# Water by Coulometric Karl Fischer Titration

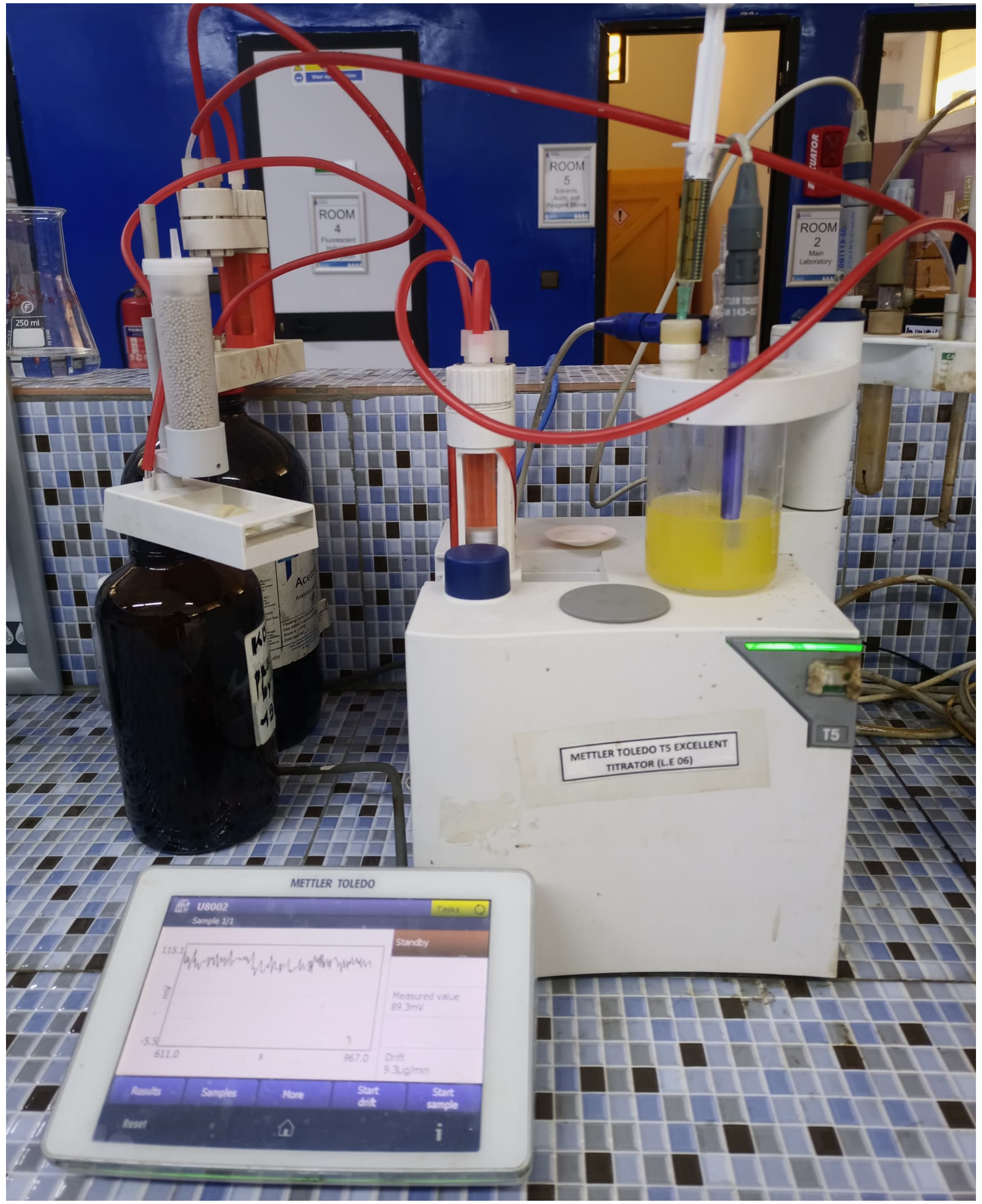
STEWART INTER SEA

## What is Water by Coulometric Karl Fischer Titration?

ASTM D6304 covers the direct determination of entrained water in petroleum products and hydrocarbons using automated instrumentation.

Karl Fischer (KF) coulometric titration is one of the most accurate methods for measuring the water content. Unlike other techniques, it can trace low levels of free, emulsified and dissolved water.

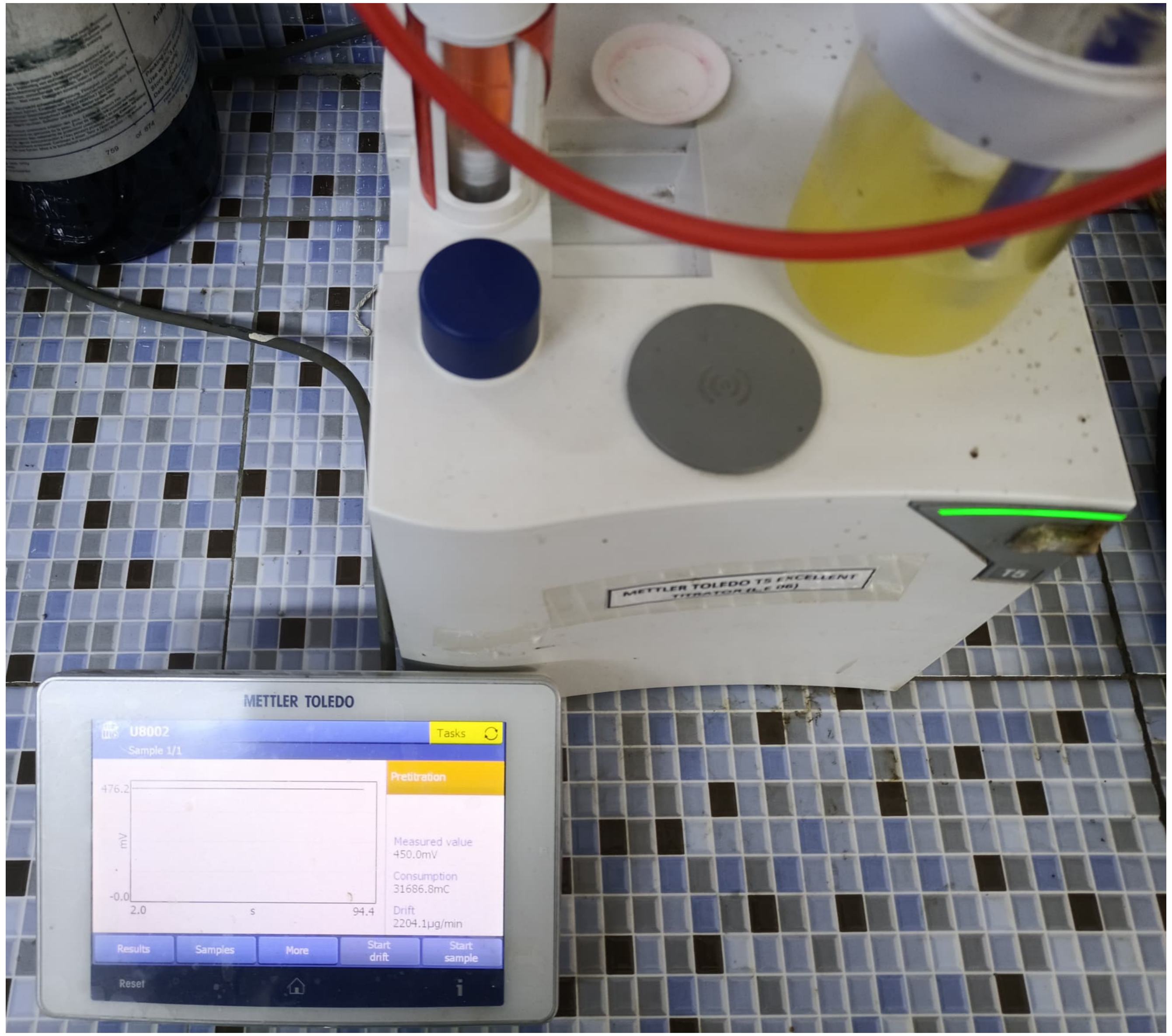
Procedure A covers the nominal range of 20 mg/kg to 25 000 mg/kg.



## Why do we test Water by Coulometric Karl Fischer Titration?

A knowledge of the water content is important in the manufacturing, purchase, sale, or transfer of petroleum products to help in predicting their quality and performance characteristics.

The presence of moisture could lead to premature corrosion and wear, an increase in the debris load resulting in reduced lubrication and premature plugging of filters, an obstruction in the effect of additives, and unwanted support of detrimental bacterial growth.



## How does it work

ASTM D6304 uses Karl Fischer titration to determine the amount of water in a sample. In the coulometric method, the titration cell consists of two parts: an anodic and a cathodic compartment.

The amount of water in the sample is calculated by measuring the current needed for the electrochemical generation of iodine (I2) from iodide (I–). When all the water has been titrated, excess iodine is detected by an electrometric end point detector and the titration is terminated.

Based on the stoichiometry of the reaction, 1 mole of iodine reacts with 1 mole of water; therfore, the quantity of water is proportional to the total integrated current according to Faraday's Law.

Potential Issues and Solutions

## Interfering Components

A number of substances and classes of compounds associated with condensation or oxidation-reduction reactions interferes in the determination of water by Karl Fischer titration. In petroleum products, the most common interferences are mercaptans and sulphides. At levels of less than 500 mg/kg as sulphur, the interference from these compounds is insignificant for water concentrations greater than 0.02 % by mass. The significance of the mercaptan and sulphide interference on the Karl Fischer titration for water in the 10 mg/kg to 200 mg/kg range has not been determined experimentally. At these low water concentrations, however, the interference may be expected to be significant for mercaptan and sulphide concentrations of greater than 500 mg/kg as sulphur. The indirect analysis using a water vaporizer accessory (Procedure B and C) may minimize interferences.

# Potential Issues and Solutions

## Sensitivity to Humidity

Humidity is probably the largest source of error during the titration. Special precautions should be taken during setup and testing, especially in coastal or tropical regions. The air conditioning system should be equipped with a moisture condenser. Also, a Karl Fischer titrator should not be installed near an air conditioner vent.

The titration cells are enclosed to help ensure that water does not enter from the atmosphere; however, a very small amount of water almost always makes it into the titration cell. The amount of water that enters over a period of time is known as the drift. Many manufacturers will give specifications on drift values and maximum allowable air humidity.

## Potential Issues and Solutions

### Diaphragm vs. Diaphragm-less Titration

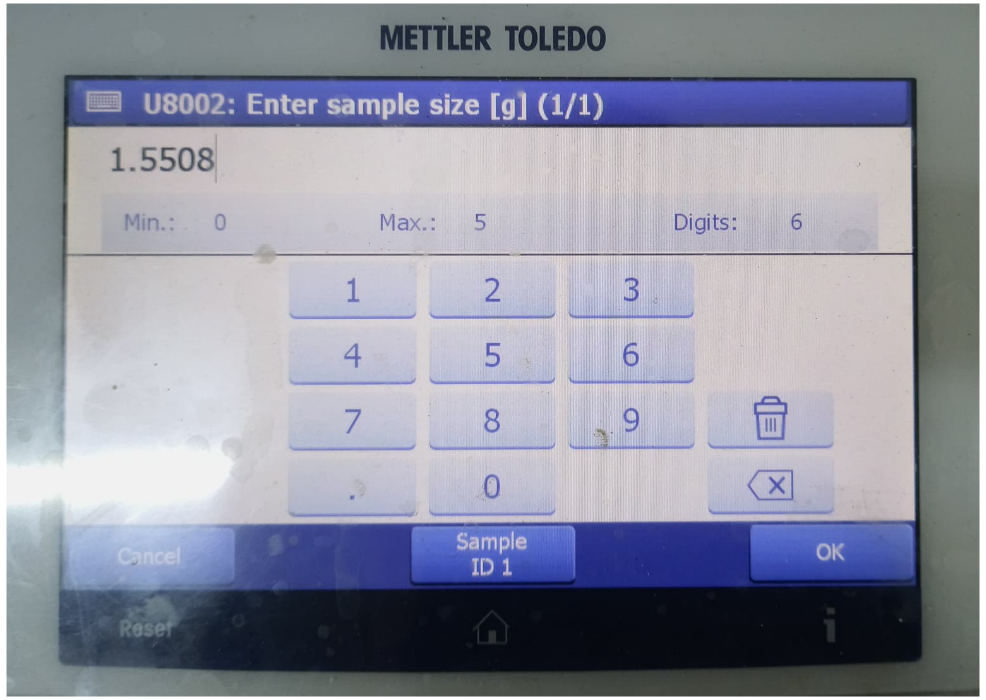
The diaphragm separates the anodic and cathodic compartments. Its purpose is to prevent the electrochemically generated iodine from reversing back to iodide at the cathode instead of reacting with the water. The diaphragm-less titrator uses a different geometric construction to prevent the generated iodine from reversing back to iodide (Figure 2). As hydrogen gas is generated in the cathodic compartment, it creates a layer of gas bubbles on the surface of the cathode. This layer of gas prevents the iodine from being reduced at the cathode. However, it is still possible for small amounts of iodine to be reversed to iodide when reaching the cathode.

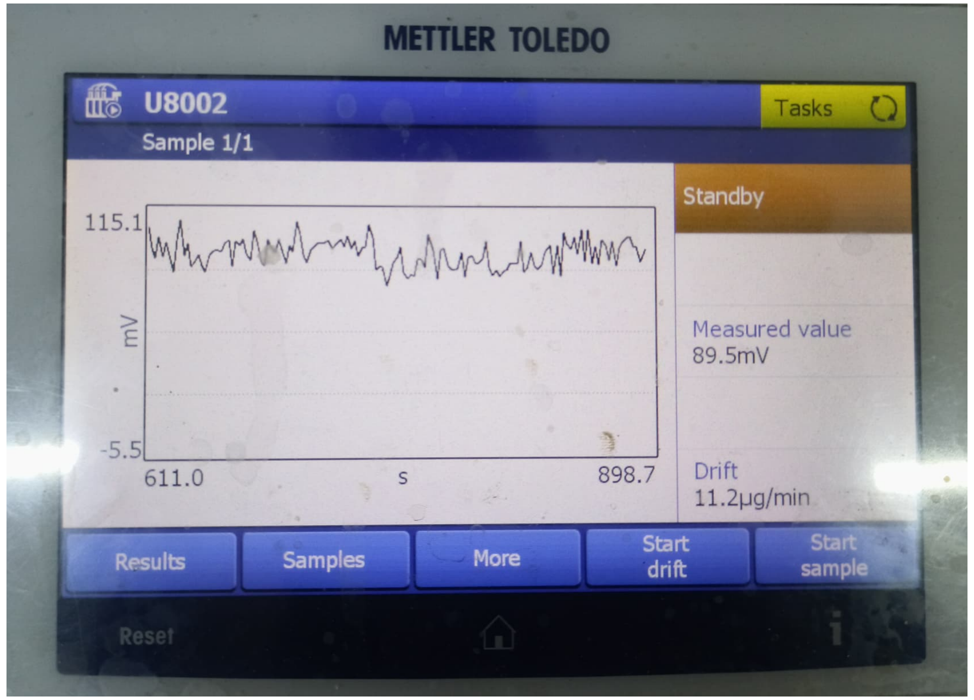
Diaphragm-less titration is advantageous because there is no diaphragm to become contaminated; it is easier to clean; and a lower drift can be used (this relates to how quickly the reaction completes).

## Potential Issues and Solutions

### Built-in Pumps

It is important that the reagents do not become contaminated. Some coulometric titrators come with a built-in pump that can fill and drain reagents. This helps eliminate reagent contamination and reduces the number of steps required for the procedure.

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