

Site Survey with the FROG-5000™ in Ellinwood, Kansas

Doug Adkins and Pat Bingaman, Defiant Technologies, Inc. Albuquerque, NM

Background:

In mid-February 2018, the Kansas Department of Health and Environment (KDHE) invited Defiant Technologies to participate in a field study along with GSI Engineering. This three day field survey took place in Ellinwood, Kansas. The test sites initially were monitored for leakage from underground petroleum storage tanks. In 1999, however, testing indicated that trans-1,2-dichloroethene (t-DCE), cis-1,2-dichloroethene (c-DCE), trichloroethylene (TCE) and tetrachloroethylene (PCE) were present. It was suspected that solvents leaked into the water from a local dry-cleaning facility. The Ellinwood sites were retested at this time as part of a continued monitoring program. From earlier test results, it was known that the contamination in this area is not just chlorinated compounds, but it is a complex mixture of chemicals that also includes petroleum derived compounds (benzene, toluene, xylenes, etc.).

Equipment:

Defiant Technologies, Inc. participated in the study using a FROG-5000™ to provide on-site water testing results. The FROG is a gas chromatograph with a 5.2-meter column and a 10.6 eV photoionization detector (PID) with an integrated purge and trap for water samples. The state of Kansas also had an on-site mobile lab equipped with an Agilent 7890 with a 30-meter column, an electron capture detector (ECD) and headspace analyzer. Both GSI and Defiant collected samples for off-site lab analyses.



Figure 1. Lowering an Teflon® sampling tube down the Geoprobe casing.

Test procedures:

A total of eight sites were sampled in Ellinwood. At seven locations, samples were extracted using a Geoprobe, and at one location, samples were drawn from an existing groundwater monitoring well. In taking a sample with the Geoprobe, a hollow rod was driven to bedrock at a depth of approximately 60 feet. A screen tube then was deployed at the end of the steel tube as the probe was partially extracted. To draw a sample, Teflon® tubing with a check-valve at the bottom was lowered down the probe tube (see Figure 1) and, with several quick strokes, water was pulled up and out of the Teflon tube. After a few minutes of purging liquid from the test depth, the tubing was withdrawn and samples were transferred from the Teflon tube to sample vials. Three depths were tested at each location; one near the bedrock base, one at 40 feet below the surface, and one at 20 feet. The water table surface was about 15 feet below the ground surface. Samples were also tested from groundwater monitoring wells at three sites in Hoisington, Kansas with known issues of chlorinated solvent contamination.

Calibration and Quality Control Samples

The FROG-5000™ was calibrated for benzene, toluene, ethylbenzene, para-xylene, meta-xylene, and ortho-xylene, (BTEX), trans-1,2-dichloroethene, cis-1,2-dichloroethene, trichloroethylene (TCE), tetrachloroethylene, (PCE) in Kansas on the evening before testing began (see Figure 2). Collectively the chlorinated compounds are known as chlorinated alkenes (CA). Figure 2 shows that the separation is sufficient to easily distinguish between the compounds.

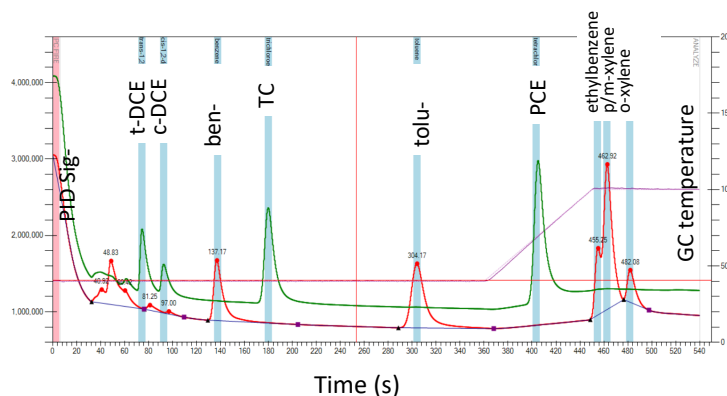


Figure 2. Chromatogram of BTEX (red) at 8 ppb and CA analytes (green) at 12 ppb from calibration runs. Compounds were well separated in these runs.

Table 1. R-squared values for each target analyte calibration.

Analyte	R ²	Fit
Vinyl Chloride	0.99953	Linear
t-1,2-Dichloroethene	0.99963	Linear
c-1,2-Dichloroethene	0.99817	Linear
Benzene	0.99988	Linear
Trichloroethene	0.99982	Linear
Toluene	0.99972	Linear
Tetrachloroethene	0.99997	Linear
Ethylbenzene	0.99992	Non-Linear Quadratic
p/m-Xylene	0.99977	Non-Linear Quadratic
o-Xylene	0.99974	Non-Linear Quadratic

The calibration consisted of five concentrations for each analyte over a range from 0.4 to 36 µg/L (ppb). The R² and fit for each compound is shown in table 1, each well above the EPA recommended 0.995.

Tests with known concentrations were also conducted periodically in the field to determine if the instrument performance was acceptable. Results of those calibration verifications (CCV) are shown in table 2. Tables 3 and 4 show the % recovery for the continuing calibration verification samples analyzed at the beginning of each test day. There were no chlorinated alkenes analyzed on day 1 so there is no CCV for those compounds on day 1. Each compound on day 1 passes the 70% to 130% as recommended by EPA 8000. On day 2, each compound passes the same criterion except for t-DCE and toluene. t-DCE is biased high and since all samples on that test

Table 3. Day 1 Continuing Calibration Verification

Analyte	Measured	Actual	%Rec
Benzene	2.0	2.00	100%
Toluene	1.6	2.00	80%
Ethylbenzene	1.9	2.00	95%
p/m-Xylene	4.1	4.00	103%
o-Xylene	2.5	2.00	125%

Table 4. Day 2 Continuing Calibration Verification

Analyte	Measured	Actual	%Rec
t-DCE	3.4	2.00	170%
c-DCE	2.3	2.00	115%
Benzene	2.3	2.00	115%
TCE	2.2	2.00	110%
Toluene	1.2	2.00	60%
PCE	2.2	2.00	110%
Ethylbenzene	1.4	2.00	70%
p/m-Xylene	3.2	4.00	80%
o-Xylene	1.9	2.00	95%



Figure 3. To the left is a FROG-5000™ running a water sample in Ellinwood, Kansas. The battery-operated FROG™ uses scrubbed ambient air as sparge and carrier gas for the GC. While not necessary, attaching to the computer allows data to be studied in real-time with the Ellvin™ software.

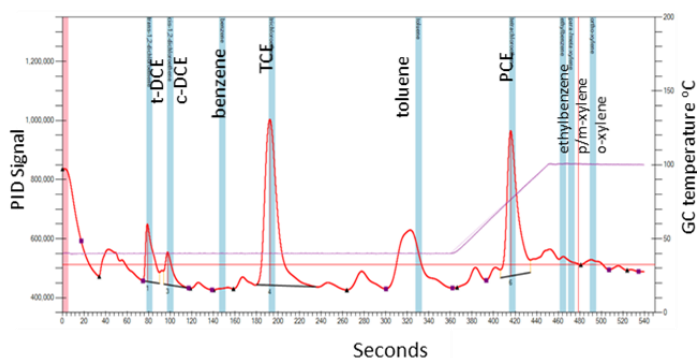


Figure 4. Chromatogram of HMW-21 sample produced on the FROG. In this sample, peaks for the CA materials were clearly visible and easily distinguished in a complex background even

Table 5. FROG and Kansas Health & Environmental Laboratories (KHEL) test results from Hoisington, KS test site.

Location	t-DCE		c-DCE		TCE		PCE		Log #
	FROG	KHEL	FROG	KHEL	FROG	KHEL	FROG	KHEL	
HMW-15	ND	ND	ND	ND	0.7	1.0	1.6	1.6	565
HMW-14	116	91	111	120	123	110	29.4	13	579
HMW-21	94.5	53	93.5	60	191	66	92.4	57	571

day were ND, there is no effect on the field sample data. Toluene is biased slightly low in the CCV, so one would expect a slight low bias in the data for toluene measurements on day 2.

Test results:

Test results from the FROG™ were compared with the on-site KDHE mobile lab during this study.

In total, twenty-two samples were tested with the FROG™ at the Ellinwood site. Three samples from monitor wells in Hoisington, KS (HMW-15, HMW-14 and HMW-21) were also tested with the FROG. GSI sent twenty samples from Ellinwood

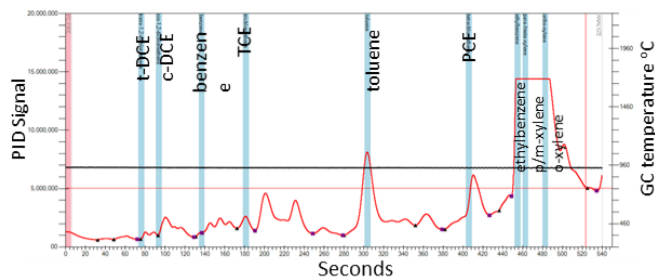


Figure 5. Chromatogram of GP-2 at 20' produced by the FROG. The sample dilution was 50x. Very complex chromatogram makes it difficult to identify and quantify compounds.

to a certified lab for testing. Ten of the twenty samples reported no detection for chemical contamination. Two samples from the same locations (GP-1(56') and GP-7(72')) had no detectable contamination when tested with the FROG. The FROG also showed that seven more samples had only benzene or toluene contamination at concentrations below one ppb. For these same samples, the result was lower than the reportable limit of the GSI lab results, so they would be reported as a non-detect. These sites were GP-1(40'), GP-3 (20', 40', 60'), GP-4(20', 40', 73'). The remaining lab-certified non-detect sample, GP-7(20') was not tested with the FROG. Overall, the non-detect lab results correlated well between the certified lab and the FROG results.

Results for the three Hoisington monitor wells are shown in Table 5. At HMW-14 and HMW-21, the samples were run on the FROG with a 25x dilution to remain within the calibration

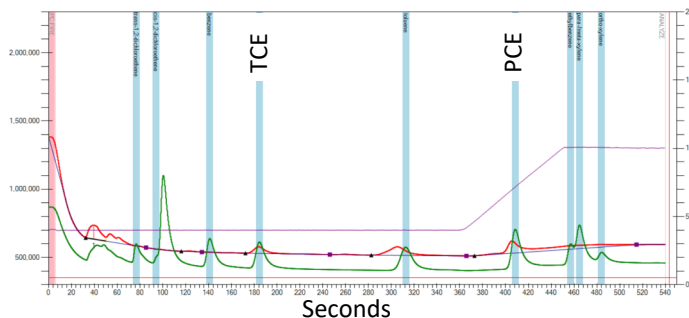


Figure 6. An overlay of the test results from MW-14 (red line) and a spiked sample with BTEX and CA (green line). The MW-14 chromatogram has one peak that aligns with the TCE peak in a spiked sample.

range. It was known from historical data that these sites had high levels of chlorinated alkenes. Samples that were sent to the Kansas Health & Environmental Laboratories compare well with the FROG results, however, the FROG typically did show higher contamination levels. The FROG was able to provide results in less than 10 minutes per sample in the field. The chromatogram for HMW-21 in Figure 4 shows the separation of compounds that was achieved on the FROG's 5.2-meter GC column.

The remaining samples from the Ellinwood sites did show water contamination, often at very high levels. Figure 5 shows a chromatogram from one site where the sample was diluted 50x. Even with this level of dilution, the instrument still reached its upper measurement limit for xylenes.

Table 6. Field test results with a comparison between the FROG-5000, the GSI testing lab, and the Hall Environmental Analytical Lab (HEAL) in Albuquerque. Results are reported in $\mu\text{g/L}$ (ppb) in the order FROG/GSI/HEAL. * indicates that the lab did not receive a sample.

Location and Depth	Benzene			Toluene			Ethylbenzene			Total Xylenes			FROG-5000 LOG #
	FROG	GSI	HEAL	FROG	GSI	HEAL	FROG	GSI	HEAL	FROG	GSI	HEAL	
GP-1(20')	2	2	3	ND	ND	ND	1.4	ND	ND	2.4	ND	ND	524
GP-2(20')	33	ND	*	2550	2140	*	>CAL	2280	*	>CAL	10700	*	536
GP-2(40')	ND	ND	ND	6.3	4.8	6	7.8	6.3	7.7	63	30.9	37	520
GP-2(58')	ND	ND	*	20.4	33.4	*	38.3	49.8	*	248	255	*	530
GP-5(20')	ND	ND	*	ND	ND	*	45	19	*	44	ND	*	582
GP-5(40')	ND	ND	*	ND	ND	*	1.7	ND	*	ND	ND	*	578
GP-5(60')	ND	ND	*	ND	ND	*	4	2	*	3.8	ND	*	574
GP-6(20')	ND	ND	ND	ND	ND	ND	432	289	190	ND	ND	ND	615
GP-6(40')	ND	ND	*	ND	ND	*	1.4	ND	*	ND	ND	*	590
GP-6(54')	ND	ND	*	ND	ND	*	1.5	ND	*	ND	ND	*	586
MW-14	ND	*	ND	ND	*	ND	ND	*	ND	ND	*	ND	520

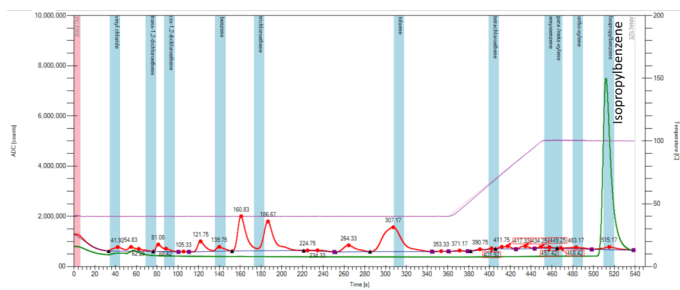


Figure 7. Chromatogram for sample GP-1(20') (red) with an overlay of an analytical standard of 40ppb Isopropylbenzene (green). HEAL reported a concentration of 2.6 ppb for isopropylbenzene in the GP-1 sample.

One complication that did arise in the testing was that the pressure into the GC column shifted by 17 Torr. This was partially the result of variations in barometric pressure that fell from 710 Torr on the first day of testing to 699 Torr on the third and final day. On average, a two Torr decrease in GC inlet pressure causes about a 1 second increase in the time it takes a compound to elute from the column. Normally, slight changes in the retention time are not critical. As illustrated in Figure 5, however, there was a very complicated mix of chemicals at high concentrations at some of the sites. With multiple peaks and many co-eluting compounds, even slight shifts in retention times can lead to the incorrect identification of compounds.

The FROG's internal pressure sensor registers both the ambient pressure and the pressure out of the pump. The pump speed is digitally controlled, so compensating for pressure variations is simple. However, for this study, the pump speed was not altered. Instead, retention time adjustments were made in the post field test analysis.

Table 6 shows the results from the FROG-5000's water analysis at 11 of the test sites. Ten of these samples had certified lab results that GSI shared with Defiant Technologies for this study. Three of the sites also had results from HEAL in Albuquerque.

Most of the lab results had compounds that were in the FROG's calibration mixture so results can be compared. Overall the comparison between results was fairly good considering the complexity of mixtures at the different sites and the sediments in many of the samples. In general, measured concentrations were no more than 25% different. There was one instance, however, when the FROG showed the presence of xylenes at a high concentration, when the lab results showed no xylenes were present (see GP-5(20')). In general, the FROG reported concentrations slightly higher than the certified labs, but this might be attributable to VOC losses incurred during

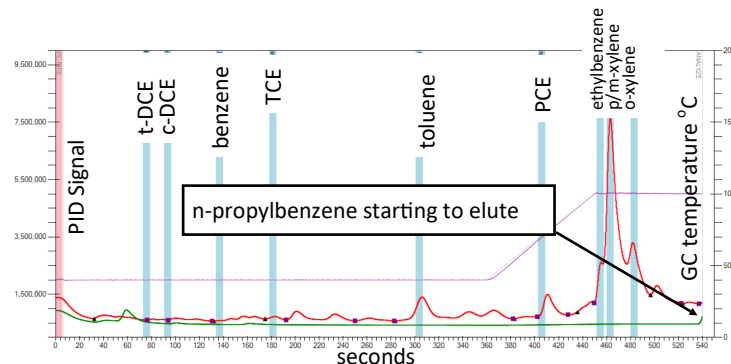


Figure 8. Chromatogram of sample GP-2(40') (red) overlays with sample spiked with n-propylbenzene (green). Here it is shown that n-propylbenzene in the sample will elute late in the analysis so longer analysis times would be warranted in future tests.

transport to the off-site labs. In one instance (GP-2(20')), the FROG was overwhelmed by the sample even with a 50x dilution. The sample could have been run with a higher dilution for measurable results, but a few run cycles were required to flush VOCs through the instrument to prepare for testing at the next site.

In the water samples with contamination, a peak periodically appeared in the FROG's chromatography near the elution time for TCE. The FROG consistently identified these peaks as TCE, however the calculated concentration was generally less than 1 ppb. This peak is illustrated in Figure 6. None of the certified lab testing showed that TCE was present in any of the samples. This was obviously a compound that had an elution time close to that of the TCE, so data from the FROG was useful in identifying that the sample warranted further examination. This illustrates the importance of sending a few samples off to a certified lab for confirmation of the final results.

When unknown peaks appear in a chromatogram, it may be interesting to analyze analytical standards after a field test to understand the collected data. While running a calibration after a field test is out of the norm for any quality assurance program, it can be informative to help identify previously unknown compounds in a chromatogram. For example, the lab results from HEAL indicated that isopropylbenzene was found in GP-1(20'). It is relatively simple to run a spiked water sample of isopropylbenzene and determine that it elutes at 515 seconds for the GC in this FROG. If a peak at 515 seconds appears in other samples, one may presume that it is isopropylbenzene. Figure 7 shows the test data for GP-1(20') and an overlay of a spiked water sample of isopropylbenzene at 40 ppb.

Both HEAL and the GSI lab also reported the presence of n-propylbenzene in several samples. Figure 8 shows a chromatogram of a sample with a reported concentration of 2 ppb

for n-propylbenzene. When a water sample spiked with 12 ppb of n-propylbenzene was tested on the FROG, it was observed that this compound elutes from the column at about 545 seconds. This elution time was slightly longer than the analysis time that was used in the field. As such, a comparison with the field data cannot be performed. Knowing the full extent of the analytes thought to be present in a field test is important in formulating a test plan. If it was determined that a compound would elute late in the analysis, then longer analysis times or higher GC temperatures could be selected for future surveys. Fortunately, these parameters are easy to change in the FROG's operating parameters, and can be altered in the field if necessary.

Conclusions:

This study demonstrated how a portable gas chromatograph can aid in a site assessment. Even test results that show non-detect can be important in directing resources during the field work and determining which samples should be sent to a fixed site laboratory for further evaluation. Despite having a very complicated matrix of contaminants in the Ellinwood water samples, the FROG did a reasonable job in matching the results from certified off-site labs.

In future field work, it is recommended that the pump pressure be checked a few times during the day and reset if needed. This is a simple adjustment to perform on the FROG-5000™ and it serve to simplify the data analysis later.

High concentrations of contaminants and multiple compounds that elute closely together will add to the complexity of the water testing. However, this is not a completely unusual situation, and hopefully some insights have been provided to assist a user of the FROG-5000™.

Acknowledgements:

The authors of this study would like to thank the Kansas Department of Health and Environment for inviting us on this field study in Ellinwood, KS. We would also like to thank GSI Engineering for coordinating this work.