

**DEVELOPMENT OF THERMAL DESORPTION GAS
CHROMATOGRAPHY/MASS SPECTROMETRY
AS A RAPID METHOD FOR AMBIENT
PARTICULATE CHARACTERIZATION**

by

Sue Anne Sheya

A dissertation submitted to the faculty of
The University of Utah
in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

Department of Materials Science and Engineering

The University of Utah

December 2002

Copyright © Sue Anne Sheya 2002

All Rights Reserved

ABSTRACT

A direct thermal desorption gas chromatography/mass spectrometry (TD GC/MS) method for air particulate matter (PM) analysis of volatile and semivolatile organic compounds was investigated. This technique uses a specially designed microdesorption GC inlet utilizing an inductively heated ferromagnetic foil with a Curie point temperature suitable for desorption, which can accommodate microgram amounts of material deposited on a thin strip of quartz fiber filter. Liquid or solid samples can be rapidly desorbed within 10 s at 315 °C, followed by 30 - 40 min of chromatography time. The results obtained by this technique were found to be statistically equivalent to those obtained by the conventional solvent extraction gas chromatography/mass spectrometry (SX GC/MS) method for analysis of aromatic and n alkane standards, single source soot particles, and PM 10 filter samples. Correlations between injecting an extract, desorbing an extract, and desorbing particles averaged $R=0.94$, with a three way correlation averaging $R=0.97$. High volume sampling conducted at 12 spatially distributed sites located along the US/Mexican border of the El Paso/Juarez metroplex supplied 24h PM 10 filters for an investigation combining thermal desorption with a rapid online chemical derivatization procedure, and multivariate methods of source attribution using principal component and canonical correlation analysis of the resultant chemical markers. Four major combustion related PM emission sources were revealed at

these sites: automotive, waste burning, biomass burning and meat cooking. A second investigation conducted in the same area used mediumvolume sampling to collect 2 h timeresolved PM 10 receptor samples for TD GC/MS analysis. Additionally, 2 h samples for inorganic analysis, multichannel particle size distribution measurements, and meteorological data were collected enabling generation of circadian PM multicharacterization profiles. Factor analysis based receptor modeling using principal component analysis of the mixed characterization data resulted in the deconvolution of temporally overlapping PM events, trends and gradients. Results of the temporally resolved PM receptor sampling profiles confirmed the results of the spatially distributed PM receptor sampling in that the major sources were attributed to automotive traffic, biomass and waste combustion. However, in the time resolved data, urban dust events – in particular a large evening PM peak– were seen to play a more prominent role.

TABLE OF CONTENTS

ABSTRACT	iv
LIST OF FIGURES	x
LIST OF TABLES	xv
ACKNOWLEDGMENTS	xvii
CHAPTER	
1. INTRODUCTION AND BACKGROUND	1
Chemical Characteristics of Ambient Aerosols	3
Physical Characteristics of Ambient Aerosols	7
Particle Emissions from Combustion Processes	9
Particles and Related Health Effects	10
Government Regulations for Particulate Matter	15
Chemical Speciation Methods	18
Analytical Methods for Inorganic Constituents	20
Analytical Methods for Organic Constituents	23
Research Objectives	30
2. DEVELOPMENT OF TIME RESOLVED THERMAL DESORPTION GAS CHROMATOGRAPHY/MASS SPECTROMETRY OF PARTICULATE MATTER IN AMBIENT AIR	32
Introduction	32
Curie Point Heating	32
Particulate Collection Methods	37
Experimental Methods	46
Sampling Procedure	46
Analytical Procedure for TD GC/MS	50
Results and Discussion	55
Analysis of Standards	55

3. CORRELATION AND INTEGRATION OF THERMAL DESORPTION GAS CHROMATOGRAPHY/MASS SPECTROMETRY WITH SOLVENT EXTRACTION GAS CHROMATOGRAPHY/MASS SPECTROMETRY	66
Introduction	66
Experimental Methods	69
Biomass Soot Extract Preparation	70
Biomass Soot Particle Preparation	71
Ambient Particulate Collection	71
Solvent Extraction of Ambient Particulates	72
Preparation of QF Filters for TD GC/MS Analysis	74
GC/MS Analysis of Extracts and Particulates	75
Results and Discussion	76
Biomass Soot Particle Analysis	79
Ambient PM 10 Analysis	85
4. SOURCE ATTRIBUTION OF PM 10 RECEPTOR SAMPLES FROM COMBUSTION RELATED SOURCES USING MULTIVARIATE DATA ANALYSIS OF THERMAL DESORPTION/GAS CHROMATOGRAPHY/MASS SPECTROMETRY PROFILES WITH AND WITHOUT ONLINE THERMAL METHYLATION	97
Introduction	97
Determination of Compound Origin	98
Biogenic and Anthropogenic Markers in Organic Aerosols	100
Derivatization of Polar Particulate Organic Material	106
Multivariate Data Analysis	107
Experimental Methods	109
Receptor PM 10 Sample Collection	109
Thermal Derivatization and TD GC/MS Analysis of PM 10 Receptor Samples	110
Multivariate Data Analysis	113
Results and Discussion	119
TD GC/MS Results for Nonderivatized and Derivatized PM 10 Receptor Samples	119
Principal Component Analysis	131
Canonical Correlation Analysis and Source Attributions	139
5. DATA FUSION AND SOURCE ATTRIBUTION	153
Introduction	153
Characterization Methods	153
Multiple Analytical Methods	154
Experimental Methods	155

LIST OF FIGURES

Figure

1.1	Illustration of the dynamic pathway between atmospheric sources of gaseous and solid matter and the potential transformation of their eventual receptor site deposition.	2
1.2	Chemical processes which influence the composition of a typical urban aerosol particle. Based on Seinfeld (1989)..	5
1.3	Schematic representation of the measured atmospheric particulate volume or mass size distribution and main sources (after Dockery 1996).	8
1.4	Deposition of particles in the major regions of the respiratory tract related to particle size (after McClellan 2000).	12
1.5	Complex chemical character of atmospheric particle, and methods for analysis.	19
2.1	Illustration of Curie point inlet used for TD GC/MS of particulates.	36
2.2	Detail of Curie point micro desorption chamber.	38
2.3	Schematic of possible analytical schemes using the Curie point desorption apparatus for ambient air.	39
2.4	Size range of particulates which are suitable for sampling instruments.	41
2.5	Schematic of commercial hiivol sampler.	43
2.6	Schematic of dichot sampling inlet used for collection of time resolved PM10 air particulates.	47

2.7	Photographs of PM10 dichot sampler used for field tests.	49
2.8	Schematic illustration of TD GC/MS analytical system.	52
2.9	Replicate analyses of a 2 h time resolved PM filter collected from the El Paso airshed and analyzed by TD GC/MS.	56
2.10	GC/MS chromatogram of alkane standard mixture.	58
2.11	Correlation of integrated peak areas of 18 n alkanes from a liquid organic standard analyzed by conventional injection on a long column using slow temperature programming of the GC oven, and by TD GC/MS from a QF filter using a short column and fast temperature programming.	59
2.12	GC/MS chromatograms of PAH standard mixture.	60
2.13	Correlation of integrated peak areas PAHs from a liquid organic standard analyzed by conventional injection on a long column using slow temperature programming of the GC oven, and by TD GC/MS from a QF filter using a short column and fast temperature programming.	61
3.1	Map segment of the El Paso/Juarez showing the four mobile and nine stationary PM10 receptor sampling sites.	73
3.2	Total ion and single ion chromatograms of selected compound groups obtained from a solvent extract of a fireplace soot.	80
3.3	Comparison of results obtained from a solvent extract of a fireplace soot analyzed by direct injection of the liquid extract into the GC/MS on a long column with slow temperature programming and desorbing the extract from a QF filter using TD GC/MS on a short column with fast temperature programming.	81
3.4	Replicate analyses of thermal desorption from a QF filter of a solvent extract prepared from fireplace soot particles.	83

3.5	Total ion and single ion chromatograms of selected compound groups obtained from TD GC/MS of fireplace soot particles.	84
3.6	Comparison of analyses for TD GC/MS of fireplace soot particles.	86
3.7	Three way comparison of analytical methods for fireplace soot particles including both direct liquid injection (standard method) and desorption of a solvent extract from a QF filter, and particles desorbed "neat" (TD GC/MS method).	87
3.8	Comparison between total and single ion chromatograms of an extract from PM10 aerosol particles obtained at the Tecnologico site in Juarez, Chihuahua, Mexico.	89
3.9	Correlation of integrated peak areas of selected compounds and compound suites obtained from a solvent extract of a PM10 receptor sample analyzed by direct injection of the liquid extract into the GC/MS on a long column with slow temperature programming and desorbing the extract from a QF filter using TD GC/MS equipped with a short column and using fast temperature programming.	91
3.10	Three way comparison of analytical methods for ambient PM10 samples, including both direct liquid injection (standard SX GC/MS method) and desorption of a solvent extract from a QF filter, and particulates desorbed directly from the QF filter (TD GC/MS method).	93
3.11	Thermal desorption of QF filter from PM10 receptor sample of A) 24 h hivol filter after three solvent extractions (TD GC/MS removes and additional ~20% more organics) and B) 2 h medium vol filter after one thermal desorption.	95
4.1	Map of 12 sites near the El Paso/Juarez metroplex where PM10 receptor samples were collected.	111
4.2	Schematic representation of online TMAH derivatization procedure in combination with TD GC/MS.	112

4.3	Total ion chromatograms from PM10 receptor samples obtained on the American side fo the El Paso/Juarez metroplex and analyzed by TD GC/MS.	126
4.4	Total ion chromatograms from PM10 receptor samples obtained on the Mexican side of the El Paso/Juarez metroplex and analyzed by TD GC/MS.	127
4.5	Selected single ion chromatogram profiles from PM10 receptor samples obtained at the Socorro site on the American side of the El Paso/Juarez metroplex and analyzed by TD GC/MS.	128
4.6	Selected single ion chromatogram profiles from PM10 receptor samples obtained at the Club 20/30 site on the Mexican side of the El Paso/Juarez metroplex and analyzed by TD GC/MS.	129
4.7	“Scree” and cumulative variance plots for nonderivatized and derivatized organic data from PCA of 12 PM10 receptor samples from the El Paso/Juarez metroplex airshed.	132
4.8	“Scree” and cumulative variance plots for nonderivatized and derivatized organic data calculated from CCA of six principal components of the nonderivatized and derivatized organic data sets.	140
4.9	First three canonical variate loadings plotted in three dimensions.	145
4.10	Two selected projections of the CV 1/CV 2/CV 3 score space of directly desorbed and TMAH derivatized receptor sample data sets.	147
4.11	Clustering of scores and loadings as a VarDia diagram of the CV 1/CV 2 and CV 1/CV 3 factor space for nonderivatized (dashed lines) and derivatized (dotted lines) data, and source attributions.	149
4.12	Semiquantitative source apportionment map of the Paso del Norte airshed.	150
4.13	Approximate tetrahedral shape of four combustion sources found from CCA of PM10 receptor samples obtained at the el Paso/Juarez metroplex, as	

	outlined in the CV1 vs CV 2 score plot by the sites which are dominated by the specific source signals.	157
5.1	Meteorological data for the period of the scoping study.	163
5.2	Two h time resolved volumetric particle data which as been subdivided in PM10, PM2.5, and coarse size (dPM) fractions.	165
5.3	Volumetric total PM10 particle data and mass based Beta gauge measurements of PM10 data for the time period of scoping study.	167
5.4	The linear relationship between calibrated Beta gauge (particle mass based) and the eight channel (particle count based) volume data.	168
5.5	Comparison of real time PAS 2000 data (measuring particle bound PAH) with real time particle density data measured by the CLIMET as volumetric particle size distribution at the Sun Metro site.	169
5.6	Four high PM10 "urban dust" events measured in the evening hours at three locations during three winter receptor sampling studies.	170
5.7	Two h time resolved ("skyline plot") receptor profiles of seven selected organic PM10 components, as represented by specific GC/MS ion peak signals.	172
5.8	Two h time resolved ("skyline plot") receptor profiles as in Figure 5.7, but representing inorganic data analyzed by the PIXE technique.	175
5.9	Plot of eigenvalues and cumulative variance accounted for by each principal component from Varimax rotated mixed characterization data set.	184
5.10	Skyline score plots as a function of time for 7 of 10 factors resulting from Varimax rotation of the mixed characterization data set, with their main sources of variance.	190

LIST OF TABLES

Table

1.1	Summary of common chemical characterization methods for PM 10 particulates.	21
2.1	Summary of sampling conditions for dichot samplers..	51
2.2	Compounds in polyaromatic hydrocarbon (PAH) standard	63
3.1	Selected compounds and compound suites from fireplace soot particulates used for comparison between SX GC/MS and TD GC/MS analytical methods.	77
3.2	Selected compounds and compound suites from ambient PM used to compare the SX GC/MS and TD GC/MS analytical methods.	78
3.3	Qualitative comparison between current status of TD GC/MS technique and the conventional SX GC/MS method for characterization of organic constituents from ambient PM 10 aerosols.	92
4.1	Marker compounds used for source identification, and their common known sources.	105
4.2	Compounds from TD GC/MS analysis of PM10 filters used in principal component analysis.	114
4.3	Compounds from TMAH derivatized TD GC/MS analysis of PM 10 filters used in principal component analysis.	117
4.4	Summary of the normalized data matrix for the nonderivatized compounds used in the PCA.	120
4.5	Summary of the normalized data matrix for the derivatized compounds used in PCA.	124

4.6	Principal component loadings ¹ of nonderivatized data set from TD GC/MS analysis of PM 10 receptor samples.	133
4.7	Principal component loadings ¹ of TMAH derivatized data set from TD GC/MS analysis of PM 10 receptor samples.	135
4.8	Scores from factor analysis of the nonderivatized TD GC/MS data set.	137
4.9	cores from factor analysis of the TMAH derivatized TD GC/MS data set.	138
4.10	Nonstandardized canonical variate loadings of nonderivatized data set from TD GC/MS analysis of PM 10 receptor samples.	141
4.11	Nonstandardized canonical variate loadings of TMAH derivatized data set from TD GC/MS analysis of PM 10 receptor samples.	143
5.1	Summary of physical and chemical characterization methods described according to sampling types and numbers obtained during the scoping study at the Paso del Norte airshed.	157
5.2	Organic compounds identified from TD GC/MS analysis of PM 10 2 h receptor samples used in mixed characterization data set for principal component analysis.	173
5.3	Data set of mixed PM 10 characterization variables used for principal component analysis.	177
5.4	Principal component loadings from factor analysis after Varimax Rotation of the combined mixed characterization data set.	186
5.5	Scores from factor analysis of the combined mixed PM characterization data set.	188