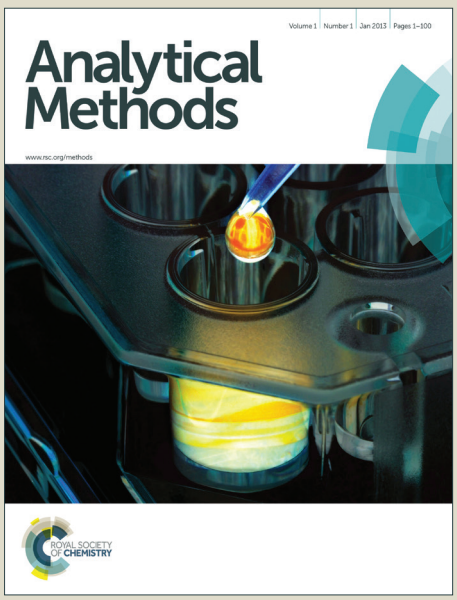
Analytical Methods

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/methods

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Characterization of Selected Oxidation Inhibitors in Transformer Oils by Multidimensional Gas Chromatography with Capillary Flow Technology

Taylor Hayward[a], Ronda Gras[a], Jim Luong[a]

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

Oxidation inhibitors such as 2,6-ditertiary-butyl para-cresol (DBPC, also known as butylated hydroxytoluene) and 2,6-ditertiary-butyl phenol (DBP) are used in transformer oils to prevent radical auto-oxidation of hydrocarbon species in the oil, prolonging the transformer's life. Routine monitoring of these compounds is recommended as a diagnostic tool for measuring the health of the transformer. Typically these compounds are analyzed by spectroscopic methods or gas chromatography with extensive sample preparation steps. A multidimensional gas chromatographic method using a Capillary Flow Technology (CFT) planar microfluidic device and a Deans switch is demonstrated to analyze these compounds in the oil matrix. The two oxidation inhibitors are separated from the matrix on the analytical column and can be easily identified and distinguished from each other. Practical limits of detection were established at 25 ppm (w/w) of each inhibitor, which are well below warning and action limits of these compounds. These compounds produced a linear calibration over the concentration range found in transformer oil. Relative standard deviations of area from each compound were determined to be below 1.5% at the 95% confidence level (*n=10*).

Introduction

Electrical rectifiers are essential to an industrial plant, which is provided through the use of transformers. Monitoring the oil of a transformer can provide indications to the health and condition of this device, and when done routinely can increase longevity and effectiveness of the transformer. Failure of a transformer can be catastrophic to an industrial plant, resulting in production and revenue losses[1].

One way transformers fail is from oxidation and polymerization of hydrocarbon components that comprise the oil, ultimately leading to loss of its function. In order to prevent this from occurring, oxidation inhibitors such as 2,6-ditertiary-butyl para-cresol (DBPC, also known as butylated hydroxytoluene) and 2,6-ditertiary-butyl phenol (DBP) are added to the oil prior to use. These compounds are designed to suppress the auto-oxidation process by terminating chain reactions. Characteristics of these compounds include very sterically hindered molecules that are resonance stabilized[2-4].

In transformer oils, the optimal concentration of DBP and/or DBPC is 0.3% by weight. Unacceptable levels for these compounds are below 0.1% by weight. This means that below 0.1%, the transformer oil is subject to undergo oxidation, aging the oil significantly. Initially the transformer oil is composed of straight chain and branched alkanes ranging from decane to tetracontane. As oxidation occurs, the oil matrix becomes more complex with multiple bonds and oxygenated functional groups, which could cause potential interferences in testing. The institute of Electrical and Electronics Engineers (IEEE) recommends an actionable limit of 0.2% to be set to signify the addition of more inhibitor[1].

In order to monitor these species, the American Society for Testing Materials (ASTM) sanctioned two separate tests, either of which can be implemented, but are instrumentally very different. For example, these methods use either infrared (IR) spectroscopy (ASTM 2668)[5] or gas chromatography (GC) with prior sample extraction and pre-treatment (ASTM 4768)[6]. Both methods are acceptable to meeting the figures of merit set by IEEE standards; however, spectroscopy measurements can be subject to false positives due to interfering species that mask the selected wavelengths. Furthermore, this method does not distinguish between the two compounds. Gas chromatography as a technique can be employed to individually identify and quantitate the components of interest; however, due to the complex and interfering matrix from the transformer oil, a sample pre-treatment and extraction of the oxidation inhibitors is necessary. According to the ASTM procedure, extraction efficiencies are between 60-70% for DBP and DBPC. This adds extra variability resulting in poor precision. The method states that the results should not differ by 30% from the same sample run by two different operators on the same equipment[6].

Here, an alternative method for the analysis of DBP and DBPC in transformer oils is proposed by using multidimensional gas chromatography (MDGC) with a Deans switch. In this setup, the oil will be isolated in the first column and the second column will be used to separate the oxidation inhibitors from interferants. Additionally, a backflush can be applied to further preserve the first column by eluting the higher molecular weight species out the split vent of the GC's inlet.

Experimental

Chromatographic Conditions

An Agilent 6890 (Agilent Technologies, Wilmington, Delaware, USA) equipped with two split/splitless inlets, two flame ionization detectors (FID), an Agilent 7683 autosampler and tray, and an auxiliary pressure control module were used. To perform the Deans switching, a capillary flow technology (CFT) plate with 5 ports was used along with a 24V 5W DC switching valve (Agilent G2399-60610) and support kit (Agilent G-2399-67610).

A schematic diagram of the column configuration is shown in figure 1. Column 1 is a 14 m x 0.250 mm i.d. x 0.10 µm film thickness DB-1HT (Agilent), column 2 is a 30 m x 0.320 mm i.d. x 0.25 µm film thickness VF-WAXms (Agilent), and the restrictor is a 1.45 m x 0.150 mm i.d. deactivated fused silica (Agilent) tube. High purity helium (Air Liquide, Edmonton, AB, Canada) is used as the carrier gas and set at pressures of 13.5 psi and 10.1 psi for columns 1 and 2, respectively and operated at a ramped flow. The flow is negatively ramped after 12.5 minutes in the first column from 2.5 mL/min to 0.2 mL/min at a rate of 100 mL/min and positively ramped in the second dimension from 2.1 mL/min to 5.0 mL/min at a rate of 100 mL/min. This ramped flow enables the backflush mode, where the higher molecular weight components of the oil elute out the split vent.

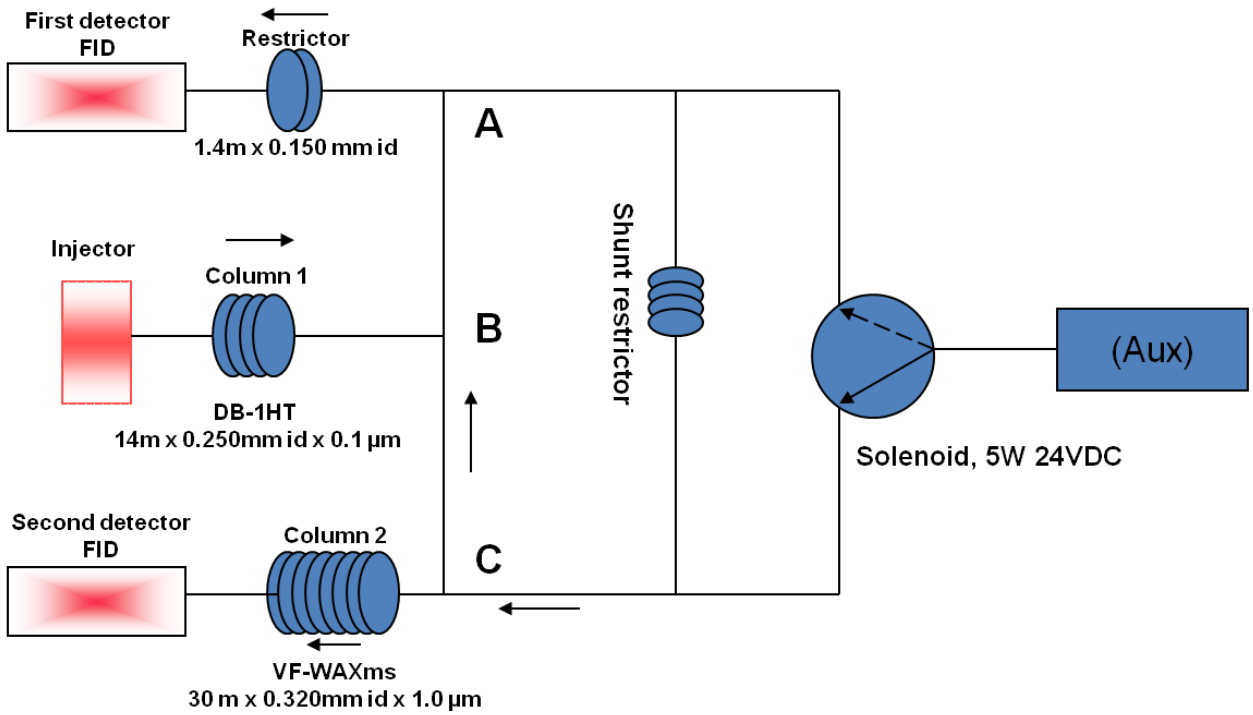


Figure 1: Schematic diagram of MDGC configuration.

The pressures delivered to both columns were set at the initial starting temperature program of 50°C. A temperature program of 50°C held for 2 minutes, then to 230°C at a rate of 20°C/min and held at 230°C for 4 minutes. The inlet temperature was maintained at 250°C and operated in split mode with a split ratio of 15:1. Both FIDs were operated at 250°C and use hydrogen, air, and nitrogen (Air Liquide) as flame gases at flow rates of 30 mL/min, 350 mL/min, and 30 mL/min, respectively.

Sample Preparation

DBP and DBPC were purchased from Sigma-Aldrich (99%, Oakville, ON, Canada). Transformer oils were obtained from transformers at Dow Chemical, Fort Saskatchewan Site. Cyclohexane (Fisher Scientific, Edmonton, Canada) was used as a solvent for sample and standard preparation.

Transformer oil samples were diluted by a factor of twenty in cyclohexane. This was achieved by weighing 0.5g of oil and adding 10g of cyclohexane. A portion of this diluted transformer oil was then analyzed by the MDGC instrument.

Results and Discussion

Analysis of oxidation inhibitors in transformer oil using a conventional column, such as polydimethylsiloxane, displays co-elutions and interference between the components of oil and the target analytes as demonstrated in figure 2. A multidimensional gas chromatographic (MDGC) analysis approach was initiated to selectively target these analytes. MDGC has key advantages that can be utilized for successful separation of the oxidation inhibitors. First, MDGC improves overall system selectivity and peak capacity by using two columns of varying selectivities. Chromatographic system integrity is also improved by isolating unwanted matrix in the first dimension column as well as being able to backflush unwanted sample out to vent[7-10]. Recently, similar phenolic compounds were investigated in fuels using an MDGC approach, which included a high phase ratio non-polar column as the first dimension and a polar column as the second, analytical column[11].

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

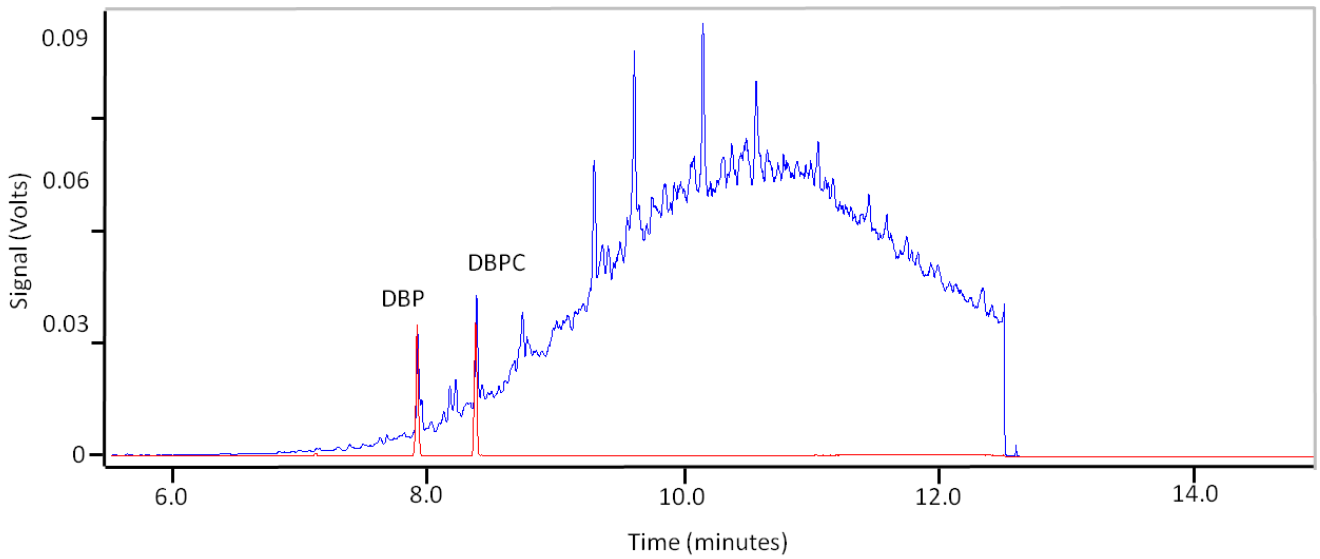


Figure 2: Overlay of the elution of transformer oil spiked with 100 ppm (w/w) oxidation inhibitors (blue) on column 1 and oxidation inhibitors in cyclohexane (red).

Stemming from this work, a first dimension, non-polar column was chosen. Additionally, this column contained a high phase ratio (β = 625) to quickly elute the oxidation inhibitors and not permanently retain the larger molecular weight components of the transformer oil. The second, analytical column used was a polyethylene glycol (wax) column, which was able to separate the two oxidation inhibitors of interest from each other as well as the matrix. The matrix is primarily non-polar hydrocarbons and will quickly elute off the wax column, while the oxidation inhibitors are more retained. A chromatogram of blank oil is displayed in figure 3, which is overlaid with a chromatogram of the inhibitors in cyclohexane. The majority of the cut displays the non-polar portion of the matrix, which is only slightly retained in the second dimension column. However, there are also low levels of compounds with similar retention indicies to the analytes of interest; therefore the baseline shows a response which may overlap with the oxidation inhibitor response. It can also be seen from this that, the responses of these inhibitors in the second dimension are clearly defined, especially when comparing these peaks to those in a single dimension analysis.

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

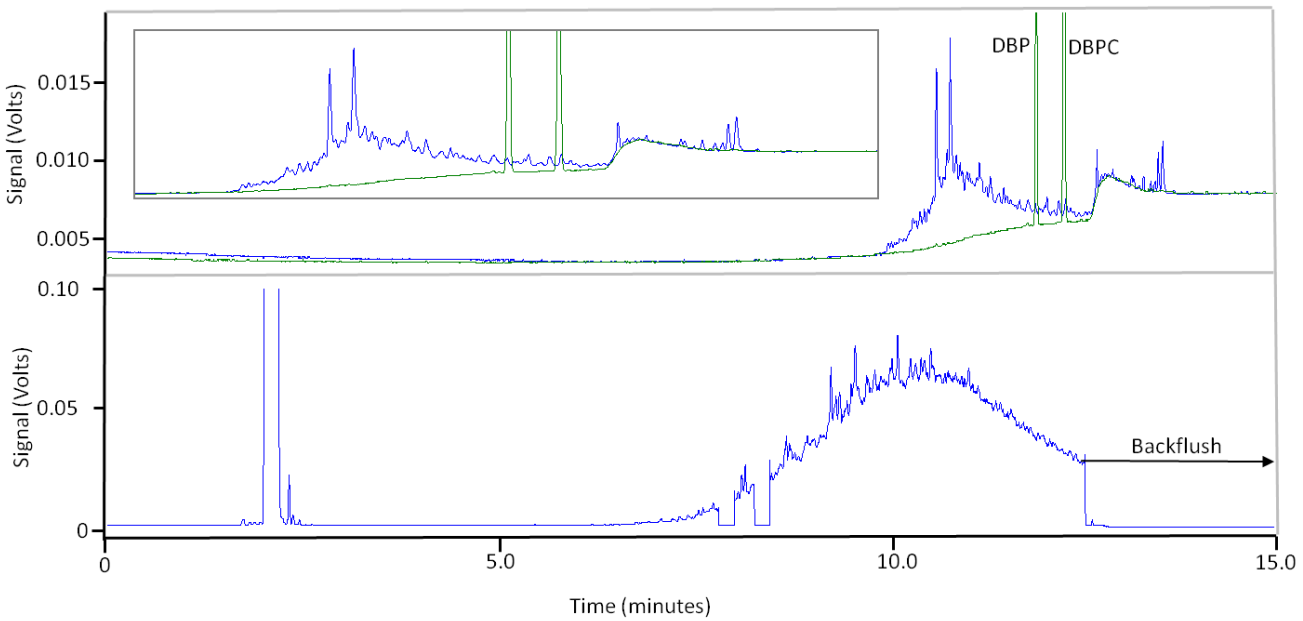


Figure 3: Chromatogram of blank oil containing no inhibitors (blue trace) overlaid with oxidation inhibitors in cyclohexane (green trace). The first dimension chromatogram is shown on bottom while the top displays the second dimension chromatogram after heart-cutting. Insert: Magnified view of second dimension.

The selectivity gained from the second column allows for these two inhibitors to be distinguished from one another, unlike the case in analysis by IR spectroscopy. Furthermore, the columns' differing selectivities reduce the potential for false positive identification and peak masking as the bulk of the oil sample remains on the first dimension column while only a fraction enters the second dimension. The polar nature of the second column aids in quickly eluting the potentially interfering oil portion and retaining the analytes of interest.

A backflush mode was employed after elution of the oxidation inhibitors. A time of greater than two times the holdup time was used for backflushing, which exceeds the recommended length of time required for complete removal of injected species[10]. This longer time period was chosen as the molecular weight range may change between transformer oils; therefore this time should be acceptable to all transformer oils tested. Subsequent thermal blank analyses each after three different transformer oils show no eluting peaks, meaning the backflush was complete in the previous run.

The backflush capability helps to reduce the need for sample preparation steps prior to analysis. When analyzed by conventional means, the hydrocarbon components in the transformer oil are largely removed by extraction prior to the GC analysis. By utilizing the benefits of the 5-port CFT plate, the extraction steps are eliminated resulting in faster analysis time and more through-put with the benefit of increase accuracy of analysis.

Analytical figures of merit for this MDGC method are comparable or better than those described in the ASTM methods. A practical detection limit was set to 25 ppm (w/w) of each inhibitor in the diluted oil sample. Figure 4 shows a spiked used oil sample present at this level, and as seen in the chromatogram, the analytes of interest shows high signal to noise ratios (25:1). This conservative detection limit was determined as it minimizes the effects of oil interference that can vary widely through different oils and degrees of use. Additionally this detection limit meets the requirements for the actionable levels set by the IEEE. Calibration produces linearity with a correlation coefficient greater than 0.999 over a range from 25 ppm (w/w) to 5000 ppm (w/w). This range encompasses all that which would be found in used and unused transformer oil.

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

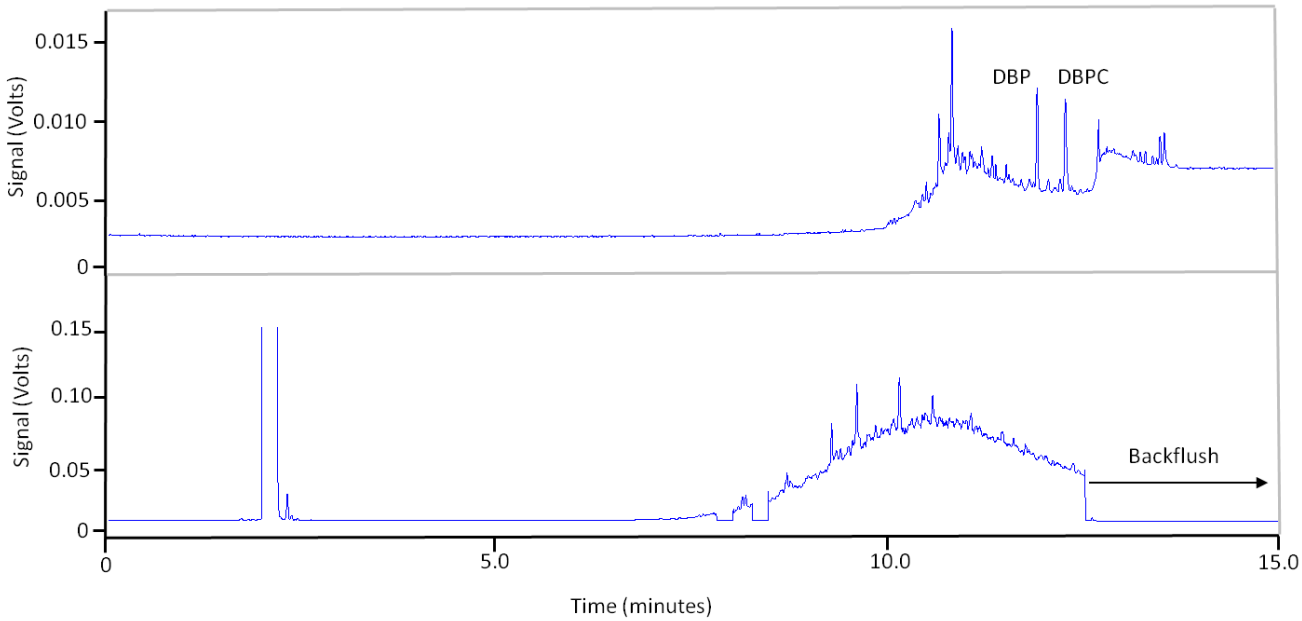


Figure 4: Chromatogram of 25 ppm (w/w) oxidation inhibitors spiked into uninhibited transformer oil.

As previously mentioned ASTM 4678, analysis by GC, produces poor intra-day and inter-day precision, which can be attributed largely to the extraction step; therefore by eliminating this step overall system precision can be improved. This was evaluated at two different levels (100 ppm w/w and 1000 ppm w/w), resulting in excellent reproducibility with relative standard deviations (RSD) of less than 1.5% with respect to peak area, as displayed in table 1. Furthermore, the method was evaluated over 4 days, which showed no significant deviations in terms of response. Additionally, retention time precision was observed to have %RSD of less than 0.05% at the 95% confidence levels for both analytes tested. Accuracy was measured by spiking an oil sample at various levels, resulting in excellent recoveries averaging 100% and 102% across the linear range tested. This data represents consistent day to day operation of the system displaying the robustness of the method, which is a significant improvement over conventional GC analysis with extraction.

Conclusions

A new method utilized multidimensional gas chromatography for the separation and quantitation of DBP and DBPC has been successfully developed and implemented. A backflush mode was employed to maintain system cleanliness by eluting larger molecular weight components via the split vent line. Limits of detection were determined to be 25 ppm (w/w) for each compound in the transformer oil. The response is linear over the range of encountered in transformer oils.

Table 1: Retention time and area data for DBP and DBPC at 100ppm (w/w) and 1000ppm (w/w) on 10 consecutive injections on 4 consecutive days.

	DBP				***DBPC***			
	100 ppm (w/w)		1000 ppm (w/w)		100 ppm (w/w)		1000 ppm (w/w)	
	Retention Time (min)	Area	Retention Time (min)	Area	Retention Time (min)	Area	Retention Time (min)	Area
Day 1 (*n=10*)	11.892	30899	11.892	309052	12.251	30404	12.250	304673
Day 2 (*n=10*)	11.887	32071	11.893	309625	12.246	31676	12.250	311435
Day 3 (*n=10*)	11.888	33591	11.893	321152	12.247	33105	12.252	315976
Day 4 (*n=10*)	11.888	33301	11.891	313781	12.246	32602	12.249	307634
Average	11.889	32466	11.892	313403	12.247	31947	12.251	309930
%RSD	0.020	3.39	0.011	1.65	0.022	3.31	0.014	1.67
At 95% confidence	0.044	7.58	0.023	3.70	0.050	7.41	0.032	3.75

Acknowledgements

The authors like to thank those involved with the transformer oil analysis program at the Fort Saskatchewan site of Dow Chemical Canada. This includes Vicki Carter, Maria Hicks, Richard Brausen, Dawn Brown, and Andy Szigety from the Analytical Team and Dan Thompson, Rene Santiago, Frank Jansen, Neil Tune, Lenny Karakushan, Mathew Grande, and Terry Keizer from the Electrical Team. Further thanks go to Martine Stolk, Director of the Analytical Technology Center for support of this program.

Notes and references

[a] Dow Chemical Canada ULC. P.O. Bag 16, Highway 15, Fort Saskatchewan, AB, Canada, T8L 2P4.

1. M. Horning, J.Kelly, S. Myers, R. Steddins, *Transformer Maintenance Guide*, S.D. Myers, Inc., USA, 3rd ed., 2004.
2. S. Ege, *Organic Chemistry: Structure and Reactivity, Cengage Learning*, Lexington, ME, USA, 3rd ed., 1994.
3. S. Zabarnick, Energ. *Fuel*., 1998, **12**, 547.
4. S. Zabarnick, *Ind. Eng. Chem. Res.*, 1993, **32**, 1012.
5. ASTM 2668-07, *Annual Book of ASTM Standards, Petroleum Products, Lubricants, and Fossil Fuels*, ASTM, Harbour Drive, West Conshohocken, PA 19428, USA, 2000.
6. ASTM 4768-11, *Annual Book of ASTM Standards, Petroleum Products, Lubricants, and Fossil Fuels*, ASTM, Harbour Drive, West Conshohocken, PA 19428, USA, 2000.
7. G. Schomburg, *J. Chromatogr. A*., 1995, **703**, 309.
8. W. Bertsch, *J. High Resolut. Chromatogr.*, 1999, **22**, 647.
9. P.Q. Tranchida, D. Sciarrone, P. Dugo, L. Mondello, *Anal. Chim. Acta*, 2012, **716**, 66.
10. M. Klee, *J. Sep. Sci.*, 2009, **32**, 88.
11. J. Luong, R. Gras, H.J. Cortes, R.A. Shellie, *J. Sep. Sci.*, 2013, **36**, 2738.

