Investigation of gassing behavior, electric and dielectric properties of different insulating fluids

Master thesis
of
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2012

Work program for the Master's thesis

of Omid Ansari

„Investigation of gassing behavior, electric and dielectric properties of different insulating fluids"

In the field of the condition monitoring of electrical equipment and systems, the knowledge of aging behavior and investigation of the decomposition products of the insulating materials are essential. Due to that background the following master thesis task is assigned to Mr. Ansari:

First of all, dissolved gas analysis method have to be done for some service aged Silicone and Midel 7131 samples that were used in some distribution power transformers. Along with DGA method the AC breakdown voltage at different temperatures (ϑ=RT, 40°C, 60°C, 90°C and 110°C), the dielectric loss factor, the specific conductivity and the relative permittivity at ϑ=20°C and ϑ=90°C should be performed for mentioned specimens. Furthermore, the surface tension, density and partial discharge inception and extinction voltage at room temperature have to done as complementary diagnostic methods to obtain more information about insulation state. Finally, all of the mentioned measurements should be applied for new Silicone and Midel7131. Then, the obtained results should be compared with aged ones at the same absolute water content.

The measured results have to be presented in the usual way and explained in their theoretical background. In addition to the observed changes as a function of the breakdown quantity, water content, temperature, as well as the fluid type, conclusions for the reasons of these changes have to be drawn. The elaboration has to follow the existing guidelines. The submitted copies remain property of the institute.

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Matriculation Number: 2839550
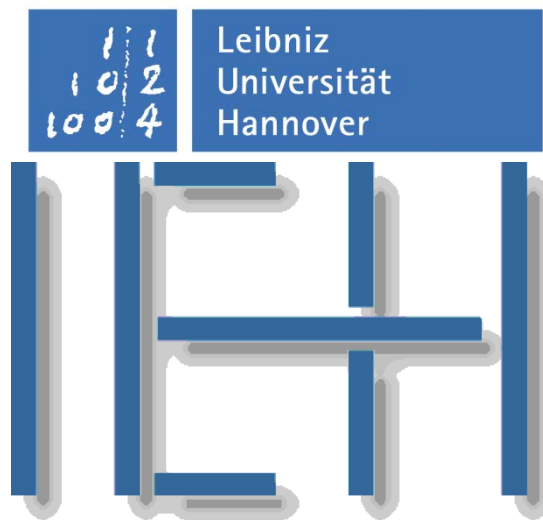
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Here I, Omid Ansari, declare that I have written this work independently and used no words and ideas from any other person, otherwise I announced it as references in this master thesis.

Hannover, September 2012

Contents

1 Introduction

Generally insulating materials in high voltage engineering have different responsibilities. The most important responsibility of them is to providing enough insulation between live and ground sections. Besides, they usually play some other roles according to their mechanical and chemical characteristics. Liquid insulation fluids are utilized widely for filling transformers, circuit breakers and also as impregnate in high voltage cables and capacitors. For power transformers, the liquid dielectric beside providing enough insulation between live and ground parts, it is utilized for cooling and carrying out the heat from the transformer to the ambient atmosphere. For circuit breaker, again besides providing insulation, the liquid dielectric can play an important role for quench the arc developed between the breaker contacts [1].

Transformers are a vital part of the power supply system. The reliable operation of transformers is an important factor. Consequently, it is essential to detect any incipient fault as early as possible and enable planned replacement of the endangered transformer with the minimum interruption of service [2].

The most common method of transformer condition monitoring is the dissolved gas analysis (DGA). In addition to dissolved air, transformer oils contain dissolved gases produced during the normal service life and by localized faults. Conditional upon the type of fault, different gases can be generated in the oil. The composition of the gases caused by a fault can vary within a wide range depending on nature and intensity of the fault. In service transformers are subjected to thermal and electrical stresses, which degrade both oil and paper and producing moisture that together with oxygen (air) damages the insulating liquid. Resulting in deterioration of the physical, chemical and electrical properties of the oil, this cycle continues and cause a undesirable situation for liquid and equipment. Oxygen, in contact with oil, oxidizes the oil and produces acids and polar compounds. The process accelerates by heat and finally sludge is produced. sludge and acids attack the insulating material, resulting in a weakening of the insulating system. Oxidation increases the viscosity of the oil which in turn leads to weak cooling and

transformer overheating. The damaged oil loses its dielectric stability and become not suitable for further use [2]. So as conclusion, it can be said that beside of DGA investigation of electrical and dielectric properties of the insulating oil is necessary and can be very helpful to monitoring and fault detection of the power transformers.

This project tries to investigate the condition of some aged Silicone and Ester fluid samples that were used in some power transformers and find out possible existing faults. So for reaching this goal some kinds of tests such as: dissolved gas analysis, breakdown voltage, dielectric loss factor, specific dc resistance, relative permittivity, partial discharge inception and extinction voltage, absolute, relative and saturation water content, density and surface tension are going to be accomplished. Results of each test will be compared with unused Silicone or Ester samples in the same water content.

In the second chapter of this thesis, general and required information about the insulation fluids is given and specially the chemical and electrical properties of silicone and ester fluids that are used in this work is discussed. The third and fourth chapters explain the preparation of oil samples, theoretical background and laboratorial setups as well as measuring procedure for every test. In chapter five, the obtained results are published and are survived in individual diagrams. Finally, in the last chapter all the results are come in to conclusion and some views are offered.

2 Liquid insulations in high voltage engineering

Liquid dielectrics, because of their inherent properties, appear to be more useful as insulating materials than either solids or gases. This is because both liquids and solids are usually 103 times denser than gases and hence, from Paschen's law it should follow that they possess much higher dielectric strength of the order of 107 V/cm. Furthermore, liquids, like gases, fill the complete volume to be insulated and simultaneously can dissipate heat by convection [3].

Some of the important properties of insulation fluids are viscosity, density, loss tangent, thermal stability, thermal conductivity and flash point but three most important properties that have determinant role in expression of the dielectric fluid's quality are dielectric strength, dielectric constant and electrical conductivity. Presence of water and the fibrous impurities can extremely affect the dielectric strength of the liquid insulations. Therefore, whenever these oils are used as dielectric fluids, in order to have high efficiency they should be free from products of oxidation, moisture and other contaminants. Breakdown voltage value of highly purified liquids is about 1 MV/cm but under actual service conditions, this value decreases significantly because of the presence of moisture and impurities. In the selection of a liquid dielectric some consideration such as: chemical stability, cost, saving in space, susceptibility to environmental influences and so on should be taken into account [1].

Between the existing oils, petroleum oils have most utilization. Some others such as Synthetic hydrocarbons and halogenated hydrocarbons are also consumed for certain implementations. For very high temperature application, less flammable liquids such as silicone oils and fluorinated hydrocarbons are also employed. In recent times, some vegetable oils and esters are also tried to be used instead of petroleum oils. In recent years, a synthetic ester fluid which has trade name 'Midel' has been manufactured as a replacement for askerels. Insulation fluids are normally made by mix of hydrocarbons and are weakly polarized [3]. Insulating oils should fulfill the following minimum health and environmental requirements: non-toxic, biodegradable, stable thermally, recyclable, readily disposable, and not listed as a hazardous material [4].
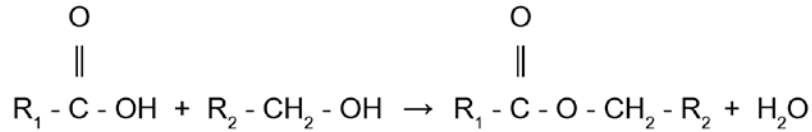
In this thesis different aged and new samples of Silicone and Midel 7131 fluids were tested and investigated to meet the influence of aging on these fluids and recognize the existing faults in power transformers. The production process beside the different characteristics of these oils describe in the following sections.

2.1   Ester fluids

Since many years ester liquids have been used in distribution transformers as an alternative insulating liquids. The major advantage, forcing the application of these fluids, is their improved environmental compatibility. In addition, these liquids comprise several additional advantages such as lower inflammability. Power transformers contain several tens or hundreds of tons of insulating liquids, that may cause a long lasting pool fire in case of a transformer tank rupture due to winding failures. Ester liquid and mineral oil possess an almost similar density. They are completely miscible at any ratio. Almost many electrical and dielectric properties of ester liquids are similar to mineral oils despite the relative permittivity ε_r, which is higher (3.3) than those of mineral oils (2.2). This is an additional benefit if the ester liquid is used for impregnating cellulose as the relative permittivity is closer to the one of cellulose (about 6), thus resulting in a more uniform electrical field distribution within the combine insulation system [5].

Ester insulation liquids divide to two major categories: The synthetic and natural ester fluids. Natural ester fluids can be broken down into saturated, single, double and triple unsaturated fatty acids. Saturated fatty acids are chemically stable, but have a high viscosity. Triple fatty acids have a lower viscosity but they are very unstable in oxidation. To reach an acceptable value of oxidation stability of natural esters, it is necessary to add suitable antioxidants. In addition to DBPC specific antioxidants that use complex phenols amines are in operation. The total amount of antioxidants is limited to 1% and below due to the increase of the conductivity to unacceptable value. Fluids with high percentage of single unsaturated fatty acids have proven suitable. Viscosity of natural ester is about four times higher than the viscosity of mineral oils. Their flash and fire points are significantly higher than mineral oil [6].

Chemical reaction between an organic acid such as carboxylic acid, and an alcohol cause to creation of ester and release of water. figure 2.1 illustrates schematically this process where the radicals R1 and R2 depict a pure connection of C_xH_y [7].

$$R_1 - \overset{\overset{\displaystyle O}{\|}}{C} - OH \ + \ R_2 - CH_2 - OH \ \rightarrow \ R_1 - \overset{\overset{\displaystyle O}{\|}}{C} - O - CH_2 - R_2 \ + \ H_2O$$

Figure 2.1: Formation of an organic ester [7]

Formation of Midel 7131 as a synthetic ester need complete esterification of the molecules of pentaerythritol The chemical structure of Midel 7131 is represented in figure 2.2 [8].

$$R_4COOCH_2 - \overset{\overset{\displaystyle CH_2OOCR_1}{|}}{\underset{\underset{\displaystyle CH_2OOCR_3}{|}}{C}} - CH_2OOCR_2$$
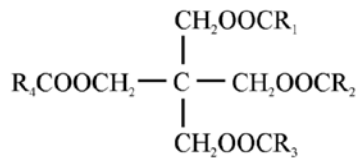
Figure 2.2: The chemical structure of Midel 7131 [8]

R1 to R4 are here partially branched fatty acid radicals with the structure of $C_{6-8}H_{13-17}$ that this structure do not contain halogens such as chlorine or fluorine, therefore the impact of this oil on the environmental totally is reduced. Midel 7131, is a synthetic ester fluid which has high utilization because of its good properties such as: an auto ignition temperature of $\vartheta = 435°C$, very high fire point of $\vartheta = 310°C$ and excellent lubrication which make possible to use of fluid with forced cooled (i.e. pumped) units of all types. Midel 7131 have very low toxicity because it is produced from some compounds that can be largely vegetables in origin, this property and also the biodegradability of this oil makes it harmless to ecosystem life [9].

The electrical and dielectric properties of Midel 7131 are shown in the following table 2.1.

Table 2.1: The electrical and chemical properties of the insulating Midel 7131 with an absolute water content of 50 ppm [39]

Density at $\vartheta = 20°C$	$\gamma = 0.97$ kg/dm^3
Permittivity at $\vartheta = 20°C$	$\varepsilon_r = 3.2$ at 50 Hz
Dielectric dissipation factor at $\vartheta = 90°C$	$\tan \delta < 0.008$ at 50 Hz
Specific DC resistance at $\vartheta = 90°C$	$\rho > 30$ GΩ·m
Breakdown Voltage	$U_d > 75$ kV
Kinematic viscosity at $\vartheta = 40°C$	$\eta = 28$ mm^2/s
Thermal conductivity at $\vartheta = 20°C$	$\lambda = 0.144$ W/m·K

2.2   Silicone fluids

Silicone filled transformers meet mostly environmental and fire protection requirements. Indeed, silicone fluid is environmentally inoffensive and flame retardant. It possesses good aging and oxidation properties. Moreover, it does not endanger living organisms in case of emission. As far as its cooling and insulating properties are concerned, Silicone can be compared with mineral oils [10].

Silicone fluids have higher viscosities than transformer grade mineral oils and thus their overall heat transfer rates are lower than of mineral oils. In the worst case scenario the rated temperature rise will be achieved with 90 percent of the nominal rating. Thus, transformers that will be run at nominal rating would not be suitable candidates for retrofiling with Silicone fluids [11].

Silicone fluids are synthetic linear polymers having the molecular structure shown in figure 2.3 [11].

Figure 2.3: Molecular structure of synthetic Silicon fluids [11]

The organic groups, shown as R, can be virtually of any type and the R groups attached to any one Silicone atom can be the same or different. The polymer terminating groups are generally trimethyls. The average value of n and the molecular weight of attached organic groups determine the molecular weight of the polymer. Critical physical properties of Silicone fluid such as viscosity, volatility and thermal conductivity are determined by the molecular weight. Increased molecular weight results in increased viscosity, lower volatility and lower thermal conductivity. Silicone polymers in which both of the organic groups are methyl groups, CH_3, are called Polydimethysiloxanes (PDMS). The value of n in these fluids can vary from 0 to over 2000. Despite this very large range of molecular weights the PMDC fluids do not solidify over a wide range of temperature. Viscosity increases from 0.65 to 2500000 centistokes as n goes from 0 to 2000. This wide range of viscosities allows the PMDC fluids to be used in a variety of applications such as dielectric fluids, anti-foam agents and heat-transfer fluids. A typical PMDC fluid, for use in transformers, in which all of the R groups are methyl groups have a viscosity of 50 centistokes [11].

The electrical and dielectric properties of Silicone fluids are shown in the following table 2.2.

Table 2.2: The electrical and chemical properties of the insulating Silicone fluid with an absolute water content of 50 ppm [11]

Density at $\vartheta = 20°C$	$\gamma = 0.96 \text{ kg/dm}^3$
Permittivity at $\vartheta = 20°C$	$\varepsilon_r = 2.7$ at 50 Hz
Dielectric dissipation factor at $\vartheta = 90°C$	$\tan \delta < 0.001$ at 50 Hz
Volume resistivity at $\vartheta = 20°C$	$\rho > 10^{14} \ \Omega \cdot \text{cm}$
Breakdown Voltage	$U_d > 50 \text{ kV}$
Kinematic viscosity at $\vartheta = 25°C$	$\eta = 50 \text{ mm}^2/\text{s}$
Thermal conductivity at $\vartheta = 50°C$	$\lambda = 0.151 \text{ W/m} \cdot \text{K}$

3   Preparation of the oil samples

As it mentioned before in this thesis two different kinds of insulation fluids were put to various tests. These fluids are Midel 7131 and Silicone fluid. Four aged samples of each kind of these fluids after sampling had sent to Schering institute through a company for investigation and find existing faults. These samples had different levels of water content. To clarify the influence of the aging on these samples, it was needed to compare the results of various tests on these aged samples with the results of the same tests on new ones in the equal level of water content. For obtaining the favorable absolute water content, I have to make a mixture of both dried and wet insulation fluids in a specific ratio. I calculated this ratio in the base of absolute water content. Function of drying and degassing of insulating fluids, storage of the prepared oil samples, the methods of measuring the absolute water content and the calculation of the mixing ratios of dry and wet samples will come into investigating in this chapter.

3.1   Drying and degassing processes for insulating fluids

Figure 3.1 represents the schematic representation of the apparatus which is used in Schering institute for filtering, drying and degassing of the insulating fluids. The function of different parts of this device are described below step by step.

The main features of filtering, degassing and drying system are depicted in the table 3.1.

Table 3.1: The main features of filtering, degassing and drying system

Specification of apparatus	
Oil flow rate	0.5 L/h
Oil temperature	55°C
Pressure of packing vessel 1	$\leq$ 0.3 mbar
Pressure of packing vessel 2	$\leq$ 0.2 mbar
Residual moisture after the process	$\leq$ 5 ppm
Residual gases after the process	$\leq$ 1% Vol.
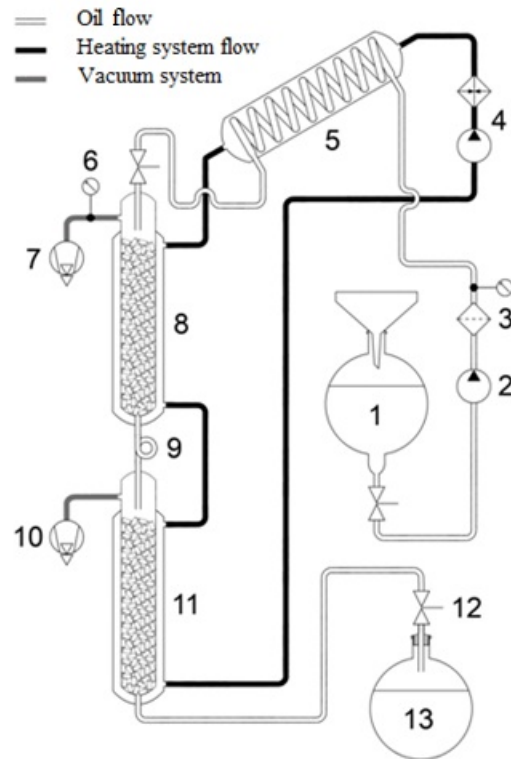
Figure 3.1: Schematic representation of a processing plant for insulating liquids [7]

First of all, by using a funnel untreated insulation liquid is poured into the collection flask (1). the temperature of the heat exchanger (5) and two packed columns (8, 11) reach to 55°C by using a heating system (4) and the temperature remains constant. Via two vacuum pumps (7, 10), the air inside the two columns (8, 11) are removed and by means of an analog pressure measurement device (6), vacuuming procedure is monitored. The pressure in the first column (8) reaches to 0.4 mbar and in the second packed column (11) it drops even lower than 0.1 mbar. The siphon (9) maintains the differences of pressure between the two columns at a constant level. The pump (2) transports the fluid through the filter (3) and the fluid is entered. By decreasing the viscosity of fluid in this step a better distribution of oil is assured when it reaches to the vacuum column. For increasing of the oil surface and so make the degassing and drying procedure in the high efficient, two columns are filled with some kind of cylinders fillers what are called Rasching rings which are made of borosilicate. The primary degassing and drying procedure is done in the first column and then in the second column, lower pressure causes this process repeated extremely , so that the insulation oil ultimately is lost a large amount of the

dissolved water and dissolved gases impurities. Finally, we have dried and degassed oil in the glass flask (13).

3.2 Storage of the dried and degassed insulating fluids

After finishing of the filtering, drying and degassing procedure of the insulating oil, the last vessel include the desired dried and degassed oil that can be separated from related apparatus. In this step by using of a plastic disposable syringe, 5 mL oil is taken for measurement of absolute water content and then the glass container should be completely closed and sealed. After the measurement of the absolute water content of the fluid, the result should be labeled on the related glass container and it should be put in the place where is not encountered directly with the sun shine.

3.3 Measurement of the absolute water content

To reach the desirable absolute water content for each insulating oil sample, we should mix the dried and wet fluids with a definite ratio. This ratio is calculated after the definition of the level of absolute water content of the both dried and wet oils. In this thesis, measurement of the absolute water content for insulating fluids is done by using of coulometric Karl Fischer titration method that full description of this method and related theoretical background will come in section 4.1.2.

3.4 Calculation of the mixing ratios of dry and wet oils for reaching the desired absolute water content of the insulation fluids

By using the following equations, we can calculate the mixing ratios of wet and dried insulation fluids for reaching to the sightly absolute water content.

$$w_{abs,1} \cdot V_1 + w_{abs,2} \cdot V_2 = w_{abs,3} \cdot V_3 \tag{3.1}$$

$$V_1 + V_2 = V_3 \tag{3.2}$$

Which $w_{abs,1}$: Absolute water content of wet fluid in ppm

V_1 : Volume of the wet fluid in L

$w_{abs,2}$: Absolute water content of dry fluid in ppm

V_2 : Volume of the dry fluid in L

$w_{abs,3}$: Desired absolute water content in ppm

V_3 : Desired volume in L

By reorganizing the equation 3.2 for V_1 and substitute into equation 3.1, I will have the following formula to calculate the corresponding volume of dry insulation liquid:

$$V_2 = \frac{w_{abs,3} - w_{abs,1}}{w_{asb,2} - w_{abs,1}} \cdot V_3 \qquad (3.3)$$

By applying equation 3.3 the volume of the wet insulation liquid could be calculated. Therefore, by calculating the needed volume of wet and dry insulation fluids by using of mentioned equations the sightly wetness for each sample is easily obtainable.

4 Theoretical background, measuring methods and laboratorial setups

This chapter describes the theoretical background of the different measurements that performed in this thesis as well as describing measuring methods and laboratorial setups.

4.1 Water content measurement

4.1.1 The role of water in dielectric fluids

Originally water in the dielectric liquids results from change in to vapor of water in the air in the case of "free breathing" or "oil-conservator" transformers, as a by-product of oxidation reactions happen in the liquid, and from thermal disintegration of cellulose-based insulating materials [12].

Water can be existed in dielectric liquids in three states:

a) Dissolved water that is joined to the hydrocarbon molecules in hydrogen link shapes.

b) Emulsified water that exist in the state of super saturation, when existing water is not totally divided from the dielectric fluid.

c) Dispersed water, which exist in the case of super saturation, while existing water in totally divided from the insulating fluid and water droplets are obvious [13].

Dielectric liquids, such as transformer oil, have a low attraction for water, in spite of the fact that the solubility increases obviously with temperature for normally refined naphthenic transformer oil. Their electrical properties are powerfully influenced by the water content, and a high moisture volume decrease the safety boundary. Moisture increases the electric conductivity and dissipation loss factor and decreases electrical strength [12].

In the normal transformers, the entire present water is dynamically stable in the liquid insulation, the solid insulation, and the gas phase. This mentioned balance protocol is

influenced by temperature, pressure, electrical load, formation of surface active compounds, metal ions, etc., in different parts of the transformer [14].

4.1.2 Absolute water content measurement

The determination of absolute water content of samples is performed under DIN 51777-1:1983-03 by means of the 831 KF coulometer. The coulometric Karl Fischer titration is a water measurement technique that has built by Karl Fischer. The idea behind this traditional method is based on a methanolic solution of: sulphur dioxide, a base as buffer and iodine. The equation (4.1) shows the overall chemical reaction that happen in the titration of water content.

As it is seen in this equation, I2 reacts with H2O that this reaction is the basic part of water content definition. In the coulometric Karl Fischer titration by using an electrochemical ways ("electronic buret") the iodine is produced directly in the electrolyte. In order to increasing of the exactness of iodine distribution, an extremely quantitative reaction is used between the amount of iodine and the electric charge. By applying of a periodic current with a constant value to a double platinum electrode, the end point is exhibited volumetrically. This leads to variation of voltage between the platinum wires of the electrode, that in presence of minimum amount of free iodine is intensely low, and by using of this fact the end point of the titration is specified [15].

$$H_2O + I_2 + [RNH] \, SO_3CH_3 + 2 \, RN \Leftrightarrow [RNH] \, SO_4CH_3 + 2 \, [RNH] \, I \qquad (4.1)$$

An outline of a coulometric titration encasement is depicted in the figure 4.1.
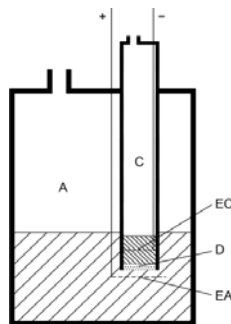
Figure 4.1: Schematic structure of a coulometric titration cell [7]

The coulometric titration cell is comprised of two main parts: a large anode (A) and a small cathode (C) that both of them include a platinum electrode (EA and EC). They can be separated by means of a diaphragm (D) [7]. In this experimental study, my case doesn't have any diaphragm. Container have a solution that is consist of iodide, sulphur dioxide and an amine in a solvent comprised of methanol/chloroform or methanol/longer chain alcohol [16].

The apparatus that is used in this thesis for measuring of the absolute water is an automatic device 831 KF coulometer from Metrohom AG. The outline of this device is illustrated in figure 4.2. It has a generator electrode without diaphragm and is suitable for use in aged oil samples that consist of polluted particles. A magnetic stirrer continues the anode reagent in moving state [15].
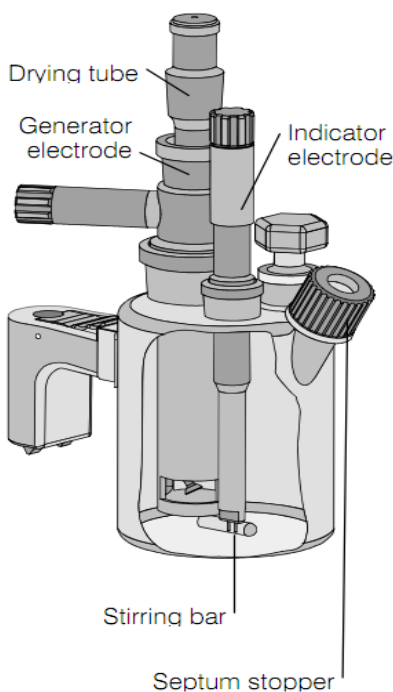
Figure 4.2: Metrohm 831 KF coulometer titration cell [15]

The coulometry reagent that is utilized in this apparatus is Hydranal-Coulomat AG-H manufactured by Riedel de Haën AG, which is built particularly for using with hydrocarbons.