PCBS
AVAILABLE OPTIONS FOR THE ANALYSIS OF PCBS

By Stephen Finch*

The many regulations applicable to PCB's (polychlorinated biphenyls) have greatly increased the number of samples requiring analysis. Electric utilities, industrial concerns, and governmental agencies are all required to do massive amounts of PCB analysis in water, oil and soil samples. Anyone who owns or operates electrical transformers at some time will need to analyze for PCBs. Although excellent techniques for PCB testing utilizing gas chromatography have been in practice for twenty years, the high cost of these methods has spurred the growth of alternate procedures.

COMPOSITION OF PCBS

All PCBs are composed of carbon, hydrogen, and chlorine. The widely used term "Aroclor" is a trademark that refers to a particular formulation of PCBs. Generally, the word Aroclor is followed by a four digit number such as Aroclor 1242 or Aroclor 1260. In most cases, the first two digits refer to the number of chlorine atoms (12) in a PCB molecule while the last two give the percentage of chlorine (42% to 60%) contained in that particular formulation.

Because these formulations contain consistent, predictable concentrations of chlorine, testing for total chlorine contamination is an accurate, though indirect method of analyzing for PCBs. In most cases, electrical insulating fluid is a pure hydrocarbon that contains no source of chlorine.

If any chlorine is present, it usually means that the oil has been contaminated by PCBs and by knowing the percent chlorine contained in these PCB formulations a "total chlorine" reading can give an accurate analysis of the concentration of PCB in the sample.

X-RAY FLUORESCENCE

Various methods of total chlorine analysis are in use for testing transformer oil. The most widely used techniques are X-ray fluorescence, microcoulometry, colorimetric methods, and electrochemistry. X-ray fluorescence is the only one of these methods that is non-destructive. For this analysis a sample is placed in a cup which is transparent to X-rays.

The sample is irradiated with a particular wavelength and if chlorine is present, radiation of a different, but specific, wavelength is radiated back to a detector, which can quantify the amount of chlorine present. This chlorine level can then be translated back into parts per million of PCB. Samples must be homogeneous as the instrument is only sensing the chlorine in a very thin layer at the bottom of the cup – this is generally not a problem with transformer oils. X ray fluorescence analyzers are expensive ($15,000) and require trained personnel to operate but can become quite economical when large numbers of samples are processed on a daily basis.

MICROCOULOMETRY

Microcoulometry is a method whereby a sample is entirely combusted at high temperature and then passed into a titration cell where the resulting chloride is titrated electrically with a silver electrode. By totaling the amount of silver that must be generated to neutralize the chloride, the total amount of chloride can be easily calculated. From this result, the original PCB concentration in the sample is found. In addition to transformer oil samples this technique can also be used on soil samples and waste oils.

Detection limits are in the low ppm range and only a very small sample is required for analysis. Instruments cost about $12,000, require some routine maintenance, and need to be operated by a trained technician.

*Dexsil Corporation

COLORIMETRIC TESTS

Colorimetric methods are the simplest and least expensive of the choride detection techniques. The sample is first reacted with a sodium compound that breaks down the PCBs into fragmented hydrocarbons and chloride. The resulting chloride is then extracted into an aqueous phase where it can be detected by a colorimetric reagent.

The most prevalent method involves adding a fixed amount of mercuric nitrate which complexes with chloride in a ratio of 1:2 Diphenyl carbazone, an indicator very sensitive to free mercuric ions is then added to the solution. If free mercuric ions are present, a deep purple color develops.

If, however, all of the mercury is complexed with chloride, then no color will appear. By adding a precise amount of mercuric nitrate to the sample, the test can be engineered to generate a specific endpoint at any chosen action level. For PCB, this level is usually 50 ppm. The advantages to the colorimetric method are speed, portability, and ease of use.

The main disadvantage is that the technique provides a go, no-go result at the chosen end point and is not quantitative. Pre-packaged kits costs about $10 per test.

ELECTROCHEMICAL METHODS

The electrochemical method is similar to the colorimetric test in that it requires an initial reaction with a sodium based compound to remove the chloride from the PCB backbone. After this has been completed, instead of adding a colorimetric reagent, an ion-specific electrode is used to quantitatively measure the concentration of chloride ions in the sample. The instrument used to make the measurement can then translate the concentration of chloride ions that it senses directly into parts per million PCB.

This is a quantitative method with a limit of detection of about 2 ppm. It is just as fast as colorimetric techniques, but requires line voltage to operate and involves an initial investment of several thousand dollars.

It requires little training by the operator and can be used outside, but does use reagents that cost about $5 per test. Extensive studies have shown this method to be comparable to gas chromatography for both oil and soil samples when testing at levels between two and two thousand ppm.

WHICH METHOD TO USE

When is the right time to use these chloride detection techniques and when should traditional gas chromatography be used? Specific techniques such as gas chromatography are most appropriate when samples may be contaminated with sources of chlorine other than PCBs.

For instance, if a motor oil sample contaminated with large amounts of chlorinated paraffins was tested for PCBs with a non-specific chlorine test, a large number of false positives would result as the non-specific test cannot distinguish between PCBs and chlorinated paraffins. A properly equipped gas chromatograph, however, would easily separate the PCBs from the other chlorinated organics.

On the other hand, with samples such as transformer oil which seldom contain chlorinated compounds at all, it is much more economical to use a non specific method which is able to find the PCBs much more quickly and right in the field. After testing over 150,000 transformers with a colorimetric test, Utah Power and Light Company found that more than eighty percent could be eliminated from further concern by using the simple test.

Before any specific test method is decided on, local regulations should be checked to make sure that one specific method is not legally specified.

If a particular sample may result in expensive remediation activity, don't hesitate to use two different methods to determine PCB levels. Even specific methods such as gas chromotography can provide widely varying results on the same sample, so a second test may end up saving thousands in remediation costs.