METHOD 9000

DETERMINATION OF WATER IN WASTE MATERIALS BY KARL FISCHER TITRATION

1.0 SCOPE AND APPLICATION

1.1 The Karl Fischer titration technique is capable of quantifying the water content of materials from 1 ppm to nearly 100%. Coulometric titration is used for direct analysis of samples with water contents between 1 ppm and 5%, while volumetric titration is more suitable for direct analysis of higher levels (100 ppm to 100%). With proper sample dilution, the range of the coulometric technique can also be extended to 100% water. Both coulometric and volumetric procedures are presented.

1.2 Multiphasic samples should be separated into physical phases (liquid, solid, etc.) prior to analysis to assure representative aliquots are analyzed.

1.3 Establishing the water content in a sample may be useful for the reasons to follow.

1.3.1 It is useful in determining the total composition of a sample. In combination with other analytical results, the mass balance of a sample can be determined.

1.3.2 It is useful in identifying which samples can be analyzed by Infrared Spectroscopy using sodium chloride cells or which require zinc selenide cells.

1.3.3 It is useful in determining the amount of alcohol in an aqueous solution.

1.3.4 It is useful when distinguishing an aqueous from a nonaqueous solution.

1.3.5 It is useful when setting the proper mixture of feed materials in the incineration of waste.

2.0 SUMMARY OF METHOD

2.1 In the volumetric procedure, the sample or an extract of it, is added to a Karl Fischer solvent consisting of sulfur dioxide and an amine dissolved in anhydrous methanol. This solution is titrated with an anhydrous solvent containing iodine. The iodine titrant is first standardized by titrating a known amount of water.

2.2 In the coulometric procedure, the sample or an extract of it, is injected into an electrolytic cell containing the Karl Fischer solvent, where the iodine required for reaction with water is produced by anodic oxidation of iodide. With this technique, no standardization of reagents is required.

2.3 In both procedures, the endpoint is determined amperometrically with a platinum electrode that senses a sharp change in cell resistance when the iodine has reacted with all of the water in the sample.

2.4 In the coulometric procedure, the coulombs of electricity required to generate the necessary amount of iodine are converted to micrograms of water by the instrument microprocessor, while in the volumetric procedure, the volume of iodine titrant required to reach the endpoint is converted to micrograms of water. Most instruments will also calculate concentration (ppm or percent) if the sample weight is keyed in.

3.0 DEFINITIONS

Refer to Chapter One and Chapter Three for a listing of applicable definitions.

4.0 INTERFERENCES

4.1 Interfering side-reactions can occur between the various species in the Karl Fischer reagent and the sample components, resulting in an overestimation of the water content in the sample.

4.1.1 Hydroxide ions will titrate as water when injected directly into the titration cell. This is a significant problem with samples having a pH > 14. When this is suspected to be a problem, a water vaporization module (furnace) should be used. The sample is heated in this module and the water vapor carried to the titration cell, while the hydroxide remains in the module.

4.1.2 Ketones can interfere with some Karl Fischer reagents by reacting with alcoholic solvents like methanol to form ketals and acetals which can decompose to form water. This problem can be avoided by substitution of a non-reactive alcohol or increasing the pH.

4.1.3 The reduction of iodine by oxidizable species such as thiols, ammonia and thiosulfate results in the consumption of iodine and an overestimation of the water content.

4.2 Undesired interfering side-reactions can also result in the underestimation of the water content in the sample. These include:

4.2.1 Sulfur dioxide, base, carbonyl functional groups on aldehydes and ketones and other substances that form bisulfite complexes.

4.2.2 Oxidation of iodide and bisulfite complexes.

5.0 SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis.

5.2 Care should be taken in avoiding the inhalation of the reagent vapors or skin contact with the reagents. If any of the reagents comes in contact with the skin, wash thoroughly with copious amounts of water. To avoid inhalation of vapors, fill and empty the cell or electrode assembly in a working laboratory hood. Once the cell is assembled, solvent vapors are contained so long as the system remains sealed.

5.3 Protective laboratory clothing, eyewear and gloves should be worn at all times.

6.0 EQUIPMENT AND SUPPLIES

6.1 Coulometric water titrator - An automatic Karl Fischer titration system with amperometric, potentiometric or potential difference end point detection. It consists of an electrolytic titration cell, dual platinum electrode, magnetic stirrer and control unit.

6.2 Volumetric water titrator - An automatic Karl Fischer titration system consisting of a titration cell, dual platinum electrode, magnetic stirrer, dispensing buret and control unit.

6.3 Syringes - 5 µL, 10 µL and 100 µL.

6.4 Analytical balance - Minimum capacity of 160 g and capable of weighing to 0.0001 grams.

6.5 Screw cap vials, 20 mL.

6.6 Furnace module for determining water in the presence of high levels of hydroxide or in samples not otherwise amenable to direct titration or extraction. This is interfaced with the titration cell. An appropriate sample introduction apparatus will also be required.

7.0 REAGENTS AND STANDARDS

7.1 Coulometric cell solutions.

7.1.1 Anode reagent - Main ingredients consisting of methanol, organic base, sulfur dioxide and a suitable iodine compound.

7.1.2 Cathode reagent - Main ingredients consisting of methanol, organic base, sulfur dioxide and possibly carbon tetrachloride.

7.2 Volumetric reagents.

7.2.1 Volumetric titrant - A mixture of an organic amine, sulfur dioxide and iodine dissolved in a non-hygroscopic solvent. Reagents with titers of 1, 2 and 5 mg H_2O/mL can be commercially obtained.

7.2.2 Karl Fischer Solvent - Typically consisting of an organic amine and sulfur dioxide dissolved in anhydrous methanol.

7.3 The reagents described in 7.1 and 7.2 are commercially available.

7.4 Methanol or other appropriate solvent for extracting samples, anhydrous, > 99.8%.

7.5 Water - Reagent water (as defined in Chapter One).

8.0 SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1 Samples should be collected and stored in containers which will protect them from changes in volume or water content. Storage in glass with Teflon-lined caps is required if analytes requiring such storage are to be determined.

8.2 Samples should be refrigerated at 4°C ± 2°C and then brought to room temperature prior to analysis if analytes requiring such storage are to be determined.

9.0 QUALITY CONTROL

9.1 For each batch of twenty samples processed, at least one duplicate sample must be carried throughout the entire sample preparation and analytical process as described in Chapter One. The relative standard deviation of the duplicate analyses should be <10%.

9.2 For each batch of twenty samples processed, at least one spiked sample must be carried throughout the entire sample preparation and analytical process as described in Chapter One. The spike recovery should be 90 to 110%. In the absence of other information, a spike of 50% water is recommended. Spikes to some matrices, e.g., paints, may not be meaningful due to their high water levels and problems with spiking emulsions. In these cases, a spike of their extract may be the best option.

9.3 Certified reference materials should be analyzed where available.

9.4 To assess the accuracy of coulometric titrators, three 5 mg injections of reagent water are to be performed daily with average recoveries of 90 to 110% and relative standard deviations of < 5% to be achieved. If the recoveries fall outside of this range, the instrument problem must be corrected before continuing with sample analysis.

9.5 Background levels of water in reagents are minimized by using anhydrous reagents and by pre-titration of reagents prior to sample analysis.

9.6 To prevent the carryover of moisture into the syringe, the syringe should be rinsed once with methanol between samples and twice with the sample prior to loading the volume to be analyzed. Alternatively, use several syringes that have been oven dried, rotating the drying/use cycle so that the syringe in use reaches room temperature prior to use.

9.7 Only small aliquots of samples should be handled near the titrator to prevent contamination of the bulk sample by Karl Fischer reagent solvents.

9.8 When methanol or other solvent extractions are performed, three solvent blanks should be analyzed with these extracts and the extract results corrected for the mean of these blanks.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Coulometric procedure - Since coulometric titrators generate iodine on demand by the titration cell, standardization of titrant is not required.

10.2 Volumetric procedure - The titer of the titrant must be checked on a daily basis. Using a 5 uL syringe, 3.0 uL of water is injected into the titration cell containing solvent that has been pre-titrated to remove residual moisture. The titer is calculated as follows:

$$\frac{3.0 \text{ mg } H_2O}{\text{mL of titrant consumed}} = \text{mg/mL } H_2O \text{ equivalent of titrant.}$$

11.0 PROCEDURES

11.1 Sample introduction - The approach which should be used will depend on the viscosity and solubility of the sample and is left to the discretion of the analyst.

11.2 Direct injection - A sample (5 µL for coulometric, 100 µL for volumetric) is weighed by difference in a cleaned and dried syringe which has the needle inserted in a small piece of silicone rubber to reduce sample evaporation. The sample is injected into the titration cell septum and the syringe reweighed to determine the actual weight injected. The sample is titrated to the endpoint and the results recorded.

11.3 Extraction - A 500 mg sample is extracted with 10 mL of an appropriate solvent by shaking in a 20 mL vial for 2-3 minutes. The mixture is allowed to settle. Centrifugation may be required. A 100 µL aliquot of the supernatant is titrated. The volume of the aliquot to be titrated can be varied to achieve results within the linear range of the titrator. Methanol is most commonly used, but is not appropriate for all materials. Toluene, DMF, pyridine and diglyme are suitable for paints.

11.4 Water Vaporization - A 10 to 100 mg sample is weighed into a sampling tube and introduced into the furnace or injected into hot mineral oil and the water vapor carried by a gas stream into the titration cell. This approach is most commonly used with samples which cannot be directly titrated or extracted or for samples containing high levels of hydroxide ion as described in 4.1.1. Consult the instrument instruction manual for proper use.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 The water content in ppm or percent in the sample is either calculated by the instrument, if sample weight was keyed in, or the instrument readout in g H_2O found is divided by the g of sample injected with appropriate corrections for any dilutions or extractions performed.

12.2 Data analysis worksheets should be prepared for all samples analyzed. The information to be included is the sample identification, sample weight, water content measured, water content in the original sample and results of quality control tests performed as described in Section 9.

13.0 METHOD PERFORMANCE

13.1 Coulometric Procedure: Crude oil analysis: In ASTM Method D4928-89, crude oils containing 0.02 to 5% water were tested in an interlaboratory study. Within laboratory precision was 5 to 10% and between laboratory 7 to 20% relative standard deviation between 0.1 and 5% water.

13.2 Volumetric Procedure

13.2.1 Used oil analysis: A series of used oil standards was prepared by spiking dried used oil with water over the range 0 to 20%. Additional standards were made by spiking a hydrocarbon based cutting fluid at 25% and 50%. The results in w/w percent are shown in Table 1. Over the range 1 to 50% water, a linear regression of the results by the method vs. the spiked water content followed the relationship: $y = 1.0137x + 0.0917$ with $R^2 = 0.9997$.

Certified reference materials covering the range 2 to 90% water were analyzed using the direct injection procedure and volumetric titration. The results are shown in Table 2 and agreed with those obtained using Method 9001 and the certified value. The relative standard deviations ranged from 1 to 10% for 6 to 10 determinations.

13.2.2 Paint analysis: A certified reference material, ERM-19, Water and Volatiles in Latex Paint, was analyzed 10 times by the extraction procedure and volumetric titration. A 500 mg sample was extracted with diglyme, centrifuged and 125 µL of the supernatant titrated. The results agreed with results determined by Method 9001:

	ERM-19, %w/w
Method 9000	42.34 ± 1.25
Method 9001	44.91 ± 0.31

In ASTM Method D4017-90, paints containing 25 to 75% water were tested in an interlaboratory study. Within laboratory precision was 1.7% and between laboratory 5.3% relative standard deviation.

13.2.3 Other wastes: In ASTM Method D5530, hazardous waste fuels containing 13 to 32% water yielded within laboratory precision of 1.3% and between laboratory of 4.3% relative standard deviation.

13.2.4 Soil analysis: A marine sediment was dried and spiked with water over the range 0 to 40% (w/w). The results are shown in Table 3 and followed the relationship $y = 0.9972x + 0.1103$ with $R^2 = 0.9991$.

13.2.5 Alcohol analysis: Mixtures of ethanol and water covering the range 0 to 100% water and three distilled spirits were analyzed by this method and Method 9001. The results are given in Table 4. Because total dissolved solids like sugars and other carbohydrates often present in beers, wines and distilled spirits will be counted as “alcohol” when water content is used to estimate alcohol content, their contribution must be considered and if necessary, determined and subtracted from the non-water content to determine the alcohol content.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When waste cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions, consult *Less is Better: Laboratory Chemical Management for Waste Reduction*, available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036, (202) 872-4477.

15.0 WASTE MANAGEMENT

15.1 Spent reagents and samples should be stored and disposed appropriately.

15.2 The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly with hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult the *Management Manual for Laboratory Personnel*, available from the American Chemical Society at the address listed in Section 14.2.

16.0 REFERENCES

1. ASTM Method D3401-92, Standard Test Method for Water in Halogenated Organic Solvents and Their Admixtures.

2. ASTM Method D4017-90, Standard Test Method for Water in Paints and Paint Materials by Karl Fischer Method.

3. ASTM Method D5530-94, Standard Test Method for Total Moisture of Hazardous Waste Fuel by Karl Fischer Titrimetry.

4. ASTM Method D4928-89 Standard Test Methods for Water in Crude Oils by Coulometric Karl Fischer Titration.

5. ASTM Method D4377-93a Standard Test Method for Water in Crude Oils by Potentiometric Karl Fischer Titration.

6. Validation Data for Draft Methods 9000 and 9001 for the Determination of Water Content in Liquid and Solid Matrices, Dexsil Corp., Hamden, CT.

7. MacLeod, Steven K. “Moisture Determination Using Karl Fischer Titrations.” Analytical Chemistry. Volume 63. Pages 557-566. May 15, 1991.

8. U.S. EPA NEIC Method. “Water Content of Waste Material Samples by Coulometric Karl Fischer Titration.” Pages 1-12, August 1991.

17.0 TABLES, DIAGRAMS, FLOW CHARTS AND VALIDATION DATA

The following pages contain Tables 1 through 4 and a method procedure flow diagram.

TABLE 1

DETERMINATION OF WATER IN USED OIL
(w/w %)

Expected	Method 9001	Method 9000
0	0.161	0.061
0.1	0.149	0.145
0.2	0.226	0.255
0.5	0.459	0.561
1.0	0.948	1.07
2.0	2.36	2.46
5.0	5.03	5.05
10.0	9.82	9.97
20.0	20.2	20.0
25.0	26.37	26.05
50.0	50.05	50.60

Source: Reference 6

TABLE 2

ANALYSIS OF USED OIL CERTIFIED REFERENCE MATERIALS[a]

CRM	Certified Value, wt %	Method 9001, wt %	Method 9000, wt %
ERM-34	1.95	1.92±0.02	1.86±0.09
ERM-35	5.86	5.91±0.61	6.13±0.55
ERM-36	10.3	10.30±0.85	10.3±0.81
ERM-41	87.4	88.4±6.7	86.4±6.6

[a] ERM-34 to 41 Water Content in Used Oil Mixtures from Environmental Reference Materials, Inc.

Source: Reference 6

TABLE 3

DETERMINATION OF WATER IN MARINE SEDIMENT
(w/w%)

Expected	Method 9001	Method 9000
0	1.14	0.579
10	10.06	9.74
20	18.99	19.67
30	28.52	29.95
40	38.47	40.34

Source: Reference 6

TABLE 4

DETERMINATION OF ALCOHOL IN WATER/ALCOHOL MIXTURES

Expected % Alcohol, v/v	Method 9001 (% v/v)	Method 9000 (% v/v)
0	0	0
10	10.0	10.3
25	25.6	25.0
40	40.9	38.7
50	48.5	49.1
80	80.6	79.8
100	99.9	100.0
Vodka, 40	41.9	42.0
Whiskey, 40	40.0	41.9
Gin, 47	47.2	48.7

Source: Reference 6.

METHOD 9000

DETERMINATION OF WATER IN WASTE MATERIALS BY KARL FISCHER TITRATION