Water Determination Using Karl Fischer Titration

Water content needs to be determined at all stages of the manufacturing process from raw materials to finished goods. The quality of the product depends on it. In products such as kerosene, transformer insulation oil or brake oil, the presence of unwanted moisture can have disastrous consequences.

In the pharmaceutical industry, it is essential to know the amount of water contained in the ingredients of a drug in order to correctly predict its lifetime, stability and effectiveness.

In the food industry, the water content of both raw materials and the finished foodstuff needs to be carefully monitored.

The technique most commonly used for these analyses because of its rapidity, accuracy and ease of use is Karl Fischer titration. The titration is based on the oxidation of sulphur dioxide by iodine in the presence of water. It is the same reaction as the iodometric titration of sulphur dioxide in water.

$$I_2 + SO_2 + 2H_2O \rightarrow 2HI + H_2SO_4$$

In 1935, Karl Fischer published a description of “a new procedure for the titration of water” using the above reaction in an anhydrous nonaqueous solvent. However, in order to shift the equilibrium to the right, it was necessary to neutralise the acids produced. Originally pyridine was used as the neutralising base. Later on, diethanolamine followed by imidazole were used as buffers.

Recent studies show that methanol, which is the most commonly used solvent, contributes in the reaction. The Karl Fischer titration can therefore be described by the two following reactions (“B” designates the base used):

$$CH_3OH + SO_2 + B \rightarrow [BH]SO_3CH_3$$

$$H_2O + I_2 + [BH]SO_3CH_3 + 2\,B \rightarrow [BH]SO_4CH_3 + 2[BH]I$$

The working medium

Two types of reagents are available:

One-component reagents

One-component reagents contain all the reactants (iodine, sulphur dioxide and a base) dissolved in a suitable solvent. The working medium (i.e. the solvent required), can be freely chosen by the user depending on the dissolution properties of the sample to be investigated. The stoichiometry 1:1 of the Karl Fischer reaction is only fulfilled if there is more than 25% methanol in the reaction mixture. A methanol-free working medium can be used, however it is important to determine the titre of the KF reagent in the same working medium.

Two-component reagents

The solvent

The modern solvents available today present a high buffer and dissolution capacity. These solvents consist of sulphur dioxide, a base and methanol. The main advantages of these solvents are:

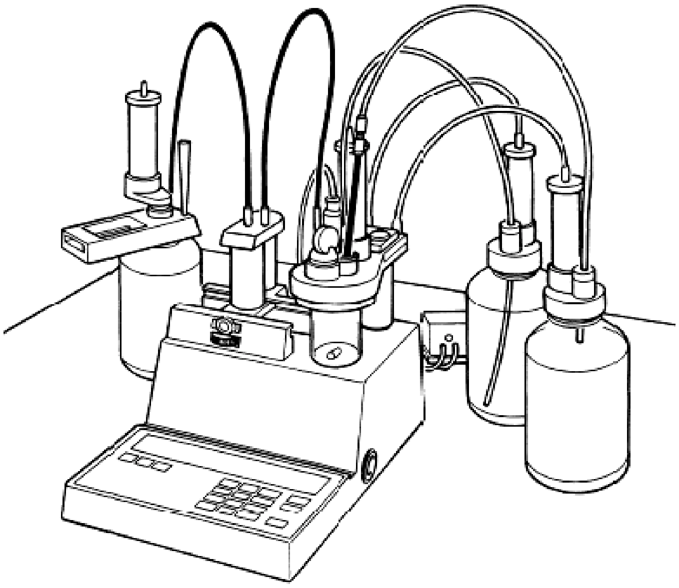
- A more rapid titration due to better reaction kinetics. An advantage especially for the titration of large amounts of water.
- A better reproducibility, because the reaction environment is stable. The pH and the sulphur dioxide concentration remain constant.

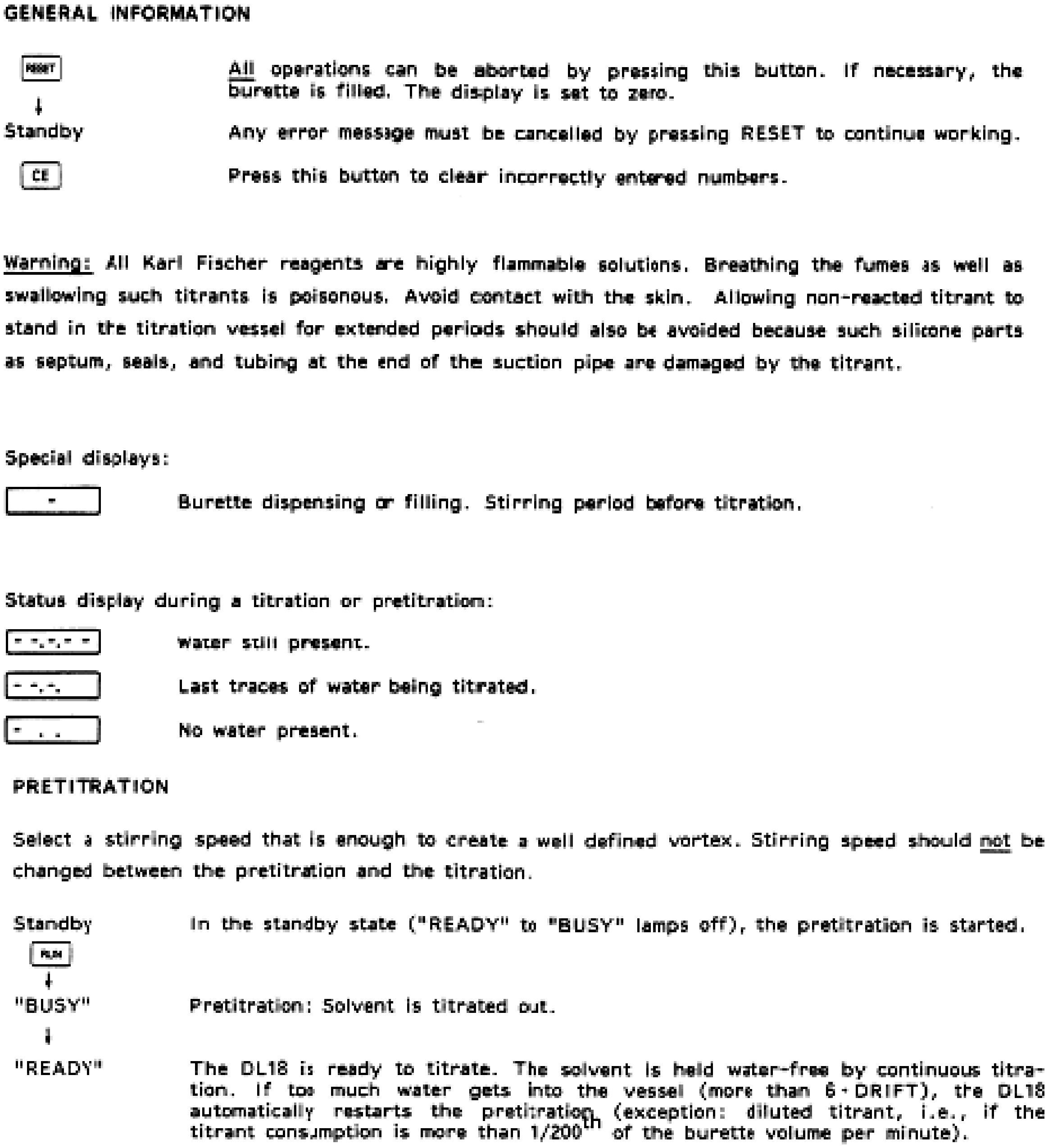
For the titration of samples producing side reactions (aldehydes, ketones and silanols), it is necessary to use an appropriate solvent. Most reagent manufacturers include the letter **K** in the commercial name of such solvents.

The titrant

The titrant consists of iodine dissolved in methanol. We often find that the titrant has three titres 1, 2 and 5 mg of water per ml titrant. Even if it is possible to perform a titration with more than one stroke of the burette piston, it should be avoided by an appropriate reagent titre and choice of sample size. This allows the titration time to be reduced and therefore improves the reproducibility. As for two component reagents, the titration of samples producing side reactions (aldehydes, ketones and silanols), require an appropriate solvent.

DL18 Karl Fisher Titrator:





GENERAL INFORMATION

RESET — All operations can be aborted by pressing this button. If necessary, the burette is filled. The display is set to zero.

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Standby — Any error message must be cancelled by pressing RESET to continue working.

CE — Press this button to clear incorrectly entered numbers.

Warning: All Karl Fischer reagents are highly flammable solutions. Breathing the fumes as well as swallowing such titrants is poisonous. Avoid contact with the skin. Allowing non-reacted titrant to stand in the titration vessel for extended periods should also be avoided because such silicone parts as septum, seals, and tubing at the end of the suction pipe are damaged by the titrant.

Special displays:

-	Burette dispensing or filling. Stirring period before titration.

Status display during a titration or pretitration:

- -.-.- -	water still present.
- -.-.	Last traces of water being titrated.
- . .	No water present.

PRETITRATION

Select a stirring speed that is enough to create a well defined vortex. Stirring speed should not be changed between the pretitration and the titration.

Standby — In the standby state ("READY" to "BUSY" lamps off), the pretitration is started.

RUN

↓

"BUSY" — Pretitration: Solvent is titrated out.

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"READY" — The DL18 is ready to titrate. The solvent is held water-free by continuous titration. If too much water gets into the vessel (more than 6 · DRIFT), the DL18 automatically restarts the pretitration (exception: diluted titrant, i.e., if the titrant consumption is more than 1/200th of the burette volume per minute).

Your laboratory experiment:

1. Receive the sample.
2. Follow sample preparation and handling instructions to weigh the sample or measure its volume.
3. Follow the titration instruction to determine the amount of water in mg.
4. Calculate the amount of water in your sample in mg/mL, or in %%.

Report the results of titration.

SAMPLE PREPARATION

Goal: The water contained in the sample is to be made as freely available as possible for the titration reaction.

Liquid samples	Generally, they need no preparation. (With oils and other samples that are not very soluble in methanol, dispensing of a suitable solvent that is as free of water as possible is added.) Samples that react with components of the Karl Fischer titrant (iodine, sulfur dioxide, alcohol) can cause problems. In particular, this applies to aldehydes, ketones, carbonates, merkaptanes and certain amines. In spite of this, they generally can be titrated using suitable measures. We refer you to the Mettler Application Bulletins (for Order Nos., see Page 25).
Solid samples	No sample preparation if the sample is fine-grained or is soluble in methanol or a suitable solvent mixture that is as free of water as possible (e.g. sodium citrate, sodium tartrate dihydrate need no preparation; for butter or margarine, addition of chloroform is necessary).
Insoluble samples	Pulverize the sample using a ball mill, grinder, mixer (e.g. grain, coffee beans and many other food items). Extract the sample (e.g. wood, paper samples) with a suitable solvent that is as water-free as possible. Heat sample (e.g. certain plastics) and transfer the vaporized water into the titration vessel.

HANDLING SAMPLES

Several samples can be titrated in sequence in a dispensed amount of solvent (capacity limit generally 100 mg water per 20 ml KF solvent).

It is easiest to determine the amount of sample by differential weighing:

- Place the sample in a container (syringe, pipette, weighing boat, etc.) and place it on the balance pan.
- Press tare (set the balance display to zero).
- Introduce the sample into the titration vessel.
- Place the container back on the balance pan.
- Trigger transfer of displayed weight to the DL18 with RUN (negative sign is ignored).

In particular with trace analysis and when working in a high humidity environment, care should be taken to assure that the titration head is well sealed.

When introducing the sample, the titration head should be opened for only a brief moment. On this subject, we make the following recommendations (see also Accessories, Appendix B).

Liquid samples	Samples that have a water content of more than 10 mg can be pipetted directly into the titration head opening using a Pasteur pipette (plastic, disposable pipette) or a syringe. For trace analysis, the titration head should remain sealed. The sample should be introduced by injecting it through the septum with a syringe. For viscous liquids, a larger needle should be used.
Solid samples	Weighing boats made of glass and plastic are listed under Accessories. These allow the sample to be introduced easily into the titration head opening because of the funnel-shaped opening. Depending on the sample, it may be easier to use a glass or plastic weighing boat. It is very important that the sample pours out of the boat easily so that the opening can be closed again very quickly. Fine-grained samples that are not immediately immersed in the solvent can be spun onto the walls of the titration vessel because of the stirrer speed. The following procedure helps in such situations: When the "READY" lamp is on, switch off the stirrer by pressing RESET and start the input dialog with 1 RUN.
Pastes, greases	For these, wide-mouthed Pasteur pipettes are suitable (plastic disposable pipettes) or syringes without needles. Slightly warming the sample facilitates drawing it into the pipette.

TITRATION INSTRUCTIONS:

TITRATION

"READY" ↓	Start the analysis by pressing RUN when the "READY" lamp is on.
"BUSY" blinks RUN ↓	When the sample is introduced into the titration vessel, the actual titration is started by pressing RUN.
"BUSY" ↓	A brief press of any of the numeral buttons causes the intermediate result reached up to this moment to appear in the display. (This intermediate result can be retroactive in a prolonged end phase due to the drift correction.)
Resultat	The result is displayed in the unit selected and is recorded by the printer.

Attention: Do not add your sample until BUSY light blinks!

Titre ("CONC") value is stored in computer memory:

Check of the stored CONC value:

Standby	("READY" lamp off)
CONC	The value stored in memory is displayed for as long as the CONC button is held.

Manual entry of the CONC value:

Standby	("READY" lamp off).
5 . 7 CONC	Key in the value in mg/burette and press the CONC button.

If the titrant concentration as stated by the manufacturer on a bottle of fresh reagent is to be used, this value (usually stated as mg water/ml), multiplied by the burette volume, is entered.

Example:

Reagent	5 mg water/ml
Burette	5 ml
CONC	25 mg water/burette

The effect of external moisture is taking into account by DRIFT value:

Check of the stored DRIFT value:

Standby	("READY" lamp off).
DRIFT	The stored value is displayed for as long as the DRIFT button is held.

Manual entry of the DRIFT value:

Standby	("READY" lamp off).
1 4 DRIFT	Key in the value in µg/min and press the DRIFT button.

The drift is typically between 5 and 50 µg/min. Reasons for a value that is too high are:

- Titration head not well sealed
- Drying agent on titration head is no longer effective.
- Moisture on the underside of the titration head. Titrating out absorbed water at such places can last a long time → remove titration vessel (see Page 13) and dry out the wet spots.
- Samples with a water-binding matrix can release traces of water over an extended period. → Under normal circumstances, determine drift with fresh solvent only. The so-called subsequent consumption can be printed out for control purposes (see Appendix D, Page 27).
- Sample residues on the walls of the titration vessel that are not detected by the titration.