California Environmental Protection Agency

Air Resources Board

Special Analysis Section
Northern Laboratory Branch
Monitoring and Laboratory Division

MLD SOP SAS03

STANDARD OPERATING PROCEDURE FOR THE KARL FISCHER (KF) DETERMINATION OF WATER WITH A KF DRYING OVEN IN CONSUMER PRODUCTS

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1 INTRODUCTION

This procedure is used for the measurement of water in consumer products and is based on the Karl Fischer (KF) procedures specified in ASTM D 4017-96 and ASTM D 3792-91. Water is determined by using commercially available standard Karl Fischer reagent integrated with a drying oven. Use of trade names or commercial products are examples only, and any equivalent products may be substituted.

2 SUMMARY OF METHOD

The principle of the method involves heating a sample aliquot diluted in 1-Methoxy-2-propanol (MPA) in an oven, where the moisture from the sample is carried from the oven into a titration vessel by a stream of dry, inert carrier gas (or dried ambient air). The moisture in the titration vessel is titrated continuously until the designated endpoint is reached. Although traditional direct injection sample introduction may be appropriate for some products, the use of the oven provides more consistent and more precise values when interferences are present (see references 8.1 and 8.2).

The traditional KF reagent contains iodine, sulfur dioxide in pyridine and methanol. New pyridine-free KF reagents use amines and glycol ethers to replace the pyridine and methanol. The iodine in the presence of water is reduced to colorless hydrogen iodide. The end point is the appearance of free iodine. The basic reaction of the KF reagent with water is given as:

$$H_2O + SO_2 + I_2 \rightarrow 2HI + S0_3$$

The method requires the dilution of a pre-weighed aliquot of the consumer product with MPA. The solvent, MPA, is completely miscible with water forming an azeotrope boiling at 97.5^{o}C. As the water in the sample is heated in the oven it is transferred quantitatively to the titration vessel as the azeotrope, where it is titrated.

3 INTERFERENCES AND LIMITATIONS

Interferences in the titrimetric water determinations are associated with condensation or oxidation-reduction reactions with a number of substances and compounds (For more information refer to ASTM E 203 "Standard Test Method for Water Using Karl Fischer Reagent" 1986).

Use of certain reagents will minimize or eliminate the interferences of many classes of compounds. For example the use of non-methanol containing KF reagent and solvent will reduce the interference from aldehydes and ketones. Ammonia and amines can be eliminated by the addition of salicylic acid to the solvent.

Other possible interferences to the KF reagent are certain active metals, metal oxides, metal hydroxides, chromates, melamines, etc. (Ref. 8.1 and 8.2).

4 INSTRUMENTATION AND EQUIPMENT

4.1 Karl Fischer Titration System

4.1.1 Metrohm Titrino 784 Volumetric KF titrator with 10 mL “snap-in” buret unit

4.1.2 A Karl Fischer titration cell with double platinum electrode and 300 mL vessel

4.1.3 Metrohm model 703 magnetic stirrer titration stand with pump

4.1.4 Metrohm oven sample processor 774

4.2 Volumetric flask, 10 mL

4.3 Rainin pipettor, 250 μL and 1.0 mL with pipette tips

4.4 Hamilton syringes, 50 μL and 250 μL

4.5 Glass vials, 10 mL with Teflon-lined caps

4.6 Sartorius MC1 analytical balance

4.7 Variable-speed lab vortex/mixer

4.8 Transfer tube/combination pipette

4.9 Headspace vials with 21mm outer diameter and crimp caps with PTFE insert

5 REAGENTS AND MATERIALS

5.1 Reagent grade, ASTM Type 1 deionized water, 18.0 MΩ

5.2 1-Methoxy-2-propanol (Aldrich #26,889-5)

5.3 Disodium tartrate dihydrate (water content 15.61-15.71%)

5.4 Pyridine-free Karl Fischer titration reagent, Hydranal Comp-5K, 1.0 mL = 5 mg water for aldehydes and ketones

5.5 Titration solvent, Hydranal Ketosolver, used with the Comp-5K

6 PROCEDURE

The following describes the analysis of water in consumer products using the KF oven.

6.1 To determine the KF water titer (mg water per mL of titrant), directly inject 25 μL (25-μg) water into the titration vessel and initiate the titration. The titer value is automatically calculated from three titrations of the water standard. This calibration factor is used for subsequent analyses. The KF reagent is standardized to 1 mL per 5 mg water (5.000 mg/mL).

6.2 Load the tartrate method into the oven sample processor and insert the transfer probe from the oven sample processor into the titration vessel. The oven should be equilibrated to 130^{o}C.

6.3 To check on the operation of the oven, weigh two 200.0 mg disodium tartrate dihydrate aliquots (containing about 15.66 $\pm$ 0.05% water) into two headspace vials. Cap the headspace vials and initiate the titration. The analysis takes about 10 minutes. Record the results on the procedure Control Chart.

6.4 The percentage of water in ambient air (AIR blank) is determined by sealing a clean headspace vial and titrating. The value obtained for the air blank is subtracted from the percentage of water in the MPA blank. The analysis is run in triplicate.

6.5 The percentage of water in the MPA solvent (MPA blank) is determined by pipeting 250 μL of solvent into a clean headspace vial and titrating. The analysis is run in duplicate. The value obtained for the MPA, less the value obtained for the air blank, is subtracted from the percentage of water in the sample.

6.6 A check solution of 25% H_2O in MPA is analyzed. The check solution is prepared by diluting 1.0 mL of the check stock standard to 10 mL with MPA. Pipet 250 μL of the check solution into a headspace vial, cap the vial, and titrate. Run the analysis in duplicate. The check solution value should be with in $\pm$ 3 s of the expected value.

6.7 A trip solution of 60% H_2O in MPA is analyzed. The trip solution is prepared by diluting 1.0 mL of the trip stock standard to 10 mL with MPA. Pipet 250 μL of the trip solution into a headspace vial, cap the vial, and titrate. Run the analysis in duplicate.

6.8 A weighed aliquot (1.0 mL) of the consumer product sample is diluted to 10 mL with MPA. Pipet 250 μL of the diluted sample into a headspace vial, cap the vial, and titrate. The analysis is run in duplicate.

6.9 The amount of water in the consumer product sample is calculated by averaging the percent water results of the two analyses.

7 QUALITY CONTROL

7.1 The sensitivity, precision, and accuracy will depend on several factors, particularly the nature of the consumer product material being analyzed.

7.2 All consumer product sample analyses are done in duplicate and should have a relative difference of less than ±2%.

7.3 A control chart of the disodium tartrate and the 25% check solution is made with the upper and lower control limits set at ±3 s of the historical value. If an analysis is out of the control limits, the conditions are evaluated and the control and any affected samples will be re-analyzed.

7.4 A trip sample of 60 % water is run with each sample set. The recovery for the trip sample should be within the error of the method (± 3 %).

8 REFERENCES

8.1 ASTM E 203 "Standard Method for Water Using Karl Fischer Reagent" 1986.

8.2 ASTM D 4017 "Standard Test Method for Water in Paints and Paint Materials by Karl Fischer Method" (EPA Method 24).

8.3 Jenkins, V.C., Reilly, Joseph C., Sypowiez, Bob, and Wills, Max T. "VOC Testing Comparison: EPA Method 24 Versus the Cal Poly Method" Journal of Coatings Technology 67(84), 53-59 (1995).

8.4 Metrohm 784 KFP Titrino Instructions for Use. Metrohm 774 Oven Sample Processor Instructions for Use.

8.5 Brinkmann Lab, "Karl Fischer Water Determination with the KF Drying Oven" Applications Bulletin No. 109/1e

APPENDIX A

Operation of the Metrohm KF Titrator and KF Drying Oven

1. Turn on the 784 KF Titrator and the 774 oven sample processor.

2. Check that there is sufficient titrating reagent and solvent. Also empty the waste reservoir if necessary. The titrating reagent is COMP 5K, where 1.0 mL titrant = 5 mg H_2O. The reagent (Comp-5K) is the most likely one to be replenished and add only when the reservoir is nearly empty.

3. Drain and refill the titration vessel with fresh Ketosolver solvent using the toggle switch on the 703.

4. Verify that the single injection plug is in the titration vessel. The injection plug should already be in place. At the end of each analytical set, the oven probe is removed and the injection plug put in place.

5. Open the KF software on the PC. Click on the icon for the instrument you are using. The KF unit to the left of the PC is KF-1 and the KF unit on the right is KF-2. Initialize the titrator by clicking on the black back arrow (first box on left of tool bar). Answer "yes" to the prompt.

6. On the 784 keypad select the water titer method by pressing

   - User method
   - Recall method, enter
   - Select water titer, enter (use ARROW keys)
   - Press start

   The stirrer is automatically turned on and the system will titrate any moisture present in the titration vessel (drift). The display will indicate when the drift is OK.

7. Once the drift is OK, press start on the 784 keypad and inject 25 μL of water into the titration vessel. It is absolutely essential to maintain consistency in how the sample is drawn up in the syringe. Using a 50 μL syringe, displace the plunger of the syringe to about 10 μL. Place the tip of the needle into the container of H_2O and draw up the plunger. Observe the meniscus and draw up the water until the bottom of the meniscus is at 24 μL. Remove the needle and draw the plunger up to be able to read the total amount of water in the syringe barrel. You should have 25 μL in the syringe (approximately 1 μL is in the needle). The water titer is run three times (3X) to obtain a statistical average. The water titer determines the average amount in mLs of titrant required to titrate the water.

8. Press stop on the 784 keypad.

9. Remove the single injection plug and replace with the transfer probe from the sample oven.

10. Check the solvent level in the titration vessel. If necessary, drain some of the solvent using the toggle switch on the 703.

11. WEEKLY CHECK: Disodium tartrate (15.66% H_2O) is used to check on the operation of the oven. Weigh two 200mg aliquots of Disodium Tartrate into two headspace vials. Record weights – these will be entered into the silo (sequence list) entries for the tartrate samples.

12. Place a conditioning vial (a clean, empty, and sealed headspace vial) into autosampler position 36.

13. Place three air blank vials (clean, empty, and sealed headspace vials) into autosampler positions 33 – 35. The air blanks account for the atmospheric water present in the headspace vial.

14. Place the vials containing Na Tartrate into autosampler positions 1 and 2.

15. Load the Tartrate method using the 774-oven sample processor keypad.

    - Press user method, enter
    - Select Tartrate method (use the SELECT button)

16. Enter the sample information into the silo on the PC. The silo should be empty – if it is not, the entries can be deleted. Click on the add new line box (5^{th} box from the right on the toolbar). The first three entries are air blanks. For the air blanks enter the following information into the silo.

    - For the Year ID, enter the last two digits of the current year (i.e. “01”)
    - For the Sample ID, enter “airblank”
    - ***Important note: The sample ID field is limited to eight alphanumeric characters. If your sample name is too long the instrument will not work properly!***
    - For the Dilution, enter the sample dilution values (“0”)
    - The Sample Size comes from the method so you do not need to enter anything (sample size is 0.250 μL)

17. The 4^{th} and 5^{th} entries in the silo are the Na Tartrate samples.

    - For the Year ID, enter the last two digits of the current year (i.e. “01”)
    - For the Sample ID, enter “tartrate”
    - For the Dilution, enter the sample dilution values (“0”)
    - For the Sample Size, enter the Na Tartrate weights

18. Push start on the 774 keypad.

19. The value for the Na Tartrate is recorded in the lab notebook and on the QC chart for the KF method. The values should be within the control limits.

20. Sample Analysis: Weigh a 1 mL aliquot of consumer product into a 10 mL volumetric flask and dilute to 10 mL with MPA. Place 250 μL of each diluted sample into labeled headspace vials and cap the vials. The samples are analyzed in duplicate. Place a conditioning vial into autosampler position 36 and three air blank vials into positions 33 – 35. Add 250 μL of MPA into two headspace vials and place the vials in positions 31 and 32 – these will be solvent blanks.

21. Initialize the titrator.

22. Load the 784 method into the 774-oven sample processor keypad.

    - Press user method, enter
    - Select 784 method (use the "select" key)

23. Enter the sample info into the silo on the PC. The silo should be empty – if not the entries can be deleted. Click on the add new line box (5th box from right on the tool bar). The first three samples are air blanks. See section 16 for the sample information to enter into the silo for the air blanks.

24. Note: try not to place the cursor in the sample size column as this will cause 0.0 to be entered into the cell. This may not have any affect on the run since the sample size is set by the method.

25. The 4th and 5th samples are MPA solvent blanks. The background value obtained from the MPA analysis is subtracted from the value for ALL the sample analysis to correct for any moisture present in the MPA solvent. For the solvent blanks, enter the following information into the silo.

    - Year ID: input "01"
    - SampleID: input - "solblk"
    - Dilution: input the sample dilutions values - "0.0"
    - Sample size : the sample size comes from the method so you do not need to enter anything – (sample size is 250 μL)

26. Samples 6 and 7 are the 25% check samples. A water check is made as a control for the system. A 25% solution of water in MPA is prepared as a stock and stored in the refrigerator. Prepare the check as you would a sample by making a 1:10 dilution in MPA. This dilution will be used throughout the analyses. Transfer the diluted check sample into a capped storage vial. Pipet 250 μL of the check solution into headspace vials. Place the vials into autosampler rack positions 1 and 2. The value for the check must be with in control limits and is recorded on the appropriate control chart.

27. Samples 8 and 9 are Trip samples. Prepare the Trip sample by making a 1:10 dilution of the stock solution in MPA. Transfer into a capped storage vial. Pipet 250 μL of the diluted trip solution into headspace vials. Place the vials into autosampler

rack positions 3 and 4. The dilution value for the check and the trip samples is one (1).

28. Samples 10 and on are your samples – the samples are run in duplicate. The check sample is rerun at the end of the analysis. The value for the check sample must be within control limits. Place the samples into the autosampler rack beginning with position 5. For your samples, enter the following information into the silo.

    - YearID: input "01"
    - SampleID: input - last seven digits of sample ID
    - Dilution: input the sample dilution weight values - "0. ___"
    - Sample size: the sample size comes from the method so you do not need to enter anything – (sample size is 250 μL)

29. Print the silo listing.

30. Push reset on the 774 keypad.

31. Set the number of samples to analyze by pushing the parameter button on the 774 keypad. This setting may be set to the actual number of samples you are running or it may be set to "rack". The "rack" setting will run sample numbers 1-30 only. Rack positions 31-35 are dedicated positions so if you set the number of samples to run to 32 the sampler will sample to position 30 and then proceed to position number one (1).

32. Push start on the 774 keypad.

********* NOTES **********

1. Before adding the sample to the headspace vial, vortex/shake the sample to obtain a homogeneous mix. Some samples, particularly gels, will require using the homogenizer unit to obtain sufficient surface area to determine the water.

2. Note: When error messages appear on the 774 keypad, the KF oven sampler is placed in "hold" status. To clear the error message push "quit" on the 774 keypad and then "stop" to take the instrument out of "hold" status. Push "reset" on the 774 keypad to set the rack to its ready position.

SOP REVISION HISTORY

DATE	VERSION	NOTES
October 11, 1996	1	Clarification of QC and addition of the Trip sample.
March 10, 1998	1.1	Adjusted document font to Times New Roman 12. Inserted appendix A formerly a stand-alone document.
December 16, 2002	2.0	Modified SOP to reflect new Karl Fischer instrumentation and renumbered to new section number.
July 8, 2003	2.1	Changed document font to Arial 12. Corrected version enumeration.