

Reliability and Improvements of Water Titration by the Karl Fischer Technique

M. Koch^{1*}, S. Tenbohlen¹, J. Blennow², I. Hoehlein³

¹ University of Stuttgart, IEH, Pfaffenwaldring 47, 70569 Stuttgart, Germany

² Chalmers University of Technology, S-412 96 Goeteborg, Sweden

³ Siemens AG, PTD, Transformers, Katzwanger Str. 150, 90461 Nuernberg, Germany

*Email: maik.koch@ieh.uni-stuttgart.de

Abstract: For the measurement of moisture in oil-paper-insulations the titration by Karl Fischer is considered as a reliable state of the art method. However factors like moisture ingress during sampling and transportation, handling in the laboratory, chemical bonds of water and aging byproducts influence the result. The results of a round robin test on oil and paper samples revealed surprising differences in the water content measured by eight participating laboratories. In this investigation many of the discrepancies were explained. The influence of the heating temperature and the solvent for oil extraction for paper samples was systematically investigated. Best results obtained 160°C for paper and 180°C for pressboard samples and heptane for oil extraction. Besides three techniques for moisture in oil measurements were compared: volumetric titration with direct injection, coulometric titration with direct injection and coulometric titration with external oil heating. Coulometric titration with direct injection seems to deliver the most reliable results. Special emphasis is given to the comparison of Karl Fischer titration to results of moisture saturation measurements e.g. by capacitive probes or headspace systems. This illuminates the frequent discussions that question the validity of Karl Fischer titration in aged oils. Recommendations for reliable Karl Fischer titrations conclude this investigation.

1 INTRODUCTION

Reliable assessment of the actual condition of high voltage power transformers allow for time- and cost-saving maintenance actions. Moisture in cellulose and oil is an ageing indicator and accelerator, decreases the dielectric withstand strength and may generate gaseous bubbles in the liquid insulation. Aging gains importance since utilities keep transformers in service even if the estimated life cycle is exceeded. Hence the number of wet transformers because of aging or even inadequate maintenance increases.

1.1 Difficulties with a State of the Art Method

To evaluate the moisture content in the liquid and solid insulation the titration according to Karl Fischer is not only widely used, but also serves as a benchmark for other methods like dielectric response methods. Nevertheless it is affected by the following influences:

- (1) There is always a moisture ingress from atmosphere during sampling, transportation and sample preparation, for answers see section 5.
- (2) Cellulose binds water with chemical bonds of different strengths. It is unsure, if the thermal energy releases all the water. Heating temperature and time strictly changes the released water (section 3.1).
- (3) Laboratories differently treat constraints, that are not covered by standards, such as the solvent for oil extraction (section 3.2).
- (4) Sometimes direct injection and heating method lead to different results for moisture in oil. This might be due to the influence of oil additives and ageing by products (section 4.1).

Thus round robin tests revealed an unsatisfactory comparability of different laboratories. Additional discussions arose because of discrepancies between titration results and online moisture probes, e.g. capacitive sensors and headspace systems. This investigation will explain the difficulties and gives advice for practical problems.

1.2 Moisture Absorption in Oil

Pure mineral transformer oil consists of saturated hydrocarbons such as paraffins and naphthenes. Because of their nonpolar molecule structure pure oil can dissolve only a very small quantity of water dispersed as water vapour according to Henry's law. However insulation oil in power transformers is polluted by remains from refinery, ageing byproducts and cellulosic particles. Thus the water solubility increases; water exists in the following states:

- dispersed as water vapour in the oil bulk
- bound to ageing byproducts by Van Der Waals and hydrogen bonds
- adsorbed by impurities e.g. cellulose fibres
- small drops, when the saturation level is exceeded

The moisture content W is usually related to oil weight (ppm as $\mu\text{g water} / \text{g oil}$) or as relative moisture saturation RS to the saturation value (%).

1.3 Moisture Absorption in Cellulose

Pressboard and paper used as insulation materials consist to 85 % of cellulose, to 3-7 % of lignin and of 10 % hemicelluloses. In the following explanations cellulose should be the collective name for insulation materials such as pressboard, Transformerboard (Weidmann), Kraft paper (insulation paper) and thermally upgraded paper. Cellulose owns polar glucose

chains and therefore dissolves high quantities of water in the following states:

- Strongly bound to OH-groups of glucose chains by hydrogen bonds (at water contents below 1-2 %)
- Weakly bound by Van Der Waals bonds, water molecules may form multiple layers attracted to glucose chains (at medium water content)
- Hold by capillary forces (at high water content)

The ability to dissolve water is, depending on temperature, some thousand times higher compared to that of oil.

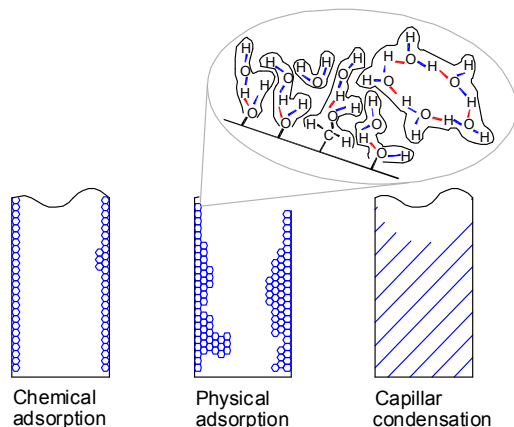


Fig. 1: Bonds of water molecules in cellulose

1.4 The Karl Fischer Titration Technique

Karl Fischer titration is a method in analytical chemistry that determines trace amounts of water in a sample using volumetric or coulometric titration. The German chemist Karl Fischer (1901-1958) introduced this titration method in 1935. Titration basically means to add a reagent of known concentration (titre) to an unknown substance until the concentrations are balanced. At *volumetric* titration the added volume is measured and the demanded value (here water content) is calculated by a stoichiometric equation. The sensitivity of volumetric titration is limited to some 10 µg water so that it is hardly applicable for dry insulation oils. At *coulometric* titration the reagent iodine is generated by a generator electrode and the need of its standardization is eliminated. (1) is a simplified stoichiometric equation illustrating the reactions taking place in the titration vessel. The detection limit of coulometric titration reaches down to some µg of water.



Equation (2) then calculates moisture relative to weight C_W as the ratio of the measured water mass to the mass of dry and oil free paper m_P multiplied with 100 %. Moisture ingress into the system as defined by the drift D (µg/min) and the humidity in an empty sample vessel (blind value $m_{\text{H}_2\text{O},B}$ in µg) must be subtracted from the total moisture income $m_{\text{H}_2\text{O}}$.

$$C_W = \frac{m_{\text{H}_2\text{O}} - t \cdot D - m_{\text{H}_2\text{O},B}}{m_P} \cdot 100\% \quad (2)$$

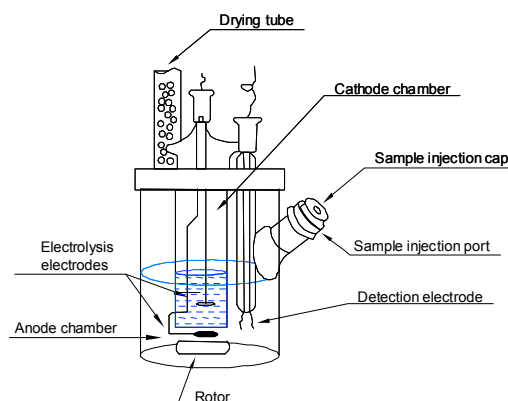


Fig. 2: Electrolysis cell for coulometric Karl Fischer titration

The moisture of the material could be brought into the electrolysis cell (Fig. 2) by three methods:

Firstly it is possible to inject the material directly into the reaction vessel, e.g. oil through a syringe. This method pollutes the reagent and side reactions of ageing products or inhibitors with the reagent are possible. Section 4.1 deals with this influence.

Secondly the water from a cellulose sample can be extracted by immersion into a hydrophilic medium, e.g. methanol. Methanol and water will then be injected into the reaction vessel. Because of the slow extraction this methanol extraction is nowadays rarely applied.

Thirdly the sample can be heated in an external oven and a gas stream with water vapour is led into the reaction vessel. Advantageously the reaction vessel remains clean from pollutions and also from ageing byproducts, depending on their boiling point. A drawback of this method is the blank value of the gas stream and of the heating vessel. This decreases the sensitivity compared to the direct injection method, especially for oil. Fig. 3 illustrates a Karl Fischer titration in a pressboard sample using an external oven.

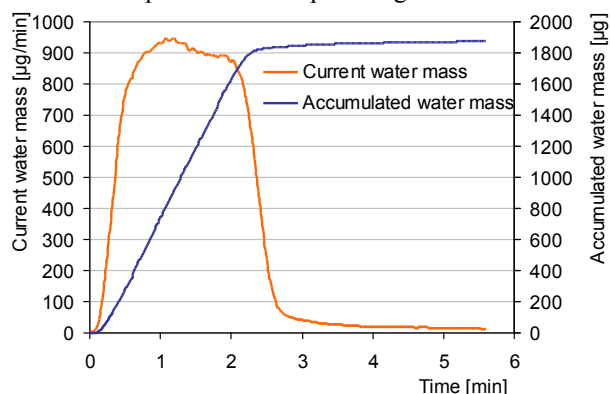


Fig. 3: Currently measured and accumulated water mass at a typical water titration in pressboard with external heating

1.5 Comparability to Other Moisture Sensing Methods

Some users compared the moisture result in oil from Karl Fischer titration to the moisture in oil in ppm obtained from capacitive probes or photo-acoustic DGA. Capacitive probes basically indicate moisture relative to saturation. They consist of two electrodes with a dielectric made by a hygroscopic polymer. Water molecules penetrate into the polymer depending on the relative saturation of the ambient material driven by equilibrium processes [1].

Some operators stated significant differences comparing results from Karl Fischer titration and capacitive probes or other instruments based on moisture equilibrium, e.g. [2]. They concluded, that Karl Fischer titration is not valid for aged oils for two reasons: Firstly, a deviation between capacitive probes and Karl Fischer titration appears only for oils with an observable acidity. Secondly, for aged oils the breakdown voltage was good, although Karl Fischer titration measured a high moisture content. Capacitive probes however indicated a low moisture content.

Contrary to this the authors of this publication argue:

Firstly, it is principally incorrect to compare the ppm-result of capacitive probes to the ppm-result of Karl Fischer titration. Karl Fischer titration measures water mass by a stoichiometric equation while capacitive probes measure moisture equilibrium and therefore the relative moisture saturation. Moisture by weight in ppm is delivered only by the mathematical equation using two constants A and B [3]. These constants depend on water saturation level of the oil (e.g. aging state, pollutions, kind of oil). Therefore to obtain reliable ppm-values the sensor must be calibrated for each oil, otherwise the comparison will fail. Because of the different measurement techniques there is no direct comparability given to KFT. This explanation applies for all techniques based on moisture equilibrium such as e.g. head space methods used in photo-acoustic DGA.

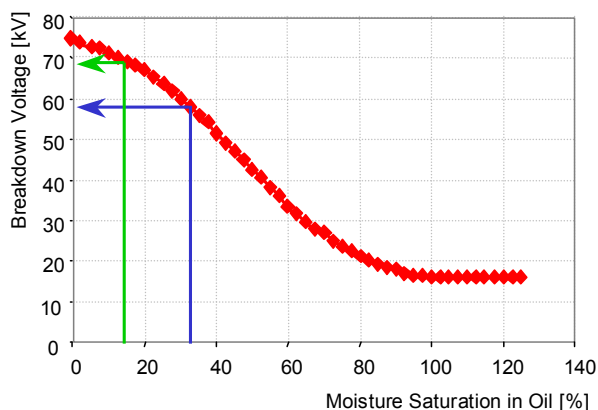


Fig. 4: Breakdown Voltage and Relative Moisture Content in Mineral Oil

Secondly, the influence of moisture on the breakdown voltage of oil depends directly on the moisture content *relative to saturation* [4]. There is only

an indirect sensitivity to moisture by weight in ppm. An example: For new oil a moisture content of 40 ppm of moisture by weight at 40°C means a RS of 33 % [1]. Therefore the breakdown value will be 58 kV (Fig. 4). For an aged oil the same moisture content follows in a RS of 16 %, the breakdown voltage will be unexpectedly high with 69 kV.

2 ROUND ROBIN TEST

2.1 Participating Laboratories

Eight laboratories from four European countries took part in a round robin test. Tab. 1 describes the equipment used in the test.

Tab. 1: Titration techniques used in the round robin test

| Lab | Instrument for Paper samples | Heating temp. | Instrument for Oil samples |
|-----|--------------------------------|---------------|--|
| A | Coulometric, heating with oven | 160°C | Coulometric, direct injection |
| B | Coulometric, heating with oven | 200°C | Coulometric, direct injection |
| C | Coulometric, heating with oven | 135°C | Coulometric, heating with oven |
| D | Coulometric, heating with oven | 135°C | |
| E | Volumetric | - | Volumetric |
| F | Coulometric, heating with oven | 140°C | Coulometric, heating with oven at 80°C |
| G | Coulometric, heating with oven | | Coulometric, direct injection |

2.2 The Samples

Three oil and paper samples filled in flasks made of PE were the measurement objects. Two of the samples consisted of new Kraft paper and new insulation oil Nynas Nytro 3000 having a relative moisture saturation in oil and paper of 2,7 % resp. 4,7 % measured at 80°C. The third sample was a service-aged paper from 1954 in service-aged Shell K 6 SX having a relative moisture saturation of 33 % at 27°C. The oils neutralization number was very high with 0,49 mg KOH / g Oil.

2.3 Measurement Results for Water in Paper

The laboratories measured the water content in paper relative to weight and the water content in oil relative to weight according to their standard procedure.

The results as depicted in Fig. 5 show a reasonable conformance compared to previous tests. One systematic influence is obvious: The heating temperature of paper in the oven increases the released mass of water. This is due to chemical bonds of different strengths which keep the water molecules in the paper. Beside this the differences could be explained by stochastic influences only. For the low water content of sample A the comparability is worst and hardly acceptable.

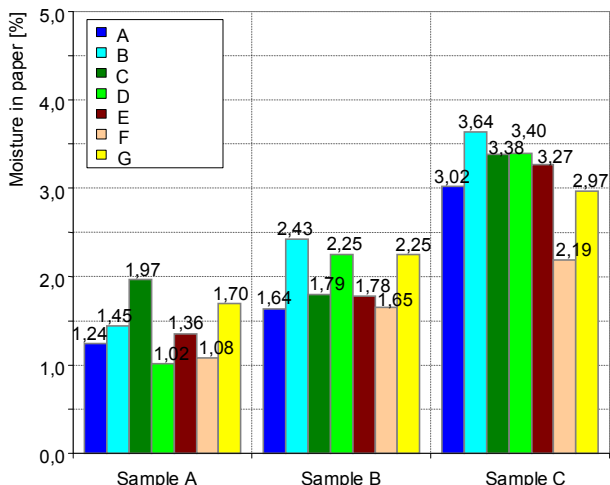


Fig. 5: Moisture in paper in % relative to weight as measured by the laboratories

2.4 Measurement Results for Water in Oil

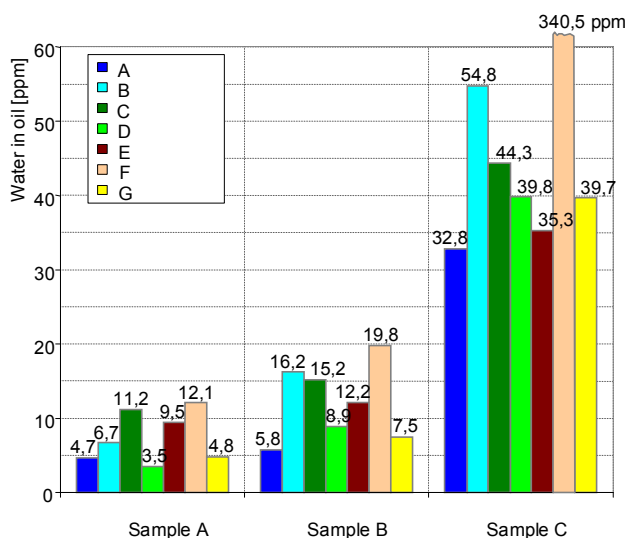


Fig. 6: Moisture in oil in ppm relative to weight as measured by the laboratories

The measurement results of Fig. 6 provide a reasonable conformance only for the wet sample C. For the rather dry samples A and B only a trend is recognizable. Systematic differences are obvious. It has to be mentioned, that at dry oils the results also scatter within one single laboratory, a standard deviation of 20% is not unusual. The following chapters of this article will investigate the influences and thus try to explain the discrepancies.

3 IMPROVED MEASUREMENTS IN PAPER

3.1 Influence of Heating Temperature

Heating with an external oven is widely used for water in cellulose measurements. Cellulose binds water

with chemical bonds of different strengths (Fig. 1). Water measurements should reveal all water from the material, however it is unsure, if the thermal energy releases all the water. Heating temperature and time strictly changes the amount of released water molecules. According to IEC 60814 the temperature should be 130-140°C. The authors of [5] found, that at pressboard samples only a temperature of 180°C leads to results comparable to the methanol extraction method (section 1.4). On the other hand the upper limit for the heating temperature is given by pyrolysis or oxidation of cellulose with subsequent water production in the heating chamber. This occurs for paper above 170°C, for pressboard above 200°C.

Several measurements at various increasing temperatures determine the heating temperature for the material to be measured. Here the optimal heating temperature was found for insulation paper to 160°C and for pressboard to 180°C. These temperatures not only detect more water, rather the measurement is faster (e.g. 5 min at 170°C instead of 12 min at 120°C) and the single measurements are less scattered.

Fig. 7 illustrates the influence of heating temperature on water content and scattering.

3.2 Solvent for Oil Extraction

After titration it is necessary to extract oil from paper in order to obtain the true dry weight of the paper sample for application in equation (2). Unfortunately the standard IEC 60814 does here only state a “appropriate chlorine-free solvent”. Some laboratories do not separate oil from paper and thus obtain a too high paper mass. Others use methanol as oil solvent. Indeed methanol cannot dissolve oil, a dispersion arises instead of a solution, a lot of oil remains in the paper. For this reason heptane was investigated in comparison to methanol. Its nonpolar molecule structure enables heptane to extract the likewise nonpolar mineral oil from cellulose. Other paraffin mixtures with boiling points of 70-90°C are applicable too (e.g. hexane).

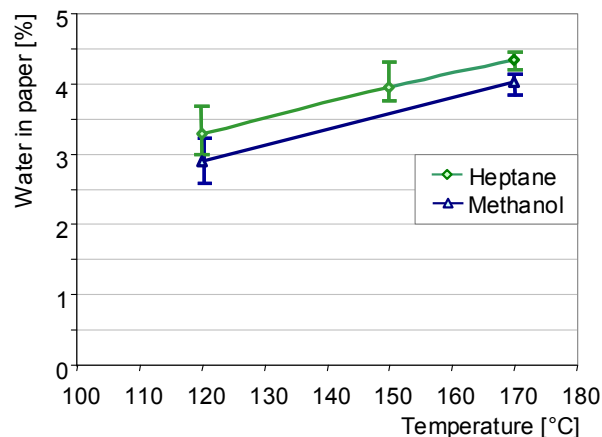


Fig. 7: Detected amounts of water in insulation paper for different heating temperatures and solvents for oil

Fig. 7 proves the qualification of heptane in comparison to methanol. Heptane releases more oil from paper, the dry weight of paper decreases, thus according to equation (2) the obtained water content increases. Here a titration system called Aqua 40.00 by ECH Germany with head space module Coulomat Oven AG from Riedel de Haen as reagent was used.

4 IMPROVED MEASUREMENTS IN MINERAL OIL

4.1 Influence of Aging Byproducts

Aging byproducts from oil degradation and inhibitors may influence the Karl Fischer reaction of oil samples with direct injection. Aging of oil causes alcohols, aldehydes, ketones, acids and sludge. It is assumed, that aldehydes and ketones react with methanol of the reagent to acetals and ketals with water as a byproduct. To prove this suspicion, a coulometric titration cell with direct injection titrated various oil samples (new, aged, inhibited). Two different reagents from Riedel de Haen were used; Hydranal Coulomat AG with methanol and Coulomat AK without, that especially suites for titrations in aldehydes and ketones preventing side reactions.

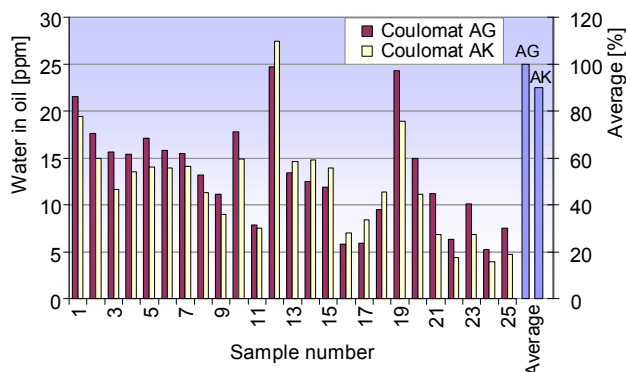


Fig. 8: Titration results comparing the reagents Coulomat AG and AK at various oil samples

Fig. 8 shows the reagent Coulomat AG in comparison to Coulomat AK, which is not sensitive to ketones. The results scatter, but the reagent AG systematically measures 10 % more water compared to AK, which might be explained by side reactions with ketones. Still one has to consider that 10 % are a minor deviation compared to that in the round robin test in Fig. 6. It is not favorable to always use reagents that are insensitive to ketones and aldehydes, since their water absorption capacity is smaller. Currently Karl Fischer reagents based on ethanol instead of methanol are introduced to the market, which promise to be non-toxic, to better dissolve mineral oil and have no side reactions with alcohols [6]. These reagents are not involved in this test.

4.2 Direct Injection versus Heating Method

Three variations of the Karl Fischer technique for oil titration were compared:

- volumetric titration using a Schott Titroline Alpha, with reagent Coulomat Solvent Oil
- coulometric titration with direct injection using an ECH Aqua 40.00 and Coulomat Oil by Riedel de Haen as reagent
- coulometric titration with heating chamber for oils using an ECH Aqua 40.00 and Coulomat Oven AG by Riedel de Haen as reagent, heating temperature 80°C, oil volume 10 ml

Of course all the techniques should come to the same moisture content in oil.

One remark about water in oil measurements by heating in an external oven: Transformer oils usually have very low water contents of sometimes less than 5 µg/g oil. Unfortunately for the heating method the water mass should exceed 50 µg to be distinguishable from the drift and the blank value. Therefore an oil volume of at least 10 ml should be heated. It is not sufficient to use the vials from paper measurements since their useable volume is 2,5 ml only, a special heating chamber for oil is necessary.

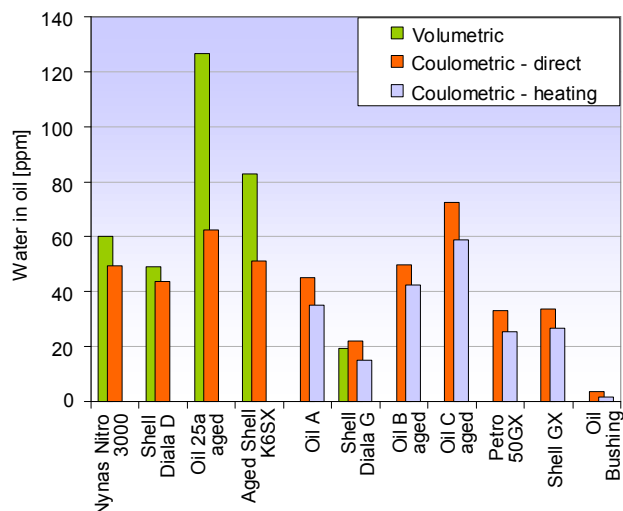


Fig. 9: Moisture in various oils for volumetric titration, coulometric titration with direct injection and coulometric titration with external heating

Fig. 9 depicts the results of the comparative measurements at various new and aged oil samples. For new oils all the three methods came to comparable results, although also here a deviation of 20 % appears. Volumetric titration indicates the highest water contents, followed by direct coulometric titration. Coulometric titration with an external heating chamber comes to the lowest water contents.

In aged oils the situation became even worse. Also here volumetric titration measures the highest water contents. Unfortunately the coulometric titration with external heating in some oils was not able to measure their water content. The drift did not decrease to the

original value but remained at 20-30 µg/min, which possibly indicates a side reaction. This leads to water contents of some 100 ppm as in the round robin test in Fig. 6. As a conclusion, the external heating method cannot be recommended for aged oils, while aged materials are the common case in transformer diagnostics.

5 RECOMMENDATIONS FOR RELIABLE TITRATIONS

5.1 Onsite Sampling

The sampling procedure determines the reliability of the moisture result, it should be performed with care.

Oil should be sampled from different levels in the transformer; if possible top, middle and bottom. Samples should not be taken at high air humidity (rain, fog). When taking the samples, a few litres of oil should be drained out for preventing sludge and standing oil to be sampled. The bottle should be dry and technically clean that moisture inside the bottle cannot contaminate the oil. For the same reason the bottle should be completely filled, leaving no space for air at the top. Since transformer oil is considered to be harmful to the environment, precautions must be taken to avoid contamination of the soil around the transformer.

Paper should be sampled as soon as possible after opening the transformer. The outer layers of the conductor insulation may be moistened by air, thus it should be removed. Remove the edge of paper and pressboard samples too for the same reason. The transformers insulation oil is useful to store paper and pressboard samples during transportation to the laboratory. Besides the cellulose samples keep the oil humidity at a low level close to the original value. When storing oil and paper together, the temperature of oil titration must be identical to that of oil sampling. Notice the oil temperature during sampling directly in the oil, don't use the transformers thermometer.

The transportation time should be short, the time between sampling and measurement ought to be below one week, depending on the tightness of the vessel. Check for the measurement date of the laboratory.

5.2 Quality Assurance in the Laboratory

- (1) Before titration the instrument should be conditioned resulting in a *stable* drift below 12 µg/min. During this the gas circulation and the oven – if available – should be active. At external heating three single measurements of the blind value will give a reliable average to compensate for this factor.
- (2) Water standards (liquid for direct injection, solid for external heating) should periodically check the reactivity of the reagent. A consumed reagent cannot be indicated by a high or unstable drift value only.
- (3) The heating temperature for paper should be 160°C, for pressboard 180°C. Thus the reproducibility

increases, the measurement time decreases and the sample will not be oxidized.

- (4) To separate oil from cellulose an oil-solving medium such as heptane suits better than methanol.
- (5) For titration of oil the coulometric titration with direct injection seems to be the most reliable method. External heating in an oil chamber cannot be recommended because of possible side reactions in aged oils. Volumetric titration owns a lower sensitivity compared to coulometric titration.

6 SUMMARY AND OUTLOOK

The titration according to Karl Fischer serves as a state of the art method for moisture determination in liquid and solid samples. Nevertheless it is subject to several influences, which lead to a bad comparability of results from different laboratories, especial for moisture determination in oils. This was revealed by two round robin tests. Four influences were investigated: heating temperature of paper/pressboard, solvent for oil separation, aging byproducts in oil, external heating of oil. This lead to a guide for reliable titrations, see section 5.

Future research might try to replace methanol in the reagent since it is toxic and sensitive to aging byproducts. The reliability of the external heating method for oils should be improved, especially in respect of aged oils. A comparison to other methods like gas chromatography might be useful, but will raise additional questions.

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