

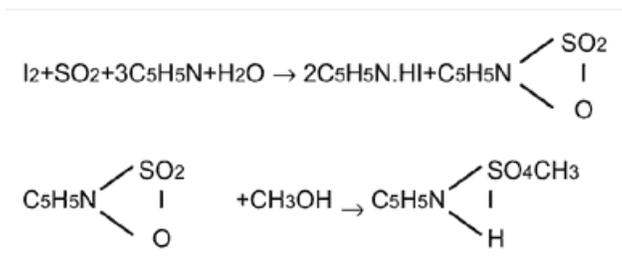
## Recent advances

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Recent advances in coulometric water content determination promote speed, portability, and most importantly, the correct result.

Since publication of his 'New Method for the Determination of Water', the name of Karl Fischer and his titration technique have been recognised throughout the world. The technique is one of the most widely used and reliable methods for the measurement of water content in a large range of samples. Karl Fischer titration is now employed as a standard method in most laboratories and can be subdivided into two main techniques: volumetric titration and coulometric titration. This article is intended to clarify the differences in the techniques and to explain how latest innovations and product designs can overcome the problems usually associated with analysis of crude oil and other petroleum products.

To explain the coulometric Karl Fischer titration it is first necessary to recap on the origins of the technique. In 1935 the German scientist, Dr. Karl Fischer, developed a titrimetric determination of water content using a reagent which contained iodine, sulphur dioxide, anhydrous pyridine and anhydrous methanol. In 1939 Smith, Bryant and Mitchell suggested that, in the presence of methanol the reaction between Karl Fischer reagent and water proceeded in two stages.



This volumetric technique involves dissolving the sample in a suitable solvent and adding measured quantities of a reagent containing iodine until an end point is reached. This end point is determined potentiometrically using a platinum electrode. However, even with the automatic or semi-automatic instruments commercially available there are certain problems associated with the technique. These problems include long analysis time, reagent calibration required, high reagent consumption rate and large sample amount required. This technique is still in widespread use today and there are a multitude of instruments, ranging from simple low cost

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manual types, to fully automated titrators.

In 1959 Meyer and Boyd were first to apply coulometry to the Karl Fischer principle. In this method the sample is introduced into a mixture of pyridine/methanol which contains iodide ions and sulphur dioxide. Using electrolysis, iodine is produced at the anode which then reacts with any water present. The production of iodine is directly proportional to the amount of electricity according to Faraday's Law as shown in the equation:



According to the stoichiometry of the reaction, 1 mole of iodine will react with 1 mole of water, and combining this with coulometry, 1 milligram of water is equivalent to 10.71 coulombs of electricity. It is therefore possible to directly determine the amount of water present in a sample by measuring the electrolysis current in coulombs. (Coulombs are a measurement of current multiplied by time).

Although the original Karl Fischer reagent contained pyridine, most reagent manufacturers now use other amines such as imidazol.

Combining coulometry with the Karl Fischer titration can provide many advantages over the volumetric technique. The main benefits that this coulometric technique offers include higher sensitivity, faster titrations, no reagent calibration required and economical operation. Indeed, unlike volumetric instruments where the solvent mixture is normally changed after each titration, coulometers can determine the water content of multiple samples on one single charge of reagent. The criteria governing reagent life are threefold:

1. The physical size of the titration cell usually allows for 50 – 60 ml of sample to be added. Sample volumes of 0.1 – 2.0 ml are typical for most oil and petroleum products therefore the maximum volume of 50 – 60ml is not usually a limiting factor.
2. The second criteria governing reagent lifetime is the total amount of water that can be analysed before saturation. A standard charge of 100 ml anode reagent can usually analyse up to 1 gram of water. Considering that the injected sample volume is normally quite small, and that usually the analysis is for the determination of low levels of water, then this water capacity should not become a limiting factor either.
3. Similar to all other Karl Fischer reagents, coulometric reagents deteriorate when left out in sunlight and with increases in temperature. Life expectancy for one charge of reagents, when left in the titration cell can be 2 – 3 weeks although this is obviously also dependent on the total amount of sample injected and the amount of water titrated.

Although all commercial coulometers use the same basic principle, the electrolysis current, which produces the iodine, has been applied in different ways.

The first method was to apply pulses of approximately 400 ma and to reduce the time for which each pulse was applied as the end point was approached. It was suggested that the end point could be overshoot when using this technique and so a variable electrolysis current was developed. This allowed the current to be reduced so that only a few milliamps was being applied as the titration neared its end point. Most recent coulometers utilise a combination of both techniques. The electrolysis current is applied in pulses but at reducing current levels (stepped pulse current). With this technique the appropriate amount of electrolysis current is automatically selected dependent upon the detector voltage signal, i.e. the amount of water present. Multiple current levels can be used, each level providing predetermined microgram per second count rates which are all automatically selected and controlled. As the end point is approached the titration rate is automatically reduced until the detector signal reaches its original baseline value. At this time the count stops and the electrolysis current is switched off. If the detector signal then increases above the baseline reference point then the titration recommences. This process continues until the signal is maintained at its baseline value for a predetermined time, at which point the titration ends and the instrument displays or prints out the calculated result.

This coulometric approach to Karl Fischer titration is becoming more widely accepted in preference to the older volumetric method but there is still one more factor to be considered when determining the water content of crude oil and other petroleum products.

The standard test methods, ASTM D4928, MPMS Chapter 10.9, IP 386, etc, for water content determination of crude oil samples by coulometric Karl Fischer titration, stipulate that the Karl Fischer anode reagent should be mixed 60:40 with xylene to improve sample miscibility and reduce waxy deposits and asphaltines from dropping out and thereby causing problems with the generator electrode. This modification to the reagent, and subsequent addition of the oil samples being analysed, affects the resistance / capacitance of the titration vessel.

When this resistance in the electrolysis cell is increased beyond certain limits the coulometer is unable to operate efficiently and provides an incorrect result, usually falsely high.

For this reason, although in principle standardisation of a coulometer is not necessary since the water 'titrated' is a direct function of the coulombs of electricity consumed, the above mentioned methods suggest that the performance of the coulometer be regularly monitored by injecting 10µl of pure water. The suggested interval is after every 10 determinations and the result obtained should be 10,000 +/- 200µg. The reagents should be changed if the result is outside these limits.

Do you then go back and retest the previous 10 samples or do you assume that they were all correctly analysed?

Can you afford to make that assumption?

The Aquamax KF coulometric Karl Fischer titrator One manufacturer of coulometric Karl Fischer titrators, G.R. Scientific, have recently overcome this problem by developing their ACE Control System, (Automatically Compensated Errors – patent pending), which guarantees that the electrolysis current produced by the coulometer and the count rate displayed are always correctly synchronised regardless of changes to the electrolysis cell resistance. This ACE control system is used in all three coulometric titrators manufactured by G.R. Scientific and the Aquamax KF shown has been specifically designed to be truly portable and for use outdoors thanks to its Low Drift Cell. By means of the ruggedised carry case supplied with these instruments operators can now easily transport their compact, battery operated titrator, with reagents already in the titration cell, so that it is ready for use immediately on arrival.

The combination of:

Cutting edge microprocessor technology

Compact product design

Special titration cells for outdoor use

Dedicated cells for crude oil and other petroleum products

Ensure that with the innovation of this recently patented technique, coulometric Karl Fischer titrators can now provide the user with fast analysis, true portability and, most importantly, the correct result every time.

