GET FAST RESULTS FOR SULFUR AND CHLORINE IN BIOFUELS IN COMPLIANCE WITH ISO 20884

The demand for biofuels has increased in recent years and is expected to continuing growing through the next decade. In Europe specifically, the EU has made it a priority to have as much as 10% of the total transport fuel from every affiliated country come from renewable sources like biofuel by the year 2020 (1). With over 220 biorefineries in operation across Europe, the industry is looking to quantify the sulfur and chlorine in their products in the most efficient, and safe way possible.

Biorefineries producing biofuels or working with biofeedstocks will still be held accountable for the total sulfur count in their finished products as per ISO 20884. Likewise, the risk of corrosion from chlorine in these products is still just as much an issue as with any traditional crude oils. However, with biofuel samples there is typically a greater concentration of oxygen than in traditional samples. This is important to note because oxygen naturally absorbs XRF signals and as a result can cause analyzers to report lower sulfur and chlorine concentrations than are actually present in the sample. For this reason, we have developed a case study that tests real world biofuel samples for sulfur and chlorine while using correction factors to eliminate bias from oxygen.

In this study, we will test three real world samples, showcase their concentrations, and then apply correction factors to mitigate biased results. The correction factors used were derived from the ASTM D7039 method, though these correction factors can still be applied for those in Europe adhering to the ISO 20884 method. As per Section 1 of ISO 20884, any sample with more than 3.7% oxygen content must be corrected for.

APPLICATION STUDY

Three real world samples were analyzed: a rapeseed oil sample, and two different palm oil samples. For this study, each sample was separated into 10 aliquots via pipette into a standard XRF cup. The samples were then sealed with sample film and vented. The two palm oil samples were heated to 42°C before being vented.

Each sample was then placed into a Sindie +Cl analyzer and measured for 30 seconds and 300 seconds. Sindie +Cl was used in this study due to its convenient ability to measure total sulfur and chlorine concurrently. Sindie +Cl is not ISO 20884 method compliant due to its lack of a proportional counter, however, it still utilizes the Monochromatic Wavelength Dispersive X-ray Fluorescence (MWDXRF) technology found in standalone Sindie and Clora analyzers. Sindie and Clora analyzers are ISO 20884 method compliant and can be used to obtain similar results as shown in this study. Sindie analyzers deliver similar detection limits to Sindie +Cl, while Clora analyzers can detect even lower chlorine levels than is achievable with Sindie +Cl.

RESULTS

Once the samples were analyzed, data was compiled for each sample type as shown in **Tables 1-3**. The concentrations throughout this data are not corrected for oxygen content and therefore contain a bias. However, separate from the bias issue, we can see that the RSD (relative standard deviation) of this data is very low. This points to a high level of precision of the technique, and this will carry over once we apply our correction factors.

TABLE 1: Rapeseed Oil Sample Concentrations On Standard Mineral Oil Curve (ppm)

Test	Sulfur (300s)	Chlorine (300s)
1	0.79	0.07
2	0.94	0.2
3	0.91	0.15
4	1.12	0.11
5	0.99	0
6	0.74	0.13
7	0.9	0
8	1.01	0.02
9	0.69	0.21
10	0.76	0.06
Average	0.885	0.095
St.Dev	0.1372	0.0776
RSD	0.1550	0.8173
Samples were analyzed using Sindie +Cl Analyzer		

TABLE 2: Palm Oil Sample A Concentrations On Standard Mineral Oil Curve (ppm)

Test	Sulfur (300s)	Chlorine (300s)
1	0.69	1.55
2	0.95	1.63
3	1	1.72
4	0.74	1.15
5	0.71	1.64
6	0.79	1.34
7	0.85	1.21
8	0.77	1.6
9	0.9	1.78
10	0.95	1.44
Average	0.835	1.506
St.Dev	0.1106	0.2138
RSD	0.1324	0.1419
Samples were analyzed using Sindie +Cl Analyzer		
Samples Were Heated To 42°C Before Being Analyzed		

TABLE 3: Palm Oil Sample B Concentrations On Standard Mineral Oil Curve (ppm)

Test	Sulfur (300s)	Chlorine (300s)
1	61.40	267.73
2	60.85	264.46
3	62.44	265.98
4	60.52	267.91
5	62.30	265.33
6	63.58	270.37
7	43.70	213.00
8	51.03	222.85
9	59.44	262.94
10	61.20	263.95
Average	58.646	256.452
St.Dev	6.2945	20.5518
RSD	0.1073	0.0801
Samples were analyzed using Sindie +Cl Analyzer		
Samples Were Heated To 42°C Before Being Analyzed		

Each sample tested has its own oxygen content. The rapeseed oil has an oxygen content of 9.1%, the first palm oil sample has an oxygen content of 10.0%, and the other palm oil sample contained 11.6%. Knowing the oxygen content of the sample of interest is crucial to determine an accurate concentration count as the oxygen number is directly correlated to the correction factor. Correction factors for each sample were calculated using the numbers provided in **Tables 4 & 5**.

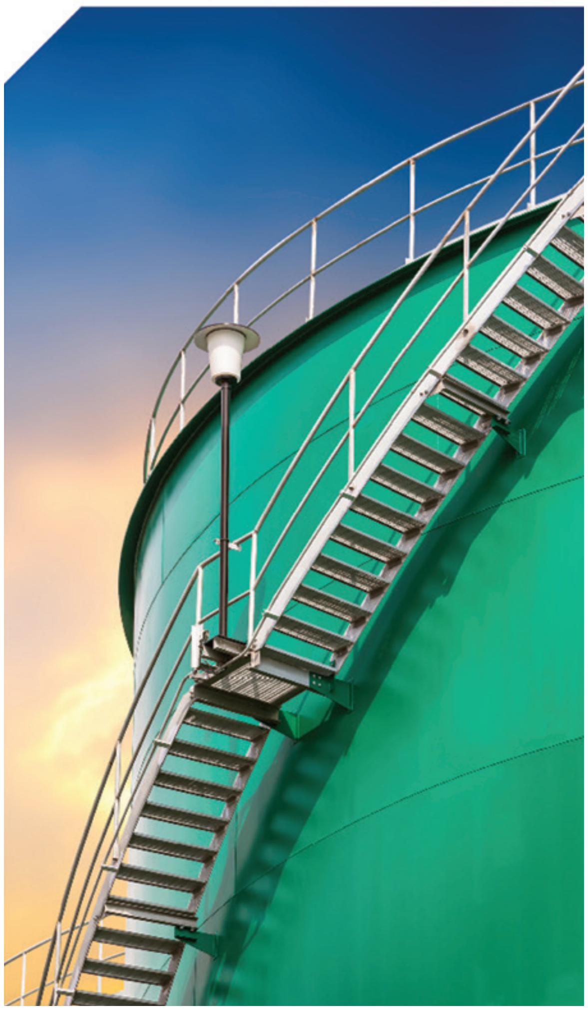

TABLE 4: Sulfur Oxygen Correction Table

Oxygen, wt%	0%	1%	2%	3%	4%	5%	6%	7%	8%	9%
0%	1.000	1.0174	1.0348	1.0522	1.0696	1.0870	1.1044	1.1218	1.1392	1.1566
10%	1.1740	1.1914	1.2088	1.2262	1.2436	1.2610	1.2784	1.2958	1.3132	1.3306

NOTE: To determine the appropriate correction factor, select the row that matches the most significant figure of the oxygen concentration, and then find the column that matches the least significant figure. The intersection of the row and the column is the correction factor. For example, a sample with an oxygen concentration of 11 wt% would use a correction factor of 1.1914. The correction factor is applied by multiplying the measured result by the correction factor to obtain the oxygen corrected sulfur value.

TABLE 5: Chlorine Oxygen Correction Table

Oxygen, wt%	0%	1%	2%	3%	4%	5%	6%	7%	8%	9%
0%	1.000	1.0178	1.0357	1.0535	1.0713	1.0891	1.1070	1.1248	1.1426	1.1604
10%	1.1783	1.1961	1.2139	1.2318	1.2496	1.2674	1.2852	1.3031	1.3209	1.3387

NOTE: Similar to ***Table 4****, to determine the appropriate correction factor, select the row that matches the most significant figure of the oxygen concentration, and then find the column that matches the least significant figure. The intersection of the row and the column is the correction factor. For example, a sample with an oxygen concentration of 11 wt% would use a correction factor of 1.1961. The correction factor is applied by multiplying the measured result by the correction factor to obtain the oxygenated correction chlorine value.*

RESULTS CONT.

These correction factors were derived from ASTM D7039, and can be applied to any sample with known oxygen content even if the user is not complying specifically with D7039 methodology. The corrected data is shown in **Tables 6-8** and as expected, we have a slight increase in total counts but have maintained our low RSD values and thus, our high level of precision.

TABLE 7: Palm Oil Sample A Results with Correction Factor Applied (ppm)

Test	Sulfur (300s)	Chlorine (300s)
1	0.81	1.83
2	1.12	1.92
3	1.17	2.03
4	0.87	1.36
5	0.83	1.93
6	0.93	1.58
7	1.00	1.43
8	0.90	1.89
9	1.06	2.10
10	1.12	1.70
Average	0.980	1.775
St.Dev	0.1298	0.2519
RSD	0.1324	0.1419
Samples were analyzed using Sindie +Cl Analyzer		
Samples Were Heated To 42°C Before Being Analyzed		
Numbers Corrected for Oxygen Content: 10.0% Correction Factor: S = 1.1740 ; Correction Factor: Cl = 1.1783		

TABLE 8: Palm Oil Sample B Results with Correction Factor Applied (ppm)

Test	Sulfur (300s)	Chlorine (300s)
1	73.15	320.23
2	72.50	316.32
3	74.39	318.14
4	72.10	320.45
5	74.22	317.36
6	75.75	323.39
7	52.06	254.77
8	60.80	266.55
9	70.82	314.50
10	72.91	315.71
Average	69.871	306.742
St.Dev	7.4992	24.5821
RSD	0.1073	0.0801
Samples were analyzed using Sindie +Cl Analyzer		
Samples Were Heated To 42°C Before Being Analyzed		
Numbers Corrected For Oxygen: 11.6% Correction Factor: S = 1.1914 ; Correction Factor: Cl = 1.1961		

TABLE 6: Rapeseed Oil Results with Correction Factor Applied (ppm)

Test	Sulfur (300s)	Chlorine (300s)
1	0.91	0.08
2	1.09	0.23
3	1.05	0.17
4	1.30	0.13
5	1.15	0.00
6	0.86	0.15
7	1.04	0.00
8	1.17	0.02
9	0.80	0.24
10	0.88	0.07
Average	1.024	0.110
St.Dev	0.1587	0.0901
RSD	0.1550	0.8173
Samples were analyzed using Sindie +Cl Analyzer		
Numbers Corrected For Oxygen Content: 9.1% Correction Factor: S = 1.1566 ; Correction Factor: Cl = 1.1604		

CONCLUSION

With the push for renewable fuel sources on the rise in regions like Europe, petroleum professionals are looking to utilize technology that allows for quick, on-site measurement of biofuels. With analyzers such as Sindie and Clora, users can analyze critical elements such as sulfur and chlorine while being method compliant with ISO 20884.

Users less concerned with method compliance can utilize Sindie +Cl for precise measurement of both elements with one instrument. By quickly and simply applying a correction factor to the results, professionals can certify their biofuel products more efficiently than with other methods.

REFERENCES:

(1) https://ec.europa.eu/energy/en/topics/renewable-energy/biofuels

PRODUCT HIGHLIGHTS

16 32.06 Sindie 2622 Sulfur Analyzer

Sindie 2622 complies with ASTM D2622, D7039, and ISO 20884 methods, enabling complete flexibility in sulfur analysis. With no compromises in detection, performance, or reliability, Sindie 2622 is the ideal sulfur analytical solution from ultra-low sulfur biodiesel and gasoline to heavy fuel oil and crudes. Utilizing MWDXRF technology, Sindie 2622 offers D2622 and ISO 20884 compliance with D7039 performance.

17 35.45 Clora 2XP Chlorine Analyzer

Clora 2XP delivers twice the precision for total chlorine analysis in liquid hydrocarbons such as biofuels, aromatics, distillates, heavy fuels, and crude oils, as well as aqueous solutions. Compliant with ASTM D7536 and D4929 methodology, Clora 2XP is ideal for testing related to catalyst poisoning in reformers, and sites with catalytic crackers and hydrocrackers. In addition, its automatic sulfur correction is perfect for high sulfur and low chlorine applications, such as crude oil and VGO. Powered by MWDXRF, Clora 2XP does not require gasses or high temperature processes, equating to easy operation and minimal maintenance requirements.

16 32.06 Sindie +Cl Sulfur and Chlorine Analyzer

Sindie +Cl delivers exceptional reproducibility for both sulfur and chlorine analysis with one push of a button and zero hassle. Samples are measured directly, which means it can analyze even the heaviest of hydrocarbons like crude oil or coker residuals, without the hassle of boats, injectors, furnaces, or changing detectors.

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