



A Fast Method for Determining PCB/Chlorine Contamination in Transformer Oils by Monochromatic X-Ray Fluorescence (MCXRF)

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Photo courtesy of : Power Substation Services, Wheeling, WV.

On an annual basis, millions of electrical transformers are removed from service in the global power grid. This activity generates many tons of solid waste and hundreds of millions of gallons of dielectric fluid / coolant (transformer oil) that can be recycled or must be incinerated as a hazardous waste. Although many chemical analysis criteria are utilised to determine the fate of both the solid and liquid reclaimed materials, the need to demonstrate regulatory compliance and control reclamation processes make testing for the presence of polychlorinated biphenyls (PCBs) contamination in used transformer oil absolutely essential.

Introduction / Abstract

Polychlorinated biphenyls (PCBs) are a liquid mixture of chemically stable chlorine containing compounds. They were widely used in the twentieth century for many electrical applications because of their excellent heat resistance and electrical insulation (dielectric) characteristics. Beginning in the late 1970's, production of high purity PCBs-based transformer oil material ceased in the United States and was eventually banned in most countries because of evidence they build up in the environment and can cause harmful health effects.

Today PCBs contamination in transformer oil is measured and controlled as millions of gallons of various dielectric/transformer oil materials are produced, recycled and traded on a global basis. Most analysis techniques take advantage of the high chlorine content in the individual compounds that comprise PCBs mixtures and measurement of specific PCBs compounds can readily be accomplished by a variety of analytical techniques, such as gas chromatography and mass spectrometry. However, analysis for the specific compounds that make up a PCBs mixture is not always practical or necessary, particularly when large number of individual samples must be characterised.

As indicated above, measurement of chlorine can be an excellent predictor for actual PCB contamination in transformer oil and other fluids of interest. X-Ray fluorescence (XRF) technology provides a reliable, fast and easy-to-use chlorine measurement methodology. The proven technique has been used for decades for primary measurement and most importantly for screening applications that reduce the need to analyse large numbers of materials with more expensive and time consuming analytical techniques.

The following describes the findings of a thorough examination of a new bench-top Monochromatic Energy Dispersive X-Ray Fluorescence (MCXRF) spectrometer. The compact (13"Wx 20"D x 16"H) and lightweight (30 lbs) analyser was found to be able to readily measure chlorine content in transformer oils to part per million levels, in duplicate, in six minutes. The analyser's performance characteristics easily meet transformer oil recycling industry requirements whenever rapid reliable chlorine measurement is essential to routine screening and process feed control activities.

Project Background and Data Origin

Analytical Services Inc. (ASI), supplies certified reference materials used for analytical instrument calibration and provides various project management and instrument validation services. They do not endorse, nor serve as an advocate for any instrument manufacturer. ASI was contracted to conduct an independent testing of the Horiba MESA 6000 chlorine in transformer oil capability and all data presented was generated by ASI personnel at their The Woodlands, TX facility. Two instruments were utilised in the study and a side-by-side testing regime

was used to demonstrate instrument agreement, accuracy, repeatability and reproducibility. The sample materials tested contained certified chlorine (Cl) content that was gravimetrically prepared in fresh transformer oil (TO) using chlorobenzene as the Cl source. Each instrument was provided separate sample sets, calibration materials, and a performance check sample. All testing was completed in less than 8 days.

Calibration – Linearity

One fundamental assessment of analytical instrument performance is verification of calibration curve linearity. Both instruments tested by ASI during the trial demonstrated excellent linearity throughout the 0-500 mg/kg Cl in transformer oil calibration range. The following graph depicts the typical near-perfect linearity exhibited by both apparatus tested and provides an indication of the quality of the calibration materials utilized (see figure 1 and note 1).

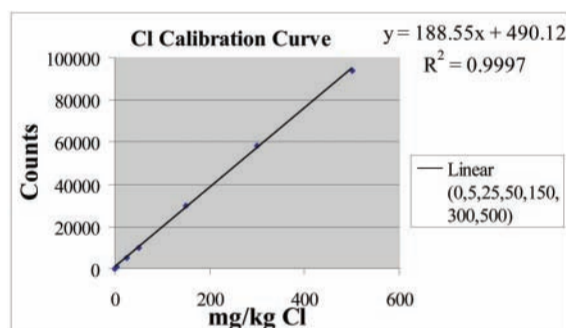


Figure 1: Chlorine Calibration Curve

Following confirmation of calibration curve linearity, instrument accuracy was demonstrated when separate performance check materials, each having a certified reference value of 40 mg/kg, were measured to contain 39 mg/kg chlorine by both apparatus (see note 1).

Note 1: The calibration, performance check and sample materials were certified to be within their assigned value at an 0.8% expanded degree of uncertainty, based on errors from assay analysis and the weighing of raw materials at a 95% confidence level (k=2).

Instrument Accuracy and Results Agreement

The ASI designed testing plan, required that both instruments measure the chlorine in each sample in their assigned sample set on 2 consecutive days. Each days result was derived from the average of two consecutive 180 second analyses of 5 mls of transformer oil in the same sample analysis cup. The day one and day two results were then averaged to yield a final result for each sample from both instruments. The test was designed to allow a close evaluation of between instrument result agreement and short-term calibration stability.

Additionally, each of the sample materials analysed had certified assigned values (see note 1) that were unknown to the analyst and were held in confidence until completion of testing. An analysis of ASI's testing results can be found in table 1 and allow the following observations.

- Final results agreement between Instrument 1 and 2 was very good as standard deviations ranged between 0.5 and 10 mg/kg Cl.
- Sample set quality and instrument accuracy were affirmed, as percent recovery values derived from the average of Instrument 1 and 2 final results were found to be very near 100% of the certified value of the samples
- No significant bias was identified as results varied above and below the certified chlorine concentrations.

All Results are Part per Million by Weight (mg/kg)						
Sample Number	Certified Cl mg/kg	Inst. #1 Final Result	Inst. #2 Final Result	Avg. #1 & #2	Avg. % Recovery	Final Result Agreement STDEV
1	4	4.2	3.5	3.85	96.3	0.5
2	20	21.0	24.5	22.75	113.8	2.5
3	75	76.0	75.6	75.80	101.0	0.3
4	200	197.4	199.5	198.45	99.2	1.5
5	325	318.9	326.1	322.50	99.2	5.1
6	490	479.4	493.6	486.50	99.3	10.0

Table 1: Two Instrument Result Comparison and Percent Recovery Data

Equivalency

In order to determine how the MCXRF methodology performance might compare to another established chlorine measurement technology, a separate but identically prepared calibration standard and sample set was analysed with Wavelength Dispersive X-ray Fluorescence (WDXRF) Instrumentation. Following instrument calibration with chlorine in transformer oil standards, the six samples were analysed in duplicate to yield the WDXRF result. An analysis demonstrates that the MCXRF and WDXRF results readily compare to each other (see table 2).

Instrument Precision and Estimation of Level of Detection

As previously discussed, during testing each instrument was supplied with a certified 40 mg/kg Cl performance check sample that was used to confirm calibration curve validity. To determine precision, ASI personnel used instrument 1 to analyse the performance check material 21 consecutive times. As with previous testing,

Sample #	Certified Cl mg/kg	Inst. #1 Result	Inst. #2 Result	WDXRF
1	4	4.2	3.5	3.4
2	20	21.0	24.5	20.1
3	75	76.0	75.6	76.9
4	200	197.4	199.5	203.6
5	325	318.9	326.1	327.0
6	490	479.4	493.6	491.1

Table 2: MCXRF and WDXRF result comparisons

results were derived from the average of two consecutive 180 second analyses of 5 mls of transformer oil in the same sample cup. This data is illustrated in Figure 2.

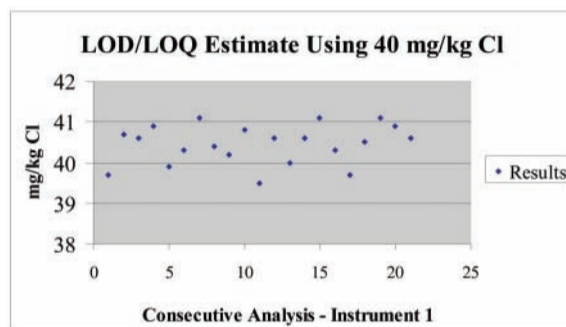


Figure 2: Precision Data

The repeatability data was then analyzed using a modified EPA method detection limit (MDL) technique to estimate level of detection (LOD) and level of quantification (LOQ) and MDL at the 95 percent confidence level. These estimates are shown in Table 3. It should be noted the elevated signal-to-noise (S/N) ratio of 84.4 indicates that a much lower concentration can be analysed and that detection limits are likely to be lower than indicated.

Instrument 1	
Mean	40.45 mg/kg
STDEV	0.48 mg/kg
LOD	1.44 mg/kg
LOQ	4.79 mg/kg
MDL-95%	0.88 mg/kg
S/N ratio	84.4

Table 3: Estimate of detection limits

Moisture Contamination Effects

Typically water contamination in new unused transformer oil is less than 10 mg/kg because of strict dielectric constant specifications and other application reasons. Additionally, water contamination can be readily visible because of its insolubility in transformer oil. However, one concern for the analyst can be the presence of a not easily visible water contamination

that might adversely affect Cl/PCB measurement capability.

In order to check for water interferences, a study was completed to shed additional light on what result bias might be documented for transformer oil containing water at various levels. Eight separate sample materials were prepared to closely approximate 25 mg/kg Cl in a fresh (unused) transformer oil (specified to be <10 mg/kg water) Water at various concentration levels was then spiked into the 25 mg/kg chlorine containing material and analysed in order to determine what water contamination level might affect MCXRF Cl measurement capability. Water visibility was judged as a film or as droplets of water obviously observable on the surface of the Mylar® sample cup film, following the analytical run (see figure 3). The results of ASI's testing can be found in table 4.

25 mg/kg Cl in transformer oil (TO)	Moisture Conc. mg/kg	Water visible to eye in sample cup after analysis	Measured CL mg/kg
1	TO neat	No	24.7
2	TO - 50 mg/kg H2O added	No	24.6
3	TO - 100 mg/kg H2O added	No	25.1
4	TO - 250 mg/kg H2O added	Yes	24.7
5	TO - 500 mg/kg H2O added	Yes	24.1
6	TO - 1000 mg/kg H2O added	Yes	25.2
7	TO - 1500 mg/kg H2O added	Yes	23.8
8	TO - 2000 mg/kg H2O added	Yes	24.1

Table 4: Cl in transformer oil, water contamination effects

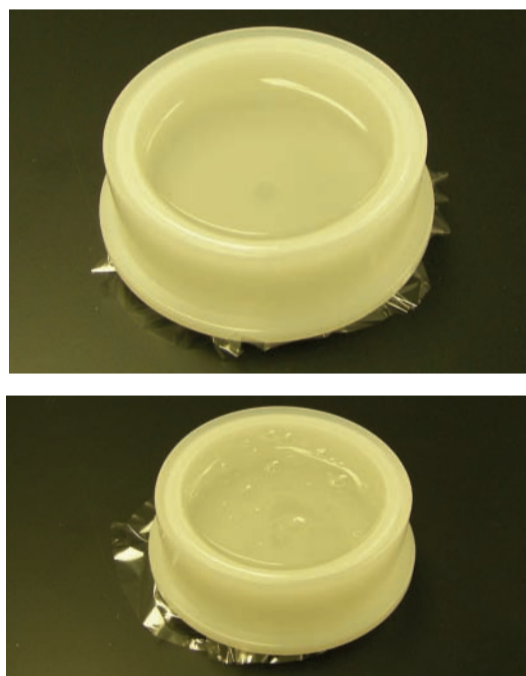


Figure 3: Photo of water droplets on cup film (Top). Cup (Bottom) spiked with water.

Water in Transformer Oil Contamination

- No discernable affect on MCXRF Cl/PCB measurement capability was noted up to 2000 mg/kg
- Contaminations up to 100 mg/kg were not readily visible to the eye
- Contaminations at 250 mg/kg and above were visible



Figure 4: Photo of Instrument

Utility – Ease of Use

The instrumentation requires only a reliable electrical source (100-250 VAC), no other utilities are required for the non-destructive and non-spark producing MCXRF technique. The apparatus features a large and responsive touch screen display that is easy to use and sample analysis can be initiated with minimum user inputs. Sample preparation and handling are eased by Mylar® film-sealed disposable plastic cups, allowing instrument use by non-laboratory trained technicians. A powerful on-board computer enables a full line-up of data handling, printing, and processing features needed for contemporary data transfer and compliance with good-laboratory practice requirements. For safe operation the instrument has an automatic control that de-powers the X-ray tube anytime the sample compartment is opened and optimum X-ray tube operating status is also ensured by an integrated, self-testing scheme that is initiated each time the instrument is started. Although not often a requirement in transformer oil applications, when desired, users can also simultaneously measure sulphur content from weight percent down to part per million levels.

Conclusion

Electrical transformers are removed from service for a whole host of reasons. Primary causes are mechanical or electrical damage, capacity upgrades, and age. For wet (oil-containing) transformers, depending on the transformer size and type of service, the condition of the fluid it contains may not be fully known and may not have been analysed or characterised in any way since being placed in service. In this case, the party having custody of the used transformer oil needs a reliable, fast and easy-to-use screening methodology. This reduces the need to analyse large numbers of materials with more expensive and time consuming testing techniques. Based on the independent ASI test findings and the performance features described, the HORIBA MESA 6000 chlorine analyser readily demonstrates the ability to meet all the fitness-for-use criteria commonly needed when inspection and classification of a large number of transformer oil materials is required.

Fully Automated Determination of TAN/TBN in Oil Samples

Metrohm presents the 864 Robotic Balance Sample Processor, an advanced system for fully automated TAN/TBN determinations in petroleum products. Capabilities include weighing, solvent addition, waiting times for complete dissolution and optimised electrode conditioning procedures between samples, as well as convenient collection of all data in a database. Results are available within minutes and even very low TAN/TBN values can be determined with reproducibilities better than 2%.

ASTM D 664 and ASTM D 2896 describe two methods for the determination of TAN and TBN based on potentiometric titration of the acidic and basic constituents, respectively.

If carried out manually, these procedures are time-consuming and labour-intensive. Further drawbacks are the handling of toxic solvent mixtures and the tedious cleaning of oil-smeared beakers and electrodes. All of this can be avoided with the 864 Robotic Balance Sample Processor, as it allows the complete automation of these procedures from sample preparation all the way to collecting and processing results in a comprehensive database. A unique feature of the system is the patented technique of weighing the sample directly on the rack. There is no simpler way to prepare a sample – just position it on the rack and press START, all other steps are carried out fully automatically. This includes taring of the titration beaker as well as transferring the correct amount of sample. This technique significantly improves the accuracy and reproducibility of results.