



AOCS Standard Procedure Ck 2-09

Revised 2011

Determination of Various Properties of Biodiesel by the QTA[®] System Method

DEFINITION

This method provides a procedure for using the QTA System for rapid determination of a variety of properties of biodiesel using a QTA-specific infrared spectrometer that uses attenuated total reflectance (ATR). The QTA System maintains a proprietary database of calibration algorithms managed centrally, and accessed by individual method users via a secure website. The spectra of the biodiesel is collected on the local spectrometer, and then transmitted to QTA's central database, where the algorithms are used for prediction. Results are then transmitted back to the user's computer.

SCOPE

This procedure describes the method that QTA Users follow when analyzing a biodiesel sample using the QTA System. A validation procedure is included, as prescribed by QTA and followed by QTA Users. The scope of this procedure does not include the development of the calibration algorithms, which is done in a proprietary process by QTA.

Calibration development by FT-IR requires knowledge of chemometric principles. This method avoids calibration development by the user, by employing a single central calibration that is used by all users. The calibration installed on the QTA Server is the result of a comprehensive calibration development program using the prescribed ASTM D6751 method for each component or property. The QTA calibrations have undergone extensive validation and have been subjected to round robin studies, as described in an AOCS Collaborative Study Report. The spectrometer specifications and operating parameters are set by QTA, and the use of central calibrations, ensure that all users access the calibrations whose performance is documented in the Collaborative Study Report. The QTA participants of the round robin were required only to scan samples and report results; the wet chemistry labs used the prescribed ASTM or EN methods.

The QTA System method is applicable to a variety of biodiesel component analyses and properties. Predictions for moisture, methanol, sulfur, total glycerin, free glycerin and monoglyceride content, as well as acid number, cloud point and oxidative stability are included. The same method may be used for other biodiesel properties when additional calibration algorithms are developed, commercialized and validated by collaborative study. This method is applicable to biodiesel B100 samples that are homogeneous, derived from animal, vegetable and/or waste feedstocks. Non-homogeneous samples cannot be analyzed using this method. The feedstocks evaluated in the 2008 international collaborative study for B100 characterization by the QTA System included two soybean oils (separate facilities), two different canola oils (separate facilities), a blend of tallow and chicken fat, two blends of choice white grease, tallow, and poultry fats (same facility but separate batches), and two blends of soybean oil and poultry fat (same facility but separate batches). For the 2010 collaborative study focusing on monoglycerides, sulfur and oxidative stability, the B100 samples included the following feedstocks: tallow, choice white grease (CWG), waste vegetable oil, canola, a blend of tallow and CWG, and four types of soybean: 1. refined, bleached, distilled; 2. crude, degummed; 3. waste; and 4. distilled after production. Additionally, two samples of unknown feedstock were included.

APPARATUS

1. QTA –specific spectrometer, provided by QTA
2. Internet-enabled computer
3. Disposable plastic pipets
4. Soft white paper towels

REAGENTS

1. 50% solution of isopropyl alcohol in distilled water

PROCEDURE

1. Log on to www.qta.com
2. Enter your secure username and password and allow system to initialize
3. On the Select Material screen, select B100 NA
4. Select the properties to be analyzed by checking the appropriate boxes

5. Click Identify Sample to be taken to the Identify Sample screen
6. Enter your sample ID information
7. Click Analyze Sample
8. When prompted by the system, clean the sampling surface. Place one drop of the isopropyl alcohol solution on a soft white paper towel. Wipe the ATR crystal with the wetted paper towel. Use a dry section of paper towel to wipe the ATR crystal three times, using a clean dry section of paper towel each time.
9. After the ATR crystal is clean, click OK. The system will collect a background file.
10. When prompted by the system, place one drop of biodiesel on the ATR crystal. Ensure that there are no bubbles in the liquid on the ATR crystal.
11. Begin the analysis.
12. Results will be returned to the computer screen within less than one minute.

CHECK SAMPLES

It is recommended that at least once per week a reference sample having known values be analyzed on QTA. The known values should be generated by a QTA-approved laboratory that utilizes approved methods.

The check sample results returned by QTA should be within 2 standard deviations of the reference value. If it does not, QTA support should be contacted.

VALIDATION

Perform the validation protocol for each new QTA System, when there are any significant changes in feedstock, and annually thereafter. The validation verifies that the sample matrix is included in the QTA central calibration, by comparing the primary method results to the QTA results to ensure that the variability is less than two standard errors. The validation includes:

1. Upon start up, send at least 4 samples of biodiesel from 4 different batches to an approved QTA primary laboratory for primary method analysis. One additional sample will be required annually. Repeat when necessary or when there is a significant feedstock or process change.
2. Analyze an aliquot of each of the above samples on the QTA System.
3. Upon completion of the primary data analysis, the QTA results should fall within two standard errors of the primary result. If true, then the system is validated for use.

If false, then

1. Check the primary data and the QTA spectra for accuracy, and repeat the process defined in step 3.
2. Check the homogeneity of the sample. If non-homogeneous, discard the sample and data and re-validate with homogeneous sample.
3. QTA will adjust the calibration to include the additional sample matrix, provided that: (a) the standard error of the system does not increase; and (b) the error of the prediction results of the other QTA Systems does not exceed two times the standard error.
4. If none of the above enables validation, then the QTA System will not be validated for that facility/process/feedstock.

PRECISION

AOCS Standard Procedure Ck 2-09 was originally published in 2009 based on a collaborative study performed in 2008 that examined the following properties: moisture, methanol, total glycerin, free glycerin, cloud point and acid number. The fuel matrices used in the 2008 study are listed in Table 1. Table 9 is the list of fuel matrices evaluated in 2009 for the validation of this Standard Procedure for the properties of monoglycerides, sulfur and oxidative stability.

REPEATABILITY

The absolute difference between two independent single test results, obtained using the same method on identical test material in the same laboratory by the same operator using the same equipment within a short interval of time, will in not more than 5% of cases be greater than the values given in Tables 2–7 and 8–12. If the difference is greater than the limit indicated in Tables 2–7 and 8–12, obtain two other test portions. Analyze one as before and keep the other for a

Table 1. Fuel Matrices

Fuel A*	Soybean Oil Methyl Esters
Fuel B [^]	Soybean Oil Methyl Esters
Fuel C	Tallow and Chicken Fat Methyl Esters
Fuel D	White Grease, Tallow, and Chicken Fat Methyl Esters
Fuel F	Canola Methyl Esters
Fuel G	Canola Methyl Esters
Fuel H	Soybean Oil and Poultry Fat Methyl Esters
Fuel I	Soybean Oil and Poultry Fat Methyl Esters
Fuel J*	Soybean Oil Methyl Esters
Fuel K [^]	Soybean Oil Methyl Esters

* Fuel A is a blind duplicate of Fuel J.

[^] Fuel B is a blind duplicate of Fuel K.

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fourth determination if necessary. In this case, take as the result the arithmetic mean of the result obtained from the third analysis and the nearest result obtained from the previous analyses, provided that the difference does not exceed the allowed limit. Failing this, analyze also the fourth test portion and take as the result the mean of the four determinations.

REPRODUCIBILITY

The absolute difference between two single test results, obtained using the same method on identical test material in different laboratories by different operators using different equipment, will in not more than 5% of cases be greater than the values given in Tables 2–7 and 8–12. Tables 8 and 13 contain the precision data generated by the ASTM D6708 statistical evaluations the precision data generated by the ASTM D6708 statistical evaluation.

Table 2. Precision Data: Karl Fischer Moisture

	A*	B [^]	C	D	F	G	H	I	J*	K [^]
Number of Laboratories	8	8	8	8	8	8	8	8	8	8
Number of Replicates	14	16	16	16	16	16	14	14	14	16
Primary Chem. XBAR ± S(R)	0.038 ± 0.005	0.047 ± 0.005	0.025 ± 0.005	0.041 ± 0.005	0.069 ± 0.007	0.069 ± 0.005	0.044 ± 0.008	0.044 ± 0.008	0.037 ± 0.004	0.046 ± 0.005
QTA XBAR	0.044	0.046	0.036	0.032	0.055	0.057	0.045	0.042	0.039	0.045
Repeatability										
QTA S(r)	0.003	0.004	0.004	0.007	0.004	0.002	0.003	0.006	0.005	0.003
QTA RSD(r)	6.41	7.60	12.11	21.07	6.55	3.31	6.53	14.75	11.94	5.57
QTA r	0.008	0.010	0.012	0.019	0.010	0.005	0.008	0.018	0.013	0.007
Reproducibility										
QTA S(R)	0.006	0.005	0.006	0.007	0.006	0.004	0.004	0.006	0.005	0.007
QTA RSD(R)	13.83	11.16	17.26	21.07	10.88	7.31	9.39	14.75	12.30	14.53
QTA R	0.017	0.014	0.017	0.019	0.017	0.012	0.012	0.018	0.014	0.018

* Sample A is a blind duplicate of Sample J [^] Sample B is a blind duplicate of Sample K

Table 3. Precision Data: Acid Value

	A*	B^	C	D	F	G	H	I	J*	K^
Number of Laboratories	8	8	8	8	8	8	8	8	8	8
Number of Replicates	16	14	16	16	16	14	14	16	14	14
Primary Chem. XBAR ± S(R)	0.313 ± 0.033	0.204 ± 0.020	0.242 ± 0.029	0.530 ± 0.039	0.092 ± 0.021	0.089 ± 0.019	0.423 ± 0.039	0.484 ± 0.045	0.334 ± 0.050	0.211 ± 0.024
QTA XBAR	0.281	0.207	0.425	0.625	0.063	0.057	0.336	0.419	0.271	0.193
Repeatability										
QTA S(r)	0.043	0.027	0.061	0.050	0.050	0.053	0.046	0.160	0.053	0.060
QTA RSD(r)	15.40	12.90	14.41	8.00	80.00	93.54	13.79	38.23	19.69	30.99
QTA r	0.121	0.075	0.171	0.140	0.140	0.150	0.130	0.448	0.150	0.167
Reproducibility										
QTA S(R)	0.055	0.049	0.069	0.058	0.063	0.053	0.050	0.169	0.085	0.060
QTA RSD(R)	19.59	23.56	16.19	9.32	100.29	93.54	14.89	40.30	31.14	30.99
QTA R	0.154	0.137	0.193	0.163	0.175	0.150	0.140	0.473	0.237	0.167

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Table 4. Precision Data: Cloud Point

	A*	B [^]	C	D	F	G	H	I	J*	K [^]
Number of Laboratories	8	8	8	8	8	8	8	8	8	8
Number of Replicates	14	16	16	16	16	16	16	16	16	14
Primary Chem. XBAR ± S(R)	0.043 ± 0.520	0.450 ± 0.788	11.679 ± 0.727	8.443 ± 1.096	-3.007 ± 0.577	-2.864 ± 0.656	1.850 ± 0.866	1.343 ± 0.759	0.043 ± 0.569	0.236 ± 1.065
QTA XBAR	-1.071	-0.125	10.125	7.688	-4.938	-4.875	1.500	1.000	-0.875	-0.286
Repeatability										
QTA S(r)	0.267	0.354	0.707	0.433	0.433	0.500	0.935	0.612	0.354	NA
QTA RSD(r)	0.010	0.130	0.250	0.150	0.160	0.190	0.340	0.302	0.130	NA
QTA r	0.748	0.990	1.980	1.212	1.212	1.400	2.619	1.715	0.990	NA
Reproducibility										
QTA S(R)	0.488	0.738	1.044	0.612	0.582	0.906	0.968	0.829	1.184	0.488
QTA RSD(R)	0.180	0.270	0.370	0.220	0.220	0.340	0.350	0.830	0.440	0.180
QTA R	1.366	2.066	2.922	1.715	1.631	2.538	2.711	2.320	3.315	1.366

* Sample A is a blind duplicate of Sample J [^] Sample B is a blind duplicate of Sample K

Table 5. Precision Data: Total Glycerin

	A*	B [^]	C	D	F	G	H	I	J*	K [^]
Number of Laboratories	8	8	8	8	8	8	8	8	8	8
Number of Replicates	16	16	16	16	16	16	16	14	14	16
Primary Chem. XBAR ± S(R)	0.147 ± 0.020	0.100 ± 0.012	0.097 ± 0.020	0.058 ± 0.013	0.200 ± 0.025	0.203 ± 0.024	0.251 ± 0.034	0.264 ± 0.027	0.148 ± 0.022	0.096 ± 0.012
QTA XBAR	0.144	0.134	0.093	0.093	0.159	0.152	0.258	0.256	0.140	0.128
Repeatability										
QTA S(r)	0.012	0.010	0.008	0.016	0.014	0.009	0.018	0.018	0.009	0.013
QTA RSD(r)	8.30	7.67	8.05	17.60	8.91	5.94	7.00	7.09	6.61	10.00
QTA r	0.034	0.029	0.021	0.046	0.040	0.025	0.050	0.051	0.026	0.036
Reproducibility										
QTA S(R)	0.017	0.017	0.019	0.019	0.017	0.017	0.019	0.042	0.016	0.016
QTA RSD(R)	11.78	12.40	20.47	20.84	10.88	11.35	7.32	16.60	11.13	12.47
QTA R	0.048	0.047	0.053	0.054	0.048	0.048	0.053	0.119	0.044	0.045

* Sample A is a blind duplicate of Sample J [^] Sample B is a blind duplicate of Sample K

Table 6. Precision Data: Free Glycerin

	A*	B [^]	C	D	F	G	H	I	J*	K [^]
Number of Laboratories	8	8	8	8	8	8	8	8	8	8
Number of Replicates	16	16	16	16	16	16	16	16	16	16
Primary Chem. XBAR ± S(R)	0.013 ± 0.001	0.006 ± 0.001	0.001 ± 0.002	0.002 ± 0.002	0.016 ± 0.003	0.016 ± 0.004	0.002 ± 0.001	0.002 ± 0.001	0.013 ± 0.001	0.006 ± 0.001
QTA XBAR	0.017	0.010	0.003	0.001	0.015	0.017	0.014	0.013	0.016	0.010
Repeatability										
QTA S(r)	0.002	0.002	0.002	0.001	0.002	0.003	0.003	0.006	0.004	0.001
QTA RSD(r)	11.99	26.05	90.67	124.72	12.65	16.37	18.73	48.89	27.09	10.50
QTA r	0.006	0.007	0.007	0.001	0.005	0.008	0.007	0.018	0.012	0.003
Reproducibility										
QTA S(R)	0.004	0.004	0.003	0.001	0.003	0.003	0.003	0.007	0.007	0.002
QTA RSD(R)	24.95	37.31	102.14	188.98	21.77	20.16	24.72	50.98	42.18	23.01
QTA R	0.012	0.010	0.008	0.003	0.009	0.010	0.010	0.019	0.018	0.006

* Sample A is a blind duplicate of Sample J ^ Sample B is a blind duplicate of Sample K

Table 7. Precision Data: Methanol Content

	A*	B [^]	C	D	F	G	H	I	J*	K [^]
Number of Laboratories	8	8	8	8	8	8	8	8	8	8
Number of Replicates	16	16	16	16	16	16	14	16	16	16
Primary Chem. XBAR ± S(R)	0.072 ± 0.034	0.099 ± 0.032	0.011 ± 0.013	0.003 ± 0.004	0.128 ± 0.044	0.135 ± 0.042	0.097 ± 0.039	0.090 ± 0.042	0.076 ± 0.027	0.095 ± 0.041
QTA XBAR	0.076	0.126	0.059	0.032	0.228	0.223	0.155	0.120	0.084	0.149
Repeatability										
QTA S(r)	0.019	0.047	0.006	0.004	0.010	0.026	0.017	0.035	0.019	0.009
QTA RSD(r)	24.54	37.56	10.42	13.58	4.40	11.57	10.77	29.17	22.73	5.82
QTA r	0.052	0.133	0.017	0.012	0.028	0.072	0.047	0.098	0.053	0.024
Reproducibility										
QTA S(R)	0.021	0.047	0.007	0.007	0.028	0.035	0.017	0.050	0.024	0.016
QTA RSD(R)	27.65	37.56	12.35	20.96	12.32	15.95	10.77	41.41	28.92	10.63
QTA R	0.059	0.133	0.020	0.019	0.078	0.099	0.047	0.139	0.068	0.044

* Sample A is a blind duplicate of Sample J [^] Sample B is a blind duplicate of Sample K

Table 8. ASTM D6708 Precision Summary

	Repeatability	Reproducibility
Cloud Point, deg C (ASTM D2500)	1.2786	2.8918
Water, % (ASTM D2709)	0.2034*(0.1-x)	0.01945
Acid Number, mg KOH/g (ASTM D664)	0.1721	0.2187
Methanol, % (EN 14110)	0.1575*(x+0.25)	0.2275*(x+0.25)
Free glycerin, % (ASTM D6584)	0.1882*(x+0.02)	0.3106*(x+0.02)
Total glycerin, % (ASTM D6584)	0.03526	0.05411

Table 9. Fuel Matrices for monoglycerides, sulfur and oxidative stability.

Fuel AZ	Crude Degummed Soybean Oil Methyl Esters
Fuel CN	Methyl Esters, unknown feedstock
Fuel GA	Methyl Esters, unknown feedstock
Fuel IL	Canola Methyl Esters
Fuel IN	Refined, bleached, distilled Soybean Oil Methyl Esters
Fuel KY	Choice White Grease Methyl Esters
Fuel MI	Waste Vegetable Oil Methyl Esters
Fuel FL	Waste Soybean Oil Methyl Esters
Fuel OH	Soybean Oil Methyl Esters, distilled
Fuel OK	Tallow and Choice White Grease Methyl Esters
Fuel TX	Tallow Methyl Esters

Table 10. Precision Data: Monoglycerides

Monoglycerides	AZ	CIN	GA	IL	IN	KY	MI	MOR	OH	OK	TX
Number of Laboratories	10	10	10	9	9	10	9	10	10	10	10
Number of Replicates	19	19	19	17	17	19	17	19	19	19	19
Primary Chem. XBAR ± S(R)	0.516 ± 0.100	0.035 ± 0.019	0.664 ± 0.118	0.586 ± 0.152	0.686 ± 0.125	0.167 ± 0.063	0.731 ± 0.154	0.358 ± 0.083	0.025 ± 0.016	0.359 ± 0.053	0.375 ± 0.048
QTA XBAR	0.588	0.067	0.583	0.425	0.595	0.229	0.708	0.45825	0.041	0.410	0.435
Repeatability											
QTA S(r)	0.037	0.037	0.030	0.021	0.026	0.043	0.021	0.025079	0.029	0.045	0.031
QTA RSD(r)	6.27	55.86	5.18	4.87	4.43	18.91	2.98	5.472726	70.13	10.98	7.18
QTA r	0.103	0.104	0.085	0.058	0.074	0.121	0.059	0.070221	0.081	0.126	0.087
Reproducibility											
QTA S(R)	0.049	0.050	0.051	0.039	0.039	0.043	0.044	0.039607	0.040	0.045	0.038
QTA RSD(R)	8.31	75.63	8.73	9.20	6.63	18.91	6.24	8.643078	95.58	11.05	8.76
QTA R	0.137	0.141	0.143	0.110	0.110	0.121	0.124	0.110899	0.111	0.127	0.107

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Table 11. Precision data: Sulfur

Sulfur	AZ	CIN	GA	IL	IN	KY	MI	MOR	OH	OK	TX
Number of Laboratories	10	10	10	8	10	9	9	9	10	10	10
Number of Replicates	19	19	19	15	19	17	17	17	19	19	19
Primary Chem. XBAR ± S(R)	1.506 ± 0.533	0.942 ± 0.273	0.771 ± 0.351	1.809 ± 0.447	1.506 ± 0.533	4.736 ± 1.570	3.699 ± 1.052	1.166 ± 0.862	0.495 ± 0.611	11.059 ± 2.032	6.053 ± 2.106
QTA XBAR	1.013	0.216	2.171	3.508	1.866	3.282	4.671	2.126	0.676	8.840	7.215
Repeatability											
QTA S(r)	0.379	0.168	0.578	0.537	0.649	0.681	0.453	0.981	0.502	0.487	0.607
QTA RSD(r)	37.45	77.93	26.62	15.32	34.80	20.75	9.69	46.14	74.21	5.51	8.42
QTA r	1.062	0.471	1.618	1.504	1.818	1.907	1.268	2.746	1.405	1.364	1.701
Reproducibility											
QTA S(R)	0.744	0.275	0.992	0.773	0.788	0.681	1.020	1.080	0.753	1.370	1.006
QTA RSD(R)	73.45	127.38	45.71	22.03	42.24	20.75	21.84	50.80	111.34	15.50	13.95
QTA R	2.083	0.770	2.779	2.164	2.207	1.907	2.857	3.024	2.107	3.836	2.818

Table 12. Precision Data: Oxidative Stability

Oxidative Stability	AZ	CIN	GA	IL	IN	KY	MI	MOR	OH	OK	TX
Number of Laboratories	10	10	8	9	9	10	10	10	10	9	10
Number of Replicates	19	19	15	17	17	19	19	19	19	17	19
<i>Primary Chem. XBAR ± S(R)</i>	4.340 ± 0.799	4.488 ± 1.452	5.203 ± 1.092	7.958 ± 1.487	5.614 ± 1.463	4.443 ± 1.261	1.647 ± 0.299	3.890 ± 2.103	1.263 ± 0.421	4.442 ± 1.352	11.857 ± 2.775
QTA XBAR	5.070	2.935	6.613	5.983	6.428	4.710	3.770	3.915	2.335	6.206	9.850
Repeatability											
QTA S(r)	0.837	0.417	0.665	0.508	0.663	0.437	0.823	0.604	0.618	0.508	0.634
QTA RSD(r)	16.50	14.21	10.06	8.49	10.31	9.28	21.84	15.43	26.46	8.19	6.44
QTA r	2.343	1.168	1.863	1.423	1.856	1.224	2.305	1.692	1.730	1.423	1.776
Reproducibility											
QTA S(R)	0.971	0.979	0.665	0.956	0.663	0.974	0.908	0.926	0.903	0.580	1.265
QTA RSD(R)	19.15	33.36	10.06	15.99	10.31	20.68	24.07	23.65	38.67	9.34	12.84
QTA R	2.719	2.742	1.863	2.678	1.856	2.728	2.541	2.593	2.528	1.623	3.543

Table 13. ASTM D6708 Precision Summary

	Repeatability	Reproducibility
Monoglycerides, % (ASTM D6584)	0.0126	0.0177
Sulfur, ppm (ASTM D6453)	0.0697*(X + 20)	0.1083*(X + 20)
Oxidative Stability (EN14112)	1.84	2.26