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This is the author's manuscript				
Original Citation:				
Availability:				
This version is available http://hdl.handle.net/2318/133694 since 2016-08-22T09:58:49Z				
Published version:				
DOI:10.1109/TDEI.2013.6508759				
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This is an author version of the contribution published on:

R.M. De Carlo; M.C. Bruzzoniti; C. Sarzanini; R. Maina; V. Tumiatti (2013) **Copper Contaminated Insulating Mineral OilsTesting and Investigations ,** IEEE TRANSACTIONS ON DIELECTRICS AND ELECTRICAL INSULATION (ISSN:1070-9878), pp. 557- 563. Vol. 20.

DOI 10.1109/TDEI.2013.6508759

The definitive version is available at:

http://ieeexplore.ieee.org/stamp/stamp.jsp?tp=&arnumber=6508759&isnumber=6508734

## Copper Contaminated Insulating Mineral Oils—Testing and Investigations

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#### ABSTRACT

Reactions between the liquid insulation and the copper conductors in power transformers and other electrical apparatus may lead to the formation of dissolved and suspended copper in the insulating oil. In this work a study concerning the correlation between the copper form and the dielectric properties of the fluid is presented.

In particular, to determine the total copper content in oil and consequently to discriminate by subtraction the presence of particulate copper, we optimized a method of oil mineralization. Moreover, by filtering the oils with PTFE filters (0.45, 1 and 5  $\mu$ m), the dimension of suspended copper content has been quantified and discriminated from the dissolved one: in such way, we investigated the influence of particulate copper on the characteristics of the oils and we determined the physical form that mostly affect the dielectric properties.

Index Terms — Copper in oil analysis, dielectric losses, transformer oil, transformers.

## **1 INTRODUCTION**

IN the last 15 years the problem of copper compounds formation within the insulation (mostly paper) of power transformers and shunt reactors was widely investigated due to the increased number of failures induced by the formation of copper sulfide [1, 2]. Being copper sulfide an insoluble product, the presence of detectable copper species in the insulating oil was not considered as a diagnostic tool to evaluate the oil's corrosiveness. In fact, the absence of correlation between copper in oil and presence of corrosive sulfur compounds was already demonstrated [3]. Nevertheless, many insulating oils suffer the problem of copper contamination to an extent that may vary from few mg/kg to hundreds mg/kg, and copper formation in transformer oil was investigated by some researchers [3, 4, 5]. Insulating oil behavior may be affected by this contamination, and advanced analytical tools are required to investigate the forms in which copper is present in the oil, and how they are capable to jeopardize the oil's dielectric properties.

The presence of conductive compounds, originating by polar

and acidic substances derived by oil aging, and by metallorganic species resulting from corrosion phenomena, cause an increase of the dielectric dissipation factor (tan  $\delta$ ). This phenomenon, related to the increased conductivity of the oil, is determined by the charge carriers within the oil. A decrease of the interfacial tension (IFT) is also often associated to the formation of conductive compounds. These trends may result in a significant worsening of the oil's insulating characteristics, with consequent risk of equipment's damage and even failure events. Therefore, maintenance and control of insulating fluids are regulated through international and national standards. The IEC 60422 guideline [6] sets the tan  $\delta$ threshold value from 0.2 to 0.5 (depending on the type and rated voltage of the equipment). Beyond this value, a maintenance action is necessary to restore good oil conditions, whereas at normal operative conditions the electrical conductivity and the dissipation factor, must be close to zero. During oil aging, and mostly in case of overheating, the number of radicals and the concentration of polar compounds increase as well as the magnitude of dielectric loss of the insulating liquid. The dielectric loss is a function of the type, concentration and mobility of the charge carriers. In addition, the increase of temperature causes a decrease of oil viscosity and, consequently, a decrease of the resistance to ions movement. Since the conductivity losses directly

depend on the movement of ions in the medium, an inverse relation exists between conductivity and oil viscosity.

Previous studies [4] have related the presence of copper metallorganic compounds to an increase of the polar character and tan  $\delta$  of mineral oils. Nevertheless, no hypothesis assessed whether the consequent worsening of dielectric properties is to be ascribed to the suspended (insoluble polar particles) or to the soluble (metallorganic soluble complexes) fractions.

In this work we have investigated the presence of metal (copper) both in the soluble and the particulate form in an heterogeneous group of oils from transformers in service. Then, we correlated the physical form (dissolved or insoluble), in which copper is present in these samples with the dielectric losses (tan  $\delta$  at 90°C) and interfacial tension of the same oils.

## 2 EXPERIMENTAL

#### 2.1 INSTRUMENTS

For copper quantification a 710-ES Varian (Lexington MA, USA) Inductively Coupled Plasma – Optical Emission Spectrometer (ICP-OES) was used. The spectrometer is provided with a radio frequency generator (40 MHz) and a Charge Coupled Device detector. For aqueous solutions, sample introduction was performed by a glass cyclonic spray chamber and a concentric glass nebulizer, whereas for organic sample, a Sturman-Masters spray chamber was coupled with a V-groove nebulizer. To facilitate the analysis of volatile organics, an AGM-1 (Auxiliary Gas Module) was used. The instrumental conditions used for analysis of organic and aqueous samples are summarized in Table 1.

Parameter	Organic setting	Aqueous setting	
Plasma power (kW)	1.5	1.35	
Plasma flow (l/min)	16.5	13.5	
Nebulizer pressure (k Pa)	110	200	
Instrument stabilization delay (s)	40	30	
Sample uptake (s)	40	30	
Acquisition wavelength (nm)	324.7 ar	nd 327.4	
Argon auxiliary flow (l/min)	1.5		
Replicate reading time (s)	5		
Sample aspiration rate (rpm)	15		
Rinse time (s)	3	0	

 Table 1. ICP-OES conditions for copper determination

A MLS 1200 MEGA Milestone (BG, Italy) digestion system was used to mineralize the 16 oils sampled from in service transformers. The microwave digestion system was equipped with sealed, pressure-proof, PTFE containers (bombs).

Polytetrafluoroethylene (PTFE) 0.45  $\mu$ m Durapore, 1 $\mu$ m FALP and 5  $\mu$ m Mitex membrane filters (25 mm, Millipore, MA, USA) were used.

A XP205DR semi-micron (5 decimal digits) balance (Mettler Toledo, Greifensee, Switzerland) was used to weigh the oils before mineralization.

A K11 Kruss (Hamburg, Germany) tensiometer, with platinum ring, was used to measure the interfacial tension (IFT).

A DTL Baur (Sulz, Austria), pre-programmed at 90 °C, according to the IEC 60247 method was used to measure the dissipation factor (tan  $\delta$ ).

#### 2.2 CHEMICALS

#### Organic copper solutions

Organic copper standard solutions were prepared in a copper-free transformer oil (Nytro Libra, Nynas, Stockholm, Sweden) from a 5000  $\mu$ g/g organo-metallic reference standard copper in hydrocarbon oil at 75 cSt (Accustandard, CT, USA). Metryk 180 (Brenntag, Belgium), commonly named isopar, was used to dilute Cu solutions and oil samples.

Chromasolv HPLC water (Panreac Quimica, Barcellona, Spain) was used for dilution of aqueous standards and samples. Nitric acid (65%, Panreac, Spain) and hydrogen peroxide (30%, Fluka, MO, USA) were used for mineralization step. Aqueous copper standard solutions were prepared from a  $100\mu$ g/ml ICP Multi-Element standard (AccuTrace Reference Standard, CT, USA).

Oil samples

Sixteen oils were sampled from in-service transformers to study the effect of the presence of copper species on the dielectric properties. All of them were uninhibited. The sampled oils presented different characteristics according to the year of production (1973 – 1993), and manufacturer. The different provenience, service conditions and aging allowed us to obtain a more heterogeneous data set. The oils were chosen on the base of the available historical information about their copper content, detected by an optimized ASTM D 7151 method [7], to cover a 1-30 mg/kg range of copper contamination (Table 2). *Agip ITE360* and *Rol OIL P-T* are specific brand names of insulating mineral oil in the market; where the actual oil type is not specified because the information was not available.

**Table 2.** Characteristics of the oils sampled from transformers in service

	Transformer		Oil Data			
Oil	D	ata				
#	Year	Power	Type/ Name	P/	TAN	$H_2O$
		(MVA)		Ν	(mg/g)	(mg/kg)
1	1973	85	Mineral oil	Р	0,163	10-15
2	1973	85	Mineral oil	Р	0,13	12-20
3	1985	18	Mineral oil	Ν	0,015	5-8
4	1989	25	Mineral oil	Ν	0,10	8-13
5	1989	27	Mineral oil	Ν	n.a.	n.a.
6	1993	18	Mineral oil	Ν	0,015	4-9
7	1989	42.3	Agip ITE360	Р	0,065	8-12
8	1991	1.6	Agip ITE360	Р	0,085	35-50
9	1988	14.5	Agip ITE360	Р	0,045	12-15
10	1992	18	Agip ITE360	Р	< 0,01	3-8
11	1992	18	Agip ITE360	Р	< 0,01	5-10
12	1989	12.7	Agip ITE360	Р	0,03	4-8
13	1989	12.7	Agip ITE360	Р	0,013	2-6
14	1999	1.6	Rol OilLP-T	Ν	0,045	17-22
15	1989	42.3	Agip ITE360	Р	0,065	35-45
16	n.a	n.a	n.a	n.a	n.a.	n.a.

n.a. = Data not available; P/N = Paraffinic/Naphtenic; TAN = Total Acidity Number,  $H_2O$  = moisture content

## 2.3 MINERALISATION PROCEDURE

ASTM D7151 method cannot by itself discriminate the

soluble metal forms from the small metal particles. Moreover, the direct injection ICP technique does not allow the determination of heavier particles, that are lost in the nebulizer due to their excessive mass. The actual size of particles that the device is not capable to nebulize depends on the type of nebulizer: the most effective is usually the V-groove type, which was the one used in this study.

For the above mentioned reasons, a microwave assisted digestion method was applied to quantify total copper content in oil (including the insoluble forms).

In the optimized method, 0.15 g of oil were mineralized in the PTFE bomb, with 2 ml of nitric acid and 0.5 ml of hydrogen peroxide solution, increasing the microwave power from 250 W to a maximum of 500 W, for a total duration of 35 minutes (5 steps).

After digestion, the solution was diluted with water up to 5 ml, and directly measured by ICP-OES in the aqueous configuration. Before and after use, the bombs were cleaned with concentrated HNO3 (5 ml) using the washing program recommended by the manufacturer (10 min, 500 W, followed by 10 min venting).

## **3 RESULTS AND DISCUSSION**

## 3.1 TOTAL COPPER CONTENT BY MINERALIZATION

The ICP-OES technique directly applied on diluted oils cannot measure the metal present as particles too big to be nebulized, even using a Babington or a V-groove nebulizer. Consequently, if the determination is carried out following ASTM D7151 method [8], just the dissolved copper species (which may originate from reactions between oil and copper promoted by overheating), and a portion of the particulate metal (generally captured by the sludge produced by oil's oxidation and degradation) can be determined. Even in the case that copper containing metallorganic complexes are trapped in the sludge, they may be undetected by ASTM D7151 based methods due to the relatively high diameter of sludge particles. This results in a possible underestimation of the actual total copper content. From an analytical point of view, it is well known that the ICP response decreases with increasing particle size of the metal present in the sample to be analyzed. In fact, large particles are difficulty nebulized and carried into the sample excitation zone. Also, the spreading of copper determination results has been found to increase in oil with high metal particle content [7, 9]. Considering the importance to accurately quantify copper content in oil while monitoring the insulating liquid condition, in this work we developed a microwave assisted mineralization method, prior to ICP analysis of the resulting aqueous solution, to evaluate also the presence of suspended particles larger than those detectable by direct ICP analysis.

Since microwaves cause molecular motion by means of migration of ionic species and/or rotation of dipolar species, the microwave heating of a material depends, to a great extent, on its "dissipation" factor, that is defined as the ratio between the dielectric loss (or "loss" factor) and the dielectric constant of the material. Transformer oils, belonging to the class of insulators, (thus expected to have very low tan  $\delta$ ) are not easy to be mineralized. Therefore we developed a digestion protocol for mineral oils, optimizing mineralization time, microwave power, sample weight and final volume of digested solution (Table 3). For this purpose, we used Nynas Nytro Libra oil spiked with 1, 10 and 30 mg/kg organometallic copper.

Table 3. Optimization of the microwave assisted digestion protocol §

Test	Program		D' ('	Sample	Final	
#	Power	Time	Digestion	weight	volume	Comments
#	(W)	(min)	solution	(g)	(ml)	
1	100	1	0.8 ml HNO <sub>3</sub> 0.2 ml H <sub>2</sub> O <sub>2</sub>	0.1	-	Not digested
2	250	1	0.8 ml HNO <sub>3</sub> 0.2 ml H <sub>2</sub> O <sub>2</sub>	0.1	-	Not digested
3	250 0 250	1 1 5	0.8 ml HNO <sub>3</sub> 0.2 ml H <sub>2</sub> O <sub>2</sub>	0.1	-	Not digested
4	250 0 250 400 500	1 1 5 5 5	2 ml HNO3 0.5 ml H2O2	0,1	10	Almost digested, but formation of a cloudy solution
5	250 0 250 400 500	3 2 10 10 10	2 ml HNO3 0.5 ml H2O2	0,1	10	Digested
6	As test # 5			0,15	5	Digested
§р.	§ Dearth and the answer 5 and UNO thread at 500W for 10 and					

**Table 4.** Copper concentrations ([Cu]) after samples mineralization

Oil #	[Cu], mg/kg * Without mineralization (optimized ASTM D7151)	[Cu], mg/kg After mineralization	[Cu] RSD% <sup>§</sup> After mineralization	Relative increase of [Cu] After mineralization
1	31.9	37.4±0.9	2.5	+ 17%
2	27.9	32.0±0.5	1.7	+ 15%
3	1.9	2.5±0.1	5.0	+ 35%
4	18.4	22.0±2.8	12.6	+ 20%
5	7.3	9.6±0.4	4.7	+ 31%
6	0.4	$1.6\pm0.3$	19.5	+ 300%
7	3.1	3.8±0.7	19.6	+ 21%
8	12.9	39.4±0.6	1.5	+205%
9	13.4	14.9±0.2	1.0	+ 11%
10	7.1	8.2±0.9	11.2	+ 16%
11	7.9	8.9±0.3	3.5	+ 13%
12	7.0	10.1±1.3	13.8	+ 44%
13	1.9	5.5±0.3	5.6	+ 187%
14	5.7	9.0±0.5	5.8	+ 60%
15	6.8	8.0±0.4	5.1	+ 17%
16	1.2	1.9±0.2	8.6	+ 55%

\* Copper without mineralization was obtained as the average of 15 replicates; the relative standard deviations range from 6.6% to 28.4%

<sup>§</sup> RSD has been obtained as the result of 3 replicates

The obtained results (tests #1 to #3 as described in Table 3) showed that a 0.8 ml HNO<sub>3</sub> + 0.2 ml H<sub>2</sub>O<sub>2</sub> solution does not provide oil digestion even setting 250 W as starting microwave power and keeping it for 5 min. By increasing the acidity and

the oxidation capabilities of the solution through a 2 ml HNO<sub>3</sub> + 0.5 ml  $H_2O_2$  solution, and by increasing the microwave power up to 500 W (tests #4 and #5), a digested and clear solution can be obtained. The oil matrix can be digested, even increasing its amount (0.15 g) and reducing the nitric acid-hydrogen peroxide solution to 5 ml, thus enhancing instrumental ICP-OES detection limit for copper.

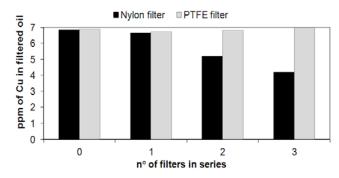
The optimized method (test #6 in Table 3) was then applied to mineralize the 16 sampled oils (0.15 g each). The resulting solution was diluted with water up to 5 ml, and analyzed for copper content by ICP-OES (aqueous configuration).

The results of copper content obtained by this procedure are reported in Table 4. The reported relative standard deviation for each sample results from 3 replicates. The same 16 samples were also tested accordingly with optimized method ASTM D7151 [7], in order to compare the copper content with and without the mineralization procedure. As results in Table 4 illustrate, copper concentration is systematically augmented, even if each oil shows a different relative increase of detected copper content. This indicates that in all of the tested oils at least part of the present copper is in a form that is not detectable with ASTM D7151 (i.e. without sample mineralization). The increase in the resulting copper concentration may vary from 10% to 300% approximately.

#### 3.2 OIL FILTRATION

To assess the presence of particulate copper in oils, not detectable with direct ICP-OES analysis [4], we evaluated the so called "filterable copper" in the 16 used oils. Filters of different porosity (5, 1, 0.45  $\mu$ m) and composition (PTFE, Nylon) were tested. Since Nylon filters showed adsorption phenomena (decrease in copper concentration with increasing number of filters posed in series), as described by the graph in Figure 1, PTFE filters, that proved to be inert through the matrix, were chosen.

The amount of copper retained on filters was determined by subtraction between metal content measured by ICP-OES before and after filtration. The results after oil filtration are reported in Table 5.

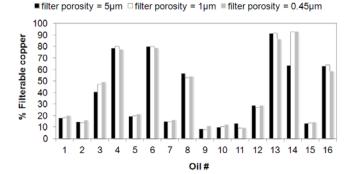


**Figure 1.** Fraction of copper retained by 0.45 nylon filters and 0.45 PTFE filters posed in series. Test performed on oil # 15.

As it can be perceived by the obtained concentrations, and from the calculated percentage of filterable copper reported in Figure 2, the majority of the tested oils contain a relevant filterable copper fraction, composed mainly by copper particles larger than 5  $\mu$ m. The only exception is oil #14, where the amount of filterable copper is markedly increased between the filtration on 5  $\mu$ m filter and the filtration on 1  $\mu$ m filter.

 Table 5. Copper concentrations ([Cu]) after samples filtration through different porpsity filters

different porosity filters					
Oil #	[Cu], mg/kg Without filtration (modified ASTM D7151)	[Cu], mg/kg Oil filtered through a 0.45 μm PTFE filter	[Cu], mg/kg Oil filtered through a 1.0 μm PTFE filter	[Cu], mg/kg Oil filtered through a 5.0 μm PTFE filter	
1	31.9	26.1	26.2	25.5	
2	27.9	23.9	24.0	23.5	
3	1.9	1.1	1.0	1.0	
4	18.4	3.9	3.6	4.1	
5	7.3	5.9	5.9	5.8	
6	0.4	0.1	0.1	0.1	
7	3.1	2.7	2.7	2.6	
8	12.9	5.6	6.1	5.9	
9	13.4	12.3	12.4	12.0	
10	7.1	6.4	6.3	6.2	
11	7.9	6.8	7.2	7.1	
12	7.0	5.0	5.1	5.0	
13	1.9	0.2	0.2	0.3	
14	5.7	2.1	0.4	0.4	
15	6.8	5.9	5.9	5.9	
16	1.2	0.5	0.4	0.5	

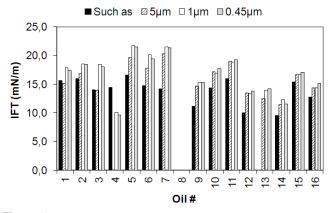


**Figure 2.** Fraction (%) of copper retained on different porosity filters for each tested oil. The percentage is calculated assuming as 100% the concentration measured according to modified ASTM D 7151 method.

## 3.3 CORRELATION BETWEEN COPPER CONTENT AND OIL PROPERTIES

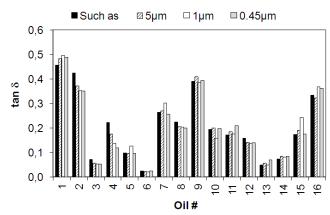
In order to verify whether copper physical form (dissolved or suspended) alters oil dielectric and physical properties or not, the interfacial tension (Figure 3) and the dielectric dissipation factor—tan  $\delta$  (Figure 4) of the 16 oils were measured both before and after filtration. Although it is well known that the presence of ionic species considerably reduces the insulating properties of transformer oils, at the best of our knowledge no study is present on the role of particulate forms in affecting insulation.

Since interfacial tension is inversely proportional to the presence of polar contaminants in the oil, the general increase of IFT values (Figure 3) observed for filtered fractions (more markedly enhanced for decreasing filter porosity) indicates an improvement of oil's condition after filtration. This behavior underlines that particles removed by filtration have a polar character; moreover, particles tend to precipitate and to accumulate at the interface between water and oil during the measurement, resulting in a decrease of the IFT. For oil labeled as 8, no data could be acquired, probably due to its particular cloudy appearance.



**Figure 3.** Interfacial Tension (IFT, mN/m) of the investigated oils before and after filtration on different porosity filters. Data for oil # 8 not available.

As far as dielectric dissipation factor (DDF) is affected by the presence of copper (see Figure 5), a direct correlation between the dissipation factor and the copper content is observable only for oils grouped in cluster A. Other three oils (namely numbers 7, 9 and 16, cluster B) can be grouped as oils with high tan  $\delta$  but relatively low copper content (< 15 mg/kg). This demonstrates that DDF is increased not only by the presence of metal, but also by other polar species, probably derived by oil oxidation. As highlighted by oil 8, high particulate copper content could also be not so detrimental of the dielectric properties. In fact, oil #8 belongs to cluster A (where tan  $\delta$  is directly related to copper concentration) if we consider the copper concentration measured. Otherwise, considering the total copper concentration (obtained after oil mineralization) the oil shows a tan  $\delta$  lower than expected on the base of the actual copper content.



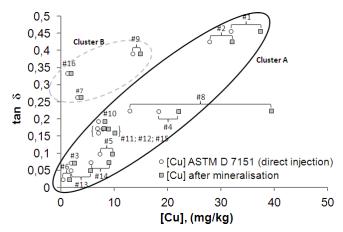
**Figure 4.** Dielectric Dissipation Factor (tan  $\delta$ ) of the investigated oils before and after filtration on different porosity filters.

This deduction was also confirmed by the evaluation of the dissipation factor trend after filtration (Fig. 4), that illustrates that copper removal by filtration does not significantly

improve the dissipation factor. In fact, significant variations in the DDF value were only observed for oils 2 and 4. Integrating this result with those coming from the filtration study, we can observe that oil 4 has a large percentage of filterable copper species, and this characteristic may explain the differences in DDF values after filtration. Nevertheless, other oils, which showed a similar variation in particulate copper, did not evidence appreciable decrease in tan  $\delta$  after filtration.

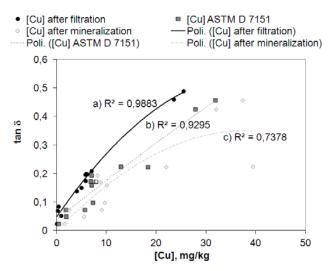
Therefore, we can state that the increase of dielectric losses for insulating mineral oils is mainly due to the soluble fraction of copper, whereas suspended copper forms, or particles, do not affect dielectric losses appreciably. These conclusions are consistent with the principle that the electrical conductivity,  $\sigma$ , and the dissipation factor, tan  $\delta$ , are determined by the charge carriers within the oil. Since the conductivity loss in a viscous medium results from the movement of ions, the conductivity of an oil is necessarily directly proportional to the number of ionic charge carriers present [10, 11]. Thus, ionic (soluble) forms of copper should be accounted for having a higher mobility within the oil, and for giving a contribution to oil's losses larger than suspended particles, even if conductive.

On the base of the above mentioned conclusion, the best correlation between copper content and DDF, in oils contaminated by copper, should be obtained when the DDF value is fitted against the soluble copper fraction. This is confirmed by the data depicted in Fig. 6, where the correlation factor  $R^2$  is reported for the three copper concentrations, respectively detected after oil filtration, on the oil as well, and after oil mineralization. The best correlation factor  $R^2$  is found between the copper after filtration (soluble fraction) and DDF values. For the same reason, the worst  $R^2$  is given by the correlation between the total copper content (after mineralization) and DDF values.



**Figure 5.** Clustering of oils: tan  $\delta$  against copper concentration obtained both with and without mineralization. Figures on the graph represent the oil's label (Oil #).

As a further demonstration of this statement, we investigated four additional oils sampled from transformers in service, with peculiar characteristics: two of them (labeled as *a* and *b*) have relatively high copper concentration and low tan  $\delta$ , while the other two samples (labeled as *c* and *d*) have both high copper concentration and high tan  $\delta$ . The four oils were filtered with a 0.45 µm PTFE filter, and copper content as well as DDF were measured before and after filtration. The obtained results, summarized in Table 6, are in agreement with our hypothesis, since oils *a* and *b* with low tan  $\delta$  exhibited a relevant amount of copper retained on the filter (>80%), confirming that, as supposed, the metal is mainly present in a particulate form, not affecting the tan  $\delta$ . In addition, oils *c* and *d* have a relatively low amount of copper retained on filter (<10%), so confirming that the high DDF has to be ascribed mainly to dissolved forms of copper. As already found in the previous experiments, no decrease in tan  $\delta$  was observed after filtration.



**Figure 6.** Correlation between copper concentrations and tan  $\delta$ . The three correlation factors,  $R^2$ , are calculated for copper concentration, [Cu] *vs* tan  $\delta$ , where [Cu] has been obtained: a) after filtration; b) following ASTM D 7151; c) after mineralization

- Regression curves equations:
  - a)  $-0,0003x^2+0,0225x+0,0463$
  - b)  $-0,00003x^2+0,014x+0,0383$
  - c)  $-0,0002x^2+0,0184x-0,0036$

**Table 6.** Correlation between filterable copper content and tan  $\delta$ 

	tan δ		[Cu], (1	Retained Cu	
Oil	Before filtration <sup>§</sup>	After filtration <sup>§</sup>	Before filtration <sup>§</sup>	After filtration <sup>§</sup>	(%)
а	0.0567	0.0534	2.6	0.5	80.7
b	0.0674	0.0680	9.1	1.0	88.6
с	0.3251	0.3241	10.8	10.0	6.7
d	0.3933	0.3853	4.8	4.4	7.8

<sup>§</sup> PTFE 0.45µm filter

## 4 CONCLUSION

New correlations between copper content in oil and insulating liquid conditions are presented in this work. At this purpose, the presence of suspended particles larger than those detectable by direct ICP analysis is investigated by a microwave assisted mineralization method and by oil filtration. The obtained results (copper concentration systematically increased with oil mineralization and relevant filterable copper fraction) indicated that a portion of copper content is present in a form not detectable with official methods (ASTM D7151), even as optimized in ref. [7] and other methods generally available in literature [5].

In order to monitor the insulating properties of transformer oils, a study concerning the role of particulate copper forms in affecting insulation is presented. In particular, IFT and tan  $\delta$ measured after oils filtration with filters of different porosity are investigated. The general increase of IFT values, observed for filtered fractions, indicated the improvement of oil's condition after filtration and showed the polar character of the removed particles, which size is sufficient to induce an accumulation of the same particles to the interface between water and oil during the measurement. Even if this may not be felt as important in actual operational conditions of insulating oil (where evidently water is not present in a free state), it must be considered that heavy particles may tend to precipitate and to accumulate in the active part (windings) of the transformer. On the other side, copper reduction by filtration did not significantly improve the dissipation factor, so demonstrating that, whilst suspended copper forms do not affect dielectric losses appreciably, soluble copper is the form that mostly influence the dielectric losses of the oil. The best correlation factor  $(\mathbf{R}^2)$  found between the copper content after filtration (soluble fraction) and DDF values further demonstrated that the increase of dielectric losses is mainly due to the soluble fraction of copper. The existing ASTM D7151 based methods do not give sufficient information to properly correlate copper content and tan  $\delta$ . Dissolved copper detected as described in this work gives better knowledge about how soluble copper species may detrimentally affect oil's dielectric properties. Moreover, filterable copper (partially undetectable by ASTM D7151) may give information on the presence of metallic or organometallic forms in which copper can increase the oil's oxidation rate by catalysis.

The existence of oils with high tan  $\delta$ , but showing a relatively low copper content (< 15 mg/kg), indicates that DDF is increased not only by the presence of metal, but also by other polar species, probably derived by oil oxidation.

In conclusion, the detection of copper in mineral oils should be carried out considering the form in which copper is present, and evaluating its correlation with the dielectric properties of the oil itself.

## ACKNOWLEDGMENT

R.M.D.C. thanks Sea Marconi Technologies (Italy) for hosting her in their laboratories. Dr. Marco Facciotti and Dr. Virginia Trento are also gratefully acknowledged for the support given.

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