

CHAPTER 7

Methods for Chemical Characterization of Air Samples — PTEAM Prepilot Study

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INTRODUCTION

A nine-home chemical characterization study was initiated by the California Air Resources Board (ARB) and was performed as a collaborative effort with the U.S. Environmental Protection Agency's (EPA's) PTEAM Prepilot Study. The purpose of this study was to evaluate the sampling and analysis methods for identifying and quantitating chemical species in air samples. Four groups of chemicals were targeted for the study, namely polynuclear aromatic hydrocarbons (PAHs), phthalates, nitrosamines, and titratable acids. Indoor and outdoor fixed-site monitoring was performed for all chemical groups in nine homes for two 12-h periods. Testing during the nine-home study was designed to estimate precision, accuracy, and limits of detection for each method. In addition, results from field monitoring were examined to determine potential interferences resulting from the sample matrix, the percentage of samples where target analytes were above the detection limits, concentration levels of target analytes, and the relative distribution of target analytes between indoor and outdoor sample locations.

The EPA is undertaking a field monitoring study to estimate frequency distributions of human exposure to airborne particles of various size ranges. This particulate TEAM or PTEAM study, is being performed in two phases. Phase 1 is a nine-home study designed to field test monitoring and data collection activities associated with the proposed program. Phase 2 is a 200-home study designed to generate data for assessing exposure of the general population in a selected study

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Table 1. Target Chemicals

Chemical Class	Compound
PAHs	Acenaphthylene, phenanthrene, anthracene
3 ring	Fluoranthene, pyrene, benzo(a)anthracene, chrysene
4 ring	
5 ring	Benzo(k)fluoranthene, benzo(a)pyrene, Benzo(e)pyrene
6 ring	Indeno(1,2,3-cd)pyrene, benzo(g,h,i)perylene
7 ring	Coronene
Nitrosamines	<i>N</i> -Dimethylnitrosamine <i>N</i> -Diethylnitrosamine <i>N</i> -Dipropylnitrosamine <i>N</i> -Dibutylnitrosamine <i>N</i> -Nitrosopiperidine <i>N</i> -Nitrosopyrrolidine <i>N</i> -Nitrosomorpholine
Acidity	Titrateable acids, NO ₃ ⁻ , SO ₄ ²⁻
Phthalates	Di- <i>n</i> -butylphthalate <i>n</i> -Butylbenzylphthalate Di- <i>n</i> -octylphthalate Di-2-ethylhexylphthalate

area to particles. Although the thrust of the PTEAM study is to evaluate particulate exposures, the target population for the Phase 2 study should also be a reasonable population for monitoring other pollutants. In this context, the ARB initiated this joint effort with EPA to use the PTEAM program as an efficient vehicle for monitoring chemicals in air inside and outside homes in California. This study was the ARB Phase 1 effort that was performed in conjunction with EPA's Phase 1 work.

The overall objective of the study was to evaluate sampling and analysis methods for monitoring selected chemical species in indoor and outdoor air samples. The selected approach was to perform a nine-home chemical characterization study using the proposed monitoring methods. Four groups of chemicals were targeted for the study: polynuclear aromatic hydrocarbons (PAHs), phthalates, nitrosamines, and titrateable acids and related species. Specific pollutants are listed in Table 1. Indoor and outdoor fixed-site monitoring were performed for all chemical groups in all nine homes for two 12-h periods.

Materials and Methods

Selection of methods for the sampling and analysis of the target chemicals was an important component of the overall study. At the outset, several important decisions were made that affected the method selection process, including:

- Chemical characterization was to be performed only for indoor and outdoor fixed site samples. Personal exposure monitoring as proposed for the

PTEAM study was eliminated because of the high burden it would place on study participants.

- For more efficient field operations and to minimize the need for multiple pump evaluations, a single type of field sampler was to be used for all chemical classes. Sample collection rates of 5 to 10 l/min were used to provide sufficient material for analysis.
- Since the physical/chemical properties of the PAHs and phthalates are similar, these two chemical classes were to be collected together to minimize the sampling equipment required and the participant burden.
- For the organics, if possible, a particulate (<2.5 μm) and a vapor phase fraction were to be collected. The two fractions were to be combined prior to sample workup and analysis. Although this would not allow us to distinguish analyte concentrations in the particulate vs. vapor phase, it was intended to provide more sample material for a single analysis to increase the number of samples with analytical concentrations above the detection limit. It was also intended to reduce analytical costs.
- For acidity, only the particulate phase was to be collected and analyzed.

Given these constraints and since standard methods were not available, methods were proposed based on our own work with similar chemicals and reported literature methods,^{1,4} our best judgement of the applicability of methods to our needs, the adaptability and simplicity of the method as used for field monitoring, and the overall method cost. Testing during this nine-home study was then intended to provide information in three important areas:

- Feasibility of field collection methods
- Performance of sampling and analysis procedures
- Approximate indoor and outdoor air concentrations of the chemicals of interest.

This paper will provide information on the analytical methods for the phthalates and the titrateable acids. Method performance data and calculated sample concentrations will also be presented for these two groups of chemicals.

MATERIALS AND METHODS

Field Monitoring

A total of nine homes from the Glendora, Azusa, San Dimas, El Monte, Covina, and Baldwin Park areas of California were monitored during this study. These homes were purposely selected to provide a variety of aerosol levels, particulate size distributions, and emission sources in order to challenge the collection and analysis protocols.

Two locations at each house were monitored. One location was in the main living area inside the house and the other was an outdoor location near the most used entrance of the house. Sampling was performed during two consecutive 12-

Table 2. Samples Collected During Field Monitoring

Type	Number of Samples		
	Phthalates/PAHs	Nitrosamines	Titrateable Acids
Indoor daytime	9	9	9
Indoor nighttime	9	9	9
Outdoor daytime	9	9	9
Outdoor nighttime	9	9	9
Field controls	4	4	8
Field blanks	4	4	4
Laboratory controls	4	4	8
Laboratory blanks	4	4	4
Duplicate samples	4	4	3

h time periods, providing overnight and daytime samples from each house. Each house was monitored for only 1 d; one house was sampled at a time. Field sampling was carried out from March 1 to March 23, 1989. The total number of samples collected is listed in Table 2.

All samples were collected using pumping systems that were designed and built by Battelle, Columbus Division. They utilized a Gast pump, a McMillan flow sensor, a Rustrak Ranger Data Logger, and a timer. Air flows were measured and recorded at the beginning and end of each 12-h sampling period using calibrated rotameters connected to the sampling heads with custom-made adapters.

Monitoring Methods for Phthalates

Particulate and vapor phase samples for phthalate analysis were collected using a quartz fiber filter backed by an XAD-resin bed. The nominal flow rate for sample collection was 15 l/min over the 12-h period to provide a sample volume of ~10 m³. Collected samples were stored in the dark at room temperature in the field, then at -5°C once they were returned to the laboratory.

Phthalates were recovered from the XAD-2 resin and quartz fiber filters by soxhlet extraction with methylene chloride over a 16-h period. An extraction thimble was not used in order to reduce background contamination. The extracts were concentrated to 7 to 10 ml by Kuderna-Danish (K-D) evaporation. The methylene chloride was then solvent exchanged with hexane and further concentrated to 1.0 ml by nitrogen blowdown. Following concentration, the extracts were first analyzed for phthalates using a Hewlett Packard gas chromatograph with an electron capture detector. A 30 m DB-5 capillary GC column temperature programmed from 100 to 260°C at 5°C/min was used to separate the compounds.

Quantitation of target phthalates in sample extracts was performed using response factors calculated relative in the internal standard 2,3', 4,4', 6-pentachlorobiphenyl which was added at the same concentration to all standards and sample extracts. The concentration of phthalates in air samples was calculated by subtracting the average mass found in the field blanks from the mass found in each sample then dividing by the sample volume.

Monitoring Method for Titrateable Acids

The titrateable acids, nitrates, and sulfates were collected using the Battelle pumping system connected to an annular denuder-filter pack (DFP). The nominal flow rate through the denuder was 10 l/min over the 12-h sampling period for a sample volume of ~7 m³. The DFP system consisted of a 120 mm annular denuder coated with citric acid and a 240 mm annular denuder coated with sodium carbonate. The filter pack contained a Teflon, a nylon, and a citric acid-coated cellulose filter. Using this method, all particles were collected on the Teflon filter. Prior to the filter collection, nitrate, sulfate, and ammonia (NH₃) gases were removed from the air stream using the sodium carbonate and citric acid denuder tubes, respectively. The Teflon filter was backed by a nylon filter and an acid-coated cellulose filter to collect nitric acid and ammonia gases that were either not collected by the denuders or vaporized off the particulate filter. Sample filters were stored in sealed plastic containers at 4°C until analyzed.

All three filters and the denuders were extracted by ultrasonication with deionized water. NO₃⁻ and SO₄⁻ were analyzed using ion chromatography (IC). The masses of NO₃⁻ and SO₄⁻ in each sample extract were calculated using response factors generated from standard solutions. Total mass of strong and weak acids in each extract was determined by Gran titration.⁵ Only the extracts from the Teflon particulate filters were analyzed. The other extracts were saved and could have been analyzed if issues such as vapor phase concentration or filter collection efficiency required further investigation. The average mass of target chemicals in the field blanks was subtracted from the amount found in field samples. Sample concentrations were calculated by dividing the corrected mass by the sample volume as described above for the phthalates.

RESULTS AND DISCUSSION

Method Performance

The primary purpose of this pilot study was to evaluate the proposed analytical methods. Several types of quality control (QC) samples were used for this purpose. Field controls were intended to assess both accuracy and precision of the overall method. Field blanks were intended to provide information on background contamination and its variability. Field blank data were also used to estimate overall method detection limits and method quantitation limits. Laboratory blanks and controls and method blanks and controls were used as additional checks on accuracy, precision, and background contamination for the methods. Results from these latter QC samples were also used to determine sources of problems when the field controls or blanks showed unsatisfactory performance. Duplicate samples were intended to evaluate overall method precision for real samples.

Table 3. Performance Evaluation Data for Phthalate Analysis

Compound	Amount (ng) Found \pm SD Field Blanks (N=4)	EMQL (ng/m ³)	% Recovery \pm SD Field Controls (n=4) ^a	Mean T RMD ^b for Duplicate Samples
Di- <i>n</i> -butyl-phthalate	385 \pm 108	41	47 \pm 23	NC ^c
<i>n</i> -Butylbenzyl-phthalate	47 \pm 10	3.8	75 \pm 16	4.5(1) ^d
Di- <i>n</i> -octyl-phthalate	9 \pm 10	3.8	83 \pm 19	25(2)
Di-2-ethylhexyl-phthalate	190 \pm 68	26	69 \pm 20 ^e	17(2)

^a All controls spiked with 1 mg of each target phthalate.

^b Percent RMD = Percent relative mean deviation.

^c Not found in any duplicate pairs.

^d Number of duplicate pairs with measurable concentrations of target chemicals.

^e N=3 — one very high value deleted.

Percent recovery for control samples was calculated as

$$\% \text{ Recovery} = \frac{M_C - M_B}{M_S} \times 100\%$$

where M_C is the mass of target found in the spiked controls, M_B is the mass of target found in the blanks, and M_S is the mass of target spiked into controls.

Estimated method quantitation limits (EMQL) were determined from the analysis of field blanks. These parameters were calculated as

$$\text{EMQL} = 3 \times \text{SD} / \text{sample volume}$$

where SD is the standard deviation of the amount of each phthalate found on field blanks. Although we had only four field blanks here, our approach is similar to that taken by the EPA where detection parameter estimates are based on the standard deviation of the calculated amount of analyte found in low level samples.

Performance evaluation data for the phthalates are shown in Table 3. Results presented here show generally acceptable precision and accuracy data. During laboratory setup, substantial effort was expended on reducing phthalate contamination that might result from sample processing. Analysis of both field and laboratory blanks showed trace levels of di-*n*-butyl- and di-*n*-octylphthalate (<50 ng per sample). Higher levels were found for butylbenzylphthalate and di-2-ethylhexylphthalate (~250 ng per sample), although these were well below the levels found on actual field samples as shown in Figure 1. The recovery of these latter two compounds was variable in control samples (percent relative mean deviation >20%) which was probably a result of sporadic background contamination. Alternate sample extraction procedures such as batch tumbling, ultrasonica-

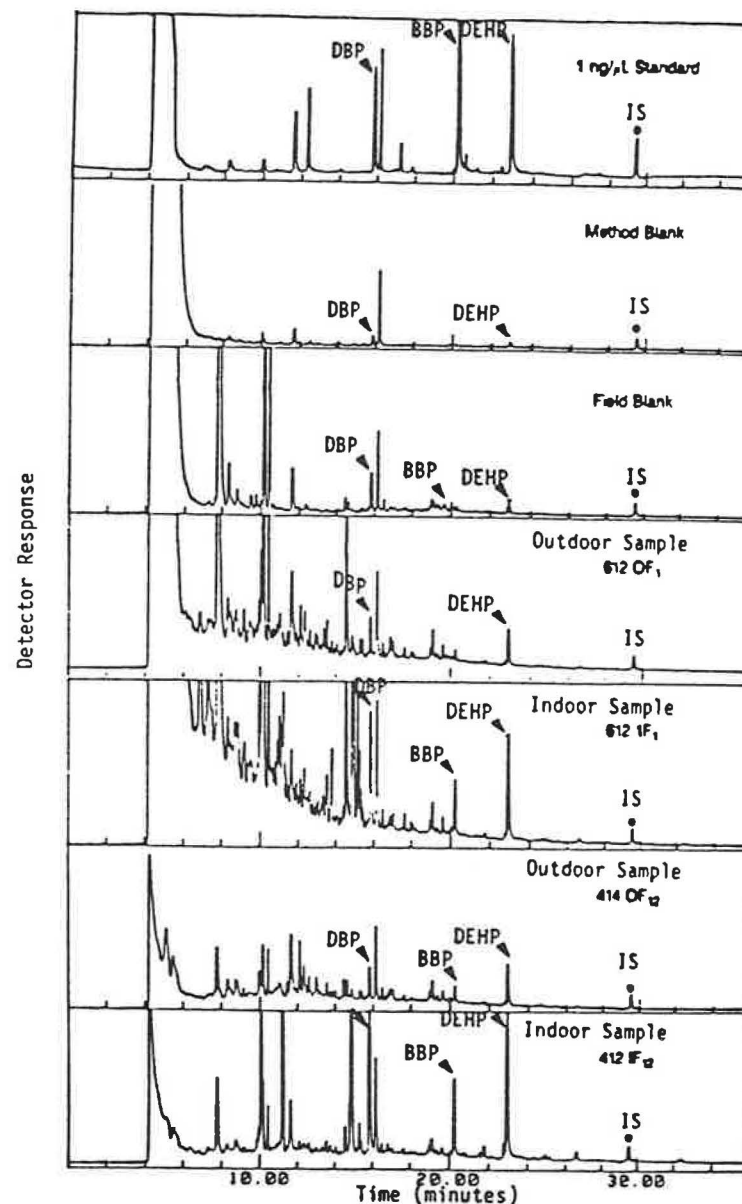


Figure 1. GC/ECD chromatographs of selected phthalate samples (IS — internal quantitation standard, DEHP — di-2-ethylhexylphthalate, BBP — butylbenzylphthalate, DBP — di-*n*-butylphthalate).

Table 4. Background NO₃⁻, SO₄⁻², and Acid Levels on Blanks and Estimated Quantitation Limits (EMQL)

Compound	Field Blanks (N=3)	EMQL (amount/m ³)
	amount/sample ± SD	
NO ₃ ⁻ (mg/sample)	1.06 ± 0.426 ^a	0.32
SO ₄ ⁻² (µg/sample)	0.24 ± 0.45 ^a	0.34
H ⁺ total (nmol/sample)	481 ± 132	99
H ⁺ strong (nmol/sample)	217 ± 63	47
H ⁺ weak (nmol/sample)	263 ± 79	59

^a n=4.Table 5. Percent Recovery for NO₃⁻, SO₄⁻², and Titratable Acid in Field Controls

	Spike Level		% Recovery	
	High	Low	High	Low
			(n=4)	(n=4)
NO ₃ ⁻	43.4 mg	4.34 mg	97 ± 5	97 ± 14
SO ₄ ⁻²	9.5 µg	.96 µg	98 ± 2.1	109 ± 29
Total H ⁺	900 nM	90 nM	126 ± 13	NC ^a
Strong H ⁺	200 nM	20 nM	360 ± 69	NC
Weak H ⁺	700 nM	70 nM	NC	NC

^a Value not calculated, spike level below the EMQL.

Table 6. Precision of Duplicate Field Samples

Parameter	% Relative Mean Deviation
Total H ⁺	9.1 (2) ^a
NO ₃ ⁻	2.9 (3)
SO ₄ ⁻²	5.5 (3)

^a Number of duplicate pairs with measurable values.

tion, or solvent elution of the resin bed are being considered to minimize contamination problems. Reproducibility of duplicate samples was considered acceptable.

Performance evaluation data for the titratable acids and related species are summarized in Tables 4 to 6. Results in these tables show excellent precision and accuracy for NO₃⁻ and SO₄⁻² for field controls. Very little contamination was found on field blanks resulting in low detection limits (0.1 µg/m³). Results of duplicate samples also compared well (average percent relative mean deviation = 4.4).

Titratable acids were analyzed using a Gran titration that was intended to provide total H⁺ concentrations plus weak and strong H⁺ concentrations. Recovery

Table 7. Phthalate Concentrations (ng/m³) in Field Samples

	Di- <i>n</i> -butylphthalate		<i>n</i> -Butylbenzylphthalate		Di- <i>n</i> -octylphthalate		Di-2-ethylhexylphthalate	
	In ^a	Out	In	Out	In	Out	In	Out
% Detected	47.4	5.3	100	26.3	57.9	26.3	89.0	47.3
Mean	110	20	47	5.5	15	3.0	81	24
D	160	19	39	12	29	3.7	38	23
Maximum	700	69	150	52	130	11	170	87
Minimum	ND ^b	ND	5.7	ND	ND	ND	ND	ND
Percentiles								
95	200	T	110	10	22	13	130	80
75	120	T	53	T	18	7.4	120	35
50	T	ND	31	ND	ND	ND	76	T
25	T	ND	16	ND	ND	ND	62	ND
5	ND	ND	7.0	ND	ND	ND	T	ND
n	17	17	17	17	17	17	17	17

^a In = indoors; out = outdoors.^b T = less than the EMQL but greater than the EMDL. ND = less than the EMQL.

data for total H⁺ was good (126 ± 13% for field controls). Unfortunately, both precision and accuracy for strong and weak H⁺ were not acceptable and, therefore, quantitation could not be performed on these species. Background H⁺ levels on field controls were high and variable, and resulted in a fairly high detection limit (33 nmol/m³). Good agreement was found for total H⁺ analysis for replicate samples (percent relative mean deviations = 10%).

Sample Analysis Results

Major emphasis for this pilot study was placed on evaluating the proposed sampling and analysis methods, although field monitoring results were examined to gather preliminary information on pollutant levels. It should be stressed that this latter information on sample analysis results represents data from only a few purposely selected homes and should not be used to draw any conclusions or make any statements about phthalate or acidic pollutant levels in the study area or any other area in California.

Percent detected and summary statistics for phthalate concentrations calculated for indoor and outdoor air samples are given in Table 7. For all data analyses, concentrations found in duplicate pairs were averaged and used as a single value. Results show high percent values, although most phthalates were detected more frequently in indoor samples than in outdoor samples. A comparison of the summary statistics also shows that indoor concentrations were higher than outdoor concentrations in every case. Highest mean indoor concentrations were reported for di-*n*-butylphthalate (110 ng/m³) and di-2-ethylhexylphthalate (81 ng/m³). The highest maximum indoor concentration was reported for di-*n*-butylphthalate (700 ng/m³), while the highest median indoor concentration was calculated for di-2-ethylhexylphthalate (76 ng/m³).

Table 8. Comparison of Indoor/Outdoor Concentration Ratios for Phthalates

	Ratio of Indoor/Outdoor Concentration			
	Di- <i>n</i> -butyl-phthalate	<i>n</i> -Butyl-benzyl-phthalate	Di- <i>n</i> -octyl-phthalate	Di-2-ethyl-hexylphthalate
Median	3.3	26	0.84	4.3
Mean	16	46	15	7.2
SD	43	52	42	10
Maximum	175	155	180	40
Minimum	0.75	0.18	0.75	0.74
No. greater than 1	14	15	7	15
No. less than 1	2	1	9	1
n	16	16	16	16

Indoor/outdoor concentration ratios for samples collected at the same home during the same time period were calculated for all four phthalates. Results given in Table 8 again show that indoor phthalate concentrations were generally higher than outdoor concentrations with mean indoor/outdoor concentration ratios ranging from 7.2 for di-2-ethylhexylphthalate to 46 for *n*-butylbenzylphthalate. Median indoor/outdoor concentration ratios were greater than one for all four phthalates, although these concentration ratios were smaller than the mean concentration ratios. For di-2-ethylhexylphthalate and *n*-butylbenzylphthalate, all but one of the indoor samples had higher concentrations than the corresponding outdoor samples (i.e., the indoor/outdoor concentration ratio was greater than 1). For di-*n*-octylphthalate, 44% of the indoor samples had higher concentrations than the corresponding outdoor samples.

To further evaluate the data, statistics were calculated for samples collected indoors during the daytime and nighttime sampling periods. These data showed no trend toward either higher daytime or nighttime concentrations in indoor samples.

Percent detected and summary statistics for concentrations of titratable acids and related species are given in Table 9. NO_3^- and SO_4^{2-} ions were detected in all of the indoor and outdoor air samples. Titratable acid results are given only for total H^+ concentrations since analytical methods for distinguishing between the weak and strong acid species did not appear to be reliable.

Percent detected for total titratable acids were much lower than for nitrates and sulfates; 42% for outdoor samples and only 17% for indoor samples. The lower percent detected for total H^+ appears to be due to the fairly high EMQL that resulted from contamination in the field blanks.

A comparison of summary statistics shows higher outdoor concentrations for NO_3^- and titratable acids. For SO_4^{2-} , slightly higher levels were reported for indoor air samples. To further investigate the relationship between indoor and outdoor samples, indoor/outdoor concentration ratios were calculated for samples collected in the same home during the same time period. Results given in Table 10

Table 9. NO_3^- , SO_4^{2-} , and Titratable Acid (nm/m^3) Levels in Field Samples

	Concentration					
	NO_3^- (mg/m^3)		SO_4^{2-} (mg/m^3)		Total Acid (nm/m^3)	
	Indoor	Outdoor	Indoor	Outdoor	Indoor	Outdoor
% Detected	100	100	100	100	17	42
Mean	4.2	8.2	4.1	3.5	61	96
SD	4.7	5.9	2.8	1.9	65	52
Maximum	16.2	18.5	11.7	8.25	233	183
Minimum	0.47	0.77	0.85	0.65	ND	19.4
Percentile						
95	9.24	14.9	6.56	4.48	100	174
75	6.10	14	5.53	4.01	T ^b	109
50	2.01	5.93	3.16	3.75	T	T
25	0.62	3.40	2.28	1.69	ND ^c	T
5	0.52	2.07	2.01	1.29	ND	T
n	13	12	13	12	11	11

^a Quantitated values greater than EMQL.

^b Concentration less than EMQL but greater than EMDL.

^c Concentration less than EMDL.

Table 10. Comparison of Indoor/Outdoor Ratios for NO_3^- , SO_4^{2-} , and Titratable Acids

	NO_3^-	SO_4^{2-}	Total H^+
Median	0.23	0.85	0.57
Mean ^a	0.51	1.48	0.71
SD	0.49	1.32	0.83
Maximum	1.7	4.4	3.0
Minimum	0.11	0.50	0
Number greater than 1	3	5	2
Number less than 1	10	8	10
n ^b	13	13	12

^a Ratios where indoor levels less than the EMQL were assigned a value of 0. Ratios were both indoor and outdoor levels less than the EMQL were assigned a level of 1.

^b Number of samples.

again show that NO_3^- and total H^+ concentrations are higher outdoors; whereas SO_4^{2-} levels are generally higher in indoor air samples.

The relationship between daytime and nighttime sample concentrations was also investigated, and although results are reported for only four homes, several trends are observed:

- NO_3^- species appear to have higher daytime concentrations in both indoor and outdoor samples

- SO_2 was slightly higher in indoor samples than in outdoor samples: there appears to be no trend for outdoor samples
- Total H⁺ may be slightly lower in daytime samples collected outdoors: no data is available for indoor samples because levels were all below the EMQL.

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