Method Development for a Simple and Reliable Determination of PCBs in Mineral Insulating Oil by SPME-GC-ECD

Massimo Santoro,[1] Sergio Guazzotti,[1] Danilo Pierone,[2] Alexandre Souza,[3] Jaqueline Lorena,[3]
[1]Thermo Fisher Scientific, Rodano, Italy; [2]Nova Analitica, San Paulo, Brazil; [3]AES, San Paulo, Brazil

Overview

Purpose: We present a simple, fast, and reliable newly developed and validated method for the determination of Polychlorinated Biphenyls (PCBs) in mineral insulating oil by Solid Phase Micro Extraction and gas chromatography with an electron capture detector (SPME-GC-ECD) using the Thermo Scientific™ TRACE ™ 1300 Series Gas Chromatograph equipped with instant connect ECD.

Methods: The identification of polychlorinated biphenyl compounds is performed on samples of insulating oil, relatively new, after oxidation and after a long period of time to perform a thorough method validation.

Results: The results of the validation study performed for determination of PCBs in the mineral insulating oil employing SPME-GC-ECD give satisfactory results in terms of selectivity, linearity, repeatability, intermediate precision, and recovery.

Introduction

Polychlorinated Biphenyls (PCBs) are synthetic organochlorine compounds used worldwide since 1929, and one of the major uses of PCBs is in insulating oils in electrical transformers and capacitors. In 1966, researchers first detected the presence of PCBs in the environment, and the levels of environmental contamination have been investigated since then because they are considered persistent organic pollutants (POP). Brazil ratified the Kyoto Protocol in 2002, so in 20 years it needs to show a decrease in PCB contamination, and in an additional 10 years must eliminate PCB contamination completely. Only in the state of San Paulo there are at least 200,000 transformers, so the determination of PCB in transformer oil is now mandatory in Brazil. The total PCB concentration now must be below 50 ppm for the oil to be transported or sold.

The Brazilian norm currently adopted uses SPE extraction according to IEC 61619 method. A work group was created in 2010 to develop a new analytical method, with an aim to increase the level of automation and to reduce consumables and glassware usage for sample clean-up, with the ultimate goal of further reducing PCB contamination. Four methods are compared[1–3]: automated SPME, manual SPME, Solid Phase Extraction (SPE) with a Florisil cartridge and SPE with sulfoxide.

FIGURE 1. The TRACE 1310 GC System and the Thermo Scientific™ TriPlus™ RSH Autosampler, with an instant connect module being installed by the user.

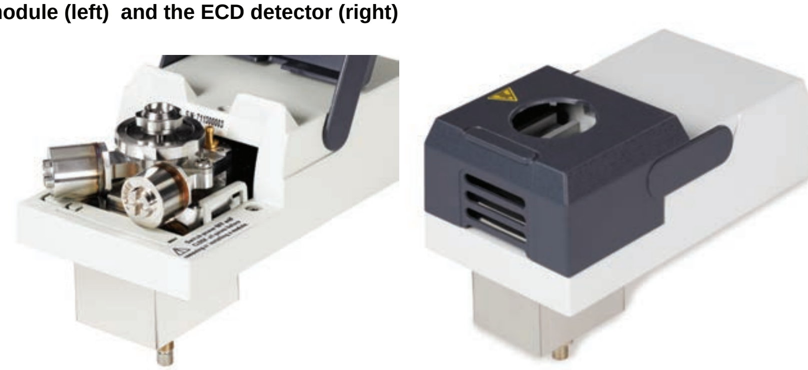
The TriPlus RSH Autosampler Capabilities

This method has been developed with the use of the innovative robotic platform of the TriPlus RSH autosampler, which has the ability to switch automatically and in an unattended fashion from liquid to headspace to SPME mode in the same sequence onto a single GC. It can also use different syringe volumes in the same run during the sample preparation phase, thus enhancing the overall laboratory productivity. Modern laboratories will benefit from this automation in terms of shorter time required for sample preparation, increased results accuracy, and reduced chance for errors.

The Instant Connect Injector and Detector Modules

The instant connect injector and detector modules are a proprietary patent-pending technology adopted on the TRACE 1300 Series Gas Chromatographs. The instant connect modules can be easily swapped with other injectors or detectors by the user to ensure extreme versatility, to accommodate new applications in a matter of a few minutes or simply to cut non-productive maintenance down time to zero. The plug-in concept of the modules allows the user to mount modules and replace them quickly and be readily operative after installation. Any instant connect module, including the ECD detector, includes the injector or detector body, the emitting source, carrier or detector and make-up gas lines, and electronics for temperature and gases control in compact and self-sufficient builds (see Figure 2).

FIGURE 2. Images of an instant connect Split/Splitless (SSL) injector module (left) and the ECD detector (right)



Benefits of Automation for PCB Determination

Appropriate automation can improve process and method consistency while also reducing the results' variability associated with human interaction. Another benefit of using the TriPlus RSH autosampler is the reduced contamination and lab personnel exposure to chemicals while also improving documentation, reporting capabilities, and sample traceability, for example, by using barcodes on the oil sample vials. Finally, the laboratory would reduce all the costs associated with the standards used, the glassware and the disposal of PCB-contaminated materials.

Materials and Methods

Sample Preparation and Separation

All the chromatograms were acquired after exposing the SPME fiber for 2 minutes into 5 mL of the neat oil samples on a TriPlus RSH autosampler mounted on a TRACE 1310 GC equipped with an instant connect SSL injector and instant connect ECD detector.

SPME fiber: PDMS 100 µm – 2 minutes sampling

Column: SGE™ HT8, 10 m × 0.1 mm × 0.1 µm

NIST Standard Reference Materials of Aroclor mixtures 1242, 1254, and 1260 in transformer oil were used.

Oil sample volume: 5 mL

Data Analysis

All the data were acquired via the Thermo Scientific™ Dionex™ Chromeleon™ Chromatography Data System..

Method Validation and Results

Method Selectivity and Accuracy

Transformer oil sample matrix may contain components that interfere with the performance of the method. PCB standards in oil were analyzed before and after a 15 day oxidation process (in an oven at 120˚ C) in order to check the matrix interference with PCB peaks and the effect of the matrix oxidation level. Aroclor 1242, 1254, and 1260 were used to artificially dope the oil samples. As shown in Figure 3, the proposed method is able to determine the total PCB content in new transformer oils, as well as in old, oxidized oils.

FIGURE 3. Total PCB concentration in oil sample before and after sample oxidation for 15 days.

	Before Oxidation (ppm)	After Oxidation (ppm)
Sample A	14.361	15.140
Sample B	14.655	15.225
Sample C	37.97	39.801

Method Linearity

The calibration curves were run with five concentrations levels of total PCBs (1, 15, 50, 75, and 100 ppm), in standard and in oil matrix. Instrumental method linearity is optimal, but a matrix interference is shown when using SPME while not shown when using SPE extraction with Florisil.

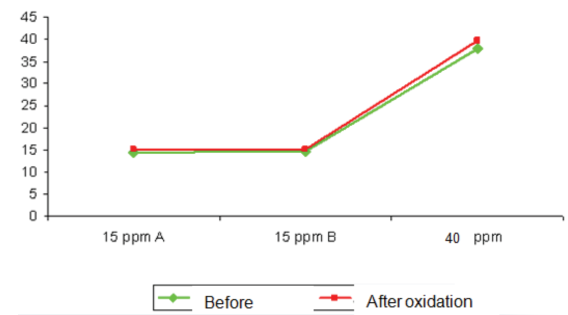
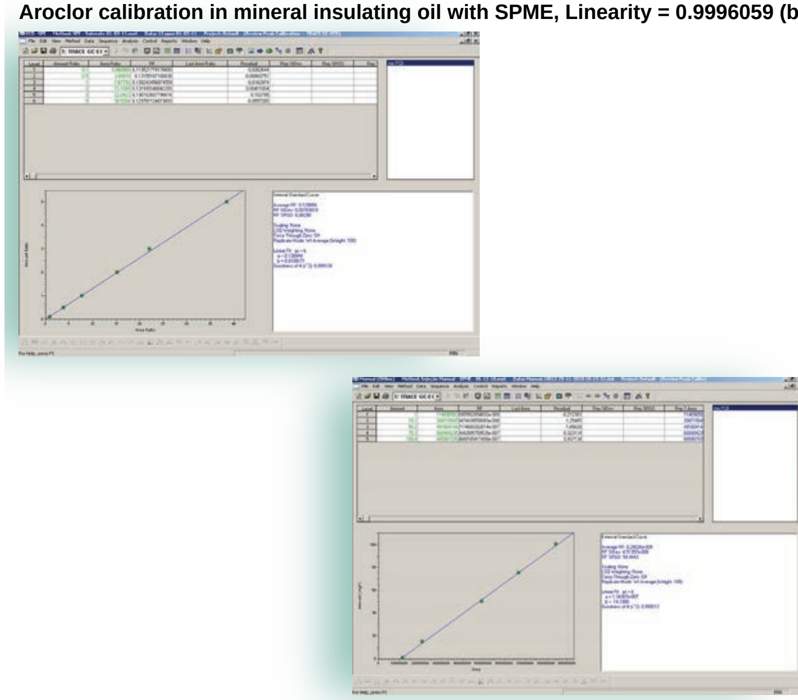


FIGURE 4. Aroclor calibration in isooctane with SPE, Linearity = 0.999653 (top); Aroclor calibration in mineral insulating oil with SPME, Linearity = 0.9996059 (bottom).



Linearity tests were also run on seven consecutive days, using Aroclor in oil matrix, obtaining a “very strong correlation”, according to the INMETRO DOQ-CGCRE-008 (Instituto Nacional de Metrologia, Brazilian Metrology Institute) definition: 0.91< r < 0.99 – very strong correlation. The results are shown in Table 1.

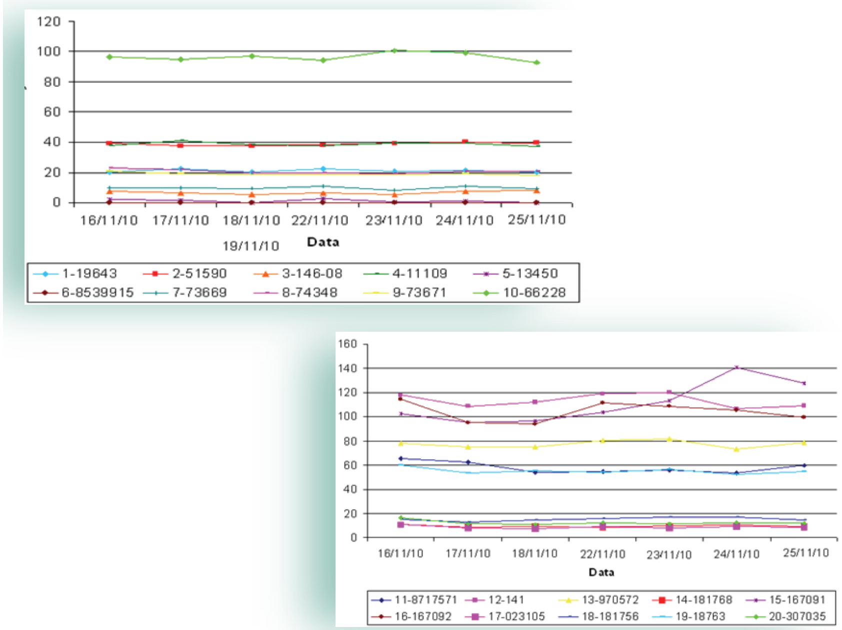
TABLE 1. Linearity results over seven days.

Date	Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7
Linearity (r)	0.998599	0.997997	0.994599	0.999886	0.998702	0.998757	0.998562

Method Intermediate Precision

Twenty-nine oil samples and two standards (at 1 and 50 ppm) were tested on different days to evaluate the intermediate method precision. Concentration of total PCBs < 1 ppm are considered “0”. Samples with concentrations > 100 ppm should be diluted before running them. The results are shown in Figure 5.

FIGURE 5. Total PCB concentration tested over 7 consecutive days on 30 oil samples at various PCB concentrations and two standards. Excellent precision was obtained.



Method Recovery

Recovery was first estimated spiking PCB-free samples with standards. Then, five oil samples were contaminated with standards in a ratio of 1:1 and homogenized for two days before the analysis. As shown in Table 2, the results obtained give 78.23 to 100.59% recovery of the standard samples.

TABLE 2. Method recovery results on standards and spiked oil samples.

Sample	Sample Concentration	Standard added	Theoretical Concentration [sample/2 + Std/2]	Measured Concentration	Recovery %
Spiked blank oil			50 ppm	51.023	
Spiked blank oil			75 ppm	67.231	
Spiked blank oil			100 ppm	99.4	
4-11109	17.7915	100 ppm	58.59575	56.673	78.23
8-74348	11.116	50 ppm	31.0695	33.799	88.91
14-181768	2.6585	100 ppm	51.02925	50.401	96.06
20-307035	5.9765	50 ppm	28.49975	29.663	92.85
26-TR12	3.327	75 ppm	35.279	37.141	100.59

PCB Extraction Methods Comparison

Experiments with PCBs in oxidized oils at 15 ppm and 50 ppm were done to compare four different extraction procedures: Automated SPME, manual SPME, SPE with Florisil cartridge and Sulfoxide SPE for PCB. As can be seen in Figure 6, SPME and Sulfoxide provide much higher accuracy then SPE with Florisil. SPME can be completely automated and allows scaling-down volumes.

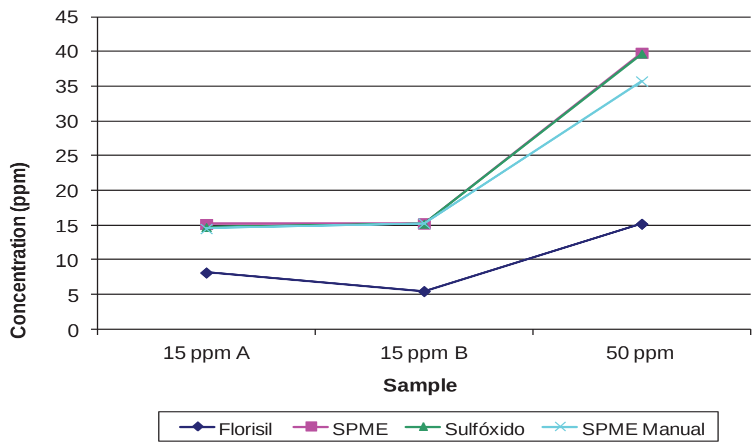


FIGURE 6. Extraction Method Comparison for PCB in transformer oil.

Conclusion

The validation study performed for determination of PCBs in the mineral insulating oil employing SPME-GC-ECD and according Guide INMETRO DOQ-CGCRE-008[4] gives satisfactory results in terms of selectivity, linearity, repeatability, intermediate precision, and recovery. Limits of quantification obtained of 1 mg/kg are well below the values controlled by the Brazilian normative 12288:2006 for disposal of electrical equipment (maximum allowable limit for mineral insulating oil 50 mg/kg). The automated SPME approach adopted provides reliable and rapid determinations of PCBs in the samples. It offers the advantages of:

- Being faster than conventional extraction techniques
- Eliminating manual sample preparation and many associated variables
- Providing a positive impact on the environmental aspects of the analysis without using solvents or chemicals and using only reduced amounts of standards and oil samples, eliminating the generation of wast3

References

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