

ONE EXAMPLE WHERE CHROMATOGRAPHY MAY NOT NECESSARILY BE THE BEST ANALYTICAL METHOD

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ABSTRACT

Three alternative methods for the analysis of polychlorinated biphenyls (PCBs) in transformer oil and soil samples are described and discussed. The first method is solely a chemical method with a final colorimetric estimation, the second a chemical method with a final electrometric measurement, and the third a GC analysis, either by direct sampling following solvent extraction or after subsequent dilution. It is shown that, depending on the nature of the sample and the analytical requirements, any of the three could be the appropriate method to use. The chemical method is preferred where speed and economy are important, where the test environment precludes the other alternatives, and where a simple yes or no answer is required to avoid expensive litigation and fines. The second method is valuable when a numerical value must be placed on the PCB concentration and where expensive capital investment is to be avoided. The second method is also the only alternative when a numerical value for the chlorine content of an oil is required and there are a large number of chlorine compounds present, a situation which renders a GC method impractical or at least very difficult to carry out. The first and second methods measure total chlorine. Thus, the third method, GC, would be chosen where the actual concentration of a specific PCB is required and any other chlorine compounds present are not critical. The first two methods can give false positive values but not false negative values, and this is important in order to be confident that legal limits are not exceeded. The cost, simplicity, accuracy, and precision of all three methods are compared and discussed.

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INTRODUCTION

Over the past decade, the use of instrumental methods of analysis has increased dramatically. Today, there is a great tendency for analysts to resort to such methods as their first choice, irrespective of their pertinence to the specific problem at hand and, sometimes, even with complete disregard for cost or the required accuracy and precision of the analysis. This biased attitude often arises from the expensive nature of the modern analytical instrument, which to some minds implies that they will provide at all times faster analyses, greater precision and greater accuracy. The complexity of the modern chromatograph, with the implied sophistication and reliability, also plays a part in convincing the analyst that chromatography, for example, should be the first choice as a suitable method to solve a particular problem. Such assumptions are of course fallacious, and it is the purpose of the paper to provide an example of one type of analysis where simple, inexpensive chemical procedures can, in fact, be preferable to alternative chromatographic methods under certain circumstances.

The advantages of alternative simple chemical tests are already being accepted by the EPA, and some such procedures have, in the face of alternative instrumental methods, been examined and subsequently become EPA approved. The examples to be described in this paper are the analyses of PCBs in transformer oils and soil, which are not as simple or straightforward as might be expected. The tests involve measurements of PCB concentration down to a few parts per million where, as a result of extensive legislation, inaccurate results would be

likely to evoke expensive litigation and heavy fines. The different methodology and apparatus will be described, the accuracy and precision of each method discussed, and the costs of each analysis reported. The three methods will then be compared, and the most appropriate areas of application of each method will be recommended.

EXPERIMENTAL

A chemical method for the determination of PCBs in oils and soil, with a final colorimetric estimation

This procedure utilizes sodium metal to remove chlorine from any PCB present in the sample, and then a color reagent is used to detect the resulting chloride that is formed (1). If the original sample contains more than 20 ppm of chlorine, a yellow color will result. If it contains less than 20 ppm of chlorine, a purple color will result. All PCB formulations that were used in transformers contain at least 42% (w/w) chlorine (e.g., Aroclor 1242). Consequently, a sample that contains less than 20 ppm of chlorine cannot contain more than 50 ppm of PCB (2).

Analytical method for oil samples. To a mix of 0.2 mL of a solution of naphthalene in diglyme and 5 mL of oil sample was added 0.2 mL of a dispersion of metallic sodium in mineral oil and the mixture was shaken for 1 min. Buffer (7 mL) was added to neutralize the excess sodium and to adjust the pH to 2.0. Then 5 mL of the aqueous layer was combined with 0.75 mL of a solution of mercuric nitrate and 0.5 mL of a solution of diphenyl carbazone in alcohol. The mixture was then shaken for 10 s. If the resulting solution is yellow or colorless then the sample may contain more than 50 ppm of PCB. If, on the other hand, the solution is purple the sample contains less than 50 ppm of PCB (3).

Analytical method for soil samples. Ten grams of the sample of soil was extracted by shaking for 1 min with 12 mL of a mixture containing 2 mL of distilled water and 10 mL of an immiscible hydrocarbon. The soil was then allowed to settle and the supernatant liquid filtered through a column containing Florisil to remove any moisture and inorganic chloride. A 5-mL measure of the dry filtrate was then treated with 0.2

mL of a solution of naphthalene in diglyme followed by 0.2 mL of solvent containing dispersed sodium, and shaken for 1 min. Buffer solution (7 mL) was then added, and the aqueous layer was separated and combined with 0.75 mL of a solution of mercuric nitrate followed by 0.5 mL of a solution of diphenyl carbazone in alcohol. The mixture was then well shaken. If the resulting solution is yellow or colorless then the sample may contain more than 50 ppm of PCB. If, on the other hand, the solution is purple the sample cannot contain more than 50 ppm of PCB.

A chemical method for the determination of PCBs in oils and soil, with a final electrometric measurement

The previous method could not provide a numerical value for the concentration of PCB in the sample and, although alerting the chemist to excessive PCB contamination, gave no idea of the extent of the contamination. However, employing the chemical procedure described above, the concentration of chloride contained in the final aqueous extract can be determined electrometrically by means of a chloride-specific electrode. By immersing a chloride-specific electrode in the aqueous extract and measuring the EMF produced, the chloride concentration, and thus the PCB content, can be estimated. The chloride concentration is exponentially related to the electrode EMF, and with a suitable electronic circuit design, the results can be presented digitally in ppm of the selected PCB on an appropriate meter (4).

Analytical method for oil samples. The measuring instrument was fitted with temperature compensation, as the output of the chloride-specific electrode varies with temperature. Initially, the temperature compensation adjustment was set to the sample/electrode temperature. The electronic measuring device was then calibrated with a solution containing chloride equivalent to 50 ppm. The electrode was immersed in 5 mL of the calibration solution, and appropriate adjustments were made to the calibration control to provide an output on the digital meter of 50 ppm of chloride. The sample was prepared in a manner similar to that described previously. A 0.2 mL volume of a solution of naphthalene in diglyme was added to 5 mL

of oil sample; to this mixture was added 0.4 mL of a dispersion of metallic sodium in mineral oil, and the mixture was shaken for 1 min. Buffer (5 mL) was then added to neutralize the excess sodium and to adjust the pH to 2.0 to ensure that the pH of the mixture was within the operating range of the electrode. Five milliliters of the aqueous layer was then carefully separated and transferred to a suitable vessel. After rinsing and drying on the paper tissue, the chloride-specific electrode was immersed into the 5-mL sample, gently stirred for 5 s, and allowed to stand for 30 s. The concentration of PCB in ppm was then read directly from the digital output meter. The dynamic range of this analytical procedure is from 5 to 5000 ppm. The precision varies with the concentration. At concentrations between 50 and 2000 ppm, it is $\pm 10\%$. Between 5 and 25 ppm, it is about ± 2 ppm.

Analytical method for soil samples. The method for the analysis of soils is very similar to that used with the colorimetric estimation. Ten grams of the sample of soil was extracted by shaking for 1 min with 12 mL of solvent containing 2 mL of distilled water in 10 mL of an immiscible hydrocarbon. The soil was then allowed to settle, and the supernatant liquid was filtered through a column containing Florisil to remove any moisture and inorganic chloride. A 5-mL measure of the dry filtrate was then treated with 0.2 mL of a solution containing naphthalene in diglyme followed by 0.4 mL of a dispersion of metallic sodium in mineral oil and shaken for 1 min. Buffer solution (5 mL) was then added and the aqueous layer allowed to separate. A 5-mL volume of the aqueous layer was then carefully separated and transferred to a suitable vessel. After carefully rinsing and drying on paper tissue, the chloride electrode was inserted into the 5-mL sample, gently stirred, and allowed to stand to 30 s. The concentration of PCB in ppm was then read directly from the digital output meter. The accuracy and precision of this method are about the same as that for the oil. The dynamic range of this analytical procedure is from 5 to 2000 ppm. The precision varies with the concentration. At concentrations between 50 and 2000 ppm, it is $\pm 10\%$. Between 5 and 25 ppm, it is about ± 2 ppm.

A method for the determination of PCBs in oils and soil by gas chromatography

A gas chromatograph equipped with an electron capture detector is a more sophisticated system that allows relatively easy identification of the Aroclor (commercially produced PCB mixture) present in an oil. The electron capture detector is extremely sensitive to chlorine containing compounds such as PCBs. Consequently, when this high sensitivity is coupled with the resolution achievable with the gas chromatograph, the analyst can determine not only how much PCB is present, but he can also identify which particular Aroclor or Aroclors are present in the oil (5).

Analytical method for oil samples. A wide range of chromatographs can be used in the analysis of oils for PCB content, but the system employed in this work was a Varian 3400 gas chromatograph fitted with an ECD detector, in conjunction with a DS654 data system and a Hewlett-Packard ThinkJet recorder. An autosampler can be employed if available. The column was 6 ft x $\frac{1}{8}$ in. o.d., packed with 3% (w/w) OV-1 on Chromasorb W. The column and injection system were operated isothermally at 195°C and at a column flow rate in the range of 30-40 mL/min. The analytical procedure was that defined in the EPA-600/4-81-045 recommended method.

A 200- μ L volume of sample was diluted to 10 mL with isooctane, and 1 mL of concentrated sulfuric acid was added. The mixture was shaken for 30 s and allowed to settle for 1 min. Then, 5 mL was removed from the top of the mixture and 100 mg of Florisil added, shaken well, and allowed to settle. For GC analysis, a 1- μ L injection was used. The time for sample preparation was about 5 min and that for GC analysis was about 35 min. The chromatograph was calibrated with an internal standard dissolved in the same type of oil. The dynamic range of the analysis is between 1 and 500 ppm of PCB; samples containing PCBs in excess of 500 ppm must be diluted to fall within the range of the analysis. The precision of the analysis is reported to be $\pm 10\%$ between laboratories, but as will be seen later, this is instead a very conservative estimate of the precision within a laboratory if good analytical practice is observed.

Analytical method for soil samples. The procedure was that defined in the EPA-8080 as the recommended method. The sample of soil was first dried at 110°C and the water content was determined. Ten grams of the sample was extracted with 69 mL of isooctane by means of a Soxhlet extractor over a period of at least 4 h. The extract was then treated in the same way as the oil samples. We diluted 200 µL of sample to 10 mL with isooctane and added 1 mL of concentrated sulfuric acid. The mixture was shaken and allowed to settle. We then removed 5 mL from the top of the mixture, added 100 mg of Florisil, shook the mixture, and allowed it to settle. Then 1 µL of the solution was injected onto the column. The dynamic range of the analysis is between 1 and 500 ppm of PCB; samples containing PCBs in excess of 500 ppm must be diluted to fall within the analysis range. Samples containing less than 5 ppm should be repeated with no dilution and, if necessary, the original extract may be concentrated by evaporation. The precision of the analysis is also reported to be ±10% (6).

RESULTS AND DISCUSSION

Chemical tests with colorimetric estimation

The samples chosen were standard EPA oil samples containing a range of Aroclor 1242 contents from 11 ppm to 109 ppm. The procedures employed were those previously described, except that a packed kit was used (Clor-N-Oil, Dexasil). All reactions with this kit are carried out in sealed plastic tubes, and all reagents are contained in crushable glass tubes to obviate any need to handle the reagents. This is advisable as some of the reagents are hazardous to handle in the normal manner. The results obtained are shown in Table 1, which includes results from the GC analyses of the same samples. The results from the two methods agree, and no false negatives were obtained. Even at a concentration of 50 ppm, an unambiguous positive result was obtained. It should be emphasized, however, that concentrations greater than or equal to 45 ppm but less than 50 ppm may sometimes give a positive value, but concentrations of 55 ppm will never give a false negative. Reagent strengths and volumes are designed to ensure that no false negatives can occur.

Table 1: Results from the Analysis of EPA Oil Samples Containing Aroclor 1242 by the Chemical Method with a Final Colorimetric Estimation

Sample concentration (ppm)	Result of colorimetric assessment
11	-
30	-
40	-
45	+
50	+
54	+
62	+
76	+
88	+
92	+
109	+

Standard soil samples were also tested in the same manner, using an analytical kit (Clor-N-Soil, Dexasil). This is a similar type of kit to the one used for oil, but also provides a simple balance for weighing out the soil. The procedures previously described were used, and the results obtained are shown in Table II, together with the GC analyses of the same samples. Agreement is good between the two methods, and again no false negative results were obtained.

The cost of each kit is \$5-10, and no capital investment in instruments is needed. The kit can easily be used in the field and will not give a false negative result. However, a positive must be checked by an alternative method (e.g., GC) to ensure that the chlorine detected does come from a PCB and not from other less toxic materials. Little skill is needed for the test, but some common sense is required on the part of the operator. The test is rapid and takes about 5 min. Today, PCBs are not so frequently found in oil at toxic levels, but their absence still needs to be confirmed; the chemical test with a final colorimetric estimation would be the first choice for a suspect oil or soil sample.

Chemical tests with final electrometric measurement

Initially, it is of interest to examine the basic response of the chloride-specific electrode (Orion Model 9617BN) used in this method. The device is a single-

Table II: Results from the Analysis of Standard Soil Samples Containing Aroclor 1242 by the Chemical Method with a Final Colorimetric Estimation and Electrometric Assessment

Sample concentration (ppm)	Result of colorimetric assessment	Concentration by electrometric assess. (ppm)
0	-	1.7
25	-	32.2
50	+	48.0
100	+	105.4

unit system that contains both half cells inside one case and can be immersed in a solution containing chloride (usually buffered to a pH of about 2.0). It provides an output exponentially related to the chloride concentration. The output from such an electrode is given in Table III. The concentration is related by a simple exponential function of the electrode EMF only to concentrations down to about 10 ppm.

Table III: Results from the Analysis of Aqueous Chloride Standards with an Electrometric Method of Measurement

Sample concentration (ppm)	Electrode potential (mv)	Concentration by electrometric measurement (ppm)
1.5	144.6	1.6
2.5	134.8	2.4
5.0	118.8	5.0
7.5	109.7	7.5
10.0	101.8	10.1
15.0	92.2	15.0
20.0	85.1	10.1
25.0	79.4	25.4
50.0	61.6	51.5
100	44.1	104
250	21.2	270
500	3.7	543
1000	-13.7	1079