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Determination of copper in liquid and solid insulation for large electrical equipment by ICP-OES. Application to copper contamination assessment in power transformers

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ABSTRACT

Copper is one of the main constituents of the components in power transformers and its presence both in liquid (mineral oil) and in solid (Kraft paper) insulators can lead to enhanced dielectric losses and to the subsequent deterioration of their insulating properties. Recently the latter have been correlated to plant failures which in turn may have severe impact on the environment. This paper describes the direct analysis of copper in insulating mineral oil by ICP-OES and how it was first optimized compared to the official American Society for Testing and Materials (ASTM) D7151 method. Detection and quantification limits of 8.8 $\mu g\ kg^{-1}$ and 29.3 $\mu g\ kg^{-1}$ were obtained. Secondly, copper determination was improved by coupling a microwave assisted dissolution procedure of the mineral oil which avoided the problems, in the real samples, due to the presence of solid species of copper which cannot be nebulized following traditional methods described in literature. Sixteen mineral insulating oils sampled from transformers in service were analyzed before and after dissolution. In order to evaluate copper speciation, size fractionation was performed by filtration on PTFE filters (0.45, 1 and 5 μm). This test was performed on all the oil samples. Finally, because of the key role of the solid insulator in failed transformers, the Authors applied the developed method to study the copper deposition tendency onto the insulating Kraft paper tapes exerted by two unused oils (a corrosive and a non-corrosive one) under defined ageing conditions.

1. Introduction

Large power transformers and reactors play a fundamental role in the production, transmission, distribution and industrial use of electric energy. Failures in transformers often have social, economic and especially environmental consequences, due to possible fire and/or explosion resulting in the introduction of pollutants in all the environment compartments. Mineral oil, the most common insulating liquid used for transformer impregnation, belongs to the class of dangerous waste [1]. In particular, in the case of polychlorobiphenyl (PCB) contaminated oil, environmental risks increase dramatically, also due to the possible formation of polychlorodibenzodioxins (PCDD) and polychlorodibenzofurans (PCDF) [2–7].

The main causes of a transformer breakdown or deficiency are over voltage or internal failures during service, and the degradation of the electric insulation (Kraft paper and oil). Furthermore, some damages have also been related to corrosion, chemical reactions which may occur between oil, copper conductors and paper [8]. Formation of copper by-products, dissolved or precipitated in the bulk oil, or deposited in the cellulose has been related to corrosion reactions [8,9].

Corrosion phenomena involving insulating fluids and other materials present in the transformer, in particular copper and cellulose, have recently received attention due to the increasing number of unexpected cases of failure observed when in service and related to the accumulation of corrosion by-products on the insulating paper tapes within the transformer windings. The so called “corrosive sulfur” is the most important cause of corrosion caused by sulfur containing organic compound, in the insulating oil [10–12]. This family of substances forms partially conductive sulfur salts deposited on insulating paper tapes, thus worsening the dielectric properties of the solid insulation, a condition that can lead to electrical failure (short circuit) between the conductors. Moreover, the formation and the accumulation of copper sulfide on bare copper may in turn lead to the formation of

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conductive particulate in the oil, which can act as *nuclei* for electrical discharge.

The presence of metals (mainly copper) in mineral oils which do not contain corrosive sulfur based compounds, has also been related to sulfur free corrosion processes. The presence of copper in oil causes an increase of the dielectric dissipation factor (tan δ), and a decrease of the interfacial tension (IFT), with a consequent worsening of oil insulating characteristics. Moreover, dissolved copper may act as a catalyzer in the oxidative degradation of insulating oils. Studies have highlighted the oxidative role of metals in oxidative degradation of automotive oils [13] as well.

The characterization of the forms in which the metal is found (dissolved or suspended) is important to understand the corrosion phenomena involved, and possibly to mitigate them. Nevertheless, to the best of our knowledge, there is no study characterizing the metal species present in oil in service. Such a characterization is of great importance in understanding if the worsening of dielectric properties is to be ascribed to the suspended (polar particles containing insoluble metal) or to the soluble fraction (metal dissolved in oil as metallorganic salts or complexes). Moreover, a reliable method for the quantification of metals in oil would be an important diagnostic tool and for the control of electrical equipment conditions.

Many studies underline the difficulties involved in the detection of metals in organic samples, which are mostly ascribed to the viscosity of the sample and to the complexity of the matrix. Brandão et al. [14] and Bakkali et al. [15], recently used electrothermal atomic absorption spectrometry (ET-AAS) to detect trace metals in petroleum and in vegetables oil. They overcame the problem using a chemical modifier (Triton-X) and sample pretreatment by microwave digestion respectively. ET-AAS, coupled with an emulsion pre-treatment step with cetyltrimethylammonium bromide (CTBA), was used for the determination of copper in gasoline [16]. Furthermore inductively coupled plasma atomic emission spectrometry (ICP-AES) is used to quantify metals in edible oils, but a pre-treating step with Triton-X is necessary to obtain an emulsification [17]. In spite of the low detection limits achievable with these techniques, the methods are time-consuming and too laborious to be applied in routine analysis. Another approach is sample dilution in suitable solvents. Aurelio et al. [18] diluted vegetable oil samples with 1-propanol and water, before direct analysis by ICP-AES. Nevertheless, the use of 1-propanol made both the introduction of sample and the plasma stabilization difficult in the afore mentioned case.

To quantify metals in insulating oils, Rodriguez et al. [19] proposed a spectrophotometric assay, in which absorption spectra of aqueous copper solution are registered between 470–550 nm. The complete procedure, that involves the extraction of metal from organic matrices, its reduction to Cu(I) and the formation of complexes with a mixture of bathocuproine- and bathophenantroline-disulfonic acids, is anyway very long and complex.

ASTM D7151 [20] is the official and most commonly used method for the above described purpose. In this procedure, the previously homogenized samples, are diluted with kerosene, and then analyzed by ICP-OES. The main drawback of this method is the difficulty to obtain a suitable viscosity, in the presence of kerosene, which causes unstable nebulizing and, finally, the plasma torch switches itself off.

The aim of this work was to improve the ICP-OES method with stable nebulization conditions, for the determination of copper in oil to be used in quality control of the insulating mineral oils throughout their useful life inside power transformers in service. An additional aim of the present work is the determination of the form (dissolved or suspended) in which copper is present in real aged oils from transformers in service. For this purpose, 16 used oils with different characteristics were sampled from transformers in service mainly in Italian and French electrical networks, analyzed and size fractionated. To overcome the problems arising from the different homogeneity of the mineral oils in service, a microwave assisted digestion procedure was also performed. The evaluation of copper content and the assessment of copper species is useful to be performed as a diagnostic tool whenever a worsening of dielectric properties of oils (IFT decrease and tan δ increase), not differently explainable, is observed.

As previously mentioned, since metals deposited and/or adsorbed by cellulose surfaces have a fundamental role in corrosion reaction [21], we also investigated the copper deposition processes on Kraft paper, the solid insulator in the transformer. For this purpose, a study on the “copper deposition tendency” (CDT test), was performed by quantification of Cu absorbed on the paper tapes wrapping Cu conductors, under different ageing conditions, to simulate the operative conditions of a energized transformer.

2. Experimental

2.1. Instrumentation

A 710-ES Varian (Lexington MA, USA) Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) was used for copper determination. The spectrometer had a radio frequency (RF) generator (40 MHz), a glass cyclonic (aqueous solutions) or a Sturman-Masters spray chamber (organic samples), a concentric glass (aqueous solutions) or a V-groove nebulizer (organic samples), and a Charge Coupled Device (CCD) detector. To facilitate the analysis of volatile organics, an AGM-1 (Auxiliary Gas Module) was used. When organic samples were analyzed, a small amount of oxygen was introduced into the plasma to improve the combustion of the matrix and to consequently avoid the deposition of carbon residues on torch capillaries. After evaluation of signal intensity and linearity, the oxygen flow rate was fixed at 4 mL min^{-1}, as the best compromise to keep the capillary clean without generating plasma instability and a decrease in sensitivity.

The instrumental conditions as optimized for analysis of organic and aqueous samples are summarized in Table 1.

A MLS 1200 MEGA Milestone (Bergamo, Italy) digester was used to mineralize the 16 real oils sampled from in service transformers. A CL10 centrifuge (Thermo Scientific Inc., USA) was used to separate the supernatant in the digested fractions. Puradisc Polytetrafluoroethylene (PTFE) 0.45, 1, 5 μm (Whatman, Kent, UK) and Econofilter Nylon 25/45 (CPS Analitica, Milan, Italy) 0.45 μm syringe filters were used.

A XP205DR semi-micron (5 decimal digits) balance (Mettler Toledo, Greifensee, Switzerland) was used to weigh the oils, the copper strips and the Kraft paper tapes.

Table 1
ICP-OES working conditions for copper determination in organic and aqueous samples.

Parameter	*Organic setting*	*Aqueous setting*
Plasma power (kW)	1.5	1.35
Plasma flow (L/min)	16.5	13.5
Argon auxiliary flow (L/min)	1.50	1.50
Nebulizer pressure (k Pa)	110	200
Replicate reading time (s)	5	5
Instrument stabilization delay (s)	40	30
Sample uptake (s)	40	30
Sample aspiration rate (rpm)	15	15
Rinse time (s)	30	30
Acquisition wavelength (nm)	324.7 and 327.4	324.7 and 327.4

2.2. Chemicals

2.2.1. Organic copper solutions

Organic copper standard solutions for ICP method optimization were prepared in a light mineral oil, (Sigma Aldrich, Milan, Italy, d (25 °C) 0.838 g mL^{-1}) from a 5000 μg g^{-1} organo-metallic reference standard copper in hydrocarbon oil at 75 cSt (Accustandard, CT, USA). Isopar M (Brenntag, Deerlijk, Belgium), a clear fluid consisting of a blend of high-purity synthetic isoparaffinic hydrocarbons with narrow boiling points ranges (225–255 °C), was used to dilute Cu solutions and oil samples.

2.2.2. Aqueous copper solutions

Chromasolv HPLC water (Panreac Quimica, Barcellona, Spain) was used during the preparation of standards and samples. Nitric acid (65%) was from Panreac; hydrogen peroxide (30%) was from Fluka (MO, USA). Aqueous copper standard solutions were prepared from a 100 μg mL^{-1} ICP Multi-Element standard (Accu-Trace® Reference Standard, CT, USA).

Isooctane (Panreac, Barcelona, Spain) and ACS grade cyclohexane (Sigma Aldrich, MO, USA) were used as cleaning solutions, to remove oil residuals from Kraft paper during CDT test.

2.3. Oil sampling

The 16 oils considered in this study were sampled from transformers in service mainly in Italian and French networks (Table 2); they were uninhibited-absence of phenolic antioxidant, accordingly to the International Electro-technical Commission (IEC) 60296 Standard- and have different characteristics according to the year of production (1973–1993), manufacturer and transformer rated power (1.6–85 MVA).

The oils used for the copper deposition tendency (CDT test, see further) were two naphthenic uninhibited unused oils, named Nytro Libra (Nynas, Stockholm, Sweden) and Mobilect 35 (Exxon-Mobil, Rome, Italy).

2.4. Oil mineralization and paper digestion procedure

Each of the 16 oils (0.15 g) was mineralized by microwave assisted digestion, using HNO_3 (2 mL) and H_2O_2 (0.5 mL), as described: 250 W for 3 min, 0 W for 2 min 250 W for 10 min, 400 W for 10 min and 500 W for 10 min. After digestion, the solution was diluted with water up to 5 mL, and measured by ICP-OES in the aqueous configuration.

Kraft paper tapes (3 cm length), obtained after CDT test (see further), were digested in sealed head-space vials (crimped with a silicone rubber septum and drilled by a needle to allow the release of mineralization steams) with 12 g of a mixture of HNO_3:H_2O_2 (5:2). Vials were sonicated at 40 °C for 3 h until complete mineralization. The solution was filtered (Nylon 0.45 μm) and centrifuged at 4000 rpm. Finally the supernatant was diluted 1:10 (w/w) with water and measured by ICP-OES.

2.5. Copper deposition tendency (CDT) on Kraft paper

12 g of Nytro Libra and Mobilect 35 oils containing three paper wrapped copper conductors were treated using accelerated ageing tests over different temperature and ageing periods in a oven; the explored range (100–180 °C) covered a temperature range from the nominal maximum temperature of a transformer in upper limit of operating conditions (about 105 °C, according to IEC Loading Guide IEC 60076) to temperatures which can be reached in moderate faulty conditions (Standard IEC 60599). The analysis was performed in 20 mL head space vials, crimped by a PTFE/butyl rubber septum and drilled with a needle 0.8 mm in diameter to allow a moderate oxygen inlet; this procedure was applied to simulate the presence of oxygen in the real transformers (*open breathing transformers*) and to increase the rate of deposition of copper onto the paper surface. After the ageing treatment, the paper was digested, treated as previously described (Section 2.4) and analyzed by ICP-OES (Table 1, aqueous setting).

Table 3
Solvent compositions tested for oil dilution during method optimization. Tests were performed in mineral light oil.

Solvent (composition)	Viscosity (cS)
1. Oil/Isopar (50:50)	3.14
2. Oil/Isopar (67:33)	4.60
3. Oil/Isopar (30:70)	2.39
4. Oil/Isooctane (50:50)	1.47
5. 50% Oil+Isopar/Isooctane (50:50)	2.07
6. Oil/Isooctane (70/30)	2.52
7. 60% Oil+Isooctane/Isopar (70:30)	2.30

Table 2
Characteristics and provenience of oils collected from transformers in service.

Oil	Holder	Year	Power (MVA)	Oil type	Provenience	Naphftenic (N) Paraffinic (P)
1	Arcelomittal	1973	85	Mineral oil	France (Fos sur Mer)	P
2	Arcelomittal	1973	85	Mineral oil	France (Fos sur Mer)	P
3	Refinery of Milazzo	1985	18	Mineral oil	Italy (Messina)	N
4	Refinery of Milazzo	1989	25	Mineral oil	Italy (Messina)	N
5	Refinery of Milazzo	1989	27	Mineral oil	Italy (Messina)	N
6	Refinery of Milazzo	1993	18	Mineral oil	Italy (Messina)	N
7	Eni	1989	42.3	AgipITE360	Italy (Pavia)	P
8	Eni	1991	1.6	AgipITE360	Italy (Pavia)	P
9	Eni	1988	14.5	AgipITE360	Italy (Pavia)	P
10	Eni	1992	18	AgipITE360	Italy (Pavia)	P
11	Eni	1992	18	AgipITE360	Italy (Pavia)	P
12	Eni	1989	12.7	AgipITE360	Italy (Pavia)	P
13	Eni	1989	12.7	AgipITE360	Italy (Pavia)	P
14	Eni	1999	1.6	Rol OilLP-T	Italy (Pavia)	N
15	Eni	1989	42.3	AgipITE360	Italy (Pavia)	P
16	n.a.	n.a.	n.a.	n.a.	Serbia (Belgrade)	n.a.

n.a. Not available.

3. Results and discussion

3.1. Determination of copper in oil

Our first aim was to optimize an ICP-OES method for the determination of copper in oil, consistent with the ASTM official method, using a light mineral oil.

3.1.1. Method optimization and analytical performance

Viscosity of mineral oils in service, usually ranging between 7–12 cSt [22], influences transformer operation and life time. The higher the viscosity values, the lower the nebulization efficiency in ICP-OES analysis, worsening both sensitivity and repeatability. In order to keep the nebulization efficiency as high as possible, different solvents (isopar, isooctane) and oil/diluent ratios were tested to dilute oil samples (Table 3). Even if composition 5 resulted in uniform and fine aerosol, isooctane vapors made plasma very unstable. Therefore, isopar was used to dilute samples before ICP-OES analysis, as the best compromise between optimal viscosity, constant nebulization conditions and plasma stability. The optimal dilution factor was 1:1 (composition 1). In fact, less diluted samples have a higher viscosity, with a consequent risk of unstable nebulization and formation of large drops in the aerosol, which may reduce analyte transfer efficiency in the plasma; on the other hand, a higher dilution, despite it leads to a better and more constant nebulization, increases the detection limits of method.

To improve the overall performance of ICP-OES analysis of oil, the operating conditions were optimized evaluating multiple responses (nebulization and plasma stability, nebulization quality, torch conditions and the presence of carbon residuals) as a function of different factors (plasma power, primary and auxiliary argon flow, nebulization pressure and pump speed for sample introduction) by a two-level half fraction of a five-factor fractional factorial design (2^{5-1}) [23]. Working conditions were fixed as described in Table 1 (organic setting) following the results obtained by the sixteen experimental runs required by the experimental design. At the optimized conditions, linearity was included within a 0.1–10 mg/kg ($n=7$) range, $R^2=0.9998$.

The limits of detection and quantification, calculated as the concentrations corresponding to three and tenfold the standard deviation of the blank ($n=18$), were 8.8 μg kg^{-1} and 29.3 μg kg^{-1} respectively. The LOQ value was verified by preparing and analyzing a Cu solution in real unused oil (Nytro Libra) not containing Cu.

The method was validated through participation in interlaboratories proficiency tests (IFQ 1109 September 2011, organized by ASTM International), obtaining a z score of -0.4 for the determination of copper in insulating oil.

Table 4
Determination of copper content in 16 used oil from transformers in service by the optimized method.

Oil	Cu (mg/kg)	RSD% ($n=15$)
1	31.9	6.6
2	27.9	9.0
3	1.9	15.5
4	18.4	7.4
5	7.3	6.5
6	0.4	14.3
7	3.1	7.9
8	12.9	15.0
9	13.4	9.3
10	7.1	7.9
11	7.9	6.7
12	7.0	9.1
13	1.9	28.4
14	5.7	10.6
15	6.8	9.5
16	1.2	7.1

3.1.2. Real sample analysis

Considering the importance of quantifying copper content in oil, with the aim of monitoring the insulating liquid condition, the method developed was applied to the analysis of 16 samples of used mineral oils from transformers in service.

Table 4 shows the average copper content obtained for each real sample, as well as the RSD% calculated for 15 different measurements. A RSD% ≥ 10 was obtained for 5 oils.

3.1.3. Total copper content by mineralization

In an attempt to improve the method reproducibility, that can vary as a function of sample composition and ageing, a microwave assisted digestion procedure was coupled.

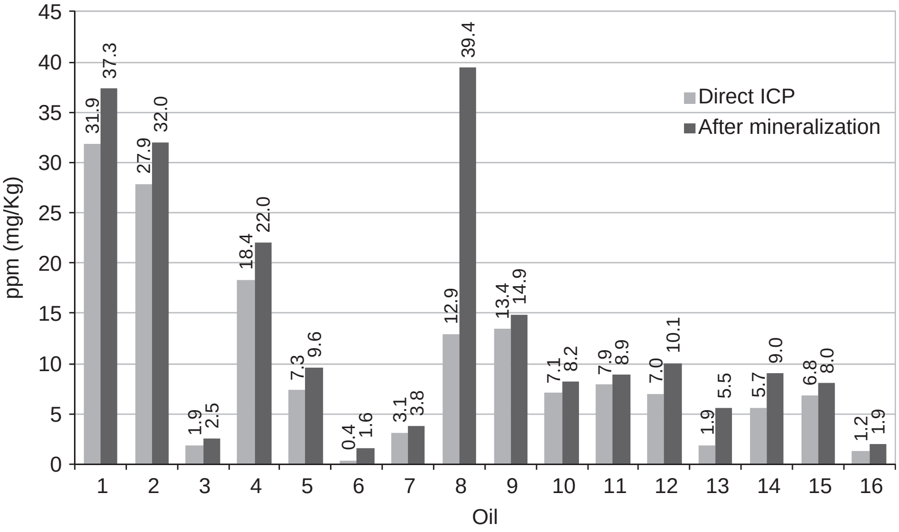


Fig. 1. Comparison of copper concentrations determined by ICP directly and after mineralization.

We hypothesized that the high relative standard deviation obtained for some of the real oil samples (Table 4) has to be ascribed to the presence of copper suspended in oil as particles larger than those detectable by direct ICP-OES, even using a Babington or a V-groove nebulizer.

Therefore, a mineralization procedure by microwave assisted digestion (§2.4) was applied before ICP-OES analysis. The total copper content obtained after mineralization was compared to copper concentration previously measured by direct ICP. Results are summarized in Fig. 1. The significant increase in copper content obtained for some samples after mineralization suggests the presence of suspended large particles, not detectable by a direct ICP measurement.

The particulate copper content, evaluated by calculating the difference between the value obtained after digestion and the value of the direct ICP, was correlated to a poor repeatability of direct ICP analysis (Fig. 2). The above results indicate that particulate copper, if present in oil, reduces reproducibility of ICP analysis, and can lead to significant errors in quantification of metals in oil even if the standard method is used.

3.1.4. Determination of filterable copper

To further investigate whether particulate copper was present in real samples, the copper content in the 16 used oils was evaluated also after filtration. A size fractionation study (Fig. 3) was performed using PTFE and Nylon filters (0.45 μm, 1 μm and 5 μm). Since nylon filter showed adsorption, PTFE filters, that proved to be inert through the matrix, were chosen.

Six of the 16 oils, namely 2, 7, 9, 10, 11 and 15, showed a copper content in the filtered fraction comparable to that measured in the unfiltered oil. These results are in agreement with data shown in Fig. 1 where about the same copper amount was measured with and without the mineralization procedure. Oil samples 3 and 14 seem to contain particles of copper within 5 and 0.45 μm, as well as some larger than 5 μm. In fact, just these two

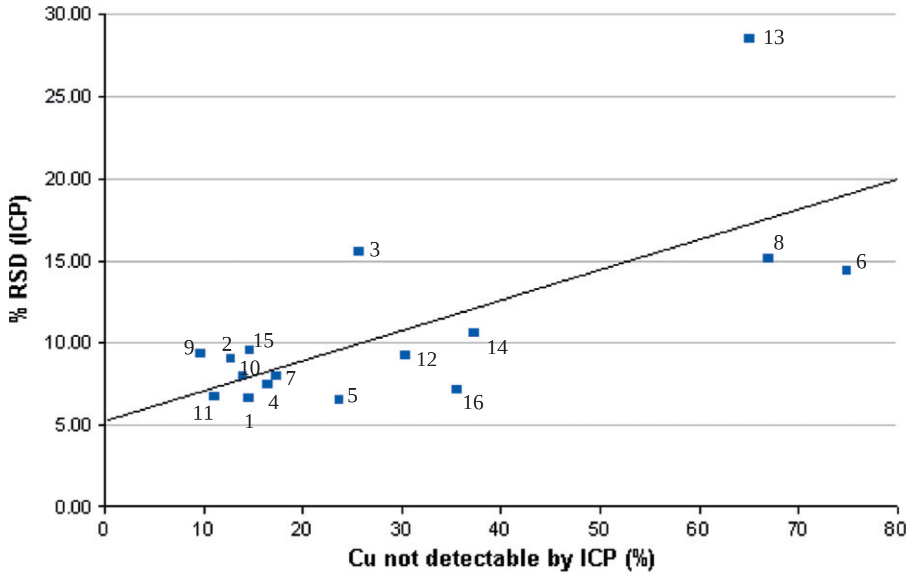


Fig. 2. Correlation between relative standard deviation by direct ICP analysis and copper percentage not detectable with this technique. The last one has been calculated according to the equation: $[(\mathrm{Cu}_{\mathrm{Mineralization}}-\mathrm{Cu}_{\mathrm{ICP}})/\mathrm{Cu}_{\mathrm{Mineralization}}]\times 100$.

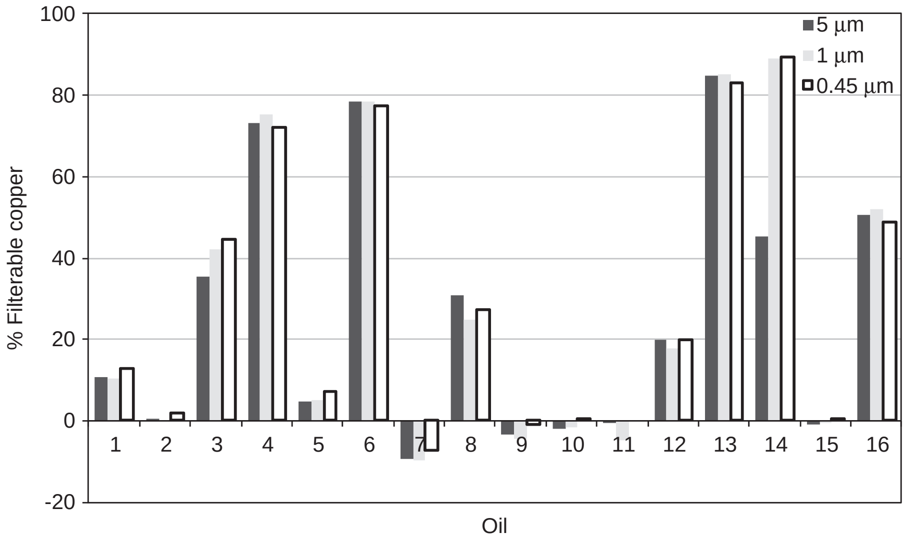


Fig. 3. Copper size fractionation, expressed as percentage of Cu retained on PTFE filters (5, 1 and 0.45 μm).

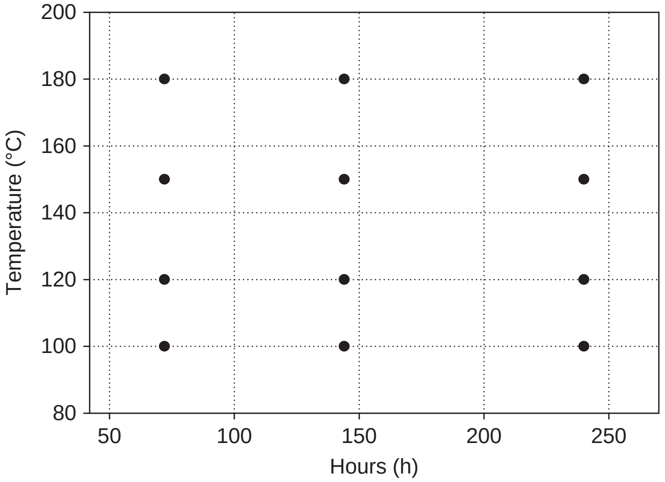


Fig. 4. Ageing conditions tested for the evaluation of copper deposition tendency.

samples showed a significantly bigger percentage of retained copper at decreasing filter porosity. On the contrary, the remaining samples showed a relevant percentage of copper retained on filters, with particles larger than 5 μm.

It is noteworthy that oils containing copper in particle form (high percentage of copper retained on filter), like oils 6, 8, 13, and 14 also showed the highest RSD% during direct ICP analysis (Table 4), hence confirming the direct correlation between the repeatability and the percentage of metal not detectable by direct ICP (Fig. 2).

3.2. *Copper deposition tendency (CDT test)*

The CDT test for the quantification of copper in the liquid (oil) and solid (paper) insulators were performed on two nafthenic uninhibited (absence of phenolic antioxidant) unused oils: Nytro Libra and Mobilect 35 which are classified respectively as non-corrosive and corrosive (due to the presence of dibenzyldisulfide)

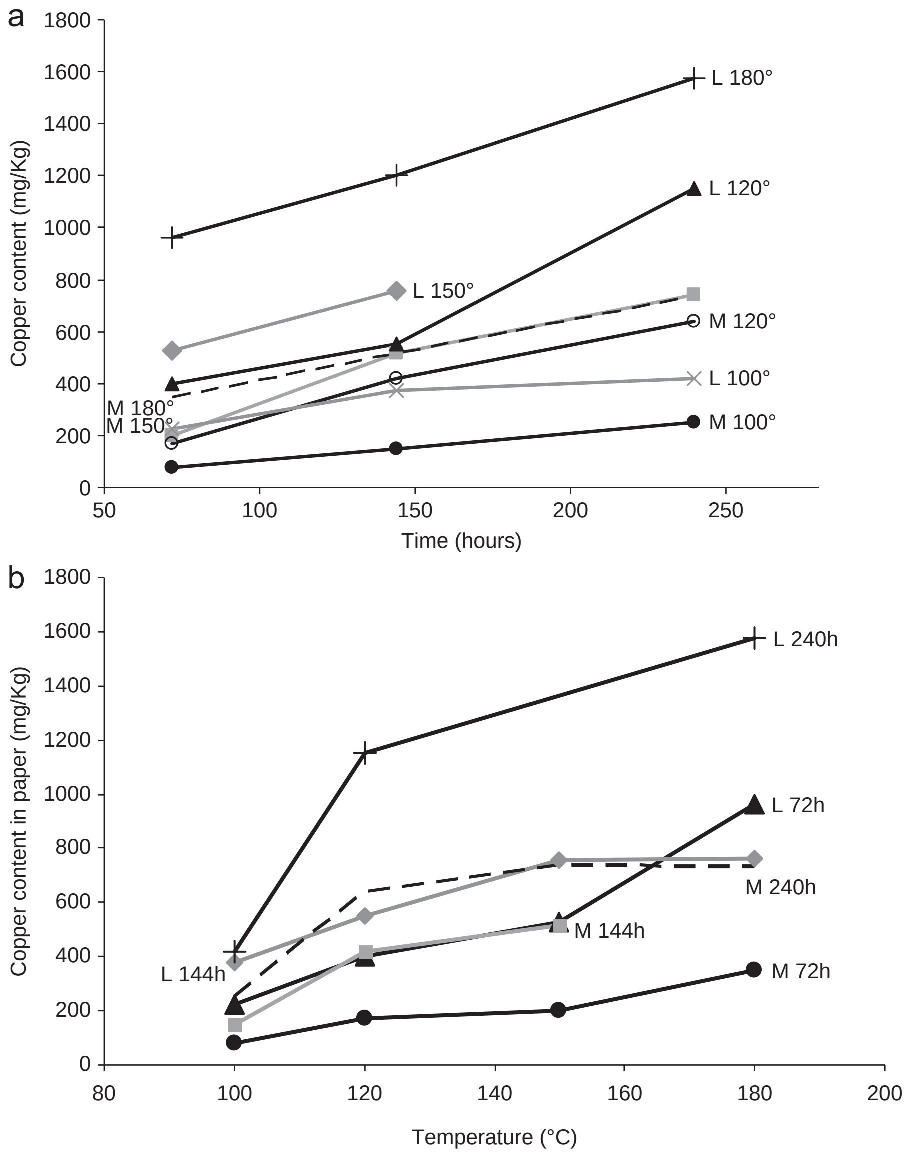


Fig. 5. (a) Copper deposited on paper surface *vs* contact time at each investigated temperature (°C). *L*=Libra, *M*=Mobilect 35. (b) Copper deposited on paper *vs* temperature at each considered ageing time. *L*=Libra, *M*=Mobilect 35.

according to the definitions of the IEC [24]. The experimental design followed for the accelerated ageing tests is shown in Fig. 4.

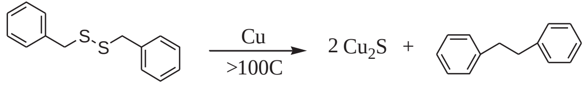
3.2.1. *Effect of ageing on copper deposition onto paper*

In both the considered oils, this study highlights a direct correlation between copper deposited on paper and the contact time: copper concentration increased almost linearly with ageing time (Fig. 5a). This means that, even in standard working operative conditions of transformers (hot-spots not exceeding 105 °C) copper tends to transfer onto solid insulation.

On the other hand, the dependence of copper deposition on temperature is less straightforward: copper concentration on paper surface increases with temperature up to ~150 °C, but, at extreme working conditions (high temperature and long time) it appears to tend to a plateau (Fig. 5b). This result is probably due to the formation of copper particles and deposits (CuO, etc) precipitated in the oil. In case of transformers affected by severe overheating, many reactions involving different forms of metal occur and many transfer paths for copper are in competition (copper-to-oil, copper-to-paper, copper from paper-to-oil).

3.2.2. *Effect of oil corrosiveness on copper deposition onto paper*

Another important information gleaned from this study is that, given the same conditions of temperature and contact time, copper concentration is generally higher in paper aged in Libra oil. This was the opposite of what expected considering the inherent characteristics of these oils. Mobilect 35 contains dibenzyldisulfide (DBDS), that is supposed to react easily with copper [10,12,25,26], causing dissolution/suspension of metal species in oil and their deposition/adsorption onto paper, according to the following reaction [27].



The fact that the corrosive oil (Mobilect 35) deposited less copper onto paper than the non-corrosive one (Libra) indicates that formation of copper sulfide salts is not the only mechanism

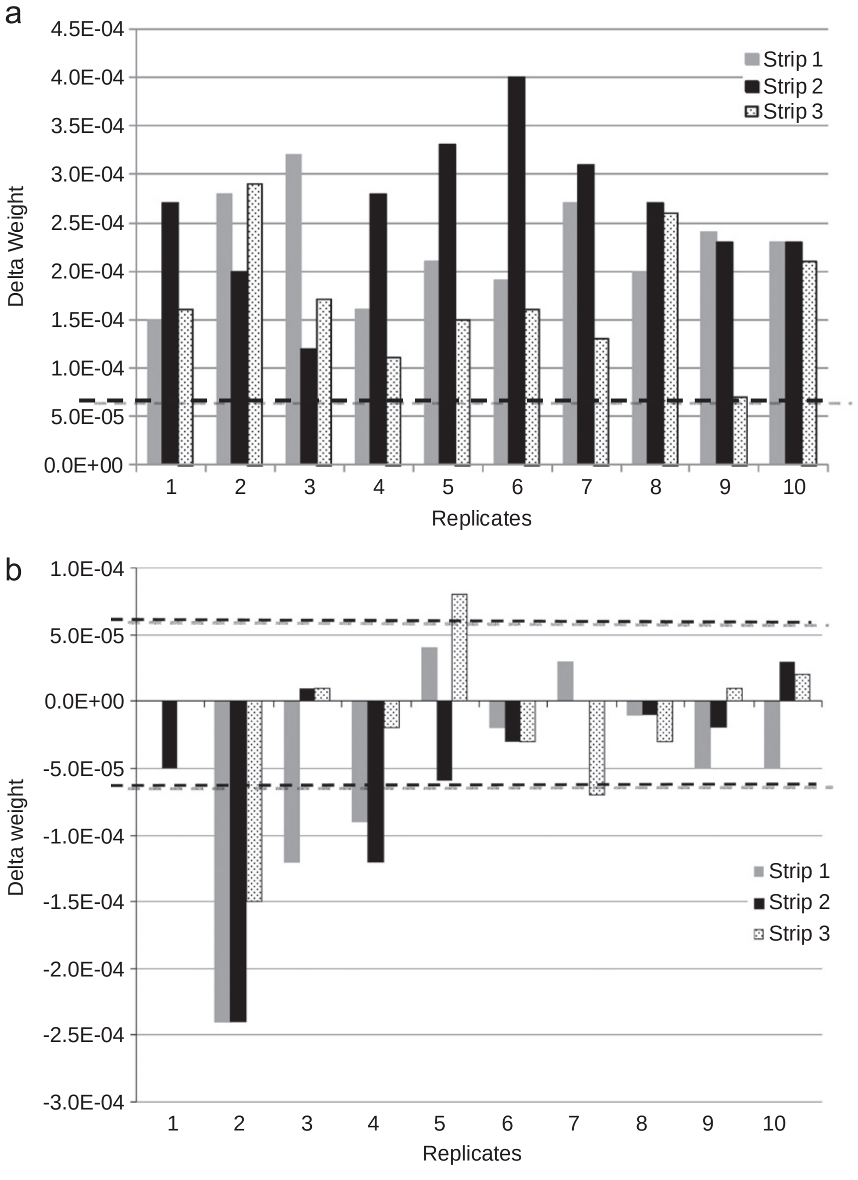


Fig. 6. (a) Change in copper strip weight (g) after ageing in corrosive oil (Mobilect 35). Conditions: 150 °C – 72 h, 3 strips for each vial, 10 replicates. The three histograms refer to the 3 conductors in each vial. The used balance was capable to weigh 0.01 mg. Weight uncertainty (dotted line): 0.06 mg (3⁎S, $n=12$).(b). Change in copper strip weight after ageing in non-corrosive oil (Libra). Conditions: 150 °C – 72 h, 3 strips for each vial, 10 replicates. The three histograms refer to the 3 conductors in each vial. The used balance was capable to weigh 0.01 mg. Weight uncertainty (dotted line): 0.06 mg (3⁎S, $n=12$).

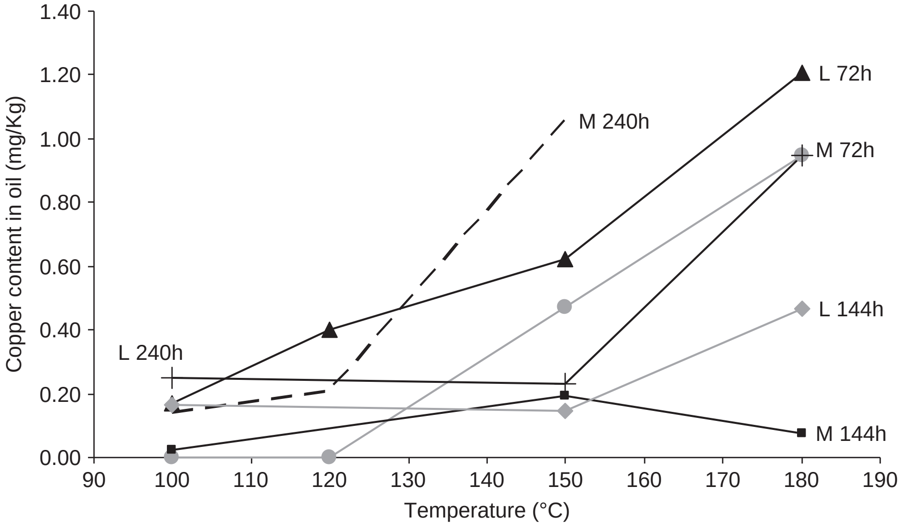


Fig. 7. Copper content in oil obtained after the ageing procedure. *L*=Libra, *M*=Mobilect 35.

underlying metal transfer to cellulose. In an atmosphere without O_2 the above reaction is quantitative, while when air can enter the system (as in our case) other reactions can occur. In particular CuO can be formed on bare copper surfaces and transferred onto paper and in oil in the form of suspended particles [28]. Another reaction that can occur in corrosive oil is the formation of insoluble copper sulfide onto conductor surface, remaining adherent to metal surface, rather than transferring on paper, as a black coat visible to the naked eye. This is confirmed by Fig. 6(a), where a significant weight increase for conductors dipped in corrosive oil (Mobilect 35) can be observed. However, this is not observed in case of copper strips dipped in non-corrosive oil (Libra), in which case their weight remain constant (if compared with balance uncertainty) in almost all replicates (Fig. 6b).

3.2.3. *Effect of ageing on copper in oil content*

The trends of copper content in oil after the described ageing treatments are shown in Fig. 7. An increase in copper content at increasing temperatures was observed, with copper concentration ranging from 0 to 1.2 mg/kg. In milder conditions (time of contact 72 h) Libra (non-corrosive, not containing DBDS) transfers more copper than Mobilect 35 in oil, while in extreme conditions (time of contact 240 h) the amount of copper transferred in oil is greater for Mobilect 35 (corrosive for DBDS presence). This can be explained by the detachment of copper salt particles (Cu_2S, CuO) from the copper surface in case of corrosive oil: such particles are small enough to be detected by ICP-OES and misleadingly simulate an increased copper dissolution.

4. Conclusions

A simple and direct ICP-OES method to quantify copper dissolved in oil was presented, with an optimization of nebulizing conditions. The optimized ICP method will provide a tool for the diagnostics of insulating oils in service, as an integration to the available maintenance guides (IEC, ASTM, IEEE (Institute of Electrical and Electronics Engineers)) to ensure the safe operating conditions.

In order to cope with the reproducibility problems that can arise with real aged oils, which may contain metal in suspended form, a microwave assisted mineralization procedure was developed. In this context, a characterization study of copper species by size fractionation was performed for the first time, on a set of real oils sampled from transformers in service. The assessment of the forms in which copper is present (dissolved or suspended) as well as the size fractionation study will provide information to be correlated with oil insulating characteristics (*e.g.* tan δ), thus allowing a better understanding of the corrosion phenomena and the possible mitigation or prevention techniques.

The optimized ICP-OES method was used to use evaluate the copper deposition on the insulating Kraft paper tapes and its dissolution in oil, under defined ageing conditions: this method demonstrates that non-corrosive oils can also deposit relevant quantity of copper on cellulose.

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