



APTI

Course 424

Introduction to Receptor Modeling

Student Manual



Notice

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Acknowledgements

Design, development and presentation activities related to this telecourse were accomplished mainly under the aegis of EPA Grant #T902784, directed by Prof. Peter A. Scheff, Ph. D., at the University of Illinois at Chicago (UIC). Overall management was provided by members of a Design Team, led by James L. Dicke in EPA's Education and Outreach Group. Ms. Kris Zierold, UIC, was highly instrumental in putting together the Student Manual. Ms. Jan Cortelyou Lee, EOG, also provided valuable assistance, especially during the instructional design phase.

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The Education and Outreach Group
Office of Air Quality Planning and Standards
U.S. Environmental Protection Agency
Air Pollution Distance Learning Network

T424-97: Introduction to Receptor Modeling
February 10, 11, 12, and March 3, 1998

COURSE DIRECTOR:

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Day and Time	Lesson number - Subject	Speaker
Tuesday, 02/10/98 (Day 1)		
11:45	Pre-test	
12:30	I. Broadcast Begins: Introduction and Objectives	P. Scheff
1:00	II. Introduction to Receptor Modeling	P. Scheff
1:50	Break	
2:00	III. Chemical Mass Balance (CMB) Receptor Model: Mathematics and Assumptions	P. Scheff
2:50	Break	
3:00	IV. Study Design	R. Wadden
3:50	Break	
4:00	V. Ambient Measurements in Support of Receptor Modeling	R. Stevens P. Scheff

4:45 **Questions and answers**

5:00 **End broadcast day 1**

T424-97: Introduction to Receptor Modeling (Day 2)

Day and Time	Lesson number - Subject	Speaker
Wednesday, 02/11/98		
12:30	VI. Introduction to Optical Microscopy	R. Draftz
1:40	Break	
1:50	VII. Optical Microscopy: Applications	R. Draftz
2:30	Break	
2:40	VIII. Introduction to Scanning Electron Microscopy	G. Casuccio
3:20	Break	
3:30	IX. Source Characterization: Sampling and Analysis Methods	R. Stevens P. Scheff
4:30	Questions and answers	
5:00	End broadcast day 2	

T424-97: Introduction to Receptor Modeling (Day 3)

Day and Time	Lesson number - Subject	Speaker
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Thursday, 02/12/98

12:30	X. Introduction to the CMB 8 software	P. Scheff
1:40	Break	
1:50	XI. Demonstration of the CMB model using CMB8 software	P. Scheff
2:40	Break	
2:50	XII. Receptor Model Evaluation and Validation	R. Wadden
3:50	Break	
4:00	XIII. CMB Model applications: Description of Homework Data Sets	P. Scheff
4:30	Questions and answers	
5:00	End broadcast day 3	

T424-97: Introduction to Receptor Modeling (Day 4)

Day and Time	Lesson number - Subject	Speaker
Tuesday, 03/03/98		
12:30	XIV. Review of Practice Exercises	P. Scheff
1:10	XV. CMB Application for VOCs	D. Kenski
1:50	Break	
2:00	XVI. Multiple Linear Regression and Carbon-14	C. Lewis
2:40	XVII. Source Allocation of Ambient Ozone	R. Wadden
3:20	Break	
3:30	XVIII. Application of Scanning Electron Microscopy to Receptor Modeling	G. Casuccio
4:20	XIX. Where to turn for help	P. Scheff
4:40	Final questions	P. Scheff
5:00	End Broadcast day 4	
5:15	Post-test and Course evaluations	
6:00	Course ends	

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SPEAKER PROFILES

Gary Casuccio

Gary S. Casuccio is a Vice President of Environmental Services with RJ Lee Group (Monroeville, PA). Mr. Casuccio received a M.S. degree in Physics and Atmospheric Sciences from Drexel University in 1976. He has been involved in the analysis of environmental samples using SEM techniques for over 15 years and specializes in the source apportionment of particulate matter using SEM data.

Mr. Casuccio has also been involved in the development of SEM instrumentation and techniques for automated detection, measurement, identification and quantitative analysis of particles. He has published extensively on the use of the SEM to characterize particulate matter and serves as a consultant to industry and governmental agencies on particle analysis methods.

Ronald G. Draftz

Ronald G. Draftz is an analytical chemist who has specialized in the application of polarized light microscopy, scanning and transmission electron microscopy and x-ray diffraction to aerosol identification, apportionment and impact assessment for more than thirty years. He is currently a Science Advisor with the IIT Research Institute (IITRI), Chicago, Illinois where he has conducted applied research studies of atmospheric aerosols related to non-attainment of TSP and PM₁₀, visibility degradation and soiling/damage assessments since 1972.

From the mid-seventies through the early eighties his group conducted more than 70% of all the source apportionment studies in the U.S. These included all non-attainment studies in EPA Regions IV, V, key areas in Regions III and VI and the Phoenix Aerosol Study. These studies led to the finding of the significance of pavement erosion plus tire emissions as the prime cause of TSP non-attainment in all major urban and industrial areas. Paved road erosion and emission coupled with tire fragments remain the key components of urban PM₁₀ aerosol fraction in non-attainment areas to this time.

His microscopical work in the U.S. EPA's 1971-1973 Denver Visibility Study led to the first discovery of elemental carbon from vehicle exhausts as the cause of visibility degradation known as the Brown Cloud. He has also developed various aerosol and dust sampling methods and media including devices for helicopters and real-time portable wind tunnel for PM₁₀. He has conducted numerous studies of soiling and damage to personal property throughout the U.S. for industry and governmental agencies applying special sampling methods to identify the source and impact of industrial and natural emissions.

Donna Kenski

Donna Kenski is an Environmental Scientist in the Air Monitoring Section within the U.S. Environmental Protection Agency Region 5's Air and Radiation Division, located in Chicago, Illinois.

Dr. Kenski analyzes air quality data for Region 5 and specializes in receptor modeling of volatile organic compounds. Her work establishes the link between ambient monitoring data and emission inventory quantification. She is the data analysis coordinator for the Region 5 Photochemical Assessment Monitoring Stations (PAMS) and is contributing to the national and regional PAMS network redesign effort. She has lectured on air quality modeling, air quality management, and industrial hygiene. She received a Ph.D. from the University of Illinois at Chicago.

Charles W. Lewis

Charles Lewis is a Research Physicist at the National Exposure Research Laboratory of the U.S. Environmental Protection Agency, Research Triangle Park, NC. Before coming to EPA in 1975 he held academic positions in physics at the University of Liverpool, Texas A&M University, and the University of Karlsruhe. His work at EPA has been concerned with a broad range of source apportionment issues: aerosol physical and chemical characterization, aerosol and VOC receptor modeling, biogenic source apportionment via radiocarbon methodology, and source apportionment of aerosol mutagenicity. He was an Editorial Board member of the Journal of Aerosol Science and Technology from 1989 to 1992. He received the B.A. degree (physics) from Reed College and the M.S. and Ph.D. degrees (physics) from the University of Minnesota.

Peter Scheff

Dr. Scheff joined the faculty of University of Illinois in 1989. Prior to this, he was on the faculty of the Department of Environmental Engineering at the Illinois Institute of Technology. He has taught courses and directed an Area Training Center for the Air Pollution Training Institute at UIC since 1991. Dr. Scheff has worked on receptor modeling studies of particulate matter and ozone precursors for urban air sheds in the United States including Chicago, IL, Detroit, MI, Beaumont, TX, and Washington, DC, and for cities around the world including Athens, Greece, Chernivtsi, Ukraine, Budapest, Hungary and Mexico City, Mexico. In addition to studies of PM₁₀ and respirable particulate matter, he has worked on the development of new receptor modeling applications including studies of ozone precursors and ozone formation, residential and industrial indoor air quality, and sources of biological aerosols. He was awarded the M.S. and Ph.D. degrees from the University of Illinois at Chicago and has published over 100 technical reports and papers.

Robert K. Stevens

Mr. Stevens has over 30 years of experience in air quality research - almost all with the U. S. Environmental Protection Agency (EPA). He served as the first Chief of ORD's Source Apportionment Branch - from 1975 to 1995. His research efforts have included: development of criteria pollutant analysis methods for SO₂, O₃, NO_x and Particulate Matter; design of field and laboratory capabilities to collect and analyze PM-10 samples to determine sample origin; and development of statistical and physical receptor models to determine sources of particulates, volatile organic compounds, and mutagenicity of aerosols. Additionally, Mr. Stevens designed and developed a new family of sampling systems that includes: annular denuders, cyclone and impactor inlets, and modified dichotomous samplers. He served as Adjunct Professor at North Carolina State University, and has published over 100 peer reviewed papers in the field of air quality monitoring and source apportionment research. He received the B. Sc. and M. Sc. degrees in chemistry from Virginia Polytechnic Institute. Presently, he is a Research Scientist with the Florida Department of Environmental Protection at the U.S. EPA in Research Triangle Park, North Carolina.

Richard Wadden

Dr. Wadden is Professor of Environmental and Occupational Health Sciences at the University of Illinois in Chicago. He is also Director of two ABET accredited training programs, in Industrial Hygiene and Hazardous Materials Management. Before entering academe he worked for 6 years in industry (Linde Co., Humble Oil and Refining) and with the State of Illinois Pollution Control Board. He is a registered Professional Engineer and a Certified Industrial Hygienist.

Dr. Wadden has extensive experience in applying the chemical mass balance receptor model. He has directed or participated in studies using this evaluation procedure in Chicago, Detroit, Tokyo, Beaumont, Atlanta, Washington D.C., and the four state Lake Michigan area, Southeast Michigan, Budapest, and Chernivtsi (Ukraine), and has published 18 papers or book chapters in this area. He is the co-author of three books, and is active in research in indoor air pollution and determination of the rates and composition of workplace emissions from such sources as offset and rotogravure printing, electroplating, welding, degreasing, and wave soldering.

Lesson I

Introduction and Objectives
Peter Scheff

INTRODUCTION TO RECEPTOR MODELING

Lesson Title: Introduction and Objectives

Lesson: I

Prepared By: P.A. Scheff

Date: February 10, 1998

Lesson Goal: The goal of this lesson is to orient students to the course, introduce instructors, describe how questions and answers will be handled, and describe requirements for the successful completion of course.

Lesson Objectives: At the completion of this lesson the student will be able to:

Describe how the course is organized.

Describe the criteria for successfully completing the course in order to receive a certificate from APTI.

Describe the qualifications of the instructors.

Explain how to submit questions and how to access the on-line materials.

LESSON I OUTLINE

- I. Introduction and Organization of Course
- II. Review of Course Requirements
- III. Introduction of Instructors
- IV. Review of Course Agenda
- V. Review of Course Objectives

Introduction and Objectives

Lesson I. Introduction and Course
Objectives

Peter A. Scheff
University of Illinois at Chicago

Introduction

- Receptor models are a group of measurement-based air quality models for identifying the concentration of specific source categories at air measurement (receptor) sites.

Introduction

- Course will present applications of receptor modeling for particulate matter and volatile organic compounds.
- Homework assignments will ask students to apply CMB model software to test data sets using their PC's.

Introduction and Objectives

Class Participants Will Learn:

- The major components of a CMB study.
- The criteria for a successful CMB study.
- Methods for ambient sampling and analysis in support of receptor modeling.

Class Participants Will Learn:

- The requirements for source profiles and how they are developed.
- The principles of receptor modeling evaluation and validation.
- How to use the CMB8 computer program for receptor modeling.

Class Participants Will Learn:

- How optical microscopy is used in receptor modeling applications.
- How scanning electron microscopy is used in receptor modeling applications.

Introduction and Objectives

Class Participants Will Learn:

- How radiocarbon analysis is used in receptor modeling applications.
- How multiple linear regression is used for receptor modeling.

Criteria For Successful Completion of the Course.

- Completion of the pre-test.
- Attendance at four days of broadcast.
- Evaluate one of the homework example data sets and submit a 5 page laboratory report.

Criteria For Successful Completion of the Course.

- Completion of the post-test with a minimum score of 70%.
- Completion of course evaluation form.

Introduction and Objectives

Course Organization

- Four day broadcast.
- Broadcast begins at 12:30 pm and ends at 5:00 pm eastern time.
- Post-test administered after broadcast ends on day four.

Course Organization

- Question and Answer session at end of each day.
- Two week break between days three and four for work on homework data sets.
- Questions on homework can be submitted by E-mail or FAX.

Agenda: Day 1

- Pre-test
- Lesson 1. Introduction and Objectives
- Lesson 2. Introduction to Receptor Modeling

Introduction and Objectives

Agenda: Day 1

- Lesson 3. Chemical Mass Balance (CMB) Receptor Model: Mathematics and Assumptions
- Lesson 4. Study Design

Agenda: Day 1

- Lesson 5. Ambient Measurements in Support of Receptor Modeling
- Questions and Answers

Agenda: Day 2

- Lesson 6. Introduction to Optical Microscopy
- Lesson 7. Optical Microscopy: Applications

Introduction and Objectives

Agenda: Day 2

- Lesson 8. Introduction to Scanning Electron Microscopy
- Lesson 9. Source Characterization: Sampling and Analysis Methods
- Questions and Answers

Agenda: Day 3

- Lesson 10. Introduction to the CMB 8 Software
- Lesson 11. Demonstration of the CMB Model Using CMB8 Software
- Lesson 12. Receptor Model Evaluation and Validation

Agenda: Day 3

- Lesson 13. CMB Model Applications: Description of Homework Data Sets
- Questions and Answers

Introduction and Objectives

Agenda: Day 4

- Lesson 14. Review of Practice Exercises
- Lesson 15. CMB Application for VOCs
- Lesson 16. Multiple Linear Regression and Carbon-14

Agenda: Day 4

- Lesson 17. Source Allocation of Ambient Ozone
- Lesson 18. Application of Scanning Electron Microscopy to Receptor Modeling

Agenda: Day 4

- Lesson 19. Where to Turn for Help
- Final Questions
- Post-test and Course Evaluations

Introduction and Objectives

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**Ronald G. Draftz, Science Adviser, IIT
Research Institute, Chicago**

Lesson II

Introduction To Receptor Modeling
Peter Scheff

INTRODUCTION TO RECEPTOR MODELING

Lesson Title: Introduction to Receptor Modeling

Lesson: II

Prepared By: P.A. Scheff

Date: February 10, 1998

Lesson Goal: The goal of this lesson is to describe the theoretical basis of receptor modeling.

Lesson Objectives: At the end of this lesson the student will be able to:

Explain the theoretical basis of receptor modeling.

Compare and contrast source-oriented and receptor-oriented air quality models.

Compare and contrast at least three different types of receptor models.

Identify at least three basic applications for receptor models.

References:

U.S. EPA, Receptor Model Technical Series, Volume I: Introduction to Receptor Models, EPA-450/4-81-016a, U.S. EPA, Research Triangle Park, NC, 27711, July, 1981.

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U.S. EPA, Receptor Model Source Composition Library, EPA 450/4-85-002, U.S. EPA, Research Triangle Park, NC, 27711, November, 1984.

U.S. EPA, Procedures for Reconciling Differences in Receptor and Dispersion Models, EPA-450/4-87-008, U.S. EPA, Research Triangle Park, NC, 27711, May, 1987.

U.S. EPA, Guidelines for PM-10 Sampling and Analysis Applicable to Receptor Modeling, EPA-450/R-94-009, U.S. Environmental Protection Agency, Research Triangle Park, NC, 27711, March, 1994.

Hopke, P.K., Receptor Modeling in Environmental Chemistry, John Wiley and Sons, New York, 1985.

Receptor Modeling in Air Quality, Philip Hopke, Editor, Elsevier Science Publishers, New York, NY, 1991.

Receptor Models Applied to Contemporary Pollution Problems, Edited by Stuart Dattner and Philip Hopke, Air Pollution Control Association, Pittsburgh, PA, 1982.

Transactions: Receptor Methods for Source Apportionment, Real World Issues, Thompson G. Pace, Editor, Air Pollution Control Association, Pittsburgh, PA, 1986.

Transactions: Receptor Models in Air Resources Management, John G. Watson, Editor, Air and Waste Management Association, Pittsburgh, PA, 1989.

INTRODUCTION TO RECEPTOR MODELING

LESSON II OUTLINE

- I. Introduction - Objectives
- II. Source Apportionment Methods
 1. Dispersion models:
 2. Receptor models:
- III. Types of Receptor Models
- IV. Approaches
 1. Direct particle identification by microscopic analysis.
 2. Statistical analysis of variability.
 3. Mass balance analysis.
- V. Mass Balance Basis of Source Apportionment.
- VI. Multiple Linear Regression model.
- VII. Factor Analysis
- VIII. Microscopy

Introduction To Receptor Modeling

Lesson II. Introduction to
Receptor Models.

Peter A. Scheff
University of Illinois at Chicago

Objectives

- Explain the theoretical basis of receptor modeling.
- Compare and contrast source-oriented and receptor-oriented air quality models.

Lesson Objectives

- Compare and contrast at least three different types of receptor models
- Identify at least three basic applications for receptor models.

Introduction To Receptor Modeling

Source Apportionment Methods

Dispersion Model:

- **Primary tool for source apportionment studies.**
- **Source oriented model.**

Dispersion Model

- **Can be solved for any specified receptor location in a modeling region.**
- **Are based on estimates (emission factors) or measurements (source tests) of emission rate and dispersion.**

Dispersion Model

- **Need to be applied to each individual source (point, line or area) in the airshed.**
- **Can be applied prospectively to evaluate the impact of new or planned sources on ambient air quality.**

Introduction To Receptor Modeling

Receptor Model

- **Ambient measurement-based model.**
- **Does not require source emission or meteorological inputs.**
- **Is solved for the air quality at the point of an ambient measurement (or set of measurements).**

Receptor Model

- **Based on the observed chemical and physical composition of pollution samples collected at a receptor sites.**
- **Is applied to all (or as many as are known) sources of a categorical pollutant (PM₁₀, NMOC).**

Receptor Model

- **Individual sources within a source-type (a specific coal fired combustor can not be directly evaluated.)**
- **Can not directly evaluate the impact of a prospective source.**

Introduction To Receptor Modeling

Types of Receptor Models

- Model that use information obtained from bulk analysis of a categorical pollutant in an ambient sample.
 - Chemical Mass Balance (CMB) Model
 - Multivariate analysis (factor analysis)
 - Multiple linear regression.

Types of Receptor Models

- Analytical methods based on analysis of the properties of individual particles.
 - Polarized light microscopy
 - Automated scanning electron microscopy.

Approaches

1. Direct particle identification by microscopic analysis.
 - Can be applied to an individual sample or small group of samples.

Introduction To Receptor Modeling

Approach 1

- Extrapolation from individual particle identification to mass concentration can be difficult.
- Has the potential to uniquely identify hundreds of particle types.

Approach 2

2. Statistical analysis of the variability (over time and/or space) in pollutant chemical composition.
- Factor analysis
 - Multiple linear regression

Approach 2

- Can be applied to gas-phase categorical pollutants (NMOC).
- Results can be complicated by the spacial variability of sources.

Introduction To Receptor Modeling

Approach 2

- **Must be applied to many samples**

(number of samples should be greater than 50 times the number of sources)

Approach 3

3. Mass balance analysis of the concentration of various chemical species measured at the receptor (CMB).

- **Deterministic model.**
- **Can be applied to individual samples.**

Approach 3

- **Uses multivariable least-squares calculations to fit source compositions (independent variables) to ambient air concentrations (dependent variable).**

Introduction To Receptor Modeling

Approach 3

- Can be applied to gas-phase categorical pollutants (NMOC).
- Each individual sample represents a sample-specific emission inventory.

Mass Balance Basis of Source Apportionment

Dispersion and receptor models have a common physical basis, that is that the pollutant measured at the receptor is the sum of the impacts from each individual source (Conservation of Mass).

Mass Balance Basis of Source Apportionment

$$M = \sum_{j=1}^P M_j$$

- where : M = Categorical pollutant mass concentration

Introduction To Receptor Modeling

Mass Balance Basis of Source Apportionment

P = Number of contributing source categories

M_j = Concentration of source "j"

Mass Balance Basis of Source Apportionment

This can be written:

$$PM_{total} = PM_{Soil} + PM_{Auto} + PM_{Steel} + PM_{Combustion}$$

Mass Balance Basis of Source Apportionment

Where:

PM_{total} = Observed particle concentration at a receptor site

PM_{soil} = Contribution of soil aerosol to measured PM concentration.

Introduction To Receptor Modeling

Mass Balance Basis of Source Apportionment

- These equations assume that we know all "important" sources of each categorical pollutant under evaluation.
- Assumption of conservation of mass must be carefully considered.

Mass Balance Basis of Source Apportionment

- Conservation of mass requires that the composition of the pollutant at the point of emission is the same as the composition at the point of collection.
- Problems include deposition and photochemistry.

Multiple Linear Regression Model

$$\frac{\mu\text{gPM}}{m^3} = \frac{\mu\text{g}_{\text{auto tracer}}}{m^3} \cdot \frac{\mu\text{gPM}_{\text{auto}}}{\mu\text{g}_{\text{auto tracer}}} + \dots$$
$$\dots + \frac{\mu\text{g}_{\text{steel tracer}}}{m^3} \cdot \frac{\mu\text{gPM}_{\text{steel}}}{\mu\text{g}_{\text{steel tracer}}}$$

Introduction To Receptor Modeling

Multiple Linear Regression Model

- Given many ambient measurements, MLR equation can be solved for the contribution of the categorical pollutant.

Multiple Linear Regression Model

- MLR equation relies on the sample to sample variation in tracer and categorical pollutant concentration. It can not be developed for an individual sample.
- Tracers must be "unique" to only one source.

Factor Analysis Model

$$M_{i,k} = \sum_{j=1}^P F_{i,j} \cdot M_j$$

Where: $M_{i,k}$ is a matrix of the measurements of i chemical components on k days.

Introduction To Receptor Modeling

Factor Analysis Model

- Factor analysis looks at the variation in the ambient measurement matrix and infers values for M_j .
- F_{ij} is not specified.

Polarized Light Microscopy

- Direct identification of particles $> 1\mu\text{m}$ diameter based on optical properties such as color, shape, and size.
- Allows for the evaluation of a greater number of features for the identification of crystalline particles.

Polarized Light Microscopy

- Dispersion staining useful in identify coarse-mode carbon particles.
- Light loading necessary to avoid overloading with multiple layers of particles.

Introduction To Receptor Modeling

Polarized Light Microscopy

- Sensitive to crystalline, noncrystalline, combusted and biological particles.
- Identification of large particles is critical. One 20 μm particle is approximately equal in weight to one thousand 2 μm particles.

Polarized Light Microscopy

- Evaluation is highly dependent on the experience of the analyst.
- Particle density and volume assumptions are required.

Computer Controlled Scanning Electron Microscopy (CCSEM)

- Technique to determine the size, shape, and elemental composition of individual particles by combining three analytical techniques under computer control:

1. Scanning electron microscopy

Introduction To Receptor Modeling

CCSEM

2. Energy-dispersive x-ray fluorescence analyzer (particle composition)
3. Digital image processor (particle morphology)

CCSEM

- Computer control allows for faster analysis and a more statistically representative sample of particles evaluated.

CCSEM

- The combination of the three techniques allows for the identification of hundreds of classes of particles.
- Physically measures particles within a broad size range (0.2 to 300 μ m).

Introduction To Receptor Modeling

CCSEM

- Elemental chemistry is obtained for each particle.
- Can overcome some of the problems of multicollinearity by including data on morphology.

X-Ray Diffraction (XRD)

- Non-destructive analytical technique that is used to identify the specific chemical structure of crystalline materials.
- May have detection limit problems. (this is changing)

XRD

- Analytical uncertainties up to 100% for minor components.
- Examples of minerals measured by XRD:

Introduction To Receptor Modeling

XRD

Graphite - Mining of metamorphic rock;
electrode and anode manufacturing;
iron and steel industry process losses

Galena - Lead mining and smelting

Sphalerite - Zinc and lead mining

XRD

Chalcocite - Copper mining and smelting

Hematite - Iron ore mining, iron and steel
manufacturing

Bauxite - Aluminum smelting

XRD

Calcite - Limestone mining, lime

Dolomite - manufacturing, cement plant

Lesson III

Chemical Mass Balance (CMB) Receptor Model:
Mathematics and Assumptions
Peter Scheff

INTRODUCTION TO RECEPTOR MODELING

Lesson Title: Chemical Mass Balance Receptor Model: Mathematics and Assumptions

Lesson: III

Prepared By: P.A. Scheff

Date: February 10, 1998

Lesson Goal: The goal of this lesson is to describe the mathematical basis and underlying assumptions of the Chemical Mass Balance Model.

Lesson Objectives: At the completion of this lesson the student will be able to:

Describe the mathematical basis of receptor modeling.

Write the basic equations for the CMB model.

Explain the data requirements of the CMB model including the independent variables (source fingerprints) and dependent variable (ambient composition).

Describe how the CMB model equation is solved.

Solve the CMB model equations and be able interpret the results of a CMB calculation.

References:

U.S. EPA, Receptor Model Technical Series, Volume I: Introduction to Receptor Models, EPA-450/4-81-016a, U.S. EPA, Research Triangle Park, NC, 27711, July, 1981.

U.S. EPA, Receptor Model Technical Series, Volume II: Chemical Mass Balance, EPA-450/4-81-016b, U.S. EPA, Research Triangle Park, NC, 27711, July, 1981.

U.S. EPA, Receptor Model Technical Series, Volume III (1989 Revision): CMB7 User's Manual, EPA-450/4-90-004, U.S. EPA, Research Triangle Park, NC, 27711, January, 1990.

INTRODUCTION TO RECEPTOR MODELING

LESSON III OUTLINE

- I. Introduction - Objectives
- II. Conservation of Mass
- III. Mass Balance Equation
 1. Categorical Pollutant
 2. Elemental or Chemical Species
 3. Units of Equation
 4. Example
- IV. Assumptions
- V. Advantages
- VI. Source Groups Identified by the CMB
- VII. Multicollinearity
- VIII. Diagnostics
- IX. Example
 1. Ambient and Source Emission Elemental Composition
 2. The receptor model equations
 3. Single Tracer Solution
 4. Ordinary weighted least squares solution
 5. Effective variance weighted least squares solution
 6. Comparison of exact and least squares solutions

Chemical Mass Balance (CMB) Receptor Model: Mathematics and Assumptions

Lesson Objectives

- Describe how the CMB model equation is solved.
- Solve the CMB model equations and be able to interpret the results of a CMB calculation.

Conservation of Mass

- Assumption of conservation of mass must be carefully considered.

Conservation of Mass

- For receptor models, conservation of mass states that the composition of the categorical pollutant at the point of emission is the same as the composition of the pollutant at the point of collection.
- Problems include deposition and photochemistry.

Chemical Mass Balance (CMB) Receptor Model: Mathematics and Assumptions

Conservation of Mass

- The mass balance equation can be written for each feature of a categorical pollutant.

$$M_i = \sum_{j=1}^P M_{i,j}$$

Conservation of Mass

M_i = concentration of pollutant component "i"

P = number of contributing source categories

$M_{i,j}$ = concentration of component i from source j

Conservation of Mass

This can be written:

$$Pb_{receptor} = Pb_{autos} + Pb_{smelter} + Pb_{foundry}$$

Chemical Mass Balance (CMB) Receptor Model: Mathematics and Assumptions

Conservation of Mass

This can be stated in terms of total source mass by substituting M_i for the product of the source impact M_j and the fraction on material i in the emission from source j .

$$M_i = \sum_{j=1}^P F_{i,j} \cdot M_j$$

Conservation of Mass

Where:

M_i = concentration of pollutant component "i"

P = number of contributing sources

Conservation of Mass

$F_{i,j}$ = fraction of component "i" in source "j" emissions

M_j = categorical pollutant concentration from source "j"

Chemical Mass Balance (CMB) Receptor Model: Mathematics and Assumptions

Conservation of Mass

- The dimensions of this equation are:

$$\frac{\mu\text{g}_i}{\text{m}^3} = \sum_{j=1}^P \frac{\mu\text{g}_i}{\mu\text{g PM}_j} \cdot \frac{\mu\text{g PM}_j}{\text{m}^3}$$

Conservation of Mass

- For an example using lead, this becomes:

$$\frac{\mu\text{gPb}}{\text{m}^3} = \frac{\mu\text{gPb}}{\mu\text{gPM}_{\text{auto}}} \cdot \frac{\mu\text{gPM}_{\text{auto}}}{\text{m}^3} +$$
$$\frac{\mu\text{gPb}}{\mu\text{gPM}_{\text{smelter}}} \cdot \frac{\mu\text{gPM}_{\text{smelter}}}{\text{m}^3}$$

Conservation of Mass

- This equation has two unknowns, the contributions of PM_{10} from autos and smelters.
- In order to solve this problem, we must write more equations than unknowns.

Chemical Mass Balance (CMB) Receptor Model: Mathematics and Assumptions

Conservation of Mass

For example

$$\frac{\mu\text{gZn}}{m^3} = \frac{\mu\text{gZn}}{\mu\text{gPM}_{\text{auto}}} \cdot \frac{\mu\text{gPM}_{\text{auto}}}{m^3} + \frac{\mu\text{gZn}}{\mu\text{gPM}_{\text{smelter}}} \cdot \frac{\mu\text{gPM}_{\text{smelter}}}{m^3}$$

Conservation of Mass

$$\frac{\mu\text{gBr}}{m^3} = \frac{\mu\text{gBr}}{\mu\text{gPM}_{\text{auto}}} \cdot \frac{\mu\text{gPM}_{\text{auto}}}{m^3} + \frac{\mu\text{gBr}}{\mu\text{gPM}_{\text{smelter}}} \cdot \frac{\mu\text{gPM}_{\text{smelter}}}{m^3}$$

Conservation of Mass

$$\frac{\mu\text{gNO}_x}{m^3} = \frac{\mu\text{gNO}_x}{\mu\text{gPM}_{\text{auto}}} \cdot \frac{\mu\text{gPM}_{\text{auto}}}{m^3} + \frac{\mu\text{gNO}_x}{\mu\text{gPM}_{\text{smelter}}} \cdot \frac{\mu\text{gPM}_{\text{smelter}}}{m^3}$$

Chemical Mass Balance (CMB) Receptor Model: Mathematics and Assumptions

Conservation of Mass

- These equations are the physical basis for receptor modeling.
- The different types of models differ only in the choice of the mathematical solution.

Assumptions

- All "major" sources of the fitting compounds are included in the model. (Secondary pollutants can not be directly included.)

Assumptions

- The number of sources impacting the receptor and emission composition must be known.

Chemical Mass Balance (CMB) Receptor Model: Mathematics and Assumptions

Assumptions

- The number of independent equations must be greater than the number of sources (number of chemical species must be greater than number of sources).

Assumptions

- All sources included in the equations are actually present in the ambient sample. Daily variation in wind direction can cause this to change.

Assumptions

- Categorical pollutant composition is conserved. That is, the source composition is the same at the point of release and the receptor.

Chemical Mass Balance (CMB) Receptor Model: Mathematics and Assumptions

Assumptions

- The composition of the source emissions are linearly independent. (sources with similar composition present a problem). This can be helped by extending the chemical and physical evaluation of source and ambient measurements by adding additional observations.

Advantages

- Simple conceptual approach to source apportionment.
- Can be applied to individual samples or short averaging times (1 to 24 hours).

Advantages

- Gives a direct measure of the emission inventory (emission history) specific for each ambient sample.

Chemical Mass Balance (CMB) Receptor Model: Mathematics and Assumptions

Advantages

- Analysis of a series of samples from a seasonal or annual monitoring program provides a distribution of predicted source coefficients. This distribution represents the effect of meteorology on the source receptor relationship and is critical for model evaluation and validation.

Advantages

- Has been validated for TSP, PM₁₀, RP, and NMOC (non-methane organic carbon).
- Has been approved by the Office of Air Quality Planning and Standards of the U.S. EPA for use in PM₁₀ SIP development.

Advantages

- May be less expensive than equivalent dispersion model applications.
- Some deviation from the basic assumptions can be tolerated (that is, the CMB model is robust.)

Chemical Mass Balance (CMB) Receptor Model: Mathematics and Assumptions

Advantages

- Receptor models do not require detailed emission or meteorological data (although this is needed for model specification and validation).

Advantages

- Receptor models are well suited to fugitive sources (or sources with uncertain emissions inventory).
- Receptor models have been able to identify previously uninventoried sources.

Source Groups Identified by the CMB Model

Geologic Sources	Soil dust
	Rock crushing
	Asphalt batching
	Marine aerosols

Chemical Mass Balance (CMB) Receptor Model: Mathematics and Assumptions

Source Groups Identified by the CMB Model

Transportation emissions	Auto exhaust
	Diesel exhaust
	Gasoline
	Gasoline vapor
	Road dust

Source Groups Identified by the CMB Model

Vegetative burning	Residential wood combustion
	Forest fires
Calcium sources	Cement, limestone, and slag dust

Source Groups Identified by the CMB Model

Point Sources	Coal-fired boilers
	Residual oil boilers
	Petroleum refineries
	Municipal incineration
	Iron and steel processes
	Non-ferrous processes
	Vapor degreasers
	Coke ovens

Chemical Mass Balance (CMB) Receptor Model: Mathematics and Assumptions

Source Groups Identified by the CMB Model

Area Sources	Graphic arts
	Architectural coatings
	Dry cleaners
	Industrial surface coating
	Liquefied petroleum gas
	Natural gas

Multicollinearity

- Linear relationships between two or more sources (sources with similar chemical profiles) may result in calculation problems.

Multicollinearity

- Methods for reducing multicollinearity errors include:
 1. Improve the accuracy and specificity of the source profiles.

Chemical Mass Balance (CMB) Receptor Model: Mathematics and Assumptions

Multicollinearity

2. Include additional fitting species that describe differences between the sources, e.g. addition of SO₂ for the resolution of coal and soil particles.

Multicollinearity

3. Avoid the inclusion of two or more sources with similar profiles. This is the classical approach used in regression analysis.

Multicollinearity

4. Removal of one or more sources from the model. Note, however, that removing a source that impacts the receptor can also introduce significant errors in the model.

Chemical Mass Balance (CMB) Receptor Model: Mathematics and Assumptions

Multicollinearity

5. Forming linear combinations of the sources which can not be resolved (a feature included in USEPA CMB7 and CMB8 software).

Example

Example: Ambient Concentration and Source Emission Composition

Element	Ambient Concentration ($\mu\text{g}/\text{m}^3$)	Soil Dust (%)	Electric Arc Furnace (%)	Auto Exhaust (%)
Si	5.00	28.0	5.0	0.8
Al	1.60	6.6	0.6	0.1
Fe	3.00	5.7	32.0	2.1
Pb	1.20	0.3	0.7	20.0
SO ₄ -2	5.00	0.0	2.5	1.3
NO ₃ -	1.00	0.0	0.0	0.7
Mass	42.0			

Example

- The receptor model equation for Fe is:

$$3.0 \frac{\mu\text{g}}{\text{m}^3} = 0.057 \frac{\mu\text{gFe}}{\mu\text{gsoil}} \cdot \frac{M_{\text{soil}}}{\text{m}^3} + 0.32 \frac{\mu\text{gFe}}{\mu\text{gsteel}} \cdot \frac{M_{\text{steel}}}{\text{m}^3} + 0.021 \frac{\mu\text{gFe}}{\mu\text{gauto}} \cdot \frac{M_{\text{auto}}}{\text{m}^3}$$

Chemical Mass Balance (CMB) Receptor Model: Mathematics and Assumptions

Example

- To solve this equation, a set of similar equations must be created using the other elements listed in the table.
- In this example, Si, Al, Fe and Pb are fitting elements.

Example

- Fitting elements are features of the categorical pollutant used as dependent variables in the CMB equations.

Example

- Non-fitting elements are feature concentrations estimated by the CMB model, but are not actually used in the regression analysis.

Chemical Mass Balance (CMB) Receptor Model: Mathematics and Assumptions

Example

- The four equations (one for each fitting element) for this example are:

$$3.0 \frac{\mu\text{gFe}}{\text{m}^3} = 0.057 \cdot \frac{M_{\text{soil}}}{\text{m}^3} + 0.32 \cdot \frac{M_{\text{Steel}}}{\text{m}^3} + 0.021 \cdot \frac{M_{\text{auto}}}{\text{m}^3}$$

Example

$$16 \frac{\mu\text{gAl}}{\text{m}^3} = 0.066 \cdot \frac{M_{\text{soil}}}{\text{m}^3} + 0.006 \cdot \frac{M_{\text{steel}}}{\text{m}^3} + 0.001 \cdot \frac{M_{\text{auto}}}{\text{m}^3}$$

Example

$$5.0 \frac{\mu\text{gSi}}{\text{m}^3} = 0.28 \cdot \frac{M_{\text{soil}}}{\text{m}^3} + 0.05 \cdot \frac{M_{\text{steel}}}{\text{m}^3} + 0.008 \cdot \frac{M_{\text{auto}}}{\text{m}^3}$$

Chemical Mass Balance (CMB) Receptor Model: Mathematics and Assumptions

Example

$$12 \frac{\mu\text{gPb}}{\text{m}^3} = 0.003 \cdot \frac{M_{\text{soil}}}{\text{m}^3} + 0.007 \cdot \frac{M_{\text{steel}}}{\text{m}^3} + 0.20 \cdot \frac{M_{\text{auto}}}{\text{m}^3}$$

Single Tracer Solution:

- The simplest solution to the set of equations is to assume that each source can be associated with a unique feature.
- If this assumption is valid, the CMB equation becomes:

$$C_i = F_{ij} \cdot S_j$$

Single Tracer Solution:

- The contribution from source j can be determined by dividing the species concentration (C_i) by the composition of source j. (F_{ij}).
- For example, if Pb is a unique tracer for leaded auto exhaust.

Chemical Mass Balance (CMB) Receptor Model: Mathematics and Assumptions

Single Tracer Solution:

- The fraction of lead in auto exhaust is 20%.
- $1.2 \mu\text{g}/\text{m}^3$ Pb is measured at the receptor.

Single Tracer Solution:

- Then the total impact of auto exhaust is:

$$\frac{1.2 \frac{\mu\text{gPb}}{\text{m}^3}}{0.20 \frac{\mu\text{gPb}}{\mu\text{gPM}}} = 6.0 \frac{\mu\text{gPM}}{\text{m}^3}$$

Single Tracer Solution:

- This approach assumes that the fraction of the tracer in the source emission is constant, the tracer can be accurately measured at the receptor, and the tracer is emitted by only one source.
- These conditions are difficult to meet.

Chemical Mass Balance (CMB) Receptor Model: Mathematics and Assumptions

Ordinary Weighted Least Squares (OWLS) Solution

- OWLS estimates source contributions based on a least-squares fit between the measured concentrations of the fitting species and the source compositions.

OWLS

- The OWLS solution is defined as the set of coefficients that minimize the following expression:

$$\chi^2 = \sum_{i=1}^n \frac{\left(C_i - \sum_{j=1}^p F_{i,j} \cdot S_j \right)^2}{\sigma_c^2}$$

OWLS

Where:

n = the number of fitting compounds

P = the number of sources in the model

σ_c^2 = the variance of the measurement error

Chemical Mass Balance (CMB) Receptor Model: Mathematics and Assumptions

OWLS

- In the OWLS solution, the CMB equation is weighted by the uncertainty of the ambient measurement.
- The advantages of this approach are:

OWLS

1. Less weight or consideration is given to features that have been measured with poor reliability.
2. More equal weight is given to all fitting features independent of their concentration.

Effective Variance Weighted Least Squares (EVWLS) Solution

- The EVWLS solution extends the OWLS solution to include uncertainties in the source profiles.
- The EVWLS solution is defined as the set of coefficients that minimize the following expression:

Chemical Mass Balance (CMB) Receptor Model: Mathematics and Assumptions

EVWLS

$$\chi^2 = \sum_{i=1}^n \frac{\left(C_i - \sum_{j=1}^P F_{i,j} \cdot S_j \right)^2}{\sigma_{C_i}^2 + \sum_{j=1}^P \sigma_{F_{i,j}}^2 \cdot S_j^2}$$

EVWLS

- This equation requires an iterative solution.
- The equation also requires that the variance of the source composition is known.

EVWLS

- Variability in source composition can include
 1. Source measurement error,
 2. Source emission variability, and
 3. Source to source variability within a category.

Chemical Mass Balance (CMB) Receptor Model: Mathematics and Assumptions

EVWLS

- Source Variability is poorly understood and complete information is frequently not available.

Comparison of Exact and Least Squares Solutions for Example

Sample ambient and source emission elemental composition data

	ELEMENT	Ambient Conc	Source Composition		
			SOIL	STEEL	AUTO
CASE 1	Fe	3.000	0.057	0.320	0.021
CASE 2	Al	1.600	0.066	0.006	0.001
CASE 3	Si	5.000	0.280	0.050	0.008
CASE 4	Pb	1.200	0.003	0.007	0.200

Example

A. Solve for Al, Si, and Pb (drop Fe)

$$1.6 \mu\text{gAl}/\text{m}^3 = 0.066 \mu\text{g}_{\text{soil}}/\text{m}^3 + 0.006 \mu\text{g}_{\text{steel}}/\text{m}^3 + 0.001 \mu\text{g}_{\text{auto}}/\text{m}^3$$

$$5.0 \mu\text{gSi}/\text{m}^3 = 0.280 \mu\text{g}_{\text{soil}}/\text{m}^3 + 0.050 \mu\text{g}_{\text{steel}}/\text{m}^3 + 0.008 \mu\text{g}_{\text{auto}}/\text{m}^3$$

$$1.2 \mu\text{gPb}/\text{m}^3 = 0.003 \mu\text{g}_{\text{soil}}/\text{m}^3 + 0.007 \mu\text{g}_{\text{steel}}/\text{m}^3 + 0.200 \mu\text{g}_{\text{auto}}/\text{m}^3$$

Chemical Mass Balance (CMB) Receptor Model: Mathematics and Assumptions

Example

A.

MODEL: $CONC = B1*SOIL + B2*STEEL + B3*AUTO$

PARAMETER	ESTIMATE
B1	30.854
B2	-74.084
B3	8.130

Example

B. Solve for Fe, Al and Pb (drop Si)

$3.0 \mu\text{gFe}/\text{m}^3 = 0.057 \mu\text{g}_{\text{soil}}/\text{m}^3 + 0.320 \mu\text{g}_{\text{steel}}/\text{m}^3 + 0.021 \mu\text{g}_{\text{auto}}/\text{m}^3$

$1.6 \mu\text{gAl}/\text{m}^3 = 0.066 \mu\text{g}_{\text{soil}}/\text{m}^3 + 0.006 \mu\text{g}_{\text{steel}}/\text{m}^3 + 0.001 \mu\text{g}_{\text{auto}}/\text{m}^3$

$1.2 \mu\text{gPb}/\text{m}^3 = 0.003 \mu\text{g}_{\text{soil}}/\text{m}^3 + 0.007 \mu\text{g}_{\text{steel}}/\text{m}^3 + 0.200 \mu\text{g}_{\text{auto}}/\text{m}^3$

Example

B.

MODEL: $CONC = B1*SOIL + B2*STEEL + B3*AUTO$

PARAMETER	ESTIMATE
B1	23.724
B2	4.790
B3	5.476

Chemical Mass Balance (CMB) Receptor Model: Mathematics and Assumptions

Example

C. Solve for Fe, Si and Pb (drop Al)

$$3.0 \mu\text{gFe}/\text{m}^3 = 0.057 \mu\text{g}_{\text{soil}}/\text{m}^3 + 0.320 \mu\text{g}_{\text{steel}}/\text{m}^3 + 0.021 \mu\text{g}_{\text{auto}}/\text{m}^3$$

$$5.0 \mu\text{gSi}/\text{m}^3 = 0.280 \mu\text{g}_{\text{soil}}/\text{m}^3 + 0.050 \mu\text{g}_{\text{steel}}/\text{m}^3 + 0.008 \mu\text{g}_{\text{auto}}/\text{m}^3$$

$$1.2 \mu\text{gPb}/\text{m}^3 = 0.003 \mu\text{g}_{\text{soil}}/\text{m}^3 + 0.007 \mu\text{g}_{\text{steel}}/\text{m}^3 + 0.200 \mu\text{g}_{\text{auto}}/\text{m}^3$$

Example

C.

MODEL: $\text{CONC} = \text{B1} \cdot \text{SOIL} + \text{B2} \cdot \text{STEEL} + \text{B3} \cdot \text{AUTO}$

PARAMETER	ESTIMATE
B1	16.618
B2	6.051
B3	5.539

Example

D. Solve for Fe, Al and Si (drop Pb)

$$3.0 \mu\text{gFe}/\text{m}^3 = 0.057 \mu\text{g}_{\text{soil}}/\text{m}^3 + 0.320 \mu\text{g}_{\text{steel}}/\text{m}^3 + 0.021 \mu\text{g}_{\text{auto}}/\text{m}^3$$

$$1.6 \mu\text{gAl}/\text{m}^3 = 0.066 \mu\text{g}_{\text{soil}}/\text{m}^3 + 0.006 \mu\text{g}_{\text{steel}}/\text{m}^3 + 0.001 \mu\text{g}_{\text{auto}}/\text{m}^3$$

$$5.0 \mu\text{gSi}/\text{m}^3 = 0.280 \mu\text{g}_{\text{soil}}/\text{m}^3 + 0.050 \mu\text{g}_{\text{steel}}/\text{m}^3 + 0.008 \mu\text{g}_{\text{auto}}/\text{m}^3$$

Chemical Mass Balance (CMB) Receptor Model: Mathematics and Assumptions

Example

D.

MODEL: $CONC = B1*SOIL + B2*STEEL + B3*AUTO$

PARAMETER	ESTIMATE
B1	31.944
B2	61.104
B3	-874.950

Example

E. Solve all four using least squares statistics.

$$3.0 \mu\text{gFe}/\text{m}^3 = 0.057 \mu\text{g}_{\text{soil}}/\text{m}^3 + 0.320 \mu\text{g}_{\text{steel}}/\text{m}^3 + 0.021 \mu\text{g}_{\text{auto}}/\text{m}^3$$

$$1.6 \mu\text{gAl}/\text{m}^3 = 0.066 \mu\text{g}_{\text{soil}}/\text{m}^3 + 0.006 \mu\text{g}_{\text{steel}}/\text{m}^3 + 0.001 \mu\text{g}_{\text{auto}}/\text{m}^3$$

$$5.0 \mu\text{gSi}/\text{m}^3 = 0.280 \mu\text{g}_{\text{soil}}/\text{m}^3 + 0.050 \mu\text{g}_{\text{steel}}/\text{m}^3 + 0.008 \mu\text{g}_{\text{auto}}/\text{m}^3$$

$$1.2 \mu\text{gPb}/\text{m}^3 = 0.003 \mu\text{g}_{\text{soil}}/\text{m}^3 + 0.007 \mu\text{g}_{\text{steel}}/\text{m}^3 + 0.200 \mu\text{g}_{\text{auto}}/\text{m}^3$$

MODEL: $CONC = B1*SOIL + B2*STEEL + B3*AUTO$

Example

DEP VAR: CONC

N = 4

MULTIPLE R = 0.997

SQUARED MULTIPLE R = 0.995

ADJUSTED SQUARED MULTIPLE R = 0.984

STANDARD ERROR OF ESTIMATE = 0.449

variable	coefficient	std error	T	P (2 tail)
SOIL	17.008	1.629	10.5	0.061
STEEL	5.957	1.484	4.0	0.155
AUTO	5.531	2.249	2.5	0.246

Chemical Mass Balance (CMB) Receptor Model: Mathematics and Assumptions

Example

ANALYSIS OF VARIANCE

SOURCE	Sum of Squares	DF	Mean Square	F Ratio	P
REGRESSION	37.799	3	12.600	62.615	0.093
RESIDUAL	0.201	1	0.201		

Example

SUMMARY OF TEST

parameter	element not included in model				
	Fe	Si	Al	Pb	all elements
Soil	30.8	23.7	16.6	31.9	17.0
Steel	-74.1	4.8	6.0	61.1	5.9
Auto	8.1	5.5	5.5	-875.0	5.5

Lesson IV

Study Design
Richard Wadden

INTRODUCTION TO RECEPTOR MODELING

Lesson Title: Study Design

Lesson: IV

Prepared By: R. Wadden

Date: February 10, 1998

Lesson Goal: This lecture describes the structure of data sets which will support a CMB analysis; The requirements of source fingerprints used in the application; And the types of weighting factors which are appropriate for solving the CMB equations.

Lesson Objectives: At the completion of this lesson students will be able to:

List the major criteria that must be satisfied in order to carry out a CMB study.

List the major components of at least 3 study designs which have been successfully used in CMB studies of suspended particulate matter, VOCs, and combinations of gaseous and particle pollutants.

Explain the rationale supporting the choice of specific sampling intervals.

Explain how source categories are chosen to be included in the CMB model.

CMB Study Design

Lesson IV. CMB Study Design

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CMB Study Design

- Form of the chemical mass balance receptor $Y = Z\beta + E$ model

where:

Y is the vector of i fitting-compound or element concentrations measured at a receptor site

CMB Study Design

Z is the pollution source composition matrix of i compounds or elements for each of the j sources modeled

E is the vector of i errors (is the residual = the difference between the measured and predicted component or element compositions)

CMB Study Design

CMB Study Design

β Is the vector representing the contribution to receptor concentration of a categorical pollutant (such as PM_{10} or NMOG) from each source category included in the model.

CMB Study Design

- The equation is solved using a least squares fit weighted with the measurement variance for each component or element.

- So need ambient measurement composition, identified source compositions (source fingerprints), and a weighting factor.

1. Collection of an appropriate data set

- Decide on the purpose of the study
 - Check or establish emission inventory
 - Determine contribution from specific source(s)
 - Check dispersion model results
 - Determine the effect of control strategy intervention

CMB Study Design

1. Collection of an appropriate data set

- Select appropriate sampling time intervals

3-4 hours for VOC's

24 hours for TSP, PM₁₀, PM_{2.5}

12 hours for day/night differences

1. Collection of an appropriate data set

- Decide on type of components to be measured (i.e. specify analytical technique), detection limit as well as components

- Choose number of samples and sampling schedule so as to characterize annual or seasonal periods

1. Collection of an appropriate data set

- Locate sampling point(s) so as to be representative of area monitored

- Include enough measurements to characterize all wind directions

CMB Study Design

1. Collection of an appropriate data set

- Be sure to make wind direction measurements (or have these available)

- Collect data simultaneously with criteria pollutant collection (whether at the same site or elsewhere in the area)

1. Collection of an appropriate data set

- At the minimum, must measure more elements or species than the number of sources to be included in the model.

2. Source identification and characterization

- Identify major sources and location

- Include sources that exist: Don't include sources that don't exist

- Need fingerprints for sources which are to be included

CMB Study Design

2. Source identification and characterization

- Examine, or at least understand, sources of fingerprint information

2. Source identification and characterization

Typical Source Fingerprints (Weight Percent of Total NMOC).
 (Partial Listing - 49 fitting compounds in all - Scheff et al,
 Air & Waste Manage.Assoc. J., 46, 1048-1057, 1996.)

Species	Vehicle	Liq Gas	Gas Vapor	Petrol. Refin.	Graphic Arts	Coke Ovens	Arch. Coatings
ethylene	6.17	0.006	0	1.45	0	0	0
ethane	1.49	0.021	0	4.95	0	0	0
propane	1.03	0.08	0.96	11.1	0	0	0
n-butane	5.40	3.23	23.7	13.2	0	2.03	0

2. Source identification and characterization

Species	Vehicle	Liq Gas	Gas Vapor	Petrol. Refin.	Graphic Arts	Coke Ovens	Arch. Coatings
isobutane	1.11	0.60	5.43	4.24	0	0.27	0
benzene	3.38	1.53	0.78	1.08	2.35	10.6	0.09
toluene	7.91	8.11	1.32	2.94	13.7	2.03	25.9
ethylbenz	1.14	1.80	0.10	0.40	0.33	0.87	0.45
n-octane	0.41	0.45	0.04	0.55	0	0.21	0
o-xylene	1.69	2.60	0.10	0.57	0.54	1.35	2.86
m&p-xylene	3.62	6.30	0.31	1.42	0.97	1.23	2.67

CMB Study Design

2. Source identification and characterization

Species	Vehicle	Liq Gas	Gas Vapor	Petrol. Refin.	Graphic Arts	Coke Ovens	Arch. Coatings
1,2,4-TM-Ibenzene							
	1.43	4.18	0.06	0.28	2.09	0.08	0
1,3,5-TM-Ibenzene							
	0.67	1.42	0.02	2.02	1.29	0.38	0
isopropylbenzene							
	0.15	0.24	0.04	0.49	0.36	0.94	0

2. Source identification and characterization

Species	Vehicle	Liq Gas	Gas Vapor	Petrol. Refin.	Graphic Arts	Coke Ovens	Arch. Coatings
n-nonane	0.24	0.21	0	0.76	0	3.14	0
n-propylbenzene	0	0.71	0.01	0.098	0.90	0.66	0

2. Source identification and characterization

Vehicles - composite of 9 Atlanta rush hour mini-tunnel samples, 12 samples from Chicago covered roadways, and EPA dynamometer study on 46 in-use cars. Includes evaporative running losses, tailpipe emissions, and diesel emissions.

CMB Study Design

2. Source identification and
characterization

- Gasoline vapor - composite of two studies: Atlanta and Chicago headspace measurements weighted by sales.

- Completely vaporized gasoline - Atlanta Precursor Study

2. Source identification and
characterization

- Petroleum Refinery - composite of three studies: refinery plume (2 aloft, 6 ground-level), refinery workers personal exposure, and refinery plume (6 ground-level).

2. Source identification and
characterization

- Coke Ovens - average composition from 8 fence-line samples collected downwind of large coke battery in Chicago area.

CMB Study Design

2. Source identification and characterization

- **Graphic Arts - composite fingerprint, based on published ink use, for lithography (47%), rotogravure (24%), flexography (18%), letterpress (7%) and miscellaneous processes (4%);**
 - lithography composite based on 68 hourly samples collected at three offset plants;
 - published fingerprint values used for other processes but rotogravure fingerprint subsequently confirmed by test of rotogravure shop (~200 hourly samples).

2. Source identification and characterization

- **Architectural coatings - based on product-use survey and sales figures.**

3. Determination of the value of the weighting factor

- **For elemental or molecular species analyzed with the same method, use variance of the analytical procedure (or even better, the variance of sampling + analysis procedures, although this value is not often available).**

CMB Study Design

3. Determination of the value of the weighting factor

See Insert:

Coefficient of Variance for Ambient Hydrocarbon Sampling and Analysis by G.C.

3. Determination of the value of the weighting factor

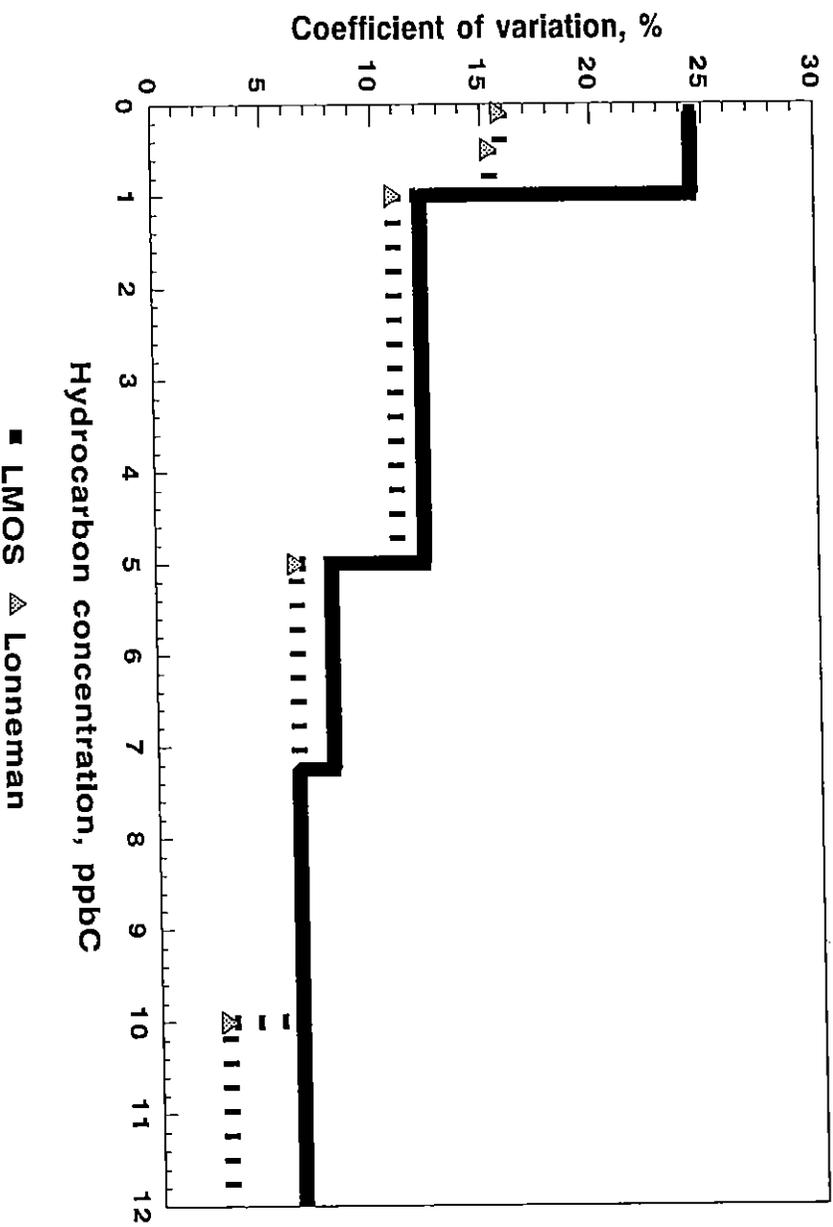
- For elemental or molecular species analyzed with different methods, use a measurement error which is a fixed fraction of the concentration, e.g., 10%.

- Variance will be the square of this value.

3. Determination of the value of the weighting factor

- Otherwise, will be making the source discrimination on the basis of differences in the variability of different techniques rather than on basis of actual composition pattern.

3. Determination of the value of the weighting factor



Coefficient of Variance for Ambient Hydrocarbon Sampling and Analysis by Gas Chromatography

(Kenski et al, J.Env.Eng., 121, 483, 1995; Kenski et al, Paper 149.01, AVMA, Nashville, 1996)

CMB Study Design

**4. Appropriate Data Set -
Designed to test CMB model**

Evaluation of Two-Phase Air Pollution Data for Receptor Modeling - Wadden et al, Paper 92-104.05, AWNA Annual Meeting, Kanas City, June, 1992.

Development of a Two-Phase Receptor Model for NMHC and PM₁₀ Air Pollution Sources in Chicago Lin et al, Paper 93-TP-58.03, AWMA Annual Meeting, Denver, June 1993.

**4. Appropriate Data Set -
Designed to test CMB model**

Source Allocation of Hazardous Air Pollutants in Chicago, Scheff et al, Paper 94-TP26B.04, AWMA Annual Meeting, Cincinnati, 1994.

**4. Appropriate Data Set -
Designed to test CMB model**

- Simultaneous measurement of PM₁₀ and NMHC.

- Development of two-phase fingerprints to better discriminate between sources.

CMB Study Design

4. Appropriate Data Set -
Designed to test CMB model

- Sources:
 - gasoline-powered vehicle emissions (running losses and tailpipe)
 - soil dust
 - diesel-powered vehicle exhaust
 - gasoline vapor
 - coal combustion emissions

4. Appropriate Data Set -
Designed to test CMB model

- Sources:
 - steel industry emissions
 - petroleum refinery emissions
 - waste incinerator exhaust
 - For winter samples: wood stove exhaust

4. Appropriate Data Set -
Designed to test CMB model

Data Set

- 80 days, 12 hour samples, equally distributed over 4 seasons, and equally divided into day/night intervals.

CMB Study Design

4. Appropriate Data Set -
Designed to test CMB model

Data Set

- Once-every-third-day sampling schedule to include all days of week equally.
- Inner city site in Chicago, 3 km west of Loop; 20 m above ground level.

4. Appropriate Data Set -
Designed to test CMB model

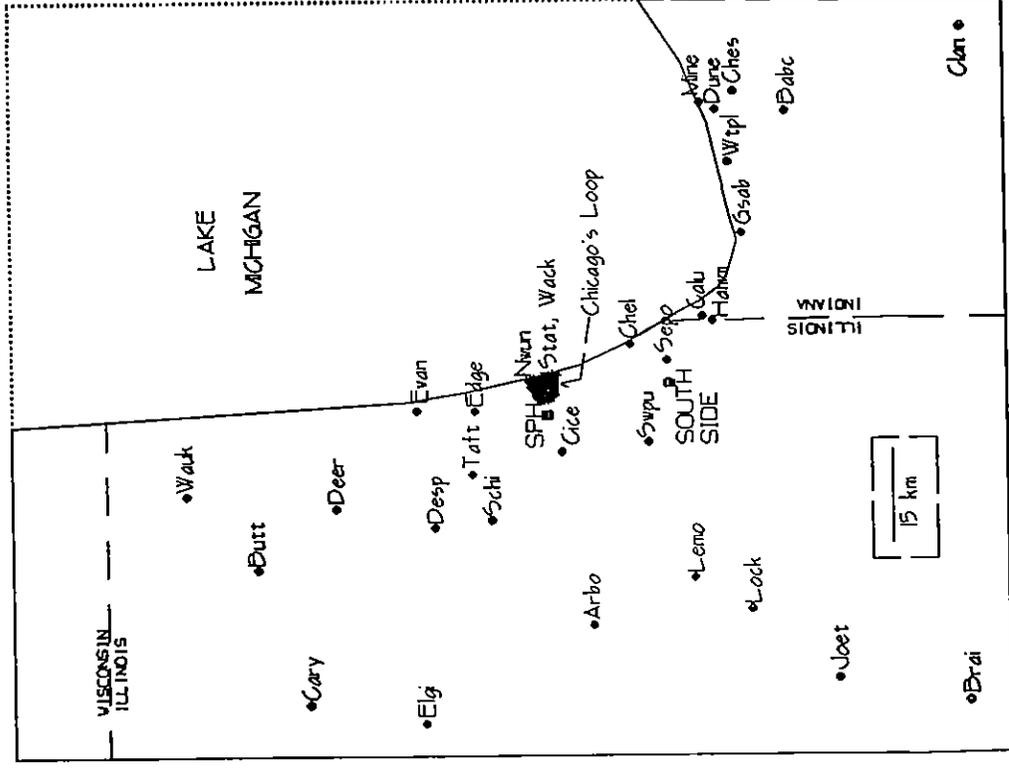
See Insert: Chicago Area Monitoring Stations

4. Appropriate Data Set -
Designed to test CMB model

Volatile Organics

- Collection in six-liter electro-polished stainless steel canisters using a constant mass-flow controlled bellows pump
- Analysis by high resolution gas chromatograph fitted with a cryogenic trap

4. Appropriate Data Set - Designed to test CMB model



Chicago Area Monitoring Stations

CMB Study Design

4. Appropriate Data Set -
Designed to test CMB model

Volatile Organics

- FID for 42 hydrocarbons, C₂'s through ethyl-toluene

- ECD for 15 non-ionizable halogenated volatiles

- FID for total NMHC

4. Appropriate Data Set -
Designed to test CMB model

Particulate Matter

- PM₁₀ gravimetrically determined with 4 cfm PM₁₀ samples, teflon filter.

- Elemental analysis on teflon filter using proton induced x-ray emission (PIXE), x-ray fluorescence (XRF), and neutron activation analyses (NAA).

4. Appropriate Data Set -
Designed to test CMB model

Particulate Matter

- Dichotomous sampler to determine respirable particulate matter (<2.5 um).

- PM₁₀ HiVol (40 cfm) sampler, fitted with a quartz filter, was used to collect samples for carbon analysis.

CMB Study Design

4. Appropriate Data Set -
Designed to test CMB model

Particulate Matter

- Organic and elemental carbon were determined by controlled stepwise volatilization.

4. Appropriate Data Set -
Designed to test CMB model

Criteria Pollutants

- Continuous monitoring carried out for CO (infra-red), O₃ (uv absorption), SO₂ (chemiluminescence) and NO/NO_x (chemiluminescence).

4. Appropriate Data Set -
Designed to test CMB model

Criteria Pollutants

- Temperature, uv, absolute humidity, windspeed and wind direction also measured at monitoring point.

CMB Study Design

4. Appropriate Data Set - Designed to test CMB model

Table I. Average Particle Characteristics

	<u>N</u>	<u>Mean</u>	<u>Sig</u>	<u>Min.</u>	<u>Max.</u>
	<u>ug/m³</u>				
PM _{2.5}	61	23.3	15.5	0	67.1
PM ₁₀	81	30.3	17	0.2	73.8
Elemental Carbon	80	1.6	1.1	0.21	5.7
Inorganic Carbon	80	0.3	0.4	<0.10	2.4
Organic Carbon	80	7.7	3.5	1.82	16.9

4. Appropriate Data Set - Designed to test CMB model

	<u>N</u>	<u>Mean</u>	<u>Sig</u>	<u>Min.</u>	<u>Max.</u>
	<u>ng/m³</u>				
Elements					
Na	81	378	574	23.8	3340
Mg	82	85.1	226	<402	880
Al	81	439	356	36.2	1760
Si	82	1210	1290	<56	7780
Cl	81	753	1000	1.5	4150
K	82	309	294	<10	2440

4. Appropriate Data Set - Designed to test CMB model

	<u>N</u>	<u>Mean</u>	<u>Sig</u>	<u>Min.</u>	<u>Max.</u>
	<u>ng/m³</u>				
Elements					
Ca	81	896	1000	22.7	6650
Ti	81	60.5	113	<6.2	654
V	81	1.8	2.4	0.1	15.7
Cr	81	3.77	4.37	<0.2	27.7
Mn	81	16.5	14.3	0.9	69.5
Fe	81	536	468	31.7	2440

CMB Study Design

4. Appropriate Data Set -
Designed to test CMB model

Elements	<u>N</u>	<u>Mean</u>	<u>Sig</u>	<u>Min.</u>	<u>Max.</u>
	ng/m ³				
Co	81	0.7	1.14	<0.01	5.76
Ni	81	2.14	3.11	<0.8	16.6
Cu	81	16.7	21.6	<2.5	160
Zn	81	93.6	108	3.8	770
As	81	0.38	0.34	<0.04	2.12
Ag	78	23.7	29.6	<0.98	134

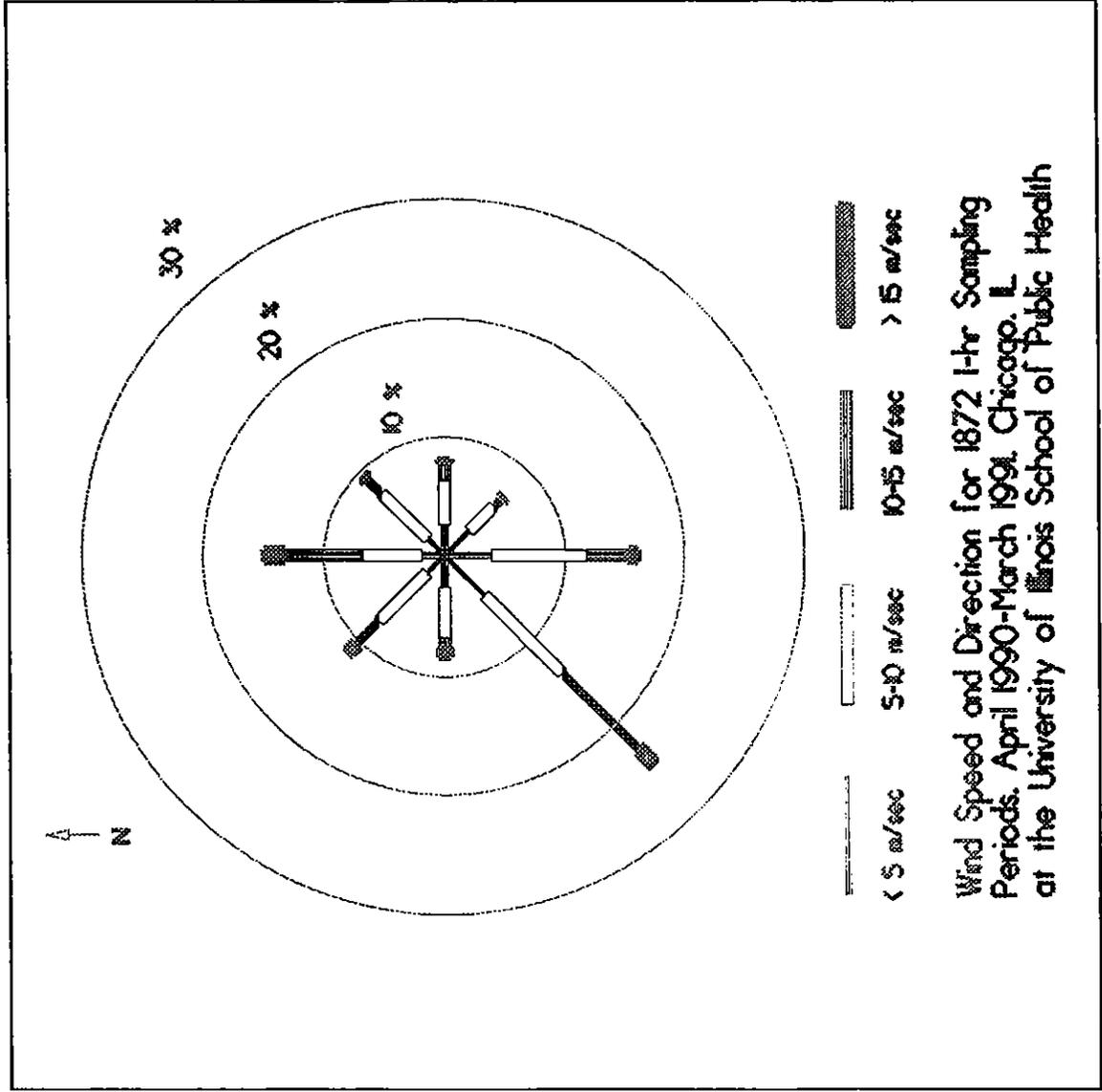
4. Appropriate Data Set -
Designed to test CMB model

Elements	<u>N</u>	<u>Mean</u>	<u>Sig</u>	<u>Min.</u>	<u>Max.</u>
	ng/m ³				
Cd	78	30.8	37.1	<0.17	192
Sn	78	52.9	97.4	<0.08	515
Sb	81	3.61	5.88	<0.13	41.4
Pb	78	246	239	9.3	1080

4. Appropriate Data Set -
Designed to test CMB model

See Insert: Wind Rose

4. Appropriate Data Set - Designed to test CMB model



CMB Study Design

4. Appropriate Data Set - Designed to test CMB model

Table II. Mean 12-Hour Values of Speciated NMOC

<u>Compound</u>	<u>N</u>	<u>Average Concentration ug/m³</u>			
		<u>Mean</u>	<u>Sig</u>	<u>Min.</u>	<u>Max.</u>
Ethane	60	9.9	5.3	<0.06	22.8
Ethylene	60	7.3	3.5	<0.06	16.7
Acetylene	60	5.2	2.7	<0.05	13.4
Propylene	60	2.2	1.4	<0.06	7.5
Propane	60	7.9	4.4	<0.06	21.9
i-Butane	64	7	12.7	<0.5	90.6

4. Appropriate Data Set - Designed to test CMB model

<u>Compound</u>	<u>N</u>	<u>Average Concentration ug/m³</u>			
		<u>Mean</u>	<u>Sig</u>	<u>Min.</u>	<u>Max.</u>
Butane	71	13	29.2	<0.5	241
2-M-butane	77	16.7	16.8	<0.5	75.8
Pentane	78	8.6	12.4	<0.5	71.6
2-M-pentane	77	7.14	8.69	<0.5	39.5
3-M-pentane	77	6.42	6.94	0.58	38.6
Hexane	78	9.19	17.9	<0.5	137
Benzene	78	7.64	6.83	1.23	38.1

4. Appropriate Data Set - Designed to test CMB model

<u>Compound</u>	<u>N</u>	<u>Average Concentration ug/m³</u>			
		<u>Mean</u>	<u>Sig</u>	<u>Min.</u>	<u>Max.</u>
Toluene	78	23.5	24.6	1.41	131
Ethylbenzene	78	8.77	22.7	<0.5	195
m&p Xylene	78	24.6	86.7	<0.5	763
o-Xylene	78	18.8	79.4	0.72	650
n-P-benzene	74	8.52	29.1	<0.5	247
Total Carbon	78	646	1010	50.9	6130
% Carbon Ident.	78	54.9	21.2	11.6	90.1

CMB Study Design

4. Appropriate Data Set - Designed to test CMB model

Halogenated Organics ug/m ³		Average Concentration			
Compound	N	Mean	Sig	Min.	Max.
Methylene Chlor.	65	19.5	34.2	<0.5	173
Chloroform	66	4.6	7.2	<0.5	40.5
Carbon Tet.	63	7.4	9.5	<0.5	33.6
Trichloroethylene	76	3.2	3.2	<0.5	13.7
1,1,1-TC-ethane	73	17.5	25.3	<0.5	124

4. Appropriate Data Set - Designed to test CMB model

12-Hour Values of Met. Observations & Crit. Pollutant Conc.

	N	Mean	Sig	Min.	Max.
CO, ppm	82	0.9	0.3	0.3	1.9
NO, ppb	82	23	21	3	112
NO ₂ , ppb	82	23	13	9	70
O ₃ , ppb	81	15	12	1	64
Max. hr. O ₃ , ppb	81	26	21	3	148
SO ₂ , ppb	82	9	8	0.3	39

4. Appropriate Data Set - Designed to test CMB model

	N	Mean	Sig	Min.	Max.
Press., mmHg	82	757	10	739	773
Temp., C	82	10.4	10	-12.6	29
Windspeed, mph	82	8.8	3.5	3.3	17.2
Abs. hum., g/kg	82	10	4	1	20

CMB Study Design

4. Appropriate Data Set - Extensive Data, CMB Application

Receptor Modeling approach to VOC Emission Inventory Validation-Kenski et al, J. Environ. Engin., **121**, 483-491, 1995.

- Purpose was to apply CMB to a speciated hydrocarbon data set collected in Detroit as part of EPA 39-city ozone precursor study; and to compare results with emission inventory.

4. Appropriate Data Set - Extensive Data, CMB Application

• Sources:

- vehicle exhaust
- gasoline vapor
- oil refineries
- graphic arts
- architectural coatings
- coke ovens

4. Appropriate Data Set - Extensive Data, CMB Application

Data Set

- Detroit, July-August 1988, central city site (inner city school).

- 39 weekdays, 1 hour samples, collected at 15ft. height, 5 times/day, 192 samples in all.

CMB Study Design

4. Appropriate Data Set - Extensive Data, CMB Application

- Analysis by Seila and Lonneman, U.S. EPA collection in 6-L, precleaned, electropolished, stainless steel canisters; cryogenic preconcentration followed by gas chromatographic separation and flame ionization detection.

4. Appropriate Data Set - Extensive Data, CMB Application

- With this sampling schedule there was a good chance to be sampling a representative wind-direction distribution.
- 29 hydrocarbons used in fingerprints

4. Appropriate Data Set - Extensive Data, CMB Application

See Insert: Major Point Sources of VOCs In Detroit

CMB Study Design

**4. Limited Data Set with CMB
Application - Budapest**

Air Pollution Source Apportionment in
Budapest - Javor et al, AWMA
Paper 92-164.04, Kansas City, 1992.

**4. Limited Data Set with CMB
Application - Budapest**

- **Very high concentrations of TSP**

- **Budapest the vehicular crossroads of the country because of limited number of bridges across the Danube.**

**4. Limited Data Set with CMB
Application - Budapest**

• **Large population of high-polluting old Trabant and Wartburg 2-stroke gas/oil-fueled cars and micro-buses previously imported from East Germany.**

• **Question to be answered was what fraction of TSP was from vehicles**

CMB Study Design

4. Limited Data Set with CMB
Application - Budapest

See Insert: Budapest Continuous Air Monitoring Stations

4. Limited Data Set with CMB
Application - Budapest

Data Set

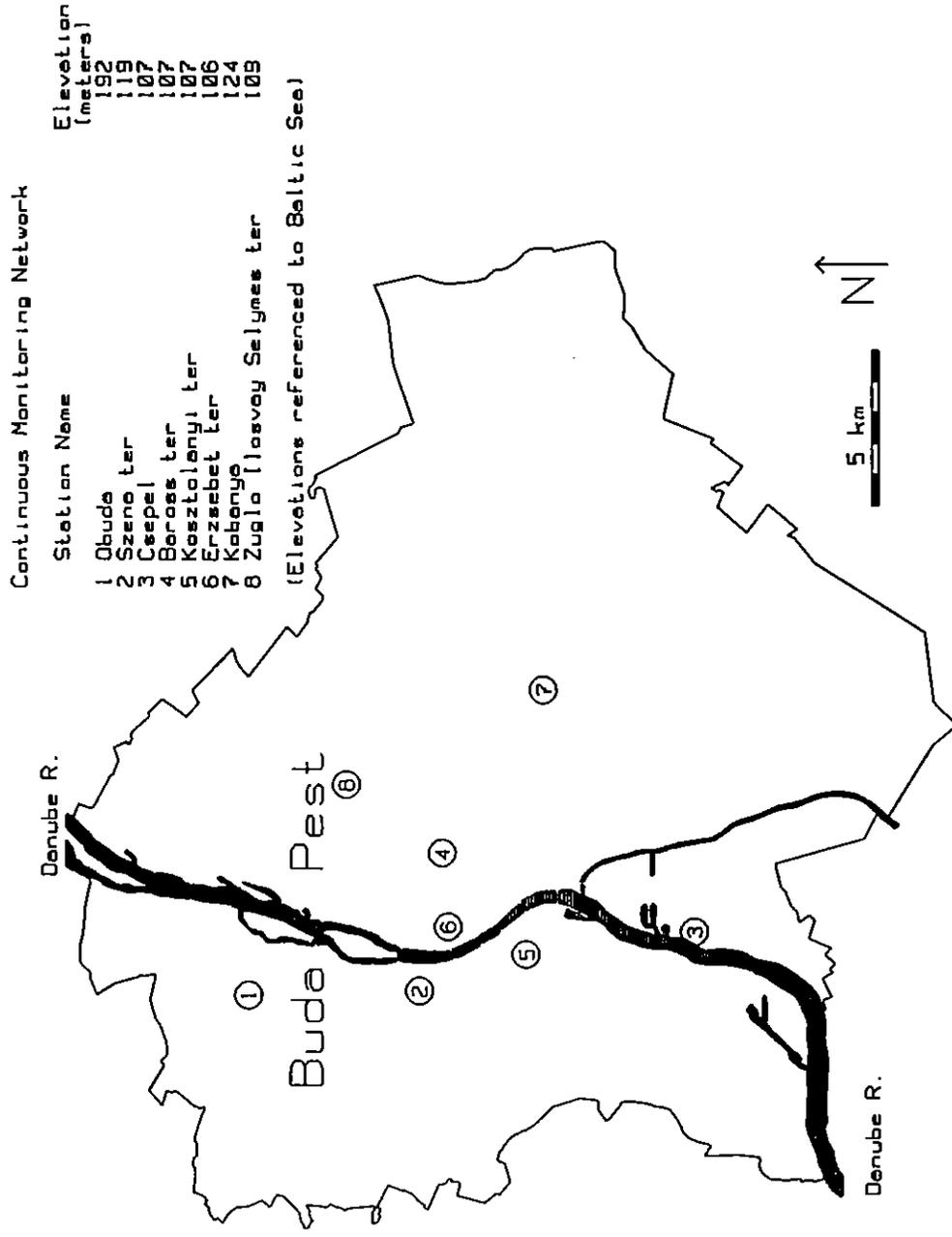
- 12, 6-hour TSP samples from a central city location (Szena Ter) collected between March and August 1991.

- Analyzed in Hungary for Pb and Cd by atomic absorption spectrometry; filters subsequently analyzed for 24 other elements by AA, XRF, and NAA.

4. Limited Data Set with CMB
Application - Budapest

- Determined fingerprints from soil samples and for vehicles from tunnel sample.

4. Limited Data Set with CMB Application - Budapest



Budapest Continuous Air Monitoring Stations

CMB Study Design

4. Limited Data Set with CMB Application - Budapest

<u>1991 Filter Collection Date</u>	<u>ug/m³</u>		
	<u>TSP</u>	<u>Cd</u>	<u>Pb</u>
March 12	451	0.0057	1.45
March 20	212	0.0027	1.07
April 10	372	0.0075	1.06
April 18	137	0.0053	0.58
May 14	224	0.0031	0.56
May 23	222	0.0043	0.81
June 6	314	0.0062	1.17

4. Limited Data Set with CMB Application - Budapest

<u>1991 Filter Collection Date</u>	<u>ug/m³</u>		
	<u>TSP</u>	<u>Cd</u>	<u>Pb</u>
June 25	208	0.0074	0.88
July 4	190	0.0020	0.44
July 31	251	0.0045	0.62
August 6	174	0.0017	0.62
August 14	219	0.0035	0.87
Average	247.5	0.0045	0.84

4. Limited Data Set with CMB Application - Budapest

Chemical composition, mg/g TSP

<u>Element</u>	<u>Budapest Soil</u>	<u>Vehicle Emissions</u>
		<u>Budapest Tunnel</u>
Al	53	4.1
Si	218	13
S	0.59	5.9
Cl	0.11	0
K	16	0

CMB Study Design

4. Limited Data Set with CMB Application - Budapest

<u>Element</u>	<u>Budapest Soil</u>	Vehicle Emissions
		<u>Budapest Tunnel</u>
Sc	0.01	0
Cr	0.066	0.044
Mn	0.52	0.16
Fe	27	6.8
Co	0.0086	0
Ni	0.026	0.037

4. Limited Data Set with CMB Application - Budapest

<u>Element</u>	<u>Budapest Soil</u>	Vehicle Emissions
		<u>Budapest Tunnel</u>
Cu	0.028	1
Se	0.0006	0
Br	0.0043	4.8
Rb	0.078	0
Cd	0.00047	0.009
Sn	0.0047	1.9

4. Limited Data Set with CMB Application - Budapest

<u>Element</u>	<u>Budapest Soil</u>	Vehicle Emissions
		<u>Budapest Tunnel</u>
Sb	0.0018	0.012
Cs	0.0055	0
Ce	0.06	0
Sm	0.005	0
Ta	0.001	0
Pb	0.084	13
Th	0.009	0

CMB Study Design

4. Limited Data Set with CMB Application - Budapest

- Based on CMB evaluation of each of the 12 samples.

- Only 22% of measured TSP was allocated to vehicular emissions and 1.8% to soil.

- 76% of TSP was likely to have come from other sources.

4. Limited Data Set with CMB Application - Budapest

- 83% of Pb could be allocated to vehicles, but most elements had large residuals indicating other sources of particulate matter.

- For example, only 13% of ambient Cd and 14% of S could be explained by vehicles and soil.

4. Limited Data Set, CMB Application - Chernivtsi, Ukraine

Scheff et al, Toxic Air Pollutants in Chernivtsi, Ukraine, Environ, International, 23, 273-290, 1997.

- City in southwest Ukraine, population of 230,000, considerable industry including factories previously operated by the military.

- Monitoring was in response to outbreak and ongoing occurrence of childhood illness.

CMB Study Design

**4. Limited Data Set, CMB
Application - Chernivtsi, Ukraine**

- **8, 24-hour particulate samples, Oct.-Nov. 1990; 1 station.**

- **Wind speed/direction available from meteorological station.**

- **Collected and analyzed vehicle exhaust and soil samples.**

**4. Limited Data Set, CMB
Application - Chernivtsi, Ukraine**

- **Analysis of ambient teflon filters and source samples by Proton Induced X-ray Emission Spectroscopy and by either X-ray fluorescence or Instrumental Neutron Activation.**

**4. Limited Data Set, CMB
Application - Chernivtsi, Ukraine**

- **Carbon determined from additional samples collected on quartz filters.**

- **25 site-specific elemental concentrations in fingerprints for vehicles and soil.**

CMB Study Design

4. Limited Data Set, CMB
Application - Chernivtsi, Ukraine

See Insert: Air Pollution Sources, Chernivtsi, Ukraine

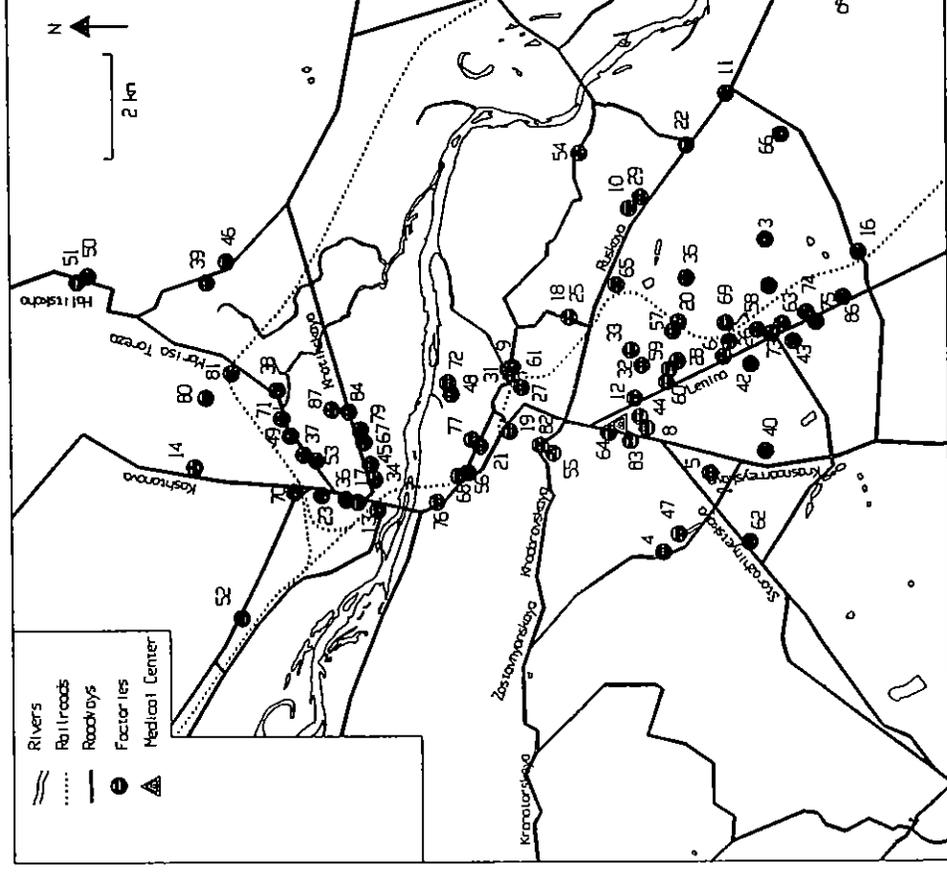
4. Limited Data Set, CMB
Application - Chernivtsi, Ukraine

<u>Element</u>	<u>Source Composition, mg/g</u>		<u>Average</u>
	<u>soil</u>	<u>vehicle</u>	<u>ambient ug/m³</u>
Na	6	17	0.48
Al	51	4.1	1.8
Si	313	13.1	7.2
S	0.59	97	5.8
Cl	0.11	3.0	0.66
K	14	1.5	1.3
Ca	12	23	2.9

4. Limited Data Set, CMB
Application - Chernivtsi, Ukraine

<u>Element</u>	<u>Source Composition, mg/g</u>		<u>Average</u>
	<u>soil</u>	<u>vehicle</u>	<u>ambient ug/m³</u>
Ti	3.2	0.079	0.27
V	0.047	0.04	0.016
Cr	0.083	0.044	0.022
Mn	0.69	0.16	0.077
Fe	22	6.8	2.1
Co	0.0098	0.0082	0.001
Ni	0.026	0.18	0.042

4. Limited Data Set, CMB Application - Chernivtsi, Ukraine



Air Pollution Sources, Chernivtsi, Ukraine

CMB Study Design

4. Limited Data Set, CMB Application - Chernivtsi, Ukraine

<u>Element</u>	<u>Source Composition, mg/g</u>		<u>Average</u>
	<u>soil</u>	<u>vehicle</u>	<u>ambient ug/m³</u>
Cu	0.025	1.6	0.041
Zn	0.2	0.87	0.16
Ga	0.0046	0	0.005
Ge	0.007	0.13	0.004
Br	0.0043	3.5	0.1
Rb	0.075	0	0.015
Sr	0.076	4.5	0.067

4. Limited Data Set, CMB Application - Chernivtsi, Ukraine

<u>Element</u>	<u>Source Composition, mg/g</u>		<u>Average</u>
	<u>soil</u>	<u>vehicle</u>	<u>ambient ug/m³</u>
Y	0.019	0	0.12
Zr	0.024	0	0.016
Mo	0.011	0	0.034
Ag	0.0011	1.3	0.062
Cd	0.0005	0.96	0.088
Sn	0.0047	16	0.58
Pb	0.068	6.3	0.22

4. Limited Data Set, CMB Application - Chernivtsi, Ukraine

<u>Element</u>	<u>Source Composition, mg/g</u>		<u>Average</u>
	<u>soil</u>	<u>vehicle</u>	<u>ambient ug/m³</u>
Th	0.008	0	0.0002
OC	20%	55%	32.3
EC	0	5.9%	4.1

CMB Study Design

4. Limited Data Set, CMB
Application - Chernivtsi, Ukraine

- Average total particulate matter was 144 $\mu\text{g}/\text{m}^3$, with a minimum of 62 $\mu\text{g}/\text{m}^3$ and a maximum of 298 $\mu\text{g}/\text{m}^3$.

- 26% of particulate matter allocated by CMB to wind-blown soil and 8.3% to vehicle emissions.

4. Limited Data Set, CMB
Application - Chernivtsi, Ukraine

- The remaining 66% due to unmodelled sources (i.e. the residual). However, a trajectory analysis combined with an existing emission inventory indicated many industrial sources were the cause of the residual.

4. Limited Data Set, CMB
Application - Chernivtsi, Ukraine

- The suspected cause of children's illnesses heavy metals, e.g., Th) was no longer present in ambient air during this sampling period.

Lesson V

Ambient Measurements in Support of Receptor Modeling

Robert Stevens

Peter Scheff

INTRODUCTION TO RECEPTOR MODELING

Lesson Title: Ambient Measurements

Lesson: V

Prepared By: R. Stevens, P. Scheff

Date: February 10, 1998

Lesson Goal: This session focuses on the ambient measurement of parameters that need to be determined from the chemical and physical analyses of PM-10 particles in order to calculate the contribution of local and regional sources from statistical receptor models, such as EPA's Chemical Mass Balance (CMB-8) model.

Lesson Objectives: At the completion of this lesson students will be able to:

Explain the requirements for ambient air measurements, including the chemical and physical analysis of PM10, to support the calculation of local and regional source concentrations using receptor models.

Explain the importance of particle size in receptor modeling studies.

Explain the characterization and operation of size selective inlets.

Explain the operation of the dichotomous sampler.

List at least five options in selecting a particulate matter sampling method.

List at least six different ways ambient samples of particulate matter are analyzed for receptor modeling studies.

Explain how to quantify uncertainty in ambient concentration measurements.

Explain how ambient volatile organic compounds (VOC) and semi-volatile organic compounds (SVOC) can be measured in receptor modeling studies.

Explain the importance of quality assurance in support of receptor modeling studies.

INTRODUCTION TO RECEPTOR MODELING

LESSON V OUTLINE

I. Introduction - Objectives

II. The Rationale for Using Dichotomous and Fine Particle Samplers to Collect Samples to Characterize Aerosols.

A. The bimodal nature of atmospheric suspended particles.

1. Size distribution
2. Chemistry of fine and coarse particles

B. The dichotomous sampler and the principle of virtual impaction.

1. The d-50 cut point of the PM-10 inlet
2. The d-50 cut point of the virtual impactor of the dichotomous sampler
3. The d-50 cut point of the fine particle sampler with cyclone inlet
4. The d-50 cut point characteristics of EPA's WINS Impactor inlet

III. Filter Characteristics for Obtaining Fine and Coarse Particle Mass Concentrations.

IV. Annular Denuder System for Collecting Acidic and Basic Gases and Particles Simultaneously.

V. Energy Dispersive X-ray Fluorescence Analyzer

A. Alternative methods for determining trace elements.

VI. Carbon Analyzer for Measuring Elemental and Volatilizable Organic Carbon.

VII. Quality Assurance Considerations in Sampling and Analysis.

VIII. Questions on This Session.

IX. Summary

***Ambient Sampling and
Analysis Methods in
Support of Receptor Modeling***

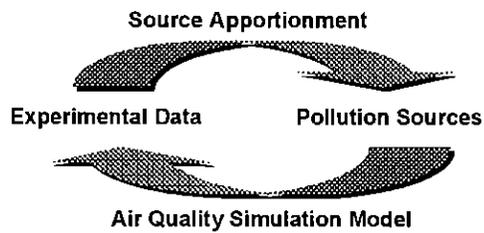
**Robert K. Stevens
FL DEP @ USEPA, RTP, NC**

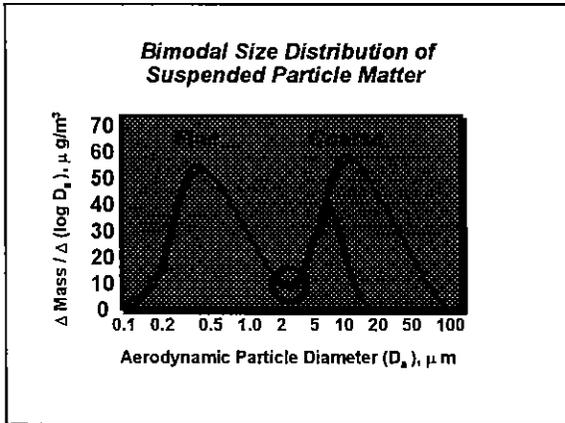
**Peter A. Scheff
Univ. of IL @ Chicago, IL**

Presentation Outline

- 1. Aerosol Characteristics and Sampling Methods**
- 2. Analysis Methods**
- 3. Quality Assurance**

Source - Receptor Modeling Approaches





- PM10 Composition & Chemical Characteristics**
- | | |
|---|---|
| <p>Fine Fraction</p> <ul style="list-style-type: none"> ▸ Acidic (pH < 7) ▸ Sulfates ▸ Organic carbon ▸ Elemental carbon ▸ Toxic metals: pb, as, cd ▸ Ammonium ions ▸ Nitrates | <p>Coarse Fraction</p> <ul style="list-style-type: none"> ▸ Basic (pH > 7) ▸ Windblown soil ▸ Roadway dust ▸ Industrial fugitive emissions ▸ Biological particles: pollen, vegetation, mold, spores. ▸ Some nitrates and sulfates |
|---|---|

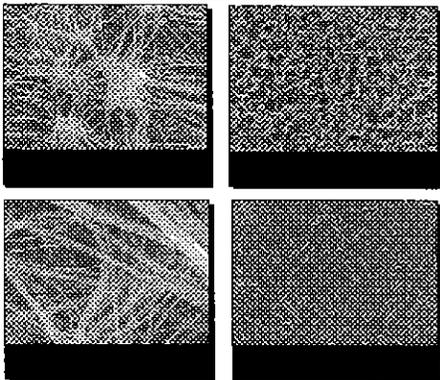
- Chemical and Physical Measurements of Aerosols Needed to Support Receptor Modeling.**
- Collect fine and coarse particles.
 - Collect samples on teflon and quartz filters.
 - Measure mass of fine and coarse particles.
 - Measure elemental composition. Measure ionic species, sulfates, nitrates.
 - Organic and elemental carbon analysis, (SEM).
 - Scanning electron microscopy analysis.

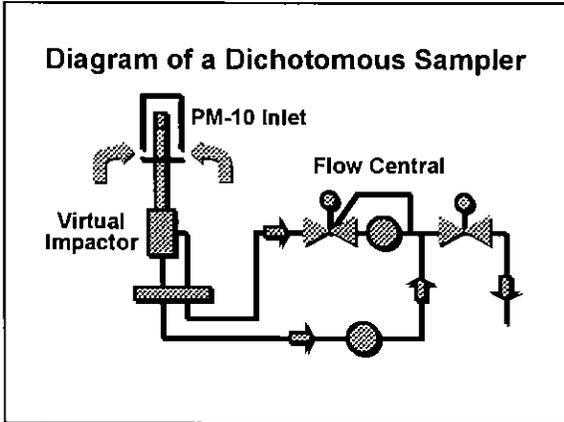
***Rationale for Use of
Dichotomous Sampler in
Receptor Modeling Studies***

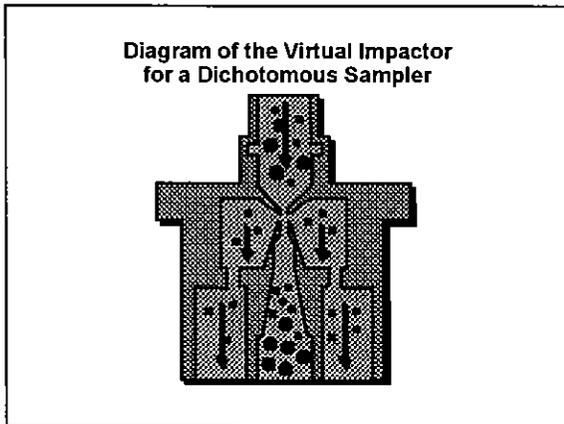
- ▶ Fine and coarse particles originate from different sources.
- ▶ Virtual impactor provides a sharp separation between fine and coarse particles.
- ▶ Provides an approved sample for both pm-10 and pm-2.5 mass measurements.
- ▶ Coarse particle fraction ideal SEM analysis.

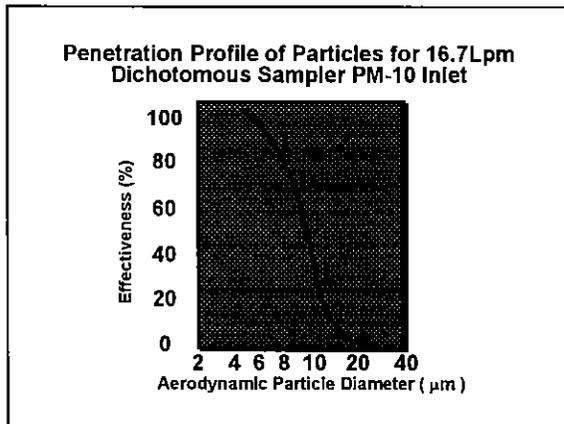
Properties of Filters Used to Collect Particle Samples

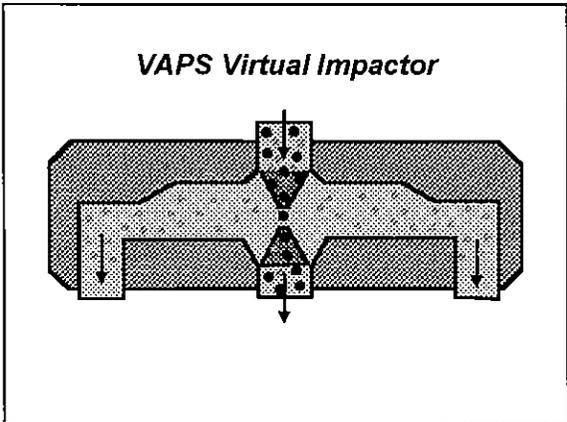
See Chart



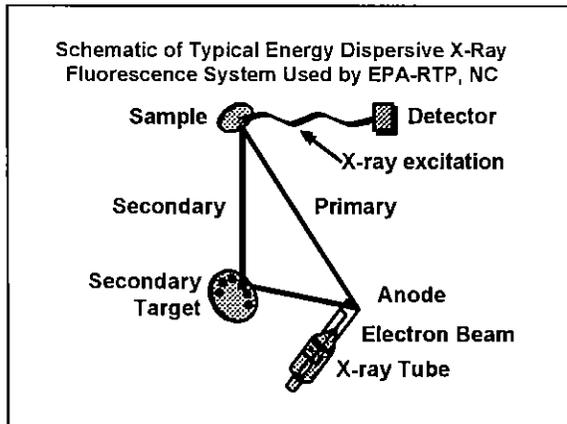




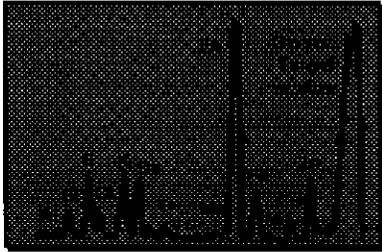




- Analytical Methods Needed in Support of PM Aerosol Characterization**
- ▶ Microanalytical balance
 - ▶ Energy dispersive x-ray fluorescence analyzer
 - ▶ Ion chromatographic analyzer for anions and cations
 - ▶ Combustion analyzer for carbon (c_o, c_v)
 - ▶ Scanning electron microscope



Example of XRF Spectra for Aerosols



*Schematic of Thermal-Optical
Carbon Analyzer*

See Handout

*Alternate Methods for
Measuring Trace Elements*

- ▶ Instrumental neutron activation analysis
- ▶ Atomic absorption spectrometry
- ▶ Proton induced x-ray emission spectroscopy
- ▶ Inductively coupled plasma emission spectroscopy

SCHEMATIC OF THERMAL-OPTICAL CARBON ANALYZER

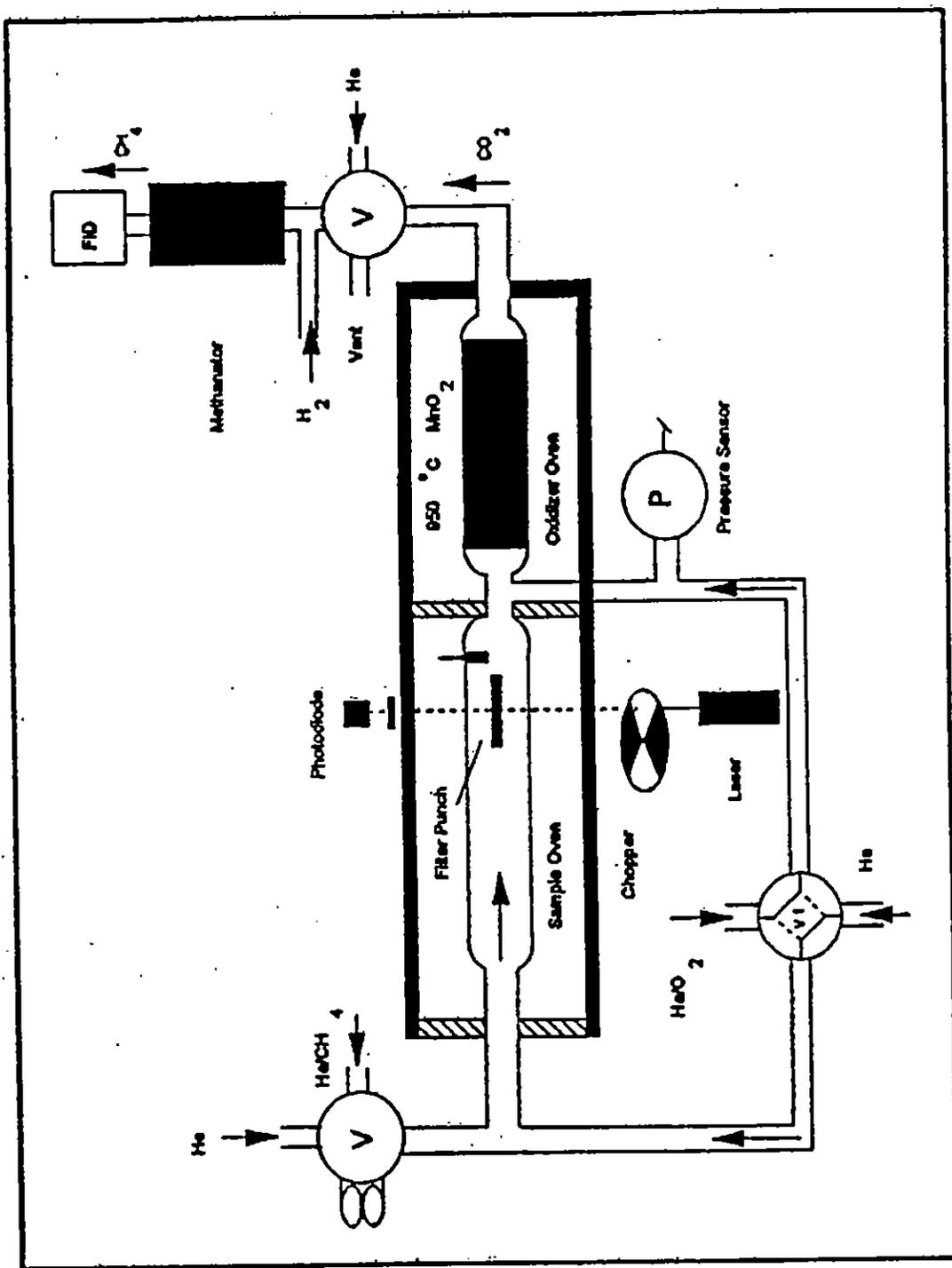
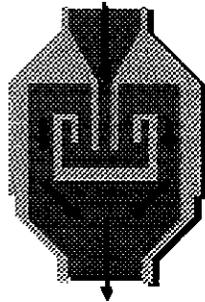


Diagram of a WINS Impactor with PM-10 Inlet

See Handout

SCHEMATIC OF 2.5um WINS IMPACTOR



Fine Particle-Annular Denuder Sampler

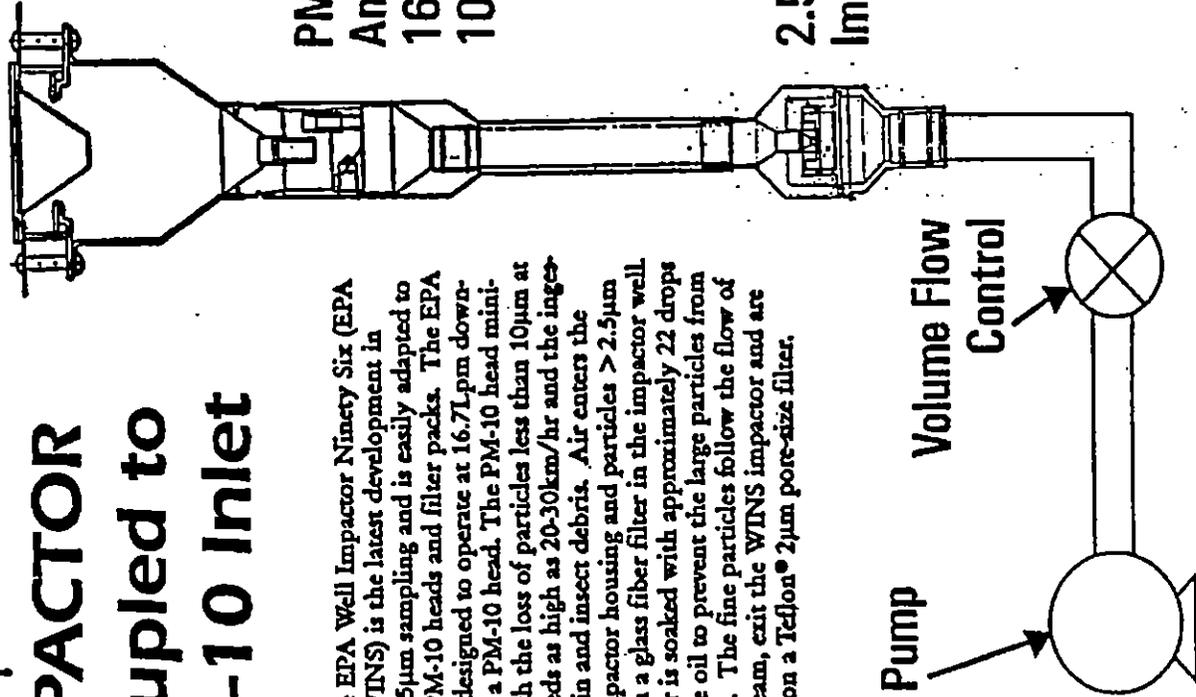
See Handout

2.5 μ m WINS IMPACTOR Coupled to PM-10 Inlet

Diagram of a WINS IMPACTOR with PM-10 Inlet

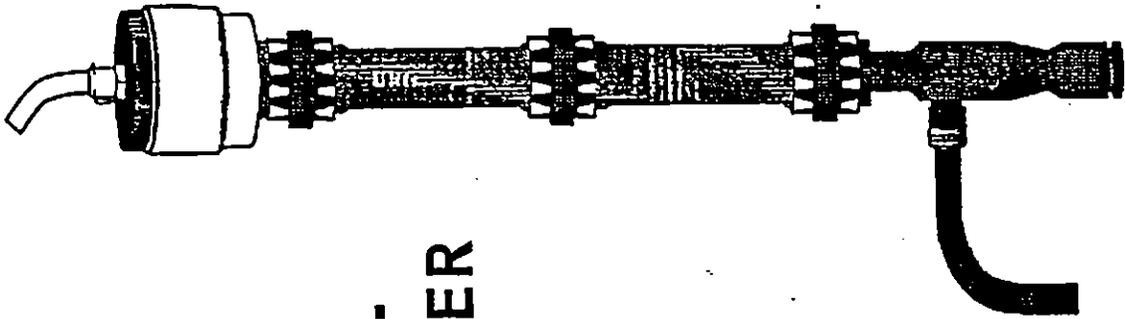
PM-10 Head
Anodized
16.7Lpm,
10 μ m

2.5 μ m WINS
Impactor



The EPA Well Impactor Ninety Six (EPA WINS) is the latest development in 2.5 μ m sampling and is easily adapted to existing PM-10 heads and filter packs. The EPA WINS is designed to operate at 16.7Lpm downstream of a PM-10 head. The PM-10 head minimizes both the loss of particles less than 10 μ m at wind speeds as high as 20-30km/hr and the ingestion of rain and insect debris. Air enters the WINS impactor housing and particles > 2.5 μ m impact on a glass fiber filter in the impactor well. This filter is soaked with approximately 22 drops of silicone oil to prevent the large particles from bouncing. The fine particles follow the flow of the airstream, exit the WINS impactor and are collected on a Teflon[®] 2 μ m pore-size filter.

**FINE PARTICLE-
ANNULAR DENUDER
SAMPLER**

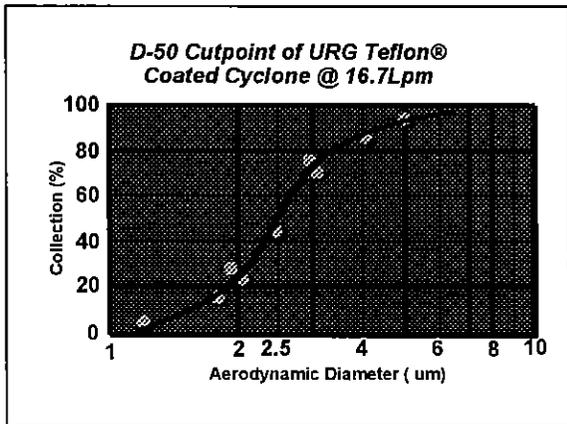


**2-STAGE FILTER PACK
47MM DIAMETER**

**ANNULAR DENUDER
COATED WITH CITRIC ACID
TO COLLECT NH_3**

**ANNULAR DENUDER
COATED WITH SODIUM CARBONATE
TO COLLECT ACIDIC GASES**

**TEFLON® COATED CYCLONE
2.5 μm**



Typical Aerosol Composition Samples Collected with VAPS, 1993 Czech Republic

	Fine	Coarse
MASS ($\mu\text{g}/\text{m}^3$)	122	19
Organic carbon ($\mu\text{g}/\text{m}^3$)	34	N/A
Elemental Carbon ($\mu\text{g}/\text{m}^3$)	2.3	N/A
Metal Oxides ($\mu\text{g}/\text{m}^3$)	6.5	14
Sulfat ($\mu\text{g}/\text{m}^3$)	42	N/A
Sum of PAHS ($\mu\text{g}/\text{m}^3$)	0.3	N/A

Typical Aerosol Composition

See Handout

TYPICAL AEROSOL COMPOSITION FROM SAMPLES
COLLECTED WITH VAPS, 1993 CZECH REPUBLIC

RESULTS
OF XRF
ANALYSIS
OF FINE
AND
COARSE
AEROSOLS

Species	January-March	
	Fine	Coarse
SO ₂ (µg/m ³)	147	
Particulate Matter (µg/m ³)	122	18.5
Trace Elements (ng/m ³)		
Al	830	2020
Si	940	3240
S	10140	nd
Cl	430	95.1
K	300	204
Ca	145	574
Ti	71.3	153
V	11.7	nd
Cr	5.9	nd
Mn	18.9	12.3
Fe	380	820
Cu	14.1	6.6
Zn	160	17.6
Ga	1.6	nd
As	44.5	nd
Se	8.1	nd
Br	18.5	4.4
Pb	108	6.8

How is the SEM used in Environmental Studies?

- ▶ As a complementary method to bulk analytical techniques
- ▶ Source identification/apportionment
- ▶ To investigate soiling of building materials

Continued on next slide

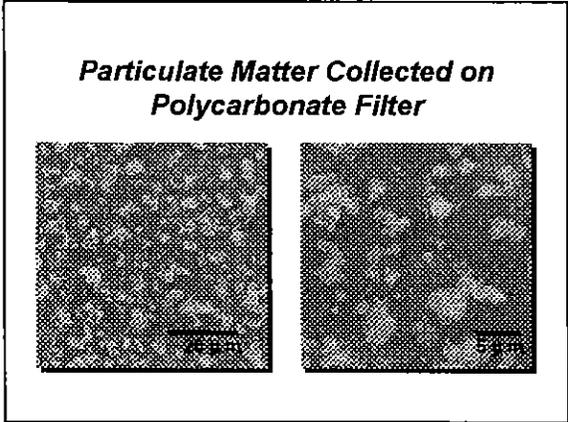
How is the SEM used in Environmental Studies?

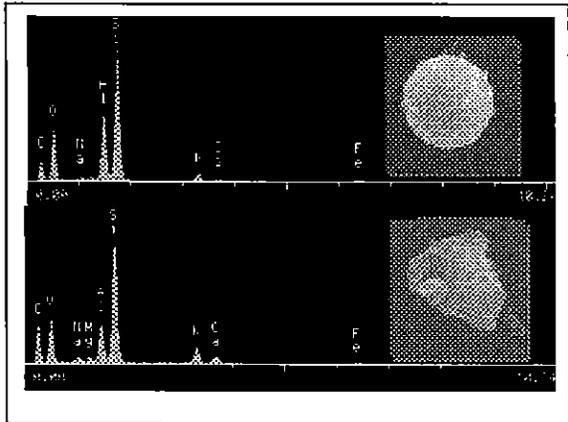
- ▶ To provide better understanding of health effects related to particulate matter
- ▶ PM_{2.5} NAAQS analysis requirements

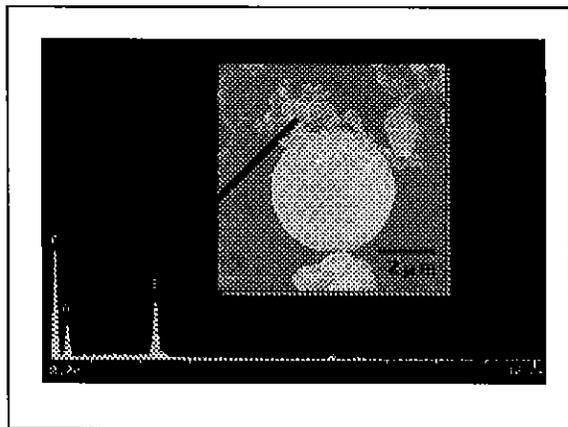
Particulate Matter Collected on Teflon Filter

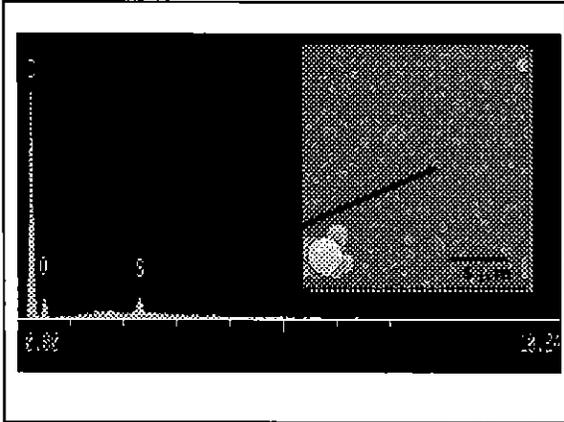


Ambient Measurements in Support of Receptor Modeling









Quality Assurance Rationale

- ▶ Detecton and control of systematic and random errors

Components of a QA Program in Support of Receptor Modeling

- ▶ Receptor site selection
- ▶ Sampling and analysis methods selection
- ▶ Written sop's
- ▶ Flow audits
- ▶ Field blanks (analysis of background)

Continued on next slide

Components of a QA Program in Support of Receptor Modeling

- ▶ Duplicate samples (analysis of precision)
- ▶ Split samples (analysis of bias)
- ▶ Calibration procedures (standard tractability)
- ▶ Analytical laboratory statistical quality control

Quality Assurance Recommendations

- ▶ Collect one field blank for every 10 samples
- ▶ Split 10% of samples to be analyzed by a reference method for measurement of bias
- ▶ Collect duplicate samples (1 set for every 10 measurements)

References on Sampling and Analysis Methods for Receptor Modeling

Whitby, K. T.; Charlson, R. E.; Wilson, W. E.; Stevens, R. K.; "The Size of Suspended Particle Matter in Air", *Science* 183: 1098-1099, 1974.

Stevens, R. K.; "Modern Methods to Measure Air Pollutants"; In: *Aerosols: Research, Risk Assessment and Control Strategies*, ed. by Lee et al., Lewis Publishers, pp 69-95, 1986.

Dzubay, T. G.; Stevens, R. K.; et al.; "A Composite Receptor Model Applied To Philadelphia"; *Environ Sci. Technol.* 22, 46-52, 1988.

Dzubay, T.G. and Stevens, R.K.; "Sampling Methods for PM-10 Aerosol" In *Receptor Modeling for Air Quality Management*, ed., Phillip K. Hopke, Elsevier Science Publ., pp 11-44, 1991.

Loo, B. W. and Cork, C.P.; "Development of High Efficiency Virtual Impactors"; *Aerosol Sci. Technol.*, 9, 167-176, 1988.

Lesson VI

Introduction to Optical Microscopy
Ronald Draftz

INTRODUCTION TO RECEPTOR MODELING

Lesson Title: Introduction to Optical Microscopy

Lesson: VI

Prepared By: R. Draftz

Date: February 11, 1998

Lesson Goal: This session provides information on the use and applicability of polarized light microscopy for identifying atmospheric aerosols and source apportionment. This lesson includes descriptions of the key microscopical characteristics of particles used to distinguish aerosols and their sources for common atmospheric constituents. Comparisons and contrasts are presented between polarized light microscopy and other frequently used analytical methods to explore the benefits and limitations of each methods.

Lesson Objectives: At the completion of this lesson students will be able to:

Explain how polarized light microscopy is used to distinguish atmospheric aerosols and their sources.

Describe the advantages and disadvantages of using polarized light microscopy to determine source impacts compared to the other commonly used analytical methods --- elemental analyses (x-ray fluorescence, etc.), x-ray diffraction and scanning electron microscopy

Explain the fundamental identifying properties used to distinguish particle types

morphology (size, shape, symmetry, surface texture, agglomeration)

physical (magnetism, solubility, melting point, combustibility)

optical (transparency, color, fluorescence, edge contrast in mounting media)

crystallography (polarization colors, birefringence, pleochroism, extinction)

Describe the compatibility of polarized light microscopy with sampling media such as quartz fiber, glass fiber, and various membrane filters.

Discuss the ability of polarized light microscopy to perform source apportionment without source samples.

INTRODUCTION TO RECEPTOR MODELING

LESSON VI OUTLINE

I. Lesson Overview

II. What polarized light microscopy provides

- A. Source Distinction
- B. Sampling Media Compatibility
- C. Source Impact Assessment without Source Sampling
- D. Mass Conservation Assumption Unnecessary

III. Particle properties used for identification of aerosols/sources

- A. Morphological
- B. Optical
- C. Physical
- D. Crystallographic

IV. Lesson Summary

- A. One of the best methods for aerosol and source distinction
- B. Can analyze historical filters without particle removal
- C. Source samples unnecessary

Lesson VI

**Fundamentals of Polarized Light Microscopy
for
Aerosol Source Apportionment**

Ronald G. Draftz

Lesson VI Objectives

- ▶ Why PLM Analyses for Receptor Modeling?
- ▶ How Are Particles Identified by PLM?

Why PLM Analyses? I

- ▶ Source Distinctiveness

Source Distinctiveness

- ▶ Can distinguish Flyash from Soils/Pavement
- ▶ Can readily distinguish biologicals, e.g., wood/paper fiber, starch, pollens/spores, etc.
- ▶ Can distinguish raw coal, coke & partially pyrolyzed coal

Why PLM Analyses? II

- ▶ Source Distinctiveness
- ▶ Can Directly Utilize Quartz/Glass Filters

Sampling Media Compatibility

- ▶ Can Be Directly Applied to Historical Samples of Concern
- ▶ Does Not Require Particle Removal for Analysis

Why PLM Analyses? III

- ▶ Source Distinctiveness
- ▶ Can Directly Utilize Quartz/Glass Filters
- ▶ Does Not Require Source Sampling

Eliminates Need for Source Sampling

- ▶ Elemental Analyses Require Ratioing Elements to Mass; PLM Does Not.
- ▶ Reference Materials (Usually) Can Be Easily Obtained
- ▶ Handbook Values Are Usually Adequate for Identification

Why PLM Analyses? IV

- ▶ Source Distinctiveness
- ▶ Can Directly Utilize Quartz/Glass Filters
- ▶ Does Not Require Source Sampling
- ▶ Does Not Presume Mass Conservation

Mass Conservation Is Unnecessary For PLM

- ▶ PLM Analyses Uses Mass Additivity for Source Components
- ▶ Mass Conservation is Necessary But Presumptive for Elemental Analyses
 - ▶ Assumes That Particle Composition Is Uniform & Constant for a Source, or
 - ▶ Sedimentation During Transport Has No Effect

What Does PLM Use to Identify A Source?

- ▶ PLM does not identify sources, per se, but identifies particles
- ▶ Knowledge of the Particles Comprising the Source Leads to Source Impact/Contribution

What Particle Properties Does PLM Use for Identification?

- ▶ Morphological
- ▶ Optical
- ▶ Physical
- ▶ Crystallographic

Morphological Properties I

- ▶ Shape/Symmetry (Slides 1-4)

Morphological Properties II

- ▶ Shape/Symmetry (Slides 1-4)
- ▶ Surface Texture (Slides 5-7)

Morphological Properties III

- ▶ Shape /Symmetry (Slides 1-4)
- ▶ Surface Texture (Slides 5-7)
- ▶ Size (Slide 8)

Morphological Properties IV

- ▶ Shape /Symmetry (Slides 1-4)
- ▶ Surface Texture (Slides 5-7)
- ▶ Size (Slide 8)
- ▶ Agglomeration/Aggregation (Slides 9-10)

Physical Properties I

- ▶ Magnetism (Slide 11)

Physical Properties II

- ▶ Magnetism (Slide 11)
- ▶ Solubility

Physical Properties III

- ▶ Magnetism (Slide 11)
- ▶ Solubility
- ▶ Melting Point/Sublimation

Physical Properties IV

- ▶ Magnetism (Slide 11)
- ▶ Solubility
- ▶ Melting Point/Sublimation
- ▶ Combustibility

Optical Properties I

- ▶ Transparency/Translucency/Opacity (Slide 12)

Optical Properties II

- ▶ Transparency/Translucency/Opaclty (Slide 12)
- ▶ Transmitted Light Color (Slide 13)

Optical Properties III

- ▶ Transparency/Translucency/Opaclty (Slide 12)
- ▶ Transmitted Light Color (Slide 13)
- ▶ Reflected Light Color/Luster (Slides 14-15)

Optical Properties IV

- ▶ Transparency/Translucency/Opaclty (Slide 12)
- ▶ Transmitted Light Color (Slide 13)
- ▶ Reflected Light Color/Luster (Slides 14-15)
- ▶ UV Fluorescence

Optical Properties V

- ▶ Transparency/Translucency/Opacity (Slide 12)
- ▶ Transmitted Light Color (Slide 13)
- ▶ Reflected Light Color/Luster (Slides 14-15)
- ▶ UV Fluorescence
- ▶ Contrast/Refractive Index (in mounting medium) (Slides 16-17)

Crystallographic Properties I

- ▶ Polarization Colors/Birefringence (Slide 18-20)

Crystallographic Properties II

- ▶ Polarization Colors/Birefringence (Slide 18-20)
- ▶ Pleochroism

Crystallographic Properties III

- ▶ Polarization Colors/Birefringence (Slide 18-20)
- ▶ Pleochroism
- ▶ Refractive Indices (Slide 21)

Crystallographic Properties IV

- ▶ Polarization Colors/Birefringence (Slide 18-20)
- ▶ Pleochroism
- ▶ Refractive Indices (Slide 21)
- ▶ Extinction Angles (Slide 22)

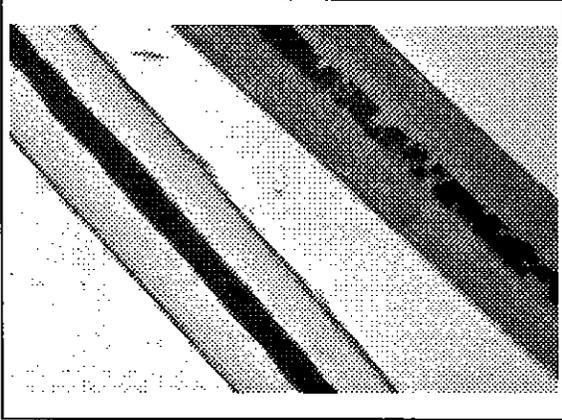
Crystallographic Properties V

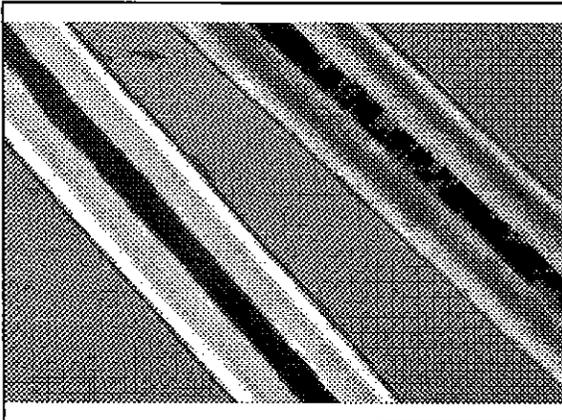
- ▶ Polarization Colors/Birefringence (Slide 18-20)
- ▶ Pleochroism
- ▶ Refractive Indices (Slide 21)
- ▶ Extinction Angles (Slide 22)
- ▶ Interference Figures

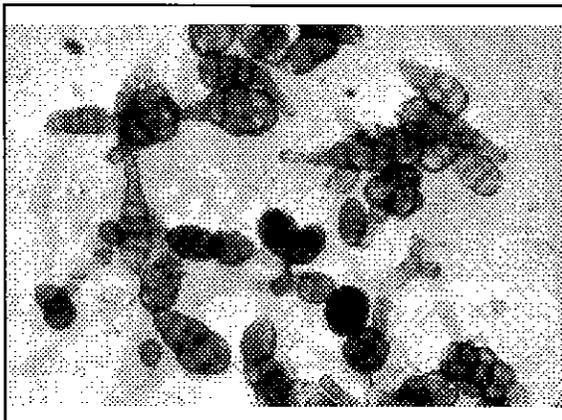
Lesson VI Summary

- ▶ PLM Offers the Best Opportunity for Source Resolution
- ▶ PLM Can Utilize Historical Filters on Glass/Quartz Fiber Eliminating the Need for Special Sampling Programs
- ▶ Few, If Any, Source Samples Are Needed, Again Reducing Program Costs

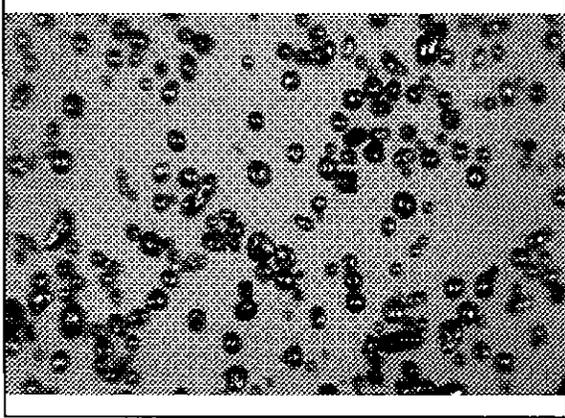
Optical Microscopy

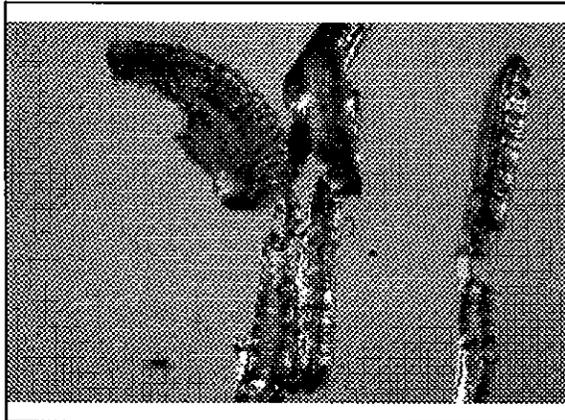






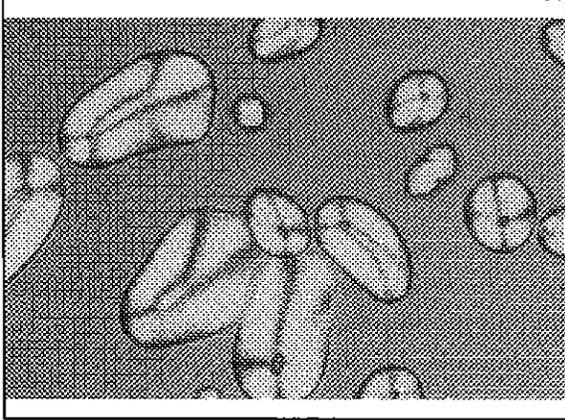
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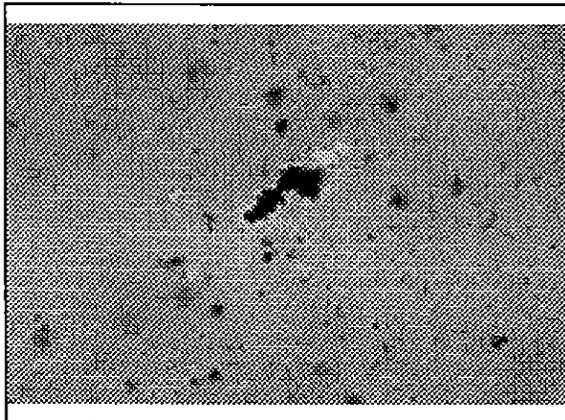


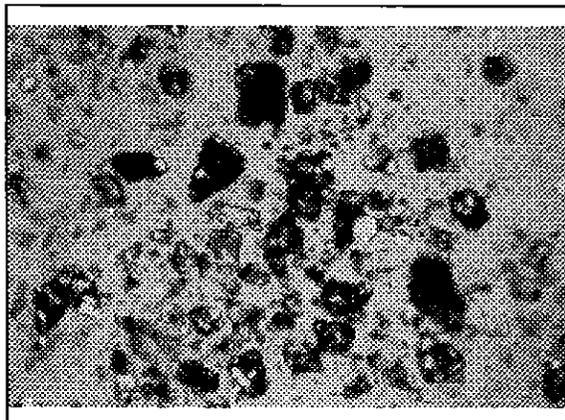




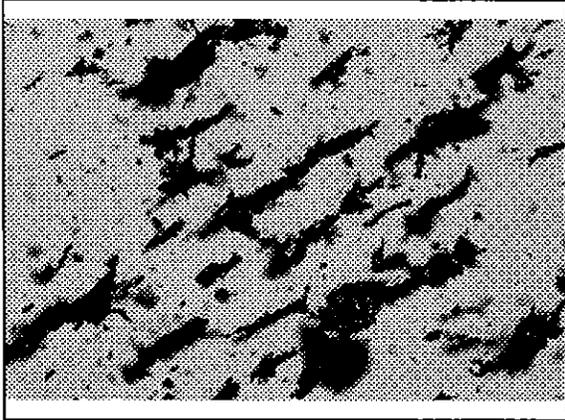
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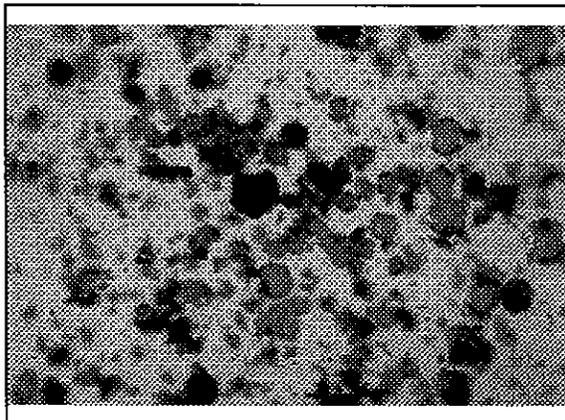


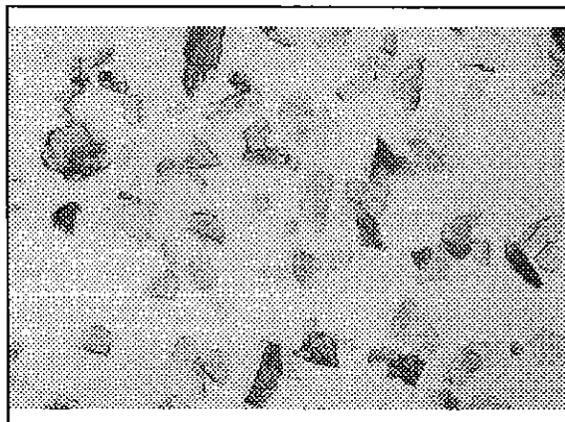




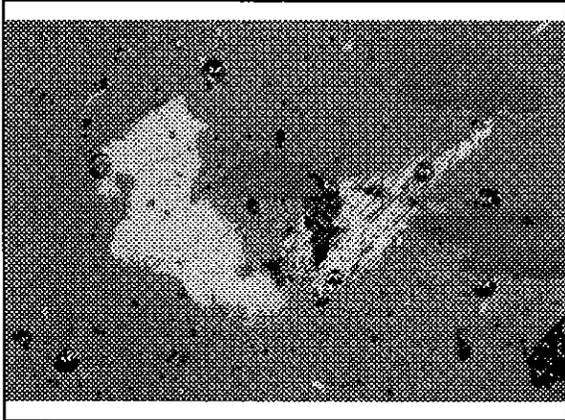
Optical Microscopy



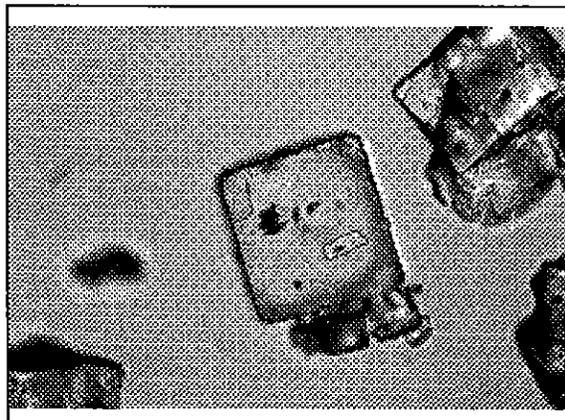




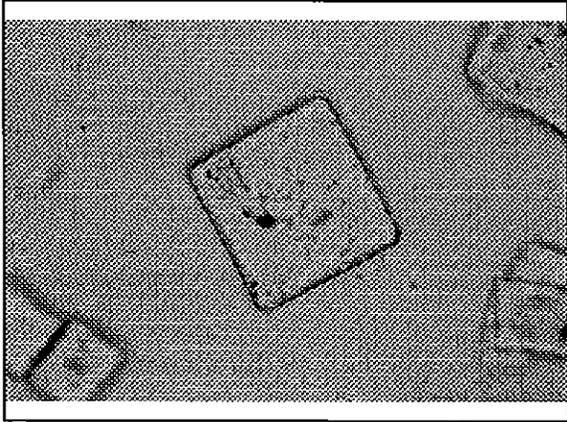
Optical Microscopy

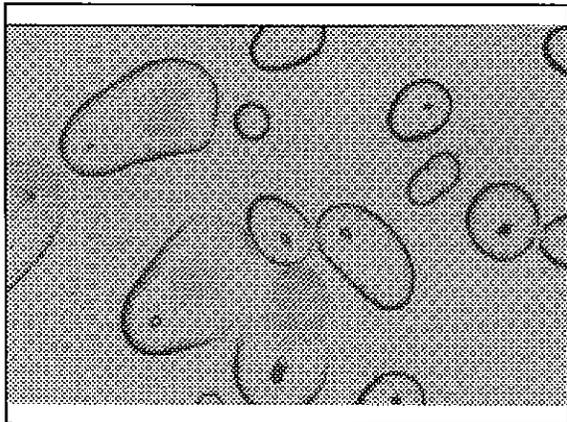


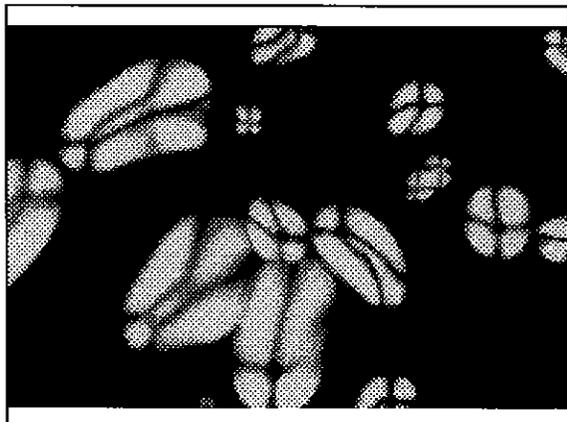




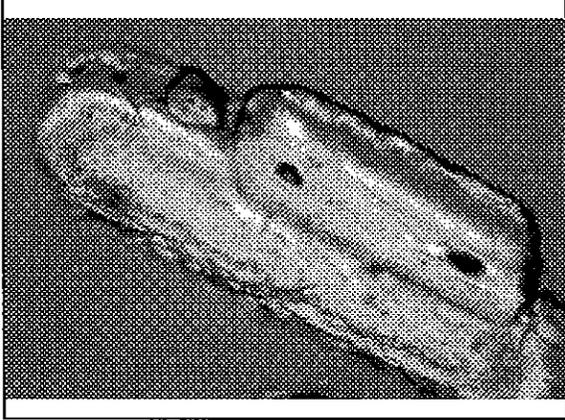
Optical Microscopy

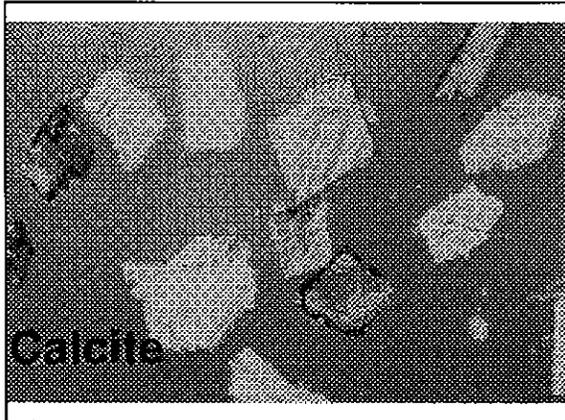


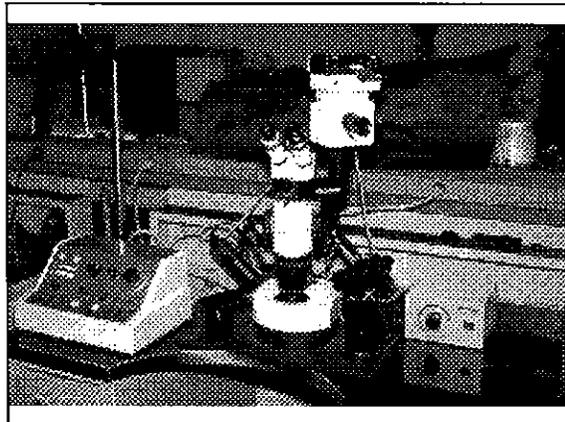




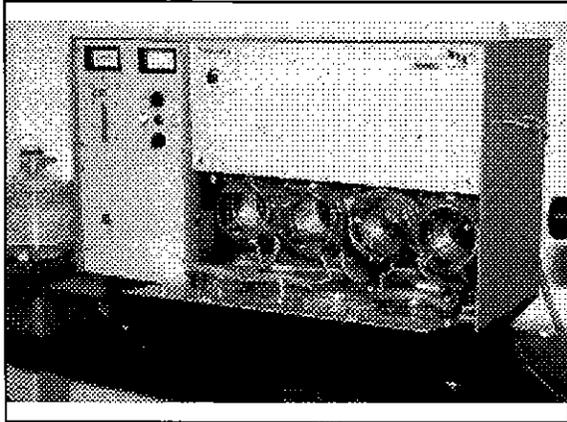
Optical Microscopy

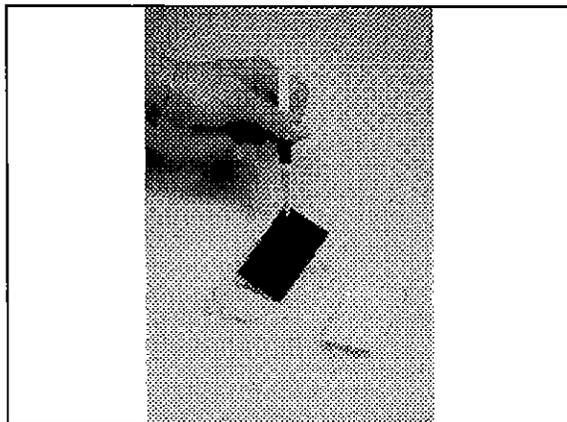


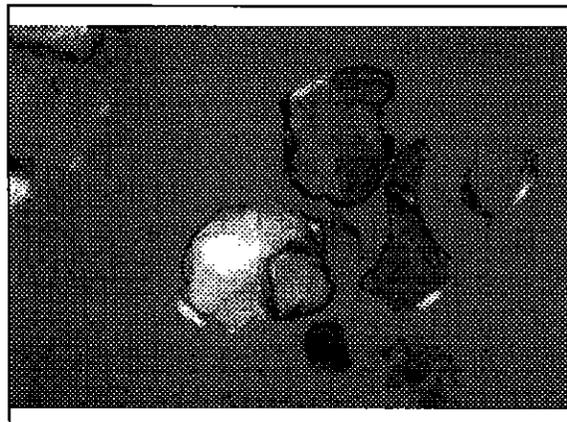




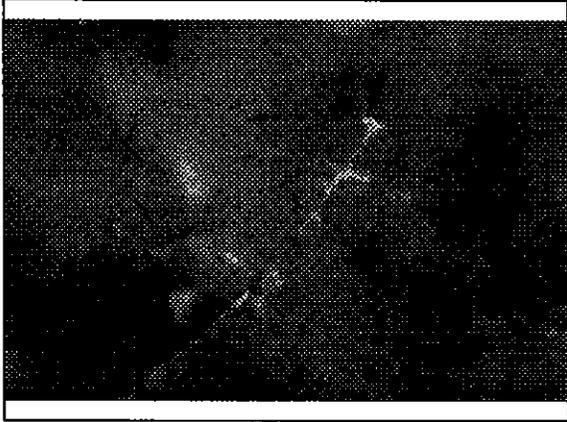
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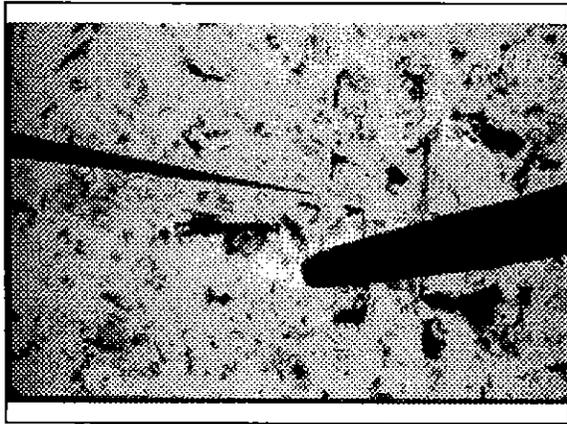


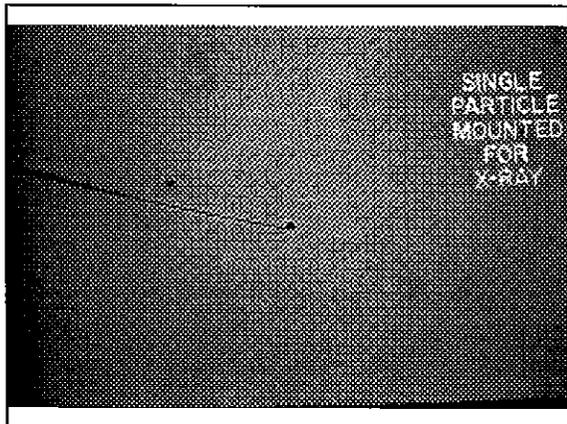




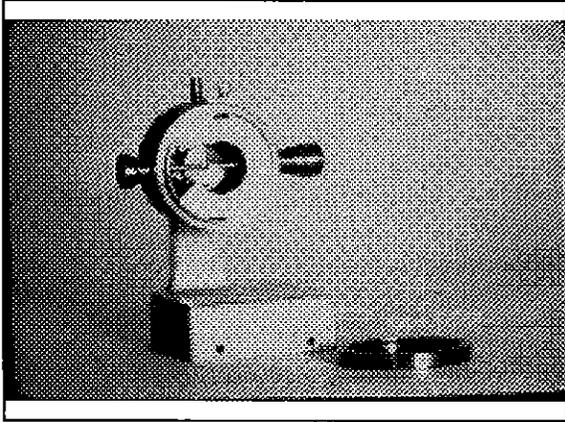
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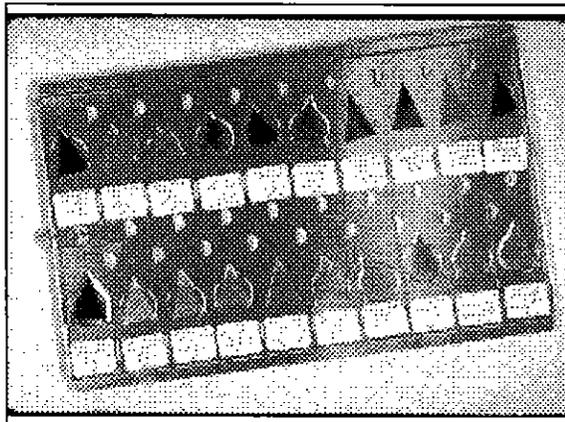




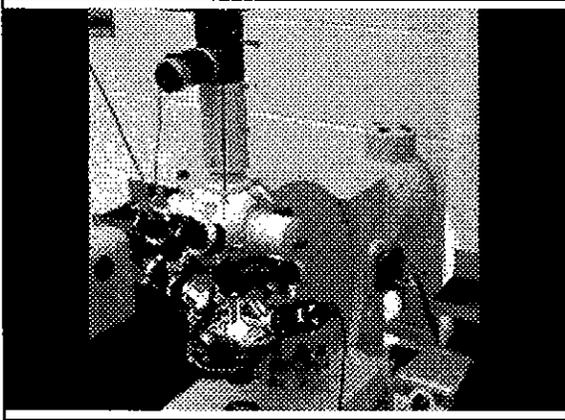
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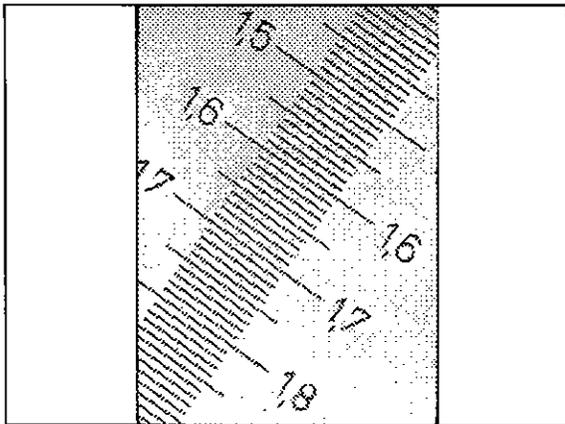


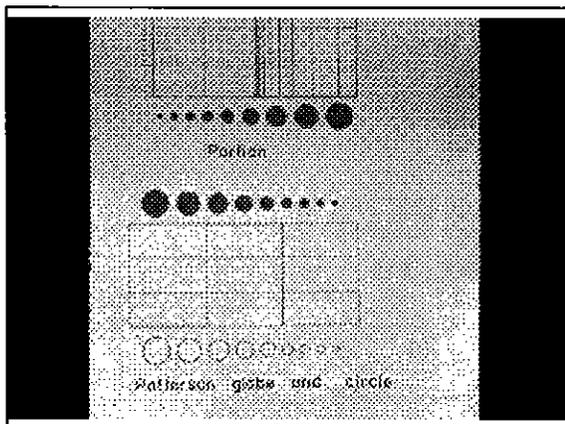




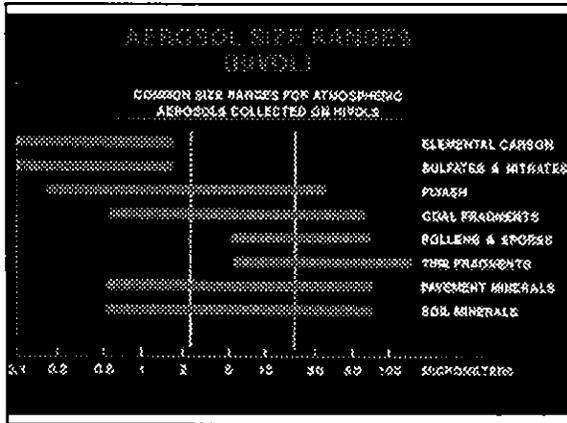
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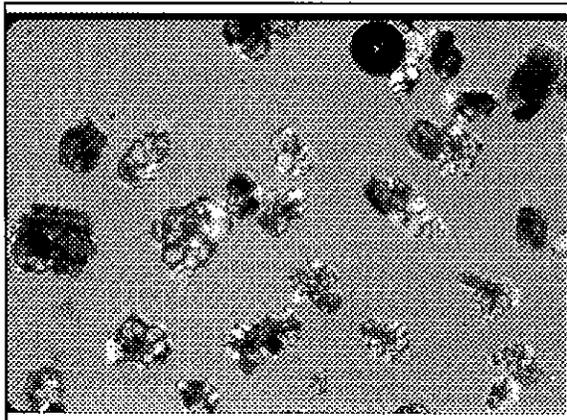


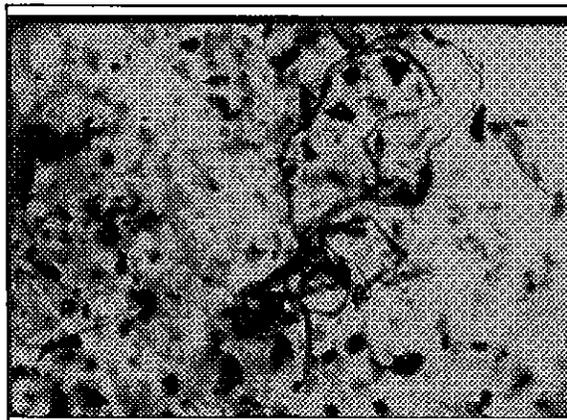




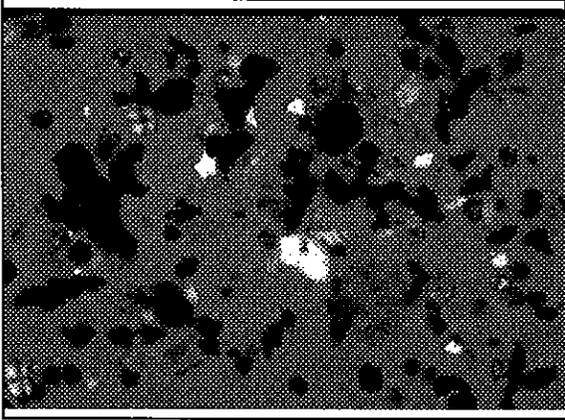
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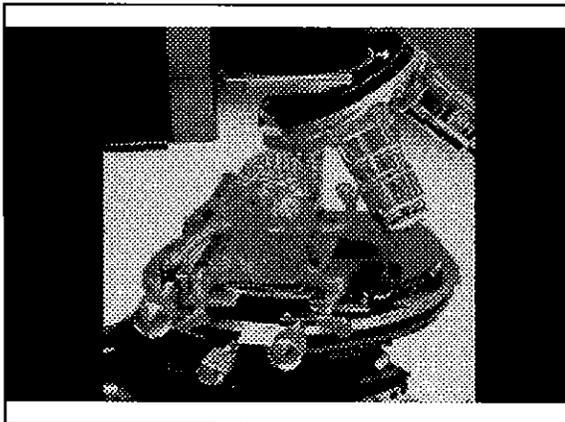






Optical Microscopy





Lesson VII

Optical Microscopy: Applications
Ronald Draftz

INTRODUCTION TO RECEPTOR MODELING

Lesson Title: Optical Microscopy: Applications

Lesson: VII

Prepared By: R. Draftz

Date: February 11, 1998

Lesson Goal: This session presents a proven, analytically integrated protocol for using polarized light microscopy with ancillary methods to identify source impacts without the need for source samples. Descriptions include sample inspection, mounting and the important features of the polarizing microscope. These features provide the ability to rapidly and easily distinguish common aerosols whose source impacts may be difficult or impossible to segregate by other methods. Some unique examples of source distinction of uninventoried emissions are presented from a major non-attainment study. Use of PLM analysis is also presented as an adjunct to CMB for validation of size selective sampling, source samples and CMB results.

Lesson Objectives: At the completion of this lesson students will be able to:

Explain why polarized light microscopy is a key method for source identification.

Explain the rationale and benefits of integrating ancillary methods with polarized light microscopy

- preliminary stereomicroscopy filter inspection
- low temperature ashing
- elemental carbon analysis
- ion chromatography
- carbonate analysis
- x-ray diffraction

Describe how to mount samples for PLM analysis.

Explain the differences between the polarizing and simple optical microscopes.

Explain how particle mass is quantitated by PLM.

List key and common atmospheric aerosols and their size ranges.

Explain how size-selective-sampling of atmospheric aerosols complicates source assignment

Study examples.

Explain the missing component in CMB ----- rubber tire fragments.

Describe how PLM can be used as an adjunct to CMB to:

- verify the size range captured by size-selective sampling

- validate source samples

- validate receptor modeling results

INTRODUCTION TO RECEPTOR MODELING

LESSON VII OUTLINE

I. Lesson Overview

II. Developing an integrated analytical protocol based on PLM

- A. Filter inspection
- B. Low temperature ashing
- C. Ion chromatography
- D. Ancillary methods
 - Scanning electron microscopy
 - Elemental carbon analysis
 - Carbonate analysis
 - X-ray diffraction

III. Sample preparation for PLM

- A. Filter sectioning
- B. Selection of immersion media

IV. Features of the polarizing microscope

V. Quantitating particle mass

- A. Stage micrometers
- B. Eyepiece graticules
- C. Counting and sizing by component

VI. Common aerosol components

VII. Ambient study examples

- A. Distinguishing limestone emissions from cement and from roads
- B. Unexpected company: Leather and paint spray
- C. Rubber tire: Missing component in CMB

VIII. Roles of PLM in receptor modeling

- A. Principal analytical tool
- B. Size-selective sampler verification
- C. Validation of source samples
- D. Validation of receptor models

Optical Microscopy: Applications

Lesson VII

**Analytical Scheme
for PLM Analysis of
Atmospheric Aerosols**

Ronald G. Draftz

Lesson VII Objectives

- ▶ **Selecting An Analytical Scheme Based on PLM**
- ▶ **The Roles of PLM in Receptor Modeling**

Integrated PLM Protocol I

- ▶ **Sample Inspection (Slide 23)**

Optical Microscopy: Applications

Integrated PLM Protocol III

- ▶ Sample Inspection (Slide 23)
- ▶ Low Temperature Ashing (Slides 24-26)

Integrated PLM Protocol IV

- ▶ Sample Inspection (Slide 23)
- ▶ Low Temperature Ashing (Slides 24-26)
- ▶ Ion Chromatography (Slide 27)

Integrated PLM Protocol V

- ▶ Sample Inspection (Slide 23)
- ▶ Low Temperature Ashing (Slides 24-26)
- ▶ Ion Chromatography (Slide 27)
- ▶ Polarized Light Microscopy

Optical Microscopy: Applications

Ancillary Methods

- ▶ Scanning Electron Microscopy
- ▶ Elemental Carbon Analysis
- ▶ Carbonate Analysis
- ▶ X-ray Diffraction (Slides 28-30)

Sample Preparation for PLM

- ▶ Sample Sectioning
- ▶ Selection of Immersion Fluids (Slides 31-32)

The Polarizing Microscope

- ▶ A Quick Look at a Polarizing Microscope (33-34)

Optical Microscopy: Applications

Quantitating Particle Mass

- ▶ Stage Micrometers (Slide 35)

Quantitating Particle Mass

- ▶ Stage Micrometers (Slide 35)
- ▶ Eyepiece Graticules (Slide 36)

Quantitating Particle Mass

- ▶ Stage Micrometers (Slide 35)
- ▶ Eyepiece Graticules (Slide 36)
- ▶ Count & Size by Component

Optical Microscopy: Applications

Common Aerosol Components

- ▶ (Slide 37)

Some Study Examples

- ▶ Distinguishing Limestone Used for Cement & for Roads (Slide 38)
- ▶ Leather & Paint (Slide 39)
- ▶ The Rubber Tire Dilemma (Slide 40)

The Roles of PLM in Receptor Modeling

- ▶ Principal Analytical Tool

Optical Microscopy: Applications

The Roles of PLM in Receptor Modeling

- Principal Analytical Tool
- Verify Size Range of Samplers

The Roles of PLM in Receptor Modeling

- Principal Analytical Tool
- Verify Size Range of Samplers
- Validation of Source Samples

The Roles of PLM in Receptor Modeling

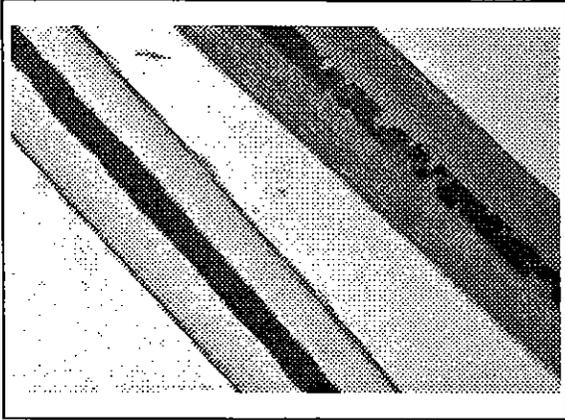
- Principal Analytical Tool
- Verify Size Range of Samplers
- Validation of Source Samples
- Validation of Receptor Models for Source Assignment & Quantity

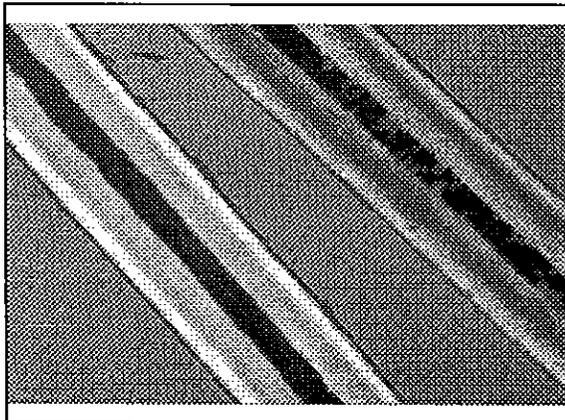
Optical Microscopy: Applications

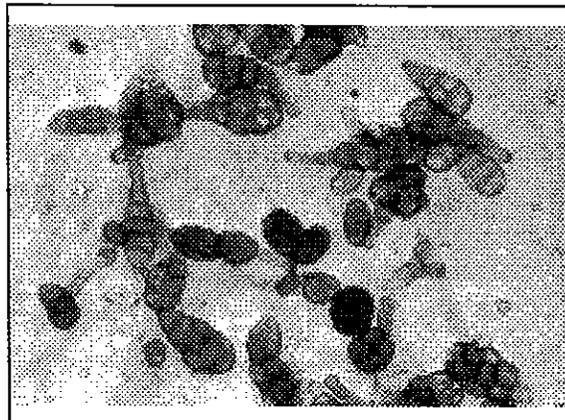
The Roles of PLM in Receptor Modeling

- ▶ Principal Analytical Tool
- ▶ Verify Size Range of Samplers
- ▶ Validation of Source Samples
- ▶ Validation of Receptor Models for Source Assignment & Quantity
- ▶ "Seeing Is Believing" (Slide 41)

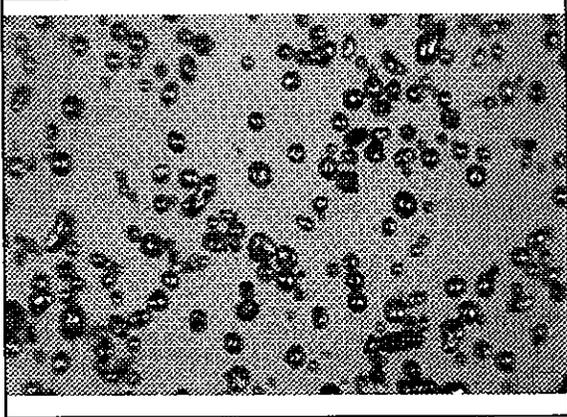
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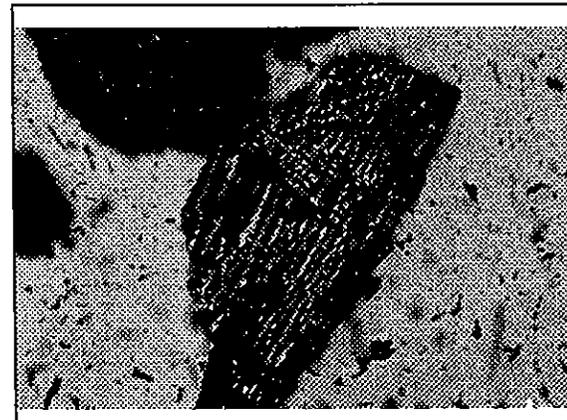




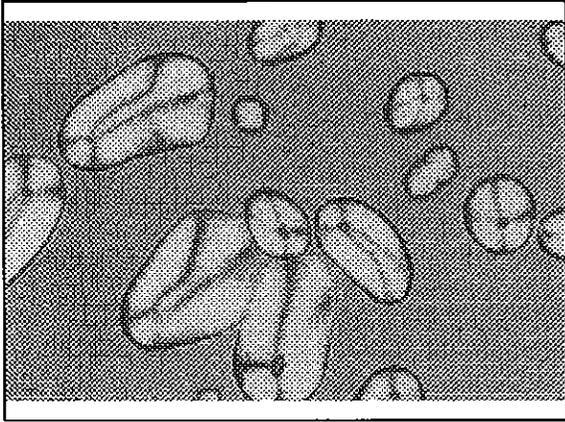
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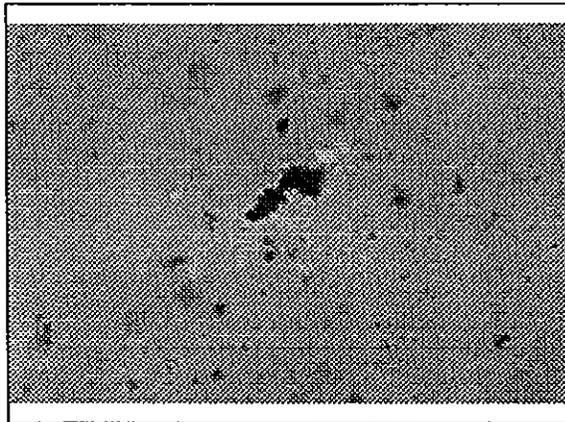


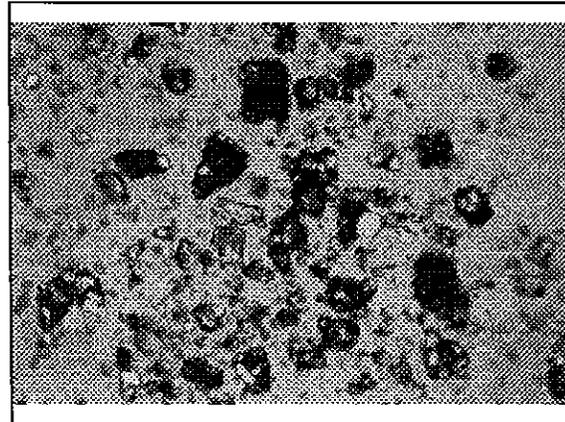




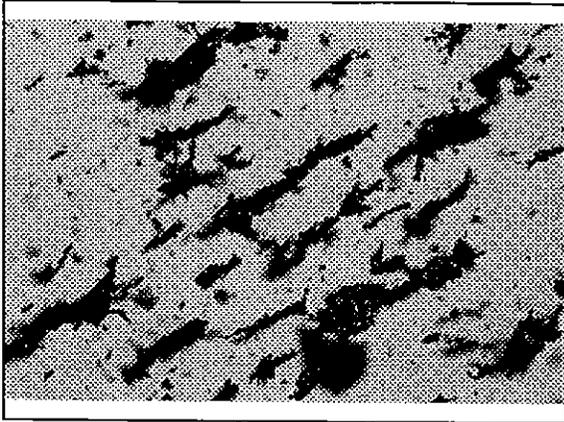
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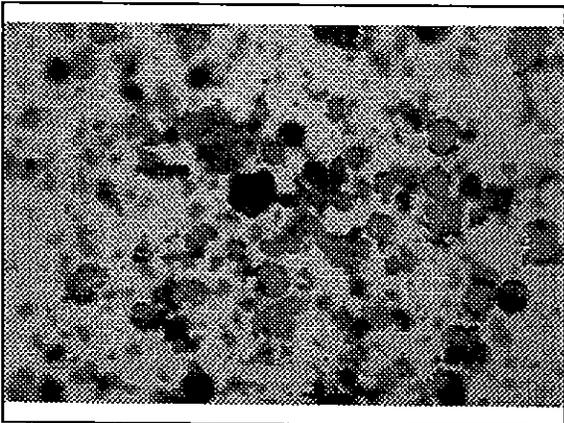


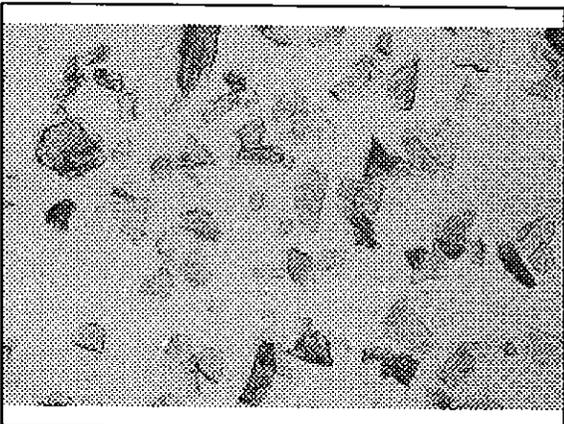




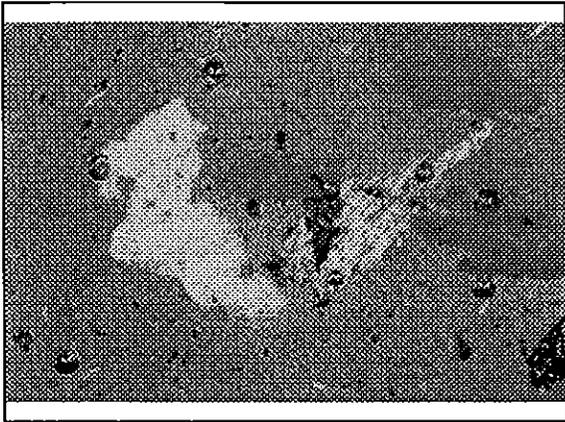
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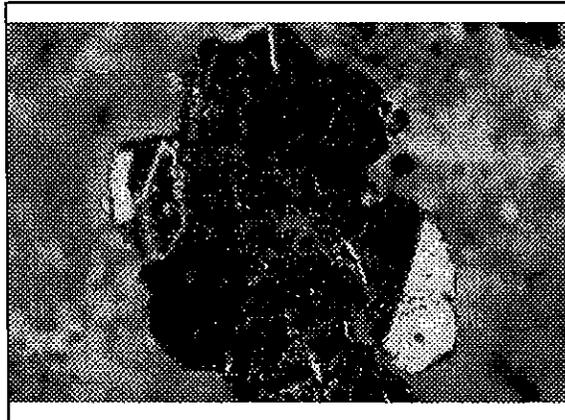


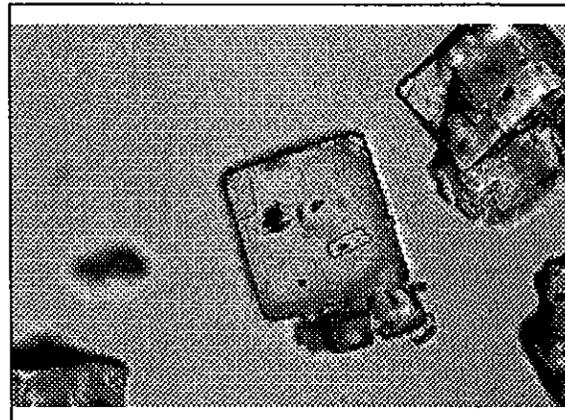




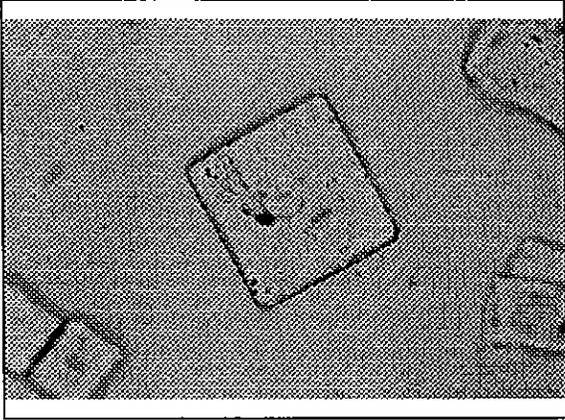
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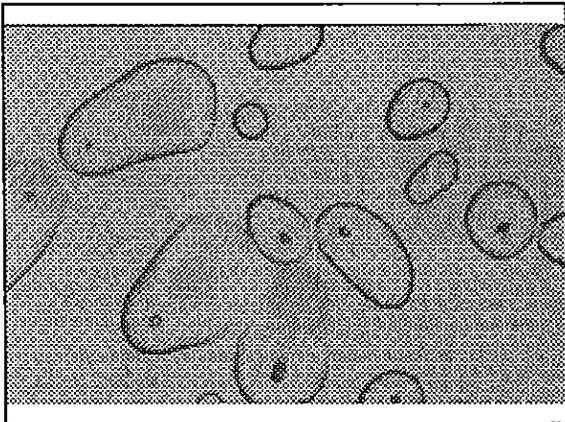






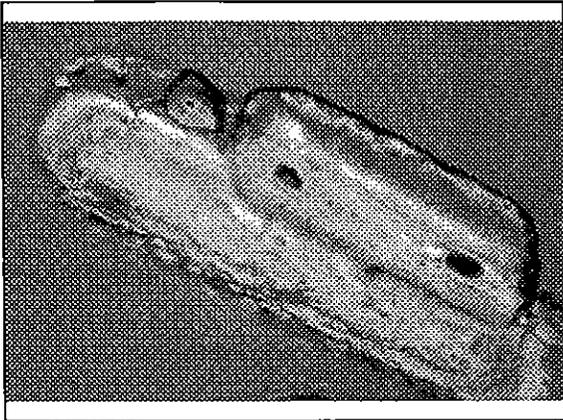
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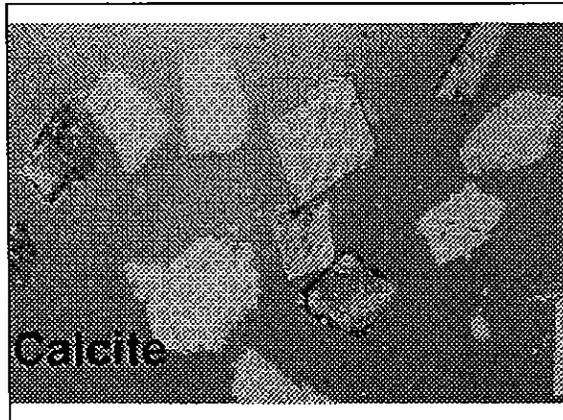


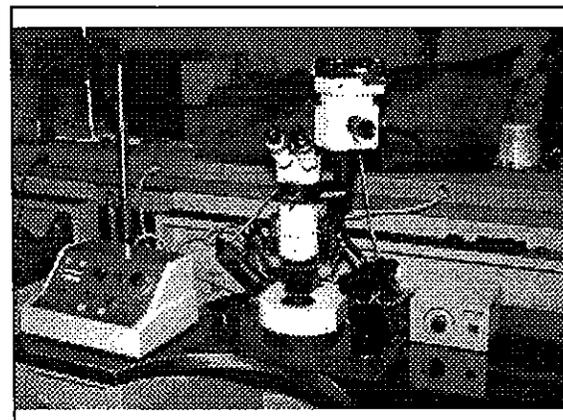




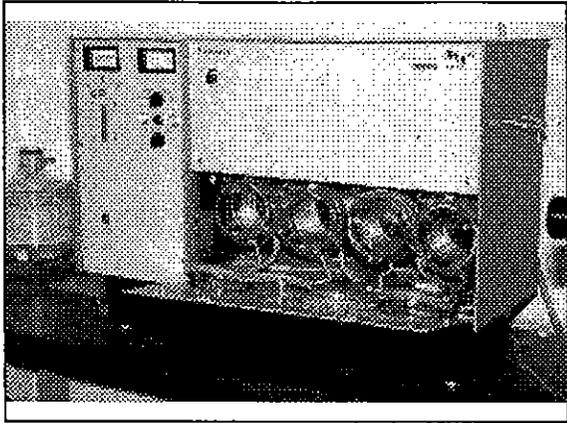
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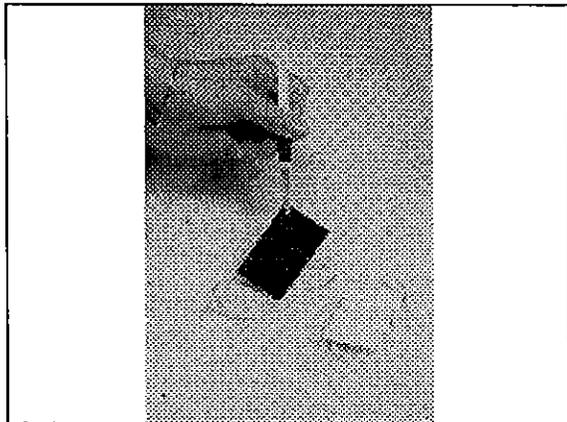


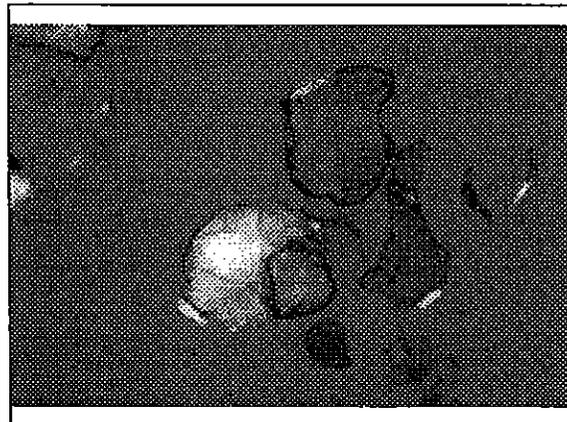




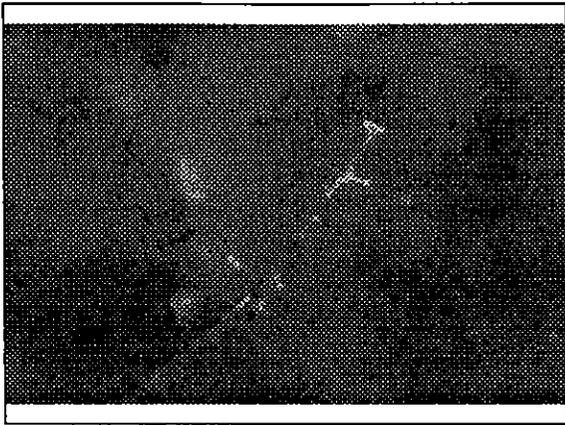
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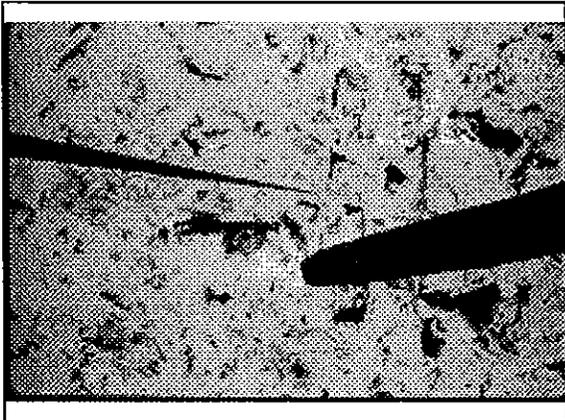


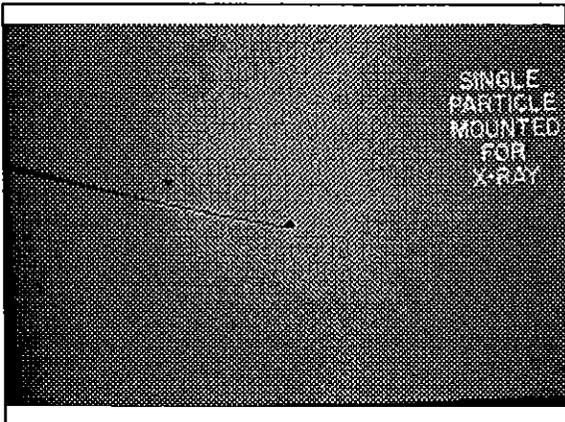




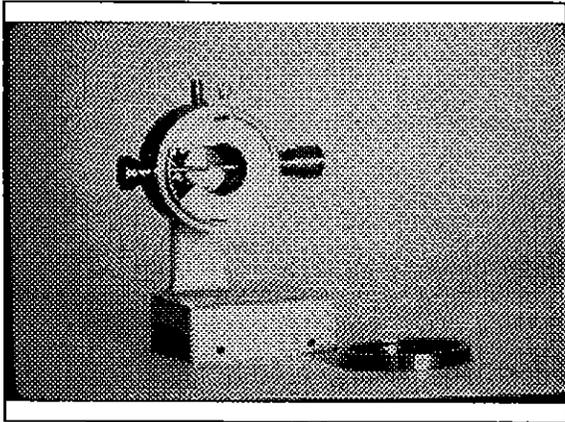
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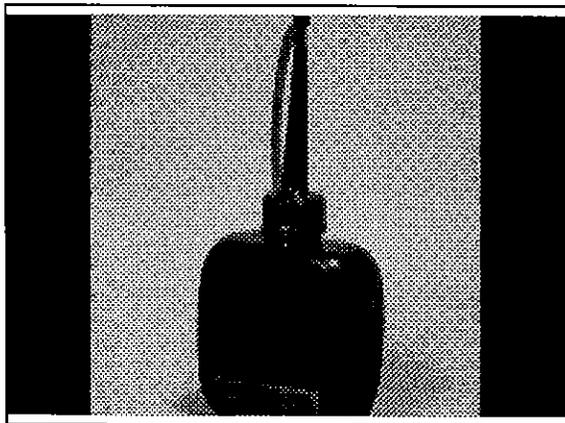


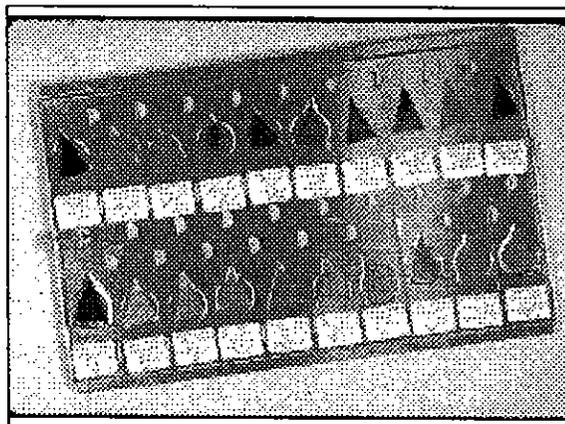




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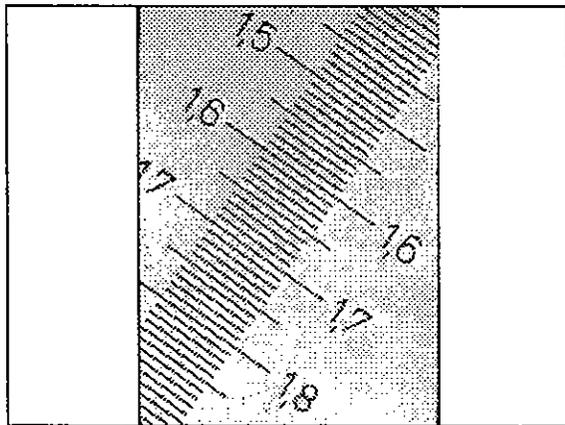


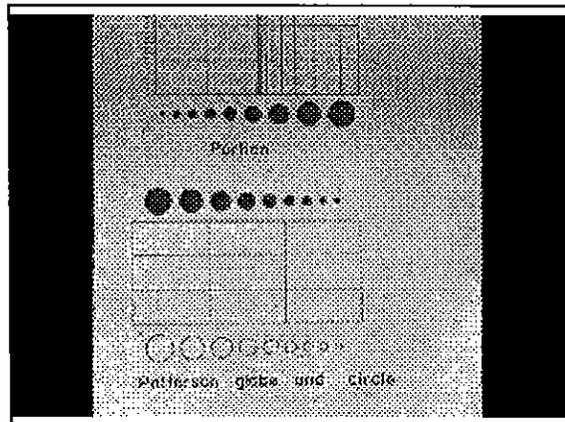




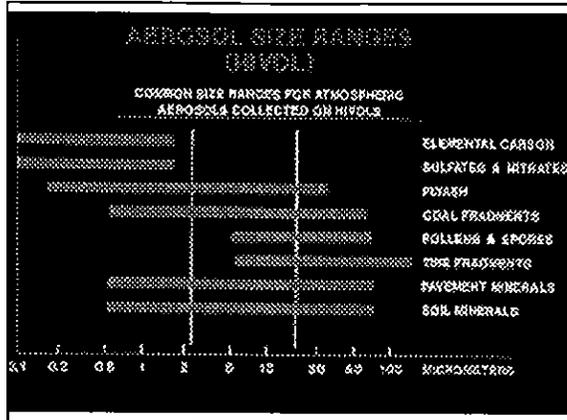
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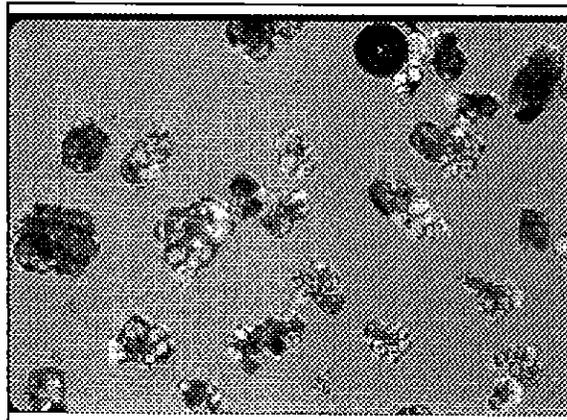


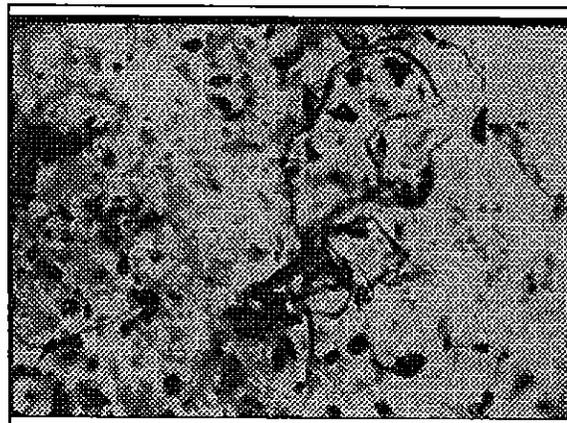




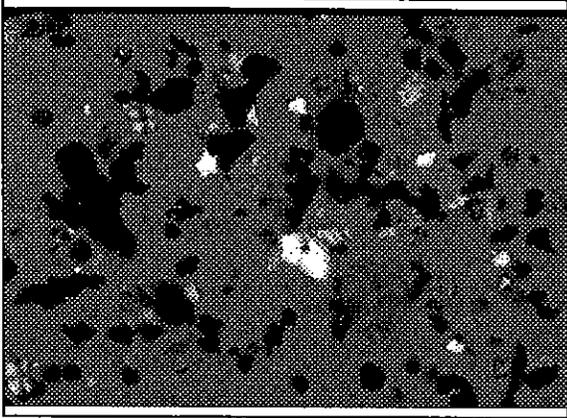
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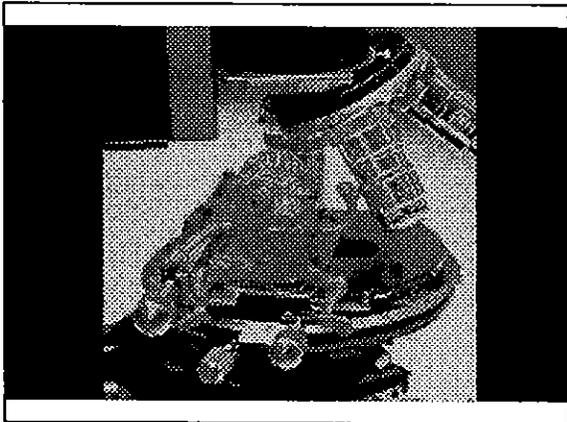






Optical Microscopy





Lesson VIII

Introduction to Scanning Electron Microscopy
Gary Casuccio

INTRODUCTION TO RECEPTOR MODELING

Lesson Title: Introduction to Scanning Electron Microscopy

Lesson: VIII

Prepared By: G. Casuccio

Date: February 11, 1998

Lesson Goal: The goal of this lesson is to introduce students to the types of information that can be obtained through analysis of particulate samples using a scanning electron microscope (SEM). Special emphasis will be placed on the use of the SEM from an environmental perspective.

Lesson Objectives: At the completion of this lesson students will be able to:

Explain the basics of how the SEM works

Discuss the types of information that can be obtained using an SEM

Describe the similarities and differences between the SEM and the optical microscope

Describe how samples are prepared for SEM analysis

List at least three ways that the SEM is used in environmental studies

INTRODUCTION TO RECEPTOR MODELING

LESSON VIII OUTLINE

- I. Introduction - Objectives
- II. What is an SEM and how does it differ from the optical microscope?
- III. What types of information are obtained with an SEM?
 - A. Image
 - Secondary electron
 - Backscattered electron
 - B. Elemental composition
- IV. How does the SEM work?
 - A. Electron gun
 - B. Magnetic lenses
 - C. Vacuum system
 - D. Secondary electron detector
 - E. Backscattered electron detector
 - F. X-ray analyzer
- V. How are the samples prepared for an SEM analysis?
 - A. Direct preparation
 - B. Resuspension
- VI. How is the SEM used in environmental studies?
 - A. Source samples
 - B. Indoor samples
 - C. Ambient samples
 - D. Soil samples
- VII. Summary

Introduction To Scanning Electron Microscopy

Introduction to Scanning Electron Microscopy

Gary S. Casuccio
RJ Lee Group
Monroeville, PA

Outline of Presentation

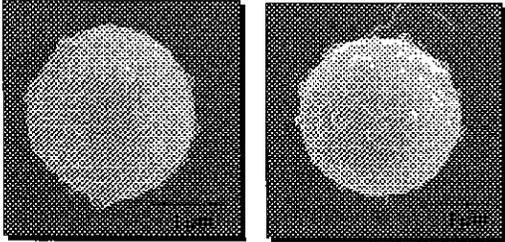
- ▶ Introduction
- ▶ What types of information are obtained with an SEM?
- ▶ Sample preparation for SEM analysis
- ▶ How is the SEM used in environmental studies?

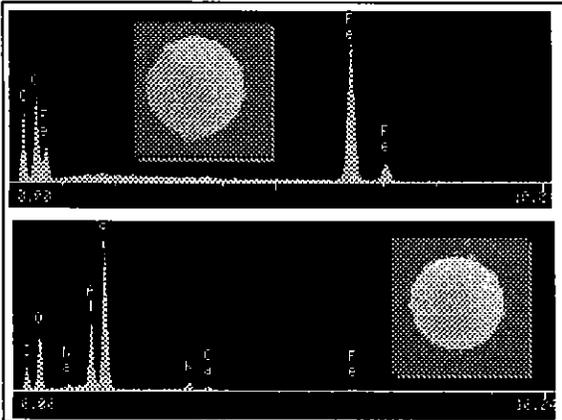
How is the SEM used in Environmental Studies?

- ▶ Provides information on individual particle characteristics
 - ▶ Image
 - ▶ Elemental chemistry

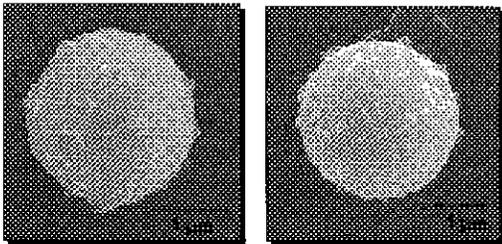
Introduction To Scanning Electron Microscopy

Particles with a Similar Shape



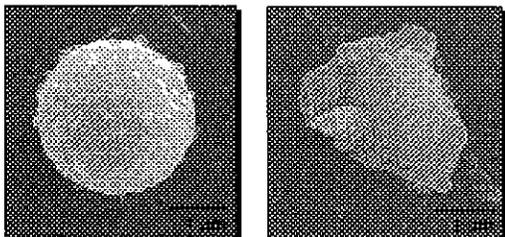


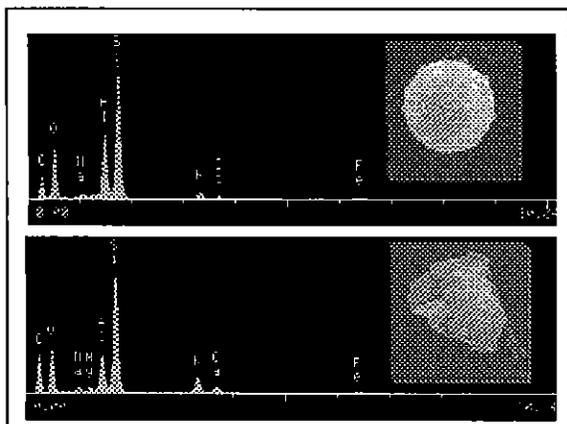
Images of Combustion Particles
Fe-rich Fly Ash



Introduction To Scanning Electron Microscopy

Particles with Different Shapes





How is the SEM used in Environmental Studies?

- ▶ As a complementary method to bulk analytical techniques
- ▶ Source identification/apportionment
- ▶ To investigate soiling of building materials

Introduction To Scanning Electron Microscopy

How is the SEM used in Environmental Studies?

- ▶ To provide better understanding of health effects related to particulate matter
- ▶ PM_{2.5} NAAQS analysis requirements

PM_{2.5} NAAQS Analysis Requirements

- ▶ Exceedance Analysis
 - ▶ "High PM_{2.5} concentration events are analyzed for particle size and composition utilizing optical or electron microscopy"

What is a Microscope?

- ▶ An instrument consisting essentially of a lens or combination of lenses, for making very small objects, as microorganisms, look larger so that they can be seen and studied.

Introduction To Scanning Electron Microscopy

What is a Microscope?

- ▶ Light microscope
- ▶ Scanning electron microscope
- ▶ Transmission electron microscope
- ▶ Scanning probe microscope

What is a Microscope?

- ▶ Each microscope has its unique capabilities and limitations and each has particular roles where its contribution is indispensable.

What is an SEM?

- ▶ Scanning Electron Microscope
- ▶ An SEM uses a highly focused beam of electrons to form a magnified image.

Introduction To Scanning Electron Microscopy

SEM Image

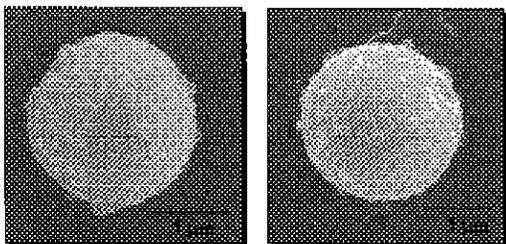
- ▶ Secondary electron (SE)
- ▶ Backscattered electron (BSE)

Secondary Electron (SE) Image

- ▶ The SE signal is sensitive to variations in surface topography (i.e., texture, surface roughness).
- ▶ The SE image provides a three dimensional perspective of the object.

Images of Combustion Particles

Fe-rich Fly Ash



Introduction To Scanning Electron Microscopy

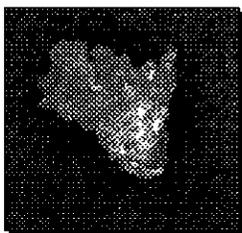
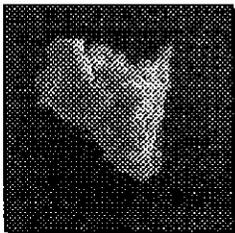
Backscattered Electron (BSE) Image

- ▶ The BSE signal is proportional to atomic number.
- ▶ The BSE image provides information on the chemical makeup of the object.

Examples of SE and BSE Images

SE

BSE



What makes the SEM a powerful analytical tool?

- ▶ Image
 - ▶ Magnification
 - ▶ Depth of Field
- ▶ Composition

Introduction To Scanning Electron Microscopy

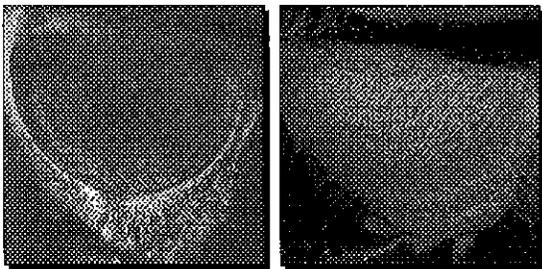
Magnification

- ▶ Wide range of magnification (10- >100,000x).
- ▶ An SEM is easily capable of resolving features in the submicron size range.
- ▶ Continuous zoom

Depth of Field

- ▶ The use of electrons to form images enables both near and distant features to remain in sharp focus.

Depth of Field
Optical SEM



Introduction To Scanning Electron Microscopy

Microchemical Analysis

- ▶ **Elemental composition is obtained through collection of x-rays using energy dispersive spectroscopy (EDS) techniques.**
- ▶ **Rapid identification of elements**

What types of information are obtained with an SEM?

- ▶ **Size**
- ▶ **Shape**
- ▶ **Elemental composition**
 - ▶ **Association**
 - ▶ **Identification**

Sample Collection and Preparation for SEM Analysis

Introduction To Scanning Electron Microscopy

Sample Collection

- ▶ Bulk powders (soil)
- ▶ Particles collected on filters
- ▶ Passive/adhesive samplers
- ▶ Liquid samples

Sample Preparation

- ▶ Direct preparation
- ▶ Resuspension
- ▶ Redeposition
- ▶ Polished mount

Direct Preparation

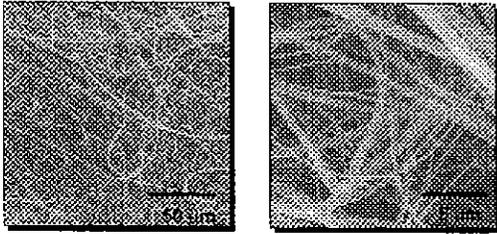
- ▶ Mount sample directly onto an SEM stub
- ▶ Coat with a thin layer of carbon
 - ▶ Ambient filter samples
 - ▶ Source filter samples
 - ▶ Powder samples (soil)

Introduction To Scanning Electron Microscopy

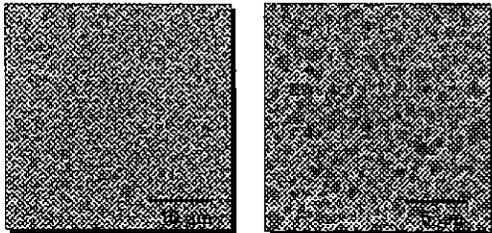
SE Images of Various Filters

- ▶ Quartz fiber filter
- ▶ Mixed cellulose ester (MCE) filter
- ▶ Teflon filter
- ▶ Polycarbonate (PC) filter

Quartz Fiber Filter

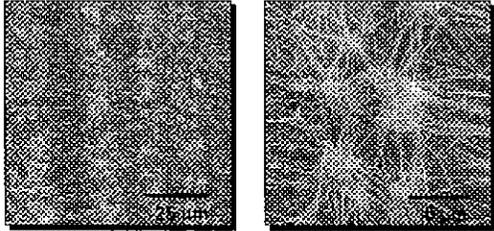


MCE Filter

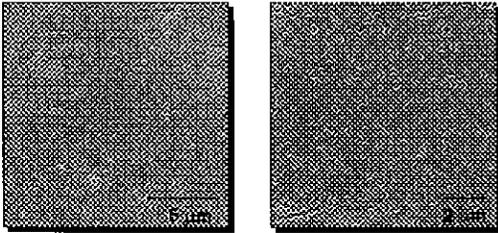


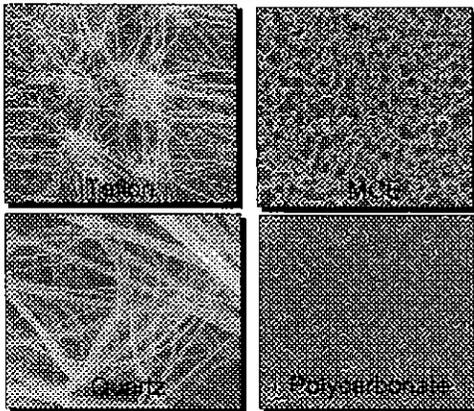
Introduction To Scanning Electron Microscopy

Teflon Filter



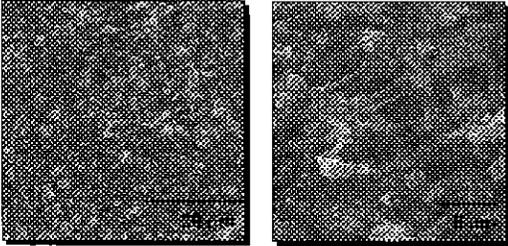
Polycarbonate Filter



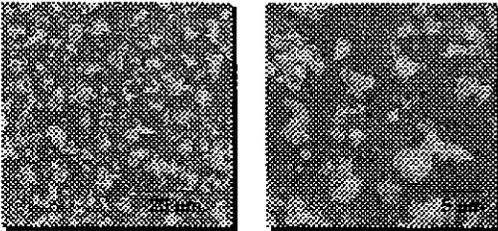


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Particulate Matter Collected on
Teflon Filter



Particulate Matter Collected on
Polycarbonate Filter



Resuspension Preparation

- ▶ Particles are resuspended and collected on a polycarbonate filter.
 - ▶ Sample chamber
 - ▶ Liquid filtration

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Redeposition Preparation

- ▶ Removal of particles from original filter and redeposit onto a polycarbonate filter.
 - ▶ Liquid filtration
 - ▶ Micro-vac

Polish Mount Preparation

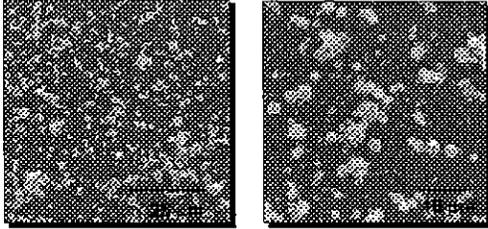
- ▶ Particles are embedded in epoxy and polished to a smooth surface to expose the internal structure of the particle.
 - ▶ Soil samples

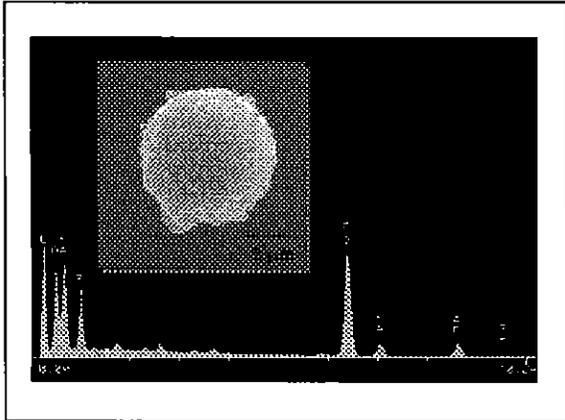
How is the SEM used in Environmental Studies?

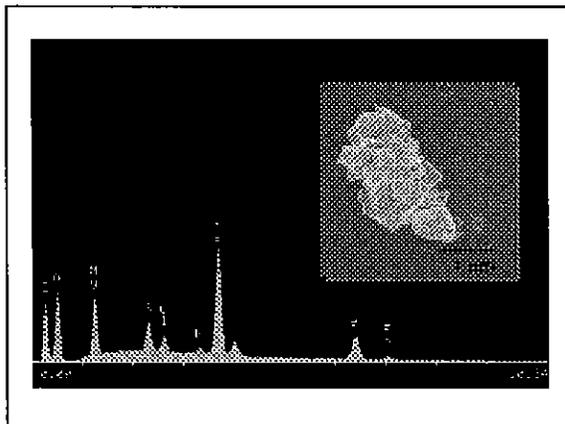
- ▶ Provides information on individual particle characteristics
- ▶ As a complementary method to bulk analytical techniques
- ▶ Source identification/apportionment
- ▶ To investigate soiling of building materials

Introduction To Scanning Electron Microscopy

Example of BOF Source Sample

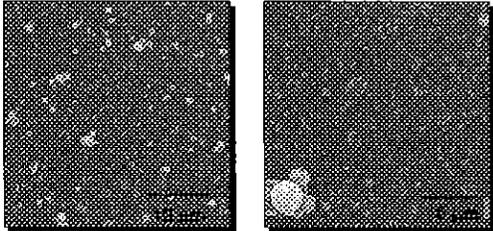


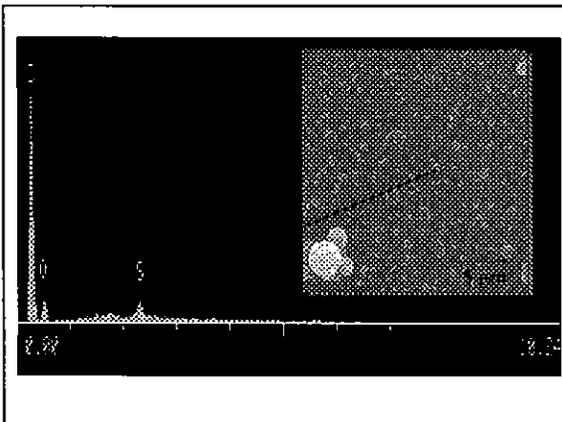




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Example of Coal Fired Power Plant Sample





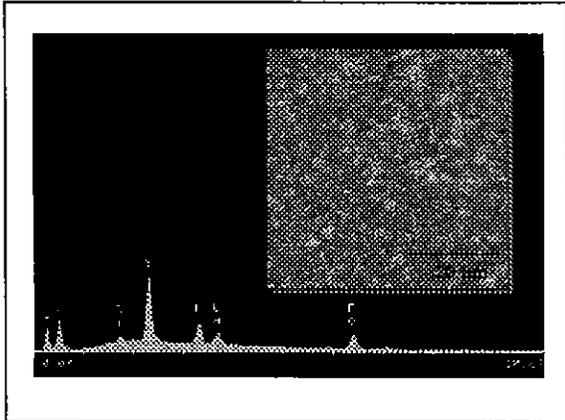
Ambient and Indoor Samples

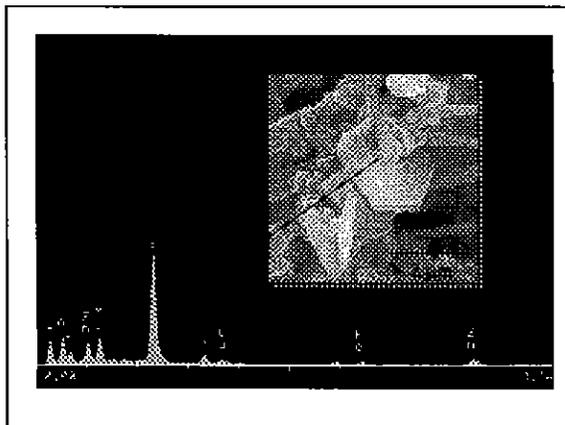
- ▶ Where did the particulate matter come from?
 - ▶ Particle identification
 - ▶ Composition
 - ▶ Image
 - ▶ Source apportionment

Introduction To Scanning Electron Microscopy

Ambient Sample
Fine Fraction

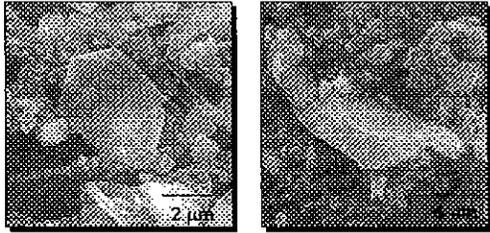


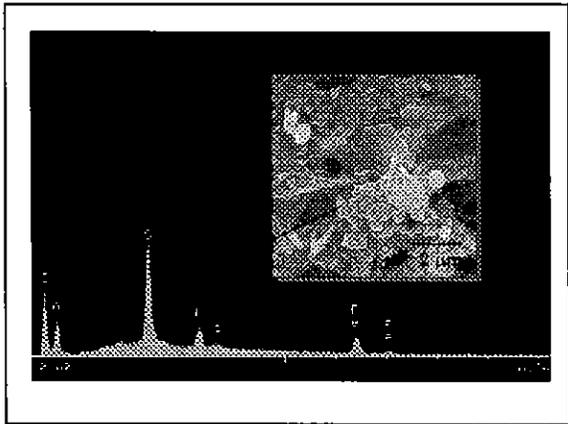


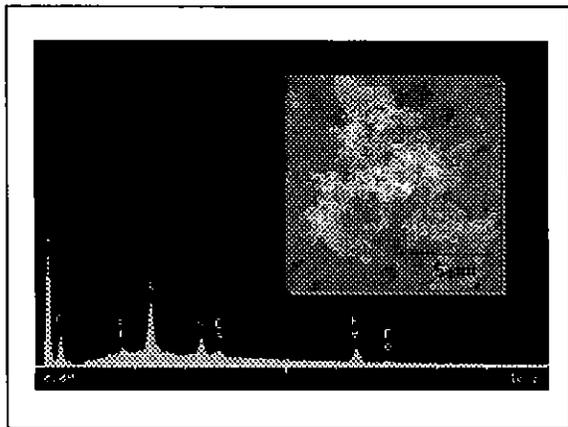


Introduction To Scanning Electron Microscopy

Examples of S-rich Particles

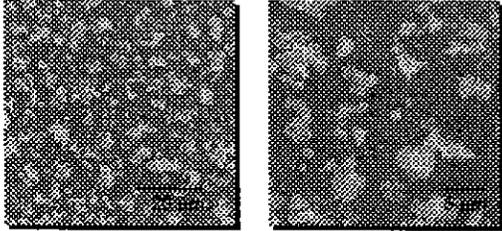


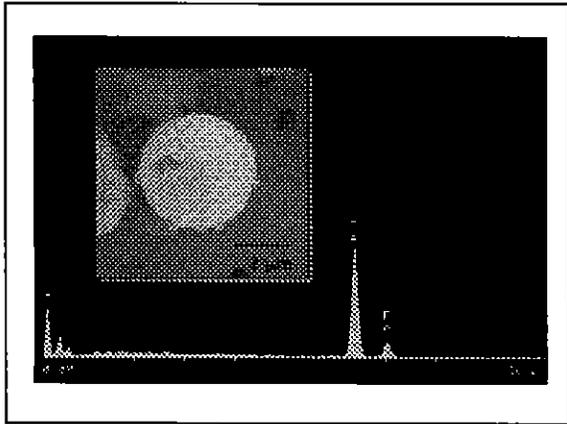


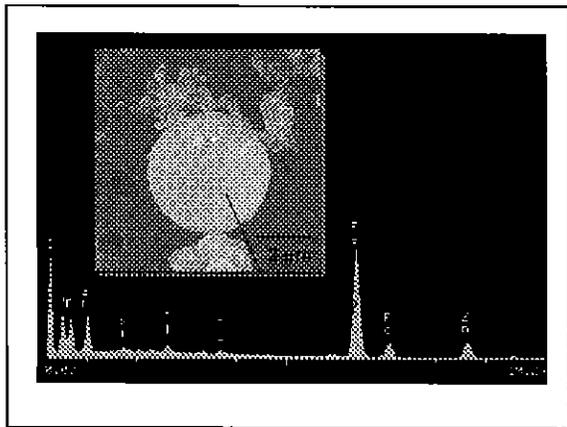


Introduction To Scanning Electron Microscopy

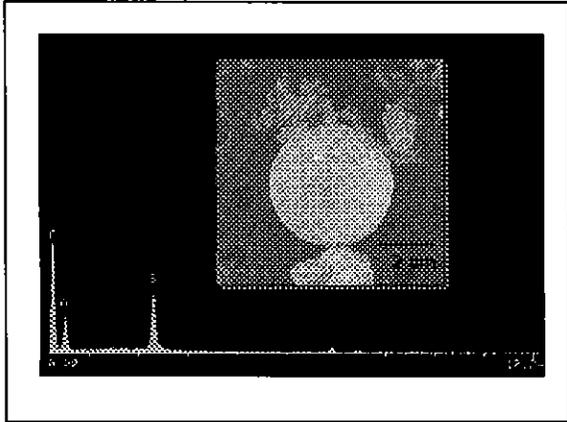
Ambient Sample
Coarse Fraction

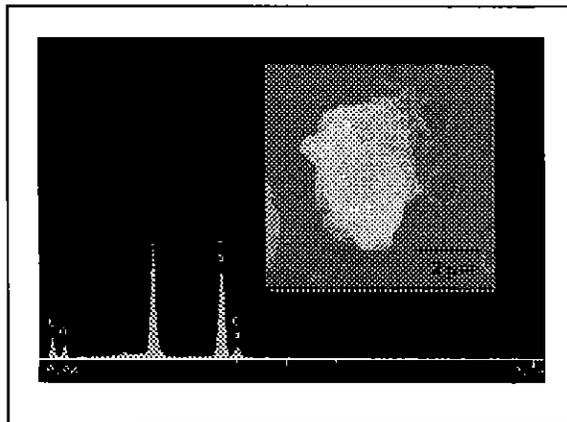






Introduction To Scanning Electron Microscopy





Example of Soil Analysis Using SEM Techniques

- ▶ Super fund site
- ▶ ~100 years mining, milling and smelting metals
- ▶ Elevated lead in local soils

Introduction To Scanning Electron Microscopy

Bulk Chemical Analysis

- ▶ Reveals areas with low (100 ppm) and high (>1000 ppm) concentrations of lead
- ▶ Lead widely distributed
- ▶ No information on the phase of the lead

Variety of (Solid) Lead Phases

- ▶ Ore minerals (galena, anglesite, cerussite)
- ▶ Processed (oxides, slags)
- ▶ Alteration products (sulfates, phosphates)

Concerns

- ▶ Adverse health effects?
- ▶ What (is/was) source?
- ▶ What is best remediation strategy?
- ▶ Concerns lead to EPA directed study to evaluate the microscopic characteristics of the lead particles.

Introduction To Scanning Electron Microscopy

Source Information

- ▶ Phase may be source specific
- ▶ Morphology may be source specific

Microscopic Analysis

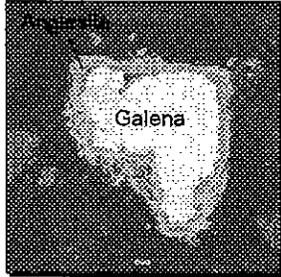
- ▶ Soil prepared as a polished mount
- ▶ BSE signal used to detect lead particles
- ▶ WDS used for phase identification
- ▶ Minimum of 100 lead particles analyzed per sample

Determination of the Microscopic Characteristics of the Lead

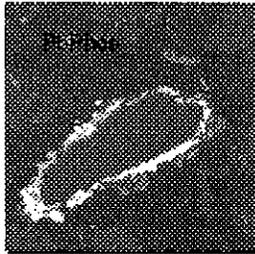
- ▶ SEM analysis reveals
 - ▶ specific elemental phases
 - ▶ size distribution
 - ▶ external morphology
 - ▶ internal morphology
 - ▶ association

Introduction To Scanning Electron Microscopy

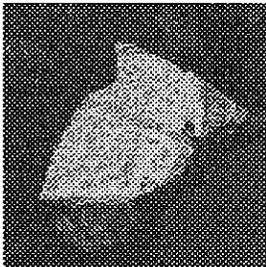
Galena Particle - Enclosed



Lead Phosphate Particle - Rim



Slag Particle - Liberated



Introduction To Scanning Electron Microscopy

Summary of SEM Results,%

▶ <u>Phase</u>	<u>Vol</u>	<u>Pb</u>	<u>Lib</u>	<u>Encl</u>	<u>Rim</u>
▶ Galena	39	87	63	31	6
▶ Slag	31	2	98	1	1
▶ Organic	4	2	95	5	--
▶ Anglesite	3	68	50	34	16
▶ PbPhos	2	27	51	35	14

Summary and Conclusions

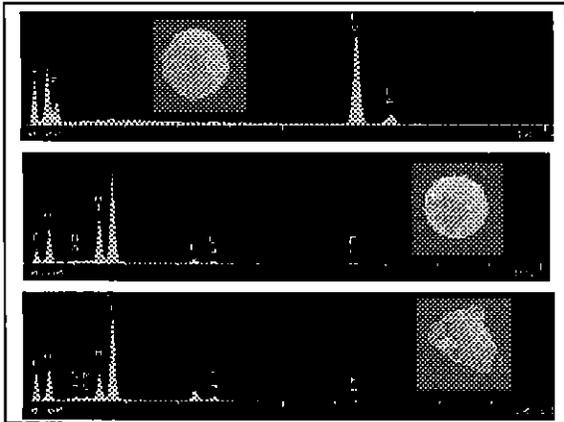
- ▶ Area could be mapped out with respect to the major sources.
- ▶ Action level adjusted based on phase and association information.

Summary

Introduction To Scanning Electron Microscopy

How is the SEM used in Environmental Studies?

- ▶ Provides information on individual particle characteristics
 - ▶ Image
 - ▶ Elemental chemistry



Advantages of SEM Analysis

- ▶ Resolution
- ▶ Depth of Field
- ▶ Zoom magnification
- ▶ Microchemical analysis

Introduction To Scanning Electron Microscopy

Advantages of SEM Analysis

- ▶ Particle x particle analysis
- ▶ can differentiate based on morphology
- ▶ can differentiate based on elemental composition

Advantages of SEM Analysis

- ▶ Eye/brain provides for the most powerful form of analysis
- ▶ Subtleties may be more easily recognized and evaluate
- ▶ Quick identification

Lesson IX

Source Characterization: Sampling and Analysis Methods

Robert Stevens

Peter Scheff

INTRODUCTION TO RECEPTOR MODELING

Lesson Title: Source Characterization: Sampling and Analysis Methods

Lesson: IX

Prepared By: R. Stevens, P. A. Scheff

Date: February 11, 1998

Lesson Goal: The goal of this session is to ensure a clear understanding of source profiles and EPA's Speciate Library of Source Profiles, including their relationship to EPA's CMB-8 receptor modeling input requirements. This includes presenting the rationale for obtaining source dilution samples from motor vehicles, coal and oil fired power plants, and incinerators, as well as how to resuspend soil and road dust samples to obtain source profiles.

Lesson Objectives: At the end of this lesson the student will be able to:

Describe what a source profile is and list at least 3 requirements for source profiles in receptor modeling.

Describe EPA's Speciate Library of Source Profiles and list at least 1 other literature source of source composition information.

Describe how source profiles are measured and explain why dilution sampling from combustion sources is important.

Explain how fence-line sampling and tunnel sampling can be used to develop source profiles.

Explain how emission factors and emissions inventory can be used to help develop and evaluate source profiles.

INTRODUCTION TO RECEPTOR MODELING

LESSON IX OUTLINE

- I. Introduction and Objectives
- II. Using EPA's Method 5 to Obtain PM10 Mass, Sulfate, Metal, and SO2 Concentrations from Stationary Sources.
- III. Using Source Dilution Samplers to Obtain Source Profiles from Stationary Sources Such as Coal Fired Power Plants.
- IV. Using Source Dilution Samplers to Obtain Source Profiles from Oil Fired Furnaces.
- V. X-ray Fluorescence Source Profiles - Elements Present in Fine Particles.
- VI. Using Wind Direction Activated Sampling Instruments in Fenceline Monitoring for Source Profile Information.
- VII. Using Versatile Air Pollution Samplers for Tunnel Sampling of Motor Vehicles to Collect Source Profile Information.
- VIII. Methods for Resuspending Soil and Road Dust Samples to Obtain Source Profiles.
- IX. The EPA Speciate Library of Source Profiles.
- X. Other Sources of Source Profile Information.
- XI. Questions on This Session.
- XII. Summary

Source Characterization: Sampling and Analysis Methods

*Source Characterization:
Sampling and Analysis Methods*

**ROBERT K. STEVENS, FL DEP
@ US EPA, RTP, NC**

**PETER A. SCHEFF UNIV. OF IL
AT CHICAGO, IL**

***Sampling and Analysis Methods
to Obtain Source Profiles***

- ▶ Source profiles should be obtained using the same sampling methods used at the receptor site.
- ▶ Samples should be collected on filter media compatible with the analytical methods.

***Sampling and Analysis Methods
to Obtain Source Profiles***

- ▶ Residence time in the source dilution apparatus should be long enough to allow the hot gases to condense / coagulate to filterable particles.

Source Characterization: Sampling and Analysis Methods

EPA Method 5

- ▶ Determination of Particulate Emissions from Stationary Sources
- ▶ For Method 5 to be valid, the sample of stack gas extracted must be a "representative" sample.
- ▶ EPA Methods 1 through 5 are designed for this purpose.

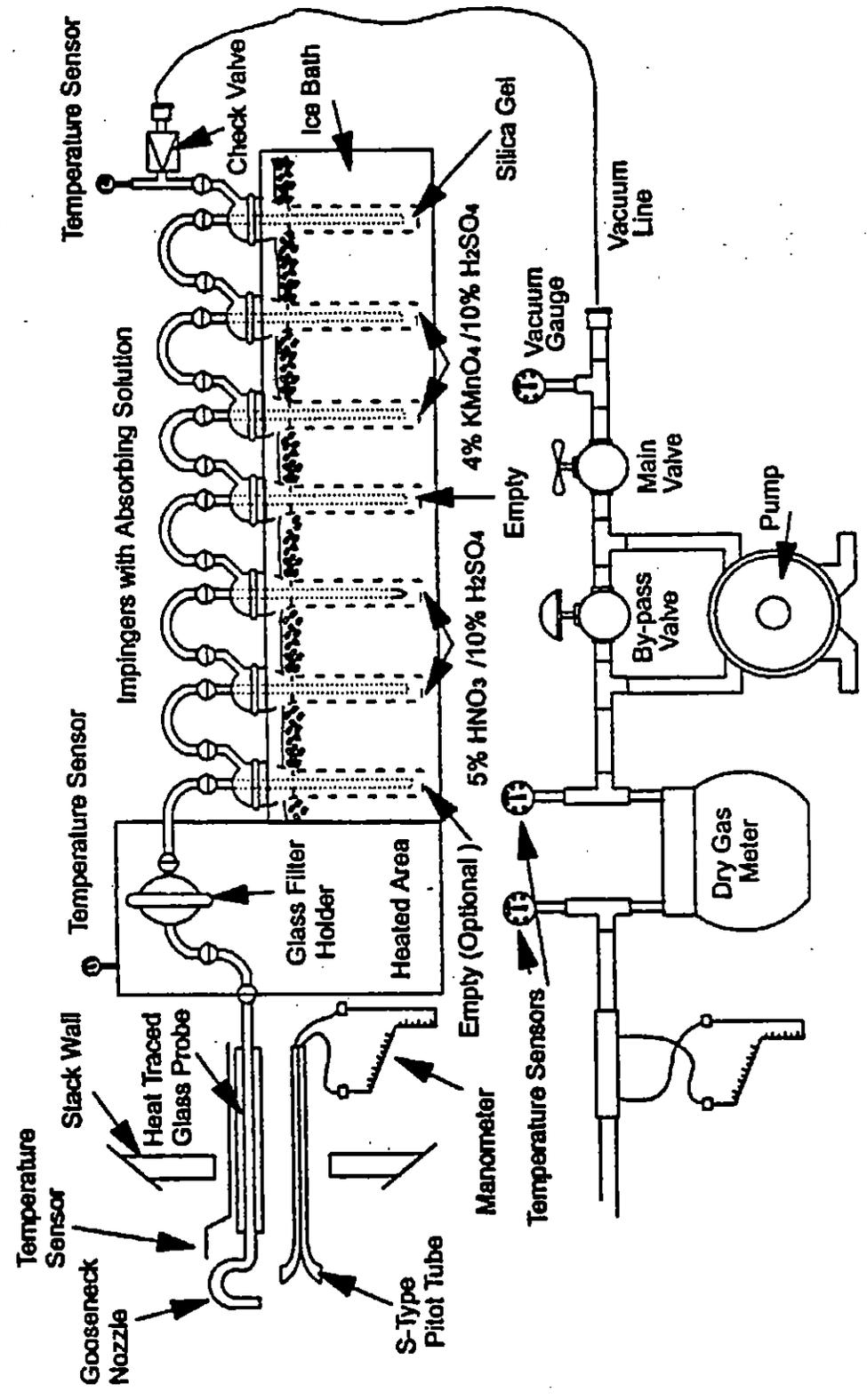
USEPA Methods 1 - 5

- 1: Determination of the number and exact location of sampling points in the stack.
- 2: Determination of stack gas velocity with a Stausscheibe (S-type) pitot tube.
- 3: Determination of the dry molecular weight of stack gas.
- 4: Determination of the moisture content of the stack gas.
- 5: Isokinetic source sampling. Velocity of stack gas approaching sampling nozzle must equal velocity in sampling.

US EPA Method 5 Sampling Train

See Insert

USEPA METHOD 5 SAMPLING TRAIN



Source Characterization: Sampling and Analysis Methods

***Teflon Coated Large Source
Dilution Sampler Used to Obtain
Incinerator Source Profiles***

See Insert

Small Teflon Coated Sampler

See Insert

***Analytical Methods Needed in
Support of Aerosol Characterization***

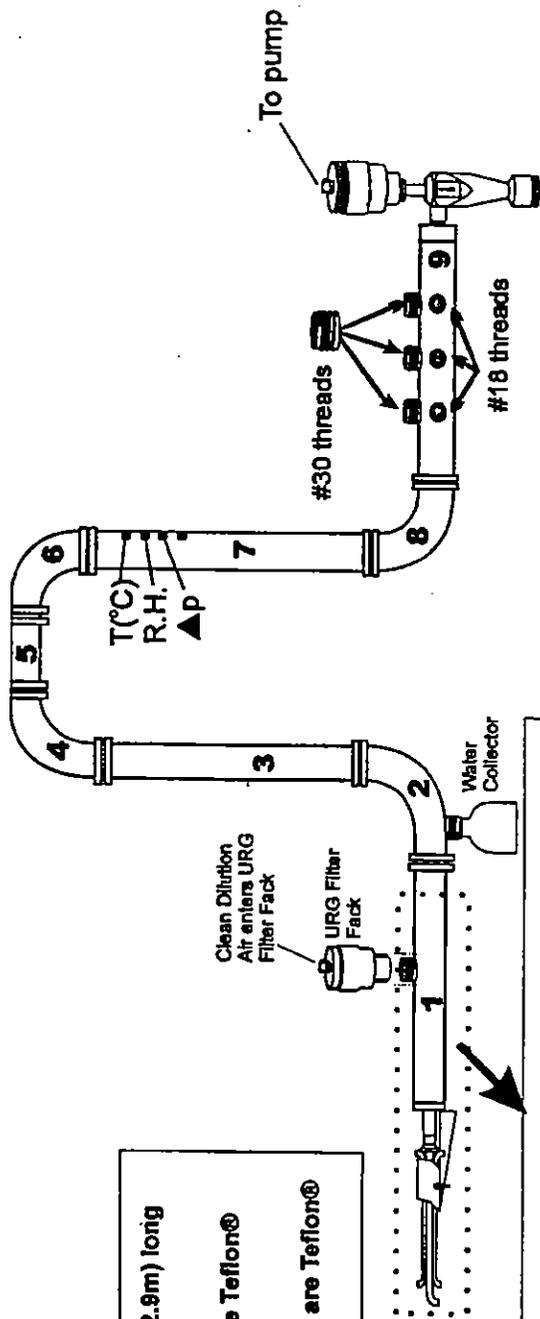
- ▶ Microanalytical Balance
- ▶ Energy Dispersive X-Ray Fluorescence Analyzer
- ▶ Ion Chromatographic Analyzer for Anions and Cations
- ▶ Combustion Analyzer for Carbon (C_{E,C_V})
- ▶ Scanning Electron Microscope

TEFLON® COATED LARGE SOURCE DILUTION SAMPLER USED TO OBTAIN INCINERATOR SOURCE PROFILES

Body of the Sampler is 12' (~2.9m) long x 3" (~7.5cm) wide

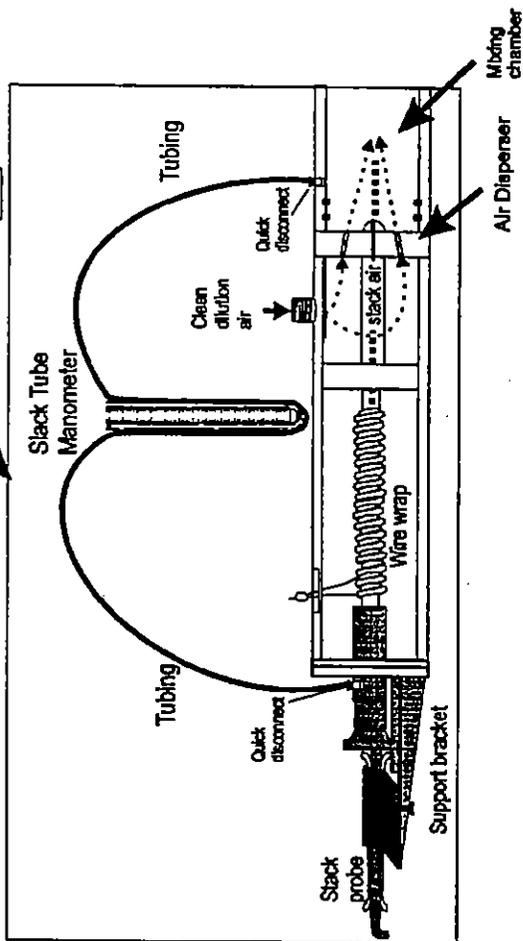
Components #2, 4, 6 and 8 are Teflon® coated glass

Components #1, 3, 5, 7, and 9 are Teflon® coated aluminum

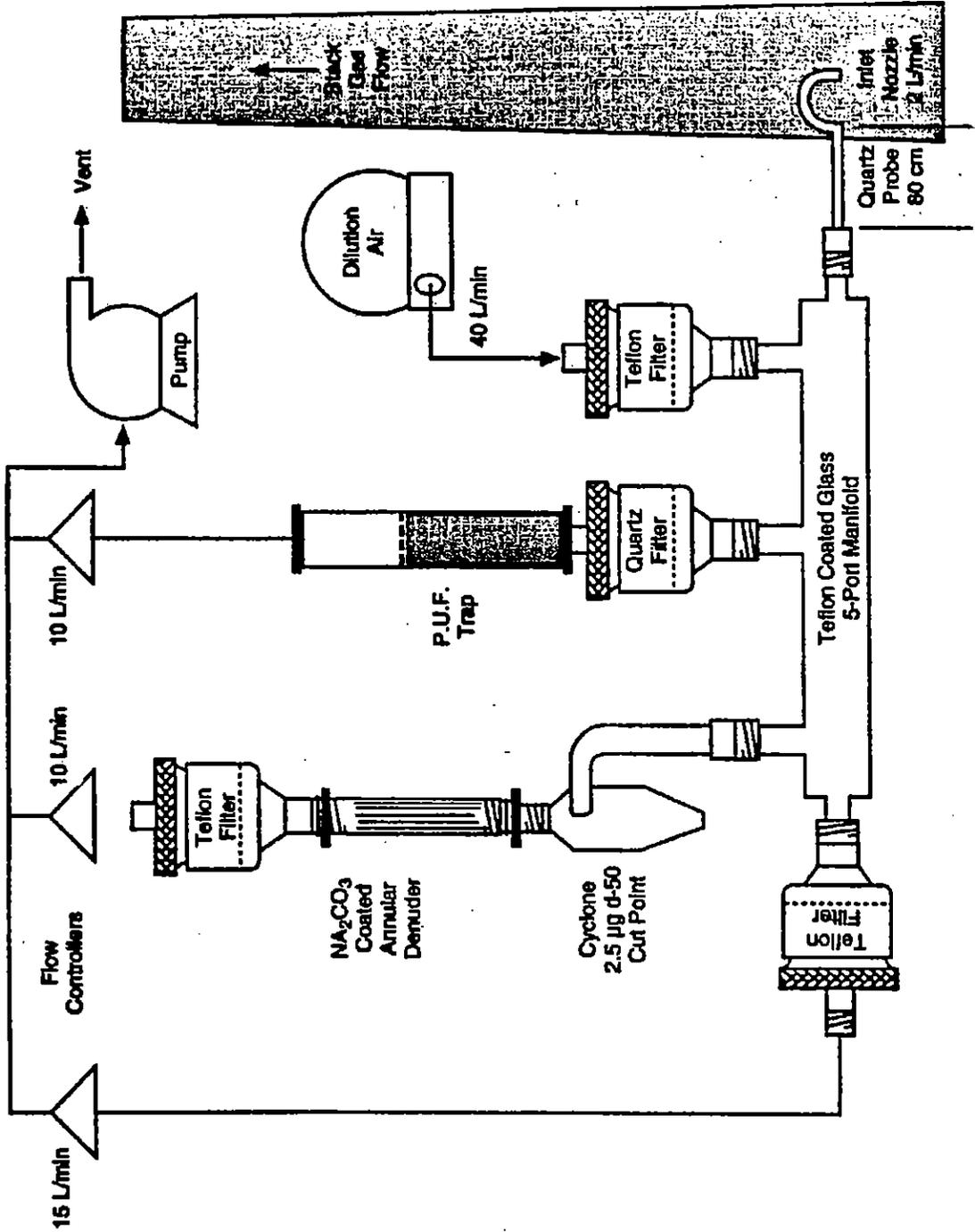


For the Collection of :
 TSP, PM10, PM2.5, PM1.0, Acid Aerosols,
 Basic Gases, Semi-volatile organics
 (Acid and Basic can all be collected
 simultaneously)

Filter Packs, Polyurethane Foam
 Traps (PUF), Cyclones and
 Elutriators may be used



SMALL TEFLON COATED DILUTION SAMPLER



Source Characterization: Sampling and Analysis Methods

Alternate Methods for Measuring Trace Elements

- ▶ Instrumental Neutron Activation Analysis
- ▶ Atomic Absorption Spectrometry
- ▶ Proton Induced X-Ray Emission Spectroscopy
- ▶ Inductively Coupled Plasma Emission Spectroscopy

Typical Source Profiles

See Insert

Fence Line Monitoring For Source Profile Determination

- ▶ Useful for sources which do not have a well defined point of release.
- ▶ Need to carefully consider wind direction.
- ▶ Simultaneous up-wind and down-wind sampling is preferable.

TYPICAL SOURCE PROFILES

	Power Plant	Home Heating-S	Home Heating-A	Mobile	Incinerator
OC	7.5%	68.0%	61.7%	53.9%	5700 ppm
EC	-	2.0%	6.2%	10.1%	3.5%
Al	15.6%	-	-	-	2500 ppm
Si	18.8%	823 ppm	-	2888 ppm	1.7%
S	1.4%	8330 ppm	1.55%	2.72%	2.9%
Cl	-	1196 ppm	2052 ppm	3838 ppm	27.0%
K	1.8%	665 ppm	2571 ppm	1001 ppm	7.6%
Ca	4262 ppm	2048 ppm	-	1040 ppm	2300 ppm
Tl	9850 ppm	298 ppm	-	-	300 ppm
V	337 ppm	-	-	-	9 ppm
Cr	288 ppm	-	-	-	-
Fe	4.2%	844 ppm	435 ppm	3886 ppm	2200 ppm
Zn	665 ppm	145 ppm	1936 ppm	946 ppm	10.4%
As	220 ppm	62 ppm	226 ppm	-	64 ppm
Se	559 ppm	25 ppm	27 ppm	-	42 ppm
Br	-	67 ppm	59 ppm	2575 ppm	2300 ppm
Pb	190 ppm	60 ppm	211 ppm	9086 ppm	5.8%

Home Heating-S = Smoldering phase.
 Home Heating-A = Active (high-temperature) phase.

Source Characterization: Sampling and Analysis Methods

Fence Line Monitoring For Source Profile Determination

- ▶ Wind direction activated samplers are available that allow for long sampling times without the need for an on-site operator.
- ▶ May need to adjust downwind concentrations with upwind measurements before determining profile.

Fence Line Monitoring For Source Profile Determination

- ▶ Examples of sources studied include:
 - ▶ Fugitive emissions from petroleum refineries. (See Sexton and Westberg, 1983 and Doskey et al, 1992)
 - ▶ Fugitive dust emissions from storage piles.
 - ▶ VOC and PAH emissions from coke batteries.

Fence Line Monitoring For Source Profile Determination

- ▶ Examples of sources studied include:
 - ▶ VOC emissions from the aeration basins of waste water treatment facilities.
 - ▶ Biological emission profiles from the turning of compost piles.

Source Characterization: Sampling and Analysis Methods

Example: Average Nmoc Composition From Metallurgical Coke Production

<u>Compound</u>	<u>% of total NMOC</u>
Butane	2.32
Pentane	0.53
Methylene chloride	0.99
Hexane	0.51
Benzene	11.46
2,3-dimethylpentane	3.99
n-Heptane	1.08
Toluene	1.73
n-Octane	0.22
Xylene	2.05
n-Nonane	1.45

Tunnel Sampling For Motor Vehicle Source Profiles

- ▶ Tunnel sampling has been used to check emission factors and develop source profiles for mobile sources.
- ▶ Concentrations at tunnel inlets can be used to adjust measured concentrations.

Tunnel Sampling For Motor Vehicle Source Profiles

- ▶ USEPA sponsored "Atlanta Ozone Precursor Monitoring Study" looked at the composition of roadway emissions from vehicles traveling from approximately 30 to 60 mph.
- ▶ Ingalls study in the Los Angeles Van Nuys tunnel (SCAQS, 1987) showed that mobile source emission models may predict low by a factor of 3 to 4 for CO and HC.

Source Characterization: Sampling and Analysis Methods

Tunnel Sampling For Motor Vehicle Source Profiles

- ▶ Average emission factors from Van Nuys Tunnel

<u>pollutant</u>	<u>emission, g/mi</u>
CO	22.9
HC	2.8
NOx	1.5
PM2.5	0.089
PM10	0.11

Tunnel Sampling For Motor Vehicle Source Profiles

- ▶ Ratios of these emission factors can be used to add CO and NOx as fitting compounds to CMB models of vehicle HC.

Soil And Roadway Dust Samples

- ▶ CMB is well suited to the identification of the sources of fugitive soil and dust particles.
- ▶ Soil samples can be resuspended with compressed air in chambers and sampled with size selective inlets coupled to appropriate filter media.

Source Characterization: Sampling and Analysis Methods

Soil And Roadway Dust Samples

- ▶ These samples should be treated with the same analytical finish that is being used for ambient measurements.
- ▶ This puts the fingerprints on the same basis as the ambient air measurements.

USEPA Speciation Data System

- ▶ Available on Internet at USEPA ftp site
<ftp://ttnftp.rtpnc.epa.gov/e-drive/chief/spec/>
- ▶ Currently only available in computerized data base format
- ▶ Air Emissions Species Manual, VOC/PM Speciation Data System (SPECIATE), Version 1.5.

USEPA Speciation Data System

- ▶ 363 PM profiles representing 23 overall source categories.
- ▶ 352 VOC profiles that span 31 industrial and non-industrial source categories.

Source Characterization: Sampling and Analysis Methods

USEPA Speciation Data System

- ▶ Data base includes identification information; data quality indicator; references; source classification codes; species identification by Chemical Abstract System number, species name or species synonym; chemical speciation in weight percent; and date.

USEPA Speciation Data System

- ▶ Requires 7.5 MB storage for SPECIATE and users guide.
- ▶ SPECIATE is a MSDOS program that runs well under Windows 95.

Major VOC Profile Source Categories

- ▶ Aircraft
- ▶ Asphalt Products
- ▶ Carbon Black Production
- ▶ External Combustion Boilers
- ▶ Food and Agriculture
- ▶ Forest Fires
- ▶ Industry-Specific Averages
- ▶ Internal Combustion Engines

Source Characterization: Sampling and Analysis Methods

Major VOC Profile Source Categories

- ▶ Jet Engines
- ▶ Mobile Sources
- ▶ Oil and Gas Production
- ▶ Organic Chemical Manufacture
- ▶ Organic Chemical Storage
- ▶ Organic Solvent Evaporation
- ▶ Paint Production

Major VOC Profile Source Categories

- ▶ Petroleum Products
- ▶ Plastics Production
- ▶ Plywood Production
- ▶ Primary and Secondary Metal Production
- ▶ Printing/Publishing Processes
- ▶ Printing Ink Manufacture
- ▶ Railcar, Tank Truck, and Drum Cleaning

Major VOC Profile Source Categories

- ▶ Solid Waste Disposal
- ▶ Storage, Transportation, and Marketing of Petroleum
- ▶ Surface Coating Operations
- ▶ Synthetic Rubber Production
- ▶ Synthetic Organic Fiber Production
- ▶ Textile Products
- ▶ Varnish Manufacture
- ▶ Wood Combustion

Source Characterization: Sampling and Analysis Methods

List Of Major PM Profile Source Categories

- ▶ Agriculture Field Burning
- ▶ Aircraft
- ▶ Chemical Manufacturing
- ▶ External Combustion Boilers
- ▶ Food and Agriculture
- ▶ Heavy Construction
- ▶ Industry-Specific Averages
- ▶ Metal Fabrication

List Of Major PM Profile Source Categories

- ▶ Mineral Products
- ▶ Mobile Sources
- ▶ Natural Sources
- ▶ Orchard Heating
- ▶ Paved Roads
- ▶ Petroleum Industry
- ▶ Primary Metal Production

List Of Major PM Profile Source Categories

- ▶ Pulp and Paper Industry
- ▶ Residential Space Heating
- ▶ Secondary Metal Production
- ▶ Solid Waste Disposal
- ▶ Surface Coating Operations
- ▶ Unpaved Roads
- ▶ Wood Combustion

Source Characterization: Sampling and Analysis Methods

Use Of Emission Inventory In The Development Of Source Fingerprints

- ▶ Fingerprints must represent broadly defined source categories. (see Scheff etal, 1989)
- ▶ Architectural coatings include solvent-based coatings (64% of VOC emissions), clean-up solvents (11%) and water-based coatings (25%). (from 1984 survey of New York/New Jersey)

Use Of Emission Inventory In The Development Of Source Fingerprints

- ▶ Graphic arts is a composite of lithography (28% of emissions), letterpress (18%), flexographic (13%) and rotogravure (41%). (from AP-42)
- ▶ Nationwide sales volumes of gasoline in 1989 were 60% regular, 10% mid-grade and 30% premium. (See Doskey etal, 1992)

Use Of Emission Inventory In The Development Of Source Fingerprints

- ▶ Individual fingerprints from SPECIATE or other literature sources can be combined with emission or consumption percentages to derive composite fingerprints for coatings, printing, and fugitive gasoline vapors.
- ▶ Solvent consumption surveys can be used to develop fingerprints for vapor degreasing and dry cleaning. (see Scheff etal, 1989)

Source Characterization: Sampling and Analysis Methods

Additional References

- ▶ USEPA: Volatile Organic Compound (VOC) / Particulate Matter (PM) Speciation Data System (SPECIATE) User's Manual, Version 1.5, February, 1993.
- ▶ Scheff, P.A., Jeng J.-Y., Graf-Teterycz, J., Keil, C., and Wadden, R.A.: Composition of Volatile Organic Compound Emissions from Spark Ignition and Diesel Vehicles, Coke Ovens, Wastewater Treatment Plants and Wood Combustion. Paper 92-66.02. Presented at the 85th Annual Meeting of the Air and Waste Management Association, Kansas City, June, 1992.

Additional References

- ▶ Doskey, P.V., Porter, J.A. and Scheff, P.A. Source Fingerprints for Volatile Nonmethane Hydrocarbons. J. Air Waste Manage. Assoc., 42:1437-1445, 1992.
- ▶ Scheff, P.A., Wadden, R.A., Aronian, P.F. and Bates, B.: Source Fingerprints for Receptor Modeling of Volatile Organics. J. Air Pollut. Control Assoc., 39:469-478, 1989.

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- ▶ Khalili, N.R., Scheff, P.A. and Holsen, T.M.: PAH Source Fingerprints for Coke Ovens, Diesel and Gasoline Engines, Highway Tunnels, and Wood Combustion Emissions. Atmos. Environ., 29(4):533-542, 1995.
- ▶ Ingalls, M.R.: On-Road Vehicle Emission factors From Measurements in a Los Angeles Area Tunnel. Paper 89-137.3, Presented at the 82nd Annual Meeting of the Air and Waste Management Association, Anaheim, CA, June, 1989.

Source Characterization: Sampling and Analysis Methods

Additional References

- ▶ Conner, T.L., Lonneman, W.A. and Seila, R.L.: Transportation-Related Volatile Hydrocarbon Source Profiles Measured in Atlanta. J. Air Waste Manage. Assoc., 45:383-394, 1995.
- ▶ Lonneman, W.A., Seila, R.L. and Meeks, S.A.: Non-Methane Organic Composition in the Lincoln Tunnel. Environ. Sci. and Technol., 20:790-796, 1986.
- ▶ Sexton, K. And Westberg, H.: Photochemical Ozone Formation From Petroleum Refinery Emissions. Atmos. Environ., 17:467, 1983.

Reference Related to Source Sampling and Analysis

- ▶ Stevens, R. K. and Pace, T. G.; Overview of The Mathematical and Empirical Receptor models workshop (Quail Roost II), Atmos. Environ., 18., 1499-1506, 1984.
- ▶ Hildemann, R. G., Cass, G. R., and Markowski, G. R., A Dilution Stack Sampler for Organic Aerosol Emissions: Aerosol Sci. Technol., 14, 1205-1209, 1989.

Reference Related to Source Profile Sampling and an Analysis

- ▶ URG Source Dilution Sampler, URG, Chapel Hill ,NC.
- ▶ Chow, J. C., And Watson, J. G., Contemporary Source Profiles For Geological Material and Motor Vehicle Emissions, DRI Document NO., 2625.2F, Feb. 1994.
- ▶ US EPA Speciate Library.

Source Characterization: Sampling and Analysis Methods

Rationale for Dilution Sampling

See Insert

Reference Related to Large Source Dilution Sampling

- ▶ Heinsohn, R.J., J.W. Davis, K.T. Knapp. *Env. Sci. Technol.*, 14, 1205-1209, 1980.
- ▶ Huynk, C.K., T. VuDuc, C. Schwab, H. Rollier, *Atmos. Env.*, 18, 155-239, 1984.
- ▶ Hildemann, L.M., G.R. Cass, G.R. Markowski, *Aerosol. Sci. and Technol.*, 10, 193-204, 1989.

Reference Related to Large Source Dilution Sampling

- ▶ Stevens, R.K., T.G. Pace, "Overview of the Mathematical and Empirical Receptor Model Workshop (Quail Roost II)," *Atmos. Environ.*, 18, 1499-1506, 1984.

RATIONALE FOR DILUTION SAMPLING

Dilution samplers have been under development for over two decades to remedy many of the difficulties inherent in conventional stack testing systems (e.g., Heinsohn et al., 1980; Huynk et al., 1984; Hildemann et al., 1989). Standard stack testing techniques collect samples at elevated temperatures, thereby missing chemical reactions and condensation which occur on the surface of fly ash. Dilution systems attempt to collect samples which are more representative of actual emissions to the atmosphere by simulating the process of cooling and condensation that occur when material leaves a stack. Because a dilution system collects samples closer to ambient conditions than do conventional methods, methods which are used to collect ambient samples can also be used to collect source samples, thereby eliminating any bias which may occur through the use of different sampling systems.

Receptor modeling applications require (Stevens and Pace, 1984) the simultaneous analysis of a wider variety of trace elements than are available from traditional stack testing techniques. Traditional stack techniques are oriented towards the collection of specific pollutants (e.g., toxic metals) and not the full range of elements that are typically used in receptor modeling (e.g., Na through Pb).

There are a number of factors to consider in the application of a dilution system. To allow for the process of condensation on particle surfaces the collision time of supersaturated metal and organic pollutant vapors with particles should be less than the residence time of air within the dilution chamber. Otherwise there may be condensation on unwanted surfaces or the vapors will pass through the system without being collected. This collision time may be estimated by knowing the total aerosol concentration and size distribution within the stack. The dilution ratio should also be adjusted to insure that water does not condense on the surface of the chamber. Needless to say, sound experimental design considerations which are used in traditional stack testing, such as obtaining representative samples over a period of time and avoiding artifacts caused by pollution control devices should also be followed.

Lesson X

Introduction to CMB 8 Software
Peter Scheff

INTRODUCTION TO RECEPTOR MODELING

Lesson Title: Introduction to the CMB 8 Software
Lesson: X
Prepared By: P.A. Scheff
Date: February, 12, 1998

Lesson Goal: The goal of this lesson is to become familiar with the CMB8 software and the commands necessary to run the model.

Lesson Objectives: At the completion of this lesson students will be able to:

Install CMB8 software on their PC

Describe the structure of the input and output files for the CMB8 computer program.

Describe the necessary inputs for the CMB calculation.

Explain the functions of the CMB8 commands

References:

U.S. EPA, Receptor Model Technical Series, Volume III (1989 Revision): CMB7 User's Manual, EPA-450/4-90-004, U.S. EPA, Research Triangle Park, NC, 27711, January, 1990.

Lewis, Charles W. A CMB8: New Software for Chemical Mass Balance Receptor Modeling. Proceedings of the EPA/A&WMA Symposium- Measurement of Toxic and Related Air Pollutants. April 29-May 1, 1997, Research Triangle Park, NC

CMB8 Tutorial

INTRODUCTION TO RECEPTOR MODELING

LESSON X OUTLINE

I. Introduction and Objectives

II. CMB8 Installation

Available for Microsoft Windows 3.x and Windows 95

Steps to installation

- Enter file manager in windows
- Click on C or hard drive
- Create directory in hard drive
- Click on drive which contains CMB8 software
- Drag CMB8.exe file to chosen hard drive
- Click on directory in hard drive to inflate files
- Click on exe. File

III. Input/Output File Options

Input Files

- Ambient Data Files
- Source Profile Data Files
- Species Selection Files
- Formats

- .txt
- .car
- .csv
- .dbf
- .wks/.wk1

Output Files

- Hardcopy Output File
- Data Analysis Output File
- Formats available

- .txt
- .csv
- .dbf
- .wks