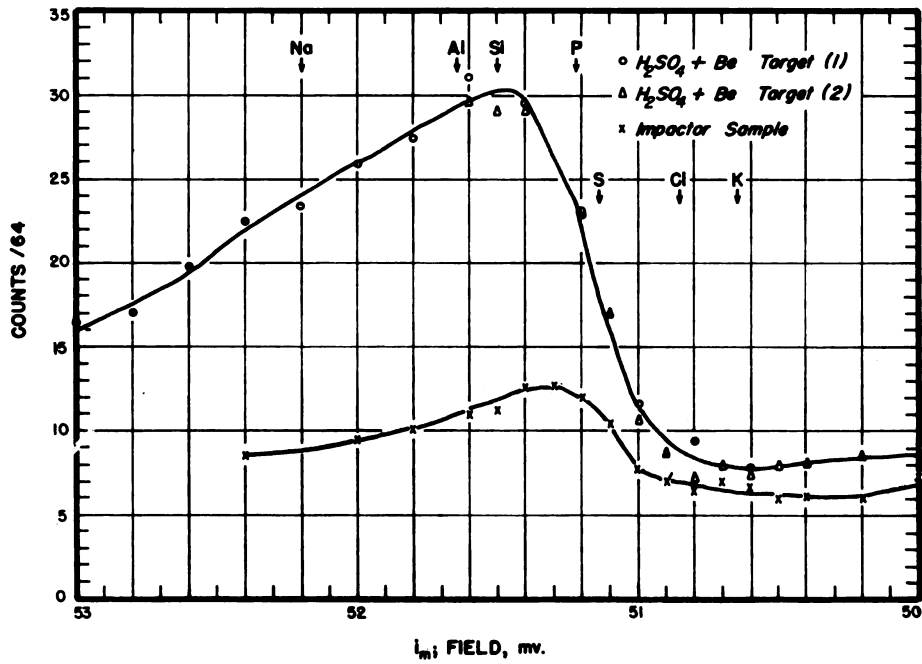


FIG. 25  
Sulfur comparison—proton bombardment

sponds to a magnet setting of 48.5 mv. Since all the elastically scattered protons are scattered by atoms of finite mass, they will all have less energy than this. The energy of protons scattered from the beryllium target corresponds to a magnet setting of 59.0 mv., so the entire atomic scale heavier than beryllium will lie between 48.5 and 59.0 mv. The heavy elements will be crowded into one end of this scale, but since there are not very many heavy elements likely to be found in significant concentration in the open atmosphere, a single peak at this end of the scale, such as was found, is not too difficult to assign.

Figure 24 shows the full scale, run both on the smog sample and on a clean area of the same piece of beryllium, away from the impactor sample. The four peaks are labeled with the element to which they are assigned. The identification of the carbon and oxygen peaks is absolutely certain, since the separation between elements of such low atomic weight is quite large. The sulfur peak was confirmed by a comparison run with a target made by treating beryllium metal with  $H_2SO_4$ , and the two curves are shown in Figure 25. A scale at the top shows where all the adjacent elements would fall compared with the standard sulfur peak at 51.12 mv., and even the closest element, phosphorus, is distinctly off the smog curve. The identification of the lead peak is less certain; however the arrow is located at the calculated position of a lead peak, and the agreement is excellent. Only the elements heavier than the rare earths would give a peak in essentially the same place as lead, within the reproducibility and resolution of these curves, and of these only lead seems to have much probability of occurrence.

It should be pointed out that the oxygen and sulfur peaks appear to correspond to "thick targets," and the carbon and lead correspond to "thin targets." Thin targets are thin in energy spread compared to the spectrograph resolution and are located by the center of the peak; thick targets have a large energy spread compared to the resolution and are located by the half-rise point of the front edge to correspond to the thin target scale. This has to do with the theory of experi-

mental "window curves" and will not be explained here in detail.

Both the relative magnitude and the similarity in shapes of the sulfur and oxygen peaks suggest that they are probably combined as  $SO_2$ , and since they appear thick compared with both carbon and lead, this probably means that they have penetrated into the beryllium, just as the  $H_2SO_4$  of the comparison target evidently did. Since no other elements heavier than beryllium were found in significant quantity and since hydrogen would not be shown, it seems most likely that the sulfur was chiefly in the form of sulfuric acid in the atmosphere sampled. Since the integral under the lead peak is only about one-tenth that under sulfur, and lead has 26 times the scattering cross section of sulfur, its atomic concentration was approximately 0.004 times that of sulfur.

Part of the background shown on the comparison curve for clean Be is due to contaminants in the Be and to reaction products, such as deuterons and alpha-particles produced in nuclear reactions between the bombarding protons and the beryllium. Some experiments on carbon and aluminum targets show them to be much cleaner than beryllium, and also it appears practical to observe carbon and oxygen on aluminum, even though the aluminum has greater atomic weight, since the curve runs quite flat on the aluminum plateau, above 51.5 mv.

Some targets with coatings of Aquadag on aluminum foil have been prepared for the impactor, to use as soon as some smog occurs. The impactor is being modified to provide means for moving the slide back and forth continuously during the run to make a uniformly thin target to obtain improved resolution of the peaks. By shortening the jet opening, the impactor can conveniently be used with existing pumps (or with an automobile windshield wiper connection) with the 0.018-inch jet.

The very helpful cooperation of Dr. C. C. Lauritsen at California Institute of Technology in providing the use of the facilities of Kellogg Laboratory and his own time in running these experiments is gratefully acknowledged.

## 5. INTERPRETING SMOG CHAMBER TEST RESULTS

FOR PURPOSES of comparison it is highly desirable that results of subjective tests be capable of being assigned a numerical value. For this purpose a method described by Roth and Swenson (Ref. 15) was employed. In this method the individual subjected to the test is requested to score his response each minute. If

the response is mild, one check is made; two checks are made for a moderate response, and three checks for severe reactions. At the completion of the test, the total number of checks in a column is added and divided by the total number of minutes the test lasted.

Thus a value of one indicates mild irritation for



## 6. SUMMARY OF WEATHER CONDITIONS FOR ALL REPORTED SMOG DAYS, 1946-MAY 31, 1949

TABLE VIII gives a summary of weather conditions as observed on all the days in the period 1946 through May 31, 1949 when smog was reported. In all cases the data have been taken from the records of the U.S. Weather Bureau. The Smog Index and the Inversion Intensity have been calculated (App. 7).

The values of the inversion intensity and the inversion height are based either upon the actual Long Beach radiosonde or upon an average of the San Diego and Santa Maria radiosondes when the Long

Beach sounding was not taken. Checks made when the three soundings were taken have shown this method to give reasonable accuracy under normal conditions. The height of the 700-millibar pressure surface and the value of the 10,000-foot wind were interpolated from the analyzed 700-millibar map. In estimating the probable time of the start of the sea breeze, the shift in the direction of the wind to a direction from south to west, inclusive, was used. Minimum visibility data cover the period 0700-1400 inclusive.

## 7. FORECASTING OF SMOG

IN THE DEVELOPMENT of a smog forecasting system a smog day was considered as a day when people within the Los Angeles area complained of eye irritation. These smog complaints, in order to be recorded as such, had to be reported to the Los Angeles County Air Pollution Board, where records were kept concerning the location of the complainant and the date of the complaint. By using these records as a basis and calling a day "smoggy" when more than a minimum of three complaints were recorded, certain characteristic weather conditions were seen to be typical of a smog day.

While the visibility on a smog day was usually quite low, a smog day was not a foggy day. This was shown rather conclusively by the observations of temperature and relative humidity on the days of reported eye irritation. The temperatures recorded on smog days were usually high, with the daily mean temperature usually above the daily normal temperature. The relative humidity observations on smog days indicated that irritation was accompanied by low relative humidity. The average noon relative humidity in downtown Los Angeles for all the reported smog days was 40 per cent, with only a few values as high as 60 per cent. In addition to high temperature and low humidity, a smog day also showed a low and usually strong inversion with weak surface wind flow. These variables—deviation of mean temperature from normal, noon relative humidity, daily surface wind movement, inversion intensity, and noon visibility—were combined into the SRI Smog Index, which was quite useful in estimating the probability that smog occurred on any certain day.

A further refinement is provided through a close inspection of the recorded hourly visibility observations

taken in downtown Los Angeles. A typical irritation day is characterized by a distinctive pattern of visibility during the morning hours. In the early morning, usually before 8 or 9 o'clock, the visibility begins to improve but then decreases to a very low value between 1000 and 1200, with improving visibility in the afternoon. During this period of decreasing visibility the relative humidity decreases, so that the lowered visibility must be the result of increased pollution and not of the presence of fog. This characteristic pattern of visibility can often be used to distinguish days when there is obvious pollution present from days when all other factors indicate a high probability of smog even though no reports of irritation are recorded.

In addition to the weather conditions on the actual smog day, the complaint data indicated that certain conditions should prevail at least 48 hours prior to the reporting of the actual irritation. These relations have been used in developing an objective smog forecasting method, the details of which follow.

### METHOD FOR FORECASTING SMOG

The objective forecasting of smog involves the problem of forecasting the days when the inversion will be low and relatively strong, the relative humidity low, wind movements small, and the temperature warm. The time interval between the forecast and the predicted occurrence for best utility should be at least 36 to 48 hours. For example, Monday's forecast should be able to predict smog for Wednesday. The method is completely objective in character, so that it may be used with accuracy by personnel untrained in meteorological techniques. All the data which are required for the several calculations are readily available from the local stations of the U.S. Weather Bu-





reau. If the method given here were used by a trained meteorological staff and in conjunction with standard synoptic forecasting procedures, it should be possible to apply the method with increased accuracy over the 48-hour range and possibly extend the range of the forecast to more than 48 hours with no loss in accuracy.

The several parts which make up the forecasting method are logically divided into those based on upper air observations (10,000-foot level, which also include temperature sounding for inversion data) and those based upon surface observations. The following discussion pertains to a description and use of the newly developed forecasting method, together with the results that have been obtained. The method is not in its finished form and is still being refined, but it is believed to represent considerable improvement over methods used in the past.

1. Upper Air Forecasting Rules

As a first consideration it is desirable to have a measure of the strength of the Pacific high-pressure area and of its changing intensity. This is useful because of the area's connection with the inversion in the lower layers in the atmosphere. Conditions at the 700-millibar pressure level (approximately 10,000 feet) have been chosen to represent changes which will be later reflected at the surface level. These conditions are represented by the following equation:

$$Z_1 = (25 + \Delta H) (H - 1000)$$

where

$\Delta H$  = change in height of 700-mb. surface over 48 hr. in units of 10's of feet

H = height of 700-mb. surface in 10's of feet

This expression states in mathematical terms that there is a tendency for smog to develop when there are rapid positive changes in the height of the 700-millibar surface simultaneously with marked deviations from the 10,000-foot level. These same conditions should contribute to the development of the inversion by increasing subsidence<sup>1</sup> in the layers above the inversion. Because of the weak wind pattern usually associated with the high-pressure cell, the weak surface winds needed for smog are a likely result. Figure 27 presents this equation in graphical form. The isopleths of  $Z_1$  on the graph correspond to the critical values of  $Z_1$  which separate "smog" and "no smog" conditions for the indicated months of the year.

The second expression based on upper air observations is:

$$Z_2 = (I - 2) (V_1 + 25)$$

<sup>1</sup>The slow settling or sinking of a mass of air.

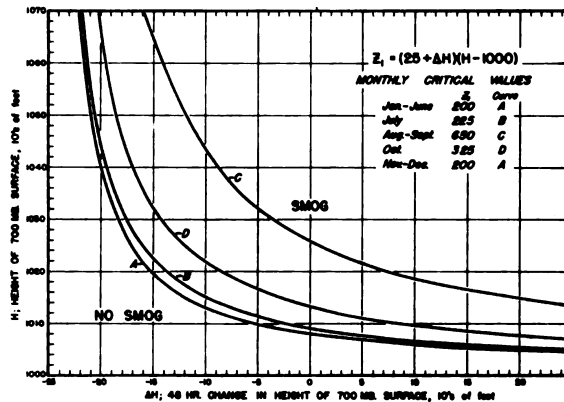


FIG. 27

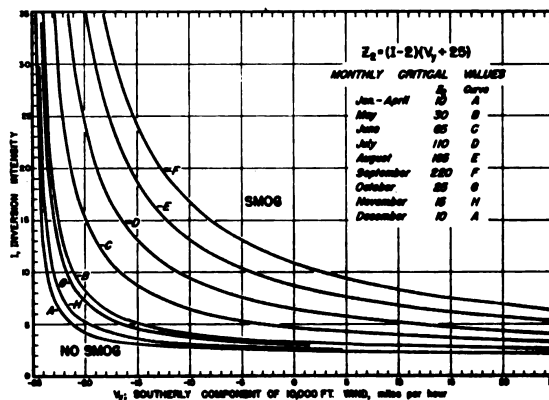


FIG. 28

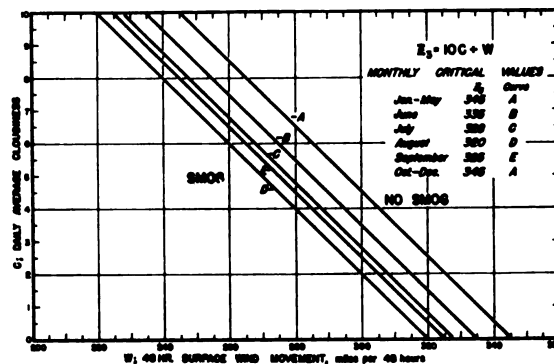


FIG. 29



where  $I$  = inversion intensity (see Section 5 below)

$V_s$  = southerly component of the 700-mb. wind in miles per hour.

This expression indicates that there is a tendency toward smog when the inversion is strong and there is southerly wind at the 10,000-foot level. Thus, an inversion at the surface above which southerly air flow is normally producing convergence<sup>2</sup> will result in a high value for  $Z_2$ . Convergence and southerly flow at this upper level can be expected by considering the vorticity theorem and assuming conservation of vorticity in the flow pattern.<sup>3</sup> Unless this resulting convergence is completely balanced by divergence<sup>4</sup> in layers other than the surface layer beneath the inversion, the inversion can be expected to become considerably more intense. Some of the most intense inversions and the more serious smog days have occurred under conditions of strong southerly winds aloft producing strong convergence above the inversion. Should the convergent flow reach the surface, the inversion itself would be destroyed, giving smog-free conditions and a negative, nonsignificant value for  $Z_2$ . Figure 28 gives this relationship in the form of a graph indicating the critical isopleths of  $Z_2$  for the various months.

## 2. Forecasting Rules Based on Surface Observations

Experience with reported smog days has shown the existence of a period of accumulation before the actual day of occurrence. During this accumulation period the inversion must be present to limit upward diffusion and the winds must be low enough to limit the pollution to the Los Angeles basin area. It has been observed that the action of the surface temperatures and sunshine seems to contribute to the formation, or at least the activity, of the irritants. Whether this is due to photochemical action or flow effects in the atmosphere is not known at this time and is outside the scope of this particular discussion. It is sufficient to note that an improvement in forecasting is possible when the factors in the following equation are taken into account:

$$Z_3 = 10 \text{ (average daily cloudiness) } + 48\text{-hr. surface wind movement}$$

(Average daily cloudiness is taken from the U.S. Weather Bureau observations using a scale of 0-10,

<sup>2</sup>The increase of mass within a given layer of the atmosphere when the winds are such that there is net horizontal inflow of air into the layer.

<sup>3</sup>*Dynamic Meteorology*, Holmboe, Forsythe, Gustin. Chap. XII.

<sup>4</sup>A net outflow of mass across a closed surface bounding a limited volume of the air.

where 0 represents a clear day and 10 is completely overcast.) This formula shows that there is a tendency for smog to be formed when the skies are clear and there is no wind.

The formula serves to separate the days on which either the wind movement was too great to allow the accumulation of the pollution or when the cloud cover was sufficient to reduce the sunshine to a minimum value. This expression resulted from a graphical combination of the variables. Better results were obtained by using data based on cloudiness rather than data representing direct sunshine measurements.

Figure 29 indicates the seasonal changes in critical values of  $Z_3$ .

The inclusion of the values of the daily maximum and minimum temperatures completes the set of forecasting rules. These are given in Table IX.

## 3. Use of Forecasting Rules

There is considerable seasonal variation in the frequency of smog days, but smog days have been recorded in every month of the year. The most favorable season as well as the season of highest frequency for smog is found in the months of August and September.

The expressions given above have been used to make smog forecasts two days in advance by applying the critical values given in Table IX and shown graphically in Figures 27, 28, and 29. The seasonal variations were determined by an examination of the complete list of reported smog days. In addition, where the number of cases warranted it, confidence limits were applied using standard statistical procedures.

The conditions for occurrence of a smog day seem to be critical enough so that should any of the considerations not be satisfied, a no-smog forecast can safely be made. The time interval between the forecast and the occurrence or nonoccurrence of smog is two days in all cases. Thus, the observations taken on a Monday will determine whether a smog will be forecast for the following Wednesday.

A no-smog forecast is made whenever any of the terms except  $Z_3$  are equal to or less than the given value. In the case of  $Z_3$  the value for a nonsmog forecast is equal to or greater than the given value.

## 4. Results of the Forecasting Method

Test forecasting by this method has been made on the period from July 1946 through December 1948. It was necessary to use this period because it is the time during which records have been kept concerning

TABLE IX.—CRITICAL VALUES FOR SMOG FORECASTS

	$Z_1$ (25+ΔH) (H-1000)	$Z_2$ (I-2) (V <sub>y</sub> +25)	$Z_3$ 10 (av. cloud) + 48 hr. wind	T Max.	T Min.
January .....	200	10	345	60° F.	40° F.
February .....	200	10	345	61	41
March .....	200	10	345	63	42
April .....	200	10	345	65	44
May .....	200	30	345	69	49
June .....	200	65	335	75	55
July .....	225	110	328	77	56
August .....	650	165	320	78	55
September .....	650	220	325	78	54
October .....	325	25	345	69	48
November .....	200	15	345	64	44
December .....	200	10	345	60	42

the irritation effects of smog. Over this length of time 84 per cent of the reported smog days fell on days when smog was forecast. Of the days for which a forecast of smog was made, 53 per cent of the days could be classified as smog days by the method given in the discussion of what constitutes a smog day. This is not a poor record in view of the fact that identifying a day as a smog day by this method is quite restricted in the type of days which may be classed as probable smog days, other than the actual reported irritation days. As even more information is gained about the mechanics of smog, the forecasts and their verifications can become more restrictive and, until it is possible to give a more complete definition of actual smog days, it will be necessary to tolerate a relatively large proportion of no-smog days on the days when smog is forecast.

The accuracy of no-smog forecasts is 96 per cent and the over-all accuracy of the forecasting method including both smog and no-smog forecasts is 85 per cent.

##### 5. Calculation of Inversion Intensity and the Stanford Research Institute Smog Index

The measure of the temperature inversion as it pertains to the smog problem is obtained by calculating the inversion intensity, I. The formula for inversion intensity is

$$I = \frac{(\Delta\theta)^2}{3 + Z\Delta Z}$$

where

$\Delta\theta$  = change in potential temperature through the inversion layer in degrees Kelvin (Potential temperature is defined by Poisson's equation:

$$\theta = T \left( \frac{100}{P} \right)^{0.286}$$

T = degrees K

P = pressure in centibars)

Z = height of inversion base in 100's of meters

$\Delta Z$  = thickness of inversion layer in 100's of meters

When Z is less than 150 meters (1.50 in formula) it is arbitrarily set equal to 150 meters and then both  $\Delta\theta$  and  $\Delta Z$  are measured from the point Z=150 meters.

The calculation of the Smog Index is given by the formula

$$S = \frac{10(T+10)}{R W} \sqrt{\frac{I}{V}}$$

where

T = deviation in degrees F of daily mean temperature from normal mean temperature for that particular date

R = noon relative humidity

W = total 24-hour wind movement in miles

I = inversion intensity (see above)

V = noon visibility in miles

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