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A COMPARISON OF CURRENT PCB ANALYTICAL TECHNIQUES

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ABSTRACT

Three primary methods of PCB analysis are currently employed in the analysis of transformer oil and soil samples. The oldest and most widely used technique is an instrumental method utilizing gas chromatography. The second method is a chemical-colorimetric test kit that simply tells whether or not the sample contains greater than 50 ppm PCB. The third, an electrochemical method, provides a quantitative result by testing for total chlorine and, like the colorimetric method, is not PCB specific. Under different conditions, each method may be more appropriate than the others. Analysis of recent data shows that the accuracy of each method is not necessarily a function of the sophistication of the technique.

INTRODUCTION

Traditionally, gas chromatography has been the method of choice for analysts who were looking for PCB in oil, soil, and water. Recently, the increase in the number of samples being tested has spurred the development of simpler methods which allow the analysis to be performed on site. Before employing any method, the prudent analyst needs to be assured of its accuracy and precision.

GAS CHROMATOGRAPHY

For analysis of PCBs with a gas chromatograph, either an electron capture detector or a Hall detector is used. Both detectors are extremely sensitive to halogens and can therefore provide low limits of detection for PCB. The gas chromatograph separates the PCBs from the other components in the mixture. The PCB compounds are then quantified by comparing the detector response to the response obtained from a standard of known concentration. Under the

same conditions, any sample should give identical results on successive runs.

CHLORIDE ANALYSIS TECHNIQUES

Clorimetric and electrochemical methods test for PCB by analyzing for total chlorine. Because all PCB contains chlorine, an absence of chlorine indicates an absence of PCB. The presence of chlorine, however, does not guarantee the presence of PCB as other sources of chlorine may influence the test. In electrical insulating fluid, other sources of chlorine are rare and total chlorine gives an excellent indication of total PCB.

The preparative steps for the chlorimetric and electrochemical test methods are identical. The PCB is reacted with a metallic sodium reagent to remove the chloride from the PCB backbone. The resulting chloride ions are then extracted into an aqueous solution where they can be easily measured.

In the colorimetric approach, a fixed amount of mercuric nitrate is added to the solution and the mercuric ions are complexed with any chloride ions that may be present. If there are more mercuric ions present than chloride ions, the addition of a small amount of diphenyl carbazone will result in a purple color. If all the mercuric ions are tied up by an excess of chloride, then no color will result after addition of the indicator.

The electrochemical method employs an ion specific electrode to detect the actual concentration of chloride that is present in the sample. The electrode puts out a millivolt potential which is inversely proportional to the log of the chloride concentration. A properly designed instrument can easily convert the millivolt output back into parts per million PCB. Like the colorimetric method, chlorinated compounds other than PCB will result in a high bias, but false negatives will not occur.

RESULTS

The first set of results (Table 1) provides a comparison between electrometric and chromatographic analysis for standard of Aroclor 1242 in transformer oil. The samples range from blanks to 500 ppm. Each sample was run three times on each method. The mean and standard deviation is given for each run. All results are in ug/g (ppm).

The second set of data provides a comparison between the electrometric and chromatographic methods on soil samples. Soil samples are actual samples obtained from a PCB remediation site. All were found to contain Aroclor 1242.

Table 1				
Results from the Analysis of Oil Samples Containing Aroclor 1242 by the Electrometric Method and by AP600/4-81-045				
Concentration Aroclor 1242	Electrometric Mean Result	Std Dev	Chromatographic Mean Result	Std Dev
(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
0	1.0	0.5	ND	—
10	9.6	0.2	10.4	0.4
50	49.4	2.8	51.4	1.0
100	98.5	5.5	95.6	1.3
500	494	26.1	484.4	11.7

Table 2				
Results from the Analysis of Soil Samples Contaminated with Aroclor 1242 by the Electrometric Method and by AP8080.				
Sample Number	Electrometric Mean Result	Std Dev	Chromatographic Mean Result	Std Dev
(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
1	52.65	1.16	38.4	2.7
2	3.2	0.3	1.4	0.2
3	55.5	9.7	57.3	7.1
4	30.3	7.1	38.1	3.2
5	15.4	0.4	10.1	0.4
6	5.8	0.9	4.25	0.5
7	100.5	5.6	98.0	2.1
8	11.6	1.4	8.3	0.9

EPA RESULTS

Twice a year, EPA sends out performance evaluation samples to laboratories performing PCB analyses. Many states use these results to certify labs so that they may legally perform PCB analyses. Each set of samples includes two water samples and two oil samples. Each laboratory is asked to analyze each sample and report the Aroclor type and quantity that is detected. After all results are received, EPA analyzes the lab data and determines a window into which a lab's results must fall for that laboratory's results to be considered acceptable.

Before looking at the aggregate EPA data it is important to note several things about this particular test.

1. Each laboratory is aware that it is being tested. The analyst knows that the sample is extremely important and that the laboratory's certification is dependent on the results.
2. The matrix being tested, transformer oil, is a clean matrix with few interferences.
3. There is enough oil provided so that the test can be run several times.

The following data are from study number WP025: The transformer oil being tested contained 50 ppm Aroclor 1260.

Number of labs reporting	522
Number deemed unacceptable	18
Number reporting below target level	327
Number reporting greater than target level	186
Number reporting below 45 ppm	275
Acceptable range	1.58 - 82.7

Any lab reporting between 1.58-82.7 ppm was found acceptable – on a 50 ppm sample. And still, 18 laboratories failed. 327 out of 504 labs (65%) that were judged acceptable gave false negative results – they reported results that were below the actual concentration of the sample. Even allowing for the ten percent error that is inherent in the method, there were still 275 labs (55%) that gave false negative results. Keep in mind that these labs knew they were being tested and that there was enough sample available to run several tests.

Recall that the colorimetric and electrochemical tests analyze for PCB by checking for total chlorine. So how does chlorine concentration translate into PCB concentration?

Fifty ppm Aroclor 1242 contains 2 ppm chlorine on a weight to weight basis. The colorimetric test (Clor-N-Oil) contains just enough mercuric nitrate to change color at 18.5 ppm. The 2.5 cushion is provided to compensate for any operator error and still avoid any chance of a false negative. By design, then, the colorimetric method reduces the rate of false negatives to zero. The number of false positives will be greater because of this conservative approach, but it is generally agreed that false positives are much preferred to false negatives when analyzing for a regulated substance.

THE ELECTROCHEMICAL METHOD

The electrochemical method also tests for chloride, but allows for a greater degree of flexibility by adjusting the response for different Aroclors. The instrument has three different settings, 1242, 1260, and Askarel A to convert the amount of chloride sensed directly into ppm for the respective Aroclors.

On the 1242 setting, 21 ppm chloride is converted to 50 ppm PCB. On the 1260 setting, 30 ppm chloride is converted to 50 ppm PCB and on the Askarel A setting, 50 ppm chloride is converted to 50 ppm PCB. The instrument compensates for the differences in composition between Aroclors so that the analyst can obtain the most accurate number for whichever PCB type is under investigation. In this manner, false negatives can be reduced to a level comparable to the colorimetric test while false positives can also be reduced to cut down on the amount of follow-up testing that is required.

DISCUSSION

A careful evaluation of the PCB testing methods that are available to analysts today indicates that the best method may not always be the most expensive. If you choose a laboratory to perform your PCB testing, ask to see their performance evaluation reports. You may be surprised. Don't hesitate to do more than one type of test on a certain sample, especially if an incorrect result could end up costing you in the long run. And remember that PCB analysis by any method is not an exact science – technique, equipment, and operator experience all play a part in determining just how good the numbers are.