AperTO - Archivio Istituzionale Open Access dell'Università di Torino

GC Methods for the Determination of Methanol and Ethanol in Insulating Mineral Oils as Markers of Cellulose Degradation in Power Transformers

This is the author's manuscript

Original Citation:

Availability:

This version is available <http://hdl.handle.net/2318/150145> since 2017-05-17T14:02:45Z

Published version:

DOI:10.1007/s10337-014-2650-8

Terms of use:

Open Access

Anyone can freely access the full text of works made available as "Open Access". Works made available under a Creative Commons license can be used according to the terms and conditions of said license. Use of all other works requires consent of the right holder (author or publisher) if not exempted from copyright protection by the applicable law.

(Article begins on next page)

UNIVERSITÀ DEGLI STUDI DI TORINO

This is an author version of the contribution published on:

Questa è la versione dell'autore dell'opera:

**GC Methods for the Determination of Methanol and Ethanol in Insulating Mineral Oils as
Markers of Cellulose Degradation in Power Transformers**

Maria Concetta Bruzzoniti*, Riccardo Maina, Rosa Maria De Carlo, Corrado Sarzanini, Vander
Tumiatti

Volume 77, Issue 15-16, Springer, pp 1081-1089

The definitive version is available at:

La versione definitiva è disponibile alla URL:

<http://link.springer.com/article/10.1007/s10337-014-2650-8>

GC Methods for the Determination of Methanol and Ethanol in Insulating Mineral Oils as Markers of Cellulose Degradation in Power Transformers

Maria Concetta Bruzzoniti^{*1}, Riccardo Maina², Rosa Maria De Carlo¹, Corrado Sarzanini¹, Vander Tumiatti²

¹University of Torino, Department of Chemistry, via P. Giuria 5, 10125 Torino (Italy)

²Sea Marconi Technologies, Via Ungheria 20, 10090, Collegno, Torino (Italy)

Corresponding Author():*

Maria Concetta Bruzzoniti

University of Torino

Department of Chemistry

via P. Giuria, 5, 10125 Torino (Italy)

Phone: +390116705277

Fax: +390116705242

Abstract

Methanol and ethanol in transformer oils have been recently proposed as new markers of thermal and mechanical degradation of cellulose (the solid insulation in power transformer). In this work, we optimized and compared the performance of two head-space gas chromatographic methods based on flame ionization (HS-GC-FID) and mass spectrometry detection (HS-GC-MS) to determine methanol and ethanol in insulating mineral oil.

For methanol and ethanol, the detection limits were $12 \mu\text{g kg}^{-1}$ and $27 \mu\text{g kg}^{-1}$ (HS-GC-FID) and $1.3 \mu\text{g kg}^{-1}$ and $3.1 \mu\text{g kg}^{-1}$ (HS-GC-MS). Repeatability was evaluated in transformer oils for both the methods at different concentration levels of analytes and was included within 1.8% and 16%. The accuracy of the methods was assessed under a proficiency test (Cigré JWG A2/D1.46).

The methods were compared by a *F*-test and a one-sided paired *t*-test performed on twenty-one transformer oils in service. Correlations of methanol and ethanol content in sampled oils against their actual time of service are provided. For each sample, the content of traditional markers (furan-2-carbaldehyde and CO_2) was also measured, finding a correlation between light alcohols and CO_2 content. This indicates that methanol and ethanol determination may be helpful in providing further information on the thermal degradation conditions of transformers' solid insulation.

The method developed is currently routinely applied by the laboratories of Sea Marconi Technologies for the assessment of transformers' conditions.

Keywords: Gas chromatography; oil analysis; methanol; ethanol; paper degradation

Introduction

Power transformers' condition assessment requires the estimation of the degradation of the electric insulation (Kraft paper and oil) [1]. Solid insulation degradation is related to its thermal ageing and the related loss of mechanical properties, that can be estimated by measuring the paper's degree of polymerization (DP). Due to the difficulty of collecting solid insulation (paper) samples, indirect estimations of paper thermal degradation are required, concerning chemical markers which are usually by-products arising from ageing of oil-impregnated paper insulation. Carbon dioxide and monoxide [2] were firstly proposed as indicators of ageing and thermal decomposition of cellulose but their applicability resulted limited since, in the time, these compounds could also be originated by the oxidative decomposition of oil. The detection of a family of furanic compounds, in particular the furan-2-carbaldehyde (2-FAL), was later proposed [3]. Although literature underlined some drawbacks in this approach, furan compounds and 2-FAL determination through high-performance liquid chromatography (HPLC) [4] remains the current reference for the analytical approach to identify cellulose ageing for which standard methods are available (IEC 61198, ASTM D5837).

Methanol and ethanol have been recently proposed [5] as new markers of ageing of oil-impregnated paper insulation in power transformers. In fact, the existence of a direct correlation between methanol production and the number of 1-4- β -glycosidic bonds broken in cellulose is remarked, which directly correlates the presence of methanol in oil to paper degradation.

Regarding methanol and ethanol analytical determination in oil matrices, current studies are hardly exhaustive. A gas chromatographic method for the determination of methanol in vegetable oil methyl esters used as diesel fuel (biodiesel) is one of the first studies reported, which nevertheless requires a complex sample dissolution in dimethylformamide and silylation with bis-trimethylsilyltrifluoroacetamide (BSTFA) [6]. An exhaustive review focusing on methods for the determination on methanol in biodiesel is available [7]. More recently, the correlation between flash points and the residual alcohol content was exploited to obtain methanol and ethanol concentration in biodiesels [8]. A standard methodology [9] that uses two-dimensional HS-GC with a flame ionization detector (FID) is so far the official procedure available for the determination of methanol in crude oil at mg/kg levels, after sample dilution with toluene. Solid-phase micro-extraction (SPME)-GC-FID was recently proposed for methanol determination in the same matrix [10], but the relatively high LOD and LOQ levels (3.9 ppm and 12.9 ppm, respectively) clearly hamper method application.

Very recently, an analytic method based on a static head space sampler coupled with a gas chromatograph equipped with a mass spectrometer has been proposed for methanol and ethanol quantification [11] at low limits of detection (about 4.0 μ g/kg for both methanol and ethanol).

Industries are currently interested in applying simple, sensitive and reliable approaches by low cost instrumentations to evaluate methanol and ethanol content in transformer insulating oils as indicators of cellulose degradation.

In this study we optimized a headspace gas chromatography method, comparing the performance of mass spectrometry and flame ionization detection, for the determination of methanol and ethanol in transformer insulating oils. Both the methods developed allow reliable identification of methanol and ethanol at concentration levels lower than existing approaches. Despite the slightly better detection limits achieved by HS-GC-MS, the HS-GC-FID method is characterized by less expensive instrumentation representing an appealing tool for laboratories in charge of solid insulation degradation surveillance of power transformers.

A tentative correlation between methanol and ethanol content with that of the traditional markers (CO₂ and 2-FAL) on oils taken from transformers with different age of service was also derived. This correlation shows its suitability to obtain additional information about the conditions of solid insulation and the related transformer's consumed thermal life.

Experimental

Instrumentation

A 6890 gas chromatograph (Agilent Technologies, PA, USA) equipped with a Head Space Gerstel MPS autosampler (Mülheim an der Ruhr, Germany) and a flame ionization detector (FID) or a 5973 Network mass spectrometer (MS) (Agilent Technologies, California, USA) were used.

The chromatography separation was performed on two capillary columns: a 30 m x 320 µm, 0.25 µm *d_f* 5% phenylmethylsiloxane (Ultra 2; Agilent, J&W) and a 30 m x 320 µm, 1.8 µm *d_f* 6% cyanopropylphenyl, 94% dimethyl polysiloxane, Rxi-624 Sil Ms (Restek, Bellefonte, PA, USA), instrumental conditions are given in the text.

For FID detection, the following conditions were adopted: 250 °C, H₂ 40 mL/min, air 450 mL/min, make-up gas He 45 mL/min.

The mass spectrometer interface was maintained at the maximum temperature of the column oven; mass range 20-100 *m/z* was scanned in total ion current count (TIC) at a rate of 14,04 scan/s. For single ion monitoring mass detection (SIM), the values 31 *m/z* [H₂C=OH]⁺, specific for methanol and ethanol fragmentation, and 33 *m/z* [D₂C=OH]⁺ specific to deuterated internal standard (ethanol-d₆) were selected. Ionization energy was 70 eV in the electron ionization mode.

For CO₂ analysis, a GC Agilent 6890 Network equipped with HS Autosampler Agilent G 1888 and injection loop 100 µL (on-column) was used with two columns system: J & W Plot Q 0.53 mm *i.d.*

30 m, 40 μ m thickness and J & W Molsieve 80-100 mesh, 5 Å, 0.53 mm *i.d.* 30 m, 50 μ m thickness. The column oven program temperature was: 6 min at 40 °C, 15°/min up to 150 °C and 150 °C for 4 min. Detection was made by a TCD detector, 250°C negative polarity coupled with a Ni-based methanizer working at 350°C, with Ar gas carrier (8 mL/min) or a FID detector (250 °C, H₂ 70 mL/min, air 450 mL/min, make-up gas Ar 6 mL/min). The analysis were performed according to the International Standard IEC 60567 [12].

The analysis of furan-2-carbaldehyde(2-FAL) was performed according to the International Standard IEC 61198 [13]. A 1100 HPLC (Agilent Technologies, PA, USA) equipped with a 4-channel pump diode-array detector was used (λ = 275 nm). The separation was performed using a Phenomenex 5 μ m, 250 x 4.0 mm end-capped C18 column (4.0 mm x 250 mm) preceded by a C18 precolumn (Phenomenex, Torrance, CA) and a gradient elution (H₂O-CH₃OH, 60-40 to 0-100% v/v) at flow rate 1.0 mL/min.

Chemicals

Extra dry 99.9% methanol and ethanol (Panreac Quimica, Barcelona, Spain), ethanol-d₆ 99.5% (Sigma-Aldrich, St Louis, USA), furan-2-carbaldehyde(2-FAL) 99% (ACROS Organics, UK), CO₂ 99.99% (Messer, TO, Italy) or CO₂ 1.000 % (v/v) in synthetic air mixture (Rivoira, TO, Italy) were used in the experiments.

Oil Samples Unused Hyvolt II oil (Ergon, Mississippi, USA) was used for method optimization. For the evaluation of HS-GC-FID and HS-GC-MS performance, as well as for correlation of markers with the transformers' years of service, twenty-one transformer oils of different provenience and of different years of first energization were sampled (see text).

Standard Solutions Preparation

In order to avoid losses of methanol and ethanol, mother solutions of the analytes were prepared by using a 50 mL gas-tight syringe containing unused degassed Hyvolt II oil avoiding the contact with the air. In order to homogenise the matrix, the syringe was properly mixed by a rotating device in the presence of glass beads. Dilution of mother solutions of ethanol and methanol was directly performed in the head-space vial containing 7.0 g of Hyvolt II oil. Vials were crimped with a Revolving Table [12] in order to minimize the loss of volatile species. Standard solutions in the range 36.0 – 3500 μ g/Kg were prepared for calibration curve in FID detection. For MS quantification the standard addition technique was used and an ethanol-d₆ mother solution (196.76 mg/Kg) was added to blanks, calibration standards and all the samples, to achieve a final

concentrations of 500 $\mu\text{g/Kg}$; the calibration curve covered the range 3.9 – 2500 $\mu\text{g/Kg}$. CO_2 standards (500 – 20000 nL/mL) were prepared by dissolution of the mother mixture in degassed oil. For furan-2-carbaldehyde, standard solutions (0.05 – 10 ppm, w/w) were obtained by dilution using the same syringe apparatus employed for methanol and ethanol standard solution preparation.

Results and discussion

Methods Optimization

To achieve the best overall performance of the analysis, a preliminary optimization using the GC-FID system was done considering both extraction and injection procedures. Separation was performed on the capillary column filled with 5% phenylmethylsiloxane.

The split ratio was initially optimized considering the following values: 50/1, 35/1, 20/1 and 5/1. As shown (Fig. 1), the reduction of the ratio results on higher peak areas, good resolution and lower retention times, so the value 5/1 was selected for further optimization.

Increasing injection volumes, 500 – 1000 μL , showed an increased sensitivity but, considering that the GC-system is equipped with a 1000 μL liner, to avoid saturation phenomena, a 500 μL injection volume was used in respect to an acceptable decrease in sensitivity.

The effect of the temperature on the head space extraction was also investigated over the range of 80-100 $^{\circ}\text{C}$. Since peak area increases with the temperature, but also co-extraction effects are enhanced over 100 $^{\circ}\text{C}$, a working temperature of 90 $^{\circ}\text{C}$ was chosen.

Finally, the performance of a column at higher polarity, Rxi-624 Sil Ms (Restek), was also investigated. Retention times resulted improved, respectively from 3.28 to 4.32 min for methanol and from 3.44 to 5.75 min for ethanol, and higher resolution was reached resulting on a separation more suitable for real samples analysis as shown in Figure 2. Table 1 shows the experimental parameters used after optimization.

For the MS detection, the optimization principally concerned the eluent flow rate, since the main problem was to reach a good separation of the analytes from the atmospheric gases. Analysis using multiple standards at 5 mg/Kg concentration were performed at flow rates values of 0.2, 0.3, 0.4, 0.5, 0.7 and 1.2 mL/min . Since 1.2 mL/min flow rate allowed us to achieve good separation and duration of analysis, this value was chosen for the next experiments.

Analytical Performance

Limits of detection (LOD) and limits of quantification (LOQ) were evaluated analysing 7 replicates samples of a transformer oil with analytes at a concentration near the expected limits. According to the EPA definition [14,15] LOD was evaluated as the standard deviation of the mean analyte

concentration multiplied by the Student's t value (99% confidence level) and LOQ as 10-fold the standard deviation. Table 2 shows the LOD and LOQ values and the linearity range obtained for methanol and ethanol respectively by HS-GC-FID and HS-GC-MS techniques. It is possible to note that the limits achieved by HS-GC-FID (12.1 $\mu\text{g/kg}$ for methanol and 26.8 $\mu\text{g/kg}$ for ethanol) are greatly improved in respect to recently developed GC-FID methods [9,10] which are set at mg/kg levels. For methanol determination, the HS-GC-MS approach here presented provides appreciable lower detection limit (1.3 $\mu\text{g/kg}$) than the MS based method recently presented [11] which allows to achieve LOD of 4.0 $\mu\text{g/kg}$, whereas detection limit achieved for ethanol (3.1 $\mu\text{g/kg}$) is comparable [11].

Repeatability of the methods was also evaluated by analysing six oils, sampled from in-service transformers, characterized by analyte concentrations inside or near the calibration range. The data obtained ($n=20$ for each sample) were verified by Grubbs's test and as shown in Table 3, we can see that a good repeatability is obtained. In fact for methanol determination by HS-GC-FID, % RSD ranges from 2.6% and 4.6% for concentrations included within 79 and 1985 $\mu\text{g/kg}$. For ethanol determination, HS-GC-FID provides % RSD of 3.6% (ethanol concentration 476 $\mu\text{g/kg}$). RSD values below 3% were obtained for both the analytes (concentration range included between 461 and 2196 $\mu\text{g/kg}$) by HS-GC-MS. Only for analyte concentrations near or below the LOQ, a relatively higher standard deviation is obtained (*e.g.* %RSD=6.8% for 13.7 $\mu\text{g/kg}$ ethanol by HS-GC-MS; %RSD=12.1% for 3.3 $\mu\text{g/kg}$ methanol by HS-GC-MS and %RSD=16.2% for 49.2 $\mu\text{g/kg}$ ethanol by HS-GC-FID).

Comparison of GC Methods

The comparison of the performance of the two methods was based on the analysis of twenty one transformer oils coming from different manufacturers and with different year of first energization (1966 – 2012, see table 4). The results obtained for methanol and ethanol determination by the HS-GC methods optimized are shown in figure 3.

Data obtained by HS-GC-FID and HS-GC-MS were evaluated by the paired t -test and F -test at a significance level $\alpha = 0.05$. Since the calculated t values for methanol (1.01) and ethanol (0.19) were lower than the tabulated t -value (2.09) no significant differences exist between the two methods. In addition, the F -test confirmed that variances of the two methods are not significantly different.

Both the methods were validated through a round robin test (RRT CIGRE JWG A2/D1.46) involving seven international laboratories. Three samples were distributed involving a blind in-service oil (sample A), the same for all the laboratories, and two unused oils spiked with methanol

and ethanol at a different concentration for each laboratory. As an example, Figure 4 (a,b) shows the chromatograms obtained for the in-service oil for the two HS-GC methods. The results for all the samples are presented in Table 5 (methanol) and in Table 6 (ethanol).

The data shown highlight that for methanol determination both HS-GC-FID and HS-GC-MS provide excellent accuracy (z-score about 0.05, real sample A). Very good performance is obtained also for ethanol determination by HS-GC-MS (z-score -0.42, real sample A). Ethanol determination by HS-GC-FID is inside the limits of acceptability of the measurement, but is most likely affected by the characteristics of the sample, as it can be gathered by the results obtained for the analysis of the spiked unused oils (samples B,C), for which the excellent performance of both the methods is assessed.

Marker Correlations

In addition to methanol and ethanol content, the concentration of traditional markers, CO₂ and furan-2-carbaldehyde(2-FAL), was also evaluated for the sampled in-service oils. Oils subjected to physical treatments (reclamation) were not considered in the comparison. The data obtained are shown in Table 7. Methanol and ethanol concentrations were determined by the HS-GC-MS method. An apparent correlation between CO₂ concentration and methanol ($y = 11.8x + 878$, $r^2 = 0.7802$) and ethanol ($y = 19.1x + 1232$, $r^2 = 0.7427$) contents was obtained as shown in Figure 5. The relevance of this correlation is the fact that further information on the thermal degradation conditions of transformers' solid insulation can be obtained. In fact, points (A,B) in Figure 5 correspond to an ethanol content higher than expected on the base of the relatively lower CO₂ production; this can be explained by the fact that the transformers to which points A and B are related suffer a faulty conditions of overheating (assessed by dissolved gas analysis interpretation, IEC60599 [16]) that may result in a higher ethanol formation.

Finally Figure 6 shows the correlation between the methanol concentration and the transformer life time where, as expected, the marker concentration increases along the time. In the inset labels, points related to anomalous situations (e.g.: oil reclamation, reduced loading of the transformer, high working temperature) are also highlighted.

Conclusions

Two gas chromatographic methods, HS-GC-MS and HS-GC-FID, were optimized and compared for the determination of methanol and ethanol in mineral insulating oil samples, as markers of degradation of cellulose inside power transformers. Detection limits noticeably better than recent literature data were achieved by HS-GC-MS. The HS-GC-FID method, characterized by less

expensive instrumentation, allowed to achieve detection limits below the value of standardized method for methanol and ethanol detection in crude oils. Both the methods were validated and provided significantly good results for working range, linearity, precision and accuracy as assessed by the inter-laboratory test. Their suitability for the analysis of in service transformer oils was also shown. A correlation derived from the comparison of traditional classic marker, CO₂, and methanol or ethanol content in in-service oils, showed its utility in defining situations of anomalous performance in power transformers.

Both the methods developed allow reliable identification of methanol and ethanol as new markers of the level of thermal degradation of cellulose. Despite the slightly better detection limits achieved by HS-GC-MS, the HS-GC-FID method is characterized by less expensive instrumentation within every laboratory reach and hence can represent a simpler tool for solid insulation degradation surveillance of power transformers. The method developed is currently routinely applied by the laboratories of Sea Marconi Technologies for the assessment of transformers' conditions.

Acknowledgements

The Authors would like to thank Dr. Giorgio Rocchia and Dr. Luca Rivoira for their valuable help. Financial support from MIUR (Ministero dell'Istruzione, dell'Università e della Ricerca, Italy) is gratefully acknowledged. Financial support from Compagnia di San Paolo and University of Torino (Progetto d'Ateneo 2012) is also acknowledged.

References

- [1] De Carlo RM, Sarzanini C, Bruzzoniti MC, Maina R, Tumiatti V (2012) Copper-in-oil Dissolution and Copper-on-paper Deposition Behavior of Mineral Insulating Oils. IEEE Trans Dielectr Electr Insul, in press
- [2] Tamura R, Anetai H, Ishii T, Kawamura T (1981) The diagnostics of the ageing deterioration of insulating paper in transformer by gas analysis. JIEE Proc. Pub. A 101:30-36
- [3] Burton PJ, Graham J, Hall AC, Laver JA, Oliver AJ (1984) Recent developments by CEGB to improve the prediction and monitoring of transformer performance. CIGRE Conf., Paper 12-09
- [4] Lessard MC et al. (2012) Furanic compounds for diagnosis. CIGRÉ Working Group D1.01(TF13), CIGRÉ Technical Brochure 494

- [5] Jalbert J, Gilbert R, Tétreault P, Morin B, Lessard-Déziel D (2007) Identification of a chemical indicator of the rupture of 1,4-b-glycosidic bonds of cellulose in an oil-impregnated insulating paper system. *Cellulose* 14:295-309
- [6] Mittelbach M, Roth G, Bergmann A (1996) Simultaneous gas chromatographic determination of methanol and free glycerol in biodiesel. *Chromatographia* 42:431-434
- [7] Knothe G (2006) Analyzing biodiesel: Standards and other methods. *J Am Oil Chem Soc* 83: 823-833
- [8] Faber Boog JH, Cardoso Silveira EL, Basílio de Caland L, Tubino M (2011) Determining the residual alcohol in biodiesel through its flash point. *Fuel* 90: 905–907
- [9] Annual Book of ASTM Standards (2009) Petroleum Products and Lubricants (IV): D6973. 05.04, Conshohocken, PA
- [10] Mokhtari B, Pourabdollah K (2012) Determination of hydrate inhibitor in crude oil by nanoextraction–gas chromatography. *J. Sep. Sci.* 35: 79–85
- [11] Jalbert J, Duchesne S, Rodriguez-Celis E, Tétreault P, Collin P (2012) Robust and sensitive analysis of methanol and ethanol from cellulose degradation in mineral oils. *J. Chrom A* 1256: 240-245
- [12] Oil-filled electrical equipment – Sampling of gases and of oil for analysis of free and dissolved gases – Guidance 60567, IEC, International Electrotechnical Commission:2005
- [13] Mineral insulating oils - Methods for the determination of 2-furfural and related compounds – Guidance 61198, IEC International Electrotechnical Commission 1993
- [14] United States Environmental Protection Agency (US EPA) (2004) Revised assessment of detection and quantitation approaches. Chapter 5.1: Detection Limit Approaches, EPA-821-B-04-005, Washington, DC
- [15] United States Environmental Protection Agency (US EPA) (2004) Definition and Procedure for the Determination of the Method Detection Limit. Revision 1.11, 40CFR-Part 136, Appendix B
- [16] Mineral oil-impregnated electrical equipment in service - Guide to the interpretation of dissolved and free gases analysis- Guidance 60599 ed 2.0 IEC International Electrotechnical Commission 1999.

Table 1. Instrumental conditions for HS-GC analysis

Head-space and injection conditions	GC temperature program
Temperature: 90 °C	T _{in} : 40 °C for 7 min, 10 °Cmin ⁻¹ to 75 °C
Injection volume: 500µL	50 °C min ⁻¹ to 300°C hold for 5 min
Split ratio: 5/1	

Table 2. Figures of merit for HS-GC-FID and HS-GC-MS analysis of methanol and ethanol in oils.

	Methanol		Ethanol	
	FID	MS	FID	MS
LOD (µg kg ⁻¹)	12.1	1.3	26.8	3.1
LOQ (µg kg ⁻¹)	36.0	3.9	79.6	9.3
Linearity (r ²)	36-3500 (0.9991)	3.9-2500 (0.9994)	80-3500 (0.9993)	10-2500 (0.9998)

Table 3. Analysis of methanol and ethanol in six transformer oils in service. Concentrations are expressed in µg kg⁻¹ and RSD are indicated in parenthesis.

Methanol (n=20)		Ethanol (n=20)	
FID	MS	FID	MS
78.9 (4.6%)	3.3 (12.1%)	49.2 (16.2%)	13.7 (6.8%)
351 (5.1%)	462 (2.7%)	476 (3.6%)	461 (3.1%)
1985 (2.6%)	2196 (2.2%)	438 (1.9%)	585 (1.8%)

Table 4. Details on the transformer oils in service analysed by the HS-GC-FID and the HS-GC-MS methods optimized.

Transformer	Holder	Application	Year of first energization
1	Romania	Network Distribution	1966
2	France	Nuclear power Generation	1974
3	Ivory Coast	Network Distribution	1975
4	Ivory Coast	Network Distribution	1976
5	France	Nuclear power Generation	1978
6	Ivory Coast	Network Transmission	1978
7	Ivory Coast	Network Transmission	1979
8	Ivory Coast	Network Transmission	1979
9	Ivory Coast	Network Distribution	1979
10	Ivory Coast	Network Transmission	1982
11	Ivory Coast	Network Distribution	1983
12	Ivory Coast	Network Transmission	1984
13	France	Hydro power Generation	1987
14	Italy	Industrial Distribution	1990
15	France	Thermal power Generation	1996
16	France	Thermal power Generation	1996
17	Italy	Thermal power Generation	1996
18	Italy	Thermal power Generation	1996
19	Italy	Network Distribution	2012
20	Ivory Coast	Network Distribution	2012
21	Italy	Network Distribution	2012

Table 5. Performance of the developed methods for methanol determination under the CIGRE JWG A2/D1.46 round robin test.

Sample	Methanol concentration ($\mu\text{g kg}^{-1}$)			Std. Dev	Z-score	
	MS	FID	Target		MS	FID
A	874	871	861	243	0.05	0.04
B	357	353	328	53		
C	1088	989	1001	160		

A: in-service oil; **B, C:** unused oils spiked with methanol and ethanol

Table 6. Performance of the developed methods for ethanol determination under the CIGRE JWG A2/D1.46 round robin test.

Sample	Ethanol concentration ($\mu\text{g kg}^{-1}$)			Std. Dev	Z-score	
	MS	FID	Target		MS	FID
A	185	275	200	36	-0.42	2.08
B	417	375	398	72		
C	1250	1042	1081	195		

A: in-service oil; **B, C:** unused oils spiked with methanol and ethanol

Table 7. New (methanol and ethanol) and traditional (2-FAL and CO_2) marker concentrations in in-service oils according to the years of service.

Years of service	Methanol ($\mu\text{g kg}^{-1}$)	Ethanol ($\mu\text{g kg}^{-1}$)	2-FAL (mg kg^{-1})	CO_2 (μLL^{-1})
38	331	321	0.81	7364
35	522	151	n.a.	5441
35	233	165	0.15	3791
34	188	83	0.13	1911
34	76	48	<0.05	1481
34	485	516	0.1	4503
32	150	63	0.3	3180
32	260	170	0.5	4597
31	120	28	<0.05	2124
30	505	211	4.69	7918
29	409	281	0.29	4367
26	533	640	n.a.	4579
17	8	14	n.a.	658
17	65	8	n.a.	1775
1	16	5	<0.05	941

n.a.: not available

Figure Captions

Figure 1. Effect of split ratio in the GC determination of methanol and ethanol in oil (Hyvolt II). Column: 30 m x 320 μm , 0.25 μm d_f 5% phenylmethylsiloxane (Ultra 2; Agilent, J&W). Carrier: He (1 mLmin^{-1}). Head-space temperature: 100 $^{\circ}\text{C}$; injection volume: 1000 μL .

Figure 2. Optimized GC separation of methanol and ethanol in oil. Column: 30 m x 320 μm , 1.8 μm d_f 6% cyanopropylphenyl, 94% dimethyl polysiloxane, Rxi-624 Sil Ms (Restek, Bellefonte, PA, USA). Carrier: He (1 mLmin^{-1}). Head-space temperature: 90 $^{\circ}\text{C}$; injection volume: 500 μL ; split ratio: 5/1.

Figure 3. Analysis of methanol and ethanol by HS-GC-FID and HS-GC-MS in the 21 transformer oils in service.

Figure 4. Analysis of methanol and ethanol by HS-GC-FID (a) and HS-GC-MS (b) in the blind in service oil (sample A).

Figure 5. Correlation between methanol, ethanol concentrations and CO_2 content in the sampled transformer oils.

Figure 6. Correlation between transformer lifetime and methanol concentrations in in-service transformer oils.

Figure 1. Effect of split ratio in the GC determination of methanol and ethanol in oil (Hyvolt II). Column: 30 m x 320 μ m, 0.25 μ m d_f 5% phenylmethylsiloxane (Ultra 2; Agilent, J&W). Carrier: He (1 mL/min). Head-space temperature: 100 $^{\circ}$ C; injection volume: 1000 μ L.

Figure 2. Optimized GC separation of methanol and ethanol in oil. Column: 30 m x 320 μm , 1.8 μm d_f 6% cyanopropylphenyl, 94% dimethyl polysiloxane, Rxi-624 Sil Ms (Restek, Bellefonte, PA, USA). Carrier: He (1 mL/min). Head-space temperature: 90 $^{\circ}\text{C}$; injection volume: 500 μL ; split ratio: 5/1.

Figure 3. Analysis of methanol and ethanol by HS-GC-FID and HS-GC-MS in the 21 transformer oils in service.

Figure 4. Analysis of methanol and ethanol by HS-GC-FID (a) and HS-GC-MS (b) in the blind in service oil (sample A).

Figure 5. Correlation between methanol, ethanol concentrations and CO₂ content in the sampled transformer oils.

Figure 6. Correlation between transformer lifetime and methanol concentrations in in-service transformer oils.