Coulometer KOH – User Manual

Acid number Determination

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1. Coulometer KOH

Coulometer KOH is instrument for acid number determination developed by Diram s.r.o.. It is an add-on module of **Coulometer WTD** – an instrument for water determination, it connects to Coulometer WTD by D-SUB 9 connector and can be controlled by **Coulometer WTD**'s touchscreen or by a computer connected to **Coulometer WTD**.

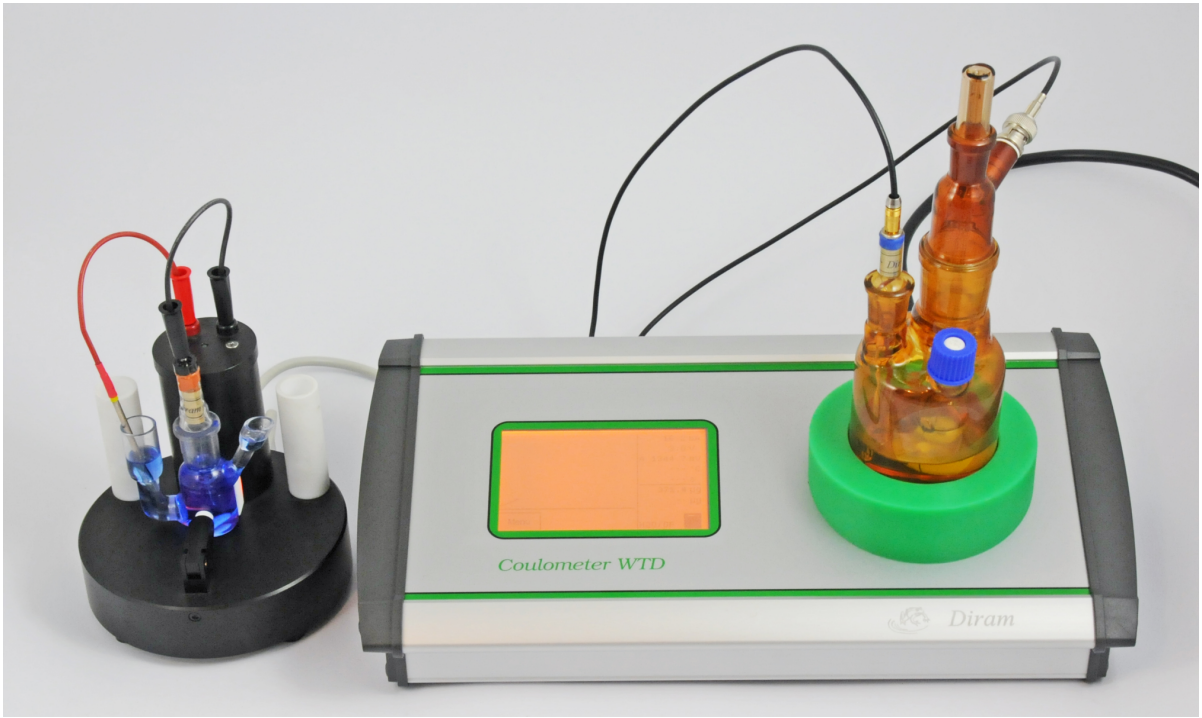

Figure 1: Coulometer WTD with Module KOH

1.1. Description

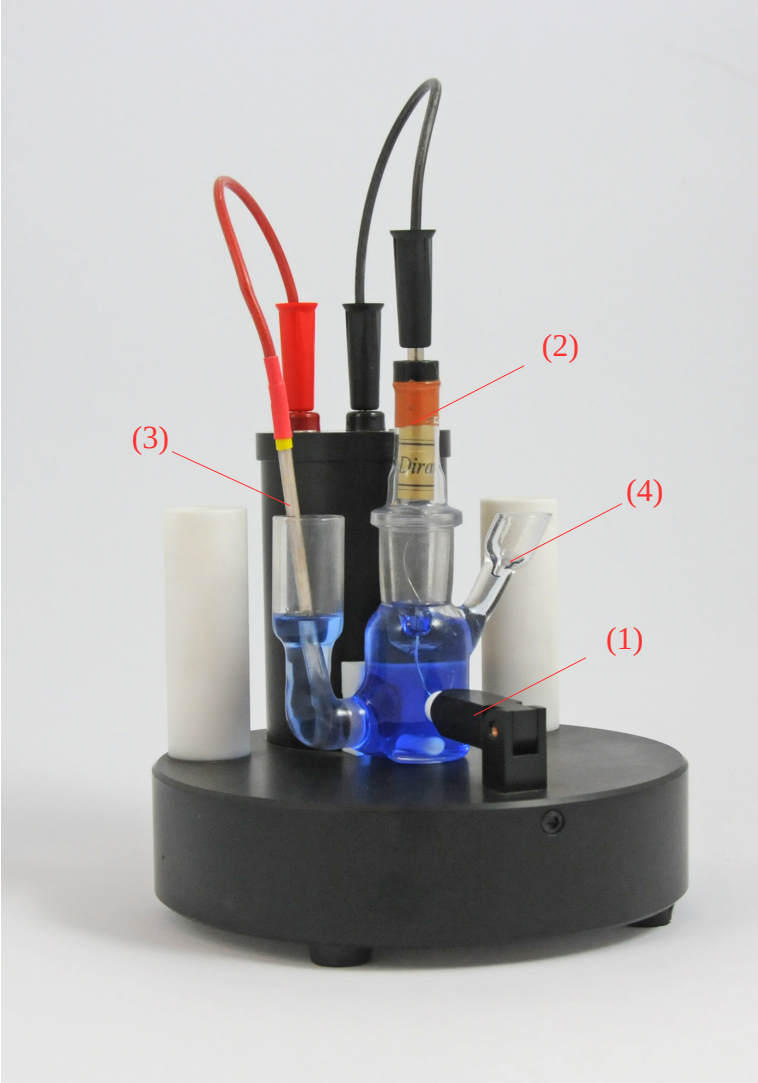

Figure 2: Module KOH

The titration vessel is adjusted by a knob (1) to the stand with integrated magnetic stirrer. The working cathode (2) is fitted to the neck in the middle, the auxiliary anode (3) is inserted to the left neck and the right neck with a capillary serves for the sample insertion (4).

1.2. Technical specification

Measurement range:	from 2 µg KOH / g
Measurement error:	< 0,4 µg to 40 µg KOH, 1 % above 40 µg KOH
Solvent consuption:	10 ml per one analysis
Sample weight:	0.01 to 0.5 g
Result:	mg KOH / g
Titration volume:	10 ml

2. Acid number determination

2.1. Method

Acid number tests are performed in petrochemical products, pharmaceutical, and food products. *Acid number* is usually defined as “The quantity of potassium hydroxide in milligrams necessary to neutralize acidic components present in one gram of oil.” As such, the *Determination of Acid number* is based on titration of acidic components, in the tested sample, by an alcoholic solution of potassium hydroxide.

The classical titration procedure involves dissolving a sample in an alcohol mixture (commonly Toluene) which then undergoes volumetric titration using Alkali blue (B6) as an indicator. The titration is performed until the color changes from blue to violet.

The main problem of volumetric titration method stems from the subjective evaluation of the color transition especially in the case of dark colored solutions. Moreover, the volumetric titration requires the use of standard solutions.

However, *Acid number* can also be determined by potentiometric titration. In this technique, the titration is performed with an alkali solution and measurement of the potential of a glass indication electrode. The weaknesses of this method include the stability of indication signal, the stringent calibration of the electrodes and involves the obligatory need standard solutions.

The Diram **Coulometer KOH** uses the convenient combination of coulometric titration with spectrophotometric indication. Coulometry enables a high precision of the measurement, without requiring the use of stock solutions nor continual calibration against standards. The titration is performed in a closed chamber avoiding the presence of unwanted CO_2 of environmental air.

The titration solution composes of an alcohol-toluene mixture with the addition of water (cca 2 %), an electrolyte and the indicator alkali blue B6. The titrant is generated electrolytically directly in the cell, and in the cathode compartment, the water is decomposed to a gaseous hydrogen and a titrant: OH^- ions. Considering sufficient water concentration in the electrolyte, the current yield of the reaction is close to 100% as the reduction of alcohol and toluene does not take place under these conditions. The total charge necessary to neutralize acid components of the tested sample is finally converted to the equivalent amount of potassium hydroxide.

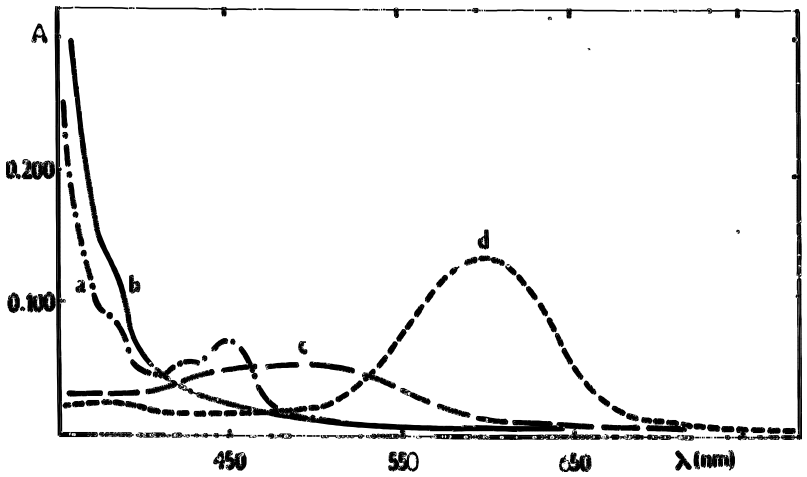

Figure 3: Absorption curves

Figure 3 depicts the absorption curves of alkali blue B6 acidobasic indicator at pH 12 (curve c) and at pH 2 (curve d) and an absorption of electrolyte with the addition of two different dark colored oils (curves a and b). The acid form of the indicator has a blue color, and its absorption maximum is at 603 nm. At this wavelength the absorption of other components of the typically tested solution is low and the orange LED emitting at this wavelength is, therefore, convenient for spectrophotometric indication.

A block-diagram representation of the titrator is shown in Figure 3. The titration vessel V is shaped so that a part of the solution is placed between a photodiode PD and a LED, of the detector D. The current source is driven by a microprocessor M is taking control feedback via the indication signal, i.e. the current of the photodiode PD.

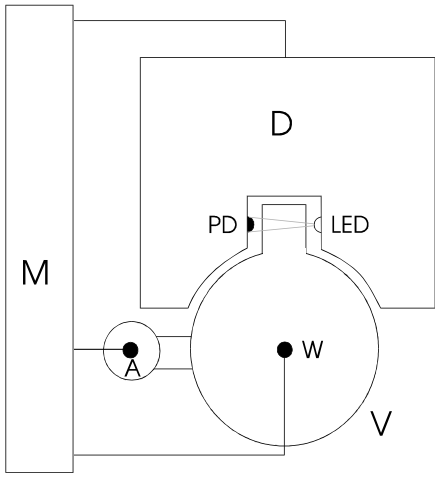

Figure 4: Block scheme of the titrator

After insertion of a sample into the vessel, there is usually an instantaneous change of the indication signal, (corresponding to an instant change of color) which automatically triggers measurement recording of the titration via the control unit. The end of the titration is established when the

indication signal returns to its original level. During the titration, the equivalent amount of KOH is constantly calculated along with continuous correction using compensation current. This value equivalent amount of KOH is displayed during the analysis, and then, once the sample weight is entered, converted to a result in mg KOH/ g.

This absolute coulometric method enables a high precision of the measurement and does not require any calibration using standards. Only a single 10 mL filling of electrolyte solution in the titration cell, is required to perform a single analysis.

Analysis of oils with a low acid number require the sample weight to be as high as possible. The sample weight of oils, with a low acid number, should be as high as possible. Unfortunately, the solubility of oils in an electrolyte solution is limited and also dependant on the type of oil. In the case of mineral oils, it is usually impossible to analyze more than 0.5 to 0.3 g of oil. Higher amounts of oil produce a suspension that disturbs the spectrophotometric indication.

On the other hand, in samples with a high acid number, the sample weight should be limited not to exceed the equivalent amount of 40 µg of KOH.

2.2. Titration vessel

The titration vessel is a special shaped silica glass chamber. The working cathode space contains 10 mL of the electrolyte and is closed by ground glass joint no 14, with sealed platinum wire representing the cathode-working electrode. A diaphragm separates the anodic space. After filling with 10 mL of Acititron B6 catholyte, the vessel is closed by the ground joint with a platinum electrode. The excess of the electrolyte is drained by a capillary which also serves for sample insertion. The anodic space is filled with 1 mL of anolyte Acititron P.

TIP: Keep a piece of cotton wool (or absorbent cloth) near the capillary vent when closing the cathode space, to absorb any excess of the electrolyte and avoid spilling of the solvents.

NOTE: It is important that the level of the solution in the anodic space is lower than the main compartment otherwise the leaching of the anolyte causes an increase in the compensation current.

2.3. Preparation of measurement

Insert the pre-filled vessel to the holder and adjust it with the knob, connect the cathode and insert the auxiliary electrode to the anode space. The instrument prepared for measurement is shown in Fig. 2. Connect the Coulometer KOH to the Coulometer WTD by cable with D-SUB 9 connector. Connect Coulometer WTD to the power source. Switch on the Coulometer WTD by the main switch.

Measurement of acid number can be, as in the case of H_2O determination, controlled both by Coulometer WTD touchscreen and by the ***Diram Measure*** program on a connected computer. The manner of control is the same as in the case of water determination. Determined amounts are given in µg of KOH. For the details, please refer to Coulometer WTD User Guide.

After switching on, it is first important to select the type of determination. Using *Setup / Device* on the touchscreen or *Device / Device selection* in *Diram Measure*, select acid number determination (KOH).

The device automatically starts to prepare for measurement: the stirring is switched on and compensation is automatically started. In the preparation phase, the compensation by current occurs until pH of the electrolyte reaches the color transition of the indicator. The originally blue color changes to violet. The instrument is ready for measurement.

IMPORTANT: The color of the solution will continually fade, so it is necessary to perform the measurement within 4 minutes otherwise there is a need to start again with a fresh solution.

2.4. Sample insertion

The instrument is ready to measure when in the right down corner there is "ready" icon displayed. When the device is ready to measure the compensation continues to maintain the constant level of the indication signal. After insertion of the sample, the titration is immediately started. The difference between the current indication signal and its set point value determines the generation current value so that the generation current decreases by the end of titration. The charge integration occurs at constant time intervals.

Insert the sample in the weight range between 0.02 and 0.5 g by syringe with needle (max. diameter 0.8 mm) through the capillary to the center of the vessel. After the insertion, the sample has to dissolve completely without formation of an emulsion. For this reason, it is not possible to perform multiple analyses and the electrolyte should be exchanged after each analysis. The sample weight is a difference of weight of the syringe before and after sample insertion.

2.5. Result

The measurement finishes automatically after reaching the initial value of the indication current. The measurement can be equally stopped manually by pressing the ***Stop*** button on the touchscreen or in the program. Such an analysis is considered as being unfinished and discarded.

After finishing the analysis, the resulting value is displayed on the touchscreen in µg KOH. Depending on the setup it is necessary to insert or confirm the sample number and the sample weight. The sample weight in grams is entered using the touchscreen and the device immediately returns a value in mg KOH/g. After that, it is necessary to press ***Cancel*** or ***Save***. When pressing ***Cancel***, all the current results are lost. When choosing ***Save***, the results are sent to a computer or stored in the internal memory of the instrument. The sample number and weight are also possible to be inserted before measurement. The values are then used for the following analysis.

2.6. Titration end point

The alkali blue B6 changes its color according to pH of the solution from blue through violet to red color. For accurate analysis, it is essential to set properly the end point of the titration. The end point of titration can be set on the display by ***Menu*** / ***Setup / Constants / Set-point*** or in the program by ***Device / End-point*** adjusting the set point level according to a visual evaluation. It is convenient to set the target level for the transition point of the color indicator – violet color. If the end point is set in the blue or red ranges, the measurement rate and/or sensitivity can be negatively affected.

2.7. Titration solutions

Acititron B6Li is a solution containing 0.12 M lithium chloride in alcohol and toluene (1:2) and 2 wt% of water. The acid-base indicator is alkali blue B6. The solution preparation is slightly complicated by limited solubility of the alkali blue. It is recommended to purchase the solution from the manufacturer.

The solution cannot be exposed to temperatures below 10ºC as this can cause precipitation of the indicator and an irreversible loss of blue color. For this reason, care should be taken when transporting/ordering during cold weather.

Acititron PLi is 0.2 M solution of lithium chloride in alcohol.

WARNINGS/PRECAUTIONS

The solutions for acid number determination are hazardous in case of

- skin contact (irritant),
- eye contact (irritant),
- of ingestion, and
- of inhalation.

Slightly hazardous in case of skin contact (permeator).

- Keep away from heat.
- Keep away from sources of ignition.
- Do not ingest.
- Do not breathe gas/fumes/ vapor/spray. Wear suitable protective clothing.
- In the case of insufficient ventilation, wear suitable respiratory equipment.
- If ingested, seek medical advice immediately and show the container or the label.
- Avoid contact with skin and eyes.
- Keep away from incompatibles such as oxidizing agents.
- Store in a segregated and approved area.

- Keep container in a cool, well-ventilated area.
- Keep container tightly closed and sealed until ready for use.
- Avoid all possible sources of ignition (spark or flame).

2.8. Testing of the device

The measurement accuracy can be tested by titration with an acidimetric standard. For example, an alcoholic solution of benzoic acid can be used. The alcohol first should be distilled with the addition of sodium hydroxide. The purified alcohol can be used for the preparation of 0.01M solution of benzoic acid.