A COMPARISON OF POPULAR SCMEENING METHODS FOR PCB CONTAMINATION IN SOIL

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ABSTRACT

A study was conducted to determine the accuracy of two test kit methods (based on the PCB RISC and L2000 kits) commonly used to quantify PCBs in soil contaminated with transformer oil, diesel fuel oil and gasoline. Laboratory generated soil samples contaminated with Aroclor 1242 over the range of 0 to 100 ppm were tested at both varying and constant levels of transformer oil (0-10%) and with diesel fuel oil and gasoline (1%). Results were compared with those obtained using an ASTM gas chromatography method. Testing at action levels of 2 and 10 ppm Aroclor 1242, the L2 00™ and GC methods correctly classified all soil samples as to containing > or < the action level, even in the presence of 2-10% transformer oil and 1% diesel fuel oil and gasoline. The PCB RISC based method failed to correctly classify such soils due to a negative interference caused by the hydrocarbons.

INTRODUCTION

Soil can become contaminated with PCBs through accidents involving the removal and maintenance of transformers and capacitors or through improper disposal of PCB containing substances. Accurate determination of the PCB content of soils suspected to be contaminated is necessary for the responsible parties to make the appropriate decisions regarding site clean up and remediation. Several proven laboratory analytical methods have been used for nearly a decade to meet this need. Most of these have involved a gas chromatographic analysis of a cleaned-up extract of the soil. More recently, field test kits and portable laboratory systems using test kits have become a popular way to identify PCB "hot spots" on-site in suspected contaminated areas, thereby reducing the number of samples requiring the more expensive and time consuming laboratory tests and limiting the extent of soil excavation required in cleaning up the site. These have included test kits based on solvent extraction of the PCBs from the soil, followed by chemical dehalogenation of the PCBs and analysis by either calorimetric reaction or specific ion electrode determination of the resulting chloride (the L2000 PCB Chloride Analyzer™ of

the Dexsil Corporation). A method based on the L2000 kit "Screening Test Method for Polychlorinated Biphenyls in Soil" has been submitted to EPA for approval.

Recently kits based on enzyme-linked immunosorbent assays (ELISA), in which a competitive reaction between PCBs and a PCB conjugate is used to determine the PCBs in a sample, have been used. A TA' t method based on one manufacturer's ELISA kit (PCB Risc Soil Test System from Ensys Inc.) has recently received a de facto endorsement by the EPA as draft Method 4020, Soil Screening for Polychlorinated Biphenyls by Immunoassay (1). Similar immunoassay-based (IA) kits are being developed and marketed by other companies who are also seeking EPA approval of their kits. However, there are at present no legal or regulatory requirements to use any particular test kit or kit-based method for the determination of PCBs in soil.

EPA's Office of Solid Waste Methods Hotline gives a recorded message that Method 4020 should not be used for regulatory purposes without the approval of a regulator. It is important that these test kit methods be properly evaluated so that regulatory agencies and industry, especially the electric power industry, will know which ones to recommend or require to meet their testing needs.

EXPERIMENTAL

Study Design

An examination of the published information on the ELISA-based kits did not indicate whether transformer oil above a given level would adversely affect the determination of PCBs in a soil sample. Ensys has reported (1,2) that transformer oil, diesel fuel oil and gasoline do not result in false positive interferences with their kits at levels greater than 1%, but the possible effect of such hydrocarbons as negative interferents has not been addressed. To test for possible negative interferences, laboratory generated soil samples contaminated with transformer oil, diesel fuel oil, gasoline and Aroclor were analyzed using this kit-based method. Comparison tests were performed using ASTM Method D3304 for PCBs in soils and by the method based on the Dexsil L2000 field test system for PCBs in soil and oil.

The experiments were designed primarily to simulate PCB contaminated oil spills covering a range of PCB and transformer oil concentrations. Additional experiments were conducted using soils contaminated with diesel fuel oil and gasoline to simulate soils found

in uncontrolled waste disposal sites or those associated with leaking underground storage tanks. All experiments were carried out using IA kits with detection levels of either 2 or 10 ppm Aroclor 1242. Aroclor 1242 was the only PCB used in the study as the IA kits used for this purpose are ordered calibrated by the manufacturer specifically for each Aroclor.

Two types of contaminated soils were prepared: those contaminated with Aroclor 1242 only and those contaminated with 1242 and transformer oil, diesel fuel oil or gasoline. Levels of 1242 in the soil containing only 1242 varied from 0 to 100 ppm. The co-contamination experiments involving transformer oil were conducted on soils contaminated with 1242 at constant levels while varying the concentration of the oil and at varying concentrations of 1242 while keeping the oil concentration constant.

To simulate a field-testing scenario, two action levels were chosen: 2 and 10 ppm Aroclor 1242. All of the results for the IA method were interpreted based on these preset action levels. A total of 20 soil samples were analyzed in triplicate by each of the three methods and the results compared to the expected concentration of the Aroclor in the soil based on gravimetric preparation. The total numbers of both correct and incorrect classifications that resulted by using each of the three methods were tabulated and used to evaluate each method. To avoid ambiguities due to possible sampling variations, the results from the analyses of soils contaminated at the action levels (i.e., 2 and 10 ppm) were used only as an indicator of the precision of the analytical methods. For concentrations other than the action level, the data were used to determine the percentage of correct determinations (i.e., the PCB concentration was identified correctly as greater than or less than the action level).

The contamination levels used for the soil containing Aroclor 1242 and no transformer oil were 0, 10t 20, 50 and 100 ppm. The first series of co-contaminant experiments was conducted using soil to which 1242 had been added at two times the 10 ppm action level (20 ppm) and to which Shell Diala A transformer oil was added at 0.5, 1, 2, 4, and 10 percent. Based on the results of the first series, a second series of co-contaminant experiments was conducted using soil containing transformer oil at 4% and 1242 levels of 0, 10, 50, and l00 ppm. All of the above soils were analyzed using the L2000^{TM} PCB Analyzer Method, the ASTM GC Method and the PCB RISC kit method (4020) at an action level of 10 ppm.

A final set of experiments was conducted at an action level of 2 ppm 1242 using soils contaminated with either 4% Diala A oil, 1% diesel fuel or 1% gasoline as the co-contaminants. The 1242 levels were 2, 5, 10 and 20 ppm. All analyses were conducted in triplicate using the three methods being evaluated, except for the fuel contamination

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samples for which duplicate determinations were performed using the L2000 method and for which no GC tests were performed.

Preparation of Spiked Soil Samples

To simulate typical soils, an 8 Kg mixture of clay soils and sand, approximately 75:25 w/w was prepared. The soils and sand were obtained from residential areas and were determined to contain less than 0.1 ppm Aroclor 1242 and less than 1 ppm total organic chlorine. In addition, the base soils were analyzed for total petroleum hydrocarbons (TPH) using EPA Method 418.1 and found to contain less than 10 ppm TPH. The clay soil was broken up by hand and allowed to air dry for 24 hours. The clay and sand were sieved to pass a 0.850 um sieve, mixed together, and tumbled for 24 hours in a rotating pail. Most of the clay particles were observed to be considerably smaller than 0.850 um. The water content of the freely flowing mixture was 1%. The soil was transferred to aluminum cake pans prior to addition of contaminants. Subsampling to generate homogeneous splits for spiking was performed according to the procedure described by Schumacher (3) in which soil was transferred from one pan to another in random order five times. The soils were then spiked with Aroclor 1242, either in hexane or in Diala A (Shell) transformer oil to generate known levels of the Aroclor and the oil in the soil. The spikes were slurried with the soils and hexane was added to facilitate mixing. The soil mixtures were air dried to a constant weight, bottled in previously unused clean Qorpak 8 oz. glass bottles with Teflon lined caps and tumbled for 4 hours on a rotating tumbler. Diesel fuel oil and gasoline were also added to separate aliquots of the PCB contaminated soils.

Results and Discussion

The antibody test upon which the ELISA-based kits rely requires that the PCBs first be extracted from a 10 g soil sample into methanol. The methanol extract is diluted with more methanol, then an aqueous buffer, and is then added to the antibody coated reaction tube. A solution of enzyme conjugates is also added to the solution and the resulting mixture is allowed to equilibrate. After the solution phase is removed and the vessel washed, a color developing agent is added. The greater the color obtained, the lower the PCB content of the original sample. The test results are interpreted by comparing optical densities (OD) obtained for the sample with that of a standard. If the OD of the sample is less than that of the standard, the sample contains more than the level of Aroclor set for the kit by the manufacturer. If the OD is greater than that of the standard, the sample contains less than the preset level of Aroclor. Other concentration ranges can be measured by serial dilution of the diluted sample or by use of kits set to respond at other-thresholds.

The specific IA kits evaluated in this study were set to respond to Aroclor 1242 at 2 ppm and at 10 ppm. While the distributors of the kit recommend that the user perform a preliminary GC screen to identify the specific Aroclor present, Method 4020 provides no such guidance. There have also been at least three versions of the kit issued and two drafts of Method 4020 since EPA endorsed 4020 for PCBs in July 1992. Method 4020 is based on a 5 ppm threshold for PCBs and refers the user to the manufacturer (in this case Ensys) for specific instructions. The various generations of the kit have added, in succession, a QC step, which may disqualify an entire set of analyses and a series of dilutions, which complicate the implementation of the test. These changes make the evaluation of Method 4020 and the Ensys kit difficult and the comparison with previously published validation data of concern. The testing described in this study at the 10 ppm level was based on the Ensys kit involving the use of the QC requirements and the double dilution of the sample extract as described in the December 1992 information supplied by the company (4) and the kits used were those set to expire in August 1993. Testing at the 2 ppm level was based on the same kit system, but without one of the dilution steps, as per the instructions accompanying the kit. Thus, the evaluation at the 2 and 10 ppm levels involves the same kit, but with a different dilution of the sample extract prior to the IA reaction.

The Dexsil Corp. L2000 ^{TM} Chloride Analyzer System was used according to the draft method and the instructions supplied with the unit (5). As was the case with the IA method, a 10 g sample of soil is extracted with a solvent. As such, both kit methods experienced equivalent sample sizes and sample homogeneities. The extract is reacted in plastic tubes with a sodium metal dispersion, which dehalogenates the chlorine from the PCBs and converts it to water-soluble chloride. The chloride is then measured by a chloride specific ion electrode system included with the kit. The electrode response is reported by the unit in terms of either specific Aroclors or chloride. When the specific Aroclor(s) of interest are unknown, the instructions recommend that results be reported in terms of Aroclor 1242 to cover the worst case. The method is simple to use and the reaction and measurement steps are not as time dependent as for the IA method. While the IA method requires strict adherence to specific reaction time schedules set forth in the instructions, the L2000 method seems less sensitive to reaction times so long as the minimum times are met. The electrode system in the L2000 method requires frequent recalibration, which is prompted automatically by the unit. A system blank, which is run daily and subtracted from all results is typically around 1-4 ppm expressed as Aroclor 1242.

ASTM Method D3304F, which involves a Soxhlet extraction of the PCBs using iso-octane, followed by gas chromatographic analysis of the extract for specific Aroclors, was used as written. The method is essentially EPA Method 3540A with iso-octane

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substituted as the extraction solvent, followed by Method 8080 and was developed specifically for PCBs in soil contaminated with insulating fluids. Approximately 30-40 g of each sample were extracted and analyzed in triplicate.

Results of analyses of three replicate aliquots from each sample by each kit method and by Method D3304 (identified as "GC" in the table) are shown in Table 1. Recoveries by the GC and L2000 methods were higher in the samples containing oil than in those without oil, probably because the PCBs tend to remain associated with the oil. When the oil is not present, the PCBs are more likely to become adsorbed to soil surfaces. While neither the GC nor L2000 methods result in 100% recoveries of the gravimetric levels of Aroclor added to the soil, in most cases the 95% confidence intervals for results by each include the gravimetric value, indicating that both methods produce acceptable quantitative measurements of Aroclor 1242 in these samples. The mean values for the GC and L2000" R results differ significantly at the 95% level of confidence TM for about half the samples, indicating that the GC and L2000 results cannot always be considered identical.

When the results from the L2000 ^{TM} and IA methods are compared with the expected values based on gravimetric preparation, both methods correctly identified soil containing 20 ppm 1242 as being above the action level of 10 ppm when the oil concentration was less than or equal to 1%. At oil levels of 2% or greater and 20 ppm Aroclor 1242, the IA method failed to detect the Aroclor as >10 ppm. At 4% oil the interference due to oil (when testing using a kit set to respond at 10 ppm) disappears when the Aroclor content increases to >50 ppm. This interference is quite severe when it is considered that the real threshold for the IA kits is around 1 ppm (2). Thus, 95% of the response to PCBs must be blocked for a false negative occur. There were no false negatives reported by the L2000 TM or GC methods. Because it isn't possible to simply look at a soil and determine if it has >2% oil, another means must be found to identify such samples prior to testing using this IA method in order to avoid excessive false negative classifications.

Subsequent testing of soil samples containing 2, 5, 10 and 20 ppm Aroclor 1242 and 4% oil using the IA kit set to respond at 2 ppm, failed to show the presence of the Aroclor at actual Aroclor levels as high as ten times the action level of the kit. As the only difference between the 2 ppm and the 10 ppm kits is the dilution made, it can be concluded that the oil is once again responsible for the interference. The L2000 method properly classified all of these contaminated soils, as did the GC method.

The IA method also failed to correctly classify soils contaminated with 1% diesel fuel oil and gasoline at 1242 levels up to five times the action level of the kit used. The L2000 ^{TM}method properly classfied both these soil types.

CONCLUSION

The results from the L2000 ^{TM} PCB Analyzer Method were not adversely affected by the presence of either transformer oil or fuels in the samples. This suggests that other hydrocarbons would also not present a problem in the analysis of contaminated soils. The co-contamination of the soil with a hydrocarbon does appear to enhance the efficiency of the L2000 method's extraction of PCBs from soil. The GC results also show an extraction efficiency enhancement due to the presence of transformer oil as a co-contaminant. In neither of these two methods did the extraction efficiency enhancements affect the accuracy of the soil classifications.

The IA method results, however, suggest that the ELISA-based kits of Method 4020 suffer from a severe negative interference due to transformer oil, as well as from other hydrocarbons at levels typically found in spill site and landfill samples. The full extent of the class of compounds capable of such a strong negative interference is not known and should be the subject of future studies. It is widely known that immunoassays can be very specific in their positive response to the analyte of interest. These experiments have highlighted a less well-advertised aspect of IA systems in that they involve complex, large molecules and may be susceptible to non-specific interferences, especially when used with non-aqueous solutions.

Reduction of the interference by dilution alone may not be possible, as the kits as presently configured are responsive over a rather narrow range of parameters. Further dilutions on the order of those predicted necessary to eliminate the oil interference would likely render the kits insufficiently sensitive to determine PCBs at the levels of interest to government and industry. While the exact mechanism of the interference observed here and its correction are beyond the scope of this study, the EPA needs to fully investigate the potential of all such possible co-contaminants to produce false negative results. The EPA or the manufacturer of the IA kits has, as yet, made no published determination of the negative interference of any compounds and should do so immediately. Oils and fuels represent only a small fraction of the possible interferents likely to be present in environmental soil samples. This will undoubtedly require reanalysis of some field samples already determined non hazardous by using draft Method 4020.

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Table 1. Comparison of GC, L2000 ™ and IA Kit Methods' Accuracy in Classifying Aroclor 1242 Levels in Soils [a,b]

Aroclor 1242, Gravimetric Value, ppm	% oil	Method Results, ppm			% correct GC &	
		GC	L2000	IA	L2000	IA
10 ppm action level						
0	0	0.1±0.04	1.4±0.6	<10	100	100
10	0	8.7±2.4	9.5±1.2	>10	100	100
20	0	15.1±1.7	13.4±2.3	>10	100	100
50	0	40.5±1.8	40.3±4.1	>10	100	100
100	0	77.3±2.0	78.9±2.3	>10	100	100
20	0.5	16.1±2.8	18.9±1.5	>10	100	100
20	1	17.3±0.9	19.5±1.7	>10	100	100
20	2	17.3±1.5	23.2±0.9	<10	100	0
20	4	18.0±1.0	21.5±0.7	<10	100	0
20	10	17.3±2.7	25.5±1.9	<10	100	0
0	4	0.1±0.04	0.0±0.0	<10	100	100
10	4	9.6±0.2	8.3±0.4	<10	100	100
50	4	46.1±4.6	49.8±0.2	>10	100	100
100	4	92.7±4.7	105.8±3.0	>10	100	100
ppm action level						
2	4	1.8±0.1	2.8±0.6	<2	100	100
5	4	4.3±0.2	5.2±0.7	<2	100	0
10	4	8.3±0.1	9.4±0.2	<2	100	0
20	4	18.0±1.0	21.5±0.7	<2	100	0
10 (Diesel)	1	NA	9.0±0.1[c]	<2	100	0
10 (Gasoline)	1	NA	9.2±1.4[c]	<2	100	0

[a]all results uncorrected for % water

[b]mean +- 1 standard deviation for GC and L2000 [TM] results; all three results from each IA method determination agreed in all cases

[c] mean of two determinations

NA: not analyzed