

METHOD 9000

DETERMINATION OF WATER IN WASTE MATERIALS BY KARL FISCHER TITRATION

SW-846 is not intended to be an analytical training manual. Therefore, method procedures are written based on the assumption that they will be performed by analysts who are formally trained in at least the basic principles of chemical analysis and in the use of the subject technology.

In addition, SW-846 methods, with the exception of required method use for the analysis of method-defined parameters, are intended to be guidance methods which contain general information on how to perform an analytical procedure or technique which a laboratory can use as a basic starting point for generating its own detailed Standard Operating Procedure (SOP), either for its own general use or for a specific project application. The performance data included in this method are for guidance purposes only, and are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

1.0 SCOPE AND APPLICATION

1.1 This method uses the Karl Fischer titration technique to quantify 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. This method presents both coulometric and volumetric procedures.

1.2 Multiphase samples should be separated into physical phases (liquid, solid, etc.) prior to analysis to assure the analysis of representative aliquots.

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 maximum amount of alcohols or other organic liquids which could be present 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.

1.4 Analysts should consult the disclaimer statement at the front of the manual and the information in Chapter Two for guidance on the intended flexibility in the choice of methods, apparatus, materials, reagents, and supplies, and on the responsibilities of the analyst for demonstrating that the techniques employed are appropriate for the analytes of interest, in the matrix of interest, and at the levels of concern.

In addition, analysts and data users are advised that, except where explicitly specified in a regulation, the use of SW-846 methods is *not* mandatory in response to Federal testing requirements. The information contained in this method is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to generate results that meet the data quality objectives for the intended application.

1.5 Use of this method is restricted to use by, or under supervision of, properly experienced and trained personnel. Each analyst must demonstrate the ability to generate acceptable results with this method.

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. This technique does not require the standardization of reagents.

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, Chapter Three, and the manufacturer's instructions for definitions that may be relevant to this procedure.

4.0 INTERFERENCES

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis (see Sec. 9.0 for specific guidance on quality control procedures). Specific selection of reagents and purification of solvents by distillation in all-glass systems may be necessary. Refer to Chapter Three for general guidance on the cleaning of glassware.

4.2 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.

4.2.1 Hydroxide ions will titrate as water when injected directly into the titration cell. This is a significant problem with samples having a hydroxide content of > 1N. 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 is carried to the titration cell, while the hydroxide remains in the module.

4.2.2 Ketones and aldehydes 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 by increasing the pH.

4.2.3 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.

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

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

4.3.2 Oxidation of iodide and bisulfite complexes by reducible species such as Cu^{2+} , Fe^{3+} , NO^2 , etc.

4.4 Suspended/undissolved solid material in a liquid sample may interfere with the electrode by blocking its contact with the solvent. Artificially high or low results can occur depending on the nature of the solid material.

5.0 SAFETY

5.1 This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals listed in this method. A reference file of material data handling sheets (MSDSs) should be available to all personnel involved in the chemical analysis.

5.2 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.

5.3 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.

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

6.0 EQUIPMENT AND SUPPLIES

The mention of trade names or commercial products in this manual is for illustrative purposes only, and does not constitute an EPA endorsement or exclusive recommendation for use. The products and instrument settings cited in SW-846 methods represent those products

and settings used during method development or subsequently evaluated by the Agency. Glassware, reagents, supplies, equipment, and settings other than those listed in this manual may be employed provided that method performance appropriate for the intended application has been demonstrated and documented.

This section does not list common laboratory glassware (e.g., beakers and flasks).

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- μ L, 10- μ L and 100- μ L.

6.4 Analytical balance -- 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 Reagent-grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. Reagents should be stored in glass to prevent the leaching of contaminants from plastic containers.

7.2 Coulometric cell solutions

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

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

NOTE: Non-methanol formulations are commercially available for the analysis of aldehydes and ketones and for general use. As indicated in Sec. 4.2.2, ketones and aldehydes interfere with the Karl Fischer titration as they undergo water-forming reactions with methanol. Use of these non-methanol Karl Fischer solvents is recommended for samples containing aldehydes and ketones.

7.3 Volumetric reagents

7.3.1 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 H₂O/mL can be commercially obtained.

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

NOTE: Non-methanol formulations are commercially available for the analysis of aldehydes and ketones and for general use. As indicated in Sec. 4.2.2, ketones and aldehydes interfere with the Karl Fischer titration because these compounds undergo water-forming reactions with methanol. The use of non-methanol Karl Fischer solvents is recommended for samples containing aldehydes and ketones.

7.4 The reagents described in Secs. 7.2 and 7.3 are commercially available.

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

7.6 Reagent water.

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 polytetrafluoroethylene (PTFE)-lined caps is necessary if analytes requiring such storage are to be determined.

8.2 Samples should be well-sealed and refrigerated at #6 EC and then brought to room temperature prior to analysis if analytes requiring such storage are to be determined.

9.0 QUALITY CONTROL

9.1 Refer to Chapter One for additional guidance on quality assurance (QA) and quality control (QC) protocols. When inconsistencies exist between QC guidelines, method-specific QC criteria take precedence over both technique-specific criteria and those criteria given in Chapter One, and technique-specific QC criteria take precedence over the criteria in Chapter One. Any effort involving the collection of analytical data should include development of a structured and systematic planning document, such as a Quality Assurance Project Plan (QAPP) or a Sampling and Analysis Plan (SAP), which translates project objectives and specifications into directions for those that will implement the project and assess the results. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated. All data sheets and quality control data should be maintained for reference or inspection.

9.2 For each batch of twenty samples processed, at least one duplicate sample must be carried throughout the entire sample preparation and analytical process. The relative standard deviation of the duplicate analyses should be set at a laboratory-derived limit developed through the use of historical analyses for the same matrix. In the absence of historical data, the relative standard deviation of the duplicate analyses should be <10%. After the determination of historical data, $\pm 10\%$ should still be the limit of maximum deviation to express acceptability.

9.3 For each batch of twenty samples processed, at least one spiked sample must be carried throughout the entire sample preparation and analytical process. Acceptance criteria should be set at a laboratory-derived limit developed through the use of historical analyses for the same matrix. In the absence of historical data, the spike recovery should be 90 to 110%. 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.

9.4 Certified reference materials should be analyzed where available.

9.5 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.

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

9.7 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.

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

9.9 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- μ L syringe, inject 3.0 μ L of water into the titration cell containing solvent that has been pre-titrated to remove residual moisture. Calculate the titer as follows:

$$3.0 \text{ mg H}_2\text{O/mL of titrant consumed} = \text{mg/mL H}_2\text{O equivalent of titrant.}$$

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 -- Weigh a sample (5 μ L for coulometric, 100 μ L for volumetric) by difference in a cleaned and dried syringe which has the needle inserted in a small piece of silicone rubber to reduce sample evaporation. Inject the sample into the titration cell septum and reweigh the syringe to determine the actual weight injected. Titrate the sample to the endpoint and record the results.

11.3 Extraction -- Extract a 500-mg sample with an appropriate solvent to a final volume of 10 mL. The solvent and sample should be shaken in a 20 mL vial for 2 to 3 min. Allow the mixture to settle. Centrifugation may be required. Titrate a 100- μ L aliquot of the supernatant. 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 -- Weigh a 10- to 100-mg sample into a sampling tube and introduce it into the furnace or inject it into hot mineral oil and the water vapor will be 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 Sec. 4.2.1. Consult the instrument instruction manual for proper use.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Calculate the water content in ppm or percent in the sample based on the instrument, if sample weight was keyed in, or divide the instrument readout in g of H₂O found by the g of sample injected with appropriate corrections for any dilutions or extractions.

12.2 Data analysis worksheets should be prepared for all samples analyzed. Include information regarding the sample identification, sample weight, measured water content, water content in the original sample and the results of quality control tests.

12.3 Results must be reported in units commensurate with their intended use and all dilutions need to be taken into account when computing final results.

13.0 METHOD PERFORMANCE

13.1 Performance data and related information are provided in SW-846 methods only as examples and guidance. The data do not represent required performance criteria for users of the methods. Instead, performance criteria should be developed on a project-specific basis, and the laboratory should establish in-house QC performance criteria for the application of this method. These performance data are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

13.2 Coulometric procedure

Crude oil analysis -- Based on ASTM D 4928-89, crude oils containing 0.02 to 5% water were tested in an interlaboratory study. "Within" laboratory precision was 5 to 10% and the "between" laboratory relative standard deviation was 7 to 20% for between 0.1 and 5% water. These data are provided for guidance purposes only.

13.3 Volumetric procedure

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

Certified reference materials covering the range of 2 to 90% water were analyzed using the direct injection procedure and volumetric titration. The results using this method 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. These data are provided for guidance purposes only.

13.3.2 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 μ L of the supernatant was titrated. The results in w/w% using this method were 42.34 ± 1.25 and agreed with results determined by Method 9001.

Based on ASTM D 4017-90, paints containing 25 to 75% water were tested in an interlaboratory study. "Within" laboratory precision was 1.7% and the "between" laboratory relative standard deviation was 5.3%. These data are provided for guidance purposes only.

13.3.3 Other wastes -- Based on ASTM D 5530, hazardous waste fuels containing 13 to 32% water yielded "within" laboratory precision of 1.3% and a "between" laboratory relative standard deviation of 4.3%. These data are provided for guidance purposes only.

13.3.4 Soil analysis -- A marine sediment was dried and spiked with water over the range of 0 to 40% (w/w). The results using this method are shown in Table 3 and followed the following relationship: $y = 0.9972x + 0.1103$ with $R^2 = 0.9991$. These data are provided for guidance purposes only.

13.3.5 Alcohol analysis -- Mixtures of ethanol and water covering the range of 0 to 100% water and three distilled spirits were analyzed by this method and Method 9001. The results are given in Table 4. These data are provided for guidance purposes only. 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. Numerous opportunities for pollution prevention exist in laboratory operations. 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 wastes 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, <http://www.acs.org>.

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 the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* available from the American Chemical Society at the address listed in Sec. 14.2.

16.0 REFERENCES

1. ASTM D 3401-92, "Standard Test Method for Water in Halogenated Organic Solvents and their Admixtures."
2. ASTM D 4017-90, "Standard Test Method for Water in Paints and Paint Materials by Karl Fischer Method."
3. ASTM D 5530-94, "Standard Test Method for Total Moisture of Hazardous Waste Fuel by Karl Fischer Titrimetry."
4. ASTM D 4928-89, "Standard Test Methods for Water in Crude Oils by Coulometric Karl Fischer Titration."
5. ASTM D 4377-93a, "Standard Test Method for Water in Crude Oils by Potentiometric Karl Fischer Titration."
6. Theodore B. Lynn; "Validation Data for Draft Methods 9000 and 9001 for the Determination of Water Content in Liquid and Solid Matrices," Dexsil Corp., Hamden, CT (not dated).
7. Steven K. MacLeod, "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 the tables referenced by this method. The tables are followed by a flow diagram of the procedure.

TABLE 1
EXAMPLE 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

Data taken from Reference 6.

TABLE 2
EXAMPLE 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

^aERM-34 to 41 Water Content in Used Oil Mixtures from Environmental Reference Materials, Inc.

Data taken from Reference 6.

TABLE 3
 EXAMPLE 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

Data taken from Reference 6.

TABLE 4
 EXAMPLE 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

Data taken from Reference 6.

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