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THOMPSON, Robert Nathan, 1923-
VEHICLE TIRE RUBBER AS AN AIR
POLLUTANT.

The University of Oklahoma, Ph.D., 1966
Health Sciences, public health

University Microfilms, Inc., Ann Arbor, Michigan

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THE UNIVERSITY OF OKLAHOMA

GRADUATE COLLEGE

VEHICLE TIRE RUBBER AS AN AIR POLLUTANT

A DISSERTATION

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the

degree of

DOCTOR OF PHILOSOPHY

BY

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Oklahoma City, Oklahoma

1966

VEHICLE TIRE RUBBER AS AN AIR POLLUTANT

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ACKNOWLEDGEMENTS

I wish to express my sincere gratitude to Dr. Carl A. Nau who served as my major professor and Chairman of my Advisory Committee. His guidance, encouragement, and resolute confidence in me provided the stimulus to pursue and complete this study.

I am also grateful to the other members of my committee--Professor W. W. Schottstaedt, Professor G. W. Reid, Professor M. J. Wilcomb, and Professor C. H. Lawrence for their counselling and assistance throughout my entire graduate program.

To Professor C. H. Lawrence must go thanks for his advice and help in editing this manuscript.

My gratitude is extended to two of my colleagues, Mr. E. L. Lichti and Mr. W. L. Sowell, for their technical assistance.

To my friend Mr. Bill Stevenson go my sincere thanks for services given so generously.

A special word of appreciation is due Mrs. Madeline Farmer who typed the manuscript.

Finally, to my wife Joanna, whose patience, understanding and sacrifice sustained me throughout all of my academic endeavors, go my deepest thanks and gratitude.

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VEHICLE TIRE RUBBER AS AN AIR POLLUTANT

CHAPTER I

INTRODUCTION AND LITERATURE REVIEW

Air pollution is a direct cause of lung cancer! This is a dramatic statement and would be a startling revelation could it be substantiated. To irrevocably state that any one of the pulmonary diseases, e.g., lung cancer, chronic bronchitis, pulmonary fibrosis, or emphysema is a direct result of the presence in our outdoor atmosphere of deleterious substances would be equally revealing and alarming. And yet a similar pronouncement indicting cigarette smoking as one certain cause of lung cancer and likely cause of numerous other disease entities was dramatically made in the report of the Surgeon General's Committee on Smoking and Health issued in January 1964 (1).

> In view of the continuing and mounting evidence from many sources, it is the judgement of the Committee that cigarette smoking contributes substantially to mortality from certain specific diseases and to the overall death rate.

This courageous statement was not a careless one nor was it hastily made. It was the culmination of a vast epidemiologic investigation which compiled an irrefutable array of evidence to establish an association between cigarette smoking and substantially higher death rates. Only after many years of investigation and the accumulation of extensive information from prospective and retrospective studies bolstered by a mass of clinical,

pathological, and experimental data were investigators prepared to openly denounce cigarette smoking as injurious to health.

As it did in the case of smoking and health the evidence to support a positive involvement of air pollution with the incidence of lung cancer is steadily mounting. In contrast, however, the likelihood of isolating any single polluting substance as the sole causative agent is very remote. The only well-defined cases in which identified air contaminants have been shown to bear a direct relationship to human health were in the often referred to and documented air pollution "episodes": the Meuse Valley, Belgium episode of December, 1930 to which 63 deaths and several hundred illnesses were attributed (2); the Donora, Pennsylvania incident which occurred in October, 1948 and accounted for 20 deaths and 7,000 illnesses. (3); and the London, England episode of December, 1952 for which there has been adduced valid statistical evidence of 4,000 deaths and a large, but uncomputed, increase in morbidity (4). In all of these acute incidents the exogenous environmental factors, i.e., biological, geographical and meteorological, have been fairly well established. In all three, concentrations of sulfur compounds produced in the process of industrial operations or residential heating became excessive due to the absence of natural ventilation in or about a river valley. This stagnant condition in each case was precipitated by a persisting temperature inversion and accompanying fog which very effectively "capped" the region and prevented dispersion of the pollutants. It should be pointed out that the morbidity and mortality data in these major disasters reveal that, in general, those persons with previously existing illnesses and the aged accounted for the majority affected.

It is not these spectacular disasters that should cause the greatest concern, though they have focused attention on an environmental health problem and provided a "point of departure" in man's attempt to define the relationship between air pollution and human health. Of more immediate interest are the chronic effects or the extent of health impairment from continued exposure to usual levels of contamination in our urban environments. The pathogenetic effects of long term exposure to the prevailing every day concentrations of man-generated gaseous and particulate emissions must be determined. Very little is known about the toxicity of new substances generated by synergistic or antagonistic interactions of these materials following dispersion into the atmosphere. The mechanisms by which these agents react to initiate disease in man are either vague or unknown and must be determined in order to establish a direct etiological association between air pollution and disease.

The increase in the incidence of lung cancer is world wide. It is an insidious disease which proves fatal to 95 per cent of its victims. Though environmental factors are recognized as contributors to its high incidence, no evidence exists for an exclusive environmental source acting in its pathogenesis. However, there already exists, in the opinion of many experts, sufficient epidemiologic and experimental data to substantially incriminate polluted urban air as a prime environmental factor. In his chapter on Effects of Air Pollution on Humans (Air Pollution, Vol. 1 by Stern) Dr. John R. Goldsmith (5) states: "In reviewing reported studies, it is clear that for large heterogeneous populations,...persons exposed to community air pollution have from 1.3 to two times as much lung cancer as comparable groups of nonexposed persons."

Mancuso (6) stated at the National Conference on Air Pollution in 1958: "I believe that air pollution represents a highly probable and important factor in the excess of lung cancer in urban areas...."

Stocks and Campbell (7) co-investigators in England have estimated that 50 per cent of the lung cancer deaths in the Liverpool area result from smoking and approximately 35 per cent from air pollution.

Known and suspected carcinogens have been detected and even quantitated in the air of essentially all cities in which they were sought. They may be divided into two distinct classes: (1) organic carcinogens of the polycyclic aromatic hydrocarbon type, and (2) carcinogenic metallic compounds such as arsenicals, chromium, nickel, etc. Of these the complex polycyclic organics are the most severely incriminated and have received the most intensive investigation very probably due to their ubiquity in community air. Sawicki et al. (8) reported finding polycyclic aromatic hydrocarbons in the atmosphere of fourteen widely separated American cities and found that concentrations were higher in winter than in summer. These investigators listed, in the same publication, 33 polycyclic compounds which have been identified in community air. They concluded that analysis of any one hydrocarbon except coronene may indicate approximately the total amount of other hydrocarbons present.

Waller (9) detected benzpyrene in smoke drawn from the air of eight English towns. He observed, as have American investigators, that the concentration generally rises during the winter months. He concluded that a large proportion seems to come from domestic fires.

Shore and Katz (10) isolated five polycyclic aromatic hydrocarbons from airborne particulates sampled in Windsor, Ontario. Dubois, Corkery

and Monkman (11) reported the detection of eight in the air of Ottawa, Ontario, while Moore and Katz (12) found nine in the atmosphere of Montreal, Quebec. D'Ambrosio et al. (13) have made similar determinations of 3,4-benzpyrene content in the air of Milan, Italy.

The carcinogenic chemical levels found in cities of the United States in the studies by Sawicki et al. (8) and Hueper et al. (14) demonstrated no direct correlation with lung cancer rates in these cities. However, a recent study by Stocks (15) in Liverpool, England demonstrated a statistically significant correlation at the 0.05 confidence level between the incidence of lung cancer and 1,12-benzperylene. In the case of 3,4-benzpyrene correlations were shown but were not quite significant at the stated confidence level.

The most universally distributed carcinogens in the atmosphere are those produced from the combustion or pyrolysis of carbonaceous material at high temperatures. Carbon black (soot), a recognized host for polycyclic aromatic hydrocarbons, is a major component of the smoke produced when solid, liquid, and gaseous fossil fuels are burned. In the past, and still in many countries, coal is the major source of fuel for domestic and industrial heating and as such it represents the primary source of the polycyclic hydrocarbons. The 3,4-benzpyrene determinations made by Waller (9) in English towns credited coal burning in residential heaters as the most probable source. In contrast the same or similar organic compounds detected in the United States come from myriad sources which can be broadly categorized as industrial, domestic, and vehicular. It is the latter which is causing increasing concern because of the ever expanding mechanization of the population of this country. Begeman (16) has reported that

the automobile contributes from 2 to 10 per cent of the total benzpyrene content in the air over cities.

Badger et al. (11) is attempting to ascertain the mechanism by which benzpyrene and the other polycyclic hydrocarbons are formed. He has demonstrated that in the pyrolysis of a complex organic molecule, a chemical bond is broken, whereupon either of the resultant fragments or free radicals may attack another molecule of the original compound. Cyclization occurs, and by way of various intermediates, benzpyrene and/or other carcinogens may result. He is able to predict with considerable accuracy where the rupture is likely to occur and what compounds are likely to be formed.

McDermott (18) has stated: "The automobile makes a further contribution to air pollution in the form of highly pulverized rubber and asphalt, generated by abrasion of tires upon streets.... This aspect of the situation has not been studied in much detail, but there is reason to believe that contamination from rubber and asphalt is appreciable."

Falk, Kotin, and Miller (19) reported that the primary source of the ubiquitous 3,4-benzpyrene is the incomplete combustion of solid, liquid, and gaseous fuels and that a secondary source is rubber tire dust. In this same publication they state: "Within the recent past there has been an increasing awareness that meaningful amounts of benzpyrene are liberated into the air incidental to the wear and tear and normal degradation of rubber tires." In their study benzpyrene was liberated rapidly from rubber tire dust by an aqueous protein solution such as is encountered in the lung.

In an earlier study Falk et al. (20) extracted portions of tire tread

rubber from an old automobile tire with benzene and identified a number of polycyclic aromatic hydrocarbons present in the extract. Some were known carcinogens and others were suspect. Table 1 gives a summary of the compounds detected by ultra-violet absorption spectroscopy and indicates their relative carcinogenicity.

TABLE 1

CARCINOGENIC ACTIVITY OF POLYCYCLIC AROMATIC HYDROCARBONS FOUND IN VEHICLE TIRE RUBBER (20)

COMPOUND	ACTIVITY
1,2-benzpyrene	very weak
3,4-benzpyrene	strong[1]
1,2-benzanthracene	weak
1,12-benzperylene	very weak
chrysene	weak
pyrene	negative
coronene	negative
anthanthrene	negative

[1] 3,4-benzpyrene is the strongest as well as the most ubiquitous of the carcinogens.

That American investigators are not alone in their inclusion of the vehicle tire as a potential source of an additional particulate pollutant, is evidenced in the following statement by Dr. Chauncey Leake (21): "It is my impression, based on a visit to Leningrad and Moscow in 1956, that Russian scientists place great emphasis on "smog" as a possible factor in

the rising incidence of lung cancer in Russian big cities, and that they have indicated that they find rubber tire tread dust in the "smog" of their big cities."

The detection of carcinogens in processed rubber led investigators to a consideration of its localization in the rubber compound. No detailed or exhaustive experiments were required to discover the most likely culprit. A literature search gave the clue. The modern automobile tire is a mixture of natural and synthetic rubbers in varying proportions whose properties are altered or modified to improve its service capabilities by numerous additives. Basic to all tire formulations is the inclusion of considerable carbon black as a reinforcing agent. It not only extends the rubber, but in contrast to other non-carbon pigments, greatly improves physical properties, particularly resistance to abrasion. The mechanism of rubber reinforcement is obscure but practical demonstration of the phenomenon is strikingly apparent in terms of tire roadwear. The average 6.00 x 16 passenger car tire contains about 4 pounds of carbon black. Ninety per cent of the carbon black produced is used in the rubber industry with the major tonnage going into rubber tires.

Carbon black (soot), in early accounts, was found to possess the capability of inducing skin cancer among chimney sweeps. Scrotal and face cancers were reported in 1775 by Pott (22) as not uncommon among the children whose task it was to sweep the soot laden English chimneys of that era. However, some confusion surrounds the attempts to incriminate carbon black as a potential occupational cancer hazard in modern industry.

Passey (23) in 1922 produced skin cancer experimentally with extracts of soot. He found that those extracts free of acidic and phenolic com-

pounds were the most potent.

Von Haam (24) produced epitheliomas in test animals with benzene extracts of carbon blacks used in the rubber industry. Von Haam and Malette (25) in 1952 identified carcinogens in extracts of carbon black and suggested that their activity would probably be insignificant in the original carbon blacks because the isolated substances would be not only too low in concentration, but also firmly adsorbed.

Benzene extracts of carbon blacks were shown by Falk and Steiner (26) (27) to contain small quantities of 3,4-benzpyrene, 1,2-benzpyrene, and five other related aromatic hydrocarbons. They found some correlation between amounts of extractable aromatic hydrocarbons and average particle diameter of the carbon blacks and proposed that the difference in extractable hydrocarbons from the blacks may be explained by the phenomenon of adsorption.

According to Falk, Kotin and Miller (19) (28) all aromatic polycyclic hydrocarbons may be eluted from soot, usually in an hour or two, after contact with plasma or other protein, and are then capable of direct epithelial cell entry and presumably of biologic activity.

In contrast to the foregoing evidence Ingalls (29) in epidemiological studies, was unable to demonstrate an increased cancer risk among carbon black workers. His conclusions were criticized by Heuper (30) because only 79 of the 677 workers evaluated had been employed for 10 years or more in that industry. Heuper further pointed out that known occupational lung cancers have an average latent period of over 10 years so Ingall's conclusions were actually based on 79 living and active workers.

Nau et al. (31) reported that the feeding of whole carbon black to

mice produced no changes from the normal. In a later study (32) they reported that carbon blacks as manufactured and used produced no observable harmful effects following skin contact. They also concluded that the carbon blacks had adsorbed a component which, when free, and applied to the skin of mice, produces skin cancer but in the adsorbed state was ineffective as a carcinogen. In a still later investigation Nau et al. (33) published results of carbon black inhalation studies. Experimental animals were exposed by inhalation for prolonged periods of time to channel or furnace blacks with no effects other than an accumulation of the dusts in the pulmonary system.

The apparent disagreement that exists among investigators has been explained somewhat similarly and separately by Nau and Von Haam who point out that carbon blacks, regardless of their method of manufacture, have remarkable adsorptive capacities which enable them to sequester the polycyclic aromatic hydrocarbons and render them wholly or partially ineffectual as cancer producers. Thus, they remain inoccuous until eluted by a substance capable of breaking the strong chemi-sorption bonds. Such elution was reported to occur by Falk et al. (34) when it was found that carcinogens disappeared from the soot in human lungs.

Falk et al. (35) in 1964 postulated that results of earlier experimenters may have been "confounded" somewhat by the fact that carbon blacks produced by different processes will contain different types and quantities of known and suspected carcinogens partly due to particle size differences but also due to variations in the manufacturing process.

The motoring public is a very large proportion of the American populace. Three out of four families each own at least one motor vehicle and

it is estimated that by 1970 there will be three automobiles for every two that were in use in 1960. In 1963, over 7-1/2 million new automobile sales were reported in this country (36). These, plus the many millions of "used" automobiles, trucks, and buses combined to transport Americans and their commodities over 800 billion miles of urban and rural roads during that year (37).

The Rubber Manufacturers Association reported in 1964 that rubber tire shipments for all classes of vehicles (cars, buses, trucks, etc.) totaled 141.9 million units, over 1.5 times the production in 1950 (38). Rubber tire companies expect shipments of new replacement automobile, truck, and bus tires to exceed 103 million units in 1965.

Millions of rubber tires are being consumed in whole or in part each year. The consumption process is one of varying rates of degradation dependent upon the service applications. Characteristics of the degradation products are also a function of service conditions. Though some of the tire tread is undoubtedly volatilized at the elevated temperatures associated with high speed driving and accelerations and decelerations, rubber dusts are formed in the wear process.

It can be demonstrated that a considerable proportion of "tire dust" produced in normal wear is composed of particles within the respirable size range. The tire treads producing these dusts contain 30 to 50 parts by weight of carbon black per 100 parts by weight of rubber (39).

It is not presumptious to postulate that the rubber tired vehicles which abound in the United States and which will conceivably only multiply in the future are actually contributing to a greater degree to the total organic carcinogen level in the atmosphere than might appear at first

glance. Some of the benzene soluble organic matter reported in air pollution measurements of the National Air Sampling Network (40) is quite probably traceable to vehicle tires.

The literature reveals that no previous attempts have been made to quantitate or qualitate, or in any way characterize vehicle tire dust. Its air pollution potential has been alluded to but slightly and only superficial evaluations have been made to implicate it.

CHAPTER II

PURPOSE AND SCOPE

This study was conceived as an important and necessary corollary to an investigation in progress at the Institute of Environmental Health in the University of Oklahoma Medical Center in which the relationship between rubber dust and health is sought. The study, initiated in January, 1962, is entitled "Occupational Health Hazards of Rubber Dust". Its specific aims are to determine if rubber dust prepared from a usual commercial rubber formulation and deposited by inhalation in significant amount in the lungs of various species of animals can be affected by the inhalation of the exhaust gases of automobiles, thus causing elution of polycyclic aromatic hydrocarbons with a resulting increase in tumor formation. It further seeks to determine if these dusts are significant occupational health hazards from the point of view of air pollution and carcinogenesis.

In the initial stages of the Institute study it became quite obvious that the production of a suitable dust in quantities sufficient for a protracted animal exposure experiment presented a formidable problem. Discussions with representatives of the tire industry revealed that there was some uncertainty about the nature of tire degradation products. Some speculated that the elevated temperatures existing at the tire-roadway contact surface are such that the rubber hydrocarbons and organic addi-

tives volatilize and enter the atmosphere in a gaseous form leaving behind only carbon black and a few inorganics. This theory has some merit as rubber oxidizes rapidly when heated in air at temperatures much above 120°C. Temperatures greater than 100°C are not uncommon in high speed running. Powell (41) has recorded temperatures up to 145°C after 9 minutes running at 102 mph. However, it seems reasonable to presume that the great majority of in-service tire wear occurs at lower temperatures, and that a sizable proportion of the tire tread is degraded in a particulate rubber form.

Other suggest that tire dust, if it exists, should have a particle size distribution not conducive to indefinite suspension in the atmosphere. But this is only speculation and no attempt has been made to substantiate or disprove the occurrence of rubber tire dust or in any manner define its features.

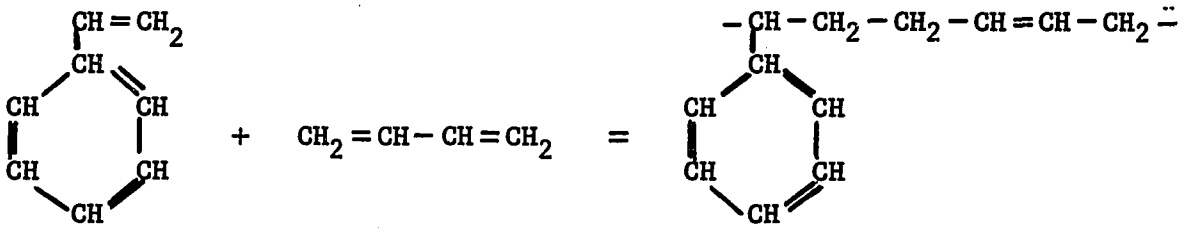
The search for a natural or manufactured tire dust containing sufficient particles in the respirable size range to sustain a chamber study, and the uncertainty surrounding the existence of respirable tire dust in the atmosphere prompted this study. Its purpose is to investigate the role of vehicle tire dust as a potential contribution to the particulate air pollution load in our atmosphere; to physically and chemically characterize the material involved; to develop an instrumental technique for qualitative analysis of that material believed to be contained in an airborne sample; and to establish a basis for its instrumental quantitation.

CHAPTER III

MATERIALS

Rubber Tires

The great majority of the vehicle tires manufactured in the United States contain synthetic rubber as well as natural rubber, each in proportions dependent upon the intended application of the tire. The most commonly used artificial rubber is known as general purpose synthetic. It is the product formed when styrene, a clear volatile liquid, is co-polymerized with butadiene, a gas at room temperature (Figure 1).



Styrene Butadiene Segment of Co-polymer Chain

Figure 1. Co-polymerization of styrene and butadiene

General purpose synthetic is usually designated as Buna S, GR-S or SBR.

Passenger car tires may contain 70 to 80 per cent SBR and small truck tires 60 to 70 per cent. In the case of large truck tires where the amount of SBR which can be used is controlled by heat build-up and tread cracking, the SBR content may be as low as 10 to 20 per cent. It is im-

portant to emphasize that SBR is so prevalent an ingredient of American rubber tires that any composite sample of abraded tire rubber, collected in the vicinity of an American roadway will most certainly contain SBR.

American tire rubber formulations vary considerably from manufacturer to manufacturer and precise ingredients are not generally publicized for obvious reasons. The component parts of the tire, i.e., the bead, the casing, the sidewalls, and the tread are compounded differently according to their assigned tasks. One typical formulation is given in Table 2.

TABLE 2

TIRE FORMULATION

Component		Parts by Weight
Rubber (Synthetic and/or natural)		100
SRF (Semi-reinforcing furnace) carbon black		15
EPC (Easy-processing channel) carbon black		20
Zinc oxide		5
Stearic acid		2
Softener		5
Antioxidant		1
Sulfur	Vulcanization	2.8
Primary Accelerator	Vulcanization	0.75
Secondary Accelerator	Vulcanization	0.15

The data in Table 2 show that the one dominant ingredient in the formulation other than rubber is carbon black. This is true of all rubber

tire formulae. Approximately one pound of carbon black is used for every two pounds of rubber, either natural or synthetic. Carbon black, the most widely-used reinforcing material, is produced in a variety of grades which differ in their particle size, in the quantities of non-carbon matter they contain, and in the extent to which their particles tend to agglomerate in chain-like structures.

Carbon blacks are manufactured by either the partial combustion or thermal decomposition of gaseous or liquid hydrocarbons. Their method of manufacture is the basis for their classification.

Channel blacks are produced when small natural gas flames are permitted to impinge on iron channels. The hard-processing, medium-processing, and easy-processing channel blacks (HPC, MPC and EPC) are the most important rubber-grade impingement blacks.

Furnace blacks are made by the combustion of natural gas, oil, or both in furnaces in a controlled air supply. All grades of furnace blacks can be used for rubber compounding.

When maximum reinforcement is essential, as in tire treads, one of the following grades of carbon black is usually used (42):

SAF Super-abrasion furnace

HAF High-abrasion furnace

HPC Hard processing channel

MPC Medium processing channel

EPC Easy processing channel

If the reinforcement requirements are less stringent, if abrasion resistance is secondary to tear strength, if high resilience is required, and if low heat build-up is desired, one of the following grades of carbon

black is preferred (42):

FEF Fast-extrusion furnace

FF Fine furnace

GPF General-purpose furnace

HMF High modulus furnace

SRF Semi-reinforcing furnace

The other materials listed in Table 2 function as activators, cure-rate controllers, softeners, antioxidants, and vulcanizing agents. Considerable variation is exercised among compounders in their selection of materials used to serve these functions.

Vehicle Tire and Roadway Dusts

Samples of rubber tire dust generated in the laboratory were contrasted to "true" and "simulated" roadway dusts in order to describe their physical and chemical characteristics, and to develop reliable analytical techniques for proving the existence of particulate rubber in the environment. The laboratory dust, made solely of vehicle tire rubber was designated for animal exposure studies. The "true" roadway samples were obtained from the Holland and Lincoln Tunnels in New York and from a parking garage in Ft. Worth, Texas. In all three locations traffic volumes were high and, to some extent, contained in a limited environment. "Simulated" roadway dusts were produced by the National Bureau of Standards in its tire testing equipment.

Holland Tunnel (H) and Lincoln (L) Tunnel Dusts

The Tunnels and Bridges Department of the Port of New York Authority provided material collected from the exhaust ducts at the bottom of grades

in the Holland and Lincoln Tunnels. The samples were collected by sweeping the floor surfaces of the ducts where the material accumulates at the rate of approximately 0.25 inch for each four years of operation.

The tunnel tubes are in operation 24 hours per day throughout the year. Traffic flow varies from a low of several hundred vehicles per hour during the early morning hours to approximately 2,700 vehicles per hour during peak hours. The estimated average daily volume of traffic using the tubes of the Holland and Lincoln tunnels from which the dust samples were collected is 29,900 and 29,300 vehicles, respectively.

Pavement in the immediate vicinity of the portals of both tunnels consists of either asphalt, concrete or paving brick. The Lincoln Tunnel sample was collected near the foot of the downgrade serving New Jersey-bound traffic, while the other was taken from the foot of the upgrade in the Holland Tunnel tube serving New York-bound traffic. Truck traffic is relatively high at both of these locations.

National Bureau of Standards (NBS) Tire Tester Roadway Dust

The National Bureau of Standards conceived, developed, and operated for a number of years a tire testing machine to study the durability of truck and automobile tires under varying roadway, loading and contact conditions. This device is used, as are its counterparts in industry, to study or test tires for tread life, cut growth, operating temperatures, and flexing fatigue. Richey, Mandel, and Stiehler (43) have reported on its development and application from its inception in October, 1951.

The tester produces a considerable quantity of solid abraded material, approximately 80 pounds per 18 tires or 4.5 pounds per tire tested. About

50 per cent of the material produced is recovered. The tester is loaded with 18 tires, 15 automobile and 3 truck tires for each test run.

This device was proposed as an ideal source of rubber tire dust for the Institute's inhalation study until it was revealed that its roadway is dusted while in operation to simulate actual service conditions and to prevent "gumming" of the track surface. The dust of choice is hydrated alumina, all of which is finer than 2 μ, 80 per cent being finer than 1 μ. Therefore, all of the dust produced is actually a two component material consisting of hydrated aluminum oxides ($Al_2O_3 \cdot 3\ H_2O$ or $Al\ (OH)_3$) and tire wear products. The inadvisability of using such a two phase material is obvious. Toxicity of aluminum compounds is still a controversial subject, and the physiological effects of respired rubber are yet to be determined. Furthermore, the possibility of interactions always exists in a heterogeneous system.

Some consideration was given to the feasibility of separating the rubber tire dust from the alumina but all attempts at deagglomeration failed or gave less than adequate results. The alumina particles clung tenaciously to the surfaces or filled the interstices of the rubber particles.

Although this dust was rejected as unsuitable for a chamber investigation it was retained for this study. It is a roadway dust containing only one adulterative material other than the tire products and as such provides an excellent material for sizing analyses and confirmation of the qualitative technique for tire rubber developed in this study.

Parking Garage (PG) Roadway Dust

Samples of roadway dust were collected from a four-story, enclosed

parking garage located in the business district of Fort Worth, Texas. This garage is in operation 24 hours per day, 7 days per week, serving only automobile traffic. Concrete ramps, which provide access between floors, are vacuumed periodically. There is no exhaust system in the building so the particulate load is retained to settle out on the interior surfaces. The material used in this study was taken from the vacuum cleaner bag.

Animal Exposure Chamber (CH) Dust

The search for a supply of vehicle tire dust suitable for the animal inhalation study first centered around tire recapping operations. Local firms use either steel clawed disc abraders or high speed wire brushes to buff tires before new treads are applied. The latter method produced the finest material but microscopic sizing revealed that all of it exceeded 50 μ in diameter. Further reduction to suitable size was found to be possible by freezing the finest fractions in liquid nitrogen (-196°C) and then grinding with mortar and pestle. Though the results were satisfactory, the method was hardly practical for production of the 5 pounds of dust required for each month of chamber operation.

The problem was resolved when it was found that the Sturtevant Micronizer, a fluid energy mill which grinds and classifies, could easily reduce recappers' grindings which had been frozen in liquid nitrogen. In this device, particles suspended in air and moving in high rotational velocity, fracture as they collide with one another. They are then classified in a cyclone separation chamber incorporated in the mill. Tire dust for chamber operation is a mixture of truck and automobile tire rubber, though predominantly the latter.

CHAPTER IV

CHARACTERIZATION OF VEHICLE TIRE AND ROADWAY DUSTS

Introduction

It is not the purpose of this portion of the investigation to establish a relationship between inhaled vehicle tire dust and subsequent physiological alterations. Microscopic sizing data, particle size distributions, and spectrographic analyses are presented to provide some characterization of the material studied and to attempt a definition of the respirable portion of each.

Brown, Cook, Ney, and Hatch (44) have made an extensive study of the significance of particle size with respect to respiratory retention of dust. Their conclusions are pertinent to any study of this kind and are presented as follows:

"1. Over-all respiratory retention is essentially complete for particles above 5 μ. It decreases with size to a minimum of about 24 per cent for approximately 0.25 μ particles and then increases again for submicroscopic particles.

2. Filtering efficiency of the nasal passages is also practically 100 per cent for particles larger than 5 μ and decreases systematically with size, reaching zero, however, for particles of finite size of about 1 μ.

3. Depth of penetration before deposition increases with decreasing

size. For those particles, larger than 1 μ which escape trapping in the upper respiratory tract, alveolar retention is complete. Smaller particles are retained in decreasing amounts but, however small the retention may be, practically all the deposition takes place in the alveoli.

4. Thus, there is an optimum particle size having the highest probabilty of alveolar deposition. This is about 1 μ. Smaller particles, down to 0.25 μ, have approximately the same probability of being retained in the alveoli as those from 1 to 5 μ. Sub-microscopic particles are deposited in the alveoli in increasing amounts as size is further reduced and, theoretically, retention approaches a maximum value corresponding to the percentage of tidal air which reaches the alveoli.
5. The relationship between particle size and penetration, and deposition of dust changes with the respiratory pattern. Retention increases with decreasing respiratory frequency. The effect is greatest for particles between 1 and 5 μ for which there is a much greater proportionate increase in alveolar deposition than in the overall retention as breathing rate decreases. The respiratory pattern has no significant effect upon the deposition of particles smaller than 1 μ."

These conclusions, which are based partially on theory and partially on experimental data, indicate a very definite relationship between particle size and degree of deposition in the lung. If it is assumed that lung damage is related to deposition of dust in the lung, it follows that particle size determinations are essential in the evaluation of any dust

hazard.

Particle Size Distributions

The Log-normal distribution is generally applied to sizes of particles obtained by breakage from large fragments of matter. This distribution is a transformation of the normal probability curve. It was adopted for the determination of particle size parameters when it was found that distribution curves of finely divided materials generally assumed an asymmetrical or "skewed" configuration and therefore the normal probability equation could not be applied since it required symmetry about a vertical axis. When the logarithms of sizes are substituted for the sizes themselves the "skewed" frequency curves, more often than not, are transformed into the familiar Gaussian normal probability curve.

Two parameters of the log-normal curve, the geometric mean and the geometric standard deviation, rigidly define that curve and also determine completely all the average diameters (45) (46). They can be determined mathematically from the particle sizing data as follows:

$$\text{Log } M_g = \text{Mean of logarithms} = \frac{\sum_i (f_i \log X_i)}{\Sigma f_i}$$

and

$$\text{Log } \sigma_g = \text{Standard deviation of logarithms} = \sqrt{\frac{\sum_i f_i (\log X_i - \log M_g)^2}{\sum_i f_i}}$$

where M_g = Geometric mean

f_i = Frequency of observations

X_i = Observation

σ_g = Geometric standard deviation

These calculations involve considerable labor which can be averted by a graphical solution in which the percentage of particles below a stated size is plotted against that size on a logarithmic-probability grid. On this paper the summation curve obtained by integration of the logarithmic size-frequency curve plots as a straight line from which the geometric mean can be read directly and the geometric standard deviation can be easily computed.

The geometric mean is the 50 per cent size and the geometric standard deviation is determined as follows:

$$\sigma_g = \frac{84.13\% \text{ size}}{50\% \text{ size}} = \frac{50\% \text{ size}}{15.87\% \text{ size}}$$

Utilizing M_g and σ_g, conversions to the more useful weight and area distributions are then easily performed as follows:

$$\text{Log } M_g' = \text{Log } M_g + 6.9078 \log^2 \sigma_g$$

and

$$\text{Log } M_{g_a} = \text{Log } M_g + 2.3026 \log^2 \sigma_g$$

where M_g' = Weight mean geometric diameter

M_{g_a} = Area mean geometric diameter

These distributions may be plotted on the same graph with the particle count distribution, all appearing as parallel lines.

Curve fitting on log-probability paper has a serious disadvantage. Each of the points plotted and used to establish visually a "line of best fit" has a different degree of reliability associated with it. It is impossible to judge the magnitude of this reliability when weighting data points for a best line. Therefore, parameters obtained from a visually

fitted line can easily be in error if the investigator puts credence in the data points lying outside the 1 per cent and 99 per cent limits and does not confine his inspection of the remaining data to those lying nearest the 50 per cent level.

In many instances the log-normal distribution does not "ideally" fit particle size distributions, but a poor correlation does not invalidate particle size measurements. Minor or even major deviations from logarithmic normality may occur where there is heterogeneity in physical and chemical properties due to cases of limited formation, multiple formation rates and/or natural and artificial separation.

Other laws and methods have been suggested for dealing with particle distributions which fail to fit the log-normal curve. Gaudin (47) and Roller (48) cited laws with a "truncated" range in which the large sizes of a distribution are excluded. Rosin and Rammler (49) demonstrated a double exponential curve suited to coal and quartz dusts in England. Irani (50) presented a semi-graphical treatment of bi-modal heterogeneous particle size distributions and artificial distributions created by cyclone separations after generation. In order to improve data reliability a statistically unbiased procedure to increase accuracy in the higher percentiles of the log-normal distribution has been proposed by Sichel (51), who terms it "Truncated Multiple Traversing".

When particle distributions which resist description either by theoretically or empirically fitted curves are encountered good representation of the data may be obtained by graphing the data as a simple histogram or frequency polygon in a recent method suggested by Corn (52). He makes the following recommendations:

"1. The original sizing data be presented, not only the total number of particles sized, but the number per defined class interval.

2. The sizing results be presented as a frequency histogram, or as a cumulative frequency distribution.

3. The errors associated with each class interval be superimposed on the frequency polygon or indicated in a table, or both."

Experimental Procedure

The roadway dust samples studied in this work are extremely heterogeneous, consisting of many materials of known and some of only suspected origin. The methods of particle generation and the post-generation alterations which may have occurred further confound application of any of the convenient distribution equations.

Attempts to fit the particle size data to the log-normal distribution were somewhat less than satisfactory for all but the Parking Garage (PG) dust, and pronounced departure from linearity on the log-probability grid plots was demonstrated in most cases. For that reason it was decided to utilize the frequency polygon method to determine and illustrate the size distribution for all of the dusts studied.

Particle Sizing and Interpretation of Particle Size Data

All particle sizing was done by light field microscopy using an American Optical Spencer Binocular microscope. The optical system consisted of a 100X oil immersion objective lens and a 10X eyepiece which permitted resolution of particles as small as 0.2 μ.

A Porton graticule (53) (ocular micrometer) was inserted at the focal plane of the eyepiece for particle size measurement. When calibrated with

a stage micrometer the size 1 Porton circle was equivalent to 0.48 μ which was rounded to 0.5 μ. Adjacent circle diameters (and reference grid line spacing) increase geometrically by a factor of $\sqrt{2}$. The unlined area on the left side of the Porton graticule provides a total viewing field of 1122 μ^2, which is subdivided into six identical rectangles of 187 μ^2.

Dust samples were prepared for microscopic measurement by dispersing a small quantity in a droplet of canada balsam diluted with xylene (1:9). The dust was dispersed in the mounting medium and the suspension spread over a microscope slide using the technique suggested by Silverman and Franklin (54). Other methods of dispersion failed to deagglomerate the dusts adequately.

The sample-bearing slide was randonly shifted on the microscope stage so that all portions of the dispersion were represented. Each particle was assigned the size of the larger of the two Porton reference circles between which the estimated projected particle area fell.

Considerable difference of opinion exists among investigators concerning the number of particles to size in a sample. Recommendations range from the 100 to 200 of Drinker and Hatch (55) to "about a thousand" suggested by Orr and Dallavalle (56). Pidgeon and Dodd (57) concluded that with samples of sub-sieve crushed quartz powders, even more than 1000 particles should be measured. Fairs (58) and Watson (59) proposed procedures to achieve any desired accuracy. For the purpose of this study an arbitrary lower limit of 200 particles has been imposed.

The (H), (L), and (PG) roadway dust sizings were made on the gross sample, i.e., every particle resolvable at the specified magnification, and no attempt was made to differentiate the rubber fraction. In the case

of the (NBS) and (CH) dusts only the rubber tire particles were sized since they were the only ones clearly defined.

Particle size data and count, area, and weight distribution calculations are shown in Tables 3, 4, 5, 6 and 7. Columns 1, 2 and 3 in each table show the Porton graticule circle number, the calibrated graticule circle size, and the number of particles (f_i) corresponding to each circle size, respectively. Column 4 shows the estimated standard deviation ($f_i^{1/2}$) for each class interval. Kottler (60) has shown that when none of the observed class frequencies is small compared with the total number of particles, and the difference between observed and expected class frequencies is small compared to either, the respective class standard deviations are calculable as:

$$\sigma_n = (f_n'^{1/2})$$

where (f_n') represents the true frequency of occurrence. Estimators are represented as (f_n), the observed frequency.

The contribution of each class to the total count distribution, together with the class standard deviation is shown in column 5. Area and weight distribution conversions are shown in columns 6-11. Columns 8 and 11 give the percentage contribution of each class to the area and weight distributions together with class standard deviations.

The calculated results in columns 5, 8 and 11 of each table have been plotted as frequency histograms representing count, area, and weight distributions in Figures 2, 3, 4, 5 and 6. The associated class standard deviations are shown in the shaded portions of each interval.

TABLE 3

PARTICLE SIZE DATA AND COUNT, AREA AND WEIGHT DISTRIBUTIONS
PARKING GARAGE (PG) DUST

Circle No.	Circle Size	f_i	$f_i^{1/2}$	$100\left[\frac{f_i \pm f_i^{1/2}}{\Sigma f_i}\right]$	d_i^2	$f_i d_i^2$	$100\left[\frac{f_i d_i^2 \pm f_i^{1/2} d_i^2}{\Sigma f_i d_i^2}\right]$	d_i^3	$f_i d_i^3$	$100\left[\frac{f_i d_i^3 \pm f_i^{1/2} d_i^3}{\Sigma f_i d_i^3}\right]$
Col. 1	2	3	4	5	6	7	8	9	10	11
1	0.5	24	4.90	8.54±1.74	0.06	1.49	0.03±0.005	0.02	0.38	0.0005±0.0001
2	0.7	56	7.48	19.93±2.66	0.36	20.16	0.36±0.05	0.22	12.10	0.02 ±0.002
3	1.0	42	6.48	14.95±2.31	0.72	30.24	0.54±0.08	0.61	25.79	0.03 ±0.005
4	1.4	34	5.83	12.10±2.07	1.44	48.96	0.87±0.15	1.73	58.82	0.08 ±0.01
5	1.9	24	4.90	8.54±1.74	2.72	65.28	1.16±0.23	4.49	107.76	0.14 ±0.03
6	2.7	23	4.80	8.19±1.71	5.29	121.67	2.16±0.45	12.17	279.91	0.37 ±0.08
7	3.8	25	5.00	8.90±1.78	10.56	264.00	4.68±0.94	34.33	858.25	1.14 ±0.23
8	5.4	20	4.47	7.12±1.59	21.16	423.20	7.50±1.68	97.34	1946.80	2.59 ±0.58
9	7.7	12	3.46	4.27±1.23	42.90	514.80	9.13±2.63	281.01	3372.12	4.49 ±1.29
10	10.9	8	2.83	2.85±1.01	86.94	695.52	12.33±4.36	804.36	6434.88	8.57 ±3.03
11	15.4	8	2.83	2.85±1.01	172.92	1383.36	24.52±8.67	2273.93	18191.44	24.22 ±8.57
12	21.8	4	2.00	1.42±0.71	345.96	1383.84	24.52±12.26	6434.86	25739.44	34.27 ±17.13
13	30.7	1	1.00	0.36±0.36	689.06	689.06	12.21±12.21	18087.89	18087.89	24.08 ±24.08
	Σ =	281			Σ =	5641.58		Σ =	75115.58	

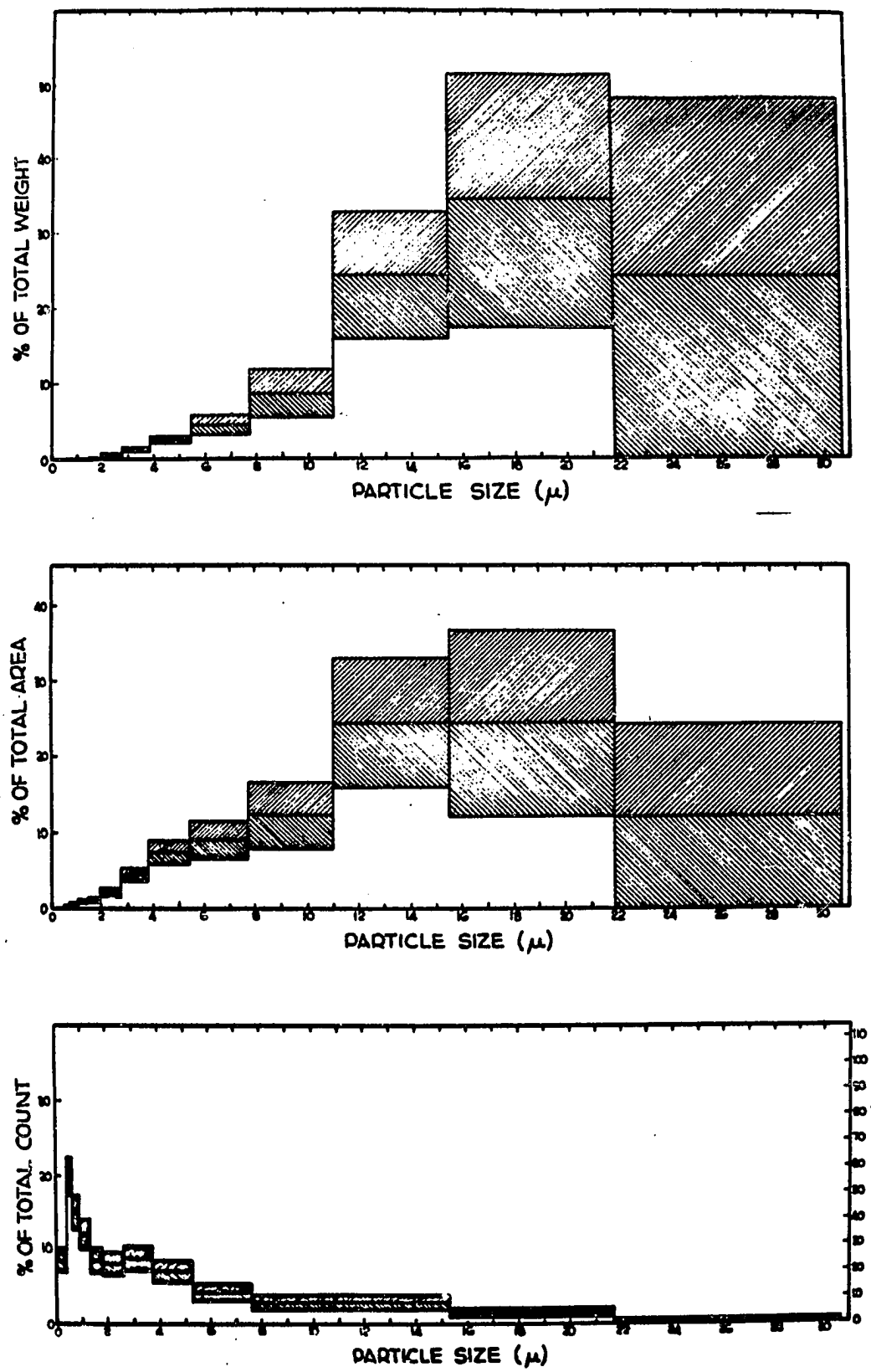


Figure 2. Frequency histograms for particle count, area and weight distributions - parking garage (PG) dust.

TABLE 4

PARTICLE SIZE DATA AND COUNT, AREA AND WEIGHT DISTRIBUTIONS
HOLLAND TUNNEL (H) DUST

Circle No.	Circle Size	f_i	$f_i^{1/2}$	$100\left[\frac{f_i \pm f_i^{1/2}}{\Sigma f_i}\right]$	d_i^2	$f_i d_i^2$	$100\left[\frac{f_i d_i^2 \pm f_i^{1/2} d_i^2}{\Sigma f_i d_i^2}\right]$	d_i^3	$f_i d_i^3$	$100\left[\frac{f_i d_i^3 \pm f_i^{1/2} d_i^3}{\Sigma f_i d_i^3}\right]$
Col. 1	2	3	4	5	6	7	8	9	10	11
1	0.5	73	8.54	26.25±3.07	0.06	4.53	0.13±0.02	0.02	1.46	0.003±0.0004
2	0.7	55	7.42	19.78±2.67	0.36	19.80	0.59±0.08	0.22	12.10	0.03 ±0.004
3	1.0	49	7.00	17.63±2.52	0.72	35.28	1.05±0.15	0.61	29.89	0.07 ±0.01
4	1.4	24	4.90	8.63±1.76	1.44	34.56	1.03±0.21	1.73	41.52	0.09 ±0.019
5	1.9	18	4.24	6.47±1.53	2.72	48.96	1.46±0.34	4.49	80.82	0.18 ±0.04
6	2.7	19	4.36	6.83±1.57	5.29	100.51	2.99±0.69	12.17	231.23	0.51 ±0.12
7	3.8	13	3.61	4.68±1.30	10.56	137.28	4.09±1.13	34.33	446.29	0.99 ±0.28
8	5.4	10	3.17	3.60±1.14	21.16	211.60	6.30±2.00	97.34	973.40	2.17 ±0.69
9	7.7	6	2.45	2.16±0.88	42.90	257.40	7.66±3.13	281.01	1686.06	3.75 ±1.53
10	10.9	3	1.73	1.08±0.62	86.94	260.82	7.76±4.48	804.36	2413.08	5.37 ±3.10
11	15.4	3	1.73	1.08±0.62	172.92	518.76	15.44±8.91	2273.93	6821.79	15.19 ±8.76
12	21.8	5	2.24	1.80±0.81	345.96	1729.80	51.50±23.07	6434.86	32174.30	71.64 ±32.09
		Σ = 278				Σ = 3359.30			Σ = 44911.94	

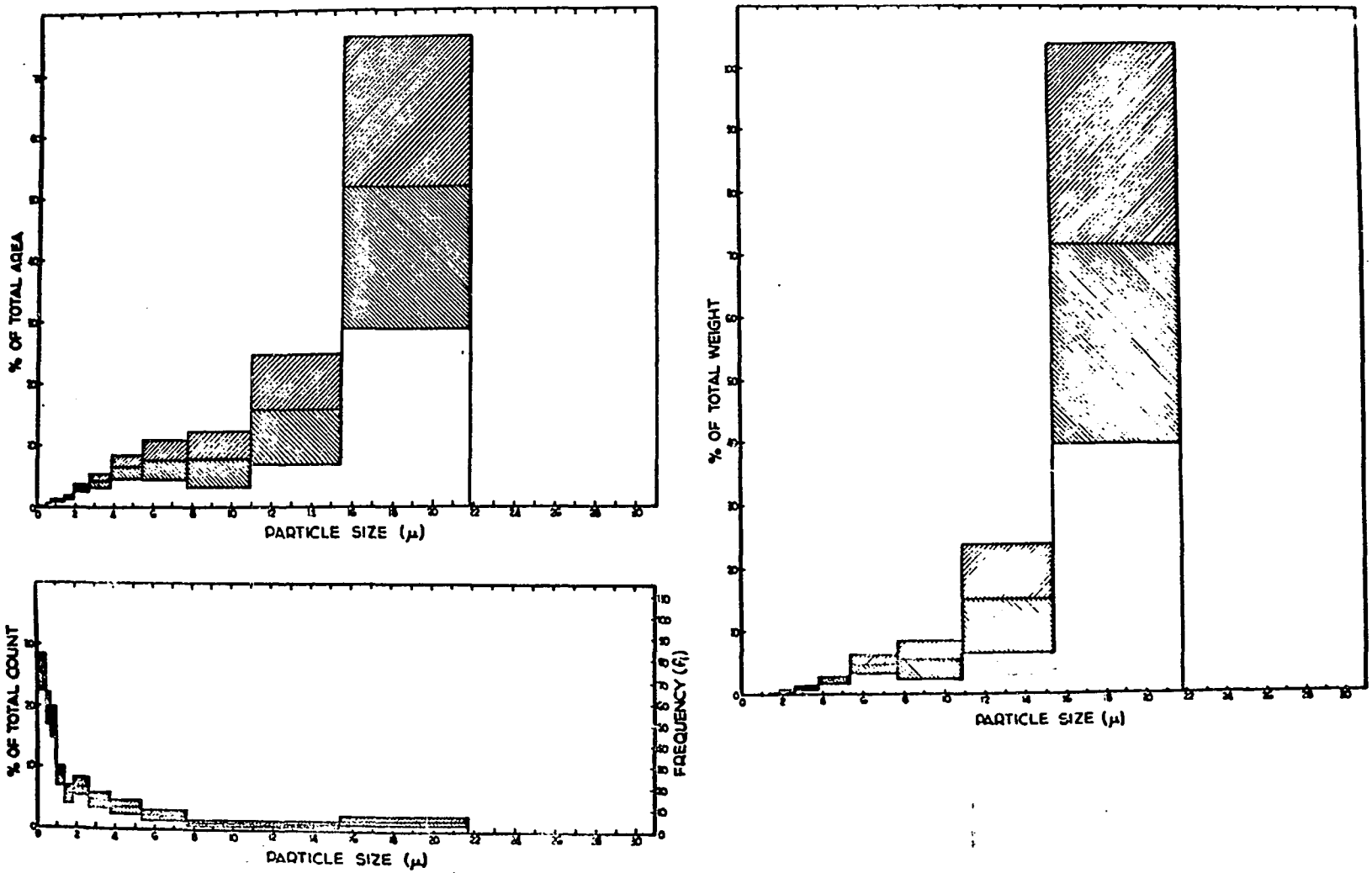


Figure 3. Frequency histograms for particle count, area and weight distributions - Holland Tunnel (H) dust.

TABLE 5

PARTICLE SIZE DATA AND COUNT, AREA AND WEIGHT DISTRIBUTIONS
LINCOLN TUNNEL (L) DUST

Circle No.	Circle Size	f_i	$f_i^{\frac{1}{2}}$	$100\left[\frac{f_i \pm f_i^{\frac{1}{2}}}{\Sigma f_i}\right]$	d_i^2	$f_i d_i^2$	$100\left[\frac{f_i d_i^2 \pm f_i^{\frac{1}{2}} d_i^2}{\Sigma f_i d_i^2}\right]$	d_i^3	$f_i d_i^3$	$100\left[\frac{f_i d_i^3 \pm f_i^{\frac{1}{2}} d_i^3}{\Sigma f_i d_i^3}\right]$
Col. 1	2	3	4	5	6	7	8	9	10	11
1	0.5	147	12.13	52.69±4.35	0.06	9.11	0.55±0.04	0.02	2.94	0.01±0.0001
2	0.7	64	8.00	22.94±2.87	0.36	23.04	1.39±0.17	0.22	14.08	0.06±0.007
3	1.0	29	5.38	10.39±1.93	0.72	20.88	1.26±0.23	0.61	17.69	0.07±0.014
4	1.4	11	3.32	3.94±1.19	1.44	15.84	0.96±0.29	1.73	19.03	0.08±0.024
5	1.9	8	2.83	2.87±1.01	2.72	21.76	1.31±0.46	4.49	35.92	0.15±0.05
6	2.7	4	2.00	1.43±0.72	5.29	21.16	1.28±0.64	12.17	46.68	0.20±0.10
7	3.8	5	2.24	1.79±0.80	10.56	52.80	3.19±1.43	34.33	171.65	0.72±0.32
8	5.4	3	1.73	1.08±0.62	21.16	63.48	3.84±2.21	97.34	292.02	1.23±0.71
9	7.7	3	1.73	1.08±0.62	42.90	128.70	7.78±4.48	281.01	843.03	3.54±2.04
10	10.9	1	1.00	0.36±0.36	86.94	86.94	5.25±5.25	804.36	804.36	3.38±3.38
11	15.4	1	1.00	0.36±0.36	172.92	172.92	10.44±10.44	2273.93	2273.93	9.54±9.54
12	21.8	3	1.73	1.08±0.62	345.96	1037.88	62.71±36.16	6434.86	19304.58	81.02±46.72
		Σ = 279				Σ = 1654.51			Σ = 23827.91	

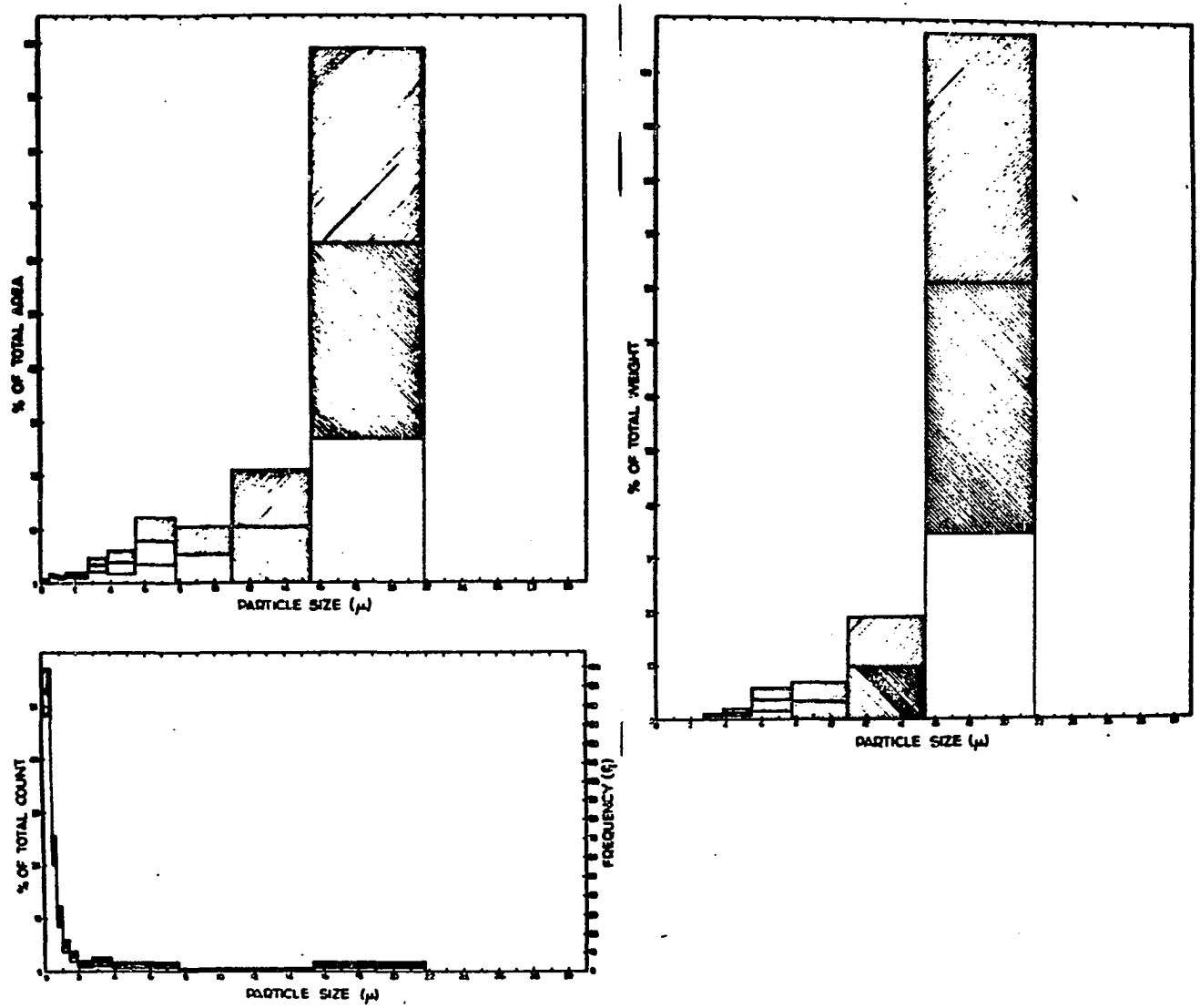


Figure 4. Frequency histograms for particle count, area and weight distributions - Lincoln Tunnel (L) dust.

TABLE 6

PARTICLE SIZE DATA AND COUNT, AREA AND WEIGHT DISTRIBUTIONS
NATIONAL BUREAU OF STANDARDS (NBS) DUST

Circle No.	Circle Size	f_i	$f_i^{1/2}$	$100\left[\frac{f_i \pm f_i^{1/2}}{\Sigma f_i}\right]$	d_i^2	$f_i d_i^2$	$100\left[\frac{f_i d_i^2 \pm f_i^{1/2} d_i^2}{\Sigma f_i d_i^2}\right]$	d_i^3	$f_i d_i^3$	$100\left[\frac{f_i d_i^3 \pm f_i^{1/2} d_i^3}{\Sigma f_i d_i^3}\right]$
Col. 1	2	3	4	5	6	7	8	9	10	11
1	0.5	37	6.08	11.78±1.94	0.06	2.29	0.10±0.02	0.02	0.74	0.002±0.0003
2	0.7	129	11.36	41.08±3.62	0.36	46.44	1.96±0.17	0.22	28.38	0.07 ±0.006
3	1.0	90	9.49	28.66±3.02	0.72	64.80	2.73±0.29	0.61	54.90	0.14 ±0.01
4	1.4	29	5.38	9.24±1.71	1.44	41.76	1.76±0.33	1.73	50.17	0.13 ±0.02
5	1.9	8	2.83	2.55±0.90	2.72	21.76	0.92±0.32	4.49	35.92	0.09 ±0.03
6	2.7	7	2.65	2.23±0.84	5.29	37.03	1.56±0.59	12.17	85.19	0.21 ±0.08
7	3.8	4	2.00	1.27±0.64	10.56	42.24	1.78±0.89	34.33	137.32	0.34 ±0.17
8	5.4	2	1.41	0.64±0.45	21.16	42.32	1.78±1.26	97.34	194.68	0.49 ±0.34
9	7.7	0	-	-	-	-	-	-	-	-
10	10.9	2	1.41	0.64±0.45	86.94	173.88	7.33±5.17	804.36	1608.72	4.02 ±2.84
11	15.4	3	1.73	0.96±0.55	172.92	518.76	21.87±12.61	2273.93	6821.79	17.07 ±9.84
12	21.8	2	1.41	0.64±0.45	345.96	691.92	29.17±20.57	6434.86	12869.72	32.19 ±16.10
13	30.7	1	1.00	0.32±0.32	689.06	689.06	29.05±29.05	18087.89	18087.89	45.25 ±45.25
		Σ = 314				Σ = 2372.26			Σ = 39975.42	

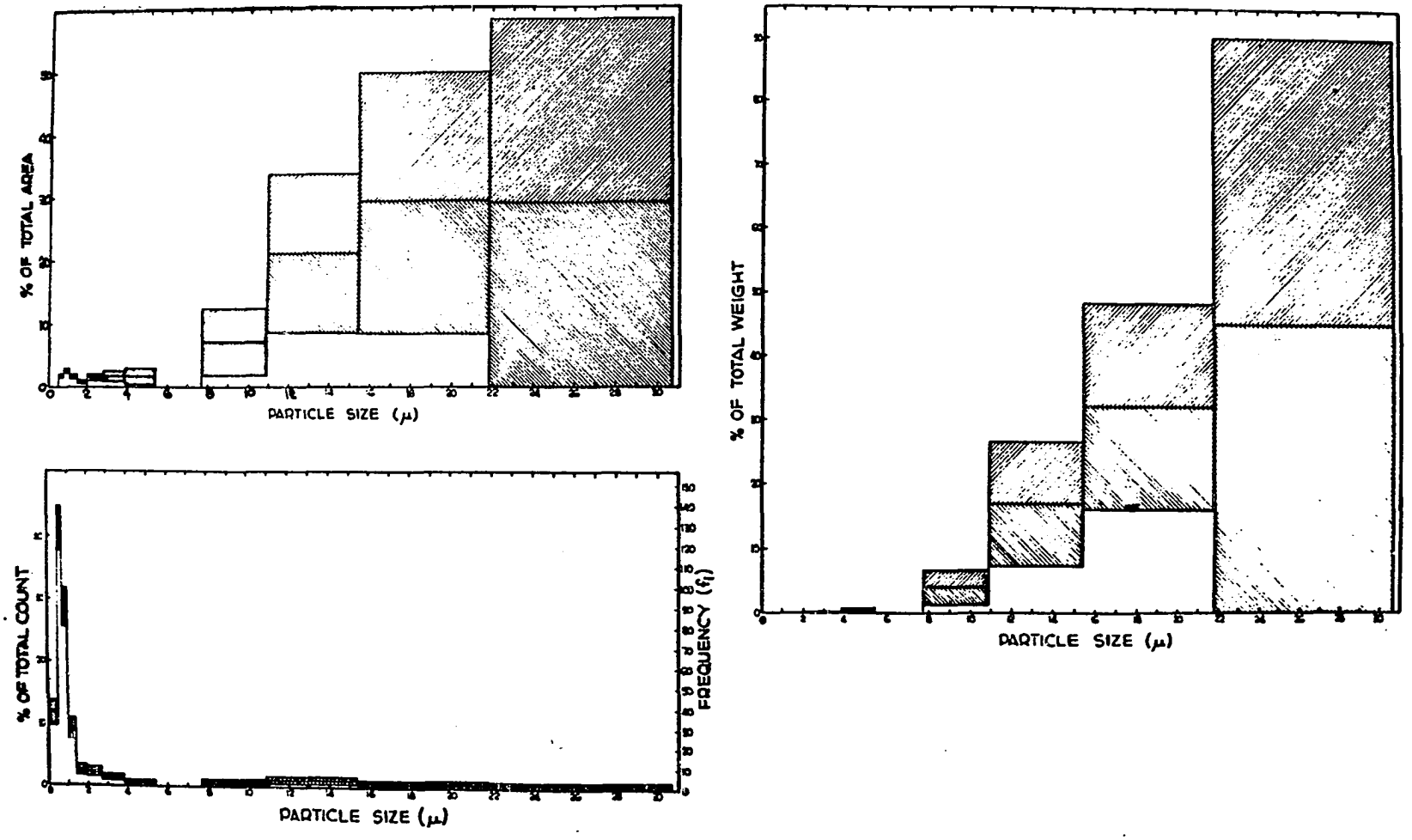


Figure 5. Frequency histograms for particle count, area and weight distributions - National Bureau of Standards (NBS) dust.

TABLE 7

PARTICLE SIZE DATA AND COUNT, AREA AND WEIGHT DISTRIBUTIONS
ANIMAL EXPOSURE CHAMBER (CH) DUST

Circle No.	Circle Size	f_i	$f_i^{\frac{1}{2}}$	$100\left[\frac{f_i \pm f_i^{\frac{1}{2}}}{\Sigma f_i}\right]$	d_i^2	$f_i d_i^2$	$100\left[\frac{f_i d_i^2 \pm f_i^{\frac{1}{2}} d_i^2}{\Sigma f_i d_i^2}\right]$	d_i^3	$f_i d_i^3$	$100\left[\frac{f_i d_i^3 \pm f_i^{\frac{1}{2}} d_i^3}{\Sigma f_i d_i^3}\right]$
Col. 1	2	3	4	5	6	7	8	9	10	11
1	0.5	63	7.94	15.79±1.99	0.06	3.91	0.95±0.11	0.02	1.26	0.10±0.01
2	0.7	150	12.25	37.59±3.07	0.36	54.00	13.09±1.07	0.22	33.00	2.55±0.21
3	1.0	108	10.39	27.07±2.60	0.72	77.76	18.85±1.81	0.61	65.88	5.09±0.49
4	1.4	50	7.07	12.53±1.77	1.44	72.00	17.46±2.47	1.73	86.50	6.68±0.94
5	1.9	20	4.47	5.01±1.12	2.72	54.40	13.19±2.95	4.49	89.80	6.93±1.55
6	2.7	4	2.00	1.00±0.50	5.29	21.16	5.13±2.57	12.17	48.68	3.76±1.88
7	3.8	2	1.41	0.50±0.35	10.56	21.12	5.12±3.61	34.33	68.66	5.30±3.74
8	5.4	1	1.00	0.25±0.25	21.16	21.16	5.13±5.13	97.34	97.34	7.52±7.52
9	7.7	0	-	-	-	-	-	-	-	-
10	10.9	1	1.00	0.25±0.25	86.94	86.94	21.08±21.08	804.36	804.36	62.11±62.11
		Σ = 399				Σ = 412.45			Σ = 1295.48	

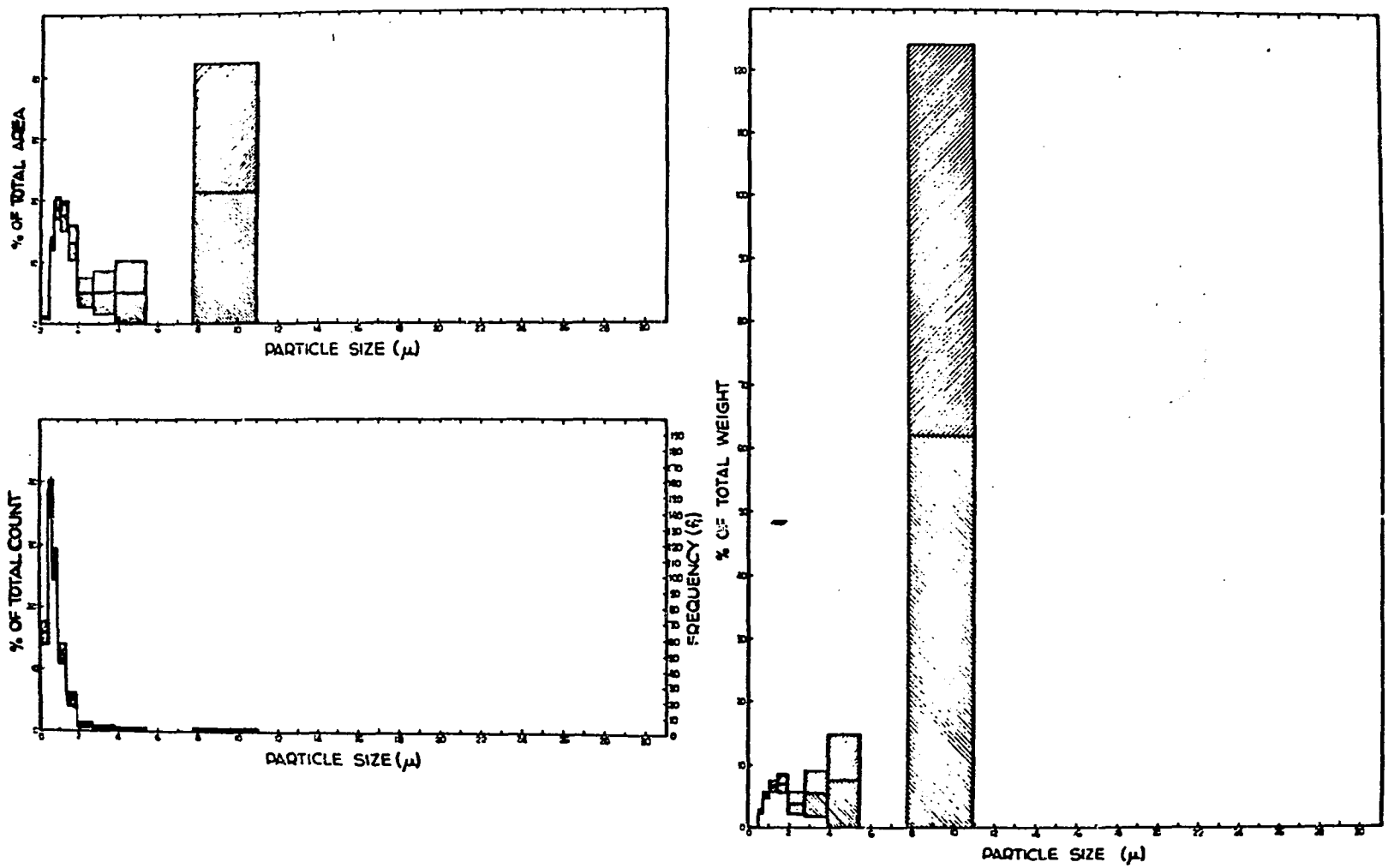


Figure 6. Frequency histograms for particle count, area and weight distributions - Animal Exposure Chamber (CH) dust.

Spectrographic Analysis of Roadway and Vehicle Tire Dusts

Spectrographic analyses of the roadway and vehicle tire dusts are shown in Table 8. Dust samples were placed in Coors crucibles and ashed at 600°C for 6 hours in a muffle furnace. Ashed samples were then analyzed in a Bausch and Lomb Dual Grating Emission Spectrograph. Spectral lines of individual elements were identified and evaluated using a densitometer with a direct reading projection comparator microphotometer. If the specific lines of an element were present in the unknown's spectrum, intensities were visually compared with corresponding standard line intensities and recorded as a percentage of the ash contents.

Discussion

It is extremely difficult, if not impossible, to examine a sample of roadway dust with the unaided eye and do any more than speculate on its composition. The assumption would be that it should contain particles of abraded tire rubber, bits of bituminous material, particulates exhausted from gasoline and diesel engines, soil constituents characteristic of foreign as well as local surface geology, and numerous other fragments of organic and inorganic material.

The appearance of roadway dusts should vary as the concentrations of its components vary. Samples of dust from the exhaust ducts of the Lincoln (L) and Holland (H) tunnels were virtually black. This is due to the large volumes of smoke soot and rubber and asphalt particles collected and vented from the tunnels. These samples were taken from the duct systems in the vicinity of entry grades where maximum accelerations and decelerations occur and where the tire tread dust contribution should be highest. On

TABLE 8

SPECTROGRAPHIC ANALYSIS OF ROADWAY AND VEHICLE TIRE DUSTS

ELEMENT	(H)	(L)	(PG)	(CH)
Silver	T	T	< 0.001	T
Aluminum	Min.	Maj.	> 2.0	Maj.
Boron	T	T	< 0.005	T
Barium	0.2	0.1	< 0.01	-
Calcium	Min.	Min.	> 2.0	Min.
Cobalt	-	T	< 0.005	-
Chromium	0.1	0.2	0.02	0.05
Copper	0.4	0.2	0.02	0.02
Iron	Min.	Min.	1.4	2.0
Magnesium	1.0	0.8	0.6	Min.
Manganese	0.05	0.08	0.2	0.05
Molybdenum	0.005	0.01	< 0.005	0.01
Sodium	Min.	Min.	0.4	Min.
Nickel	0.02	0.03	0.01	0.05
Lead	∿ 1.0	∿ 1.0	∿ 1.0	0.5
Silicon	Min.	Maj.	> 2.0	Maj.
Tin	0.01	0.02	0.01	0.03
Titanium	0.2	0.3	0.2	0.2
Vanadium	0.08	0.2	0.04	0.05
Zinc	0.1	0.2	0.2	Min.
Zirconium	< 0.01	0.01	0.03	-
% Ash Content	48.7	54.6	63.3	4.1

Min. = 3.0 to 10.0% Maj. = > 10.0% T = Trace

the other hand, the automobile parking garage (PG) dust was much lighter in color and could be described as a dark grey, the lightening probably due to a decrease in the automobile exhaust soot contribution. The National Bureau of Standards (NBS) dust occurred in varying shades of grey as it was an exclusive mixture of hydrated alumina and vehicle tire rubber. The animal chamber (CH) dust was a single source material composed entirely of tire rubber and as such was black.

Little improvement in the identification of rubber dust in a sample can be expected when a portion is dispersed on a glass slide and examined with the ocular microscope. A search of the literature reveals no morphology for vehicle tire abrasion products. Sixty to seventy per cent of the particles observed in the true roadway samples using a light field technique were black suggesting the presence of soot in their composition.

In the (NBS) and (CH) dusts the individual particles greater than approximately 6 μ in diameter appear to be non-uniform and erose. Their shredded appearance is characteristic of their process of generation, a tearing action imposed on a resilient material extended beyond its elastic limit. The many particles smaller than about 6 μ in diameter, which were resolvable, appeared as black dots in the light field. These tiny particles in the (NBS) and (CH) dusts were rubber dust. However, in the case of the (H), (L), and (PG) dusts, it could only be assumed, with some degree of certainty, that all of the smallest black particles which appeared in the microscope field were a combination of automobile exhaust soots, tire dust, and asphalt particles.

In general it can be stated that rubber particles tend to agglomerate with one another and with other materials. What appeared, at first glance

to be a large "spongy" rubber particle, very often was found to be a conglomerate of finer rubber particles or a mixture of rubber and non-rubber materials. It was quite common to find materials of mineral origin in the interstices of the erose rubber particles.

Only the (PG) dust sample conformed to the classical log-normal distribution from which the usual size parameters could be calculated or observed. However, it was treated as the other dust samples, to obtain count, area, and weight frequency histograms. Ninety-five per cent of the (PG) particles counted were equal to or less than 11 μ in diameter and 88 per cent were equal to or less than 5 μ. The particles equal to or less than 11 μ represented 38 per cent of the total area but only 17 per cent of the total weight of the sample. The 5 μ and below sizes represented 17 per cent of the area and only 4 per cent of the weight distribution.

The (H) dust data and histogram show that 97 per cent of the particles counted were equal to or less than 11 μ in diameter and 94 per cent were equal to or less than 5 μ in diameter. Those equal to or less than 11 μ accounted for 33 per cent of the surface area and 13 per cent of the weight of the material. Those particles in the 5 μ and below size range represented 18 per cent of the area and but 4 per cent of the weight distribution.

The (L) dust was extremely fine. The sizing showed that 99 per cent of the particles counted were equal to or less than 11 μ in diameter and 98 per cent were equal to or less than 5 μ in diameter. However, the large number of particles in the broader range accounted for only 27 per cent of the area and a scant 9 per cent of the total weight. It is significant that the 0.5 μ size accounted for over 50 per cent of the particles counted

and contributed virtually nothing to total area or weight. On the other hand, only 3 particles, 22 μ in diameter, accounted for 63 per cent of the total area and 81 per cent of the total weight. However, there is a high degree of unreliability contributed to the area and weight distributions by these large particle sizes as evidenced by the wide error bands superimposed on the histograms.

Large rubber particles occasionally appeared when sizing the (NBS) dust. The size data show that one particle approximately 30 μ in diameter contributed to 29 per cent of the area and 45 per cent of the weight distributions. For the most part the sample represented a very finely divided material. Ninety-eight per cent by count was equal to or less than 11 μ and 97 per cent was equal to or less than 5 μ in diameter. The former size range accounted for 20 per cent of the surface area and only 1.5 per cent of the weight distribution. The 5 μ and below range contributed 13 per cent of the area and 5.5 per cent of the weight distributions.

The (CH) dust is classified to some extent as it is produced. For that reason particles larger than 11 μ in diameter are almost non-existent in any randomly selected sample. Very nearly all of the sample counted was equal to or less than 5 μ in diameter, and that range represented 79 per cent and 38 per cent of the area and weight distributions, respectively.

Large proportions of the "true" roadway samples (L, H, and PG) were mineral in origin. In addition the (PG) dust contained some fibrous material and fragments of apparent organic composition.

The (CH) dust had the highest content of volatile material and the spectrographic analysis (Table 8) of the ashed sample was consistent with

general rubber tire formulations. The high aluminum content (> 10.0%) is derived from hydrated alumina or any clay reinforcing material. Calcium (3.0 to 10.0%) derived from the calcium silicate often used as a reinforcer. Iron (2.0%) is originally present in rubber as a pigment. Magnesium (3.0 to 10.0%) results from the decomposition of talc, asbestos and chemically allied products. Sodium (3.0 to 10.0%) can be traced to the emulsifiers used in the synthetic rubbers, to polymerization initiators, and to the carbon black. Free silica is finding increasing use as a reinforcing filler in rubber but the high silicon content (> 10.0%) found in the (CH) dust is more likely traceable to naturally occurring silicates appearing as fillers in the form of clay, talc or asbestos or in the manufactured silicates of aluminum and calcium. Lead (0.5%) and titanium (0.2%) compounds are used as pigments in rubber formulations. The most widely used activator is zinc oxide. The high zinc content (3.0 to 10.0%) can be traced to the activator and to zinc coloring and reinforcing compounds.

Most of the metallic elements detected in the "pure" tire dust were found in approximately equivalent amounts in the roadway dusts. As would be expected the ubiquitous iron was found in higher concentrations. Lead, found higher in all roadway dusts, is probably due to the exhaust particulates from vehicles burning leaded fuels. The zinc content decreased drastically and consistently in all of the roadway samples.

All of the roadway samples showed a marked increase in non-volatile compounds compared to the laboratory produced tire dust.

CHAPTER V

IDENTIFICATION OF VEHICLE TIRE RUBBER IN A DUST SAMPLE

Introduction

All of the chemical and instrumental methods of analysis for rubber and rubber products include or are preceded by tedious and time-consuming extractions to produce a sample rubber hydrocarbon free of pigment and filler. Once free of carbon black and other compounding ingredients the elastomer can be identified and assayed by chemical analysis using either the ASTM methods (61) or the more sophisticated physical methods developed by Barnes et al. (62) and perfected in the now classical work of Dinsmore and Smith (63). The ASTM procedures are naturally detailed and exhaustive as they were developed for control and specification. As such their use as a method for rapid determination of rubber is prohibited. The absorption spectroscopy methods developed by the above mentioned investigators offered a more rapid and accurate analytical technique for identification and quantitative determination of the elastomer composition of industrial rubber products. Dinsmore and Smith investigated seven classes of gum rubber and six classes of compounded and cured rubber using infrared spectroscopy. They developed a spectral basis for identification of elastomers and a satisfactory technique for spectral examination of compounded and cured rubber. It is interesting to note that they stressed

the necessity of removing fillers which rendered their samples too opaque for quantitative spectral study. In this connection much of their work involved the evaluation of various solvents in regard to their ability to dissolve the elastomer and retain their purity and inertness on prolonged heating (24 to 36 hours). These lengthy extraction procedures preliminary to infrared examination of rubber polymers prompted the search for a more rapid and a "cleaner" analytical method.

In 1954, Davison, Slaney and Wragg (64) reported on a simplified method for identification of polymers. They pyrolyzed samples of polymeric materials and subjected the pyrolyzates to gas-phase partition chromatography and utilized the pattern of peaks on the recorded chromatogram as a method of identification. They pointed out that it is not necessary to identify individual components but merely to recognize the pattern obtained. Typical chromatograms of polymers were illustrated. One comment made by these investigators, which is particularly important to this work, should be stressed: "The time at which the various peaks appear is more characteristic than their relative heights; the latter depend to some extent upon compounding, and, in the case of elastomers, the vulcanization." This factor is vital to the application of the methods developed in this study.

In 1959, Radell and Strutz (65) used pyrolysis and gas chromatography for the identification of acrylate and methacrylate polymers. They too utilized patterns and retention times for identification.

Janak (66), the following year, reported on the identification of the structure of non-volatile organic substances by gas chromatography of their pyrolytic products. He specifically studied olive oil, hardened olive and

coconut oil, and sodium salts of barbituric acid derivatives.

The most recent paper describing the combination of pyrolysis and gas chromatography was reported by Virus (67) in 1963. It describes the analysis of natural and synthetic rubbers and presents typical chromatograms.

In order to establish a basis for proof of the existence of vehicle tire abrasion products in a sample of roadway dust some reproducible identifying characteristic of the tire material must be found. It has been pointed out that virtually all tire rubber contains SBR to a greater or lesser degree. Therefore, any method which would permit identification of SBR in a dust sample would, in like manner, prove the presence of tire rubber in that sample.

The successes of predecessors in combining pyrolysis and gas chromatography to identify complex polymers and the accessibility of the appropriate equipment have respectively prompted and facilitated the development of a very clean, fast and reliable technique for the positive identification of vehicle tire products in a sample of roadway dust.

Equipment

Introduction

Gas-liquid chromatography is a relatively new aid in air pollution investigations. It shows great promise for the identification of trace amounts of organic pollutants. The conglomerates heretofore reported as "benzene soluble organic matter" can, via gas-liquid chromatography, be readily separated as individual components, identified, and quantitated. Industrial and vehicular gaseous emissions are easily analyzed for their

organic constituents, even when collected in minute quantities. Complex mixtures of compounds which otherwise rigidly resist separation and identification very often yield meekly to gas-liquid chromatographic partitioning.

Gas-liquid chromatography, gas-liquid partition chromatography, gas-partition chromatography and vapor fractometry are all synonymous designations for a process designed for separation and analysis of gases and volatile materials. It is basically a two-phase system. Separation of the components of a mixture is accomplished when a mobile phase, composed of an inert gas and a small sample of the mixture, passes over a stationary phase or sorbent which is a non-volatile liquid thinly coated on an inert solid support. Sample components traverse the stationary phase at rates dependent on their respective volatilities and/or interaction with the non-volatile liquid sorbent. The various molecules tend to dissolve and re-vaporize as they pass through the stationary phase. Molecules of the component having the greater solubility on the liquid sorbent are retarded in their passage and under suitable conditions the partition process between the moving and static phases results in a situation in which each component of the sample mixture emerges in time from the stationary phase as a binary mixture with the carrier gas. Each component moves through the stationary phase at a rate depending on its partition coefficient between the mobile phase and the stationary phase. The partition coefficient is defined as the ratio of the concentration of molecules in the liquid phase, to the concentration in the gas phase at any given moment. In a more convenient form it is expressed as:

$$K = \frac{\text{Weight of solute/ml stationary phase}}{\text{Weight of solute/ml mobile phase}}$$

If K for a compound is small the traverse time is short since it is not retarded by the stationary liquid. Conversely, a large K value indicates that a greater proportion of the compound resides in the stationary phase and the traverse time is longer. Therefore, the material with the lower K value will be eluted prior to one with a higher K value.

Two properties affect the partition coefficient of a component:

1. Boiling point: The partition coefficient is directly proportional to the boiling point.
2. Chemical affinity: A secondary effect exerted on the partition coefficient is the strength of the chemical affinity which exists between a sample component and the liquid phase. This fact enables certain stationary phases to effect wide separations of two components with identical boiling points.

The stationary phase is a liquid of low volatility supported on an inert finely divided material. It is commonly housed in a glass or metal tube which may be straight, U-shaped or coiled and of varying lengths and diameters. This column is the very heart of a system consisting of four basic units: (1) a carrier gas supply and flow control, (2) an injection port and means of introducing the sample, (3) the column (or columns) and oven, and (4) the detector and recorder.

Carrier gas supply and flow control. Three gases are commonly used: helium, hydrogen, and nitrogen. Of these, helium is the most commonly used because of its high thermal conductivity, small molecular size (gives higher flow rates than other gases at equal pressures), and its inertness. If reproducible and stable results are to be obtained the flow rate must remain constant during sample runs. The carrier gas flow rate will affect

both the retention time of the sample components and the magnitude of the signals obtained.

Injection port and sample introduction. The conventional method is to introduce both gases and liquids with a hypodermic, or other type, syringe through a self-sealing serum cap located near the inlet to the column. Rapid introduction of precise amounts of the sample is vital to good resolution of chromatogram peaks. Injection port temperatures are pre-set to a point just above the boiling point of the highest boiler in the sample. For non-volatile substances special equipment and techniques permit pyrolysis of the sample suspended in the injection port.

Column and oven. The column which contains the stationary phase and its solid support is commonly 2 to 6 mm (ID) glass tubing or 0.125 to 0.375 in. (OD) metal tubing. Its length varies over a wide range. In general, separating power of a column improves with length but not necessarily to a proportional degree. Column configuration is usually determined by the geometry of the thermostatted chamber (oven) in which it is contained. The longer columns are usually coiled to achieve compactness and convenience of installation and removal. Columns are housed in chambers in which temperatures may be controlled accurately. In some analyses of samples with wide boiling ranges gradually increasing column temperatures may be desirable to attain optimum separation or resolution of sample peaks.

Detector and recorder. Numerous devices are available to detect the separated components and translate their time of elution from and relative magnitude in a sample. The output signal from the detector actuates a recorder which produces a chromatogram consisting of a series of peaks

characteristic of the separated sample components. Positions of the peaks allow identification of components and peak amplitude or area permit quantitation. Of the many types of detectors available including the automatic recording burette, nitrometer, gas-density balance, infra-red analyzer, surface potential detector, mass spectrometer, electron capture detector, hydrogen flame detector, and thermal conductivity cell, the last two are most generally used.

Hydrogen flame detector. When a carrier gas introduces an organic component into a hydrogen flame through the jet supporting the flame the compound is burned and ionized, thereby forming both positive ions and negative electrons. If a voltage is applied across the jet and a collector ring mounted above it the electrons and ions may be collected. The collected electrons flow through a biasing circuit and thereby create a voltage drop across an input load resistor which is in turn measured by an electrometer and the output presented on a potentiometric recorder in the form of a chromatographic peak. A well designed flame detector is about 1000 times more sensitive than a good thermal conductivity detector. It is applicable to a wide range of solutes. It is reasonably stable, moderately flow insensitive, and linear over a wide range.

Thermal conductivity cell. The thermal conductivity cell is the most commonly used of all the detectors. It consists of a hot wire filament or thermistor held in the center of a small tube or metal block through which the gas passes. The filament is heated with electric current and the temperature rises to some constant value which depends on the current applied, the resistance of the filament, the temperature of the cell block, the nature of the gas and to some extent on the flow rate of the gas. If

the cell block is held at some temperature below the temperature of the filament, heat will be conducted away from the filament to the cell block at a rate which will depend on the thermal conductivity of the gas and the difference in temperature between the side walls of the cell block and the filament.

Absolute measurements of thermal conductivity are not attempted. A differential procedure is used in which two gas channels and two filaments are employed. Pure carrier gas flows through one channel, and the same (or an equal) current of gas, which has passed through the column, through the second. Any difference of resistance of the two filaments due to the presence of volatile components in the column effluent is then recorded as peaks on a moving chart.

Gas-Liquid Chromatograph

All chromatographic analyses were performed with the F & M Scientific Corporation Model 810-19 instrument shown in Figure 7. It is a versatile, sensitive, dual column instrument designed to take advantage of the sensitivity available with dual flame detector systems. This installation used simultaneous detector operation, with dual hydrogen flame as the prime detector and dual thermal conductivity as its auxiliary. The latter received the column flow from a 1 to 1 effluent splitter housed in the oven. Simultaneous detector operation affords the versatility of differential analysis. However, in this study the exit ports of the thermal conductivity detector were used for collection of selected sample components.

The instrument consists of two basic cabinet groups. The oven cabinet group houses the column oven, the sample injection port assembly, dual

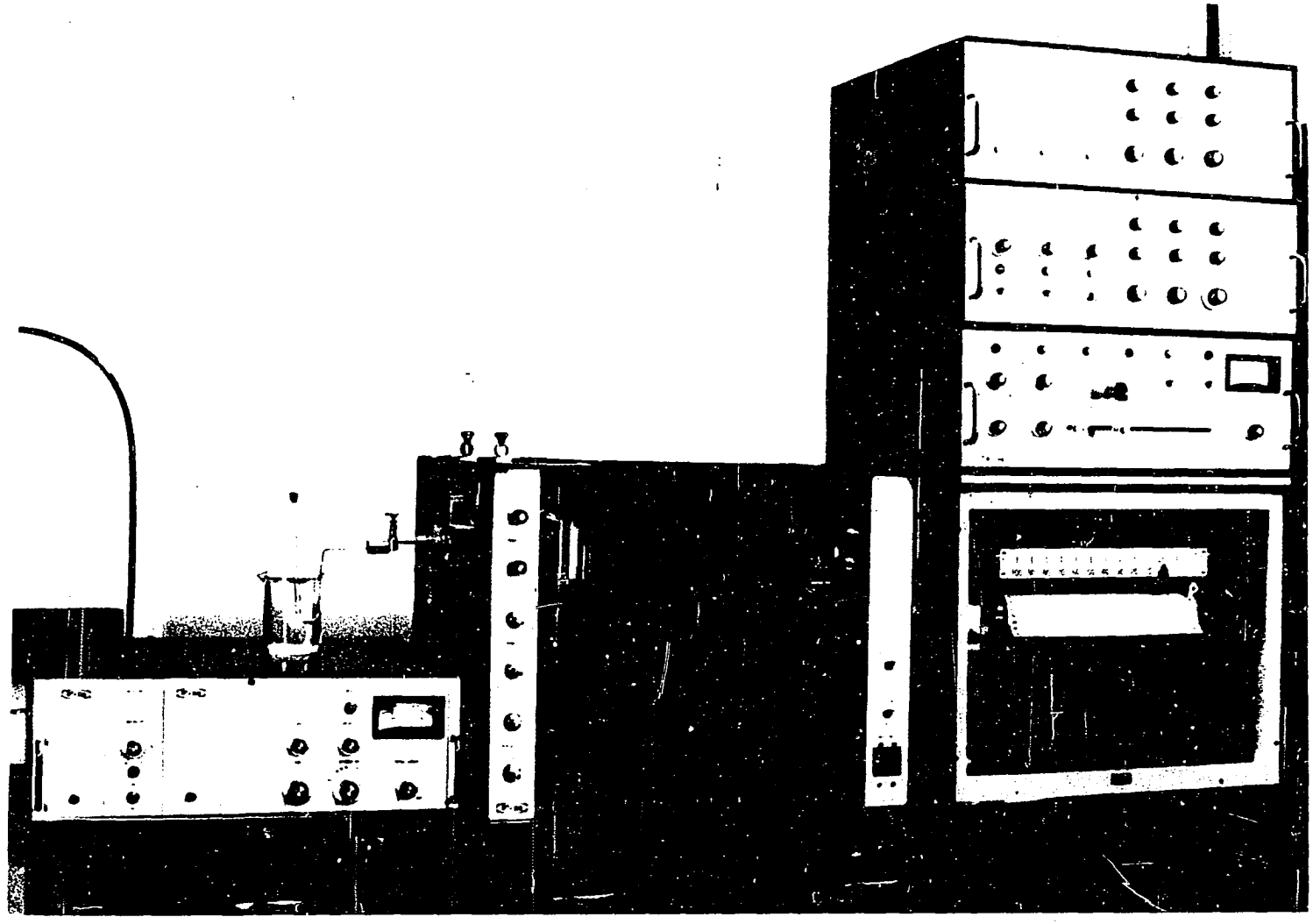


Figure 7. F & M Scientific Corporation Model 810-19 Gas-Liquid Chromatograph

flame detectors, dual thermal conductivity detectors, and the carrier gas, detector gas, and purge gas flow systems.

The control cabinet group is composed of three separate modules: (1) the electrometer drawer which contains controls for selecting the detection sensitivity and controlling the operating temperature of the injection port assembly and detector assembly, (2) the programmer drawer which contains controls, meters and timers to completely preset and automate a column oven "program" or to operate the columns isothermally, and to completely monitor the run, and (3) the recorder compartment which houses a Minneapolis-Honeywell Class 15 recorder. For this study an additional cabinet group housing a drawer for thermal conductivity detector controls and a second recorder were included.

Gas flow systems. Commercial high purity helium was used as the carrier gas. A molecular sieve removed moisture and hydrocarbon impurities that might have been present in the carrier gas supply. High purity hydrogen gas was used for the flame detectors. Oxygen, rather than "house" air, supported the hydrogen flame combustion and purged the detector housing of combustion products.

Columns and column packings. The columns were F & M Scientific Corporation 0.25 in. (O.D.) stainless steel columns 4 ft. long. Both were packed with a 60-80 mesh Diatoport S solid support. Diatoport S is diatomaceous earth specially treated and silanized to minimize adsorption and tailing of polar compounds. The liquid phase or adsorbent was Apiezon L, a grease, which is particularly good for the separation of aromatic hydrocarbons. Its maximum recommended operating temperature is 300°C.

Both columns were fitted with 1 to 1 effluent splitters which per-

mitted the gas flow from the columns to be divided into two equivalent streams for simultaneous analysis in the two dual detector systems.

Pyrolysis Unit

All non-volatile samples were thermally decomposed for chromatographic analysis using the F & M Scientific Corporation Model 80 Pyrolysis Unit shown in Figure 8. It consists of a control cabinet, a probe assembly, and an interconnecting cable. Samples for pyrolysis were placed in the platinum-rhodium foil jaws of the probe, Figure 9. The probe was inserted into the injection port of the gas-liquid chromatograph and automatically fired at a pre-set temperature for 12 seconds after which the pyrolyzates were swept onto the column where separation began.

Collection Systems

Certain pyrolyzate components represented by specific well-defined chromatogram peaks were collected for identification by other techniques as they emerged from the thermal conductivity detector ports. The thermal conductivity cell permitted the sample components to pass unaltered and the heat of the block prevented their condensation so that they could be collected as vapors. Though more sophisticated sample collection systems were available for this purpose it was found that either of two very simple techniques utilizing a minimum of equipment proved quite satisfactory.

The first system, which is shown in Figure 10, was a simple "bubble trap" designed to collect the eluted component in a suitable solvent. As the eluent emerged from the heated thermal conductivity cell it passed through a short length of 0.125 in. (O.D.) copper tubing which retained

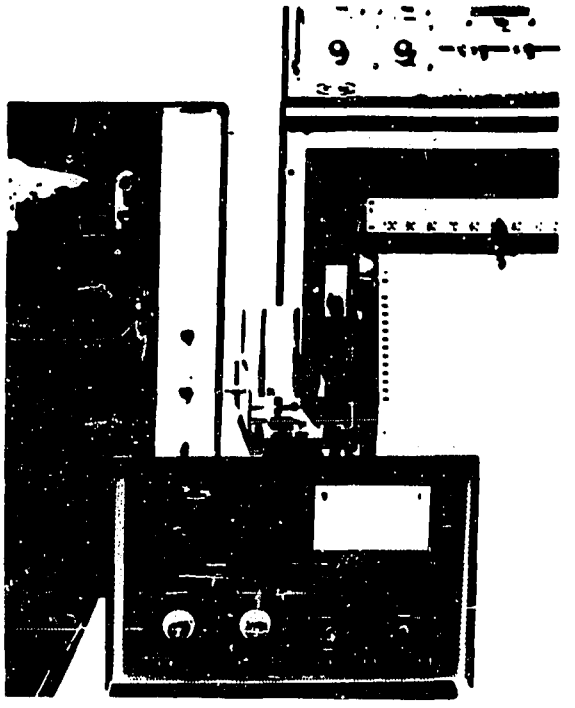


Figure 8.

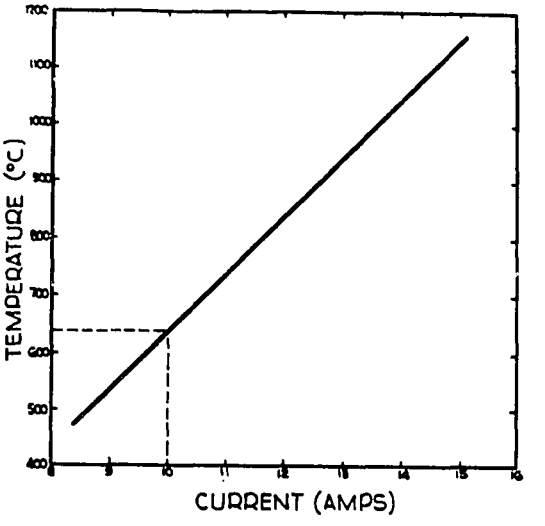


Figure 12.

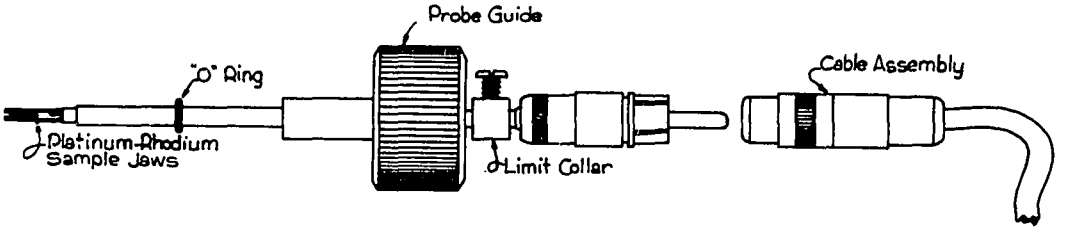


Figure 9.

Figure 8. F & M Scientific Corporation Model 80 Pyrolysis Unit

Figure 9. Pyrolysis Probe

Figure 12. Pyrolysis Probe Calibration Curve

the conducted heat from the cell block. The end of the tube was submerged in a scrubbing solvent contained in a 100x13 mm pyrex test tube which was sealed with an aluminum foil covered cork stopper between "peak" collections.

A slight elaboration of the bubble trap design as shown in Figure 11 permitted better control of the collection procedure and more sample yield with each "peak" collected. A stainless steel manifold needle valve fitted in the system allowed close control of the column effluent so that all but the desired component could be easily bypassed to the atmosphere. The use of rubber serum stoppers in the collecting tube kept the solvent and its collected fraction continually in a helium environment. This is especially important when collecting monomers which readily polymerize on exposure to air. Condensation of the sample was aided by immersing the collection tube in a wet ice (0°C.) bath.

Experimental Procedure

Identification of vehicle tire rubber in a sample of roadway dust involved three clearly defined steps:

1. Production of Standard Chromatograms - The production of standard chromatograms of the pyrolyzates of materials known to be used in rubber tires and of other materials which might be found in a roadway dust.

2. Identification of SBR and/or Natural Rubber in Compounded Materials and Roadway Dusts - The chromatographic separation of the pyrolyzates of compounded tire rubber and samples of roadway dust in an attempt to locate one or more of the standard patterns developed in (1).

3. The Identification of Chromatographic Components - The identification of chromatographic pyrolyzate components to confirm the presence

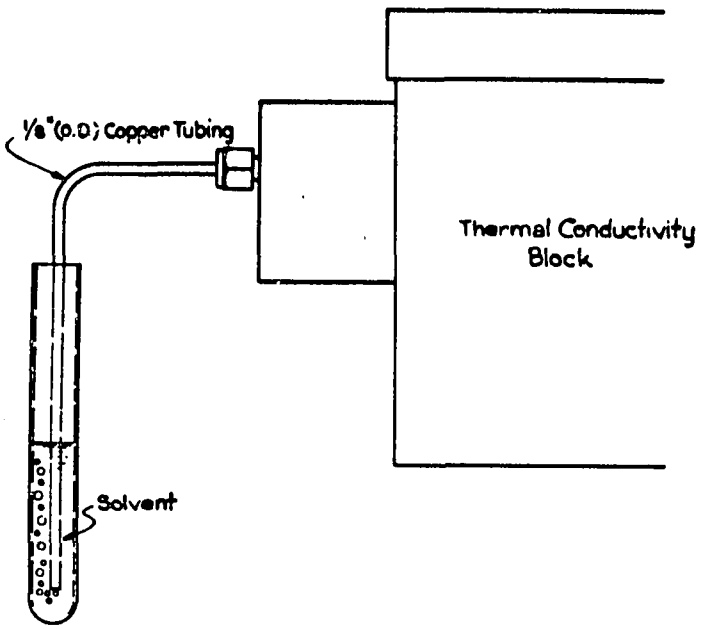


Figure 10. Collection System No. 1

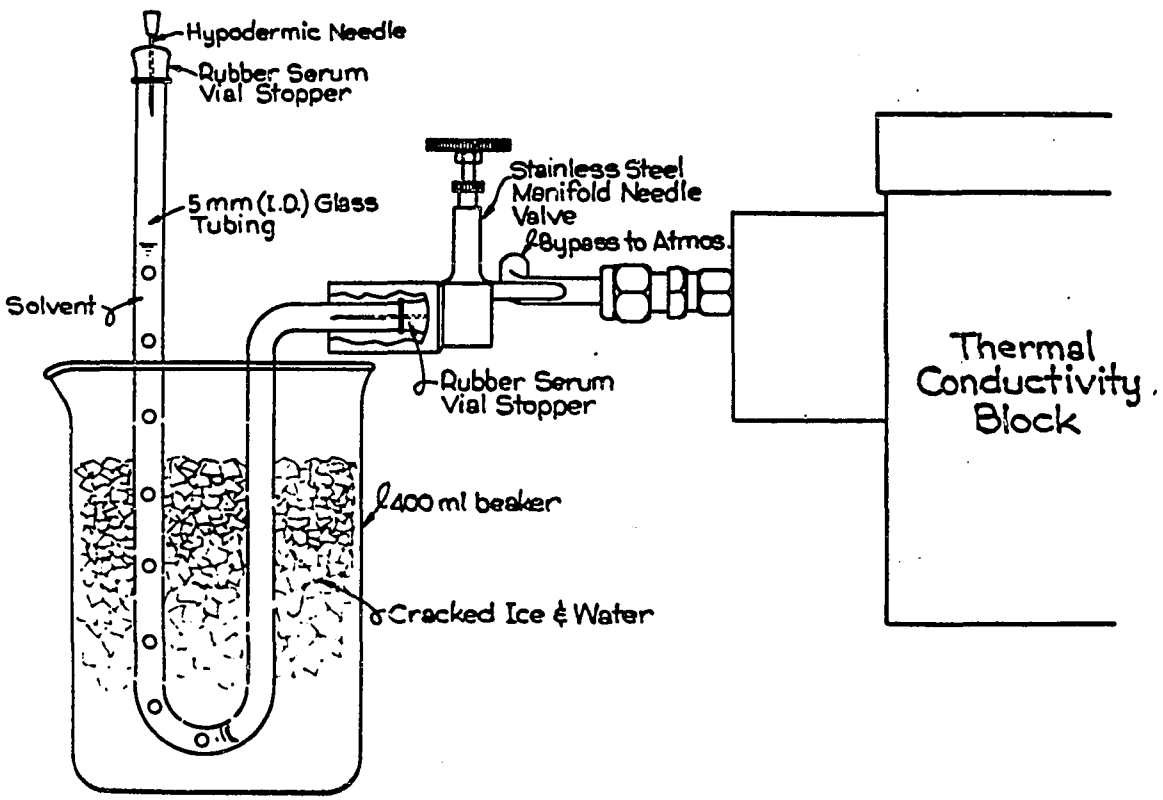


Figure 11. Collection System No. 2

of a specific monomer in the pyrolyzates of the raw elastomers, the compounded rubbers, and the roadway samples.

The Production of Standard Chromatograms

A sample of raw SBR elastomer containing only an anti-oxidant was obtained from a leading tire manufacturer. Small pieces (10 mg) of the synthetic rubber were placed in the platinum-rhodium jaws of the pyrolysis probe. The probe had previously been calibrated, Figure 12, and programmed to yield a pyrolytic temperature of 640°C. at 10 amps. The probe containing the sample was then inserted to its maximum depth into the injection port chamber of the chromatograph column. The injection port assembly then became the pyrolysis chamber. An automated pyrolysis cycle provided a sixty second delay before firing to allow any air entrapped at insertion of the probe to pass through the column and to completely reestablish the helium environment. After the delay the sample was ignited at the pre-set temperature for 12 seconds and its pyrolyzates permitted to flow onto the column.

Chromatographic separation was accomplished isothermally at 108°C. To achieve sharp definition of component peaks the carrier gas flow rate was held to 25 ml/min.[1] The injection port and detector temperatures were held constant at 240°C. and 305°C., respectively.

At a recorder chart speed of 0.25 in./min., approximately 46 minutes were required for the pyrolyzates to traverse the column and provide a characteristic pattern for SBR. Many replications of the SBR pyrolyzate

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[1]In general, resolution of peaks is, in part, a function of column temperature and carrier gas flow rate. Decreasing both (within limits) will provide better separation.

separation were made to establish the reproducibility of the technique.

Samples of numerous other carbonaceous compounds were treated in like manner to the SBR to test the applicability of the process and to provide a series of standard patterns for future reference and identification purposes. Materials "fingerprinted" include butyl rubber, latex (natural rubber), neoprene, polyurethane, polystyrene, asphalt and carbon black.

Pyrolysis temperatures, column temperatures, and carrier gas flow rates for all of the standard materials were unchanged from those used on the SBR elastomer. Only the detector range (sensitivity) and attenuation varied from sample to sample in order to improve the "readability" of each chromatogram.

Identification of SBR and/or Natural Rubber in Compounded Materials and Roadway Dusts

Identification of elastomers in compounded rubber materials has been done most effectively using the methods of infra-red absorption spectroscopy but only after lengthy extractions of the fillers (61) (62). Pyrolysis and chromatography eliminates the need for preliminary preparation of a sample and permits the analysis of polymeric materials in their compounded states.

Compounded rubbers treated to pyrolysis and chromatographic separation include: (1) a sample of rubber from a new Continental 5.70 x 16 automobile tire; (2) a sample of grindings collected from an automobile tire recapping operation; and (3) a sample of grindings collected from a truck tire recapping operation.

Samples of roadway dusts previously identified as (H), (L), (PG), and (NBS) were tested in the same manner and at essentially the same

pyrolysis and chromatography operating conditions used in previous analyses. Detector sensitivity was increased in order to detect rubber patterns in the chromatograms of the heterogeneous samples, particularly in the case of the Holland and Lincoln Tunnel dusts. Concentrations of tire rubber in any roadway sample are relatively low and delicate sensing is necessary to define their presence.

The Identification of Chromatographic Components

Degradation of polymers may occur when they are exposed to any one, or a combination, of heat, ultra-violet radiation, neutron radiation, oxygen, or ozone.

Random degradation is analogous to stepwise polymerization. In this instance chain rupture or scission occurs randomly along the chain producing fragments which are usually large compared to the monomer units which joined to form the polymer.

Chain depolymerization involves the successive release of monomer units from a chain end in a depropagative reaction which is essentially the reverse of chain or addition polymerization.

Thermal alterations may occur as random degradation or chain depolymerization or a combination of both. Madorsky (68) has shown that the chemical nature and relative amounts of the products of thermal degradation are remarkably independent of the temperature and the extent of the degradation reaction.

When the synthetic rubber SBR is subjected to thermal degradation the monomer yield is approximately 12 weight per cent and 52 mole per cent. This is contrasted with other polymeric materials in Table 9 (69).

TABLE 9

PER CENT MONOMER FROM THERMAL DEGRADATION OF POLYMERS

Polymer	% Monomer	
	Weight	Mole
Polystyrene	42	65
Polybutadiene	14	57
SBR	12	52
Polyisoprene	3	21

Pyrolytic chain depolymerization of the co-polymer of styrene and butadiene (SBR) followed by chromatographic separation and identification of the resultant monomers is the basis for this technique. Identification of all of the pyrolyzate peaks appearing in the chromatograms would be ideal and, in all probability, the goal of the analytical chemist. In this study, time and equipment limitations prohibited the luxury of such thoroughness. Furthermore, it was not considered mandatory to identify all of the column eluents in order to confirm monomer restoration.

One pyrolyzate component consistently appeared in all samples known or suspected to contain SBR. It manifested itself in each chromatogram as a large, well defined peak, having a 17 min. retention time under the previously stated "run" parameters. The position of this peak, its amplitude, and its relatively slow elution velocity made it a logical choice for collection and identification.

Each time a peak appears in a chromatogram it represents but a minute

quantity of that component and not enough for identification by other methods. Therefore repeated collections from replicated separations were necessary to concentrate sufficient peak material for identification purposes. Using the sampling traps illustrated in Figures 10 and 11, each identification required 12 to 14 collections.

The first accumulated peak sample was collected in carbon tetrachloride using the simple bubble trap of Figure 10. This initial sample was intended for separate identification by infra-red absorption spectrophotometry (carbon tetrachloride and chloroform are relatively I-R transparent), but in this first attempt an insufficient quantity of the unknown component was collected to obtain any identifiable spectra. However, the sample yielded the strong, unmistakable, penetrating odor of styrene, completely masking that of the solvent. It appeared that pyrolysis of SBR or compounded rubber products containing SBR caused depolymerization of the copolymer styrene butadiene to release the monomer styrene. In order to confirm that the isolated and collected peak represented styrene, two recognized chromatographic techniques were used.

Comparison of retention times. The basis of classical qualitative analysis in gas-liquid chromatography is a comparison of the retention times (or retention volumes) of a pure compound with those of the unknown. When operating variables are maintained constant, the retention time is characteristic of a compound. Retention time for a component of a mixture may be defined simply as the time interval from sample injection to appearance of the eluted component. Its equivalent volume of gas for that time interval is called the retention volume. The time axis of a constant-speed recorder chart can conveniently be used to compare retention times

of an unknown with that of a standard.

Five μL samples of reagent grade chloroform and reagent grade carbon tetrachloride were chromatographed to obtain "blank" patterns in which no elution peaks appeared after the first 10 minutes.

Using the bubble trap of Figure 11, twelve replications of the suspected styrene component of the SBR pyrolyzates were collected in the chloroform. Similarly, 14 replications of the suspected styrene component appearing in the (PG) pyrolyzates were collected in carbon tetrachloride. Five μL portions of each collection were injected into the chromatographic column to obtain chromatograms of the collected components. Two 1:10 dilutions of pure styrene in chloroform and carbon tetrachloride were prepared and five μL samples analyzed to produce chromatograms of pure styrene for retention time comparisons.

Addition of a suspected component. If a pure compound, that is suspected of corresponding to a specific peak of the sample chromatogram, is added to the sample, a new chromatogram obtained under identical run conditions of that of the sample chromatogram will reveal an increase in the amplitude of the original peak. Such is the basis for the second chromatographic confirmation of the identity of the suspected styrene peak. The addition of a pure liquid compound to a liquid sample is a simple procedure and one which can be done quantitatively with confidence in the results. However, the quantitative addition of a pure compound to a solid sample prior to pyrolysis is quite another matter. The technique adopted is simple and entirely suitable for the purposes of this study, but suffers somewhat in reproducibility.

The solid samples were placed in the jaws of the probe as before but

just prior to insertion into the injection port a 1 μL droplet of a 1:10 or 1:50 styrene in chloroform dilution was placed on the solid sample. The altered sample was then quickly inserted into the chamber and pyrolyzed as before under the same operating conditions to obtain an amplified styrene peak.

Discussion

The standard chromatograms of the pyrolyzates of the raw elastomers of SBR, latex (natural rubber) and butyl rubber were the basis for identification of vehicle tire rubber in a sample of roadway dust. They are the rubbers used most frequently in tire manufacture. The chromatograms illustrated are typical of many replications of test runs on each of the polymeric materials. Each compound, when subjected to this method of analysis produces an identifiable and consistent "fingerprint" which can be used to qualitatively characterize that compound. This method is of particular value in its application to analysis of the high polymers or "giant molecules". At constant carrier gas flow rate and constant column temperature, retention times for the series of elution peaks were identical. Only the amplitude of the peaks varied from run to run as no attempt was made to exactly duplicate sample sizes.

The chromatogram of "raw" SBR is shown in Figure 13. It features seven clearly resolved major peaks, one of which, labeled "S", predominates consistently in all of the chromatograms of SBR - the major rubber material used in tire manufacture.

Latex (natural rubber), which is present in practically all tires produced the pattern of Figure 14. Raw elastomer butyl rubber containing only an antioxidant yielded the chromatogram of Figure 15. Some vehicle

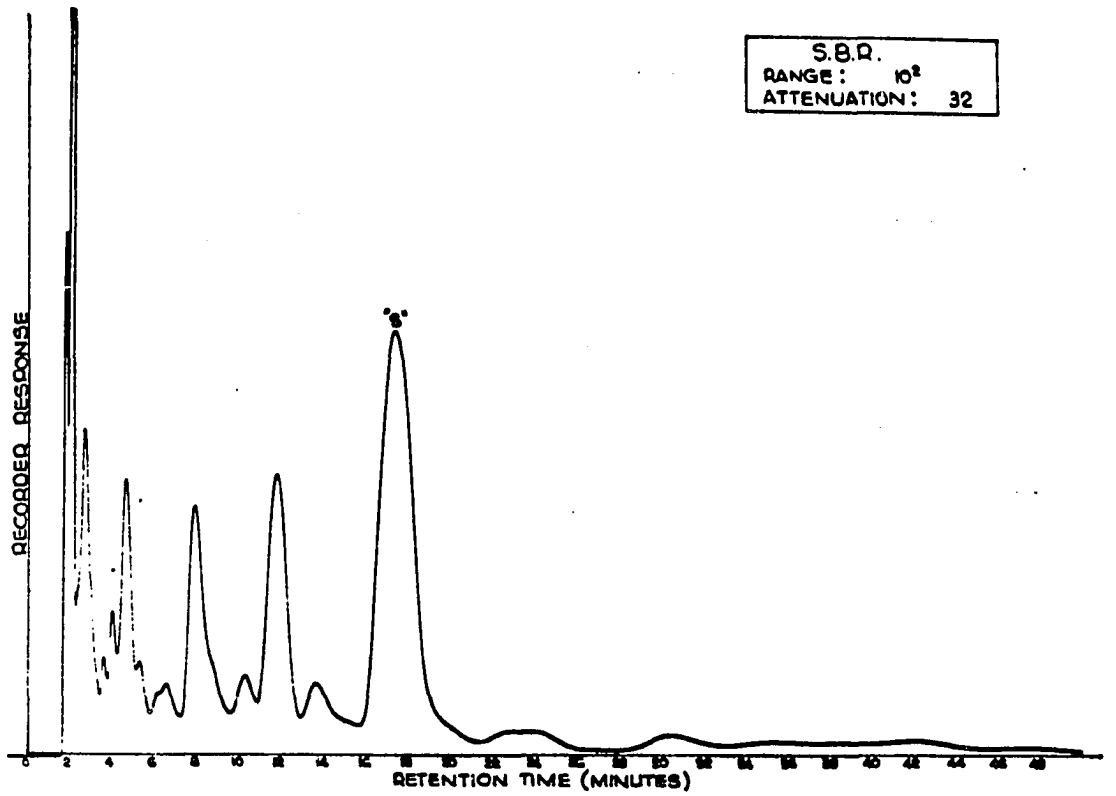

Figure 13. Chromatogram of SBR pyrolyzates.

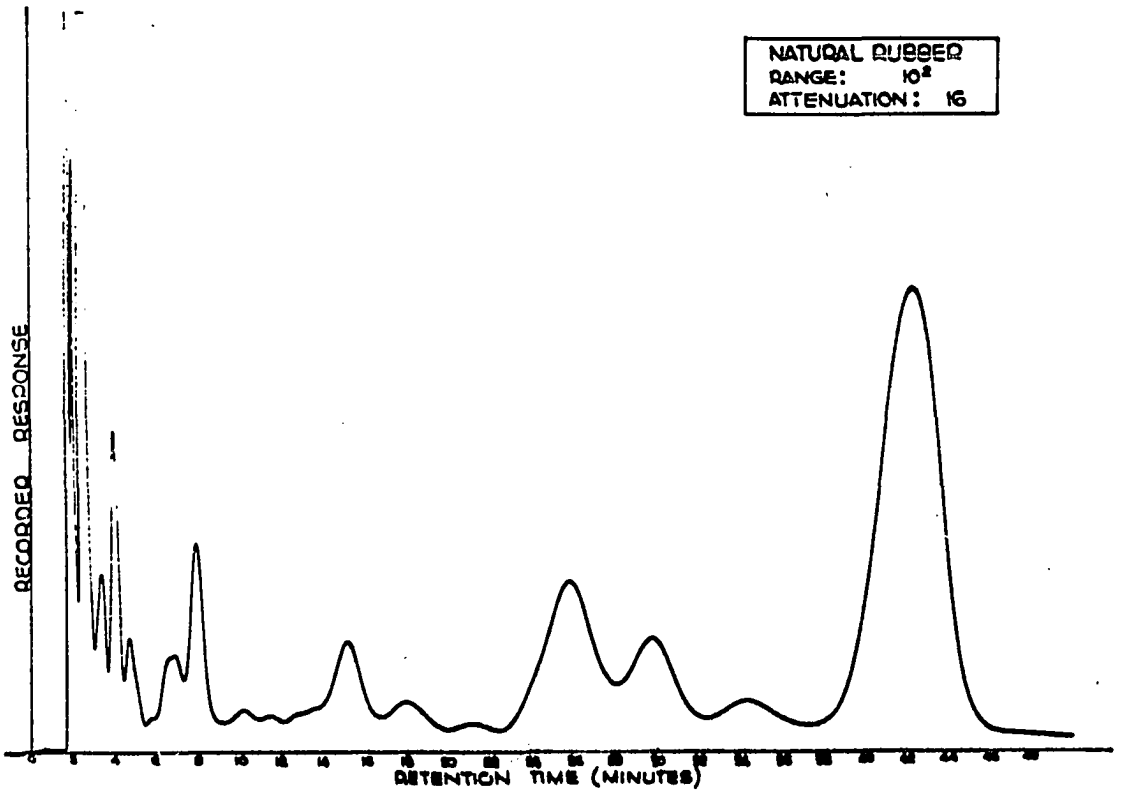

Figure 14. Chromatogram of natural rubber pyrolyzates.

tires are now made almost entirely of butyl rubber or at least contain significant amounts in their formulation. This synthetic is used exclusively in the manufacture of the obsolescent inner tube.

Numerous other hydrocarbons were chromatographed to aid in the identification of rubber in dust mixtures and to provide a basis for characterization of polymers. These include neoprene, Figure 16; polyurethane, Figure 17; polystyrene, Figure 18; asphalt, Figure 19; and carbon black, Figure 20.

Samples of compounded tire rubber from three sources were pyrolyzed, chromatographed, and analyzed for evidence of the standard elastomer patterns.

A pyrolyzed sample of rubber from a new Continental 5.70 x 16 tire yielded the chromatogram of Figure 21. Excellent reproduction of the SBR pattern is observable at once. Relative peak height determinations were not attempted because they vary from sample to sample as vulcanization and compounding vary.

The SBR pattern is again strongly evident in the chromatogram of Figure 22 which represents the pyrolyzates of automobile tire grindings from a recapping operation.

Truck tire rubber, which is predominantly natural rubber, produced the chromatogram of Figure 23. The truck tire pattern which is remarkably identical to the natural rubber chromatogram of Figure 14 attests to the high natural rubber content.

Using the techniques previously described, little difficulty was encountered in the identification of SBR or natural rubber present in compounded materials. The most rigid test for the technique was in the de-

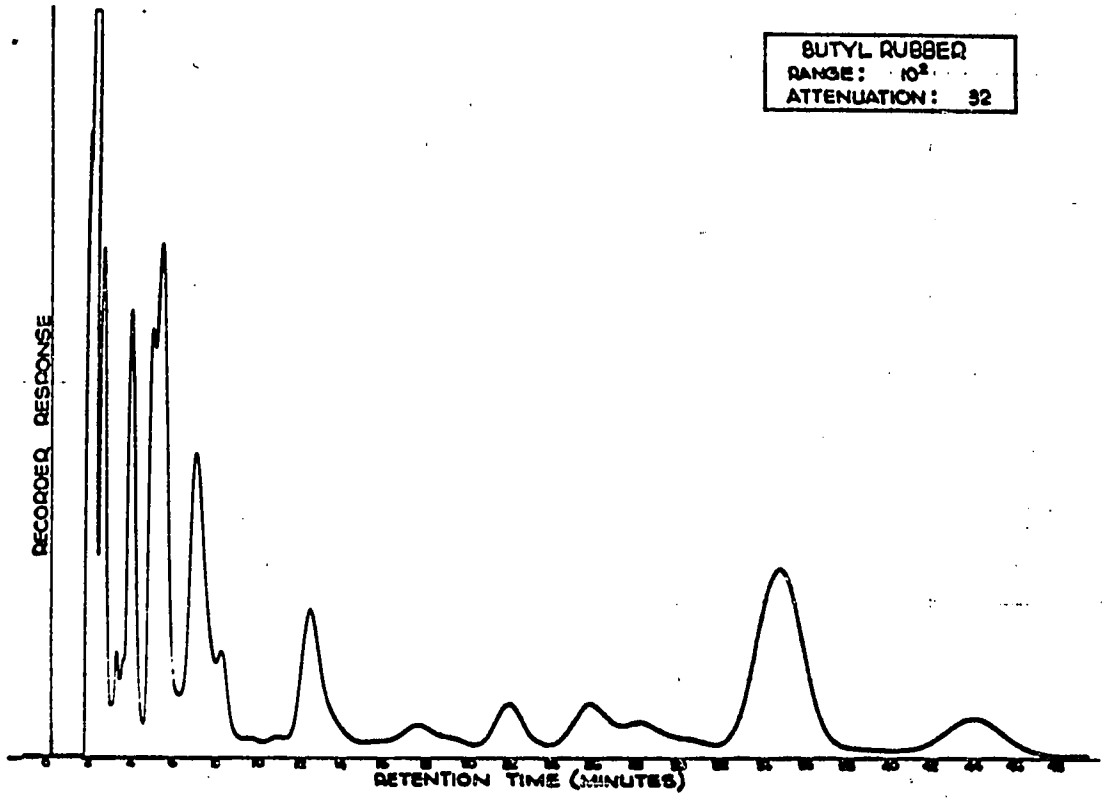

Figure 15. Chromatogram of butyl rubber pyrolyzates.

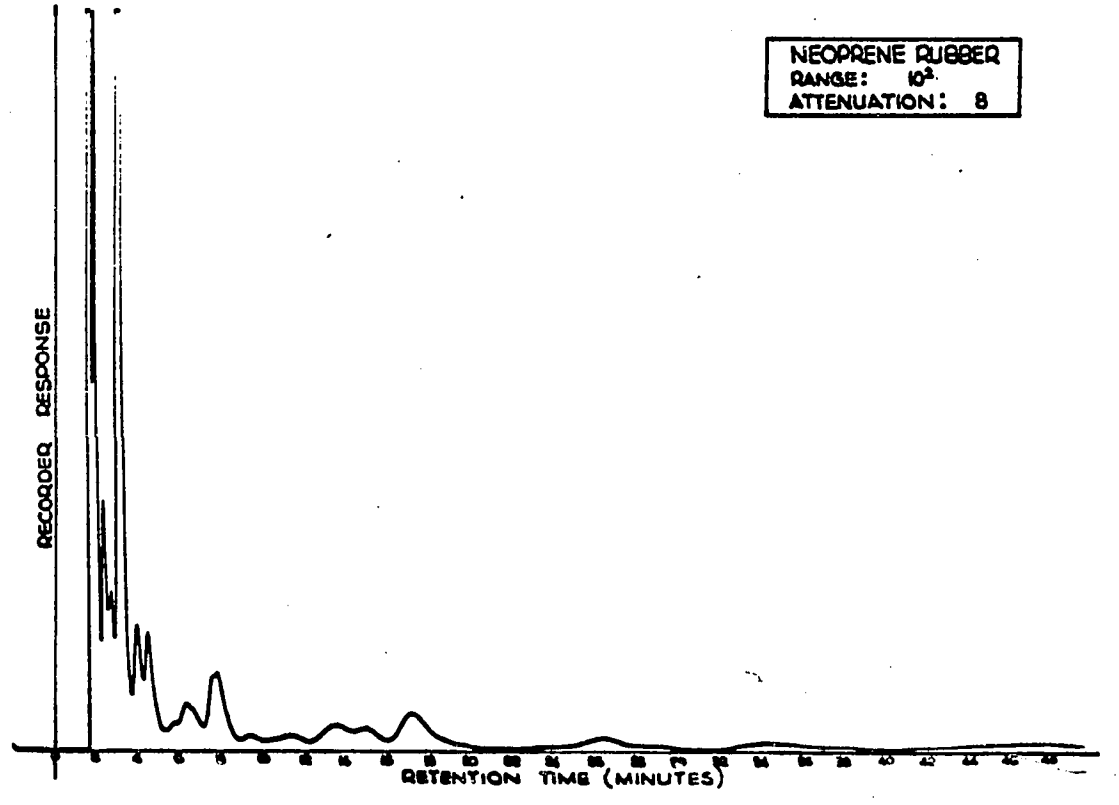

Figure 16. Chromatogram of neoprene rubber pyrolyzates.

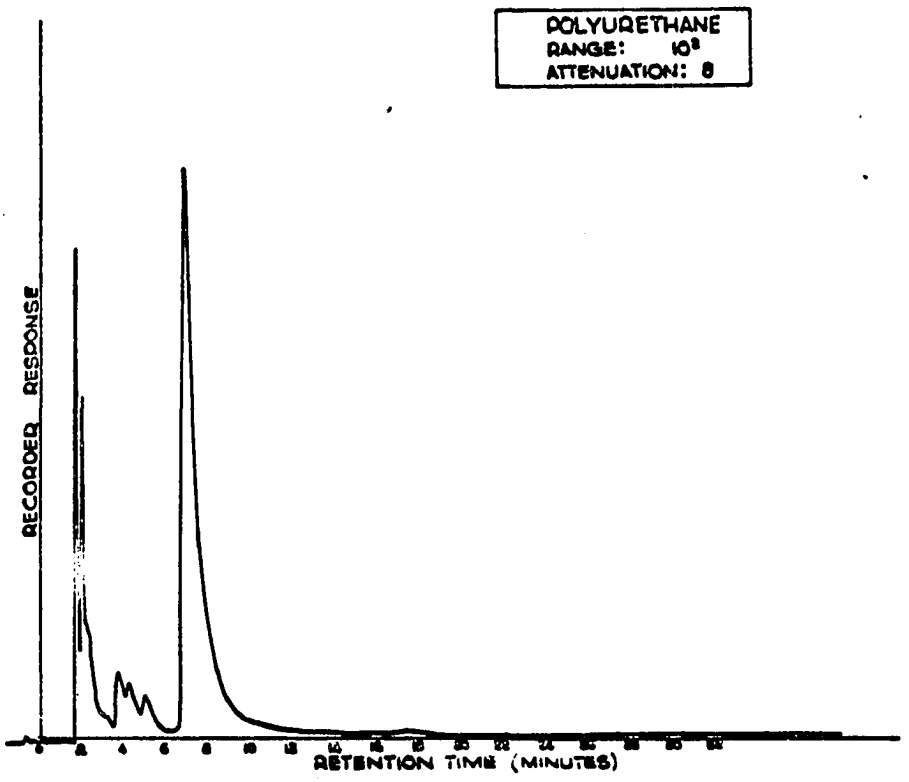

Figure 17. Chromatogram of polyurethane pyrolyzates.

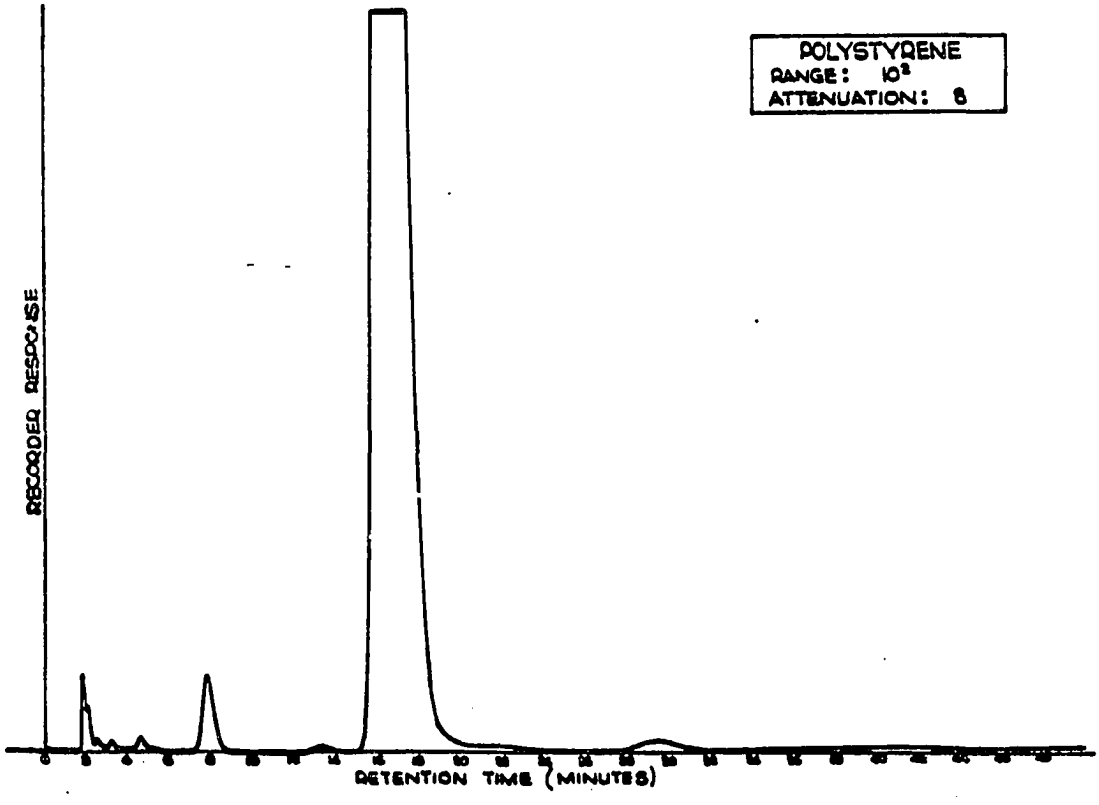

Figure 18. Chromatogram of polystyrene pyrolyzates.

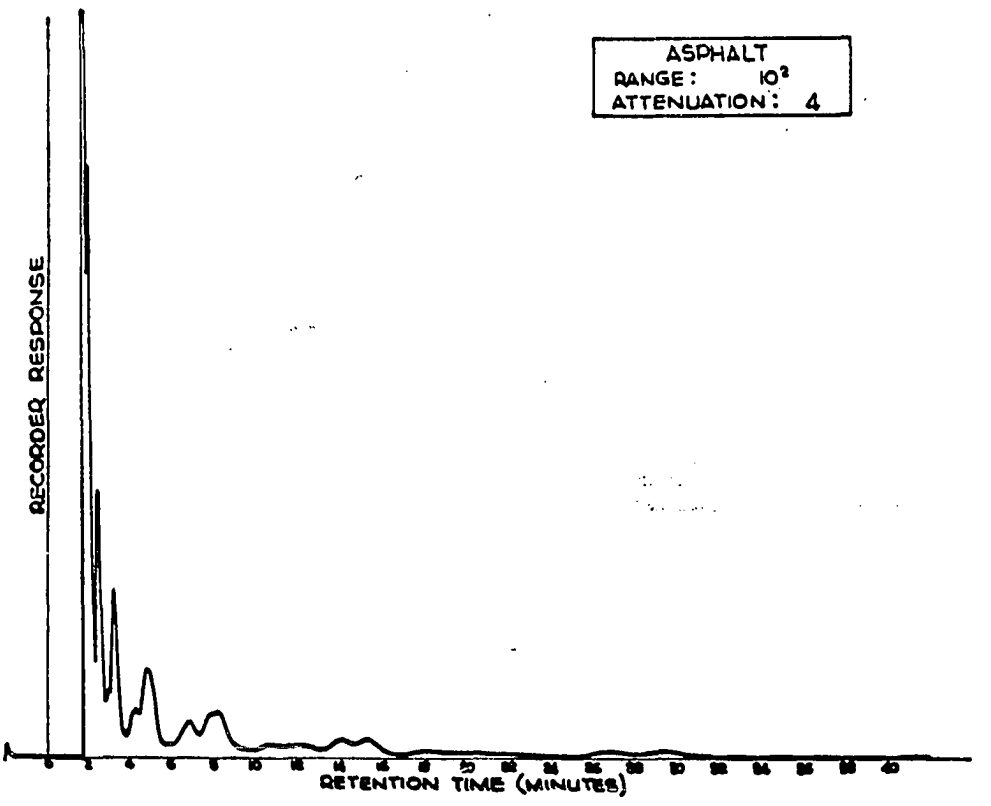

Figure 19. Chromatogram of asphalt pyrolyzates.

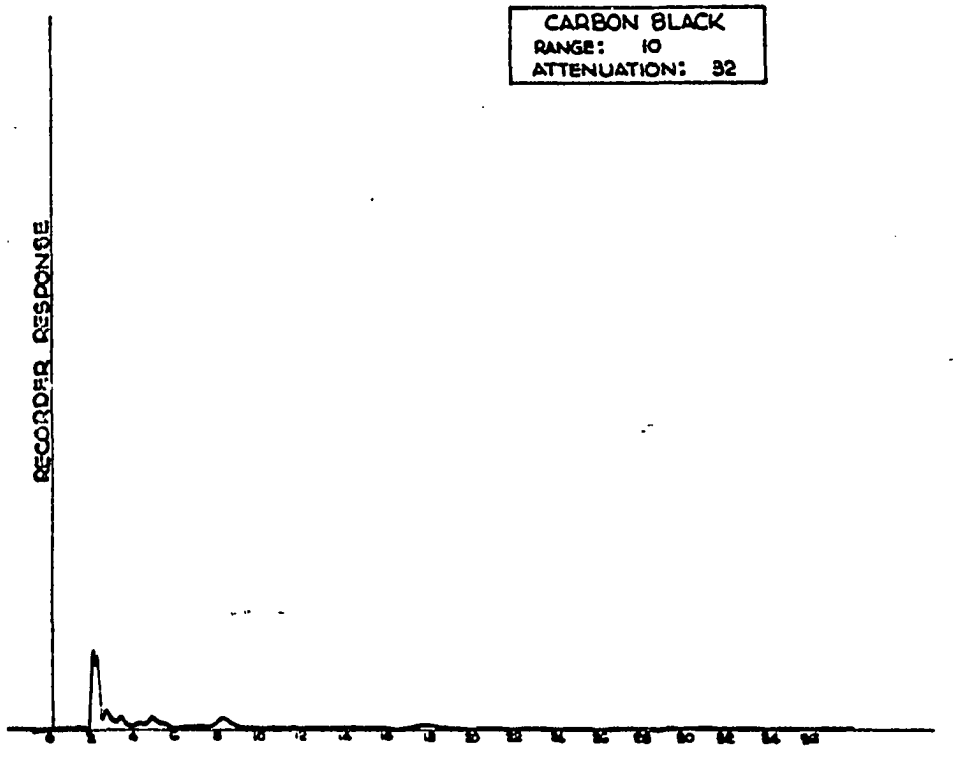

Figure 20. Chromatogram of carbon black pyrolyzates.

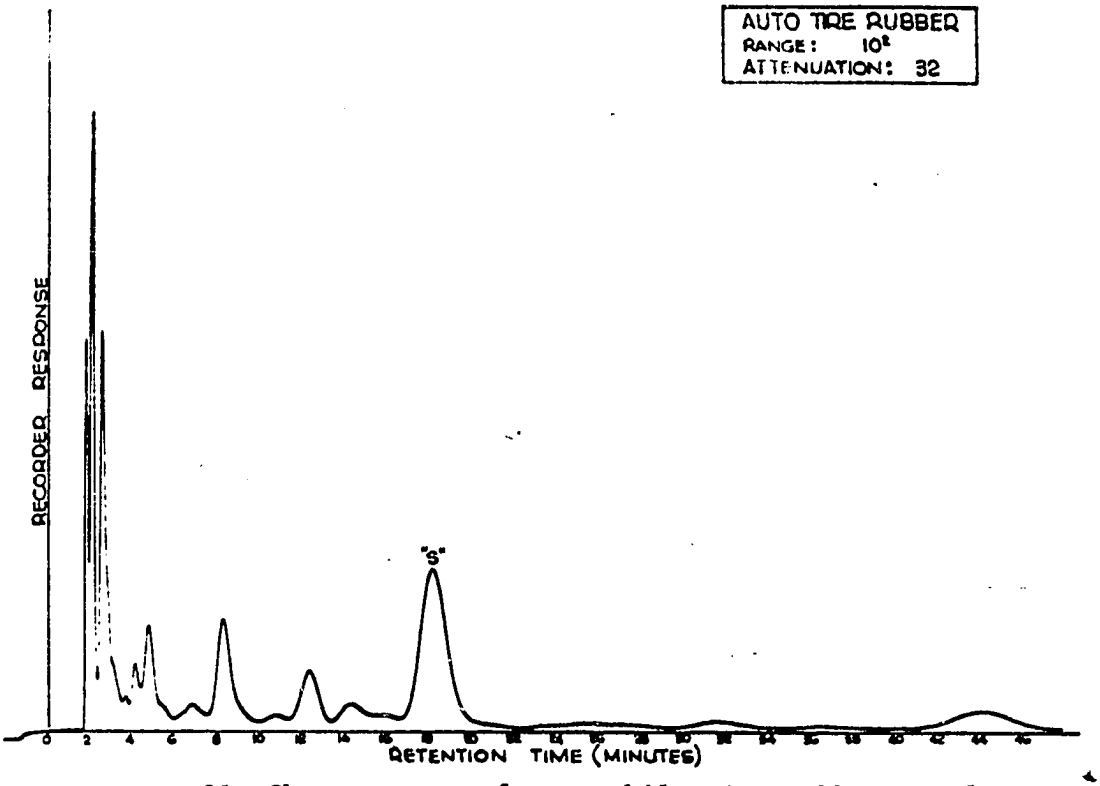

Figure 21. Chromatogram of automobile tire rubber pyrolyzates.

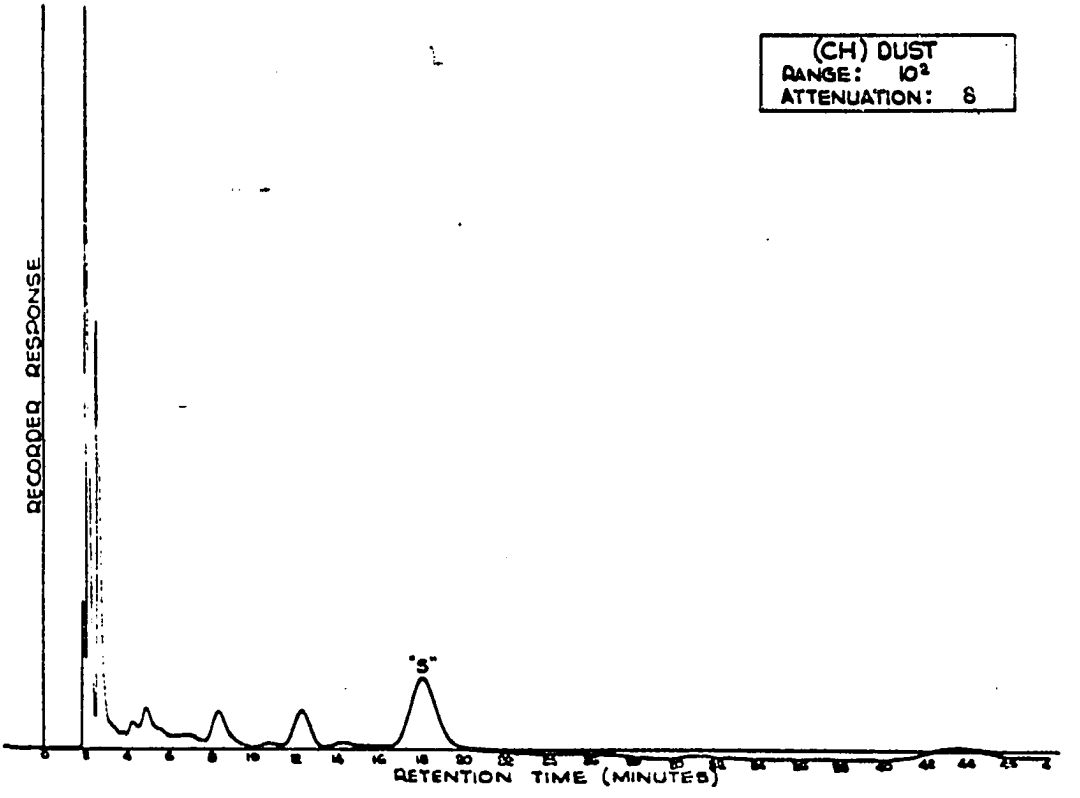

Figure 22. Chromatogram of (CH) dust pyrolyzates.

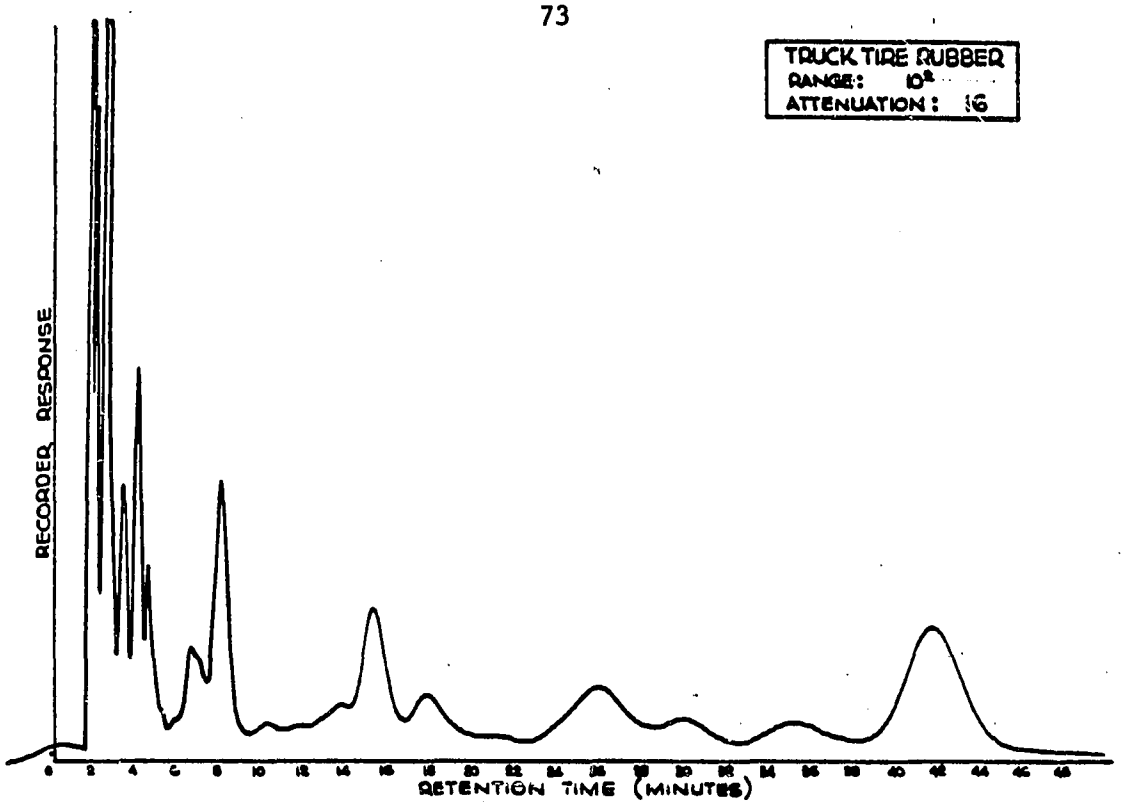

Figure 23. Chromatogram of truck tire rubber pyrolyzates.

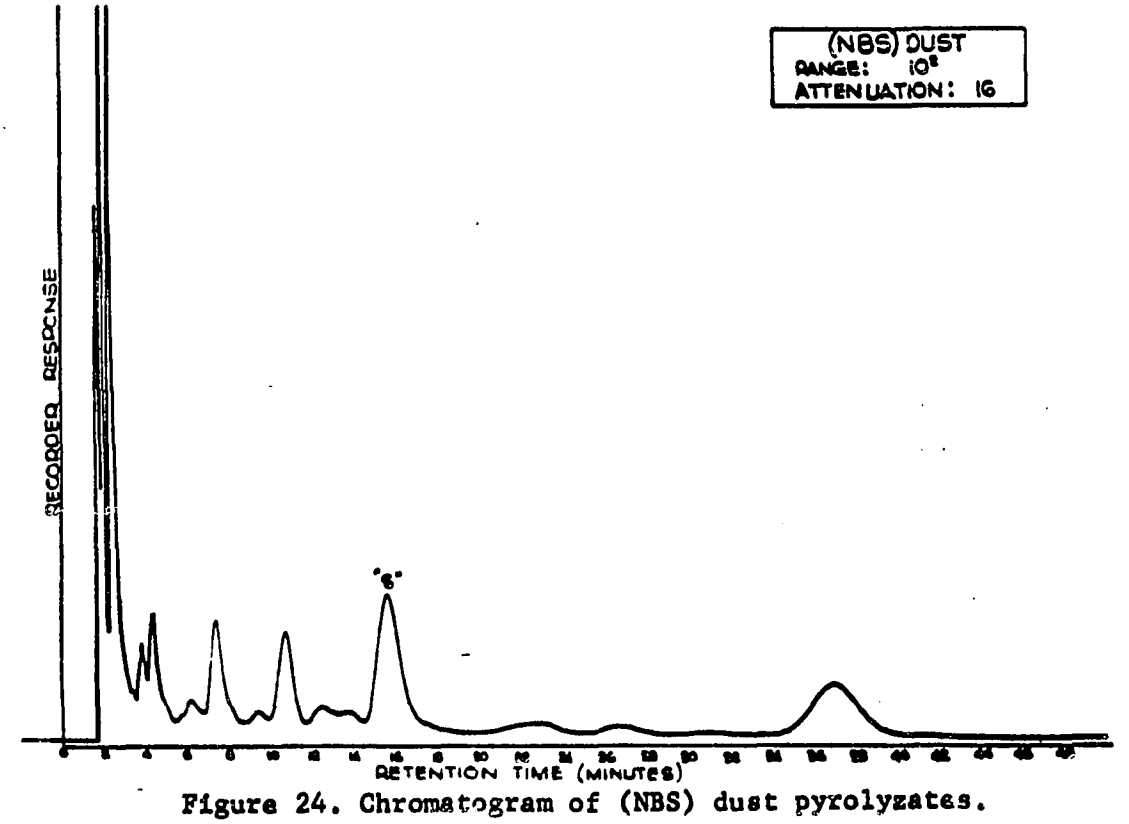

Figure 24. Chromatogram of (NBS) dust pyrolyzates.

tection of SBR and/or natural rubber in the "true" roadway dusts (H, L, and PG) and in the "simulated" roadway dust (NBS).

The (NBS) dust is a two-phase mixture of tire rubber dust and hydrated alumina in varying proportions. The SBR pattern appears very strongly in Figure 24 because the rubber dust was the only pyrolytically degradable substance present. It is especially important to note that the natural rubber pattern is evident to some extent in this chromatogram. An inquiry into the National Bureau of Standards tire testing procedure revealed that one of every five tires tested in the giant apparatus was a truck tire. As emphasized earlier, American truck tires contain 80 to 90 per cent natural rubber.

The (PG) dust sample yielded a strong SBR configuration as seen in Figure 25. This was not unexpected as automobiles were known to be the only vehicles traversing the parking garage ramps.

The (H) and (L) dusts contained many materials other than the suspect tire rubber; consequently, these materials produced complex chromatograms. However, the SBR pattern was still discernible in Figure 26 and Figure 27 and the presence of tire rubber in each of these "true" roadway dusts was confirmed. Though the identifying peaks do not have the striking magnitude of those of compounds more heavily loaded with the basic polymers, the full sensitivity of the detector was never completely utilized in producing the included chromatograms. Under full sensitivity the electrometer is capable of sensing very minute currents of electricity not attributable to ionization current from the flame detector. A random recorder pen movement, called "noise", resulting from the detection of electron movement in the electrometer circuitry, interferes with the production of

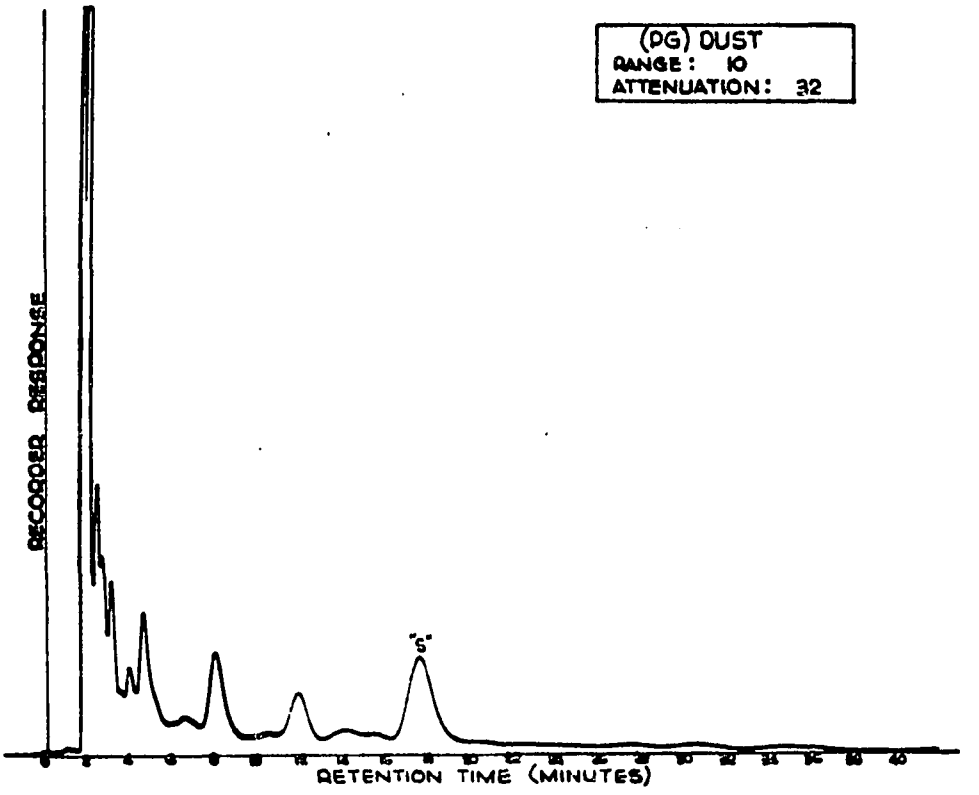

Figure 25. Chromatogram of (PG) dust pyrolyzates.

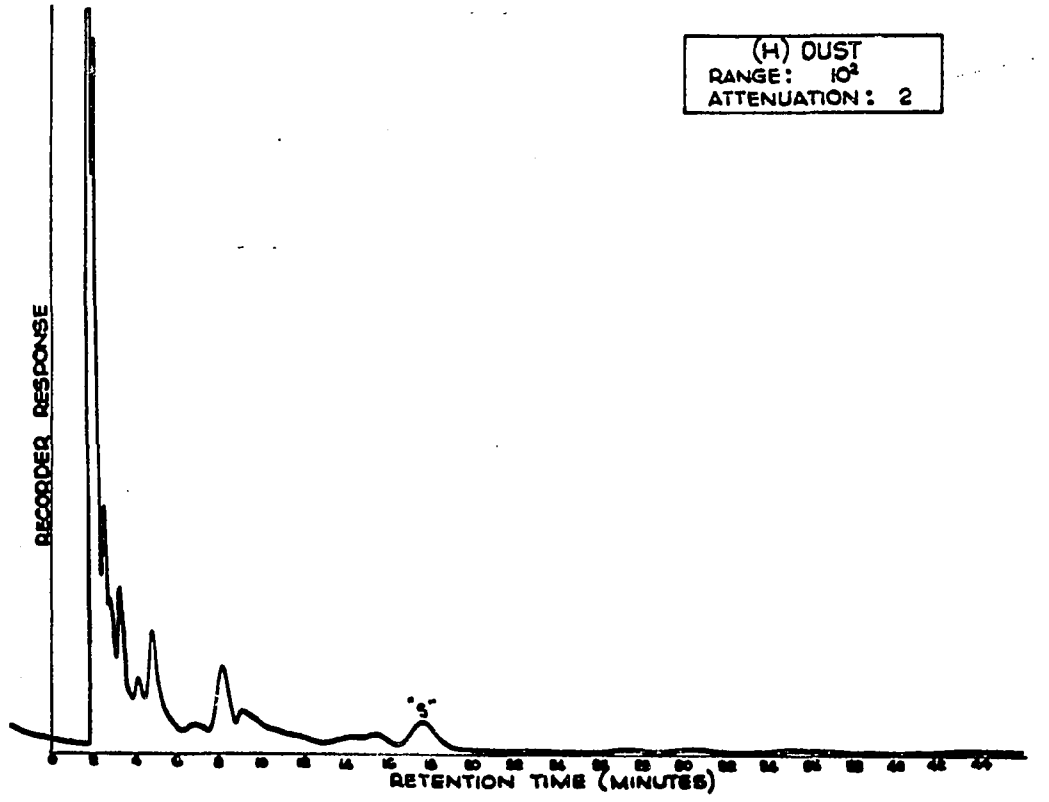

Figure 26. Chromatogram of (H) dust pyrolyzates.

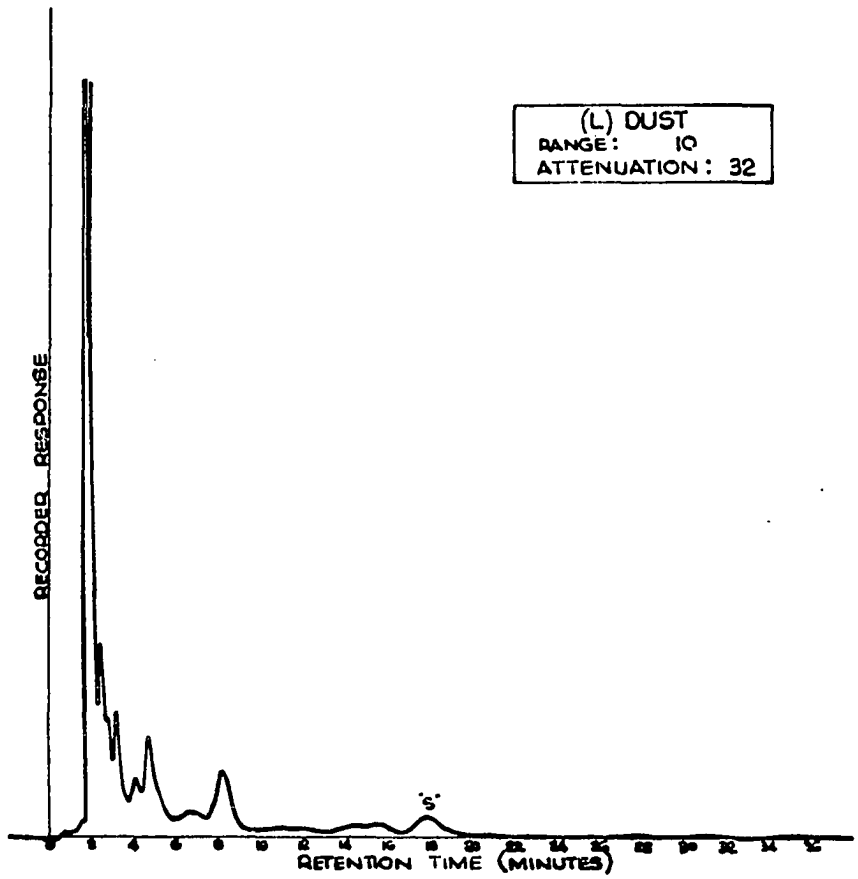

Figure 27. Chromatogram of (L) dust pyrolyzates.

smooth chromatographic peaks.

The identification of SBR and consequently tire rubber in a roadway dust was not considered conclusive until one or more of the pyrolyzate components were identified. As mentioned in the description of experimental procedure, one strong peak appeared consistently in all of the chromatograms of the pyrolyzates of material known to contain or suspected of containing SBR. In all of those chromatograms that peak is labeled "S". Suspected of being the monomer styrene, the component was collected for identification by comparison of its retention time with that of the pure styrene.

When collected in chloroform and injected again into the column the "S" component of the SBR pyrolyzates produced the chromatogram shown in Figure 28 (b). Its retention time is identical to the retention time of the pure styrene in chloroform as seen in Figure 28 (c). In like manner, when collected in carbon tetrachloride and reinjected in the column the "S" component of the (PG) pyrolyzates produced the chromatogram shown in Figure 29 (b). Again, its retention time is identical to the retention time for pure styrene in carbon tetrachloride as shown in Figure 29 (c). By comparison of retention times the peak "S" component was identified as the styrene monomer.

Using one further recognized technique for identification of chromatographic components the monomer styrene was shown to exist as one of the pyrolyzates of four of the roadway dusts. Each of the dusts were bolstered with pure styrene prior to being pyrolyzed and chromatographed. In Figure 30 the amplification of peak "S" in the (CH) dust is illustrated. Figures 31, 32 and 33 illustrate the amplication of peak "S" in (NBS),

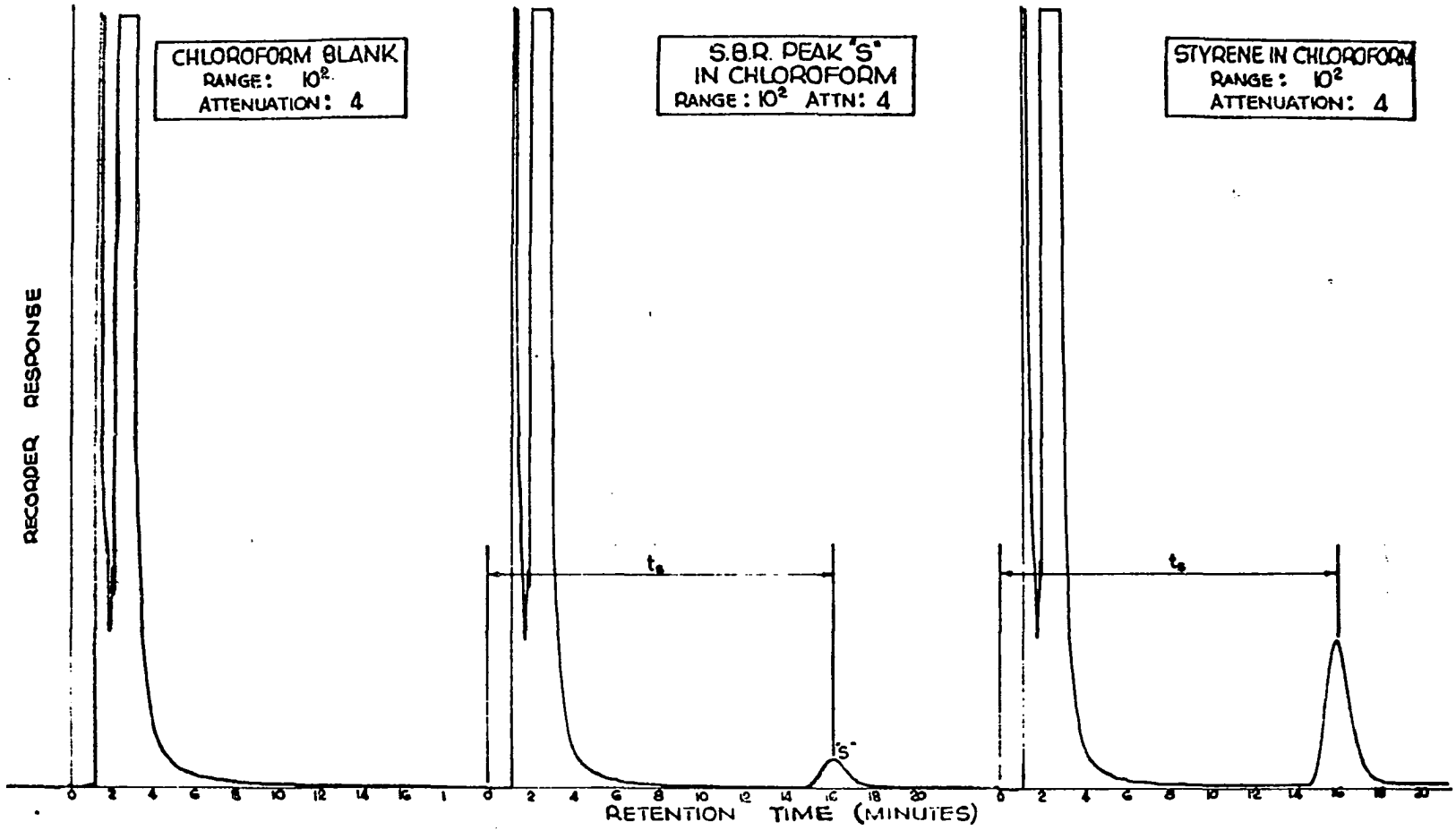

Figure 28. Identification of styrene in SBR - comparison of retention times.

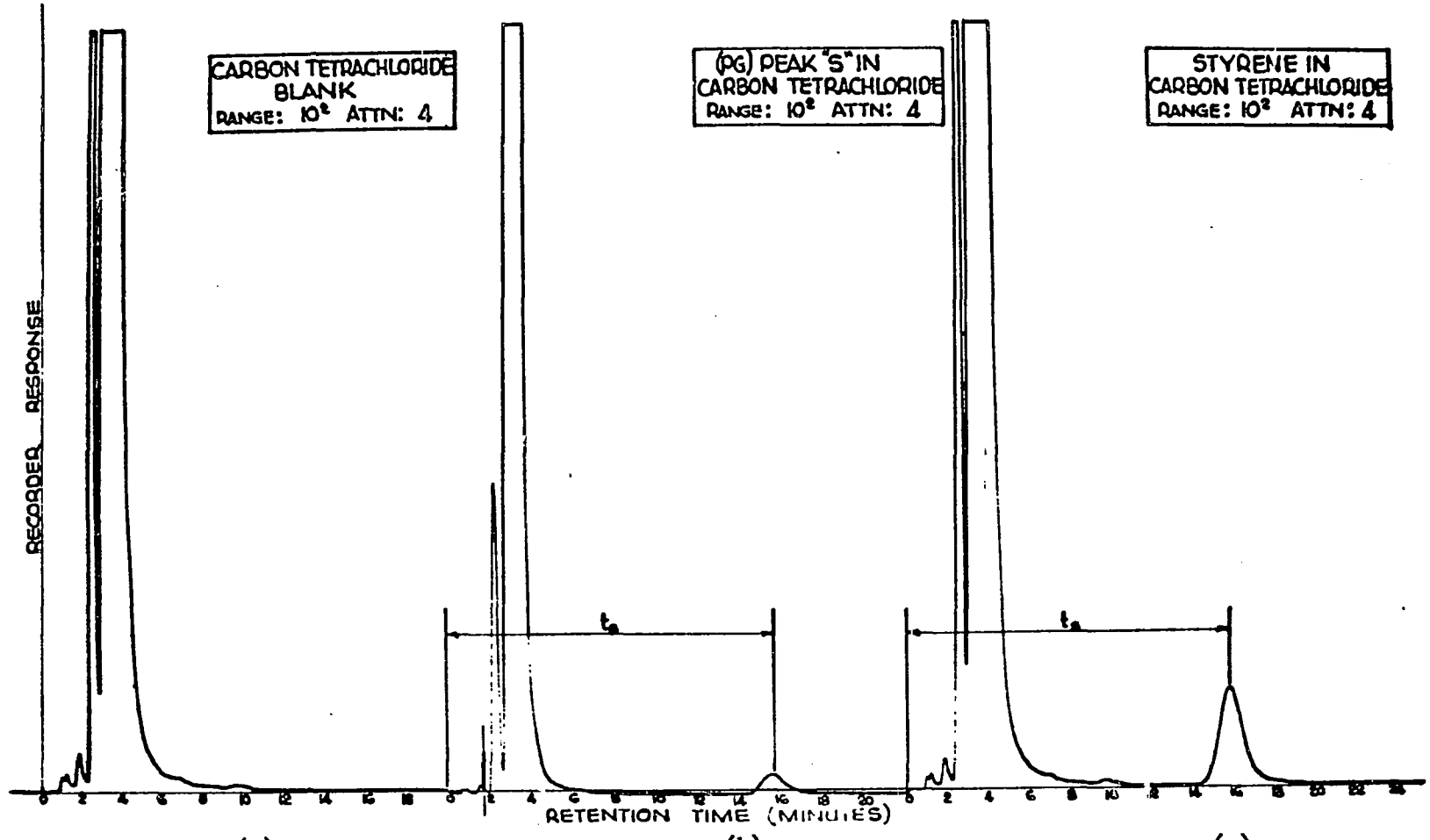

Figure 29. Identification of styrene in (PG) dust - comparison of retention times.

(PG), and (H) dusts, respectively. By the methods of "addition of a suspected component" the peak "S" component was further identified as the styrene monomer.

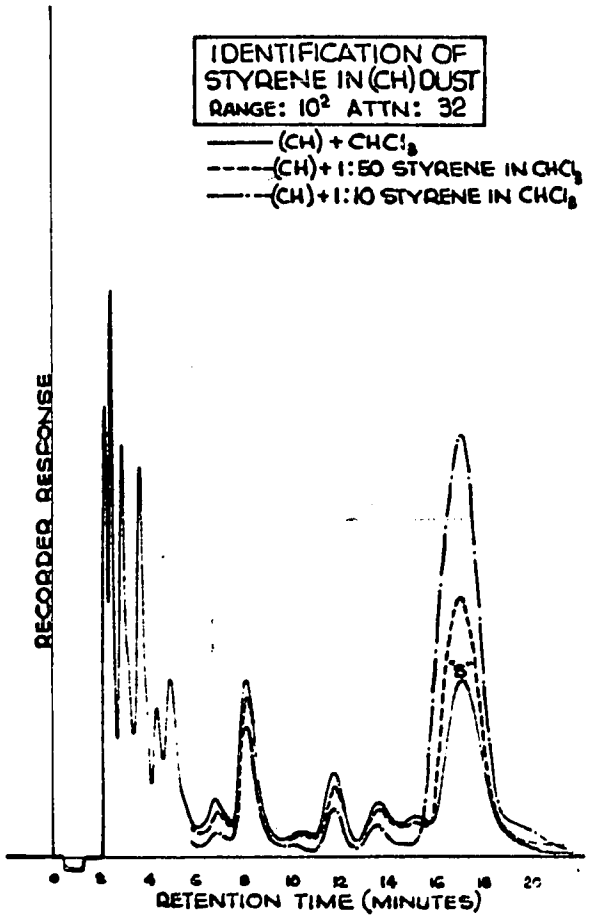

Figure 30. Identification of styrene in (CH) dust - addition of a suspected component.

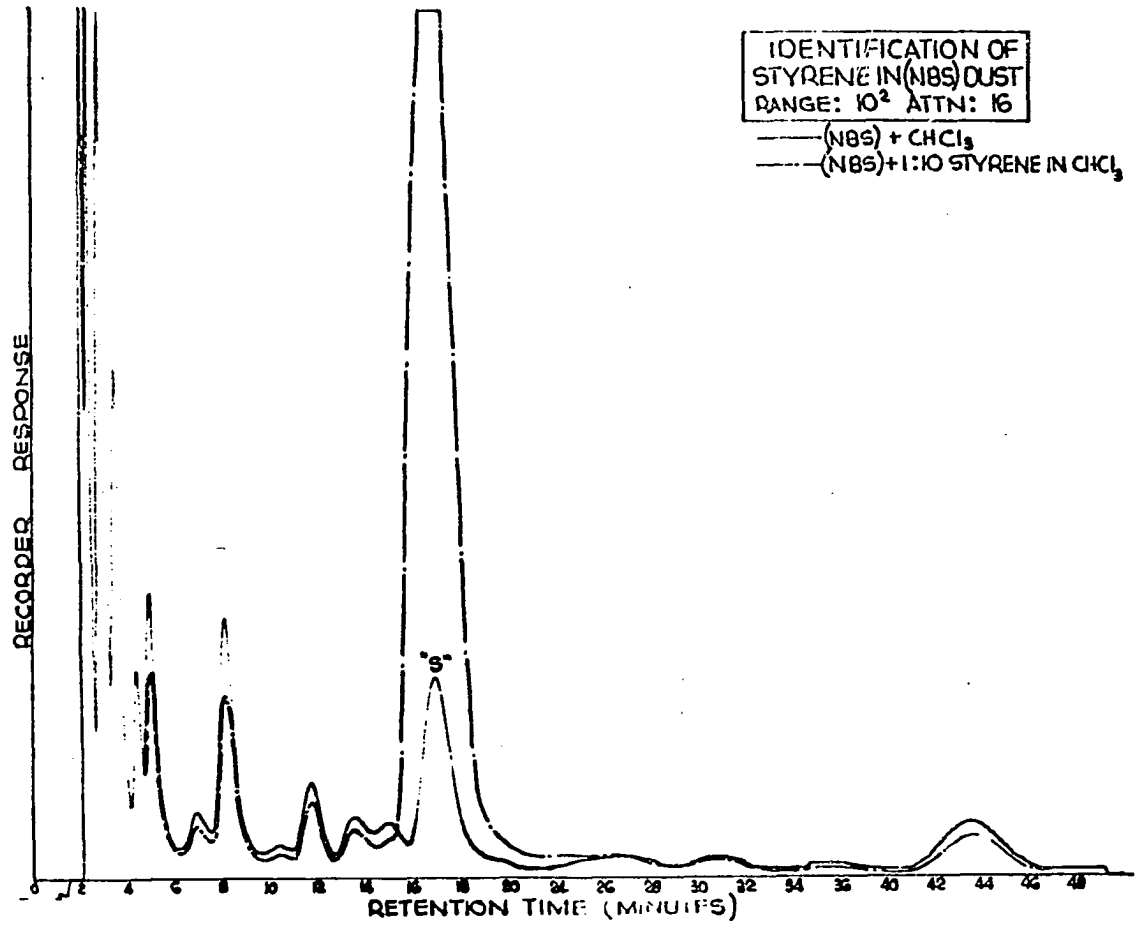

Figure 31. Identification of styrene in (NBS) dust - addition of a suspected component.

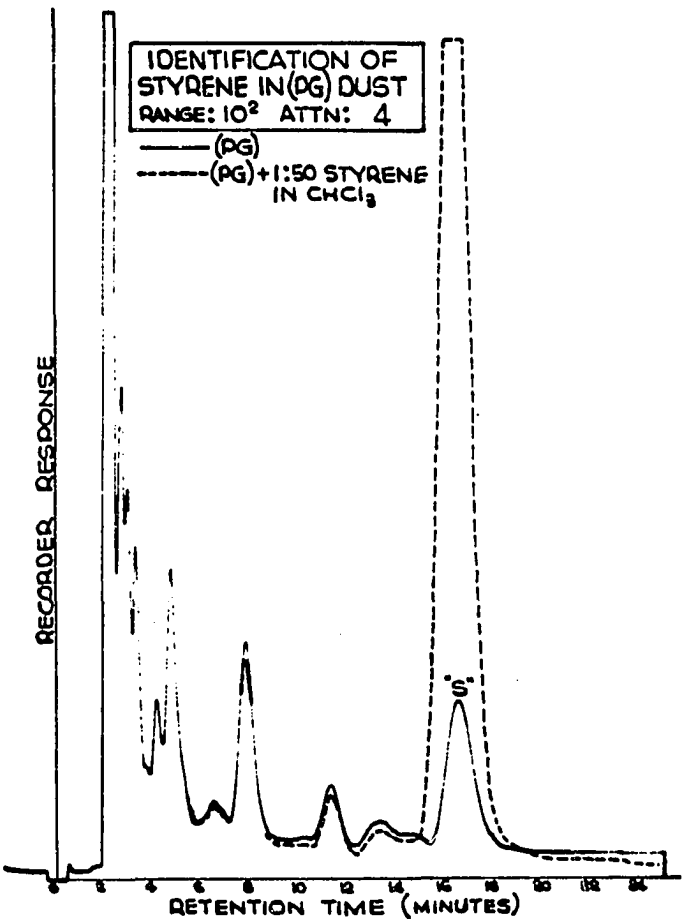

Figure 32. Identification of styrene in (PG) dust - addition of a suspected component.

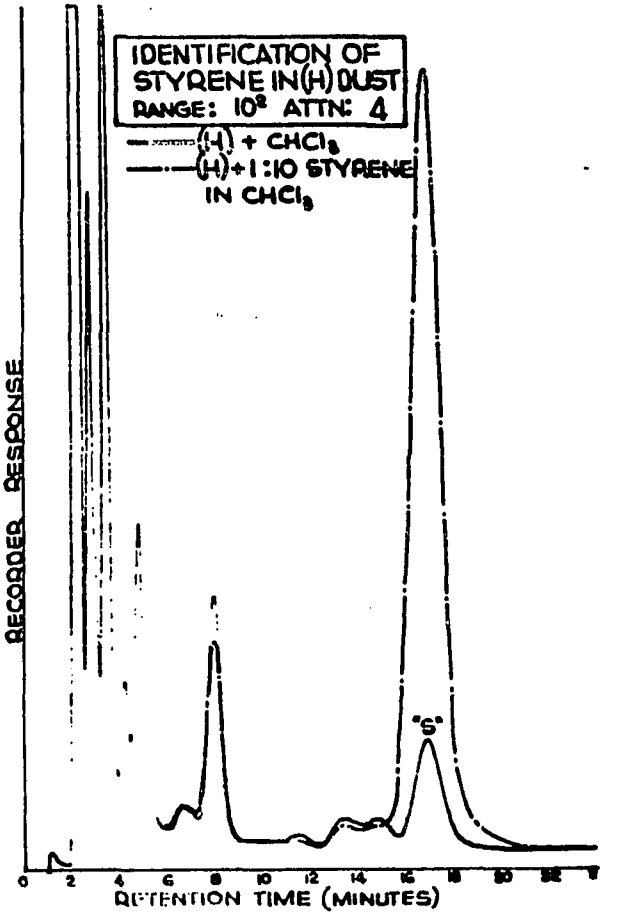

Figure 33. Identification of styrene in (H) dust - addition of a suspected component.

CHAPTER VI

SUMMARY AND CONCLUSIONS

Allusions to vehicle tire rubber as a potential source of a particulate air pollutant have appeared briefly in the literature from time to time over the past ten years. Until 1962 no investigator had gone beyond these inferences to determine if rubber tire dust is truly an aerosol pollutant of public health significance or to determine if rubber tire degradation products even exist in a particulate form in our environment. In that year the Institute of Environmental Health at the University of Oklahoma Medical Center initiated an investigation into the physiological effects of inhaled vehicle tire dust. A companion study was conceived to eliminate the obvious deficiency of information concerning the existence of and the chemical and physical nature of this suspected air pollutant. It further sought to evolve and confirm an efficient and reproducible instrumental procedure for the identification of vehicle tire rubber in a sample of roadway dust.

Based on the evidence accumulated, the techniques developed and confirmed, and the data collected and analyzed in this investigation, the following conclusions have been drawn:

1. Rubber tire degradation products definitely contribute to the pollution of our environment. They constitute a potential source of polycyclic aromatic hydrocarbons known or suspected of being carcinogenic.

Dusts collected from, or in close proximity to, actual as well as simulated roadways contain respirable solid aerosols identifiable as particulate tire rubber.

2. Sizing of gross samples of roadway dusts reveals that their heterogeneity prohibits representation of data in the commonly used log-normal distributions. The data can be presented and analyzed most realistically using frequency histograms. When the dusts are well dispersed it is found that 90 per cent of each dust size distribution, by count, is represented by particles equal to or less than 5 μ in diameter. The count majority of each dust studied lies within the range for retention in the human lung. However, from the standpoint of chemical activity potential, it is significant that 85 to 100 per cent of the total area distributions of the roadway dusts are represented by particle sizes in excess of 5 μ in diameter. It is generally accepted that filtering efficiency of the upper respiratory passages is essentially 100 per cent for sizes greater than 5 μ in diameter. Ninety-five to 100 per cent of the total weight distributions result from particle sizes in excess of 5 μ. This factor will be significant in future evaluations of the quantitative contribution of rubber tire dust to the total respirable particulate load in the atmosphere.

3. In addition to rubber tire dust, free silica, talc, asbestos, lead and zinc may be liberated to the environment as tires are abraded. These further contributions to the complex mixture of organic and inorganic substances create, in roadway dust, a conglomeration that resists qualitation or quantitation of its respirable rubber fraction

by usual analytical methods.

4. A new instrumental technique capable of detecting vehicle tire rubber in a sample of roadway dust has been developed. This quick, reliable and extremely sensitive procedure combines the expediency of pyrolysis and the versatility of gas-liquid chromatography to volatilize and separate for identification the organic components of roadway dust.

5. The methods developed in this study are readily adaptable to the detection of other non-volatile particulate pollutants which might invade the atmosphere. Asphalt, for example, can be treated similarly to permit identification of pavement abrasion products.

6. Although this is a qualitative technique, with some modification and refinement it can be developed as a quantitative method to permit evaluation of the vehicle tire dust contribution in terms of "vehicle miles" or "tire miles".

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