In-field Screening Techniques for PCBs in Transformer Oil: US-EPA Field Trial Results for the L2000DX Analyzer

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Presented at the 2002 Meeting of MY TRANSFO in Torino, Italy, October, 2002

ABSTRACT

The US-EPA, through the ETV, SITE and other programs, routinely evaluates innovative field testing technologies for measuring environmental contaminants. In August of 2000 Oak Ridge National Laboratory (ORNL), through the ETV program, investigated technologies for measuring PCB contamination in transformer oil. During the field trials the Dexsil L2000DX analyzer successfully analyzed 152 oil samples -- 52 performance evaluation (PE) samples and 100 environmental samples. In comparison with laboratory results for all environmental samples, the L2000DX generated only one false positive and no false negatives. The mean relative percent standard deviation (RPSD) was 11% and the average recovery for PE samples was 112%. The overall comparison with the laboratory resulted in a correlation coefficient (R^2) of 0.87, for single Aroclor samples the correlation with the lab was 0.92. Unlike the laboratory, the L2000DX was determined to be unbiased for both single Aroclor and mixed Aroclor samples.

INTRODUCTION

The L2000DX analyzer has been in use in the field since 1989. Primarily developed for the analysis of transformer oils, the L2000DX is capable of also analyzing soils, wipes and water samples. The soil method eventually became SW-846 Method 9078[1] and has been evaluated in two different forms, first, through the SITE program[2] and, most recently, under the ETV program.[3]

The L2000DX is a total chlorine analyzer; all chlorinated compounds are quantified as the suspected contaminant. A requirement for the system is that all chlorine must be chemically converted to inorganic chloride for quantification. By changing the sample preparation steps either total chlorine or total organic chlorine will be measured. There are three elements to the analysis: sample preparation/extraction, converting the organic chlorine present into inorganic chloride using metallic sodium and the quantification of the resulting chloride using a chloride ion selective electrode (ISE). Over the 12 years of its use in the field, the L2000DX has proven to be a very reliable instrument and the ISE based system has been shown to be accurate and relatively free of interferences. (NOTE: All organic chlorine is quantified as the target analyte, however, this is the nature of a TOC measurement and is not, per se, an interference. Inorganic chloride can be an interference, but can be removed in the matrix cleanup step and, therefore, would not interfere in soil, water or wipe samples.) Because transformer dielectric fluid is relatively free of inorganic chloride, there is no specific sample preparation for oil samples, the oil is simply pipetted into the reaction tube and the test is run on the oil itself. Knowing something about the source of the contamination facilitates the conversion from chloride to the equivalent PCB concentration. If the Aroclor is known, the percent chlorine is used to calculate the final PCB concentration or, if the Aroclor is not known, a conservative conversion factor is used. In the worst case, using a conversion factor of 42% chlorine on a sample actually contaminated with 1260 will over estimate the concentration by 40% but will not result in a false negative if the sample is contaminated with Aroclor 1242, the least chlorinated Aroclor in common use.

For this study Aroclor information was provided with each sample. This information was used to convert the chloride results to PCB concentrations. In the case of mixed Aroclors the lower chlorine percentage was used for conversion to provide a conservative estimate.

Prior to the beginning of the field trials, pre-demo samples were sent to both Dexsil and the reference lab. The results from the analysis of these samples indicated that the reference lab was not accurately quantifying mixed Aroclors. This was traced to the way this lab was running SW-846 Method 8082. More specifically, overlapping peaks from the mixed Aroclor samples were not counted resulting in an under estimation of the PCB contamination. Further work with the lab did not improve the performance. ORNL personnel running the study decided to switch labs to a different commercial lab running USEPA Method 600/4-81-045.[4] Because this method is widely used in

industry and routinely performed by this lab, it was assumed by ORNL that the lab could run the method correctly. This assumption is made often by many companies trying to find a good lab but, as is not uncommon in the laboratory business routine analysis does not equate to accurate analysis.[5] As will be seen this lab too had a problem with mixed Aroclors but in the other direction.[6]

The field trials were conducted at ORNL in Oak Ridge, Tennessee, in August of 2000. The final report and data analysis was complete and published in August of 2001. Sample preparation, data collection and data reduction were conducted by ORNL personnel. Samples were delivered to Dexsil personnel as blind samples for analysis outdoors using the L2000DX without access to AC power. A total of 152 oil samples, including PE and environmental samples, were analyzed in 2 ½ days for an average throughput of eight samples per hour. Samples were analyzed in replicates of 4, therefore, there were 25 different environmental oils analyzed and 13 unique PE samples including 5 blank oils. Identical samples were analyzed by gas chromatography by an outside laboratory using EPA Method 600/4-81-045. For PE samples, the results from both the lab and the L2000DX were compared to the certified values to assess the accuracy of the two methods. For environmental samples comparisons were made between the two methods.

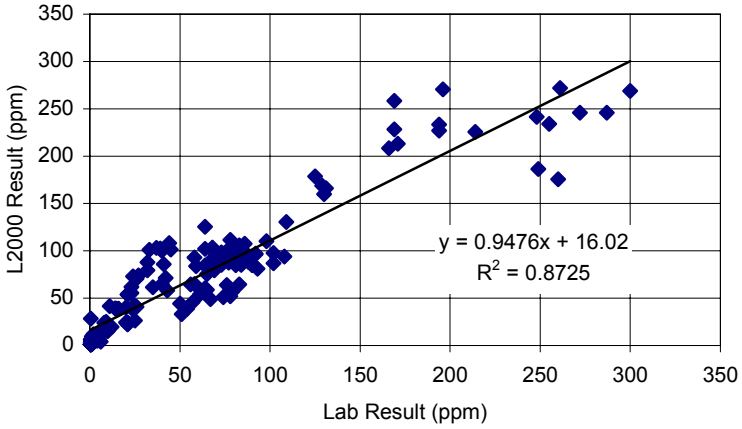
The selected technologies were evaluated according to five major criteria: precision, accuracy, false positive/false negative rates, completeness and comparability. The metric for precision was RPSD. This is a measure of how reproducible the results were and the comparison is within the replicate data generated by the field technology. To determine accuracy, the comparison is made with the certified values supplied with the standards. The resulting recovery is then the measure of the methods accuracy. The false positive/negative rate is calculated in two ways. A result is considered a false positive when a detectable level of PCB was detected for a sample where either the certified value is zero on a PE sample or there was a "non-detect" reported for an environmental sample. On the other hand, a false negative is registered if the L2000DX fails to measure a detectable amount of PCB in a sample where either the certified value for a PE sample is non-zero or the lab returned a detectable result on an environmental sample. Completeness is simply the percentage of samples for which valid results were returned. Both the L2000DX and the lab returned 100% of the possible results. Comparability was determined using both a regression analysis and by calculating the relative percent difference (RPD) between the lab and field results. The regression analysis is by far the more powerful tool for comparison. Although the relative percent difference was calculated for each data point, it is only of limited value. See the final ITVR for RPD data.

RESULTS AND DISCUSSION

The final results for the field samples were calculated as each batch was processed so that a new set of samples could be obtained. These data are then, in effect, generated in "real time" for use by field personnel. The laboratory returned their results in approximately three weeks. As can be seen in Table 1, the L2000DX results agreed well with the laboratory. In addition, the L2000DX precision was the same as the laboratory's (Average PRSD = 11).

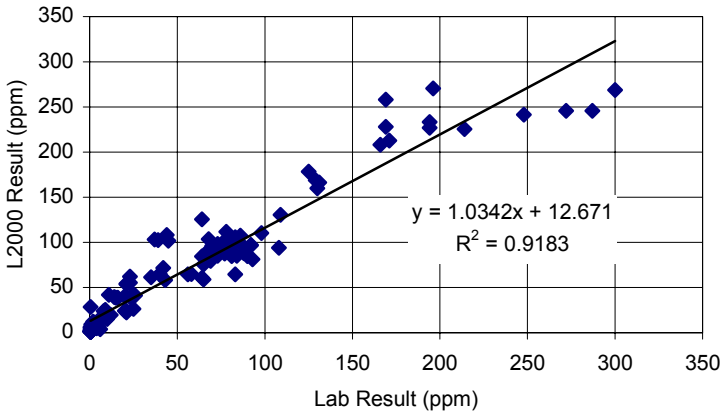
To evaluate the accuracy of the L2000DX Analyzer the PE sample data was analyzed in three groups, either single Aroclor, mixed Aroclor or all data together. The average recovery for the L2000DX for the three groups was 119%, 105% and 112% respectively. By comparison the laboratory recoveries were 97%, 134% and 115%. The performance on the mixed Aroclor samples by the laboratory indicated a problem with the integration of peak areas for overlapping Aroclor peaks. In this case, the error was in "double counting" the areas of peaks that occur in both Aroclors resulting in an over estimation of the true concentration. As mentioned in the introduction, this is the

Figure 1: L2000DX vs Lab (All Data)



opposite problem to that encountered with the first lab. Due to the high bias on the mixed Aroclor samples, consideration was taken when comparing the L2000DX results to the lab results.

Figure 2: L2000DX vs Lab (Single Aroclor Data Only)



In distinguishing contaminated oils from "clean" oils, with an effective action level of 3 ppm, the L2000DX correctly classified all contaminated oils resulting in no false negative results. The analysis of the blank oils resulted in a statistically significant result for 5 out of the 20 analyses for a 25% false positive rate. Using this same criterion, there was one statistically significant result in the field on an unknown oil where the lab returned a non-detect; Out of a total of eight non-detects for all unknown oils this would be a 12% false positive rate for environmental oils. NOTE: The above discussion does not address the issue of correct identification of contaminated oil at an action level other than the MDL for the method. See the final ITVR for an explanation of the application of the L2000DX precision and accuracy data to the decision making process for oils contaminated at the regulatory limit of 50 ppm.

Figure 1 shows the L2000DX results plotted versus the reference lab results for all data. For this comparison all non-detect data were replaced with a value of one half of the method detection limit for the corresponding method to facilitate a regression analysis and plotting. As can be seen from the regression analysis results on the figure, the correlation with the lab was very good for all data. The slope and intercept were not statistically different from one or zero respectively and the R^2 was 0.87. This correlation indicates that the L2000DX is capable of providing reliable data in the field. Due to the high bias of the lab exhibited on the analysis of PE samples containing mixed Aroclors, the single Aroclor data should be looked at separately. Figure 2 shows the comparison of the L2000DX data with the lab for the single Aroclor data only. The regression analysis indicates that the correlation improves (R^2 = 0.92) and the slope and intercept, although statistically not different, improve slightly.

CONCLUSIONS

The field trials at Oak Ridge have demonstrated that the L2000DX is an accurate and unbiased analytical tool for the analysis of PCBs in transformer oil. The operation of the L2000DX under field conditions also demonstrates that the technique of total halogen analysis can be applied in the field with the same precision and accuracy as laboratory techniques. The lack of bias for mixed Aroclor also validates the point that the most sophisticated laboratory method is not always better than a field method based on simple, well founded, principals.

Table 1: All L2000DX and Lab Data

Sample ID	Aroclor	Replicate	Dexsil PCB (ppm)	Ref. Lab PCB (ppm)
101	1254	1	ND < 3	ND < 1
101	1254	2	ND < 3	ND < 1
101	1254	3	ND < 3	ND < 1
101	1254	4	ND < 3	ND < 1
102	1254	1	ND < 3	ND < 1
102	1254	2	3.0	ND < 1
102	1254	3	ND < 3	ND < 1
102	1254	4	ND < 3	ND < 1
103	1260	1	10.4	3.0
103	1260	2	10.0	2.0
103	1260	3	9.3	1.0
103	1260	4	9.4	2.0
104	1260	1	9.1	4.0
104	1260	2	11.1	3.0
104	1260	3	12.0	2.0
104	1260	4	7.5	2.0
105	1260	1	23.9	8.0
105	1260	2	25.1	9.0
105	1260	3	19.6	12.0
105	1260	4	15.2	10.0
106	1260	1	38.8	15.0
106	1260	2	41.7	11.0
106	1260	3	39.3	14.0
106	1260	4	38.8	16.0
107	1260	1	54.2	21.0
107	1260	2	53.7	21.0
107	1260	3	55.4	23.0
107	1260	4	61.9	23.0
108	1260	1	39.4	23.0
108	1260	2	42.1	25.0
108	1260	3	40.4	20.0
108	1260	4	41.0	26.0
109	1242/1254	1	70.8	26.0
109	1242/1254	2	74.2	27.0
109	1242/1254	3	73.2	24.0
109	1242/1254	4	79.4	32.0
110	1254/1260	1	100.2	40.0
110	1254/1260	2	85.8	41.0
110	1254/1260	3	87.9	32.0
110	1254/1260	4	101.0	33.0
111	1260	1	103.1	37.0
111	1260	2	101.6	45.0
111	1260	3	108.3	44.0
111	1260	4	102.4	39.0
112	1260	1	58.3	43.0
112	1260	2	61.4	35.0
112	1260	3	71.5	42.0
112	1260	4	64.8	40.0

Table 1(continued): All L2000DX and Lab Data

Sample ID	Aroclor	Replicate	Dexsil PCB (ppm)	Ref. Lab PCB (ppm)
113	1260	1	89.8	80.0
113	1260	2	96.2	70.0
113	1260	3	81.1	93.0
113	1260	4	75.4	65.0
114	1260	1	60.6	64.0
114	1260	2	59.0	65.0
114	1260	3	65.0	58.0
114	1260	4	64.6	56.0
115	1260	1	85.4	66.0
115	1260	2	84.8	90.0
115	1260	3	89.4	67.0
115	1260	4	125.4	64.0
116	1254/1260	1	93.1	58.0
116	1254/1260	2	84.0	59.0
116	1254/1260	3	102.2	64.0
116	1254/1260	4	97.6	75.0
117	1260	1	103.5	68.0
117	1260	2	84.8	81.0
117	1260	3	79.6	69.0
117	1260	4	89.4	69.0
118	1254/1260	1	98.2	79.0
118	1254/1260	2	97.8	102.0
118	1254/1260	3	90.8	83.0
118	1254/1260	4	86.8	102.0
119	1260	1	178.5	125.0
119	1260	2	166.2	131.0
119	1260	3	168.9	129.0
119	1260	4	159.8	130.0
120	1242	1	103.5	78.0
120	1242	2	88.7	77.0
120	1242	3	87.5	77.0
120	1242	4	85.1	84.0
121	1260	1	98.3	82.0
121	1260	2	105.8	83.0
121	1260	3	96.4	92.0
121	1260	4	97.1	92.0
122	1242	1	88.1	88.0
122	1242	2	97.6	79.0
122	1242	3	110.4	98.0
122	1242	4	111.6	78.0
123	1260	1	245.8	287.0
123	1260	2	245.8	272.0
123	1260	3	241.6	248.0
123	1260	4	268.7	300.0
124	1260	1	212.9	171.0
124	1260	2	258.3	169.0
124	1260	3	208.3	166.0
124	1260	4	228.1	169.0

Table 1(continued): All L2000DX and Lab Data

Sample ID	Aroclor	Replicate	Dexsil PCB (ppm)	Ref. Lab PCB (ppm)
125	1260	1	233.3	194.0
125	1260	2	225.4	214.0
125	1260	3	227.0	194.0
125	1260	4	270.6	196.0
126	1254	1	4.7	ND < 1
126	1254	2	ND < 3	ND < 1
126	1254	3	6.4	ND < 1
126	1254	4	28.4	ND < 1
127	1254	1	ND < 3	ND < 1
127	1254	2	ND < 3	ND < 1
127	1254	3	ND < 3	ND < 1
127	1254	4	6.0	ND < 1
128	1254	1	ND < 3	ND < 1
128	1254	2	ND < 3	ND < 1
128	1254	3	ND < 3	ND < 1
128	1254	4	ND < 3	ND < 1
129	1254	1	ND < 3	ND < 1
129	1254	2	ND < 3	ND < 1
129	1254	3	ND < 3	ND < 2
129	1254	4	ND < 3	ND < 1
130	1254	1	ND < 3	ND < 1
130	1254	2	ND < 3	ND < 1
130	1254	3	ND < 3	ND < 1
130	1254	4	3.4	ND < 1
131	1254	1	4.0	6.0
131	1254	2	5.1	4.0
131	1254	3	7.0	5.0
131	1254	4	15.7	6.0
132	1260	1	24.2	21.0
132	1260	2	22.3	21.0
132	1260	3	24.2	20.0
132	1260	4	26.4	25.0
133	1254/1260	1	33.1	51.0
133	1254/1260	2	39.0	54.0
133	1254/1260	3	44.3	50.0
133	1254/1260	4	39.7	54.0
134	1254/1260	1	45.8	57.0
134	1254/1260	2	51.1	74.0
134	1254/1260	3	54.2	61.0
134	1254/1260	4	49.1	67.0
135	1254/1260	1	59.6	78.0
135	1254/1260	2	63.8	76.0
135	1254/1260	3	56.7	79.0
135	1254/1260	4	52.0	78.0
136	1260	1	64.6	83.0
136	1260	2	84.4	64.0
136	1260	3	98.3	73.0
136	1260	4	85.2	73.0

Table 1(continued): All L2000DX and Lab Data				
Sample ID	Aroclor	Replicate	Dexsil PCB (ppm)	Ref. Lab PCB (ppm)
137	1254	1	107.4	86.0
137	1254	2	98.8	86.0
137	1254	3	94.1	108.0
137	1254	4	130.6	109.0
138	1254/1260	1	175.4	260.0
138	1254/1260	2	271.9	261.0
138	1254/1260	3	233.9	255.0
138	1254/1260	4	186.2	249.0

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