RESEARCH TRIANGLE INSTITUTE
Contract Number 68-01-7075
Work Assignment Number 58
RTI Project Number 472U-3255-05

August 1987

Evaluation of Techniques for Determining Chlorine in Used Oils

Volume I

Contractor: Research Triangle
Institute Task Request: Denise A. Zabinski

Prepared by
Alvia Gaskill, Jr.
Eva D. Estes
David L. Hardison

Prepared for
Office of Solid Wage
U.S. Environmental Protection Agency
Washington, DC 20460

POST OFFICE BOX 12194 RESEARCH TRIANGLE PARK, NORTH CAROLINA 27709

8.13 TEST KITS
8.13.1 Dexsil Test Kit
8.13.1.1 Analytical Evaluation

Both RTI and Dexsil evaluated the Dexsil test kit on the 40 oil samples. The complete reports from Dexsil and RTI are given in Appendix C-12. The results are summarized in Tables 8.24 and 8-25.

Outside of the 1,000-1,200 _g/g transition zone, the kits gave correct and repeatable results for 90 percent of the samples for both laboratories. Between 1,000-1,200 _g/g the kit was accurate 80 percent of the time, depending on the assignment of concentration to the color observed samples.

The only samples which posed a problem were the spiked used crankcase oils. These oils typically contain sediment, dirt, grease, metals, and various other materials not reatily removed by the sulfuric acid dehydration step or the other separations that the kit involves. Sometimes some of these materials survive all of these steps and obscure the color change endpoint. It was found that omitting the sulfuric acid step reduced the occurrence of this problem. Dexsil addressed this in their modified kit.

Dexsil's results were reported in terms of the color observed at the endpoint of the test for three separate aliquots of each sample. The precision of their determinations was good, with the same color reported for each of the three aliquots for all but one sample. The colors reported correspond to the following ranges in _g/g less than 1,000 (dark purple); 1,000 1,100 (medium to light purple); 1,100-1,200 (pink); greater than 1,200 (yellow). The reporting of results is probably somewhat subjective in the transition range of 1,000-1,200 since different observers may report shades of purple differently.

TABLE 8-24. RESULTS OF DEXSIL ANALYSES USING DEXSIL TEST KIT

Sample	Expected	Expected color	Reported color	Correct Identification
STD-LA	156	Dark purple	Dark purple	Yes
STD-2A	500	Dark purple	Dark purple	Yes
STD-3A	1,140	Yellow pink	Yellow pink	Yes
STD-4A	2,123	Yellow	Yellow	Yes
STD-5A	5,075	Yellow	Yellow	Yes
STD-6A	9,994	Yellow	Yellow	Yes
Blank-B	<50	Dark purple	Dark purple	Yes
Blank-C	5	Dark purple	Dark purple	Yes
Blank-D	58	Dark purple	Dark purple	Yes
Blank-E	91	Dark purple	Dark purple	Yes
A-1	717	Dark purple	Dark to medium purple	Yes
A-2	1,758	Yellow	Yellow	Yes
A-3	1,197	Yellow pink/yellow	Yellow pink	Yes
A-4	1,156	Yellow pink/yellow	Medium to light purple	No
A-5	675	Dark purple	Dark purple	Yes
A-6	1,759	Yellow	Yellow	Yes
A-7	580	Dark purple	Dark to medium purple	Yes
A-8	1,197	Yellow pink	Yellow	Yes
A-9	1,660	Yellow	Yellow	Yes
A-10	1,071	Light purple	Dark to medium purple	Unclear
A-11	645	Dark purple	Dark purple	Yes
A-12	1,559	Yellow	Dark to medium purple	No
A-13	1,610	Yellow	Yellow pink	Yes
A-14	1,032	Light purple	Dark purple	Unclear
A-15	791	Dark purple	Dark purple	Yes
B-1	7,350	Yellow	Yellow	Yes
C-1	3,910	Yellow	Yellow	Yes
D-1	1,193	Yellow pink	Yellow	Yes
E-1	1,101	Light purple	Dark to medium purple	Yes
F-1	1,321	Yellow	Medium to light purple	No
F-2	1,817	Yellow	Yellow	Yes
F-3	1,226	Yellow pink	Dark to medium purple	Yes
F'4	2,076	Yellow	Medium to light purple	No
F-5	1,476	Yellow	Yellow	Yes
F-6	1,726	Yellow	Yellow	Yes
G-1	7,722	Yellow	Yellow	Yes
H-1	4,027	Yellow	Yellow	Yes

I-1	998	Dark purple	Dark to medium purple	Yes
CW-1	734	Dark purple	Dark purple	Yes
MW-1	1,472	Yellow	Yellow	Yes

TABLE 8-25. RESULTS OF RTI ANALYSES USING DEXSIL TEST KIT

Sample	Expected	Expected color	Reported color	Correct Identification
STD-LA	156	Dark purple	Purple	Yes
STD-2A	500	Dark purple	Purple	Yes
STD-3A	1,140	Yellow pink	Purple (3), yellow (1)	Yes
STD-4A	2,123	Yellow	Yellow	Yes
STD-5A	5,075	Yellow	Yellow	Yes
STD-6A	9,994	Yellow	Yellow	Yes
Blank-B	<50	Dark purple	Purple	Yes
Blank-C	5	Dark purple	Purple	Yes
Blank-D	58	Dark purple	Purple	Yes
Blank-E	91	Dark purple	Purple	Yes
A-1	717	Dark purple	Purple	Yes
A-2	1,758	Yellow	Yellow	Yes
A-3	1,197	Yellow pink/yellow	Yellow	Yes
A-4	1,156	Yellow pink/yellow	Purple	No
A-5	675	Dark purple	Purple	Yes
A-6	1,759	Yellow	Yellow	Yes
A-7	580	Dark purple	Purple	Yes
A-8	1,197	Yellow pink	Purple	No
A-9	1,660	Yellow	Yellow	Yes
A-10	1,071	Light purple	Purple	Yes
A-11	645	Dark purple	Purple	Yes
A-12	1,559	Yellow	Purple (8), yellow (4)	No
A-13	1,610	Yellow	Yellow	Yes
A-14	1,032	Light purple	Purple	Yes
A-15	791	Dark purple	Purple	Yes
B-1	7,350	Yellow	Yellow	Yes
C-1	3,910	Yellow	Yellow	Yes
D-1	1,193	Yellow pink	Yellow	Yes
E-1	1,101	Light purple	Purple	Yes
F-1	1,321	Yellow	Purple	No
F-2	1,817	Yellow	Yellow	Yes
F-3	1,226	Yellow pink	Purple	No
F'4	2,076	Yellow	Purple (2), yellow (1)	No
F-5	1,476	Yellow	Purple (3), yellow (2)	No
F-6	1,726	Yellow	Yellow	Yes
G-1	7,722	Yellow	Yellow	Yes
H-1	4,027	Yellow	Yellow	Yes
I-1	998	Dark purple	Purple	Yes
CW-1	734	Dark purple	Purple	Yes
MW-1	1,472	Yellow	Yellow	Yes

The kit provided correct identification of the sample as greater than or less than 1,000 _g/g for all of the standards spiked with trichlorobenzene and for all of the unspiked virgin oils and fuels. Correct identifications were also made for all but one of the "A" series spiked virgin crankcase oils. Results for A-10 (COD plus 25 percent water) and A-14 (NaCl plus 25 percent water) could not be evaluated as these were within the transition zone of the test. The result for A-4 (COD) was reported as medium to light purple (1,0001,100) when it should have been pink. However, this is not considered a serious error. The only one of the A series samples clearly identified incorrectly was A-12 (COD plus 25 percent water). All of the other samples except the used crankcase oils were correctly identified. Samples F-1 (TeCE), F-3 (COD) and

F-4 (COD) were incorrectly identified as below 1,200 when they were actually above it. Of these, only F-4 was well above 1,200.

The error in the identification of a threshold level is dependent on several assumptions, including density of the oil and complete dehalogenation of all halogenated organics. In general, this error mav be expected to be *100 #g/g. Thus, the transition zone may actually include the range 900-1,300 ,_g/g. If this is correct, then only two of the oils were incorrectly identified.

RTI's results (Table 8-25) were reported only in terms of yellow or purple. Thus, there is somewhat less of a discrimination seen in these results. Unless otherwise indicated, the results refer to identical triplicate identifications of color at the endpoint. The results were in general agreement with those reported by Dexsil. RTI also incorrectly reported A-4, A-12, F-1, F-3 and F-4 as purple. In addition, RTI incorrectly reported A-8 and F-5 as purple.

The kit as originally conceived was to be applied only to organic chlorine in used oil fuels, i.e., No. 4 or No. 6 fue'. oil to which used oil was blended at around 10 percent. However, the performance of the kit on these samples including used oils, oil fuels, blends of used oil and oil fuels, and metalworking fluids indicates a much broader applicability. It detects all forms of chlorine equally. The kit can probably be used as a screening tool throughout the used oil industry, from the generator to the recycler to the transporter and burner. There are few false positives or negatives and minimal matrix effects.

8.13.1.2 Economic Evaluation--

The kit requires no setup time. A complete test requires around 10-15 min to complete. It is simple to use and little skill is required. Training requirements are minimal. The user need not understand the chemistry of the test to obtain accurate results. The kit is entirely field portable. The kit is small enough that truck drivers, small generators, and enforcement personnel in unmarked vehicles can easily carry it to the sampling location. Dexsil has informed RTI (Appendix C-12) that they plan to market their kit according to the following schedule:

# of Kits	Price per kit
10	$8.00
20-60	$7.00
80-380	$6.00
400-1,980	$5.50
>4,000	$5.00

The estimate of cost per analysis for the Dexsil Test Kit assumes 15 min per test; 4 tests per h and a labor rate of $25/h. This translates into a labor charge of $6/h. Over a year 8,000 tests could be performed at $5 per kit. This represents a fixed cost of $40,000. The cost per test is then estimated to be around $11.

Only a few of the more than 150 test kits evaluated were found to be defective. The defects were leaking reagent (isooctane or buffer containers), cracked capillary tubes, or svringes with holes in them such that the oil sample could not be collected.

8.13.1.3 Technique Evaluation Summary--

The evaluation of the Dexsil Test kit is summarized in Table 8-26. Several recommendations were developed as a result of this testing. Dexsil should include in their kit a color chart assigning colors to specific concentration ranges as noted earlier. The kit only identifies colors as above or below 1,000 /Ag/g. This is also somewhat misleading since the threshold for a positive determination is 1,200 ug/g. The acid dehydration step should be omitted. It does not appear to remove inorganic chlorine well and the samples containing mostly water were not affected by it, nor did they consume all of the sodium before it could react with chlorinated organics. The only effect it seemed to have was a negative one in causing problems with the used crankcase oils.

Dexsil addressed this concern by eliminating the H_2S0_4 treatment step; this led to reduction in the number of tubes from four to two and the number of boxes from two to one. Reagents were included to mask potential interferences in used oils. The aqueous extraction system was modified to improve the phase separation. The threshold was also adjusted to be at 1,000 *uglg*.

Dexsil conducted a limited field evaluation of the modified kit. As part of this evaluation, seventy samples of used crankcase oil were sent to Dexsil by generators and recyclers. The oil samples were analyzed with Dexsills new kit called CLOR-D-TECT and the results from the kit were compared to results obtained with the COSA TSX-10 analyzer. The results indicated that the modified kit and the MCT analyzer agreed for 68 out of 70 samples tested. These results are given in Appendix A-11.

RTI also evaluated several of the modified kits on samples which previously gave false or equivocal results. The results were as follows:

Sample	Expected Ug/g	CLOR-D-TECT
Std3a	1,140	Yellow
E-1	1,101	Dark purple
F-I	1,321	Yellow
F-4	2,076	Yellow
I-1	998	Yellow
# 6 fuel oil	800	Dark purple

Since these tests were conducted, Dexsil has conducted several additional 4-n-house studies to improve the applicability of the kit to more oil types (Appendix D-1). Specifically, their in-house testing suggested that low recoveries may occur with certain No. 6 fuel oils. For example, in a comparison of the new kit with MCT using the TSX-10 analyzer, the following results were obtained:

TABLE 8-26. TECHNIQUE EVALUATION SUMMARY FOR DEXSIL TEST KIT

Criterion	Result
Analytical	
Sample size (oil)	0.6 g
Bias	+ 10%at 1000 ug/g
Precision (% RSD)	10%
Quantitation range	1,000 ug/g
Technique detection limit	1,000 ug/g
False positives at 1,000#g/g	Few (5%)
False positives at 4,000#g/g	None
False negatives at 1,000 /ig/g Few (5%)	
False negatives at 4,000/;g/g	None
Effect of water None	
Effect of chlorine form	None
Effect of oil type	None
Economic	
Setup time	None
Training time	30min
Unit sample analysis time	10 min
Ease of use	Simple
Education required	High school graduate
Laboratory space	Not required/NA
Field portability	Yes
Equipment cost	Not applicable
Consumables cost	$5-8/kit
Unit cost per analysis	$11-14

Samples	Cl by Kit (,Ug/g)	Cl by MCT (#g/g)	% difference from MCT
#2 fuel oil	1021	970	+5
#6 fuel oil	787	1065	-26
#6 fuel oil	878	1600	-45
#6 fuel oil	1119	1090	+3

In this testing, the kit was used except in the very final step. Instead of using the fixed-point titration to give a go/no-go result, the extracted chloride was titrated with the mercuric nitrate reagent to obtain an exact result using a Mettler photometric titrator to determine the endpoint. The microcoulometric method (MCT), using the COSA instrument, was used as a referee technique.

Based on these results, kit performance was reassessed on a range of typical chlorine containing species that might be found in used crankcase oils.

Compound	Kit (/Ag/g)	Cl by MCT (Ag/g)	Cl by difference from MCT
Chlorooctadecane	852	967	-12
Trichlorobenzene	913	1060	-14
Monochlorobenzene	733	800	-8
T-richloroethane	926	978	-6

These results indicated that the form of chlorine was not the source of the problem. The problem was associated with the solvent system. The solvent has to (1) suitably dissolve the entire sample to present a medium for reaction with the sodium, and (2) permit a clean phase separation with the aqueous extraction svstem. In addition, the solvent system must have a sufficiently high flash point to make it safe for handling and shipment.

To improve the existing isooctane solvent system, a solvent study was conducted. The basic criteria for evaluationwere whether an emulsion or solids formed in the aqueous separation step, and whether the analysis on used lubricating oils and various types of #6 fuel oils would yield acceptable results.

As a result of this study the solvent system used with the Chlor-D-Tect kit was modified. Analyses obtained for various chlorine containing species in a wide range of oils are given below.

Samples	Kit (Aglg)	Cl by MCT (,Og/g)	Cl by from MCT	% difference
Used Lube Oil				
Chlorooctadecane		974	967	+1
Trichlorobenzene		1172	1090	+8
Virgin Lube Oil		927	970	-4
Hydraulic Oil		6455	6050	+7
#6 Fuel Oil				
Sample No. I		1100	1065	+3
Sample No. 2		1689	1650	+2
Sample No. 3		1079	1100	-2

Additional analyses conducted using the test kit with the modified solvent system in the fixed endpoint mode also compared well with MCT and results from photometric titration of the extract:

Sample	Kit	Photometric titration (.Ug/g)	MCT ug/g)	% difference from MCT
1.F-6 RTI crankcase	Yellow	1625 + 16	1650	-1
2.E-Blank with TCB spike (RTI No. 6 fuel oil)	Yellow	1258 + 94	1100	-14
3.#6 Fuel oil	Yellow	1476 + 22	1650	-11
4.#6 Fuel oil	Yellow	995 + 12	1090	-9
5.Crankcase oil with COD spike	Indeterminate	827 + 14	960	-14
6.Crankcase oil with TCE spike	Yellow	910 + 32	1000	-9
7.Crankcase oil with COD spike	Purple	--	531	--
8.Crankcase oil with COD spike	Light purple	--	800	--
9.#6 Fuel oil, unspiked	Dark purple	--	40	--
10.Unspiked crankcase oil	Dark purple	--	166	--
11.Crankcase oil spiked with monochlorobenzene	Light purple	--	900	--

In a further validation of the Clor-D-Tect methodology, various hologen species were added to a # fuel oil sample and analyzed by photometric titration of the kit extract. Results obtained were:

Material added	Halogen added (ug/g)	Halogen found (ug/g)	% rec.
Bromobenzene	1100	1090	99
Iodobenzene	1100	1074	97
Fluorobenzene	1100	34	3

The results indicate excellent recoveries of both bromo- and iodo-species in used oils. As expected, no of the fluoro- species was recovered since the mercuric nitrate titrant is known not to react with fluoride ions in solution. It is quite possible that the chemical reaction sequence converted organic fluoride to ionic fluoride but that this species was not quantified.

Analysis of a mixed halogen organic, trichlorotrifluoroethane, gave the following results:

Sample	Cl added (ug/g,)	F added (ug/g)-	Halogen found as Cl (ug/g)
Used crankcase oil	832	446	833

This shows that the chlorine in a mixed halogen containing organic will be accurately determined. By modifying the solvent used in the Clor-D-Tect analytical system, kit performance has been improved, ar the range of materials that can be analyzed, which is just as important, has been extended.

These results coupled with the results of the RTI studies indicate that the modified CLOR-D-TECT kit can effectively screen used crankcase oils for chlorine.

The Dexsil Test Kit can provide acceptable qualitative results with a detection threshold set at 1,000 /ug/g and a transition zone between 900 and 1,100 /ug/g. The kit is immediately applicable to all oil types.