

Electrochemical Analysis of Chlorine Concentration as a Screening Method for PCBs in Oil and Soil

Stephen Finch
Dexsil Corporation
One Hamden Park Drive
Hamden, CT 06517 USA

ABSTRACT

Electrochemical analysis of oil and soil samples using a chloride ion specific electrode provides an accurate screening method for PCBs that correlates well with standard gas chromatographic methods.

INTRODUCTION

Traditional methods of sample preparation and analysis for PCBs in oil and soil require at least several hours to complete and often must be shipped off site for analysis. A screening method that could accurately predict PCB concentrations in several minutes would be extremely helpful, especially at remediation sites where waiting time can be very expensive.

PROCEDURE

Oil and soil samples are prepared differently although the analysis procedure after sample preparation is the same.

1) Transformer oil.

Measure five mL of transformer oil into a 20-30 mL reaction tube fitted with a dispensing closure. Add approximately 200 uL of a solution consisting of 25% percent naphthalene in diglyme. Shake the mixture well for ten seconds and add 400 uL of a dispersion of sodium metal in light oil. Shake the mixture and allow it to react for one minute. Pipette in five mL of an aqueous buffer solution containing 5% sodium sulfate and enough sulfuric acid to reduce the pH

to approximately 2.0. Cap the reaction tube tightly and shake it well for at least a minute. Allow the oil phase to separate from the aqueous portion and dispense the aqueous portion into a clean glass vial.

An instrument to convert millivolt output to ppm PCB (L2000, Dexsil Corporation, Hamden, CT) is used in conjunction with a chloride ion specific electrode (Orion Research, Boston, MA or Phoenix Electrode Co., Houston, TX) to determine the original concentration of PCB in the oil sample. Calibrate the instrument on a 50 ppm chloride standard and set the instrument to the appropriate Aroclor setting (Aroclor 1242, Aroclor 1260, or Askarel A) for the type of PCB that is anticipated. If the Aroclor type is unknown, set the instrument to read "1242" as this will provide the most conservative reading. Place the electrode into the vial containing the solution being tested and allow it to equilibrate. Read the concentration of PCBs in the original sample directly off the LCD readout.

2) Soil samples

Weigh ten grams of the soil being tested into an empty reaction tube. Add ten grams of a suitable extraction solvent such as isooctane and shake the sample well to assure complete mixing. Allow the soil to settle out of the solvent. Decant off the extraction solvent and proceed with the sodium reaction as described above for oil. Wet soil samples require that the extraction solvent be dried first using Florisil or sodium sulfate. A Soxhlet Extraction procedure is not required for this test.

Samples were also run by gas chromatography using EPA method 600/4-81-045 for oil and EPA 8080 for soil. A direct comparison is made between the results obtained using EPA methodology and the electrometric method.

Results

The first set of results (Table 1) provides a comparison between electrometric and chromatographic analysis for standards 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).

Table 1

Results from the Analysis of Oil Samples Containing Aroclor 1242 by the Electrometric Method and by EPA 600/4-81-045

Concentration Aroclor 1242 <u>(ppm)</u>	Electrometric Mean Result <u>(ppm)</u>	Std Dev <u>(ppm)</u>	Chromatographic Mean Result <u>(ppm)</u>	Std Dev <u>(ppm)</u>
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

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 1248 (or partially degraded 1242).

Results from the Analysis of Soil Samples Contaminated with Aroclor 1248 by the Electrometric Method and by EPA 8080.

Sample Number	Electrometric Mean Result <u>(ppm)</u>	Std Dev. <u>(ppm)</u>	Chromatographic Mean Result <u>(ppm)</u>	Std Dev <u>(ppm)</u>
1	7.1	0.7	48.5	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

Discussion

The electrometric measurement of chloride as an indicator of PCB content is an excellent screening method when time of analysis is an important factor. Results on samples of oil spiked with Aroclor 1242 correlate very well with GC results. Soil samples do not give as good an indication of exact PCB content, but keeping in mind the heterogeneity of the samples, the results are reasonably accurate. Soil samples were wet when run using the electrometric method, but were air dried before the EPA method could be used. Moisture accounted for two to eight percent of sample weight. The limit of detection for the electrometric method with the electrodes used in this study appears to be about 2 ppm. The GC method has an LOD of 1 ppm.

Samples contaminated with chlorine sources other than PCBs give false positive results with the electrometric/sodium technique so it should be used primarily on samples that are uncontaminated by chlorinated solvents or chlorinated paraffins. Results will also be skewed when the Aroclor being analyzed is unknown. The instrument being used has chloride to PCB conversion factors for 1242, 1260, and Askarel A (1260 and trichlorobenzene), but if the Aroclor that is present is not known before the analysis, the prudent analyst must leave the instrument set on 1242 to provide the most conservative result. If the sample actually contains more highly chlorinated Aroclors (1254 or 1260), the instrument will read high.

When time and expense are important factors in analyzing for PCBs, the electrometric method provides a good alternative to gas chromatographic analysis. In PCB remediation in particular, the time saved by utilizing this new technique can cut total costs significantly.

References

- 1) M.D. Erickson, "Analytical Chemistry of PCBs," Butterworths Publications, Boston, MA (1986)
- 2) E.D. Handel, Canadian Patent 1219203 (1987)