

DETERMINATION OF WATER IN WASTE MATERIALS
BY QUANTITATIVE CALCIUM HYDRIDE REACTION

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 quantitative calcium hydride reaction method is capable of determining water in the concentration range from 0.1% to 100% in liquid and solid materials including oils, paints, soils and water/alcohol mixtures. It is intended to be used as either a field or laboratory method.

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 amount of water 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 the distinction of 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 aqueous from nonaqueous solutions.

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 A sample of the material to be tested is treated with a specially formulated calcium hydride reagent which reacts with water in the sample to liberate hydrogen gas as shown below:



2.2 The reaction is carried out in a sealed pressure vessel and the resulting pressure is then measured using a specially designed meter. The results are displayed directly in weight or volume percent, depending on the sampling method used.

2.3 The reaction is quantitative, measuring all water present in the sample over the range of 0.1 to 100%.

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 This method has no known positive interferences. Tests conducted on 20% (w/w) solutions of the compounds listed below using twice the normal sample size produced no response. The compounds listed below are representative of substances either known to react with calcium hydride and/or which are likely to be present in materials to be tested using this method.

- Ethanol
- Methanol
- Acetone
- Methyl ethyl ketone
- Tetrahydrofuran
- Diethylene glycol dimethyl ether
- Ethylene glycol
- Diethylene glycol
- Dipropylene glycol
- Stearic acid
- 2-Ethyl hexanoic acid
- Lead oxide (II and III)
- Aluminum oxide (Brockman I)

4.2 Nitric acid reacts with calcium hydroxide to form calcium nitrate tetra-hydrate crystals, which trap water in the acid before it can react with calcium hydride. This reaction may yield results as much as 80% lower than the actual water content. This interference is only significant when determining the water content of concentrated nitric acid mixtures.

5.0 SAFETY

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

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

5.4 The amount of hydrogen gas generated is minimal and is not a hazard to the user.

6.0 EQUIPMENT AND SUPPLIES

6.1 Quantitative calcium hydride reaction test kit -- Hydrosout test system (Dexsil Corporation, One Hamden Park Drive, Hamden, CT), or equivalent.

6.2 Each commercially-available test kit will supply or specify the apparatus and materials necessary for successful completion of the test.

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 Each commercially available test kit will supply or specify the reagents necessary for successful completion of the test. Reagents should be labeled with appropriate expiration dates.

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 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 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 Follow the test kit manufacturer's instructions for additional quality control procedures.

9.3 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 determinations should be <10%. After the determination of historical data, $\pm 10\%$ should still be the limit of maximum deviation to express acceptability.

9.4 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., oils and 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.

9.5 A test sample provided with the kit should be analyzed to verify proper performance of the test and meter operation.

9.6 A method blank correction for water content is unnecessary. Reagents are ampulized instead of bulk packaged and thus are less likely to absorb water from the air.

9.7 Certified reference materials should be analyzed where available.

10.0 CALIBRATION AND STANDARDIZATION

The meter provided with the kit is factory calibrated to read directly in percent water. Every time the meter is turned on, a new zero calibration point is determined.

11.0 PROCEDURE

11.1 Follow the directions provided by your kit manufacturer.

11.2 Oil samples are analyzed by directly reacting a measured 0.4- to 0.8-mL (for v/v measurements) or 1-g (for w/w measurements) sample with the calcium hydride reagent. Samples up to 5 mL can be used to determine water in the 0.1 to 1.0% range. The resulting pressure due to hydrogen gas is converted by the meter to percent water. The meter has separate programs for reporting results in v/v or w/w percent water.

11.3 Paint and soil samples are analyzed after extracting 1-g samples with a dilution solvent. A 0.8-mL aliquot of the extract is reacted with the calcium hydride reagent. The meter results are reported in w/w percent water.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 The meter provided with the kit is factory calibrated and the equations converting pressure to percent water are stored in designated programs. The matrix and sample size determine the appropriate program to use.

12.2 Data analysis worksheets should be prepared for all samples analyzed. Include information to be regarding the sample identification, sample weight or volume, water content (as read from the instrument readout), water content in the original sample (accounting for any dilutions or extractions) and 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 goals for users of the methods. Instead, performance goals 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 Used oil analysis -- A series of used oil standards were prepared by spiking dried used oil with water over the 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: $y = 1.007x + 0.1024$ with $R^2 = 0.9993$. These data are provided for guidance purposes only.

Certified reference materials covering the range of 2 to 90% water were analyzed using this method and Method 9000. The results are shown in Table 2. The relative standard deviations ranged from 1 to 10% for 6 to 10 determinations and the results using this method agreed with the certified value and those determined by Method 9000. These data are provided for guidance purposes only.

13.3 Paint analysis -- A certified reference material, ERM-19, "Water and Volatiles in Latex Paint," was analyzed 10 times using this method. The results in w/w% were $44.91 \pm$

0.31%. The RSD of the measurements was 0.7%. The results from using this method agreed with those obtained using Method 9000. These data are provided for guidance purposes only.

13.4 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: $y = 0.9311x + 0.8149$ with $R^2 = 0.9994$. These data are provided for guidance purposes only.

13.5 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 9000. 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.

13.6 Other wastes -- Concentrated sulfuric and nitric acids and 10 N sodium hydroxide were analyzed using this method. The following results were obtained: the water content of the sulfuric acid was determined to be 4.33% vs. the bottle assay value of 4.2%; while the water content of 10 N NaOH was found to be greater than 20%, the upper limit of the method for undiluted samples. This is expected for 10 N NaOH, which has a nominal water content in excess of 50%. The example water content of concentrated nitric acid was determined to be around 6% vs. the assay value of 30%. These data are provided for guidance purposes only.

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 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, <http://www.acs.org>.

15.0 WASTE MANAGEMENT

15.1 On completion of a test, the reaction tube will contain water, the original sample matrix and a solution of calcium hydroxide. Samples requiring dilution with an organic solvent will also require disposal of the solvent. Reacted samples and spent solvents 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 Sec. 14.2.

16.0 REFERENCES

1. Operating Manual, Hydroscoat System, Dexsil Corporation.
2. 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).

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 method 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 2.

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.

Source: Reference 2

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 2.

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 2

METHOD 9001

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