PCB DETERMINATION, SIMPLE/LOW COST OR COMPLEX/EXPENSIVE, WHICH METHOD IS THE MOST RELIABLE IN THE FIELD?

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The reliability of a low cost, simple method for the determination of polychlorinated biphenyls (PCB) in oil is compared with that obtained from a more complex method using expensive analytical instrumentation.

The inexpensive method involved the use of a simple chemical test kit consisting of two plastic tubes (each containing crushable glass ampoule(s)) and a polyethylene bellows-type pipette. The analysis was carried out using the following procedure.

(1) 5 ml of oil is pipetted into tube 1 and the cap secured

(2) The lower ampoule is broken, releasing the catalyst, and the tube shaken for 10 seconds. The upper ampoule is then broken, releasing the dispersed sodium that reacts with the chlorine in the PCB. The tube is then shaken for a further 10 seconds. The tube is then periodically shaken over a period of 60 seconds.

(3) The buffer in tube 2 is-poured into tube-1 and 5 ml of the aqueous layer is separated by a decanting system and passed back into tube 2.

(4) Two ampoules in tube 2 are broken and the tube shaken for 10 seconds. If the color is mauve or purple there is less than 50 ppm of PCB present. If the color is yellow or white there is more than 50 ppm of PCB present.

The samples that were tested were identical to those used by the EPA in their WP (water pollution) series proficiency test and consisted of six oils containing traces of PCBs, the details of which are shown in table 1. The six samples were tested by 50 different field personnel, 25 having had prior experience with the kit and 25 who were not only completely new to the method, but who had little or no knowledge of chemistry or chemical analysis. The nature and the concentration of the PCBs in the samples were completely unknown to the participants. The personnel with previous experience were merely given the samples and the kits and asked to proceed with the tests. The personnel who had no previous experience with the kit were given a single demonstration using a separate sample and then given the kits and the samples and asked to carry out the tests using the instructions provided. The results obtained from the tests are summarized in table 2.

Table 1
Samples Used in Study

Sample	Aroclor	Concentration (ppm)
A	1242	21
B	1242	45
C	1254	50
D	1254	26.3
E	1260	8.2
F	1260	50

Table 2
Results from the Simple Chemical Tests

Number of Tests	300
Number of operators	50
Number of samples reported below target level (false negatives)	1
Number of samples reported above target level (false positives)	52

The Water Pollution (WP) series of performance tests are performed semi-annually by laboratories which have asked to participate. Although the federal EPA does not certify laboratories, many states use the results from this series of tests in their own certification programs. Each series includes two oil samples in which the participants are asked to identify both the type and quantity of PCB present. The samples are analyzed by GC or GC-MS and reported back to EPA for evaluation. Each lab is asked to specify which method (EPA, ASTM, Standard Methods, etc.) was used. Acceptable limits are determined by tabulating the results from only EPA and state laboratories and calculating the 95% confidence limits for each sample. Each laboratory is then evaluated by checking if its results fall into those acceptable limits.

The actual method used specifies the type of column, the correct temperatures, the proper dilution ratio, the sample preparation procedure, and the integration technique. The majority of laboratories report using EPA procedure 600/4-81-045 to perform the analyses.

The six samples, as defined in table 1, were circulated to 522 laboratories and analyzed. As in the simple chemical tests, the nature and concentration of the PCBs in the samples were completely unknown to the participants. The results obtained on one sample that contained 50 ppm 1260 are summarized in table 3.

Table 3
Results from the EPA Proficiency Tests (50 ppm 1260)

Number of Laboratories Reporting	522
Number Deemed Unacceptable	15
Number Reporting below Target Level (False Negatives)	327
Number Reporting above Target Level (False Positives)	186
Acceptable Range (95% Confidence Limits)	1.58-82.7 ppm

Table 4 shows the acceptable ranges that EPA calculated for each of the samples used in this study.

Table 4

Sample Conc.(ppm)	Aroclor	Acce2tance Limits (ppm)
21.2	1242	1.80 - 30.8
8.2	1260	0.727 - 12.2
45.0	1242	7.35 - 69.3
50.0	1254	3.77 - 63.4
26.3	1254	4.04 - 46.7
50.0	1260	1.58 - 82.7

Discussion of Results

In order to conform to the EPA regulations, any transformer oil must contain less than 50 ppm of PCB to be considered non-PCB and, if more is found, then special procedures must be adopted. Furthermore, if oils are found to contain in excess of 50 ppm PCB, then very expensive litigation can ensue followed by heavy fines. It follows that the essential question that the analysis must answer is simple. Is the PCB concentration in excess of 50 ppm or less than 50 ppm? It is not important to know the exact concentration of PCB in the sample, only if it is in excess of 50 ppm or not.

The GC method of analysis can, without doubt, provide a very accurate measurement of the PCB concentration of an oil and for this reason, the method was chosen by the EPA as a preferred method of analysis. The equipment is very expensive ($15,000 to $30,00 depending on the instrument and accessories chosen) but modern GC instruments are well designed and reliable. The results, therefore, obtained from the EPA proficiency tests are, to say the least, very unexpected.

The modern GC is a very complex instrument and the specific detectors recommended by the EPA for PCB analysis are particularly susceptible to contamination and must be maintained with care. The sample preparation and analytical procedure require considerable analytical skill. More importantly, extensive GC experience is essential if the validity of the analysis is to be confirmed by the correct interpretation of the chromatogram. It follows that the analyst operating the instrument must be well trained and well qualified. The salary of such a staff member, together with overhead, can be in excess of $100,000 a year. However, it must be emphasized that a gas chromatograph cannot be operated successfully by an unqualified technician, however dedicated and enthusiastic he/she may be and certainly not for PCB analysis. Assuming the instrumentation purchased for the analysis is adequate, the results obtained from the EPA tests can only be explained by procedural mistakes made by inadequately trained operators.

Unfortunately, as a result of their enthusiasm for the product, their own experience in GC, and a strong desire for a sale, the instrument company's sales agents tend to exaggerate the simplicity of the analytical procedure and do not stress the need for skilled operators. As a result, the purchaser of a GC instrument may not recognize the need to hire an appropriate analyst to operate the device and as a consequence never achieves the accuracy and precision that the equipment can provide. Furthermore, although the initial capital outlay necessary to buy the instrument may be acceptable to a given organization, the large increase in operational costs that are necessary to permanently employ a trained analyst may not be acceptable. It follows that although GC may be, theoretically, the ideal method for PCB analysis, in practice, the advantages of the technique may not be realized

due to appropriately trained operators not being available. An interesting corollary arises from this discussion. Due to-the limited availability and high cost of well trained gas chromatographers and the increasing scope of the EPA, it may not be practical to continue to recommend GC as the method of choice for the analysis of environmental contaminants even though it may be technically appropriate. This argument will also apply to other instrumental methods of analysis.

It is seen from the EPA test results that, should the samples have been real, there would be a large number of customers taking steps to deal with a PCB concentrations in excess of 50 ppm when, in actual fact, the concentrations were acceptable. Conversely, and more importantly, there would be even more customers unaware that they are breaking the law and, as a consequence liable to litigation procedures, due solely to analytical error. This situation must be considered completely unacceptable, particularly as the responsibility for meeting the EPA regulations lies with the customer and a faulty analysis is not an acceptable explanation or excuse despite a recommended EPA method being used.

In contrast, the simple chemical test that answers the EPA question of contamination with a simple yes/no reply appears to meet all the analytical needs of the customer. It gives an extremely small number of false negatives (0.33% or one false negative in three hundred tests), is very inexpensive and the test can be carried out by unqualified operators or operators with very little training. It can be used in the field, requires no services or laboratory facilities and, most important of all, is highly reliable.

The results from the chemical tests suggest that it would be appropriate to make some recommendations to the EPA. The suggestions are not meant to be impertinent and are submitted with the honest intent to help the public at large and the EPA to reduce pollution and as a result to help improve the environment. The recommendations are as follows.

When recommending a test procedure for a particular environmental contaminant, do not propose the most sensitive and sophisticated method available but one that provides adequate, but not excessive accuracy and precision. The test must be simple and should not require the use of costly equipment or the support of highly trained and expensive staff so that the cost to the industry concerned is minimized and thus, encourages their cooperation. Instrumental methods of analysis should be avoided wherever possible and in cases where simple inexpensive tests are not available, a suitable method should be developed exclusively for the compound(s) of interest. Such method development could be carried out by the EPA itself, or through contracts arranged with appropriate university departments or companies involved with the development and manufacture of such tests. Finally, when defining pollution limits, an attempt should be made to enunciate the regulations in such a manner that any tests that are necessary can be designed to give a simple yes/no answer and, consequently, not require the reporting of numerical data.