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Moisture content of tall oil by coulometry

Scope

This test method covers the determination of water in liquid organic materials containing <2% water. The moisture content of tall oil is determined by automatic titration with coulometrically generated Karl Fisher reagent. In the Karl Fisher reaction, iodine reacts with water in the presence of sulfur dioxide, an organic nitrogen base like pyridine and an alcohol:



With coulometric titrators the required iodine is produced by anodic oxidation of an iodide contained in the cell reagents. The sample water content is then determined directly by electronically integrating the current required to generate sufficient iodine to precisely react with the water in the sample.

Safety precautions

Always operate the titrator in a fume hood. Most of the reagents, including some of the pyridine-free systems are noxious or toxic and inhalation or direct skin contact with them should be avoided.

Apparatus

1. Coulometric Karl Fisher titrator.
2. Sample vials, 8-nt or 4-dram.
3. Medicine droppers.
4. Disposable plastic syringes, 1-cc with 16, 18 or 20 gauge needles.
5. Syringe, 10-uL.

Reagents

Karl Fischer pyridine-free reagent. Reagents are available from the manufacturer of the apparatus.

Instrument preparation

Prior to sample analysis the analyst must become familiar with the operation of the titrator which differs slightly depending on the manufacturer of the apparatus.

1. Prepare and calibrate the apparatus as specified in the operating manual supplied by the manufacturer. This generally includes the following steps:
 - a. Clean and assemble the titration chamber.
 - b. Pour the titration solution into the chamber.
 - c. Add the iodine generator solution to the generator assembly.
 - d. Put the instrument in STANDBY position.
 - e. Slowly add neutralizing solution normally by injection with a syringe)
 - f. Continue the addition until the instrument indicates by a light or a message on an LCD that excess water is present.
 - g. Stop the addition of neutralizing solution.
 - h. Let the instrument stabilize for 1 hour in the STANDBY position.
2. Verify the instrument by injecting a known amount of water, usually 1 uL to 5 uL below the surface of the titration solution.
3. Put the instrument in the TITRATE or RUN position and record the reading when the END light comes on or a message appears that the titration is complete.

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Moisture content of tall oil/2

- Record the reading. This reading is usually in micrograms or milligrams of water and should be within $\pm 5\%$ of the amount of water that was added.

Example: for 5 uL of water the reading should be 5000 ug \pm 250 ug.

Procedure

- Some coulometric titrators require that the sample be injected through a septum. If this is the case proceed as follows:
 - Draw approximately 0.5 ml, of the tall oil into a 1-cc disposable syringe. Wipe the needle clean with a dry paper towel.
 - Weigh the syringe with the sample to the nearest 0.001 g. Record this weight.
 - Inject about 0.1 to 0.2 mL of the sample into the titrator. Withdraw the syringe.
 - Weigh the syringe to the nearest 0.001 g and record this weight.
 - Proceed to step 6.

For instruments which do not require through-septum injections go to step 2.

- Put approximately 4 mL of tall oil into a small sample vial. Do not allow the sample to touch the outside of the vial.
- Put a medicine dropper into the vial and weigh the vial, sample and medicine dropper together on an analytical balance to the nearest 0.0019. Record this weight.
- Using the medicine dropper, introduce one to two drops of the sample into the coulometric titrator.
- Put the medicine dropper back into the vial and weigh to the nearest 0.001 g.. Record this weight.
- Begin the titration.

Calculation

Moisture, % = $\frac{\text{micrograms of water found}}{\text{weight of sample in g} \times 10,000}$

Report to the nearest 0.001%.

Alternate methods

PCTM 4A, PCTM 4C

References

ASTM D1364 "Water in Volatile Solvents."
ASTM D890 "Water in Liquid Naval Stores."

Appendix

In general, the coulometric reaction cell consists of a small vessel which houses an iodine generating electrode and a

sensing electrode. To keep out moisture, the vessel is sealed except for a sample and reagent introduction port which may be opened as needed. The iodine generating electrodes consist of an (inner) cathode and an (outer) platinum screen anode, separated by a glass frit. Iodine generation takes place at the anode. An equivalent amount of reducing species is created at the cathode. The glass frit and spatial arrangement of the electrodes prevents unwanted migration of the reducing species.

The sensing probe is a dual platinum electrode to which a voltage is continuously applied. A sharp decrease in cell resistance is recorded when the highly conductive excess iodine appears, after all the water in the sample has reacted. This is the equivalent of the end point in the volumetric titration with Karl Fisher reagent. (Reference ASTM D1364).

In the stand-by mode a coulometric titrator continues to generate iodine on demand as trace quantities of atmospheric moisture enter the apparatus. Between samples, the end-point is always held in this way and the instrument is always ready for use, provided reagent solutions are replenished when needed. All current models of coulometric Karl Fisher titrators have warning indicators to alert the analyst when reagents need replacement.