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

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ABSTRACT

Organic aerosols comprise approximately 30% by mass of the total fine particulate matter present in urban atmospheres. The chemical composition of such aerosols is complex and reflects input from multiple sources of primary emissions to the atmosphere, as well as from secondary production of carbonaceous aerosol species via photochemical reactions. To identify discrete sources of fine carbonaceous particles in urban atmospheres, analytical methods must reconcile both bulk chemical and molecular properties of the total carbonaceous aerosol fraction. This paper presents an overview of the analytical protocol developed and used in a study of the major sources of fine carbon particles emitted to an urban atmosphere.

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 paper describes the experimental methods that have been developed for: (1) the collection of fine organic aerosols from combustion sources; (2) the construction of chemical mass balances based on the mass of fine organic aerosol emitted from major urban sources of particulate carbon; and (3) the generation of discrete emission source chemical profiles derived from chromatographic 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.^{11,12} 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. To ensure collection of a representative aerosol sample, the following design goals were established for the sampler: (1) choose

dimensions of the sampler to minimize the loss of particles and the condensation of supersaturated vapors onto wall surfaces; (2) simulate atmospheric dispersion processes by ensuring that the emissions are highly diluted and cooled to ambient temperature before sample collection; and (3) include a residence time in the sampler sufficient to allow complete condensation of the supersaturated vapors to occur.

Rigorous checks of sampler performance were conducted for quality control/quality assurance (QA/QC) purposes. To minimize sample contamination and artifact collection, the following strategies were adopted: (1) exclude use of rubber, plastics, greases, and oils as sampler components to avoid off-gassing of organic materials into the sampled airstream (use Teflon for all gaskets and o-ring seals); (2) construct the sampler entirely from stainless steel to facilitate thorough cleaning between field experiments; (3) preclean the dilution air using activated carbon and HEPA filtration; and (4) store filters containing the collected organic aerosol in annealed glass containers. Between field tests, the entire sampling system was cleaned before a new source type was measured. Large system pieces were vapor-degreased with tetrachloroethylene, and subsequently heated (70 °C for 4 hrs) to volatilize possible remaining organic impurities. All open ends were wrapped in clean aluminum foil to prevent recontamination. Small sampler parts were immersed in an ultrasonic cleaner and were cleaned sequentially with high purity (glass-distilled) methanol and hexane for 5 minutes in each solvent. The small pieces were covered with aluminum foil immediately after cleaning to protect the interior surfaces during storage and transport. Before collection of a sample from a new source type, the clean assembled sampler was evaluated for leaks. A system blank was then collected by passing precleaned dilution air through the system for the same

length of time that would be required for collection of an actual source sample. Filtered samples of the dilution air were analyzed for artifacts by the same analytical methods used for the actual source samples and included measurement by high-resolution gas chromatography with flame ionization detection (HRGC-FID) and high-resolution gas chromatography/mass spectrometry (HRGC/MS). Further details of sampler design and sample 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. Details of the quantitative mass emission characteristics corresponding to each of the source types are available.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 analytical protocol must be applicable to a wide range of aerosol mass loadings and chemical compositions. Here, the objective is to generate analytical methodologies which are dynamic with respect to sample size, thus placing fewer constraints on field sampling operations, to recognize 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 QA/QC procedures which adequately evaluate laboratory protocol 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. The total fine aerosol mass is collected on preweighed Teflon filters. The total mass of fine aerosol is determined gravimetrically under conditions of constant temperature and humidity using a microbalance. Total carbon (TC) analysis is performed by a combined pyrolysis/combustion

measurement technique.¹⁵ The method provides a quantitative measurement of the mass concentrations of elemental carbon (EC) and organic carbon (OC) present on a sampled quartz microfiber filter and uses laser transmittance to correct for the conversion of OC to EC during the initial pyrolysis step. Quantitation of total solvent-soluble, elutable organics (*i.e.*, lipids having 6 to 40 carbon atoms) is achieved by HRGC-FID analysis which uses both a surrogate standard (*i.e.*, internal recovery standard) and a suite of *n*-alkane external standards.¹⁶⁻¹⁸ Individual molecular tracers present in the total extracts from the source aerosol filters are identified and quantitated by HRGC/MS analysis.¹⁸⁻²⁰ In this paper we summarize the results of the first 3 mass balance resolution steps listed (*i.e.*, TC, OC, and total elutable organics) for the source samples, the analytical blanks, and the sampling system blanks. An example of the fourth step, molecular characterization of the source samples, is given in reference 20. The mass emission characteristics of the investigated sources and their chemical composition are reported and discussed at length 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. To provide sufficient organic mass for the HRGC-FID and HRGC/MS analyses (*i.e.*, minimum of 300 μg OC per filter composite for a single source type), up to 18 separate parallel filters were configured into the source sampling device to produce the samples necessary for the above mass determinations. 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 (neutral elutable 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.^{16,18} 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 (total acid+neutral elutable organics). The mass of the acid fraction (acidic elutable organics) of the solvent-soluble organics is determined by difference. Quantitation of the total extracts is accomplished by computerized HRGC-FID analyses that incorporate the combined application of: (1) area counts relative to a coinjection standard (1-phenyldodecane); (2) relative response factor for the perdeuterated surrogate standard ($n\text{-C}_{24}\text{D}_{50}$); (3) recovery of the perdeuterated surrogate standard for each source sample extract; and (4) relative response factors for a suite of n -alkane external standards (17 n -alkane homologs from $n\text{-C}_{10}\text{H}_{22}$ to $n\text{-C}_{36}\text{H}_{74}$).¹⁶⁻¹⁸

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 range over 3 orders of magnitude, from 13 μg to 20 mg. Diverse compositions of the source samples are evident based on 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),^{1,21} and total elutable organics measured.

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.*, $< 5 \mu\text{g}/\text{filter}$ total weighable mass). Total carbon, organic carbon, and total organics masses are $< 2 \mu\text{g}/\text{filter}$ for the laboratory blank analyses and 10 to 11 $\mu\text{g}/\text{filter}$ for the dynamic system blanks, while elutable organics mass loadings for these blanks average 7 and 9 $\mu\text{g}/\text{filter}$, respectively. The three independent measurements used to quantitate mass confirm the upper bound mass estimates for the blank samples as 9 $\mu\text{g}/\text{filter}$ for the laboratory analytical blanks and 11 $\mu\text{g}/\text{filter}$ for the dynamic sampling blanks. The standard deviation of the blanks is also given in Table 2, and is seen to be 2 $\mu\text{g}/\text{filter}$ or less for the source system sampler blanks, and 4.5 $\mu\text{g}/\text{filter}$ 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 and quantitation limits of the procedures used according to the method of Keith et al.²²

The replicate analyses of blank samples via HRGC-FID 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-FID 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.

An assessment of the QA/QC achieved for the entire sampling and analytical methodology used for the carbonaceous aerosol emissions study can be obtained from the observed total mass loadings of the source sampler system blanks (Table 2). These blank samples represent the best measure of the combined residual artifacts associated with the sampling and analytical protocols. The reproducibility with which the organic compound distribution from a single source can be characterized using these techniques is evaluated by Hildemann *et al.*¹⁷ Briefly, mass distributions of replicate pairs as filter composites were analyzed for six separate source types. Using the percent of total eluted mass falling between the elution points of adjacent *n*-alkanes as the common unit of measure, it was estimated that the standard deviation of a single step within the mass histogram plot (e.g., Figure 1b) was equal to 0.66% of the total eluted organic mass comprising the whole sample. This degree of agreement between sample replicates for the final mass distributions, as represented by the histogram plots, represents the reliability of sampling, analytical, and chromatographic data reduction procedures used in the present study of carbonaceous source emissions.

Preliminary Test Filters

Test aerosol samples were evaluated and consisted of authentic fine ambient aerosol samples and replicate source samples. Following the procedure developed by Mazurek,¹⁶⁻¹⁸ $n\text{-C}_{24}\text{D}_{50}$ was used as an internal standard to facilitate quantitation of the organics present. The amount of $n\text{-C}_{24}\text{D}_{50}$ 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 filter (collected in parallel) that was analyzed by pyrolysis/combustion; the ratio of OC mass to the mass of added $n\text{-C}_{24}\text{D}_{50}$ was chosen to be 150 $\mu\text{g OC} : 1 \mu\text{g } n\text{-C}_{24}\text{D}_{50}$.

Results of the test samples provided performance evaluations of the analytical protocol. These analytical procedures were conducted to eliminate blind analyses of the critical source samples. First, the efficiencies of the extraction procedures could be checked using the perdeuterated surrogate standard. The recoveries of $n\text{-C}_{24}\text{D}_{50}$ obtained for the source sample filter composites ranged typically (within ± 1 standard deviation) between 59 and 93%. Second, by knowing the organic carbon concentration by combustion plus the likely extraction efficiency prior to extraction, the mass of organic material eluting through the HRGC analytical column could be estimated in advance. This estimate provided 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-FID. Based on these preliminary extractions of the test filters, it was determined that a minimum of 300 μg of OC for a single source type provided a quantity of total elutable organics sufficient for mass distribution measurement by HRGC-FID and for molecular tracer identification by HRGC/MS. However, if available, a target

quantity of 800 μg OC per source type was adopted for the extraction of an actual source composite. This higher OC mass level for a given source type facilitated quantitation and identification by HRGC/MS of single molecular species present in a complex mixture of total elutable organics. 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.

HRGC-FID plots of the total compound distributions ($n\text{-C}_{10}\text{H}_{22}$ to $n\text{-C}_{36}\text{H}_{74}$) for the preliminary test filters of the sources sampled showed very different elution profiles. Although the original surrogate spike ratio of 150 μg OC : 1 μg $n\text{-C}_{24}\text{D}_{50}$ was, in general, a good estimate for most source composites, slight adjustments were necessary for a few of the filter composites. The adjustment in the mass of surrogate standard was scaled such that the $n\text{-C}_{24}\text{D}_{50}$ peak observed in a HRGC-FID plot of total elutable organics for a given source type, was twice the height of the tallest resolved peak within the mixture. Although not critical in the case of HRGC/MS analyses of the source extract mixtures, this scale factor was necessary for HRGC-FID quantitation of the extract mixtures.

Mass Quantitation

Mass determinations of the carbonaceous materials from urban sources of fine aerosol are given in Table 2. All the data shown are blank-corrected. It is possible to compare the total organics (determined by pyrolysis/combustion) and total elutable organics (determined by HRGC-FID) mass values for the source samples because the results of both analyses are

blank-corrected, and the elutable organics values are corrected for the mass contributions of extraction artifacts and standards.

The chemical nature of urban organic aerosol emissions vary greatly from source to source, as shown by the ratios of total elutable organics mass to total organics mass (Table 2). These percentages range from <20% to 100%. Differences between the mass determinations obtained by combustion to those obtained by HRGC-FID 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.^{1,21} While this factor is considered appropriate for ambient samples taken in urban areas (based on a survey of the elemental compositions of organic particulate matter sampled in urban atmospheres), it may vary from source to source. Hence, the values calculated for the total organics mass may be somewhat high or low for certain source emissions that have unusual organic composition relative to an average urban aerosol composition. For example, in the case of the roofing tar pot emissions, the ratio of >150% obtained indicates that the total organics mass (by combustion) has been underestimated significantly for this one source test.

Elutable Organics Mass Distributions

Besides mass determinations, the total elutable organics fraction determined by HRGC can be characterized by subdividing the HRGC-FID trace into discrete mass segments. An external standard mixture containing 17 normal alkane homologs that range between $n\text{-C}_{10}\text{H}_{22}$ to $n\text{-C}_{36}\text{H}_{74}$, is used to quantitate the mass corresponding to each portion of the complex organic mixture eluting between C_n and C_{n+1} . The HRGC-FID relative response factor corresponding to the C_n normal alkane (RRF- C_n) is used for quantitation of the total integrated area eluting between C_n and C_{n+1} . Consistent response factors were obtained for multiple injections of the n -alkane standard mixture throughout the total time period needed to analyze all standard and source samples by HRGC-FID. Relative response factors for the $n\text{-C}_{12}\text{H}_{26}$ to $n\text{-C}_{18}\text{H}_{38}$ homologs ranged typically from 0.9 to 1.3 (average value of 1.1). Higher homologs from $n\text{-C}_{20}\text{H}_{42}$ to $n\text{-C}_{34}\text{H}_{70}$ showed a systematic increase in RRF with increasing carbon number with RRF values of 1.2 for the smaller homologs up to 2.1 for the larger homologs. RRF values for $C_{36}\text{H}_{74}$ were in the range of 2.2 to 3.3. Use of the RRF- C_n was adopted instead of an average RRF determined for a C_n and C_{n+1} homolog pair to maintain a consistent mathematical conversion over the entire range of mass elution (beyond $n\text{-C}_{20}\text{H}_{42}$, RRFs for even-numbered homologs only were obtained since odd-numbered homologs were not present in the standard mixture). By using the RRF- C_n instead of an average RRF for two adjacent n -alkane homologs, the underestimation of the total mass eluting between two alkane standards with high carbon numbers $> n\text{-C}_{24}\text{H}_{50}$ is $< 3\%$ for the worst case example.

A HRGC-FID elution pattern and its computed mass distribution histogram can be utilized as "fingerprint" profiles for a single source emission type. As an example, Figure 1 shows the HRGC-FID plot for the underivatized extract (neutral elutable organics) of heavy-duty diesel truck fine aerosol (Fig. 1a) and the computed organic mass distribution (Fig. 1b) of the neutral elutable organics.

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-FID plots has been accounted for in the computed elutable organic mass distribution. This adjustment is apparent when comparing the distributions corresponding to $> n-C_{24}H_{50}$ 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-FID 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 refs. 20, 23).

SUMMARY AND CONCLUSIONS

An analytical 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 $\mu\text{g}/\text{filter}$ are analyzed, and individual organic compounds in the range of C_6 to C_{40} are characterized further via HRGC-FID 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 to 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.

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Table 1. Urban Sources of Fine Carbonaceous Aerosol

Anthropogenic Sources

Oil-fired boiler -- No. 2 fuel oil
Fireplace -- natural wood; synthetic log
Vehicles -- catalyst and noncatalyst cars; diesel trucks
Home appliances -- natural gas
Meat 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 (%)
<u>BLANKS</u>							
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
<u>ANTHROPOGENIC^f</u>							
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	171g
Roofing tar pot (Experiment 2)	2	10,600	6,350	6,350	7,650	11,800	154g

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

Sample	Combined Filters ^a	Fine Mass $\mu\text{g}/\text{filter}$	Total Carbon $\mu\text{g}/\text{filter}$	Organic Carbon $\mu\text{g}/\text{filter}$	Total Organics ^b $\mu\text{g}/\text{filter}$	Total Elutable Organics ^c $\mu\text{g}/\text{filter}$	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	---	---	14	---
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 $\mu\text{g}/\text{filter}$	Total Carbon $\mu\text{g}/\text{filter}$	Organic Carbon $\mu\text{g}/\text{filter}$	Total Organics ^b $\mu\text{g}/\text{filter}$	Total Elutable Organics ^c $\mu\text{g}/\text{filter}$	Ratio of Elutable Organics to Total Organics (%)
<u>BIOGENIC^f</u>							
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	13
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.^{1,21}

^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. Organic mass distributions obtained from heavy-duty diesel truck fine particulate emissions. X denotes a known solvent artifact; S_C is the coinjection standard (1-phenyldodecane); and S_R is the recovery standard ($n\text{-C}_{24}D_{50}$). (a) HRGC plot of the neutral elutable organics, and (b) the computed mass distribution of neutral elutable organics plotted versus normal alkane carbon number.

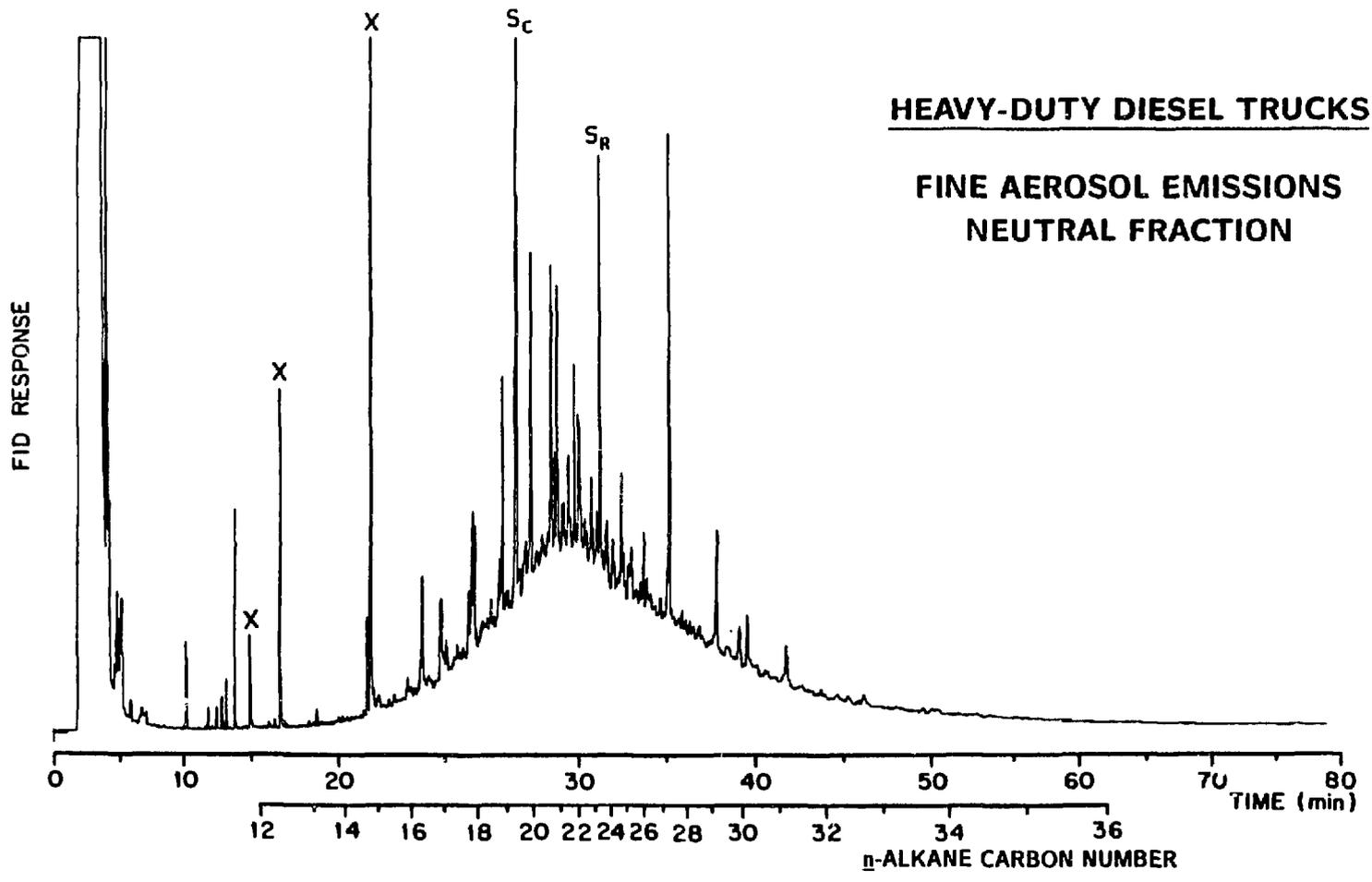


FIGURE 1a

FIGURE 1b

