

CIGRE TF A2-32-03 Sulfur Speciation in Insulating Oil - Final Report, June 2010

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## **CIGRE TF A2-32-03**

### **SULFUR SPECIATION IN INSULATING OIL**

#### **INTRODUCTION AND BACKGROUND**

In recent years corrosive sulfur in insulating oils has been blamed for many transformer failures. The problem has now become worldwide and considerable effort is underway to address this issue. ASTM has revised their test for corrosive sulfur and CIGRE has several working groups and task forces looking at various aspects of the problem. More specifically, CIGRE TF A2 32 03 has looked at what specific sulfur compounds are present in insulating oils and that may be responsible for copper corrosion.

There is no lack of useful methods to determine total sulfur content in oil, which are also applicable to insulating oil. However, among users and producers of such oil there are few well known and universally accepted methods to determine the content of groups of organo-sulfur compounds or that of individual sulfur species known to be of interest from a corrosivity point of view such as dibenzylidene disulfide (DBDS). Even oil suppliers seem to have limited experience of such analyses.

There are numerous sulfur compounds in insulating oil and complete identification would be a daunting task. The traditional consensus was that the activity of such sulfur compounds towards corrosion of copper decreases in the following order: elemental sulfur > mercaptans > sulfides > disulfides > thiophenes. It is not clear if this still holds true, nevertheless it is in the interest of the whole transformer community and of WG A2-32 to find out what methods could be used for these classes of compounds or specific compounds. A summary of this report was included in CIGRE Brochure 378, prepared by WG A2-32.

IEC may have need for standardized methods for sulfur speciation in future revisions of some standards, especially oil specifications and maintenance guides. Thus, the recommendations of the TF may be used by IEC in the preparation of a new standard.

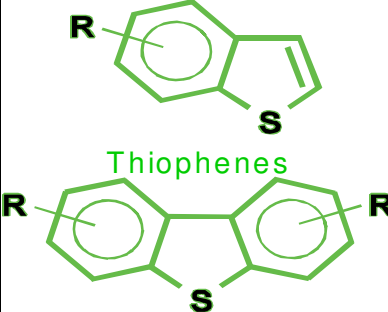
#### **SOURCE AND NATURE OF CORROSIVE SULFUR**

Sulfur compounds are indigenous to oils of petroleum origin. Crude oil contains sulfur and sulfur compounds at concentrations up to 20%. It is important to note that not all sulfur compounds are corrosive and in fact many of them are natural oxidation inhibitors and beneficial to oil aging.

The vast majority of sulfur compounds present in oil can be divided into five classes based on their corrosive nature. These are listed in Table 1 in accordance to their activity towards corrosion. We can see from Table 1 that elemental sulfur and mercaptans are the most corrosive compounds. It was reported by Clark [12] that elemental sulfur is corrosive even at the 1-ppm level. Sulfides are the second most reactive class of sulfur compounds followed by disulfides followed by thiophenes. The latter two classes are considered stable and very stable. In fact some

disulfides have been used as metal passivators and deactivators reducing the catalytic effect on oil oxidation in transformers.

**Table 1**  
**Classes of Sulfur Compounds and Their Activity Towards Corrosion**

<b>Very Reactive</b>	<b>Reactive</b>	<b>Stable</b>	<b>Very Stable</b>
<p style="text-align: center;"><b>S</b> Elemental Sulfur</p> <p style="text-align: center;"><b>R-SH</b> Mercaptans</p>	<p style="text-align: center;"><b>R-S-R<sub>1</sub></b> Sulfides</p>	<p style="text-align: center;"><b>R-S-S-R</b> Disulfides</p>	<p style="text-align: center;">   Thiophenes                 </p>

## ROUND ROBIN TEST (RRT) PROGRAM

### Introduction

The intent of the program was to evaluate methods that may be suitable for the analysis of specific sulfur compounds or classes of compounds in insulating oils. This was done by conducting a round robin test by laboratories that are proficient with this type of analysis.

### Scope

Task Force A2 32 03 on Sulfur Speciation was set up to survey and evaluate, refine or develop if necessary, and recommend methods suitable for the analysis of specific sulfur compounds or classes of compounds in insulating oils.

The analytical methods selected for evaluation included the analysis of insulating oils for:

- Total sulfur content
- Total mercaptans and disulfides
- Dibenzyl disulfide (DBDS)
- Other sulfur compounds: dibenzyl sulfide (DBS), octadecylmercaptan (ODM), didecyl sulfide (DDS)

This was done by conducting a round robin test (RRT) program with 12 participating laboratories proficient with this type of analysis. The program evaluated both aged and un-aged oil samples in their original state and after spiked with known amounts of the above sulfur compounds. The participating laboratories were asked to analyze each oil sample with analytical instruments at their disposal as follows:

- Inductively coupled plasma (ICP) – total sulfur
- Silver/Silver sulfide (Ag/Ag<sub>2</sub>S) electrode titration – total mercaptans and disulfides

- Gas chromatography/electron capture detector (GC/ECD) – DBDS
- Gas chromatography/atomic emission detector (GC/AED) – DBDS, DBS, ODS, DDS, other sulfur compounds
- Gas chromatography/mass spectrometry (GC/MS) – DBDS, DBS, other sulfur compounds
- Other methods as available

Not all participating laboratories were able to perform all the above analysis, but the response was sufficient to evaluate most of the methods above.

Due to time constraints and available analytical methods, the scope of the program has been limited to the analysis of: DBDS, total mercaptans and disulfides, and total sulfur. The results of analysis will be used to select what or if these methods are suitable for sulfur speciation of insulating oils. The scope has been limited to oils of petroleum origin from several manufacturers and oils that had been in service in electrical equipment.

### Participants

Based on information provided by members of TF A2 32 03, a list of participating labs and their capability was compiled. This can be found in Appendix A. The final list consisted of 12 labs; the level of their participation varied depending on their resources availability.

### Samples

Insulating oils used to prepare samples for the study were supplied by the members. These were commercially available mineral insulating oils commonly used at their facility or oil from in-service transformers at their utility. This included three different new (unused) oils that tested non-corrosive, one aged oil that tested non-corrosive and two different aged oils that tested corrosive. Details of the oils used for the RRT are given in Table 2. Additional samples were prepared from the above by adding sulfur compounds representative of disulfides (DBDS), mercaptans (ODS), sulfides (DBS, DDS), and bibenzyl (BiBZ) at two concentration levels. All the samples for the study were prepared by Powertech Labs and distributed to the participating labs.

**Table 2**  
**Details of Oils Used for RRT Samples**

Oil Description	Supplier/Manuf.	Source	Corrosive Sulfur Test	Comments
New Voltesso 35	Imperial Oil	Powertech	Non corrosive	New stock, low sulfur, contains triazole,
Aged Voltesso 35	Imperial Oil	Powertech	Non corrosive	Old stock, in-service oil from BCH. No triazole, high sulfur
New Nynas, 10XN	Nynas	ABB, Sweden	Non corrosive	Low sulfur,
Aged Nynas, 10GBN	Nynas	ABB, Sweden	Corrosive	
New Laborelec,		Laborelec	Non Corr.	
Aged Laborelec		Laborelec	Corrosive	

Each participating member was provided with 13 bottles containing 75 g of oil samples for analysis. The samples consisted of the following:

- Three new oils as received
- Three new oil spiked with DBDS, DBS, OCM, DDS and BiBZ at concentration C1 (0-25ppm)
- One new oil sample spiked with same compounds to a concentration C2 (25-50ppm).
- Three aged oil samples from different sources as received
- Three aged oil samples spiked with the above compounds to concentration levels C2.

Details of the sample composition are given in Appendix B.

### **Analysis**

Each lab was asked to analyze each sample for as many parameters as they were able to and using as many analytical methods as they wished. For example, a lab may wish to analyze the oil samples for DBDS by GC-ECD, and GC-MS, or for total sulfur by ICP and GC-AED. Also they may wish to analyze for other specific compounds such as DBS, OCM and DDS by GC-AED or GC-MS – these were optional.

The methods of analysis to be used may be in-house methods but should be similar to those provided. However, analysis for total mercaptans and disulfides should be done by titration as per method provided by ABB. Whenever possible the samples should be analyzed in duplicate. Specific methods of analysis used by individual labs are given in Appendix C.

### **Reporting**

Results were to be reported using the Excel template provided. For consistency and ease of comparison, all result reported were converted to **sulfur content** as  $\mu\text{g S/g}$  (ppm) oil.

## **RESULTS OF ROUND ROBIN**

### **Analysis for DBDS by GC-ECD**

Analysis for DBDS in oil by GC-ECD is relatively simple, requires little sample preparation and can be carried out using equipment and conditions normally used for PCB analysis. As a result most participating labs were able to perform this analysis. Typical GC-ECD chromatograms of new, aged and spiked oils are shown in the Appendix. We can see from these chromatograms that there is little to no interference from other oil constituents, aging products and other sulfur compounds deliberately added (DBS, DDS ODS).

The results of analysis from participating labs are summarized in Table 3 below. The results show that all labs were able to determine DBDS in the spiked samples with a standard deviation of 10-15%. Considering this was an inter-laboratory study with each lab using their own method and calibration standard, the precision is well within acceptable limits.

### **Analysis for DBDS, DBS and Other Compounds by GC-MS**

This method is more definitive and has the capability of analyzing other compounds of interest concurrently. However, it requires more sophisticated and more expensive equipment which many laboratories do not have. Only two laboratories reported results of analysis by this method.

Lab No1 extracted the sample with a polar solvent prior to GC-MS analysis. Sample chromatograms are shown in Figure C3 of Appendix C. Lab No 6 analyzed the samples using three different ways; a) dilution with a solvent, b) solvent extraction as per lab No 1 and c) using SPE cartridges. Although both labs reported results of analysis for DBDS, DBS, DDS, and ODM, for simplicity, only DBDS is shown in Table 4.

The results show that simple dilution with solvent as used by Lab 6 provided more accurate results but poorer detection limits than solvent extraction as used by Lab 1. Results for other compounds showed a similar trend.

**Table 3**  
**Results of Analysis of Oil Samples from RRT Program**

Sample Code	Sulfur Content in DBDS by GC-ECD ( ppm as S)									
	Amnt Added	Lab 1	Lab 2	Lab 6	Lab 8	Lab 10	Lab 11	Lab 12	Ave.	Std. dev
V35N	0	<	<	<	<	<2.6	<1.3	<2		
V35N50	50	46.9	40	45	48.2	39.4	35.5	39.0	42.0	4.72
10XN	0	<	<	<0.9	<	<2.6	<1.3	<2	0.0	0.00
10XN25	25	22.9	20	23	21.9	20.5	15.6	15.8	20.0	3.12
10XN50	50	44	39	46	45.3	40	30.1	39.2	40.5	5.45
LBLN	0	0.17	0	<0.9	<	<2.6	<1.3	<2	0.1	0.12
LBLN25	25	21.7	19	22	22.9	19.7	14.4	18.7	19.8	2.86
V35O	0	0.3	3	<0.9	<	<2.6	1.7	1.3	1.6	1.12
V35O50	50	48.1	39	46	46.1	40	28.9	43.0	41.6	6.51
10GBN	0	58	50	57	53.7	46.8	42.4	55.0	51.8	5.71
10GBN50	50	110.8	93	108	81.3	89.6	79.7	104.4	95.3	12.66
LBLO	0	45	37	40	42.7	36.9	31.8	38.0	38.8	4.31
LBLO50	50	95.6	78	85	83.9	80.5	67.3	86.0	82.3	8.63

**Table 4**  
**Analysis of DBDS in Oil by GC-MS**

Sample Code	Sulfur Content in DBDS (ppm as S) by GC-MS				
	Amnt Added	Lab 1	Lab 6	Lab 6*	Lab 6**
V35N	0	0.13	<5	<10	<0.6
V35N50	50	56.25	49	30	24
10XN	0	0	<5	<10	<0.6
10XN25	25	22.6	24	15	15
10XN50	50	80.68	49	31	33
LBLN	0	0.2	<5	<10	<0.6
LBLN25	25	20.69	22	15	15
V35O	0	0.08	<5	<10	<0.6
V35O50	50	77.83	49	33	26
10GBN	0	75.1	62	36	23
10GBN50	50	132.4	102	50	<44
LBLO	0	50.54	42	25	20
LBLO50	50	141.7	85	43	40

\*: Powertech Method; \*\* SPE Extraction

### Analysis for Sulfur Compounds by GC-AED

Analysis of oil by GC-AED in the sulfur mode is capable of detecting all sulfur compounds with little interference from hydrocarbons. Figure C4 shows a typical GC-AED chromatogram of new Voltesso 35 mineral oil spiked with selected sulfur compounds, each containing 50ppm sulfur. In low sulfur oil, all these compounds are easily detected and quantified. However, as can be seen from Figure C4, oils containing a large number of sulfur compounds at higher levels, the analysis is prone to some interference.

The results of analysis of oil samples for DBDS as reported by three labs are shown in Table 5. All three labs were able to measure DBDS with reasonable accuracy and agreement among them. None of the labs reported measurable levels of DBDS for the new oils tested but did so for the aged oils.

Results of analysis for other sulfur compounds, although detected, were not reported.

**Table 5**  
**Results of Analysis of Oil Samples for DBDS by GC-AED**

Sample Code	Sulfur Content in DBDS by AED (PPM)			
	Amnt added	Lab 1	Lab 11	Lab 12
V35N	0	<2	<2	<2
V35N50	50	49.7	41.6	39
10XN	0	0	<2	<2
10XN25	25	25.1	21	15.8
10XN50	50	48.7	41.6	39.2
LBLN	0	0	<2	<2
LBLN25	25	25.3	18.2	18.7
V35O	0	9.3	1.3	1.3
V35O50	50	59.3	41	43
10GBN	0	57.9	53.5	55
10GBN50	50	101.6	91.4	104.4
LBLO	0	34.8	39.7	38
LBLO50	50	89.7	77.4	86

### Analysis for Total Sulfur by ICP

A total of 5 labs reported results of RRT oil samples for total sulfur by ICP analysis. These are summarized in Table 6 below. There appears to be reasonable agreement among most labs for some samples (New VE 35 and New Nynas), but in the majority of samples, there is considerable scatter. In some cases the results variation is more than 100%. Given the poor inter laboratory results and that no correlation exists between total sulfur and corrosivity of the oil, there seems to be little merit in pursuing this test.

**Table 6**  
**Results of Analysis of Oil Samples for Total Sulfur Content by ICP**

Sample Code	Total S Content (ppm) by ICP Analysis					
	Amnt added	Lab 1	Lab 2	Lab 6	Lab 7	Lab 11
V35N	0	104	135	140	108	550
V35N50	200	348	420	530	319	560
10XN	0	29	35	30	29	40
10XN25	100	152	200	235	154	230
10XN50	200	274	356	430	255	350
LBLN	0	489	702	745	436	735
LBLN25	100	587	995	1085	555	970
V35O	0	450	550	750	416	730
V35O50	20	696	856	1405	631	1040
10GBN	0	1432	1600	not done.	1236	1990
10GBN50	200	1626	1965	not done.	1443	2200
LBLO	0	350	458	665	322	660
LBLO50	200	573	952	1295	530	850

**Analysis for Total Mercaptan and Disulfide Sulfur by Titration**

Four labs reported analysis for total mercaptans and disulfides by silver/silver sulphide electrode titration. The results are shown in Table 7. We can see that labs 6 and 8 are in good agreement with each other and close to the expected concentrations. Lab 5 reported somewhat lower than expected results whereas lab 9 reported somewhat higher than expected results.

The amounts of mercaptans and disulfides added are much higher than expected in new oils. For this reason, some labs indicated they had to modify the method to cope with such high levels. Also for consistent results, the electrodes require frequent cleaning. It is worthwhile noting that sulfides gave little to no response.

Overall, the method gave reasonable results and with minor refinements can become a useful test.

**Table 7**  
**Results of Analysis of Oil Samples for Total Mercaptan and Disulfide Sulfur by Titration**

Sample Code	SH & SSH Content by Titration Method (ppm as S)				
	Amnt added	Lab 5	Lab 6	Lab 8	Lab 9
V35N	0	0	<1	<	3.58
V35N50	100	55.8	100	93.2	112
10XN	0	3.5	<1	<	2.44
10XN25	50	41.5	50	49.7	67
10XN50	100	67.4	93	91.7	121
LBLN	0	7.8	6	<	16.7
LBLN25	50	35.1	54	52.5	79.8
V35O	0	6.1	<1	<	5.27
V35O50	100	52	91	88.8	111
10GBN	0	34	56	52.5	73.2
10GBN50	100	0	147	131.2	171
LBLO	0	29	42	46.5	57.5
LBLO50	100	0	104	108.6	153

## SUMMARY AND CONCLUSIONS

Results of the RRT program to date indicate the following:

- Analysis for DBDS by GC/ECD is simple, sensitive and fairly reliable. The method can be applied to new and aged oils with little interference and minimal sample preparation to levels below 1 ppm.
- Analysis for DBDS can also be accomplished by GC/MS and GC/AED. Analysis by GC/MS is more definitive and can identify other target compounds (DMS etc.) concurrently, but is less sensitive and not as readily available. Analysis by GC/AED has the advantage of detecting all sulfur compounds but is prone to more interference and is a more expensive and less common laboratory instrument.
- Analysis for total mercaptans and disulfides was successfully achieved by Ag/Ag<sub>2</sub>S electrode titration. The method is more tedious and requires frequent electrode cleaning, and adjustments need to be made for higher concentrations.
- Determination of total sulfur by ICP gave poor reproducibility among labs. Other methods are available as substitutes but since total sulfur has little or no correlation to corrosive sulfur, it is not worthwhile pursuing further.

## RECOMMENDATIONS

The mandate of the Task Force was limited to identifying methods suitable for the identification and quantitation of specific sulfur compounds or classes of compounds. Although several methods were identified for this purpose, their suitability has not been rigorously evaluated. Before these methods can be used as standards, they will need to be properly validated through a controlled inter laboratory program using stricter protocols. This will require that each lab adheres to the same analytical procedure, test split test samples from the same source and apply it to a wider range of insulating oils.

## REFERENCES

1. J. Hajek, M. Dahlund, L. Paterson, "Quality of Oil Makes the Difference, ABB Discovers the Solution to Transformer Breakdowns", ABB Review, No 3-2004.
2. L. Lewand, "The Role of Corrosive Sulfur in Transformers and Transformer Oil", Proceedings of the 69<sup>th</sup> International Conference of Doble Clients, Boston, MA, 2002.
3. L. Lewand, "Investigating Copper Sulfide Contamination in a Failed Large GSU Transformer", Proceedings of the 72<sup>nd</sup> International Conference of Doble Clients, Boston, MA, 2005.
4. C. Bengtsson *et al.*, "Oil Corrosion and Cu<sub>2</sub>S Deposition in Power Transformers", CIGRE Moscow Symposium, 2005.
5. L. Lewand, "The Evolving Problem of Corrosive Sulfur In Transformer Oil". Presentation at the IEEE/PES Transformer Committee Fall 2005, Memphis TN.
6. ABINEE, Workshop on Corrosive Sulfur in Oil, June 2005, Sao Paulo Brazil, presentations by ABB, Toshiba, Doble, Nynas, Siemens, Terna and Areva.

7. A. Hjortsberg and Jose-Carlos Mendes, "Oil Corrosion & Cu<sub>2</sub>S Deposition, - ABB Testing, Passivation and Diagnostics", Presented at the ABINEE Workshop June 2005, Brazil
8. L. Lewand and P. Griffin, "Update On the Corrosive Sulfur Issue in Oil-Filled Electrical Equipment", Proceedings of the 73<sup>nd</sup> International Conference of Doble Clients, Boston, MA, 2006.
9. M. Dahlund, *et al.*, "Oil Corrosion and Cu<sub>2</sub>S Deposition in Power Transformers", CIGRE Study Committee A2, Session V – Paper 8, 2006
10. T. L. Machado Junior, "Corrosive Sulphur", Presentation at the IEEE/PES Transformer Committee Fall 2005, Memphis TN
11. J Baldauf, "corrosive Sulfur in Oil", Presentation at the IEEE/PES Transformer Committee Fall 2005, Memphis TN
12. Clark, F.M. and Raab, E.L. "The Detection of Corrosive Sulfur Compounds in Mineral Transformer Oil", ASTM Publication, Presented at the Society Meeting, June 21-25, 1948, pp. 1201-1210.
13. V. Tumiatti, *et al.* "Corrosive Sulphur in Mineral Oil: Its Detection and Correlated Transformer Failures", IEEE International Symposium on Electrical Insulation, 2006, p 400
14. W. G. Brown, "Review of Results of Corrosive Sulfur Testing Using Doble Engineering's Amended ASTM Method D 1275", Proceedings of the 73<sup>nd</sup> International Conference of Doble Clients, Boston, MA, 2006.
15. V. Tumiatti, "Condition Monitoring by Oil Chemical Analysis", presented at the CIGRE General Meeting, Paris, 2000
16. F. Scatiggio "Corrosive Sulphur", Proceedings of IEC TC 10 Plenary meeting, Cape Town, 2005
17. CIGRE Task Force Report A2-31, on "Copper Sulphide in Transformer Insulation", Electra No 224 Feb. 2006.
18. C. Clairborne, " Specification & Testing of Transformer Oils with Respect to Corrosion". Presentation at the IEEE/PES Transformer Committee Fall 2005, Memphis TN.
19. M. Eklund and K. Sundkvist, "Transformer Oils-An Orientation About Sulphur and its Characteristics and Effects", Proceedings of the 72<sup>nd</sup> International Conference of Doble Clients, Boston, MA, 2005.
20. T. V. Oommen, *et al.*, "Sulfur Corrosion Tests and Corrosion Effects in Transformers", Presented at the TechCon 2003
21. C Bengtsson, *et al.* "Oil Corrosion and Conducting Cu<sub>2</sub>S Deposition in Power Transformer Windings", CIGRE 2006 Paris Meeting

22. N. Dominelli, S. Kovacevic, E. Hall and M. Lau, "The Presence, Fate and Removal of Corrosive Sulfur in Transformer", Presented at the EPRI Substation Equipment Diagnostics Conference XIV, San Diego, July. 2006.
23. R. Maina *et al.*, "Corrosive Sulfur in Insulating Oils. Detection, Faults, Statistics and Countermeasures", Presentation at the Oslo CIGRE meeting, Dec. 2005.

**APPENDIX A**

**Table A1**  
**List of Participating Laboratories**  
**CIGRE TF A2 32 03 RRT Participating Laboratories**

Lab/Affiliation	Contact/Name	DBDS			Other	SH/SSH	Total S	
		GC-ECD	GC-MS	GC-AED		Titration	ICP	Other
ABB - Sweden	Mats Dahlund/Hans Önnerud	X	X			X	X	
Areva, France	Christophe Perrier	X	X			X	X	
DOBLE, USA	Paul Griffin	X						
Labelec, Portugal	Maria Augusta	X				X		X
Laborelec, Belgium	Julie Van Peteghem	X	X			X		
Nicola Tesla, Serbia	Jelena Lukic				X	X		
Powertech Labs, Canada	Nick Dominelli	X	X	X			X	X
Repsol YPF, Spain	Maria Aparicio	X	X	X	X	X	X	
Siemens, Germany	Vladyslav Mezhvynskiy	X	X			X		
SINTEF, Norway	Marit-Helen G. Ese					X		
SEA Marconi, Italy	Riccardo Maina	X		X			X	
Terna, Italy	Fabio Scatiggio	X		X				

**APPENDIX B**

**Table B2  
Details of Samples Used in RRT Program**

Sample Description	Sample Code	Added Amount of Sulfur Compound (ppm as S)					
		DBDS	DBS	BiBZ	DDS	ODM	S Added
New VE 35	V35N	0	0	0	0	0	0
New VE 35-C2	V35N50	50	50	50	50	50	200
New Nynas	10XN	0	0	0	0	0	0
New Nynas-C1	10XN25	25	25	25	25	25	100
New Nynas-C2	10XN50	50	50	50	50	50	200
New Laboralec	LBLN	0	0	0	0	0	0
New Laboralec-C1	LBLN25	25	25	25	25	25	100
Aged VE 35	V35O	0	0	0	0	0	0
Aged VE 35-C2	V35O50	50	50	50	50	50	20
Aged Nynas	10GBN	0	0	0	0	0	0
Aged Nynas-C2	10GBN50	50	50	50	50	50	200
Aged Laboralec	LBLO	0	0	0	0	0	0
Aged Laboralec-C2	LBLO50	50	50	50	50	50	200
Conversion factor from S to Comp.		3.84375	6.6875	NA	9.9375	8.9375	NA

DBDS-Dibenzylsulfide

DBS-Dibenzylsulfide

BiBZ- BiBenzyl

DDS-Didecylsulfide

ODM- Octadecylmercaptan

## APPENDIX C

### Methods of Analysis

#### POWERTECH LABS

##### Standards Preparation

All sulfur compounds were purchased from Alfa Aesar and used as received.

Standard samples were prepared in New Nynas oil that has been treated to remove any sulfur compounds using the following compounds:

- Dibenzyl disulfide (DBDS),
- Benzyl sulphide (DBS),
- Octadecyl mercaptan (ODM),
- Di-n-decyl sulfide (DDS) and
- 1,2-Diphenylethane (BiBZ)

The above compounds were dissolved in New Nynas oil that has been treated to remove any sulfur compounds to give a sulfur concentration of 100 ppm (except 1,2-diphenylethane). The concentration of calibration sample of 1,2-diphenylethane is compound concentration. The calibration sample was heated at 50°C to allow complete dissolution of the reagents.

##### Analysis of Calibration Standards

1. For analysis using GC-AED, 25 µL of the calibration oil was diluted with 1 mL of cyclohexane. Then, the diluted samples were measured by GC-AED (HP 6890 GC systems attached with G2350 A Atomic Emission Detector)

1 µL of the sample was injected by the automatic liquid sampler, with splitless injection mode, and the analyzing column was HP-5 (250 µm ×30 m from Agilent). The temperature of injection was 280 °C and the column temperature was initially at 60 °C, which was ramped to 200 °C at 8 °C/min and then to 310 at 20 /min.

The same conditions were used to measure the amount of sulphur compounds in the spiked solutions.

2. For GC-MS analysis, 10 mL of the standard oil samples were extracted by 1 mL of methanol. 1 µL of the methanol extract was injected in the GC-MS (Agilent 7890 A GC System) using the automatic liquid sampler. The analyzing column was HP-5 (250 µm ×30 m from Agilent). The temperature of injection was 250 °C and the column temperature was initially 60 °C, which was ramped to 220 °C at 10 °C/ min and then to 320 at 15 °C/min. The same conditions were used to measure the amount of sulfur compounds on the spiked solutions.

**Note:** Only DBS and DBDS were extracted by the methanol.

The selected ion monitoring (SIM) method was used for analyzing the different sulfur compounds.

## Analysis of Insulating Oil Samples for Sulfur Compounds

### Reagents

All chemicals and solvents used were reagent grade or better. For ECD analysis the solvent was pesticide grade.

### Analysis for DBDS by GC-ECD

#### Sample Preparation

One hundred microliters of oil were diluted with isooctane. A sample of the diluted oil was transferred to a vial, capped and placed in the liquid autosampler. The amount injected for analysis was 1  $\mu$ L using the following conditions.

Instrument: HP 5890 A GC with automatic liquid sampler  
Detector: ECD  
Column: Narrow Bore DB5 (250  $\mu$ m  $\times$  30 m)  
Carrier: Ar/methane,  
Injector: 300  $^{\circ}$ C; Splitless  
Detector Temp: 320 $^{\circ}$ C;  
Oven Temp: 120  $^{\circ}$ C with no retention, to 285  $^{\circ}$ C at 25  $^{\circ}$ C/min, then to 320 C at 25 C/min, with a hold time of 2 minutes  
Volume injected: 1  $\mu$ L

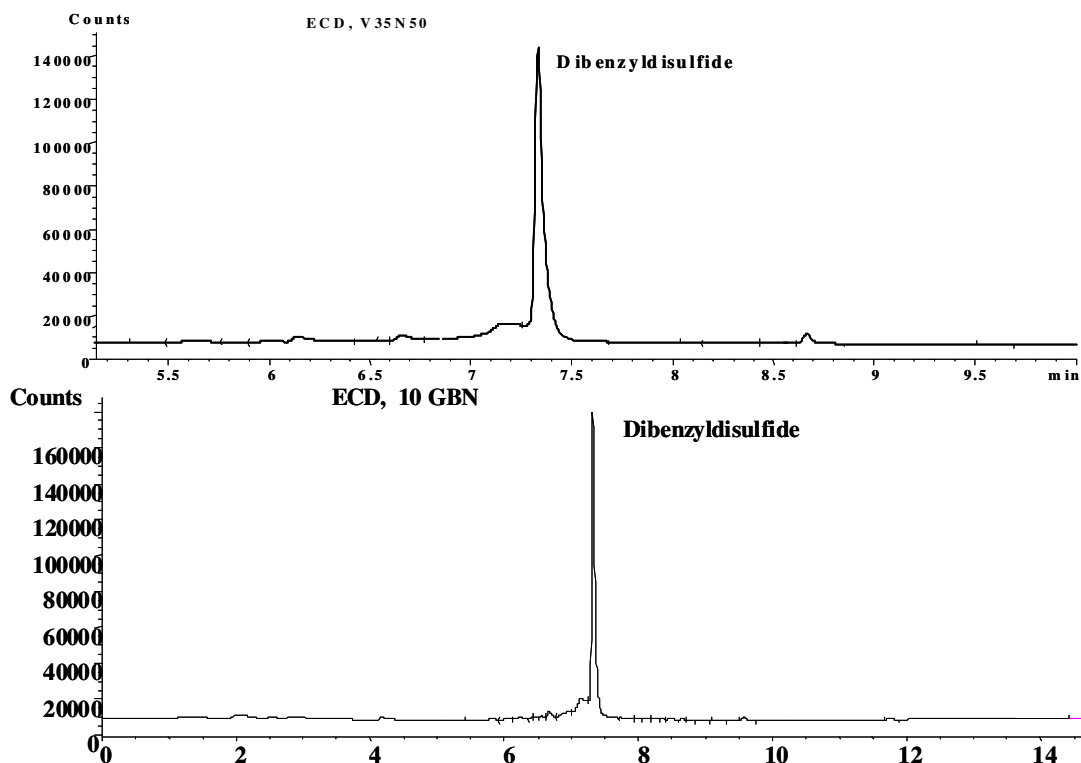
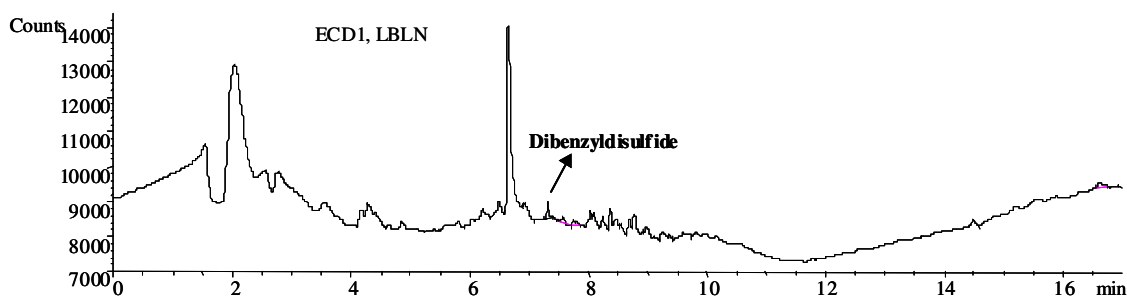


Figure C1. GC-ECD Chromatograms of DBDS in Unaged Voltesso 35 oil (top) and aged Nynas oil (bottom)



**Figure C2. GC-ECD Chromatogram of DBDS in aged Oil**

**Analysis for DBDS, DBS by GC- MS**

Sample Preparation

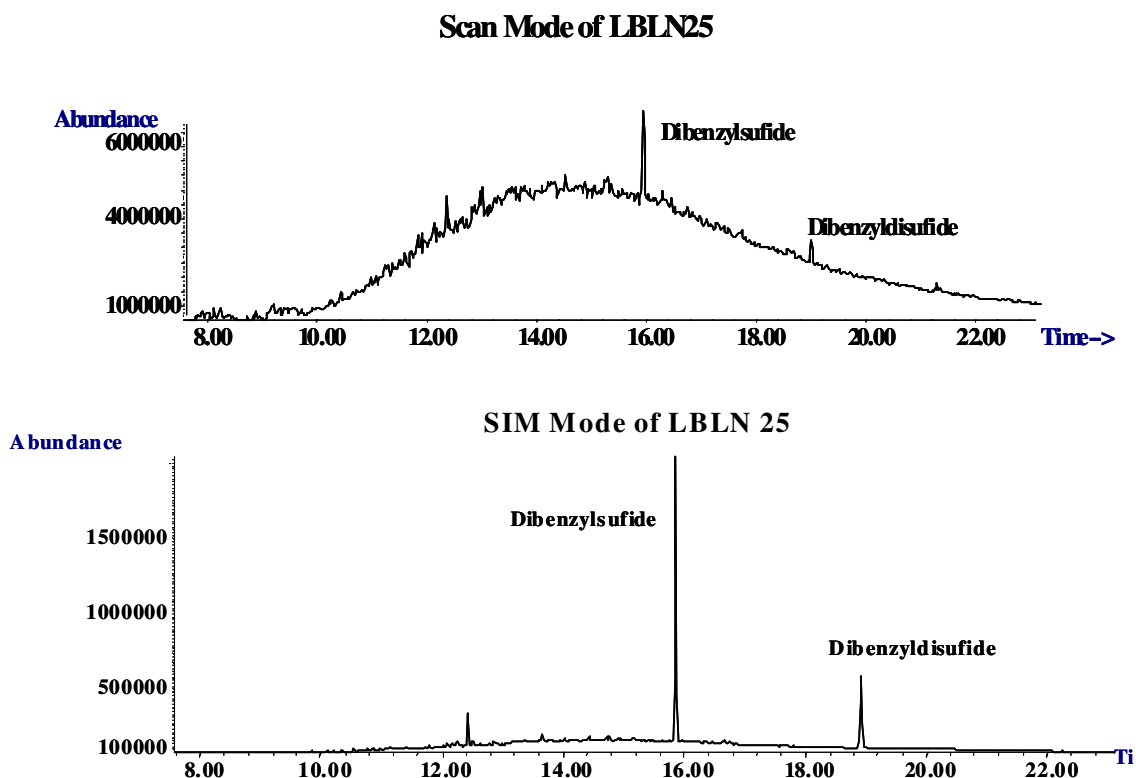
For GC-MS analysis, 10 mL of the standard oil samples were extracted by shaking with 1 mL of methanol. 1  $\mu$ L of the methanol extract was injected in the GC-MS (Agilent 7890 A GC System) using the automatic liquid sampler. The following conditions were used.

- Instrument: Agilent 7890 GC with automatic liquid sampler
- Detector: MS (5975 C, Inert XL MSD)
- Column: HP-5 (250  $\mu$ m  $\times$ 30 m)
- Carrier: He,
- Injector: 250  $^{\circ}$ C; Split, Solvent delay: 1.5 minutes
- Detector Temp 230  $^{\circ}$ C
- Oven Temp: 60  $^{\circ}$ C with no retention time, to 220  $^{\circ}$ C at 10  $^{\circ}$ C/min, then to 320  $^{\circ}$ C at 15  $^{\circ}$ C/min
- Volume injected: 1  $\mu$ L

**Note:** Only DBS and DBDS were extracted by the methanol.

The standards and samples were analyzed using selected ion monitoring (SIM) method using the conditions below.

Mass range:	15 to 1000 (SCAN)
Monitoring Ions (M/Z, SIM)	
1,2-Diphenylethane	91, 182
Dibenzyl sulfide	91, 214
Dibenzyl disulfide	91, 246
Octadecyl sulfide	83, 286
Di-n-decyl sulfide	173, 314



**Figure C3. GC-MS Analysis of 25ppm of selected sulfur compounds added to new oil; Total ion chromatogram (top), selected ion chromatogram (bottom)**

#### **Analysis of DBDS and Other sulfur Compounds by GC-AED**

The oil samples were prepared and analyzed using the same conditions as the calibration standards. The amount of each compound present in the samples was determined by comparing the peak area of each compound from the samples to that of the standard.

#### Sample Preparation

For analysis using GC-AED, 25  $\mu\text{L}$  of the standard oil was diluted with 1 mL of cyclohexane. The diluted standards were analyzed by GC-AED (HP 6890 GC systems attached with G2350 A Atomic Emission Detector) at the following conditions.

- Instrument: HP 6890 GC with automatic liquid sampler
- Detector: AED (G2350 A), sulfur mode
- Column: HP-5 (250  $\mu\text{m}$   $\times$  30 m)
- Carrier: He, N<sub>2</sub>
- Injector: 280 °C; Splitless
- Detector Temp: 300 °C
- Oven Temp: 60 °C with no retention time, to 200 °C at 8 °C/min, then to 310 C at 20 C/min
- Volume injected: 1  $\mu\text{L}$

AED, Sulfur 181, V35N50

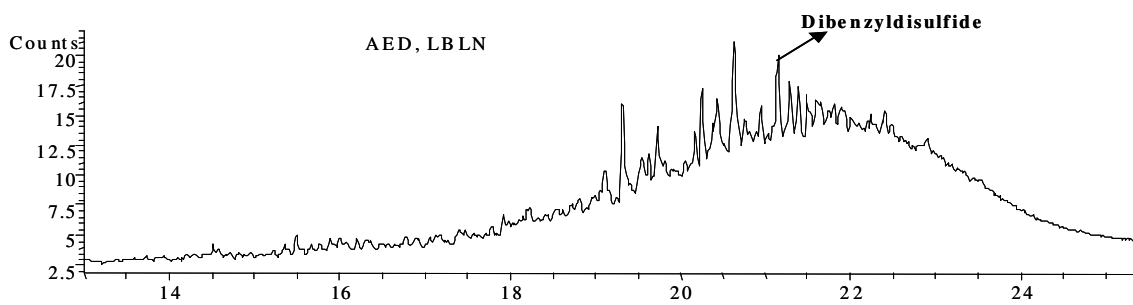
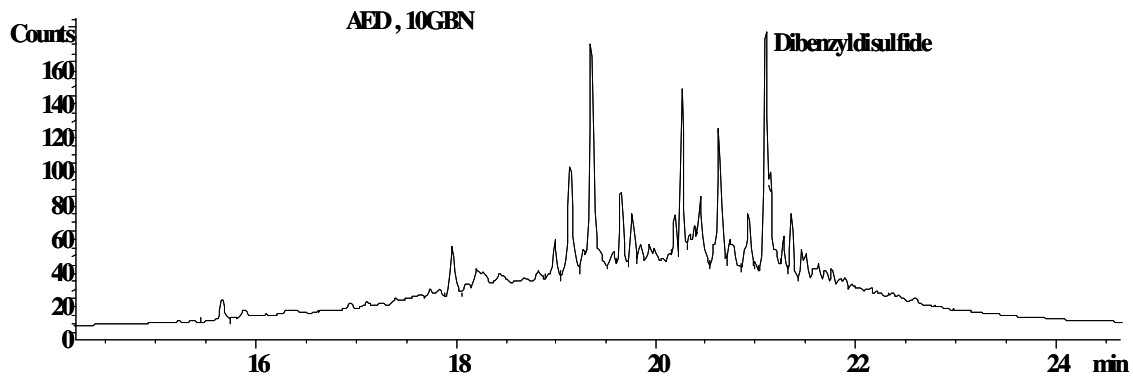
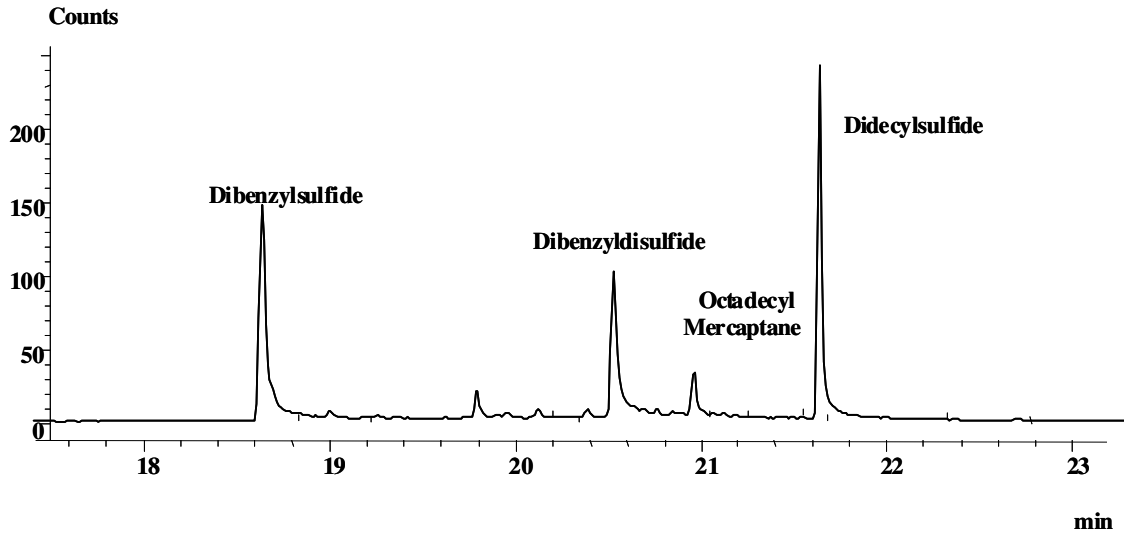


Figure C4. Analysis of sulfur compounds by GC-AED; Chromatogram of selected sulfur compounds in new oil (Top), Chromatogram of DBDS in aged Nynas oil (Middle), and Chromatogram of DBDS in new oil from Laborelec (Bottom)

Analysis for Total Sulfur Content by Inductively Coupled Plasma (ICP)

Sample Preparation

The total sulfur content was measured using the ICP (Vista-MPX, CCd Simultaneous ICP-OES). 2 g of the oil samples were diluted with Conostan Oil Analysis Standard PremiSolv ICP solvent and then analyzed by following the ASTM D5185 method.

## Methods of Analysis

### LABELEC – EDP Group -Insulating Materials Department

#### METHOD FOR THE DETERMINATION OF DIBENZYLDISULFIDE IN TRANSFORMER OIL

##### GC-method

GC Thermo - Chromatograph

Injection volume - 1  $\mu$ l

Syringe size - 10 $\mu$ l

Splitless Injection

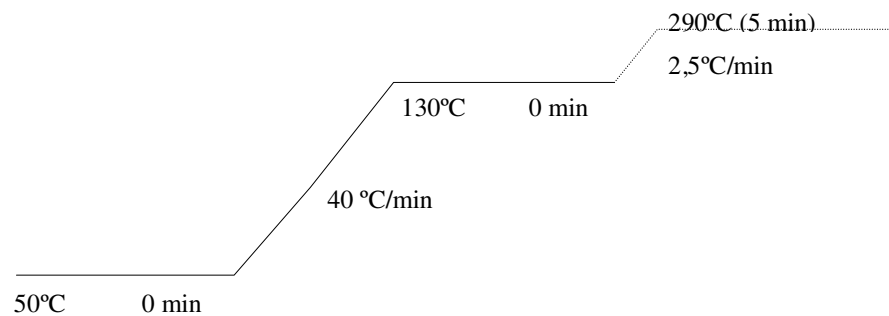
Carrier gas - He

Flow - 1 ml/ min

**Column** – Reference: - Thermo TR 5 Ref<sup>o</sup> 260-3154P - - 350°C - máx temperature.

Column type: - Capillary 60.0m x 0,25mm x 0.25 $\mu$ m

##### Oven



Equilibration Time 3.00 min

##### ECD

Heater 350°C

Make up N<sub>2</sub>

##### Procedure

- 0.1g oil
- 10 ml Isooctane

##### Standard Solutions

Standard solutions of Dibenzyldisulfide are prepared in blank insulating oil, between the following concentrations: 10 to 350 mg/kg.

##### Reagents

- Isooctane , p.a.

- Dibenzylsulfide From SIGMA-ALDRICH, Reference B21805-100G.
- Blank oil - Oil free of Dibenzylsulfide (for example Shell Diala S).

## Methods of Analysis

### ABB POWER TRANSFORMERS

Prepared by Hans Önnnerud for CIGRE A2-32-03 RRT spring 2008

### METHOD TO DETERMINE SUM OF MERCAPTAN AND DISULPHIDE SULPHUR

#### Apparatus

The apparatus used comprises a titration vessel with a magnetic stirring device, a 10 ml burette, an Ag/Ag<sub>2</sub>S electrode, a pH electrode used as reference, a pH-meter or a high quality digital voltmeter and basic glassware and laboratory equipment.

#### Chemicals

The chemicals used are isopropanol, glacial acetic acid, silver nitrate, zinc granules, distilled water and argon gas. All chemicals are of *pro analysi* quality or equivalent grade.

#### Titrant

The titrant used should be a fresh 0.5 mM AgNO<sub>3</sub> solution in isopropanol, e.g. 1 ml of 0.1 M AgNO<sub>3</sub> is diluted to 200 ml using isopropanol (0.1 M AgNO<sub>3</sub> can be prepared by dissolving 16.99 g AgNO<sub>3</sub> in 1000 ml of water). The titrant flask should be covered with alumina foil for the protection from the daylight. A standard of octadecylmercaptan in mercaptan-free oil corresponding to about 70 µg S/g oil is prepared (for example, 54.6 mg octadecylmercaptan can be dissolved in 87 g oil).

#### Procedure

Between every titration the Ag/Ag<sub>2</sub>S electrode should be polished gently using fine abrasive paper and washed with isopropanol. All equipment that is put in the titration vessel for each sample should be rinsed with isopropanol before (electrodes, burette tips and argon gas hose). The titrations are performed under an Argon gas curtain as well as the reductions.

#### Conditioning titrations

The titrations are started by performing three conditioning titrations. 30 ml isopropanol and three drops of the octadecylmercaptan standard are put in the titration vessel for titration. The shape and inflection point of the titration curve is monitored and should give a distinct, typical for titrations, inflection point.

#### Standardisation

The standardisation of the 0.5 mM AgNO<sub>3</sub> solution are performed by weighing the octadecylmercaptane standard in oil to four decimals in a titration vessel (about 1 g). 30 ml of isopropanol, 150 µl acetic acid and a magnetic stirring bar are added. This is followed by the titration and calculation of the concentration of the titrant.

#### Reagent blanks

Before the samples are titrated two reagent blanks are titrated. The reagent blanks are prepared by mixing 3 ml methanol, 150 µl acetic acid and 0.1 g zinc granules in a 20 ml headspace vial. The air is removed by allowing a gentle stream of Argon to be passed just above the surface of

the solution for a few minutes. The headspace vial is capped using a butyl cap. The capped vial is put on a shaking table for 30 minutes (frequency 200 rpm). When the shaking is finished, the vial is decapped and immediately rinsed with three portions of 10 ml isopropanol with each portion being successively transferred to the titration vessel. The zinc granules are not transferred to the titration vessel. The reagent blank titrations are performed directly after all of the solvent was transferred to the titration vessel.

### Samples

The titrations of the samples are performed by weighing 1 g of oil sample (to four decimals) in a 20 ml headspace vial. 3 ml of methanol, 150 µl acetic acid and 0.1 g zinc granules are subsequently added. The reduction was performed in analogy to the procedure above for the reagent blank titrations followed by the titration.

### Calculation

The calculation of the total amount of disulphides and mercaptans in the oil sample are performed by taking the volume of the titrant for the sample and subtract this volume with the average value for the titrant volumes for the reagent blank titrations. This corrected titrant volume was used in the calculation of the amount of total disulphides and mercaptans in the oil. The reported amount is expressed as µg S/ g oil.

### **Notes:**

- 1) During the method development work it was discovered that plastic disposable titration vessels were convenient to use and that the repeatability was improved by this type of equipment.
- 2) For samples having a lower amount of the sum of disulphides and mercaptans (<20 ppm) a better repeatability for the method could be obtained by increasing the sample amount titrated from 1 g oil to 3 g oil and also increasing the amounts of methanol, acetic acid and zinc granules by the same factor.