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FOURIER TRANSFORM INFRARED (FTIR) SPECTROSCOPY ANALYSIS OF COMBUSTION AEROSOL

Gary Jacquin

Introduction

In conjunction with my co-op program at McDonnell-Douglas, my current OURE project is the analysis of combustion aerosols using Fourier Transform Infrared (FTIR) Spectroscopy. Aerosol science is a very important field as it is concerned with atmospheric chemistry, atmospheric physics, climate, public health, and environmental issues.

In the Cloud and Aerosol Sciences Laboratory (CASL) at UMR, combustion aerosols are generated by an in-house designed torch or burner. The fuels, JP4 and JP5, are provided by McDonnell-Douglas. Some other commercial fuels are also used.

The primary objective of my OURE project was to generate and collect combustion aerosols for chemical analysis. I was also involved in the construction of an automated cloud condensation nucleus (CCN) counter. A more thorough description of these efforts is now offered.

Redesigning the Liquid-Fuel Burner

Background

One question that arose early on was whether or not the carbon aerosol from the UMR burner truly simulates the emissions from a jet aircraft. The size distributions found in earlier works (Refs. 1-3), dealing with jet engine exhaust, indicated that the mean carbon particle diameter Dp was approximately 0.04 microns. Figure 1 shows the basic set-up of the UMR burner. Before the improvements were made to the burner, carbon produced by the burner was deposited onto slides coated with Au-Pd and examined by scanning electron microscopy. The carbon was found to be huge strands (about 1 microns in diameter) of interconnecting carbon conglomerates. This was believed to be a characteristic of the flame, which frequently turned yellow. Clearly the UMR torch needed to be improved before it would simulate a jet engine.

Actual Work

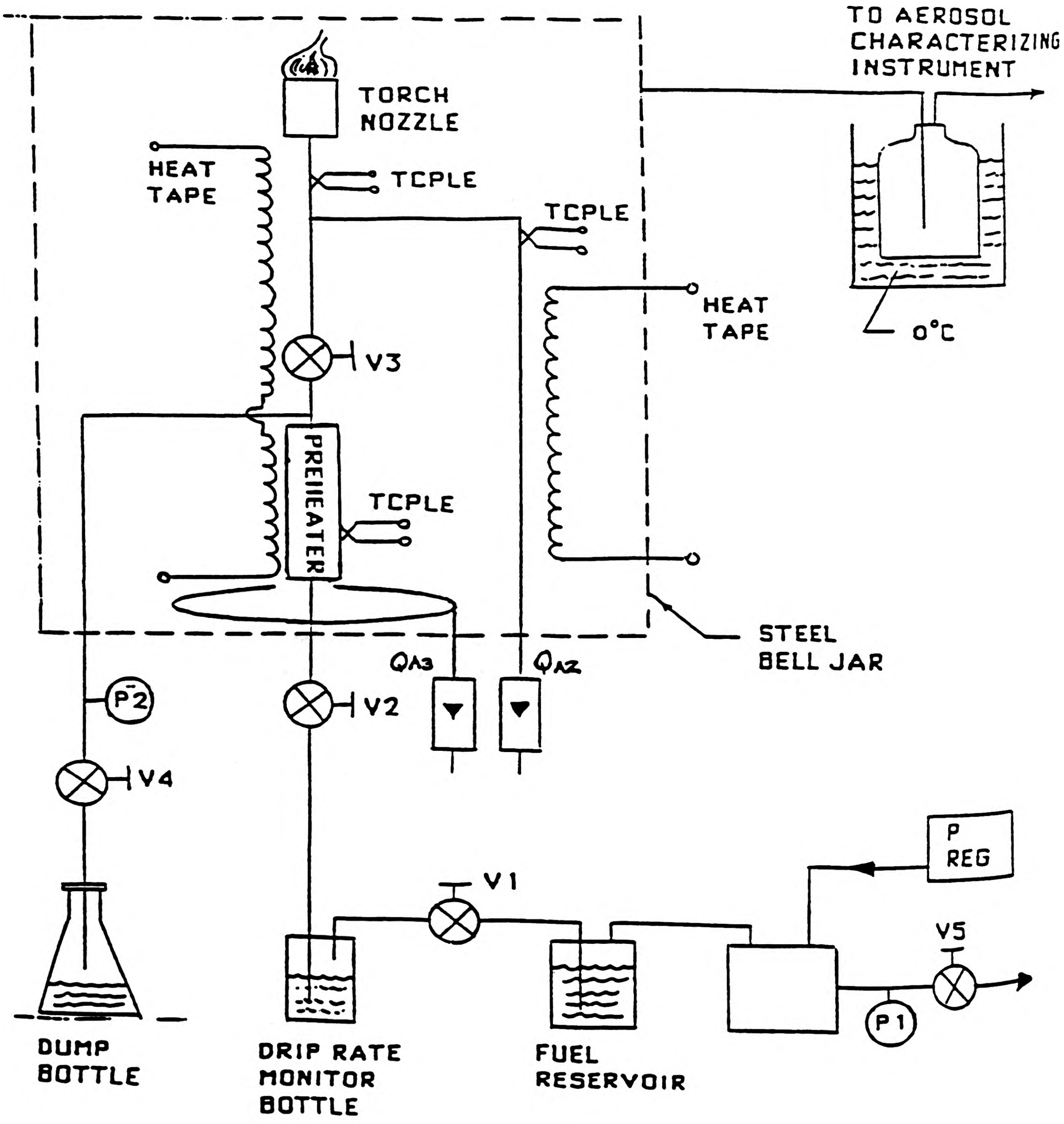
Many internal improvements were made to the torch or burner head to obtain a highly-controllable flame. There were also improvements made to the external mechanism. These include:

1) A port used as a pressure tap and fuel dump was added to the fuel injection system. This greatly decreases start-up and shut-down times, and allows the monitoring of fuel pressure, thus enhancing day to day reproducibility.

2) A shaft with several universal joints was installed to allow external control of the final fuel valve, and an externally operated ignition system was designed and implemented. These modifications allow the torch to be operated without raising and lowering the bell jar.

3) A photoresistance circuit was designed and partially installed to monitor the flame and sound an alarm should the flame go out. This is a big safety improvement.

FIGURE 1


TO AEROSOL CHARACTERIZING INSTRUMENT
TORCH NOZZLE
HEAT TAPE
TCPLE
TCPLE
HEAT TAPE
0°C
V3
PREHEATER
TCPLE
STEEL BELL JAR
Q_{A3}
Q_{A2}
P2
V2
V4
P REG
V1
V5
P1
DUMP BOTTLE
DRIP RATE MONITOR BOTTLE
FUEL RESERVOIR

4) The most significant improvement, however, was the design of a new burner tip. Previously the burner used to use a porous ceramic tip which produced a ball-shaped flame consisting of many individual flames that flickered out of each pore. This was unsuitable for the McDonnell-Douglas experiment which required a single large stable flame with all distinct areas of the flame accessible for probing. A new burner tip and inserts were then constructed of aluminum. This new design offers the following features:

   a) It accepts "inserts" of differing diameters to allow for variation of burn surface areas.

   b) It holds the inserts in place by pulling a fine stainless steel wire screen down over it. The screen causes the base of the flame to sit slightly above the burner head giving access to all parts of the flame.

   c) It has a threaded hole in the bottom for easy installation of fuel jets of various orifice size. The orifice forces the fuel-air mixture to become turbulent, thus ensuring a thorough mixing. Having different diameter orifices provides the ability to use different fuels having different vapor pressures for a given torch temperature.

There was some concern that the high temperature of the flame might cause some of the aluminum in the tip to sublimate away contaminating the aerosol. Thus the final version was machined from stainless steel. As a result of the improvements, the burner is now able to produce a wide variety of very stable flames, from a pure blue flame with an inner bright blue cone and an outer dark blue cone (premixed flame) to a sooty, yellow flame. This is desirable because we can now simulate the jet engine (premixed flame) for McDonnell-Douglas. It is also able to simulate other combustion aerosol sources such as an uncontrolled oil refinery fire (sooty, yellow flame). Such a flame is at the center of the nuclear winter controversy.

After the improvements to the burner, a sample was again taken and there were no longer any strands of carbon conglomerates, and the vast majority of the particles were single spheres with diameter in the .02 to .1 microns range. Thus the UMR liquid fuel burner produces carbon aerosol with size distribution simulating the carbon from jet aircraft. This is clearly a direct effect of the burner modifications.

Aerosol Samples From the Torch

Once the torch was finished, samples of the combustion aerosol were sent to McDonnell-Douglas for Fourier Transform Infrared (FTIR) analysis. This was accomplished with an Electrostatic Aerosol Sampler (EAS). The EAS charges the aerosol, then electrically deposits the particles onto slides. The aerosol was sampled directly from the burner and after passing it through an Electric Aerosol Classifier (EAC), which discards from the aerosol stream all particles except those within a very narrow range of diameters. Such an aerosol is termed monodisperse. The slides were then sent to McDonnell-Douglas to undergo FTIR analysis to determine the aerosol's chemical nature. The main focus of the chemical analysis was on the aerosol's hydration properties. This is part of an ongoing effort to determine the effect of jet exhaust on the atmosphere.

The origin of hydration properties of combustion aerosols is a heated topic. One school of thought believes it is based on the amount of soluble material in the aerosol particles, while others argue that it is mainly due to morphological effects. This was the main topic of discussion at the Third International Conference on Carbonaceous Particles in the Atmosphere held at Lawrence Berkeley Laboratory in October, 1987 and at the conference titled Lab Studies of Smoke/Cloud Microphysical Processes Workshop held in Los Angles, Calif. in December

1987. The present research at UMR is helping to uncover the answer by investigating whether certain soluble materials do actually exist on combustion aerosols. Initial results of the FTIR analysis do show the presence of soluble sulfates in the combustion aerosols. This is a positive and exciting result (I plan to monitor further developments in the future).

Infrared spectroscopy was chosen to analyze the aerosol because it is a powerful tool for chemical characterization, since it is capable of detecting picogram quantities of material for both organic and inorganic functional groups. This makes it possible to collect enough aerosol to perform a chemical analysis in a day.

Figure 2 shows the size distribution of carbon from JP4 aviation fuel that is available downstream of the EAC. The octagons denote the size distribution of the aerosol with the combustion air flow rate (QA2) of 5.5 liter per minute. The mean particle diameter (Dp) is about 0.045 microns. The crosses denote the size distribution for QA2 equal to 2.1 liter per minute. The mean particle diameter (Dp) is about 0.06 microns. Thus at higher combustion air flow rate, the mean carbon particle diameter is slightly smaller. Although not shown here, similar characteristics are also found for JP5. This seems to indicate a more thorough combustion of the fuel as expected. For the sake of comparison, the size distribution of the aerosol produced by the combustion of ethanol is also shown. Note that both its mean size Dp and the concentration of particles are smaller than those of JP4. One might very well expect oily fuels such as JP4 and JP5 with long chain-like molecules and many carbon atoms/molecules to provide more unburned carbon than a fuel such as ethanol.

Figure 3 shows the size distribution of carbon from JP4 that is available just after the burner. Although the mean particle diameter Dp is approximately the same for the octagons and crosses here, the crosses (lower QA2) still have a higher concentration of large particles. Again ethanol is shown for comparison.

The data for Figure 3 is obtained from the data in Figure 2 through a somewhat sophisticated computer inversion. The basic premise of this inversion is that what exits the EAC at a particular diameter Dp is only a fraction f of what enters the EAC at that Dp. Boltzmann's distribution correctly describes the charge distribution on aerosol particles. At a given Dp only the fraction f of those particles carry a charge and can thus be extracted from the rest of the aerosol.

Note that the Dp in Figure 3 (at exit from torch) is approximately 0.03 microns, which is smaller than that in Figure 2 (exit of EAC). This is because the value of f is smaller for the smaller particles, and the EAC is less efficient, therefore, in extracting them.

While collecting the samples, a part of the aerosol was extracted by the EAC (i.e., a particular Dp) and put through a Continuous Flow Diffusion Chamber (CFD). This instrument introduces the particles to a precisely controlled supersaturation. An optical particle counter counts drops that are grown from the aerosol. This allows the calculation of the critical supersaturation (SSc) for the particle of a certain diameter and chemical species. This is necessary to correlate the results of the chemical analysis with the results predicted by theory. Figure 4 shows the critical supersaturation (SSc) vs. carbon particle diameter (Dp) produced by burning ethanol, JP4, and JP5. For reference, the behavior of NaCl is also shown. First note that for a given Dp, NaCl has lowest SSc. The carbon from ethanol has the highest SSc. This is entirely to be expected since the pertinent theory states that the more soluble material there is in the particle, the lower the SSc. All of the material in an NaCl particle is soluble and one would expect very little, if any, soluble material in a carbon particle from burning reagent grade ethanol. The carbon from JP4 and JP5 is another matter though. Such fuels contain small amounts (about 0.1%) of sulfur. When burned, these fuels give rise to sulfur oxide which combine with the water of combustion forming sulfuric acid. The sulfuric acid is, of course,

FIGURE 2

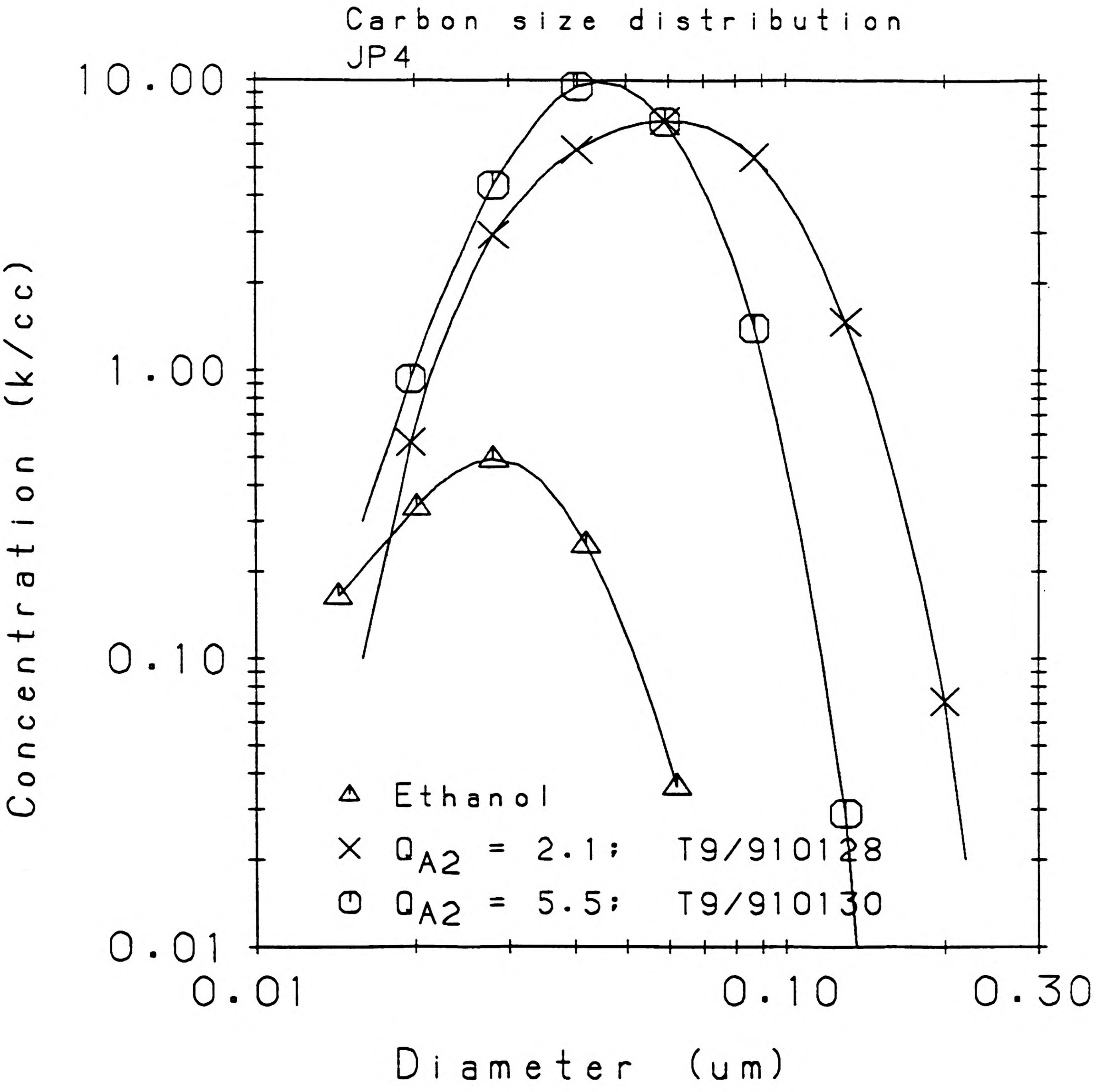

Carbon size distribution
JP4
10.00
1.00
0.10
0.01
Concentration (k/cc)
0.01
0.10
0.30
Diameter (um)
△ Ethanol
× Q_{A2} = 2.1; T9/910128
○ Q_{A2} = 5.5; T9/910130

FIGURE 3

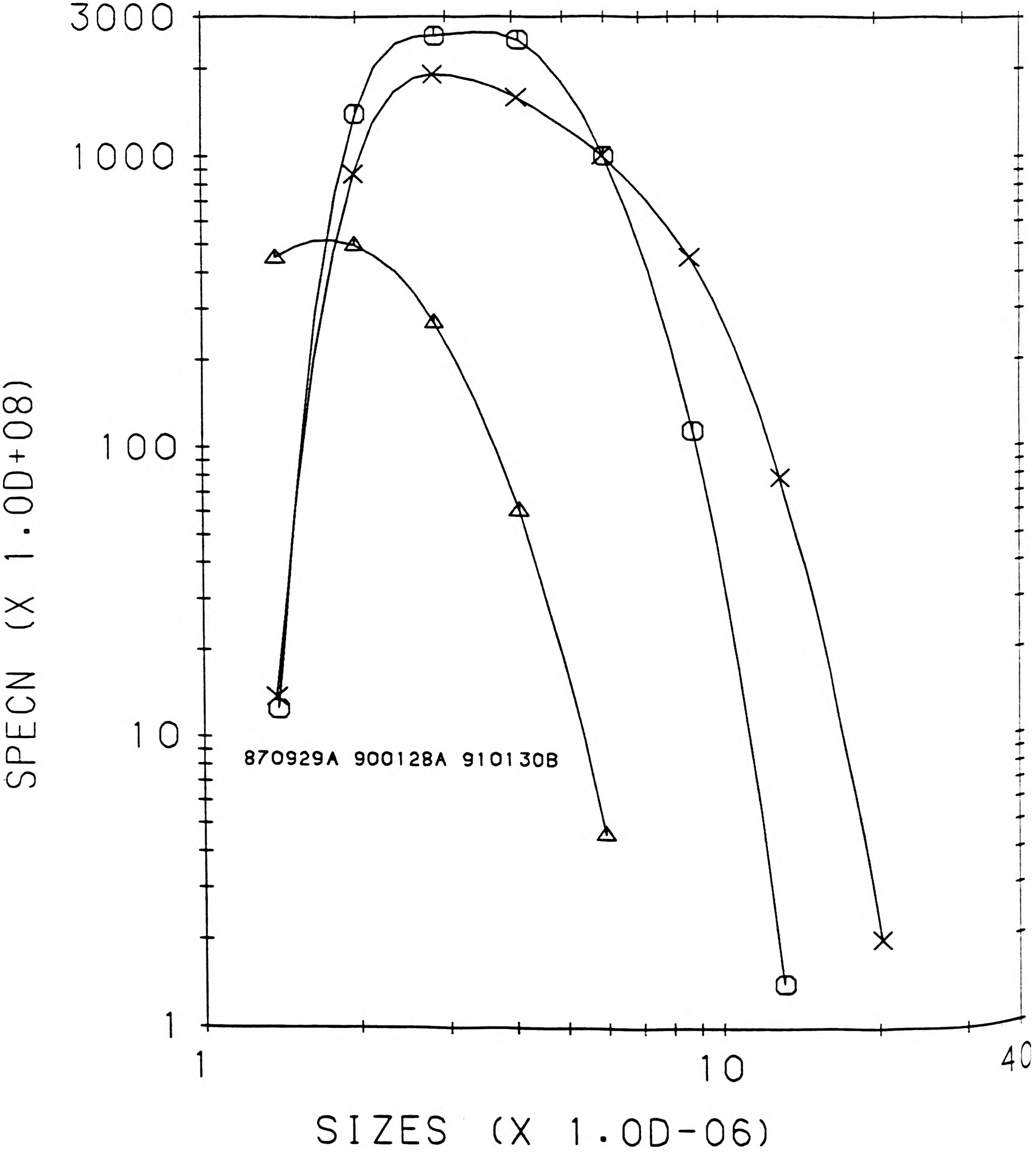
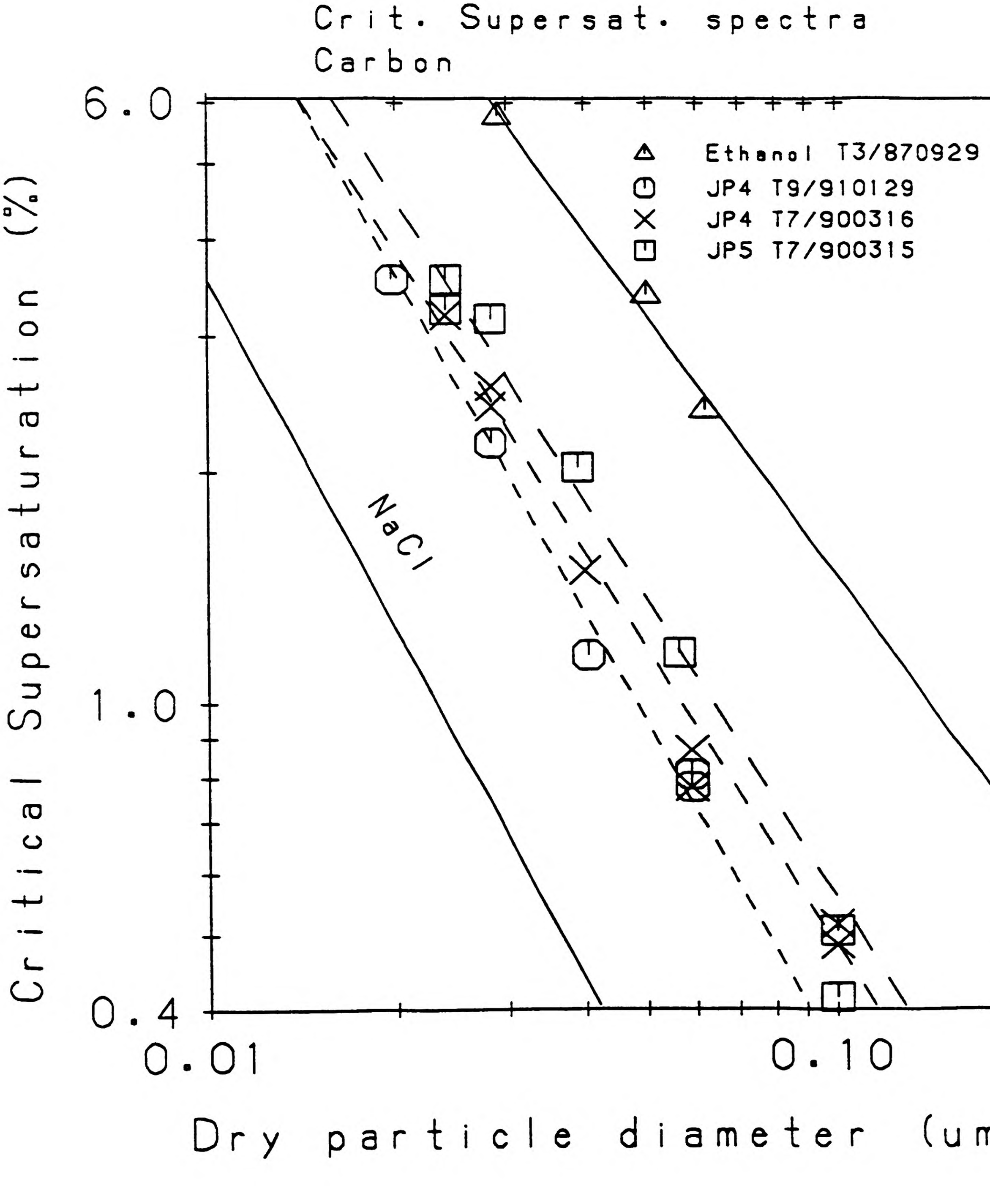

3000
1000
100
10
1
SPECN (X 1.0D+08)
870929A 900128A 910130B
1
10
40
SIZES (X 1.0D-06)

FIGURE 4


Crit. Supersat. spectra
Carbon
6.0
1.0
0.4
0.01
0.10
Critical Supersaturation (%)
Dry particle diameter (um)
Ethanol T3/870929
JP4 T9/910129
JP4 T7/900316
JP5 T7/900315
NaCl

soluble. If it finds its way to a carbon particle, as some of it surely must, it would then cause the carbon particle to have a lower SSc than that from ethanol.

Note that the highest SSc value (the squares) are for JP5. The two batches of JP4 provide particles with lower SSc values. This also is to be expected since the analyses of sulfur content of JP4 and JP5 revealed that the JP4 had more sulfur than the JP5.

Other Experimental Work

There was considerable turn around time between supplying McDonnell-Douglas with samples and getting instructions from them on what type of samples to take next. Therefore, I also worked on a project designed to determine the chemical composition of cloud condensation nuclei (CCN). CCN make up only about 1% of the atmospheric particulate matter, yet are responsible for cloud condensation, fog, etc. Thus, these are very important particles. The problem is that they are at the extreme small end of the aerosol size spectrum. This makes it difficult to collect the mass required to do a chemical analysis. Recent advances in chemical analysis now make it possible to perform quantitative analysis on the amount of material that can be obtained by collecting these CCN over a reasonable of time (about 24 hours).

This project requires the design and construction of a much larger and improved version of the fore mentioned CFD. I was involved in the construction and initial testing of a smaller prototype of the new instrument. Figure 5 shows a diagram of the prototype. We are having good initial success with the still uncompleted prototype.

In addition to the FTIR McDonnell Douglas experiment and the CCN chemical composition experiment, I was involved on a smaller scale in many other experiments. One such experiment was the study of scavenging rate. Scavenging is a process whereby one aerosol particle captures another particle of smaller diameter. This process creates a third particle with Dp and SSc different from either of the original two. As stated earlier, this is of considerable importance in environmental issues. This experiment again made use of both the EAC and CFD. The burner produced carbon particles which were then sent to the EAC and a monodisperse slice of diameter Dp1 extracted. Meanwhile the nebulizer atomized a solution of polystyrene latex (PSL) particles and this aerosol was sent to a second EAC where a monodisperse slice of diameter Dp2 was extracted. These two aerosols were put in a 200 liter plastic bag for a few hours. Then the resulting aerosol was extracted from the bag, and its SSc measured using the CFD. Repeating this procedure many times using different diameter particles and varying scavenging times allowed the scavenging rate and resulting SSc to be measured as a function of Dp1 and Dp2 and scavenging time.

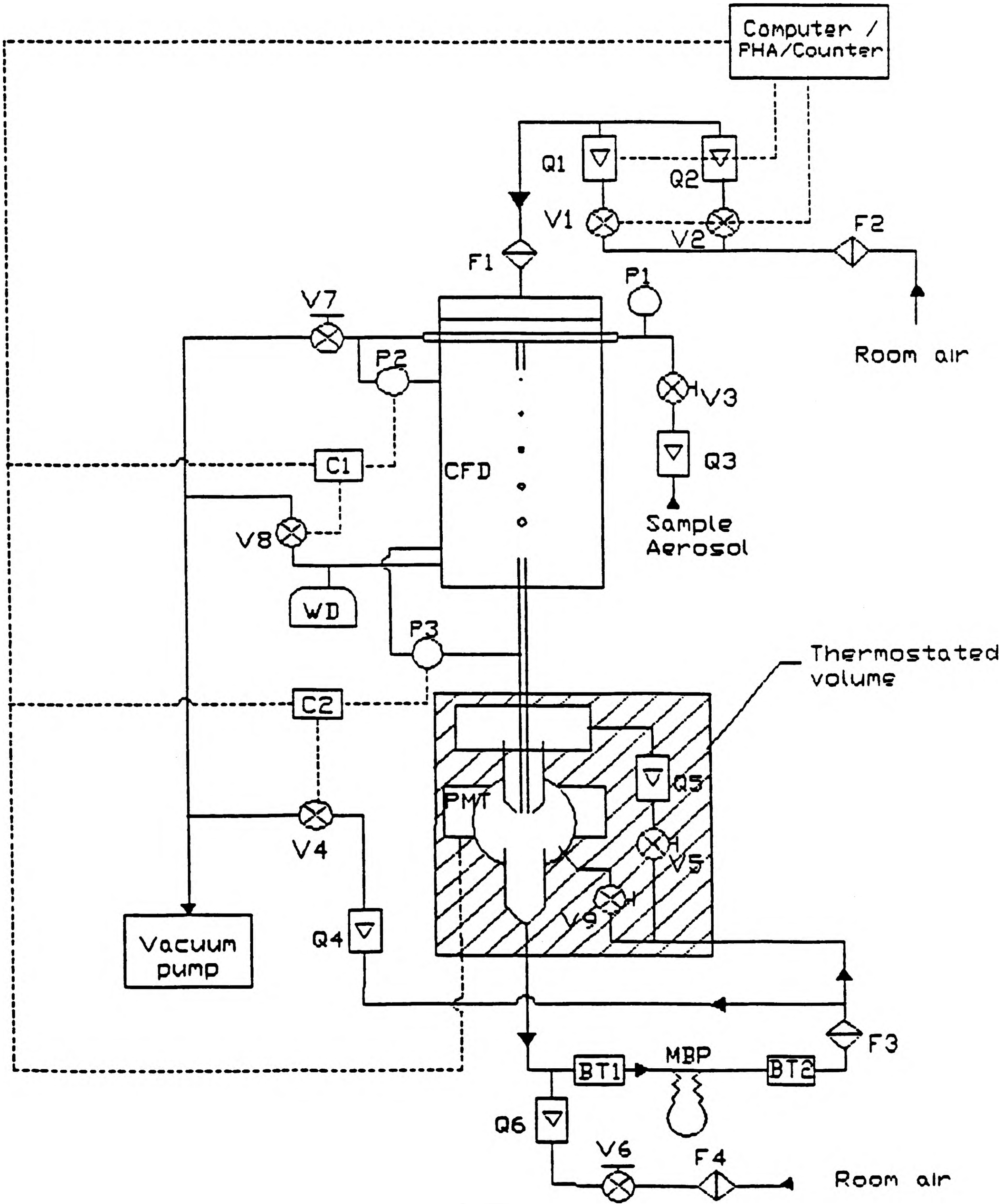
I also spent some time developing a drop generator to be used in ice nucleating experiments. A drop generator is an instrument that can create drops of liquid of various diameter at various rates. The drop generator I worked on used a ball-tipped wire connected to a motor driven cam to pull a drop away from a meniscus of liquid.

In addition, Ron Holland, another OURE student with whom I worked closely over last summer, and I spent a week learning to use an image processor called JAVA. Ron Holland plans to use the processor to analyze Scanning Electron Microscope results of his morphology experiments.

Conference Presentations

With the support of Dr. Donald Hagen and Max Trueblood, I have entered a paper in the Missouri Academy of Sciences (MAS) meeting to be held April 19. Ron Holland is also presenting a paper at the meeting. I have included a copy of my abstract in this report. I feel

FIGURE 5


Computer / PHA/Counter
Q1
Q2
V1
V2
F2
F1
P1
V7
P2
V3
Room air
Q3
C1
CFD
V8
Sample Aerosol
WD
P3
Thermostated volume
C2
Q5
PMT
V4
V5
V9
Vacuum pump
Q4
F3
MBP
BT1
BT2
Q6
V6
F4
Room air

this will be a very valuable experience for me and I look forward to participating in the meeting. This work will also be reported at the 9th Midwest Association for Cloud and Aerosol Physics Meeting, May 1991, at the University of Wisconsin-Madison, in a paper entitled "A laboratory liquid fuel burner and the properties of the associated combustion aerosols".

With the MAS meeting being April 19, I will not be able to participate in the UMR Undergraduate Research Symposium being planned for the same date. I regret not being able to present a talk at both events.

Postscript

I have restrained from introducing the theoretical and mathematical aspect of the experiments in favor of simple, direct explanation of the subject in the belief that this approach would better serve prospective future OURE students who may read this report in trying to decide where they may want to work. Along these same lines I would like to conclude by saying I had a very enjoyable and beneficial OURE experience. Everyone I worked with on a daily basis was extremely helpful and supportive. I have gained immeasurable knowledge from the project, not only in cloud physics, but also in research methods and the many difficulties involved in research. Therefore, I strongly recommend future OURE involvement in the Cloud and Aerosol Science Laboratory.

References

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3) "Electrical Aerosol Analyzer: Operation, Maintenance, and Application." Taken from Aerosol Measurement, D. A. Lundren ed., University Press of Florida, Gainesville 1979.