KF Coulometric Troubleshooting Tips and Routine Maintenance

General

This document details Karl Fischer troubleshooting tips, good practices and routine maintenance.

Procedure

A. Coulometric cell

1. Inspect the generator electrode
    a. If using without diaphragm, 6.0345.100, then the mesh should be flat and not concave into the cylinder. Carefully flatten the mesh. The mesh should be about 5-7mm from the anode.
    b. If black deposits are present on the mesh, then clean the generator electrode, see Appendix I. These black deposits are effects of continual use of the Coulomat reagent past the limit. Refer to the technical specifications of the reagent for replacement.
    c. If using with diaphragm, 6.0344.100, then the ceramic diaphragm should have a cream or white color. Routine cleaning is recommended every 1 - 6 months or depending on the number and type of analyzed samples, see Appendix I.
2. Inspect the Indicator [double platinum wire] electrode, 6.0341.100.
    a. The pins should be 3 mm apart. Adjust with care since the pins are fragile.
    b. The pins should be straight. Adjust with care since the pins are fragile.
    c. Routine cleaning is recommended every 1 – 2 months or depending on the number and type of analyzed samples, see Appendix I.
3. Molecular sieve replacement
    a. Every 4 – 8 weeks for controlled humidity.
    b. Every 1 – 2 weeks if humidity is greater than 70 %.
    c. The sieve can be regenerate in a 200 C oven for 48 hrs or 300 C oven for 24 hrs.
    d. If sieve becomes saturated with volatiles, then replace with dried sieve.
4. Cleaning and Inspecting the vessel – perform this quarterly or more often due to samples throughput or matrix.
    a. Ensure that o-ring is intact and not corroding. In older systems, this is Teflon Top.
    b. Verify that the Teflon sleeves seal both the generator and indicator electrodes.
    c. Properly empty the vessel and clean the vessel
        i. Soap and water
        ii. Flush with water 3 – 5 times to remove soap residue
        iii. Rinse with about 20 - 30mL methanol or acetone for ketone system
        iv. Rinse with about 20 mL coulomat reagent.
        v. Direct injection KFC system, fill with about 100 mL Hydranal Coulomat reagent.
        vi. Oven KFC system, fill with 150 mL Hydranal Coulomat AG-OVEN reagent
    d. Tighten all connections
    e. Replace septum regularly
    f. Don't forget the stir bar.
        i. For a 800 or 700 series stirrer, the stir rate should create a wave on the surface or mini vortex but not exposed the two wires of the platinum electrode

B. Oven, if applicable

1. Tighten all connections with the 3" wrench
2. For a 800 series stirrer, the stir rate should be very high 12-15 with the standard 1" stir bar to create a snow global effect.

3. For a 700 series stirrer, the stir rate should be very high 6-7 with the standard 1" stir bar to create a snow global effect.
4. If using nitrogen, then a moisture scrubber/filter must be connected and replaced every 6-12months depending on usage and drift stability of KFC oven system.
5. If using nitrogen, then the main nitrogen source regulator should be < 4PSI; otherwise, the flow sensor can be damaged.
6. Heatable transfer tube.
   a. The tube should be warm to touch.
   b. The connection of the buret tip to the transfer tube should be inspected for loss of seal and moisture.
   c. The heatable transfer tube should be positioned in the vessel such that it isn't bubbling into the generator. It should be positioned over the stir bar for best delivery.
   d. The heatable transfer tube is a consumable part which should be replaced based on sample through put and loss of seal, typically, 12-18 months.
7. Molecular sieve
   a. Every 8 - 12 weeks for controlled humidity.
   b. Every 2 – 4 weeks if is greater than 70 %.
   c. The sieve can be regenerate in a 200 C oven for 48 hrs or 300 C oven for 24 hrs.
8. Inspect the outer and injection needle for blockage.
9. The injection needle can be sonicated in appropriate solvent.
10. The outer needle can be cleaned with a brush.
11. If there is a blockage, then inspect the needle assembly block and heatable transfer tube.

C. Good Coulometric practices

1. Direct injection system
   a. Run a standard to check the functionality of the KF system. See Appendix II.
   b. If the drift is 0, then don't start a sample but review Part A for root source of error.
   c. If the vessel solution is brownish or reddish, then determinations shouldn't be started. Review Part A to locate root source of error.
2. Oven system
   a. Run 2 old blanks using a sample method. This is a system purge. These used vials can be from previous day.
   b. Run 3 blanks using the blank method. The average is saved to a common variable for subtraction from samples and standards
   c. Run 3 Hydranal oven standards using a sample or standard method or follow QA or SOP requirements.
   d. Run 1 new blank using a sample method. This is a blank verification. The water content should be ±5ppm after blank subtraction. Always follow QA or SOP requirements.
   e. Depending on the sample type a solvent rinse might be required to maintain a clean needle and transfer tube.

KF Coulometric Troubleshooting Tips and Routine Maintenance

1. **If error "check generator electrode" is generated by the coulometer, then try the following:**
    a. Check cable connections are connected to correct electrode.
    b. Check that method parameters are correct.
        i. Generator assignment is correct, refer to manual
    c. Check if generator is broken, dirty or bent, refer to step A.1 and A.2
    d. Clean vessel and electrodes, refer to step A.4 and Appendix I
    e. Replace cable.
    f. Replace generator electrode
2. **If error "overtitration" is generated by the coulometer. This indicates that there is too much Iodine generated either by the chemistry of the sample or titration is too fast.**
    a. Check stirring. If stirring is too low, then iodide can pool around the generator electrode and create an access.
    b. Check both electrode cable connections are connected to correct input and electrode.
    c. Clean electrode and vessel, refer to step A.4 and Appendix I, then replace reagent.
    d. Check if either electrode is misaligned or bent, refer to step A.1 and A.2
    e. Replace generator electrode.
3. **If error "sample unfit" is generator, then this indicates that the required max generator rate is higher than max.**
    a. Sample or film is on indicating electrode. Cleaning is required, refer to Appendix I.
    b. Check electrodes for damage, refer to steps A.1 and A.2
    c. Exhausted reagent so clean vessel, see step A.4, then refill with fresh reagent.
    d. The ratio of sample to coulomat is excess [20%] which effects the KF chemistry. Meaning the coulomat has to be changed even though it hasn't reached its water capacity because the %organic solvent or sample in the vessel is >20%.
    e. Stirring not sufficient such that the sample creates a "field" around the indicator electrode. Increase stir rate required, unless already at max.
    f. Failed electrode cable(s).
    g. If using an oven, the air is flowing up into the generator electrode
4. **If the drift is greater than the titration rate, then either the cable or Polarizing input has failed.**
    a. Meaning if the titration rate equals 1200 and the drift maintains at any value greater than 1400.
5. **If the drift equals zero, then check the following:**
    a. Clean indicator electrode
    b. Check pin alignment of indicator electrode
    c. Replace reagent
    d. Replace indicator electrode

Appendix I Cleaning Karl Fischer Electrodes – excerpt from Metrohm KF leaflet

2.2 Cleaning the indicator electrode

CAUTION

Use caution when cleaning the indicator electrode in order not to bend the Pt pins.

Contaminated indicator electrodes can be cleaned with an abrasive agent such as aluminum oxide powder (6.2802.000 polishing set) or toothpaste. Afterwards, rinse first with water and then with methanol.

2.3 Cleaning the generator electrode and the glass cell

If the anode or the cathode should show discoloration or deposits, then they should be cleaned with concentrated nitric acid (or chromic acid in the case of persistent contamination). It is also recommended to apply the same cleaning procedure for the glass cell. Afterwards, rinse the electrode and the cell first with water and then with methanol.

2.4 Cleaning the diaphragm of the generator electrode

CAUTION

Make sure not to damage the platinum grid.

Sticky residues on the diaphragm: Place the generator electrode in an upright position, fill with concentrated nitric acid and leave over night. First rinse with water twice, then with methanol. If the contamination is particularly persistent, you may use chromic acid for cleaning. Afterwards, rinse first several times with water and then with methanol.

Oily contamination: Clean with solvent (e.g. hexane) and then rinse with methanol.

Salt-like residue: First clean with water and then rinse with methanol.

To rinse the diaphragm, fill the cathode chamber of the generator electrode with methanol and let the content flow out. Repeat two or three times. Carry out this procedure after each cleaning. After the last rinsing cycle, dry the cell in the drying oven at 50 °C or with a hair dryer.