

PCB ANALYSIS BY GAS CHROMATOGRAPHY

What do the Numbers Mean?

INTRODUCTION

Twice a year, the United States Environmental Protection Agency (USEPA) sends out performance evaluation samples as part of a program to check laboratories' ability to analyze for polychlorinated biphenyls. Many states use the results to certify laboratories to perform PCB analysis as this is by far the most widely used evaluation program in the United States. Results for this report provided by the USEPA show that gas chromatography provides only an approximation of the PCB level in the samples and suggest that when PCB quantification is critical, other test methods should be considered.

THE PERFORMANCE EVALUATION PROCEDURE

Each WP (water pollution) series consists of two water samples and two oil samples which must be analyzed. Water samples are sent as ampules of PCB in acetone and the analyst is required to dissolve the sample into one liter of water. Oil samples are ampulized and can be run directly. Laboratories are requested to report the type and the amount of each Aroclor detected, as well as what method was used (EPA, ASTM, Standard Methods, etc.). When EPA has received all the results, the numbers are tabulated and acceptance limits are determined. Acceptance limits are calculated by determining the 99% confidence interval on data obtained only from EPA and state laboratories. If a lab's results fall outside of that confidence interval, then those results are considered unacceptable. Results that are within the 99% confidence interval but outside of the 95% confidence interval are considered to be within warning limits and should be reviewed for possible problems.

THE LABORATORY'S PREPARATION

The following factors should all contribute to the laboratory obtaining the best results possible on a WP transformer oil sample:

- 1 The WP samples are sent out every six months and laboratories have 30 days to send results. They are not rushed.
- 2 The analyst knows that the sample is important and that generally the laboratory's certification is dependent on the results.
- 3 The matrix being tested, in this case transformer oil, is a clean matrix with few interferences.
- 4 There is enough oil provided so that the test can be run several times.
- 5 Several of the sample are very close to 50 ppm which is the most critical level for PCB analysis as this level determines if a sample is non-PCB or PCB contaminated. Extra care is usually taken with samples at this level.

Keep these factors in mind when reviewing the data summarize below.

Transformer Oil Results from WP023, WP024, and WP025

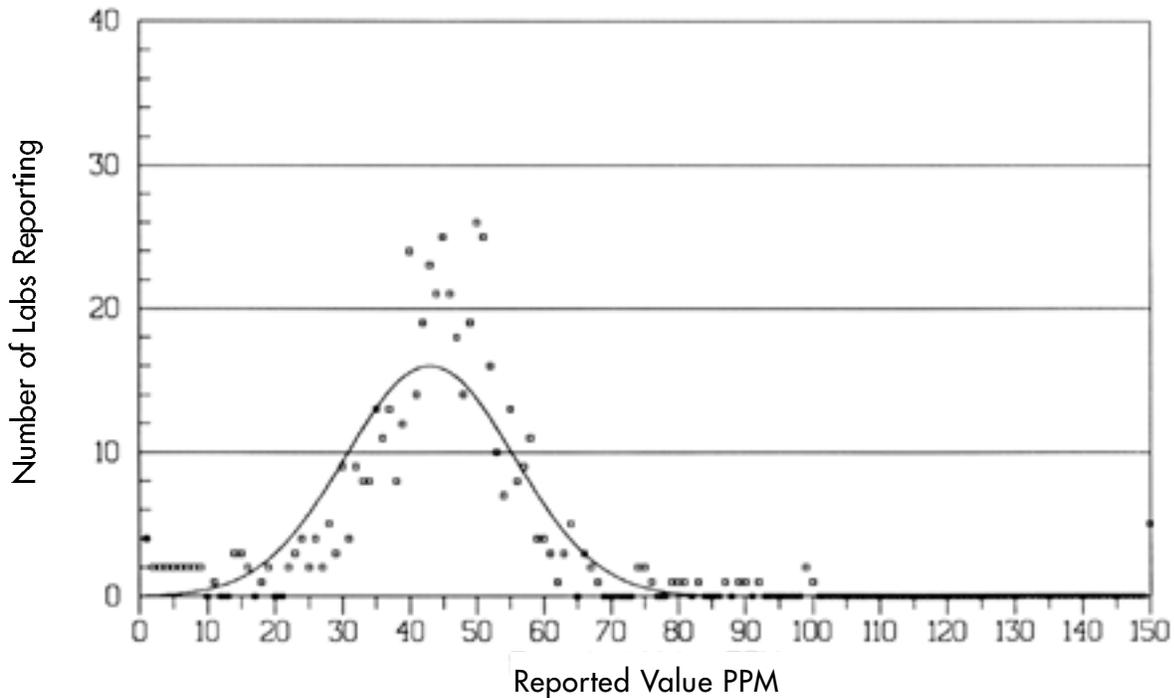
Test Number	Sample Number	Aroclor	True Value	Acceptance Limits
WP023	1	1260	8.20	0.727-12.2
WP023	2	1242/1016	21.2	1.80-30.8
WP024	1	1242/1016	45.0	7.35-69.3
WP024	2	1254	50.0	3.77-46.7
WP025	1	1254	26.3	4.04-46.7
WP025	2	1260	50.0	1.58-82.7

Take a careful look at the acceptance limits. The narrowest limits for the entire group span over 10 ppm and that's for the sample with the lowest concentration, 8.2 ppm 1260. For the two samples that should read exactly 50 ppm (the most critical level for PCB in oil), the acceptance limits cover ranges of 60 and 80 ppm. This means that on one sample that contains 50 ppm PCB, one lab could report 2 ppm, another lab report 80 ppm, and both be considered

within acceptance limits. On sample number 2 in test WP025 one lab reported a result as low as 0.05 ppm while another reported 43,000 ppm. Neither of these labs was within the acceptance limits, but that doesn't mean they are not performing commercial PCB analysis on a daily basis. The following curve illustrates the dis-

tribution of the acceptable results received for sample number 2 (50 ppm) in study WP025. All results lying outside of the 99% confidence limit (unacceptable results) have been eliminated. Note that the mean is well below the true value and that the distribution is much wider than expected.

NORMAL DISTRIBUTION OF TEST WP025



The following table gives a breakdown of all labs reporting data for sample 2, test WP025:

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

Analysis of this data shows that of the 522 labs providing results for this test, 327 gave false negative results—that is, 65% of the labs reported that the sample contained less than 50 ppm when in fact it contained exactly 50 ppm and should have been considered a contaminated oil. Even allowing for 10% error which is inherent in the method, 55% of the labs still gave false negative results. If this type of error is made in the field, it could be extremely costly if it is found that a PCB contaminated oil was treated as non-PCB. Remember, it's not the lab that assumes the liability for incorrect results but the owner of the equipment being tested.

ALTERNATIVES

All PCBs are composed partially of chlorine and an absence of chlorine in an oil sample guarantees specifically for PCB. Testing for total chlorine is a much simpler procedure than analyzing specifically for PCB and can be performed accurately in a less sophisticated laboratory or even in the field by untrained personnel. Microcoulometry, x-ray fluorescence, colorimetric and electrochemical techniques can all provide accurate total chlorine readings in a matter of minutes. If any of these techniques can show that an oil sample contains less than 21 ppm chlorine, then the sample must contain less than 50 ppm PCB because even the least chlorinated of the PCBs (1242, 1016) contains at least 42% chlorine. If chlorine is found at a level greater than 21 ppm, PCBs may be present, but the chlorine could be from another source and a more specific test (GC) should probably be run. Although these total chlorine methods are less specific than GC, their simplicity, improved accuracy, low cost, and tendency to fail only on the “safe side” of the 50 ppm limit mean that under many conditions a PCB screen for total chlorine is preferable to a gas

chromatographic analysis. The general absence of interfering chlorinated compounds in electrical insulating fluid makes these methods even more attractive.

RECOMMENDATIONS

Many utilities and contractors have relied on gas chromatography to provide accurate results for their PCB tests. When a result came back from the lab it was assumed that the numbers were accurate and that the sample actually contained what the lab reported. But performing a gas chromatographic test is not a simple task – many variables can influence the final result. Sample preparation, instrument integrity, and the training of the analyst all play a role in what results are reported. Sometimes a simpler, more direct test may provide more reliable results than a complicated instrumental analysis. Whatever method is used, don't hesitate to test a sample two or three times if the result is close to the action level, and ask your laboratory for a copy of their performance evaluation results. Make sure that your sample is indeed below 50 ppm. Remember, the laboratory isn't responsible for PCB results – you are.