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DATE: November 17, 2003

SUBJECT: Data Review, Ahmanson Ranch Sample
AMEC Data Review Report, September 19, 2003
Advanced Technology Laboratories Revised Report, Oct. 16, 2003

The Hazardous Materials Laboratory (HML) of the Department of Toxic Substances Control (DTSC) has been requested to review a data package for an Ahmanson Ranch sample; an AMEC data review report, September 19, 2003, on the sample; and an Advanced Technology Laboratories revised report, Oct. 16, 2003. The parameter of interest is perchlorate, and the sample at issue and other related samples were analyzed according to method 314.0.

We have reviewed the documents and our comments are as follows:

Ahmanson data package

According to the materials available to us, the sample information is provided as follows:

Project: 14834
Client Sample ID: 90682
Matrix: Water
Lab ID: 058251-004
Collection Date: 8/1/2002
Sample Availability: Disposed of
Perchlorate Found: 28 ug/L
Analyzing Laboratory: American Scientific Laboratories/Advanced Technology Laboratory

The method blank, laboratory control sample, matrix spike/matrix spike duplicate results are within the control limits.

A run log is shown in Table 1. Table 1 also shows the retention times and the perchlorate concentrations for some samples.

Using the results of AutoCal 2 through AutoCal 6 in Table 1, the average retention time for a five-point calibration is 9.18 minutes (m). The five calibration standards are used, even though there was a time gap about 1.5 hours between AutoCal 3 and AutoCal 5, because method 314.0 indicated that the retention times of the "standards" analyzed over "several days" can be used to calculate the average retention time. With a retention time window of +/- 5%, the retention time window would be 8.73 m to 9.64 m (the retention time window is almost identical if we use the average retention time +/- 3 standard deviations). The retention time for the sample peak is 9.42 m as shown in Figure 1. In Figure 1, the chromatogram shows a high background from 0 up to about 7 m of elapsed run time. The sample peak at 9.42 m shows some tailing. Since the retention time of 9.42 m of the sample peak is within the retention time window of 8.73 m to 9.64 m, the laboratory reported the presence of perchlorate as specified by method 314.0. Compared to the standard calibration, the amount of perchlorate in the sample was determined to be 28 ug/L.

Another analysis was carried out for the sample with a 5 times dilution. It appears that the diluted sample was analyzed in order to obtain a chromatogram with a lower background. The resulting chromatogram is shown in Figure 2. In Figure 2, the background is lower compared to the chromatogram in Figure 1. However, the signal at 9.63 m is hardly discernible. It consisted of what looks like a 1 mm little dark line with no definitive shape or peak, similar to a common background noise. Therefore, we call it a signal instead of a peak. This result would be expected because the diluted sample would have a calculated perchlorate concentration of 5.6 ug/L [(28 ug/L)/5]. The concentration of perchlorate found according to the chromatogram in Figure 2 is 2.96 ug/L. These concentrations are close to the reporting limit given as 4 ug/L. Generally, the data generated at or near the detection limit are highly variable and not very reliable. As we see here, a calculated value of 5.6 ug/L was experimentally determined to be 2.96 ug/L. Our available materials indicated that the laboratory did not use this analysis for any purpose such as for perchlorate identification or quantitation, probably due to the negligibility of the signal at 9.63 m and the data unreliability. In other words, the chromatogram including its data as shown in Figure 2 is less reliable than the test on the undiluted sample.

Since no confirmation test, such as spiking the actual sample with a perchlorate standard, analysis with a second column, or ion chromatography/mass spectrometry technique, was performed (sample reanalysis is not possible now because the sample was disposed of); we cannot rule out the possibility that the peak at 9.42 m in Figure 1 is due to an interferent. Thus, we consider that perchlorate may or may not be present in the sample in the amount of 28 ug/L.

AMEC data review report (9/19/03)

In summary, the AMEC data review report stated that perchlorate reported for the sample (Lab ID: 058251-004 or Client Sample ID: 90682) is a false positive. They offered two reasons for their conclusion: (1) the peak identified as perchlorate is outside of the retention time window and therefore not perchlorate, and (2) the peak area to height (A/H) ratios for the sample are significantly dissimilar to the perchlorate standards and may indicate that the peak identified by the laboratory as perchlorate is actually an interferent.

For item (1), AMEC excluded AutoCal 2 and AutoCal 3 due to the time gap about 1.5 hours and used the retention times of AutoCal 4, AutoCal5, AutoCal 6, and six quality control samples to calculate the average retention time. However, as we mentioned above, method 314.0 indicated that the retention times of the "standards" analyzed over "several days" can be used to calculate the average retention time. It follows that a time gap of 1.5 hours is immaterial compared to a permitted duration of several days. It would appear that method 314.0 does not contemplate the use of quality control sample retention times to calculate the average retention time, because a standard calibration needs to be available and the average retention time be established before quality control samples can be analyzed and quantitated. Thus, the approach taken by AMEC to exclude AutoCal 2 and AutoCal 3 and to include six quality control samples in its average retention time calculation is not consistent with method 314.0.

To complete our discussion, we can use the average retention time of 9.0 m calculated by AMEC. For an average retention time of 9.0 m, the retention time window should be 8.55 m to 9.45 m. As the retention time for the sample peak as shown in Figure 1 is 9.42 m, the peak is within the retention time window. Also, as the retention time for the sample signal as shown in Figure 2 is 9.63 m, the signal is outside the retention time window.

As we discussed above, the chromatogram in Figure 2 is not as useful as the chromatogram in Figure 1 due to the insignificant signal and data unreliability. However, AMEC used the retention time in Figure 2 to conclude that the peak identified as perchlorate is outside of the retention time window. Therefore, AMEC claimed that no perchlorate was present for the sample at issue. At the same time, AMEC did not consider the obvious sample peak as shown in Figure 1. In fact, the information provided in Figure 1 would show that the sample peak identified as perchlorate is within the retention time window calculated by AMEC itself, as we discussed above. Thus, the retention time at 9.42 m would be regarded as a positive test for perchlorate according to method 314.0.

For item (2), the peak area to height (A/H) ratios are discussed in method 314.0, section 9.2.8.6 et seq. Generally, the changes in the A/H ratios may affect the accuracy of the peak areas. Method 314.0 uses peak areas for quantitation purpose. It does not use A/H ratios for identification of perchlorate. Retention time is the criterion specified to

determine the presence or absence of perchlorate in a sample. Thus, the use of the A/H ratios for perchlorate identification is not relevant.

We also wish to point out two minor matters regarding the AMEC report. On page 8, it stated that the sample was diluted 10 times in the text while it also stated in the table for the same sample as diluted 5 times. On page 9, it stated that it was only the reviewer's professional opinion that the reported perchlorate was a false positive. It appears that without further substantiation, this professional opinion is transformed in the cover letter into a factual assertion that the sample reported with a concentration of 28 ug/L is a false positive.

Thus, AMEC incorrectly calculated the average retention time for the perchlorate standards because it omitted two calibration standards and picked six quality control samples. AMEC used inappropriate data to justify that retention time of a sample run is outside of the retention time window (see Figure 2). AMEC did not consider crucial data that indicated the presence of perchlorate in the sample (see Figure 1). AMEC used the peak area to height (A/H) ratios as criteria for perchlorate identification. These criteria are not valid because method 314.0 specified the retention time as the criterion for perchlorate identification.

It appears that the retention times of perchlorate standards are dependent on the perchlorate concentrations. As shown in Table 1, low concentration standards (4 ppb, 10 ppb, and 25 ppb) have higher retention times than higher concentration standards (50 ppb and 100 ppb). Aside from method 314.0 procedures, we can compare the retention time of a sample with the retention times of standards with similar concentrations. Since the diluted sample as shown in Figure 1 has an estimated concentration about 3 to 6 ug/L, we can compare its retention time with the average retention times of 4 and 10 ppb standards. From Table 1, the average retention time of these two standards would be 9.32 m. For an average retention time of 9.32 m, the retention time window would be 8.85 m to 9.79 m. Since the retention time of the diluted sample has a retention time of 9.63 m, it is within the retention window. This adds support that perchlorate could be present in the sample at issue.

Advanced Technology Laboratories revised report (10/16/03)

This revised report changed the perchlorate in the sample at issue from 28 ug/L to non-detect (ND) with a reporting limit of 4 ug/L. No explanation was given for the revision.

CONCLUSIONS

For the reasons discussed above, HML has the following conclusions:

1. The reported perchlorate of 28 ug/L for the sample (Lab ID: 058251-004 or Client Sample ID: 90682) is inconclusive because no confirmation test, such as

spiking the actual sample with a perchlorate standard, analysis with a second column, or ion chromatography/mass spectrometry technique, was performed.

2. AMEC incorrectly calculated the average retention time for the perchlorate standards. AMEC used inappropriate data to show the sample retention time is outside of the retention time window while it did not use appropriate data that revealed the possible presence of perchlorate. AMEC also used invalid criteria [peak area to height (A/H) ratios] for perchlorate identification because method 314.0 only specifies retention time as the criterion for perchlorate identification.

3. HML strongly and emphatically disagrees with AMEC's conclusion that the reported perchlorate of 28 ug/L for the sample (Lab ID: 058251-004 or Client Sample ID: 90682) is a false positive.

4. The revised report issued by Advanced Technology Laboratories does not provide any explanation for changing its reported perchlorate of 28 ug/L for the sample (Lab ID: 058251-004 or Client Sample ID: 90682) to non-detect with a reporting limit of 4 ug/L.

If you have any questions, please contact me or Lorna Garcia at (510) 540-3003.

Cc: Bart Simmons, Ph.D.
Lorna Garcia
Cindy Dingman
James Cheng

Table 1: Run log and sample analysis results (8/7/2002)

Sample	Time	Retention Time (minute)	Perchlorate Concentration (ppb)	
AutoCal 1	9:52:51	-----	0	
AutoCal 2	10:07:37	9.30	4	
AutoCal 3	10:22:27	9.35	10	
AutoCal 5	12:00:36	9.02	50	(about 1.5 hr gap)
AutoCal 6	12:15:25	9.03	100	
AutoCal 4	12:33:54	9.22	25	
ICV	12:51:36	9.08	51.785	
ICB	13:06:21	----	0 (ND)	
Method Blank	13:21:05	----	0 (ND)	
LCS	13:35:53	9.02	53.208	
58251-001A	14:05:46	----	0 (ND)	
58251-002A	14:20:35	----	0 (ND)	
58251-003A	14:35:25	----	0 (ND)	
58251-004A	**14:50:15**	**9.42**	**27.778**	
58252-001AMS	15:55:37	8.97	53.848	
58252-001AMSD	16:10:24	8.92	53.983	
CCV	16:25:08	8.92	53.015	
CCB	16:39:53	----	0 (ND)	
58251-004A*5	**16:54:41**	**9.63**	**2.960**	
CCV	17:39:02	8.82	55.063	
CCB	17:53:49	----	0 (ND)	

Data Reprocessed On 08/11/2003 09:26:21

Sample Name:	58251-004A	Date:	08/07/2002 14:50:15
Data File :	C:\DX\DATA\02080701.D15		
Method :	C:\DX\METHOD\020807.MET		
ACI Address: 1	System: 1 Inject#: 15	Detector:	PED-Cond.
Analyst :	Column:		

Calibration	Volume	Dilution	Points	Rate	Start	Stop	Area Reject
External	1	1	3600	5Hz	0.00	12.00	1000

********** Component Report: All Components **********

Pk. Num	Ret Time	Component Name	Concentration UG/L	Height	Area	Bl. Code	%Delta
2	9.42	Perchlorate	27.778	52947	1964237	1	2.17
		Totals	27.778	52947	1964237		

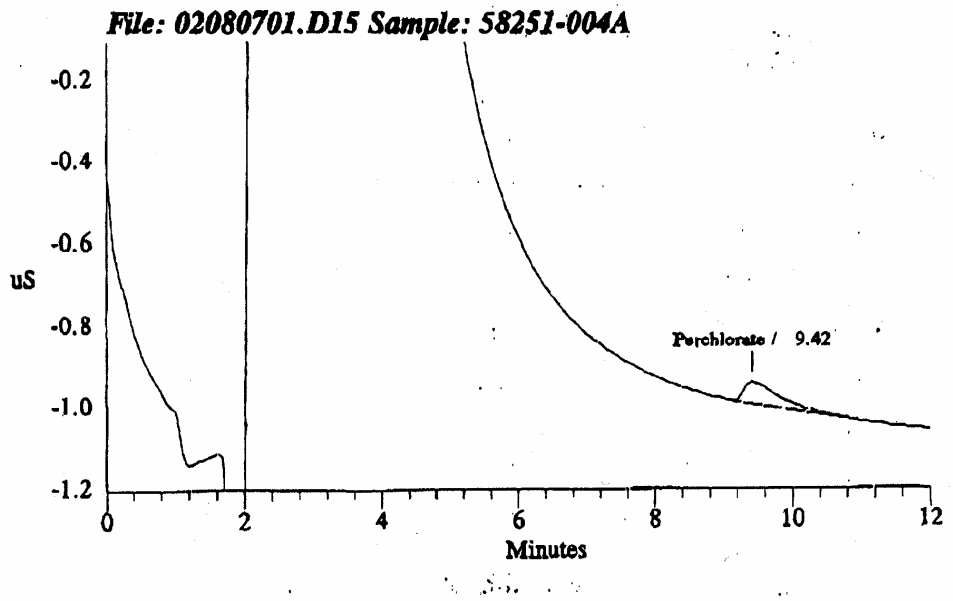

Figure 1: Ion Chromatogram for sample (Lab ID: 058251-004 or Client Sample ID: 90682) at issue.

Data Reprocessed On 08/11/2003 09:28:43

Sample Name:	58251-004A*5	Date:	08/07/2002 16:54:41
Data File :	C:\DX\DATA\02080701.D22		
Method :	C:\DX\METHOD\020807.MET		
ACI Address: 1	System: 1 Inject#: 22	Detector:	PED-Cond.
Analyst :	Column:		

Calibration	Volume	Dilution	Points	Rate	Start	Stop	Area Reject
External	1	1	3600	5Hz	0.00	12.00	1000

********** Component Report: All Components **********

Pk. Num	Ret Time	Component Name	Concentration UG/L	Height	Area	Bl. Code	%Delta
1	9.63	Perchlorate	2.960	8565	219775	1	4.52
		Totals	2.960	8565	219775		

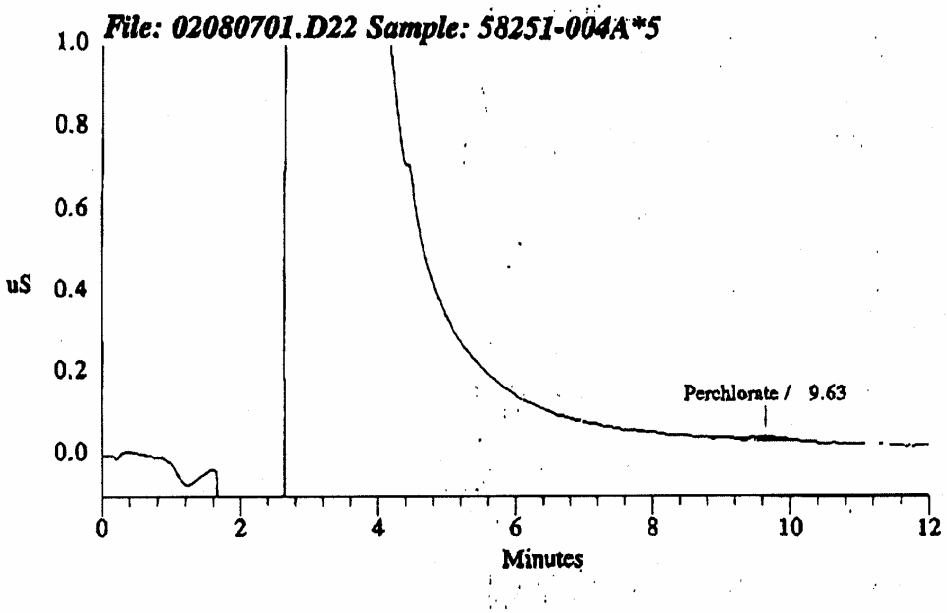

Figure 2: Ion Chromatogram for sample (Lab ID: 058251-004 or Client Sample ID: 90682) at issue with a dilution factor of 5.