Karl Fischer method
Measuring the water content in transformer oil
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Traditional oil sampling:
Oil samples taken from the transformer, sent to the laboratory for water in oil analysis will not provide accurate dissolved water results. Sampling contamination, “bound” water in particles and other oxidation by-products plus the normal dissolved water, overstates the true water in oil position for our diagnostic purposes. The more oxidised (acid) the oil becomes, the more the water in oil results are distorted because the oxidation by-products bind more water.

Background:
The water content of an insulating fluid in high voltage devices can adversely affect the physical, chemical, and electrical properties of the fluid. Water and oil are not mutually soluble in each other due to their large difference in polarity. Mineral oil is essentially non-polar while water is highly polar. However, up to a certain limit, a small amount of water will dissolve in the oil. This limit is a function of the oil temperature. The solubility of water in oil increases exponentially with temperature. Some typical values for the solubility of water in oil are 52, 82, 132, and 206 ppm at 20, 30, 40, and 50^{o}C respectively. When the amount of water present exceeds the solubility limit of the oil, a separation into two layers occurs. Since the density of water is greater than that of the oil, the water will separate out at the bottom of the unit and appear as free water. The oil above this free water will be saturated with respect to dissolved water.

The solubility values above are the saturation values for new oil; however, as the oil becomes oxidized, the increased level of polar oxidation products in the oil allow more water to be dissolved in the oil.

Significance:
The water content of an insulating fluid will directly affect the physical, electrical, and chemical properties of the fluid. There is a general inverse relation between the water content of an oil ,and its dielectric strength. It will also have the same type relationship with regard to the IFT of the oil. The higher the water content of the oil the more likely will be reactions of the water with certain metals that are present such as iron, e.g. rusting. This will especially be the case when the water content exceeds the solubility limit and there is a separation of a lower layer of free water.

Karl Fischer procedure:
The details of the entire procedure for determining the water content of an insulating fluid by the Karl-Fischer method are given in the ASTM D 1533 standard and are only briefly mentioned here. The Karl-Fischer method is based on the oxidation of sulfur dioxide, SO_2, by iodine, I_2, as shown in the following equation:

$$SO_2 + I_2 + ROH + H2O ==> 3\ H^+ + 2\ I^- + ROSO_3^-$$

This equation essentially states that one molecule of iodine requires one molecule of water in order to oxidize one molecule of sulphur dioxide. The most common method of carrying out this reaction is to generate the iodine needed for the reaction electrochemically and to monitor the reaction potentiometrically. Thus the entire process can be done automatically in an electrochemical cell. The amount of current needed to generate the iodine is measured and related to the amount of water used in the reaction mixture.

Therefore the Karl Fischer method will measure both the dissolved water in the oil and the water in the oxidation by-products (bound water). It does not differentiate.

The IEEE has suggested guidelines for the water content depending on the type of oil and the unit it is being used in (IEEE C57.106-1991). Some representative values are given below:

Type of Oil/Unit	Water Content
Shipments of New Mineral Oil as Received from Refinery	Maximum 35 ppm
New Oil Received in New Unit	
< 69 kV 69 - 230 kV	Maximum 25 ppm Maximum 20 ppm
New Oil Processed for use > or = 345 kV	Maximum 10 ppm
Limits for Continued Use	
< or = 69 kV 69 - 288 kV > 345 kV	Maximum 35 ppm Maximum 25 ppm Maximum 20 ppm
New Oil for Circuit Breakers	Maximum 35 ppm
Processed Oil for Circuit Breakers	Maximum 20 ppm