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METHODS OF ANALYSIS FOR COMPLEX ORGANIC AEROSOL MIXTURES FROM URBAN EMISSION SOURCES OF PARTICULATE CARBON

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1.

ABSTRACT

Extractable organic compounds having between 6 to 40 carbon atoms comprise an important mass fraction of the fine particulate matter sampled from major urban emission sources. Depending on the emission source type, this solvent-soluble fraction accounts for <20% to 100% of the total organic aerosol mass, as measured by quantitative high-resolution gas chromatography (HRGC) with flame ionization detection. In addition to total extract quantitation, HRGC can be applied to further analyses of the mass distributions of elutable organics present in the complex aerosol extract mixtures, thus generating profiles that serve as "fingerprints" for the sources of interest. This HRGC analytical method is applied to emission source samples that contain between 7 to 12,000 μg/filter organic carbon. It is shown to be a sensitive technique for analysis of carbonaceous aerosol extract mixtures having diverse mass loadings and species distributions.

DISCLAIMER

INTRODUCTION

Study of the sources of organic aerosols found in urban atmospheres is of key importance because organic particulate matter comprises typically 30% of the fine aerosol mass (*i.e.*, nominal particle diameter < 2.1 μm).[1] These airborne carbonaceous particles contribute to visibility reduction[2,3] and have complex chemical compositions that include carcinogenic and mutagenic organic compounds.[4-10] In the past, a few of the organic aerosol compounds present in urban atmospheres have been traced back to their origin, but the vast proportion of the aerosol material remains to be assigned to its source. This study describes the analytical chemical methods that have been applied to: (1) the construction of chemical mass balances based on the mass of fine organic aerosol emitted from major urban sources of particulate carbon; and (2) the generation of discrete emission source chemical profiles derived from chomatographic characteristics of the organic aerosol components.

EXPERIMENTAL APPROACH

Source Sampling

A dilution stack sampler was designed and field-evaluated for collection of fine organic aerosols from combustion sources. Strong emphasis was focused on minimizing sample loss and contamination due to collector components and to sample handling.[11] The sampler simulates the cooling and dilution processes that occur in the plume downwind of a combustion source, so that the organic compounds which condense onto pre-existing particles under ambient conditions are collected in the sampler as particulate matter. Details of the the organic aerosol acquisition procedures are presented elsewhere.[11,12] Urban emission sources were selected on the basis of previous mass emission inventories of particulate carbon compiled for metropolitan Los Angeles, sufficient to account for close to 80% of the organic aerosol emissions in that air basin.[13,14] The urban emission sources of particulate carbon examined in this study are summarized in Table 1. The quantitative mass emission characteristics corresponding to each of the source types are reported elsewhere.[12]

Analysis

Several considerations are important to the overall design of the emission source characterization study. First, quantitative links between the total fine aerosol mass and the carbonaceous subfractions must be developed. This is a critical requirement for relating the mass of potential molecular tracers to the total fine particle mass emission rate of a given source type. Second, the source sampling and analytical protocol must be applicable to a wide range of aerosol mass loadings and chemical compositions. Here, the objective is to generate source sampling and analytical methodologies which are dynamic with respect to sample size, thus placing fewer constraints on field sampling operations, in spite of the fact that source emission rates and hence sample sizes, often will not be known until after the source test has been conducted. An additional benefit of a broad measurement capability is the ability to assess in a quantitative fashion as many carbonaceous compounds as possible that are associated with a given emission source. A third design consideration is the incorporation of quality assurance/quality control (QA/QC) procedures which adequately evaluate laboratory procedures as well as sampling background (including dynamic and static system blanks). Without close scrutiny of laboratory and sampling blanks at the molecular level (*i.e.*, individual organic compound analysis by mass spectrometry), it is not possible to identify definitively the carbonaceous chemical components that are present as fine aerosol emissions. Fourth, the precision of the analytical protocol must be within acceptable limits. As a final design consideration, the analytical method must generate data which are suitable for computer manipulation. This last requirement is intended to facilitate quantitative comparisons of the different chemical attributes that characterize the sampled emission sources of fine particulate carbon.

The analytical objective of this study is to construct a mass balance for each emission source by examining the relationships between total aerosol mass and certain carbonaceous fractions:

Total Mass : Total Carbon (Organic+Elemental) : Elutable Organics : Molecular Tracer.

An array of analytical methods are required for the above mass determinations: (1) gravimetric determination of the total mass of aerosol collected on a sampled filter; (2) total carbon analysis by a combined pyrolysis/combustion measurement technique;[15] (3) quantitation of total solvent-soluble, elutable organics (*i.e.*, lipids having 6 to 40 carbon atoms) by high-resolution gas chromatography (HRGC);[16] (4) quantitation of single organic compound peaks by HRGC with flame ionization detection (FID)[16]; and (5) molecular tracer identification and quantitation by high-resolution gas chromatography/mass spectrometry (HRGC/MS).[16] To provide sufficient organic mass for the HRGC and HRGC/MS analyses, up to 18 separate parallel filters were configured into the source sampling device to produce the samples necessary for the above mass determinations.[11] In this paper we summarize the results of the first 3 mass balance resolution steps listed (*i.e.*, total carbon (TC), organic carbon (OC), and total elutable organics) for the source samples, the analytical blanks, and the sampling system blanks. The mass emission characteristics of the investigated sources and the organic source "fingerprints" for sources other than the diesel truck data of Figure 1 are discussed elsewhere.[11,12]

Micro-methods have been developed for the quantitative recovery of extractable organic matter in the atmospheric fine aerosol fraction.[16-18] The analytical protocol is designed to monitor losses associated with volatilization, incomplete extraction, or instrumental bias. The organics are extracted from the filters by ultrasonic agitation using successive additions of hexane (2 volume additions) and benzene/isopropanol (3 volume additions). The serial extracts are filtered and then combined. The total extracts are reduced to volumes of 150-2500 μL. The neutral fraction of the organics is defined operationally as that fraction which elutes from the bonded phase (DB-1701) of the analytical column and is detected by the FID of the HRGC without further derivatization. An aliquot of the total extract is derivatized by addition of diazomethane.[16] This step converts reactive organic acids to the respective methyl ester or methyl ether analogues. Injection of this derivatized fraction onto the HRGC column produces chromatographic data for the acid plus neutral (acid+neutral) fraction. The mass of the acid fraction of the solvent-soluble organics are determined by difference. Quantitation of the total extracts is accomplished by computerized HRGC analyses that incorporate the combined application of: (1) area counts relative to a coinjection standard (1-phenyldodecane); (2) relative response factor for the perdeuterated recovery standard (n-$C_{24}D_{50}$); and (3) recoveries of the perdeuterated recovery standard.

RESULTS

The mass determination per filter for the various emission source samples, along with averages of the laboratory blanks and system blanks, are presented in Table 2. The mass loadings of the source samples on a per filter basis ranges over 3 orders of magnitude, from 13 μg to 20 mg. The diverse carbonaceous compositions of the samples become evident when considering the relative proportions of the TC, OC, total organics (*i.e.*, OC mass multiplied by a factor of 1.2 provides a lower mass estimate of the hydrogen, oxygen, nitrogen, etc., atoms that are bound or bonded with operationally-determined atomic organic carbon),[19] and total elutable organics (*i.e.*, organics that are detected by HRGC).

Quality Control/Quality Assurance

Source sampling system blanks and laboratory blank filter composites were generated routinely throughout the source testing and analytical work-up procedures adopted for this study. All blanks were evaluated by analytical procedures identical to those used for the collected source filter samples. Mass loadings of the principal carbon-containing fractions for the laboratory blank filter composites (each containing 4, 8, or 16 of the 47mm quartz microfiber filters) and the dynamic source sampler system blanks are listed in Table 2. Both types of blanks contain total masses which are below the detection limit of the gravimetric measurement method (*i.e.*, < 5 μg/filter total weighable mass). Total carbon, organic carbon, and total organics masses are < 2 μg/filter for the laboratory blank analyses and 10 to 11 μg/filter for the dynamic system blanks, while elutable organics mass loadings average 7 and 9 μg/filter, respectively. The three independent measurements used to quantitate mass confirm the upper bound mass estimates for the blank samples as 9 μg/filter for the laboratory analytical blanks and 11 μg/filter for the dynamic sampling blanks. The standard deviation of the blanks is also given in Table 2, and is seen to be 2 μg/filter or less for the source system sampler blanks, and 4.5 μg/filter for the total elutable organics in the laboratory blanks. These data on the variability of the blanks can be used to assess the detection limits (LOD) and quantitation limits (LOQ) of the procedures used according to the method of Keith et al.[20]

The replicate analyses of blank samples via HRGC also enabled identification of and correction for contaminant peaks. Using HRGC/MS analyses, spurious compound peaks seen in the blank analyses were identified and determined to be solvent artifacts. Consequently, during HRGC analyses of the source samples, the retention times of the principal contaminant peaks were monitored routinely, and when found, the respective resolved areas were subtracted from the total integrated area.

Preliminary Test Filters

Test aerosol samples were evaluated and consisted of authentic fine ambient aerosol samples and replicate source samples.[12,16] In the procedure of reference (16), n-$C_{24}D_{50}$ is used as an internal standard to facilitate quantitation of the organics present. The amount of n-$C_{24}D_{50}$ to be added to the sample filter as a surrogate standard before sample extraction was determined from the total mass of organic carbon (OC) contained on a replicate filter that was analyzed by pyrolysis/combustion; the ratio of OC mass to the mass of added n-$C_{24}D_{50}$ was chosen to be 150 μg OC : 1 μg n-$C_{24}D_{50}$. Results of the test samples provided performance evaluations of the analytical protocol. First, the efficiencies of the extraction procedures could be checked, using the perdeuterated surrogate standard. Second, the mass of organic material eluting through the HRGC analytical column could be quantified, providing the opportunity to determine the appropriate number of source sample filters to be extracted, and/or the appropriate degree to which the extracted material should be concentrated for measurement by HRGC. Last, the amount of surrogate standard to be added before extraction could be adjusted based on the nature of the HRGC trace for each source, ensuring that the mass of elutable organics present could be quantitated accurately. In this manner, blind analyses of the critical source samples were eliminated.

Mass Quantitation

Mass determinations of the carbonaceous materials from urban sources of fine aerosol are given in Table 2. All the data shown have been blank-corrected. It is possible to compare the total organics and total elutable organics mass values for the source samples, because the results of both analyses have been blank-corrected, and the elutable organics values have been corrected for the mass contributions of extraction artifacts and standards. Differences between the results can be attributed to several factors. Most importantly, a portion of the total organics present from some sources may not be solvent-soluble, or may not elute through the HRGC analytical column. One would expect that a fraction of the organic material in vegetation fragments and in tire dust, for example, will be insoluble or of such high molecular weight that it will not pass through the HRGC analytical column. When this fraction is significant, then the ratio of total elutable organics to total organics is much less than 100%. Second, the mass of total organics is calculated based on the organic carbon mass present, multiplying by a factor of 1.2 to account for the associations of hydrogen, oxygen, nitrogen, etc., with the carbon atoms. While this factor is considered appropriate for ambient samples taken in urban areas, it may vary from source to source. In addition, the precision with which the combustion/pyrolysis technique distinguishes OC from EC may be influenced by the degree to which the associated organics are oxidized during the procedure. Hence, the values calculated for the total organics mass may be somewhat high or low for certain source emissions that have unusual organic composition.

The ratios of total elutable organics mass (by HRGC) to total organics mass (by combustion) are given in Table 2. The percentages shown range from <20% to 100%, indicating that the nature of urban area organic aerosol emissions varies greatly from source to source. For sources with a low percentage of total organics eluting, like the vegetative detritus, paved road dust, and meat cooking emissions, a significant fraction of the organic compounds present must be either unextractable or nonelutable with the methodology used. At the opposite extreme, the ratio of >150% obtained for two samples of roofing tar pot emissions indicates that the total organics mass (by combustion) has been significantly underestimated.

Elutable Organics Mass Distributions

Besides mass determinations, the total elutable organics fraction determined by HRGC can be characterized by subdividing the HRGC trace into discrete mass segments. An external standard mixture containing normal alkane homologs that range between n-$C_{10}H_{22}$

to n-$C_{36}H_{74}$, is used to quantitate the mass of each of the fractions of the complex organic mixture eluting between C_n and C_{n+1}. The HRGC relative response factor corresponding to the C_n normal alkane is used for quantitation of the total integrated area eluting between C_n and C_{n+1}. In this manner, HRGC elution patterns can be utilized as "fingerprint" profiles for the emission sources evaluated in this study. Figure 1 shows an example of the HRGC plot for the underivatized extract (neutral fraction) of heavy-duty diesel truck fine aerosol (Fig. 1a) and the computed organic mass distribution (Fig. 1b) of the neutral elutable organics. The precision of the computed organic mass distribution technique was evaluated for six replicate pairs of samples that corresponded to six different emission sources. The standard deviation associated with a single computed value (*i.e.*, a single histogram step) was 0.66% of the total mass of elutable organics present in a given source type.[12,21]

Generation of the computed organic mass distribution profile has the advantage of producing a simplified, quantitative fingerprint for each sample of interest. First, because the mass of the species that elutes between the C_n and the C_{n+1} n-alkanes is adjusted for relative response of the HRGC-FID, the computed profile shown in Figure 1b, for example, reflects a more accurate distribution of species concentrations within the complex mixture. Chromatographic bias against the higher molecular weight components which occurs routinely for HRGC plots has been accounted for in the computed elutable organic mass distribution. This adjustment is apparent when comparing the distributions corresponding to > n-C_{24} for Figures 1a and 1b. A second advantage to the computed profile is that the data on the hundreds of unknown peaks present in the original chromatogram are compressed into a well-defined smaller number of compound groups (*i.e.*, histogram area segments) that can be tracked by computer models for the atmospheric transport of aerosol emissions. Although hundreds of individual resolved compound peaks can be detected in a HRGC profile, these raw data (*i.e.*, retention time versus area counts) are too numerous to be handled easily by computer-based mathematical models. Formulation of the computed organic mass distribution profiles allows a quantitative representation of urban emission sources. Hence, this approach provides a data base on organic aerosol source emission characteristics that can be related to the composition of ambient aerosol samples that have been processed in a similar fashion (see ref. 12).

SUMMARY AND CONCLUSIONS

A procedure has been developed which provides quantitative links between the total fine aerosol mass and the carbonaceous subfractions that are associated with urban sources of fine aerosol. The method is applicable to a variety of emission sources, where both organic carbon mass loadings and the organic chemical compositions are highly diverse. Emission source samples having organic carbon mass loadings of 7 to 12,000 μg/filter are analyzed, and individual organic compounds in the range of C_6 to C_{40} are characterized further via HRGC and HRGC/MS. Low levels of analytical and sampling derived artifacts are observed. Highly reproducible computed mass distribution profiles (*i.e.*, source "fingerprints") are obtained for the total elutable organics fraction. These features of the analytical protocol permit a very accurate approach in describing the key chemical attributes of organic aerosols that are emitted to urban atmospheres from major emission sources. This approach, as applied to fine aerosol emissions, will assist in determining the origin of organic particulate matter present in urban atmospheres via atmospheric transport modeling techniques.

Acknowledgements

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Table 1. Urban Sources of Fine Carbonaceous Aerosol

Anthropogenic Sources

- Fireplace -- natural wood; synthetic log
- Vehicles -- catalyst and noncatalyst cars; diesel trucks
- Home appliance -- natural gas
- Hamburger cooking -- charbroiling (extra-lean and regular meat); frying
- Road dust
- Brake dust
- Tire dust
- Cigarettes
- Roofing tar pot

Biogenic Sources

- Vegetative detritus -- dead leaves; green leaves (cultivated and native plant species composites)

Table 2. Mass Determinations of Carbonaceous Materials from Urban Sources of Fine Particulate Carbon

Sample	Combined Filters^a	Fine Mass µg/filter	Total Carbon µg/filter	Organic Carbon µg/filter	Total Organics^b µg/filter	Total Elutable Organics^c µg/filter	Ratio of Elutable Organics to Total Organics (%)
BLANKS							
Blank filters (avg of ≥ 7 analyses)	4 to 16	$< 3^d$	$< 2^e$	$< 2^e$	$< 2^e$	8.9 ± 4.5	---
Source sampler system blanks, (avg of ≥ 7 analyses)	15	< 3	10.3 ± 2.0	9.5 ± 1.6	11.4 ± 1.9	7.0 ± 1.7	49 ± 17
ANTHROPOGENIC^f							
Boiler, #2 fuel oil, (Experiment 2)	18	1,230	323	44	52	26	50
Boiler, #2 fuel oil, (Experiment 5, residence chamber)	9	2,330	408	56	67	29	43
Boiler, #2 fuel oil, (Experiment 5, tunnel)	9	2,340	388	59	70	38	54
Automobiles, catalyst-equipped	45	30	23	17	21	25	119
Automobiles, non-catalyst	45	83	60	52	63	87	138
Trucks, heavy-duty diesel	21	197	147	63	76	66	87
Roofing tar pot (Experiment 1)	2	19,700	11,900	11,900	14,300	24,500	171^g
Roofing tar pot (Experiment 2)	2	10,600	6,350	6,350	7,650	11,800	154^g

Table 2. Mass Determinations of Carbonaceous Materials from Urban Sources of Fine Particulate Carbon (Cont.)

Sample	Combined Filters[a]	Fine Mass µg/filter	Total Carbon µg/filter	Organic Carbon µg/filter	Total Organics[b] µg/filter	Total Elutable Organics[c] µg/filter	Ratio of Elutable Organics to Total Organics (%)
Tire wear (Experiment 1)	4	2,290	1,180	825	990	419	42
Tire wear (Experiment 2)	1	9,630	4,940	3,470	4,160	1,970	47
Fireplace, oak	15	1,750	873	827	987	439	44
Fireplace, pine	15	2,850	1,460	1,370	1,650	841	51
Fireplace, synthetic log	15	947	659	543	651	497	76
Cigarette smoke (Experiment 1)	3.75	2,500	1,500	1,490	1,790	1,420	79
Cigarette smoke (Experiment 2)	3.75	2,470	1,490	1,470	1,770	1,520	86
Burgers, extra-lean beef, charbroiled	15	68	41	41	49	15	31
Burgers, regular beef, charbroiled	15	381	218	217	261	65	25
Burgers, mixed beef, fried	30	13	7	7	9	3	33
Brake wear	4	8,080	1,080	---[h]	---[h]	14	---[h]
Natural gas home appliances	39	17	15	14	17	14	82
Paved road dust (Experiment 1)	4	3,350	488	453	543	144	27
Paved road dust (Experiment 2)	4	3,880	565	523	628	111	18

Table 2. Mass Determinations of Carbonaceous Materials from Urban Sources of Fine Particulate Carbon (Cont.)

Sample	Combined Filters[a]	Fine Mass µg/filter	Total Carbon µg/filter	Organic Carbon µg/filter	Total Organics[b] µg/filter	Total Elutable Organics[c] µg/filter	Ratio of Elutable Organics to Total Organics (%)
BIOGENIC[f]							
Vegetative detritus, green leaves (Experiment 1)	4	595	180	176	211	36	17
Vegetative detritus, green leaves (Experiment 2)	4	360	109	106	128	21	16
Vegetative detritus, dead leaves (Experiment 1)	4	1,038	340	328	393	53	12
Vegetative detritus, dead leaves (Experiment 2)	4	378	140	136	163	20	12

[a] Value represents the number of 47-mm diameter quartz fiber filters that were grouped for the elutable organics mass determinations. Fine mass, total carbon, organic carbon, and organics values were determined for samples collected on single 47-mm diameter Teflon or quartz microfiber filters.[12]

[b] Calculated as 1.2 times the mass of organic carbon present.[19]

[c] Quantified as the sum of all area counts eluting between 16 and 80 minutes. Values corrected for contributions of artifacts and surrogate standard additions.

[d] Below detection limit of gravimetric measurement method.

[e] Below detection limit of pyrolysis/combustion method.

[f] Mass determinations for Anthropogenic and Biogenic sources have been blank-corrected on a per sample basis for the Elutable Organics and on a per filter basis for the other measurements.

[g] Underestimation of organic carbon by pyrolysis/combustion method.

[h] Quantity uncertain due to interference with organic carbon measurement.

Figure Captions

Figure 1. (a) HRGC plot of the neutral elutable organics obtained from heavy-duty diesel truck fine particulate emissions; and (b) the computed mass distribution of neutral elutable organics plotted versus normal alkane carbon number.

Fig 1a

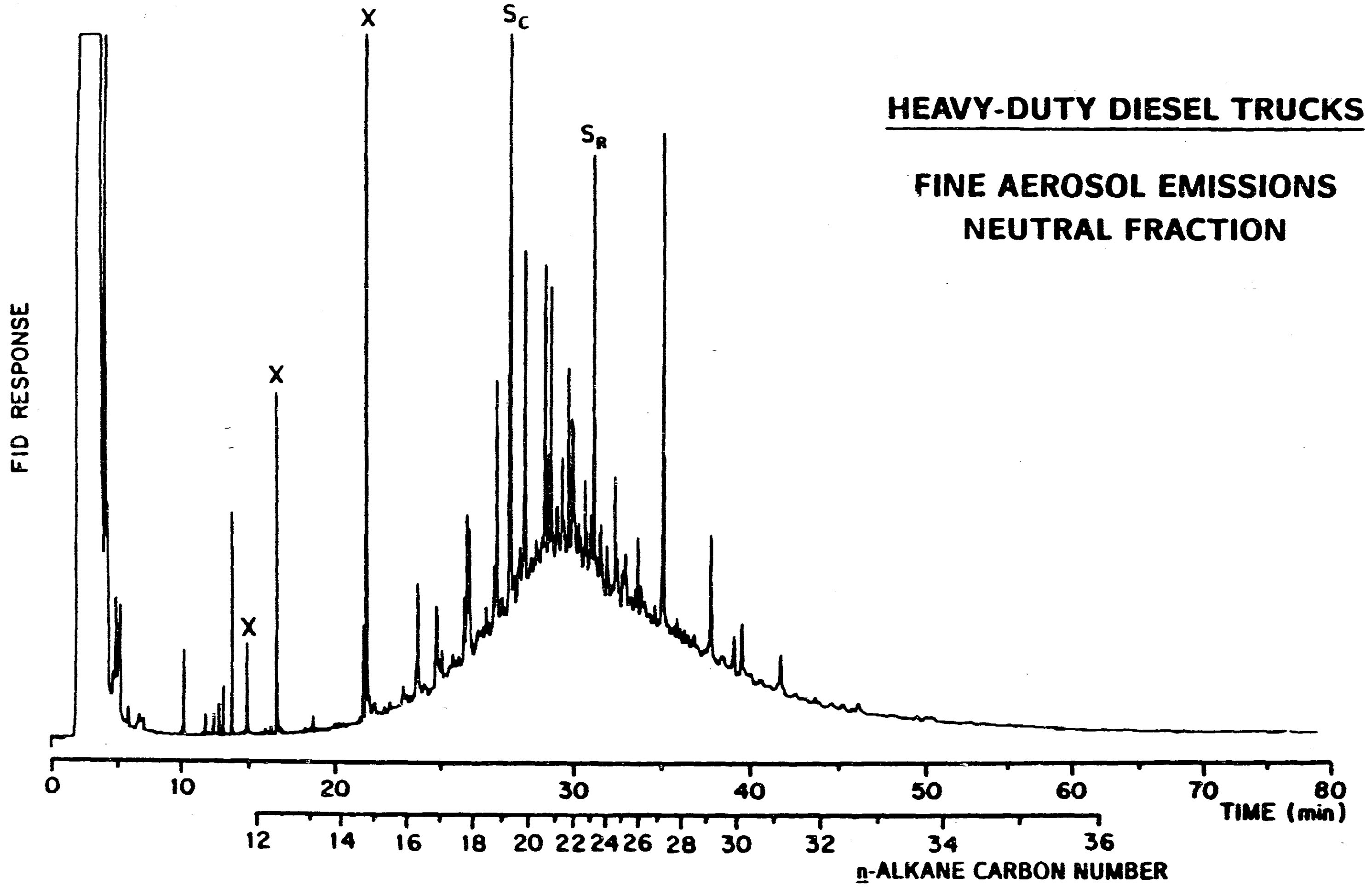
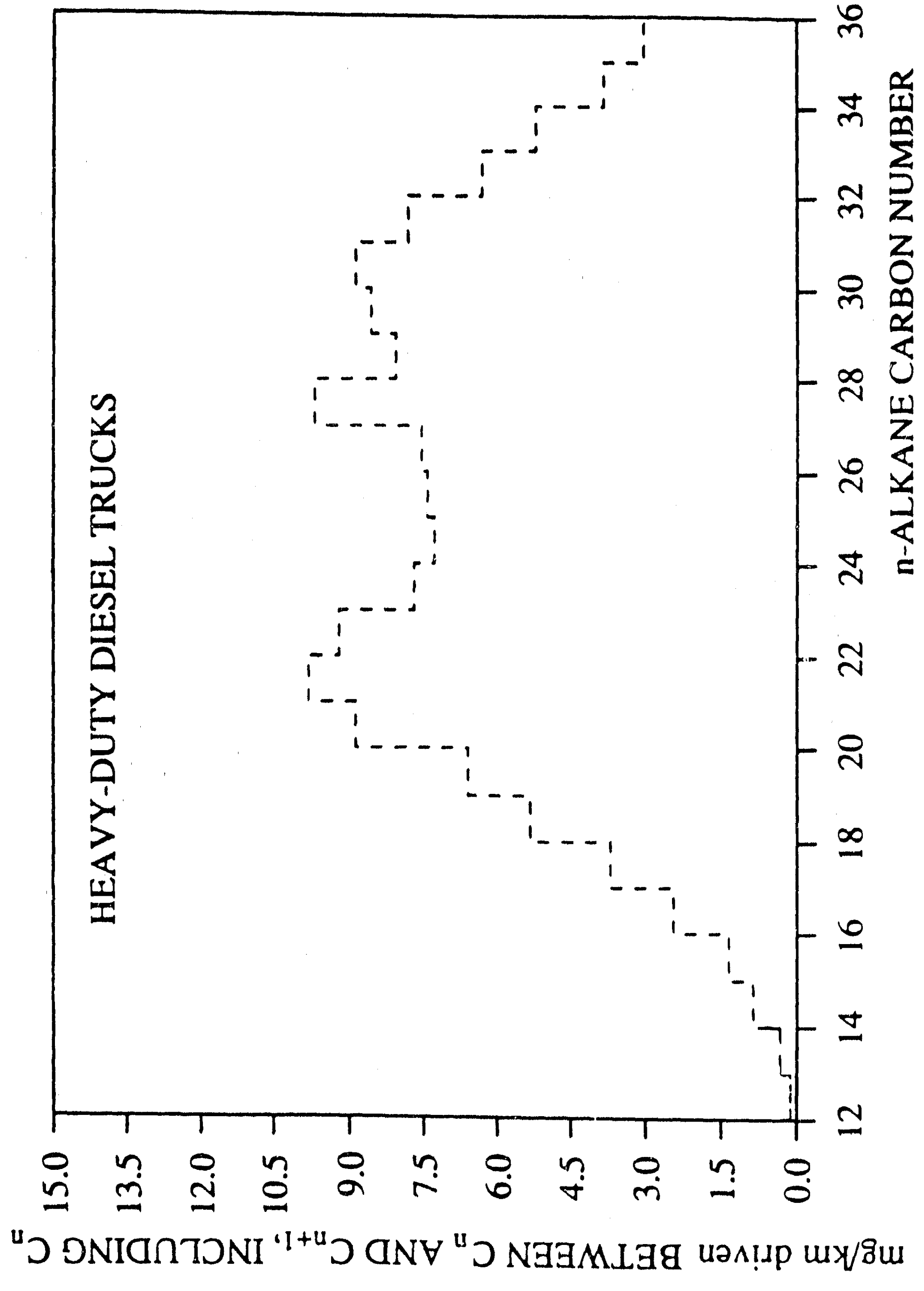

HEAVY-DUTY DIESEL TRUCKS
FINE AEROSOL EMISSIONS
NEUTRAL FRACTION
FID RESPONSE
X
X
X
S_C
S_R
0
10
20
30
40
50
60
70
80
TIME (min)
12
14
16
18
20
22
24
26
28
30
32
34
36
n-ALKANE CARBON NUMBER

Fig. 1b


HEAVY-DUTY DIESEL TRUCKS
mg/km driven BETWEEN C_n AND C_{n+1}, INCLUDING C_n
15.0
13.5
12.0
10.5
9.0
7.5
6.0
4.5
3.0
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