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REVIEW OF DIESEL ODOR AND TOXIC VAPOR EMISSIONS

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FINAL REPORT

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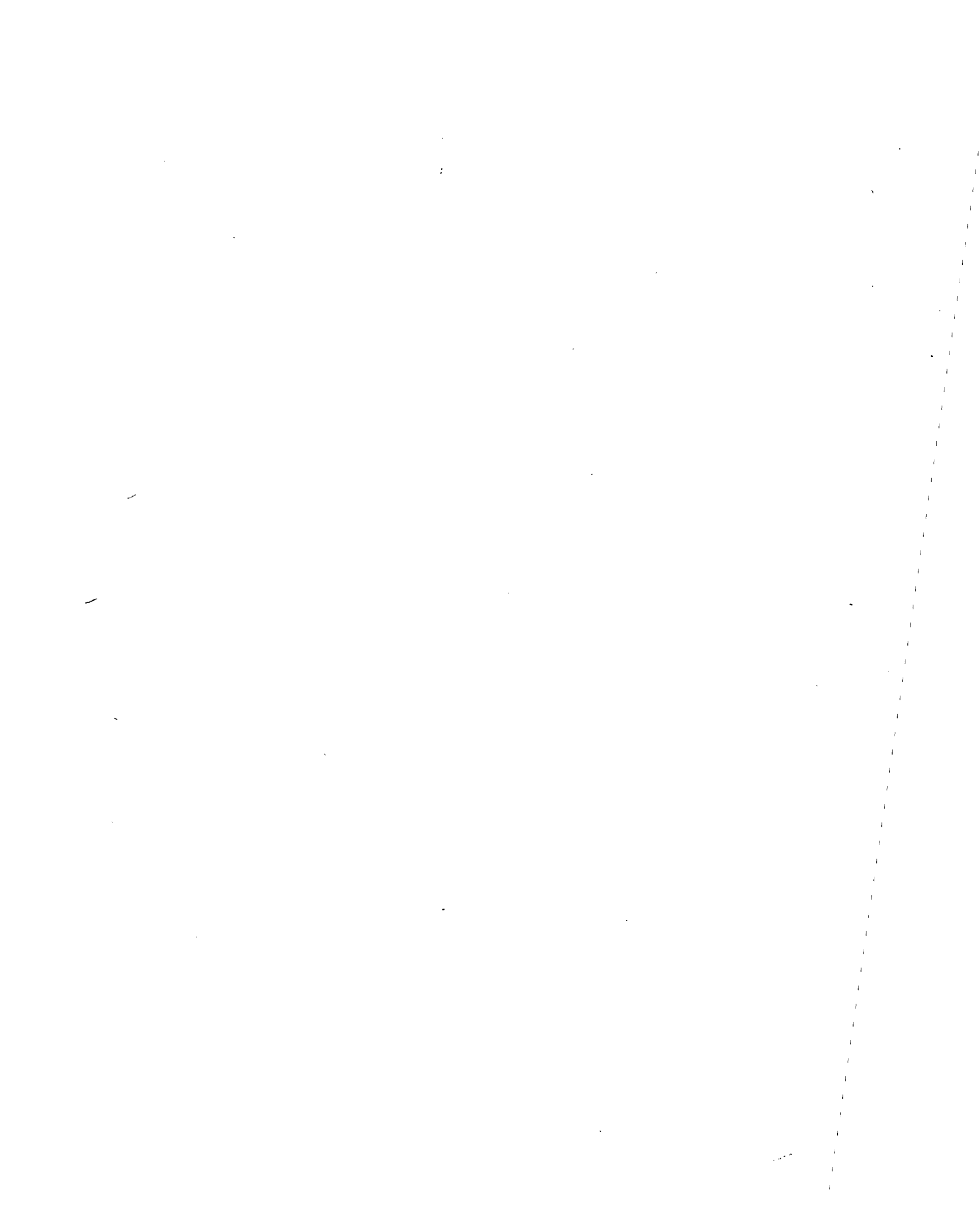
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PREFACE

A review of the chemical composition and analysis methods has been carried out for the species in diesel exhaust. Emphasis was placed on chemicals giving rise to sensory response, odor and irritation, and toxic chemicals. The review consisted of a literature search and interviews with researchers in currently active programs.

The review is organized by chemical, sensory and physical groups including carbon monoxide, carbon dioxide, nitrogen oxides, sulfur oxides, hydrocarbons, oxygenates subdivided into carbonyls, phenols and odorants, irritants, polynuclear aromatic hydrocarbons, particulates, and health effects/exposure studies.

The chemical information was found to be adequate for many groups and almost non existent for others. Analysis procedures were found to vary from continuous on-line instruments to laborious batch type manual methods.

Recommendations have been made for various levels of research programs for each of the groups of chemicals.

The following individuals have been contacted for information and opinions in preparation of this review. Their assistance has been most valuable and their cooperation is gratefully acknowledged:

Dr. Ronald Bradow	U.S. Environmental Protection Research Triangle Park
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Mr. Ralph Slone	Cummins Engine Company, Inc.
Dr. Joseph Sommers	U.S. Environmental Protection Agency, Research Triangle Park
Mr. Karl Springer	Southwest Research Institute
Dr. I.H. Suffett	Drexel Institute

Approximate Conversions to Metric Measures

Symbol	When You Know	Multiply by	To Find	Symbol
<u>LENGTH</u>				
in	inches	2.5	centimeters	cm
ft	feet	30	centimeters	cm
yd	yards	0.9	meters	m
mi	miles	1.6	kilometers	km
<u>AREA</u>				
in ²	square inches	6.5	square centimeters	cm ²
ft ²	square feet	0.09	square meters	m ²
yd ²	square yards	0.8	square meters	m ²
mi ²	square miles	2.6	square kilometers	km ²
	acres	0.4	hectares	ha
<u>MASS (weight)</u>				
oz	ounces	28	grams	g
lb	pounds	0.45	kilograms	kg
	short tons (2000 lb)	0.9	tonnes	t
<u>VOLUME</u>				
teaspoon	teaspoons	5	milliliters	ml
tablespoon	tablespoons	15	milliliters	ml
fluid ounce	fluid ounces	30	milliliters	ml
cup	cups	0.24	liters	l
pint	pints	0.47	liters	l
quart	quarts	0.95	liters	l
gallon	gallons	3.8	liters	l
cubic foot	cubic feet	0.03	cubic meters	m ³
cubic yard	cubic yards	0.76	cubic meters	m ³
<u>TEMPERATURE (approx)</u>				
°F	Fahrenheit temperature	5/9 (also subtract 32)	Celsius temperature	°C

*1 in. = 2.54 exactly. For other exact conversions and more detailed tables, see NBS-604, Page 206, Units of Weight and Measure, Price 17.75. SD Coll.-No. C13-10-206



Approximate Conversions from Metric Measures

Symbol	When You Know	Multiply by	To Find	Symbol
<u>LENGTH</u>				
mm	millimeters	0.04	inches	in
cm	centimeters	0.4	inches	in
m	meters	3.3	feet	ft
mi	miles	1.1	yards	yd
km	kilometers	0.6	miles	mi
<u>AREA</u>				
cm ²	square centimeters	0.16	square inches	in ²
m ²	square meters	1.2	square yards	yd ²
km ²	square kilometers	0.4	square miles	mi ²
ha	hectares (10,000 m ²)	2.5	acres	ac
<u>MASS (weight)</u>				
g	grams	0.035	ounces	oz
kg	kilograms	2.2	pounds	lb
t	tonnes (1000 kg)	1.1	short tons	sh
<u>VOLUME</u>				
ml	milliliters	0.03	fluid ounces	fl oz
l	liters	1.1	quarts	qt
l	liters	1.06	quarts	qt
l	liters	0.26	gallons	gal
m ³	cubic meters	35	cubic feet	ft ³
km ³	cubic kilometers	1.3	cubic yards	yd ³
<u>TEMPERATURE (approx)</u>				
°C	Celsius temperature	9/5 (also add 32)	Fahrenheit temperature	°F

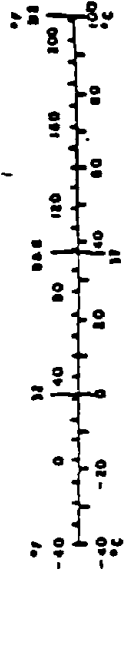


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1. INTRODUCTION

The purpose of the study was to attempt to assess the adequacy of the diesel engine exhaust chemical composition data base and instrumental analysis methods for the measurement of chemicals giving rise to sensory response, especially odor and irritation. The review would then constitute the basis for recommendations as to areas for future research.

A further objective was to relate the chemistry of the species giving rise to sensory response (odor, irritation) to those also known to have other toxic effects, such as the polynuclear aromatic hydrocarbons.

The results of the first toxicity tests of diesel particulate extract carried out using the Ames salmonella test was announced after the goals of this review had been established. Considerable experimental activity relating to diesel particulate and other unregulated emissions has been initiated during the course of this review. The Environmental Protection Agency has initiated a significant comparative health effects study of diesel exhaust particulate, and in addition is conducting a number of chemical characterization studies.

At the time of writing this report, much of the additional chemical and health effects information which is now recognized as being significant for diesel engines is still underway and preliminary findings have not been confirmed.

The material presented in this report is thus restricted primarily to information which was published prior to 1978, with some attempt to integrate information developed since that time. The status of information available on odor and irritation has not changed in the last few years and the review is thus current in that regard. A review focusing on the results of the current diesel particulate health effects and chemistry studies will be appropriate in the early 1980's.

The scope of the review was thus to determine whether the currently available instrumentation was adequate for measurement of those species. Those species, such as the regulated emissions (CO, HC, NO_x, Smoke) are covered extensively in a number of engineering reports and reviews and receive minimal attention in this review. The engine design and operating parameter cause and effect relationships are also deferred to other engineering reports.

The approach used for the review included several different methods for obtaining information including:

1) Conducting an updated literature search. The computerized on-time data bases were searched for

- odor
- irritants
- toxic species (or chemicals)
- polynuclear aromatic hydrocarbons

The computer search update focused on the period from 1970.

2) Review of the Arthur D. Little, Inc., literature files on diesel exhaust, especially odor.

3) Personal interviews with researchers currently active in the field. The interviews included telephone conversations and in-depth trip interviews. A list of individuals contacted is given in the Preface. Their assistance is gratefully acknowledged and their perspective was invaluable in completing this review. The interview sheet shown in Table 1 was used as the basis for questions in these interviews.

During the course of this review, the Coordinating Research Council (CRC) CAPI-1-64 composition of diesel exhaust panel and chemical characterization sub-panel have been active in summarizing available information and identifying research needs. Active participation in that panel has further helped in summarizing the information for this review.

Arthur D. Little, Inc., has just completed (Menziez, 1979) a comprehensive review of state-of-the-art methodology for measuring diesel exhaust contaminants, performed for the U.S. Bureau of Mines. This review covers in detail the various alternative methods for measurement of regulated and unregulated emissions. Sampling procedures are also discussed in detail. Because they have been covered thoroughly in that report, the information is not repeated in this review. The currently preferred methods identified in that report are identified in this review. Sampling and analysis methods for the following contaminants were evaluated:

- carbon monoxide (CO)
- carbon dioxide (CO₂)
- nitric oxide (NO)
- nitrogen dioxide (NO₂)
- hydrocarbons (HC)
- particulates
- polynuclear aromatic hydrocarbons (PNA)
- sulfate (SO₄)
- oxygenates

In addition, the Southwest Research Institute (SwRI) has recently published (Dietzmann, 1979) a description of the analytical procedures being used by EPA and SwRI for the characterization of unregulated emissions from gasoline fueled motor vehicles. That report includes detailed descriptions of methods and validation results for:

- aldehydes and ketones
- organic amines

sulfur dioxide
nitrous oxide
individual hydrocarbons
hydrogen sulfide
total cyanides
organic sulfides
nickel carbonyl
ammonia

While these methods have been selected for, and demonstrated to be valid with gasoline engine exhaust, the procedures for most of the methods would also be appropriate for diesel engine exhaust.

TABLE 1. INTERVIEW QUESTIONS: REVIEW OF TOXIC DIESEL ENGINE EXHAUST EMISSIONS

PURPOSE: Describe existing methodology and identify research needs in chemical understanding and measurement technique development.

QUESTIONS:

- What species (or groups) are most important to health?

CO

HC

SO₂/SO₄

NO/NO₂

Particulates

PAH

Aldehydes

Odor

Irritants

} focus of study

- What groups have sufficient information/monitoring methods?
- What groups need greatest development (research) effort?
- What area do we need more chemical information in?
- What area needs (is ready for) instrument development?

2. DISCUSSION

2.1 COMPOSITION OF DIESEL EXHAUST - OVERVIEW

Any review of diesel exhaust, or efforts to initiate new research programs to study diesel exhaust, should recognize that diesel exhaust has been the subject of intensive research programs for many years at the Bureau of Mines, and recently the Department of Energy. The Environmental Protection Agency also maintains active research programs at its Ann Arbor and Research Triangle Park facilities, as well as contractor laboratories such as Southwest Research Institute. Individual engine manufacturers also have continuing research programs on the composition and control of diesel exhaust emissions. Programs have also been active in the research laboratories of several European research institutes and engine and vehicle manufacturers.

A large amount of the diesel exhaust research has been carried out in connection with the use of diesel powered equipment in mines, and the associated potential health hazards.

It is not possible, nor was it intended, to begin to represent the extensive results of these programs in a review such as this one. The programs and organizations are mentioned as a reminder to those beginning work in this area that there is a substantial amount of valuable information already available with which one should become familiar.

In early studies of diesel exhaust it was convenient and sufficient to talk about species or physical state in terms of simple descriptors such as gases, particulate, hydrocarbons, odor etc. As more has become known about the composition of the various groups some confusion has developed in using the same words as previously, because more effort has been made to attach descriptive or interpretive modifiers. In fact, it is now being recognized that such simple terms as "hydrocarbons" span the composition range from CH_4 to $\text{C}_{40}\text{H}_{82}$ and gases to particulate. The follow-

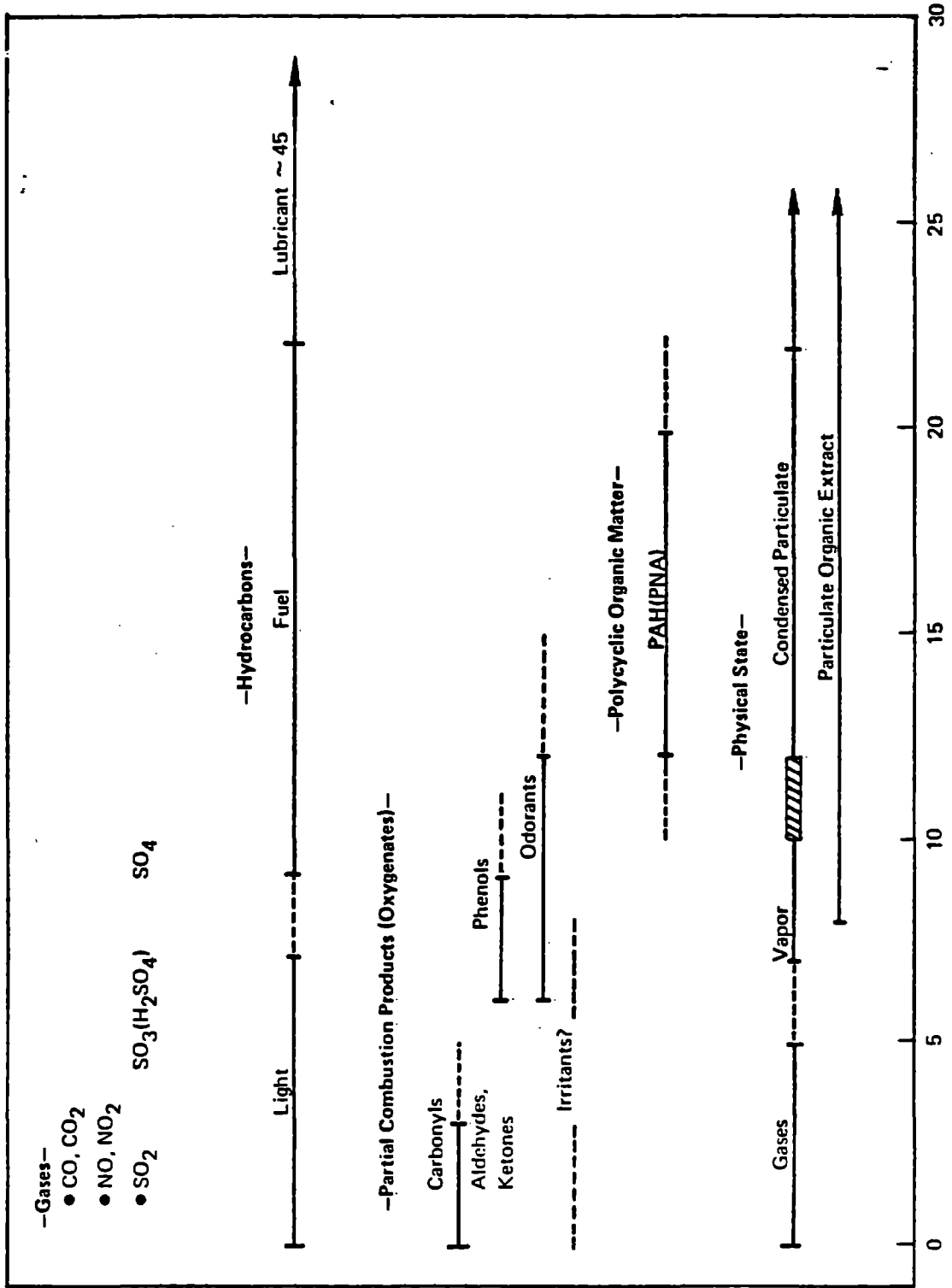


FIGURE 1. SPECIES OBSERVED IN DIESEL EXHAUST IN RELATION TO CARBON NUMBER AND PHYSICAL STATE

ing discussion sections are divided according to familiar groupings. The display in Figure 1 has been prepared in an attempt to show the relationship between the various chemical groups, their conventional descriptive terms and their physical state.

The physical and chemical information implied in Figure 1 has been displayed according to carbon number. The carbon number is meant to indicate ranges of chemical composition, but also indicates the boiling point range of chemicals.

The measurement of gases in diesel exhaust normally means the carbon oxides, nitrogen oxides and hydrocarbons. It has been recognized for some time, however, that the hydrocarbons in diesel exhaust contain a large portion of unburned fuel and must be sampled and measured in a heated system to avoid condensation. Recent studies have focused on the hydrocarbon, or extractable portion of particulate. Thus, hydrocarbons are seen to be comprised of a wide range of species including combustion fragments (methane, etc.), unburned fuel and lubricants. As a result, the hydrocarbons may be observed in several phases, depending on the sampling conditions, media and temperature.

Similarly, sulfur dioxide is readily measured as a gas, but sulfur trioxide may be collected as sulfuric acid either as a vapor or particulate, dependent on the sampling system and temperatures. Inorganic sulfate is collected entirely as particulate. The physical state (gas, vapor, combustible or adsorbable) or particulate in which a species will be found depends largely upon its boiling point or volatility and its concentration or partial pressure in the exhaust system. In particular, there is overlap between species which may be collected by condensation or adsorption (vapors) and particulates which are collected by filtration due to variables in sampling system temperature and exhaust dilution. This area of overlap is indicated approximately on the vapor - condensed particulate line of the Figure. The recent shift from undiluted exhaust to dilution tunnels or CVS systems for sampling diesel exhaust and the inherent or designed lower temperatures has resulted in the collection of more

condensable or adsorbed species on the particulate.

The incomplete or partial oxidation products (oxygenates) of the hydrocarbons include a wide variety of oxygen (and some nitrogen) containing organic compounds. The group can generally be divided into subgroups of light and heavy oxygenates. The light oxygenate group contains the simple aldehydes and ketones such as formaldehyde, acetone and acrolein and they are normally treated as gases in sampling and analysis. The heavy oxygenates contain species which are condensable or may be collected by adsorption. All of the species primarily responsible for the characteristic odor of diesel exhaust fall in this latter group. The phenols are also in this group. Very recent studies of the organic extract of particulates suggest that even higher molecular weight oxygenated species are observed in those samples.

The primary purpose of this overview has been to emphasize that many species may exist in different physical states, dependent upon exhaust and sampling conditions. Thus, it may be possible to measure the same species as a gas, vapor or particulate. Similarly, many of the species may be part of several different measurements such as hydrocarbons, odor and particulate.

2.2 CARBON OXIDES (CO, CO₂)

The concentration of carbon monoxide in diesel exhaust is in the range of 100-3000 ppm with typical values of 300-500 ppm. Carbon dioxide is normally observed at 2.4-8.7 percent.

Both CO and CO₂ are reliably measured in exhaust using non-dispersive infrared (NDIR) instruments. A Coordinating Research Council cooperative study (Perez, 1971) demonstrated that measurements were reproducible within a 5 percent standard deviation. No reliable instrumentation exists for field (portable) measurement of exhaust levels.

2.3 NITROGEN OXIDES (NO, NO₂)

Total nitrogen oxides (NO, NO+NO₂) are found in diesel exhaust in the concentration range of about 100-1200 ppm. Typical values are 500-700 ppm. Because the regulations limit only total NO_x, reliable separate data on nitric oxide (NO) and nitrogen dioxide (NO₂) are not readily available. It is generally recognized that the majority of the total NO_x in diesel exhaust is NO. The total NO_x values increase considerably approaching rated engine conditions. Some studies indicate (Springer, 1979) that the NO₂ level is held relatively constant at 10-50 ppm while the NO level increases with engine load. Because of the possibility of setting a new short term ambient air quality standard for NO₂, some concern has been expressed that NO₂ may constitute as much as 50 percent of the NO_x emissions. While the statement is basically true, the NO₂ emission level still represents a low and relatively steady concentration.

The chemiluminescence based instrument is the preferred means for measurement of NO_x and NO and then NO₂, by difference. Some conflicting data have been reported for NO and NO₂ values when using these instruments. In this technique, NO is measured directly by the ozone induced fluorescence. NO₂ is measured indirectly after thermal and/or catalytic conversion to NO.

In raw exhaust, some quenching of fluorescence has been attributed to high levels of CO₂ and H₂O. High concentration levels of hydrocarbons or CO appear to saturate the NO₂-NO converter capacity and thus also lead to erroneous values. Reliable results do appear to be obtained on diluted exhaust, either from CVS or dilution tunnel systems.

The chemiluminescence analyzers should be operated with heated sampling lines and the converter's efficiency should be checked frequently.

Because of the feeling of uncertainty among some researchers, a systematic study should be carried out on the reliability of this procedure for NO and NO₂ measurement in diesel exhaust.

2.4 SULFUR OXIDES (SO_2 , SO_3 (H_2SO_4))

Diesel fuel contains low levels of sulfur, typically about 0.2 percent, in an organically bound form. During combustion most of this sulfur is converted to sulfur dioxide (SO_2). Typically SO_2 concentrations are about 40 ppm. A small fraction of the sulfur oxides is present as sulfuric acid - typically 5-10 percent of the SO_2 level or 2-4 ppm.

SO_2 is readily measured as a gas, using a flame photometric detector. Sulfate and sulfuric acid should be collected as particulate in a dilution tunnel and measured after extraction from the filter. The barium chloranilate (BCA) colorimetric procedure has been widely used for SO_4 analysis in exhaust, but the newer ion chromatography procedure is rapidly gaining popularity as the preferred method. The BCA procedure is reported to have some interferences from organic species in diesel exhaust. Insoluble sulfate, such as may be formed when using barium full additives, will not be determined by these procedures.

2.5 HYDROCARBONS

As indicated in Figure 1, hydrocarbons are now known to represent a very wide range of species. Generally, diesel exhaust hydrocarbons are taken to mean those species which are measured with a heated flame ionization detector. Hydrocarbon values range from 50-3000 ppm.

A good perspective on the composition of the total range of hydrocarbons observed in diesel exhaust is seen in the work of Black and High (Black, 1979), a portion of which is shown in Figure 2. This figure shows the gaseous, condensable and particulate bound exhaust fraction observed from three different diesel engines. The gaseous hydrocarbons are in the C_1 - C_7 range. Diesel fuel accounts for most of the C_{10} - C_{20} hydrocarbons, while the engine lubricant appears to account for most of the C_{20} plus hydrocarbons. The particulate for these studies was collected from a dilution tunnel with a typical gas temperature of 99°F.

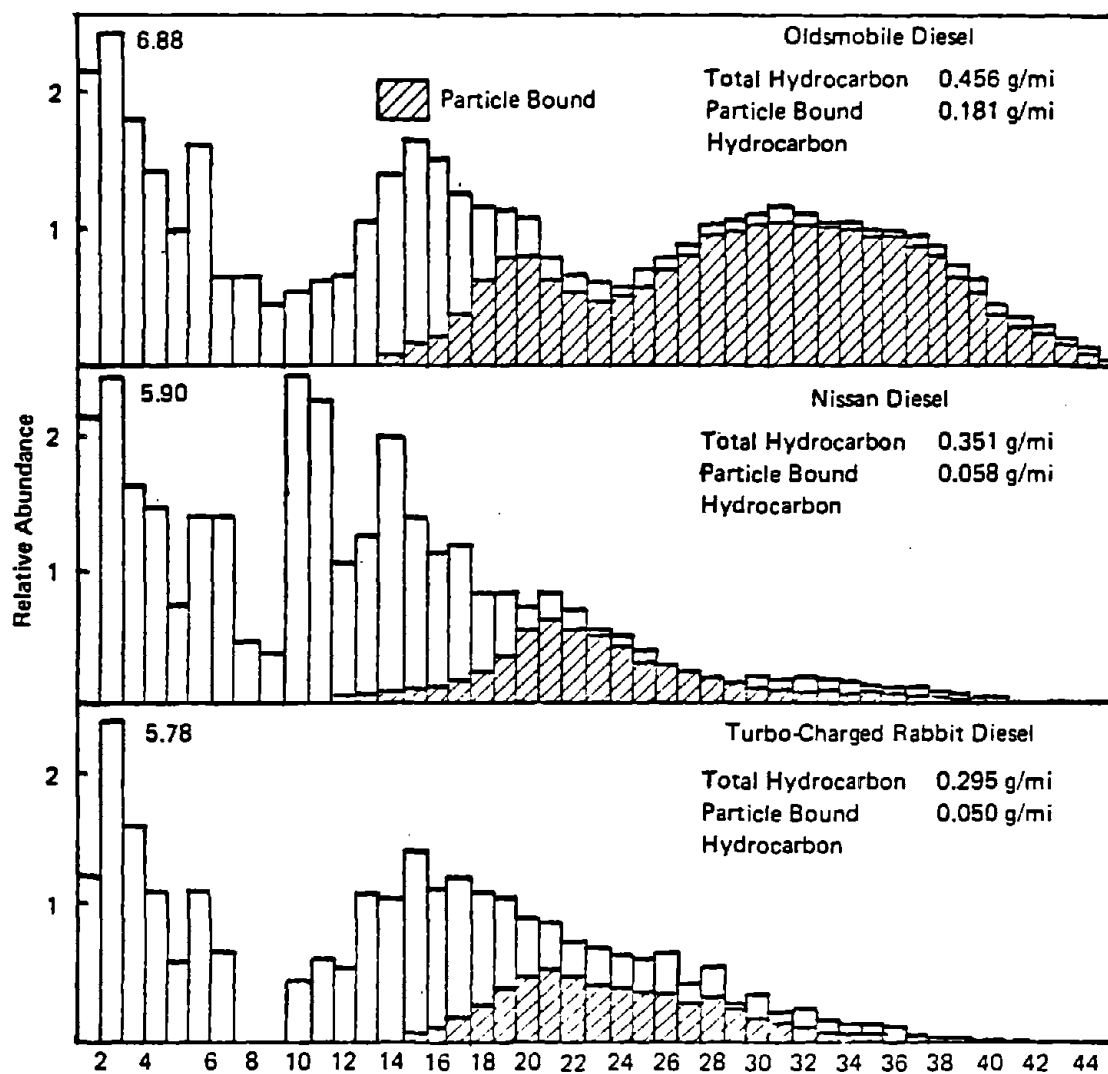


FIGURE 2. DIESEL HYDROCARBON MOLECULAR WEIGHT DISTRIBUTION

The condensed or adsorbed portion of the diesel fuel associated with the particulate can also be seen from this Figure. Further discussion of the heavier hydrocarbons will be deferred to the section on particulates.

A typical example of the composition of the light (gaseous) hydrocarbon portion of diesel exhaust is given in Table 2. Unsaturated hydrocarbons represent the largest portion of the light hydrocarbons, and these are known to be photoreactive. Landen and Perez (Landen, 1974) have reviewed the light diesel hydrocarbon emissions and conclude that they are unlikely to make any significant contribution to photochemical smog, if diesels are maintained at the present low proportion of the vehicle fleet. Since total diesel hydrocarbon emission levels are so much lower than gasoline vehicles it is unlikely that diesels would represent a reactivity problem even in a largely dieselized fleet.

A typical composition of the exhaust hydrocarbons in the C_{10} - C_{20} range is given in Table 3. The chemical class composition of the exhaust species is seen to be nearly the same as the No. 1 fuel used in the experiments. The small amount of oxygenates formed during combustion is also indicated.

The consensus during the interviews was that there was sufficient information about the composition of diesel exhaust hydrocarbons and that they in themselves did not constitute a problem. No further research was indicated. The classes of trace toxic species associated with the particulate represent a special case and need considerable research, as will be discussed later.

The heated flame ionization detector method for total hydrocarbon measurement is reliable and was shown to give an exhaust measurement with about a 22 percent standard deviation in a CRC collaborative study (Wagner, 1975).

2.6 OXYGENATES - CARBONYLS

The chemicals normally considered in this group are the lower molecular weight aldehydes and ketones. They are treated

TABLE 2. EXAMPLE OF DIESEL EXHAUST LIGHT HYDROCARBON DISTRIBUTION

<u>Carbon No.</u>	<u>Compound</u>	<u>Concentration</u> <u>ppm</u>	<u>% of Light</u> <u>Hydrocarbon</u>
2	Ethylene	10.7	48
2	Acetylene	4.0	18
3	Propylene	3.9	18
3	Propane	0.07	0.3
4	1-Butene	1.1	5
4	1,3-Butadiene	0.7	3
4	Isobutylene	0.5	2
4	2-Butene	0.2	1
4	n-Butane	<0.05	<0.2
5	1-Pentene	0.7	3
5	n-Pentane	0.1	0.4
5	Isopentane	<0.05	<0.2

Ref.: Linnell, 1972

TABLE 3. CHEMICAL CLASS COMPOSITION OF EXHAUST HYDROCARBONS IN C₁₀ - C₂₀ RANGE AND COMPARISON WITH DIESEL FUEL

<u>Principal Classes</u> ^a	<u>No. 1 Fuel</u>	<u>Organics Collected from Exhaust</u>
Paraffins	79	80
Aromatics	21	17
Oxygenates	0	3
<u>Aromatic Subclasses</u> ^b		
Alkylbenzenes	32	45
Indans/tetralins/indenes	38	17
Naphthalenes	32	40

^aClass separation based on silica gel liquid column chromatography (LC)

^bSubclass assignments based on low resolution mass spectroscopy of aromatic fraction from LC

Ref. Levins, 1979

as gases in sampling systems. The measurement techniques for carbonyls are not well established and as a result there is a sparcity of data concerning these species.

The predominant species in this group are the aldehydes, with formaldehyde, acetaldehyde and acrolein the most abundant. Total aldehyde values range from 1 - 30 ppm with typical values in the 15-20 ppm range. Formaldehyde is observed at 1 - 20 ppm, with typical values of 3 - 7 ppm; acrolein is observed at 0.1 - 17 ppm, with typical values of 0.3 - 3 ppm. The aldehyde composition of diesel exhaust reported by Vogh (Vogh, 1969) included

- formaldehyde
- acetaldehyde
- acrolein
- acetone
- propionaldehyde
- iso-butylaldehyde
- n-butylaldehyde
- crotonaldehyde
- valeraldehyde
- hexanaldehyde
- benzaldehyde

Most of these species, plus methyl ethyl ketone, are included in the DNPH chromatographic procedure used by EPA (Dietzmann, 1979). That procedure does not separate, and thus measure independently, acetone, acrolein and propionaldehyde.

The available carbonyl composition data was reviewed thoroughly by Spicer and Levy (Spicer, 1975) in their review of diesel exhaust smog reactivity, but very little data was found. In their review, it was estimated that the aldehydes in diesel exhaust might account for about 50 percent of its photochemical reactivity.

Certain of the aldehydes are known irritants, notably formaldehyde and acrolein, and they are present in diesel exhaust above their OSHA standard (or Threshold Limit Value) concentra-

tions - acrolein: 0.1 ppm, formaldehyde: 3 ppm.

The sampling and analysis procedures for carbonyls are labor intensive and need further development. The best currently available procedure is the gas chromatographic dinitrophenylhydrazine (DNPH) derivitization method.

2.7 OXYGENATES - PHENOLS

Phenols are known to be present in diesel exhaust at low levels. However, there is only a brief reference to date on these species in the literature. In the early Gulf Research Work (Spindt, 1974) total phenols were reported at a concentration of about 100 $\mu\text{g}/\text{cu m}$.

Although little data is available on the phenols in diesel exhaust they are mentioned here because they are known to cause membrane irritation and are a small portion of the odorant oxygenate group (Levins, 1971).

This chemical group is not known to be as important as other groups at this time, and thus analysis methods need not be developed. However, should the phenols be found to contribute to irritation, an analysis method will be needed. A sensitive gas chromatographic method based upon an acid deactivated column is available (Supelco SP 1240 DA) and could probably be used for analysis of these species in diesel exhaust.

2.8 OXYGENATES - ODORANTS

Significant diesel exhaust odor research programs have been carried out since the early 1950's with the studies initiated at the General Motors Research Laboratories. The major odor research studies carried out since that time have been conveniently summarized in a review by Savery, Matula and Asmus (Savery, 1974). A definitive study of the chemicals responsible for diesel exhaust odor was carried out by Arthur D. Little, Inc., during the period from 1968-1971 (Levins, 1969-1971; Kendall, 1974; Caragay, 1974). Subsequently Arthur D. Little developed an instrument for the

measurement of diesel exhaust odorants (Levins, 1972-1974). This instrument, referred to as a Diesel Odor Analysis System (DOAS) has been evaluated in a collaborative study conducted by members of the odor panel of the Coordinating Research Council, during the period from 1973-1977 (CRC, 1979).

Since the development of the DOAS odorant instrument, odor research programs have been carried out at a number of the manufacturers and research institute laboratories. Odor measurement studies are active at the Institute Francois de Petrole (Degohert) and Ricardo Engineers (Lesley, 1976). Odor chemistry and analysis programs are active in Daimler-Benz (Dandel, 1979). Engine parametric and odor formation mechanism studies are active at Drexel University (Cermansky), Cummins, John Deere, Detroit Diesel and Fiat. Contract supported studies continue at Arthur D. Little, Inc., and Southwest Research Institute.

The warning issued by the Environmental Protection Agency in 1978 has halted all direct human odor studies. The demand for studies to understand the diesel particulate problem has brought most diesel odor studies to a standstill since 1978.

Two different human panel rating scales have been used to measure diesel exhaust odor intensity. A scale based upon bottles of reference chemicals was developed by Dr. Amos Turk (Turk, 1967). This scale ranges from 1-12. The TIA (total intensity of aroma) has been used by Arthur D. Little, Inc., in their studies. The DOAS instrument readings are also based upon the TIA scale. The TIA scale is based upon 7 steps ranging from 0-3 as described below:

<u>TIA</u>	<u>Odor Intensity</u>
0	Not detectable
½	Very slight
1	Slight
1½	Slight to moderate
2	Moderate
2½	Moderate to strong
3	Strong

The relationship between the D and TIA diesel odor intensity scales has been investigated in a limited study (CRC, 1979) and the comparison is shown in Figure 3.

One of the most important factors to remember about diesel odor is that the odor intensity is an exponential function of odorant concentration (as is the case for most sensory responses). The odor intensity increases (or decreases) in proportion to the logarithmic function of concentration. This dependence is shown in Figure 4 for the exhaust from an engine operating at mid speed and load using No. 1 fuel. This exponential dependence is very important to recognize for control studies, since a factor of 10 reduction in odorant concentration only gives rise to a 1 TIA unit reduction.

The odor profile of a diesel exhaust (Kendall, 1974) can be described as

TIA	2
Smoky-burnt	2
Oily-kerosene	1½
Nose and eye irritation	perceived

The unique and characteristic odor of diesel exhaust is associated with the smoky-burnt fraction, with a smaller odor contribution from an oily-kerosene fraction. Eye and nose irritation are perceived in the odor studies and noted, when present.

The chemical analysis studies (Levins, 1969-1971) showed that collected exhaust samples could be separated into three primary fractions by silica gel liquid column chromatography. The aromatic fraction thus isolated contained the smoky-burnt odor species. Subsequent identification of the odorous chemicals in these fractions revealed the odorant composition information which is summarized in Tables 4 (oily-kerosene odorants) and 5 (smoky-burnt odorants).

It was estimated that about 200 distinct chemicals may contribute to the oily-kerosene odor, while approximately 2000

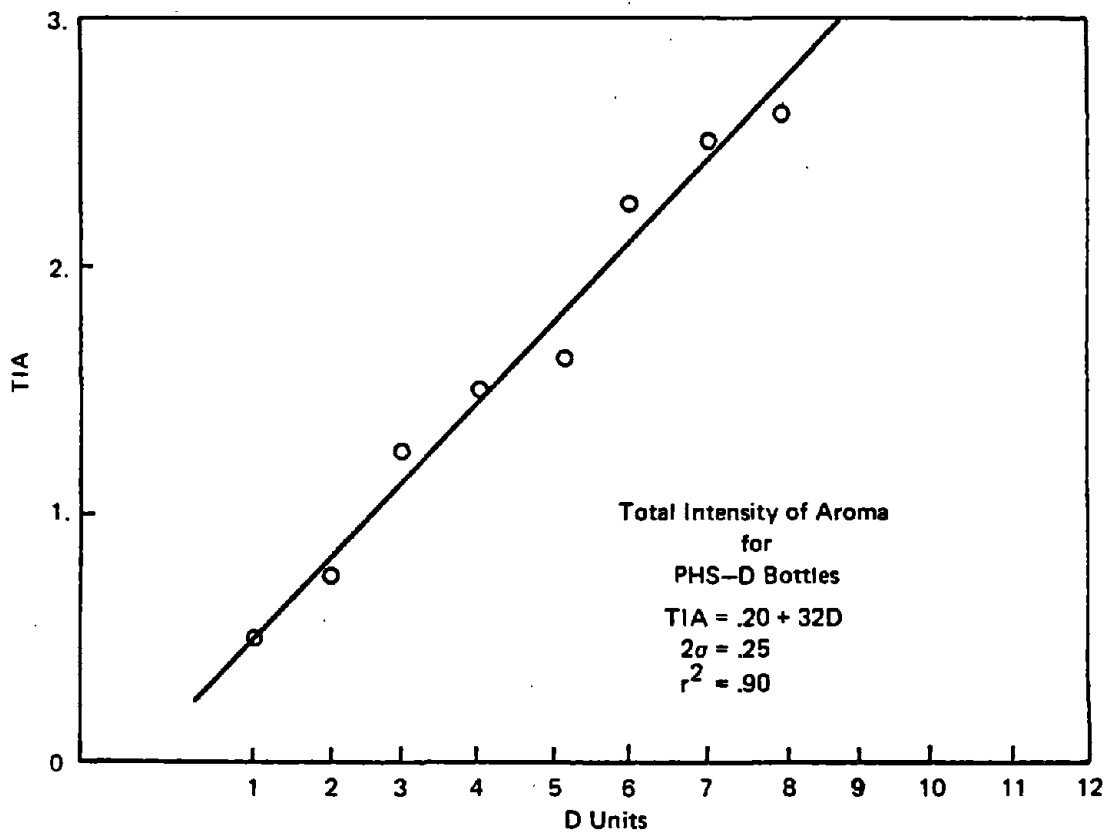


FIGURE 3. COMPARISON OF D AND TIA DIESEL ODOR INTENSITY SCALES

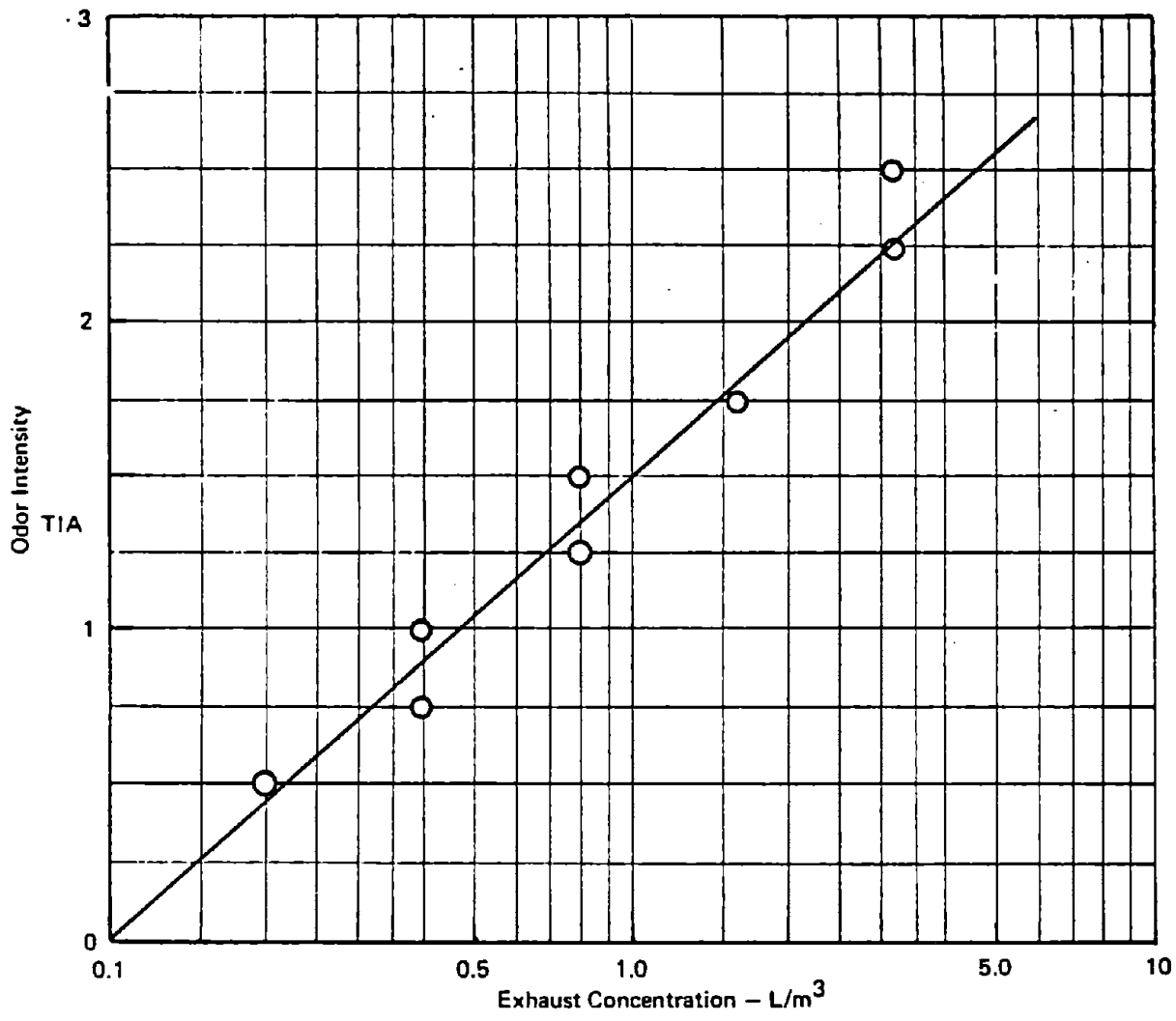


FIGURE 4. DOSE/RESPONSE DEPENDENCE OF DIESEL EXHAUST ODOR

TABLE 4. CHEMICAL COMPOSITION OF THE OIL-KEROSENE ODOR COMPLEX

<u>STRUCTURES</u>	<u>ODOR</u>
ALKYL BENZENES ALKYL INDENES	OILY
ALKYL INDANS ALKYL TETRALINS	KEROSENE
METHYL NAPHTHALENES	SENSATION (FEEL, IRRITATION)

TABLE 5. CHEMICAL COMPOSITION OF THE SMOKY-BURNT ODOR COMPLEX

<u>STRUCTURE TYPE</u>	<u>ODOR</u>
ALKENONE DIENONE	OXIDIZED OILY OXIDIZED OILY
FURAN FURFURAL	IRRITATION BURNT
BENZENES METHOXY HYDROXY CARBONYL	SMOKY, PUNGENT BURNT, IRRITATION BURNT, PUNGENT
BENZOFURAN	PARTICLE SIZE
INDANONE INDENONE	SMOKY METALLIC LEATHERY TARRY BURNT
NAPHTHALDEHYDE	PARTICLE SIZE

discrete chemicals contribute to the smoky-burnt odor. The odor-chemical studies demonstrated that it is important to measure the odorants as a group in order to reflect the odor intensity and character accurately.

A good correlation was observed between the concentration of the oxygenate group of smoky-burnt odorants (frequently referred to as LCO for liquid chromatography oxygenates) and the total diesel exhaust odor intensity, as shown in Figure 5. The correlation represented by this data is

$$\begin{aligned} \text{TIA} &= 1.0 + 1.0 \log \text{LCO (mg/cu m)} \\ r^2 &= 0.996 \\ 2\sigma &= 0.32 \end{aligned}$$

The ± 0.32 TIA 95 percent confidence limits are better than normally observed (0.4) in the odor observation itself.

Concentration estimates for diesel exhaust odor species are as indicated below

	Total (mg/cu m)	Individual Species ($\mu\text{g/cu m}$)
oily-kerosene odorants	20	40-400
smoky-burnt odorants (LCO)	5	0.1-10

The total concentrations will vary of course with engine and fuel conditions. The oxygenate LCO group has been reported to vary by a factor of 10 (1 TIA unit) between engine models (CRC, 1979).

The DOAS instrument has been shown to give a good correlation with odor intensity for light duty vehicles (Springer, 1975) and heavy duty vehicles (Levins, 1973). Later studies on heavy duty vehicles (Springer, 1977) show a more scattered correlation.

Recent studies at Drexel University (Cermansky, 1978) and by the CRC odor panel (CRC, 1979) indicate that details of the sampling conditions in collection of samples for analysis by the DOAS should be more carefully defined.

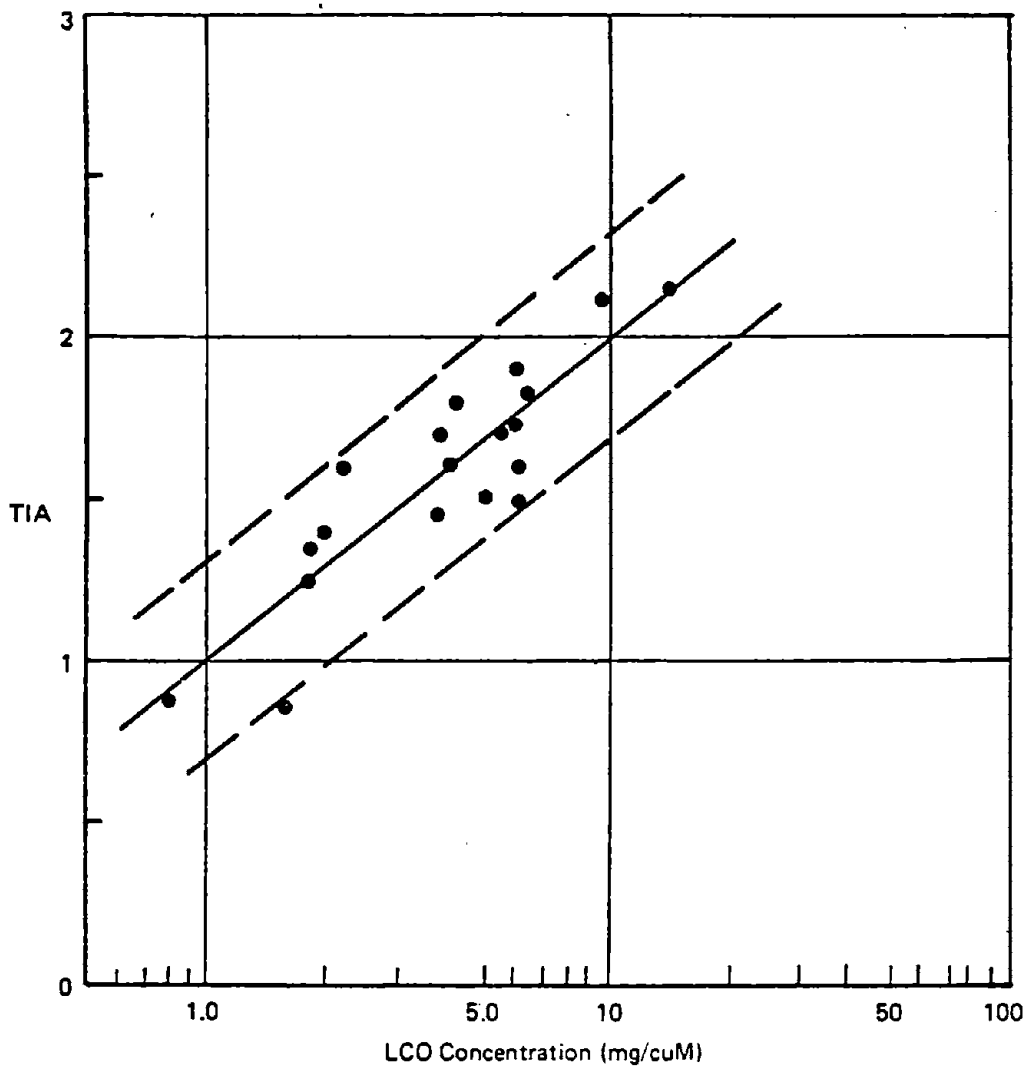


FIGURE 5. SUMMARY CORRELATION OF EXHAUST ODOR INTENSITY AND LCO

The CRC collaborative study (CRC, 1979) showed that it is possible to obtain precise measurements of diesel exhaust odor intensity. The smoky-burnt oxygenate group (LCO) measurement gave an interlab precision of about 10 percent with a TIA prevision of 0.15 units.

While the DOAS approach does provide a reliable measurement of diesel exhaust odor from steady state conditions, the sampling requirements are not well suited for measurement of transient conditions.

2.9 IRRITANTS

There are no reported studies of the chemical composition of the species giving rise to the irritation associated with diesel exhaust. As the portion of diesels in the vehicle fleet grows, however, it may be the irritation associated with diesel exhaust which becomes more important than odor in terms of public acceptance and potential health effects. While diesel odor is an instantaneous effect and disappears when the source is removed, the irritation from diesel exhaust can linger for a considerable period of time.

While the term "irritant" is also used in the early diesel exhaust odor studies (Rounds, 1964; Reckner, 1967) no specific studies were carried out to separate the effects.

Species known to be present in diesel exhaust which are irritants include

- nitrogen dioxide
- sulfuric acid
- formaldehyde
- acrolein
- phenol

Each of these chemicals is very different in character and probable combustion origin. It seems unlikely that any new chemicals will be found which are primarily responsible for the irritation in diesel exhaust. Rather, it is likely that it is a

combination of the already known species which give rise to the irritation response.

A research program should be initiated which would systematically measure the sensory irritation and find the chemicals primarily responsible for the effect.

The eye irritation approach used in the photochemical smog studies may be one approach to measuring diesel exhaust irritation. The review by Spicer and Levy (Spicer, 1975) indicates that aldehydes may be responsible for up to 50 percent of diesel exhaust photochemical reactivity. It is probable that they also may be at least a partial direct contribution to irritation. The change in respiration rate method used by Barrow, Alarie and Stock (Barrow, 1978) to measure the irritation of polymer decomposition products may also be appropriate for the study of diesel exhaust.

2.10 POLYNUCLEAR AROMATIC HYDROCARBONS (PNA OR PAH)

A great deal of work has been done on the measurement of PAH in a wide variety of samples, including diesel exhaust and much of this work has been published. Relatively recent examples are the work by Gulf Research (Spindt, 1977), the Department of Energy - Bartlesville (Seizinger, 1977) and the General Motors research labs (Williams, 1979).

The analysis procedures used to identify and measure the PAH's has included gas chromatography/ultraviolet, high performance liquid chromatography (HPLC)/fluorescence and gas chromatography/mass spectrometry (GC/MS). Most of these procedures have, in themselves, been reliable and give accurate results. However, the samples used in all of these studies have been extracted from particulate collected in filters.

Programs sponsored under project CAPE-24-72 by the Coordinating Research Council have shown that PAH cannot be sampled reliably from diesel exhaust as particulate on filters, due to what appears to be an unusual PAH reactivity associated with diesel exhaust (Spindt, 1977). Typical losses of benzo(a)pyrene

ranged from a factor of 10 to 400. Further studies to find a reliable PAH procedure for diesel exhaust are currently being sponsored at the Battelle Columbus Laboratories under the same CRC project.

Since there is such a great deal of uncertainty at the present time concerning the reliability of PAH data in diesel exhaust, it was decided to postpone expanded coverage of the topic in this review. It is expected that reliable PAH data in diesel exhaust will become available in the next few years. PAH are a small portion of diesel particulate, whose composition is currently being studied in great detail. Some PAH which have been reported in diesel exhaust are

- phenanthrene
- pyrene
- fluoranthene
- benzo(a)anthracene (BaA)
- benzo(a)pyrene (BaP)
- benzo(j)fluoranthene
- benzo(b)fluoranthene
- chrysene
- benzo(ghi)perylene

Concentration estimates in exhaust are 0.3-0.6 $\mu\text{g}/\text{cu m}$ for BaP and 0.70-1.1 $\mu\text{g}/\text{cu m}$ for BaA.

A variety of reliable analysis methods are available for PAH. The most attractive procedures appear to be HPLC/fluorescence and capillary column GC/MS. Once a reliable sampling procedure is established, the development of a PAH procedure should be straightforward.

2.11 PARTICULATES

Particulates in diesel exhaust have long been of interest because of the smoke problem. Recently, they have gained new attention because of the possibility of adverse health effects associated with diesel particulate. Initial studies focused on

diesel particulate as a relatively inert, insoluble solid. Gradually the research community has learned that diesel particulate has a very complex chemistry. With the trend to collect particulate samples from dilution tunnels it has been seen that from 10 to 80 percent of the particulate mass may be soluble in organic solvents.

The research necessary to fully understand diesel particulate as it relates to health effects has only been initiated since 1978 and much of the available information is preliminary in nature. Any attempt to interpret that tentative information at this time would be an error. The type of studies being conducted and the directions of the research are presented briefly to act as a guide to the reader in following future developments in this area.

The character of diesel particulate has been reviewed thoroughly in an excellent paper by Lipkea, Johnson and Vuk (Lipkea, 1978). Key points noted in that review are that there are significant differences in particulate from raw and diluted exhaust. Particulate from diluted exhaust has agglomerated and collected organic compounds (fuel, lubricant, partial combustion products) and inorganic compounds (H_2SO_4) due to the cooler temperatures. Individual particulate particles vary from 100-600 Å in diameter. The sampled aerodynamic particle size varies from 0.1-3 µm diameter, but most of the particles are less than 1 µm diameter.

Chemical analysis of diesel particulate is being pursued generally along the type of scheme outlined by Funkenbusch, Leddy and Johnson (Funkenbusch, 1979) and shown in Figure 6. Key to this type of analytical scheme is that several separate fractions (heavy outlines in Figure) are isolated which, when analyzed, represent the entire sample. Attention has recently been focused on the transitional fraction which has the highest Ames test biological activity of all the fractions tested.

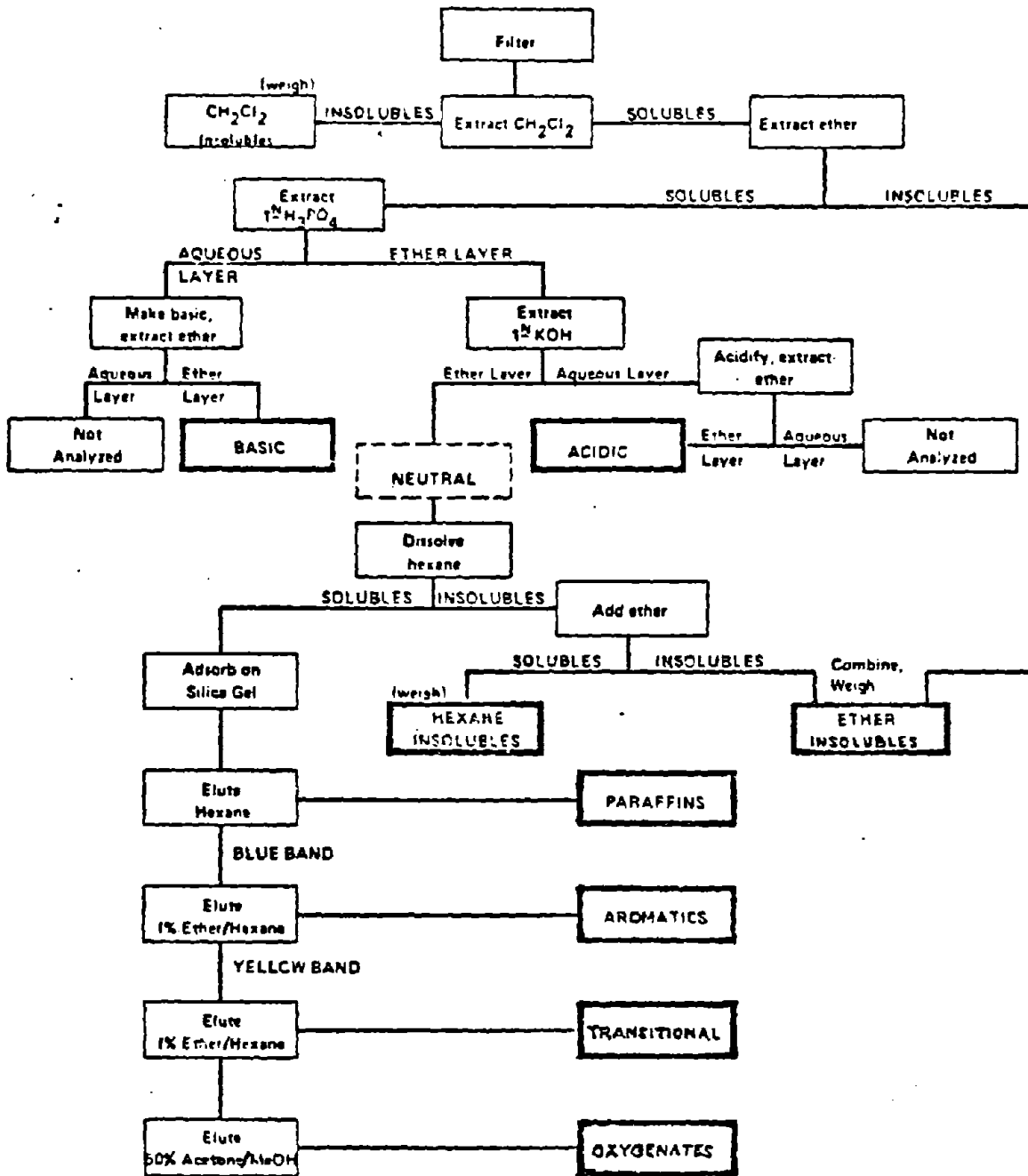


FIGURE 6. SCHEME FOR EXTRACTION OF SOLUBLE ORGANIC FRACTION OF DIESEL PARTICULATES

The relative distribution of the fractions for three fuel types is shown in Figure 7 (Funkenbusch, 1979). The fuels used are a normal No. 1 and No. 2 and a special heavy oil gas blend.

A detailed chemical characterization of the particulate organic fractions has been initiated by EPA and preliminary results have been published in an interim report (Erickson, 1979). The analyses summary from that report is shown in Table 6. The acid fraction consists mainly of alkyl aromatic oxidation products. The OXY (oxygenates in Figures 6 and 7) fraction showed the presence of aromatics oxidized to carbonyls. The most polar oxygenated fraction (oxygenates in Figure 6) is expected to have the same general type of functional chemical composition as the oxygenate group isolated in the odor studies, but shifted to a higher molecular weight because of volatility considerations.

The primary species characterized in the transition (TRN) fraction were a series of fluorenones.

Appropriate measurement procedures for particulates await the completion of the chemical analysis studies before convenient sampling and analysis methods can be developed. Sample collection from a dilution tunnel does appear to be the best means of treating particulate to represent the ultimate public exposure.

2.12 HEALTH EFFECTS/EXPOSURE STUDIES

Most health effects studies of diesel exhaust have been carried out in connection with their use in mines. Many of these studies have been reviewed recently for the American Mining Congress (Lassiter, 1978). In that review, few studies were found which provided a direct measure of health effects; most were inferential. One NIOSH study showed no additional deaths due to the use of diesels. A more recent study indicated a moderate excess of lung cancer among coal miners working in a dieselized mine.

A recent study (Reger, 1979) reported that coal miners in dieselized mines experienced 41 percent more coughing and 20 percent had more phlegm. The health effects of diesel exhaust

was the topic of a recent conference held by NIOSH at Morgantown, West Virginia (Wagner, 1978). During that workshop, coal mine exposure concentrations were summarized and that data is given in Table 7. Many of the values in that table were derived from the information gathered during a study by Arthur D. Little, Inc., for the Bureau of Mines (Lawter, 1977). Table 8 presents a comparison for the personal exposure data obtained during the Arthur D. Little study with the threshold limit values (TLV) for the chemicals. It can be seen that the highest observed concentrations are generally lower than the TLV. One potential area of concern is with the aldehydes which were observed close to the acrolein TLV. Acrolein comprises a larger fraction of the total aldehydes.

The Environmental Protection Agency Program to determine the health effects of diesel emissions has been described recently (Barth, 1978).

TABLE 6. SUMMARY OF PARTICULATE EXTRACT ANALYSIS RESULTS

Sample Type	Sample ^a Code	Predominant Compounds/Classes Found	Additional Data
Unfractionated Extract	I-DCM, II-DCM		Upper m/z > 1000 C:H ratio ~ 45:80 with N and/or O present
Acid	E 1.1	alkyl phthalic anhydrides hydroxy benzoic acids naphthoic acids naphthalic anhydrides anthracene dicarboxylic anhydrides	upper m/z = 700
	E 1.1-M	methyl benzoates methyl naphthoates dimethyl naphthalates	upper m/z = 600
	E 1.1-DM	dimethyl phthalates methyl benzoates methyl naphthoates dimethyl naphthalates	upper m/z = 920
	C1 1.1		upper m/z = 750
	E 6.5		upper m/z = 810
	E 6.5-M	methyl fatty acid esters methyl alkylnaphthoates methyl anthroates and/or phenanthroates	
	E 6.5-M	methyl fatty acid esters methyl alkylnaphthoates methyl anthroates and/or phenanthroates	

TABLE 6. SUMMARY OF PARTICULATE EXTRACT ANALYSIS RESULTS (CONT'D)

Sample Type	Sample ^a Code	Predominant Compounds/Classes Found	Additional Data
OXY	OXY 11		upper m/z = 900
	OXY 11-F1	naphthaldehydes anthraldehydes fluorenones	
	OXY 11-DM	nothing found	
Transition	TRN-11B-FC1	alkanes fluorenones	
	TRN-11B-FC2	alkanes, fluorenones	
	TRN-11B-FC3	alkanes, fluorenones	upper m/z >> 500
Fuel	FAR	alkyl benzenes alkyl naphthalenes alkyl phenanthrenes alkyl anthracenes	
	FOXY	alkyl phenols C _n H _{2n} O (n = 13-17) C _n H _{2n} N (n = 12-14)	
	FTRN	alkanes alkyl aromatics C _n H _{2n} N (n = 13-16)	

Notes:

- (a) DCM = unfractionated dichloromethane extract of diesel exhaust particulate
- E 1.1 = acid fraction, ether extract at pH = 1.1
- G1 1.1 = acid fraction, dichloromethane extract at pH = 1.1
- E 6.5 = acid fraction, ether extract at pH = 6.5
- OXY = OXY fraction
- F = fuel extract
- AR = aromatic fraction
- TRN = transition fraction
- M = dimethylsulfate methylation
- DM = dimethylmethane methylation

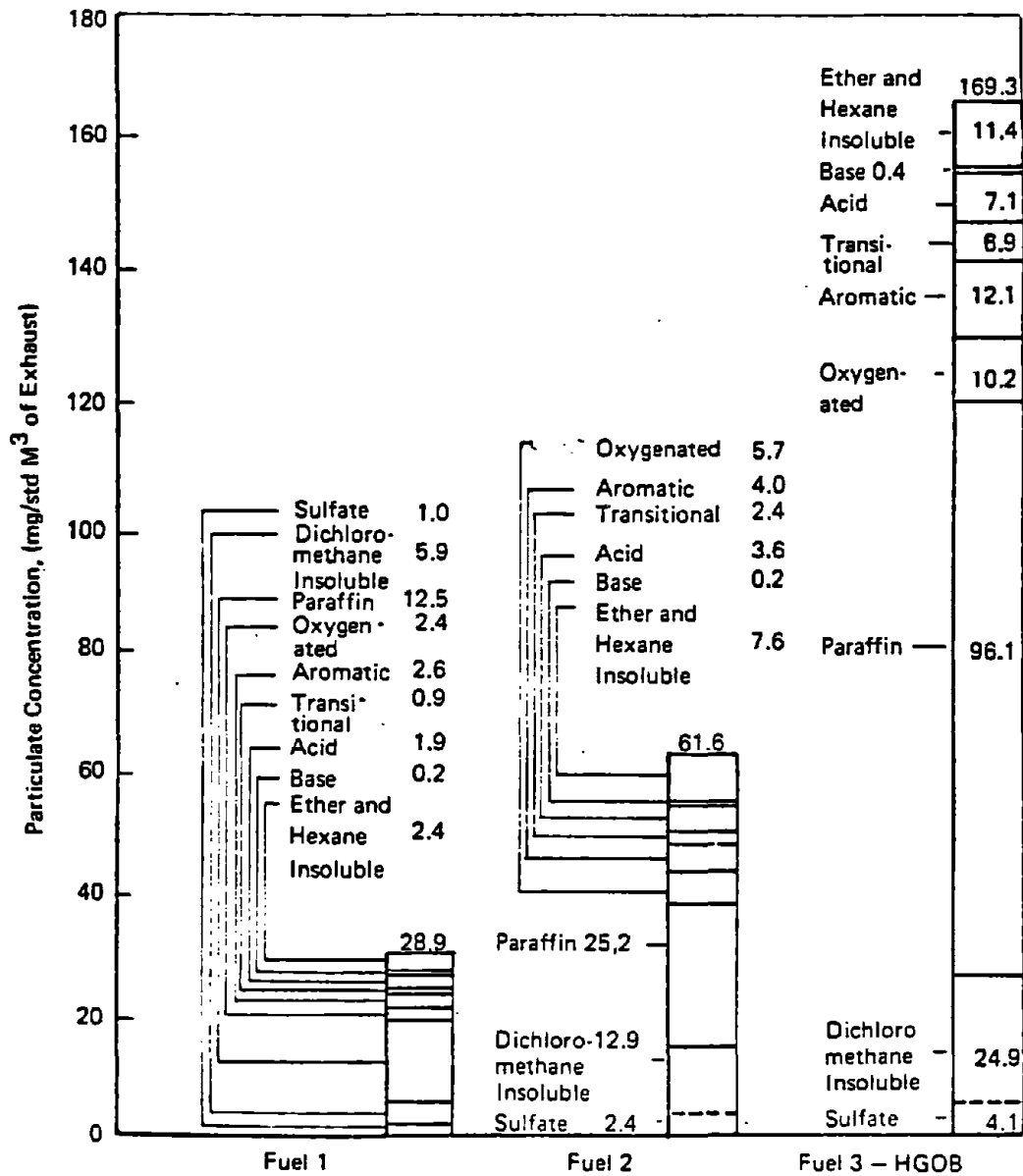


FIGURE 7. FRACTIONAL BREAKDOWN BY MASS CONCENTRATION OF SOLUBLE ORGANIC FRACTION MODE 3 AT 8:1 VOLUME DILUTION RATIO

TABLE 7. COAL MINE EXPOSURE CONCENTRATIONS

Component	Range, Undiluted (1)	Units	Exposure Median	Exposure Values Range	Confidence in exposure values	Calc Dil'n factor (avg.)	Comments
CO ₂	6.1-7.2%	ppm*	700	500-1100	Good	(165)	Dil'n factor is baseline for comparison of all values. Exposure values include 300 ppm background CO ₂
CO	114-513 ppm	ppm	10	0-20	Good	10-50(30)	Suggest undiluted values low.
NO	225-735 ppm	ppm	3	1-5	Good	75-245(160)	
NO ₂	36-84 ppm	ppm	0.3	0.1-0.5	Good	120-280(200)	
SO _x	7.7 ppm	ppm		0.5			No mine data.
SO _x (2)	40 ppm	ppm		0.5	Good upper limit	80	No mine data. Base on 0.2 sulfur in fuel.
H ₂ SO ₄		mg/m ³		0.2	Unknown		Used 10% of SO _x value as basis.
Hydrocarbons (3)		ppm		5-20	Poor		Measured values as methane but unverified

(NOTE: Values in this table are approximations subject to change as more accurate data become available.)

TABLE 7. COAL MINE EXPOSURE CONCENTRATIONS (CONT'D)

Component	Range, Undiluted (1)	Units	Exposure Values Median	Range	Confidence in exposure values	Calc Dil'n factor (avg.)	Comments
Benzene	(3)	ppm		0.01			Rough estimate.
Aromatics		mg/m ³	0.7	0.13-2.1	Unknown		
Oxygenates	(3)	mg/m ³	0.04	0.006-0.11	Unknown		
Total Aldehydes	(3)	mg/m ³	0.045	0.007-0.19	Unknown		
Formaldehyde	(3)	mg/m ³	0.04	0.007-0.06	Unknown		
Diesel Particulate	0.12-9.47 g/BHP-HR	mg/m ³		0.1-1	Unknown		
Respirable Coal Particulate		mg/m ³	1.3	0.1-10	Good		Compliance values

Others: a) PNA
 b) Organic Acids
 c) Organo-Sulfur Compounds
 d) Organo-Nitrogen Compounds
 e) HNO₃, HNO₂
 f) Trace Metals

Insufficient data to estimate exposures.

Footnotes:

- 1) Emission work group data
- 2) Without scrubber
- 3) Emission work data questionable or no data

TABLE 8. COMPARISON OF PERSONAL SAMPLE DATA WITH THE THRESHOLD LIMIT VALUES

Species	Concentration Units	Measured Concentrations				Threshold Limit Value
		Lowest	Mean	Highest		
Aldehydes	mg/m ³	0.004	0.045	0.19	$\left\{ \begin{array}{l} 3 - \text{ formaldehyde} \\ 180 - \text{ acetaldehyde} \\ 0.25 - \text{ acrolein} \end{array} \right.$	
Aromatic Hydrocarbons	mg/m ³	0.13	0.69	2.1	50 - naphthalene	
Carbon Dioxide	ppm	450	650	1150	5000	
Carbon Monoxide	ppm	1.5	7.6	14	50*	
Formaldehyde **	mg/m ³	0.007	0.038	0.059	3	
Nitric Oxide	ppm	1	3	5	25*	
Nitrogen Dioxide	ppm	0.10	0.34	0.47	5	
Oxygenates-odorants	mg/m ³	0.006	0.039	0.11	$\left\{ \begin{array}{l} 19 - \text{ phenol} \\ 22 - \text{ cresol (all isomers)} \end{array} \right.$	

* Ceiling Value

** Estimated from the average NO/NO₂ ratio (10 to 1) obtained with direct reading instruments.

3. CONCLUSIONS AND RECOMMENDATIONS

The purpose of this review has been to determine if sufficient chemical information existed for groups of chemicals in diesel exhaust and if instrumentation was available for measurement of the groups or individual chemicals. Areas needing future research efforts were to be identified. This section is organized according to the groupings presented in the Discussion section, although not necessarily on a one-to-one basis.

A. CO_x, SO_x, HC

Conclusion: The chemistry of these species is sufficiently well established. Reliable instrumentation of analysis methods are available for all species.

Recommendation: No new programs need be initiated for these chemicals.

B. NO_x

Conclusion: The chemistry of NO and NO₂ is well established. The potential of a new or revised health standard for NO₂ places new emphasis on it. The analysis procedure (chemiluminescence) is probably reliably established, but should be checked further.

Recommendation: Initiate a systematic study of NO/NO₂ measurements by chemiluminescence, including a study of interferences and converter efficiency.

C. CARBONYLS

Conclusion: Relatively little is known about the aldehydes and ketones in diesel exhaust. They could make significant contributions to reactivity and irritation. No convenient methods are available for the analysis of carbonyls, although the DNPH method does give accurate results.

Recommendations: A research program should be initiated to establish the composition of carbonyls (aldehydes and ketones) in diesel exhaust and develop a convenient method for their measurement.

D. PHENOLS

Conclusion: Very little information is available about the phenols in diesel exhaust, but there is no current indication that they are present at levels which are significant.

Recommendation: No programs for this group of chemicals is indicated.

E. ODORANTS

Conclusion: The chemistry of the odorants is well established. The diesel odor analysis system (DOAS) instrument works well for measurement of steady state conditions. Sampling system conditions need to be specified in greater detail.

Recommendation: A limited program should be carried out to specify the conditions for collection of samples to be analyzed on the DOAS. A program should be developed to build an instrument capable of continuous measurement of odorant levels. Such an instrument should have a response time sufficient to measure transient levels.

F. IRRITANTS

Conclusion: There is no systematic sensory/chemical information available concerning the irritation associated with diesel exhaust.

Recommendation: A basic study of the chemicals primarily responsible for diesel exhaust irritation should be initiated. Once the primary sources of irritation are known an analysis approach should be developed. The analysis of irritants may involve the combination of a number of methods in order to measure all of the chemicals which may be involved in the phenomenon.

G. POLYNUCLEAR AROMATIC HYDROCARBONS (PAH)

Conclusion: The sampling procedures for PAH are unreliable. Various analytical procedures are well established.

Recommendation: A program should be designed to develop a reliable sampling procedure for PAH. This program should coordinate with, and utilize the results of the present CRC CAPE-24-72-study.

H. PARTICULATES

Conclusion: Particulates have just recently been recognized as a serious potential health problem. While relatively little is currently known in detail about the composition of particulates, a number of research programs are now underway.

Recommendation: Support on-going programs in this area. Additional programs should probably be initiated to determine the chemical composition in detail.

APPENDIX
REPORT OF NEW TECHNOLOGY

The work performed for this report, while leading to no new inventions, has provided detailed information on exhaust emissions of small, high speed diesel engines. Particular emphasis is given to odors, irritants, and toxic vapors and the procedures for measuring and controlling them.

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