Section 5.20 Title: Karl Fischer Titration **Revision Date:** 11/01/19
Prepared By: Michael Roy **P.I.:** Prof. John F. Berry

Prior Approval: This procedure is NOT considered hazardous enough that prior approval is needed from the Principal Investigator.

Involves Use of Particularly Hazardous Substance (PHS)? No
___ Carcinogen ___ Reproductive Toxin ___ High Acute Toxicity
Does this procedure require medical surveillance? No
Does this require use of a fit-tested respirator? No

Brief Description of Procedure:
Determination of water content in organic solvents by coulometric Karl Fischer Titration.

Location: *List the locations (buildings/rooms) where this procedure may be performed. For use of a PHS indicate a more precise location within the room, if appropriate, as a designated area.*
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Chemicals Involved:

Chemical	Physical or Health Hazard (e.g. carcinogen, corrosive)
Organic Solvents	Consult relevant SDS for more details
Coulomat AG (methanol solution)	Flammable, toxic.

Other Hazards: *Include hazards, other than chemical, that may be present during operation of the procedure.*
Sharps (needles)

Exposure Controls: *(Check all that apply)*
PPE: _X_ Safety Glasses ___ Face Shield ___Chemical Splash Goggles
___Chemical Apron _X_ Gloves (Nitrile) _X_ Lab Coat
___Respirator (type) ___Other:

Engineering Controls:
___Fume Hood ___Biosafety Cabinet ___Glove box
___ Vented gas cabinet ___Other:

Administrative Controls: *List any specific work practices needed to perform this procedure (e.g., cannot be performed alone, must notify other staff members before beginning, etc.).*

N/A

Task Hazard Control Table: *For procedures involving numerous steps, it may be convenient to indicate specific requirements for individual tasks in the table below:*

N/A

Waste Disposal: *Describe any chemical waste generated and the disposal method used.*

Excess solvent should be disposed of in the appropriate carboy. Used Coulomat solution should be disposed of in the halogenated waste carboy.

Accidental Spills: *Describe the procedure for handling small chemical spills that may occur during this procedure. Note that for large spills it may be appropriate to call 911.*

Small spills may be cleaned with an absorbing material. The material should be placed in a fume hood to dry after the spill has been cleaned.

Decontamination Procedures (required for PHS use): *Describe the procedure for decontamination of personnel and equipment.*

N/A

Training: *Describe any training needed prior to performing this procedure. Include training performed in-lab and any required demonstrations of competency.*

Training is required. Training is performed by the group member(s) responsible for this apparatus or another lab member they have approved. The procedure will be demonstrated at least once and new members will be supervised their first time.

Principle Investigator Approval: I have reviewed this procedure and approved it for use. Note: Modifications to the procedure may require update to this form.

Name: John F. Berry Signature: _____ Date: _____

Karl Fischer Titration

1. Turn on the instrument by pressing the red stop/power button.
2. When the main menu loads, press the green start button to begin conditioning the cell. This will electrochemically oxidize I^- to I_2, which is necessary for the titration. The solution will develop a yellow color indicative of I_2.
3. The system will display a drift value. This is the current rate of water titration. It needs to be steady and below 5 µg/min for an accurate titration.
4. As the conditioning improves, gently swirl the titration cell to wet the sides. This helps to remove trace water from the glass that could interfere with titration.
5. If the system overshoots the amount of I_2 it generates, it will say "overtitrated". Simply wait, and background water from the atmosphere will bring the cell back to a properly conditioned state.
6. Acquire a clean gas-tight syringe. See the table below to determine the appropriate volume for the syringe.
7. In a nitrogen atmosphere, draw a small volume (<1 mL) of the solvent to be titrated into the syringe. Draw nitrogen into the syringe to fill the rest of the volume. Swirl the solvent around the syringe barrel to draw any surface-bound water into the solvent. Dispense this solvent as waste.
8. Draw up the desired volume of solvent into the syringe. If possible, draw up an additional volume of nitrogen to buffer the syringe from atmospheric water.
9. Place the filled syringe on the balance near the Karl Fischer titrator. You may need to open the top of the balance to fit the syringe.
    a. If you used a reusable needle to draw solvent into your syringe, you need to replace it with a 4" 22 G needle before placing the syringe on the balance. The straight 22 G needle minimizes the wear on the instruments septum, reducing the frequency at which it needs to be replaced.
10. Tare the syringe so that the balance reads 0.0000 g.
11. Press the green start button on the Karl Fischer titrator to ready the instrument. It will begin a 10 second countdown. You do *not* need to insert your sample within this time. You can ignore the countdown.
12. Carefully pierce the instrument's septum with the needle. Do not insert the needle into an existing hole. Insert the needle until it is near the surface of the titration solution.
    a. If the needle drips at all as you prepare to pierce the septum, wipe down the needle with a lab wipe and re-tare the syringe.
13. Gently depress the syringe plunger to dispense solvent into the cell. If the solvent is particularly wet or the cell less than half full, the yellow color of iodine will fade, indicating sufficient sample has been added. If the color does not fade, dispense all of the solvent.
14. Replace the syringe on the balance. On the Karl Fischer keypad (you may need to press the numlock key to activate the keypad), press enter and then enter the mass of solvent dispensed. This is simply the number displayed on the balance, without the negative sign. Press enter again. The screen on the instrument should display the correct sample mass.
15. Press the green start button. The system will begin titrating and will show a curve and the total water content titrated.
16. When the titration is finished, the system will beep and display the water content in PPM.

17. Record your name, the date, the solvent, and the water content in the Karl Fischer log book.
18. Press the back button to return to the main menu to run another sample or power down the system.
19. Titrate any additional solvents by repeating steps 6-18 once the cell has reached a stable conditioned state.
20. Press the red stop/power button to end the conditioning and stirring.
21. Press and hold the red stop/power button to power down the system.

2.7.1 Sample size

The sample size should be small so that as many samples as possible can be titrated in the same electrolyte solution and the titration time kept short. However, take care that the sample contains at least 50 µg H_2O. The following table provides guidelines for the sample weight.

Content of sample	Sample weight	H_2O to be determined
100000 ppm = 10 %	50 mg	5000 µg
10000 ppm = 1 %	10 mg... 100 mg	100 µg...1000 µg
1000 ppm = 0.1 %	100 mg... 1 g	100 µg...1000 µg
100 ppm = 0.01 %	1 g	100 µg
10 ppm = 0.001 %	5 g	50 µg

Troubleshooting and Maintenance

1. Water content standards are available with the Karl Fischer supplies. These can be used to verify the accuracy of the instrument.
2. Replace the septum after 10-20 injections, or when the septum has enough puncture marks.
3. With dry solvents, the Coulomat AG solution should contain enough iodide to last until the cell has been filled. If the cell is full or the instrument is no longer detecting water, dispose of the solution (halogenated waste) and replace it with 100 mL fresh Coulomat AG solution. This fresh solution will likely take a long time (>30 minutes) to condition.
4. If conditioning or titration takes a very long time, replace the molecular sieves in the electrode cell. If this does not solve the problem, replace the PTFE sleeves around all joints.
5. If the cell needs to be cleaned, it should be carefully disassembled and rinsed with methanol and DI water. It can then be cleaned with 50 % nitric acid and rinsed with water and methanol. The electrodes can be cleaned in the same manner.