

Maine Department of Environmental Protection

SUMMARY OF THE 2006 RIDOHL ACROLEIN ANALYSIS STUDY

Revision of June 21, 2007

OBJECTIVES:

Near Term – 8 Samples to Rhode Island (RIDOHL): Maine DEP currently lacks the necessary lab equipment to accurately measure Acrolein in its TO-15 HAP samples. A substantial capital outlay is necessary to upgrade the laboratory equipment. Before proceeding with the capital upgrade, MEDEP intends to send eight samples to the RI laboratory to make sure that ambient levels of Acrolein will be found at levels above the detection limits for the equipment that will be purchased. This will include four sample canisters from the Rumford area, and four from Portland (EMPACT site). MEDEP intends to send the samples to the Rhode Island lab during the fall of 2006.

JUNE 2006 RIDOHL - approval to analyze 8 cans, 4 from Rumford, 4 from Portland's EMPACT site to screen for the presence of Acrolein and at what concentrations. Before doing an analysis on these cans they would reduce the pressure to 4 psi. MEDEP must analyze the cans first before they are shipped to RIDOHL in order to get their HAPS results.

AUGUST/SEPTEMBER 2006 – Silco glass lined canisters were purchased and phased into MEDEP's clean can analysis process to prepare them for the Acrolein sampling events. MEDEP had to clean them in their laboratory and analyze them for a cleaning certification on their analytical system to fulfill their HAP's sampling requirements. Since they are conducting the clean certification requirements for TO/15 compounds it was thought that RIDOHL would not have to re-analyze them as clean a second time to meet their needs for the cleaning certifications.

While preparing the canisters for cleaning certifications MEDEP struggled to get their analytical system fully operational after their attempts to analyze for Acrolein back in April 2006. The New England EPA lab that often supports MEDEP when they are experiencing instrument problems was unavailable to provide these services because they too were experiencing analytical system malfunctions of their own. MEDEP had to wait until they could get things operational again before Acrolein sampling could begin.

OCTOBER 2006 – MEDEP has a sampling protocol that is more extensive than some of the protocols established today. MEDEP does not use a blank to represent the clean can backgrounds from a group or batch of cans. Instead, every can gets a complete analysis after a cleaning to establish the level of background contaminants in each canister before it goes out into the field. This goes beyond having one can chosen as a blank to represent an entire batch of cans cleaned at one time. Since we were analyzing all of the cans as clean for the TO/15 compounds that our system provides we did not anticipate the need to ship blanks to the RIDOHL.

After we were ready to begin sampling for Acrolein, RIDOHL suggested sending a blank with the planned sample events so they could check the can backgrounds with their analytical instrument. MEDEP had to work out a system to accommodate. Since it wasn't suggested earlier in the study, an adequate supply of Silco glass lined cans needed to include the blanks was not purchased or cleaned in their respective batches. MEDEP had to borrow Silco cans planned for future sampling events to provide RIDOHL with blanks for the first two samples. As a result of this, sample events had to be skipped until new cans arrived and were worked into the schedule to cover the remaining sample events for the intended study. After the first two samples were analyzed by RIDOHL, they too experienced some instrument malfunctions of their own and had to put MEDEP's project on hold until they could get their instrument back online.

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NOVEMBER 2006 – We took advantage of the time that the RIDOHL was offline to get a better understanding of what we would expect to happen when trying to sample for Acrolein. RIDOHL felt that the sampling protocols and the ways in which the sample is handled in a canister environment play a major role as to how much Acrolein is really measured in a sampling event. RIDOHL learned from their experiences that such things as sample hold times, and contamination in the canister itself may be effecting the Acrolein results. For instance as hold times increased they found increased levels of Acrolein in their results. They also conducted some canister media comparison studies of their own and determined that it may not necessarily be the canister media (i.e. Silco glass lined vs. Summa Polished) that plays a role in the increased levels of Acrolein but perhaps the canister itself. If there are active sites on the canister walls that do not clean well that provides more opportunity for contaminants to remain in the can that may react to inflate the Acrolein levels after they are collected.

After discussing the effects of different hold times on the Acrolein sample results with RIDOHL, it was decided that RIDOHL would receive the sample canisters from the MEDEP sites a.s.a.p. MEDEP would analyze them when they were returned if there was enough pressure remaining in the sample. Worst case scenario would be to substitute RIDOHL's data into MEDEP's database to fulfill MEDEP's commitment to analyze their samples for their HAP's monitoring program.

Since MEDEP has more of the Summa Polished canisters in their inventory they thought it would be worth looking at some samples collected in these types of canisters and comparing them with the samples collected in Silco glass lined canisters. If MEDEP were to monitor for Acrolein on a full time basis then they wanted to have some way of knowing how the Summa Polished canisters would work in an Acrolein sampling program. If it is determined that they are not appropriate then a considerable investment would have to be made to purchase more Silco glass lined canisters for future sampling.

To achieve this task of comparing the two types of canister media, MEDEP arranged to ship the Portland EMPACT sites collocated sample to RIDOHL along with the reporting sample. One sampler would always use a Summa Polished canister and the other would have the Silco glass lined canister. Everything else regarding the sample remained the same. Each sampler operated at the same flow rate, times and sampling dates.

To further assess how contamination plays a roll in the Acrolein results, MEDEP would continue to send blanks. However, the blanks would be cleaned in the same group as the sample cans. MEDEP would continue to analyze every can as clean using their analytical system which captures the TO15 compounds. The blank would be treated as though it were a sample can and would be evacuated with the sample cans leaving it under vacuum until the intended sample date. On the sample date or as close to it as possible, it would be filled with the nitrogen used to clean the cans originally. This would allow us a chance to observe how much activity occurred within the canister environment in between sampling and analysis. If there were any compounds residing in the cans that are not detected in the cleaning certifications then we would have some way of knowing how much they contribute to the Acrolein levels.

As we began to understand all of the variables within the sampling protocols that affect the Acrolein levels in a canister environment we thought it would be better if we could gather more samples than originally planned. Since we had experienced some difficulties in our first attempts to gather 4 samples from two sites we asked if we could increase the number of sampling events. RIDOHL did not have a problem with our request to extend the amount of samples taken for our study. We were able to begin sampling in November and continue through the entire month of December. The following table contains the sample events and analysis information for the Acrolein study conducted by MEDEP and analyzed by RIDOHL.

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SIP DATE	SITE	S/N	CLEAN DATE	SIP/FILL DATE	SHIP DATE	RIDOHL ANALYSIS DATE	MEDEP ANALYSIS DATE	ME #####	RIDOHL 2nd analysis	RIDOHL 3rd analysis
*10/8/06	Blank	2464	09/28/06	10/11/06	10/17/06	10/23/06	*N/A	ME00883		
	RAP	2521	08/09/06	10/08/06	10/17/06	10/23/06	10/16/06	ME00869		
	EMP#2	22151	08/09/06	10/08/06	N/A	N/A	10/25/06	ME00865		
	EMP#1	2523	08/09/06	10/08/06	10/17/06	10/23/06	10/16/06	ME00866		
*Did not use this data, Blank from different batch. N/A - MEDEP was not able to analyze these cans.										
*10/14/06	RAP	13049	09/28/06	10/14/06		01/03/07	10/30/06	ME00887		
* This sample was not part of the intended study. We did not have silco cans available for this sample event and we intended to skip the Acrolein sample for this SIP date. IT was actually a can we requested RIDOHL to analyze as part of a split analysis comparison study we did with the NEEPA lab. NOTE THE HIGH LEVELS OF ACROLEIN. THIS MAY BE DUE TO THE LONG HOLD TIMES. NEEPA AND MEDEP ANALYZED THE CAN FIRST INCREASING THE HOLD TIME TO 81 DAYS UNTIL THE RIDOHL ANALYSIS.										
*10/20/06	Blank	2560	10/18/06	10/20/06	10/24/06	10/25/06	11/06/06	ME00905		
	RAP	2467	10/11/06	10/20/06	10/24/06	10/25/06	11/06/06	ME00899		
	EMP#2	2522	10/11/06	10/20/06	10/23/06	10/25/06	11/06/06	ME00895		
	EMP#1	No can available for this sampler for this SIP sample date.								
*Did not use this data, Blank from different batch.										
RIDOHL instrument was down for repairs so we re-grouped and started back up in November. We decided to use blanks from the same cleaning run that the sample cans were taken from whenever possible. We also decided to evacuate the blanks with the sample cans and hold them evacuated until the SIP date. If possible they were filled on the SIP day or as close to the SIP day as possible if it occurred on a holiday or weekend.										
11/19/06	Blank	2521	10/30/06	11/20/06	11/20/06	11/24/06	*N/A	ME00918	12/5/2006	
	RAP	2464	10/30/06	11/19/06	11/20/06	11/24/06	12/18/06	ME00917	12/5/2006	
	EMP#2	2523	10/30/06	11/19/06	11/20/06	11/24/06	*N/A	ME00916	12/5/2006	
	EMP#1	10872	10/30/06	11/19/06	11/20/06	11/24/06	12/20/06	ME00913	12/5/2006	
*N/A - MEDEP not able to analyze these cans.										
11/25/06	Blank	2467	11/07/06	11/27/06	11/27/06	12/05/06	12/18/06	ME00921		
	RAP	2559	11/07/06	11/25/06	11/27/06	12/05/06	*N/A	ME00920		
	EMP#2	2560	11/07/06	11/25/06	11/27/06	12/05/06	*N/A	ME00919		
	EMP#1	14103	10/24/06	11/25/06	11/27/06	12/05/06	*N/A	ME00907		
*N/A - MEDEP not able to analyze these cans.										
12/1/06	Blank	2465	11/07/06	12/01/06	12/04/06	12/07/06	12/27/06	ME00924	12/18/2006	
	RAP	2524	11/07/06	12/01/06	12/04/06	12/07/06	12/27/06	ME00923	12/18/2006	
	EMP#2	2561	11/07/06	12/01/06	12/04/06	12/12/06	12/27/06	ME00922	12/18/2006	
	EMP#1	10868	10/24/06	12/01/06	12/04/06	12/12/06	12/27/06	ME00908	12/18/2006	
12/7/06	Blank	2522	11/08/06	12/07/06	12/08/06	12/11/06	12/27/06	ME00926	12/18/2006	
	RAP	2466	11/08/06	12/07/06	12/08/06	12/11/06	12/27/06	ME00927	12/18/2006	
	EMP#2	2562	11/08/06	12/07/06	12/11/06	12/14/06	12/27/06	ME00925	12/18/2006	
	EMP#1	22154	11/08/06	12/07/06	12/11/06	12/15/06	12/27/06	ME00930	12/18/2006	
12/13/06	Blank	RI1462	11/21/06	12/13/06	12/13/06	12/14/06	01/22/07	ME00948	12/15/2006	12/28/2006
	RAP	RI1441	11/21/06	12/13/06	12/14/06	12/15/06	01/22/07	ME00947	12/28/2006	
	EMP#2	RI1453	11/21/06	12/13/06	12/14/06	12/15/06	01/22/07	ME00946	12/28/2006	
	EMP#1	10812	11/21/06	12/13/06	12/14/06	12/15/06	01/22/07	ME00945	12/28/2006	
*12/16/06	CKP	10757	11/21/06	12/13/06		01/03/07	12/20/06	ME00944		
* This sample was not part of the intended study. It was actually a can we requested RIDOHL to analyze as part of a split analysis comparison study we did with the NEEPA lab.										
*12/19/06	Blank	RI119	11/28/06	12/19/06	12/20/06	12/21/06	01/23/07	ME00950	12/21/2006	
	RAP	RI1444	11/28/06	12/19/06	12/20/06	12/21/06	01/22/07	ME00949	12/28/2006	
	EMP#2	RI1445	11/28/06	12/19/06	12/20/06	12/21/06	01/22/07	ME00951	12/28/2006	
	EMP#1	10869	11/28/06	12/19/06	12/20/06	12/21/06	*N/A	ME00952	12/28/2006	
* Contamination noted in blank, did not use this run since all cans are cleaned with blank.										
*N/A - MEDEP not able to analyze these cans.										
12/25/06	Blank	2559	12/14/06	12/26/06	12/26/06	12/28/06	01/25/07	ME00961	1/3/2007	
	RAP	2560	12/14/06	12/25/06	12/26/06	12/28/06	01/25/07	ME00962	1/3/2007	
	EMP#2	2523	12/14/06	12/25/06	12/26/06	12/28/06	01/25/07	ME00963	1/3/2007	
	EMP#1	21558	12/14/06	12/25/06	12/26/06	12/28/06	01/25/07	ME00964	1/3/2007	
*12/31/06	Blank	2467	12/21/06	01/02/07	01/02/07	01/03/07	01/25/07	ME00967		
	RAP	2464	12/21/06	12/31/06	01/02/07	01/03/07	01/25/07	ME00968		
	EMP#2	2521	12/21/06	12/31/06	01/02/07	01/03/07	01/25/07	ME00969		
	EMP#1	13050	12/21/06	12/31/06	01/02/07	01/03/07	*N/A	ME00970		

*** Did not use these results since EMP#1 looks like an outlier. We suspect the summa canister is old and may have some active sites that do not clean well anymore. This could increase the contamination in the can that may react to increase the Acrolein levels. We will ship the can to RIDOHL as cleaned blank again to see if it happens again.**

*N/A - MEDEP not able to analyze these cans.

SUMMARY OF THE RESULTS:

This particular study set out to establish if the Rhode Island Department of Health Lab (RIDOHL) would find levels of Acrolein that they could accurately measure above their instruments detection limits in Maine's Ambient Air to help us evaluate the need to purchase new equipment in the future. It also evolved to determine if hold times and contamination levels in the blanks influenced Acrolein measurements, test the differences between two types of canister media used in the sampling method and compared Acrolein values to 1,3-Butadiene.

RIDOHL was able to detect the presence of Acrolein at levels that exceed Maine's Ambient Air Guideline of (0.009ppb/v) in all of the samples collected from the Portland and Rumford areas. The levels measured were detected well above the instruments method detection limit (MDL) of (0.045 ppb/v). To make accurate measurements, the detection levels must occur between the ranges used to calibrate the instrument. The Acrolein results measured in this study were detected below the lowest calibration standard in the extrapolated portions of the instruments calibration curve so they are considered estimated.

Most of the instruments used today are very capable of measuring results at the levels where we are finding Acrolein but it is often qualified because the measurements cannot be verified against a calibration curve. In fact most of the HAP's data measured in the environment on the National level is highly qualified or flagged.

One reason for this is that the master standards that are available on the market today are well above the concentrations needed to calibrate an instrument for the ranges where HAP's compounds are measured. When these gases are mixed to generate the levels needed for a calibration curve, the amounts of dilutions used to mix these standards will create inaccuracies. Gas companies are just beginning to conduct research on the stability's of these compounds as they are mixed at the lower concentrations needed for these types of programs. In reality, until they are verified all of the data below the lowest calibration standard for any given instrument must be considered estimated.

The following illustrates the detection capabilities of the RIDOHL instrumentation and compares them to the level established in Maine's Ambient Air Guidelines.

Laboratory Chemical CAS #	MDL (ppb/v)	Lowest	Highest	Qualified Region Estimated Concentrations (ppb/v)	Quantified Region Accurate Concentrations (ppb/v)	Ambient Air Guideline (ppb/v)
		Calibration Standard (ppb/v)	Calibration Standard (ppb/v)			
RIDOHL Acrolein 107-02-8	0.045	0.422	10.25	0.045 -0.422	0.422-10.25	0.009

The levels established in the guideline are actually below the detection limits of the RIDOHL instrument. Anything that is below 0.045ppb/v is considered to be undetectable. Measurements detected above the MDL and below the lowest calibration standard are considered estimates and are normally qualified. All detection's found within the ranges of the instruments calibration curve are considered accurate quantifiable measurements. (Figure 1.)

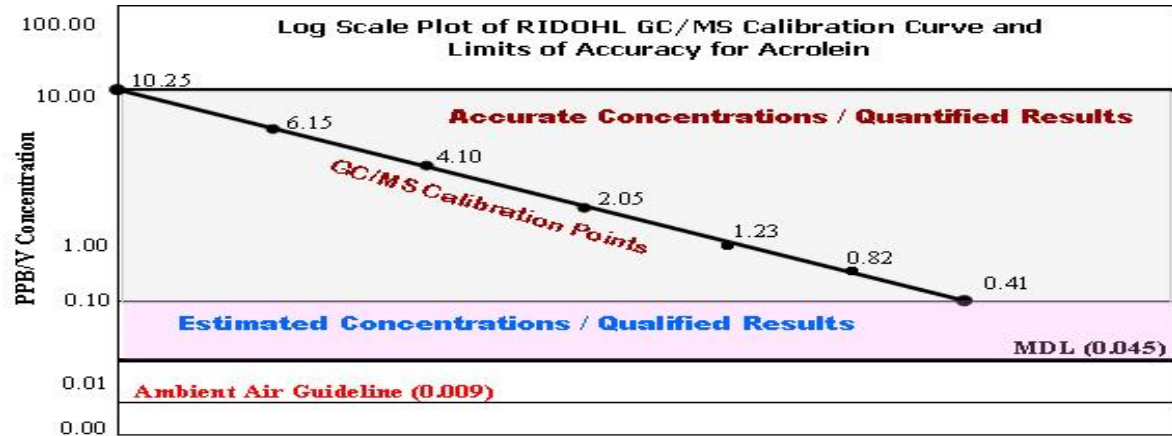


Figure 1. - Illustrates where the estimated regions are on the RIDOHL calibration table. RIDOHL uses 7 standards ranging from 0.41ppb/v to 10.25 ppb/v. All data detected above their MDL and below the lowest calibration standard are considered estimated.

ACROLEIN RESULTS FOR THIS STUDY:

These results were taken from a very small but extremely good set of sampling events. Most notably, we have an extraordinary group of individuals performing this analytical task who are by far the most experienced group of professionals in the country.

Except on two occasions, the levels detected by the RIDOHL are well below their lowest calibration standard. This being said, it would be very difficult to present the results from this data set by giving you a quantitative measurement. Like most of the HAP's compound that we analyze for today, these values are to be considered as qualitative measurements.

Due to the instabilities of Acrolein when it is collected in a canister media, it was much more difficult to estimate so we provided a different kind of assessment for these results. The following table (Figure 3.) gives a visual representation of the data in a chart and table format. The results in the chart and table represent the analytical results. Once we determined what types of variables affect the results, we established a estimated range for these results and placed highlighted bar in the chart view to indicate where the estimated results for Acrolein actually are based upon our assessments of the data..

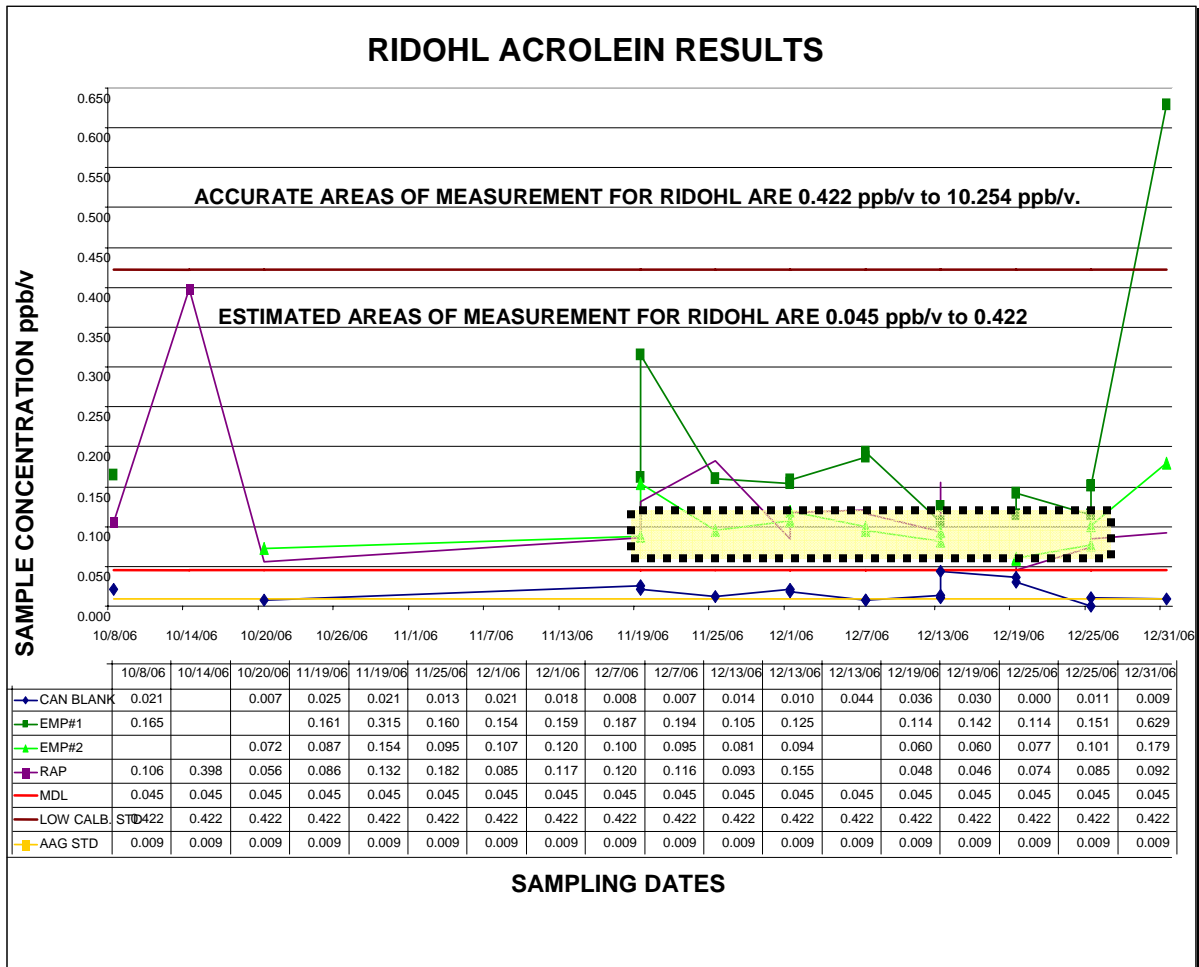


Figure 3. – Illustrates where we placed the highlighted bar in the chart view to indicate where the estimated results for Acrolein actually occur based upon our assessments of the data. This assessment took into consideration some of the known variables that may have influenced the results obtained for Acrolein in this study and omitted them from the final averages. The highlighted area on the chart represents our most conservative estimate for Acrolein.

FINAL RESULTS TABLE

SITE	Total # samples collected	Total # of Detections above AAG	Total # samples used for Averages	AVG. ppb/v	* NET AVGS. ppb/v	Ambient Air Guideline ppb/v	FINAL RESULTS Estimated Ranges		
							LOW -34% ppb/v	NET. AVG. ppb/v	HIGH +34% ppb/v
EMP#1	9	9	6	0.144	0.130	0.009	0.086	0.130	0.174
EMP#2	10	10	6	0.090	0.076	0.009	0.050	0.076	0.102
RAP	10	10	6	0.091	0.077	0.009	0.051	0.077	0.103
CAN BLANK	10	7	6	0.014	n/a	n/a	n/a	n/a	n/a

* NET AVGS. Are the total averages minus potential influences from the canister blank average in ppb/v.

Figure 4. - This table illustrates that we intentionally subtracted the blank averages from the final Acrolein results. In most assessments the blanks have little or no influence on the final results. In this particular instance, the blank average is above the Ambient Air Guideline established for Acrolein. Because contaminants in a canister have the potential to influence Acrolein results, we attempted to provide the most conservative results for the actual field samples. That is, provide results that are least likely to have false positives.

The conclusions we reached from the study is dependent on our approach to assessing the ranges of error for the instruments used to measure the results, choosing the sample events with Acrolein measurements least influenced by holding times, and elimination of outliers that could have been influenced by contaminants in the blanks or possible the canisters themselves.

OUR APPROACH TO ASSESSING THE RANGES FOR THE ACROLEIN ESTIMATES:

To make our assessments regarding the ranges of error for the instrument, we based our decisions on the RIDOHL recommendations. RIDOHL has been able to conduct test to evaluate how well their instruments measure in the extrapolated portions of their calibration curve. They have found that their Gas Chromatograph Flame Ionization Detector (GC/FID) and Gas Chromatograph Mass Spectrometer (GC/MS) are very linear. Based upon their results they have concluded that the ranges of error resulting from the instruments calibration are minimal. Since all of the results in the data set from RIDOHL came as an average as it was detected on both of these instruments, RIDOHL felt the best means of determining the ranges of error due to the instrumentation would be to look at its repeatability over long periods of time.

RIDOHL is currently working up the results from their co-located samplers for 2006 so it was not available for this report. Instead they provided results for 2005 (Figure 5) which they noted was very similar to what they are finding for 2006. This data shows how well the instrument estimates two samples taken from the same air mass on the same dates and times. Ideally, they should produce the same results. However, due to all of the variables known to influence these results, this is the best means we have of knowing how precise the instrument is when it estimates the values being measured in the extrapolated portions of the calibration curve that are illustrated in figure 1.

Precision data for 2005 East Prov VOC co-located samplers data in % diff		All data pairs with a non-detect are excluded				
		n	average	first quartile	median	third quartile
43505	acrolein	58	34%	15%	33%	46%

Figure 5.

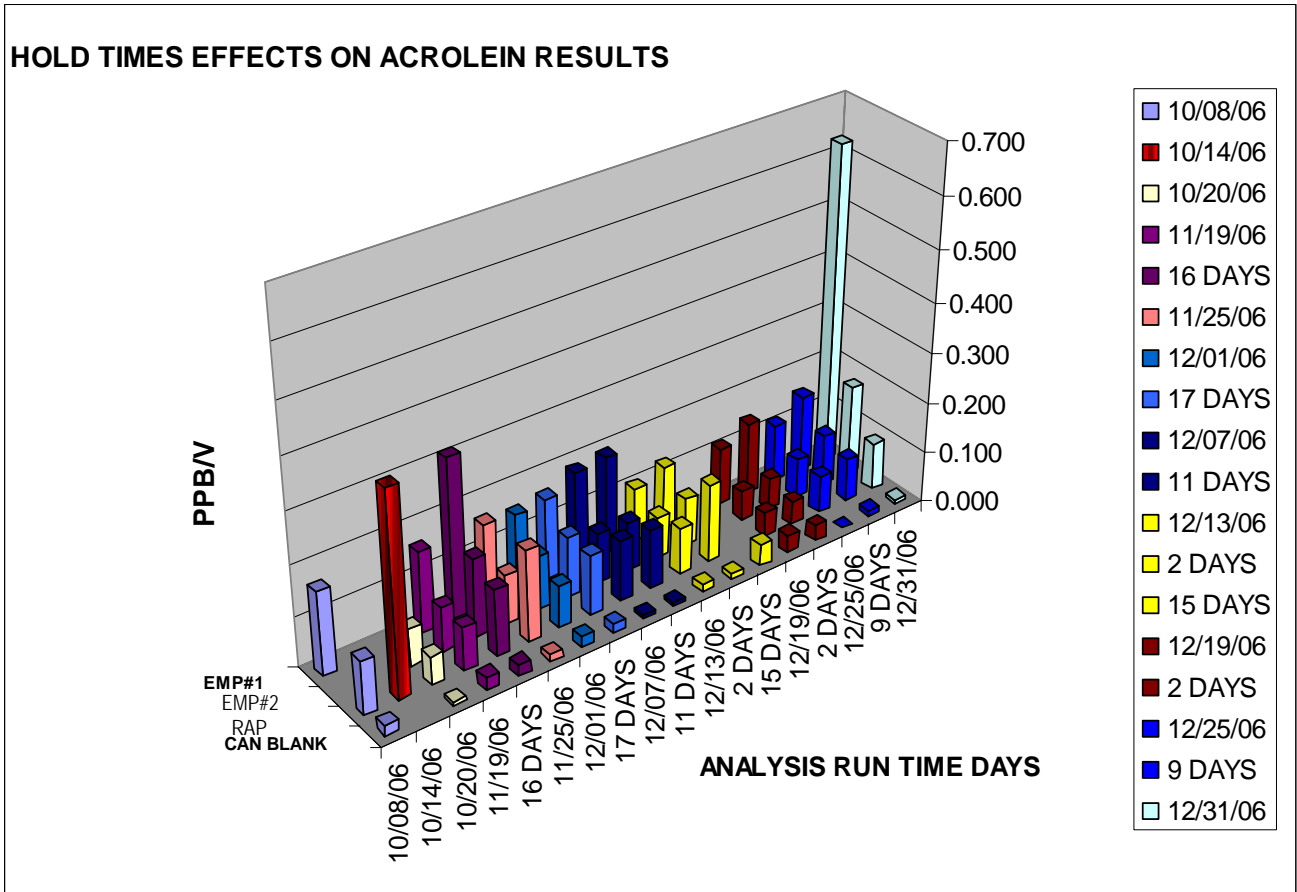
The average percent differences between the reporting and co-located sample results for an entire year range from 15 to 46 percent. The median for these was 33 percent and the entire year averaged out to 34 percent.

For data assessment purposes we established ranges for the estimated measurements based on the averages of the percent errors between the reporting and co-located samples from 2005. This takes into account other variables that we have not even considered at this time such as seasonal variation. Because RIDOHL has found that Acrolein levels tend to be greater during the PAMS season we feel we are including the most challenging pairs of precision results in the averages, thereby giving us a more realistic range of error for the instrumentation. When looking at the FINAL RESULTS TABLE you will find ranges indicating that the measurements could be as much as +/- 34% above or below the estimated averages.

SAMPLE HOLD TIME ASSESSMENTS

To make our decision regarding these assessments we were able to utilize information that was not factored into the original objectives for this study. We included replicate samples that were analyzed at different holding times and results that were not part of the intended study.

Some of these results are replicated runs from intended sampling events conducted at different hold times. We did not plan to include replicate analyses originally for this study. RIDOHL was concerned about the hold times for some of our samples because the analysis schedule was interrupted briefly when they experienced some hardware problems with their instrumentation. When they were not able to produce immediate results, they factored in the time differences between the sampling events and analyzed them a second time to determine if the Acrolein results were influenced by the longer hold times.



Several of the samples were analyzed on two different occasions and we found very little difference between the two results. What is interesting though is that the highest levels of Acrolein occurred in the sample results that had hold times beyond 10 days. You will also find two samples in this data set that were included that are not part of the intended sample events. While we were shipping cans for this study to

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RIDOHL we wanted to do some verification checks on two of our other canisters. What we later learned was interesting so we felt it was worth including. One of the two canisters (10/14/06) had a hold time of 81 days before it was analyzed by RIDOHL. The Acrolein value from this particular sample was at least two times higher than the ones reported with hold times under 10 days.

This sample result is very close to the RIDOHL lowest calibration standard. The closer these results are to being above the lowest calibration standard, the more accurate the results are for the Acrolein concentrations. If hold times were not influencing the results and/or the concentrations of the samples in the ambient air are as concentrated as with this particular event, then we would have no problem meeting the objects for this intended study.

Since this is such a small data set, it would be difficult to say for certain that there are real differences between the two data sets when the samples are analyzed within the first two weeks after collection. All we can do is make generalized assessments regarding these results. When we compared the 6 day averages to the 10 day averages for the Portland site, there was little or no difference between the results. When we compared these two averages for the Rumford site the 10 day hold time averages were slightly higher.

For data assessment purposes, based upon what the RIDOHL had experienced and what we learned regarding hold times from our sample set, we took the most conservative approach (that is erred on preventing false positives) and chose the results from all of the samples that were analyzed within one week of sample collection. Since there is only a slight difference in these averages between the one and two week intervals, we are confident that the one week hold times had little or no effect on the averages we collected for our data set.

ACROLEIN AVERAGES FOR ALL SAMPLES ANALYZED WITH HOLD TIMES OF 10 DAYS OR LESS							
(Maine Ambient Air Guideline for long-term exposure is .009 ppb/v)							
SIP SAMPLE DATES	11/19/06	11/25/06	12/01/06	12/07/06	12/13/06	12/25/06	AVG.
SITE	ppb/v	ppb/v	ppb/v	ppb/v	ppb/v	ppb/v	ppb/v
EMP#1 -summa can	0.161	0.160	0.154	0.187	0.105	0.114	0.147
EMP#2 - silco can	0.087	0.095	0.107	0.100	0.081	0.077	0.091
RAP - silco can	0.086	0.182	0.085	0.120	0.093	0.074	0.107
CAN BLANK - silco can	0.025	0.013	0.021	0.008	0.014	0.000	0.013

ACROLEIN AVERAGES FOR SAMPLES WITH HOLD TIMES OF 6 DAYS OR LESS							
(Maine Ambient Air Guideline for long-term exposure is .009 ppb/v)							
SIP SAMPLE DATES	11/19/06	12/01/06	12/07/06	12/13/06	12/25/06	AVG.	
SITE	ppb/v	ppb/v	ppb/v	ppb/v	ppb/v	ppb/v	
EMP#1	0.161	0.154	0.187	0.105	0.114	0.144	
EMP#2	0.087	0.107	0.100	0.081	0.077	0.090	
RAP	0.086	0.085	0.120	0.093	0.074	0.091	
CAN BLANK	0.025	0.021	0.008	0.014	0.000	0.014	

OUTLIER ASSESSMENTS

As noted in the initial sample event and analysis table in the objectives, we made a decision to not utilize samples that did not have representative blanks, unusual levels of contaminants in the blank, and a sample event in which the summa canister sample suddenly spiked way above the remaining sample concentrations.

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OCTOBER RESULTS OMITTED DUE TO INADAQUATE REPRESENTATION OF THE BLANKS

We did not include the October results in the Acrolein averages because we did not feel the blanks adequately represented the clean canister backgrounds for each of the intended October sampling events. Since we were analyzing all of the cans as clean for the TO/15 compounds that our system provides we didn't expect that RIDOHL would find contaminants in the blanks, hence the October blanks were originally thought to be suitable for the study. When we later learned in our 12/19/06 results that the blank had a fair amount of contaminants that were found in the TO/14 analysis conducted by RIDOHL, we excluded the October results from the study because we had no way of knowing what types of TO/14 contaminants were present in the batches of sample cans we provided for the October sampling events.

12/19/06 RESULT OMITTED DUE TO BLANK CONTAMINATION- POSSIBLE NITROGEN TANK

Further into the study we learned from our 12/19/06 sampling event that the blank had a fair amount of contaminants found in the TO/14 analysis conducted by RIDOHL. We looked into the matter further and learned that the gas company contracted to provide the nitrogen tanks we used to clean our canisters, was shipping industrial grades instead of ultra pure grades called for in our contract. When the tank gets low, it is possible to pull contaminants out of the liquid into the canisters when they are being filled. We suspect the contamination came from the Nitrogen tank which was changed over just after the blank was filled. It is apparent that we do not have the ability to detect the types of contaminants noted in method TO/14. These are the types of contaminants found in the industrial grade versions of the nitrogen tanks.

12/31/06 RESULT OMITTED DUE TO SUSPECTED CONTAMINANTS ON THE CANISTER WALL

On 12/31/06 we noticed that the Summa Polished canister levels for Acrolein suddenly spiked. Since the Summa Polished canister spiked at much higher levels than the remaining canisters, this was regarded as suspicious data and noted as an outlier. We suspect this result was demonstrating how the canister media influences the Acrolein result. This Summa Polished canister may contain active sites that host contaminants making them readily available to react, potentially increasing the levels of Acrolein in the canister. Since we had no way of knowing if the other canisters cleaned in the same batch as the Summa Polished canister contained some of the same contaminants, to be cautious we noted them all as potential outlier's and omitted the 12/31/06 results from the final averages.

CANISTER MEDIA COMPARISON

In this data set we were trying to determine if there were any differences in the canister media (Silco glass lined vs. Summa Polished). It should also be noted that our collocated sample study was designed to specifically test the differences between the canister media and not the instruments repeatability at levels detected in extrapolated portions of the instruments calibration curve.

These results demonstrate that there are noticeable differences between the types of canister media being used. The EMP#1 sampler produced results that were greater than the EMP#2 results every time it sampled and in every replicate analysis.

Since this is such a small sample set, we do not know with absolute certainty that this proves true, however it does indicate that it is probable. To investigate this matter further, we looked at the percent differences between the two samplers in our 2005 database and concluded that the samplers themselves showed less than a 1 percent differences for most compounds. The differences noted in the overall comparisons of these two samplers are no where near the differences indicated in this test series so the apparent differences may be caused by the canister types.

To eliminate any bias a more extensive study would need to be evaluated by randomly selecting the sampler chosen for the canister media. If the summa polished canisters always produce greater results then it would be confirmed that the canister media could potentially inflate the Acrolein results.

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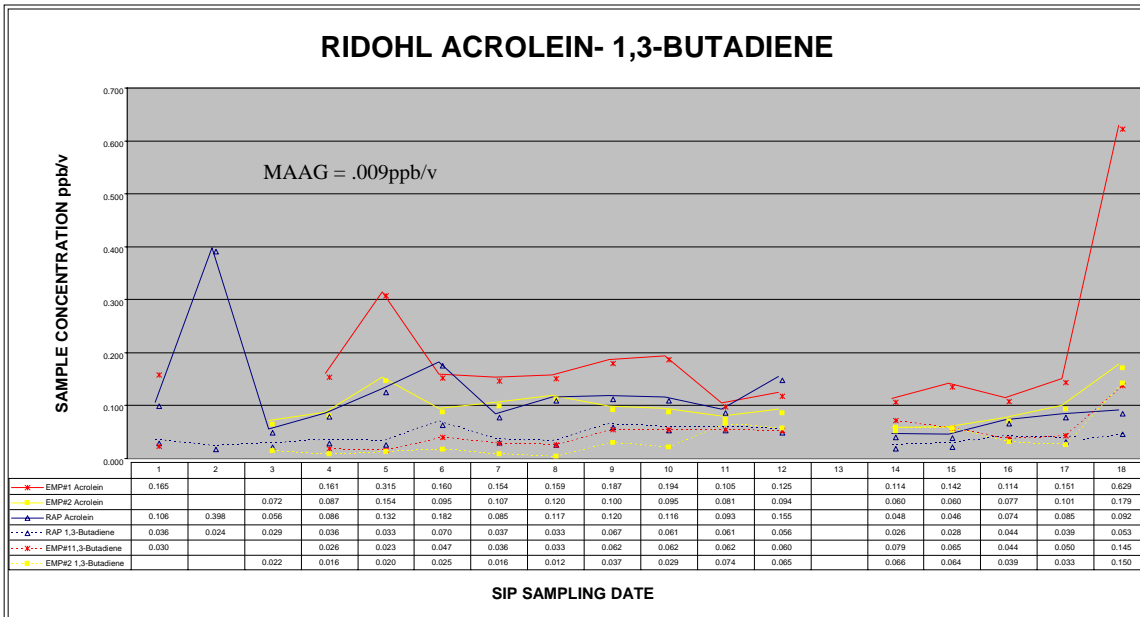
ACROLEIN RESULTS for samples analyzed within 6 days of sample collection.						
SIP SAMPLE DATES	11/19/06	12/01/06	12/07/06	12/13/06	12/25/06	AVG.
SITE	ppb/v	ppb/v	ppb/v	ppb/v	ppb/v	ppb/v
EMP#1 Summa Polished	0.161	0.154	0.187	0.105	0.114	0.144
EMP#2 Silco glass lined	0.087	0.107	0.100	0.081	0.077	0.090
Differences between samples	0.080	.047	.087	.024	.037	.054
% Differences	59.67%	36.01%	60.63%	25.81%	38.74%	46.15%

This table shows the reporting and co-located sample results from our study. Our results ranged from .024ppb/v to .087ppb/v. The averages of these percent differences are 46.15%. The average ppb/v differences between the two media are 0.054ppb/v.

PLOTTED 1,3-Butadiene vs. Acrolein

We also wanted to make a special note that MEDEP does not have the ability to actually find 1,3-Butadiene in their analytical results for ambient samples. We suspect it is there because RIDOHL has detected it and we asked the New England EPA laboratory (NEEPA) to go below their lowest calibration standard to see if they can detect it and they have confirmed what RIDOHL has detected. For some reason we have two compounds that co-elute in the ambient samples where we would expect to find 1,3-Butadiene so without actually finding the peak in the mass spectra MEDEP has to report their 1,3-Butadiene results as not found.

We felt it was important to make it known that we have acknowledged that there are levels of 1,3-Butadiene in the ambient air that could be contributing to the Acrolein levels that we are detecting. However our long term trends in data show that MEDEP has not found it in their ambient sample analyses.



Finally, we plotted 1,3-Butadiene levels out on the graph with the Acrolein results. Even though the data being used are estimated values that have been determined from the extrapolated portion of the calibration curve, for the most part we could conclude that there is some type of correlation taking place between these two compounds.

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CONCLUSIONS: By conducting a data assessment designed to interpret the results measured in the extrapolated proportions of the instruments calibration curve, we could still conclude conservatively that our estimated values may be above the levels established in Maine's Ambient Air Guideline. To purchase an analytical system at this time might not change the fact that the levels being measured are going to be more accurate; however if the levels remain the same or increase we could/should continue to monitor these results as we do with the majority of our other HAP's compounds by making these qualitative assessments to define how meaningful the estimated measurements are in the data that is collected.

In this manner the intended values of measurement that are given should take into account all of the known variables such as the instruments repeatability, blank contamination, canister background, and difficulties pertaining to the compound of interest before it can reasonably be assessed. Failing to conduct these types of assessments could potentially artificially inflate these results or in some instances indicate that compounds are not detected when they have the potential to exist in the environment at levels that we should be concerned about.

In this particular study we were able to look at some of the variables recommended by the RIDOHL that could influence Acrolein results. These included looking at different hold times, the differences between canister media, and contamination levels in blanks.

In general, all cans had little or insignificant increases in Acrolein levels when the hold times were kept less than two weeks. As the hold time increased such as the sample that was analyzed 81 days after collection, you will note a significant difference in the results for this sample compared to the samples intended to be used for this study.

During our assessment of the results from this study we observed that there are noticeable differences between the two types of canister media used in the sampling protocol. With all of the variables factored out of the final results such as outliers and contamination, the samples collected with a summa polished canister averaged out to be approximately .050ppb/v higher. However, the results of this study do not definitively show which type of canister media provides for the most accurate measurement of Acrolein in ambient air. Further comparative studies will need to be conducted to determine this.

Since this study does not take into account the analysis of the TO-14 compounds for each individual can after a cleaning we do not know for certain if it is due to the background in each of the canisters themselves or a direct result of the type of canister media being used. It is also interesting to note that the summa polished canisters with the highest amount of PAMs compound in the blanks had the biggest changes in Acrolein levels after being analyzed at different hold times.

All measured Acrolein values fell within the estimated range (below the lowest calibration standard) of the analytical instruments used in this study. Currently there is no technology available that can measure Acrolein concentrations at or near the Maine ambient air guideline of 0.009 ppb/V within its calibration range.

To provide more meaningful results for this kind of data we were able to establish potential ranges of error for the instrument as it detects compounds that are measured in a qualitative manner. All samples collected in this study were collected from Acrolein influenced areas, i.e., areas containing significant amounts of air pollution from automobile exhaust and/or industrial activities. This study did not determine ambient Acrolein concentrations at background sites and whether or not they are above the Maine ambient air guideline.

The average percent differences between the reporting and co-located sample results (from RIDOHL 2005 precision data set) for an entire year averaged out to 34 percent. This indicates that the average reproducibility or precision between reporting and co-located samplers varied by an average of 34 percent. However, this does not definitively prove that measured Acrolein concentrations were within plus or minus 34 percent of the analytical results. The exact degree of accuracy of the analytical results could not be determined in this study.

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It is apparent that there is some type of correlation taking place between 1,3-Butadiene and Acrolein. RIDOHL's data show that 1,3-Butadiene is present in Maine's ambient air, however MEDEP does not have the ability to report it because it co-elutes with other compounds in the chromatographic column in the Maine DEP GC/MS. These co-eluting compounds interfere with the interpretation of the mass spectrum of 1,3-Butadiene. It should be noted that Acrolein is also a photo-oxidation product of various hydrocarbons including 1,3-Butadiene. However, due to the two compounds different mass spectra and different retention times in the chromatographic column it is impossible to misidentify 1,3-Butadiene as Acrolein.

Acrolein is an extremely challenging compound to measure in the environment at the levels were established within the Ambient Air Guidelines. With a study as limited as this one, we are not able to make a fair and reasonable assessment about the levels of Acrolein in the ambient air. We don't feel that our sampling protocols are suitable at this time to really understand how much is in the environment. Additional research is needed to develop a sampling protocol that will give an accurate representation of Acrolein levels in Maine's ambient air. What we do know is we may have under estimated the true measurement for Acrolein. Focusing on a long term trend with seasonal variations, and better sampling procedures would give us more conclusive results.

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