FIELD DETERMINATION OF PCB IN TRANSFORMER OIL CLOR-N-OIL™ KIT

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Askarel is a generic term for a group of non-flammable synthetic chlorinated hydrocarbons used as electrical insulating fluids in transformers and capacitors. Most contain poly-chlorinated biphenyls (PCB). PCB have been judged to be harmful in the environment and their manufacture, use and disposal have been subject to Government regulation since 1978. This regulation extends not only to askarel filled transformers containing PCB, but also to the much larger number of mineral oil-filled transformers which may have been contaminated with PCB during manufacture or service. Oils containing less than 50 ppm when taken from transformers are defined as non-PCB liquids and have no unusual limitations on their handling and disposal (except that oils contaminated with any detectable PCB may not be used in widely dispersed applications such as dust control). Oils containing 50 to 500 ppm PCB are considered "contaminated" and those containing more than 500 ppm are considered to be totally PCB. Handling and disposal of oils in these last categories requires special techniques.

Ultimately, each of the 35 million oil-filled transformers now in service in utility and industrial applications may have to be tested for PCB content to assure proper disposal. While adequate analytical methods exist for determining the PCB content of oils in the laboratory, this process is time-consuming. Samples must be packed, sent to the laboratory doing the analyses and the analysis must be performed. The aim of the work reported here has been to reduce this problem by developing techniques for the measurement of PCB in transformer mineral oils by non-chemists in the field.

A number of instrumental approaches were evaluated and the most promising for immediate field use was x-ray emission using the Horiba MESA-200 analyzer (1). This instrument determines the total amount of chlorine present in oil and, hence, gives an indirect measure of the upper limit on the PCB content. Field testing of the MESA-200 instrument firmly established the concept of using the total chlorine content in transformer oil as an indication of the PCB concentration. It appears that the chlorine screening approach can eliminate 50-70% of the transformers tested from further concern.

Initial cost of the x-ray emission analyzer is relatively high and the instrument is best transported by automobile. Recent attention in this program has focused on developing a smaller disposable means of screening PCB by determination of chlorine content of transformer oil. This has led to the CLOR N-OIL™ PCB screening kit.

The kit developed here is based on the quantitative conversion of the chlorine atoms in PCB in transformer oil to chloride ions which in turn are extracted into an aqueous solution and measured colorimetrically. The conversion of chlorine to chloride ions is done by sodium salts formed by naphthalene together with the dimethyl ether of diethylene glycol ("diglyme") as stabilizing ligand (2). The chloride ions are extracted into an aqueous buffer solution and reacted with a carefully controlled amount of dissolved mercuric nitrate. Diphenylcarbazone is added. If the mercuric ion content is greater than that taken up by the chloride ion in forming slightly dissociated mercuric chloride, a vividly blue complex is formed by the excess mercuric ion and the diphenylcarbazone. If the chloride ion content exceeds that taken up by the available mercuric ion, the complex is not formed and the reaction mixture remains colorless to pale yellow. The reactions are carried out in soft plastic test tubes containing premeasured reagents in breakable glass ampules. Proper control of the sample size and of the quantity of mercuric nitrate allows the blue-colorless response level in the mineral transformer oil to be set at levels from a few ppm to several thousand ppm.

The test is performed in two soft sided polyethlyene tubes. The conversion of PCB to chloride ion is done in the first tube by breaking ampules containing naphthalene-diglyme and then sodium dispersion into the oil. Buffer solution is added from the second tube, the chloride ion is extracted into the aqueous phase and any excess sodium is eliminated. A minor amount of hydrogen is vented. A measured amount of the aqueous solution is returned to the second tube containing the mercuric nitrate and the indicator in separate ampules. The color development process id done by breaking these last ampules in turn. A convenient way of transferring the aqueous phase back and forth is provided by a flip top cap on the first tube. The tube is capped and allowed to settle after extraction of the chloride into the buffer. It is gently inverted so that the heavier aqueous phase moves to the bottom over the cap, the flip top is opened and a measured quantity of buffer is squirted back into the second tube. When done carefully, virtually all of the oil phase is retained in the first tube above a residual aqueous layer. Only the aqueous phase is returned to the tube where the indicator is finally contacted and the color observed.

The lowest ration of chlorine to PCB found in an askarel is 0.42. Therefore, an oil sample containing less than 21 ppm chlorine cannot contain more than 50 ppm PCB. A color response level set at 21 ppm chlorine for the kit should assure that no contaminated oil gives blue responses. The chlorine to PCB ratio for other askarels is as high as 1.34. Oil samples containing as little as 15.7 ppm askarel contamination can result in colorless responses as can samples containing other sources of chlorine contamination-but no PCB. Samples giving colorless responses can be checked by gas chromatography to determine whether they actually contain more than 50 ppm PCB.

The standard deviation on kits in prototypical production was found to be <2 ppm chlorine at a response level of 18.5. The kit then can be quite reliable Actual field experience is needed to judge the overall performance of the kit. A field test is being conducted by EPRI to provide this experience.

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1 R. G. Hirst, Field Determination Of PCB In Transformer Oil, Final Report – Part 1, Chlorine Analysis by X-Ray Emmision, EPRI RP 1713-1 (in preparation) ; also J. M. McQuade, PCB Analysis By X-Ray Fluoresence, Proc. PCB Seminar, EPRI EL-2572 (1982) ; also A. L. Schwalb and A. Marquez, Salt River Project Experience with the Horiba Sulfur/Chlorine-In-Oil Analyzer, Proc. PCB Seminar, EPRI EL-2572 (1982).

2 J. F. Brown, M. E. Lynch, J. C. Carnahan, J. S. Singleton, Chemical Destruction of PCB In Transformer Oil, Detoxification of Hazardous Wastes, p. 201, Ed. J. H. Exner, Ann Arbor Sci. Pub. (1982).; also T. O. Rouse, Removal Of PCB From Transformer Oil, Proc. PCB Seminar, EPRI EL-2572 (1982).

DISCUSSION

Q1. What is the shelf life of the kits?

A. Kits have shown no sign of deterioration in the 6 months now in use. There is no reason to suspect that shelf life will not be quite long, but time is needed to establish the shelf life.

Q2. Has a national policy regarding test methods been addressed?

A. EPA does not endorse any method, but there is no reason why the method can not be accepted.

Q3. What is the effect of moisture on the test results?

A. The solubility is approximately 60 ppm. There have been no attempts to dry the oil and no problems have been experienced to that level.

Q4. What is the cost/test?

A. $4 to $6 depending upon quantities.

Q5. Has the method been tried on hydraulic oil?

A. Some, but test results are not available. Additives could create a problem.

Q6. There was a request for a show of hands regarding interest in a test kit at the 500 ppm PCB level. 15 to 20 people indicated interest.

CLOR-N-OIL™ FIELD TEST PROGRAM

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Eighty-seven utilities have participated in the test program, and so far (as of the end of November 1983) we have received test results back from 40 of them. This report presents the summary of these test results.

A total of 879 oil samples have been tested both with the CLOR-N-OIL test kit as well as on a gas chromatograph. Whenever a CLOR-N-OIL kit user recognized that he erred on his test procedure, either through breaking the capsules in the wrong order or spilling some fluid, the test results were discarded for this summary report.

Of the 879 samples, 424 tested negative (with a blue color at the end of the test) indicating less than 50 ppm of PCB. The remaining 455 tested positive (turned clear). However not all of these samples were drawn randomly, since many users wanted to explore this test method in a narrow critical range of pcb contamination. This led to a larger percentage of oil samples testing clear.

If we were to choose only randomly picked samples, the test results show 372 (51%) blue and 352 (49%) clear. Of the 355 clear samples 161 (22% of the total) did contain more than 50 ppm of PCB and 194 samples (27% of the total) gave a false positive test. This in comparison to 51% of the samples being eliminated from any further tests is quite small. Of course one would like this percentage to get even smaller but in order to safeguard against contaminated samples testing negative, this is the best we can do.

A total of 18 tests showed false negatives, i.e., the CLOR-N-OIL test gave a negative (blue) test, but a subsequent PCB test indicated a contamination level greater than 50 ppm. While we continue to examine the reasons and retest many of these samples, we do have an explanation for many of the tests.

A user who reported four false negative readings in a batch of 20 tests subsequently found that the PCB tests carried out by an independent outside lab gave high PCB readings. The PCB test reported by the lab gave readings between 53 and 26 ppm, whereas the subsequent tests carried out on these same samples at General Electric tested between 2 and 11 ppm.

There were two other problems early in the test program that were rectified through appropriate changes in the instructions. One change was to show through a photograph that if a test sample has a substantial percentage of PCB (above a few hundred thousand ppm) the test sample being heavier than water will sink below the water and this test method will not work.

Another problem was eliminated through the removal of a photo showing a test resulting from a sample contaminated with 40 ppm of Askarel 1242. Here the photograph showed a slight purple ring at the top of the water layer which would look similar to a test sample if some oil was transferred to tube #2 (in step 4 of the instructions). Since the instructions were revised only two false negatives have been reported.

CONCLUSIONS:

Through the use of the CLOR-N-OIL screening test one can typically eliminate half of the oil samples from any further testing. The general experience, especially since the instructions were revised, has been exceptionally good. This test method can offer a significant cost savings to the utility industry.

Number of Utilities Participating	87
Number of Utilities that have Reported to Date	40
Total Oil Samples Tested	879
Blue	424 (48%)
Clear	455 (52%)
Random Sampling	
Blue	372 (51%)
Clear	355 (49%)
False Positives	194 (27%)
PCB Contaminated	161 (22%)
False Negatives	18 (2.3%)