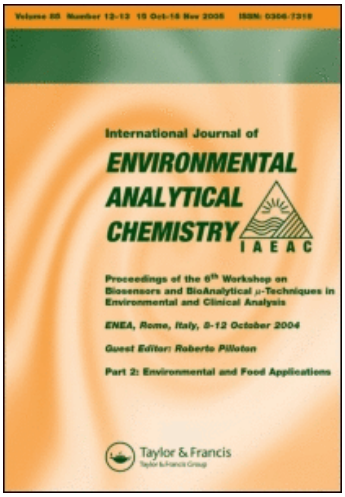

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Quantitative High - Resolution Gas Chromatography and High - Resolution Gas Chromatography/Mass Spectrometry Analyses of Carbonaceous Fine Aerosol Particles

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To cite this Article Mazurek, Monica A. , Simoneit, Bernd R. T. , Cass, Glen R. and Gray, H. Andrew(1987) 'Quantitative High - Resolution Gas Chromatography and High - Resolution Gas Chromatography/Mass Spectrometry Analyses of Carbonaceous Fine Aerosol Particles', International Journal of Environmental Analytical Chemistry, 29: 1, 119 — 139
To link to this Article: DOI: 10.1080/03067318708078415
URL: http://dx.doi.org/10.1080/03067318708078415

Intern. J. Environ. Anal. Chem., 1987, Vol. 29, pp. 119–139

Printed in Great Britain

Quantitative High-Resolution Gas Chromatography and High-Resolution Gas Chromatography/Mass Spectrometry Analyses of Carbonaceous Fine Aerosol Particles

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(*Received July 9, 1986; in final form September 15, 1986*)

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Methods have been developed for the quantification of low-microgram levels of the extractable organic matter contained in the atmospheric fine aerosol fraction. Extract quantification is accomplished by computer-assisted high-resolution gas chromatography (HRGC) used in conjunction with a procedural recovery mixture containing perdeuterated compounds of differing polarity and molecular weight. Recovery data for these species indicate that relative volatility rather than functional group classification is the primary factor affecting overall recovery. Routine quality control analysis is performed on a per-sample basis by high-resolution gas chromatography/mass spectrometry (HRGC/MS) for confirmation of the standard components and for identification of procedural contaminants. By the way of illustration, fine aerosol samples have been analyzed from Anaheim, California. The absolute solvent extract yields range from 49 to 346 μg of organic carbon, and demonstrate a seasonal variation with winter maximum and summer minimum concentrations.

KEY WORDS: Carbonaceous fine aerosols, extractable organic carbon, organic acids, quantitative analysis, quality control, atmospheric particles.

INTRODUCTION

Recent studies of atmospheric aerosol composition show that carbon-containing particles constitute up to 50% of the fine particle burden in the atmosphere of cities.[1-4] These carbonaceous aerosols scatter and absorb light, contributing to visibility reduction.[4-9] Individual compounds found within the airborne organic fraction may be carcinogenic, mutagenic or teratogenic.[10-12] As a result, there is great interest in ascertaining how the fine carbonaceous aerosol can be described and controlled.

Atmospheric dispersion models are convenient tools that can be applied to the development of control strategies for the abatement of fine aerosol particles. Such models assess the relationship between pollutant emission sources and airborne carbon particle concentrations, but must be verified and tested by comparison against quantitative data on airborne aerosol organic levels. Likewise, urban visibility models and receptor-based models that determine the origin of organic aerosols also require quantitative input data on aerosol organic levels. Bulk carbon measurements (e.g. total carbon, elemental carbon, organic carbon, or solvent-extractable carbon) have been employed and have generated quantitative results (in $\mu g\,m^{-3}$ of aerosol carbon).[1-4,8,9,13-21] Such measurements expose relatively little of the underlying information concerning the nature

of the actual organic compounds present. This additional data could be used to confirm or infer the emission sources that contribute to ambient concentrations. Conversely, most previous attempts at organic compound identification by gas chromatography/mass spectrometry,[19,22-27] direct probe thermal desorption mass spectrometry,[13,28-31] high-pressure liquid chromatography fluorescence detection,[11,32-34] and by liquid chromatography with IR detection,[35] have focused on selected groups of target compounds, resulting in partial quantitative or qualitative analyses. These data are of marginal utility for use in design of pollutant abatement programs where the result of control efforts must be expressed in terms of changed aerosol component concentrations, stated in $\mu g\,m^{-3}$, and where one must account for the total of the aerosol that is present. Consequently, there is a clear and pressing need for analytical procedures that are directed toward achieving a carbon balance on the samples of interest (in order to maintain a link to absolute atmospheric mass loadings), while at the same time providing information on both the bulk characteristics and molecular nature of the organic compounds that are present.

Developed here is a solvent isolation and quantification method which employs computer-assisted high-resolution gas chromatography (HRGC) for direct sample extract measurement and is used in conjunction with computer-assisted high-resolution gas chromatography/mass spectrometry (HRGC/MS) for quality assurance analysis. Internal controls have been applied that assess solvent extraction efficiency and absolute recovery on a per-sample basis by the application of an eight-component recovery mixture. The standard suite is comprised of perdeuterated compounds that together represent a range of polarity and molecular weight. Overall, the described analytical protocol has been designed in order to monitor component losses associated with volatilization, extraction efficiency or with instrumental bias, and has been applied to the analysis of low microgram levels of total extractable organic aerosol material. Fine aerosol samples acquired from Anaheim, California, have been analyzed using this method and data are presented for illustrative purposes. In addition, this procedure has been tailored to aerosol filter samples that have been acquired using currently-available low-volume collectors. This feature will enable detailed organic chemical data to be generated from low flow-rate size-segregated aerosol

samples and therefore has important applications to air pollution monitoring programs.

EXPERIMENTAL METHODS

Apparatus

The in-line filtration and collection apparatus developed for this extraction procedure is shown in Figure 1. This device is specially designed to reduce surface adsorptive losses, to minimize transfer steps, and to reduce the potential inclusion of procedural contaminants. All-glass and Teflon components are used, with the exception of a 2 μm porosity stainless steel filter frit (Valco Instruments, Houston, Texas). The vacuum side-arm adapter is modified from a commercially available standard taper 14/20 joint (Ace Glass, Vineland, New Jersey) and is attached to the vacuum system using a 6.35 mm (1/4 inch) Swagelok brass union (Crawford Fitting Company, Solon, Ohio) connected to a 6.35 mm (1/4 inch) o.d. corrugated Teflon tube (Penntube Plastics Company, Clifton Heights, Pennsylvania). The Teflon transfer unit consists of 1.59 mm (1/16 inch) o.d. tubing that is connected to an enlarging adaptor (1.59 mm to 6.35 mm o.d., Chemplast, Wayne, New Jersey). This adaptor contains two Viton o-rings and is attached by way of compression fit to the Teflon and glass tubing. The 6.35 mm (1/4 inch) glass tubing, stainless steel frit, and glass transfer pipet are connected using Teflon heat-shrink tubing (Chemplast, Wayne, New Jersey). The filtrate is collected into a standard taper 14/20 ground glass graduated test tube with a capacity of 15 ml (Ace Glass, Vineland, New Jersey), which is removable for direct attachment to a rotary evaporator for extract concentration. Prior to assembly, all glass components are annealed at 500°C for eight hours and the Teflon and stainless steel parts are solvent-extracted with methylene chloride using ultrasonic agitation.

Reagents

Distilled-in-glass solvents are used throughout the analytical sequence and also for the preparation of the standard solutions (Burdick and Jackson, Muskegon, Illinois). Perdeuterated standard compounds

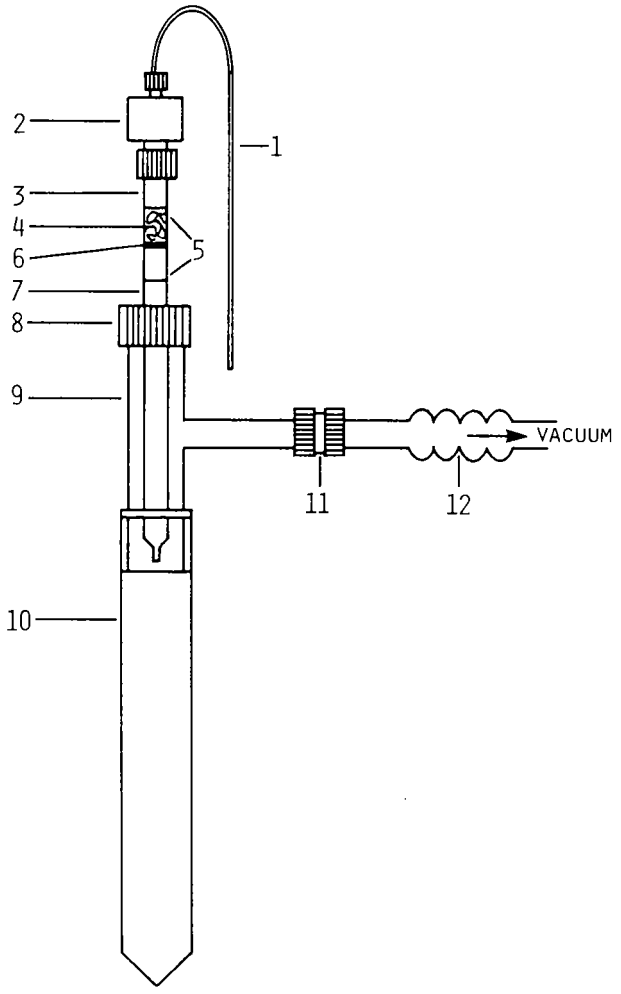

Figure 1 In-line transfer and filtration apparatus. Numbered components correspond to the following: (1) 1.59 mm (1/16 inch) o.d. PTFE tubing; (2) 1.59 mm to 6.35 mm (1/16 inch to 1/4 inch) Teflon enlarging adaptor; (3) 6.35 mm (1/4 inch) o.d. glass tubing; (4) glass wool; (5) Teflon heat-shrink tubing connection; (6) 6.35 mm (1/4 inch) o.d. stainless steel filter frit; (8) Teflon bushing; (9) 14/20 vacuum side-arm adaptor; (10) 14/20 graduated test tube; (11) 6.35 mm (1/4 inch) brass union with Teflon TFE ferrules; and (12) 6.35 mm (1/4 inch) o.d. corrugated Teflon PTFE tubing.

have atomic purities of 98–99% (Merck, Sharpe and Dohme, Montreal, Quebec, Canada and Cambridge Isotope Laboratories, Cambridge, Massachusetts). The precursor used for diazomethane preparation is 1-methyl-3-nitro-1-nitrosoguanidine (MNNG; Aldrich Chemical Co., Milwaukee, Wisconsin). This chemical is handled with great precaution due to its potent mutagenicity and flammability.

Sample acquisition

Fine particulate air samples were acquired from Anaheim, California, a metropolitan Southern California location, during the 1982 calendar year.[3] Acquisition began in January, and 24-hour average fine aerosol samples were obtained at 6-day intervals throughout the year. Ambient air at a flow rate of 26 *l*pm was drawn through an AIHL-cyclone separator[36] designed to remove particles with an aerodynamic diameter greater than 2.1 μm. The fine particle fraction remaining in the air downstream of the cyclone was split between several parallel filter holders. The fine aerosol sample of interest here was collected by filtration at a rate of 10 *l*pm on 47 mm diameter quartz fiber filters (Pallflex 2500 QA0, Putnam, Connecticut) that had been pre-fired to 600°C for two hours to reduce possible organic background contaminants. The typical air volume sampled was 14 m^3 per 24-hour organic carbon filter. After collection, each filter was sealed in an air-tight petri dish and refrigerated at 4°C until analysis.

Procedural standard recovery mixture

The perdeuterated recovery mixture is prepared by combining volume aliquots of the standard solutions as indicated in Table I. These initial solutions are either single-component standards or binary homolog mixtures as in the case of the alkane and fatty acid methyl ester compounds. Standard solutions are prepared in toluene with the exception of isoquinoline which contains benzene as solvent. The individual standard solution concentrations and also the final procedural standard mixture concentrations for each deuterated compound, are indicated in Table I. Proportions are determined by the relative flame ionization detector (FID) response, such that an individual peak plots within the range of 30–70% full scale height at

Table I Concentrations of perdeuterated recovery standards

Perdeuterated component	Unmixed concentration (ng/μl)	Mixing volume ratio	Mixture concentration (ng/μl)
Isoquinoline (C_9D_7N)	122.0	1	7.19
N-Dodecanol ($C_{12}D_{25}OH$)	64.8	3	11.49
Methyl tetradecanoate ($C_{15}D_{27}O_2H_3$)	99.0	1	5.38
Anthracene ($C_{12}D_{10}$)	117.6	2	13.90
Tetracosane ($C_{24}D_{50}$)	103.5	2	12.23
Methyl eicosanoate ($C_{21}D_{39}O_2H_3$	115.0	(1)[a]	6.25
Dotriacontane ($C_{32}D_{66}$)	83.9	(2)[b]	9.92
Perylene ($C_{20}D_{12}$)	11.8	8	5.58

[a]Binary mixture of methyl tetradecanoate and methyl eicosanoate.
[b]Binary mixture of tetracosane and dotriacontane.

a constant detector millivolt range (10 ^{12} millivolts) and attenuation (attenuation = 32). These final concentrations are amenable to recovery assessment of the unknown sample mixtures through previous analyses of representative test filters.

Fatty acid methyl ester standards are synthesized from the perdeuterated acid using freshly prepared diazomethane.[37] A 100-fold milliequivalent excess of diazomethane is added in order to achieve quantitative yields of the methyl ester homologs. Extreme care is taken in order to ensure that accidental detonation of the diazomethane does not occur. This is accomplished by the use of specially designed glassware for generation of the reagent (Pierce Chemical, Rockford, Illinois) and a micro-transfer pipet which consists of smooth-sided glass capillary tubing with a Teflon plunger (Drummond Scientific, Broomall, Pennsylvania). Known-volume sample aliquots are also subjected to this methylation procedure for conversion of acidic hydroxyl groups to the respective methoxy derivatives.

Sample preparation

The analytical sequence used to isolate the extractable aerosol components is outlined in Figure 2. Prior to analysis, the filters are composited according to calendar month with the resultant monthly samples containing from 1 to 6 filters. Composites are then spiked with 6.5 μg per filter of the standard recovery mixture. The filters are extracted in heavy-walled flint glass jars (30 ml capacity) which have been annealed at 550°C for eight hours and are equipped with tightly-fitting Teflon-lined caps. Samples are extracted sequentially over a period of 15 minutes with each solvent addition using an ultrasonic bath maintained at room temperature. Each time, the extract is filtered to remove filter and aerosol particulate matter, and is concentrated to a volume of approximately 1 ml using rotary

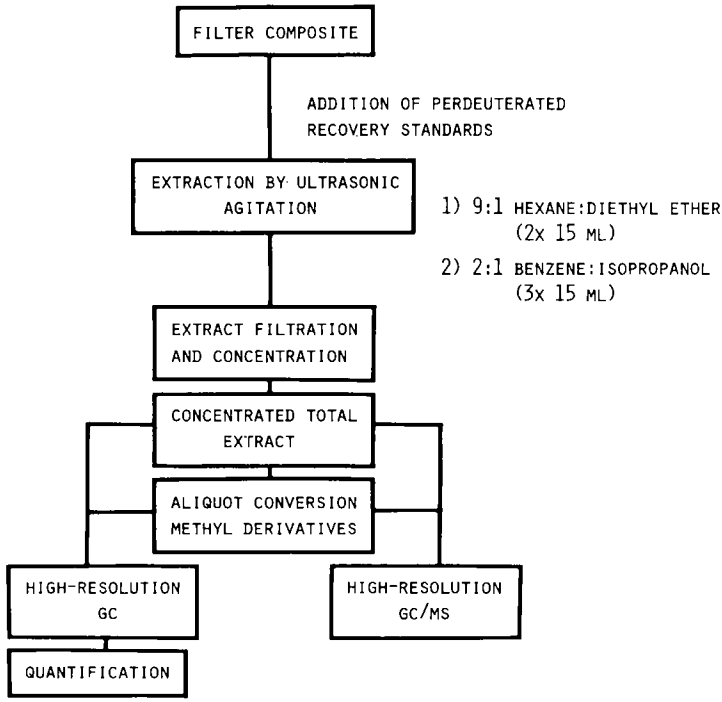

Figure 2 Fine aerosol isolation and quantification scheme for the extractable organic fraction.

vacuum distillation and having a constant temperature water bath (27°C) and controlled vacuum conditions (640 mm Hg). After the final extraction and volume reduction, the total aerosol extract is further reduced in volume by a slow stream of filtered ultra-pure nitrogen gas. The final extract volume is adjusted to the original volume of the added standard recovery mixture.

High-resolution gas chromatography quantification

Aerosol extracts are analyzed with a Varian 4600 high-resolution gas chromatograph equipped with a Grob injector (splitless mode) and a 30 meter fused silica OV-1701 column (bonded 86% dimethyl-(14%)-cyanopropyl phenyl polysiloxane, 25 μm film thickness, 0.4 mm o.d., J&W Scientific, Rancho Cordova, California). The linear velocity is 29 cm sec^{-1} using helium as the carrier gas and having nitrogen make-up gas. Temperature programming consists of injection at 65°C, an isothermal hold for 10 minutes at 65°C, a temperature ramp of 10°C min^{-1} up to the final temperature of 275°C, and a final isothermal hold for 49 minutes at 275°C. A segmented, hot injection technique is adopted and it involves the following sequence: (1) 1 μl solvent; (2) 0.5 μl air plug; (3) 0.5–0.6 μl coinjection standard (1-phenyldodecane at 5.6 ng μl^{-1}); (4) 0.5 μl air plug; (5) 1.0–1.2 μl sample extract; and (6) 1.5 μl air plug. The injection syringe used for this purpose is a guided-plunger model having an extended barrel with a 5 μl capacity and is graduated in 0.1 μl units (Scientific Glass Engineering, Austin, Texas). The injection procedure is followed rigorously for this critical aspect of the extract quantification step. Three injections of the standard component mixture are used to establish retention times and relative response factors (RRF) for the individual perdeuterated components. RRF are computed according to the equation:

$$\text{RRF} = \frac{\text{Amount standard component (ng)}}{\text{Counts standard component}} \times \frac{\text{Counts 1-phenyldodecane}}{\text{Amount 1-phenyldodecane (ng)}}$$

Table II lists the mean RRFs for the individual standards together

Table II Mean relative response factors for perdeuterated recovery standards

Perdeuterated component	RRF (s.d.) ($N=3$)	Mean injected Ng
Isoquinoline (C_9D_7N)	1.60 (0.12)	8.05
N-Dodecanol ($C_{12}D_{25}OH$)	-	—
Methyl tetradecanoate ($C_{15}D_{27}O_2H_3$)	1.86 (0.20)	6.03
Anthracene ($C_{12}D_{10}$)	0.96 (0.11)	15.57
Tetracosane ($C_{24}D_{50}$)	1.13 (0.16)	13.70
Methyl eicosanoate ($C_{21}D_{39}O_2H_3$)	1.47 (0.22)	7.00
Dotriacontane ($C_{32}D_{66}$)	1.25 (0.15)	11.11
Perylene ($C_{20}D_{12}$)	1.03 (0.11)	6.25

with the relative standard deviations. Also included are the mean quantities of the injected standard components that are used in the RRF determinations. RRF values are not evaluated for alternate concentration points since previous analyses of fine aerosol test samples indicate a generally uniform concentration range. Therefore, only a single concentration point for each of the perdeuterated standards is necessary.

Peak integration is performed electronically using a Varian Vista 401 computerized data system (CDS). Two modes of integration are conducted with this instrument since the raw data are recalculated at signal-to-noise (SN) ratios which either incorporate (SN = 1) or exclude (SN = 30) the nonbaseline-resolved portion or unresolved complex mixture (UCM). Quantification of the UCM and the resolved components is facilitated by an automatic baseline subtract feature which removes the effect of temperature-programmed column bleed. Recovery standards are quantified at a SN = 30 since it was determined that all extracts contain a UCM profile to some degree, which elutes within the range of standard species elution times. The contribution of the standard is represented by the resolved portion extending above the UCM.

High-resolution gas chromatography/mass spectrometry analysis

Perdeuterated recovery standards contained in the aerosol samples are confirmed by the comparison of retention times and mass spectra with those for the authentic standards. A Finnigan 4000 high-resolution gas chromatograph/mass spectrometer interfaced with an INCOS data system is used, and has chromatographic conditions identical to those used for HRGC quantification. Mass spectrometric data pertaining to the standard peaks are analyzed for all samples for positive confirmation of the perdeuterated compounds. Determination of spurious analytes incorporated into the individual samples and procedural blanks is also conducted by HRGC/MS analysis.

Molecular assignments are performed by (1) comparison to the authentic standards, where possible; (2) fundamental interpretations of mass spectrometric fragmentation patterns for the assignment of compound empirical molecular weights and plausible molecular structures; and (3) comparison to the relative HRGC retention times, especially in the case of homologous series or of stereoisomers.

Procedural blanks

Two procedural blanks are analyzed in conjunction with the twelve monthly composites. These blank determinations each consist of two filters which have been subjected to identical pretreatment and storage conditions as the sample collection filters. Before extraction, the blank filters are spiked individually with 6.5 μg (90.0 μl) of the standard recovery mixture. Recoveries and background contaminants are monitored cumulatively using these procedural blanks.

RESULTS AND DISCUSSION

Quality assurance analysis

A comprehensive quality control procedure was developed prior to the isolation and quantification of the collected aerosol samples. This was performed by the combined analyses of representative aerosol filters and procedural blanks which, together, provide an indication of total organic extract yields and also the actual levels of back-

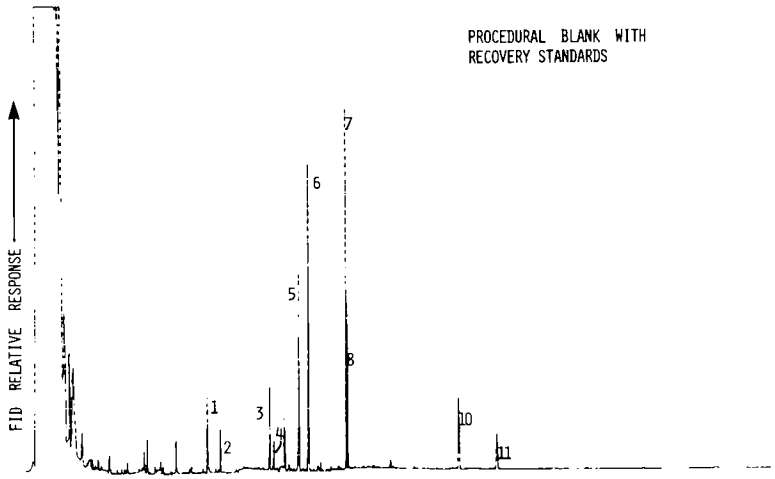

Figure 3 HRGC trace of an unmethylated procedural blank aliquot spiked with the perdeuterated recovery standards. Peak identifications are: (1) isoquinoline-d_7; (2) 1,1′-biphenyl (solvent impurity); (3) methyl tetradecanoate-d_{27}; (4) diethyl phthalate (filter background); (5) 1-phenyldodecane (coinjection standard); (6) anthracene-d_{10}; (7) tetracosane-d_{50}; (8) methyl eicosanoate-d_{39}; (9) dioctyl phthalate (filter background); (10) dotriacontane-d_{66}; and (11) perylene-d_{12}. Chromatographic conditions are as follows: splitless injection at 300°C onto a DB1701 column with an isothermal hold at 65°C for 10 minutes; temperature program is 10°C min^{-1} to 275°C and with an isothermal hold for 49 minutes.

ground contamination contributed by the analytical procedures. Test aerosol samples were used to determine the final concentrations of the perdeuterated recovery standards which were prepared in the concentrations listed in Table I. Minor amounts of procedural contaminants were identified by HRGC/MS analysis. Figure 3 demonstrates a representative procedural blank for the unmethylated aliquot spiked initially with the standard recovery mixture. Peak areas associated with the standards correspond to 7.2–17.6 ng per component, while those related to the identified contaminants are on the order of 0.6–3.2 ng per component. Solvent and solvent impurities comprise the peaks eluting before isoquinoline. These respective peak areas are suppressed from the total area integration by an automatic solvent-reject function included with the Varian 401 CDS. Contaminants eluting within the retention time range defined by the recovery

standards are subtracted manually from the total area counts. These inclusions are 1,1'-biphenyl, a component of diethyl ether, and low levels of C_2, C_4 and C_8 phthalate esters. One other type of background contamination is evident and occurs only in actual aerosol samples. Inclusions of the C_8 phthalate ester are evident in each sample (e.g. Figures 4a and 4b), and averages 0.47 μg of carbon m^3 of air sampled (equal to 6% of the average total airborne fine particle carbon as determined by combustion analysis). These contributions demonstrate a seasonal dependence having summer maximum and winter minimum concentrations. Based on the foregoing observations, we ascribe the C_8 phthalate ester presence to sampling artifact incorporation. However, as a well-resolved peak, the area contribution is easily measured and then subtracted from the sample total area counts. Routine HRGC/MS spectral analysis and retention time comparison are used to positively confirm the presence of the C_8 phthalate ester as well as other additional background contaminants which have been observed and also identified in the procedural blanks. A correction for analytical artifacts is performed on all methylated extract aliquots. Here, low-molecular weight inclusions principally from the solvent, diethyl ether, are monitored and subtracted from sample area integrations. This quality control process is conducted for all fine aerosol samples.

Standard component recovery

Average recoveries for the individual perdeuterated standards are given in Table III. These values are calculated from data derived from the unmethylated monthly composites and from the procedural blanks. A variance is demonstrated with respect to the mean recovery determinations. The combined aspects of differential volatility during extract concentration and losses due to transfer and surface adsorption are the principal factors affecting recovery precision. Such losses are inevitable when dealing with trace-level material, however, by using this mixture, an estimate of the overall magnitude of these factors can be assessed. In the worst-case example of the mean recovery determination for the most volatile constituent, isoquinoline, the standard deviation corresponds to a 38% variance, while that for the least variable component, methyl eicosanoate, equates to a 14% variance.

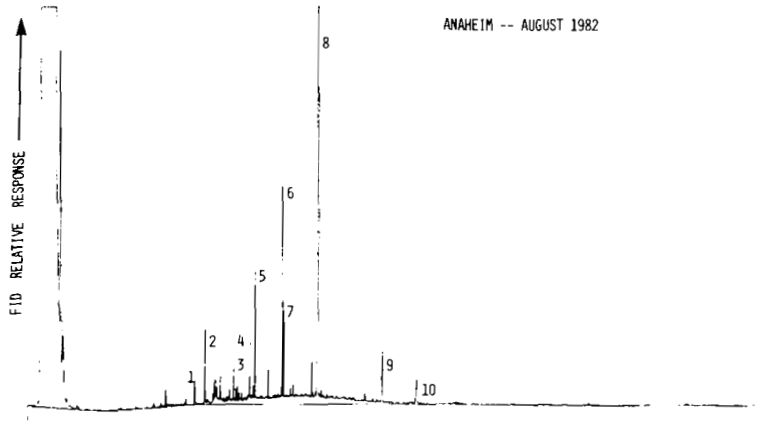

Figure 4a HRGC trace of the unmethylated total extractable fraction for Anaheim, California, sampled during August 1982. Peak identifications are: (1) isoquinoline-d_7; (2) 1,1′-biphenyl (solvent artifact); (3) methyl tetradecanoate-d_{27}; (solvent artifact); (3) methyl tetradecanoate-d_{27}; (4) 1-phenyldodecane (coinjection standard); (5) anthracene-d_{10}; (6) tetracosane-d_{50}; (8) dioctyl phthalate (sampling artifact); (9) dotriacontane-d_{66}; and (10) perylene-d_{12}.

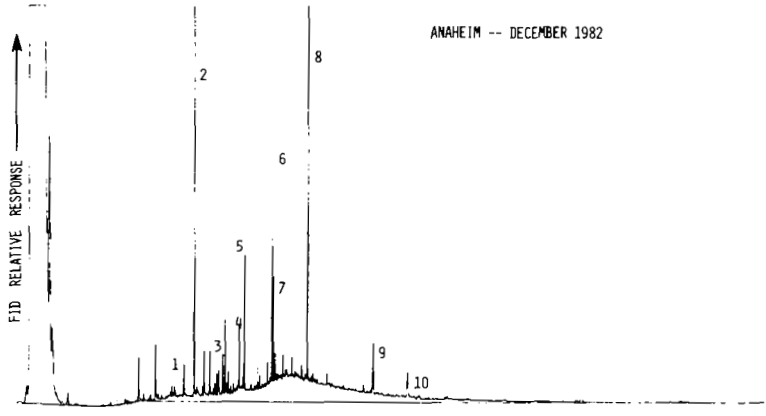

Figure 4b HRGC trace of the unmethylated total extract aliquot from Anaheim, California, sampled during December 1982. Peak assignments are the same as those for Figure 4a.

Table III Mean recoveries of standard components in underivatized total extract

Perdeuterated component	Spike (ng) (Per filter)	Recovery % ($N=14$)	(s.d.)	95% Confidence interval
Isoquinoline (C_9D_7N)	647	47.6	(17.9)	47.6 ± 10.3
N-Dodecanol ($C_{12}D_{25}OH$)	1034	—		
Methyl Tetradecanoate ($C_{15}D_{27}O_2H_3$)	484	50.8	(10.6)	50.8 ± 6.1
Anthracene ($C_{12}D_{10}$)	1251	41.7	(8.2)	41.7 ± 4.7
Tetracosane ($C_{24}D_{50}$)	1100	73.4	(11.1)	73.4 ± 6.4
Methyl eicosanoate ($C_{21}D_{39}O_2H_3$)	563	78.4	(10.9)	78.4 ± 6.3
Dotriacontane ($C_{32}D_{66}$)	893	70.0	(11.4)	70.0 ± 6.6
Perylene ($C_{20}D_{12}$)	502	67.8	(10.0)	67.8 ± 5.8

Further comparison of the standard component recoveries indicate that relative volatility rather than the functional group classification is the primary factor affecting overall recoveries, with the exception of *n*-dodecanol. Given the HRGC operating conditions, the underivatized alcohol is significantly retained by the column bonded phase, as indicated by severe peak tailing. Accurate and consistent peak integration is not possible for this compound, therefore the average recovery is not determined. In general, however, the mean recoveries of the relatively volatile components (e.g. isoquinoline, methyl tetradecanoate, anthracene) range from 42% to 51%, while those corresponding to the less-volatile compounds (e.g. tetracosane, methyl eicosanoate, dotriacontane, perylene) are 68% to 78%. Examination of the 95% confidence intervals associated with the mean recoveries indicates a distinction in overall recovery based on volatility. Given this, a division is made between compounds eluting prior to anthracene (RT = 28 minutes) and for those eluting after the compound. The median standard recovery is determined for the volatile group as represented by isoquinoline, methyl tetradecanoate, and anthracene. A separate median standard recovery is also cal-

culated for the less-volatile components represented by tetracosane, methyl eicosanoate, dotriacontane and perylene. Median values are evaluated for each sample in order to calculate absolute recoveries of the total extract corresponding to the chromatogram area segments occurring between 14–28 minutes and between 28–60 minutes. These median results are listed in Table IV, for both the methylated and unmethylated sample aliquots. In general, the standard median values fall within the 95% confidence limits that are shown in Table III for the individual perdeuterated standard components. Based upon this concurrence, the approximation for compound recovery as a function of elution time (i.e. RT < 28 minutes and RT > 28 minutes) is considered valid.

Extract quantification

Quantification of the fine aerosol extracts require the following information: (1) area counts relative to a coinjection standard (e.g. 1-phenyldodecane); (2) relative response factors for the individual standard recovery components; and (3) median standard recoveries of the perdeuterated species determined for the 14–28 minutes and 28–60 minutes HRGC chromatogram segments. It is important to note that the calculation of total extract yields involves the underlying assumption that the chemical species comprising these complex mixtures exhibit chromatographic behavior that is similar to the standard components. In a rigorous sense, this is not the case. However, recent work on multicomponent organic mixtures has shown that the use of a single, averaged response factor for the quantification of each group of homologous compounds is an acceptable approach for the quantitative analysis of complex mixtures.[38] Therefore, by using a recovery mixture which includes species of varying carbon content and aromaticity, an approximate measure is obtained for the relative response factors for related homologous constituents in the aerosol extract.

Total extract yields (μg units) are listed in Table IV for both methylated and unmethylated aliquots. These values are corrected for procedural losses by factoring in the median recoveries of the standard compounds. A graphic distribution of the average monthly ambient concentrations is given also in Figure 5, where a winter maximum ($5.86\,\mu g\,m^{-3}$ total extractable organic carbon) and a

Table IV Median recoveries and corrected total solvent yields for Anaheim, California. Fine aerosol monthly composites.

Sample (Number filters)	Unmethylated		Methylated		Total corrected yield (unmethylated fraction) (μg)	Total corrected yield (methylated fraction) (μg)
	Median recovery (%) 14–28 minutes	Median recovery (%) 28–60 minutes	Median recovery (%) 14–28 minutes	Median recovery (%) 28–60 minutes		
January (1)	53	79	40	62	49	85
February (5)	54	69	44	53	159	151
March (5)	54	81	43	54	93	129
April (5)	44	59	39	57	156	177
May (5)	52	81	39	56	99	158
June (5)	36	60	32	50	118	162
July (5)	44	78	28	49	112	153
August (5)	43	87	44	75	91	144
September (5)	33	65	31	57	111	202
October (5)	35	68	36	70	127	213
November (5)	32	54	28	51	143	206
December (6)	32	58	22	41	206	346

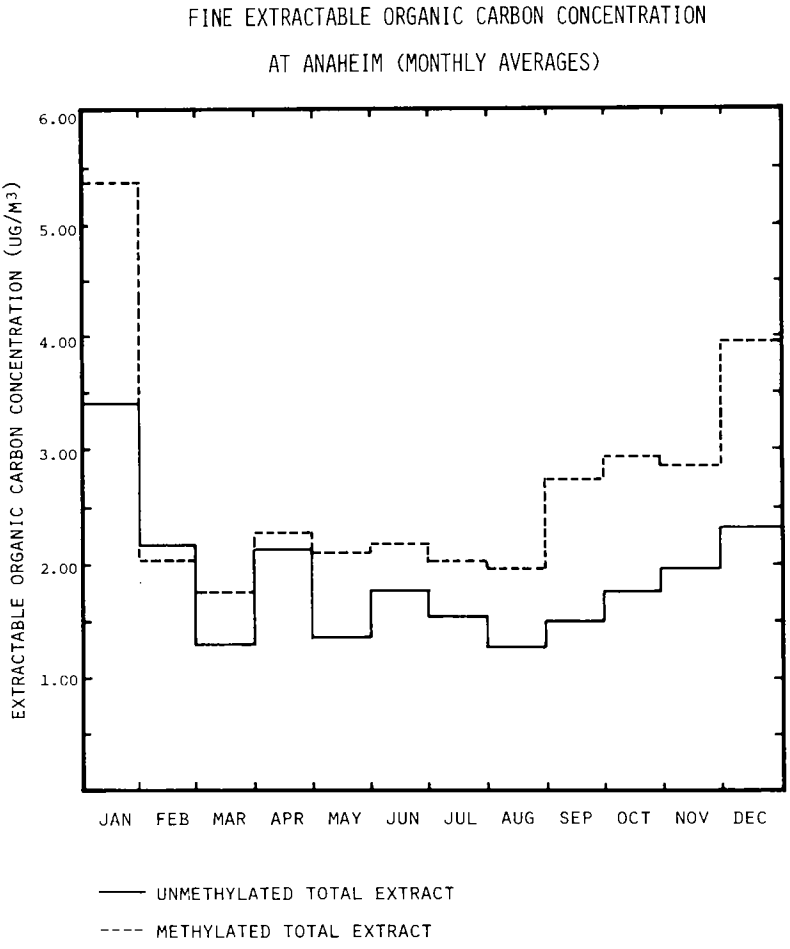

Figure 5 Distribution of monthly averages for ambient concentrations of total extractable organic species in the fine aerosol fraction. The solid line indicates the total unmethylated fraction (neutral and basic components) and the broken line indicates the combined methylated (acidic fraction) plus unmethylated total extractable organic carbon concentrations.

spring/summer minimum (1.73–1.95 $\mu g\,m^{-3}$ total extractable organic carbon) are evident. In Figure 5 it is also seen that the acid fraction of the organic aerosol is present year round. Comparison of the acid and neutral fractions mass contributions to the carbonaceous fine aerosol burden yields valuable information for use in source correlation discussions.[39] Therefore, in addition to the generation of bulk organic carbon ambient concentrations, the described analytical method permits the determination of the relative chemical composition (i.e. acidic or neutral) of the fine aerosol extractable organic carbon.

As indicated in Figures 4 and 5, a sizeable portion of the total extract is not detected in the unmethylated fraction due to selective retention by the column bonded phase. Therefore, derivatization of the acidic hydroxy species to the methoxy analogs is necessary for a more accurate assessment of the total solvent-extractable organic yield. Overall, these concentrations are a low estimate for the extractable carbon species, since compounds characterized by high polarity and/or molecular weight also are not amenable to measurement by the described techniques. This analytical bias is demonstrated by comparison to independent measurements of the organic carbon fraction in samples acquired simultaneously to those samples analyzed in this study. Thermal combustion analysis was utilized as an alternate measurement technique for the total organic carbon content.[3] These results also indicate winter maximum (8.8 $\mu g\,m^{-3}$ organic carbon) and spring/summer minimum (3.6 $\mu g\,m^{-3}$ organic carbon) concentrations. Values determined by the combustion technique are higher overall, but differ by a factor of less than two. This difference is attributed to the presence of organic species which are not efficiently extracted and/or detected by HRGC procedures due to extremes in polarity or molecular weight (e.g. pollen, rubber tire fragments, soil humic matter, etc.).

CONCLUSIONS

The described solvent isolation and quantification procedure provides a sensitive method by which trace-level organic species associated with the fine aerosol fraction can be measured. Absolute concentrations are obtained through the application of a perdeuterated

standard recovery mixture that estimates solvent extraction efficiency and overall recovery on a per-sample basis. In addition, detailed information is obtained for bulk characteristics of the total solvent extract (as was illustrated for acidic and neutral species concentrations). Many other bulk characteristics can be determined via data processing efforts from these quantitatively correct HRGC traces (e.g. carbon preference index, unresolved-to-resolved component ratio) and from the HRGC/MS analysis that was applied here only to quality control and standard recovery analyses. Together these parameters generate an enhanced level of analytical capability that facilitates determinations of organic source contributions to the fine carbonaceous aerosol fraction.

Acknowledgements

We thank Ed Ruth and Gary Taghon for their valuable comments and suggestions. Thanks are also given to Karen Dykes and Celeste Correia for their assistance in the manuscript preparation. Financial support from the Atmospheric Research Section, National Science Foundation (Grants ATM 81-16622, ATM 81-18101 and ATM 85-09184) and from the California Air Resources Board under agreement A1-071-32, is gratefully acknowledged.

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