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## Summary

The Optimum WDS system features used to efficiently measure unused lubricating oil and additive products are listed below. The precision, Lower-Limit-of-Detection, and regression analysis are also summarized below.

- 1) The close coupled ultra-thin (75 $\mu$ ) end window X-ray tube operating at 4000 watts with up to 150 mA provides maximum intensity for the harder to analyze lighter elements found in these samples (Mg, P, S).
- 2) The sample handling capabilities of the S4 PIONEER allows both liquid and solid samples to be analyzed simultaneously decreasing the overall analyzing time. Random access of any position in the sample changer allows "rush" samples to be processed in a priority data collection mode.
- 3) A fail-safe vacuum interlock between the sample and the spectrometer chamber eliminates the risk of contaminating the optical path from accidental spills.
- 4) The standard deviation of the calibration curves were as follows:

Ca	0.0020% (20 ppm)
Cl (Ge)	0.0023% (23 ppm)
Cl (PET)	0.0022% (22 ppm)
Cu	0.0007% (7 ppm)
Mg	0.0015% (15 ppm)
P (Ge)	0.0010% (10 ppm)
P (PET)	0.0016% (16 ppm)
S (Ge)	0.0065% (65 ppm)
S (PET)	0.0095% (95 ppm)
Zn	0.0017% (17 ppm)

This is an indication of the accuracy of the method since it includes all errors associated with the measurement process (errors in the known concentration values of the standards, errors from preparing the specimens and errors in the measurements).

- 5) A repeatability test performed on two known samples showed the repeatability of the S4 PIONEER to be within the guide lines outlined in the ASTM Test Method D6443.

- 6) The Lower-Limits-of-Detection (LLD) based on 100 seconds of counting time were calculated to be:

Ca	0.00005% (0.5 ppm)
Cl (Ge)	0.00011% (1.1 ppm)
Cl (PET)	0.00009 (0.9 ppm)
Cu	0.00004% (0.4 ppm)
Mg	0.000013% (1.3 ppm)
P (Ge)	0.00003% (0.3 ppm)
P (PET)	0.00004% (0.4 ppm)
S (Ge)	0.00005% (0.5 ppm)
S (PET)	0.00005% (0.5 ppm)
Zn	0.00004% (0.4 ppm)

The S4 PIONEER fully meets the requirements for the determination of calcium, chlorine, copper, magnesium, phosphorus, sulfur, and zinc in unused lubricating oils and additives as outlined in ASTM D6443. The S4 PIONEER is ideally suited for the wide range of process control applications found in the petroleum industry.

## References:

- (1) D6443-99 Standard Test Method for Determination of Calcium, Chlorine, Copper, Magnesium, Phosphorus, Sulfur, and Zinc in Unused Lubricating Oils and Additives by Wavelength Dispersive X-ray Fluorescence Spectrometry (Mathematical Correction Procedure), American Society for Testing and Materials, West Conshohocken, PA, Copyright 1999.
- (2) Analytical Services, Inc, Woodlands, Texas 77387, (409) 273-1780
- (3) Bruker AXS liquid sample cells, 35 mm inside diameter, 40 mm outside diameter, part number 7KP19018FA
- (4) Prolene is a registered trademark of Chemplex Industries, Inc., Palm City, Florida 34990, (772) 283-2700

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## S4 PIONEER

# ASTM D6443 Standard Test Method for Determination of Ca, Cl, Cu, Mg, P, S, and Zn in Unused Lubricating Oils and Additives.

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### Introduction

Lubricating oils are generally formulated with additives, which act as detergents, anti-oxidants, anti-wear agents, etc. These additives can contain calcium, copper, magnesium, phosphorus, sulfur, and zinc. Chlorine can also be present in these oils as a contaminant. The ASTM Standard Test Method D6443<sup>(1)</sup> can be used to determine if the oils, additives, and additive packages meet specifications with respect to the added elements, and with respect to chlorine contamination.

The analysis of lubricating oils by WDS provides a non-destructive method that is easily incorporated into a production environment. This Lab Report covers the performance of the Bruker AXS S4 PIONEER for ASTM D6443, including precision and Lower-Limits-of-Detection (LLD).

### Instrument Configuration

The Bruker AXS S4 PIONEER is an ideal solution for analyzing petroleum products. The S4 PIONEER has a very small foot print and comes with casters. This allows the instrument to be placed into tight quarters and easily moved whenever service is required.

The S4 PIONEER uses a 4kW end-window X-ray tube with an ultra-thin 75 $\mu$  beryllium window. A closely coupled optical path helps provide high intensities and low detection limits for all elements. Automatic computer control of the X-ray generator allows the kV and mA settings to be adjusted automatically for each element. This optimization of the voltage and current settings provides maximum sensitivity for all elements. The lower atomic number elements are typically analyzed using low kV and high mA settings, while the higher atomic number elements are analyzed with high kV and lower mA settings.



Figure 1 - Bruker AXS S4 PIONEER wavelength dispersive X-ray spectrometer.

The S4 PIONEER has all of the features one expects for a complete Bruker AXS instrument in this class: a 10-position primary beam filter changer, up to 4 primary collimators, and up to 8 analyzer crystals. It uses two detectors mounted side-by-side in the vacuum chamber. One is a scintillation detector, which is used to measure the higher energy lines, and the other is a gas flow proportional detector for measuring the lower energy lines.

Traditional liquid sample analysis requires the entire optical path in the X-ray spectrometer to be flushed with helium gas. Bruker AXS has developed a unique vacuum seal that utilizes a thin window between the spectrometer chamber and the sample chamber. This allows the spectrometer chamber to remain under vacuum at all times, and only the sample chamber needs to be flushed with helium when measuring liquids. This arrangement minimizes the time required to switch between vacuum and helium modes of operation. The vacuum seal also provides a safety interlock between the sample and spectrometer chambers preventing liquids from contaminating the optical path in the event of sample cup leakage. This arrangement always keeps the flow detector in a vacuum atmosphere allowing ultra thin entrance windows to be used without the risk of them breaking. A software interlock is also provided to prevent a liquid sample from being analyzed while the spectrometer is in a vacuum mode. The software will not allow the introduction of a sample identified as a liquid into a vacuum path, and can be set to require a password for all samples that will be measured in a vacuum path.

Table 1 - Calibration standard compositions in mass %.

Standard	Ca (%)	Cl (%)	Cu (%)	Mg (%)	P (%)	S (%)	Zn (%)
LOE10-01	0.0200	0.0301	0.0100	0.2002	0.2561	1.0480	0.0205
LOE10-02	0.0200	0.0200	0.0501	0.2000	0.0204	0.0202	0.2566
LOE10-03	0.0200	0.2025	0.0100	0.0401	0.2560	0.1535	0.2566
LOE10-04	0.0200	0.2030	0.0500	0.0400	0.0206	1.0680	0.0205
LOE10-05	0.4000	0.0200	0.0100	0.0402	0.0201	1.0540	0.2567
LOE10-06	0.4010	0.0200	0.0500	0.0405	0.2568	0.0204	0.0204
LOE10-07	0.4010	0.2013	0.0100	0.2012	0.0205	0.0203	0.0507
LOE10-08	0.4000	0.1999	0.0507	0.2000	0.2582	1.0520	0.2569
LOE10-09	0.2002	0.1000	0.0250	0.0800	0.1520	0.5120	0.1025
LOE10-10	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

The Bruker AXS S4 PIONEER's automatic sample loader is designed to handle both liquid and solid samples at the same time with random access capabilities. Priority levels can be set for individual samples, which controls the measurement sequence of these samples. This allows samples, which have just been loaded to become the very next samples to be measured without interruption of the current running sample. An immediate mode also is available which allows rush samples to be analyzed immediately by interrupting the current measurement without loss of data collected up to the point of interruption. These features allow a wide variety of samples to be handled routinely without any modifications to the system.

Operation and data reduction for the S4 PIONEER are easily handled with the Bruker AXS SPECTRA<sup>plus</sup> software package. This is a true 32-bit program designed for use on the Windows-2000/XP platform for maximum stability. Its standard features include a "standardless" analysis package, sophisticated matrix corrections with integrated Fundamental Parameters, flexible data storage and retrieval, and full network capability.

### Experimental

Ten lubricating oil standards, which included a blank, were obtained from a commercial laboratory<sup>(2)</sup>. These standards had been prepared gravimetrically using reagents traceable to NIST Standard Reference Materials. Compositions for the calibration standards used are listed in Table 1.

Table 7 - Precision test for Cl, P and S from twenty measurements of Lubricating Oil Check Sample 1 with the S4 PIONEER and a PET analyzer crystal.

Sample	Cl (PET) mass %	P (PET) mass %	S (PET) mass %
Check Sample 1	0.0957	0.1522	0.5059
Check Sample 1	0.0941	0.1528	0.5082
Check Sample 1	0.0952	0.1533	0.5108
Check Sample 1	0.0969	0.1544	0.5139
Check Sample 1	0.0945	0.1510	0.5063
Check Sample 1	0.0967	0.1535	0.5096
Check Sample 1	0.0966	0.1532	0.5098
Check Sample 1	0.0963	0.1539	0.5149
Check Sample 1	0.0949	0.1527	0.5073
Check Sample 1	0.0957	0.1527	0.5074
Check Sample 1	0.0946	0.1536	0.5082
Check Sample 1	0.0959	0.1536	0.5107
Check Sample 1	0.0949	0.1532	0.5140
Check Sample 1	0.0951	0.1543	0.5161
Check Sample 1	0.0953	0.1531	0.5126
Check Sample 1	0.0955	0.1536	0.5106
Check Sample 1	0.0938	0.1517	0.5123
Check Sample 1	0.0936	0.1519	0.5126
Check Sample 1	0.0945	0.1527	0.5090
Check Sample 1	0.0943	0.1530	0.5094
Number of Tests	20	20	20
Maximum	0.0969	0.1544	0.5161
Minimum	0.0936	0.1510	0.5059
Range	0.0033	0.0034	0.0102
Average	0.0952	0.1530	0.5105
Abs. Std. Dev. ( $1\sigma$ )	0.0010	0.0009	0.0029
Rel. Std. Dev. ( $1\sigma$ )	1.0	0.6	0.6
True Concentration	0.1000	0.1520	0.5120
Abs. Difference	0.0048	-0.0010	0.0015
Rel. Difference	5.0	-0.7	0.3
ASTM Repeatability	0.0039	0.0057	0.0130
Actual Repeatability	0.0033	0.0034	0.0102

Table 8. Precision test for Cl, P and S from twenty measurements of Lubricating Oil Check Sample 2 with the S4 PIONEER and a PET analyzer crystal.

Sample	Cl (PET) mass %	P (PET) mass %	S (PET) mass %
Check Sample 2	0.0186	0.0204	0.0202
Check Sample 2	0.0187	0.0198	0.0204
Check Sample 2	0.0183	0.0203	0.0200
Check Sample 2	0.0189	0.0201	0.0205
Check Sample 2	0.0190	0.0201	0.0200
Check Sample 2	0.0190	0.0204	0.0204
Check Sample 2	0.0188	0.0204	0.0205
Check Sample 2	0.0188	0.0204	0.0201
Check Sample 2	0.0187	0.0201	0.0202
Check Sample 2	0.0186	0.0203	0.0201
Check Sample 2	0.0188	0.0202	0.0205
Check Sample 2	0.0187	0.0205	0.0203
Check Sample 2	0.0186	0.0208	0.0205
Check Sample 2	0.0189	0.0204	0.0207
Check Sample 2	0.0188	0.0208	0.0207
Check Sample 2	0.0187	0.0207	0.0205
Check Sample 2	0.0182	0.0202	0.0200
Check Sample 2	0.0185	0.0202	0.0202
Check Sample 2	0.0183	0.0202	0.0200
Check Sample 2	0.0184	0.0203	0.0202
Number of Tests	20	20	20
Maximum	0.0190	0.0208	0.0207
Minimum	0.0182	0.0198	0.0200
Range	0.0008	0.0010	0.0007
Average	0.0187	0.0203	0.0203
Abs. Std. Dev. ( $1\sigma$ )	0.0002	0.0002	0.0002
Rel. Std. Dev. ( $1\sigma$ )	1.2	1.2	1.1
True Concentration	0.0200	0.0204	0.0202
Abs. Difference	0.0013	0.0001	-0.0001
Rel. Difference	7.2	0.3	-0.5
ASTM Repeatability	0.0010	0.0014	0.0007
Actual Repeatability	0.0008	0.0010	0.0007

Table 6 - Precision test from twenty measurements of Lubricating Oil Check Sample 2 with the S4 PIONEER with a Ge analyzer crystal.

Sample	Ca mass %	Cl (Ge) mass %	Cu mass %	Mg mass %	P (Ge) mass %	S (Ge) mass %	Zn mass %
Check Sample 2	0.0197	0.0191	0.0252	0.0798	0.0204	0.0192	0.1025
Check Sample 2	0.0198	0.0188	0.0251	0.0807	0.0202	0.0194	0.1023
Check Sample 2	0.0199	0.0188	0.0254	0.0813	0.0206	0.0196	0.1041
Check Sample 2	0.0198	0.0187	0.0254	0.0813	0.0204	0.0195	0.1044
Check Sample 2	0.0200	0.0195	0.0251	0.0806	0.0204	0.0198	0.1020
Check Sample 2	0.0200	0.0192	0.0252	0.0824	0.0202	0.0196	0.1022
Check Sample 2	0.0201	0.0189	0.0253	0.0817	0.0204	0.0198	0.1024
Check Sample 2	0.0201	0.0192	0.0253	0.0814	0.0206	0.0196	0.1044
Check Sample 2	0.0199	0.0193	0.0252	0.0804	0.0202	0.0197	0.1021
Check Sample 2	0.0197	0.0193	0.0251	0.0802	0.0203	0.0196	0.1023
Check Sample 2	0.0199	0.0188	0.0251	0.0804	0.0202	0.0195	0.1028
Check Sample 2	0.0200	0.0192	0.0255	0.0819	0.0205	0.0198	0.1041
Check Sample 2	0.0199	0.0191	0.0254	0.0817	0.0203	0.0199	0.1044
Check Sample 2	0.0202	0.0194	0.0251	0.0794	0.0206	0.0198	0.1038
Check Sample 2	0.0201	0.0191	0.0252	0.0810	0.0206	0.0196	0.1025
Check Sample 2	0.0197	0.0185	0.0254	0.0790	0.0202	0.0192	0.1030
Check Sample 2	0.0199	0.0188	0.0250	0.0815	0.0202	0.0194	0.1023
Check Sample 2	0.0199	0.0188	0.0250	0.0804	0.0204	0.0196	0.1020
Check Sample 2	0.0200	0.0187	0.0254	0.0803	0.0204	0.0197	0.1044
Check Sample 2	0.0201	0.0190	0.0251	0.0814	0.0205	0.0197	0.1025
Number of Tests	20	20	20	20	20	20	20
Maximum	0.0202	0.0195	0.0255	0.0824	0.0206	0.0199	0.1044
Minimum	0.0197	0.0185	0.0250	0.0790	0.0202	0.0192	0.1020
Range	0.0005	0.0010	0.0005	0.0034	0.0004	0.0007	0.0024
Average	0.0199	0.0190	0.0252	0.0808	0.0204	0.0196	0.1030
Abs. Std. Dev. ( $1\sigma$ )	0.0001	0.0003	0.0002	0.0009	0.0002	0.0002	0.0009
Rel. Std. Dev. ( $1\sigma$ )	0.7	1.4	0.6	1.1	0.7	1.0	0.9
True Concentration	0.0200	0.0200	0.0250	0.0800	0.0204	0.0202	0.1025
Abs. Difference	0.0001	0.0010	-0.0002	-0.0008	0.0000	0.0006	-0.0005
Rel. Difference	0.3	5.2	-0.9	-1.0	0.1	3.1	-0.5
ASTM Repeatability	0.0010	0.0010	0.0005	0.0070	0.0014	0.0007	0.0025
Actual Repeatability	0.0005	0.0010	0.0005	0.0034	0.0004	0.0007	0.0024

Individual specimens were prepared by pipetting about 12 mL of each sample into a Bruker AXS 40 mm diameter liquid sample cell<sup>(3)</sup> that was fitted with a 4µ Prolene<sup>®</sup> window<sup>(4)</sup>. The sample cells used have vented caps to prevent the window from bulging during sample analysis. These liquid cells were then placed into sample cups fitted with stainless steel masks having openings of 34 mm in diameter.

The intensities at the peak and off-peak background angles were measured from the liquid samples using the operating parameters listed in Table 2. Data was measured for phosphorus, sulfur and chlorine using both the PET and

Ge analyzer crystals for comparison purposes. The counting time listed in this table was a maximum time to count each peak and off-peak background position. The Bruker AXS SPECTRA<sup>plus</sup> software has provisions for doing an optimized counting time. In this mode the user enters a target statistical error and a maximum counting time. Each intensity is then measured to the desired statistical error or the maximum counting time, whichever is shorter. A statistical error of 0.9% 3-sigma was used for all lines. This is equivalent to collecting 100,000 counts for each line measured. The total time required to measure each sample was from 3½ to 6½ minutes, which includes sample introduction time.

Table 2 - Instrument operating parameters used to measure the lubricating oil samples.

El.	Analyzer Crystal	Peak Angle (deg. 2θ)	Bkgd. Angle (deg 2θ)	Collimator	Detector	Beam Filter	kV/mA	Count Time (sec)
Mg	OVO-55	20.41	23.22	0.46°	FC	None	30/135	30
P	Ge(111)	140.92	145.35	0.46°	FC	None	30/135	10
P	PET	89.41	92.38	0.46°	FC	None	30/135	10
S	Ge(111)	110.68	116.75	0.46°	FC	None	30/135	10
S	PET	75.78	78.82	0.23°	FC	None	30/135	10
Cl	Ge(111)	92.75	94.20	0.23°	FC	None	30/135	20
Cl	PET	65.44	66.40	0.23°	FC	None	30/135	20
Ca	LiF(200)	113.07	116.20	0.23°	FC	None	50/81	10
Cu	LiF(200)	45.00	46.50	0.23°	SC	Al 500µm	50/81	10
Zn	LiF(200)	41.77	47.03	0.23°	SC	Al 500µm	50/40	10

Calibration coefficients were calculated using the 10 calibration standards by regressing the concentration data with the measured intensity data for each analyte. Matrix corrections (influence coefficients) were applied using a concentration based calibration model with the form:

$$C_i = a_i + b_i I_i (1 + \sum \alpha_{ij} C_j)$$

Where:

- $C_i$  = concentration of the analyte element  $i$ .
- $a_i$  = intercept of the calibration line for analyte element  $i$  on the concentration axis.
- $b_i$  = slope of the calibration line for analyte element  $i$  in %/kCPS
- $I_i$  = net measured intensity for analyte element  $i$  in kCPS.
- $\alpha_{ij}$  = influence coefficient for the effect of an absorbing element  $j$  on the the analyte element  $i$ .
- $C_j$  = concentration of an interfering element  $j$  as a weight fraction.

Theoretical influence coefficients (alphas) were calculated using a "Fundamental Parameters" program and the Variable Alphas model that is a standard part of the SPECTRA<sup>plus</sup> software. The Variable Alphas model calculates the alpha coefficients individually from each samples composition instead of using an average composition. This gives more appropriate alpha factors and allows accurate calibrations over wide concentration ranges. The results of the regression analysis using the 10 standards have been summarized in Table 3

Table 3 - Calibration summary for Unused Lubricating Oils and Additives.

Analyte	Conc. Range (mass %)	Calibration Line Offset (mass %)	Calibration Line Slope (mass %/kCPS)	Standard Deviation (mass %)
Mg	0 - 0.2012	-0.00679	0.01862	0.0015
P (Ge)	0 - 0.2582	-0.00042	0.01214	0.0010
P (PET)	0 - 0.2582	-0.00044	0.02500	0.0016
S (Ge)	0 - 1.0680	-0.00318	0.01859	0.0065
S (PET)	0 - 1.0680	-0.00227	0.03079	0.0095
Cl (Ge)	0 - 0.2030	-0.00344	0.06692	0.0023
Cl (PET)	0 - 0.2030	-0.00439	0.04376	0.0022
Ca	0 - 0.4000	-0.00112	0.03506	0.0020
Cu	0 - 0.0507	-0.00354	0.02349	0.0007
Zn	0 - 0.2569	-0.00231	0.03787	0.0017

Table 4 lists the estimated Lower-Limit-of-Detection (LLD) for each of the analyte elements. These LLD's were calculated based on the actual counting times used, and have also been expressed based on a counting time of 100 seconds for comparison purposes. The SPECTRA<sup>plus</sup> software estimates the LLD for each of the calibration standards by calculating 3 standard deviations of the background intensity, and converting this to a concentration. This is consistent with the generally accepted formula given below, except instead of using "m" to convert the intensity to a concentration the calibration coefficients are used.

$$LLD = \left( \frac{3}{m} \right) \left[ \frac{I_b}{T_b} \right]^{1/2}$$

where:

- $m$  = sensitivity of analyte in CPS/mass-%
- $I_b$  = background intensity for analyte in CPS
- $T_b$  = counting time in seconds at the background angle.

Table 4 - Lower Limits of Detection for Unused Lubricating Oils.

Analyte	Count Time (seconds)	LLD Actual Time (ppm)	LLD 100 Sec. (ppm)
Mg	30	2.4	1.3
P (Ge)	10	1.1	0.3
P (PET)	10	1.4	0.4
S (Ge)	10	1.6	0.5
S (PET)	10	1.6	0.5
Cl (Ge)	20	2.5	1.1
Cl (PET)	20	2.0	0.9
Ca	10	1.7	0.5
Cu	10	1.3	0.4
Zn	10	1.4	0.4

A precision test was performed on twenty individual sample preparations for two Check Samples with known concentrations. The results of this precision test, and statistical evaluation of the data is summarized in Table 5 through Table 8. These tables include a comparison to the known chemical concentrations for each analyte in the sample. The table also includes the ASTM expected

repeatability limits along with those determined from the measured data. This repeatability is the difference between successive test results for the same sample obtained from a single operator using the same instrument. Over the long run 19 out of 20 values are expected to be within the prescribed limits. The results produced by the S4 PIONEER were all within the prescribed limits.

Table 5 - Precision test from twenty measurements of Lubricating Oil Check Sample 1 with the S4 PIONEER and a Ge analyzer crystal.

Sample	Ca mass %	Cl (Ge) mass %	Cu mass %	Mg mass %	P (Ge) mass %	S (Ge) mass %	Zn mass %
Check Sample 1	0.2013	0.0993	0.0484	0.1972	0.1526	0.5162	0.2497
Check Sample 1	0.2015	0.0999	0.0488	0.2013	0.1533	0.5178	0.2508
Check Sample 1	0.2017	0.1008	0.0486	0.2013	0.1533	0.5199	0.2513
Check Sample 1	0.2026	0.1010	0.0488	0.1999	0.1541	0.5201	0.2531
Check Sample 1	0.2002	0.1001	0.0492	0.2010	0.1526	0.5131	0.2522
Check Sample 1	0.2013	0.0997	0.0486	0.1981	0.1528	0.5185	0.2498
Check Sample 1	0.2028	0.1009	0.0489	0.2019	0.1542	0.5234	0.2535
Check Sample 1	0.2029	0.1019	0.0489	0.2034	0.1540	0.5234	0.2540
Check Sample 1	0.2009	0.1001	0.0485	0.1991	0.1527	0.5162	0.2498
Check Sample 1	0.2006	0.0994	0.0484	0.2015	0.1524	0.5136	0.2502
Check Sample 1	0.2000	0.1001	0.0486	0.1994	0.1535	0.5179	0.2510
Check Sample 1	0.2026	0.1002	0.0491	0.2019	0.1550	0.5207	0.2531
Check Sample 1	0.2029	0.1005	0.0489	0.1992	0.1531	0.5201	0.2508
Check Sample 1	0.2025	0.1004	0.0485	0.2029	0.1535	0.5205	0.2522
Check Sample 1	0.2022	0.1004	0.0489	0.2023	0.1530	0.5209	0.2539
Check Sample 1	0.2002	0.0981	0.0483	0.1991	0.1508	0.5186	0.2503
Check Sample 1	0.2011	0.0981	0.0483	0.2008	0.1524	0.5153	0.2504
Check Sample 1	0.2002	0.1001	0.0484	0.1995	0.1518	0.5156	0.2506
Check Sample 1	0.2018	0.0983	0.0483	0.2043	0.1535	0.5201	0.2503
Check Sample 1	0.2030	0.0988	0.0490	0.1984	0.1537	0.5231	0.2534
Number of Tests	20	20	20	20	20	20	20
Maximum	0.2030	0.1019	0.0492	0.2043	0.1550	0.5234	0.2540
Minimum	0.2000	0.0981	0.0483	0.1972	0.1508	0.5131	0.2497
Range	0.0030	0.0038	0.0009	0.0071	0.0042	0.0103	0.0043
Average	0.2016	0.0999	0.0487	0.2006	0.1531	0.5188	0.2515
Abs. Std. Dev. ( $1\sigma$ )	0.0010	0.0010	0.0003	0.0019	0.0009	0.0030	0.0015
Rel. Std. Dev. ( $1\sigma$ )	0.5	1.0	0.6	0.9	0.6	0.6	0.6
True Concentration	0.2002	0.1000	0.0501	0.2000	0.1520	0.5120	0.2566
Abs. Difference	-0.0014	0.0001	0.0014	-0.0006	-0.0011	-0.0067	0.0051
Rel. Difference	-0.7	0.1	2.9	-0.3	-0.7	-1.3	2.0
ASTM Repeatability	0.0031	0.0039	N/A	0.0094	0.0057	0.0130	0.0047
Actual Repeatability	0.0030	0.0038	0.0009	0.0071	0.0042	0.0103	0.0043