VALIDATION DATA FOR DRAFT METHODS 9000 AND 9001 FOR THE DETERMINATION OF WATER CONTENT IN LIQUID AND SOLID MATRICIES

Theodore B, Lynn, Ph.D., Dexsil Corporation Publication DTP-17-01
One Hamden Park Dr., Hamden, CT 06517

INTRODUCTION

Performance data for SW-846 draft methods, 9000 ("Determination of Water in Waste Materials by Karl Fischer Titration") and 9001 ("Determination of Water in Waste Materials by Quantitative Calcium Hydride Reaction Test Kit"), were collected by Dexsil personnel for submittal in support of the two methods. Standards spiked at known levels of water were used for all matrices in order that any systematic bias or interference would be detectable. The exception to this would be the commercially available distilled spirits and the certified reference materials for water content in paint and used oil which were also analyzed. The liquid matrices tested were: used lube oil, latex paint, alcohol and water mixtures and commercially available distilled spirits. Other liquid matrices tested for were: concentrated sulfuric and nitric acids and 10 normal sodium hydroxide. The solid matrix analyzed was a marine sediment.

EXPERIMENTAL

Method 9000 is based on the Karl Fisher technique for titrating water in non-aqeous matricies. The method describes two types of test: a coulometric method, recommended for low concentrations of water (1 ppm to 5%) and a potentiometric method for determining water content over the range 1-100%. The latter method was employed in these experiments, as the quantifiable range of the two methods would be most similar. Titrations were performed using a standard automatic titrator (TitroLine Alpha, Schott Inc.) configured for Karl Fisher analysis. The Karl Fisher reagents used for the testing were Pyridine-free Hydranal-Composite 5 and Hydranal Solvent, obtained from Crescent Chemical Co., Inc., Hauppauge, NY.

Method 9001 describes a method for determining water content by reacting the sample, in a closed container, with calcium hydride and measuring the pressure of the resulting hydrogen gas. The method is employed in a commercially available system (HYDROSCOUT System, Dexsil Corporation) using prepackaged reagents and a portable pressure meter calibrated to read in parts per million. The meter is configured with two operation ranges, 0-20% and 10-100%. The standard reagents are used for analyzing samples in both ranges and an additional dilution step is required for analysis of samples in the high range (dilution reagents are included in each refill pack). The standard meter is calibrated to read in volume percent. For these experiments a meter programmed to read directly in pressure was used and calibrated using either gravimetric or volumetric standards. Field units are also available with direct pressure readout by request.

RESULTS

Used Oil

A large quantity of mixed used oil obtained from various company vehicles was first dried by heating to >100°C for 1 hour while bubbling dry nitrogen gas through the oil. This stock "dry" oil was then spiked at various levels, up to 20% (w/w) water, for testing using both draft methods. Additional standards were prepared using a commercially available hydrocarbon based cutting fluid (Chem-Tool 250) at concentrations of 25 and 50% (w/w). These additional standards were necessary to achieve an acceptable degree of homogeneity in the samples containing greater than 20% water. The results of the comparison are presented in Table 1. Over the range 1 to 50% water, a linear regression of the results by method 9001 vs. The spiked water content followed the relationship: $y=1.007x+0.1024$ with $R^2=0.9993$. Over the range 1 to 50% water, a linear regression

of the results by method 9000 vs. the spiked water content followed the relationship: y = 1.0137x + 0.0917 with R^2 = 0.9997.

In addition to the above standards, water in used oil certified reference materials were obtained with water contents from 2 to 86% (w/w) (Environmental Reference Materials, Inc., Research Triangle Park, NC). Each aliquot of each reference material was analyzed in duplicate by each method. The results are presented in Tables 2-5.

Water in Alcohol

Reagent grade denatured ethyl alcohol was dried over night using Molecular Sieves (5A, Aldrich Chemical Co.). The dried alcohol was then used to prepare as series of volumetric standards from 0 - 100% water in alcohol. These standards were then analyzed using both methods. In addition samples of three commercial distilled spirits were also analyzed. The results are presented in Table 6.

Paint

A latex paint reference material was obtained from Environmental Reference Materials containing approximately 45% (w/w) water. The paint standard was analyzed 10 times by each method. The sample preparation procedure was the same for each method and consisted of accurately weighing a 0.5 gram sample of paint into a vial containing 10 mL of diglyme. The vial was thoroughly mixed and an aliquot was taken for analysis. The results of the analysis are presented in Table 7.

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%.

Soil

A large quantity of marine sediment was dried at 120°C for 2 hours. The soil was allowed to cool and then spiked alequots were prepared at concentration from 0 to 40%. A 1 gram sample of each aliquot was extracted with 10 grams of dry solvent and analyzed in duplicate by each method. The solvent used for method 9000 was methanol and 20% methanol in THF was used as the solvent for method 9001. The results are presented in Table 8. A linear regression of the results by method 9001 vs. the spiked water content followed the relationship y = 0.9311x + 0.8149 with R^2 = 0.9994. A linear regression of the results by method 9000 vs. the spiked water content followed the relationship y = 0.9972x + 0.1103 with R^2 = 0.9991.

TABLE 1: DETERMINATION OF WATER IN USED OIL, w/w%

Expected	Method 9001	Method 9000
0	0.132	0.062
0-D	0.190	0.060
0.1	0.139	0.143
0.1-D	0.158	0.146
0.2	0.240	0.248
0.2-D	0.212	0.263
0.5	0.463	0.576
0.5-D	0.454	0.546
1.0	0.991	1.13
1.0-D	0.905	1.01
2.0	2.41	2.46
2.0-D	2.30	2.46
5.0	5.06	5.05
5.0-D	5.00	5.05
10.0	9.80	9.94
10.0-D	9.83	10.0
20.0	20.4	20.0
20.0-D	20.0	20.1
25.0	26.1	26.2
25.0-D	26.7	25.9
50.0	49.9	50.7
50.0-D	50.2	50.5

TABLE 2: ANALYSIS OF CERTIFIED REFERENCE MATERIAL ERM 34 (%w/w)

Sample ID	Method 9001	Method 9000
1	1.92	2.02
1-D	1.94	1.88
13	1.92	1.84
13-D	1.96	1.78
26	1.90	1.80
26-D	1.90	1.84
Mean	1.92	1.86
Std Dev	0.0259	0.0895

TABLE 3: ANALYSIS OF CERTIFIED REFERENCE MATERIAL ERM 35 (%w/w)

Sample ID	Method 9001	Method 9000
1	5.10	5.55
1-D	5.24	5.32
13	6.08	6.51
13-D	6.69	6.38
26	6.12	6.44
26-D	6.23	6.59
Mean	5.91	6.13
Std Dev	0.6148	0.5507

TABLE 4: ANALYSIS OF CERTIFIED REFERENCE MATERIAL ERM 36 (%w/w)

Sample ID	Method 9001	Method 9000
1	9.27	9.26
1-D	9.55	9.34
7	9.43	9.34
7-D	9.32	9.6
13	10.87	10.90
13-D	11.52	10.98
21	10.88	10.81
21-D	11.29	11.33
27	10.28	10.64
27-D	10.54	10.81
Mean	10.30	10.30
Std Dev	0.8516	0.8108

TABLE 5: ANALYSIS OF CERTIFIED REFERENCE MATERIAL ERM 41 (%w/w)

Sample ID	Method 9001	Method 9000
1	87.11	86.67
1-D	89.07	85.79
7	93.58	87.36
7-D	93.25	91.40
14	76.24	75.56
14-D	74.87	73.58
20	90.18	90.01
20-D	92.90	90.10
27	93.69	91.43
27-D	92.87	91.69
Mean	88.38	86.36
Std Dev	6.744	6.56

TABLE 6: DETERMINATION OF ALCOHOL IN WATER/ALCOHOL MIXTURES

Expected % Alcohol, v/v	Method 9001, (%v/v)	Method 9000, (%v/v)
0	0	0
10	9.45	11.6
10	10.7	8.97
10	9.76	--
25	25.8	25.0
25	25.0	25.08
25	26.1	--
40	41.4	38.5
40	39.5	38.9
40	41.7	--
50	50.6	49.4
50	48.2	48.8
50	46.8	--
80	80.4	79.8
80	80.5	79.7
80	80.8	--
100	100	100
100	99.7	100
Smirnoff Vodka, 40	41.6	41.9
Smirnoff Vodka, 40-D	42.1	42.0
Seagrams VO, 40	39.2	41.8
Seagrams VO, 40-D	40.3	41.9
Beefeaters Gin, 47	47.6	48.8
Beefeaters Gin, 47-D	46.8	48.6

TABLE 7: DETERMINATION OF WATER CONTENT IN LATEX PAINT (%w/w)

Sample ID	Method 9001	Method 9000
1	45.57	44.23
1-D	45.11	42.20
13	44.58	40.15
13-D	44.72	40.97
16	44.73	41.99
16-D	45.09	41.75
27	44.90	42.43
27-D	44.79	42.85
31	44.57	44.01
31-D	45.08	42.84
Mean	44.914	42.342
Std Dev	0.3062	1.2490

TABLE 8: DETERMINATION OF WATER CONTENT IN MARINE SEDIMENT (%w/w)

Sample ID	Method 9001	Method 9000
Blk	1.14	0.796
Blk-D	--	0.361
10	10.06	9.626
10-D	--	9.859
20	18.99	20.13
20-D	--	19.20
30	28.52	30.03
30-D	--	29.87
40	38.47	40.18
40-D	--	40.49