

Measurement of Emissions from Air Pollution Sources. 1. C_1 through C_{29} Organic Compounds from Meat Charbroiling

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A dilution source sampling system was used to quantify the organic air pollutant emissions from commercial-scale meat charbroiling operations. Emission rates of gas-phase volatile organic compounds, semivolatile organic compounds, and high molecular weight particle-phase organic compounds were simultaneously quantified on a single compound basis. Fine particle mass emission rates and fine particle elemental chemical composition were measured as well. Emission rates of 120 organic compounds, spanning carbon numbers from C_1 to C_{29} were quantified including *n*-alkanoic acids, *n*-alkenoic acids, carbonyls, lactones, alkanes, aromatics, polycyclic aromatic hydrocarbons, alkenes, and steroids. Ethylene, formaldehyde, and acetaldehyde were found to be the predominant light gas-phase organic compounds emitted from the charbroiling operations. *n*-Alkanoic acids, *n*-alkenoic acids, and carbonyls made up a significant fraction of the quantified semivolatile and particle-phase organic compound emissions. Meat charbroiling is one of the few sources identified to date that contributes to the high molecular weight aldehydes measured in the urban atmosphere. Semivolatile and particle-phase organic compounds were collected for quantification by two simultaneous sampling protocols: (1) quartz fiber filters followed by polyurethane foam (PUF) cartridges, and (2) XAD-coated annular denuders followed by quartz fiber filters and PUF cartridges. Good agreement was observed for the total mass emissions collected by the two different sampling procedures; however, the partitioning of the semivolatile organic compounds between the gas phase and particle phase, as measured by the two sampling procedures, showed significant differences for *n*-alkanoic acids, indicating that significant artifact adsorption of these compounds occurs to the filter in the filter/PUF sampling system.

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Introduction

Atmospheric dispersion models (1, 2) and an atmospheric receptor model that uses organic compounds as tracers (3) have been used to understand the relationship between fine particulate matter emitted from meat cooking operations and atmospheric fine particle concentrations. In the Los Angeles area, meat cooking operations were found to contribute up to approximately 20% of the annual average fine organic particle concentrations in the atmosphere at four air quality monitoring sites in 1982 (3). Although the relationship between ambient fine particle concentrations and primary particle emissions from meat cooking (4) are relatively well characterized, little is known about the relationship between the emissions from meat cooking operations and other aspects of air pollution such as photochemical smog formation, secondary organic aerosol formation, and the ambient concentrations of toxic air pollutants. The lack of understanding of the effect of meat cooking emissions on these aspects of air quality is largely due to two reasons: (1) the lack of data on the emissions of gas-phase and semivolatile organic compounds from meat cooking operations, and (2) the previous inability of air pollution models to address the role of semivolatile organic compounds in secondary aerosol formation and photochemical smog.

Significant progress has been made in recent years toward understanding the atmospheric behavior of semivolatile organic compounds (5, 6). In addition, air pollution models are now capable of better addressing the role of secondary organic aerosol formation from reactive organic gases (7). These two developments have laid the foundation for the development of comprehensive air pollution models which will be able to simultaneously track the gas-phase and particle-phase organic compound concentrations and the chemistry and physics of the interaction of gas-phase organic compounds with the associated particulate matter. A limiting factor in the application of these models to studying specific air pollution problems is the scarcity of emissions inventory data for the semivolatile organic compounds covering virtually all major urban air pollution sources. To this end, a series of air pollution source tests is being conducted to obtain comprehensive emissions source profiles covering gas-phase, semivolatile, and particle-phase organic compounds, including hydrocarbons, carbonyls, and organic acids, plus fine particle emission rates and fine particle elemental composition. The current paper addresses the measurement of such emissions from meat charbroiling operations.

Experimental Methods

Comprehensive Source Sampler. An advanced source sampling system has been developed which facilitates the simultaneous measurement of gas-phase, semivolatile, and particle-phase organic compound emission rates; fine particle mass emission rates and fine particle elemental composition. The portable dilution tunnel was originally developed for fine particulate measurements by Hildemann et al. (8) and has been extended with additional equipment that allows single compound quantification of gas-phase and semivolatile organic compound emissions. In this dilution source sampler, which can operate as a single-stage dilution tunnel or a two-stage dilution tunnel, hot exhaust emissions are mixed with a 25- to 180-fold excess of activated carbon-filtered and HEPA-filtered air which in the presence of sufficient residence time causes those organic vapors that

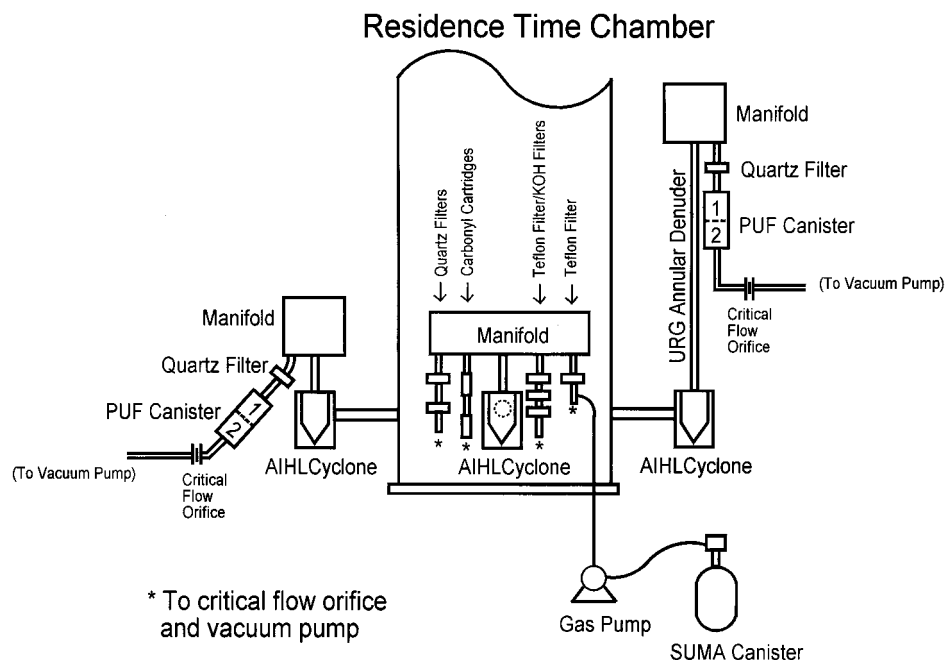


FIGURE 1. Sampling equipment connected to the comprehensive dilution source sampler for the measurement of gas-phase, semivolatile, and particle-phase organic compounds, and fine particle mass and chemical composition.

will form particulate matter upon cooling in the atmosphere instead to condense onto preexisting particles in the source exhaust within the dilution sampler itself. The emissions thus can be sampled at near atmospheric temperature and pressure to obtain data on the partitioning of organic compounds between the gas and particle phases.

A diagram of the front portion of the dilution source sampler used here is shown in Figure 1 of Hildemann et al. (8). Modification of that sampler begins as the diluted mixture of particles and gases is withdrawn from the residence time chamber located at the far downstream side of the sampling system. As shown in Figure 1 of the present paper, sample was withdrawn through AIHL-design cyclone separators (9) which were operated at a flowrate of 30 L min^{-1} such that fine particles with aerodynamic diameters smaller than $1.8 \mu\text{m}$ in diameter pass through the cyclones along with all gas-phase species. Semivolatile organic and fine particle-phase compounds were then collected with two different sampling trains that operate in parallel. The first sampling train begins with a XAD-coated annular denuder (URG, Inc.; 400 mm long, four-channel denuder), shown on the right side of Figure 1. The flow next was divided between three quartz fiber filters (47 mm diameter, Pallflex Tissuequartz 2500 QAO) operated in parallel at a flowrate of 10 L min^{-1} each. The flow out of each of the three quartz fiber filters was then combined and passed through two polyurethane foam (PUF) cartridges (Atlas Foam; density = 0.022 g cm^{-3} , ILD = 30; 5.7 cm diameter by 7.6 cm long) operated in series. The gas-phase semivolatile organic compounds were collected by the annular denuder while particles and particle-phase organic compounds pass through the denuder and were collected on the filters downstream of the denuder. The PUFs downstream of the filters collect any semivolatile organics that blow off the filters.

The XAD coated annular denuders were prepared by a modified version of the procedure originally developed by Gundel et al. (10) and were operated at a flowrate of 30 L min^{-1} . Briefly, the XAD-coated annular denuders were coated as recommended by Gundel et al. (10) with a slurry of XAD-4 (Sigma Amberlite XAD-4). The XAD-4 was ground with a mortar and pestle to pass through a 400 mesh sieve ($38\text{-}\mu\text{m}$ mesh openings), cleaned, and then slurried into a solvent

mixture of dichloromethane/acetone/hexane (2:3:5) (Fischer Optima Grade). The internal walls of the denuder were wetted with an aliquot of the XAD slurry and then rinsed with four successive batches of a clean XAD-free dichloromethane/acetone/hexane mixture (denuder solvent). The denuder was then dried with high purity nitrogen. The slurry application was repeated five more times. The XAD-4 adheres directly to the etched glass denuder walls, and no adhesive is required (10). Within 12 h prior to being used in a source test, the denuder was cleaned by four successive extractions with the denuder solvent in the presence of mild shaking of the solvent-filled denuder assembly. The denuder was then dried with high purity nitrogen. Denuders were sealed with Teflon-lined end caps from the time of preparation until use.

Particle losses in a similar URG annular denuder have been evaluated at operating conditions similar to those used in the current study, and it has been shown that electrically neutral fine particle losses are less than 5% for particles with diameters between 0.015 and $0.75 \mu\text{m}$ (11). Experimental results reported by Gundel et al. (10) and experiments conducted in the course of the present project also demonstrate low fine particle losses in the denuders. Likewise, experiments conducted by Kamens and Coe (12) have shown that outgassing of particles does not occur at the denuder residence times of the present study. Typically only one denuder/filter/PUF sampling unit was placed in operation during a source test. A single denuder was used for a sampling time of up to approximately 30 min. The denuders were changed during source tests lasting longer than 30 min to ensure that sampling was almost continuous throughout the source test cycle.

Prior to the current project, the use of XAD-coated denuder technology has only been reported for the collection of PAH (10), nitro-PAH (13), and dioxin (14). The current research requires that the technology be applicable to many classes of organic compounds. For this reason, tests were conducted to demonstrate the ability to extract and recover a broad range of organic compounds from these denuders. A denuder was spiked with a standard suite containing over 100 compounds including series of *n*-alkanes, *n*-alkanoic acids, *n*-alcohols, PAH, fatty acid methyl esters, phenol, and benzaldehyde. All of these compounds were found to be

TABLE 1. Sampling Trains Used with Comprehensive Source Sampler

sample train	substrate and flowrate	followed by	followed by	chemical analysis
denuder/filter/PUF (one per cyclone)	XAD-coated annular denuder (URG, 400 mm long, four channel) 30 L min ⁻¹ 0.2 s residence time	47-mm quartz fiber filters (three in parallel) 10 L min ⁻¹ per filter	PUF cartridges (two in series) 30 L min ⁻¹	organic compounds by GC/MS
filter/PUF (three per cyclone)	47-mm quartz fiber filters 10 L min ⁻¹	PUF cartridges (two in series) 10 L min ⁻¹		organic compounds by GC/MS
inorganic and VOC (all four sampling trains in parallel downstream of one cyclone)	47-mm quartz fiber filter 10 L min ⁻¹ 47-mm Teflon membrane filter 10 L min ⁻¹ 47-mm Teflon membrane filter 10 L min ⁻¹ DNPH-impregnated C ₁₈ cartridge 0.2 L min ⁻¹	47-mm quartz fiber filter 10 L min ⁻¹ KOH-impregnated 47-mm quartz fiber filter 10 L min ⁻¹ SUMA canister DNPH-impregnated C ₁₈ cartridge 0.2 L min ⁻¹	KOH-impregnated 47-mm quartz fiber filter 10 L min ⁻¹	EC/OC Teflon filter: mass emissions rate and trace metals by XRF KOH impregnated filters: organic acids Teflon filter: mass emissions rate and soluble ions by AA and IC SUMA canister: VOC carbonyls by LC

quantitatively extracted from the denuders by four successive extractions with denuder solvent as described above, with no residual compounds remaining as measured by a second round of this extraction procedure. In addition, results will be presented in the current study showing good agreement between the total mass emission rates (but not necessarily phase separation) measured by the denuder/filter/PUF sampling train and a less complex filter/PUF sampling train.

A second type of semivolatile and particle-phase organic compound sampling train was operated simultaneously in parallel with the denuder/filter/PUF system. In this second system, an AIHL-design cyclone separator operated at 30 L min⁻¹ was followed by three filter/PUF units in parallel each operated continuously at a flowrate of 10 L min⁻¹ throughout the source test cycle. Each of the filter/PUF units consisted of a quartz fiber filter (47 mm diameter, Pallflex Tissuequartz 2500 QAO) followed by two PUF cartridges (Atlas Foam) operated in series as shown on the left side of Figure 1. Each PUF consisted of a 5.7-cm-diameter by 7.6-cm-long cylinder of polyurethane foam which was sized to retain 95% of the gas-phase naphthalene entering the PUF when operated at 10 L min⁻¹ over the entire source test (15). Less volatile, heavier organic compounds were collected with even higher efficiencies than seen for naphthalene. During a typical source test, one denuder/filter/PUF sampling train and four cyclones each with three-filter/PUF assemblies were connected to the residence time chamber of the dilution tunnel; the extra filter/PUF units were intended for collection of excess sample to be used in further method development efforts.

In addition to the above sampling trains, a third type of cyclone-based filter sampler combined with VOC canisters and cartridges was operated for the collection of fine particulate matter, carbonyls, organic acids, and gas-phase organic compounds. A schematic of this system is shown in the center of Figure 1 pictured with the dilution tunnel's residence time chamber located behind the cyclone, and the sampling substrates are listed in Table 1. Three stacked filter units and one carbonyl sampling line were connected to the outlet of an AIHL cyclone that drew air at a flowrate of 31 L min⁻¹ from the residence time chamber of the source sampler. The first stacked filter unit consisted of two quartz fiber filters (47 mm diameter, Pallflex Tissuequartz 2500 QAO)

in series which were used for elemental and organic carbon (EC/OC) analysis by thermal evolution and combustion analysis as described by Birch and Cary (16). The OC measured on the back-up quartz fiber filter was used to help understand the adsorption of semivolatile organic compounds onto the front filter (17, 18). The second filter stack contained three filters, a Teflon membrane filter (47 mm diameter, Gelman Teflo, 2 μ m pore size) followed by two KOH-impregnated quartz fiber filters in series. This Teflon membrane filter was used for gravimetric determination of the fine particle mass emissions rate and was analyzed by X-ray fluorescence for 35 trace elements (19). The tandem KOH-impregnated quartz fiber filters were used to collect vapor-phase organic acids which will be analyzed in association with other research activities and will not be reported here. The third filter holder assembly contains one Teflon membrane filter which was used for a duplicate fine particle mass emissions measurement and for inorganic ion measurements by ion chromatography (20), atomic absorption spectroscopy, and colorimetry (21). Downstream of that single Teflon filter the sample flow was divided, and a small portion of the flow was used to fill a 6-L polished stainless steel SUMA canister for the collection of non-methane volatile hydrocarbons ranging from C₂ to C₁₀. The 6-L SUMA canister was filled continuously at a constant flowrate set to fill the canister over the entire source test cycle. Carbonyls were collected at the outlet of the AIHL cyclone separator by two C₁₈ cartridges impregnated with dinitrophenylhydrazine (DNPH) that were operated in series (22). The air flowrates through the DNPH impregnated cartridges are typically in the range 0.3 to 0.5 L min⁻¹.

The flowrates through each of the sampling substrates were controlled with the use of critical orifices and were measured before and after each source test with rotameters that have been calibrated using an electronic bubble flowmeter (Gilian Instrument Corporation Model 800268). The sample and the dilution air flowrates into the dilution tunnel were monitored throughout the source tests with a venturi meter and an orifice meter, respectively. The venturi meter and the orifice meter have been calibrated using dry gas meters. From these sample and dilution air flowrates and the analytical measurements described above, quantitative

emissions rates were determined for chemically speciated fine particulate matter, as well as for individual gas-phase, semivolatile, and particle-phase organic compounds.

Dilution Sampler Preparation and Evaluation. Prior to the meat charbroiling source tests the dilution source sampler was completely disassembled and cleaned by vapor degreasing. Directly after degreasing, the sampler pieces were immediately wrapped with clean aluminum foil which had been baked at 550 °C for 12 h. After the dilution sampler was reassembled, clean dilution air was passed through the sampler as the sampler was heated to approximately 95 °C by wrapping the stainless steel sections with electrical heating tape. The sampler was maintained at 95 °C for a minimum of 4 h to remove any residual light hydrocarbons remaining after vapor degreasing. All of the small sampler pieces, including the filter holders and cyclones, were thoroughly cleaned with a detergent solution, next rinsed with deionized water, and then cleaned by sonication with hexane, methanol, and dichloromethane.

The dilution air supply to the dilution tunnel consists of ambient air that has been cleaned by passage through a HEPA filter and an activated carbon bed (8). A comprehensive blank test was conducted at the onset of the source sampling program to determine the ability of the dilution air cleaning system to remove particles, semivolatile organic compounds, carbonyls, and VOCs. The dilution air cleaning system was found to have very high removal efficiencies for particulate matter, semivolatile organic compounds, and all carbonyls. As expected, the lightest VOCs were not completely removed by the activated carbon bed, so a system for measuring the residual VOCs in the dilution air was added to the source sampler. Dilution air was sampled and analyzed by the same procedures as used for the diluted sample gas stream described above, and source test results were then corrected by subtraction of any VOC background concentration present in the dilution air. VOC background concentrations present in the diluted air were all less than 10% of the concentrations contributed by the exhaust from the charbroiler except for ethane, ethylene, acetylene, and propane.

Particle losses in the comprehensive dilution sampler were evaluated by extracting a section of the dilution tunnel walls immediately following the completion of a cigarette source test in our laboratory. The extract was handled by the same procedures that will soon be discussed for the sample extracts, and compounds deposited per centimeter squared of dilution sampler interior wall area were quantified by GC/MS. The mass of individual organic compounds that were deposited onto the entire sampler internal surface area was calculated by scaling up the mass deposited onto the extracted area of the sampler walls to represent the entire interior surface area of the sampling system. The semivolatile organic compounds that are predominantly present in the gas phase showed no detectable losses to the walls, while the predominately particle-phase organic compounds showed losses of approximately 7%, which is consistent with earlier particle loss experiments reported by Hildemann et al. (8). The compounds which were partitioned between both the gas-phase and the particle-phase were found to have losses between the pure particle-phase compounds and the pure gas-phase organic compounds. These results indicate that there are no preferential losses of semivolatile organic compounds in the comprehensive dilution source sampler and that those losses that do occur affect primarily particulate matter, accounting for approximately 7% of the fine particle mass emissions.

Source Testing Procedure. The meat charbroiling source tests were conducted in the field at a large institutional-scale natural gas fired charbroiler that is in current commercial use. Emissions were sampled downstream from the filter and grease extractor that exist in the charbroiler exhaust ventilation system, which was operated at flowrate of 400 m³

min⁻¹. The filter and grease extractor are expected to have a particle mass removal efficiency of approximately 60% (23). The source effluents were diluted by a second stage of dilution within the dilution sampler to bring the organic vapor/particle mixture to ambient conditions at 29 °C. Two charbroiler tests were conducted using commercially distributed preformed hamburger patties (Kraft Premier, 114 g of meat per patty, 20% fat); one test was conducted with defrosted hamburgers and the second test was conducted using hamburgers that were still frozen when placed on the grill as is the common practice at the facility tested. Eighty hamburger patties were cooked, in batches of eight at one time, over a period of 85 min during the test in which the frozen hamburgers were not defrosted prior to cooking. One hundred twelve hamburger patties were cooked, in batches of eight at one time, over a period of 72 min during the test where the hamburger patties were completely defrosted prior to cooking. No cooking oils were used in the charbroiling process.

Organic Chemical Analysis. Extraction of particle-phase organic compounds collected on quartz fiber filters during the source tests was based on the previous work by Mazurek et al. (24) and Rogge et al. (4, 25–30) and Rogge (31). Prior to sampling, the quartz fiber filters were baked at 550 °C for a minimum of 12 h to reduce residual carbon levels associated with new filters. Immediately after sampling, the filters were stored in a freezer at –21 °C until the samples were extracted. The filters were typically extracted within one to two weeks following sample collection. Before the quartz fiber filters were extracted, they were spiked with a mixture of seven deuterated internal recovery standards: *n*-decane-*d*₁₂, *n*-pentadecane-*d*₃₂, *n*-tetracosane-*d*₅₀, *n*-hexanoic acid-*d*₁₁, *n*-decanoic acid-*d*₁₉, phenol-*d*₅, benzoic acid-*d*₅, and benzaldehyde-*d*₆. The samples were extracted under mild sonication twice with hexane (Fischer Optima Grade), followed by three successive benzene/2-propanol (2:1) extractions (benzene—high purity lots of E&M Scientific benzene; 2-propanol—Burdick & Jackson). Extracts were filtered, combined, and reduced in volume to approximately 250 μL, and were split into two separate fractions. One fraction was then derivatized with diazomethane to convert organic acids to their methyl ester analogues which are amenable to GC/MS identification and quantification.

The procedures developed for the identification and quantification of organic compounds collected on the XAD-coated annular denuders and the PUF plugs were based on the methods previously developed for the analysis of air pollution samples collected on the quartz fiber filters. The analytical methods developed for the XAD-coated annular denuders and the PUF plugs can be used to quantify vapor-phase semivolatile organic compounds that are as heavy as dodecane for alkanes, heptanoic acid for *n*-alkanoic acids, and naphthalene for polycyclic aromatic hydrocarbons under appropriate sampling conditions.

After the completion of each source test, the denuders used for sampling were extracted within 12 h. During sample extraction, the denuder was first spiked with the same deuterated internal standard mix used for the filter extraction, and was then extracted with the use of four aliquots of 40 mL each of denuder solvent by pouring each aliquot into the denuder and shaking the Teflon-capped denuder for approximately 30 s per aliquot. The four aliquots were composited and reduced to a volume of approximately 250 μL and then split into two separate fractions. One fraction was derivatized with diazomethane.

Prior to source sampling, the PUF plugs were cleaned by four successive extractions with a solvent mixture of dichloromethane/acetone/hexane (2:3:5) (Fischer Optima Grade). The foam plugs were repetitively compressed during the extraction. After the cleaning procedure, the PUFs were air-

dried in the dark in an organics clean room and were then stored in annealed borosilicate jars with solvent-washed Teflon lid liners in the freezer at -21°C . After sampling, the PUF plugs were spiked with the same internal standard mix used for the filter and denuder extractions, and then were extracted with four successive aliquots of a mixture of dichloromethane/acetone/hexane (2:3:5). The extracts were filtered, combined, reduced in volume to approximately 250 μL , and then split into two separate fractions. One fraction was derivatized with diazomethane as was done with the filter extracts and the denuder extracts.

Filter, PUF, and denuder field blanks were analyzed with each set of source samples. The field blanks are prepared, stored, and handled by exactly the same procedures as used for the source samples. Average extraction recoveries for the internal standards after extraction and reconcentration were 85% for low volatility tetracosane- d_{50} and 60–65% for higher volatility pentadecane- d_{32} , hexanoic acid- d_{11} , and decanoic acid- d_{19} . The smaller recoveries for the higher volatility compounds reflect losses during blowdown, and all data are corrected according to the internal standard recoveries.

Both the derivatized and underivatized sample fractions were analyzed by GC/MS on a Hewlett-Packard GC/MSD (GC Model 5890, MSD Model 5972) using a 30-m 0.25-mm-diameter HP-1701 capillary column (0.25 μm film thickness, Hewlett-Packard). 1-Phenyldodecane was used as a co-injection standard for all sample extracts and standard runs. The deuterated n -alkanes in the internal standard were used to determine extraction recovery for the compounds quantified in the underivatized samples. The deuterated acids were used to verify that the diazomethane reactions were driven to completion. In addition, the deuterated n -alkanoic acid recoveries were used in conjunction with the recovery of deuterated tetracosane to determine the recovery of the compounds quantified in the derivatized fraction.

Semivolatile and particle-phase organic compounds collected during the source test program were identified and quantified by gas chromatography/mass spectrometry (GC/MS). Although not all organic compounds emitted from air pollution sources were solvent extractable nor were they all elutable from a GC column, hundreds of compounds can be identified and quantified in source emissions (4, 25–30). Hundreds of authentic standards have been prepared for the positive identification and quantification of the organic compounds found in the current source test program. When quantitative standards could not be obtained for a given compound or compound class, significant effort was made to obtain a nonquantitative secondary standard that could be used for unique identification of the organic compounds. An example of such a secondary standard was the use of petroleum candle wax as a source of isoalkanes and ante-isoalkanes that can then be used to help identify their presence when found in cigarette smoke particulate matter. Quantification of compounds identified using secondary standards has been estimated from the response factors for compounds having similar retention times and chemical structure. When neither quantitative nor secondary standards could be obtained, compound identification was classified as either (1) *probable*, when the sample mass spectrum was identical to the library spectrum but no standard was available, and (2) *possible*, same as probable except that the spectrum contained additional information due to coelution with another compound. Compounds having probable and possible identifications were noted but their emission rates are not quantified. Estimated measurement uncertainties attached to the measured emissions of individual organic compounds by the GC/MS technique used in the present study were $\pm 20\%$ (1 σ).

Total non-methane organic gases (NMOG, EPA method TO12) and individual organic vapor-phase hydrocarbons

TABLE 2. Average Fine Particle Emission Rate and Fine Particle Chemical Composition from Meat Charbroiling^a

fine particle mass emissions rate (avg + std): 18.8 \pm 2.0 g kg ⁻¹ of meat cooked			
X-ray fluorescence (wt % of fine particle mass)			
aluminum	0.039 \pm 0.019	selenium	0.00 \pm 0.01
silicon	0.082 \pm 0.018	bromine	0.00 \pm 0.01
phosphorus	0.066 \pm 0.018	rubidium	0.00 \pm 0.01
sulfur	0.19 \pm 0.012	strontium	0.00 \pm 0.01
chlorine	0.16 \pm 0.030	yttrium	0.00 \pm 0.01
potassium	0.34 \pm 0.030	zirconium	0.00 \pm 0.01
calcium	0.01 \pm 0.03	molybdenum	0.00 \pm 0.02
titanium	0.00 \pm 0.12	palladium	0.00 \pm 0.04
vanadium	0.00 \pm 0.05	silver	0.01 \pm 0.05
chromium	0.00 \pm 0.01	cadmium	0.00 \pm 0.05
manganese	0.00 \pm 0.01	indium	0.00 \pm 0.06
iron	0.01 \pm 0.01	tin	0.00 \pm 0.08
nickel	0.01 \pm 0.01	antimony	0.00 \pm 0.09
copper	0.00 \pm 0.01	barium	0.02 \pm 0.33
zinc	0.00 \pm 0.01	lanthanum	0.01 \pm 0.44
gallium	0.00 \pm 0.01	mercury	0.00 \pm 0.01
arsenic	0.00 \pm 0.01	lead	0.00 \pm 0.02
elemental and organic carbon (wt % of fine particle mass)			
organic carbon ^b	33.8 \pm 2.0	elemental carbon	0.0 \pm 0.5
ionic species by ion chromatography (wt % of fine particle mass)			
chloride	0.17 \pm 0.08	ammonium	0.00 \pm 0.15
nitrite	0.00 \pm 0.06	sodium	0.37 \pm 0.11
nitrate	0.38 \pm 0.01	calcium	0.00 \pm 0.59
sulfate	0.00 \pm 0.10	magnesium	0.00 \pm 0.06

^a Values shown in boldface are greater than zero by at least two standard errors. ^b Measured downstream of the organics denuder. Organic carbon measured on undenuded filter is 56.6% of fine particle mass.

ranging from C_1 to C_{10} were analyzed from the SUMA canisters by gas chromatography/flame ionization detection (GC/FID) as described by Fraser et al. (32). Carbonyls collected by the C_{18} cartridges were analyzed by liquid chromatography/UV detection as described by Grosjean et al. (33). The measurement uncertainties of the VOC measurements and the carbonyl measurements are expected to be approximately $\pm 15\%$ (1 σ) (33).

Results and Discussion

Fine Particle Mass and Chemical Composition. Fine particle emission rates and bulk chemical composition were found to be very similar in both meat charbroiling source tests in this study with an average fine particle mass emission rate of 18.8 ± 2.0 g per kilogram of meat cooked and an aerosol organic carbon content of $56.6 \pm 3.3\%$. The average emission rate was approximately half the 39.8 g per kilogram of meat cooked reported by Hildemann et al. (34) when cooking hamburgers on the same charbroiler at longer cooking times, 7–8 min per burger patty as compared to the approximate 5 min cooking duration in the current study for comparable defrosted hamburgers. The emission rate per unit of meat charbroiled thus scales approximately in proportion to cooking time on the grill, which seems logical. The fraction of organic carbon in the particle emissions in the present test was not statistically different from the 58.8% measured by Hildemann et al. (34). Table 2 shows the average fine particle emission rate and fine particle elemental and inorganic ion composition obtained during the present meat charbroiling tests. The fine particulate matter emitted from meat charbroiling contained virtually no elemental carbon and very little inorganic matter. Potassium was measured at a level of 0.34% of the fine particle mass, much less than

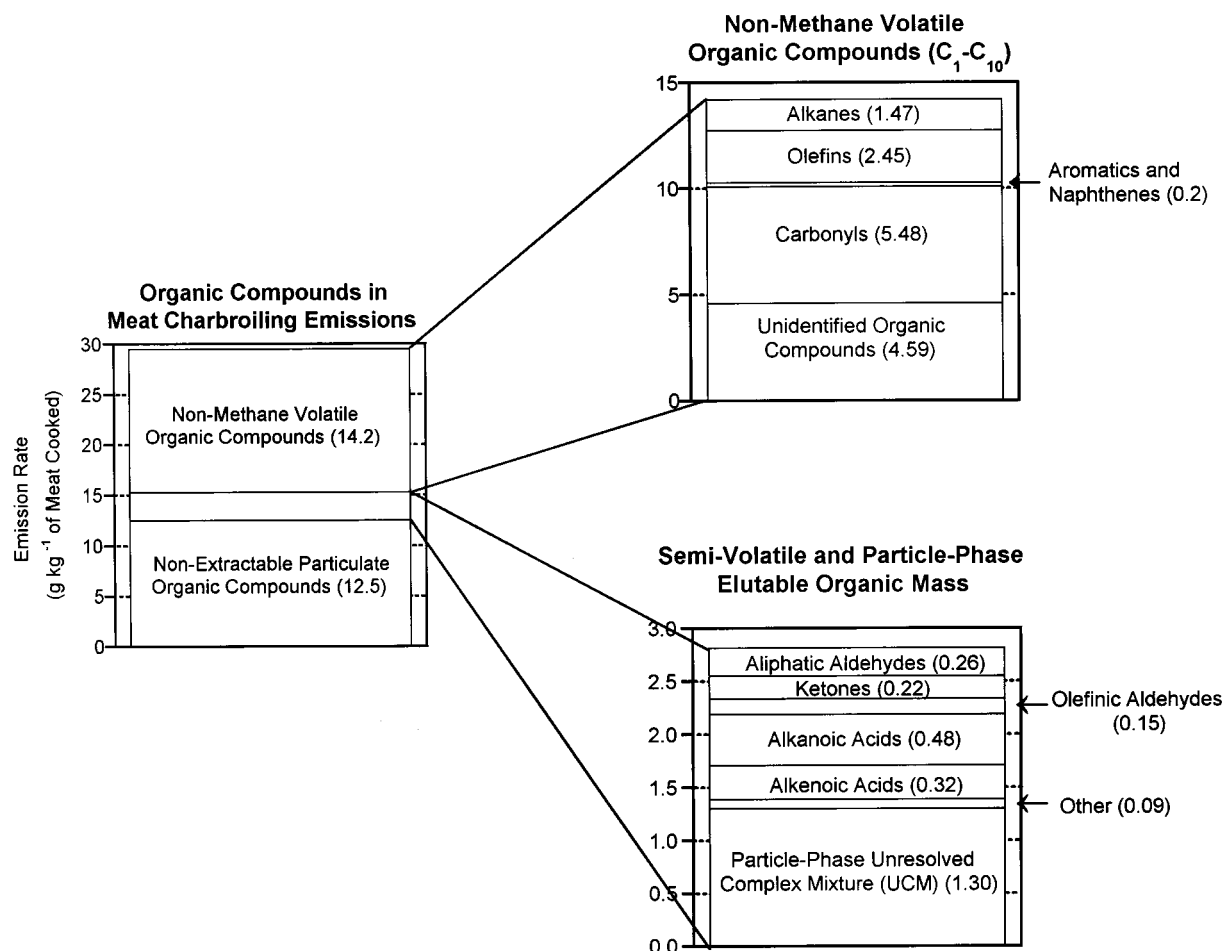


FIGURE 2. Material balance on the gas-phase, semivolatile, and particle-phase organic compound emissions from meat charbroiling measured by the comprehensive source sampler.

organic carbon but in a higher concentration than any of the other inorganic species except sodium. Knowledge of the potassium content of meat smoke is important because nonsoil potassium has been used in the past as if it were a nearly unique tracer for woodsmoke (35). In some cases, the potassium content of meat smoke should be considered as well. Smaller quantities of nitrogen as nitrite, aluminum, silicon, phosphorus, sulfur, and chloride also were detected in meat smoke, as shown in Table 2.

Non-methane Organic Compounds. Single compound quantification of the gas-phase, semivolatile, and particle-phase organic compound emissions was performed only on the source test which utilized defrosted hamburgers for cooking. A material balance on gas-phase and fine particulate organic compounds measured by the comprehensive dilution source sampling system during the defrosted hamburger charbroiling test is shown in Figure 2. These emissions include 14.9 g of fine particulate organic compound mass per kilogram of meat cooked, 8.67 g kg⁻¹ of identified C₂-C₁₀ volatile hydrocarbon gases, 1.0 g kg⁻¹ of higher molecular weight vapor-phase organics collected by the XAD-coated denuders, and 5.48 g kg⁻¹ of C₁-C₁₀ carbonyls.

Volatile Organic Compounds. The emissions rate of non-methane C₁-C₁₀ volatile organic compounds (VOC) from meat charbroiling was measured to be 13.6 g per kilogram of meat cooked, which includes formaldehyde and other C₁-C₁₀ carbonyls. Although the VOC emissions from charbroiling were relatively small on a mass basis compared to other urban sources, the emissions contained noticeable amounts of several very reactive light olefinic hydrocarbons. The VOC emissions were found to consist of 2.0% propene, 1.6%

butenes, and 0.8% 1,3-butadiene by mass, accompanied by less reactive unsaturated organics including 10.5% ethylene and 2.4% acetylene. It is unclear if these olefinic compounds were formed from the meat that was being charbroiled or were formed directly from the natural gas combustion used in the charbroiler. Table 3 lists the contribution of 41 volatile organic compounds to the non-methane C₁-C₁₀ VOC emissions from charbroiling. The quantified volatile hydrocarbons made up 30% of the VOC emissions and another 36% of the VOC emissions consisted of C₁-C₁₀ aldehydes.

Formaldehyde and acetaldehyde were emitted from meat cooking operations at 1.38 and 1.09 g per kilogram of meat cooked which was higher than all other emissions rates for individual VOCs except ethylene. Propanal, crotonaldehyde, and glyoxal were also emitted in significant quantities at 0.50, 0.50, and 0.55 g kg⁻¹ of meat cooked. The emissions of these carbonyls add significantly to the reactivity of the VOCs emitted from meat cooking operations.

Semivolatile and Particle Phase Organic Compounds. Seventy-one vapor-phase semivolatile and particle-phase organic compounds have been quantified in samples collected on the denuders, filters, and PUFs during the charbroiled meat cooking test as shown in Table 3. *n*-Alkanoic acids, *n*-alkenoic acids, and carbonyls made up a significant fraction of the semivolatile and particle-phase organic compounds emitted from meat charbroiling that were extractable and elutable. 9-Octadecanoic acid (oleic acid) and *n*-hexadecanoic acid (palmitic acid) were emitted at by far the largest rates, with average emissions of 214 000 and 174 000 µg kg⁻¹ of meat cooked, respectively. *n*-Alkanoic acids as light as *n*-heptanoic acid and as heavy as *n*-docosanoic

TABLE 3. Organic Compound Emission Rates from Hamburger Meat Charbroiling over a Natural Gas Fired Grill

compound	gas phase (µg kg ⁻¹ of meat cooked)			fine particle (µg kg ⁻¹ of meat cooked)			total	notes ^{a-e}
	VOC canister	DNPH cartridge	XAD denuder	filter	PUF1	PUF2		
n-Alkanes								
methane	18 000 000						18 000 000	a
ethane	663 000						663 000	a
propane	190 000						190 000	a
n-butane	107 000						107 000	a
n-pentane	87 000						87 000	a
n-hexane	44 000						44 000	a
n-heptane	46 000						46 000	a
n-octane	38 000						38 000	a
n-nonane	13 000						13 000	a
n-decane							<5 000	a
n-tridecane			3 100	330			3 430	b
n-tetradecane			3 110	580	1 320		5 000	a
n-pentadecane			4 490	520	1 240		6 240	b
n-hexadecane			3 110	135			3 240	a
n-heptadecane							<400	b
n-octadecane			1 290	160			1 450	a
n-nonadecane			400		320		720	b
n-eicosane			1 020		170		1 190	a
n-heneicosane			390	130	360		880	b
n-docosane			450	160			610	a
n-tricosane			500	60			560	b
n-tetracosane			430	260			690	a
n-pentacosane			110	380	290		780	b
n-hexacosane				260			260	a
n-heptacosane				650			650	b
n-octacosane				1 140			1 140	a
n-nonacosane				770			770	b
Branched Alkanes								
isobutane	54 000						54 000	a
isopentane	74 000						74 000	a
2,3-dimethylbutane	5 000						5 000	a
2-methylpentane	22 000						22 000	a
2,4-dimethylpentane	5 000						5 000	a
2-methylheptane	5 000						5 000	a
2,2,4-trimethylpentane	11 300						11 300	a
Alkenes								
ethene	1 485 000						1 485 000	a
propene	289 000						289 000	a
1-butene	73 000						73 000	a
Branched Alkenes								
isobutene	159 000						159 000	a
Diolefins								
1,3-butadiene	105 000						105 000	a
Alkynes								
ethyne (acetylene)	336 000						336 000	a
Saturated Cyclic Hydrocarbons								
cyclopentane	5 000						5 000	a
methylcyclopentane	9 000						9 000	a
cyclohexane							<5 000	a
methylcyclohexane	13 000						13 000	a
Biogenic Hydrocarbons								
isoprene	3 000						300	a
squalene				342			342	a
Aromatic Hydrocarbons								
benzene	83 000						83 000	a
toluene	40 000						40 000	a
ethylbenzene	11 000						11 000	a
m-xylene + p-xylene	12 000						12 000	a
styrene							<5 000	a
o-xylene	11 000						11 000	a
1,3,5-trimethylbenzene							<5 000	a
1,2,4-trimethylbenzene	24 000						24 000	a
naphthalene ^f			5 860		1 690	1 440	8 990	a
phenanthrene			1 120	34	90		1 220	a
anthracene			110	51			160	a
fluoranthene			400	120			520	a
pyrene			570	100			670	a
chrysene/triphenylene			330	270			600	a

TABLE 3 (Continued)

compound	gas phase ($\mu\text{g kg}^{-1}$ of meat cooked)			fine particle ($\mu\text{g kg}^{-1}$ of meat cooked)			total	notes ^{a–e}
	VOC canister	DNPH cartridge	XAD denuder	filter	PUF1	PUF2		
Aliphatic Aldehydes								
formaldehyde		1 382 000					1 382 000	a
acetaldehyde		1 092 000					1 092 000	a
propanal		504 000					504 000	a
butanal/isobutanal		373 000					373 000	a
hexanal		203 000					203 000	a
heptanal		125 000					125 000	a
octanal		146 000					146 000	a
nonanal ^g		141 000	115 000	32 700			148 000	a
decanal ^g		70 000	29 500	4 060			33 600	a
undecanal			13 600	3 550			17 200	a
dodecanal ^g		35 000	26 200	3 830			30 000	a
tridecanal ^g		38 000	15 300	2 680			18 000	a
tetradecanal			14 400	3 580			18 000	a
pentadecanal			12 850	1 570			14 400	b
hexadecanal			3 490				3 490	b
heptadecanal			2 510				2 510	b
Dicarbonyls								
glyoxal		550 000					550 000	a
methylglyoxal		334 000					334 000	a
biacetyl		28 000					28 000	a
Ketones								
nonan-2-one ^f			55 700		15 400	6 200	77 300	c
decan-2-one			65 500	10 000			75 500	c
undecan-2-one			107 000	3 430			107 000	c
tridecan-2-one			39 000	3 250			42 300	c
tetradecan-2-one			61 900	3 400			65 300	c
pentadecan-2-one			64 500	5 200			69 700	c
heptadecan-2-one			21 300	1 680			23 000	c
Unsaturated Carbonyls								
crotonaldehyde		495 000					495 000	a
methacrolein		52 000					52 000	a
furaldehyde		81 500					81 500	a
2-decenal			98 200	5 950			104 000	a
2-undecenal			80 600	5 530			86 100	a
n-Alkanoic Acids								
heptanoic acid			26 000	6 190			32 200	a, e
octanoic acid			29 400	9 290			38 700	a, e
nonanoic acid			42 400	6 030			48 400	a, e
decanoic acid			8 890	2 220			11 100	a, e
dodecanoic acid			4 610	1 850			6 460	a, e
tetradecanoic acid			4 040	17 700			21 700	a, e
pentadecanoic acid			220	5 750			5 970	a, e
hexadecanoic acid			11 400	163 000			174 000	a, e
heptadecanoic acid				10 300			10 300	a, e
octadecanoic acid			2 150	96 900			96 100	a, e
nonadecanoic acid				600			600	a, e
eicosanoic acid				860			860	a, e
docosanoic acid				350			350	a, e
n-Alkenoic Acids								
9-hexadecenoic acid				18 400			18 400	b, e
9-octadecenoic acid				214 000			214 000	a, e
9,12-octadecadienoic acid				32 000			32 000	a, e
Alkanedioic Acids								
hexanedioic acid				1 990			1 990	a, e
octanedioic acid				3 900			3 900	a, e
Furanones (γ -Lactones)								
5-ethyldihydro-2(3 <i>H</i>)-furanone			6 490	2 850			9 370	a
5-propyldihydro-2(3 <i>H</i>)-furanone			7 020	1 800			8 820	b
5-butyldihydro-2(3 <i>H</i>)-furanone			9 540	1 420			11 000	a
5-pentyldihydro-2(3 <i>H</i>)-furanone			4 770	1 290			6 060	b
5-hexyldihydro-2(3 <i>H</i>)-furanone			3 120	920			4 040	a
5-heptyldihydro-2(3 <i>H</i>)-furanone				390			390	b
5-octyldihydro-2(3 <i>H</i>)-furanone				480			480	b
5-nonyldihydro-2(3 <i>H</i>)-furanone				800			800	b
5-decyldihydro-2(3 <i>H</i>)-furanone				1 750			1 750	b
5-undecyldihydro-2(3 <i>H</i>)-furanone				780			780	b
5-dodecyldihydro-2(3 <i>H</i>)-furanone				670			670	b
Other Compounds								
cholesterol				3 970			3 970	a
hexadecanamide				<i>h</i>				<i>d</i>
octadecanamide				<i>h</i>				<i>d</i>
9-octadecenamide				<i>h</i>				<i>d</i>
Unresolved Complex Mixture								
				1 300 000			1 300 000	

^{a-e}Identification notes: (a) authentic quantitative standard; (b) authentic quantitative standard for similar compound in series; (c) secondary standard; (d) probable identification; and (e) analyzed as a methyl ester. ^fNaphthalene and nonan-2-one are too volatile for complete collection by denuder. Mass of these compounds collected on PUF is from the gas phase. ^gEmissions shown are for two parallel sampling techniques, total is taken from denuder/filter/PUF. ^hDetected but not quantified.

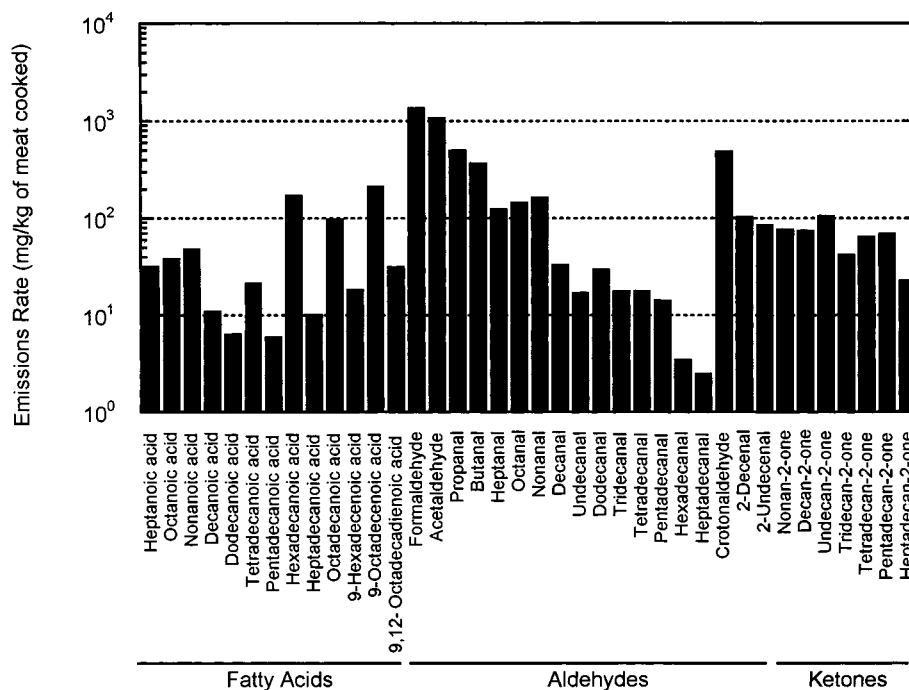


FIGURE 3. Emission rates of fatty acids and carbonyls from meat charbroiling operations.

acid have been identified and quantified. The high emission rates of the *n*-alkenoic acids and *n*-alkanoic acids were not surprising since meat fat contains glycerol esters of these fatty acids (36).

Significant quantities of heavy aliphatic *n*-aldehydes and alkan-2-ones also were found in the meat cooking exhaust, spanning the range from nonanal to heptadecanal and nonan-2-one to heptadecan-2-one. In addition, two semivolatile olefinic aldehydes have been identified and quantified, 2-decenal and 2-undecenal. 2-Decenal and 2-undecenal have been previously identified in the headspace vapor of heated peanut oil (37). Grosjean et al. (33) measured the atmospheric concentration of aliphatic aldehydes spanning the range from formaldehyde through tetradecanal in the South Coast Air Basin of California during a period of poor air quality and found noticeable quantities of the high molecular weight aliphatic aldehydes. They also showed that the chemical reactivity of the high molecular weight aldehydes taken as a group was comparable to that of formaldehyde or acetaldehyde separately. Although low molecular weight aldehydes are known to be both emitted by primary sources of air pollution as well as formed by chemical reaction in photochemical smog (38), the high molecular weight aliphatic aldehydes have not been previously measured in the emissions from air pollution sources. We now know from the present study that the high molecular weight aldehydes are emitted in large quantities from meat charbroiling. Food preparation could be a significant contributor to the high molecular weight aldehydes and hence to the photochemical reactivity of the urban atmosphere. Other sources (e.g., the cooking oil fumes mentioned above) should be sought as well through further source testing. Figure 3 shows the distribution of emissions for semivolatile and particle-phase fatty acids (*n*-alkanoic acids and alkenoic acids) and carbonyls, as well as the low molecular weight gas-phase carbonyls measured by the DNPH-impregnated C₁₈ cartridges.

n-Alkanes, low molecular weight PAH, and alkanedioic acids also were present in the meat charbroiling emissions. In addition, squalene and cholesterol were found at levels of approximately 342 and 3970 μg per kilogram of meat cooked, respectively.

As previously indicated, the fine particle mass emission rate per unit of meat cooked as measured by Hildemann et al. (34) when charbroiling meat for approximately twice the cooking time used here, was reported to be approximately twice the emission rate per hamburger patty cooked in the current study. The individual organic compounds present in the particle phase during the meat charbroiling source tests conducted by Hildemann et al. (34) were reported by Rogge et al. (4). The individual organic compound emission rates normalized to fine particle organic carbon emissions for the test conducted by Hildemann et al. (34) averaged 1.12 ± 0.21 (mean \pm standard deviation of the mean) times those observed in the present study as measured by the undenuded filter sample. Thus the relative chemical composition of the particulate organic compounds measured in the two sets of tests were found to be quite similar. The earlier tests of Hildemann et al. (34) lack vapor phase and semivolatile compound emissions data so no comparison was possible in these cases.

The collection efficiency of the denuder as operated in the present study was approximately 65% for naphthalene, greater than 90% for *n*-tridecane and higher boiling range *n*-alkanes, and greater than 90% for phenanthrene and higher boiling range PAH.

Comparison between Measurement Methods for Semivolatile Organics. The total mass emission rate of each individual organic compound determined from the denuder/filter/PUF sampling train showed good agreement with the total mass emission rate determined from the filter/PUF sampling train. Figure 4 provides a comparison of the total measured emission rates obtained by the two sampling methods for individual compounds within the following compound classes: alkanolic acids, alkenoic acids, aldehydes, ketones, PAH, lactones, and alkanes. The linear regression fit through the points in Figure 4 has a slope of 1.0 ± 0.1 and an intercept of $2000 \pm 2400 \mu\text{g kg}^{-1}$, with an R^2 of 0.85.

The distribution between the gas- and particle-phase of each of the 71 organic semivolatile and particle-phase organic compounds which were identified and quantified by the denuder/filter/PUF sampling train is given in Table 3. The phase distribution of the lactones, the carbonyls, and the *n*-alkanoic acids as measured by the denuder/filter/PUF

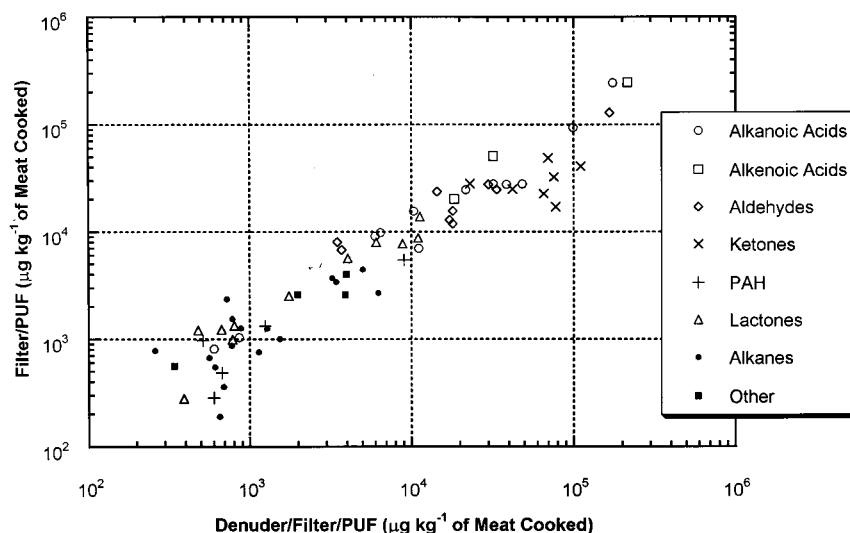


FIGURE 4. Comparison of the total mass of individual organic compounds collected by the denuder/filter/PUF and filter/PUF sampling trains during the charbroiled meat cooking source tests.

sampling train is compared to the filter/PUF sampling train in Figure 5. The compounds that are quantified in Table 3 but not shown in Figure 5 were either completely in one phase or were not measured at concentrations high enough to obtain a good description of their phase distributions by either method. For the denuder/filter/PUF sampling train the gas-phase fraction of each compound was taken as the fraction of that compound collected on the XAD-coated denuder, while the particle-phase fraction was the fraction collected on the combined filter plus PUF samples. In the case of the filter/PUF sampling train, the fraction of the mass collected on the filter was taken as the particle-phase portion and the gas-phase fraction was the fraction collected on the two PUFs in series located downstream of the filter.

Although the total compound masses collected by the two sampling trains showed good agreement, there were significant differences in the phase distributions measured by the two sampling methods when operated simultaneously in parallel. As seen in Figure 5, the fraction of compound mass measured to be in the particle phase by the filter/PUF sampling system was much greater than observed by the denuder/filter/PUF sampling system for the higher molecular weight compounds in each of the compound classes. The likely explanation for this observation was that adsorption of vapor-phase semivolatile organic compounds occurred on the filter, or on organic particulate matter previously collected on the filter, as those vapors first passed over the filter in the filter/PUF sampling train (39). As seen in Figure 5, virtually complete sorption of the vapor-phase semivolatile organic compounds onto the filter in the filter/PUF system occurred for the highest molecular weight species in each group. This finding has significant implications for the interpretation of the low OC loading that was found on the back-up quartz fiber filter of the tandem EC/OC filter stack. The back-up filter contained only 2.0% of the organic carbon found on the front filter. Traditionally, this might have been interpreted to mean that the potential for sampling artifacts was low since there was little vapor phase material collected on the back-up filter. Instead just the opposite was true: the adsorption artifact was so great that certain vapor phase species do not pass through the filter at all. This suggests that the use of the back-up filter as a measure of the adsorption to the front filter may not be applicable when taking source samples from sources similar to meat smoke exhaust.

Gas/Particle Partitioning: Experiment versus Theory. Gas/particle partitioning theory (5, 40, 41) holds that the

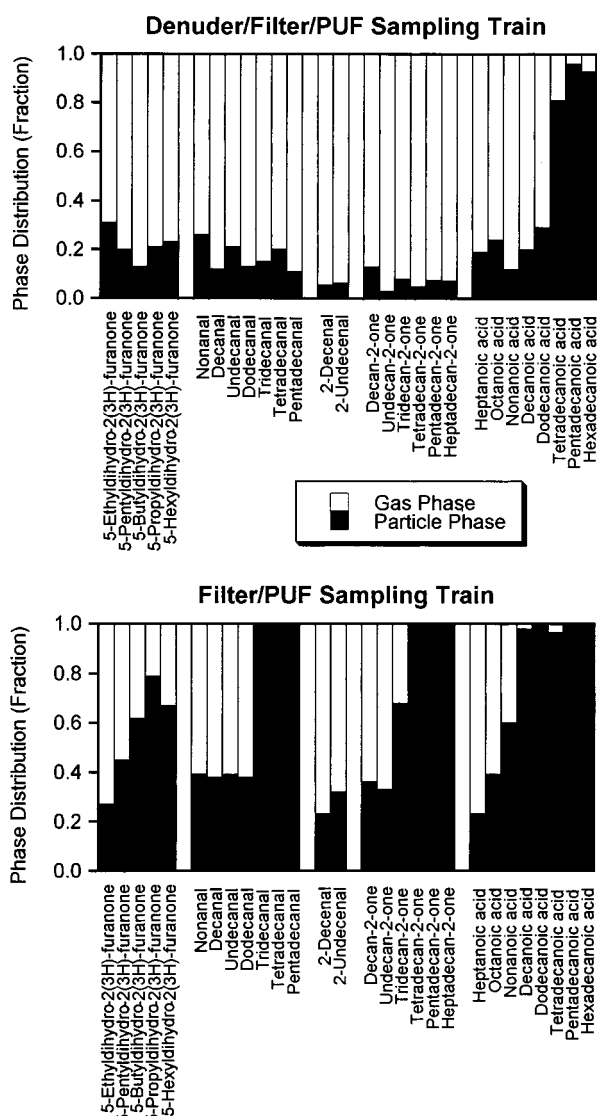


FIGURE 5. The distribution of organic compounds between the gas phase and particle phase in the diluted exhaust from meat charbroiling as measured by the denuder/filter/PUF and filter/PUF sampling trains.

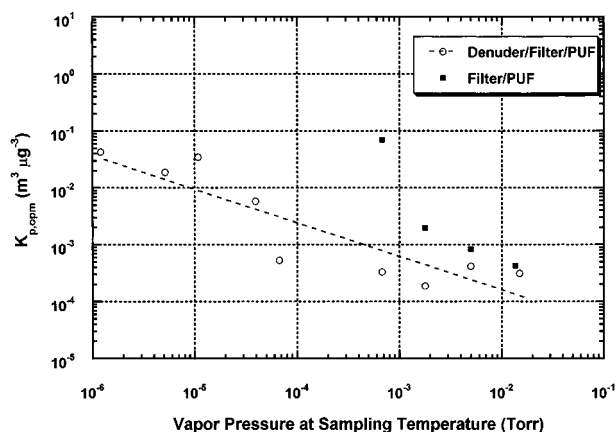


FIGURE 6. Partitioning coefficient, $K_{p,opm}$, for the n -alkanoic acids in the diluted exhaust from meat charbroiling operations as measured by the denuder/filter/PUF and filter/PUF sampling train plotted as a function of the vapor pressure of the pure compounds

phase distribution of a semivolatile organic compound is determined by its absorption into the particle-phase matrix, and that this phase distribution can be described by a partitioning coefficient, $K_{p,opm}$, defined as

$$K_{p,opm} = \frac{F/OPM}{A} \quad (1)$$

where $K_{p,opm}$ is the gas/particle partitioning coefficient based on organic particulate matter as the receiving particle phase substrate (in units of $m^3 \mu g^{-1}$); F is the particle-associated mass concentration of the semivolatile organic compound of interest (in $\mu g m^{-3}$); OPM is the total organic particulate matter concentration into which the compound can partition (in $\mu g m^{-3}$), and A is the gas-phase mass concentration of the compound of interest (in $\mu g m^{-3}$). It is expected that the gas/particle partitioning coefficient, $K_{p,opm}$, will depend on the vapor pressure of the various organic compounds (41):

$$\log(K_{p,opm}) = m_{r,opm} \log(p_L^0) + b_{r,opm} \quad (2)$$

where p_L^0 is the vapor pressure over a liquid pool of the semivolatile organic compound of interest (in Torr), and $m_{r,opm}$ and $b_{r,opm}$ are coefficients that can be estimated by regressing a series of experimentally measured values of $K_{p,opm}$ on the corresponding liquid vapor pressure values, p_L^0 , for the members of a given organic compound class. If the compounds have similar activity coefficients when present in the particulate organic matrix and the partitioning process has reached equilibrium, then $-m_{r,opm}$ should be close to unity. Under this condition, $b_{r,opm}$ is a constant characteristic of the partitioning for that class of compounds with the specific particle matrix.

Figure 6 shows the gas/particle partitioning of the alkanic acids during these source tests as a function of the vapor pressure of each of the organic acids as measured by the filter/PUF and the denuder/filter/PUF sampling trains. The best fit curve through the denuder/filter/PUF data has a slope of -0.62 , suggesting that the partitioning is not at equilibrium as described by Pankow and Bidleman (5). This suggests that the semivolatile organic compounds had not equilibrated between the gas and particle phases either because of insufficient residence time or because the mass transfer between phases was inhibited. In similar measurements made while testing the emissions from cooking with lighter seed oils, the n -alkanoic acids were found to be partitioned as would be predicted at equilibrium (42). In those tests, the seed oil cooking samples had significantly less time to equilibrate than did the charbroiled meat cooking exhaust

prior to sampling (42). For this reason it seems likely that the semivolatile organic compounds in the charbroiled meat exhaust were inhibited from transferring to the gas phase from the particle phase or into the particle phase from the gas phase. The fact that the mass transfer to and from the meat smoke particles may have been inhibited is consistent with the possibly solid character of meat fat at room temperature; meat fat is a major constituent in the diluted particle mass emissions from meat charbroiling.

The phase distribution of the n -alkanoic acids measured by the filter/PUF sampling train during the meat charbroiling test is also shown in Figure 6. The phase distribution measured by the filter/PUF system was significantly shifted as compared to the phase distribution measured by the denuder/filter/PUF system. All of the n -alkanoic acids were found in much higher percentages on the filter when sampled by the filter/PUF method. In fact, all of the n -alkanoic acids with vapor pressures less than n -decanoic acid were not even detected on the PUF downstream of the particle filter in the filter/PUF system. This again suggests that a strong filter adsorption artifact exists for moderate volatility n -alkanoic acids within a meat smoke matrix when sampled by the filter/PUF method. The K_p , defined in eq 1, as determined from measurements made using the two parallel sampling techniques differs by more than 2 orders of magnitude for some of these moderate volatility n -alkanoic acids.

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