METHOD 9001

DETERMINATION OF WATER IN WASTE MATERIALS BY QUANTITATIVE CALCIUM HYDRIDE REACTION

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

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 amount of alcohol in an aqueous alcohol 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.

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:

$$CaH_2 + 2H_20 \rightarrow Ca(OH)_2 + 2H_2 \uparrow$$

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 0.1 to 100%.

3.0 DEFINITIONS

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

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

5.3 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 - Hydroscout test system (Dexsil Corporation, One Hamden Park Drive, Hamden, CT), or equivalent. 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 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 PTFE-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 brought to room temperature prior to analysis if analytes requiring such storage are to be determined.

9.0 QUALITY CONTROL

9.1 Follow the manufacturer's instructions for quality control procedures.

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 as described in Chapter One. The relative standard deviation of the duplicate determinations should be <10%.

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 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., 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.

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

9.5 A blank correction for water is not required. Reagents are ampulized instead of bulk packaged and thus are less likely to absorb water from the air.

9.6 Certified reference materials should be analyzed where available.

10.0 CALIBRATION AND STANDARDIZATION

10.1 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. The information to be included is 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 performed as described in Section 9.0.

13.0 METHOD PERFORMANCE

13.1 Used oil analysis: A series of used oil standards were 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: $y = 1.007x + 0.1024$ with $R^2 = 0.9993$.

Certified reference materials covering the range 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 agreed with the certified value and those determined by Method 9000.

13.2 Paint analysis: A certified reference material, ERM-19, Water and Volatiles in Latex Paint, was analyzed 10 times. The results in w/w% were 44.91 ± 0.31%. The RSD of the measurements was 0.7%. The results by this method agreed with those obtained using Method 9000 (43.38 ± 1.29%).

13.3 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 $y = 0.9311x + 0.8149$ with $R^2 = 0.9994$.

13.4 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 9000. 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.

13.5 Other wastes: Concentrated sulfuric and nitric acids and 10 N sodium hydroxide were analyzed. The water content of the sulfuric acid was determined to be 4.33% vs. the bottle assay value of 4.2%. 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 water content of concentrated nitric acid was determined to be around 6% vs. the assay value of 30%.

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 operation. 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 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 Section 14.2.

16.0 REFERENCES

1. Operating Manual, Hydroscout System, Dexsil Corporation.

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

17.0 TABLES, DIAGRAMS, FLOW CHARTS AND VALIDATION DATA

The pages to follow 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 2

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 2

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 2.

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 2

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