



CALSPAN—UNIVERSITY AT BUFFALO RESEARCH CENTER, INC.

**NOPP Aerosol Process Experiments:
Phase II Data Report**

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I. Introduction

This report presents the data obtained by the Calspan University of Buffalo Research Center (CUBRC) during the National Oceanographic Participation Program (NOPP) Phase II Aerosol Process Experiments. These experiments were performed in Calspan's 600 m³ Atmospheric Research Chamber. In May-June of 1998 a preliminary series of experiments were performed in the chamber to characterize its operation and performance prior to the Phase II experiments which were performed in October-November 1998. The results of the Phase I experiments were reported earlier.⁽¹⁾ This earlier report includes a complete description of the chamber, its operation and performance and is reproduced in this data report for completeness. A number of recommendations were made as a result of the Phase I Chamber and which were deemed necessary in preparation for the Phase II experiments. These improvements are also summarized in this report. CUBRC was responsible for the IR Transmissometer-Liquid Water Content (LWC) Measurements and the Measurement of Hydrocarbon (HCs) in experiments designed to study aerosol formation in the presence of HCs. These included experiments where known concentrations of cyclohexene, cyclopentene and alpha-pinene were introduced into the chamber.

CUBRC was also responsible for providing the chamber interfaces and operating infrastructure for the principal investigators, from the Naval Research Laboratory and University of Washington and the participating scientists from the National Center for Atmospheric Research, Aerodyne, Environment Canada and the University of Delaware. The liquid water content and HC data are available to all of the organizations that participated in the Phase II experiments.

II. The 600 m³ Atmospheric Research Chamber

A. *Physical dimensions of the chamber:*

Diameter: 9.1 m (30 ft)

Height: 9.1 m (30 ft)

Volume: 590 m³

Surface area: 394 m²

Steel walls 0.5 inches thick

Inside covered with Teflon coating

B. *Chamber Pressurization and Expansion, Fog Cycles.*

The chamber can be pressurized and expanded to create clouds. Initially the chamber is pressurized by pulling air in through the charcoal filter bank and into the chamber. The rate of pressurization is controlled by manipulating a blower damper. The chamber can be pressurized to a maximum of 25 millibars which can be accurately controlled and held at plus or minus 0.5 millibars. The pressure limitation is dictated by the strength of the windows covering the irradiation lamps. During the characterization experiments leaks in ducting and valves resulted in a over-pressure decay time of about 5 minutes; i.e., after over-pressuring, the chamber pressure fell to e^{-1} the maximum value in 5 minutes when the over-pressure blower was turned off. While this was adequate for cloud processing experiments, improvements were made prior to the Phase II series.

C. *Washing and Humidification System*

Chamber Humidification. The chamber is equipped with a wall wetting ring located along the top circumference of the chamber. Deionized water is supplied to the ring by a high pressure pump. Wetting the walls in two, 3 minute intervals over a 30 minute period can elevate the chamber relative humidity to over 97%.

Chamber Dehumidification. The chamber has two copper finned dehumidification coils. These are capable of reducing the relative humidity in the chamber from 100% to < 35% operated over a 12 hour interval. Lower RH values can be achieved with longer cycle time.

Chamber Wash System. Wash water for the chamber is processed through a filtered deionizing system. Tap water is passed through a 5 micron filter into a charcoal filter bed. It then passes through two resin beds and finally through a 5 micron filter before being transfer to a 300 gallon holding reservoir.

The chamber is equipped with an automated pneumatic articulating spray nozzle mounted from the center of the ceiling . When in operation, the entire chamber can be wetted by the spray nozzle every 6 minutes. A thorough wash is accomplished by spraying the chamber interior with a mild soap solution followed by two rinse cycles using deionized water. Each wash and rinse cycle consume approximately 50 gallons of water. The chamber is typically put through a fresh water rinse at the end of each operation day.

D. Filtering and Air Purification System.

The 600 m³ chamber facility incorporates a system of pre and absolute filters to permit virtually the total removal of particulates. Impregnated charcoal filter panels enable the removal of gaseous contaminants. Some of the most difficult to remove contaminants, such as CO and CH₄, are present only at minimum concentrations in the unpurified ambient air due to the rural location of the test facility. The air purification system is thus capable of preconditioning the chamber for studies of tropospheric pollutant and aerosols even at minute concentrations. The chamber "air" system can be operated in various modes depending on the nature of the investigation.

Fresh Air Flush. In this operating mode chamber air is exhausted outdoors via an exhaust blower, makeup air is supplied through a Farr 30/30 pre-filter followed by a 95%, efficient Ashrae filter.

Charcoal (absolute) filtering. In this operating mode chamber air is circulated through a copper finned dehumidifier coil and downstream through a Hepa filter bank. The air then passes through a 30/30 pre-filter and a 95% Ashrae filter followed by a series of two absolute charcoal filters. Finally the air is circulated through a Hepa filter before being returned to the chamber. This is a closed cycle configuration.

Filtering reduces the concentration in half about every 10 minutes for substances which are removed with about 100% efficiency with the filters. This is shown for the total aerosol concentration in Figure 1.

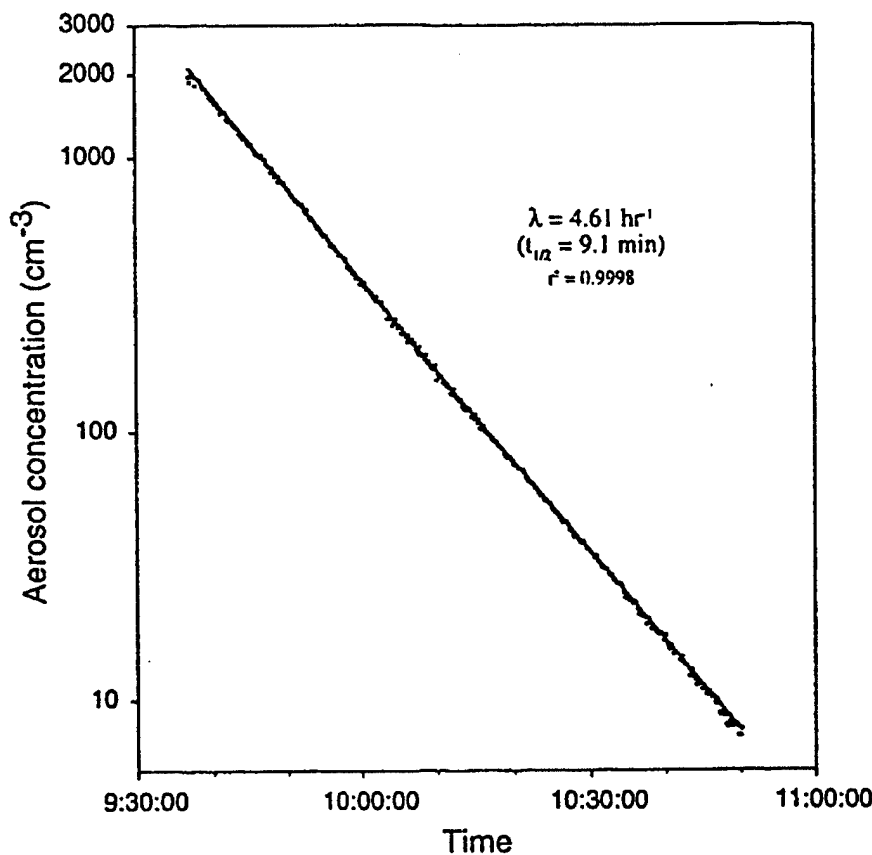


Figure 1 Filtering efficiency for total aerosol concentration

E. Cloud formation in the Chamber.

After the desired seed nuclei are generated in the chamber, the chamber is humidified by injecting deionized water from a tube around the top of the chamber wall. A series of nozzles directs a stream of water against the wall and the water flows down the wall and puddles on the floor of the chamber. The initial increase in humidity is fairly rapid and approaches saturation exponentially. When the chamber is nearly saturated (dew point depression is less than a degree) the chamber is over-pressured to about 20 mb for ten minutes. The compression slightly heats the chamber but the dew point depression recovers its low value within ten minutes. The air providing the overpressure is supplied through the charcoal and absolute aerosol filters, and a small amount of air must continually be supplied during the compression to maintain the pressure against small leaks in the air handling system. During the overpressure period any required reactants can be supplied to the chamber and the mixing fan remains on until just before the start of the expansion. During the characterization experiments, the expansion of the air in the chamber was accomplished by exhausting air from the chamber through a three inch diameter ball valve connected to a vacuum blower. The expansion through the blower is continued until the pressure in the chamber is about

10 mb below ambient. Expansion by this system was not adequate for all desired expansions, so during the characterization experiments an additional two inch ball valve was installed which could be used during the initial expansion while the chamber pressure was still above ambient pressure. After the cloud is held the desired length of time (usually 3 to 4 minutes) the chamber is allowed to come back to ambient pressure by admitting air through the filters. The purpose of the compression at the end is to evaporate the cloud in a definitive manner.

F. Characterization of the Chamber Irradiation System.

The spectral irradiance characteristics of the 600 m³ Chamber lamp system was determined by direct measurement using a calibrated Optical Multi-Channel Analyzer (OMA).

The chamber contains 3 types of lamps:

- | | |
|---|-----------------------|
| 1. Very high output (VHO), 96" long F96T12 Sylvania | 2 Lamps per enclosure |
| 2. High output (HO), 72" long F72T12 Blacklamps GE | 8 Lamps per enclosure |
| 3. FS40 (FS), 40" Long Sunlamps Westinghouse | 2 Lamps per enclosure |

There are a total of 8 lamp banks containing three enclosures each for a total of 24 enclosures. All enclosures are covered with a borosilicate glass (PyrexTM) window. Each enclosure measures 17 ½ inches wide by 8 ½ ft. tall. These lamps were investigated separately and collectively. The data represent the relative intensity and spectral profiles of the ultra violet wavelength region of these various lamps.

An Optical Multi-channel Analyzer (OMA) was used to determine the relative spectral intensity of the chamber lamp system. This instrument consist of a spectrometer with a 25 micron entrance slit and a 1200 grooves per millimeter grating blazed at 300 nanometers. The measured radiation is focused onto a photo sensitive micro-channel plate. The optical signal is then stored into a computer for additional processing. Exposure times where set to 16 milliseconds in order to average out the AC effects of the lamps. The instrument's field of view was approximately 17 inches by 24 inches when located 12 ft. from the desired source. The relative spectral intensity of the instrument was determined with a deuterium lamp standard.

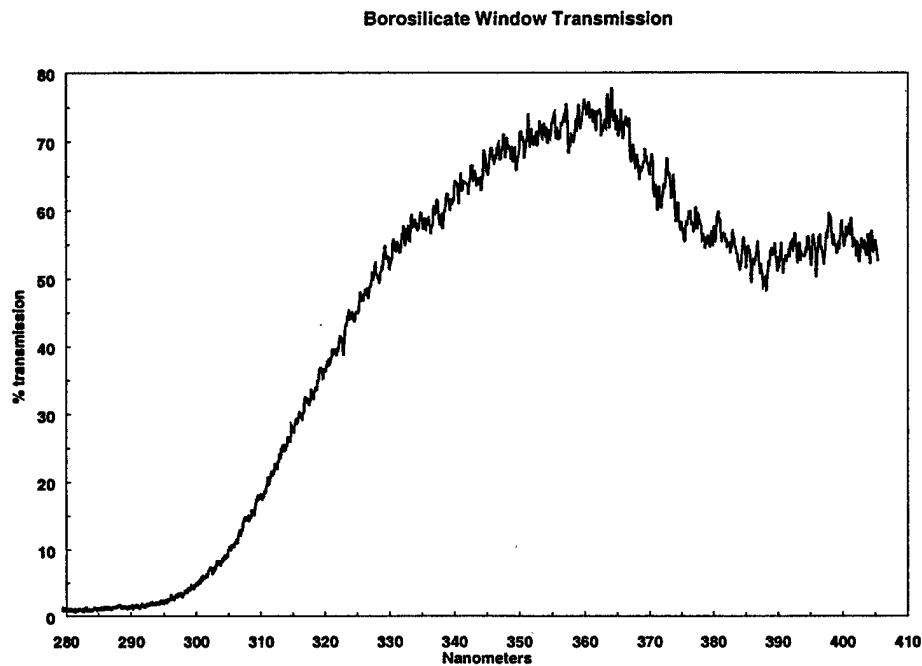


Figure 2 Window spectral transmission

The measured transmission of the borosilicate window is displayed in Figure 2. A deuterium lamp standard was used as the light source for this measurement and also to correct for the spectral response of the instrument. The UV transmission begins to fall off at 320 nm and decreases to 10% of the maximum by 300 nm.

Figure 3 depicts the relative intensity of a single lamp enclosure with all chamber lamps operating. The instrument field of view was centered on the middle 2 ft. section of a 8 ½ ft. enclosure. The actual OMA field of view represents roughly 25% of the enclosure's active area.

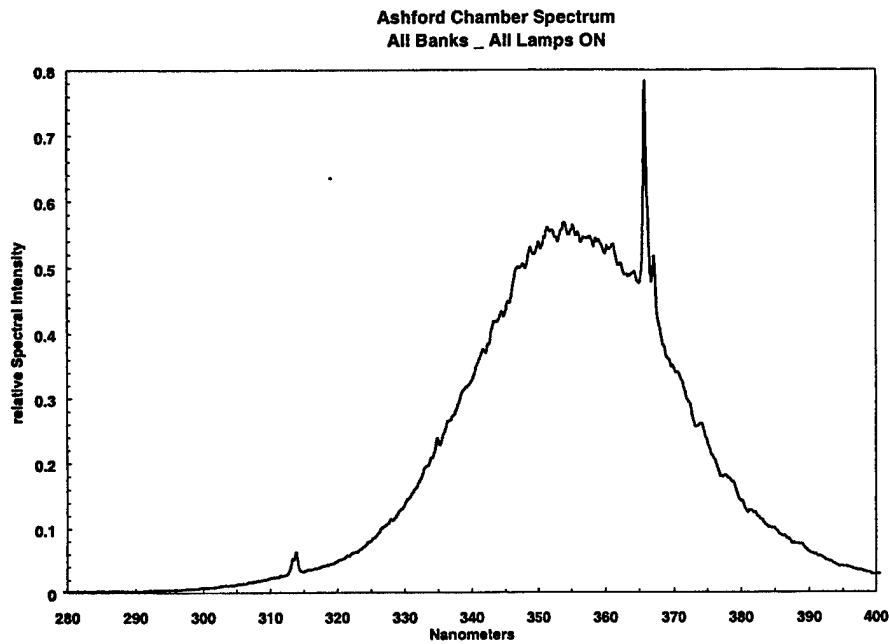


Figure 3 Relative intensity of a single enclosure with all lamps on

The spectrum clearly shows that the bulk of the radiation consists of the fluorescent continuum of interest, with superimposed atomic mercury lines at 365 and 312 nanometers. This fluorescent continuum appears centered and symmetric about the peak intensity at 355 nanometers. This relative spectral intensity displayed in Figure 3.

Figure 4 shows the spectral profile of the HO lamps. Figure 5 is the spectral profile of the VHO lamps. The spectral shape appears to be very similar. Figure 6 is the spectral profile of the FS40 lamps. The radiation peak is centered at 320 nanometers dropping off more rapidly in the shorter wavelength direction due to the window transmission limitations. Although this spectral intensity is not large, it is the major source of short wavelength UV radiation.

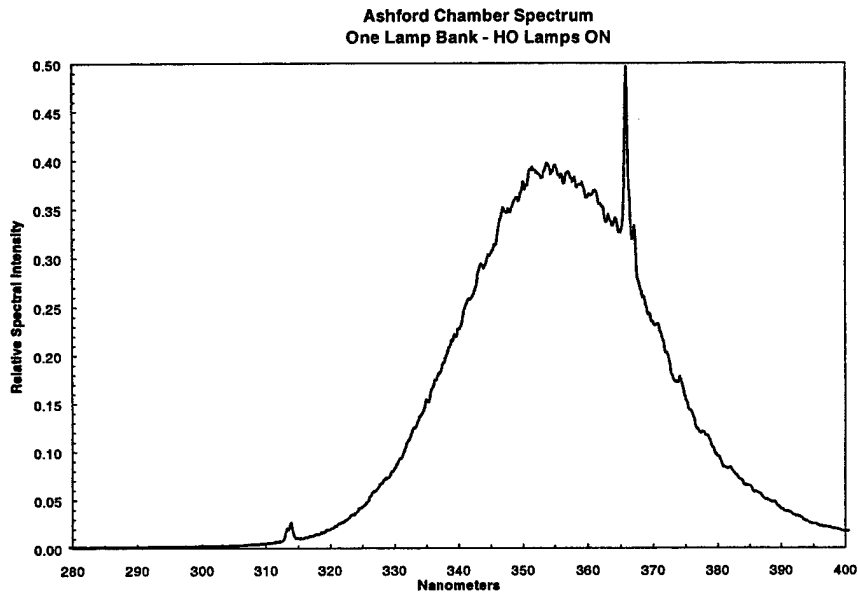


Figure 4 Spectral profile of the HO lamps

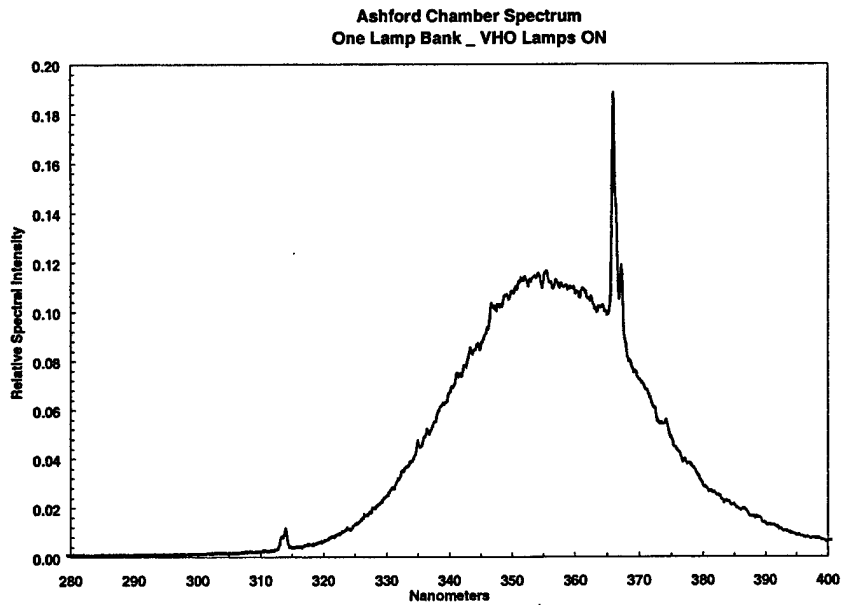


Figure 5 Spectral profile of the VHO lamps

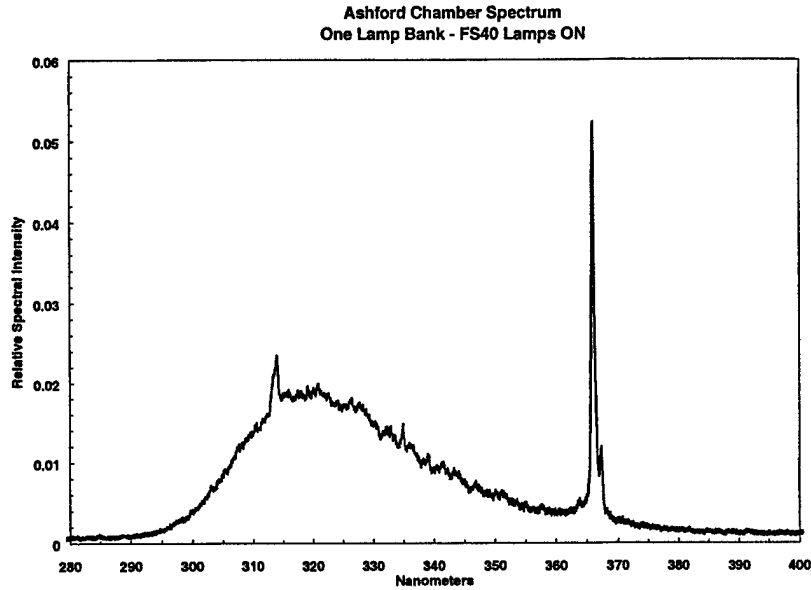


Figure 6 Spectral profile of the FS40 lamps

Figure 7 is a spectral distribution with the OMA field of view shifted to a section of the chamber wall. All lamps were operating for this measurement. In comparison with Figure 3 the spectral distribution remains unchanged. Thus, the chamber walls are spectrally neutral; they do not alter the spectrum of the incident radiation.

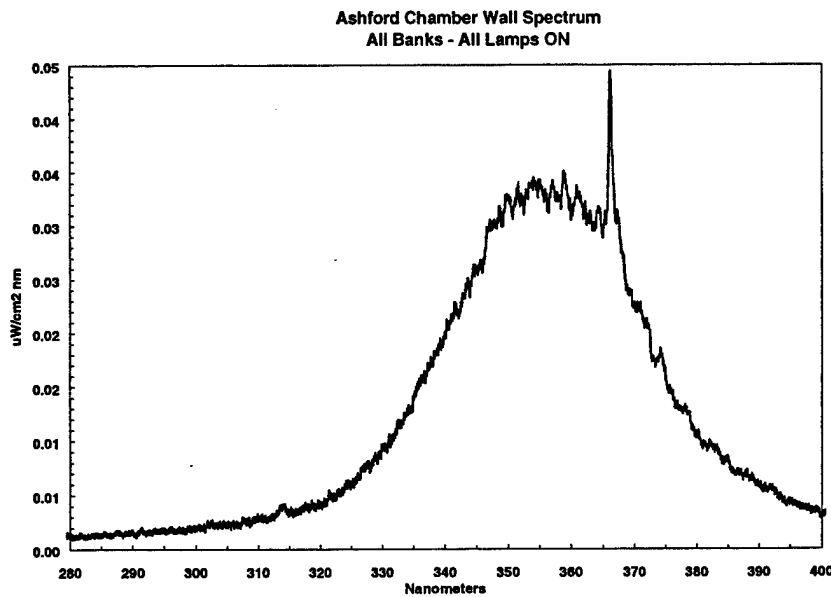


Figure 7 Spectral distribution with the OMA field of view shifted to a section of the chamber wall.(ordinate should be "relative Spectral Intensity")

Figure 8 depicts an overlay of all spectra for a comparison of relative spectral irradiance. From this plot it can be seen that the HO and VHO lamps are the major radiation sources. While the FS40 lamp intensity is small, it is the dominant contributor at the shorter UV wavelengths.

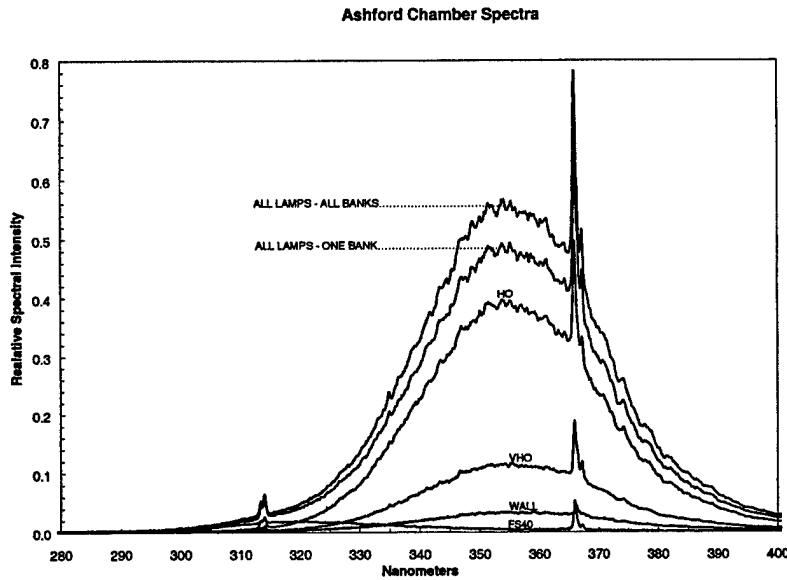


Figure 8. Overlay of all spectra for a comparison of relative spectral irradiance

Spectra of the lamps were also taken without the borosilicate windows in place. The relative spectral profiles of the HO and VHO lamp intensities were not much different than the spectra taken with the windows in place. However, the FS40 lamp showed substantially more radiation below 300 nanometers (Figure 9).

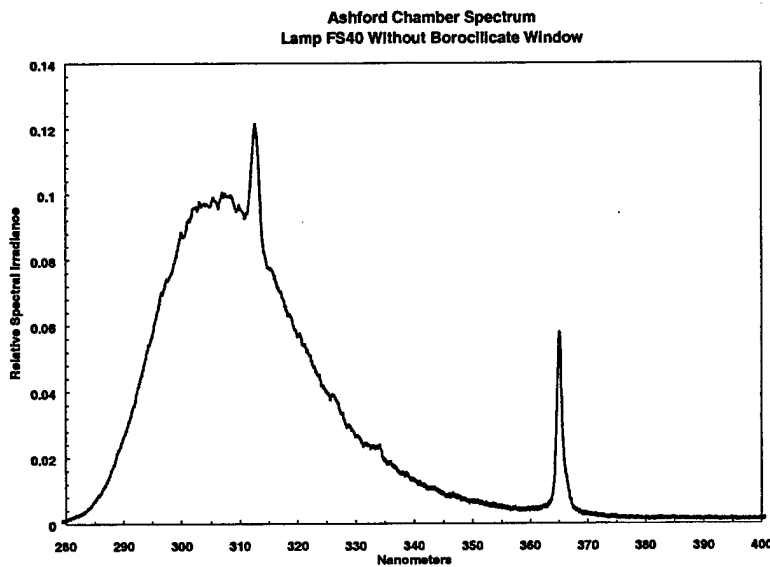


Figure 9 Spectra of the FS40 lamp without the borosilicate windows

At the conclusion of the Phase II experiments a 4II Actinic Flux head was procured and was to be interfaced to the OMA to obtain the total integrated light intensity spectrum from the chamber lamp system. Difficulties with the head and component failures in the OMA precluded making these measurements.

G. Recommendations and Facility Improvements

As a result of the Phase I experiments, specific recommendations were made in the Phase I report, to improve the physical operation and performance of the chamber prior to the Phase II experiments. The recommendations are reiterated here and the actions taken to address them are summarized:

- Concern was expressed about low level hydrocarbon emissions possibly emanating from the gear box of the chamber mixing fan. To eliminate this possibility, the gear box and motor of the fan were enshrouded with a Tedlar bag and placed under slight negative pressure (relative to the chamber). Subsequent GCMS analysis of the chamber background atmosphere showed no discernable difference, however, between Tedlar bag system on or off.
- It was determined that background aerosols were being introduced into the chamber by the introduction in unfiltered air into the chamber to make up for the volume removed by the instruments employed by the various investigators. To resolve this, a passive air make up unit was fabricated consisting of an absolute filter and 4-Dorex type H charcoal canister filters. The total flow capacity of this system was significantly greater than the total sampled air flow rate and resolved this issue.
- Improvements of the overall tightness of the air handling system were made to improve the facility performance for cloud processing. Repairs to the ductwork, flange seals, and filter box assemblies were made which resulted in an overpressure decay time of 10 minutes relative to the 5 minutes reported for the Phase I experiments.
- In order to improve the cloud formation process, a six inch butterfly valve was procured and ducted to the chamber blower to allow for a more rapid expansion than was possible during the Phase I experiments. The valve was equipped with a hand-lever operator having fixed detents that permitted discrete valve open positions to be set. This improved the overall run to run reproducibility in the rate of expansion and control during the closed formation process. The rate of expansion was monitored using Magnehelic pressure gauges.

- While the spectral response of the chamber irradiation system is similar to the solar spectrum at ground level, concern was experienced that it might not be adequate to photoze O_3 in the spectral region to yield OH concentrations sufficient for some of the proposed Phase II experiments. Therefore eight FS40 lamps were installed, mounted vertically from the chamber floor in preparation for these experiments. By not being deployed behind pyrex windows, the spectral output extended below 200 nm as shown in Figure 7. The resultant effectiveness of these lamps in the Phase II experiments is not known to the authors and is to be addressed in the data reviews by the NRL and NCAR investigators.
- During the Phase II experiments elevated concentrations of background ammonia were detected in the chamber by the NRL TDLAS system. Considered unacceptable for the intended nucleation experiments it was decided to attempt to reduce this level, initially, by spraying two of the charcoal filters with a phosphoric acid solution. This treatment appeared to be effective, which led to the decision to procure and install two commercially available Ammoniasorb II filters in the filter train assembly. Subsequent measurements indicated Ammonia concentrations below the detectable limit of the TDLAS supporting a significant decrease. The absolute levels of measured ammonia in the chamber, however, remain under investigation, at NRL, through continuing calibration and data reduction efforts.
- During the Phase I cloud processing experiments difficulty was noted in getting the dew point depression as small as had been achieved during prior programs performed in the chamber. It was suggested that this was being caused by the chamber floor being cooler than the walls and ceiling evident by puddles on the floor during humidification. To remedy this, thermocouples were installed on the floor, wall and ceiling to monitor differences, and a heater was installed in the crawl space beneath the chamber to increase the floor temperature. These actions were intended to shorten the time required to humidify the chamber and provided a nearly saturated chamber atmosphere at the start of the expansion process.

III. Phase II Deployment

A. Index of Experiments

Table I, provided by the Naval Research Laboratory, is an index of the Phase II experiments grouped by type. Table II, also provided by NRL, contains detailed information and observations pertinent to each experiment and is also presented here to serve as a cross reference for the liquid water content and hydrocarbon data presented in the next two sections.

Table I
INDEX OF EXPERIMENTS BY TYPE FOR OCTOBER AND NOVEMBER DEPLOYMENTS
TO CALSPAN CHAMBER

I. Cloud processing:

1. SO₂ oxidation by Ozone – Sulfuric acid formation in the liquid phase
2. SO₂ oxidation by Ozone in cloud droplets formed on sea salt – liquid phase conversion and chloride depletion
3. SO₂ oxidation by Ozone – with NH₃ added to reduce acidity of cloud droplet
4. SO₂ oxidation by H₂O₂ – Sulfuric acid formation in the liquid phase
5. Effect of organics on cloud microphysics

II. Nucleation of sulfuric acid aerosol starting with oxidation of SO₂

III. Nucleation in Hydrocarbon-ozone systems

- A. Alpha-pinene/ozone system
- B. Cyclopentene/ozone system
- C. Cyclohexene/ozone system

IV. DMS oxidation by NO₃

V. Heterogeneous reaction of SO₂ with sea-salt aerosol

Table II
PHASE II EXPERIMENTS

I. Cloud processing: (r_p/R_p is the ratio of the radii where the peaks in the processed mode and the cloud droplets occur, for pure SO₂-O₃ system, this ratio is predicted by theory to be about 0.009-0.013)

Date/Time	Cld#	Ozone ppb	SO ₂ ppb	H ₂ O ₂ ppb	NH ₃ ppb	Type of nuclei / comment	r_p/R_p
1. SO₂ oxidation by Ozone – Sulfuric acid formation in the liquid phase							
10/6/98(PM)	1	100	~0.4	none	?	CCN produced by sulfuric acid nucleation – before we installed phosphoric acid filters to eliminate NH ₃ . Saw strong cloud processing mode. May have been SO ₂ limited here	.006-.007
	2	90	~3-4	none	?	No additional mass increase	0.021
10/13/98(PM)	1	80	~5	none	none	CCN formed by sulfuric acid nucleation produced by SO ₂ & O ₃ , Saw cloud processing mode develop	0.010
	2	yes	yes	none	none		0.009
	3	yes	yes	none	none	LW sample	0.013
11/3/98(PM)	1	80	~2.1	none	none	CCN formed by OH oxidation of SO ₂ via CH ₂ O photolysis. Cloud processing mode developed.	.009
	2	72	~1.9	none	none	Faster expansion	.010
	3	60	~1.4	none	none	LW sample	.011
11/4/98(PM)	1	~75	~3.6	none	none	CCN formed by OH oxidation of SO ₂ via CH ₂ O photolysis. Cloud processing mode developed	.012
	2	~75	~2.7	none	none		.013
	3	~50	~2.2	none	none		.017
2. SO₂ oxidation by Ozone in cloud droplets formed on sea salt – look at chloride depletion as well as sulfate formation. Analyze filter samples for chloride depletion							
10/9/98(AM)	1	90	~3	none	none	Sigma sea-water nebulized with TSI nebulizer – saw cloud processing mode; i.e. mass conversion	0.018
	2	66	~5	none	none		.020
(PM)	3	92	~3	none	none	After filtering and nebulizing 1/10 solution of sea water – saw conversion	.016
	4	80	~5.5	none	none	LW and filter sample	.019
10/15/98(AM)	1	85	~5.5	none	none	Sigma sea-water nebulized with TSI nebulizer – saw cloud processing mode; i.e. mass conversion	.012
	2	~80	~5	none	none		.015

Table II
PHASE II EXPERIMENTS (cont.)

Date/Time	Cld#	Ozone ppb	SO ₂ ppb	H ₂ O ₂ ppb	NH ₃ ppb	Type of nuclei / comment	r _p /R _p
3. SO₂ oxidation by Ozone – with NH₃ added to reduce acidity of cloud droplet							
10/21/98(PM)	1	90	~2.4	none	none	CCN formed by OH oxidation of SO ₂ via CH ₂ O photolysis. Cloud processing mode developed.	.006
	2	67	~0.6	none	~4?		.007
	3	54	~2.5	none	?	For LW sample	.014
11/6/98(PM)	1	77	~4.0	none	none	CCN formed by OH oxidation of SO ₂ via CH ₂ O photolysis – no NH ₃ for the first cloud	.007
	2	~50	~1.6	none	10?	NH ₂ needs calibration	.020
	3	~45	~2	none	?	For LW sample	.025
11/19/98	1	~80	~2	none	none	CCN formed by sulfuric acid nucleation produced by SO ₂ & O ₃ , Saw cloud processing mode develop – no NH ₃ for first cloud	.006
	2	~70	~1	none	~4?	SO ₂ disappeared fast after NH ₃ was added – large conversion in cloud processing mode	.031
	3	~60	~?	none	?	LW sample	.035
4. SO₂ oxidation by H₂O₂ – Sulfuric acid formation in the liquid phase							
10/14/98(PM)	1	~7	yes	yes	none	CCN formed by sulfuric acid nucleation produced by SO ₂ & O ₃ , Saw cloud processing mode develop	
	2	~6	yes	yes	none		
10/20/98(PM)	1	none	~4	~3	none	CCN formed by OH oxidation of SO ₂ via CH ₂ O photolysis – large amount of conversion	
	2	none	~5	~4	none	LW sample	
11/5/98(PM)	1	none	~1.8	~6	none	CCN formed by OH oxidation of SO ₂ via CH ₂ O photolysis – large amount of conversion	
	2	none	yes	yes	none	LW sample	
11/16/98	1	none	~2.2	yes	none		
	2	none	~1.6	yes	none		
	3	none				LW sample	

Table II
PHASE II EXPERIMENTS (cont.)

Date/Time	Cld#	Ozone ppb	SO ₂ ppb	H ₂ O ₂ ppb	NH ₃ ppb	Type of nuclei / comment	r _p /R _p
5. Effect of organics on cloud microphysics							
10/8/98 (1115)	1	none	none	none	?	Generated ammonium sulfate aerosol by nebulizing solution of 7 g/liter with TSI nebulizer - but discovered leak and found it in valve	
(1700)	2	none	none	none	?	Generated ammonium sulfate aerosol by nebulizing solution of 7 g/liter with TSI nebulizer - ?U of WA sample?	
(1845) 2nd run	3	none	none	none	?	Generated ammonium sulfate and succinic acid aerosol by nebulizing solution of 3.5g/liter of (NH ₄) ₂ SO ₄ and succinic acid each with TSI nebulizer - ?U of WA sample?	
11/13/98(AM) Amm. sulfate	1	none	none	none	none	Generated ammonium sulfate aerosol by nebulizing solution of 7 g/liter with TSI nebulizer - too few CCN	
	2	none	none	none	none	Added more CCN and slowed up expansion rate	
	3	none	none	none	none	Repeat 2 on same CCN- no LW sample	
2nd run mixture	4	none	none	none	none	Nebulize solution of 3.5 g/l each of ammonium sulfate and pinonic acid	
	5	none	none	none	none	Repeat of 4 on same CCN	
	6	none	none	none	none	#6 is for LW sample	
3rd run - pinonic acid	7	none	none	none	none	Nebulize 7 g/l solution of pinonic acid	
	8	none	none	none	none	Repeat of 7 on same CCN	
	9	none	none	none	none	Repeat of 8 for LW sample	

Should Include cloud processing on organic aerosol produced in HC nucleation experiments here.

II. Nucleation of sulfuric acid aerosol starting with oxidation of SO₂ (an X in the last column indicates NRL has chosen these events to analysis - a double X indicates we also are looking at a 2nd nucleation event after particles have grown in. These events are particularly interesting because we can calculate growth rates of existing particles during a nucleation event.)

Table II
PHASE II EXPERIMENTS (cont.)

Date/time	Ozone ppb	SO ₂ ppb	CN max 3025/3022	T(C)/ RH%	Method of SO ₂ oxidation/Comments/Evaluation	
10/6/98-1022	180	defunct	os/180K	24/33	Added ozone to chamber - SO ₂ instrument defunct - Canadian instrument didn't arrive until afternoon - not yet added NH ₃ filter	
10/12/98	100	see comment		23/50	Added SO ₂ in small steps 1,2,4,5 ppb, with SF-40 lamps on - Had installed phosphoric acid filters to remove NH ₃	
10/13/98-0920	145	10	os/125K	24/35 24/84	Added humidity after 3025 was OS - also turned on NRL uv lamps and FS-40 lamps	
10/17/98-0850	various	~5	81K/47K os/207K	24/36	2 methyl-2 butene was added at 1033- this produced a second nucleation event which drove 3025 off scale	
10/17/98-1400	98	0	38K/9.4K		Here we added 30 ppb of 2M-2B We got particle formation with only ozone and 2M-2B - concluded that 2M-2B is not good way to get OH	
10/17/98 - 1620	0	22	os/130	25/50	Here we turned on big chamber lights and photolyzed background aldehydes to get OH from HO ₂ and background NO - later added NO which gave trailing nucleation mode	
10/20/98 0927-1012 2nd event 1024	0	100	os/200	25/12	Here we added CH ₂ O (~26ppb) and photolyzed it with main chamber lights using background NO of about 1ppb also added SO ₂ to get trailing mode	XX
10/21/98 0927-1026 2n event 1026	0	100	os/152	25/45	Here we repeated the previous experiment with CH ₂ O (~22 ppb) but reduced the illumination by using only the VHO lamps in 8 banks to reduce illumination to about 1/6	XX
11/3/98 1107-1205	0	80	os/104K	24/51	Here we again repeated the CH ₂ O experiment with only four banks of the VHO lamps and about 15 ppb of CH ₂ O	X
11/4/98-0944	0	35	1000/130	23/48	Here we further reduced concentrations and used only 2 banks of VHO lamps and 13 ppb CH ₂ O - got very small nucleation event which we increased increasing light intensity and reactants until 3025 went off-scale.	X
11/5/98 0917-0951	0	70	67K/17K	24/43	Here we used ~10 ppb of CH ₂ O and 4 banks of VHO lamps. The nucleation event stayed on scale even with the 3025, but it took 30 minutes to reach the max concentration - then increased illumination and reactants and got trailing mode.	X
11/6/98 1007-1045	0	90	os/65K	25/30	This was very good event. 4 banks of VHO lamps - ~20 ppb of CH ₂ O - 1.2 ppb of NO. The max increase in 3025 was reached before it went off scale in about 15 minutes after lights were turned on - started to see particles in DMA after about 20 minutes. Induced trailing mode by adding SO ₂ . This was first day when we keep NO and humidity low by running dehumidifier until chamber was sealed.	X
11/16/98 1109-1159 2nt event 1159	0	70	94K/40K	20/77	Tried to repeat last run but at higher humidity. CH ₂ O~20 ppb, 4 banks of VHO lamps, NO~1.2 ppb. Saw on DMA after about 30 min. Increased reactants and illumination to grow them in and produced trailing mode.	XX
11/19/98 0845-0953 2nd event 0954	150	9.5	os/110K	25/28	This event happened when we looked at reactivity of chamber with new charcoal filters of ozone and SO ₂ . Dark reaction. Produced trailing mode by adding 5 ppb of SO ₂ - good data - look at growth at time trailing mode is nucleated and infer H ₂ SO ₄ concentration.	XX

Table II
PHASE II EXPERIMENTS (cont.)

III. Nucleation in Hydrocarbon-ozone systems

A. Alpha-pinene/ozone system (NRL is analyzing all but 5/19/98)

Date/time	Ozone ppb	α -pinene ppb	CN max 3025/3022	T(C)/ RH%	SO ₂ ppb	NH ₃ ppb	[O ₃] x [a-pin.]	Comment
5/19/98	100	12	os/200K	/34	?	?	1,200	I suspect we had some SO ₂ coming in through leaks as make-up air. Also we know we had some NH ₃ which was not filtered out but later showed NH ₃ probably did not effect result
10/19/98 1048-1120	115	20	54K/43K	26/48	none	none	2,300	This was after we eliminated NH ₃
11/9/98 0938-1020	95	16	20K/14K	25/29	none	none	1,520	
11/10/98 0920-0955	100	15	31K/25K	25/29	none	abt8?	1,500	Added NH ₃ to see if that would give us 5/19 result - it didn't but 5/19 result may have been due to trace amounts of SO ₂ . NH ₃ needs to be calibrated to see if it was 8 or less than 8.
The following three runs are with decreasing SO ₂ added to the alpha-pinene / ozone system								
11/11/98 0948-1015	100	15	os/380K	25/47	6	none	1,500	
11/12/98 1330-1350	110	15	os/187K	24/43	2.5	none	1,650	This run complicated by residual larger particles which we did not take time to completely filter out - these also grew
11/18/98 1238-1320	110	15	79K/73K	25/30	0.5	none	1,650	Wanted to add trace amounts of SO ₂ to see effect!
The following experiment shows that when pre-existing particles are present the products condense on the existing particles								
11/12/98 0950-1020	110	15		24/49	none	none	1,650	We generated particles by nebulization 11K/9K (3025/3022) prior to introducing reactants. No new particles were formed but existing particles grew.

Table II
PHASE II EXPERIMENTS (cont.)

B. Cyclopentene/ozone system

Date/time	Ozone ppb	Cyclo- pentene ppb	CN max 3025/3022	T(C)/ RH %	SO ₂ ppb	NH ₃ ppb	Comment
5/14/98	100	50	57K/42K	23/35	?	?	In May we may have had trace amounts of SO ₂ and NH ₃
10/10/98 (PM)	100	50	24K/18K	27/66	?	none	Check data there may have been trace of SO ₂ in chamber - For this experiment we mistakenly added ozone first
11/10/98 (PM)	100	50	2800/2400	26/29	yes	none	Injected NH ₃ to see if that increased nucleation - did not - NH ₃ needs to be calibrated
11/14/98	90	50	14K/9.4K	23/64	no	none	Made this run at higher humidity to see if we got same as on 10/10/98
For the following run we purposely added 1 ppb of SO ₂							
11/14/98 (PM)	100	50	os/120K	24/67	1	none	SO ₂ has a huge effect - note also higher humidity

C. Cyclohexene/ozone system

Date/time	Ozone ppb	Cyclo- hexene ppb	CN max 3025/3022	T(C)/ RH %	SO ₂ ppb	NH ₃ ppb	Comment
5/13/98	100	50	os/100K	25/33	?	?	There may have been some background SO ₂ and NH ₃ in the chamber
10/16/98	135	30	2000/1900	25/43	none	none	Very weak nucleation event over long period
11/10/98	170	29	300/255	25/31	none	yes	We added NH ₃ thinking it was responsible for May result - it was not - need to calibrate NH ₃
Now tried adding 2.5 ppb of SO ₂							
11/18/98	165	30	77K/69K	25/29	2.5	none	Here saw large nucleation event

Table II
PHASE II EXPERIMENTS (cont.)

IV. DMS oxidation by NO₃

Dates:

7 November. We started by trying OH oxidation by photolyzing CH₂O and after adding large concentration of reactants we produced ultra fine particles (25K/9.7K) which had not grown into DMA size. We then added NO₂ (50 ppb) to 60 ppb of DMS with residual ozone of 160 ppb and observed what looked like a large nucleation and growth event (OS/100K). However many of the particles may have been formed in first part of experiment - which was probably sulfuric acid nucleation and then grew with other (probably MSA) products. We saw a little (0.3 ppb) of SO₂ during first part of experiment but much larger yield during the second part of the experiment where the concentration reached about 5 ppb by end of the experiment - at which point there was probably balance with wall loss.

17 November. On this day we made two runs. In the first experiment we put the NO₂ in first and did photolysis of NO₂ to characterize the lights.

Run #1: Added 32 ppb of NO₂, 50 ppb of DMS, and 110 ppb of ozone, Temperature and RH were 25 C and 39%.

Result: Particle formation and growth was much smaller than on 7 May (max concentration of 57K/45K) and it took 30 minutes to see them on the DMA.

Run #2: Since the result of run #1 was so different than 7 November, we decided to run with concentrations more like those of 7 November.

DMS=60 ppb, NO₂=50 ppb, RH=60%, Ozone=220 ppb.

Result: Particle concentration maxed out at 83K/73K and they appeared in DMA after about 20 minutes. The particles grew much faster than H₂SO₄ particles would have for the same concentration formed.

V. Heterogeneous reaction of SO₂ with sea-salt aerosol.

Thursday, 10/22/98 . These experiment basically repeat the heterogeneous experiments carried out during the Characterization Experiments with sea water, and described in the Characterization Report, pp. 61-64 but with the addition of single particle analysis and filter samples which hopefully will identify any chemical reactions which have taken place in the sea salt particle. The predictions found in the literature is that in the case of sea-water the high pH causes the O₃ - SO₂ reaction to proceed rapidly converting enough SO₂ (by O₃) to use up the alkalinity before the reaction terminates. The first run is with NaCl solution (no buffering) whereas the following three runs are with two types of sea water: real sea water from Sigma which has been filtered and sterilized, and raw sea water taken off the Delaware coast. With real sea-water we saw the rapid decrease of SO₂, whereas with NaCl no measurable uptake of SO₂. We saw no uptake of O₃. In light of all the hype in the recent literature about the importance of O₃, I think this simple and straight forward result has the potential to make an easy and significant contribution. If the aerosol samples show that the SO₂ was converted to S(VI) which I would expect (since O₃ was not used up), then someone needs to look at sea water and see what is responsible for the conversion of SO₂ {S(IV)} to S(VI). The point here is not that the alkalinity may be able to account for the uptake of SO₂, but that no O₃ is reacted

IV. IR Transmissometer - Liquid Water Content Measurements

Measurements of Liquid Water Content (LWC) during the phase I experiments were made using the Calspan developed IR Transmissometer System.

A. Instrument Description

Path length = 18.3 meters (folded path)

Source = 1000 ° C Blackbody

Detector = HgCdTe

Optical filter = 11 micron narrow band pass filter,
CWL = 10.939 μm , HBW = 0.655 μm

Chamber windows = Kodak Irtran (zinc sulfide), 75% transmittance, 1.25 and 3 in dia.

Mirrors = Two 6 inch diameter gold coated collimating spherical mirrors
Four flat gold coated turning mirrors.

B. Calculation of Liquid Water Content (LWC)

The relation between liquid water content and IR extinction coefficient is developed in a paper by Chylek (1978). This relationship is:

$$\text{LWC} = \frac{\beta}{C}$$

LWC = Liquid water content (g/m^3)

β = extinction coefficient (km^{-1})

C = Constant (= 128 for 11 μm extinction)

This linear relationship holds for IR extinction at 11 μm wavelength and for fog drop size distribution with maximum drop radii of 14 μm .

From Beer's Law,

$$\delta \tau = \frac{\ln(\frac{I_o}{I})}{0.0183} \quad .0183 = \text{Path length of IR transmissometer in km.}$$

Substituting

$$\text{LWC} = \frac{\ln(\frac{I_o}{I})}{2.34}$$

I_o = clear chamber IR signal

I = IR signal in cloud

C. Liquid Water Content Data

Figures 10 through 69 are plots of liquid water content for all of the cloud cycle experiment data obtained by CUBRC during the Phase II experiments. These data are presented chronologically starting with the data obtained on 10/9/98. No data was obtained for the two cloud cycle experiments on 10/6/98 due to instrument difficulties. Note that there are LWC data contained in this data set that are not listed in the index of experiments provided by NRL. The IR transmissometer data were also recorded (in parallel) by NRL during the Phase II experiments and LWC was computed in the same manner as outlined here. These results are also contained in the archived NRL data set.

Liquid Water Oct 9 1998 Cloud 1

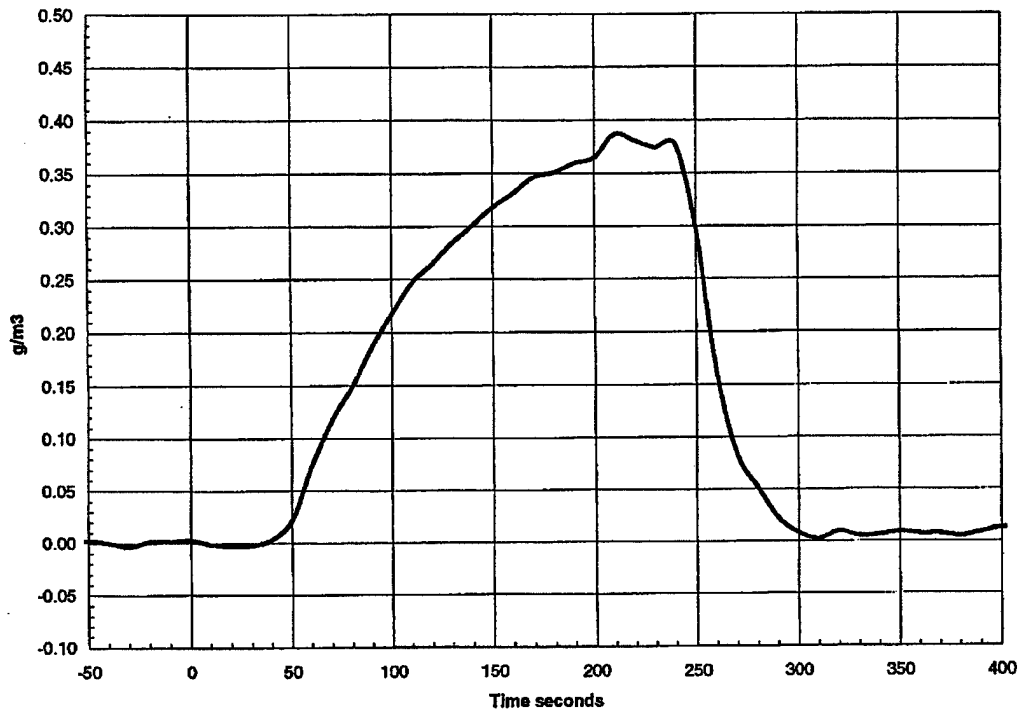


Figure 10

Liquid Water Oct 9 1998 Cloud 2

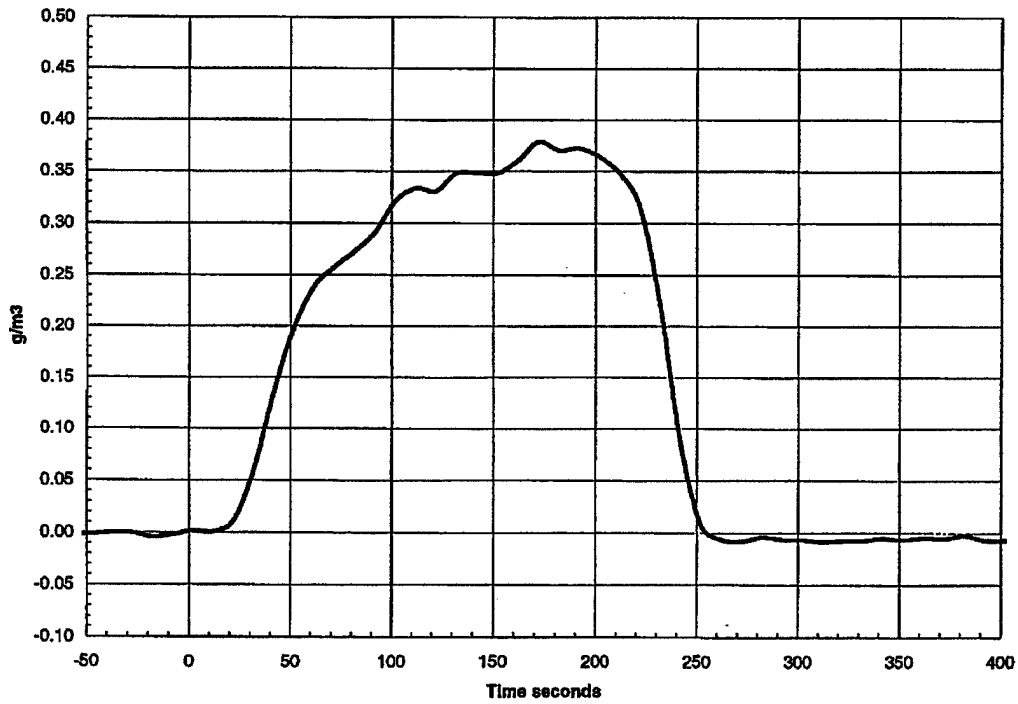


Figure 11

Liquid Water Oct 8 Cloud 3

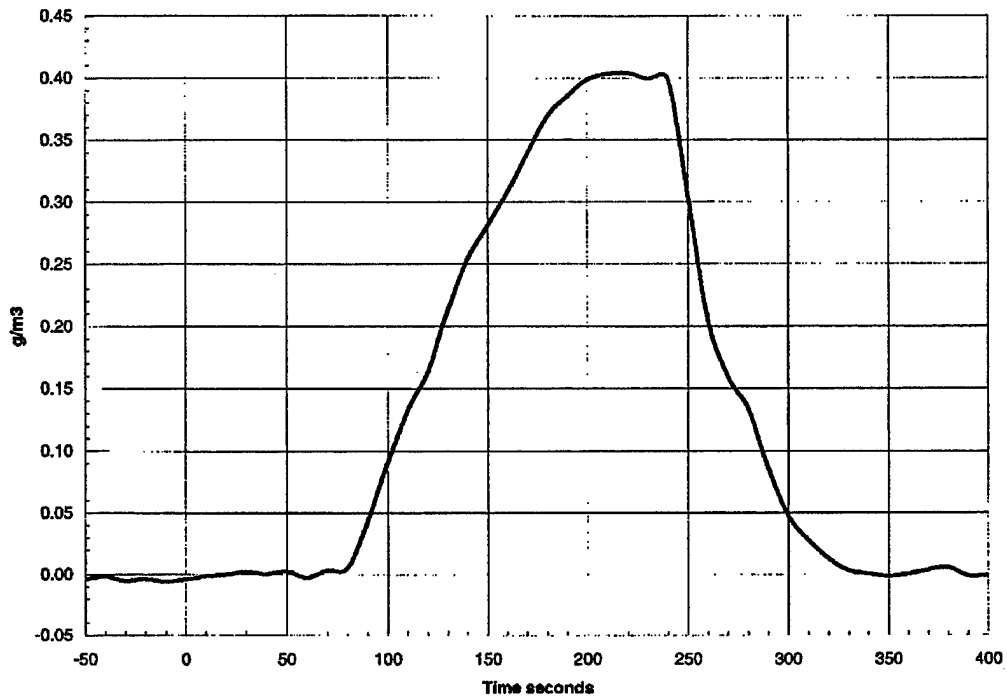


Figure 12

Liquid Water Oct 9 1998 Cloud 1

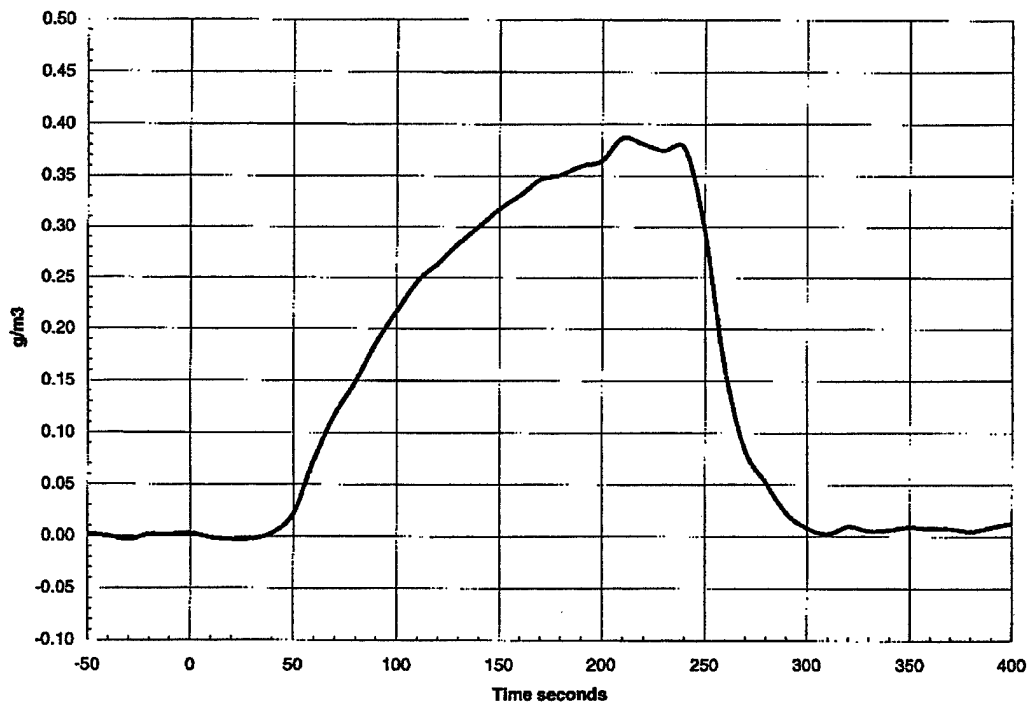


Figure 13

Liquid Water Oct 9 1998 Cloud 2

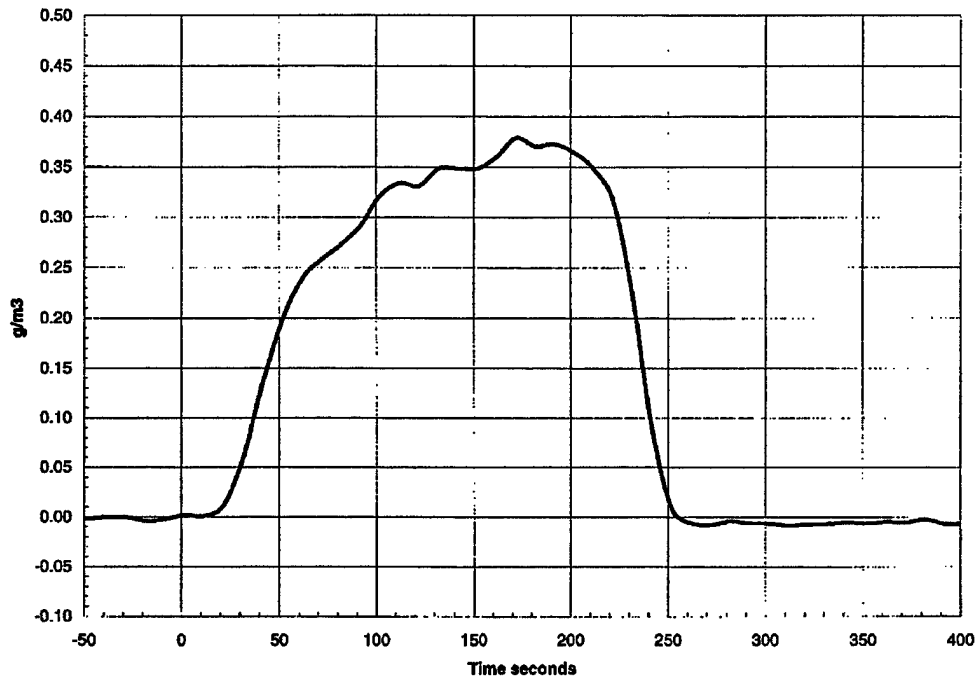


Figure 14

Liquid Water Oct 9 1998 Cloud 4

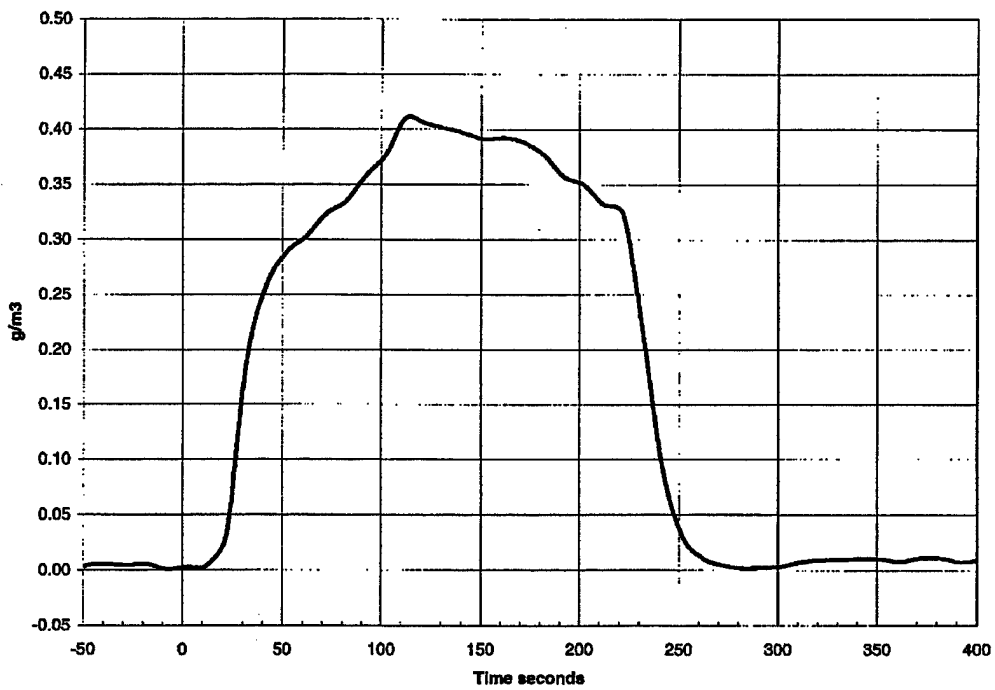


Figure 15

Liquid Water Oct 9 1998 Cloud 3

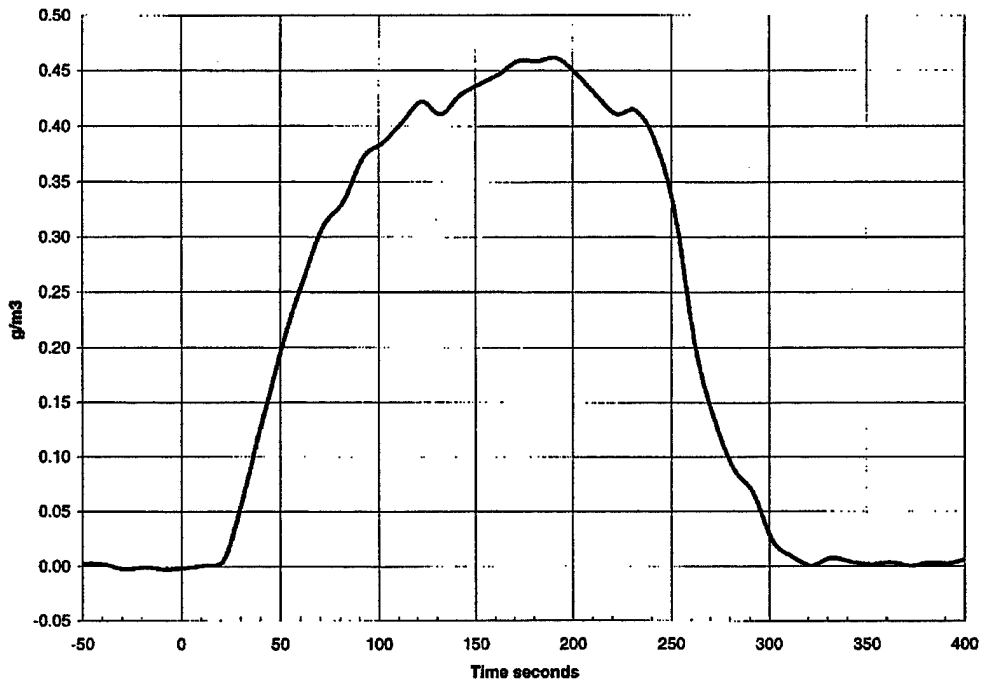


Figure 16

Liquid Water Oct 13 1998 Cloud 1

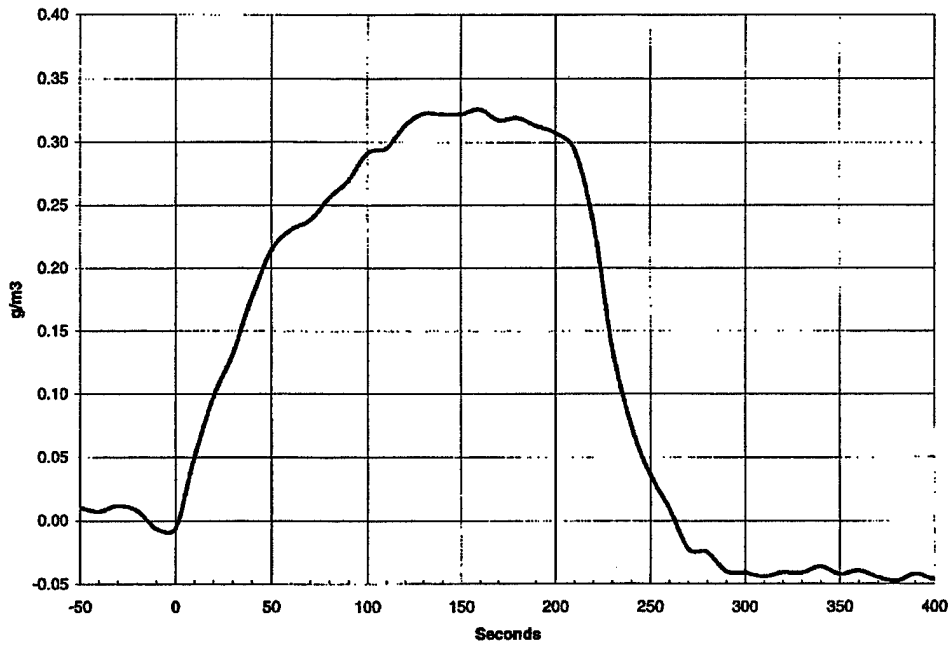


Figure 17

Liquid Water Oct 13 1998 Cloud 2

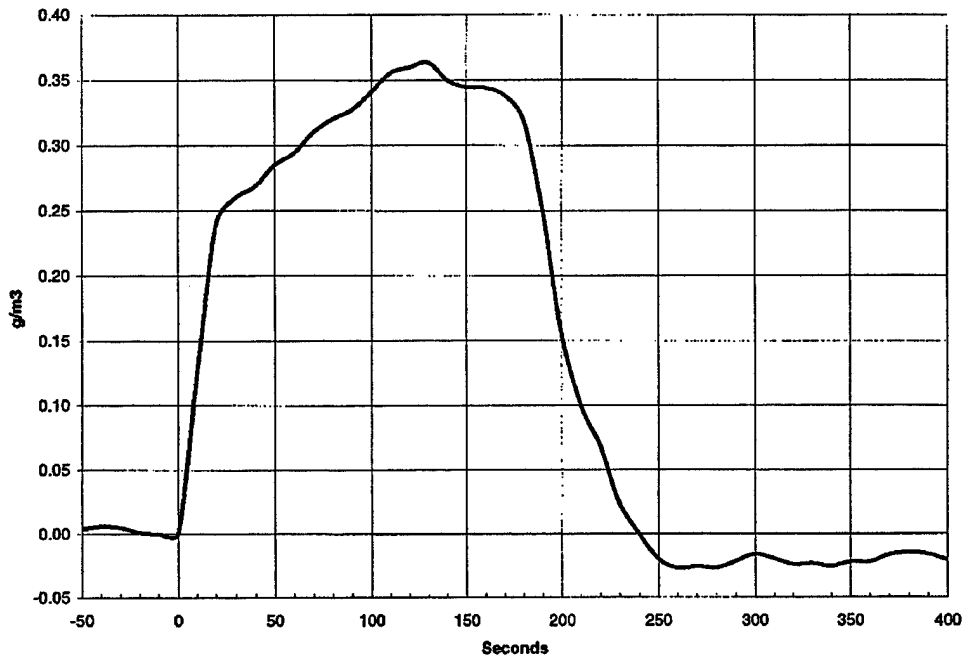


Figure 18

Liquid Water Oct 13 1998 Cloud 3

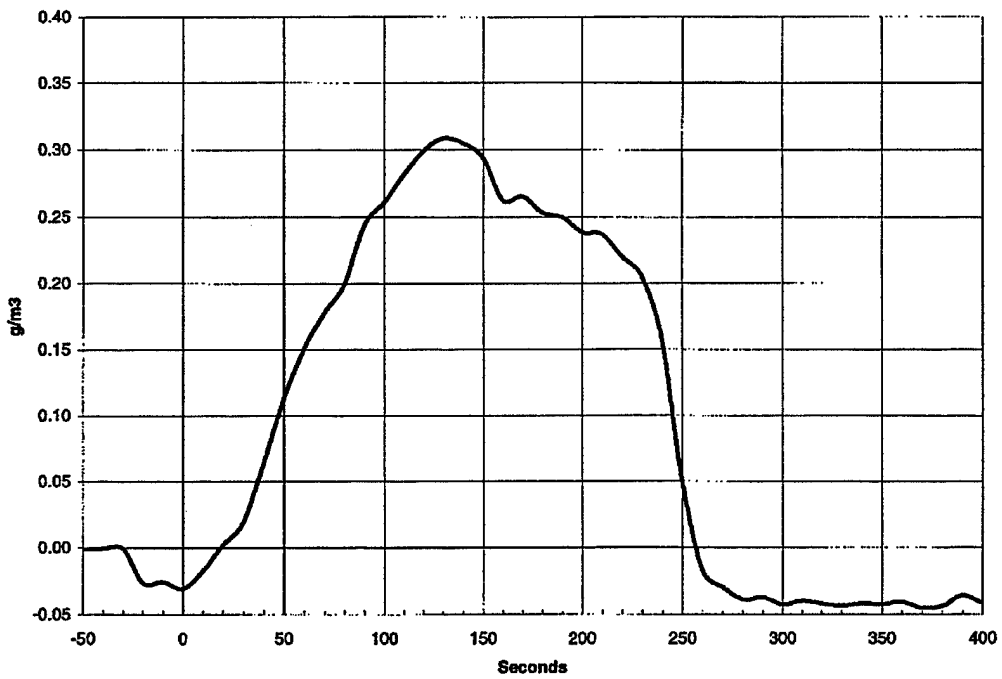


Figure 19

Liquid Water Oct 14 1998 Cloud 1

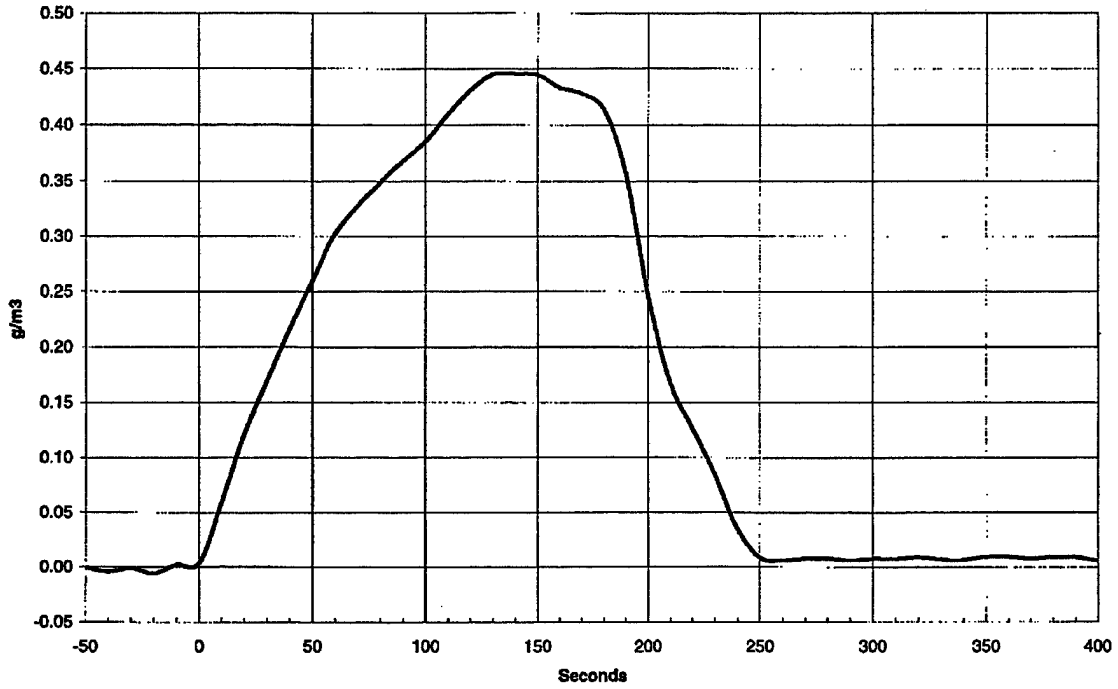


Figure 20

Liquid Water Oct 14 1998 Cloud 2

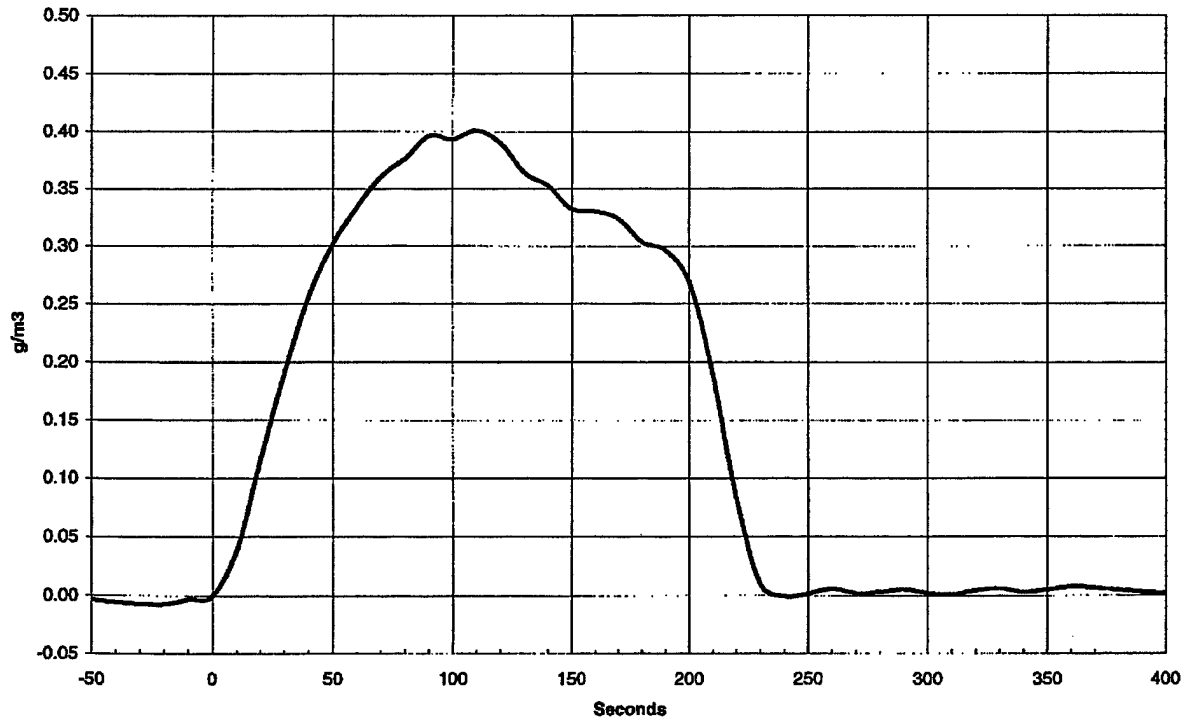


Figure 21

Liquid Water Content g/m3
Oct 15 1998 Cloud 1

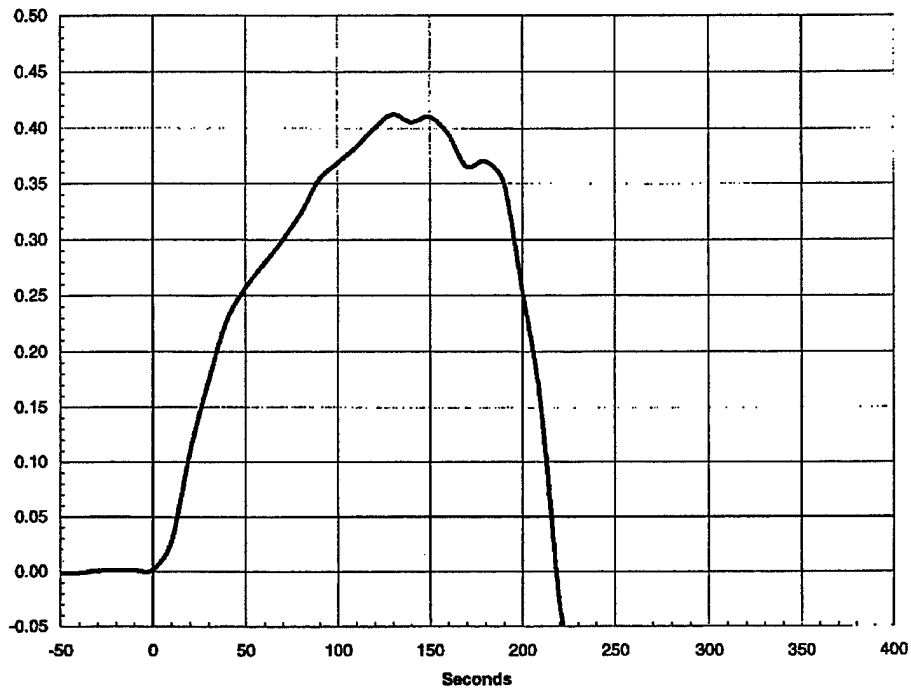


Figure 22

Liquid Water Content g/m3
Oct 15 1998 Cloud 2

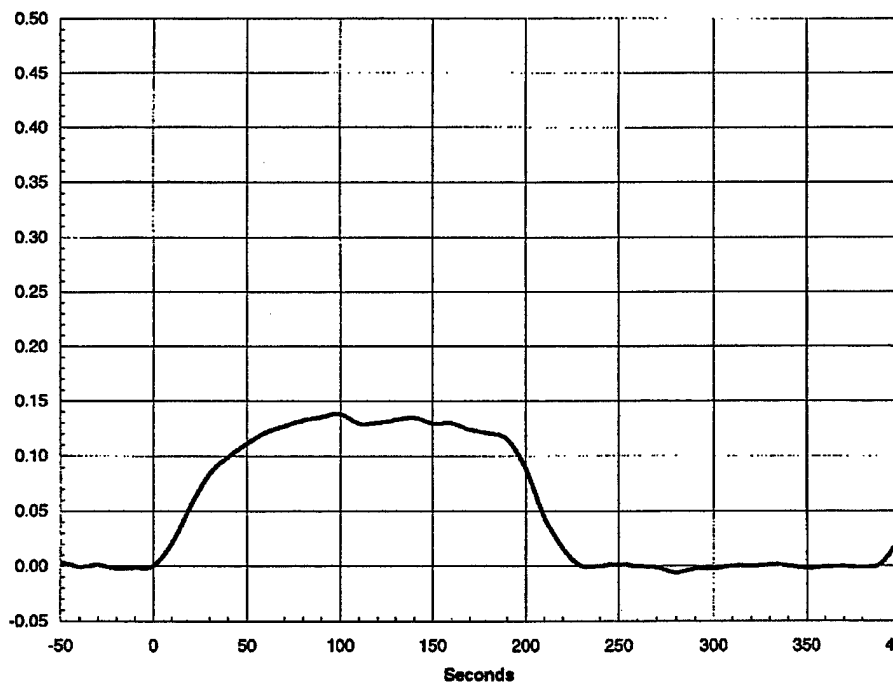


Figure 23

Liquid Water Content g/m3
Oct 15 1998 Cloud 3

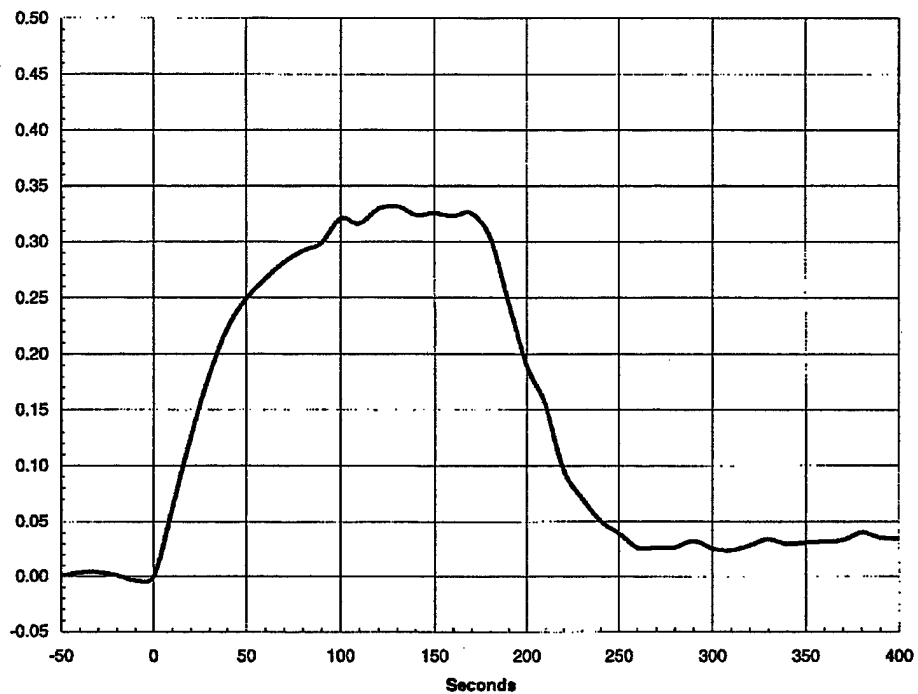


Figure 24

Liquid Water Content g/m3
Oct 15 1998 Cloud 4

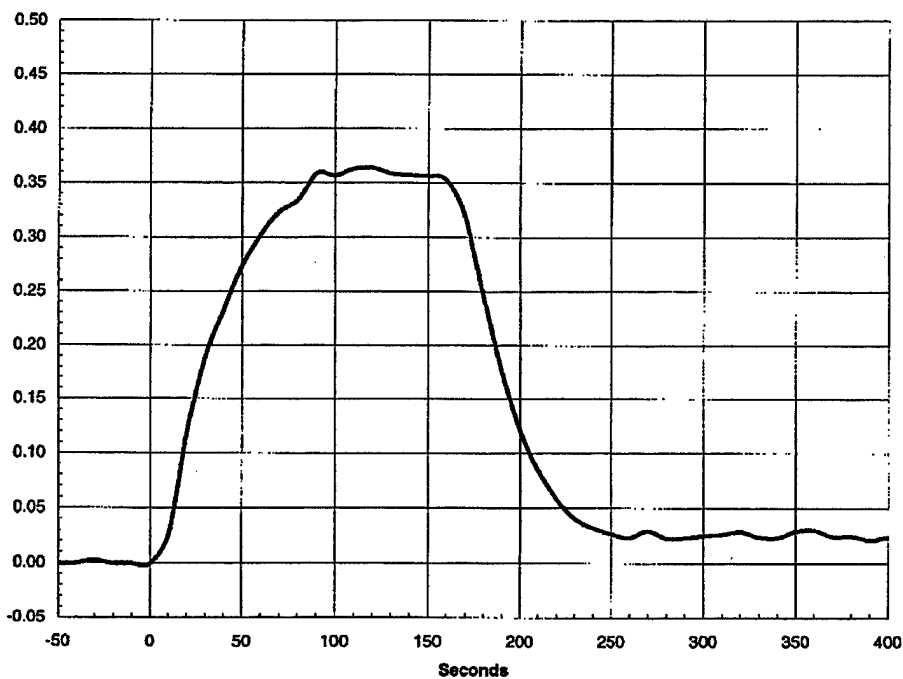


Figure 25

Liquid Water Content g/m3
Oct 15 1998 Cloud 5

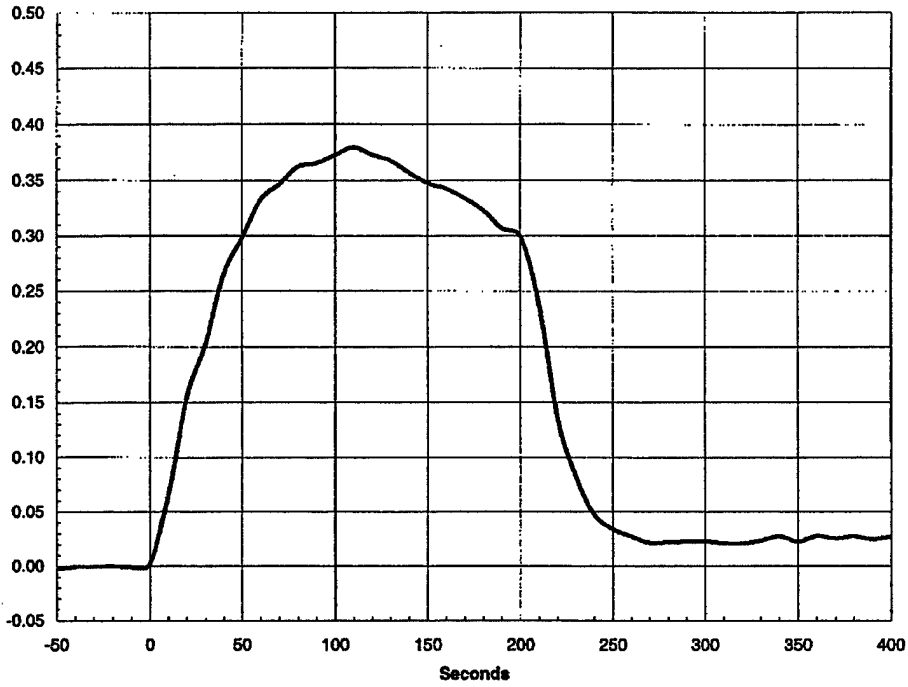


Figure 26

Liquid Water Content g/m3
Oct 15 1998 Cloud 6

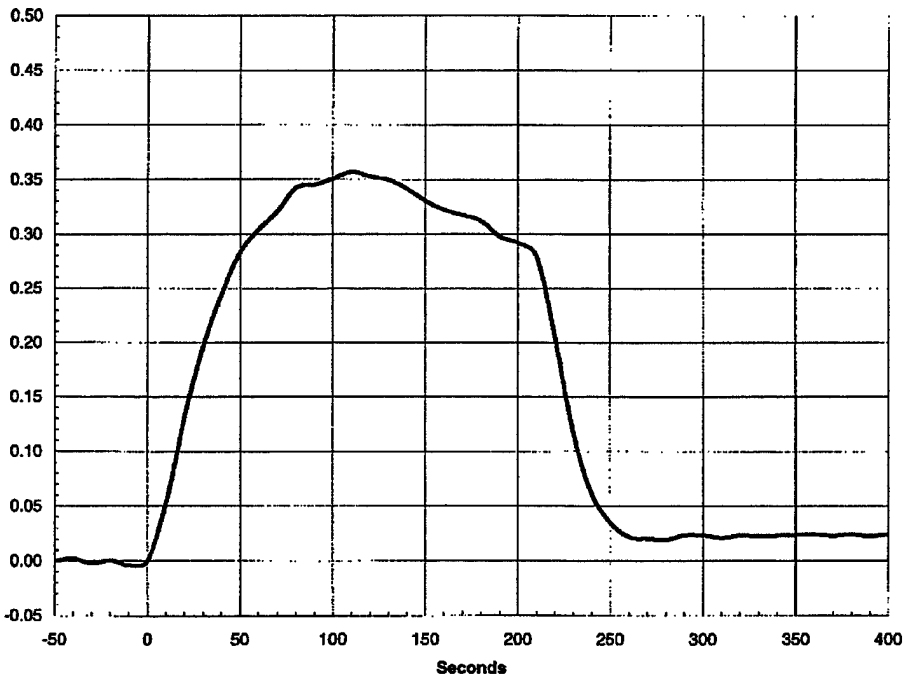


Figure 27

Liquid Water
Oct 16 Cloud 1

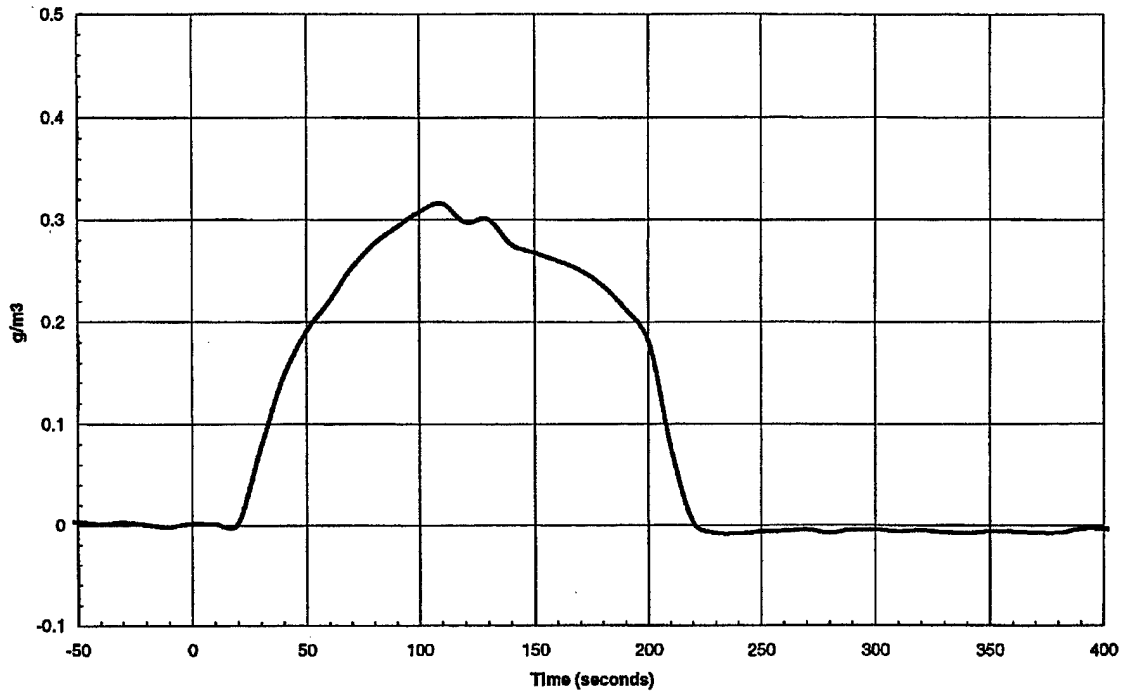


Figure 28

Liquid Water
Oct 16 Cloud 2

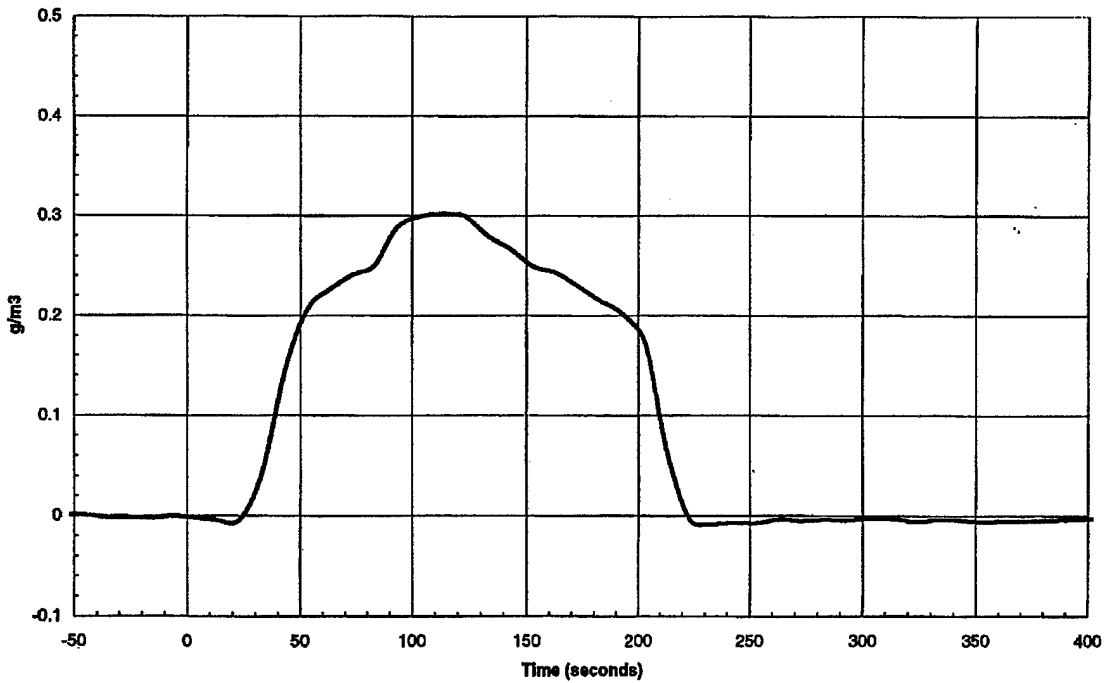


Figure 29

Liquid Water Content
Oct 21 1998 Cloud 1

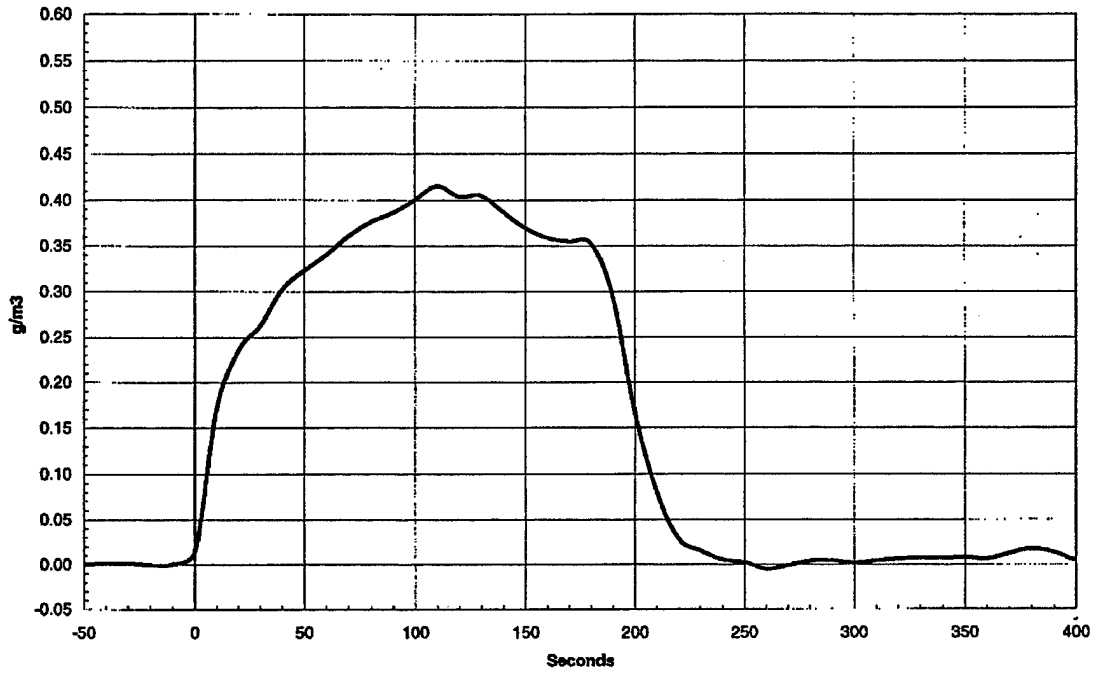


Figure 30

Liquid Water Content
Oct 21 1998 Cloud 2

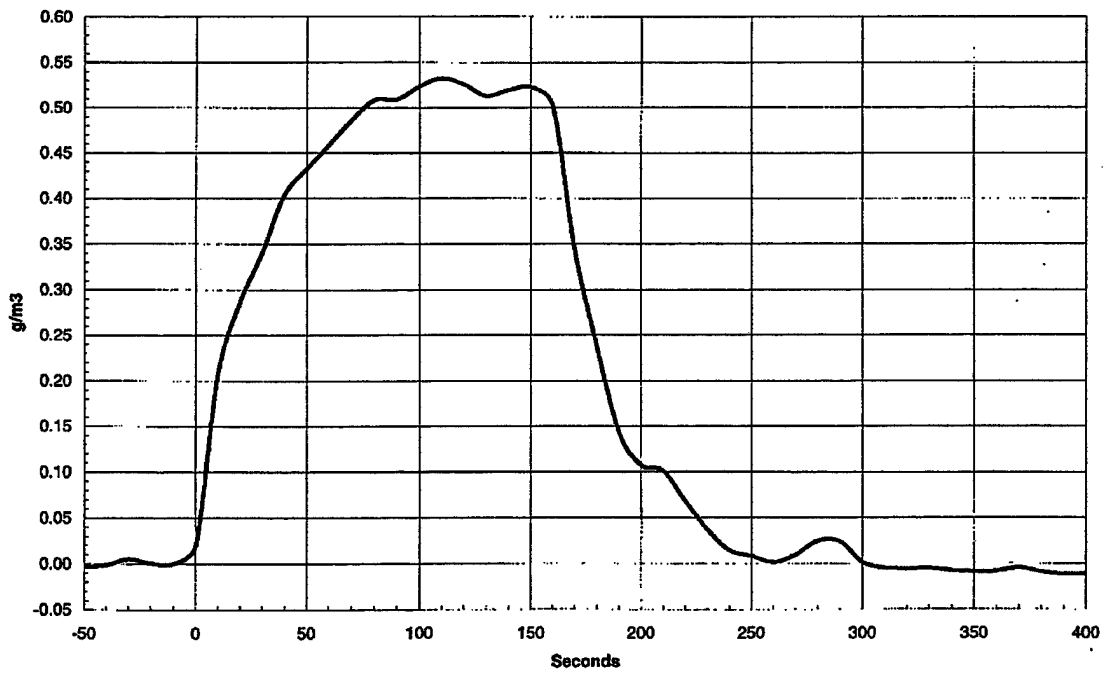


Figure 31

Liquid Water Content
Oct 21 1998 Cloud 3

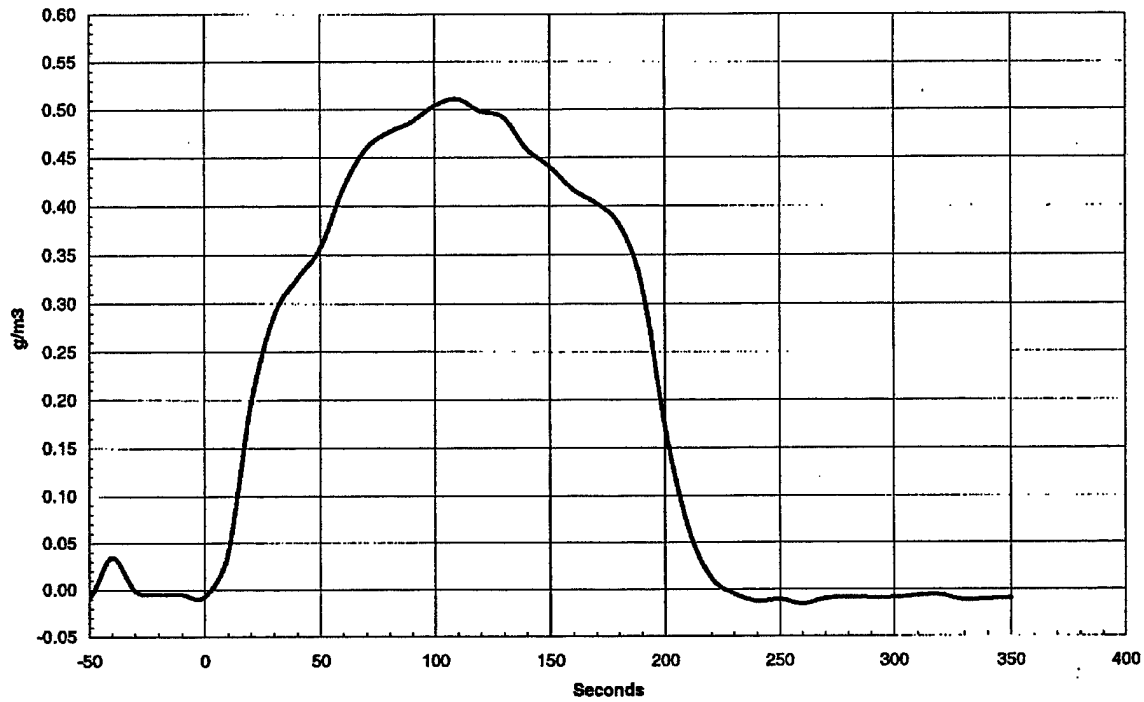


Figure 32

Liquid Water Content
Oct 19 1998 Cloud 1

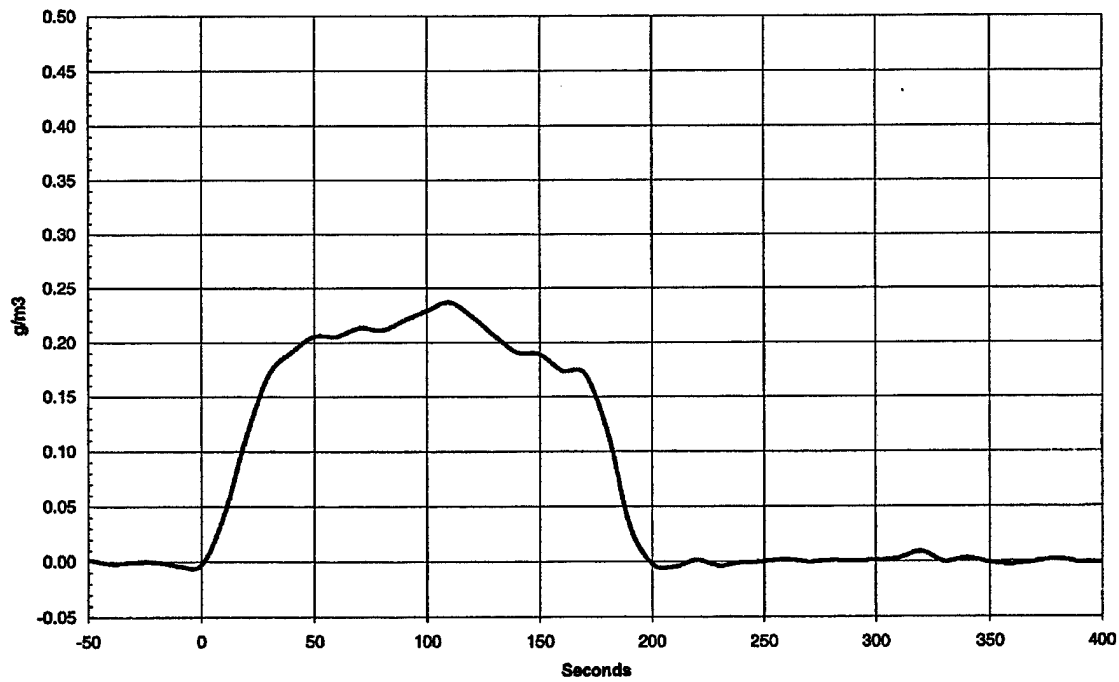


Figure 33

Liquid Water Content
Oct 19 1998 Cloud 2

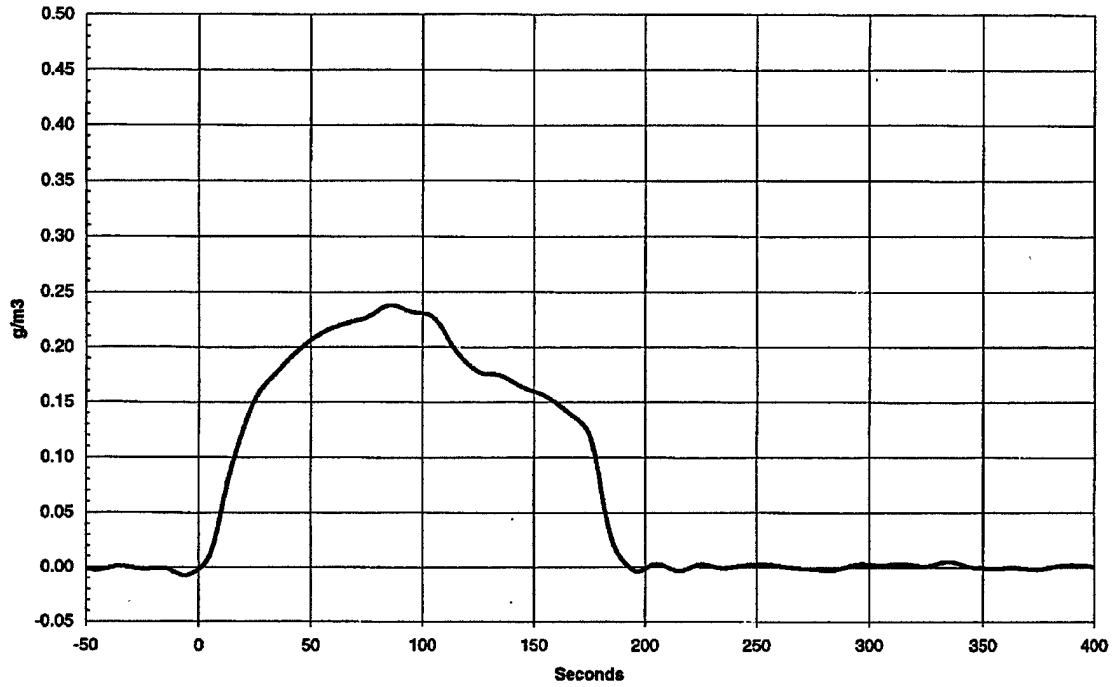


Figure 34

Liquid Water Content
Oct 19 1998 Cloud 3

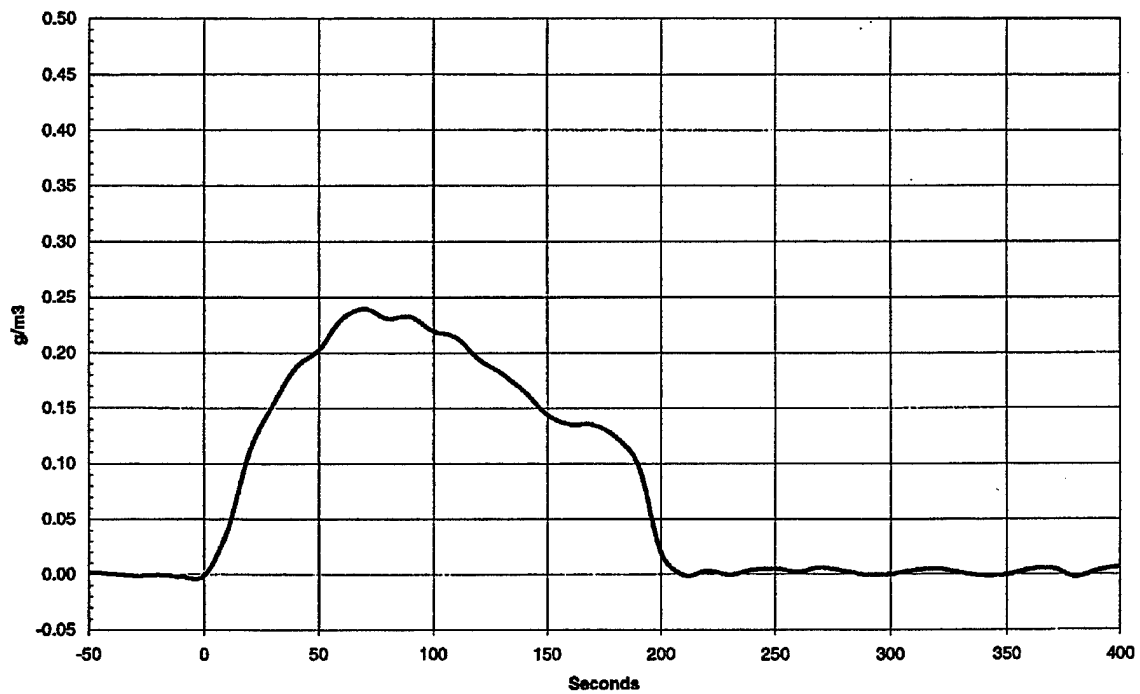


Figure 35

Liquid Water Content
Oct 20 1998 Cloud 1

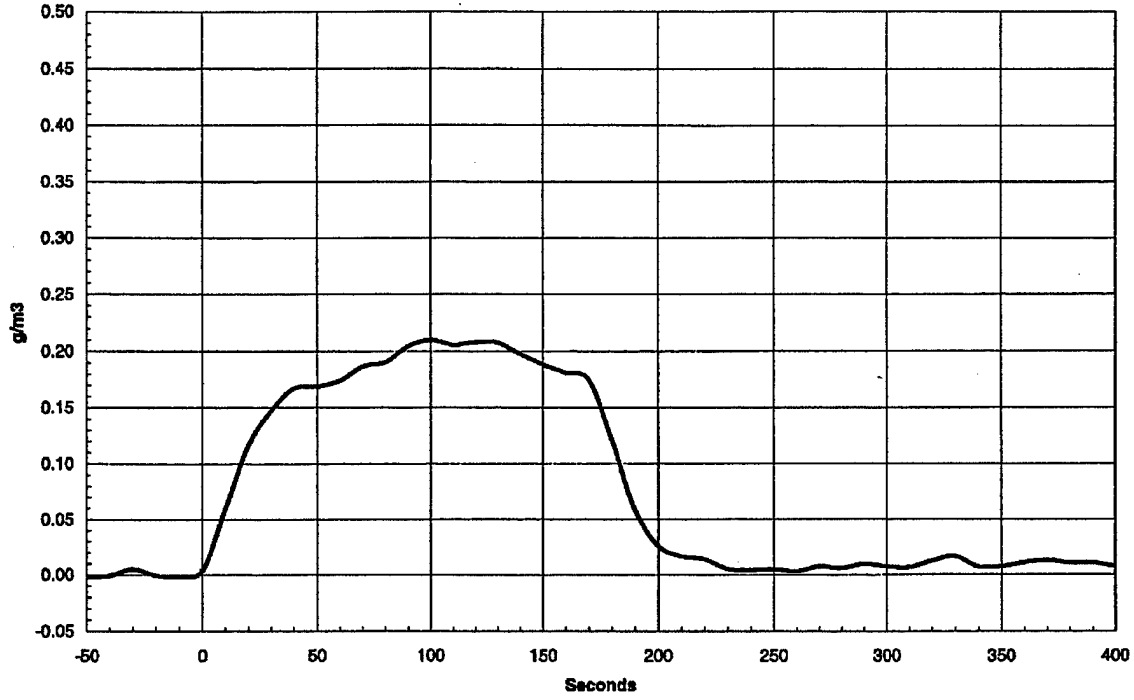


Figure 36

Liquid Water Content
Oct 20 1998 Cloud 2

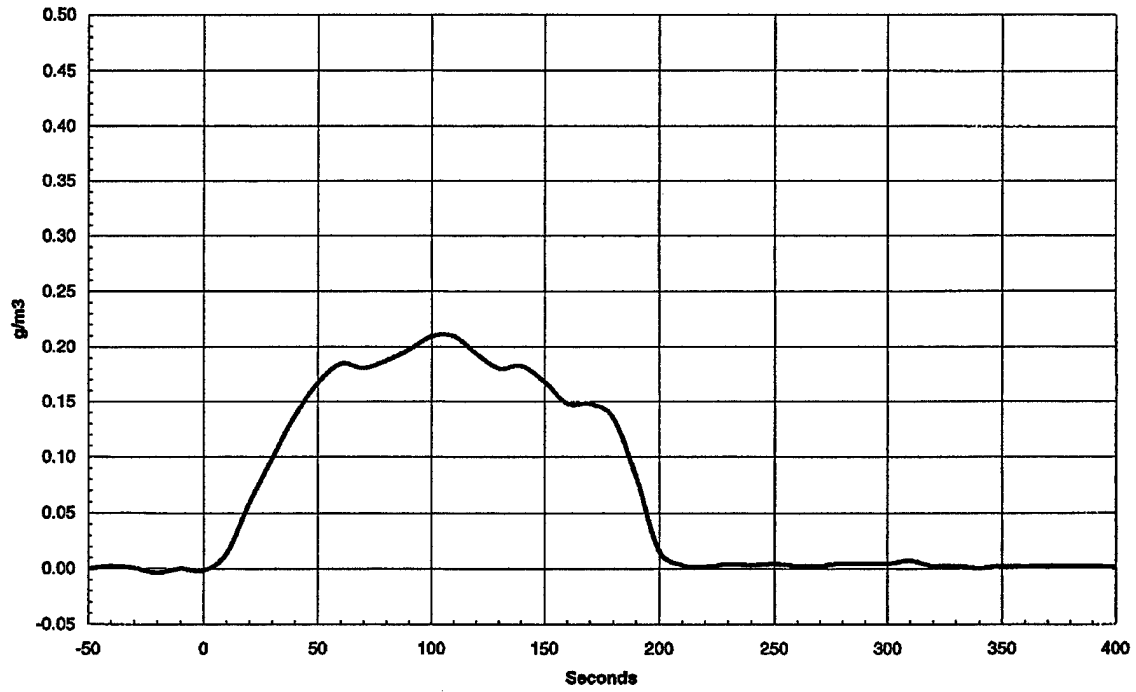


Figure 37

Liquid Water Nov 3 1998
Cloud 1

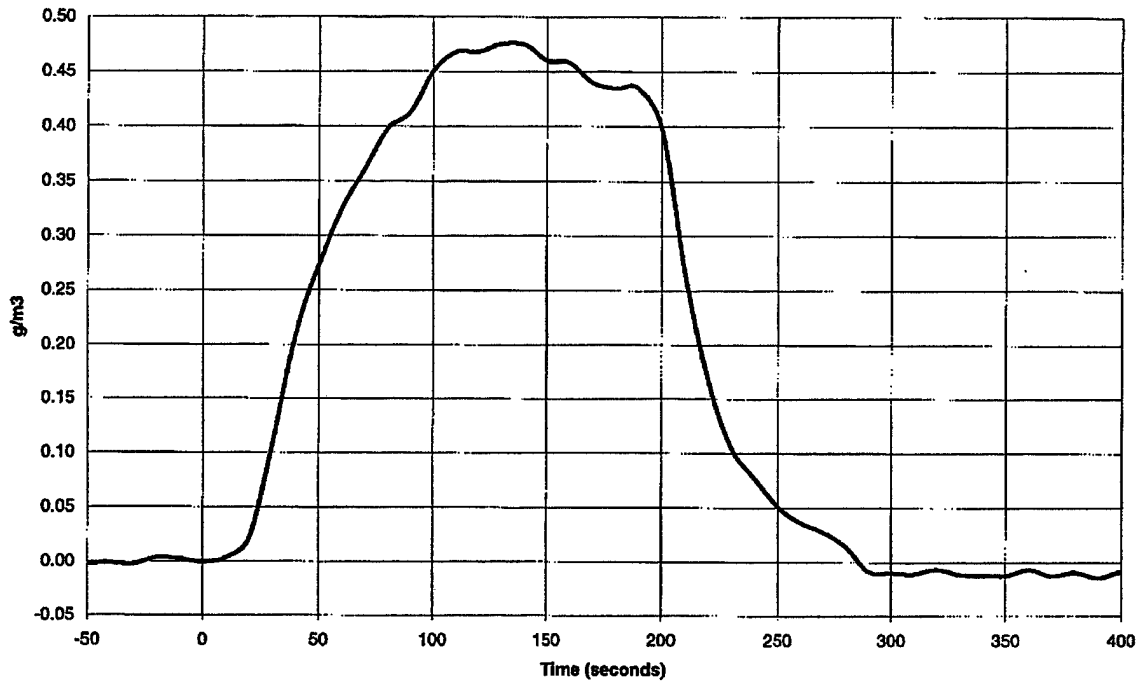
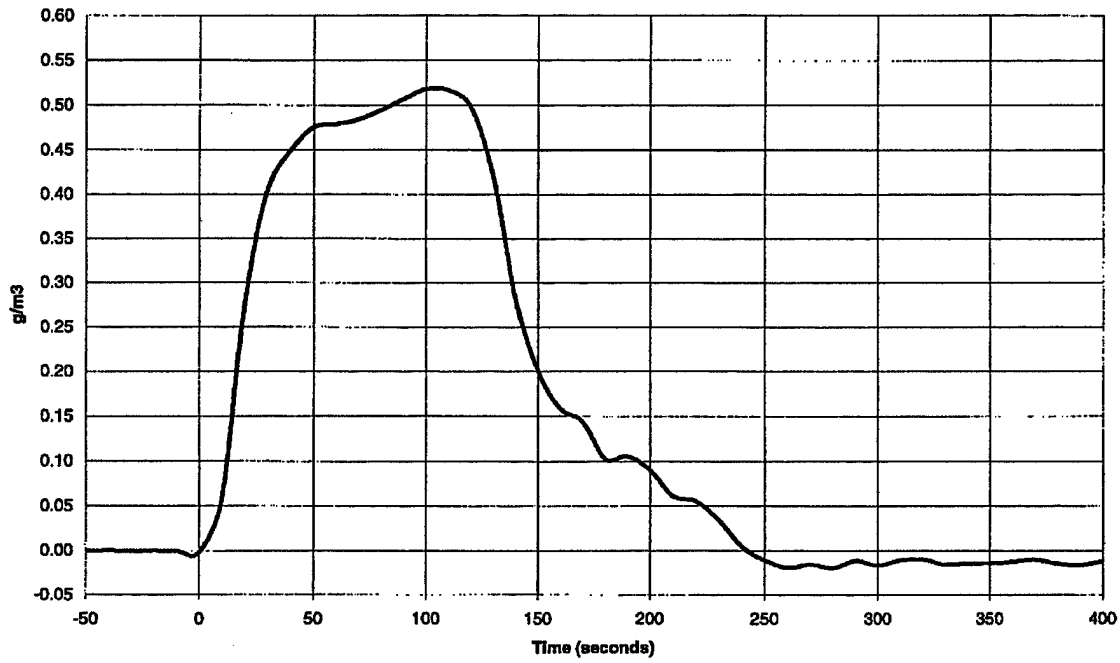


Figure 38

Liquid Water Nov 3 1998
Cloud 2



Figure

39

Liquid Water Nov 3 1998
Cloud 3

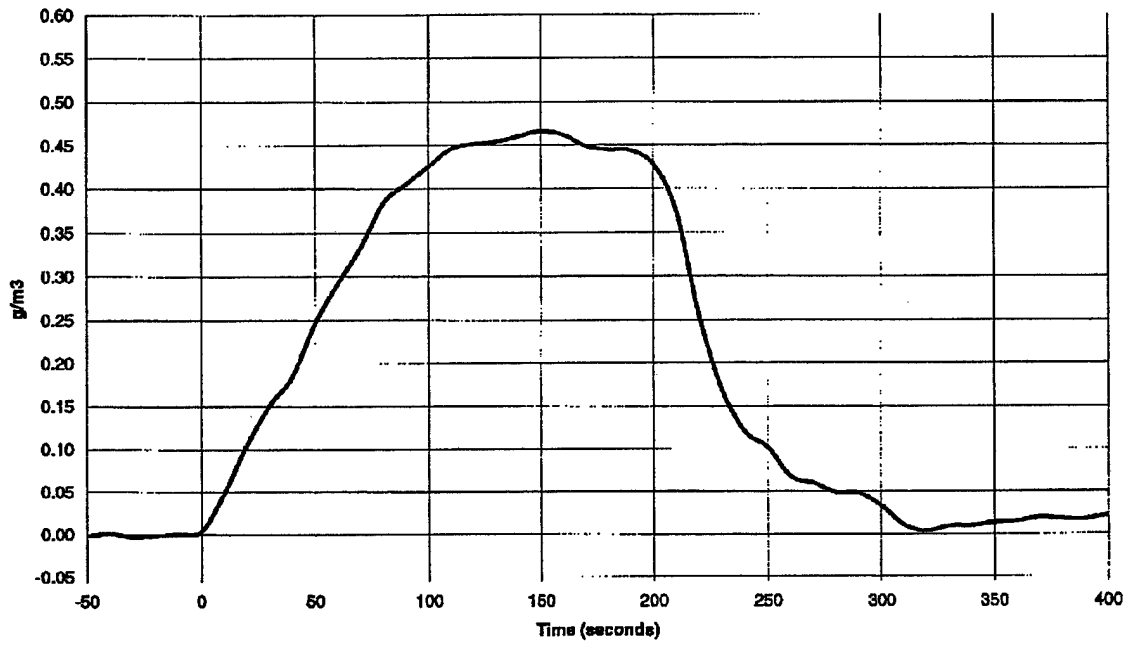


Figure 40

Liquid Water Content
Nov 4 1998 Cloud 1

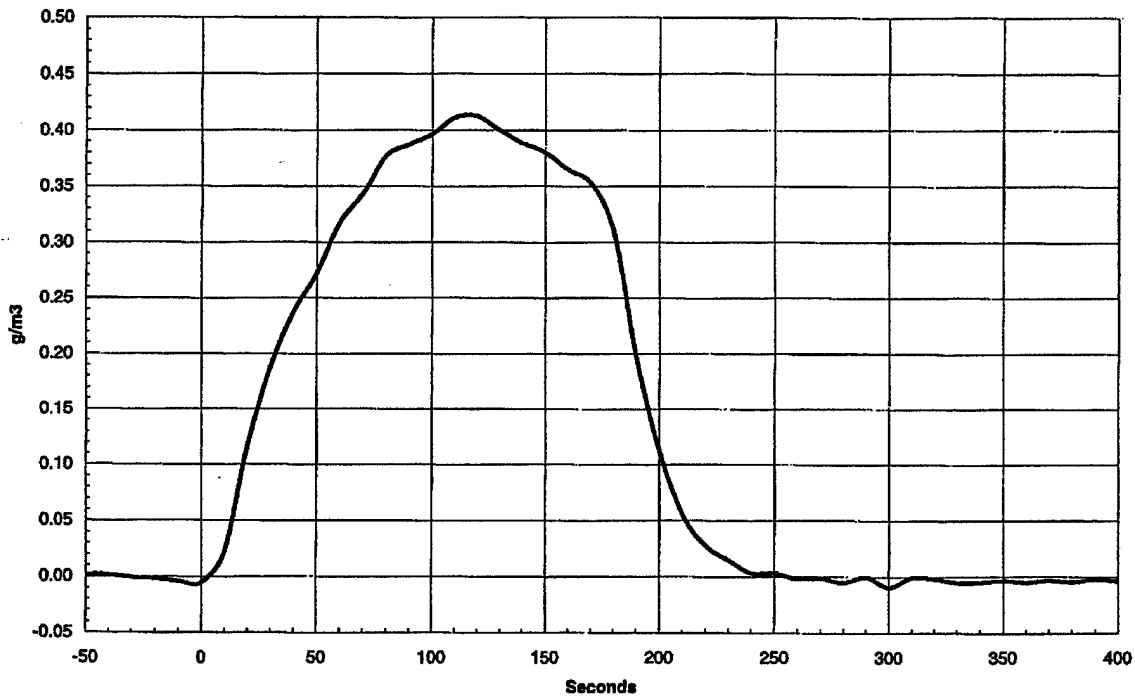


Figure 41

Liquid Water Content
Nov 4 1998 Cloud 2

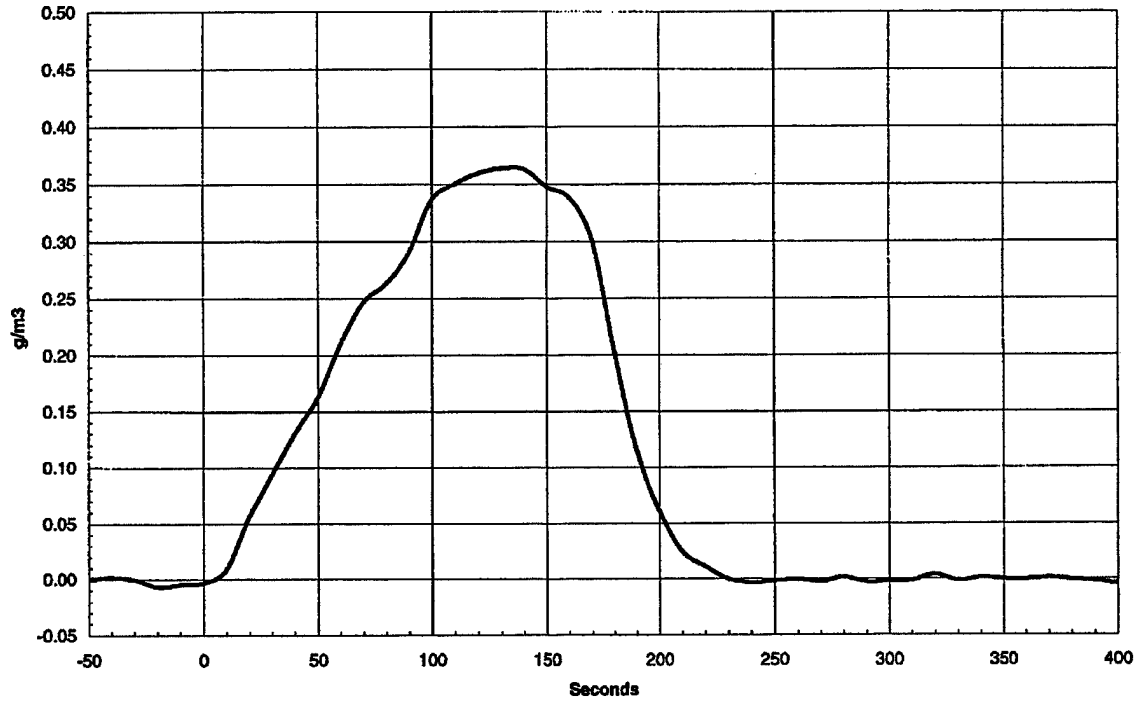


Figure 42

Liquid Water Content
Nov 4 1998 Cloud 3

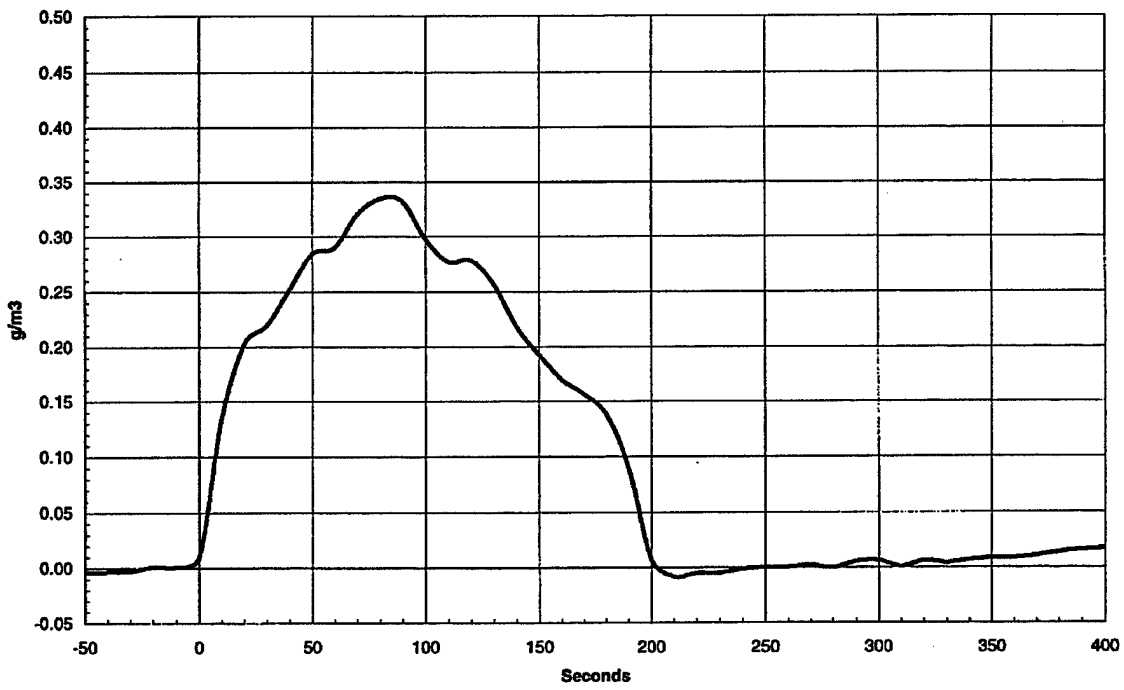


Figure 43

Liquid Water Content
Nov 5 1998 Cloud 1

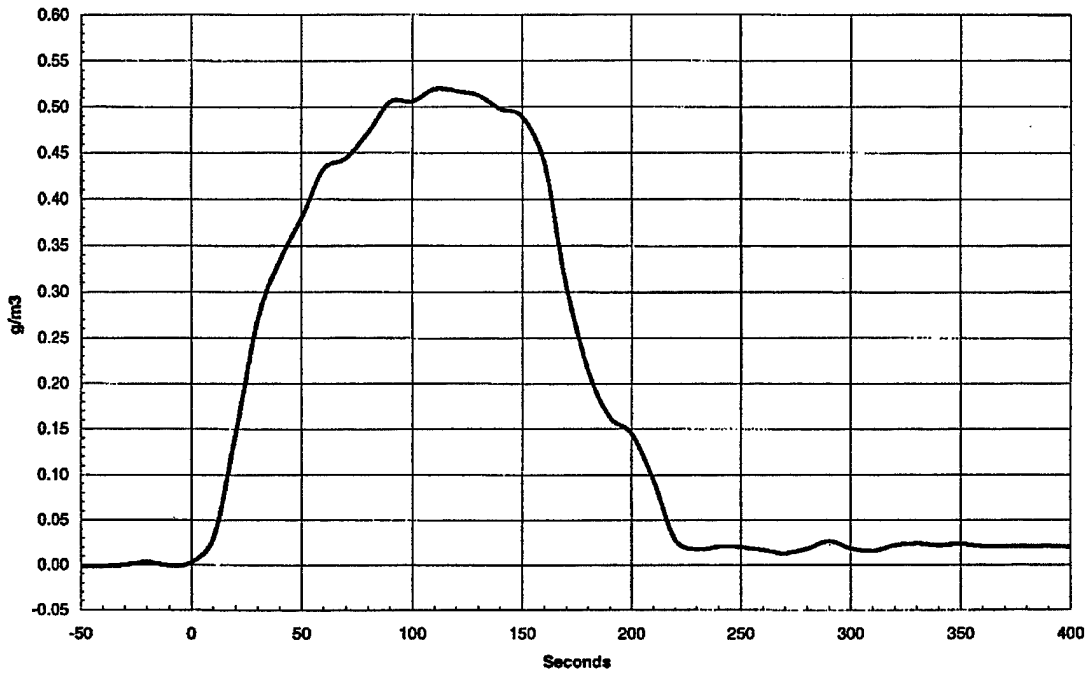


Figure 44

Liquid Water Content
Nov 5 1998 Cloud 2

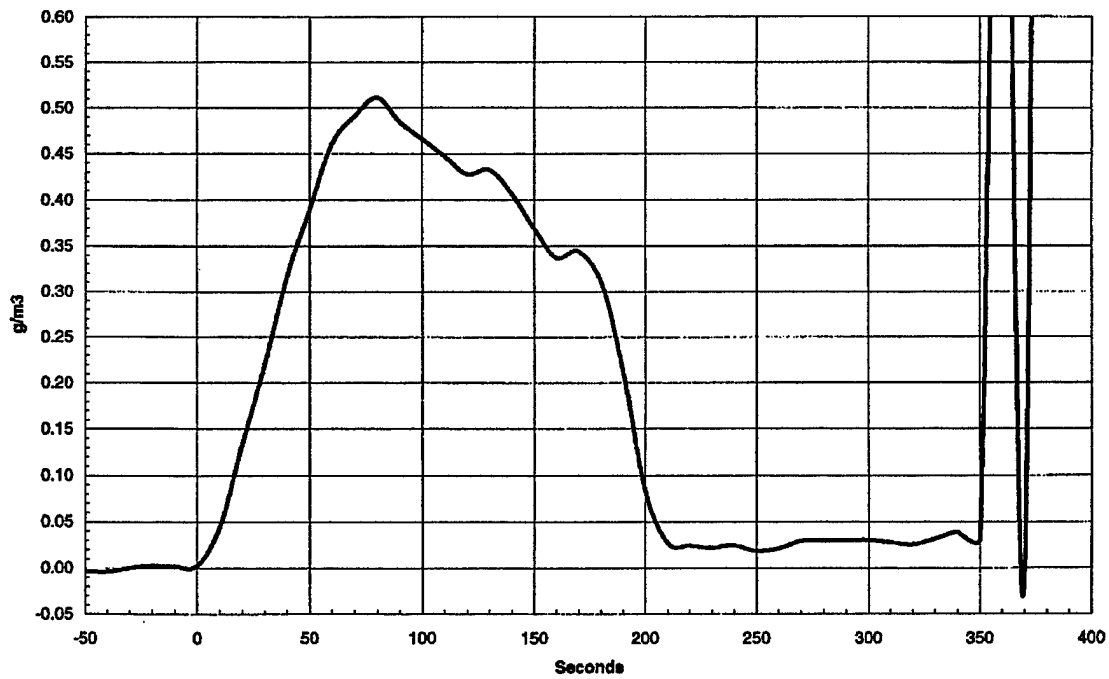


Figure 45

Liquid Water Content
Nov 6 1998 Cloud 1

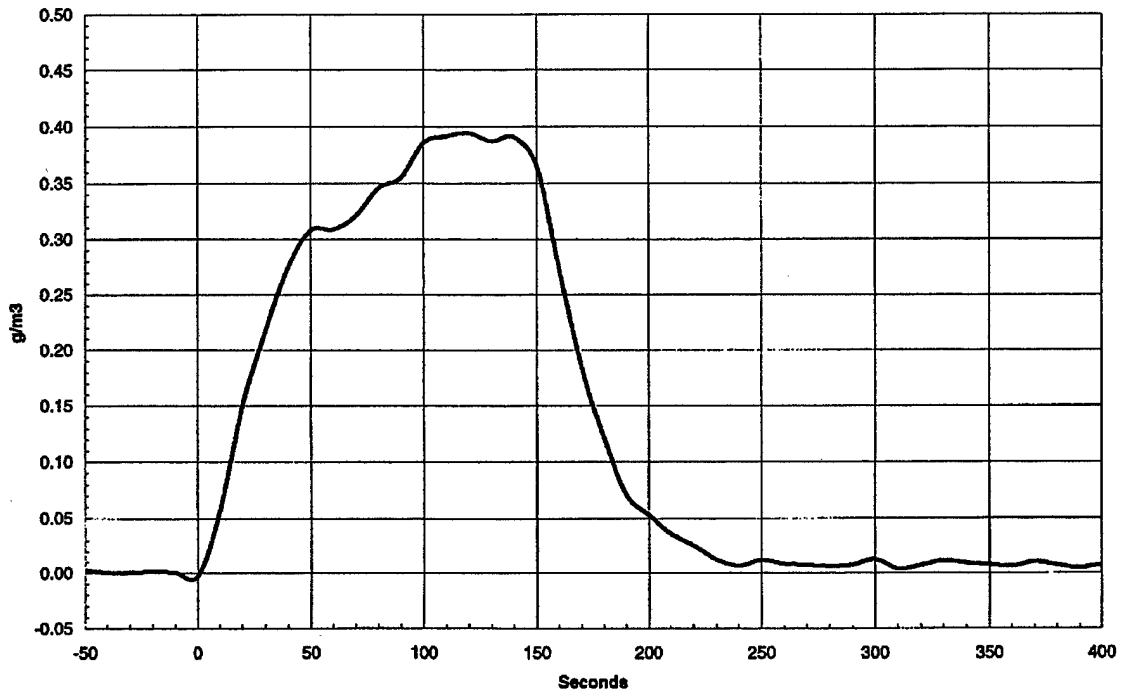


Figure 46

Liquid Water Content
Nov 6 1998 Cloud 2

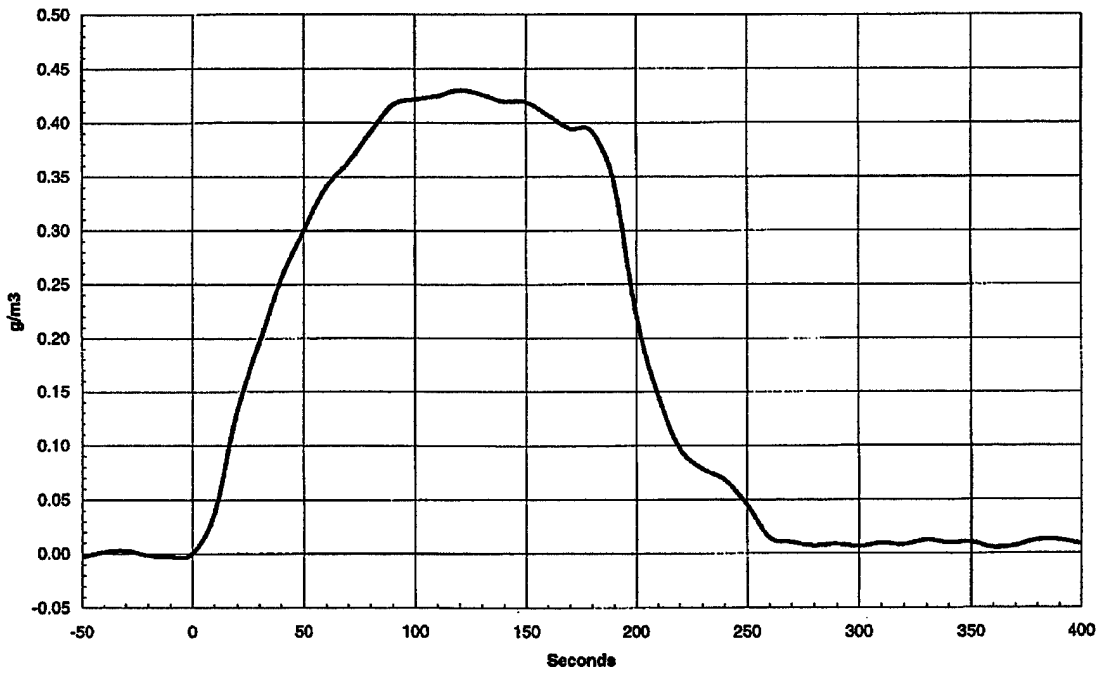


Figure 47

Liquid Water Content
Nov 6 1998 Cloud 3

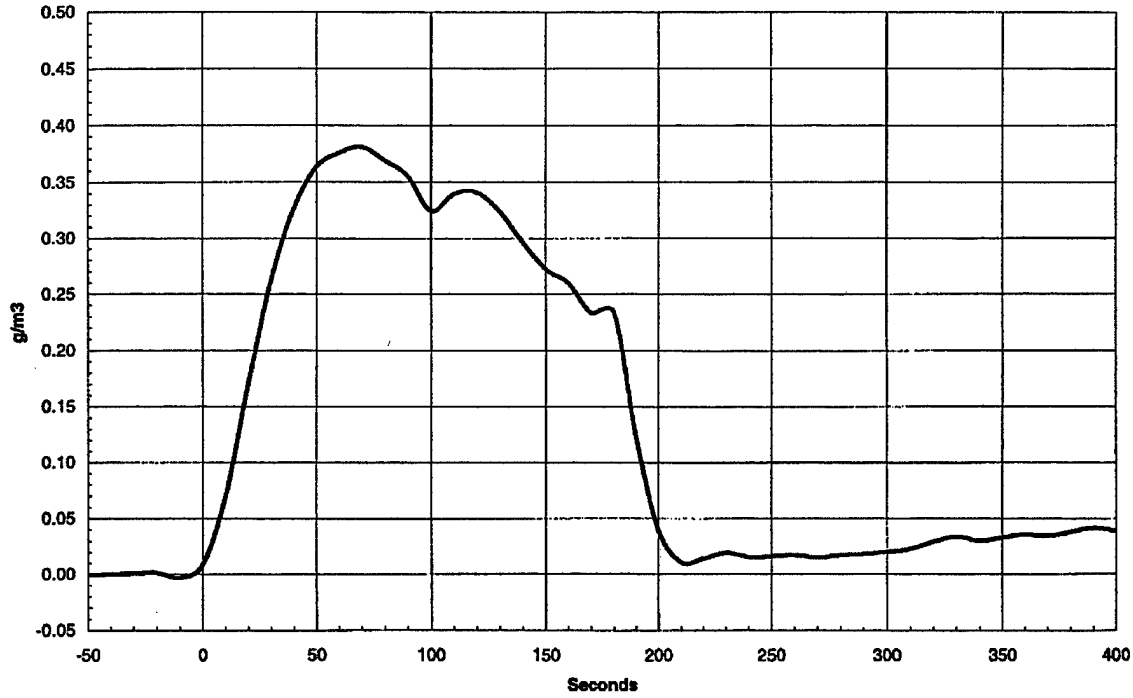


Figure 48

Liquid Water Content
Nov 9 1998 Cloud 1

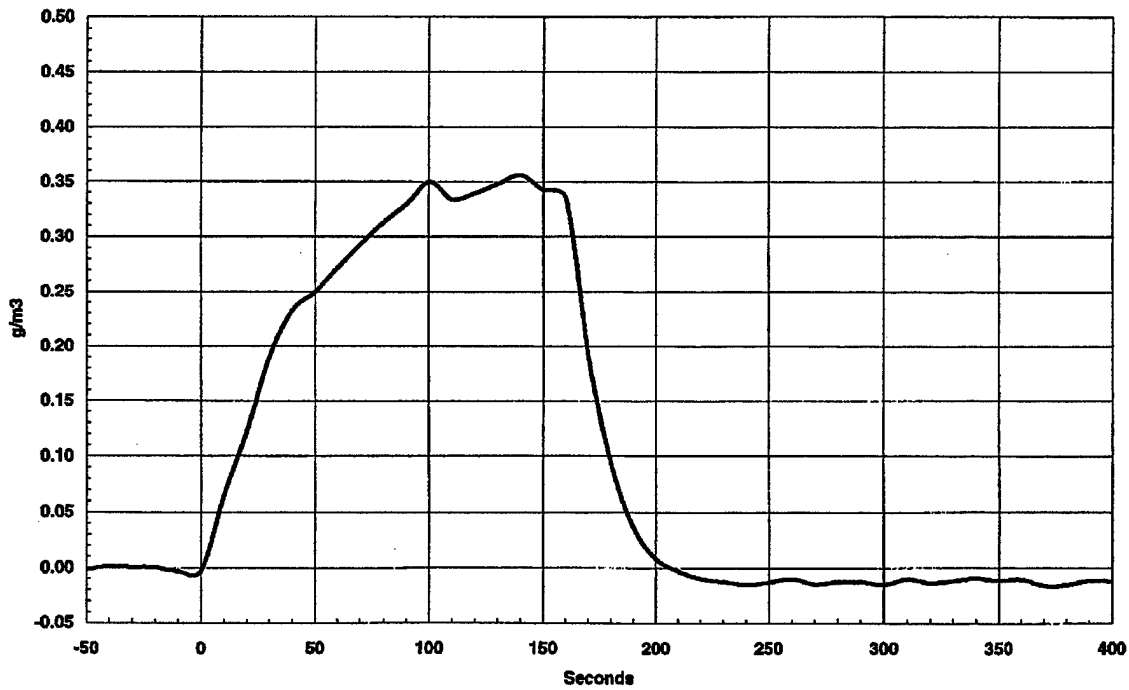


Figure 49

Liquid Water Content
Nov 9 1998 Cloud 2

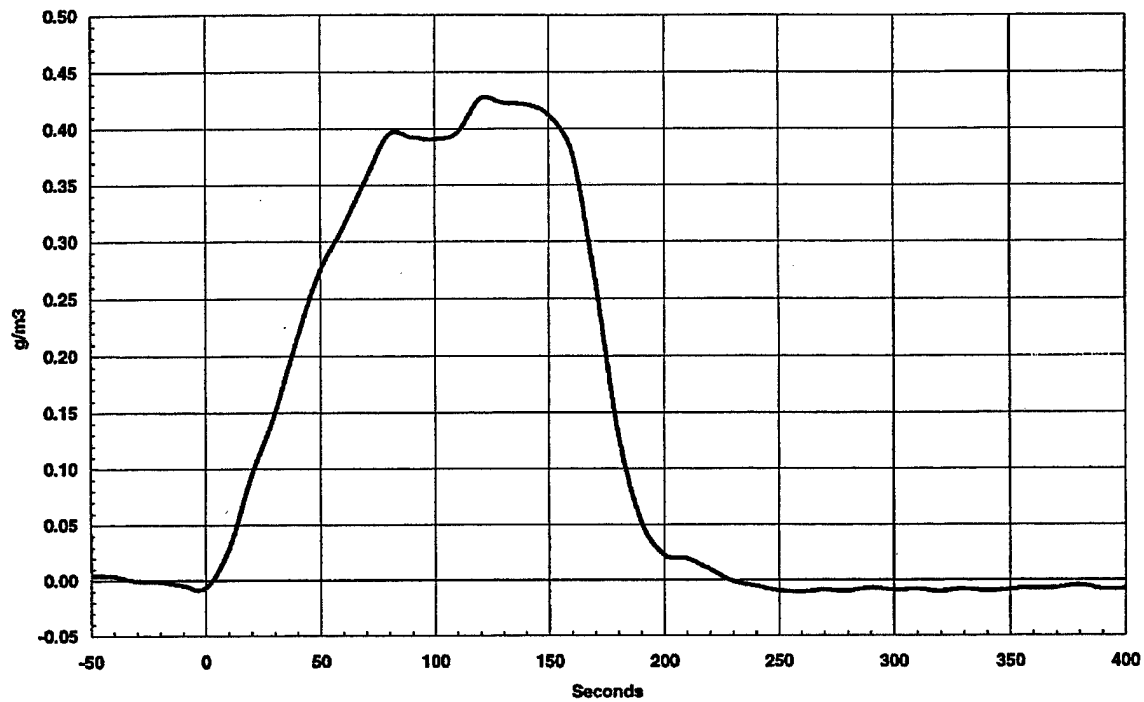


Figure 50

Liquid Water Content
Nov 9 1998 Cloud 3

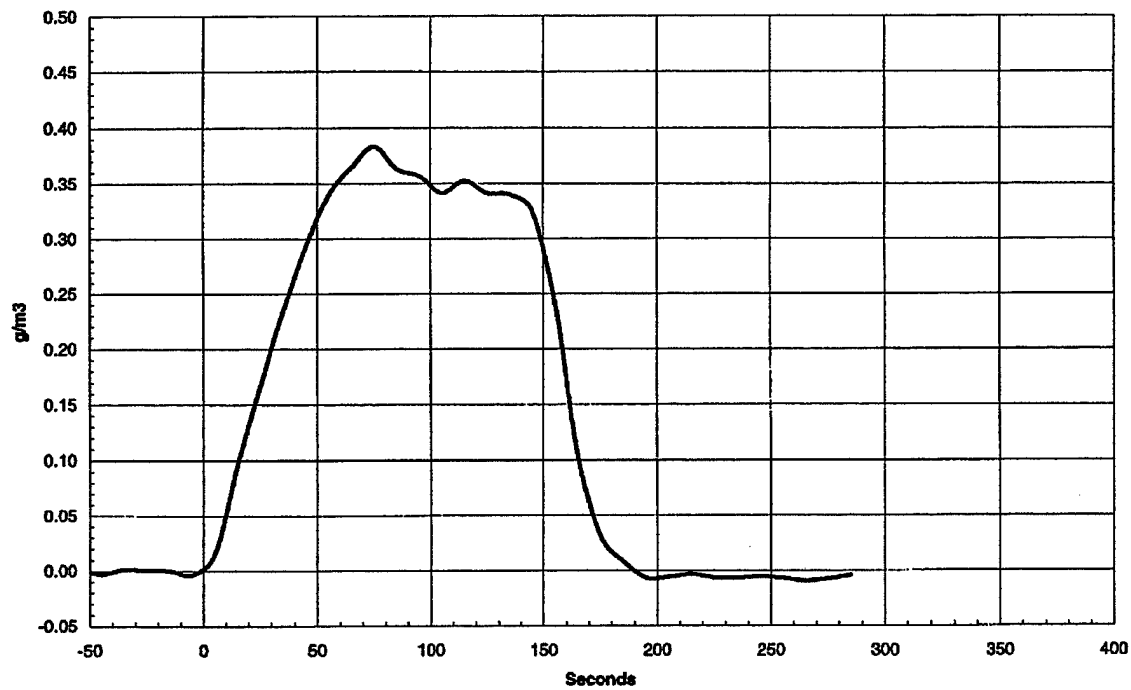


Figure 51

Liquid Water Content
Nov 11 1998 Cloud 1

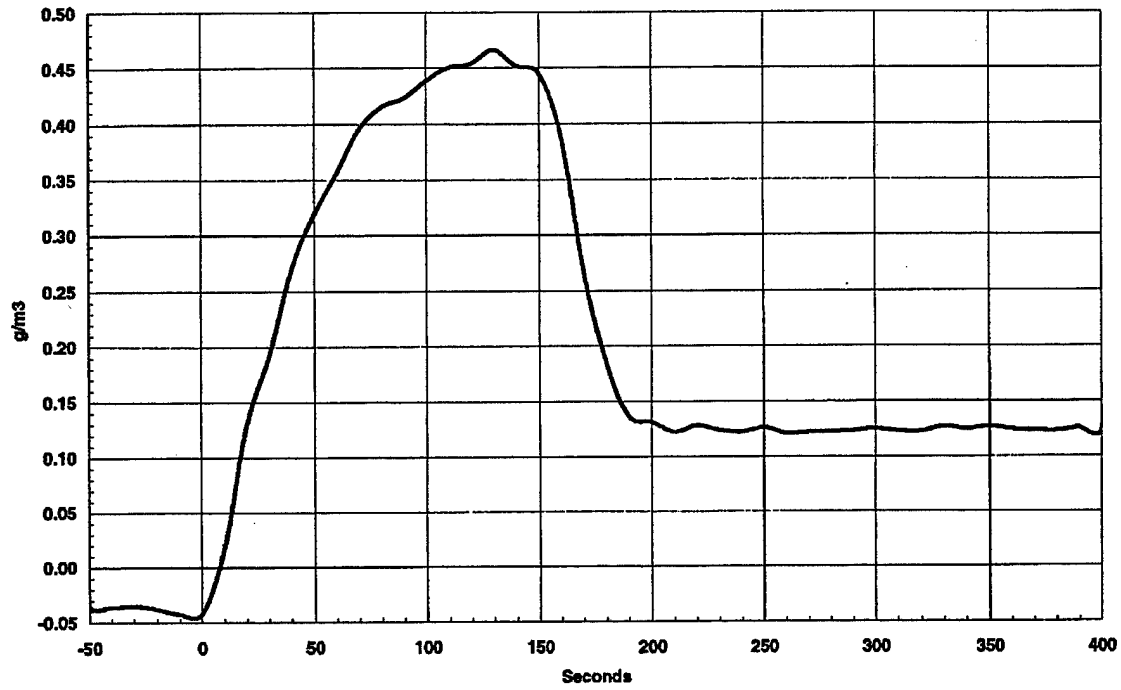


Figure 52

Liquid Water Content
Nov 11 1998 Cloud 2

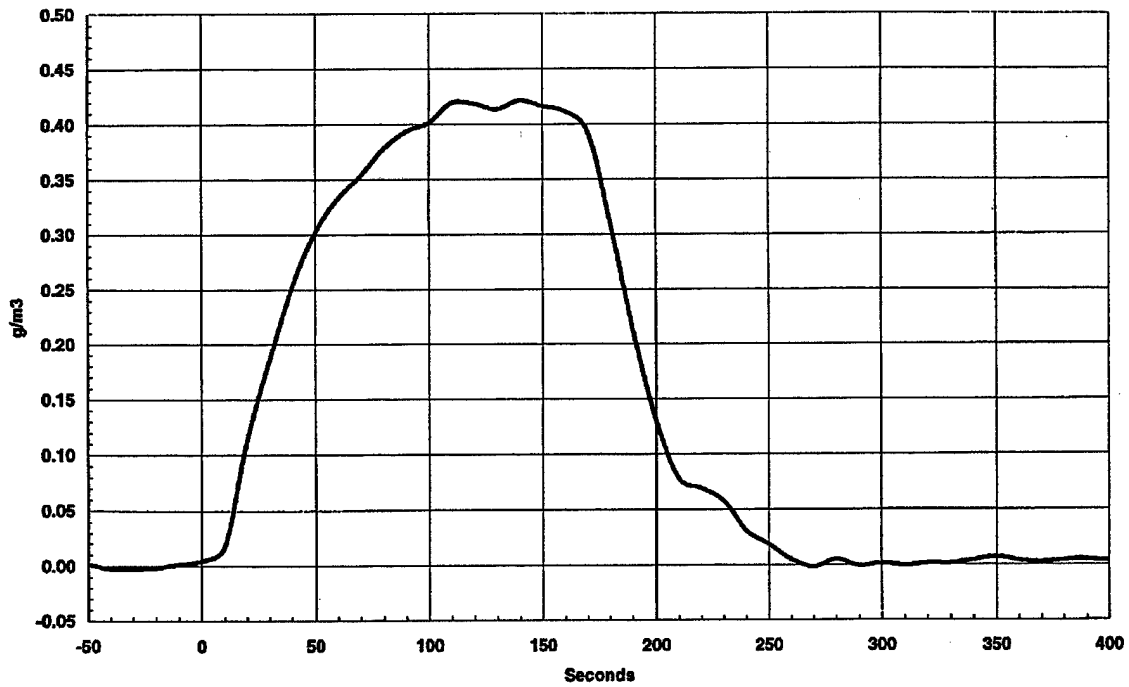


Figure 53

Liquid Water Content
Nov 11 1998 Cloud 3

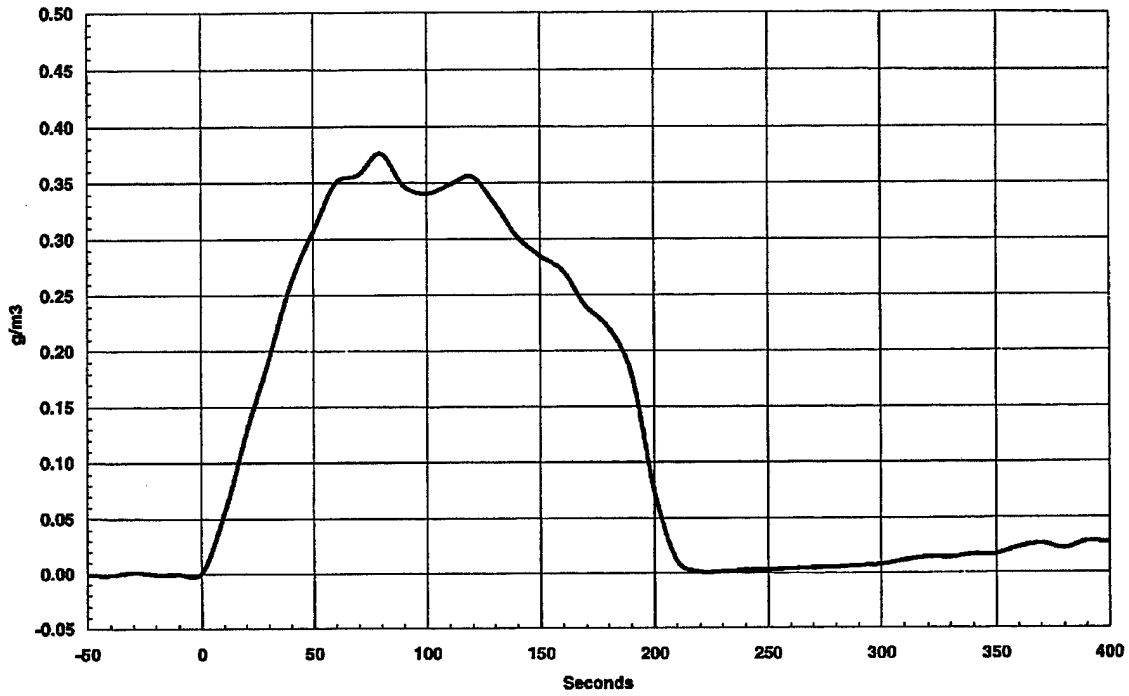


Figure 54

Liquid Water Content
Nov 13 1998 Cloud 1

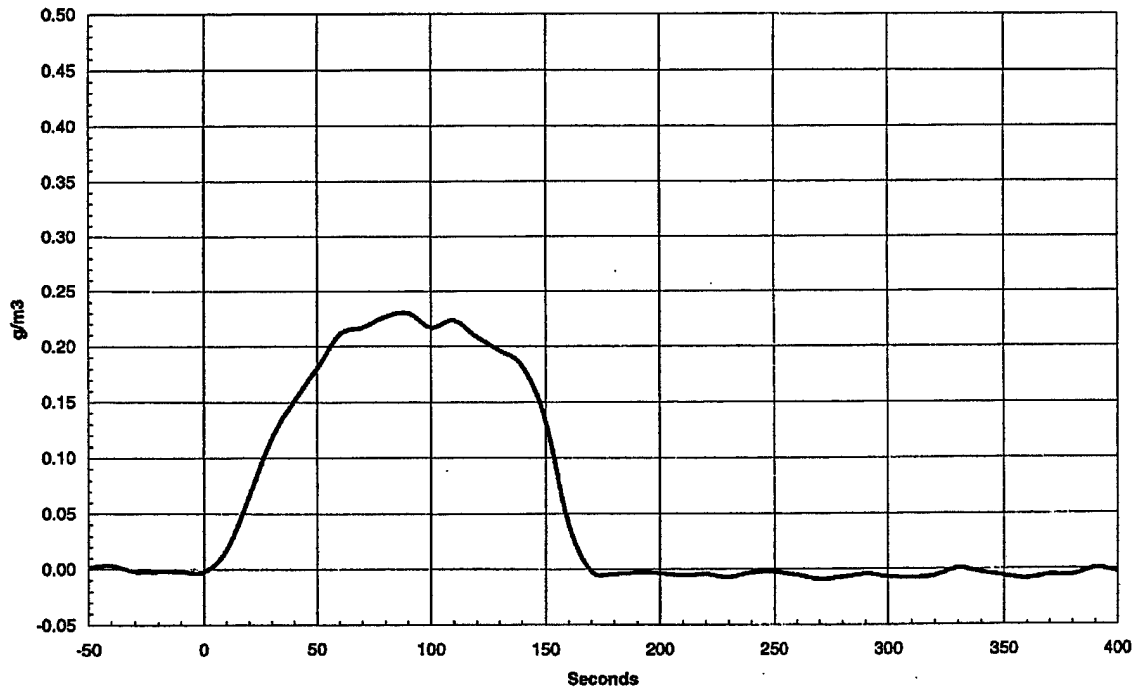


Figure 55

Liquid Water Content
Nov 13 1998 Cloud 2

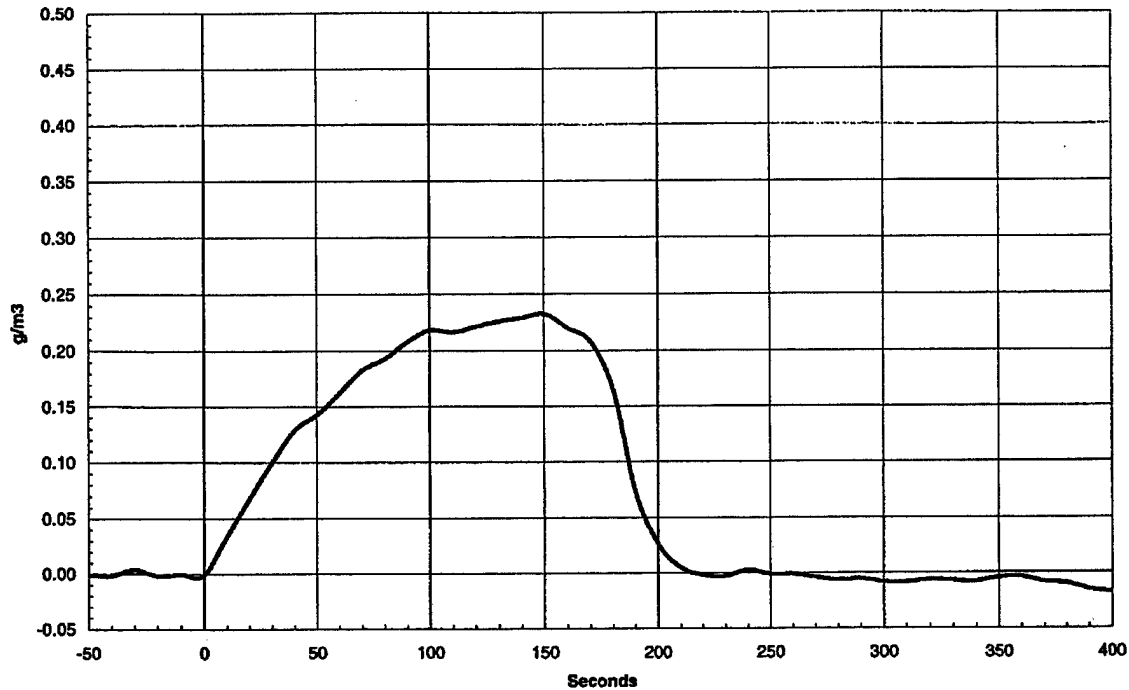


Figure 56

Liquid Water Content
Nov 13 1998 Cloud 3

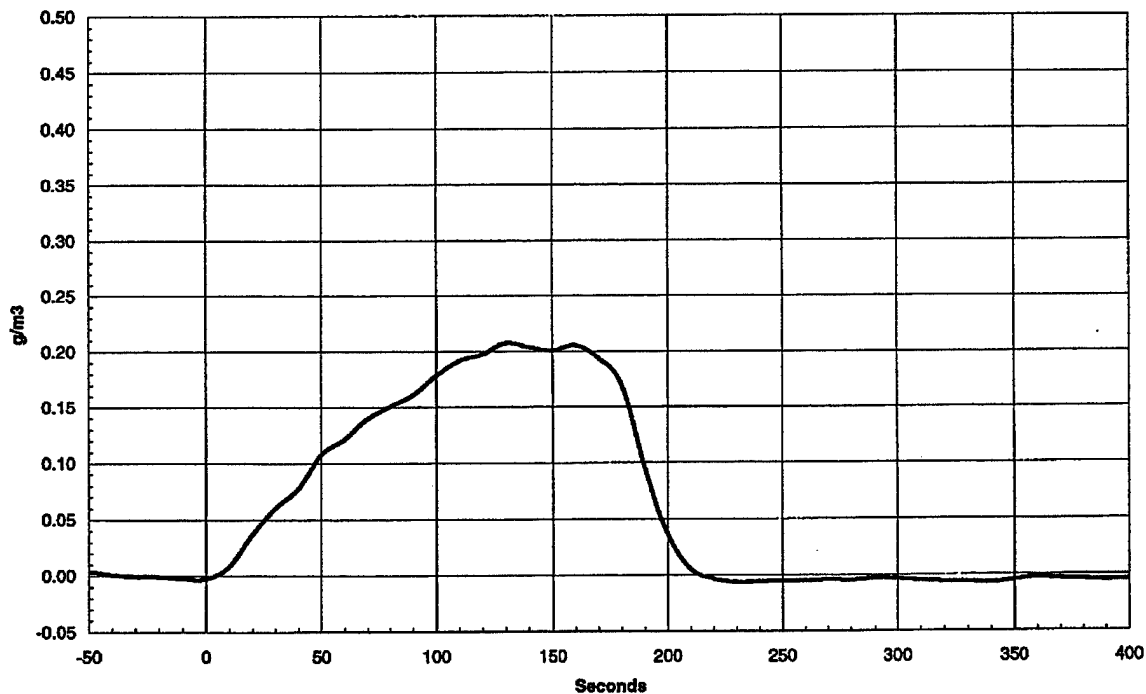


Figure 57

Liquid Water Content
Nov 13 1998 Cloud 4

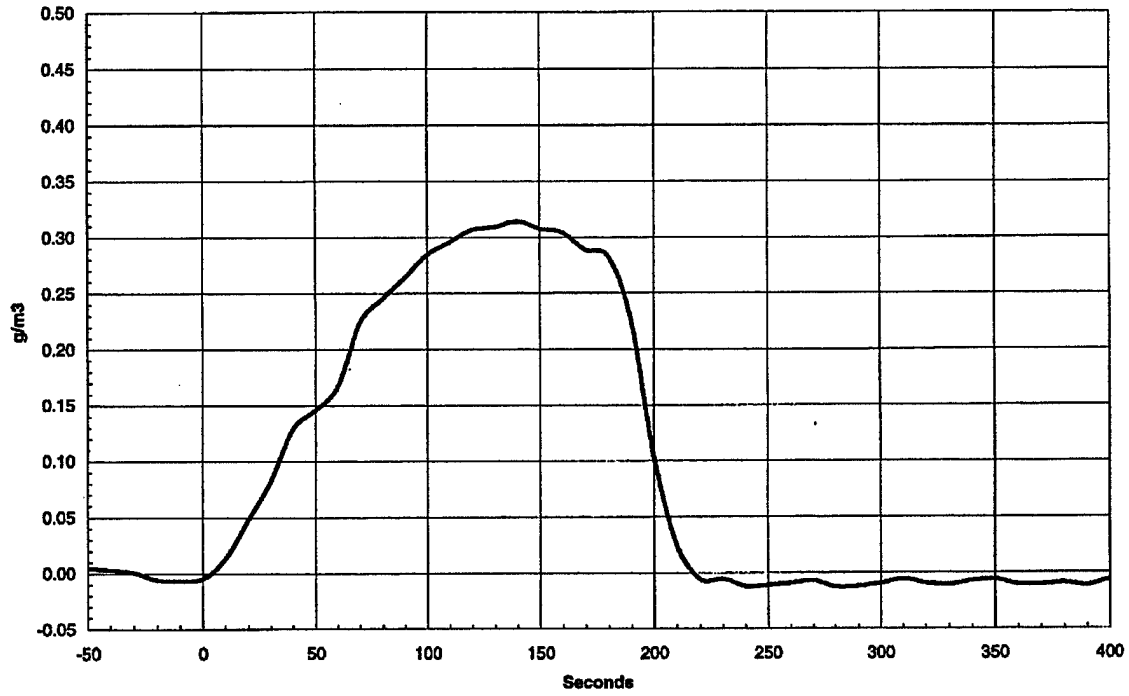


Figure 58

Liquid Water Content
Nov 13 1998 Cloud 5

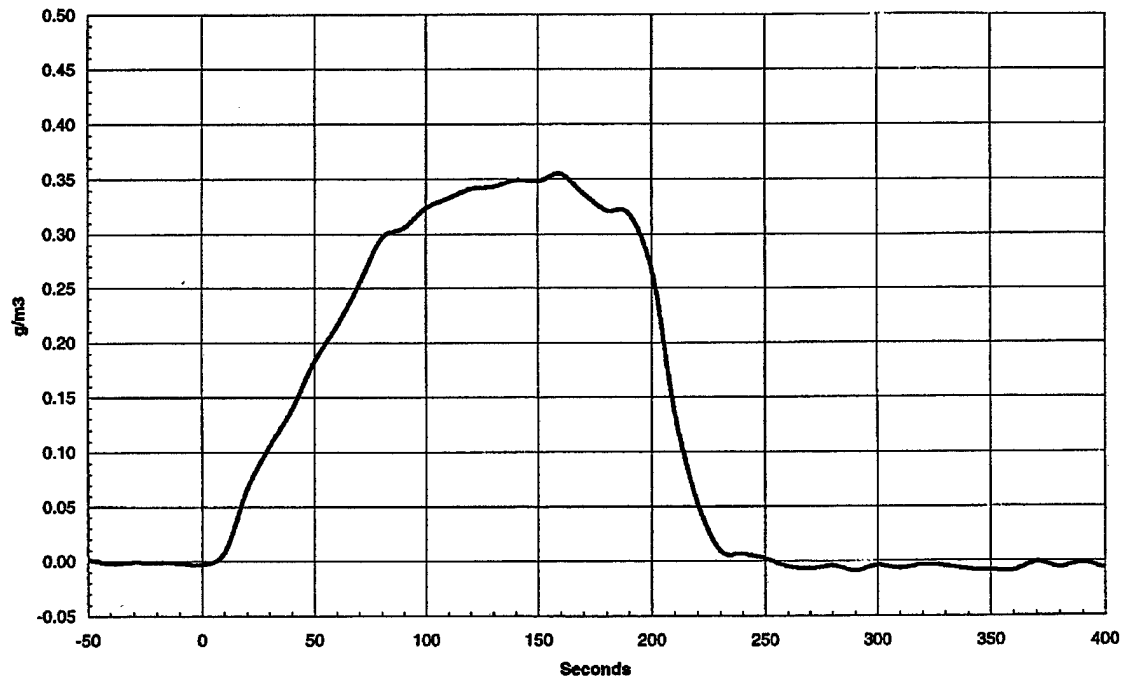


Figure 59

Liquid Water Content
Nov 13 1998 Cloud 6

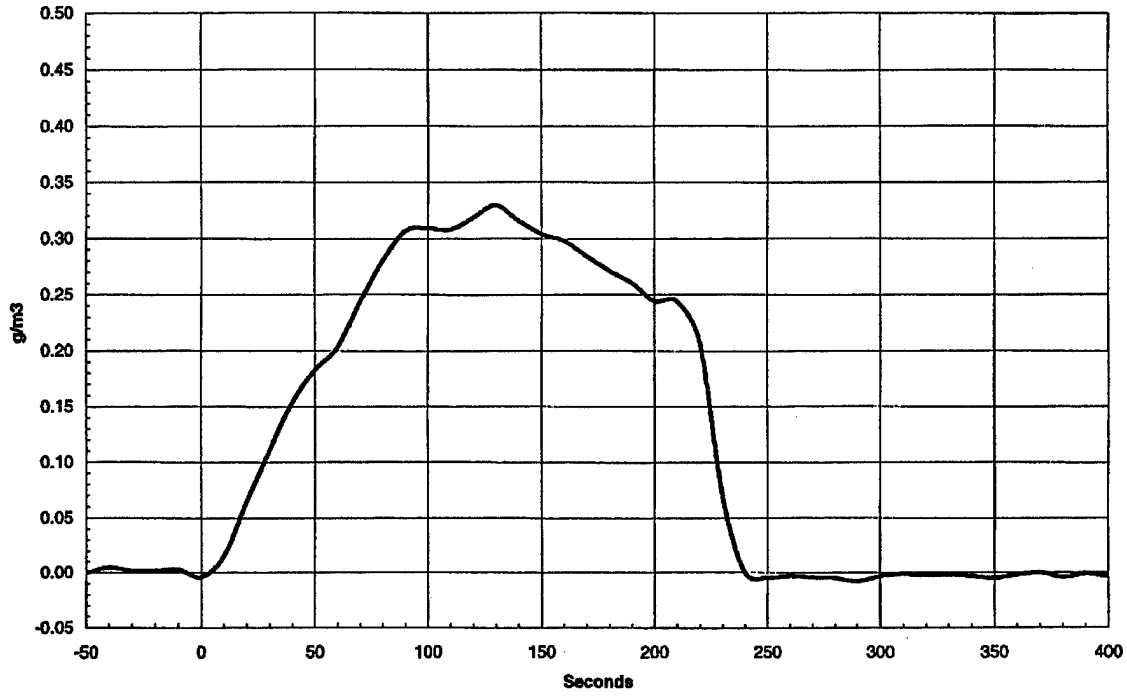


Figure 60

Liquid Water Content
Nov 13 1998 Cloud 7

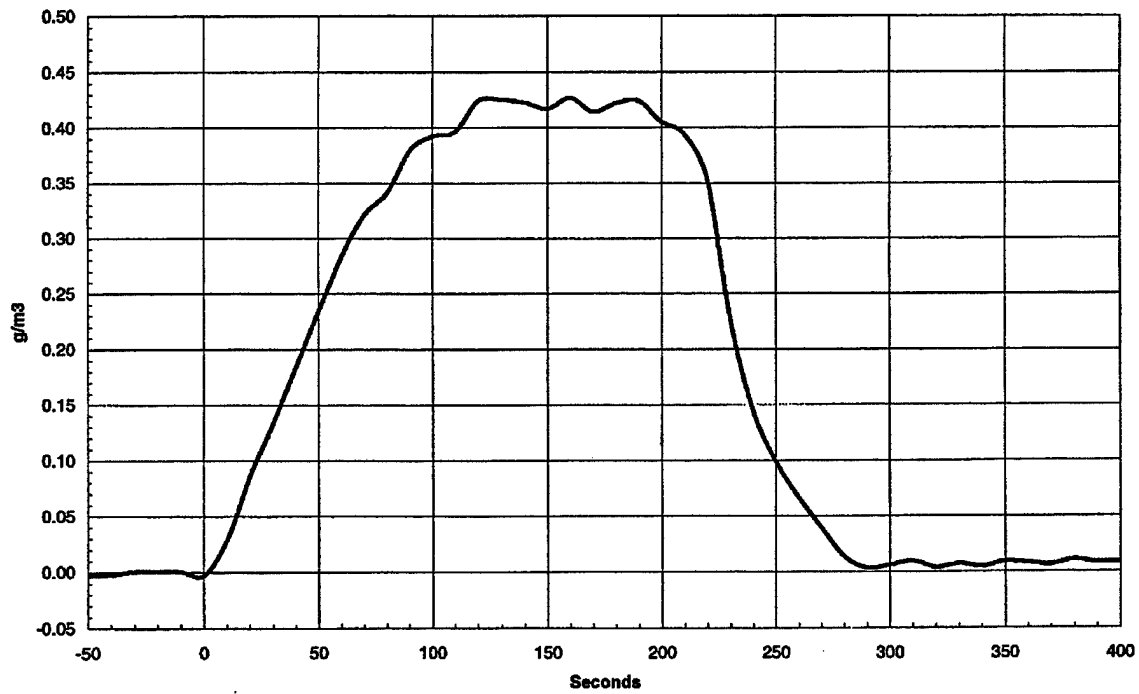


Figure 61

Liquid Water Content
Nov 13 1998 Cloud 8

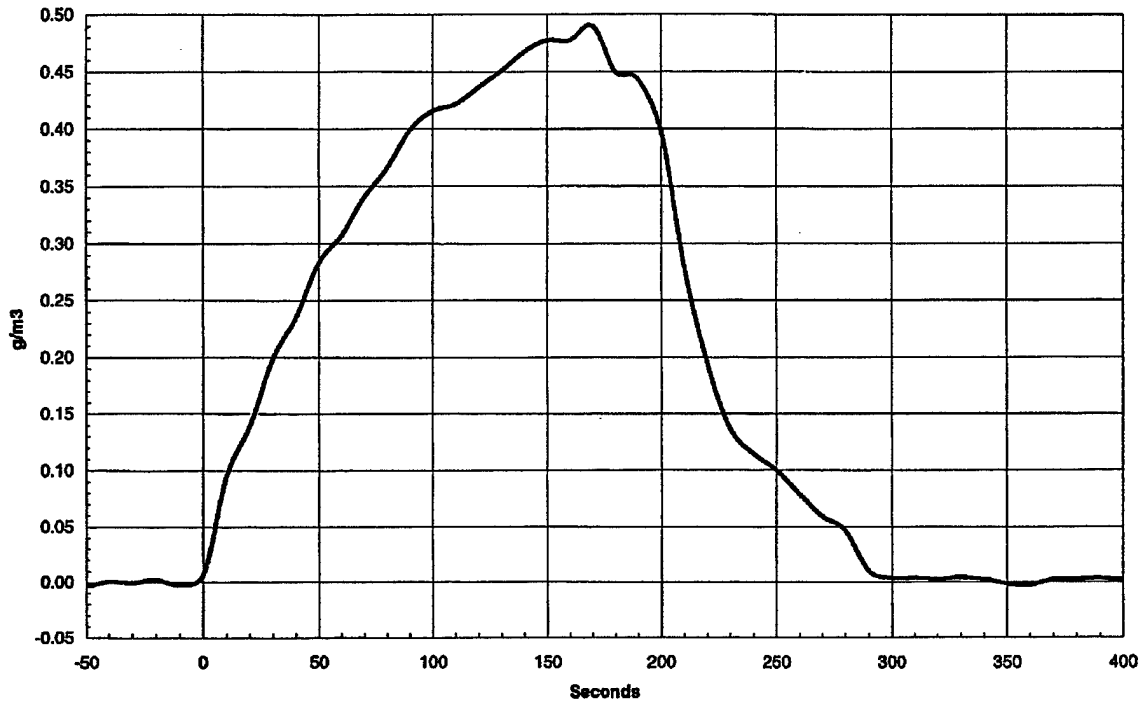


Figure 62

Liquid Water Content
Nov 13 1998 Cloud 9

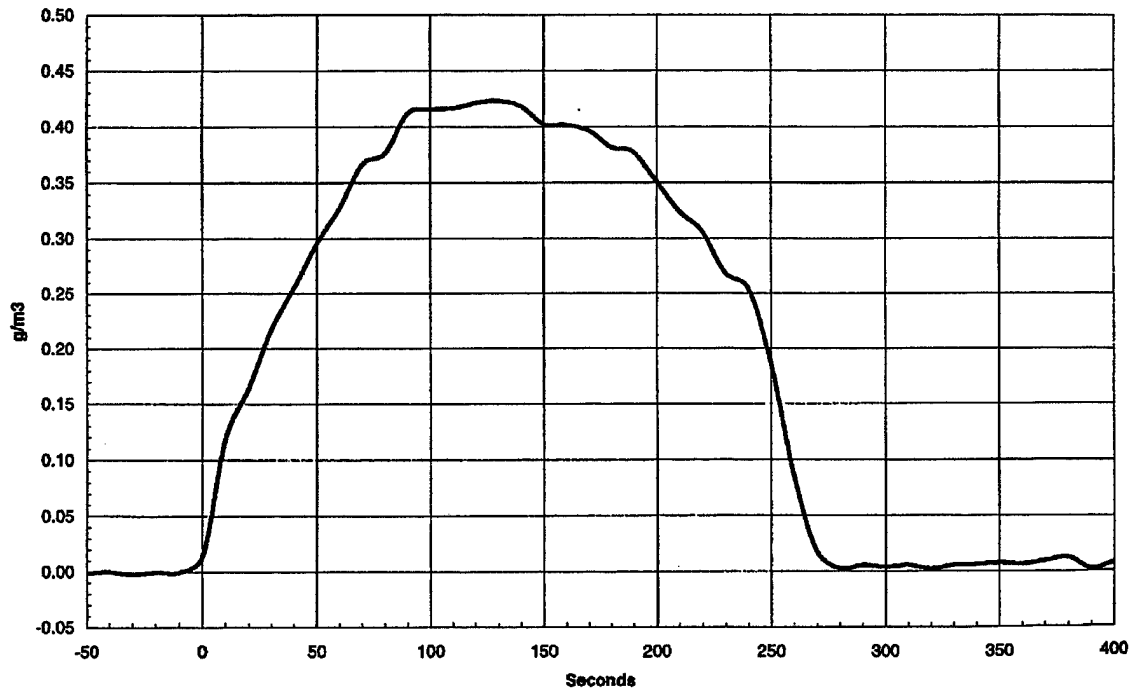


Figure 63

Liquid Water Nov 16 1998
Cloud 1

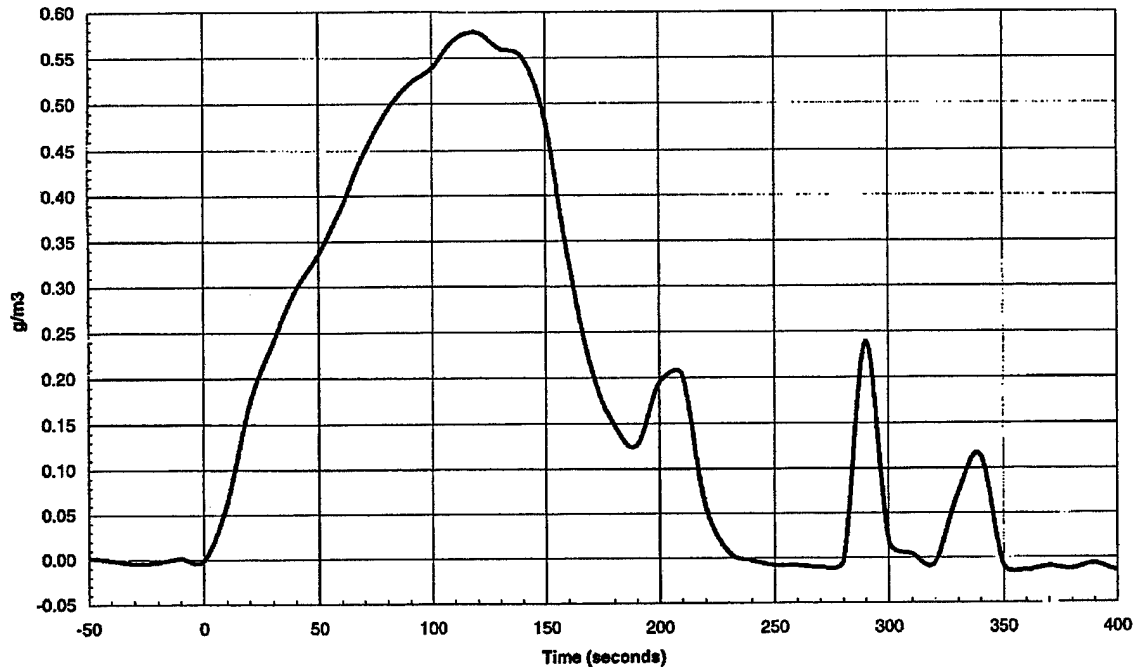


Figure 64

Liquid Water Nov 16 1998
Cloud 2

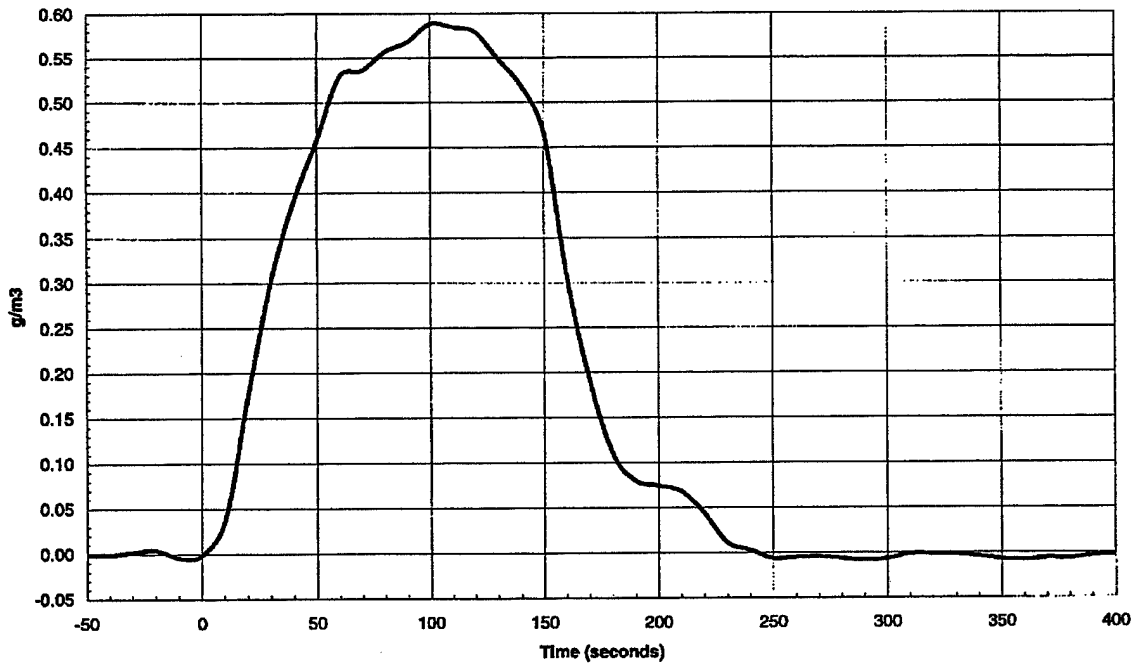


Figure 65

Liquid Water Nov 16 1998
Cloud 3

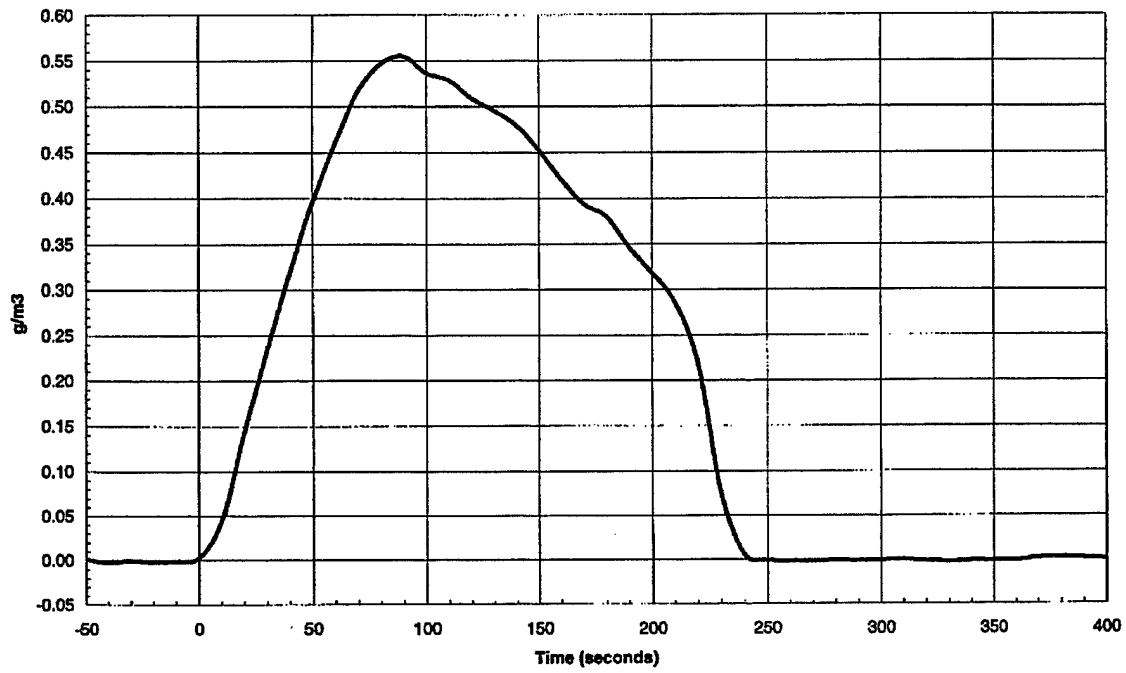


Figure 66

Liquid Water Content
Nov 19 1998 Cloud 1

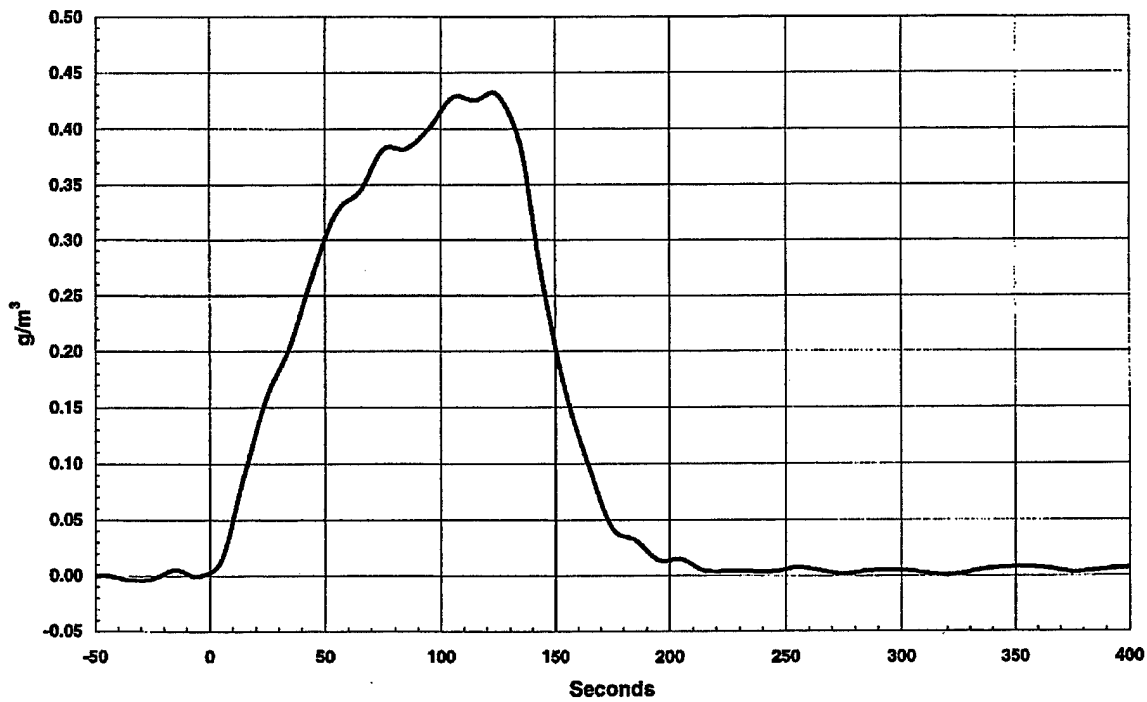


Figure 67

Liquid Water Content
Nov 19 1998 Cloud 2

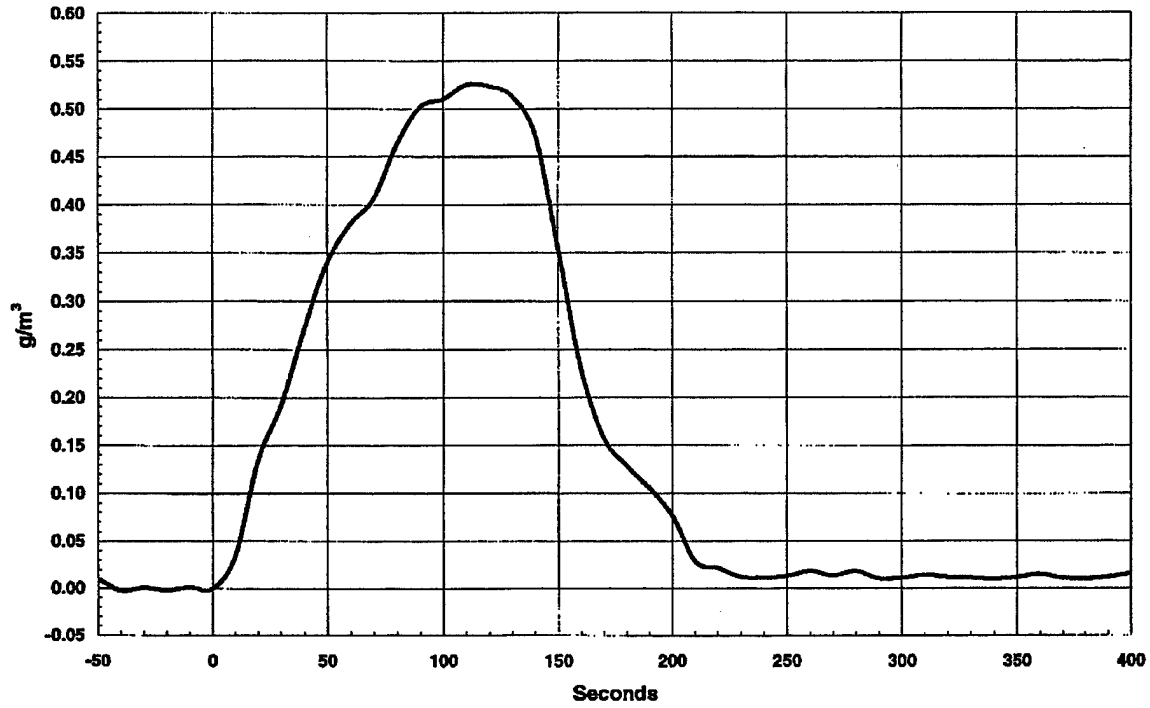


Figure 68

Liquid Water Content
Nov 19 1998 Cloud 3

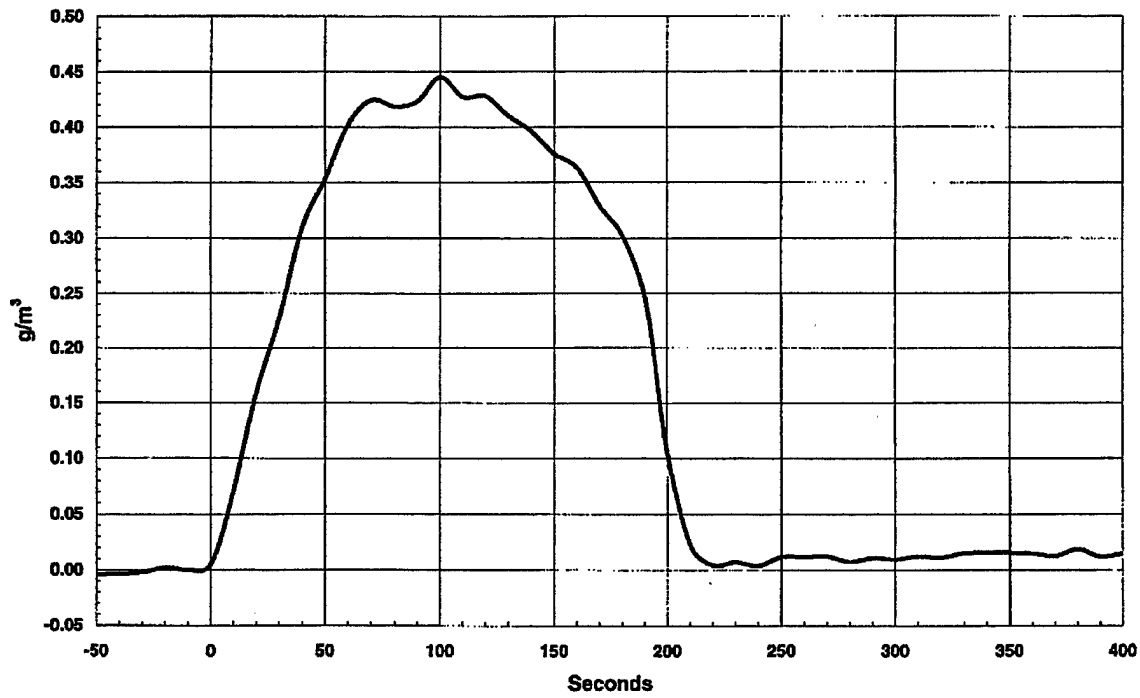


Figure 69

V. Hydrocarbon Measurements

A. GC/MS Analytical Approach and Techniques

Measurements of gas phase hydrocarbon compounds in the atmospheric chamber during the Phase 2 experiments were performed by Calspan employing GC/MS in conjunction with thermal desorption. This instrumental system was used to qualitatively, and semi-quantitatively identify background hydrocarbons in the chamber. The system was also used to quantitatively monitor hydrocarbons for decay during the Phase 2 experiments. The portion of the hydrocarbon backgrounds taken representing benzene-based compounds was calculated as a "cumulative benzene" approximation based on the response of toluene and xylene standards.

Thermal desorption followed by GC was chosen to collect and concentrate, and then separate the various hydrocarbon species present in these experiments. Mass spectrometry was the method of choice for detecting and quantifying the various hydrocarbon species since it allowed for more positive identification of the peaks, aided quantification in the presence of interferents and allowed some identification or characterization of unknown species.

The gas chromatograph (GC) used for the hydrocarbon measurements was a Hewlett-Packard model 5890 Series II+ in conjunction with a Discovery2 quadrupole ion trap mass spectrometer (MS) from Teledyne Electronic Technologies Inc. The thermal desorption was accomplished with a Dynatherm ACEM900 single tube thermal desorption system.

Sampling was performed using a vacuum pump pulling ~25" Hg on a manifold having 4 ports, each with it's own critical orifice limiting flow to 132cc/min. Critical orifices were #13 sapphire from O'keefe Controls Co., Trumbull CT. The orifices are rated at 0.13LPM when critical (vacuum >15"Hg). The value used here was obtained by averaging readings from the 4 orifices using a soap bubble flowmeter (100cc read to the nearest second; all reading were either 45 or 46 seconds). O'Keefe Controls guarantees performance within a test band not exceeding one-half the difference between adjacent orifices (120-145cc/min or -8%/+12%); while our results indicate a much tighter range. Sampling time was generally 10 minutes; any variations are noted. A Galab model 300 timer was used to control the vacuum pump to eliminate operator errors in timing. 6mm diameter glass tubing was extended into the chamber ~28" as sampling probes.

Thermal Desorption of collected samples was performed using the Dynatherm ACEM900 unit described previously. Drying and thermal desorption steps were performed with a nominal helium flow of ~20cc/min. A needle valve flow controller supplying approximately 5cc/min. to the GC analytical column governed the helium carrier gas flow. The following conditions were generally used (any variations are noted):

Valve	210°C
Transfer Line	250°C
Dry Time	5 min.
Desorb	5 min. @250°C
Cool Time	2 min.
Trap Desorb	2 min. @300°C

Carbotrap-300 sorbent tubes were used for all but a couple of the alpha-pinene experiments that utilized Tenax-TA traps. It had been suggested that the Carbotrap-300 tubes could adversely affect the alpha-pinene results; but that was shown not to be a problem during post-test chamber calibration work. Carbotrap-300 tubes were conditioned on Dynatherm single tube conditioning units at 375-400°C, while Tenax-TA tubes were conditioned at 250-280°C. During some of the later experiments, the Carbotrap-300 tubes were precleaned with a set of solvent rinses prior to thermal conditioning; 2 rinses each with chloroform, followed by acetone and finally methanol. Tube blank runs were performed on tubes used for chamber background analyses.

Potassium iodide (KI) traps were installed in the glass sampling probes on November 10th after an alpha pinene and a cyclohexene experiment had been run; but prior to the cyclopentene experiment that was run. It was surmised that some samples might be degrading on the thermal desorption tubes prior to analysis due to residual ozone. The KI traps were made after a very helpful discussion with Dr. Jim Greenberg of NCAR regarding our problem. The traps consisted of a dry coating of the KI on glass wool, and were used on all subsequent samples.

The following GC parameters were generally used throughout the Phase II test series.

Column:	Supelco Petrocol-DH 25mX0.25mm
Carrier gas:	Helium at 5cc/min (est'd)
Det. Temp. :	200°C
Oven:	
Initial:	50°C
Hold:	2 min.
Ramp1:	to 200°C @15°/min.
Hold:	2 min.
Ramp2:	to 250° @50°/min.
Hold:	0 min.

MS parameters for the Teledyne Discovery-2 ion trap were generally as follows:

Ionization step:

Ion time: varied by ASC (Automatic Sensitivity Control)
Pre/post: 0 / 4msec.
Low RF: m/z=42
Endcap excitation: No Signal

Acquisition step:

Time: 13.08msec.
RF (m/z): 42-200
Scan rate: 12khz/sec
Endcap excitation: FAST frequency 540khz/3.15V
Averaging: 10 uScans
EMT: 1900 volts
Current: 30 uAmps
Threshold: 5

B. Hydrocarbon Experiments

Quantification for alpha-pinene, cyclopentene and cyclohexene was based on the response relative to that of the initial injection at the test concentration. This approach assumes a linear response and a negligible y-intercept and the "In Chamber" calibration data in Appendix A illustrates this assumption. The cyclopentene experiment run on October 10 is an exception because ozone was added before the cyclopentene, and no "t=0" sample was taken. The t=0 value was instead derived from an exponential regression.

Several background benzene compounds were present in the chamber during the experiments. Attempts to flush and filter the chamber air were unsuccessful in removing the compounds to below detectable limits of the analytical instrumentation. The substituted benzene compounds were estimated using the calibration curve obtained from the xylene standard prepared in a gas bulb and run on 11/6/98. This method is reasonable as an estimate only, because the identities and the exact response factors of the benzene compounds are unknown. The compounds are suspected of having 1 to 3 carbon substitutions on the ring (i.e. toluene, xylenes (or ethylbenzene) and trimethyl (or methyl-ethyl) benzenes). A subsequent calibration experiment performed in our chamber on 3/17/99 indicates that the actual levels of benzene compounds may have been even lower than estimated, but by no more than an order of magnitude.

Alpha pinene/ozone experiments

A series of alpha pinene/ozone decay experiments were performed during the October and November campaigns. Samples were taken to provide a measure of the decay rate and decay function of the alpha pinene. Most samples were 5-minute duration due to the relatively good response factor of the alpha pinene. The sampling intervals were based on an estimate of what the decay rate might be. Calibration was based on the concentration initially injected into the chamber. Response was shown to be linear, so decay samples could be calculated relative to the starting concentration. Potential byproducts have been detected with some idea of the chemical formula coming from mass spectral library searches, and possibly an order of magnitude estimate of their concentrations coming from the ion peaks present.

Cyclopentene/ozone experiments

A total of four cyclopentene/ozone decay experiments were performed. Samples were taken to measure decay rate and function for the cyclopentene/ozone system. The normal sampling period was 10 minutes, but occasional exceptions were made and noted. Most samples were taken in rapid succession due to the normally fast reaction rates.

Cyclohexene/ozone experiments

Three Cyclohexene/ozone decay experiments were run. Most samples were 10-minutes duration, some as little as 5-minutes; all times were noted. Sample intervals tend to be greater, since decay rates were generally slower.

DMS experiments

Two sets of two DMS experiments each were run during the second campaign, one on November 7th and the other on November 17th. While the collection and analysis of DMS is known to be quite difficult, the results obtained were acceptable. DMS was quantified using $m/z=61-63$ ions for the first three experiments. However due to some minor interferences encountered during the fourth experiment, the $m/z=62$ ion alone to quantify the DMS. The November 7th experiments consisted of a photolysis with CH_2O at 10-15 ppb and NO at 2 ppb, followed by an ozone reaction with 50 ppb NO_2 and 160 ppb O_3 . The chamber was challenged with 3-20 ppb doses of DMS for a total of 60 ppb for the first experiment. The chamber was sampled after each addition, and those samples were used as a calibration for both experiments. The responses of the 60 ppb samples were extremely variable though. Both DMS experiments run on 11/17 were ozone oxidation reactions.

C. Cloud Processing Experiments

Prior to the cloud processing and sulfuric acid nucleation experiments samples were obtained to characterize the HC⁺ contained in the chamber background. These results are summarized as follows:

SO₂ oxidation by Ozone – Sulfuric Acid formation in the liquid phase

10/13: 10min. background sample taken at 08:51 showed an estimated 8ppb cumulative benzene compounds.

11/3: A 10min. background sample taken at 09:15 showed an estimated 7ppb of cumulative benzene compounds.

11/4: A 10min. background sample taken at 08:47 showed an estimated 7ppb of cumulative benzene compounds.

SO₂ oxidation by Ozone in cloud droplets formed on sea salt...

10/9: A 10min. background sample taken at 08:47 showed an estimated 3ppb of cumulative benzene compounds.

10/15: A 10min. background sample taken at 08:33 showed an estimated 7ppb cumulative benzene compounds.

SO₂ oxidation by Ozone – with NH₃ added to reduce acidity...

10/21: A 10min. background sample taken at 08:44 showed an estimated 2ppb cumulative benzene compounds.

11/6: A 10min. background sample taken at 09:31 showed an estimated 29ppb of cumulative benzene compounds.

SO₂ oxidation by H₂O₂ – Sulfuric Acid formation in the liquid phase

10/20: A 10min. background sample taken at 08:49 showed an estimated 4ppb cumulative benzene compounds.

11/5: A 10min. background sample taken at 08:47 showed an estimated 2ppb of cumulative benzene compounds.

Effect of organics on cloud microphysics

10/8: A 1min. background sample taken at 010:29 showed an estimated 11ppb of cumulative benzene compounds.

11/13: A 10min. background sample taken at 08:33 showed an estimated 7ppb cumulative benzene compounds.

D. Nucleation of Sulfuric Acid Aerosol

10/12: A 10min. background sample taken at 08:27 showed an estimated 2ppb cumulative benzene compounds.

10/13: A 10min. background sample taken at 08:51 showed an estimated 8ppb cumulative benzene compounds.

10/17: A 10min. background sample taken at 08:36 showed an estimated 10ppb cumulative benzene compounds.

10/20: A 10min. background sample taken at 08:49 showed an estimated 4ppb cumulative benzene compounds.

10/21: A 10min. background sample taken at 08:44 showed an estimated 2ppb cumulative benzene compounds.

11/3: A 10min. background sample taken at 09:15 showed an estimated 7ppb of cumulative benzene compounds.

11/4: A 10min. background sample taken at 08:47 showed an estimated 7ppb of cumulative benzene compounds.

11/5: A 10min. background sample taken at 08:47 showed an estimated 2ppb of cumulative benzene compounds.

11/6: A 10min. background sample taken at 09:31 showed an estimated 29ppb of cumulative benzene compounds.

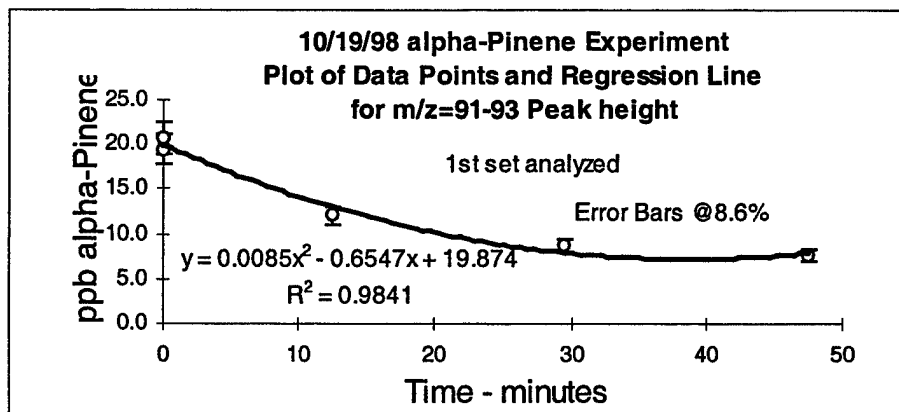
11/16: A 10min. background sample taken at 09:25 showed an estimated 4ppb of cumulative benzene compounds.

E. Nucleation in Hydrocarbon-Ozone Systems

E.1 Alpha-pinene/ozone system

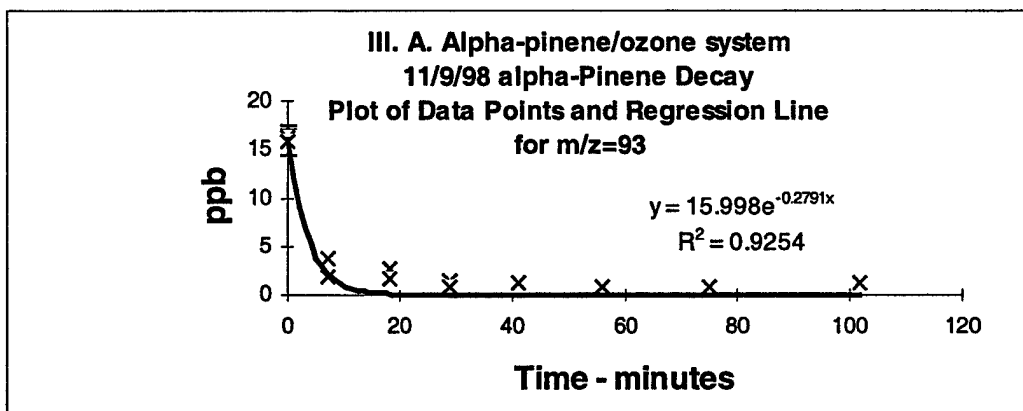
October 19, 1998; Figure 70

A nucleation study was run with an alpha-pinene concentration of 20ppb. Ozone was added at 115ppb, and decay was monitored. 5-minute samples were taken at 10, 27 and 45 minutes into the reaction. The first set of tubes analyzed gave the most consistent results as shown here; while the second set had more scatter. The best fit seems to be a second order polynomial which shows leveling off at about 40 minutes. The error bars are based on the post test chamber calibration. KI filters were not in place at this time. Early morning background levels were estimated at less than 10ppb cumulative benzene compounds.



November 9, 1998; Figure 71

The alpha-pinene was added in two increments of 8ppb each to allow a calibration check. The nucleation study was begun after sampling the 16ppb atmosphere, which had a relative humidity of 29%. Ozone was added at 95 ppb to initiate reaction. 10-minute samples were taken at 2, 13, 24, 36, 51, 70 and 97 minutes into the reaction. The samples begun at 2 minutes ($t_{ave}=7$ minutes) gave results between 2-4ppb, indicating a very fast reaction. The results are shown with an exponential trendline indicating a 4-minute time constant. KI filters were not in place at this time. Early morning background levels were estimated at less than 10ppb cumulative benzene compounds.

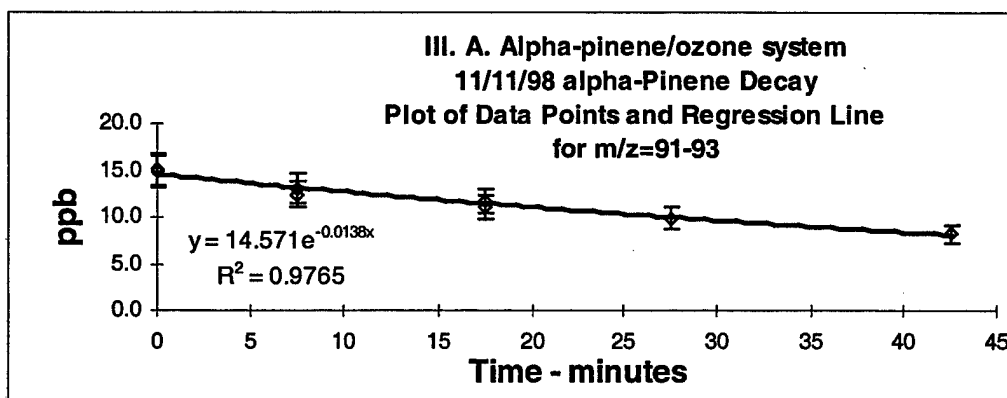


November 10, 1998

Alpha-pinene was added to the chamber at a level of 15ppb for a nucleation study. However, the analytical results are questionable and are not presented.

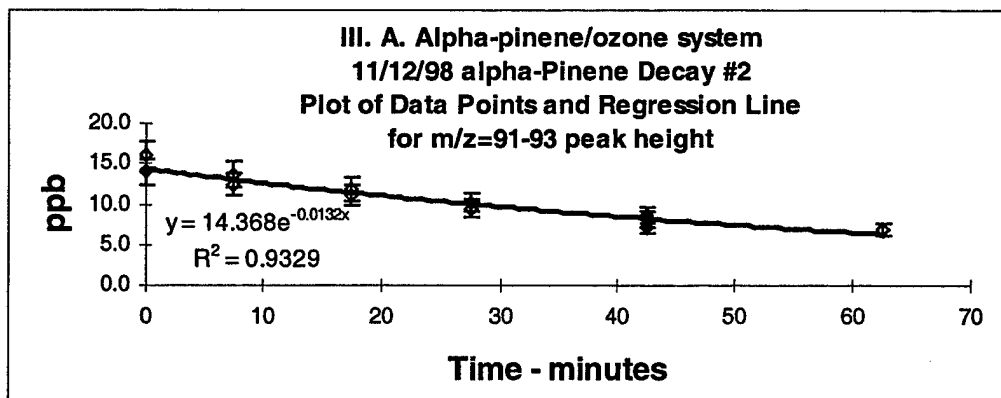
November 11, 1998; Figure 72

Alpha-pinene was added to the chamber at a level of 15ppb for a nucleation study. The relative humidity was 47%, and sulfur dioxide was present at 6ppb. T=0 samples were taken before ozone was added at 100 ppb to initiate reaction. 5-minute samples were taken at 5, 15, 25 and 40 minutes into the reaction. KI filters were in place at this time. The results are shown with an exponential trendline indicating a 72-minute time constant. Early morning background levels were estimated at less than 10ppb cumulative benzene compounds.



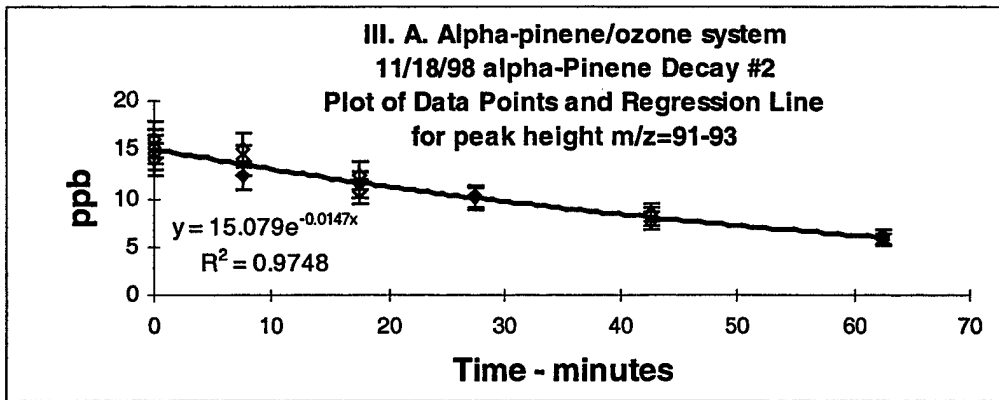
November 12, 1998; Figure 73

Alpha-pinene was added to the chamber at a level of 15ppb for a nucleation study. The relative humidity was 43%, and sulfur dioxide was present at 2.5ppb. T=0 samples were taken before ozone was added at 110 ppb to initiate reaction. 5-minute samples were taken at 5, 15, 27, 40 and 60 minutes into the reaction. KI filters were in place at this time. The results are shown with an exponential trendline indicating a 76-minute time constant. Early morning background levels were estimated at less than 10ppb cumulative benzene compounds.



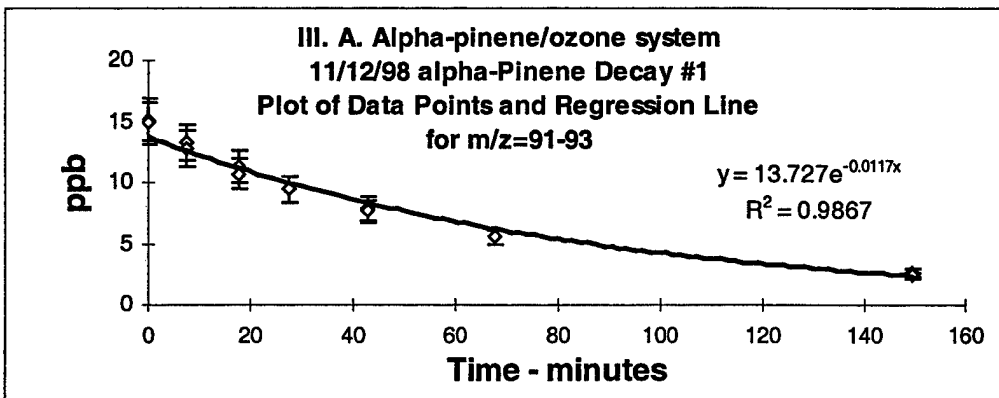
November 18, 1998; Figure 74

Alpha-pinene was added to the chamber at a level of 15ppb for a nucleation study. The relative humidity was 30%, and sulfur dioxide was present at 0.5ppb. T=0 samples were taken before ozone was added at 110 ppb to initiate reaction. 5-minute samples were taken at 5, 15, 25, 40 and 60 minutes into the reaction. KI filters were in place at this time. The results are shown with an exponential trendline indicating a 68-minute time constant. Early morning background levels were estimated at less than 10ppb cumulative benzene compounds.



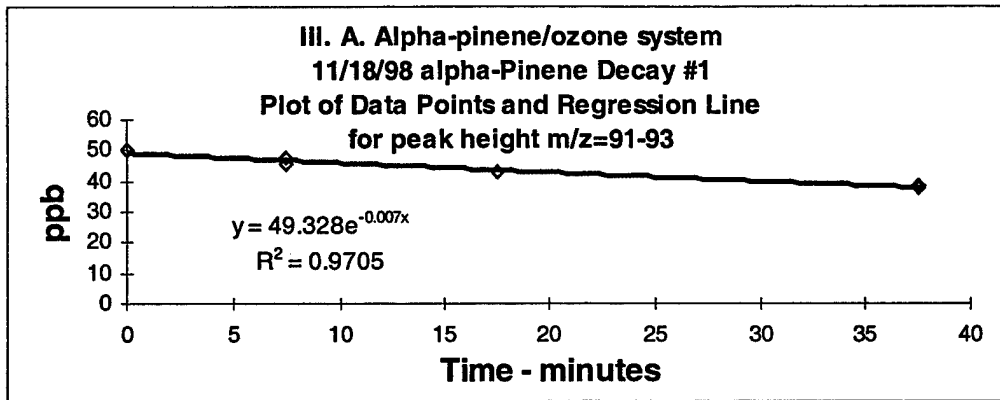
November 12, 1998; Figure 75

Alpha-pinene was added to the chamber at a level of 15ppb for a nucleation study. The relative humidity was 49%. T=0 samples were taken before ozone was added at 110 ppb to initiate reaction. 5-minute samples were taken at 5, 15, 25, 40, 65 and 147 minutes into the reaction. KI filters were in place at this time. The results are shown with an exponential trendline indicating an 85-minute time constant. Early morning background levels were estimated at less than 10ppb cumulative benzene compounds.



November 18, 1998; Figure 76

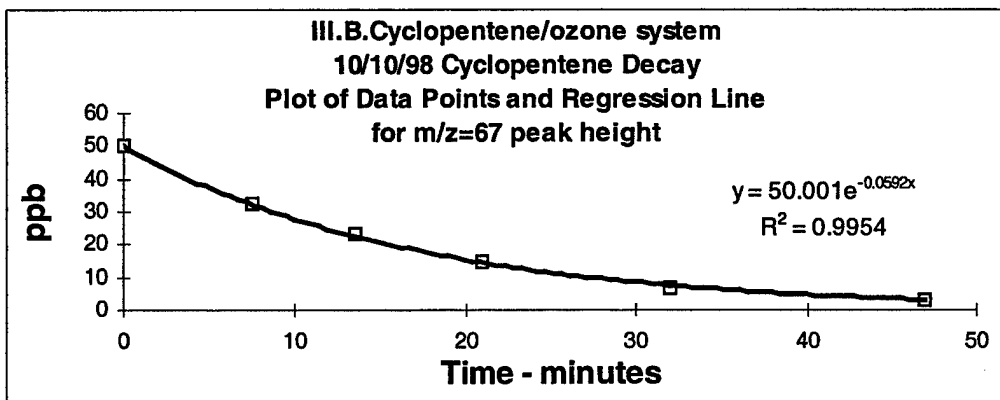
Alpha-pinene was added to the chamber at a level of 50ppb for a nucleation study. NO₂ was present at 100ppb. T=0 samples were taken before ozone was added at 30 ppb to initiate a reaction. 5-minute samples were taken at 5, 15 and 35 minutes into the reaction. KI filters were in place at this time. The experiment was terminated at 50 minutes. The results are shown with an exponential trendline indicating what would be a 143-minute time constant. As stated earlier, morning background levels were estimated at less than 10ppb cumulative benzene compounds.



E.2 Cyclopentene/Ozone System

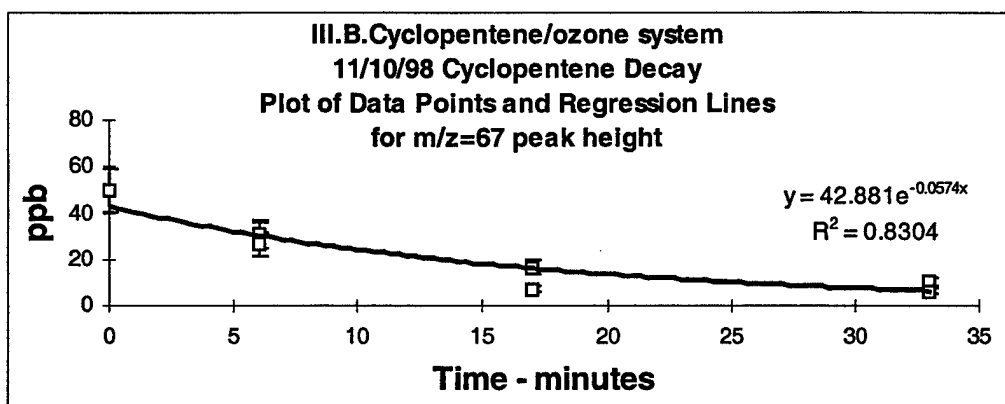
October 10, 1998; Figure 77

Cyclopentene was added to the chamber at a level of 50ppb for this nucleation study. Samples for t=0 were not taken before initiating the reaction since 100ppb ozone was added prior to the 50ppb of cyclopentene. The t=0 value was derived from the regression of the other data points. 5-minute samples were taken at 5 and 11 minutes; 10-minute samples at 16 and 27 minutes, and a 20-minute sample at 37 minutes. The results are shown with an exponential trendline indicating a 17-minute time constant. KI filters were not in place at this time.



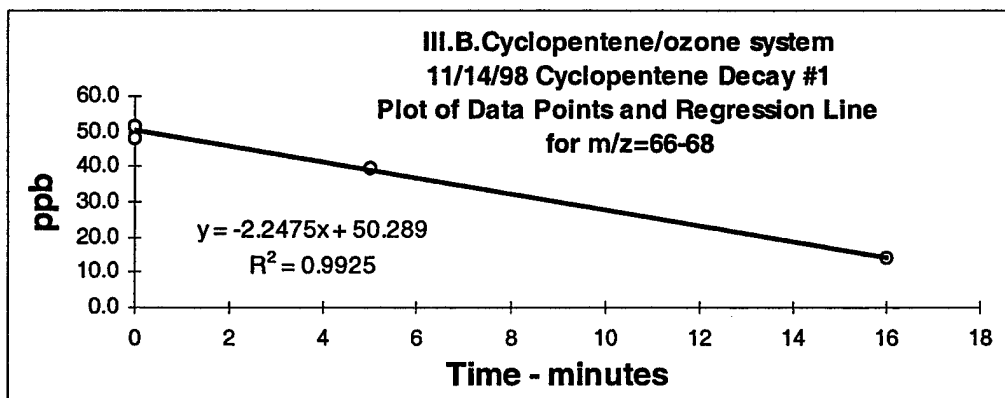
November 10, 1998; Figure 78

Cyclopentene was added to the chamber at a level of 50ppb for a nucleation study. SO₂ was present. A 10-minute t=0 sample was taken before ozone was added at 100 ppb to initiate a reaction. 10-minute samples were taken at 1, 12, 28 and 40 minutes into the reaction. KI filters were in place at this time. The 40-minute sample was not used due to the low level at this time. The results are shown with an exponential trendline indicating a 17-minute time constant. The R² value is a little low, but increases dramatically if the low 12-minute (17 minutes average) sample is omitted.



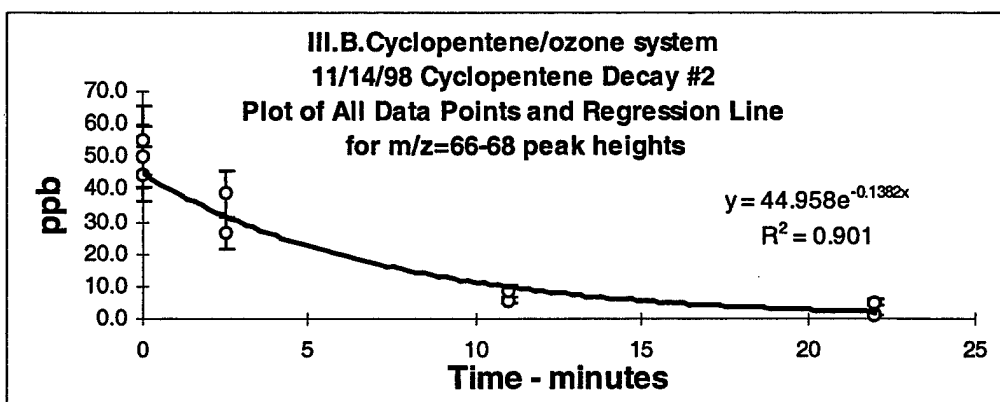
November 14, 1998; Figure 79

Cyclopentene was added to the chamber at a level of 50ppb for a nucleation study. The relative humidity was at 64%. A set of 10-minute t=0 samples was taken before ozone was added at 90ppb to initiate a reaction. 10-minute samples were taken at 0, 11, 22, 32 and 43 minutes into the reaction. KI filters were in place at this time. The 22, 32 and 43 minute samples were not used, due to an MS malfunction. A linear regression produced the best fit to this limited data set, however, yielding a time constant of approximately 14 minutes.



November 14, 1998; Figure 80

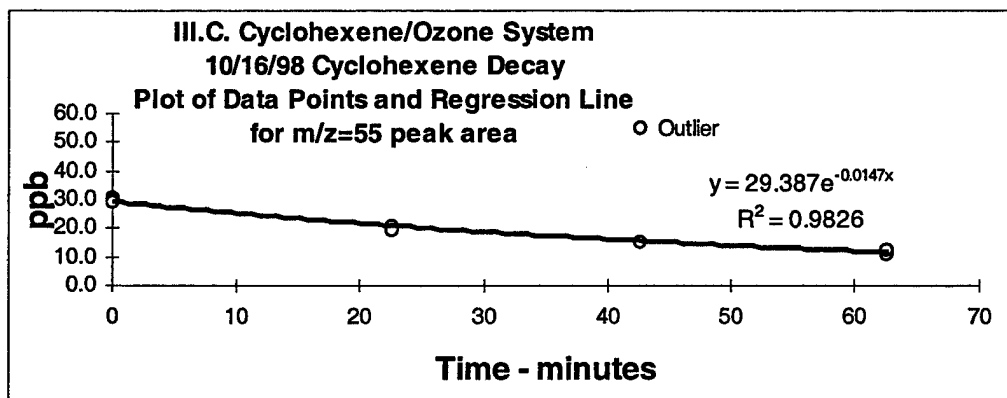
Cyclopentene was added to the chamber at a level of 50ppb for a nucleation study. The relative humidity was at 67%, and SO₂ was at 1ppb. A set of 10-minute t=0 samples was taken before ozone was added at 100ppb to initiate a reaction. A 5-minute sample was taken beginning at t=0 and 10-minute samples were taken at 6, 17, 28, 37, 60 and 78 minutes into the reaction. KI filters were in place at this time. Only samples through t=17 (22 minutes average) were included since cyclopentene could not be detected and/or quantified in later samples. The reaction appeared to be quite fast as evidenced by the 7-minute time constant as shown in the plot below.



E.3 Cyclohexene/Ozone System

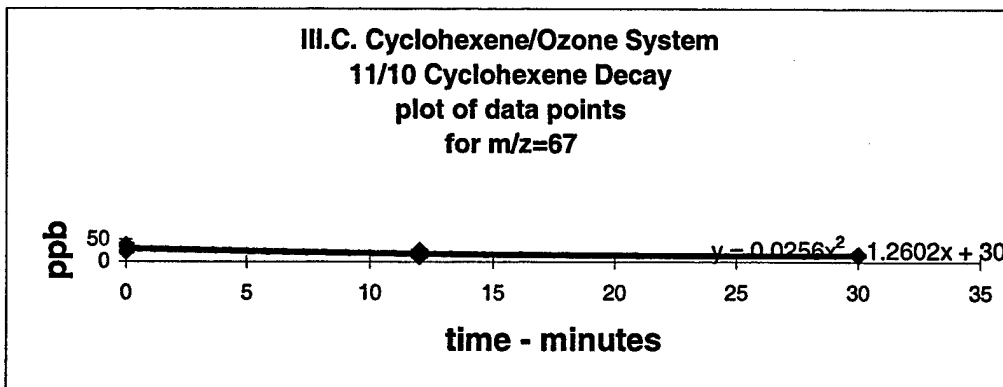
October 16, 1998; Figure 81

The chamber was charged with 30ppb cyclohexene for this nucleation experiment. A set of 5-minute t=0 samples was taken, then ozone was injected into the chamber at a level of 135ppb. 5-minute samples were then taken at t=20, 40 and 60 minutes. KI filters were not in place at this time. The decay curve fits an exponential regression with a 68-minute time constant.



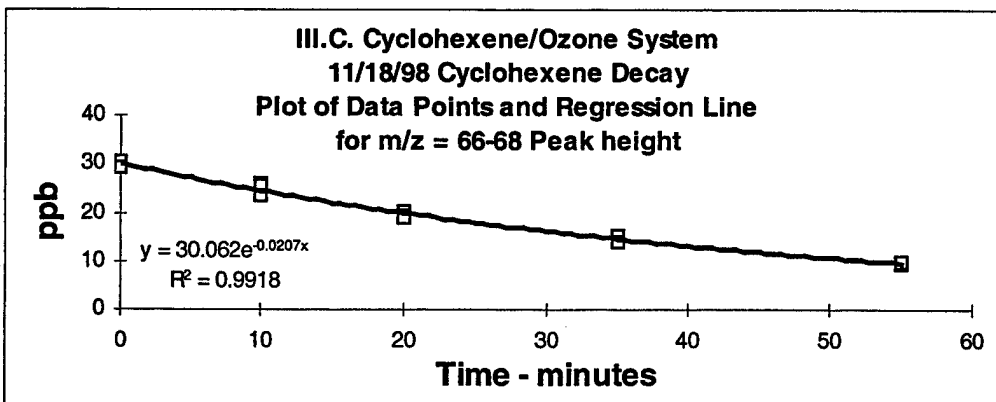
November 10, 1998; Figure 82

The chamber was charged with 29ppb cyclohexene for this nucleation experiment. The relative humidity of the chamber was 31%, and ammonia was present. A set of 10-minute, $t=0$ samples was taken; then ozone was injected into the chamber at a level of 170ppb. A 10-minute sample was then taken at $t=7$ and an 18-minute sample was taken at 21 minutes. KI filters were not in place at this time. The decay curve as shown approximates a 2nd order polynomial fit, which would indicate a leveling off at 37% of the original concentration in 25 minutes. The reason for the spread in analytical results for $t=0$ and $t=7$ -minute samples is unclear.



November 18, 1998; Figure 83

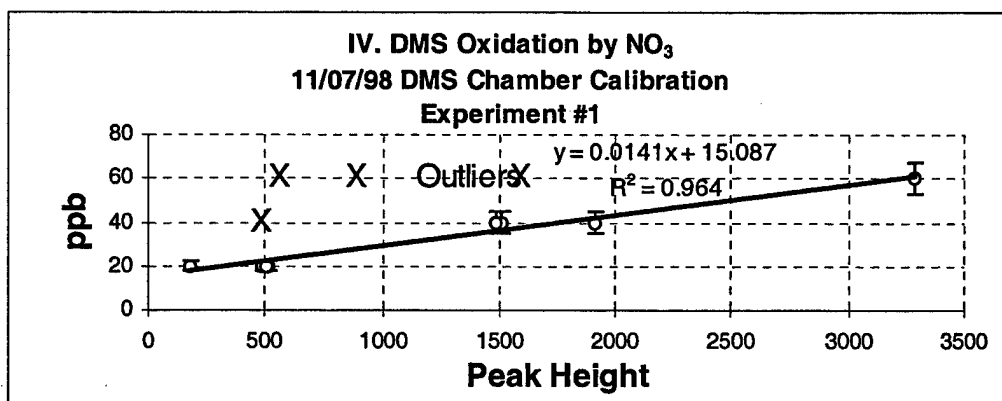
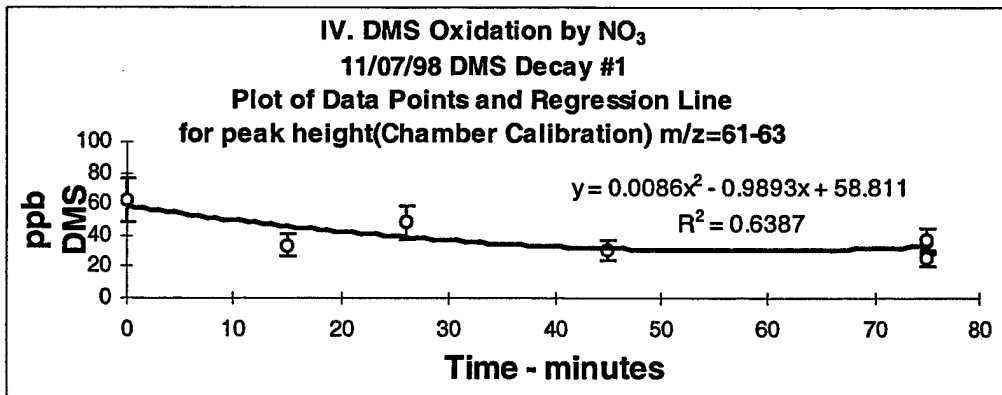
The chamber was charged with 30ppb cyclohexene for this nucleation experiment. The relative humidity of the chamber was 29%, and SO_2 was present at 2.5ppb. A set of 10-minute $t=0$ samples was taken, then ozone was injected into the chamber at a level of 165ppb. 10-minute samples were then taken at $t=5, 15, 30$ and 50 minutes. KI filters were in place at this time. The decay curve fits an exponential regression with a 48-minute time constant.



E.4 DMS Oxidation by NO₃

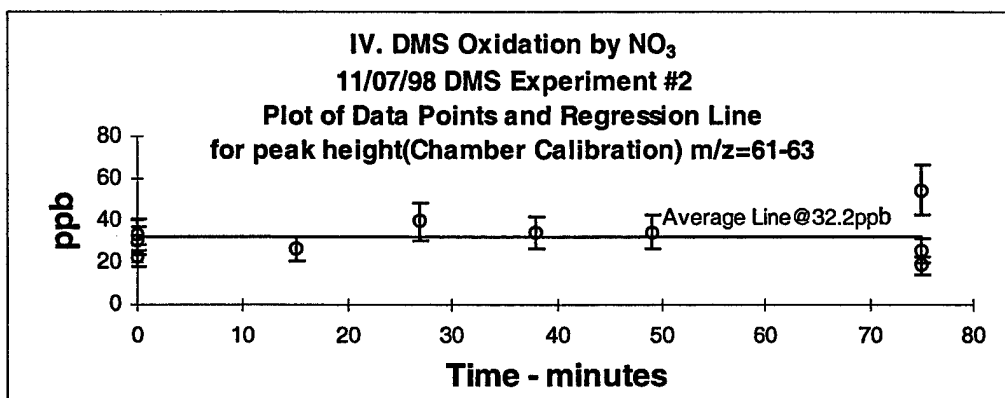
November 7, 1998 part 1; Figures 84a and 84b

The DMS was added in three increments of 20 ppb each to allow a calibration check. Four sorbent tubes were taken at each calibration level (i.e., 20, 40 and 60 ppb) for a total of 12 samples. The samples taken at the 60 ppb level were extremely variable, and three of them were not used in the calibration. One of the 40 ppb samples was also dropped from the calibration. The nucleation study began after sampling the 60 ppb atmosphere, which contained NO at 2 ppb and CH₂O at 10-15 ppb. The UV lamps were turned on to initiate the reaction. 10-minute samples were taken at 10, 21, 40 and 70 minutes into the reaction. The figure below shows the data approximates a 2nd order polynomial with decay to 50% of original in 57 minutes. Figures 84b shows the calibration of the three DMS levels prior to the test.



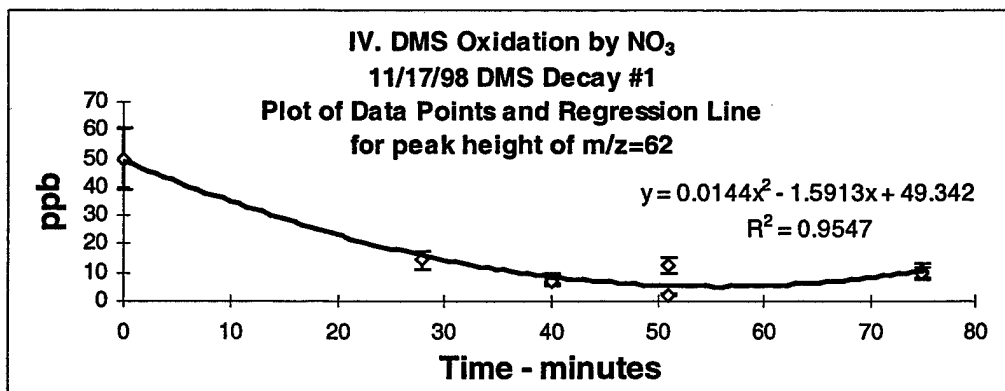
November 7, 1998 part 2; Figure 85

A second experiment began by using the atmosphere already existing in the chamber. NO_2 was added to the chamber at 50 ppb followed by 160 ppb O_3 to initiate the reaction. 10-minute samples were taken just prior to beginning, as well as at 10, 22, 33, 44 and 70 minutes. There is scatter in the data, but there appears to be no appreciable reaction.



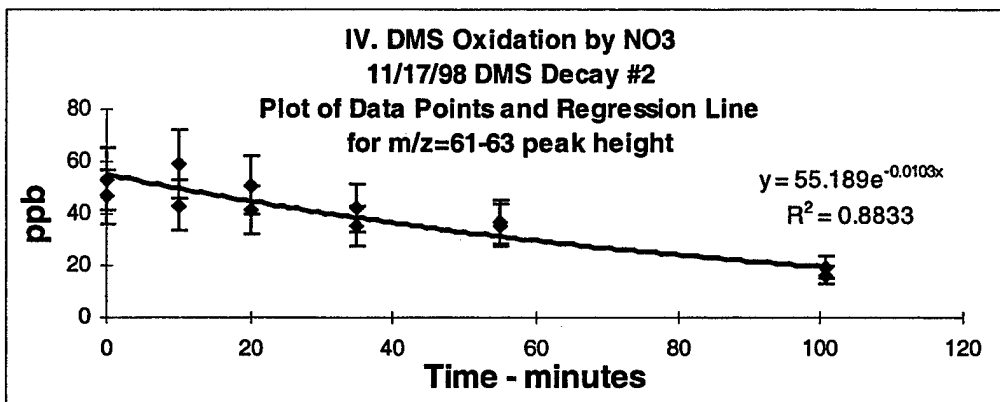
November 17, 1998 #1; Figure 86

The DMS was added at 50ppb for this nucleation study. The nucleation study was begun after sampling the atmosphere, which contained NO_2 at 32ppb and had a relative humidity of 39%. Ozone was added at 110ppb to initiate reaction. 10-minute samples were taken at 23, 35, 46 and 70 minutes into the reaction. KI filters were in place at this time. The chart below shows that the data approximates a 2nd order polynomial with decay to 11% of original in 55 minutes. The apparent slight rise for the 70-minute (75 minutes average) point is presumably coincidental, and more likely a "leveling off".



November 17, 1998 #2; Figure 87

The DMS was added at 60ppb for this nucleation study. The nucleation study was begun after sampling the atmosphere, which contained NO₂ at 50ppb and had a relative humidity of 60%. Ozone was added at 220ppb to initiate reaction. 10-minute samples were taken at 5, 15, 30, 50 and 96 minutes into the reaction. KI filters were in place at this time. The chart below shows that the data fits an exponential decay with a time constant of 100 minutes.



F. Heterogeneous Reaction of SO₂ with Sea-Salt Aerosol

10/22: A 10min. background sample taken at 08:36 showed an estimated 4ppb cumulative benzene compounds.

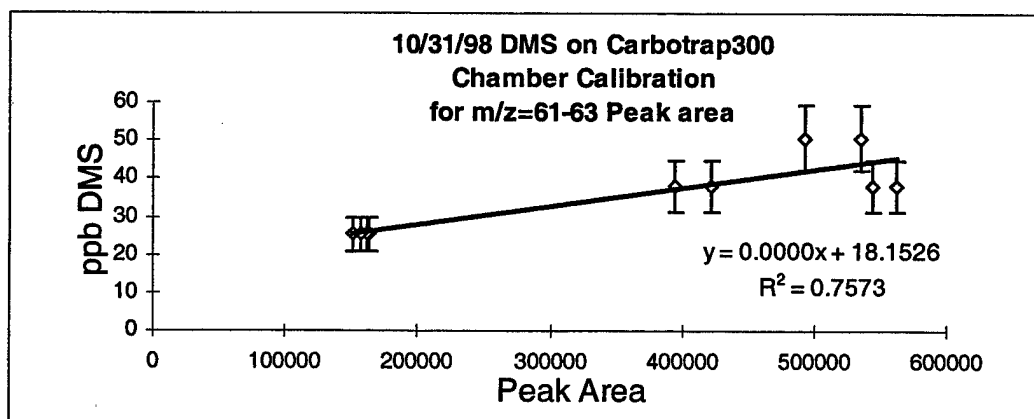
Appendix A

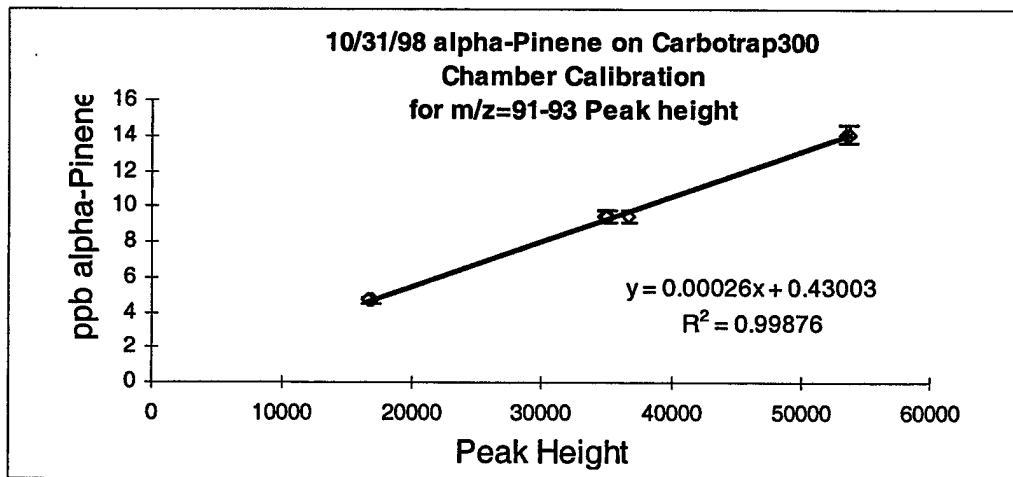
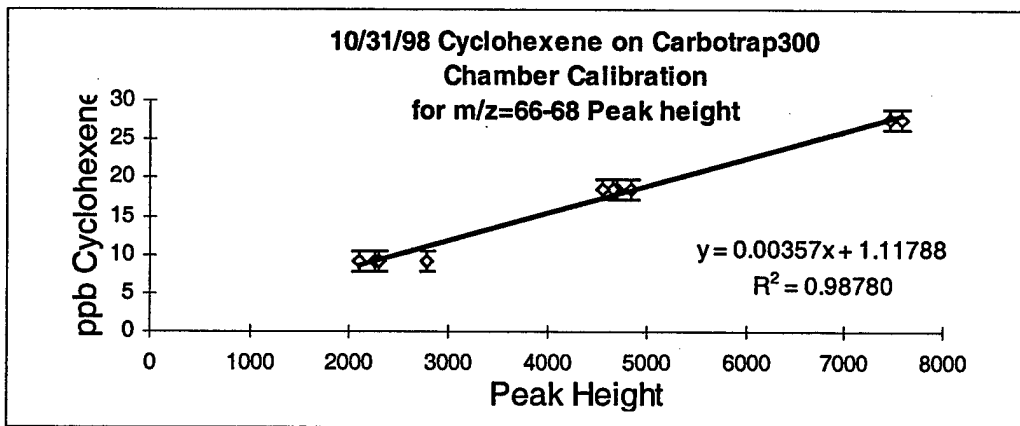
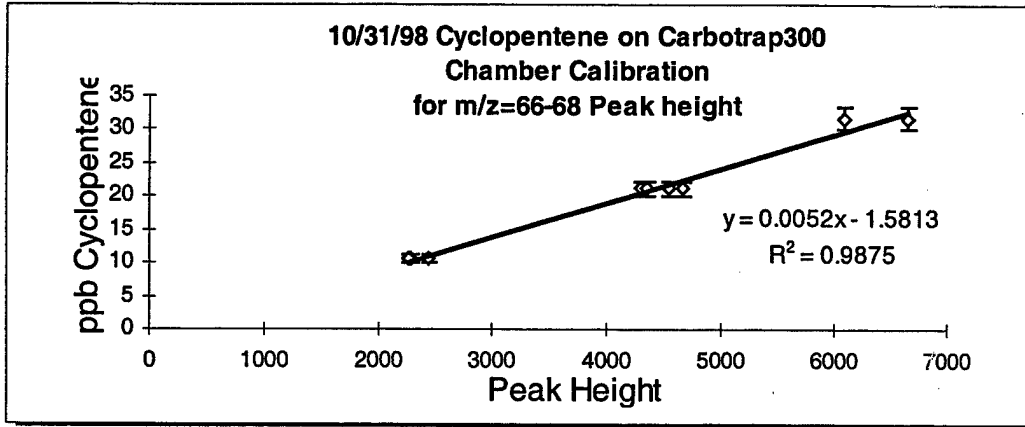
In-chamber Calibrations

Two sets of chamber calibrations were run in conjunction with the experiments. The first set was run on 10/31/98 between the two 3-week test series. This first set was run by introducing the four components at one time for each level, with successive additions incrementing the total concentration. The second set was run a little differently and ran from 1/19/99 through 1/21/99. Alpha-pinene and DMS were injected into the chamber at the same time on 1/19 in four increments. Tenax-TA tubes were used to sample for alpha-pinene using a 5-minute sample time. Carbotrap-300 tubes were used to sample the DMS and additionally the alpha-pinene for comparison with the Tenax-TA results using a 10-minute sample time. Cyclohexene additions were made on 1/20/99, also at 4 levels. Finally 4 additions of cyclopentene were made on 1/21/99. The tables below list the levels of components calibrated. Figures are shown along with tables of components/concentrations.

October 31, 1998

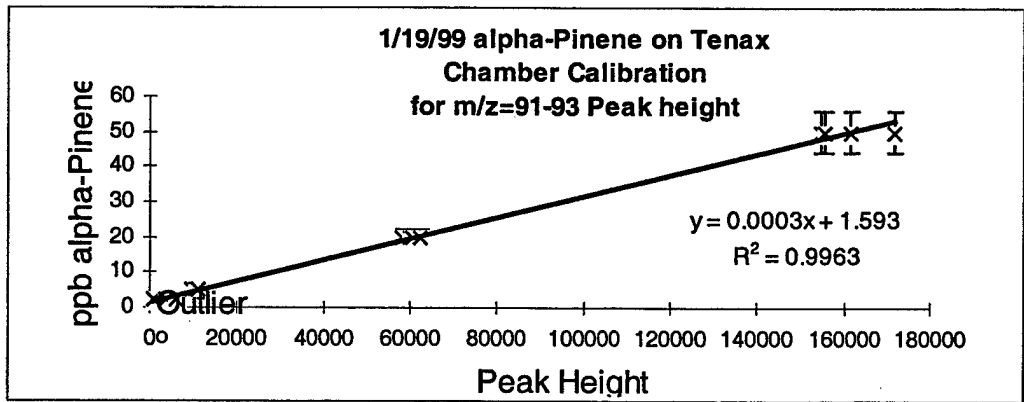
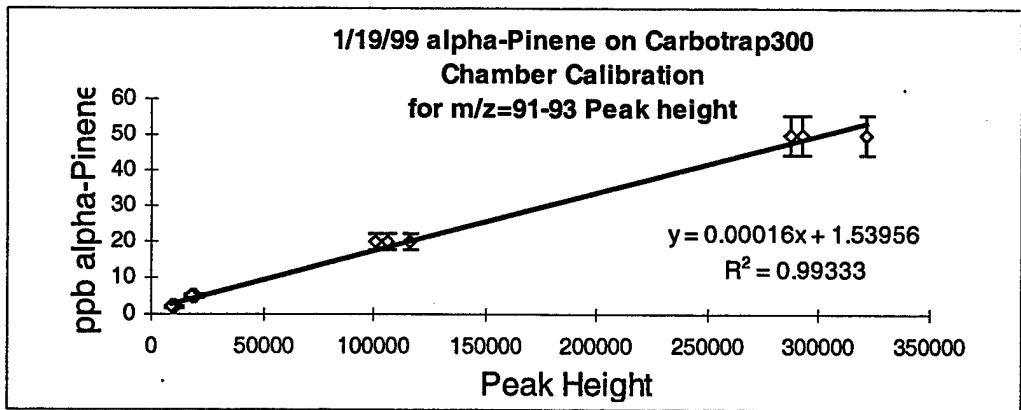
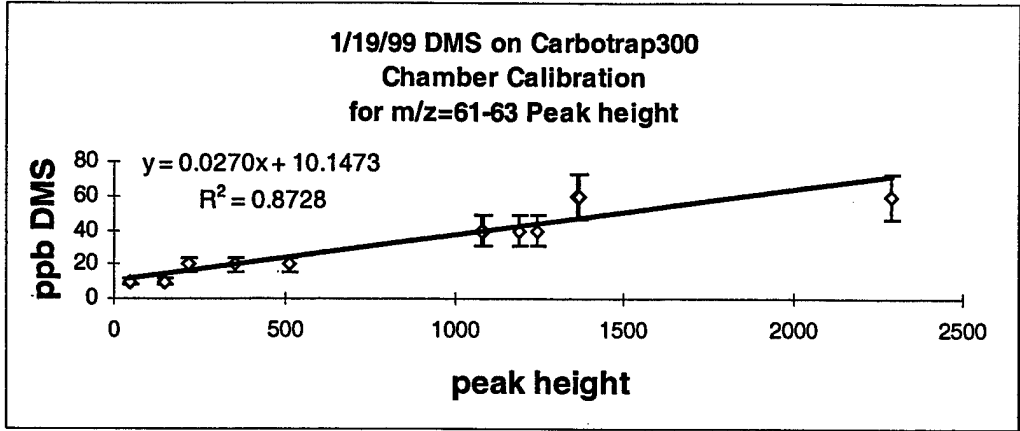
ppb	<u>DMS</u>	<u>cyclopentene</u>	<u>cyclohexene</u>	<u>alpha-pinene</u>
Level 1	25.4	10.6	9.2	4.7
Level 2	38.1	21.2	18.4	9.4
Level 3	50.8	31.7	27.6	14.1





January 19, 1999

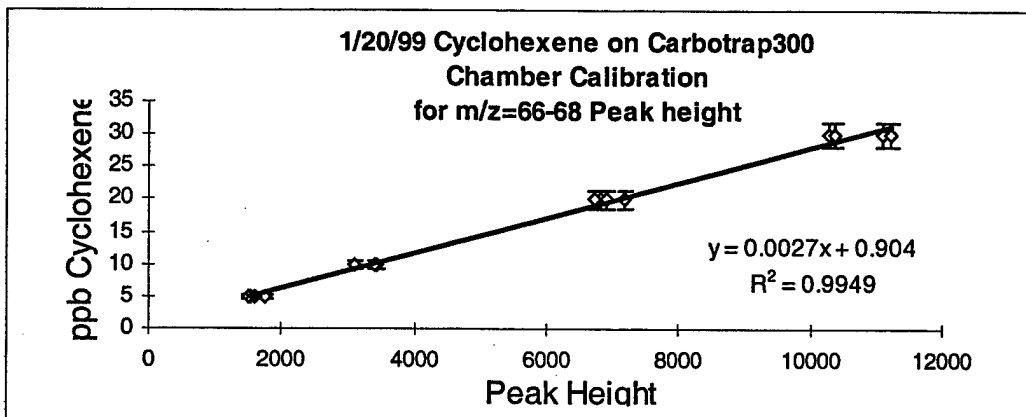
ppb	DMS	alpha-pinene
Level 1	10	2
Level 2	20	5
Level 3	40	20
Level 4	60	50



Note: The Carbotrap-300 tubes represent 10 min. samples(1.32L), whereas the Tenax-TA tubes represent 5 min. samples(0.66L). The unit response, therefore, for alpha-pinene is the same for both types of tubes. Not only are the slopes proportional, but the intercepts are nearly identical.

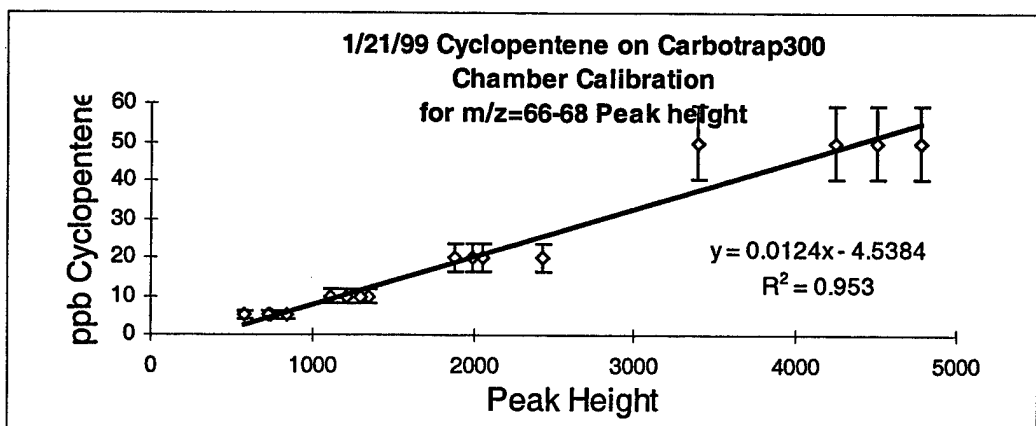
January 20, 1999

<u>ppb</u>	<u>cyclohexene</u>
Level 1	5
Level 2	10
Level 3	20
Level 4	30



January 21, 1999

<u>ppb</u>	<u>cyclopentene</u>
Level 1	5
Level 2	10
Level 3	20
Level 4	50



References

1. Hoppel et al, April 1999: Report on the Characterization of Calspan's 600 m³ Chamber in Preparation for the NOPP Aerosol Processes Experiments. *Naval Research Laboratory*, NRL/MR/6110—99-8370.
2. Chylek, P., 1978: Extinction and Liquid Water Content of Clouds. *J. Atmos. Sci.*, **34**, 296-300.