Summary of UT Special Audit Report

GAD Number 582-8-86245-FY10-06

Ozone Precursors and Toxic Chemical Compound Monitoring

October 6, 2010

On August 24, 2010, staff from The University of Texas Center for Energy and Environmental Resources (CEER) conducted an independent performance audit of the DISH and Eagle Mountain Lake (EML) air quality monitors. A performance audit consists of analyzing a control sample, with an assigned concentration of each chemical compound to be measured, and comparing the analytical result (observed value) to the expected concentration. The control sample was comprised of a selection compounds whose identity and concentration were unknown to the instrument operator at the time of analysis and reporting.

Even state-of-the-art monitors like these automated gas chromatographs (AutoGCs) have analytical measurement uncertainties. Scientific acceptance criteria for this analytical technique are (+/-) 30 percent from an expected or assigned value. It is important to note that these percentages are being applied to observed values in the parts per billion range, and represent fractions of those very low concentration measurements.

Any measurements that are more than 30 percent from the expected value warrant further investigation to determine an assignable cause for the exceedance and implement corrective action if appropriate. For purposes of this evaluation, an even more conservative investigation level is being used, and any audit results that are more than 15 percent from an expected value are compiled and reported as well.

Summary of Results

The DISH AutoGC observations were within 9 percent of the control sample for benzene, an absolute difference of only 0.1 ppbv (1.5 ppbv expected vs. 1.4 ppbv observed). An absolute difference of 0.4 ppbv (1.5 ppbv expected vs. 1.1 ppbv observed) was reported at the EML monitor. These differences are many times lower than the levels of interest for health effects evaluation.

The DISH monitor had 43 out of 46 reported compounds within 30 percent of the expected concentration and an average absolute difference of 10 percent (and 0.2 ppbv) across all compounds. Three compounds were outside of the 30 percent range. These were isoprene, methylcyclopentane, and styrene. According to CEER, isoprene and styrene are inherently difficult to measure by this technique, and the methylcyclopentane variance may be due to interference of chlorinated compounds present in the standard that are not on the target list. Even though these compounds exceeded the 30 percent criterion, they differed by small amounts from the expected value and are as follows:

Compound	Expected Value (ppbv)	Observed Response (ppbv)	Absolute Difference (ppbv)
isoprene	1.4	0.9	0.5
methylcyclopentane	1.4	1.9	0.5
styrene	1.3	0.9	0.4

The EML monitor had 41 out of 46 reported compounds within the 30 percent range with an average absolute difference of 13 percent (and 0.2 ppbv) between the expected and observed measurements. Five compounds were outside the 30 percent range. These were ethylene, isoprene, 2-methylhexane, n-octane, and styrene and are as follows:

Compound	Expected Value (ppbv)	Observed Response (ppbv)	Absolute Difference (ppbv)
ethylene	3.5	2.1	1.4
isoprene	1.4	0.9	0.5
2-methylhexane	1.4	0.8	0.6
n-octane	1.5	1.0	0.5
styrene	1.3	0.7	0.6

Conclusion

While results for some compounds differed by more than predefined limits, most compounds, including benzene, compared closely to expected values. It is important to note that compounds exceeding the 15 percent range does not necessarily imply problems with the equipment nor that the data is not useful. In fact, these concentration levels and observed differences are significantly lower than applicable Ambient Monitoring Comparison Values (AMCVs) that are used to assess the potential for exposure to measured concentrations to be of human health concern and are conservative in terms of health protectiveness (i.e., they are not set at concentrations right above which you would expect effects).

The CEER report recommends that TCEQ, “continue operating in the current configuration without making any system changes as a result of this audit to affect data quality until after” the EPA completes their independent assessment of the DISH and EML sites. As such, TCEQ has not initiated changes as a result of the CEER audit. Results of the EPA assessment are pending at the time of this report.

Special Audit Report, September 14, 2010
Partially Satisfying Tasks 3 & 4

WORK ORDER UNDER THE CONTRACT BETWEEN TCEQ AND CONTRACTOR:
The University of Texas at Austin

GAD Number 582-8-86245-FY10-06

Ozone Precursors and Toxic Chemical Compound Monitoring

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1. Background

This is the special report on performance audits conducted at the DISH CAMS 1013 and Eagle Mountain Lake (EML) CAMS 75 auto-GCs on August 24, 2010.

2. Summary of Results

A standard gas canister was prepared at The University of Texas at Austin, Center for Energy and Environmental Resources, in a laboratory that follows the National Environmental Laboratory Accreditation Program (NELAP) standards. Only the lab chemist knew the composition of the canister. The canister was shipped following standard chain of custody conventions to the Fort Worth, TX office of the ORSAT contractor. This canister was used to challenge the DISH CAMS 1013 and Eagle Mountain Lake (EML) CAMS 75 auto-GCs on August 24, 2010. The procedure for running the canister in the field was to introduce the pressurized sample using the same manner that the weekly second source Laboratory Control Standard (LCS) is introduced. This is the same approach used by TCEQ in conducting performance audits. The challenge occurred at one site, followed by a blank run, after which the canister was taken to the other site to repeat the procedures, and then taken back to the first site for a repeat, and then back to the second site for a repeat. Repeatability was very good at both sites: the correlation coefficient at DISH was 0.997 and at EML was 0.994. At both sites the operator also ran the standard Calibration Verification Standard and the second source Laboratory Control Standard on the day of the audit. The canister was returned to Austin and again was analyzed in the UT CEER lab on August 30.

Table 1 summarizes the audit results. Table 1 contains the following:

- the list of 46 chemical species measured by the auto-GCs,
- the concentration measured in the canister standard in the UT CEER laboratory on August 18 (Standard ppbV),

- the absolute value of the relative percent difference between the first UT CEER lab run on August 18 and the second on August 30 (%RDP),
- the concentration measured on the first challenge at DISH (DISH ppbV) and the first challenge at EML (EML ppbV),
- the number of carbon atoms per molecule (#C), and
- the percent difference between the auto-GC results and the August 18 lab result (%DISH, %EML).

Table 2 summaries the precision (reproducibility) in the field. Table 2 contains the following:

- the list of 46 chemical species measured by the auto-GCs,
- the concentration measured on the first challenge at DISH (DISH-1, ppbV) and the second challenge at DISH (DISH-2, ppbV),
- the concentration measured on the first challenge at EML (EML-1, ppbV) and the second challenge at EML (EML-2, ppbV),
- the number of carbon atoms per molecule (#C), and
- the percent difference between the repeat challenges (%DISH, %EML), calculated as "relative percent difference" (RPD) = ratio of absolute difference to the average of the two observations.

Table 3 summaries the precision (reproducibility) in the UT CEER laboratory. Table 3 contains the following:

- the list of 46 chemical species measured by the auto-GCs,
- the concentration measured in the canister standard in the UT CEER laboratory on August 18 (*8/18/2010* ppbV),
- the concentration measured in the canister standard in the UT CEER laboratory on August 30 (*8/30/2010* ppbV), and
- the percent difference between the repeat canister standard runs in the laboratory calculated as "relative percent difference" (RPD) = ratio of absolute difference to the average of the two observations (also included in Table 1).

The Quality Assurance Project Plan cites in section D3 as data quality objectives for *accuracy* that "UT compiles audit results, compares to 15%." Thus, in Table 1, cells in the last two columns are shaded if greater than 15 percent (pink) or less than -15 percent (green). Of the 46 species, 10 are outside this margin at DISH, and 13 are outside this margin at EML. Acetylene at EML would also be out of range, but this species is already known to be poorly measured at the site. It should be noted that the EML site equipment had been "retired" from service, then repaired to use in this project. The auto-GC has been in service for ten years. A value outside the 15 percent range is not failure; it is simply an indication that a high standard goal is not met.

The actual acceptance criteria for auto-GC data under the weekly second source LCS runs is plus or minus 30 percent. Three species are out of this range at DISH:

- Isoprene
- Methylcyclopentane
- Styrene

Five species are out of this range at EML:

- Ethylene

- Isoprene
- 2-methylhexane
- n-Octane
- Styrene

Unsaturated hydrocarbons such as acetylene, styrene, and isoprene have traditionally been harder to measure than other species due to reactions with active sites in the analytical system and in the standard cylinders themselves.

Methylcyclopentane was the only species with recovery higher than 30 percent, and an assignable cause may be co-elution with a chlorinated species.

In Table 2 comparing the results of two challenges with the standards canister at each site, only toluene at the EML site appears to have had a problem, with a 21 percent RPD. This may have been a random error, as there is no evidence from the audit or from recent calibration verification precision calculations or second source laboratory control runs that there is an issue with toluene data quality at this site.

The blanks runs with zero-air after each canister challenge showed very little carry-over or detection. Note that zero-air will always contain some minor contamination. The species with highest response at EML was t-2-butene with a blank response of 0.1 ppbV in both runs. The species with highest response at DISH was n-hexane with a blank response of 0.04 ppbV in both runs. At EML, 37 out of 46 species had non-detect responses on the first blank run, and 43 out of 46 had non-detect responses on the second blank run. At DISH, 36 out of 46 species had non-detect responses on the first blank run, and 37 out of 46 had non-detect responses on the second blank run.

In Table 3 comparing the two analysis runs on the standard gas canister on August 18 before the audit and August 30 after the audit, the mean RPD is 3 percent. The maximum RPD is 6.8 percent with styrene, the second high is 6.6 percent with 1,3,5-trimethylbenzene, and third high is 6.4 percent with isoprene.

EPA will be visiting the site on September 14, 2010. It may be advisable to continue operating in the current configuration without making any system changes as a result of this audit to affect data quality until after their independent assessment of the two sites.

Table 1. August 24, 2010 audit results summary

Compound	Standard (ppbv)	%RPD	DISH ppbV	EML ppbV	#C	%DISH	%EML
ethane	3.03	1.9%	2.63	2.65	2	-13.2%	-12.7%
ethylene	3.49	1.2%	2.94	2.14	2	-16.0%	-38.7%
propane	2.74	0.2%	2.73	2.68	3	-0.4%	-2.1%
propylene	2.61	1.5%	2.12	1.84	3	-18.8%	-29.7%
isobutane	1.28	0.5%	1.35	1.28	4	5.4%	0.1%
butane	1.37	0.5%	1.44	1.41	4	5.4%	3.2%
acetylene	2.41	1.0%	1.87	1.18	2	-22.5%	
trans-2-butene	1.25	3.1%	1.29	1.30	4	3.3%	4.1%
1-butene	1.24	1.1%	1.30	1.24	4	5.1%	0.0%
cis-2-butene	1.39	5.1%	1.39	1.34	4	-0.5%	-3.6%
cyclopentane	1.37	1.6%	1.42	1.41	5	3.6%	2.7%
isopentane	1.38	0.6%	1.39	1.37	5	0.7%	-0.6%
pentane	1.38	0.3%	1.38	1.37	5	0.5%	-0.8%
1,3-butadiene	1.28	5.6%	1.23	1.16	4	-3.9%	-9.7%
trans-2-pentene	1.47	3.6%	1.45	1.45	5	-1.4%	-1.5%
1-pentene	1.35	1.0%	1.14	1.11	5	-15.5%	-17.9%
cis-2-pentene	1.42	3.7%	1.21	1.25	5	-15.3%	-12.0%
2,2-dimethylbutane	1.35	0.8%	1.15	1.11	6	-15.0%	-18.0%
isoprene	1.40	6.4%	0.88	0.88	5	-36.7%	-36.9%
hexane	1.47	1.4%	1.62	1.30	6	10.0%	-12.0%
methylcyclopentane	1.40	2.3%	1.88	1.48	6	33.6%	5.3%
2,4-dimethylpentane	1.42	3.4%	1.46	1.46	7	2.4%	2.5%
benzene	**1.47**	1.1%	**1.35**	**1.09**	**6**	**-8.2%**	**-25.6%**
cyclohexane	1.41	1.9%	1.41	1.36	6	-0.5%	-3.6%
2-methylhexane	1.41	1.9%	1.25	0.79	7	-11.3%	-43.9%
2,3-dimethylpentane	1.47	2.5%	1.48	1.70	7	0.6%	15.3%
3-methylhexane	1.43	1.8%	1.30	1.10	7	-8.9%	-23.3%
2,2,4-trimethylpentane	1.40	3.4%	1.32	1.30	8	-6.3%	-7.5%
heptane	1.55	3.1%	1.48	1.37	7	-4.5%	-11.4%
methylcyclohexane	1.39	1.2%	1.35	1.42	7	-2.4%	2.6%
2,3,4-trimethylpentane	1.43	5.0%	1.30	1.29	8	-9.4%	-9.8%
toluene	**1.43**	4.9%	**1.29**	**1.35**	**7**	**-10.4%**	**-6.0%**
2-methylheptane	1.42	3.8%	1.30	1.29	8	-8.6%	-9.6%
3-methylheptane	1.46	3.7%	1.33	1.33	8	-8.6%	-8.6%
octane	1.45	4.0%	1.23	1.00	8	-15.2%	-31.0%
ethylbenzene	1.53	4.0%	1.55	1.44	7	1.6%	-6.0%
m/p-xylene	**3.35**	5.1%	**2.88**	**2.74**	**8**	**-14.0%**	**-18.2%**
styrene	1.26	6.8%	0.87	0.71	8	-31.0%	-43.2%

Compound	Standard (ppbv)	%RPD	DISH ppbV	EML ppbV	#C	%DISH	%EML
o-xylene	**1.45**	4.2%	**1.61**	**1.62**	**8**	**11.1%**	**12.2%**
nonane	1.37	4.2%	1.24	1.19	9	-9.7%	-13.4%
isopropylbenzene	1.20	4.4%	1.07	1.04	9	-10.5%	-13.1%
n-propylbenzene	1.25	3.6%	1.15	1.10	9	-7.9%	-12.2%
1,3,5-trimethylbenzene	1.23	6.6%	1.09	1.11	9	-11.4%	-9.8%
1,2,4-trimethylbenzene	1.23	4.9%	1.11	1.02	9	-9.6%	-16.5%
decane	1.31	4.3%	1.26	1.20	10	-3.7%	-8.7%
1,2,3-trimethylbenzene	1.18	4.9%	1.05	1.01	9	-11.4%	-14.3%

Table 2. August 24, 2010 results for reproducibility (precision) at the sites

Compound	DISH-1 ppbV	DISH-2 ppbV	EML-1 ppbV	EML-2 ppbV	#C	%DISH RPD	% EML RPD
ethane	2.63	2.53	2.65	2.60	2	4.1%	1.9%
ethylene	2.94	2.84	2.14	1.92	2	3.5%	11.1%
propane	2.73	2.68	2.68	2.75	3	2.0%	2.6%
propylene	2.12	2.09	1.84	1.87	3	1.6%	2.0%
isobutane	1.35	1.34	1.28	1.30	4	0.6%	1.2%
butane	1.44	1.47	1.41	1.42	4	1.7%	0.5%
acetylene	1.87	1.79	1.18	1.14	2	4.4%	3.9%
trans-2-butene	1.29	1.30	1.30	1.33	4	0.6%	2.7%
1-butene	1.30	1.31	1.24	1.24	4	0.2%	0.2%
cis-2-butene	1.39	1.39	1.34	1.33	4	0.2%	1.1%
cyclopentane	1.42	1.44	1.41	1.42	5	1.1%	1.1%
isopentane	1.39	1.38	1.37	1.39	5	1.0%	1.0%
pentane	1.38	1.39	1.37	1.39	5	0.3%	1.7%
1,3-butadiene	1.23	1.24	1.16	1.17	4	0.8%	1.1%
trans-2-pentene	1.45	1.39	1.45	1.43	5	4.2%	1.4%
1-pentene	1.14	1.12	1.11	1.11	5	2.1%	0.4%
cis-2-pentene	1.21	1.23	1.25	1.26	5	1.6%	1.0%
2,2-dimethylbutane	1.15	1.08	1.11	1.08	6	6.2%	2.3%
isoprene	0.88	0.86	0.88	0.90	5	2.8%	2.2%
hexane	1.62	1.65	1.30	1.32	6	1.8%	1.9%
methylcyclopentane	1.88	1.91	1.48	1.49	6	1.7%	1.0%
2,4-dimethylpentane	1.46	1.45	1.46	1.49	7	0.3%	2.0%
benzene	1.35	1.34	1.09	1.11	**6**	0.1%	1.8%

Compound	DISH-1 ppbV	DISH-2 ppbV	EML-1 ppbV	EML-2 ppbV	#C	%DISH RPD	% EML RPD
cyclohexane	1.41	1.37	1.36	1.34	6	2.4%	1.4%
2-methylhexane	1.25	1.23	0.79	0.80	7	1.4%	1.4%
2,3-dimethylpentane	1.48	1.46	1.70	1.74	7	1.7%	2.4%
3-methylhexane	1.30	1.30	1.10	1.13	7	0.7%	3.0%
2,2,4-trimethylpentane	1.32	1.31	1.30	1.34	8	0.3%	2.8%
heptane	1.48	1.33	1.37	1.44	7	10.9%	4.9%
methylcyclohexane	1.35	1.35	1.42	1.45	7	0.0%	2.2%
2,3,4-trimethylpentane	1.30	1.28	1.29	1.24	8	1.8%	3.9%
toluene	1.29	1.25	1.35	1.09	**7**	2.8%	21.2%
2-methylheptane	1.30	1.28	1.29	1.25	8	1.5%	2.9%
3-methylheptane	1.33	1.31	1.33	1.31	8	1.5%	1.5%
octane	1.23	1.21	1.00	1.04	8	1.7%	3.6%
ethylbenzene	1.55	1.54	1.44	1.48	7	1.1%	2.7%
m/p-xylene	2.88	2.83	2.74	2.81	**8**	2.0%	2.5%
styrene	0.87	0.86	0.71	0.73	8	0.6%	2.6%
o-xylene	1.61	1.53	1.62	1.58	**8**	5.0%	2.5%
nonane	1.24	1.22	1.19	1.20	9	1.4%	1.0%
isopropylbenzene	1.07	1.06	1.04	1.04	9	1.6%	0.5%
n-propylbenzene	1.15	1.14	1.10	1.12	9	1.0%	1.7%
1,3,5-trimethylbenzene	1.09	1.09	1.11	1.15	9	0.7%	3.4%
1,2,4-trimethylbenzene	1.11	1.06	1.02	1.03	9	4.6%	0.8%
decane	1.26	1.22	1.20	1.17	10	3.7%	2.3%
1,2,3-trimethylbenzene	1.05	1.02	1.01	1.00	9	3.1%	1.2%

Table 3. Laboratory results for reproducibility (precision)

Compound	8/18/2010 ppbV	8/30/2010 ppbV	%RPD
ethane	3.031	3.088	1.9%
ethylene	3.493	3.452	1.2%
propane	2.742	2.748	0.2%
propylene	2.611	2.571	1.5%
isobutane	1.281	1.274	0.5%
butane	1.366	1.373	0.5%
acetylene	2.414	2.391	1.0%
trans-2-butene	1.247	1.209	3.1%
1-butene	1.24	1.254	1.1%
cis-2-butene	1.392	1.323	5.1%
cyclopentane	1.37	1.348	1.6%
isopentane	1.38	1.372	0.6%
pentane	1.377	1.373	0.3%
1,3-butadiene	1.28	1.21	5.6%
trans-2-pentene	1.472	1.42	3.6%
1-pentene	1.354	1.341	1.0%
cis-2-pentene	1.423	1.371	3.7%
2,2-dimethylbutane	1.348	1.337	0.8%
isoprene	1.397	1.311	6.4%
hexane	1.473	1.452	1.4%
methylcyclopentane	1.404	1.372	2.3%
2,4-dimethylpentane	1.423	1.376	3.4%
benzene	1.465	1.449	1.1%
cyclohexane	1.412	1.385	1.9%
2-methylhexane	1.405	1.379	1.9%
2,3-dimethylpentane	1.471	1.434	2.5%
3-methylhexane	1.431	1.406	1.8%
2,2,4-trimethylpentane	1.404	1.357	3.4%
heptane	1.551	1.504	3.1%
methylcyclohexane	1.386	1.369	1.2%
2,3,4-trimethylpentane	1.434	1.364	5.0%
toluene	1.434	1.365	4.9%
2-methylheptane	1.423	1.37	3.8%
3-methylheptane	1.457	1.404	3.7%
octane	1.449	1.392	4.0%
ethylbenzene	1.53	1.47	4.0%
m/p-xylene	3.353	3.185	5.1%

Compound	8/18/2010 ppbV	8/30/2010 ppbV	%RPD
styrene	1.257	1.174	6.8%
o-xylene	1.447	1.387	4.2%
nonane	1.373	1.316	4.2%
isopropylbenzene	1.199	1.147	4.4%
n-propylbenzene	1.252	1.208	3.6%
1,3,5-trimethylbenzene	1.235	1.156	6.6%
1,2,4-trimethylbenzene	1.227	1.168	4.9%
decane	1.311	1.256	4.3%
1,2,3-trimethylbenzene	1.183	1.126	4.9%