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Instrumental methods of analytical chemistry applied in power transformer condition assessment

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Abstract **– The application of analytical methods in power transformer (PT) condition assessment enables the separation, identification and quantification of degradation products or contaminants, which are present in mineral transformer oils in low concentrations (mg/kg, µg/kg). This paper presents a review of the key instrumental methods applied in the laboratory of the Nikola Tesla Institute (NTI) and emphasizes the importance of their application during transformers life cycle. Gas chromatography (GC) is applied for assessment of PT operating condition and fault detection, cellulose degradation and for quantification of contaminants (PCB) and corrosive sulphur compounds (DBDS, S_8) in insulating liquids. Liquid chromatography (LC) is applied for testing the presence of specific additives, such as metal passivators and degradation products such as furanic compound in oils. The importance of applying infrared spectrophotometry (IR) is reflected in the analysis of the chemical composition and antioxidant content (DBPC) in the oils. The results of Round Robin Tests (RRT) are also presented in this paper.**

I. INTRODUCTION

Mineral insulating oils used in transformers, beside the basic role to insulate, dissipate heat, suppress corona discharge and arcing, also represent a diagnostic medium for PT condition assessment, estimation of moisture content in the paper-oil insulation system and degree of degradation. For the adequate use of oil as an insulating and cooling agent, the most important thing is the quality of oil itself, which is monitored by testing the characteristics of the oil in a chemical laboratory. New technologies for transformer manufacturing set increasingly strict requirements for high quality of insulation materials in order to have long service life. Therefore, testing the condition and quality of both, unused and used, transformer oil is extremely important.

Unused and recycled mineral insulating oils must comply with the criteria defined in IEC standard 60296, while in-service mineral insulating oils can be classified as “Good”, “Fair” or “Poor”, acc. to IEC 60422 standard, based on the evaluation of oil properties.

During exploitation the oil degrades, which leads to significant changes in oil properties. By applying instrumental methods in oil testing, with high reliability, better insight into the condition and quality of new transformer oils is achieved on the one side, as well as monitoring the PT service condition and insulation system (IS) degradation trend, on the other.

II. INSTRUMENTAL METHODS OF TESTING MINERAL TRANSFORMER OILS

Following chapters provide an overview of the instrumental methods of analytical chemistry applied in the NTI laboratory regularly, in testing the new mineral insulating oils and oils from service, the parameters that are tested, their significance and use.

III. GAS CHROMATOGRAPHY (GC)

Gas chromatography is the most applied analytical technique in transformer oil analysis for determination the following oil characteristics and contaminants: 1. Dissolved gas analysis (DGA), 2. Low molecular weight alcohols dissolved in the oil (methanol/ethanol), 3. PCB content, 4. Corrosive sulphur compounds in the oil (such as dibenzil disulphide, DBDS and elemental sulphur, S_8).

A. Dissolved gas analysis (DGA)

DGA in unused mineral insulating oils gives the information of oil tendency to create gasses ("stray gassing") and provides the insights about the PT condition, during the factory acceptance tests (FATs). On the other side, monitoring the content of the gasses during the PT operation, in oils from service, provides the information of the PT operating condition assessment and fault detection.

The analysis of the gases dissolved in transformer oil is carried out using the TOGA GC system with a head space autosampler on a temperature-programmed column, according to IEC 60567 standard. The detection of organic components is performed using a flame ionization detector (FID) and inorganic components with thermal conductivity detector (TCD) (Figure 1). Argon is used as carrier gas [1]. The defined limit of detection (LOD) is from 0.1 mg/kg (for hydrocarbons) to 10 mg/kg (for carbon oxides) – for acceptance tests and from 1 mg/kg (for hydrocarbons) to 25 mg/kg (for carbon oxides) – for service tests acc. to IEC 60567.

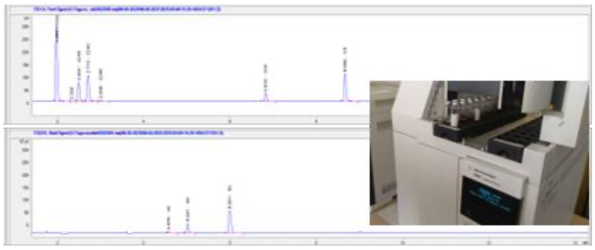

Fig. 1. TOGA GC TCD&FID (left) and chromatogram of DGA (right).

B. Methanol/ethanol in the oil

For PT condition assessment and diagnostics in real time, monitoring of said compounds is of great importance to enable stable, reliable and normal operation of PT during its lifetime. Low molecular-weight alcohols (LMA), methanol and ethanol represent the aging markers of cellulose degradation in early stage of transformer operation and it could be useful in PT fault diagnostic.

On the other hand, furans are more inert and could be formed in higher amounts in later stages of paper aging. Both, can be used as a complementary tool, for detection of thermal faults that include solid insulation, in lower and medium temperature range as well as detection of dysfunctions in transformer cooling system, thus avoiding potential transformer failure [2].

Quantification of methanol and ethanol is performed using gas chromatograph (TOGA GC FID system) as an integrated analysis with DGA in transformer oil. This approach was found to be very convenient and effective method in transformer fault diagnostic [2]. Dissolved gases, methanol and ethanol, quantified together in the same chromatographic run are shown in Figure 2.

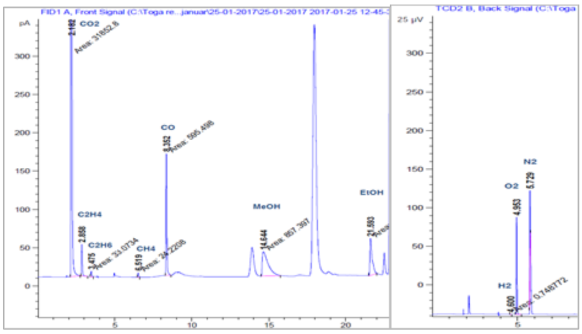

Fig.2. Chromatogram of DGA and LMA [2].

The integrated method reaches very low LOD and LOQ in both unused and used mineral insulating oils. For new mineral oils, established LODs are 2 ppb and 4 ppb, while LOQs are 7 ppb and 14 ppb, for methanol and ethanol respectively. On the other side, for the aged oils from service the limits are a bit higher: LODs - 5 ppb and 7 ppb and LOQs - 15 ppb and 22 ppb, for methanol and ethanol respectively [2].

C. PCB content in the oil

Quantification of polychlorinated biphenyls (PCB) in transformer oils is performed using the capillary column gas chromatography with micro electron capture detector (µECD), according to IEC 61619 standard. The method is based on the separation and identification of individual PCB congeners followed by calculation of the total PCB content by summing the masses of each individual PCB congener in the oil sample. Analyzes are performed on a temperature-programmed capillary column, with helium as carrier gas (Figure 3). The LOD is 2 mg/kg for total PCB content and 0.1 mg/kg for each individual PCB congener.

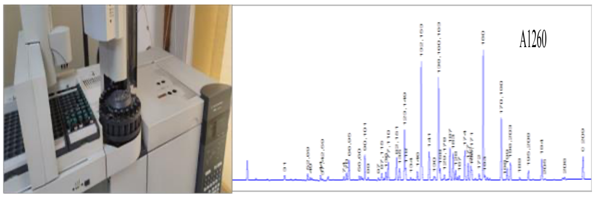

Fig. 3. GC-µEC (left) and chromatogram of PCB congeners in mineral oil (right).

In order to meet the defined oil quality criteria in terms of safety and environmental protection, it is necessary to measure the content of PCBs in unused and used oils. By quantifying PCBs, proper identification of equipment is achieved, which further leads to more adequate maintenance and handling during storage, cross contamination prevention and to appropriate mitigation measures, i.e. decontamination of equipment.

The low LOD of the method provides a reliable assessment of PCB contamination of the transformer related to the prescribed limit values defined in the legal regulations [3].

D. Corrosive sulphur compounds in the oil (DBDS, S_8)

The presence of corrosive sulphur compounds in the mineral insulating oil, such as DBDS and S_8, increases the risks of power transformers failures, due to deposition of electro-conductive metallic (copper and silver) sulphides in transformer active part. Reactive disulfides (DBDS) can be detected in new oils and oils in service, while S_8 can be introduced into the oil, during oil reclamation when reactivation of adsorbent is applied during the process [4]. Brochures of the CIGRE international committee and international standards (CIGRE TB 378, CIGRE TB 625, IEC 60296 and IEC

60422) provide a detailed analysis of the phenomenon and mechanism of the formation of copper (I) sulfide, a description of risk factors, recommendations and criteria for the exploitation of recycled mineral insulating oils.

Quantification of both corrosive sulphur compounds is performed using the GC with µECD, acc. to IEC 62697-1, for DBDS and acc. to IEC TR 62697-3, for S8. Analyzes are performed on a temperature-programmed column, with helium as carrier gas. GC-µECD chromatograms of DBDS and S_8 are presented in Figure 4.

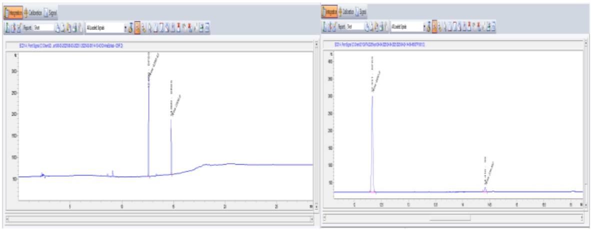

Fig. 4. GC-µECD chromatograms of DBDS (left) and S_8 (right).

The LOD (0.30 mg/kg for DBDS and 0.07 mg/kg for S_8) and LOQ (1 mg/kg for DBDS and 0.24 mg/kg for S_8) established in NTI laboratory for mineral insulating oils are much lower than prescribed limits in standards and typical values found in oils, thus ensuring reliable diagnostics.

Testing the presence of mentioned corrosive sulphur compounds and their quantification, present a first key step in PT corrosive sulphur risk assessment with the aim to apply appropriate corrective measures.

IV. LIQUID CHROMATOGRAPHY (LC)

High-performance liquid chromatography (HPLC) is analytical technique, mostly used in oil analysis to determine furanic compound and metal passivators in mineral insulating oils.

A. Furanic compounds

Furanic compounds present specific markers of cellulose insulation degradation. Unused oils usually do not contain furan derivatives, but traces of these compounds can remain dissolved in oil, due to insufficient separation of solvent from oil, during oil refining procedures in refineries, that most often use 2-furfural as solvent. Testing of these compounds in new oils should be performed to check the purity of the new oil and to establish an initial, reference value for further monitoring in PT exploitation [5].

Regular, periodical measurement of 2-furfural and related compounds represent main diagnostic tool in PT maintenance. It is used as a trend analysis therefore it is very important to establish precise method with low LOD [5].

The analysis of furan derivatives in transformer oils is performed by liquid chromatography (HPLC) on a reverse-phase column with a mobile phase gradient flow. The oil sample is prepared by solid-liquid extraction on columns filled with silica gel. Polar compounds, retained on silica gel, are eluted with the appropriate mobile phase and analyzed. The method is standardized in IEC 61198. The LOD is 0.05 mg/kg for each individual furan compound. Figure 5 shows the HPLC and hromatogram of 2-furfural.

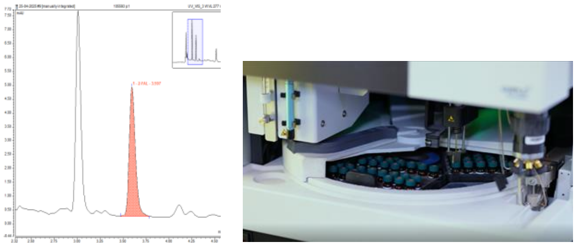

Fig. 5. HPLC (left) and chromatogram of 2-furfural (right).

B. Metal passivator content

The HPLC technique is also used to determine the content of metal passivators (based on benzotriazole, BTA and toluyltriazole, TTA) in new and used oils. This type of inhibitors has a dual protective role, in inhibiting oil oxidation process and passivating the copper surface (oil oxidation catalyst), making it unavailable for chemical reaction with sulfur compounds (e.g. DBDS) [6]. The addition of metal passivators has been found to be an efficient mitigation technique in the suppression of copper corrosion in the transformer windings, but ineffective in mitigation of silver corrosion in oils containing corrosive sulphour compounds, such as DBDS, S_8 and other reactive disulfides, i.e. other than DBDS [7,8]. Regular monitoring of the concentration of passivator is necessary, as it is consumed during PT operation.

Quantification of metal passivator in the oil is performed acc. to IEC 60666 standard. Figure 6 shows the chromatogram and spectrum of metal passivator (Irgamet 39) in mineral insulating oil.

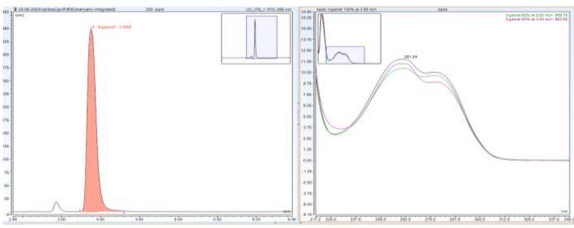

Fig. 6. Chromatogram and spectrum of Irgamet 39 in mineral oil.

Monitoring the concentration of metal passivator in the unused and oils in service is essencial in the assessment of the quality of new oils and the eventual corrosivity of the oil, which is ensured by the low LOD (5 mg/kg).

V. INFRARED SPECTROPHOTOMETRY (IR)

Fourier transform infrared spectroscopy (FTIR) is analytical technique applied mostly for determination of inhibitor content, such as: 2,6 di-tert-butyl-p-crezol (DBPC) or 2,6-di-tert-butyl-phenol (DBP) and hydrocarbon composition of the mineral oil, i.e. paraffinic, naphthenic, and aromatic hydrocarbons in mineral oils.

A. Inhibitor content, DBPC

FTIR is commonly used technique to determine specific additives in the oil, antioxidants based on aromatic hydrocarbons, which are added to new oils in order to improve its oxidation stability and extend service life. The most frequently used antioxidants are phenolic compounds, DBPC and DBP.

According to the IEC 60296 standard, oils containing less than 0.01 wt.% of inhibitor are considered uninhibited, oils containing from 0.01 wt.% to 0.08 wt.% of inhibitor are trace inhibited, while oils containing an oxidation inhibitor in the range from 0.08 – 0.40 wt.% are inhibited oils [9].

During exploitation, the inhibitor is consumed in oxidation reactions, which is monitored by the FTIR analysis. Change in inhibitor consumption during the service life, may indicate abnormal oil aging [10].

The concentration of DBPC or DBP in oils is determined acc. to IEC 60666 standard, by quantifying adsorption peaks at wavelength of 3650 cm^{-1} (Figure 7). The low detection limit of the method (0.02 wt. %) enables reliable monitoring of DBPC consumption in oils during operation.

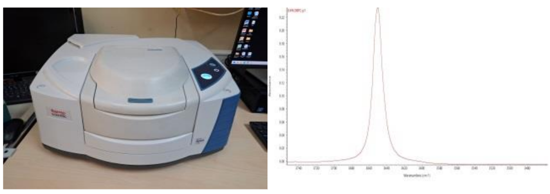

Fig. 7. FTIR (left) and spectrum of DBPC in mineral oil (right).

B. Hydrocarbon composition of the oil

IR spectrophotometry enables the determination of hydrocarbon (HC) content of new oils, i.e. paraffinic, naphthenic, and aromatic hydrocarbons. The hydrocarbon composition of the oil, especially the content of aromatic hydrocarbons, is very important for oil oxidation stability, gas-absorption characteristics and degree of solubility of water in the oil.

Oils with a relatively high content of aromatic compounds dissolve water and other polar compounds more extensively and have a higher potential for gas absorption. Moreover, the aromatic hydrocarbons are one of the key parameters for determining the oxidation stability of the oil. Certain aromatics are very good natural antioxidants (monocyclic and pure polycyclic aromatic hydrocarbons). On the other side, a high content of paraffinic hydrocarbons adversely affects the pour point, kinematic viscosity and other low-temperature characteristics of the oil [1].

The determination of aromatic hydrocarbons is performed by FTIR acc. to IEC 60590 standard, by quantification of the absorption peaks of aromatics at 1605 cm^{-1}, while the content of paraffinic hydrocarbons is determined by quantification of the absorption peaks at 725–730 cm^{-1} of the IR spectrum. Finally, the content of naphthenic compounds is determined from a difference up to 100%.

VI. OVERVIEW OF INSTRUMENTAL METHODS OF ANALYTICAL CHEMISTRY USED IN PT CONDITION ASSESSMENT

A comparison of instrumental methods, presented in this paper, used in PT condition assessment, is shown in Table 1.

Table 1. Instrumental methods of analytical chemistry in PT condition assessment.

Method	Properties	Significance and Use
GC	DGA	Oil tendency to generate gases; FATs; PT operating condition assessment; Fault detection;
	LMA	Paper aging markers in early stage; Fault detection;
	PCB	Oil contamination; Maintenance of PCB contaminated transformers; Decontamination; Environmental protection;
	DBDS, S_8	Contamination; Consumption monitoring; Corrosive sulphur risk assessment; Mitigation measures;
LC	Furans	Contamination; Paper ageing markers in later stages; Fault detection;
	Passivator	Consumption monitoring; Reduction of risk of copper sulphide formation;
IR	DBPC	Inhibitor consumption and oil ageing monitoring;
	HC	Degree of oil refining; Oxidation stability; Oil capacity to absorb gases, dissolve water and aging products;

VII. INTERLABORATORY COMPARISONS OF INSTRUMENTAL METHODS (RRT)

By participating in comparative interlaboratory tests (Round Robin Test - RRT) for different oil testing methods, the laboratory improves the level of testing, verifies its own measurements, validates methods and expresses measurement uncertainty. Validating new test methods the laboratory makes an active and significant contribution to the development of new and revision of existing IEC standardized methods.

Interlaboratory tests are organized by distributing the same samples to all participating laboratories, using the same test procedure and technique for oil testing. Statistical analysis of the results determines the reproducibility and applicability of the particular method.

Table 2 shows the results of comparative measurements of laboratories which participated in RRT, for following mineral oil analyses: 1. Quantification of corrosive sulphur compound (DBDS), acc. to IEC 62697-1, 2. Metal passivator content (Irgamet 39), acc. to IEC 60666 and 3. Inhibitor content (DBPC) by FTIR, acc. to IEC 60666 standard.

Table 2. RRT results.

Labs	DBDS, mg/kg	Irgamet 39, mg/kg	DBPC, wt. %
L.01	65.3	126.3	0.3664
L.02	99	116	0.34
L.03	79	-	0.38
L.04	87.9	117.4	0.3244
L.05	96.4	59.9	0.34
L.06	-	-	0.335
NTI	92.2	117	0.38
L.08	-	-	0.388
L.10	100	92.5	0.405
L.11	114	98	0.368
L.12	111	41	0.373
L.14	91	-	0.38
Avg.	92.344	96.013	0.363
St.Deviat.	14.216	30.616	0.027
ZScore	0.0	0.7	0.6
Results	Satisfactory	Satisfactory	Satisfactory

Since the Zscore values of all three testing methods presented in Table 2, are between -2 and 2, the results are classified as satisfactory. This confirms the validity of the applied methods as well as the good agreement of the oil testing results, performed in different laboratories.

VIII. CONCLUSION

Instrumental methods of analytical chemistry plays an important role in monitoring of PT during its life cycle. Their application contributes to the improvement of diagnostics of the PT operating condition and insulation system and the PT life assessment. The introduction of new, precise measurement techniques led to the revision of a large number of test methods, with the aim to decrease the detection limit and to achieve a higher class of accuracy. Moreover, the standards for new, unused oils and oils from service are constantly expanded with new test methods, in order to improve the assessment of the quality of new and used oils, their usability and degree of degradation. Early prevention in diagnosis of the PT condition is of great importance in system planning, assessment of reliability and availability of equipment, which has a great economic influence.

Participation in comparative interlaboratory testing (RRT) enables a realistic determination of the measurement uncertainty of the methods and ensures confidence in the precision and quality of the test results.

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