Early Engine Exhaust Particle Size Distribution Measurements

Gilmore J. Sem, TSI Incorporated, Shoreview, Minnesota, USA
Oliver F. Bischof, TSI GmbH, Aachen, Germany
David B. Kittelson, University of Minnesota, Minneapolis, Minnesota, USA

John Frey, Mine Safety Appliances Company, Pittsburgh, and Morton Corn, University of Pittsburgh, published a paper in *American Industrial Hygiene Association Journal* in 1967 entitled "Physical and Chemical Characteristics of Particulates in a Diesel Exhaust." It described virtually all that was known at that time about the subject. It serves today as a landmark paper summarizing the state-of-the-art up to that date. Measuring methods included cascade impactors, microscopy, electron microscopy, and scanning electron microscopy. With such tedious methods, not much information was known with any certainty.

During the period 1964-1967, Kenneth Whitby, University of Minnesota, Minneapolis, along with his students, Carl Peterson, William Clark, and Gilmore Sem, was developing a new instrument that could measure in about 2 minutes the size distribution of aerosol particles in the size range between 5nm and 1µm. In 1967, TSI introduced a commercial version as Model 3000 Whitby aerosol analyzer (WAA). It was designed primarily for aerosol measurements of urban outdoor atmospheres. While the WAA was not used extensively, it did make a set of landmark measurements of atmospheric aerosol about 50 meters from Harbor Freeway, near the University of Southern California campus in Los Angeles. The intent was to measure the contribution of freeway traffic on Los Angeles aerosol. This data confirmed the multimodal nature of atmospheric aerosol that was developed after similar measurements on the California Institute of Technology campus, Pasadena, in 1969 using another WAA.

Meanwhile, Benjamin Liu and a student, David Pui, University of Minnesota, developed a miniaturized electrical aerosol size analyzer and tested it in California in 1972 during the Aerosol Characterization Experiment (ACHEX). TSI introduced the commercial Model 3030 EAA in 1973, again intended primarily for measuring atmospheric aerosols. Soon, young David Kittelson and his colleagues adapted the instrument for measurements of diesel exhaust. Dan Dolan, Kittelson, and Whitby published the first paper about this work in 1975 in the American Society of Mechanical Engineers proceedings. This appears to be the first attempt to use near-real-time instruments to measure diesel exhaust aerosol without any other aerosol interfering with the sample.

Very soon, John H. Johnson and colleagues of Michigan Technological University, Houghton, began making similar measurements. Both Kittelson's group and Johnson's group described new aerosol sampling, dilution, and sample treatment methods in nearly each paper they published throughout the latter half of the 1970s. Kittelson's group also attempted to solve the problem of changing aerosol size distributions during a dynamic drive cycle by use of a batch sampling system.

In 1975, Kittelson's group contributed measurements to a major measurement program at the General Motors test track in Michigan. The purpose was to see the effect of new catalytic converters on the aerosol produced by a large fleet of new cars as they traversed the GM test track. Once again, the tri-modal aerosol size distribution was confirmed, with nuclei mode, accumulation mode, and coarse mode all produced by the fleet of cars.

During the 1970s, Liu and Pui at U of MN and Sem at TSI were hard at work developing hardware and methods for calibrating EAAs and condensation nucleus counters. Earl Knutson and Whitby developed and extensively evaluated a differential mobility analyzer (DMA) to produce highly monodisperse aerosol in the EAA size range. U of MN also developed an aerosol electrometer with noise level of about 10^{-15} amperes that measured the concentration of unipolarly-charged aerosol particles exiting a DMA. TSI introduced commercial versions in 1975 - 1978. Meanwhile, TSI developed a commercial version of a condensation particle counter developed in 1975 by Jean Bricard, Guy Madelaine, and Michel Pourprix, Atomic Energy Commission, Paris. TSI's instrument, Model 3020 CPC introduced in 1978, was capable of detecting and counting single airborne particles. It soon became obvious that combining a DMA and a CPC would permit a new type of submicrometer particle sizer capable of substantially greater size resolution. To make this practical required use of a personal computer that became available just in time. TSI engaged Heinz Fissan and colleagues at U of Duisburg to develop the algorithm to process the data from the first differential mobility particle sizer spectrometer in 1982. Harry ten Brink and André Plomp, Petten, Netherlands, also worked on this algorithm. We believe the first application of DMPS technology to sizing of diesel exhaust particles was by Georg Reischl et al, University of Vienna, Austria, around 1983.

In the early 1980s, TSI introduced a commercial version of David Sinclair's screen diffusion battery. Combined with a CPC, it offered another method of measuring size distributions in the submicrometer size range. With help from the Alex Ankilov group, Novosibirsk, Russia, to develop a very good data reduction algorithm, the fundamental lack of size resolution of diffusion batteries made them impractical for most diesel aerosol measurements. In 1984, Cheng et al, Lovelace, Albuquerque, New Mexico, also tried to use a diffusion battery with a TSI 3020 CPC to measure diesel exhaust.

In 1992, TSI introduced a commercial version of the scanning mobility particle sizer (SMPS) spectrometer software developed by Rick Flagan et al, Caltech, to improve the size resolution and time resolution of a DMPS. In 2002 - 2003, Cambustion introduced a fast particulate spectrometer and TSI introduced an engine exhaust particle sizer to greatly improve the time resolution for dynamic engine drive cycle measurements. While the time resolution is now down to below 200milliseconds, the size resolution of these fast instruments does not match that of SMPS or DMPS.

The power point slides below include references to key papers.

Early Engine Exhaust Particle Size Distribution Measurements

Gilmore J. Sem, TSI Inc, Shoreview, MN, USA
Oliver F. Bischof, TSI GmbH, Aachen, Germany
David B. Kittelson, U of Minnesota, Minneapolis, USA

For presentation at
9th ETH Conference on Combustion Generated Nanoparticles
Zurich, Switzerland, 15-17 August 2005

TSI

Outline of this historical review

- Motivation for this historical review
- Off-line measurement techniques
  - Impaction, microscopy, SEM, TEM
- Near-real-time measurements (1972 - 1980)
  - Who did it?
  - What instruments did they use?
  - What were some of their findings?
- Improvements of size resolution (1980 – 1984)
- Bibliography of early work
- Summary

Motivation

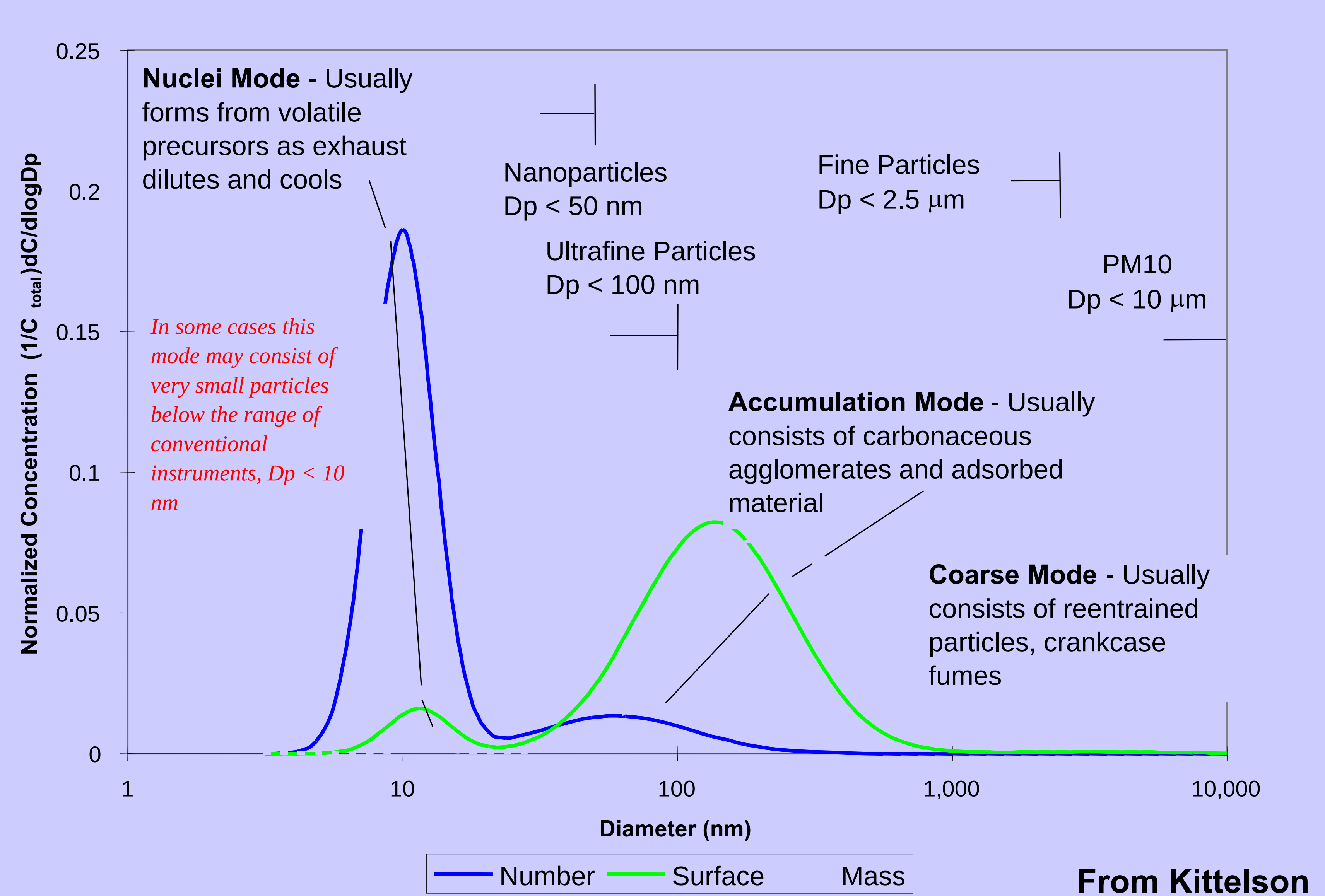
- Real-time / near-real-time aerosol particle counters & sizers are frequently used today to characterize engine exhaust particles.

  How did it get started?

- 1959: Andreas Mayer recently discovered reference to "fine particles, their number, size and surface area" in records of the Johannesburg Conference of 1959.
- 1888: John Aitkin / 1st condensation nucleus counter.
- 1978: TSI 3020, counts single aerosol particles >7nm.
- Single-particle-counting CPC is essential for DMPS / SMPS measurements of particle size.

TSI

Today's model of engine exhaust aerosol size distribution:



From Kittelson

Leaders of early exhaust measurements

- David B. Kittelson et al (University of Minnesota) & John H. Johnson et al (Michigan Technological University):
  - Developed methods for using near-real-time aerosol particle sizing instruments to measure diesel & spark-ignition exhausts (1974 - 1980):
    - Both used electrical aerosol analyzer (TSI 3030 EAA) as the primary particle sizer for early near-real-time work.
  - The combination of a CNC with differential mobility analyzer was commercially introduced in 1982 (TSI, Gilmore Sem *et al*) and was rapidly applied by others to engine exhaust particle measurement.

- Landmark papers are discussed below, in context with contemporary developments in aerosol measurement technology

Diesel exhaust characteristics, mid-1960s

Use of electron microscopy & impaction:

Frey & Corn (1967) Physical and chemical characteristics of particulates in a diesel exhaust. ***American Industrial Hygiene Association Journal*** **28:468-478.**

TABLE V
Characteristics of Diesel Exhaust Particulate—Summary

Number of Observations	Operating condition: Load:	1400I 0	1800C 0	1800L 1/2[a]
7	Weight concentration, mg/m^3	75.3	72.5	33.3
	Rate, mg/min	47.8	55.6	28.6
	mg/cm^3 fuel	6.3	5.4	1.3
7	Number concentration, 10^5 particles/cm^3	199	185	682
	Rate, 10^{12} particles/min	12.6	14.2	58.3
	10^{12} particles/cm^3 fuel	1.6	1.4	2.6
1	Specific surface, m^2/gm	28.1	37.5	50.0
	Specific surface concentration, m^2/m^3	2.1	2.7	1.7
	Rate, m^2/min	1.3	2.1	1.4
	m^2/cm^3 fuel	0.18	0.19	0.06
16	Bulk density, gm/cm^3	0.12	0.12	0.10
	Particle projected area diameter			
	Arithmetic mean size, $m\mu$	86	86	33
	Geometric mean, $m\mu$	62.0	60.5	21.0
3	Free acidity, μmoles/min	5	8	5
	μmoles/cm^3 fuel	0.8	0.8	0.2

[a]3.6 bhp.

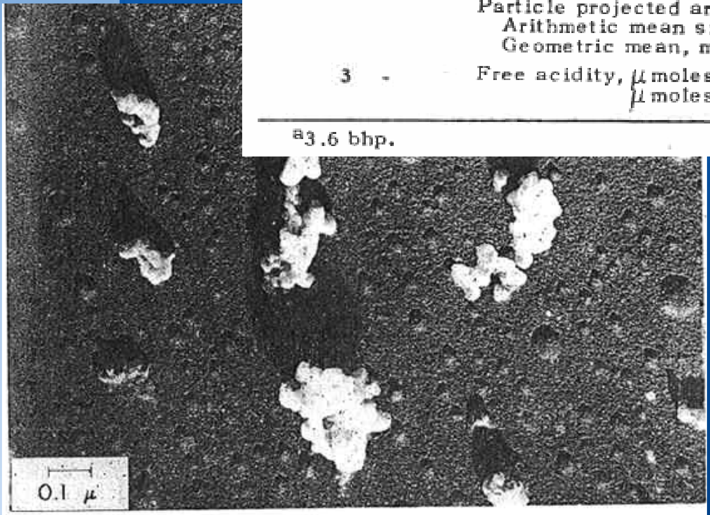


FIGURE 2. Electron photomicrograph of diesel exhaust particulate, shadowed with platinum. Sampled using a thermal precipitator 4 inches from the cylinder at engine operating condition 1400I (138, 150X).

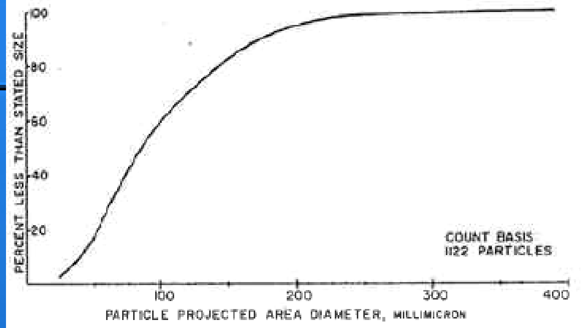


FIGURE 3. Cumulative frequency size distribution of diesel exhaust particulate at engine operating condition 1400I.

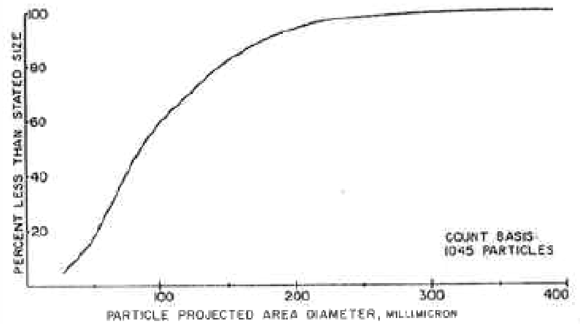


FIGURE 4. Cumulative frequency size distribution of diesel exhaust particulate at engine operating condition 1800C.

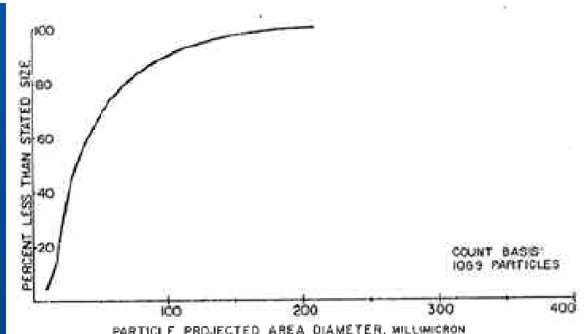


FIGURE 5. Cumulative frequency size distribution of diesel exhaust particulate at engine operating condition 1800L.

Use of electron microscopy & impaction:

Vuk, Jones, & Johnson (1976) The measurement and analysis of the physical character of diesel particle emissions. *SAE paper 760131*.

- Used Andersen cascade impactors
- Discussed problems with cascade impactors
- Used microscopy
- Used scanning electron microscopy (SEM)
- Used transmission electron microscopy (TEM)
- Performed much tedious work for limited data

Comprehensive summary prior to ~1976

Comprehensive summary of diesel particle emissions characterization methods to 1978:

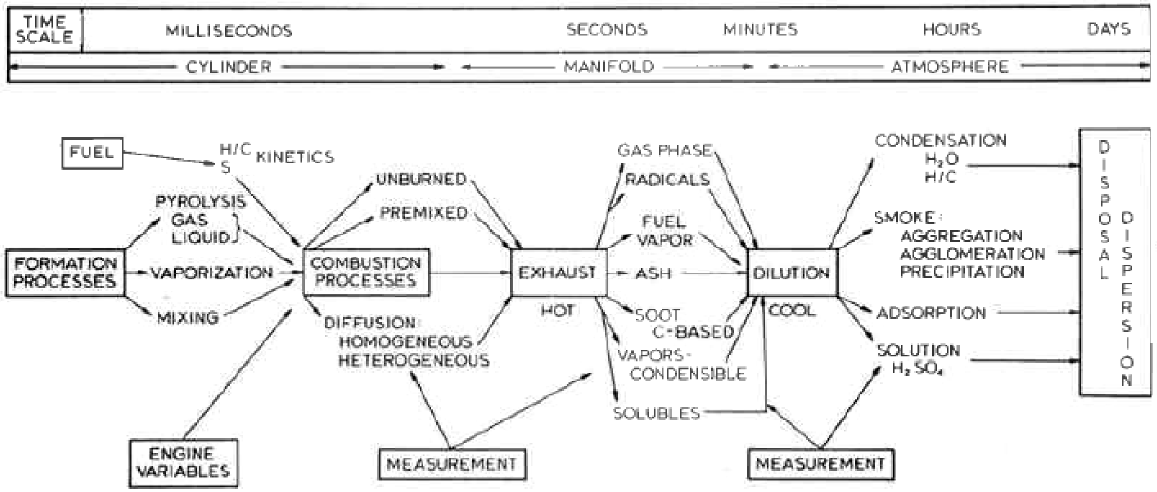


Fig. 14 - Combustion-time factors related to diesel particulate emissions

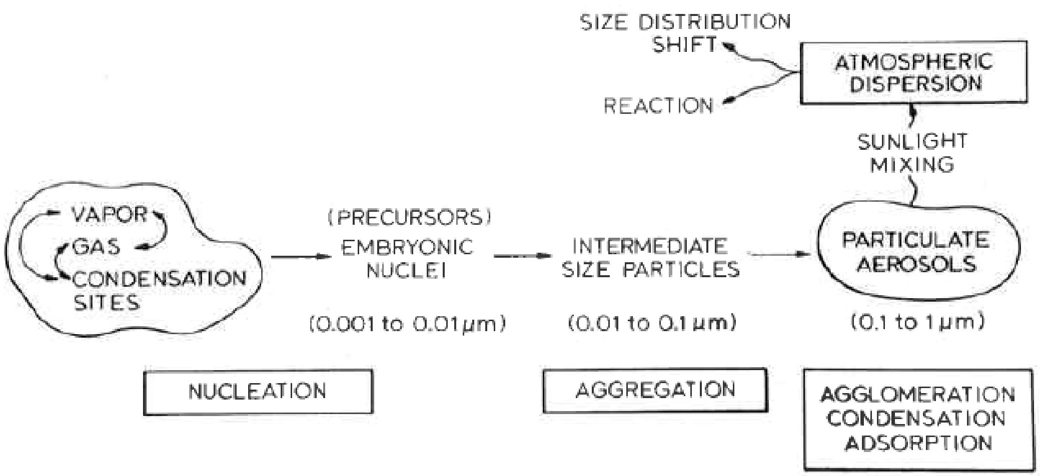


Fig. 15 - Physical processes related to diesel particulate emissions

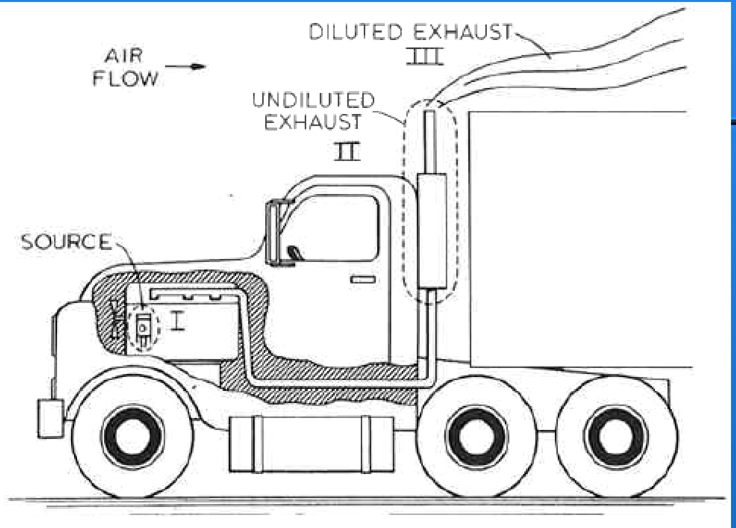


Fig. 3 - Dilution of exhaust following a diesel truck on the highway

Lipke, Johnson, & Vuk (1978)
The physical and chemical character of diesel particulate emissions – Measurement techniques and fundamental considerations. *SAE/PT-79/17*, pp1-57

TSI

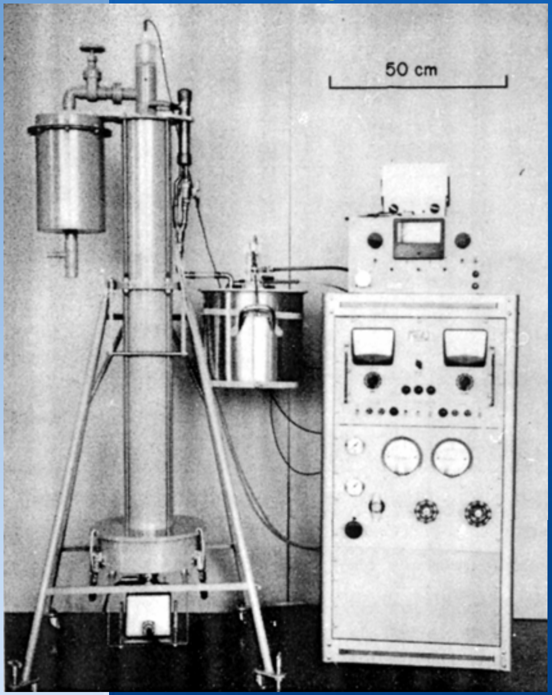
First use of aerosol sizing instruments

First use of rapid aerosol sizing instruments to measure alongside traffic using TSI electrical aerosol analyzer (EAA), Environment One Rich 100 condensation nucleus counter (CNC), & Royco 220 / 245 optical particle counters (OPC):

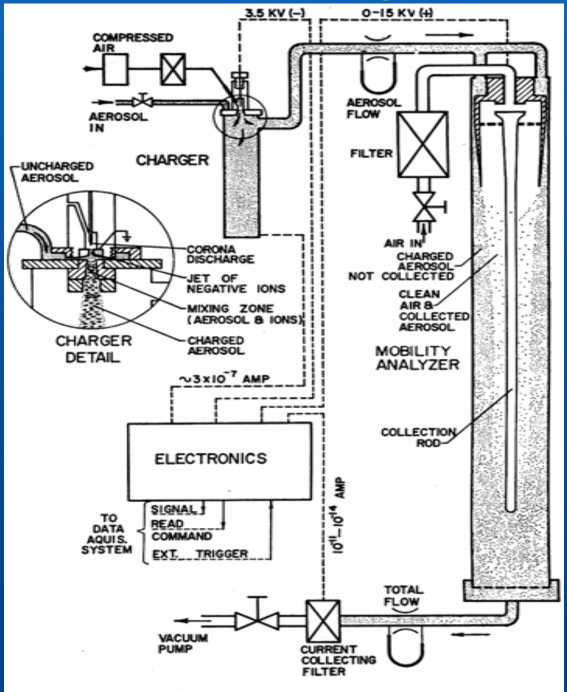
Whitby, Clark, Marple, Sverdrup, Sem, Willeke, Liu, & Pui (1975) Characterization of California aerosols - I. Size distributions of freeway aerosol. *Atmospheric Environment* 9:463-482 - used TSI 3000 Whitby EAA in 1972.

Wilson, Spiller, Ellestad, Lamothe, Dzubay, Stevens, Macias, Fletcher, J. Husar, R. Husar, Whitby, Kittelson, & Cantrell (1977) General Motors sulfate dispersion experiment: Summary of EPA measurements. *J. Air Pollution Control Association* 27(1):46-51 – used TSI 3030 EAA in 1975.

U of MN Prototype, 1966



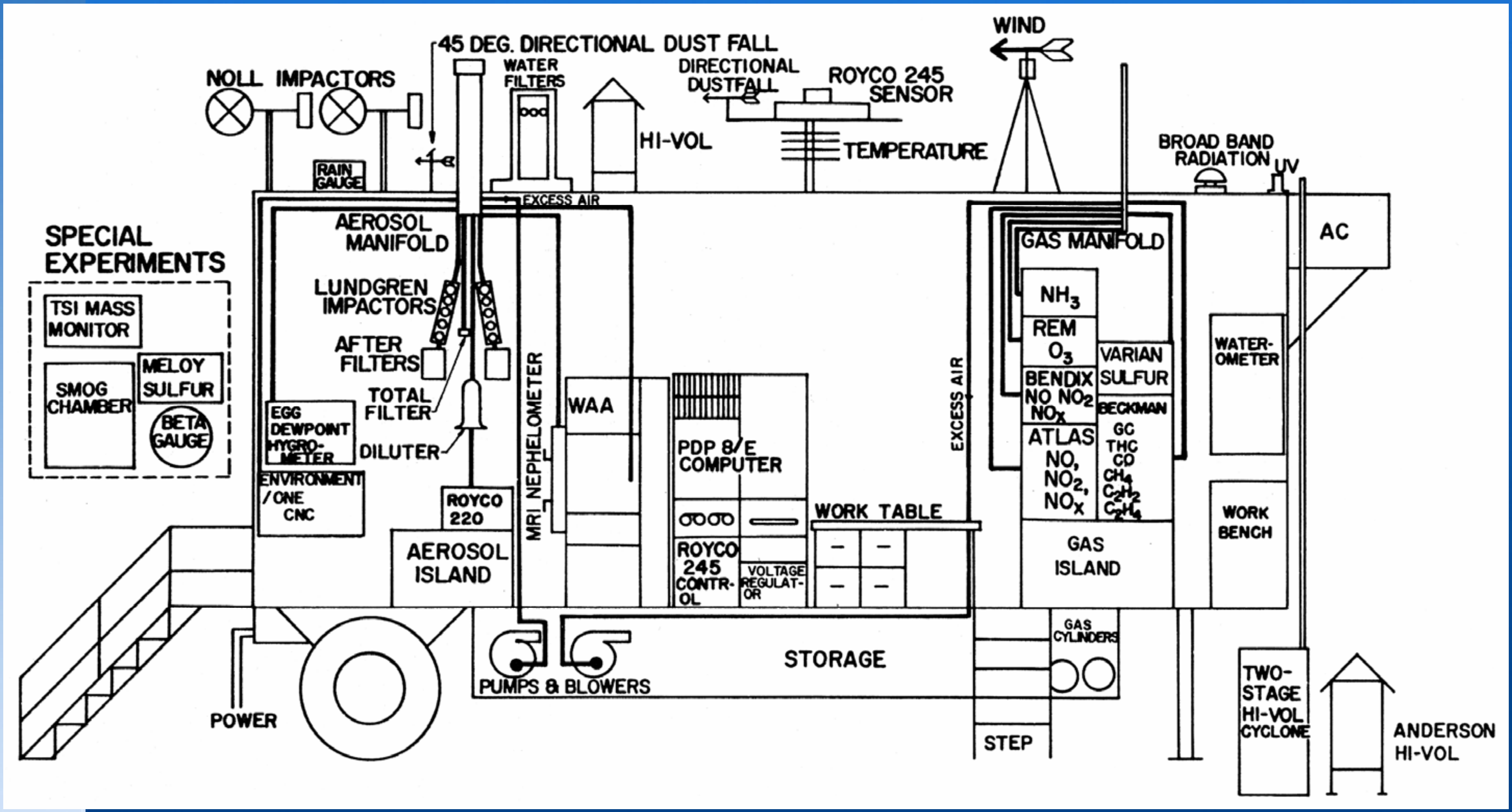
Schematic diagram



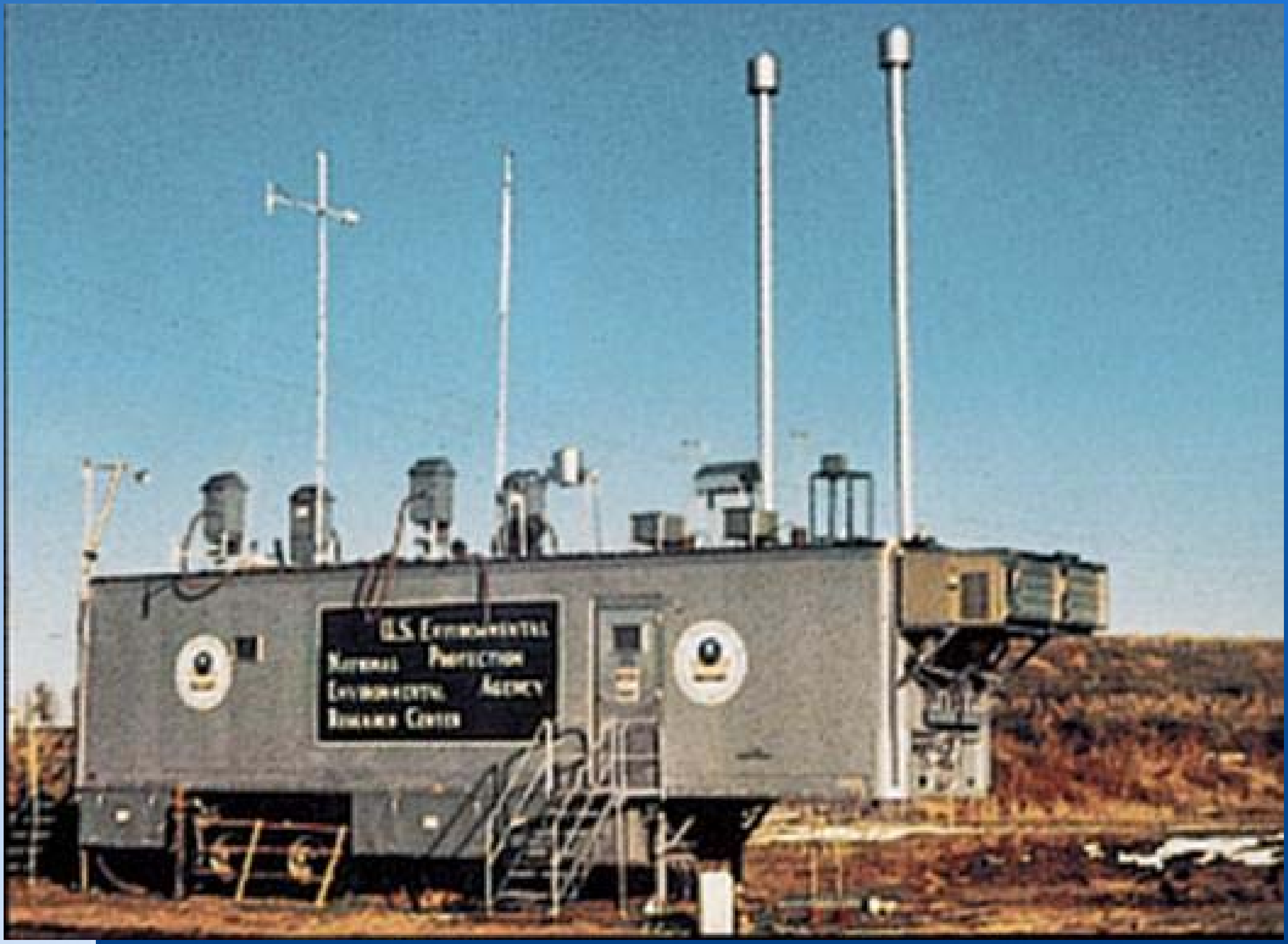
TSI 3000 Whitby aerosol analyzer, 1967

INSTRUMENT LAYOUT, 1972
U of MN / TSI AEROSOL LAB, CALIFORNIA ARB, AEROSOL CHARACTERIZATION EXPERIMENT (ACHEX)

(Whitby, Clark, Marple, Sverdrup, Sem, Willeke, Liu, & Pui (1975))



EPA Semi-trailer Aerosol Laboratory, designed / built in 1973 by TSI; used for EPA's 1975 Sulfate Experiment, GM test track, Michigan



Wilson, Spiller, Ellestad, Lamothe, Dzubay, Stevens, Macias, Fletcher, J. Husar, R. Husar, Whitby, Kittelson, & Cantrell (1977) General Motors sulfate dispersion experiment: Summary of EPA measurements. *J. Air Pollution Control Association* 27(1):46-51

TSI®

Tri-modal size distribution from GM tests

EXPERIMENTAL VALIDATION OF MULTIMODAL ATMOSPHERIC AEROSOL SIZE DISTRIBUTION AND CONTRIBUTION OF CARS TO ATMOSPHERIC AEROSOL, 1975 GM SULFATE DISPERSION EXPERIMENT

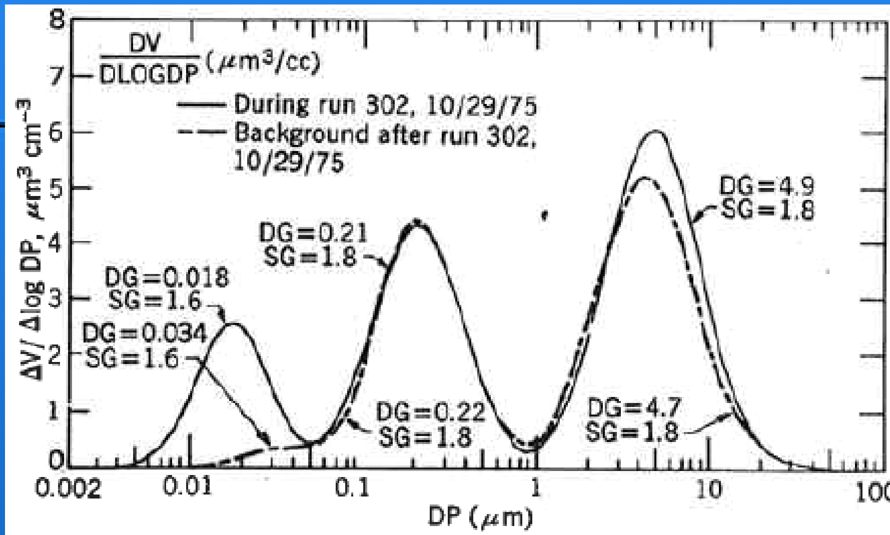
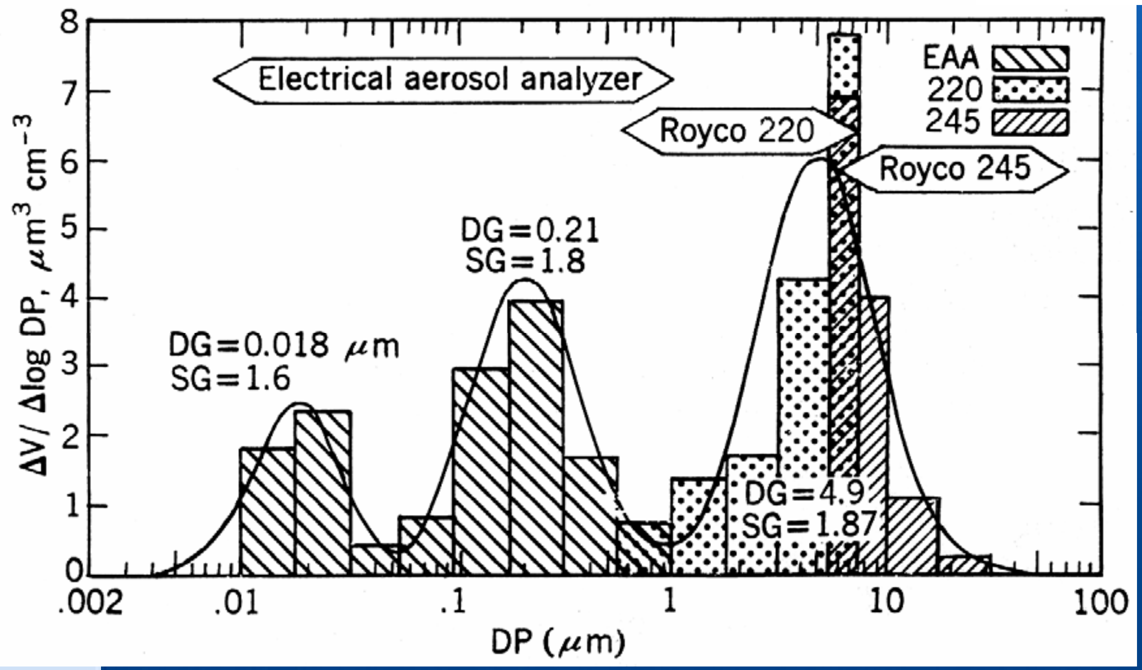


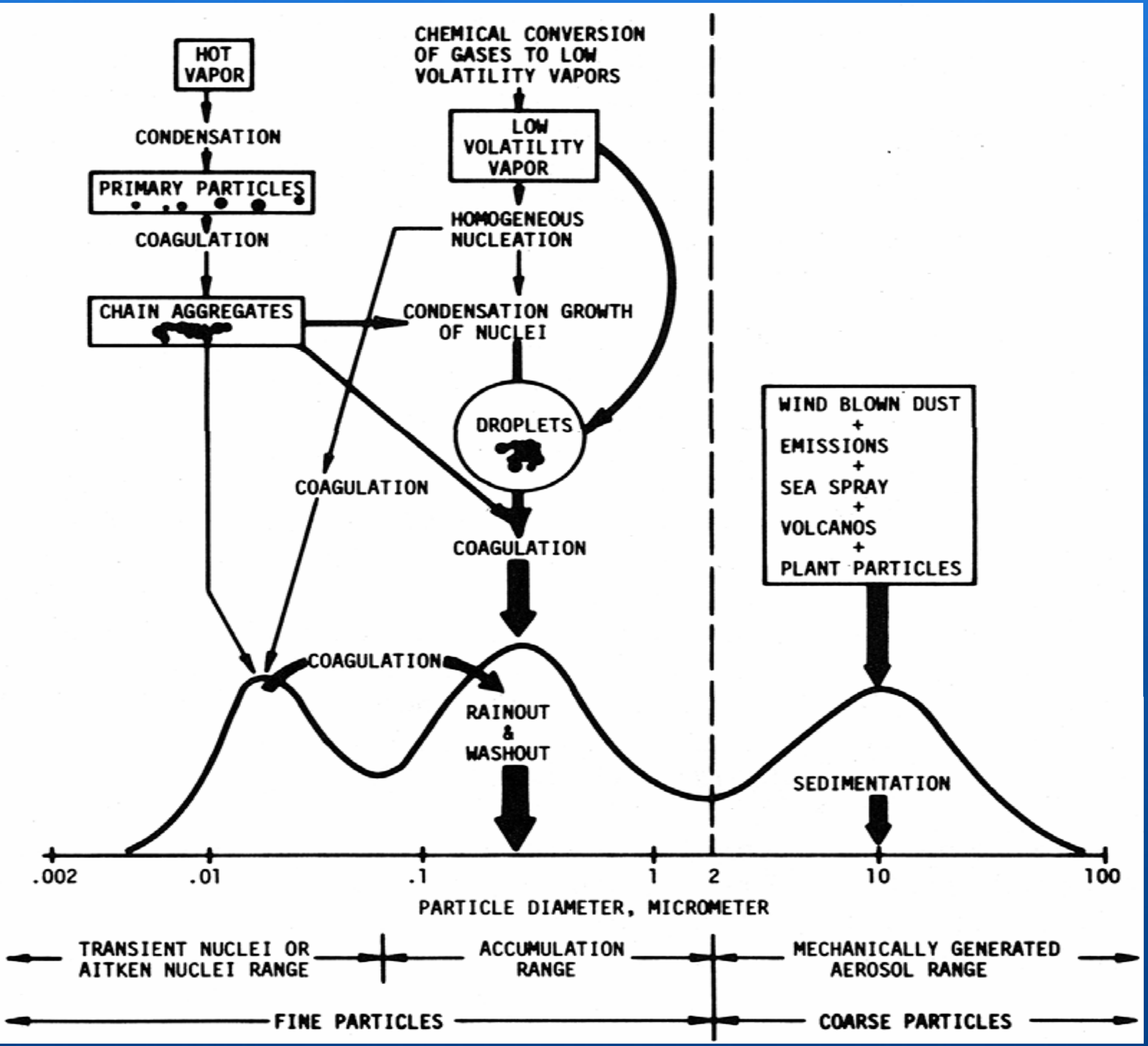
Figure 5. Trimodal model distribution measured at the EPA trailer during run 302 on 10/29/75. The model distributions were obtained by fitting the data shown in Figure 5. Note that during the test the accumulation and coarse particle modes (center and right modes) have not changed significantly from the background conditions. On the other hand, practically all of the volume of the nuclei mode (left mode) is contributed by the cars on the roadway.



Wilson, Spiller, Ellestad, Lamothe, Dzubay, Stevens, Macias, Fletcher, J. Husar, R. Husar, Whitby, Kittelson, & Cantrell (1977)

Whitby multimodal size distribution model

AEROSOL PROCESSES CAUSING MULTIMODAL SIZE DISTRIBUTIONS



Developed & introduced by:

Whitby (1978) The physical characteristics of sulfur aerosols. Atmos. Environment 12(1-3):135-159

First use of near-real-time aerosol sizing instrument (EAA) plus Environment One CNC to measure diesel exhaust:

Dolan, Kittelson, & Whitby (1975) Measurement of diesel exhaust particle size distributions. *Paper 75-WA/APC-5*, American Society of Mechanical Engineers.

Verrant & Kittelson (1977) Sampling and physical characterization of diesel exhaust aerosols. *SAE paper 770720*.

Khatri & Johnson (1978) Physical size distribution characterization of diesel particulate matter and the study of the coagulation process, *SAE paper 780788*.

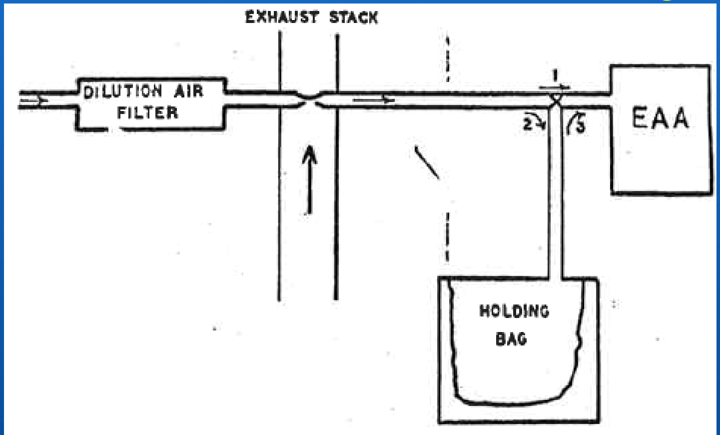
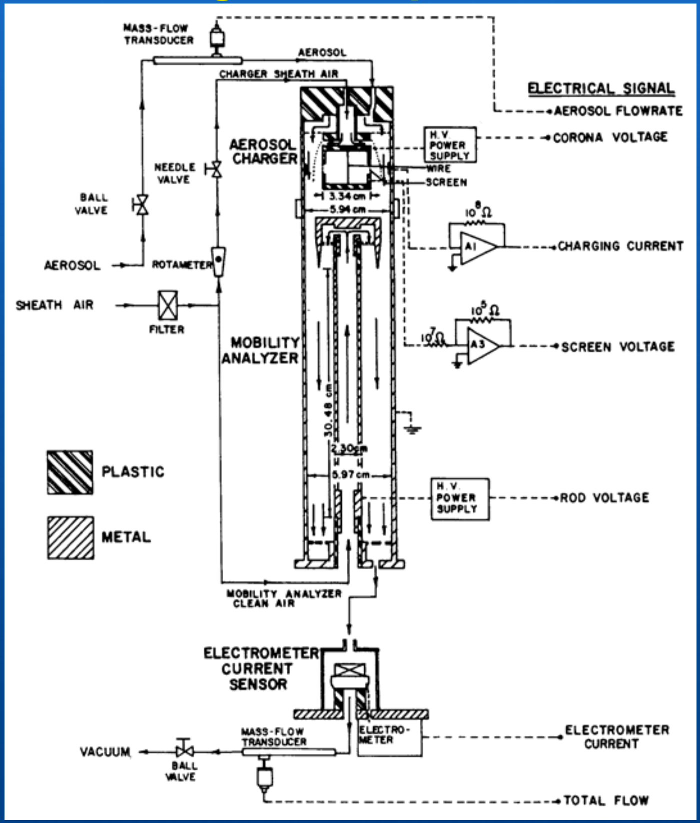


Fig. 1 Sampling system schematic

Dolan, Kittelson, & Whitby (1975) sampling system for diesel exhaust measurement ↑



← Schematic diagram, electrical aerosol analyzer (EAA, TSI introduced in 1973) ←

Evolution of engine sampling systems

Verrant & Kittelson (1977)

sampling, dilution, and sample conditioning system for measuring diesel aerosol

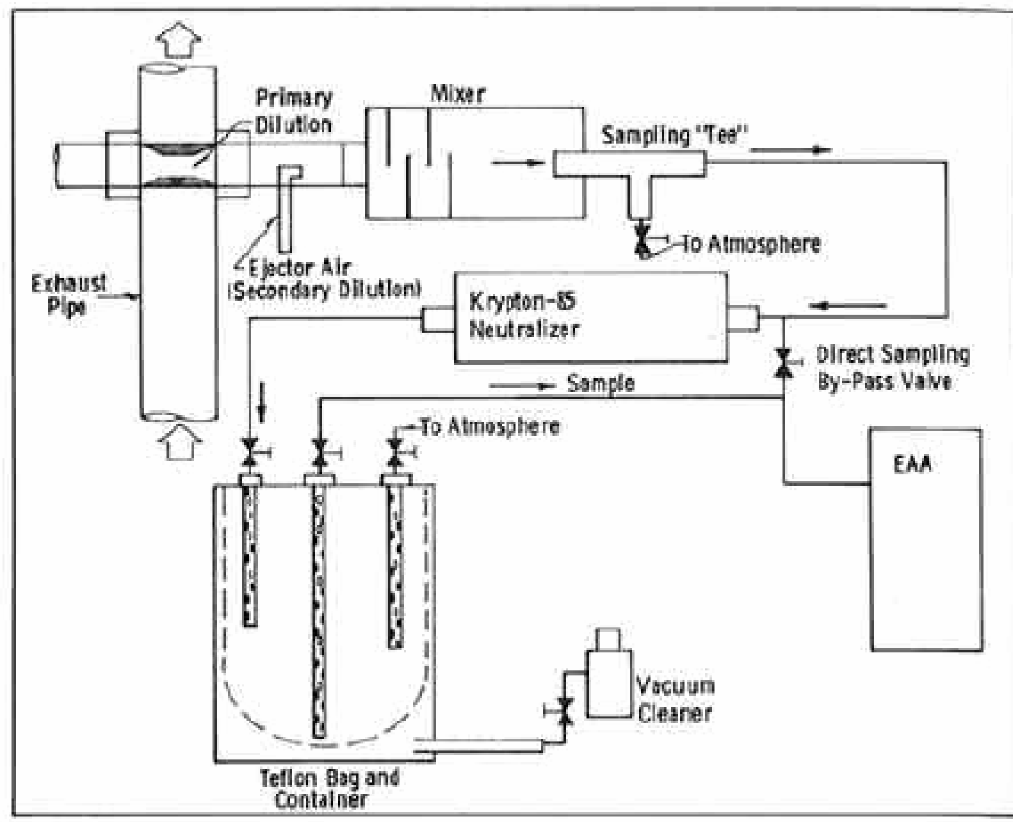


Fig. 1 - Dilution and sampling system for measuring diesel aerosols

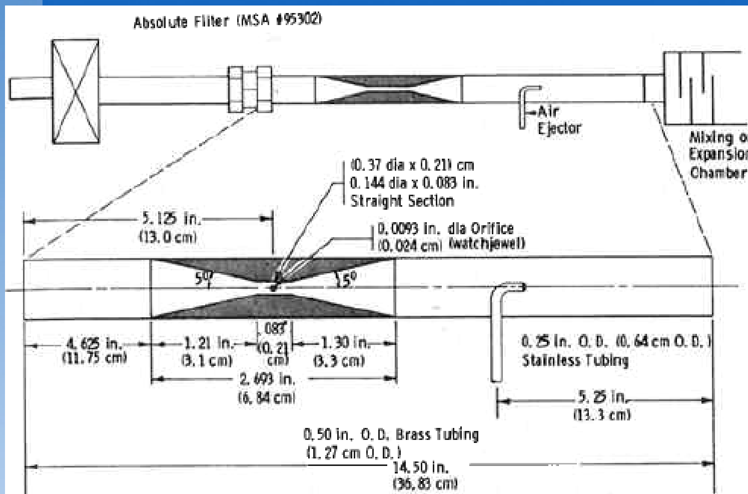


Fig. 2 - (Top) Dilution system for sampling diesel aerosols. An absolute filter (MSA#95302), diluter, and mixing chamber constitute the system
(Below) A dimensioned drawing of the diluter with primary and secondary dilution sections is illustrated

Johnson et al application of EAA

Lipke, Johnson, & Vuk (1978) The physical and chemical character of diesel particulate emissions – Measurement techniques and fundamental considerations. *SAE/PT-79/17*, pp1-57

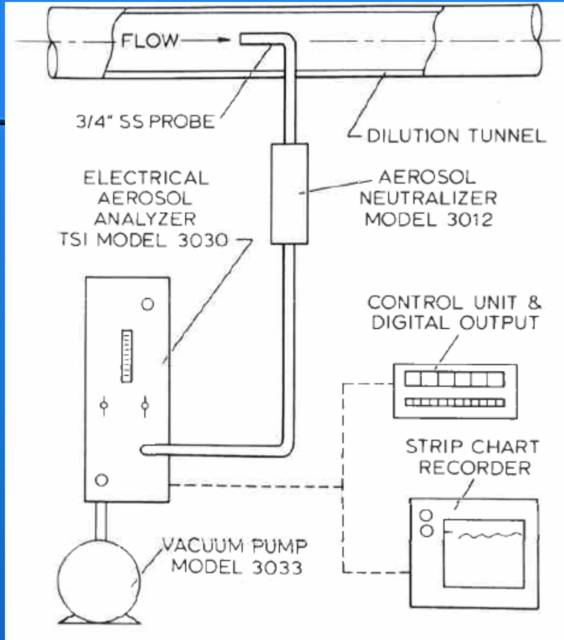


Fig. 42 - EAA installation at Michigan Technological University. Khatri (3)

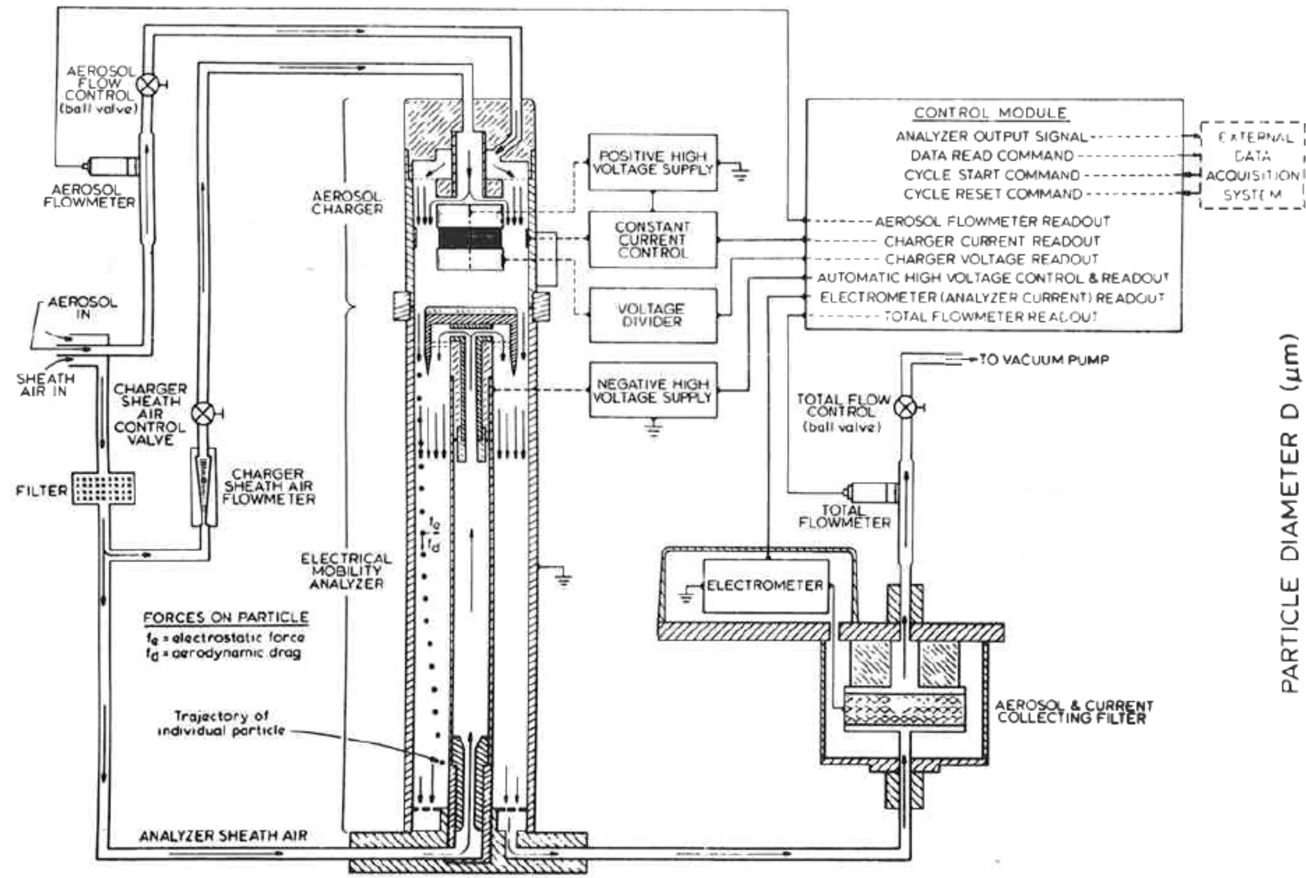


Fig. 41 - Schematic of electrical aerosol analyzer

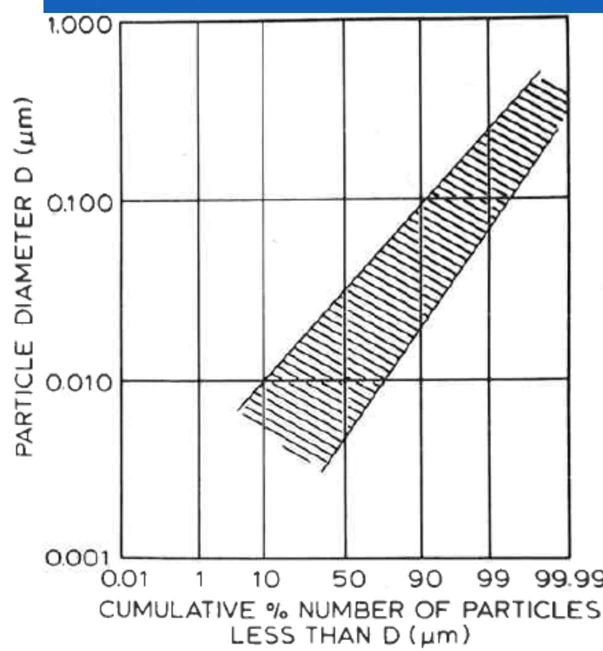


Fig. 43 - EAA results (3150 Caterpillar engine modes 2,4,5,6,8,9,10). Khatri (3)

Diesel particle sizing by diffusion battery

Dolan, Kittelson, & Whitby (1975)

Model 3040 mounted on a Model 3042 Diffusion Battery Switching Valve.

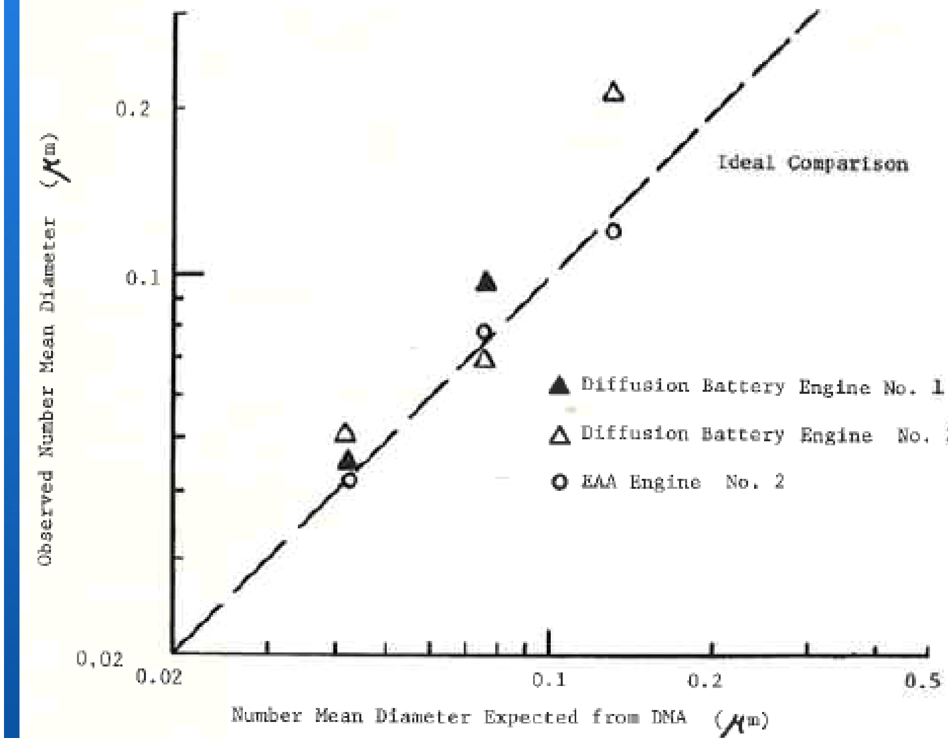


Fig. 16 – EAA-micro-orifice impactor comparison

TSI 3040 Diffusion Battery +
TSI 3042 Switching Valve

Comparison: EAA vs diffusion battery

First use of diffusion battery / condensation particle counter (TSI 3020) to measure diesel exhaust particle size distributions:

- **Dolan, Kittelson, & Pui (1980)** Diesel exhaust particle size distribution measurement techniques. *SAE paper 800187* contained in *SAE Proceedings P-86, Diesel Combustion and Emissions*.
- **Cheng, Yeh, Mauderly & Mokler (1984)** Characterization of diesel exhaust in a chronic inhalation study. *American Industrial Hygiene Association Journal* 45(8):547-555.

From Dolan, Kittelson, & Pui (1980)

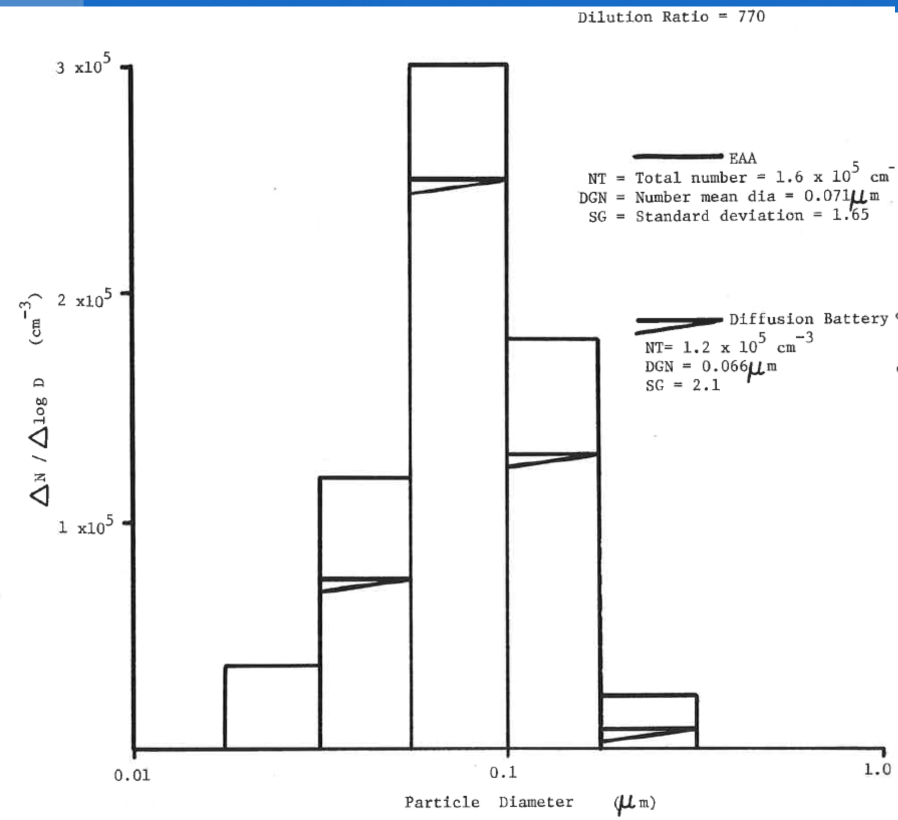


Fig. 7 - Particle number size distribution for Engine 2

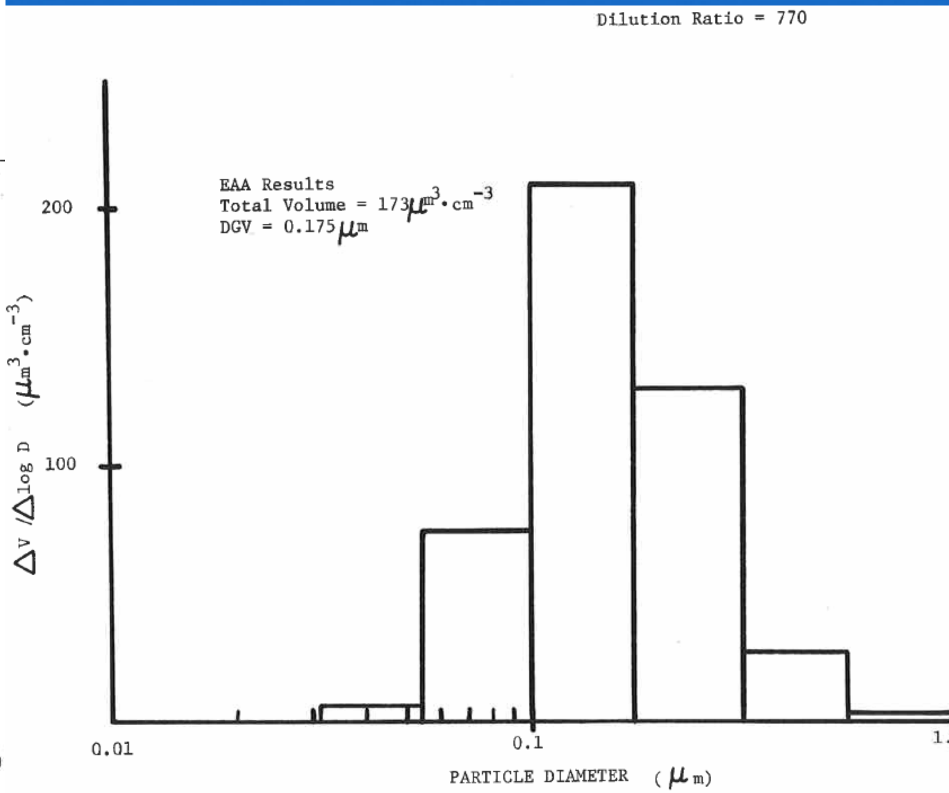


Fig. 8 - Particle volume size distribution for Engine 2

Cheng, Yeh, Mauderly, & Mokler (1984)

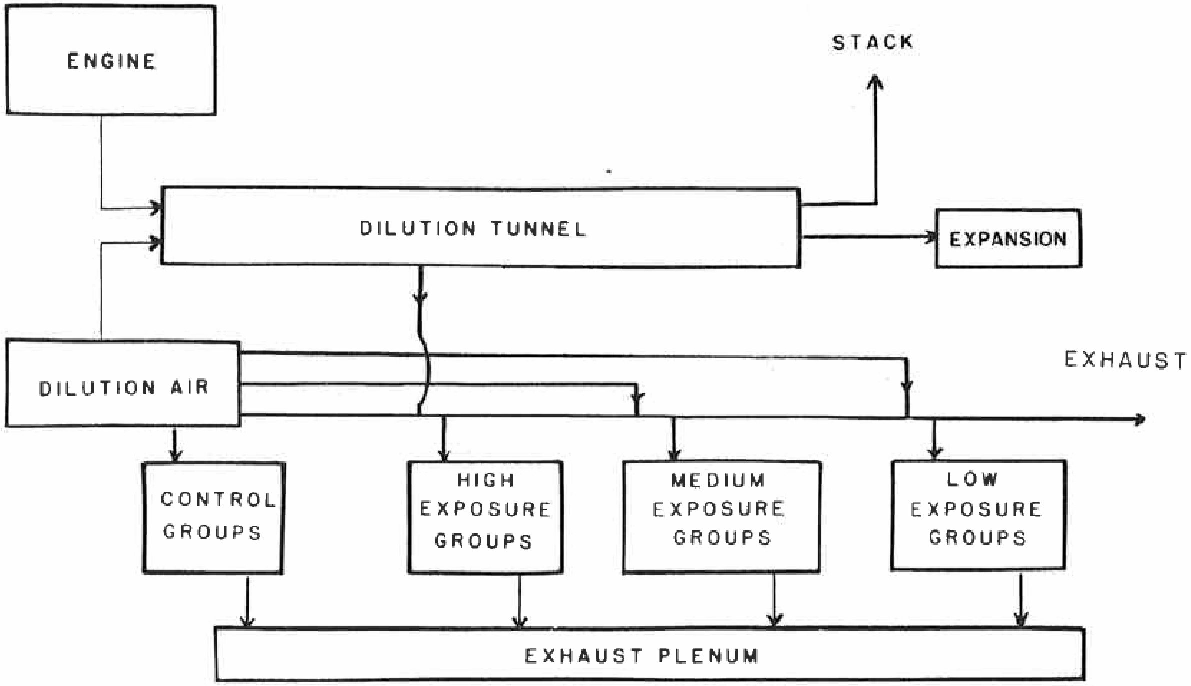


Figure 1 — Organization of the diesel exposure system.

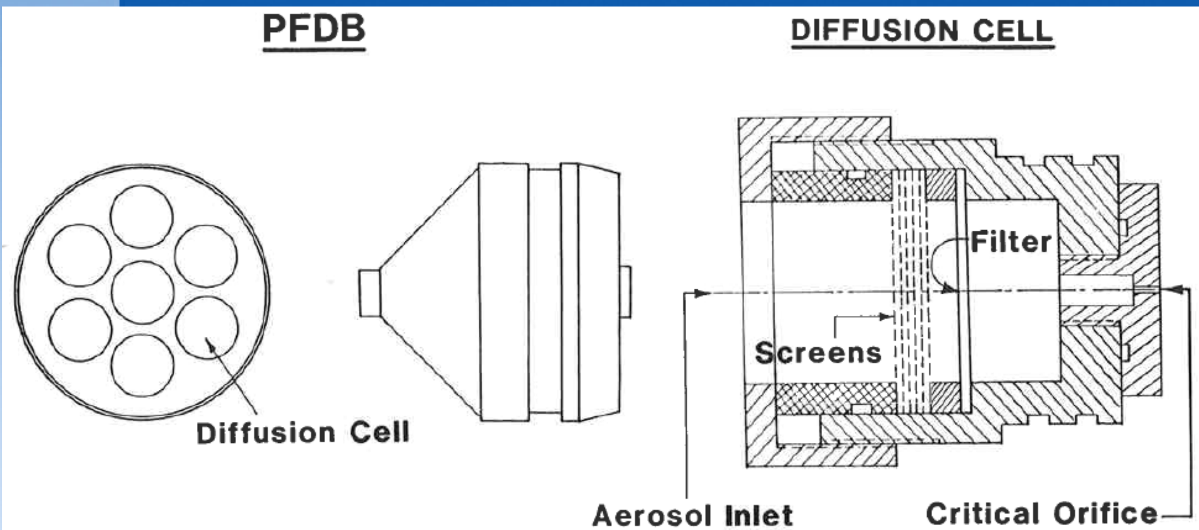


Figure 3 — Schematic of the parallel flow diffusion battery (PFDB).

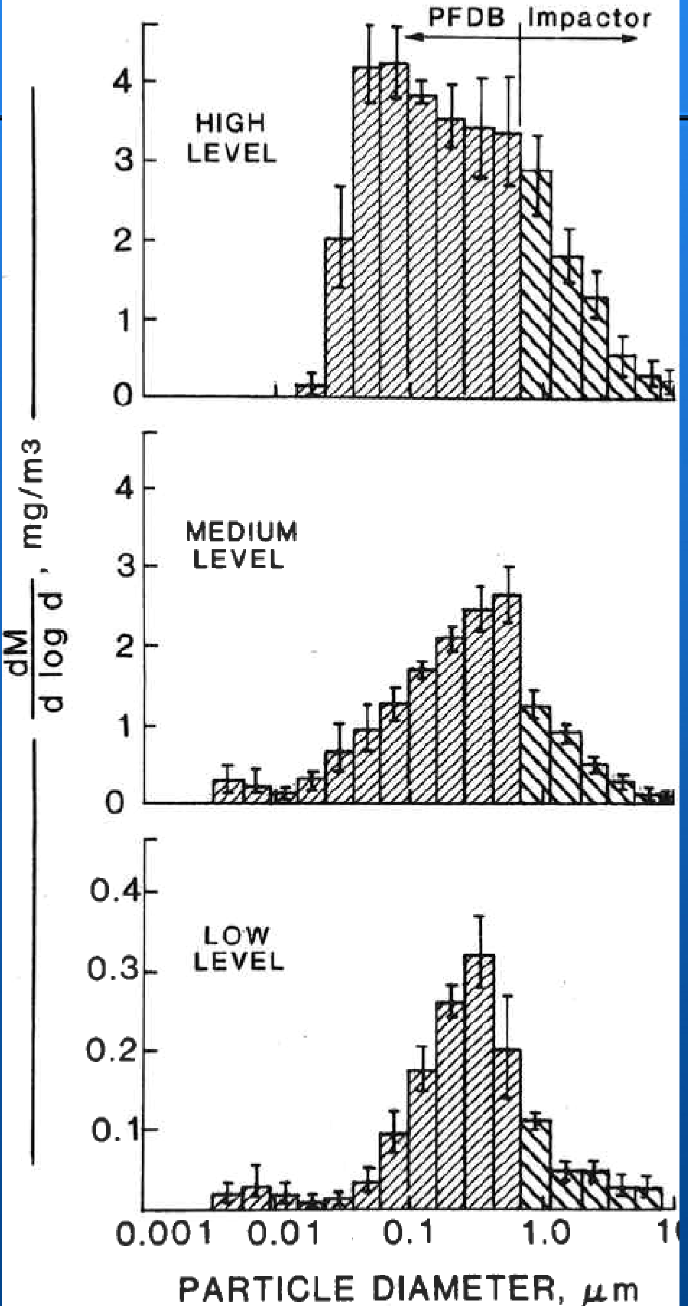


Figure 7 — Diesel particle size distributions (averaged over 3 measurements in each level) as determined by impactor/PFDB for three exposure concentrations.

(DMA + CPC) to calibrate EAA & (DB + CPC)

First use of differential mobility analyzer (TSI 3071) and condensation particle counter (TSI 3020) to calibrate particle sizing instruments:

Dolan, Kittelson, & Pui (1980) Diesel exhaust particle size distribution measurement techniques. *SAE paper 800187* contained in *SAE Proceedings P-86, Diesel Combustion and Emissions*.

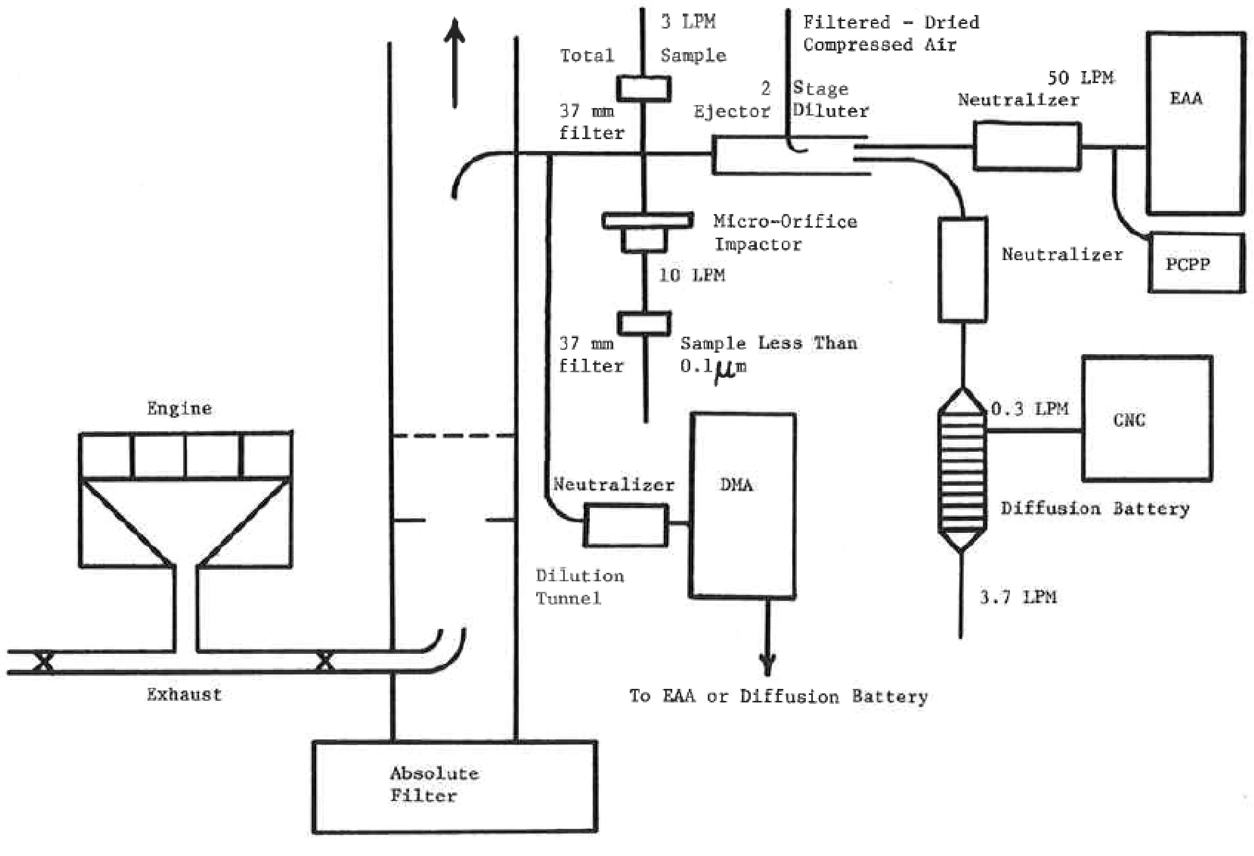


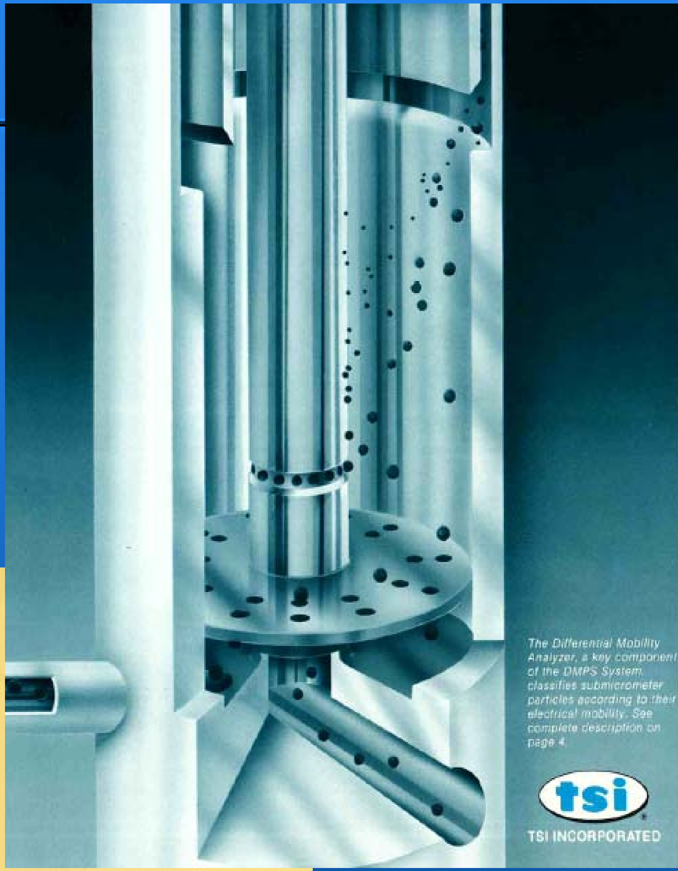
Fig. 2 - Schematic of test setup

Several years later, DMA + CPC became Differential Mobility Particle Sizing (DMPS) technique with high size resolution

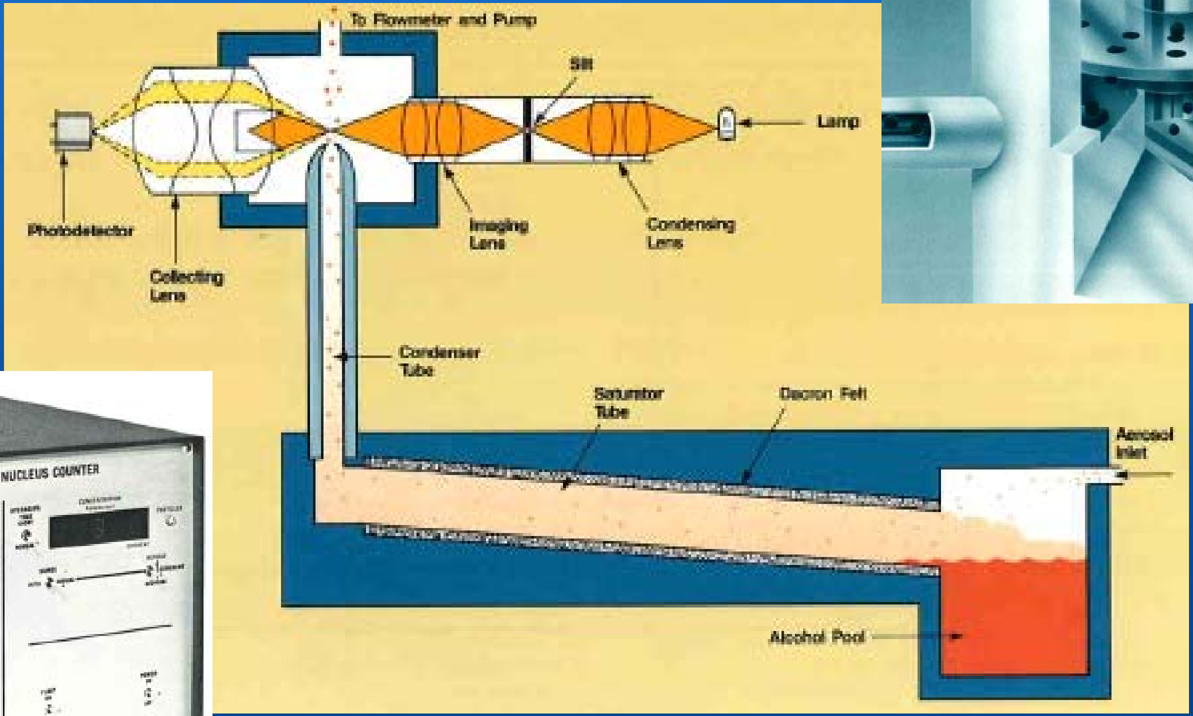
Pre-DMPS use of DMA + CPC for calibration

First use of differential mobility analyzer (TSI 3071) and condensation particle counter (TSI 3020) to calibrate particle sizing instruments:

Dolan, Kittelson, & Pui (1980) Diesel exhaust particle size distribution measurement techniques. *SAE paper 800187* contained in *SAE Proceedings P-86, Diesel Combustion and Emissions*.



↑ DMA from TSI 3071 electrostatic classifier



TSI 3020 CPC ↓→

First European rapid diesel exhaust particle measurements:

Israel, Zierock, & Mollenhauer (1981) Properties of particulate emissions from diesel engines. *J. Aerosol Sci.* 12(3):222.

- From Technische Universität Berlin
- Half-page abstract of an oral paper at a GAeF Conference
- Used cascade impactors
- Used EAA for number, surface, & volume distributions
- Used optical particle counter to supplement EAA for sizes > 1µm

First DMPS engine exhaust measurement?

- TSI introduced the 1st single-particle-counting CPC (1978).
- TSI introduced the 1st differential mobility particle sizing system (1982).
- We believe the 1st application of DMPS to engine exhaust was by Reischl & colleagues, U of Vienna. We have not found reference to such work.
- They set the stage for such measurements with the paper:

Wen, Reischl, & Kasper (1984) Bipolar diffusion charging of fibrous aerosol particles – II. Charge and electrical mobility measurements on linear chain aggregates. *J. Aerosol Sci.* 15(2):103-122.

- Used TSI 3020 CPC & Faraday cup electrometer to characterize charge / particle for chain aggregates
- Used iron oxide chain aggregate aerosol particles
- Used differential mobility analyzer (DMA) of Vienna design
- Characterized DMA transfer function

TSI

Summary

EVOLUTION OF MEASUREMENT TECHNOLOGY FOR ENGINE EXHAUST PARTICLE SIZE DISTRIBUTIONS:

- 1966: U of MN develops near-real-time size distribution system:
  - developed primarily for atmospheric applications.
  - 120 sec / measurement, 5 – 1000 nm, 4 size channels / decade.
- 1967: TSI 3000, based on Whitby U of MN instrument:
  - measurements possible by non-instrument-developers.
- 1973: TSI 3030, based on Liu-Pui U of MN instrument:
  - 90 sec / measurement, much easier to use, smaller, more practical.
- 1982: TSI Differential Mobility Particle Sizer (DMPS):
  - size resolution greatly improved, 16 channels / decade.
- 1992: TSI Scanning Mobility Particle Sizer (SMPS):
  - size resolution again improved, 64 channels / decade.
  - time resolution improved, 30 - 60 sec / measurement.
- 2003: Cambustion DMS / TSI EEPS (engine exhaust particle sizer):
  - time resolution (<200 msec) good for dynamic exhausts.
  - size resolution not comparable with SMPS.

TSI®

Contact

Gilmore J. Sem
TSI Incorporated
500 Cardigan Road
Shoreview, MN 55126-3996 (USA)

Email: GSem@tsi.com
http://particle.tsi.com