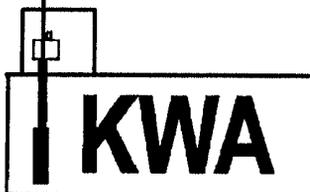


Evaluation of the FCI Fiber Optic Chemical Sensor (FOCS) for Vapor Phase Out-of-Tank Product Detector

Addendum for Lower Detection Limit

Prepared for:
FCI/Fiberchem, Inc.

December 5, 1994



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**Prepared for:
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1181 Grier Drive, Suite B
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Background

This report is an addendum to an earlier evaluation of the FCI Fiber Optic Chemical Sensor (FOCS)[™] for vapor detection. (See "Evaluation of the FCI Fiber Optic Chemical Sensor (FOCS)[™] for Vapor Phase Out-of-Tank Product Detector," March 7, 1994.) In the earlier evaluation testing was conducted at higher concentrations of the order of several hundred ppm. Because these tests were conducted at vapor concentrations well above the Lower Detection Limit (LDL), it was necessary to conduct additional tests closer to the LDL to establish the FOCS performance at low concentrations. These tests were conducted under static test conditions (as would be expected for sensors in monitoring wells) rather than with a dynamic flow system such as was used for the earlier tests. The modified EPA results forms for the LDL are contained in attachment 1 of this document.

Objectives

The primary objective of this evaluation was to determine the minimum detectable vapor concentration that could be measured by the FOCS Sensors. Several different products including xylene, gasoline, JP4, and other products were tested at low vapor concentrations. Testing was conducted using the procedures described in the EPA protocol "Standard Test Procedures for Evaluating Leak Detection Methods: Vapor-Phase Out-of-Tank Product Detectors," EPA/530/UST-90/008, particularly Section X 0006 for determination of the LDL. Modifications to the procedure are noted in this report.

Description of Equipment

The FCI FOCS Vapor Sensor is a total hydrocarbon instrument that can be calibrated to read in any units. It has a temperature compensation built into the sensor head. A calibration is readily accomplished by exposing the sensor to a test atmosphere of known product type and concentration.

Test Procedure

The concentration levels selected for this testing were based on previous experimental data obtained by FCI prior to the evaluation. Each sensor was calibrated at vapor concentrations near the expected detection limit for each product. This was followed by the measurement of an "unknown" concentration prepared by KWA. The products tested are listed in Table 1. The molecular weights and densities used in the calculation are also included in Table 1. The densities were measured by FCI for each of the products. The molecular weights were estimated by FCI.

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Calibration

Each sensor was calibrated by first exposing it to a clean atmosphere and adjusting the output to zero. The sensors were then exposed to a known atmosphere generated by injecting 0.3 μL of product into a test chamber with a volume of 3.8 L. The concentration of the atmosphere was calculated to be of the order of 10 ppm for all of the products tested. The calculations were based on estimated molecular weights for all products except xylene and synthetic gasoline. The molecular weight of the synthetic gasoline was calculated from the weighted average of the compounds used to blend the fuel. The calibration coefficients were then adjusted to give the calculated concentration.

Table 1. Products Tested with FOCS Sensors

Product	Molecular Wt. (g/mole)	Density** (g/mL)
Kerosene	97.5*	0.820
P-Xylene	106.17	0.866
Synthetic Gasoline	95.3	0.736
JP-4	115.5*	0.815
JP-8	110.75*	0.806
Diesel Fuel	115.45*	0.841
Unleaded Gasoline	95.0*	0.753

* estimated ** measured in the laboratory

Measurement of Blind Test Atmospheres

The techniques used to produce the test atmospheres was identical to that for the calibration except that the volume of liquid injected into the test cell was unknown to FCI. The sensors were first exposed to a zero atmosphere until stable readings were obtained. Vapor concentrations were prepared by KWA by injecting known volumes of liquid into each test cell using the same techniques as were used for the calibration. The test cells were then allowed to come to equilibrium and the measured concentrations were recorded.

A one μL syringe was used to introduce the liquids through a port in the lid of the test chamber. The test chamber was examined visually after injection to determine if complete evaporation had occurred as well as monitoring the time to reach stable output for each sensor.

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Eight sensors were installed in each test chamber so that simultaneous tests were conducted under identical test conditions for each run. The concentration of vapor in the test cell was calculated for each of the products using estimated average molecular weights. The concentration of p-Xylene was measured independently using a gas chromatograph that was calibrated using the same test atmosphere as the FOCS sensors. It was assumed that all of the injected product evaporated prior to obtaining the sample readings. The stabilization time varied from 15-20 minutes for Xylene to one hour for diesel fuel.

The test cell was cleaned and ventilated thoroughly between runs. In some instances the test cell was heated to approximately 110 Deg C in a drying oven to assist in removing volatile materials from the cell.

Calculations

The vapor concentrations for each product were calculated using the equation

$$\text{Calculated Conc} = \mu L * \frac{d}{MW} * \frac{22.4}{V_{cell}} * 1000$$

where μL is the micro liters of product injected into the test chamber, d is the density of the liquid product, MW is the molecular weight of the product and V_{cell} is the volume of the test chamber. The standard deviation was calculated using the difference between the mean measured value and the calculated concentration. A mean and standard deviation were calculated for each product. The lower detection limit (LDL) was calculated from the equation

$$\text{Lower Detection Limit} = K * s + B$$

where K is the tolerance limit statistic, s is the standard deviation and B is the absolute bias. Separate LDLs were determined for each product tested.

Calculations were conducted to determine the relationship between the output of the FOCS sensors and the gas chromatograph for xylene and synthetic fuel. These vapor concentrations of these two products could be accurately calculated because the molecular weights could be established. Both the GC and the FOCS sensors were calibrated using xylene standards prepared by KWA.

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Table 2. Vapor Test Data for the FOCS Sensors (In ppm)

Diesel Vapor Tests

Probe No.	Measured Conc	Meas-Calc
1174	7.26	-1.21
353	6.62	-1.85
432	6.60	-1.87
505	6.12	-2.35
513	6.66	-1.61
534	7.27	-1.20
543	4.13	-4.34
583	6.77	-1.70

Average 6.45 -2.02
 Stdev 1.01
 LDL = 5.79
 Calc Conc 8.47

JP-8 Vapor Tests

Probe No.	Measured Conc	Meas-Calc
1174	12.96	1.11
353	11.00	-0.85
432	5.45	-6.40
505	9.02	-2.83
513	8.32	-3.52
534	7.92	-3.93
543	9.95	-1.90
583	9.23	-2.61

Average 9.23 -2.62
 Stdev 2.22
 LDL = 10.89
 Calc Conc 11.85

Unleaded Gas Vapor Tests

Probe No.	Measured Conc	Meas-Calc
1056	14.52	3.46
1246	10.61	-0.45
355	12.12	1.06
422	14.94	3.88
442	11.03	-0.03
450	10.13	-0.93
488	13.69	2.63
586	15.01	3.95

Average 12.76 1.70
 Stdev 2.02
 LDL = 7.55
 Calc Conc 11.06

Kerosene Vapor Tests

Probe No.	Measured Conc	Meas-Calc
1056	15.95	6.17
1246	12.40	2.62
355	16.66	6.88
422	18.14	8.36
442	14.63	4.85
450	18.56	6.78
488	18.70	8.92
586	15.51	5.73

Average 16.32 6.54
 Stdev 2.18
 LDL = 14.65
 Calc Conc 9.78

JP-4 Vapor Tests

Probe No.	Measured Conc	Meas-Calc
1074	13.99	0.86
1108	14.70	1.57
1196		
424	12.01	-1.12
447	12.99	-0.14
555	14.20	1.07
571	11.17	-1.96
602	14.48	1.35

Average 13.36 0.23
 Stdev 1.35
 LDL = 5.26
 Calc Conc 13.13

Synthetic Gas Vapor Tests

Probe No.	Measured Conc	Meas-Calc
1174	17.82	-4.63
353	21.94	-0.52
432	20.66	-1.79
505	28.86	6.40
513	19.78	-2.67
534	19.65	-2.80
543	23.22	0.77
583	24.10	1.64

Average 22.00 -0.45
 Stdev 3.43
 LDL = 13.26
 Calc Conc 22.45

p-Xylene Vapor Tests

Probe No.	Measured Conc	Meas-Calc
1174	19.98	5.76
353	13.14	-1.09
432	21.13	6.90
505	16.16	1.94
513	15.37	1.15
534	17.98	3.75
543	18.98	4.76
583	17.19	2.96

Average 17.49 3.26
 Stdev 2.60
 LDL = 12.94
 Calc Conc 14.23
 GC Conc.-Run 1 10.06
 GC Conc.-Run 2 6.81

Physical Characteristics

Product	Density	Mol Wt.	Vol. Inj.
Xylene	0.866	106.17	0.30
JP4	0.815	115.50	0.32
JP8	0.806	110.75	0.28
Syn Gas	0.736	95.30	0.50
Kero	0.800	110.55	0.20
Diesel	0.841	115.45	0.20
UL Gas	0.753	95.00	0.24

Test Results

The test results have been provided in Table 2. The concentrations tabulated were obtained from each sensor with the appropriate calibration constants built into the measurement. Differences in sensitivity between sensors and product types have all been accounted for by the calibration. The individual sensor readings for the test atmosphere have been provided for each product. The difference between the measurements obtained from each probe and the calculated concentrations were also tabulated. A summary of the performance of the FOCS system is provided in Table 3.

Table 3. Summary of Performance

Product	StdDev	Bias (ppm)	LDL (ppm)
Diesel	1.01	-2.02	5.79
JP4	3.08	0.23	5.26
JP8	2.22	-2.62	10.89
Synthetic Fuel	3.43	-0.45	13.26
p-Xylene	2.60	3.26	12.94
Kerosene	2.18	6.54	14.65
UL Gasoline	2.02	1.70	9.25

Discussion

There were several problems associated with this testing that may have contributed to the standard deviation and biases of these measurements. Briefly stated these are:

- a) the molecular weights of most compounds had to be estimated;
- b) it was difficult to reproducibly introduce sub-microliter volumes of liquid into the test chamber; and
- c) it was necessary to assume something about the percent of evaporation of the liquid injected into the test chamber.

In spite of these technical uncertainties, it is clear that the FOCS sensors are capable of detecting vapor concentrations at in the range of 10 ppm under laboratory conditions.

To evaluate the absolute accuracy of the vapor sensors it is necessary to know the average molecular weight of the products used to generate the calibration standards. For this evaluation, reasonable estimates were made for each of the products where they could not be readily obtained. The synthetic fuel was prepared from a known blend of pure materials and could

FOCS Lower Detection Limit

therefore be estimated reasonably well. This value was also used for the unleaded gasoline that was obtained from a commercial station. The molecular weight of p-Xylene was obtained from its formula. The estimated molecular weights of kerosene, diesel fuel, JP8, and JP4 were obtained from FCI.

The difficulty in establishing the true concentration of vapor in the test chamber has little effect on the standard deviation of the readings. This is because all eight sensors were exposed to identical atmospheres for both zero and test vapor conditions. Any calibration errors would have produced identical shifts in output for all sensors for a given product. In fact the standard deviations are relatively small, usually of the order of 2 or 3 ppm, and, except for kerosene, they are equally distributed around zero.

A second, more serious limitation involved the difficulty in establishing reproducible concentrations. It is difficult to reproducibly inject sub-microliter volumes of liquid into a test chamber. Some of the deviation in concentration levels from the calculated values was no doubt due to the difficulty in reproducibly injecting the small amounts of liquid into the test chamber.

The results of injection errors are to introduce biases (either positive or negative) into the test results. Biases of this type are not related to the performance of the sensors in any way but is rather an artifact of the testing. Despite these difficulties, the absolute biases for all but one of the products are less than 3.5 ppm. The relatively large bias for kerosene is probably due to a slight discrepancy in generation of the test atmosphere.

A third potential source of bias occurs if less than 100% of the liquid injected into the test chamber evaporates. This will produce measured values less than those calibrated and result in a negative bias. Errors of this type would not have been detected during this evaluation since the calibration and test procedures were identical.

The implications of a bias for a field measurement are similar to those for the laboratory calibration. Errors in the calibration standard due to incorrect molecular weight will be reflected in the accuracy of the system. The problem is not particularly acute when the product type is known, but will result in some uncertainty when the product type is not known or when several types of products are present at the same time.

Although an attempt was made to correlate the output of the FCI sensors with the output of a gas chromatograph, the results were not as precise as expected. While there are some differences, they are not large and, again, are most likely due to experimental errors rather than any inherent problem with the FCI sensors.

Attachment 1
EPA Results Forms

Results of the U.S. EPA Standard Evaluation*
Vapor-Phase Out-of-Tank Product Detectors
(Page 3 Addendum Added December 5, 1994)

This form documents the performance of the vapor-phase product detector described below. The evaluation was conducted by the equipment manufacturer or a consultant of the manufacturer according to the U.S. EPA's "Standard Test Procedure for Evaluating Leak Detection Methods: Vapor-Phase Out-of-Tank Product Detectors."

Tank owners using this leak detection system should keep this form on file to prove compliance with the federal regulations. Tank owners should check with state and local agencies to verify that this form satisfies their requirements.

Method Description

Name Analog Hydrocarbon Probe 100

Version AHP 100

Vendor FCI Environmental, Inc. and Fiberchem, Inc.

1181 Grier Drive, Suite B

(street Address)

Las Vegas, NV 89119 (702) 361-9873

(city)

(state)

(zip)

(phone)

Detector output type: Quantitative Qualitative

Detector operating principle: Metal Oxide Semiconductor Adsistor Detector Tube
 Catalytic Gas Sensor Combustible Gas Detector Photoionization Detector Product-
 Permeable Detector IR Detector Other Fiber Optic

Detector sampling frequency: Intermittent Continuous

Evaluation Results

The detector described above was tested for its ability to detect known concentrations of test gas. The following parameters were determined:

Accuracy - How closely test gas concentration, as measured by the detector, agrees with the actual gas concentration.

Bias - Whether the method consistently over-estimates or under-estimates gas concentration. Not applicable to qualitative detectors.

Precision - Agreement between multiple measurements of the same gas concentration. Not applicable to qualitative detectors.

Detection Time - Amount of time the detector must be exposed to test gas before it responds.

Fall Time - Amount of time that passes before the detector returns to its baseline reading after test gas is removed.

Lower Detection Limit - The smallest gas concentration that the detector can reliably detect.

Specificity - Indicates the ability of the detector to detect several different test gasses.

* This evaluation includes testing using the techniques described in both EPA protocols dated March 1990 and June 1990.

Evaluation Results

>Compiled Test Results (for tests conducted with 1000 ppm of test gas)

Test	<u>March, 1990 Protocol</u>			<u>June, 1990 Protocol</u>	
	Xylene	Benzene	2-Methylbutane	Unleaded Gasoline	Synthetic Gasoline
Relative Accuracy (%)**	<u>2</u>	<u>35</u>	<u>NR **</u>	<u>12</u>	<u>22</u>
Bias* (%)	<u>1</u>	<u>-23</u>	<u>NR</u>	<u>-7</u>	<u>-2</u>
Precision* (%)	<u>1</u>	<u>11</u>	<u>NR</u>	<u>4</u>	<u>15</u>
Detection Time (hh:mm:ss)	<u><1 min</u>	<u><1 min</u>	<u>NR</u>	<u><1 min</u>	<u><1 min</u>
Fall Time (hh:mm:ss)	<u><1 min</u>	<u><1 min</u>	<u>NR</u>	<u><1 min</u>	<u><1 min</u>
Lower Detection Limit (ppm)	<u>84</u>	<u>519</u>	<u>NR</u>	<u>137</u>	<u>220</u>

*not applicable to qualitative detectors ** No Response

>Specificity Results (%)*	<u>March, 1990 Protocol</u>		<u>June, 1990 Protocol</u>
Benzene	<u>76</u>	Unleaded Gasoline	<u>93</u>
Toluene	<u>96</u>	Synthetic Gasoline	<u>98</u>
p-Xylene	<u>101</u>	JP-4 Jet Fuel	<u>105</u>
Synthetic Gasoline	<u>100</u>	n-Hexane	<u>NR</u>
Trimethylbenzene	<u>107</u>	Xylene	<u>103</u>
Methane	<u>NR</u>		
Butane	<u>NR</u>		
2-Methylbutane	<u>NR</u>		
Pentane	<u>NR</u>		

* corrected for sensitivity differences (see attached sheet)

>Safety disclaimer: This test procedure only addresses the issue of the method's ability to detect leaks. It does not test the equipment for safety hazards.

Certification of Results

I certify that the vapor-phase product detector was operated according to the vendor's instructions and that the evaluation was performed according to the standard EPA test procedure for vapor-phase out-of-tank product detectors except as noted on any attached sheets. I also certify that the results presented above are those obtained during the evaluation.

H. Kendall Wilcox, President
 (printed name)

H. Kendall Wilcox
 (signature)

March 7, 1994
 (date)

Ken Wilcox Associates, Inc.
 (organization performing evaluation)

Independence, MO 64055
 (city, state, zip)

(816) 795-7997
 (phone number)

Addendum for Lower Detection Limit for FOCS Vapor Sensors

Vapor-Phase Product Detector Fiber Optic Chemical Sensor (FOCS)TM Vapor Sensor
Version Analog Hydrocarbon Probe 100

Testing was conducted at vapor concentrations of approximately 10 ppm to determine the Lower Detection Limit (LDL) for FOCS vapor sensors when exposed to low levels of hydrocarbon vapor. The procedures used were those described in the EPA protocol for Vapor Phase Out-of-Tank Leak Detectors. The results are shown below.

Product	Std. Dev.	Bias (ppm)	LDL (ppm)
Diesel	1.01	-2.02	5.79
JP4	3.08	0.23	5.26
JP8	2.22	-2.62	10.89
Synthetic Fuel*	3.43	-0.45	13.26
p-Xylene	2.60	3.26	12.94
Kerosene	2.18	6.54	14.65
UL Gasoline	2.02	1.70	9.25

* blended as described in the EPA protocol for Liquid Phase Out-of-Tank Leak Detectors

Certification of Results

I certify that the vapor-phase product detector was operated according to the vendor's instructions and that the evaluation was performed according to the standard EPA test procedure for vapor-phase out-of-tank product detectors except as noted on any attached sheets. I also certify that the results presented above are those obtained during the evaluation.

H. Kendall Wilcox, President
(printed name)

H. Kendall Wilcox
(signature)

December 5, 1994
(date)

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(organization performing evaluation)

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