



WEEK 3.4 REPORT – PICARRO INSTALLATION

March 8th, 2017

Summary

On March 8th the Mobile Lab was used at Columbia Basin Analytical Laboratories (CBAL) from 11:30 AM to 3:40 PM. During this time the Liquid Calibration Unit (LCU) and Picarro were powered down, unplugged, and removed from the electronics cabinet. The cabinet shelves were then readjusted to accommodate the vacuum pump for the Picarro. Once this was accomplished the LCU, Picarro, Variac, and vacuum pump were placed into the cabinet. All cords were plugged in. Then all instruments that were disconnected during this process were powered on as per normal procedure for Mobile Lab use. This ensured that all instruments were operational and connections were appropriate. The goal of these activities was to protect the vacuum pump from any damage that could result by being outside of the cabinet as well as to shorten the distance between the pump and Picarro so that the manufacturer-supplied connection line could be utilized. The new configuration of the electronics cabinet is displayed in Figure Picarro 3.4.1a.

March 8th Figures

Figure Picarro 3.4.1a

Figure Picarro 3.4.1a displays the current configuration of the Picarro in the electronics cabinet.



WEEK 3.4 REPORT – PTR-MS VERIFICATION

March 9th, 2017

Summary

On March 9th the Mobile Lab was used at CBAL from 12:30 PM to 1:05 PM to evaluate if the Proton Transfer Mass Spectrometry (PTR-MS) system was capable of detecting several compounds. A standard of each compound was opened and the PTR-MS inlet tubing was exposed to the headspace of the vial to collect a sample of the compound in the gas phase. Di-n-butyl phosphonate was run as an indicator. The standards examined included tributyl phosphate, diethyl phthalate, and Aroclor 1242. Aroclor is a mixture of mono, di, and tri chlorinated congeners of polychlorinated biphenyls (PCBs) in hexane.

Spectra showing signals of these compounds from the PTR-MS are displayed in Figure PTR-MS 3.4.2a through Figure PTR-MS 3.4.2e. It is important to note that compounds with high vapor pressures are more likely to be found in the atmosphere and that the compounds examined during March 9th had very low vapor pressures. Dibutylbutylphosphonate has a vapor pressure less than 0.09 mm Hg at 25 °C. Tributylphosphate has a vapor pressure of 0.004 mm Hg at 25 °C. Diethylphthalate has a vapor pressure of 0.002 mm Hg at 25 °C. As a reference, 1-methylnaphthalene has a vapor pressure of 4.9 mm Hg at 25 °C. A vapor pressure of 3-4 mm Hg at 25 °C is about the lower limit for the analysis of compounds without experiencing issues related to condensation in the sampling lines. The Aroclor PCB mixture used has a vapor pressure of about 87.75 mm Hg at 37.8 °C. This higher vapor pressure is not indicative of the components of the mixture but rather the solvent, hexane. Figure PTR-MS 3.4.2f is a table comparing these compounds and it displays that all the compounds tested (except Aroclor) had vapor pressures below this amount. These compounds would not likely be in the atmosphere at significant concentrations unless they were aerosolized. Thus, while the PTR-MS could potentially analyze these compounds, it is unlikely to encounter them, especially considering the potential for the compounds to stick to the sampling tubes leading to the instrument. All the spectra shown in this report were obtained at a standardized E/N value of 120 Td and drift tube temperature of 60°C.

Also, for this data collection the Inlet Temperature setting on the PTR-MS was increased from 60 °C to 90°C. Future data collection will be conducted at this temperature. The increase in temperature will not affect data quality. The purpose of increasing temperature is to reduce the tendency of heavier compounds from sticking in the inlet line.

March 9th Figures

Figure PTR-MS 3.4.2a

Figure PTR-MS 3.4.2a displays the spectrum taken with the PTR-MS inlet line in the headspace of the dibutylbutylphosphonate sample bottle. Note that no peak was observed at $m/z=251$ implying that any dibutylbutylphosphonate sample analyzed was fragmented. The signal at $m/z=233$ implies the loss of water from the original protonated compound, which indicates that the compound was indeed present in the PTR-MS. A quantitative measure of the compound would require a calculation based on unique identified fragments. Further experiments with differing voltages in the PTR-MS are needed to form a set of operating parameters capable of fragmenting the compound in such a way to make quantification possible and practical.

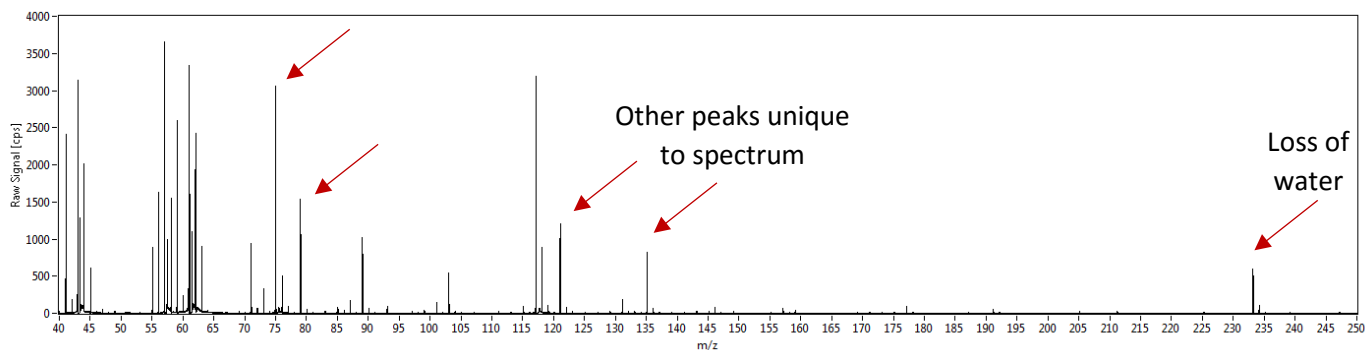


Figure PTR-MS 3.4.2b

Figure PTR-MS 3.4.2b displays a spectrum taken with the PTR-MS inlet line in the headspace of the tributylphosphate sample bottle. Note that no peak was observed at $m/z=267$ implying that any tributylphosphate sample analyzed was fragmented. Several small but apparently unique fragments may indicate that tributylphosphate was present in the PTR-MS. A quantitative measure of the compound would require a calculation based on unique identified fragments. Further experiments with differing voltages in the PTR-MS are needed to form a set of operating parameters capable of fragmenting the compound in such a way to make quantification possible and practical.

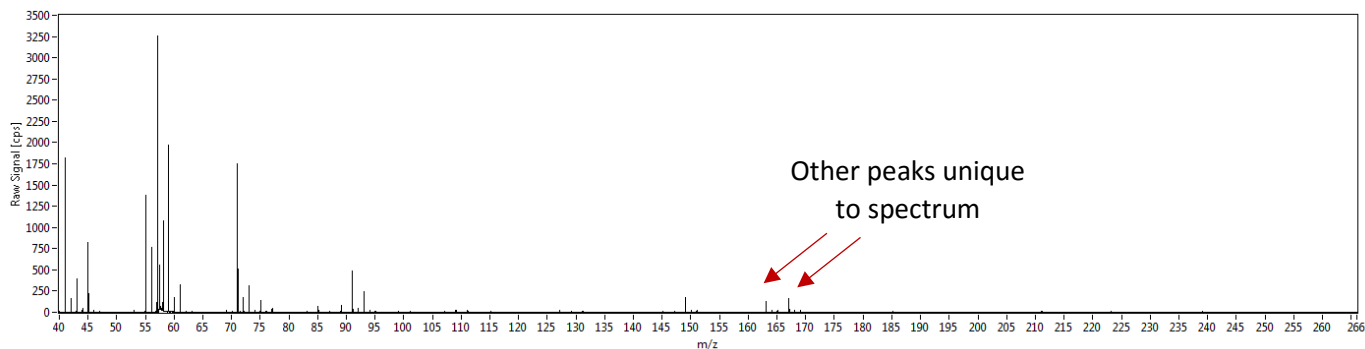


Figure PTR-MS 3.4.2c

Figure PTR-MS 3.4.2c displays a spectrum taken with the PTR-MS inlet line in the headspace of the diethylphthalate sample bottle. Note that the molecular ion, protonated diethylphthalate, is indicated by a peak at $m/z=223$. Several large peaks appeared also, see $m/z=151$ and $m/z=177$, which indicate fracturing of the compound. A quantitative measure of the compound would require a calculation based on unique identified fragments. Further experiments with differing voltages in the PTR-MS are needed to form a set of operating parameters capable of fragmenting the compound in such a way to make quantification possible and practical.

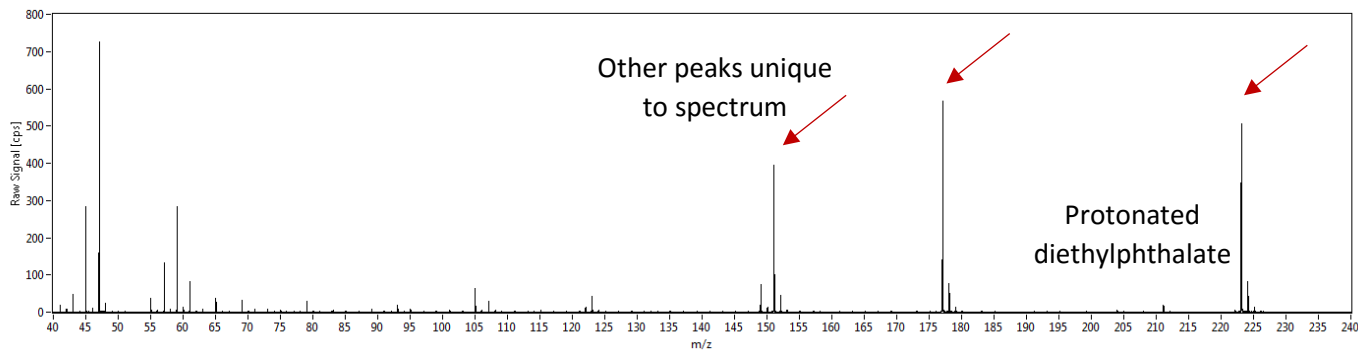


Figure PTR-MS 3.4.2d

Figure PTR-MS 3.4.2d displays a spectrum taken with the PTR-MS inlet line in the headspace of the sample bottle of PCBs. A peak at $m/z=189$ indicates the protonated mono-chlorinated congeners. The peak at $m/z=223$ indicates the protonated di-chlorinated congeners. The peak at $m/z=257$ indicates the protonated tri-chlorinated congeners. A quantitative measure of the compound would require a calculation based on unique identified fragments. Further experiments with differing voltages in the PTR-MS are needed to form a set of operating parameters capable of fragmenting the compound in such a way to make quantification possible and practical.

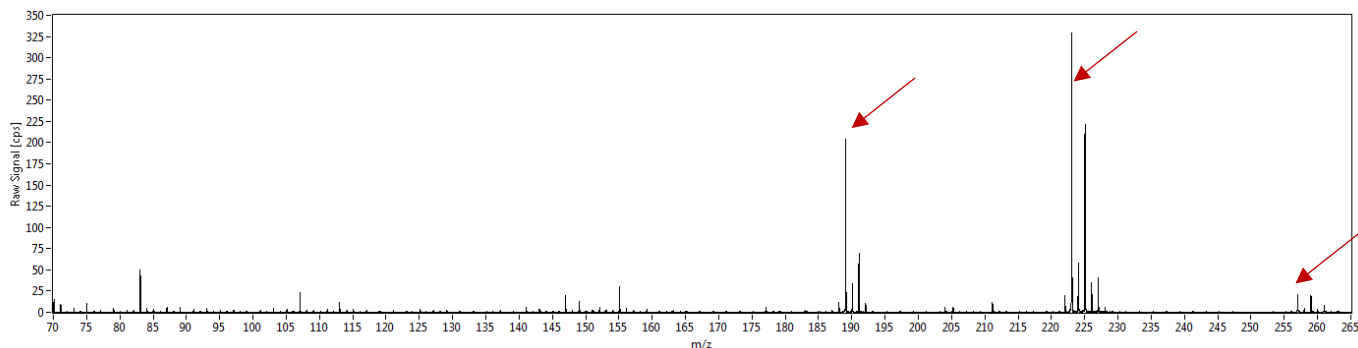


Figure PTR-MS 3.4.2e

Figure PTR-MS 3.4.2e displays a spectrum taken with the PTR-MS inlet line in the headspace of the sample bottle of PCBs. This spectrum was taken approximately 20 seconds after the inlet line was removed from the sample source. The same peaks are visible as those in Figure PTR-MS 3.4.2d indicating that these compounds, especially the heavier ones, are quite 'sticky' in the sampling system and would not provide a good real-time quantitative indication of their presence.

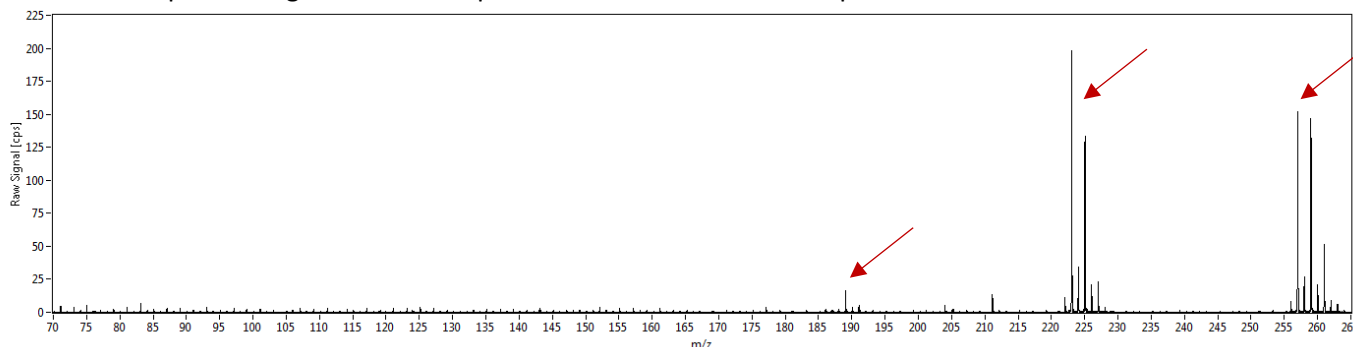
**Figure PTR-MS 3.4.2f**

Figure PTR-MS 3.4.2f displays a table of the compounds investigated in this experiment. This table shows that the vapor pressures of all the compounds tested in this experiment fell below the lower threshold of compounds that can be analyzed. Aroclor is a mixture of PCB compounds in hexane. The high vapor pressure is representative of the solvent in Aroclor, hexane. Although hexane has quite a high vapor pressure, a decreased vapor pressure is expected because of the PCBs in the mixture. Several individual PCBs are included in the table below to provide an example of the expected vapor pressures of the PCBs investigated in this experiment.

Compound	Temperature (°C)	Vapor Pressure (mm Hg)	Vapor Pressure (atm)	Vapor Pressure (torr)
Dibutylbutylphosphonate ²	25	<0.09	< 0.00012	<0.09
Tributylphosphate ²	25	0.004	0.000053	0.004
Diethylphthalate ²	25	0.002	0.000026	0.002
Aroclor 1242 PCB mixture ²	37.8	87.75	0.12	87.75
Hexane	20	132.01	0.174	132.01
4-Chlorobiphenyl	25	0.0105 ¹	0.000014 ¹	0.0105 ¹
2,3'-Dichlorobiphenyl	38	<0.1 ¹	0.00013 ¹	<0.1 ¹
2,4,5'-Trichlorobiphenyl	25	0.000975 ¹	0.0000013 ¹	0.000975 ¹
1-methylnaphthalene	25	4.9	0.0064	4.9

¹Predicted values using US Environmental Protection Agency's EPISUITE™

²Compounds tested in this experiment.

WEEK 3.4 REPORT – PICARRO VERIFICATION AND SOFTWARE INSTALLATION

March 10th, 2017

Summary

On March 10th the Mobile Lab was used at CBAL from 7:30 AM to 2:30 PM to install a remote access software and to test the Picarro. LogMeIn was installed on each computer or tablet used in the Mobile Lab for field monitoring purposes. LogMeIn was not yet usable on the Picarro analyzer. A mixed standard of ammonia and volatile organic compounds was prepared and then delivered into the sampling line for approximately 1 second at the Mobile Lab cab air canister connection. This connection was utilized to simulate entrance at the sampling port because wind gusts made ladder use unsafe. It was found that there was an approximate delay of 10 seconds between sampling and detection by the Picarro and about 0.5 seconds between sampling and detection by the PTR-MS. Also, some tailing behavior was noted in the sample behavior on the Picarro which indicates that to collect sharp data peaks it may be necessary to run a PEEK tubing line to the sampling port. Note that the ammonia used in this experiment is not traceable to a certified source. Thus, all activities on this day were strictly preliminary experiments. Ultra-high purity nitrogen and zero air were both flowed through the Picarro in another preliminary experiment to help determine the best way to perform sensitivity checks and blanks.

WEEK 3.4 REPORT – PICARRO VERIFICATION

March 13th, 2017

Summary

On March 13th the Mobile Lab was used at CBAL from 7:30 AM to 3:00 PM to test for time delays related to sampling for ammonia. These delays included both the sample lag time and the graphic delay time on the Picarro monitor which will affect ammonia sampling protocols. The end goal of these preliminary experiments is to gain knowledge of the instrument's operational characteristics to prepare a standard operating procedure for routine sampling and analysis.

These experiments were performed by sampling and analyzing a standard that contained ammonia and VOCs with the Picarro or alternatively a hand. Several variables were investigated including the method of sampling, source sampled, and the type of tubing used to sample. Note that the ammonia in the standard was not certified and thus these were strictly preliminary experiments.

It was found that there was a longer delay of the signal on the Picarro graphical interface than within the data file. This indicated that there is a graphical delay. There appeared to be no substantial difference in graphical delay based on tubing material or method of sampling. There does appear to be a difference based on the source sampled. This indicates that there is some variability in graphical delay, which is perhaps due to a difference in the overall amount of data being processed. Signals that last a longer amount of time have more data to be processed and thus may have an increased graphical delay.

The other type of delay investigated was the lag time of the sample in the tubing. There did not appear to be a difference in sample lag time due to the type of tubing or method of sampling used based on this day's experimental results. There did appear to be a difference in sample lag time based on the source of the sample. This may indicate that the composition of the sources varies, for example in humidity, causing a difference in the tubing environment and the amount of time it took ammonia to reach the Picarro. A composition difference may also indicate why peak trailing behavior is increased in canister sampling as opposed to hand sampling.

WEEK 3.4 REPORT – Tour Preparation and Verification of IH Sample Pump

March 14th, 2017

Summary

On March 14th The Mobile Lab was used at CBAL from 1:00 PM to 3:00 PM to prepare for a tour on March 15th. This included securing all loose items and instruments as well as configuring the lab for monitoring conditions. Additionally, a PEEK sample line was connected to the Picarro and run up through the sampling port to minimize dilution or loss of ammonia to the walls of the relatively wide PFA sample-line tubing. Furthermore, the LogMeIn software was installed and used successfully on the Picarro monitor.

The five sampling pumps used for the collection of air samples on alternative sampling media were charged and tested to ensure that their internal sampling clocks corresponded to a real-time measurement period. These pumps will be used for the collection of air samples on 2,4-dinitrophenylhydrazine tubes for aldehydes and ketones, Thermosorb/N tubes for nitrosamines, and CarboTrap-300 tubes for VOCs. It is expected that these pumps will be heavily used in upcoming field activities for the routine support of the PTR-MS measurements and for source emissions characterization. It was found that the sampling clocks did match real time. The results of the testing are displayed in Table 3.4.7a.

March 14th Figures

Table 3.4.7a

This table displays the results of the Evaluation of the Internal Timing Function of the IH Sampling Pumps. Note that pump elapsed time and minutes of real time match for each pump.

Pump Serial No.	A117549	A117500	A117798	A091311	A117536
Start Time	7:12	7:12	7:14	7:16	7:17
End Time	15:39	15:39	15:40	15:40	15:41
Hours	8:27	8:27	8:26	8:24	8:24
Minutes	507	507	506	504	504
Pump Elapsed Time (min)	507	507	505	504	504