Field Evaluation Of The Clor-D-Tect Q2000 Test Kit For Use In Landfill-Gas Engines To Determine Chlorine Contamination Of Lube Oil
Final Report

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Theodore B. Lynn, Ph.D.
Director of Research
Dexsil Corporation

Scope of the Study:

A joint research project was conducted to determine the acceptability of the Dexsil Clor-D-Tect Q2000 test kit as a test for chlorine contamination of engine oil exposed to chlorine containing fuels, e.g. in this case, land fill gas. Mobil has data to indicate that the condemning limit using microcoulometric titration (MCT) is 1000 ppm. Because the determination of the chlorine content of oil used in engines exposed to chlorine contaminated fuels is very time sensitive, a field test method was desired that would have the precision of MCT but eliminate the delay caused by the necessity of sending samples out for laboratory analysis.

Participating in the study were Dexsil Corporation, Mobil Corporation, Browning-Ferris Gas Services (BFGSI) and Waukesha-Dresser Inc. The test was conducted at the BFGSI facility at Chicopee, Massachusetts following the protocol outlined in the 19 November 1993 letter from Mobil. Dexsil was to provide the test kits, duplicate kit analyses and confirmatory lab analysis using MCT. Dexsil was also responsible for the final analysis of the data. BFGSI personnel performed the field tests at their facility where Waukesha engines are in use. Mobil coordinated the sampling program and provided laboratory analytical services using MCT.

The test program consisted of sampling oil from the crankcases of each of the three Waukesha L-7042GL engines at the BFGSI facility on a regular basis. The oil sample was tested on-site by BFGSI personnel using the Dexsil Q2000 kit. A split of the sample was sent to both Dexsil and Mobil-EM/PA labs for analysis using MCT. In addition to MCT analysis, Dexsil also ran the Q2000 test kit to obtain statistics on inter-operator variation. All kit analyses were run in duplicate.

Over the course of the study two types of Mobil oil were used in the engines: Pegasus 426 and Pegasus 446. Data were collected for one complete oil cycle for the Pegasus 426 and for two oil cycles for the Pegasus 446 oil. The testing began with the change of new Pegasus 426 oil on 2 December, 1993, continuing until 24 December, 1993, at which time the Pegasus 426 was exchanged for Pegasus 446. The test continued until February 2, 1994.

Results and Discussion:

A total of 60 oil samples were analyzed by BFGSI, Mobil and Dexsil personnel (see table 1). Preliminary analysis of the data showed no effect due to type of oil, therefore, the data was pooled for analysis. The combined data was analyzed to determine how well the Q2000 results compare with the MCT laboratory data. The means of all the data are presented in table 1. Column 1 identifies the engine by the last digit of the EM/PA number (e.g. 1, 2 or 3) and column 2 shows the total hours the oil had been in service when the sample was taken. Columns 3 through 6 show the MCT data obtained by the Dexsil and Mobile-EM/PA labs. Columns 3 and 4 show the average result obtained by each lab for that sample. The values in column 5 are the average of both labs' results and are used for the final comparison between MCT and the Q2000. Column 6 lists the difference between the results of the two labs which are used to assess the inter-laboratory variation of the MCT data. Columns 7 through 10 contain the Q2000 results. Column 7 and 8 are the means of the BFI-Chicopee and Dexsil Q2000 results respectively. Column 9 is the average of the two Q2000 results obtained by each of the operators. These values are the ones used for the final comparison with the MCT values. Column 10 shows the difference between the two operators' Q2000 results. Column 11 shows the difference between the average Q2000 result and the average MCT result for each sample.

To establish the expected precision of the MCT results, first, a paired difference analysis was made between the MCT results for the two labs. The t statistic, as a test for significance, shows that the average difference between labs of 58 ppm (with a standard deviation of 139 ppm) was statistically significant at the 99% confidence level.

$$X_D = 58 \text{ ppm} \pm 49 \text{ ppm}$$

This indicates that there is a possible systematic difference between the laboratory results. This difference is not unusual for the method and this sample matrix (see EPA SW-846 Method 9076 "Test Method for Total Chlorine in New and Used Petroleum Products by Oxidative Combustion and Microcoulometry" for repeatability data).

A similar analysis was preformed on the inter-operator data for the Q2000, resulting in a mean difference between the BFI-Chicopee results and the Dexsil results of 28 ppm, a standard deviation of 82 ppm and a 99% confidence interval of:

$$X_D = 28 \text{ ppm} \pm 29 \text{ ppm}$$

This difference was not statistically significant as determined by the t test. The lower average difference and the smaller 99% confidence interval indicates that the field test kit is less subject to systematic variations in calibration or individual user operation.

A paired difference analysis of the mean MCT data and the mean Q2000 results in an average difference of 24 ppm, a standard deviation of 86 ppm and a 99% confidence interval of :

$$X_D = 24 \text{ ppm} \pm 30 \text{ ppm}$$

This difference was also not statistically significant at the 99% confidence level. This indicates that given the combined inter-operator variation of the two methods the difference between the two results is not statistically significant.

One of the primary objectives of this study was to establish a useable condemning limit for the chlorine content of engine oil based on the Q2000 kit. To establish the relationship between the two methods quantitatively, a regression analysis was performed on the inter-operator means for each method, i.e., the averages of the Q2000 kit results for both operators were compared to the averages of the MCT data for both operators (see figure 1). The correlation coefficient (r^2) for the regression was 0.83 indicating a reasonable correlation. The slope of the regression line was 0.95 with a standard error of 0.055 and the intercept was 54 ppm with a standard error of 87 ppm. Both the slope and the intercept were found to be not statistically different from their expected values of 1 and 0.

The regression analysis was used to establish the 99% confidence interval for comparison of MCT data and Q2000 data. The lower extent of the confidence interval is an estimate of the lowest value determined by the Q2000 for an oil that tested 1000 ppm using MCT. Because the true value of the chlorine content of the oil is not known, the accuracy and bias of each method can not be assessed individually. The regression analysis and the calculation of the confidence interval assumes that the MCT value is the known quantity. The variation in both methods extends the confidence interval of the Q2000 results to account for the combined error. The interval represents a conservative estimate because the MCT value is in fact also an experimental value with an error associated with it.

The lower value for the 99% confidence interval calculated for the Q2000 data was 966 ppm. This means that if a value of 966 ppm is determined by the Q2000 there is only 1 chance in 100 that the value as determined by MCT exceeds 1000 ppm. For this comparison, all variability was attributed to the kit method. The analysis of the inter-operator variability above shows that the variability of the MCT is at least as great as the Q2000.

If MCT were to be used exclusively to determine chlorine levels the 99% confidence interval should be calculated for the condemning limits determined by MCT. The inter-laboratory comparison discussed above indicates that the results from two labs may vary by as much as 107 ppm at the 99% confidence level. Excluding any systematic bias and applying this confidence interval would result in a condemning limit of 900 ppm for MCT analysis.

Setting the condemning limit at 900 ppm chlorine would therefore be a reasonably conservative determination. Then by either method the confidence level is at least 99%. The field method could be used with the same certainty as the laboratory method and the laboratory method could be used where a laboratory was accessible.

TABLE 1: FIELD TEST OF Q2OOO AT CHICOPEE (MOBIL PEGASUS 426 AND 446 OIL)

DATE	1 ENG #	2 HRS	3 MCT DEX PPM	4 MCT EM /PA PPM	5 AVE MCT PPM	6 DIF MCT D - EM PPM	7 Q2 BFI PPM	8 Q2 DEX PPM	9 AVE Q2 PPM	10 DIF Q2 D - BFI PPM	11 AVE DIF Q2 - MCT
12/2/93	1	22	236	132	184	104	225	188	206	-38	22
	2	22	242	137	190	105	213	200	206	-13	17
	3	365	697	435	566	262	600	675	638	75	72
12/6/93	1	110	421	443	432	-22	450	400	425	-50	-7.1
	2	110	415	457	436	-42	350	475	413	125	-24
	3	64	362	382	372	-20	400	300	350	-100	-22
12/8/93	1	157	484	582	533	-98	475	488	481	13	-52
	2	158	476	587	532	-111	425	450	438	25	-94
	3	112	463	556	510	-93	525	575	550	50	41
12/10/93	1	211	553	497	525	56	450	500	475	50	-50
	2	211	530	503	516	27	475	475	475	0	-41
	3	166	531	531	531	0	550	500	525	-50	-6
12/13/93	1	279	570	563	567	7	475	575	525	100	-42
	2	280	551	594	573	-43	500	525	513	25	-60
	3	234	738	784	761	-46	525	600	563	75	-199
12/15/93	1	327	616	530	573	86	525	525	525	0	-48
	2	326	578	570	574	8	525	550	538	25	-37
	3	282	690	597	644	93	550	750	650	200	6
12/17/93	1	376	696	547	622	149	525	625	575	100	-47
	2	375	709	515	612	194	550	600	575	50	-37
	3	330	810	692	751	118	600	800	700	200	-51

DATE	1 ENG #	2 HRS	3 MCT DEX PPM	4 MCT EM /PA PPM	5 AVE MCT PPM	6 DIF MCT D - EM PPM	7 Q2 BFI PPM	8 Q2 DEX PPM	9 AVE Q2 PPM	10 DIF Q2 D - BFI PPM	11 AVE DIF Q2 - MCT
12/20/93	1	450	699	644	671	55	500	625	563	125	-109
	2	450	660	564	612	96	500	663	581	163	-31
	3	405	719	644	682	75	675	675	675	0	-7
12/22/93	1	490	582	310	446	272	575	500	538	-75	92
	2	0	148	158	153	-10	200	238	219	38	66
	3	445	737	783	760	-46	650	750	700	100	-60
12/24/93	1	40	274	269	272	5	275	338	306	63	35
	2	65	339	400	370	-61	400	400	400	0	30
	3	20	221	282	251	-61	275	250	263	-25	11
1/5/94	1	281	544	331	438	213	650	650	650	0	213
	2	184	399	409	404	-10	525	550	538	25	133
	3	280	614	482	548	132	700	800	750	100	202
1/7/94	1	NA	547	NA	547	NA	625	650	638	25	90
	2	232	557	509	533	48	525	775	650	250	117
	3	327	661	605	633	56	775	950	863	175	229
1/10/94	1	401	637	800	719	-163	NA	850	850	NA	132
	2	302	572	676	624	-104	NA	700	700	NA	76
	3	400	662	861	762	-199	NA	925	925	NA	164
1/14/94	1	53	325	174	250	151	350	338	344	-13	94
	2	381	626	590	608	36	625	700	663	75	54
	3	NA	352	NA	352	NA	300	400	350	100	-2
1/21/94	1	192	466	654	560	-188	600	563	581	-38	21
	2	NA	532	NA	532	NA	600	550	575	-50	43

DATE	1 ENG #	2 HRS	3 MCT DEX PPM	4 MCT EM /PA PPM	5 AVE MCT PPM	6 DIF MCT D - EM PPM	7 Q2 BFI PPM	8 Q2 DEX PPM	9 AVE Q2 PPM	10 DIF Q2 D - BFI PPM	11 AVE DIF Q2 - MCT
	3	NA	595	NA	595	NA	675	725	700	50	105
1/24/94	1	63	726	711	718	15	725	700	713	-25	-6
	2	232	651	610	631	41	725	775	750	50	120
	3	253	689	651	670	38	800	775	788	-25	117
1/26/94	1	NA	914	613	764	301	775	750	763	-25	-1
	2	NA	782	534	658	248	750	750	750	0	92
	3	NA	864	681	773	183	850	850	850	0	77
1/28/94	1	NA	916	858	887	58	850	838	844	-13	-43
	2	NA	793	979	886	-186	950	675	813	-275	-73
	3	NA	909	887	898	22	950	950	950	0	52
1/31/94	1	NA	958	846	902	112	800	825	813	25	-90
	2	NA	1192	991	1091	201	925	1000	963	75	-129
	3	NA	1056	801	928	254	1000	950	975	-50	47
2/2/94	1	NA	1034	625	830	409	975	963	969	-13	139
	2	NA	1255	802	1029	453	1175	1150	1163	-25	134
	3	NA	299	NA	299	NA	275	250	263	-25	-37
Average						58				28	24
St dev.						139				82	86
t						3.091				2.610	2.135
t_{cr}, $\propto/2 = 0.005$						2.660				2.660	2.660