

An Overview of PM_{2.5}

An Informal Discussion of Fine Particulate with

Comparisons to TSP and PM₁₀

Physics

Chemistry

Sources

Transformations

Effects

**NUCLEAR UTILITY
Meteorological Data Users Group Meeting
(NUMUG)**



**Met One
Instruments**

TOM MERRIFIELD

Technical Director

Met One Instruments, Inc.
1600 Washington Blvd.
Grants Pass, Oregon 97526
Phone (541) 471-7111
Fax (541) 471-7116
<http://www.metone.com>

DISCLAIMER

**The study of particles is inherently messy, and
anything I, and**

anything I, or anybody else,

**say is certainly incorrect at some time and
place,**

probably including your own facility.

RULES OF THUMB For PARTICLES

(Which means, although they are probably not correct, they are a good first guess).

Some other comparisons, specifically focused to $PM_{2.5}$ -

- Unlike gasses, particles have size and shape,**
- Unlike gasses, you can almost never write a chemical formula for even a single particle, and every particle is different,**
- Unlike gasses, particle collection is averaged over extended periods of time, usually 24 hours,**
- In most cases, the detailed mechanisms of health impacts of particles are not known,**

Source of Material

Natural

Man-made

Suspension of Material

Wind

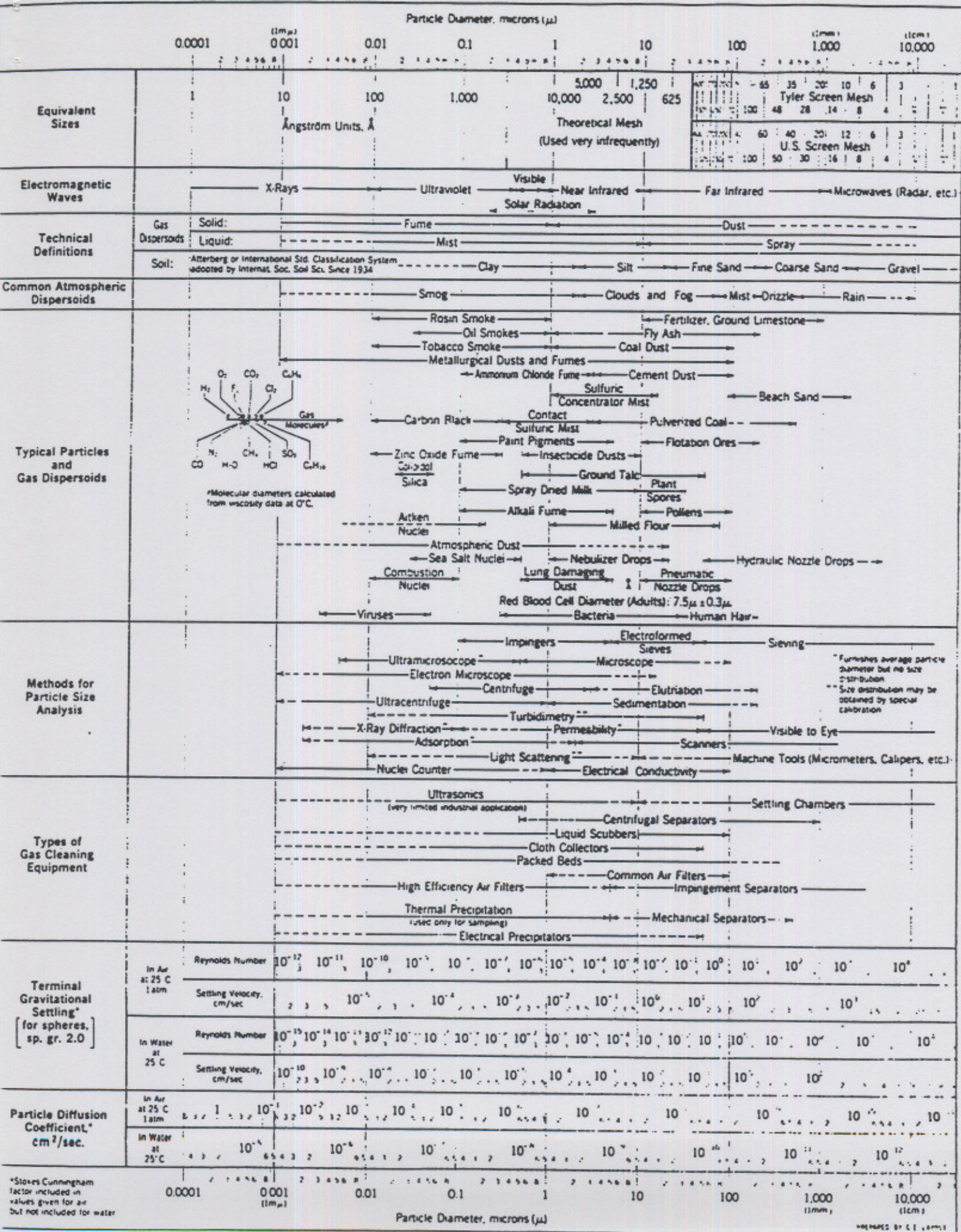
**Natural
Background**

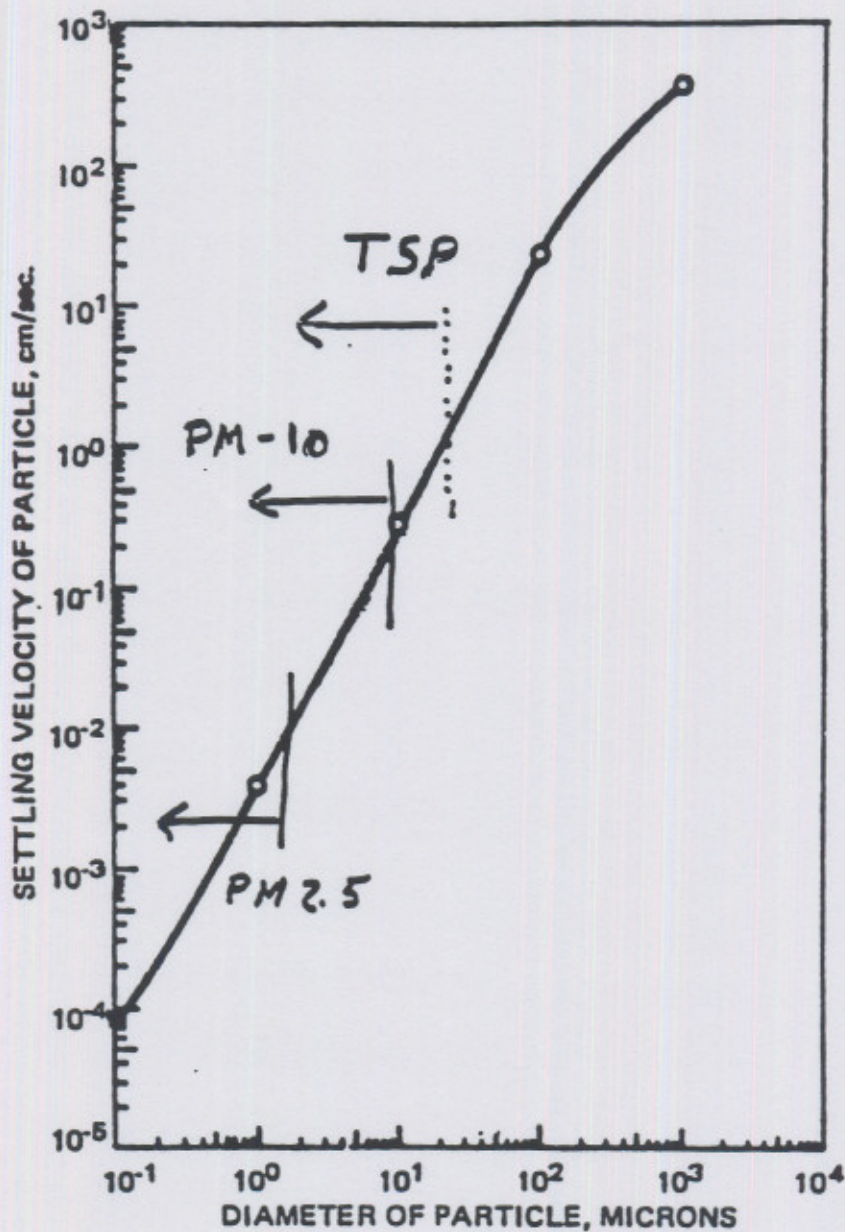
**Fugitive
Dust**

Human Activity

**Re-suspended
Dust**

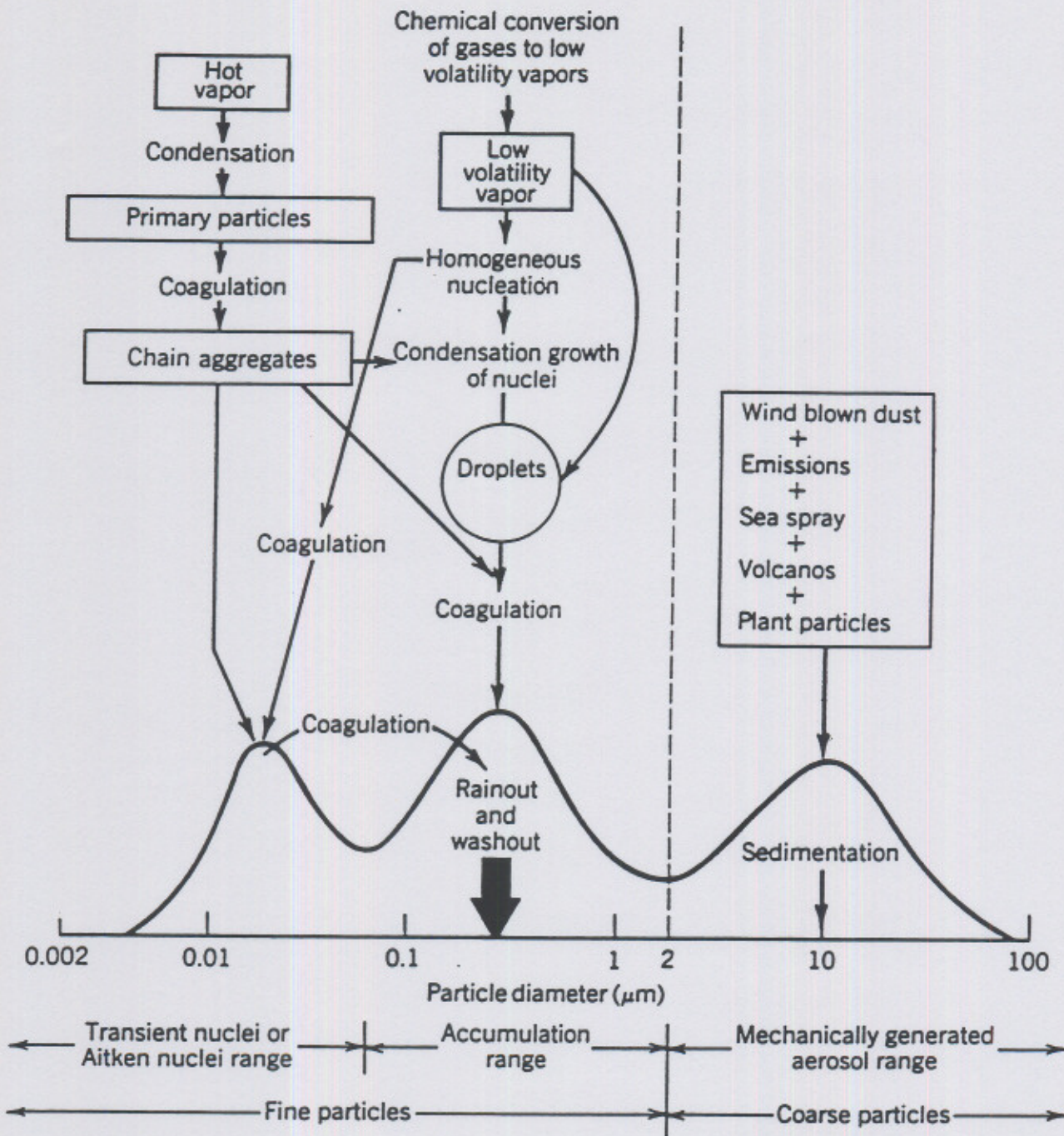
**Primary
Particulate
Pollution**





Settling velocities in still air at 0° C and 760 mm pressure for particles having a density of 1g/cm³ as a function of particle diameter. (This graph shows that, for spherical particles of unit density suspended in air near sea level, Stokes law applies over a considerable range of particle sizes, where the line is straight, but that correction is required at the extremes where the line begins to curve.)

PHYSICAL PROPERTIES



Schematic of an atmospheric aerosol size distribution showing the three modes, the main source of mass for each mode, and the principal processes involved

PM₁₀

is a Garbage Bag

of “Particles”

PM_{2.5}

is an Epidemiology “Particle”

RULES OF THUMB For PARTICLES

(Which means, although they are probably not correct, they are a good first guess).

	Size Limits		Velocity	Source	
	Upper Cut Point (μm)	Mode (μm)	(Settling) (m/hr)	Type	Location, Strength
TSP	~ 30	~ 15	3.6	Primary	Strong, Local
PM ₁₀	10	~ 7	0.4	Primary	Weaker, Sub-Regional
PM _{2.5}	2.5	~ 0.4	negl.*	Secondary	Moderate, Regional

* Efficiently removed by clouds, rainfall

Note: As PM₁₀ are transported, they rapidly (few hours) convert from PM₁₀ to PM_{2.5}.

RULES OF THUMB For PARTICLES

(Which means, although they are probably not correct,
they are a good first guess).

	Size Limits		Impacts	
	Upper Cut Point (μm)	Mode (μm)	Health Inhalability	Welfare Visibility
TSP	~ 30	~ 15	Mouth, Nose	Invisible
PM ₁₀	10	~ 7	Nose, Throat, Bronchial Tract	Invisible
PM _{2.5}	2.5	~ 0.4	Bronchial Tract, Lung	Highly Visible

Note: In wood smoke, the present 24 hr PM₁₀ standard occurs at a visibility of about 2 miles.

For the proposed 24 hr standard, this will rise to about 5 miles.

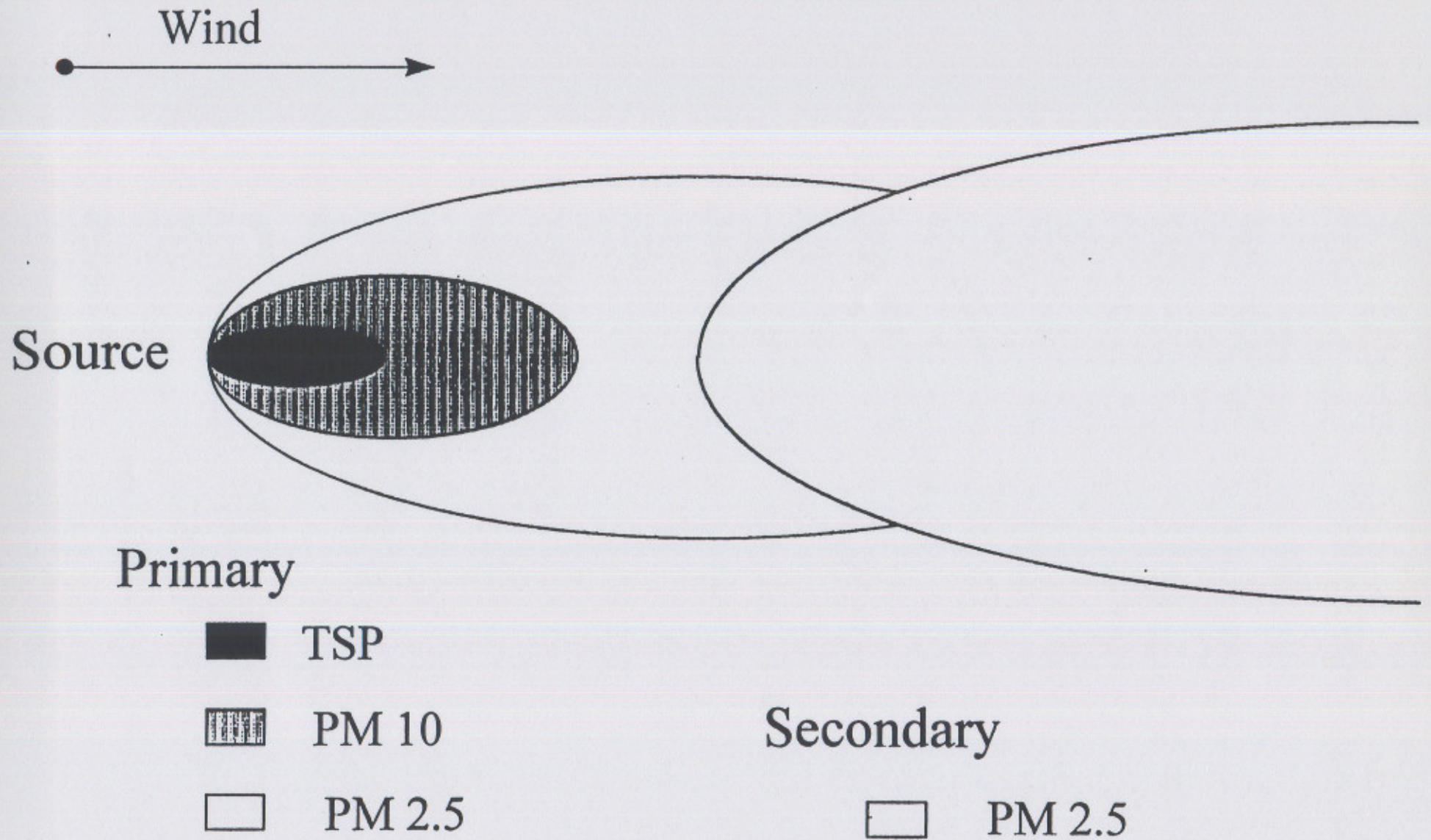
RULES OF THUMB For PARTICLES

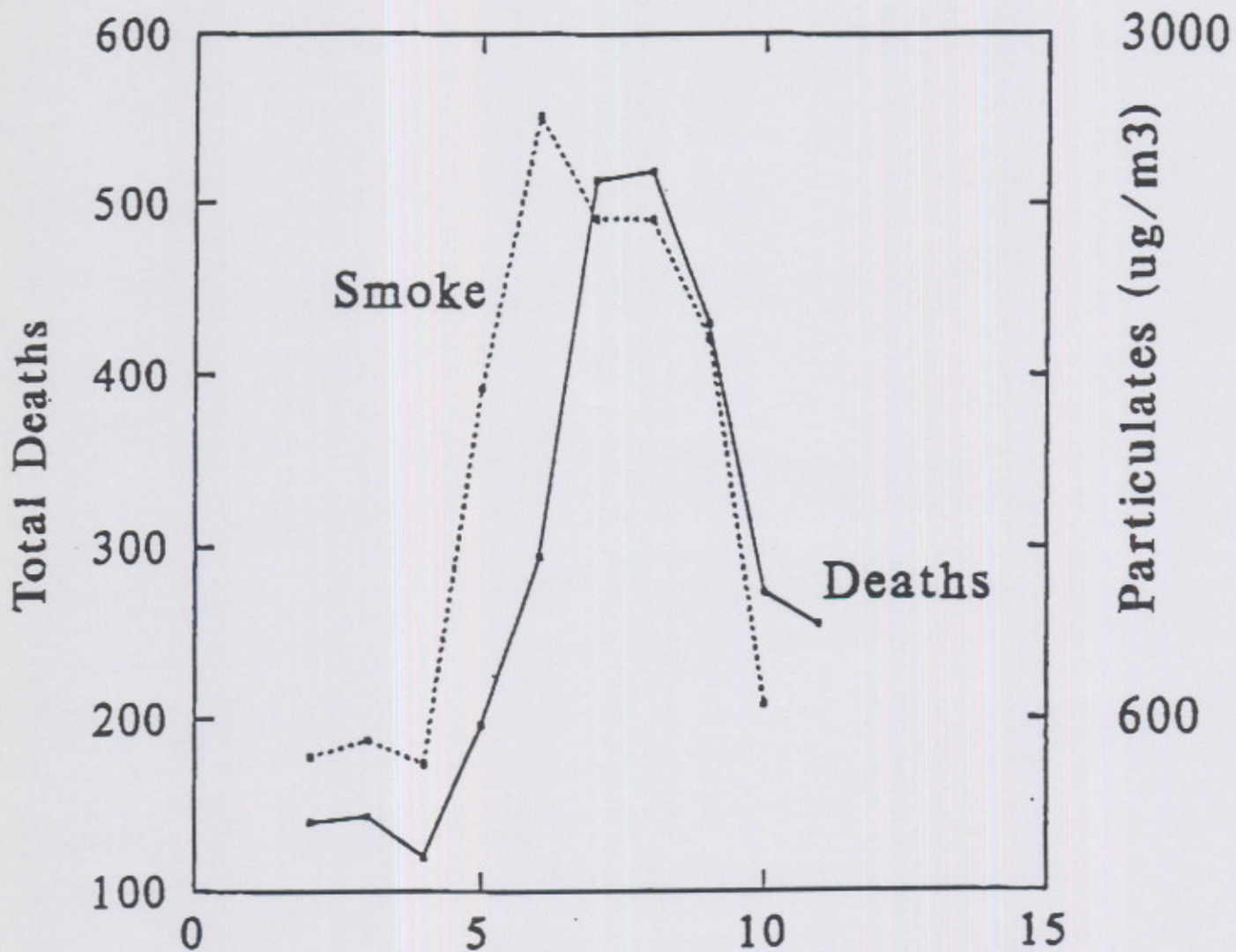
(Which means, although they are probably not correct, they are a good first guess).

	<u>Size Limits</u>		<u>Mass Concentration</u>		
	Upper Cut Point (μm)	Mode (μm)	Relative to TSP* (approx)	24 hr EPA Standards ($\mu\text{g}/\text{m}^3$)	Annual EPA Standards ($\mu\text{g}/\text{m}^3$)
TSP	~ 30	~ 15	= 1.00	260	75
PM ₁₀	10	~ 7	TSP x ~ 0.5	150	50
PM _{2.5}	2.5	~ 0.4	TSP x ~ 0.25 PM ₁₀ x ~ 0.5	50?	15?

* Major Exceptions: Wood/ Grass Smoke
 Eastern Summer Sulfate Haze
 Western Winter Valley "Fogs"
 These are as much as 90% PM_{2.5}.

Transport of Particulate Pollutants





Number of total deaths and particulate concentrations in London, England, December 2-10, 1952.

RESULTS OF HARVARD-EPA 6 CITIES STUDY (1985-1993)

This was a comparison between death rates in the cleanest city (Topeka, Kansas or Portage, Wisconsin) versus the dirtiest (Steubenville, Ohio), corrected for smoking - current smokers, past smokers, non-smokers. Note that no western cities were used.

INCREASE IN MORTALITY

Cause	Smoking		Air Pollution
	Current smokers vs non smokers	Past smokers vs non smokers	Dirty* city vs clean city
Lung Cancer	700%	154%	37%
Pulmonary Cardiovasc.	130%	52%	37%
All Others	46%	17%	1%

*Air pollution

Annual average concentrations

	Dirtiest		Cleanest	Change
PM-10	90 $\mu\text{g}/\text{m}^3$	vs	30 $\mu\text{g}/\text{m}^3$	60 $\mu\text{g}/\text{m}^3$
PM-2.5	30 $\mu\text{g}/\text{m}^3$	vs	11 $\mu\text{g}/\text{m}^3$	19 $\mu\text{g}/\text{m}^3$
Sulfates	13 $\mu\text{g}/\text{m}^3$	vs	4.5 $\mu\text{g}/\text{m}^3$	7.5 $\mu\text{g}/\text{m}^3$

Ozone ? Acidity? SO₂? No statistically sound information

NEW PROMULGATED METHOD FOR FINE PARTICULULATE PM_{2.5}

- **NAAQS JULY 18, 1997**

- **40 CFR PART 58**

**50 CHEMICAL SPECIATION SITES
OPERATIONAL BY SEPTEMBER 16, 1998**

- **REPRESENTS BEGINNING OF A NEW
NATIONAL NETWORK**
- **LIKELY CO-LOCATED WITH PM 2.5 CORE
SITES (COMMUNITY REPRESENTATIVE
SITES)**
- **EXPAND NETWORK TO 300 SITES**

PROVIDE CHEMICAL SPECIATION DATA

- **PARTICULATE MASS**
- **SULFATE CONTENT**
- **NITRATE CONTENT**
 - **AMMONIUM**
- **ORGANIC CARBON**
- **ELEMENTAL CARBON**
 - **TRACE METALS**

Chemical Speciation Approach

- Sampling

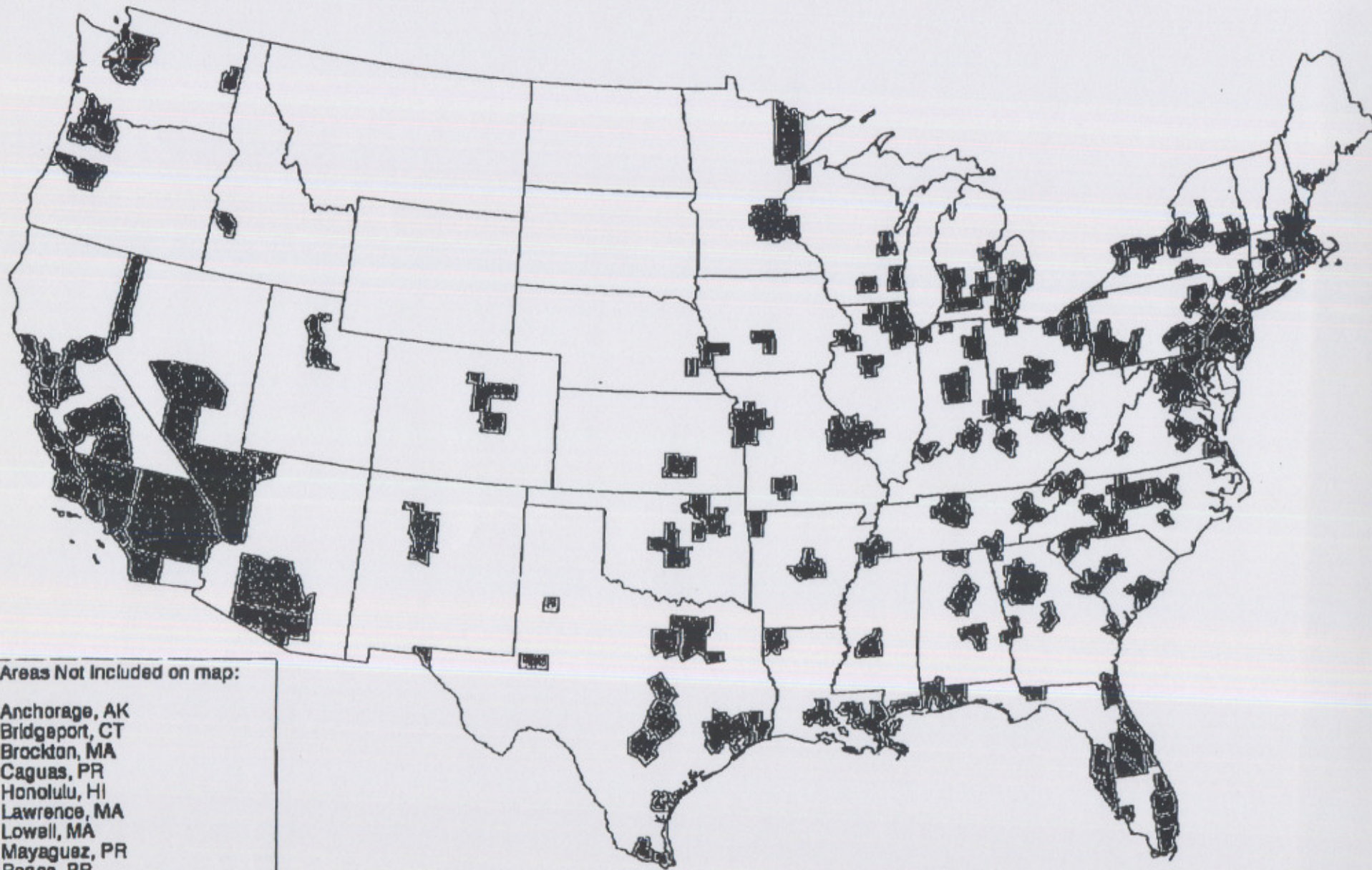
- Allow flexible and creative approaches (no FRM/FEM designations required)
- Samples similar to FRM, but can include additional filter media

- Analysis

- Routine analyses similar to IMPROVE with standardized SOPs
- Array of analytical methods with proven applications to filter samples



MSAs Required to Monitor PM2.5



Areas Not Included on map:

- Anchorage, AK
- Bridgeport, CT
- Brockton, MA
- Caguas, PR
- Honolulu, HI
- Lawrence, MA
- Lowell, MA
- Mayaguez, PR
- Ponce, PR
- Portsmouth-Rochester, NH-MA
- San Juan, PR
- Stamford, CT
- Waterbury, CT
- Worcester, MA

 **Monitored MSAs**
 **States.shp**

07.20.86 17:16 000 044 1800

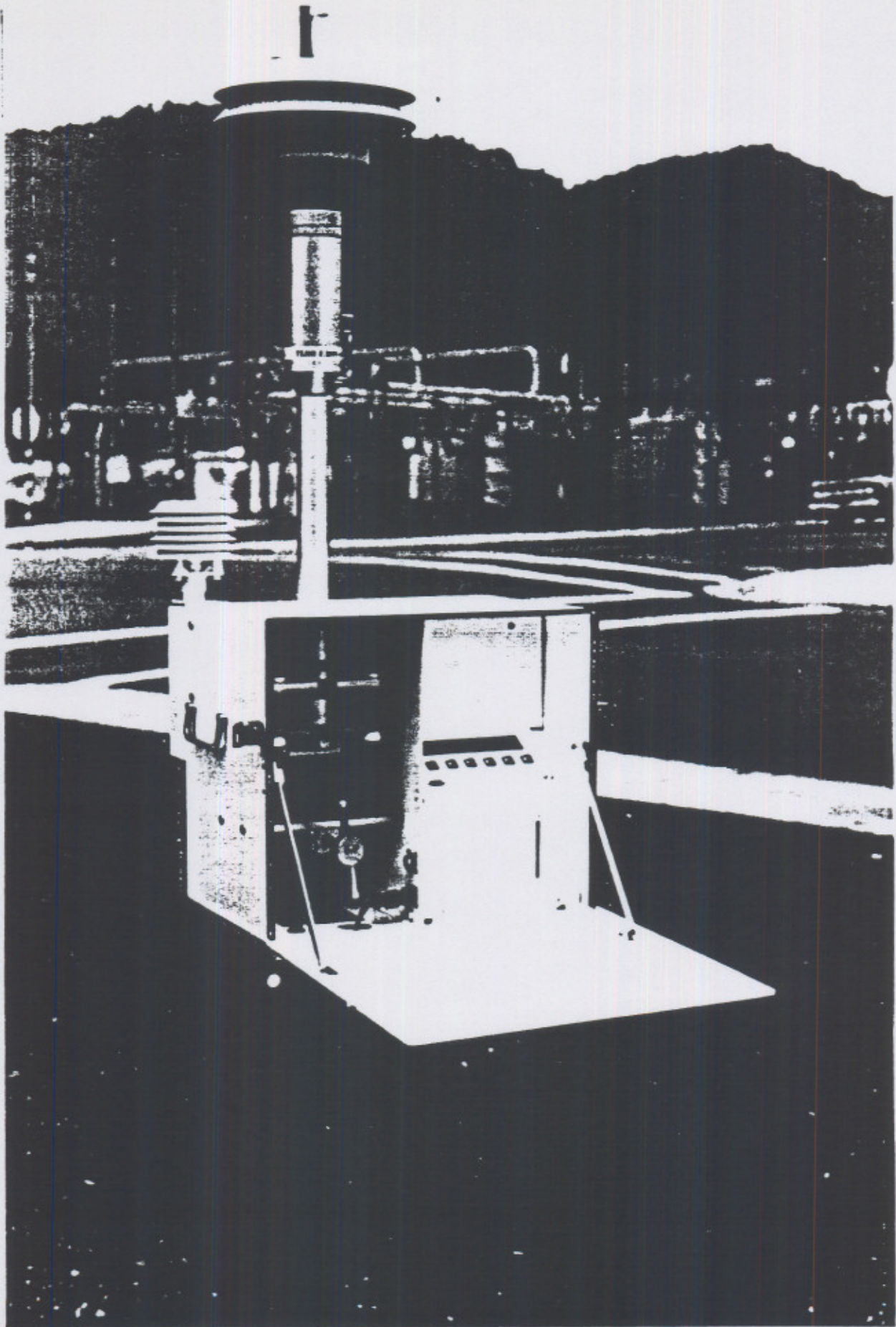
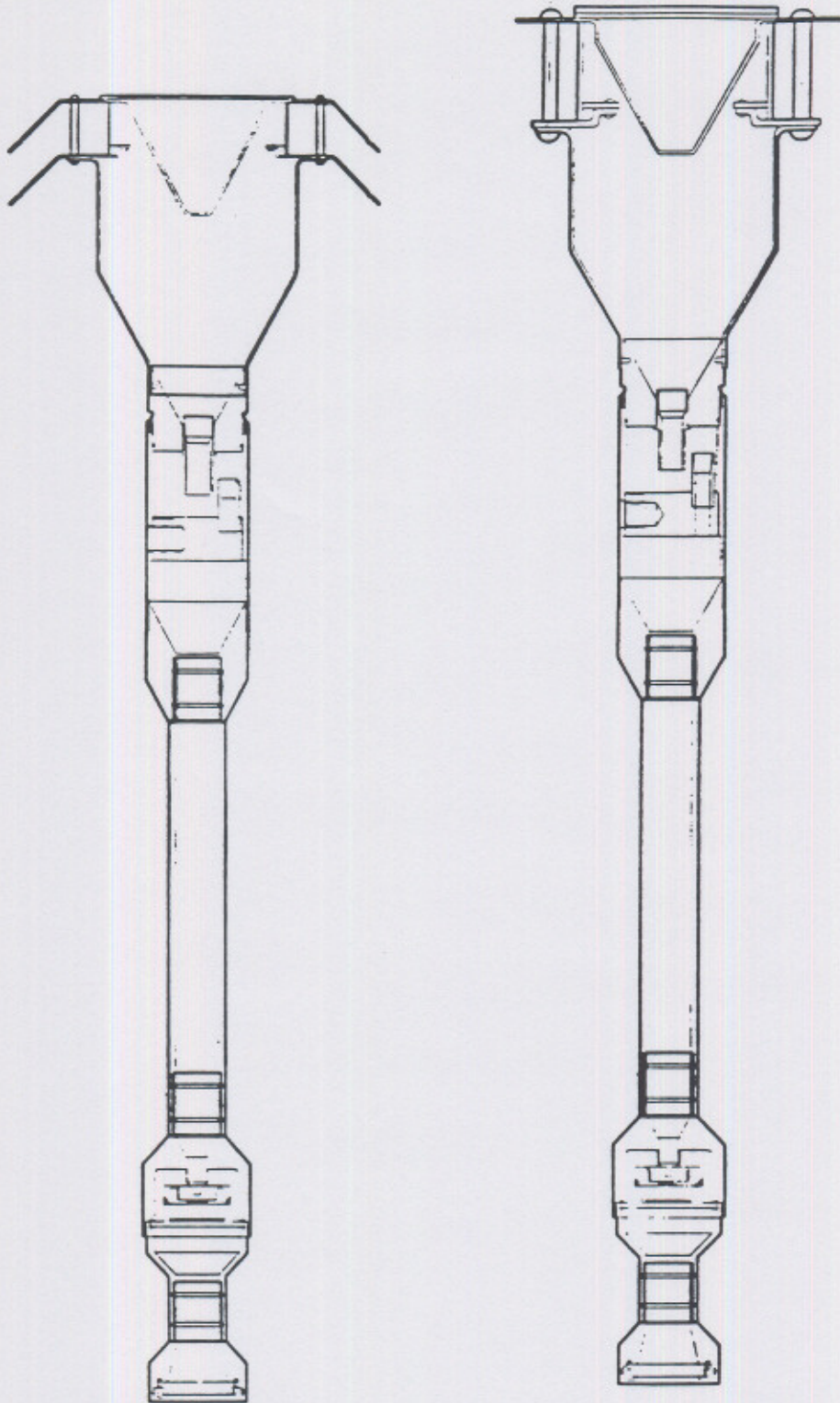
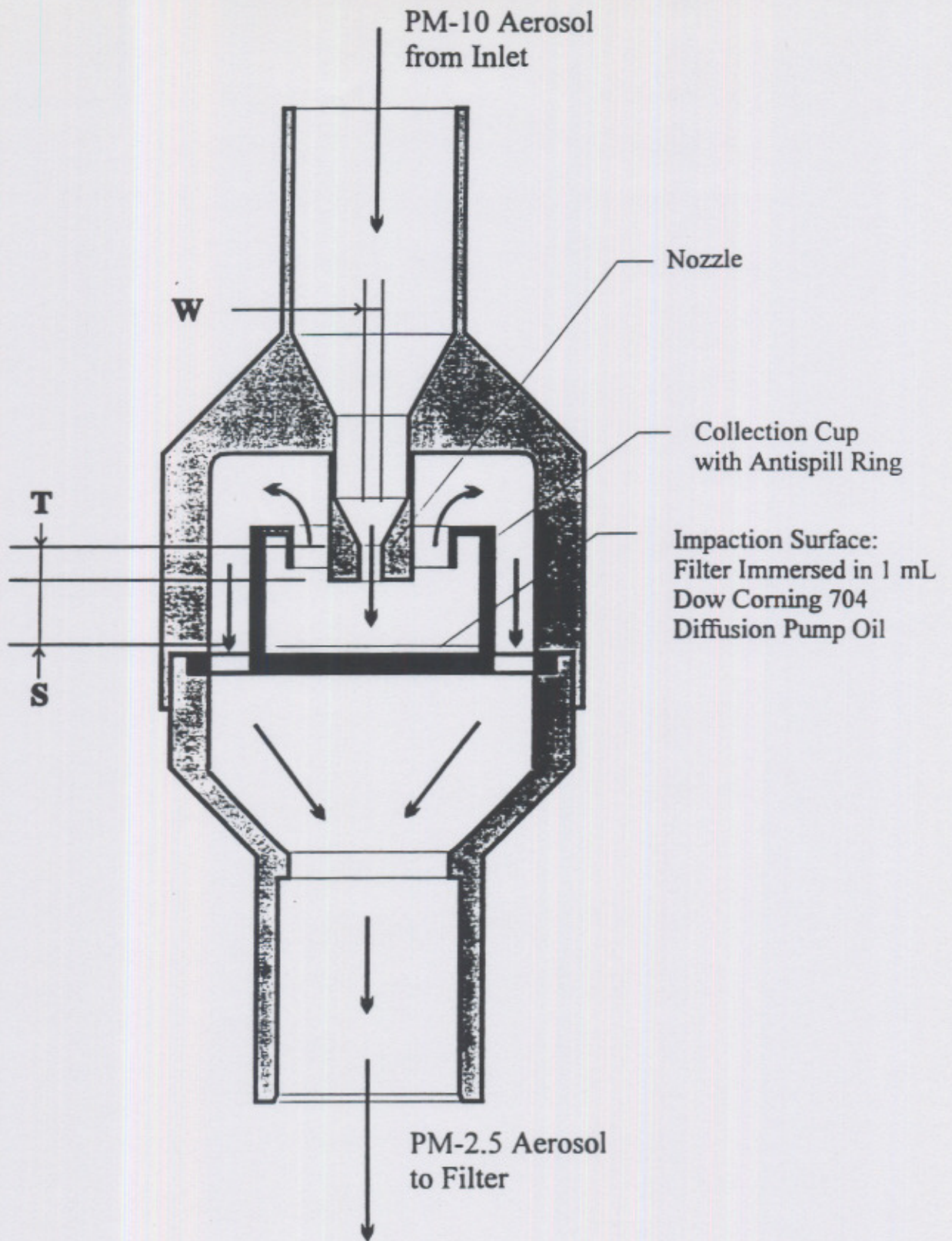
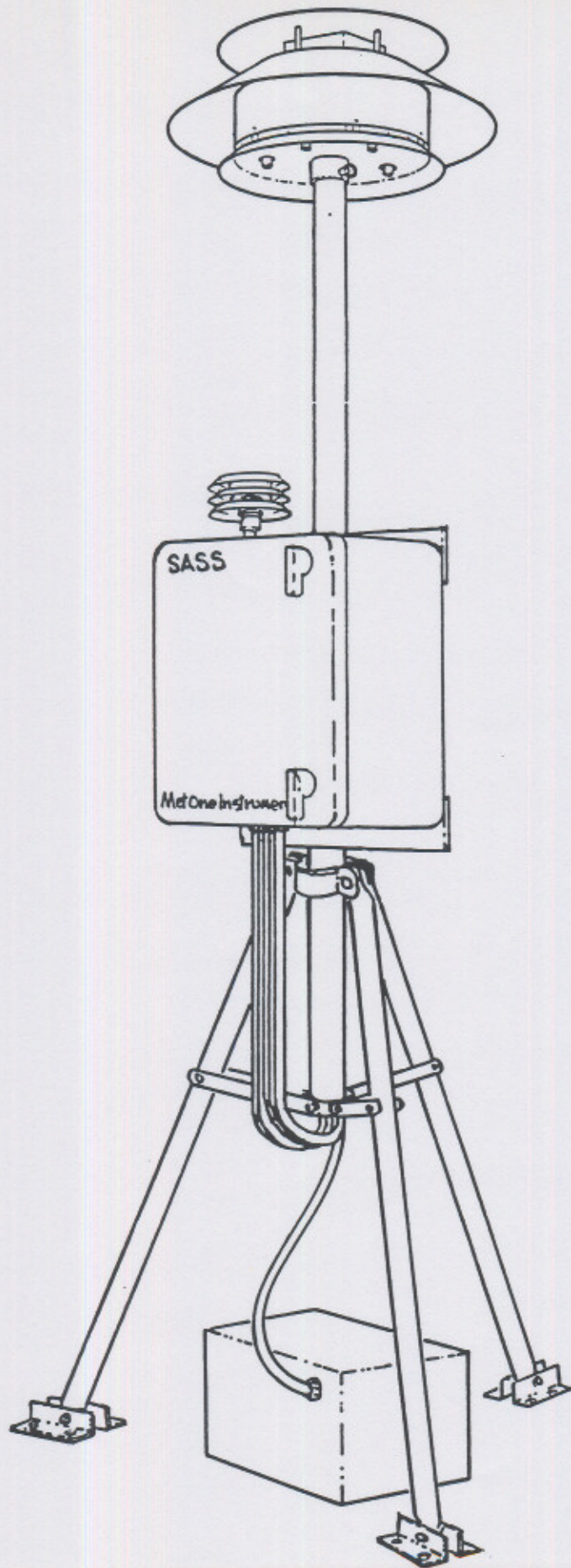


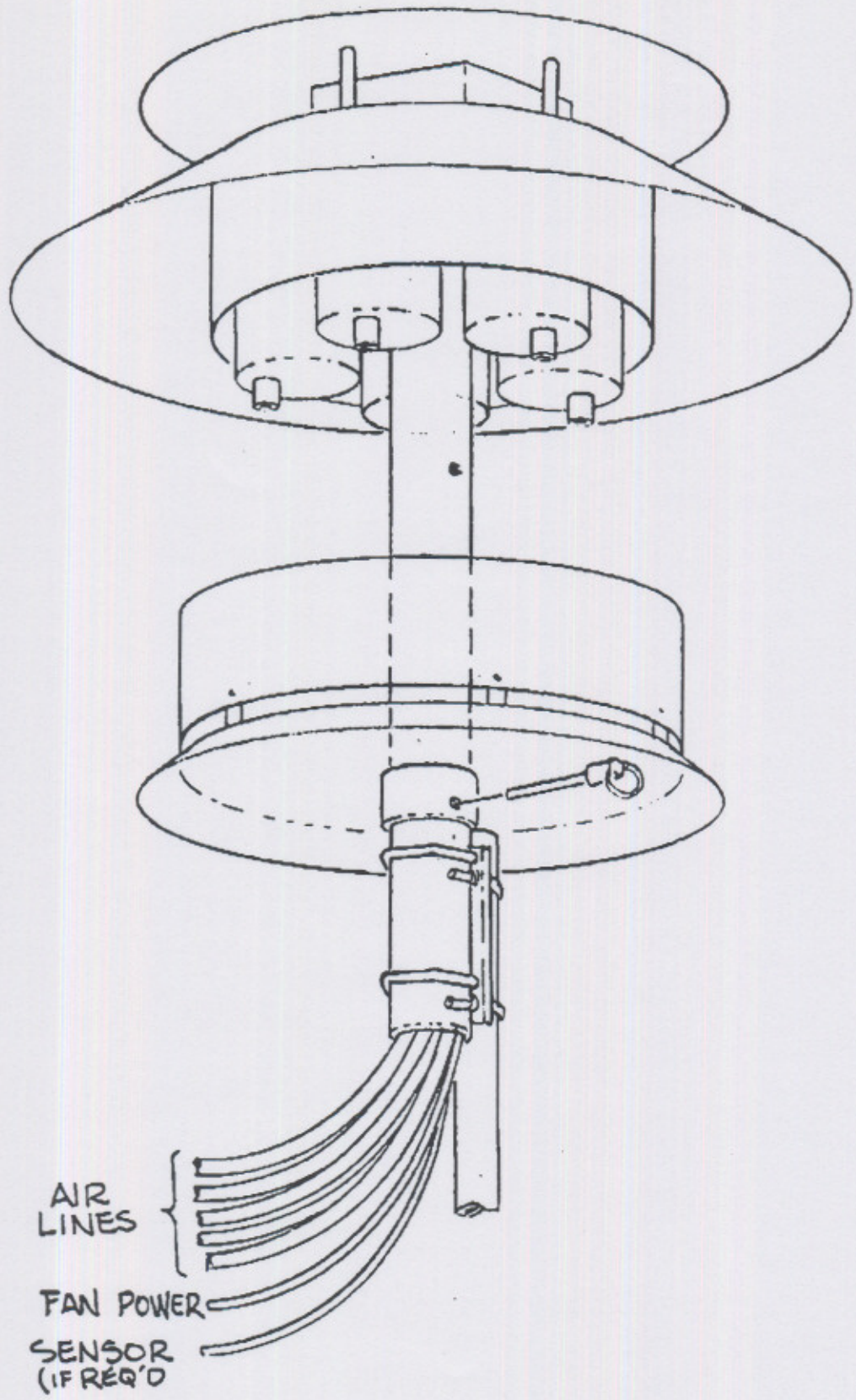
FIGURE L-1. PM2.5 SAMPLER, ASSEMBLY





RTI/EPA WINS Discriminator

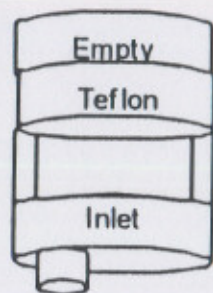




AIR
LINES

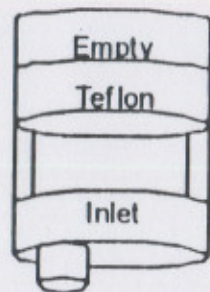
FAN POWER

SENSOR
(IF REQ'D)



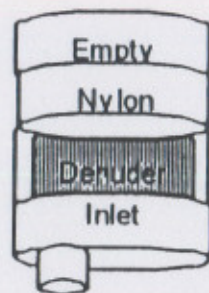
#1

Mass (grav)
Metals (XRF)



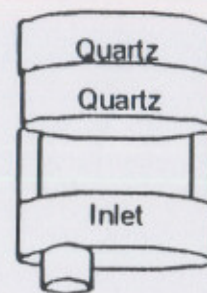
#2

Ions (IC)



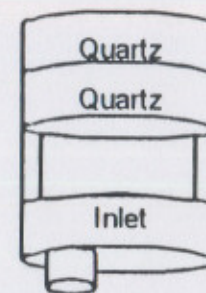
#3

Nitrate



#4

Organic
& Elemental
Carbon

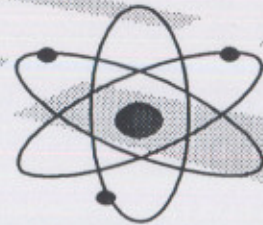


#5

Replicate
(shown
for carbon)

PM2.5 Speciation Target Analytes

- **Cations:** particulate ammonium; ionic sodium, calcium, magnesium
- **Anions:** particulate sulfate, nitrate, and chloride
- **Carbon:** organic and elemental
- **Trace Elements:** sodium, magnesium, etc., through lead
- **Semivolatile organic particles**



PM2.5 Speciation Sampling

Speciation Sampling Network

- **50 Core sites within NAMS**
 - 25 samplers collocated within PAMS
 - 25 sites selected by EPA HQ/RAs/States
- **Approximately 250 additional sites**
- **Estimated sample collection at every 6 days(NAMS) and every 12 days for others**
- **Analytes similar to those in IMPROVE**

PM2.5 Speciation Filter/Analyte Matrix

Lab Analyses

Filter Medium	Analytes	Analysis Methods
Teflon	mass, elements	gravimetry, XRF, PIXE, ICP
Nylon	nitrates, sulfate, chloride, ammonium ion, cation metals	ion chromatography, colorimetry
Quartz	elemental and organic carbon, semivolatile organics	controlled combustion, GC/MS

Table 3.
Analytical Detection Limits for Ambient Aerosols Collected with the SASS

Species	Analytical Method	Method Detection Limit ¹	SASS Detection Limit ² ($\mu\text{g}/\text{m}^3$)
Mass	Gravimetry	15 $\mu\text{g}/\text{filter}$	1.7
Chloride	Ion chromatography	0.05 $\mu\text{g}/\text{mL}$	0.06
Nitrate	"	0.05 $\mu\text{g}/\text{mL}$	0.06
Sulfate	"	0.05 $\mu\text{g}/\text{mL}$	0.06
Ammonium ion	Auto. Colorimetry	0.05 $\mu\text{g}/\text{mL}$	0.06
Soluble potassium	Atomic Adsorption	0.07 $\mu\text{g}/\text{mL}$	0.08
Organic carbon	Thermal Optical Anal.	0.82 $\mu\text{g}/\text{cm}^2$	1.07
Elemental carbon	"	0.19 $\mu\text{g}/\text{cm}^2$	0.25
Al	X-ray fluorescence	0.0025 $\mu\text{g}/\text{cm}^2$	0.0033
Si	"	0.0014 $\mu\text{g}/\text{cm}^2$	0.0018
P	"	0.0014 $\mu\text{g}/\text{cm}^2$	0.0018
Cl	"	0.0012 $\mu\text{g}/\text{cm}^2$	0.0016
K	"	0.0026 $\mu\text{g}/\text{cm}^2$	0.0034
Ca	"	0.0015 $\mu\text{g}/\text{cm}^2$	0.0020
Ti	"	0.0011 $\mu\text{g}/\text{cm}^2$	0.0014
V	"	0.00073 $\mu\text{g}/\text{cm}^2$	0.00096
Cr	"	0.00048 $\mu\text{g}/\text{cm}^2$	0.00063
Mn	"	0.0004 $\mu\text{g}/\text{cm}^2$	0.00053
Fe	"	0.00038 $\mu\text{g}/\text{cm}^2$	0.00050
Co	"	0.00022 $\mu\text{g}/\text{cm}^2$	0.00029
Ni	"	0.00022 $\mu\text{g}/\text{cm}^2$	0.00029
Cu	"	0.00027 $\mu\text{g}/\text{cm}^2$	0.00035
Zn	"	0.00027 $\mu\text{g}/\text{cm}^2$	0.00035
Ga	"	0.00048 $\mu\text{g}/\text{cm}^2$	0.00063
As	"	0.00039 $\mu\text{g}/\text{cm}^2$	0.00051
Se	"	0.00031 $\mu\text{g}/\text{cm}^2$	0.00041
Br	"	0.00025 $\mu\text{g}/\text{cm}^2$	0.00033
Rb	"	0.00024 $\mu\text{g}/\text{cm}^2$	0.00032
Sr	"	0.00028 $\mu\text{g}/\text{cm}^2$	0.00037
Y	"	0.00033 $\mu\text{g}/\text{cm}^2$	0.00043
Zr	"	0.00042 $\mu\text{g}/\text{cm}^2$	0.00055
Mo	"	0.00067 $\mu\text{g}/\text{cm}^2$	0.00088
Ag	"	0.003 $\mu\text{g}/\text{cm}^2$	0.0039
Cd	"	0.003 $\mu\text{g}/\text{cm}^2$	0.0039
In	"	0.0034 $\mu\text{g}/\text{cm}^2$	0.0045
Sn	"	0.0044 $\mu\text{g}/\text{cm}^2$	0.0058
Sb	"	0.0045 $\mu\text{g}/\text{cm}^2$	0.0059
Ba	"	0.013 $\mu\text{g}/\text{cm}^2$	0.017
Hg	"	0.00065 $\mu\text{g}/\text{cm}^2$	0.00085
Pb	"	0.00076 $\mu\text{g}/\text{cm}^2$	0.00100

¹ from Chow and Watson (1998)

² Assumes 24 hour collection at 6L/min with deposit diameter of 38 mm (11.4 cm^2) or extraction of entire filter in a volume of 10 mL

generation analysis system based on the preferential volatilization of elemental carbon compounds at different temperatures. The Model 4000 design has benefited from the experience gained in thousands of analyses of suspended particulate carbon performed over the past decade using the first three generations of hardware and software. The major features of the Model 4000 are:

peaks are integrated at 550 °C, 500 to 700 °C, and 700 to 800 °C until the FID response returns to baseline. Each of these integrals is reported separately. Analysis of source samples indicated that these different fractions may allow different carbon sources to be resolved from each other by receptor modeling.

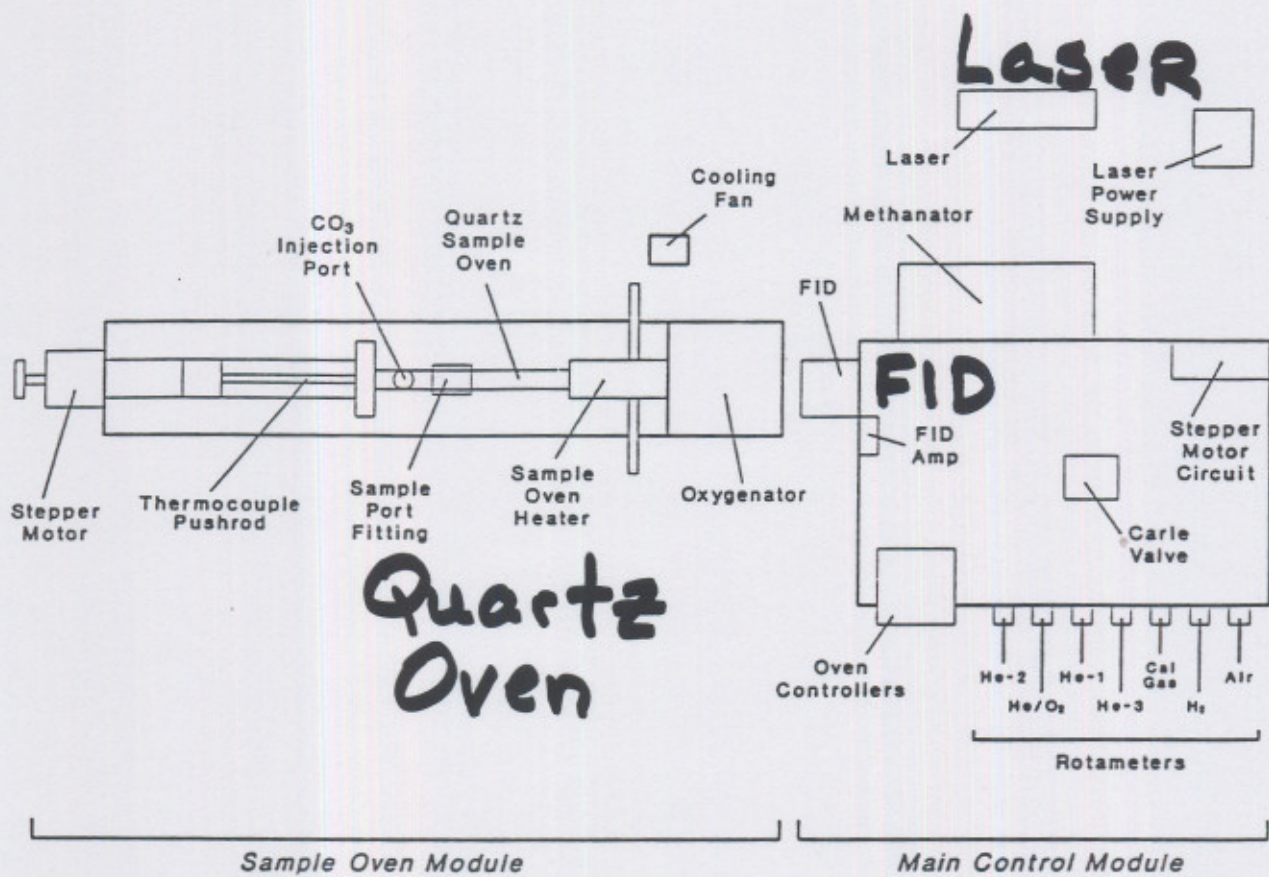
LIGHT ABSORBING FRACTION FOR VISIBILITY STUDIES The continuous monitoring of light reflectance from the sample deposit (with an option to also monitor transmission through the deposit) allows the evolved carbon to be unequivocally associated with light absorption. This fraction can be used to apportion the absorbing portion of light extinction to the sources of this carbon.

ORGANIC FRACTION FOR TOXICS STUDIES The four fractions of the organic carbon provide an inexpensive method of screening for toxic organic compounds in particulate matter. Research is being conducted to determine the chemical species which evolve in these different fractions.

CARBONATE ANALYSIS OPTION Carbonate carbon can also be measured using an optional oven design which allows acidification of the aerosol deposit prior to heating. The carbonate evolved independently of other carbonaceous material after this acidification.

FLEXIBLE SOFTWARE AND HARDWARE FOR RESEARCH STUDIES Analysis temperatures, temperature ramping, combustion atmospheres, and peak integration periods can be easily adjusted to change the carbon fractions which evolve. The oven can be replaced with other configurations (e.g., two- or three zone heating; modified sample boats to accommodate different types of samples) for fundamental study of the properties of carbonaceous materials.

The Model 4000 TOR Carbon Analyzer is available from the Energy & Environmental Engineering Center of the Desert Research Institute. Full documentation and standard operating procedures are provided with each instrument. Interested parties may contact Dr. John Watson or Dr. Judith Chow at: Energy & Environmental Engineering Center, Desert Research Institute, University of Nevada System, P.O. Box 60220, Reno, NV 89506. Phone (702) 677-3166.



Model 4000X Thermal/Optical Carbon Analyzer Overview.

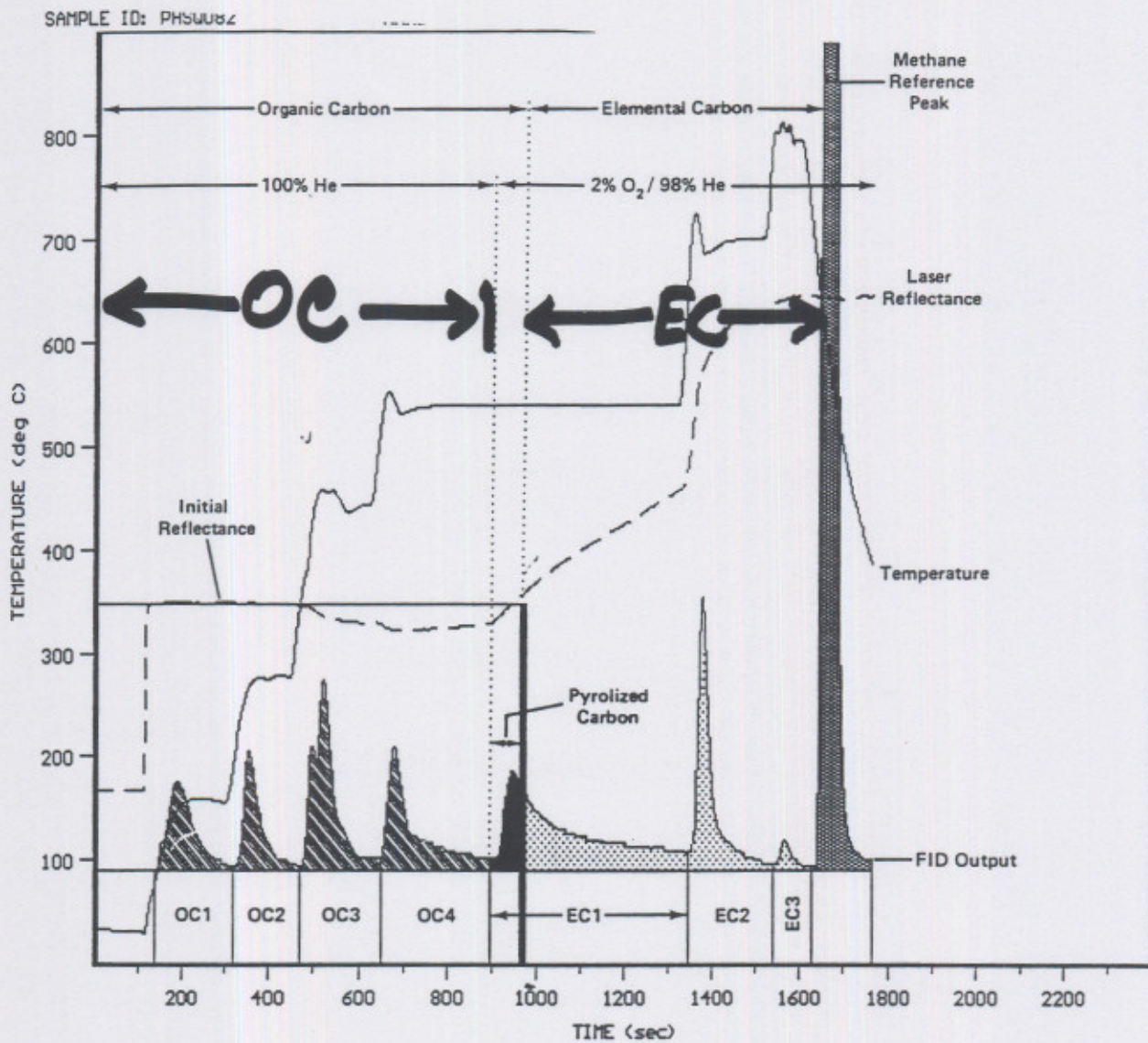


Fig. 1a.

Roadside
GASOLINE Vehicle

SAMPLE ID: PHSQ022

ANALYSIS ID: HSQ022-1

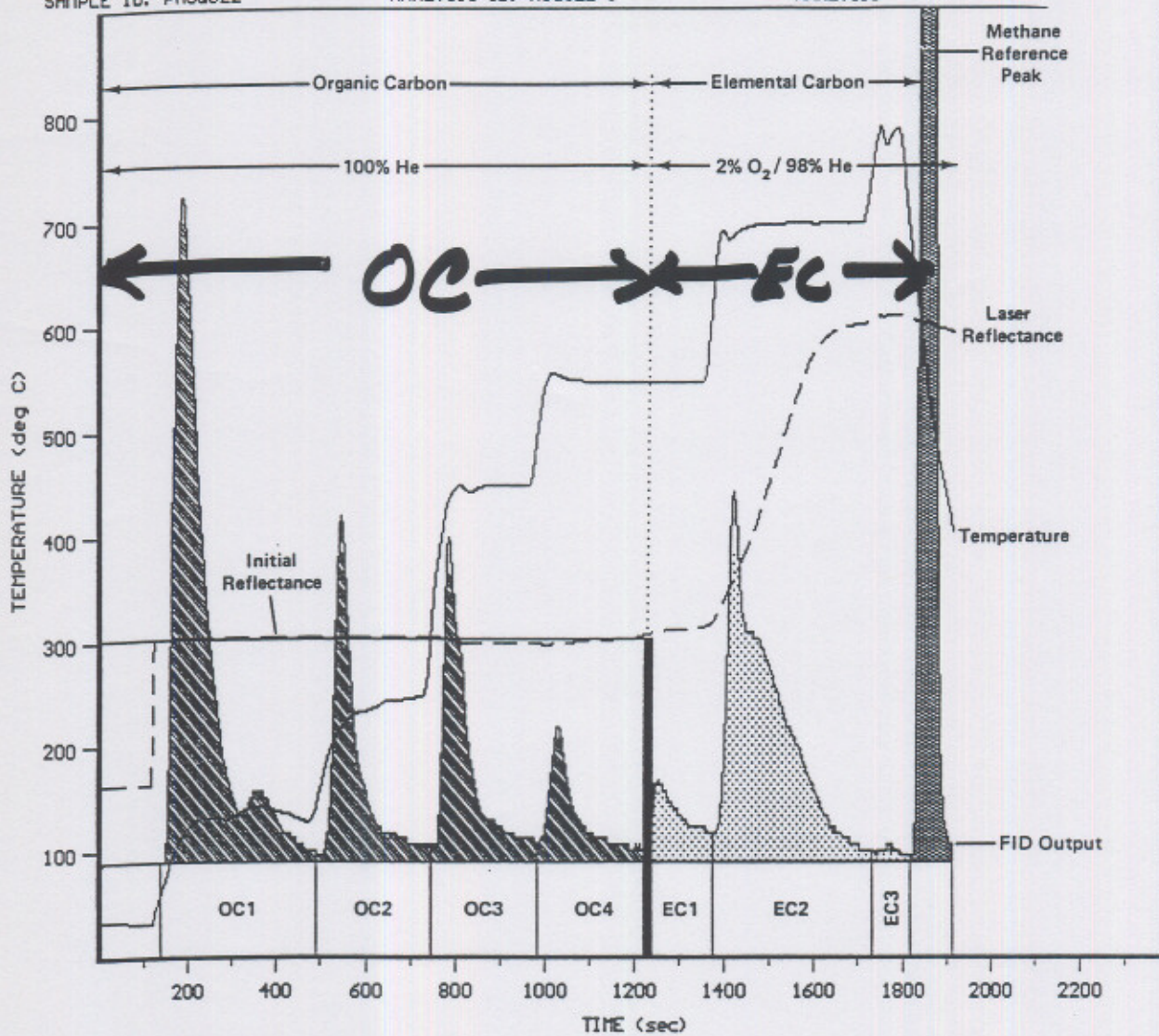


Fig. 1b.

Roadside
DIESEL VEHICLE