BRINGING CLARITY AND HAZE RATINGS INTO THE MODERN WORLD – ASTM D8148 PROVIDES THE PERFECT SOLUTION

In this article we look at the benefits of ASTM D8148 using an instrument which utilizes a proprietary spectrophotometric/nephelometer optical technology consisting of a combination of a near-infrared light-emitting diode light source and photodiode detectors positioned to measure transmission and scatter across the test specimen. This approach is critical to achieve limits of detection and sensitivity across the entire 1 to 6 haze rating range without regard to the color of the fuel. This in turn enables the ability to simultaneously determine a qualitative Instrument Haze Rating (IHR) and quantitative Haze Clarity Index (HCI). This method offers significant improvements in terms of accuracy, precision and safety over existing methods and is being proposed as an alternative to the current ASTM D4176 procedure.

Figure 1, Example of instrumentation complying with D8148. the Clarity Choice hz

Since the early days of hydrocarbon-based fuels it has been important to set standards of quality specifically linked to the performance and reliability of the product for its intended application. Furthermore, to ensure compliance with these standards there was a necessity to develop and define standard tests which has largely been under the auspices of ASTM International which today operates over 12,000 standards globally.

There has been a requirement to include in fuel specifications a standard that the distillate fuels be clear and bright and visually free of undissolved water, sediment, and suspended matter which has historically been covered by method ASTM D4176-04 (1) and also that aviation fuels can be field tested for detection of free water and solid contaminants, or any other visually apparent contamination as covered by ASTM D6986-03 (2). It has long been the practice to use these methods to rate a fuel's Haze or Clarity

However, both these methods were developed before the advent of modern routine spectroscopic techniques and are based on visual inspection of the samples. D4176 procedure 2 is performed by holding a clear 1-liter jar in front of a chart as the person performing the test rates the fuel from 1-6 and D6986 is performed by observing fuel in a white porcelain bucket. These methods are highly subjective and yield non-quantitative attribute data and variations in operator experience and lighting conditions can lead to varying interpretations with conflicting results. In addition, significant quantities of fuel (≥ 1 litre) are required which leads to concerns over safety both from the risks of ignition and also exposure to fuel vapors for operators.

Furthermore, with the increasing use of synthetic and bio derived fuels and the introduction of modern engines with sophisticated high-pressure fuel injectors the measurement of haze and freedom from particulate materials is becoming an increasingly important product specification which must be measured within stringent standards. Consequently, the determination and rating of Haze and Clarity in a wide variety of petroleum and biomass-based matrices is essential throughout the fuel supply chain.

So, what is different in ASTM D8148(3)?

ASTM subcommittee D02.14 on Stability, Cleanliness and Compatibility of Liquid Fuels promptly developed and published D8148 during just a 24-month time frame with the following scope statement:- " This test method covers a spectroscopic procedure for determining the level of suspended H2O and particulate contamination (haze) in liquid middle distillate fuels including those blended with synthesized hydrocarbons or biofuels". The method generates an ordinal, whole-number, Instrument Haze Rating (IHR) from 1 to 6 and a Haze Clarity Index (HCI) from 50.0 to 100.0 which are determined on a test specimen at a temperature of 22.0 °C ± 2.0 °C. Both are derived from the above-mentioned spectroscopic measurements and an algorithm. IHR values increase depending on the amount attributed, while HCI values increase with sample Clarity and ranges from 100 HCI (very clear and bright) to 50 HCI (very cloudy and opaque). Accordingly, a fuel with an HCI value of 90 has less Haze than a fuel with an HCI value of 80. HCI can be used to evaluate Haze intensity changes to a much finer degree than could ever be achieved with visual inspection procedures.

Utilizing simple operation and world-class spectroscopic techniques, the new ASTM test method D8148 delivers the rapid, precise and reliable Haze and Clarity determination measurement capabilities needed for today's demanding petroleum-based process control and product quality assurance applications. These applications include all light/middle distillate fuels (gasoline, jet and diesel) and biofuels. These materials are produced and transported in significant quantities and in each case the absence of Haze, and product Clarity, is an important quality control requirement.

Instrumentation

Instruments which meet this ASTM method include the Clarity Choice hz (Figure 1) which is a compact and lightweight analyzer that can readily measure Haze and Clarity in petroleum products, in just 105 seconds. The instrumentation requires only a power source with no other utilities required. The apparatus features a large and responsive touch screen display that is easy to use, and sample analysis can be initiated with minimum user inputs. Sample preparation and handling are simplified with the use of optical glass dedicated cuvettes, allowing instrument use by non-laboratory trained technicians. A powerful onboard computer allows a full complement of the data handling, printing, and processing features that are needed for data transfer and

compliance with good laboratory practice requirements.

For laboratories which also require to measure sample color there is the Color Choice hz which is the only instrument in the industry that complies with D8148-17 and provides Haze Clarity Index (HCI) along with ASTM D6045 for Saybolt and ASTM color as well as ASTM D5386 for Platinum Cobalt/APHA color.

Health and Safety Benefits As already stated the conventional ASTM D4176-04 (1) and ASTM D6986-03 (2) require significant quantities of fuel (≥ 1 litre) which leads to concerns over safety both from the risks of ignition of highly flammable samples and also exposure to fuel vapors for operators. The Choice analytical instruments described here require only 10mls of sample to make a measurement and therefore bring with them significant reductions in risk and the need to store, handle and transport relatively large volumes of fuel samples when testing.

Calibration The instrument is factory-calibrated and may also be field calibrated as required depending on the specific application. The calibration plot is arranged so that quantitative HCI measurement is on the y axis with the ordinal relevant haze standard value on the x axis. The plot shown in Figure 2 reveals the non-linear nature of the D4176, 1-6 haze rating range and in particular, the circa 20 HCI unit change for the transition from Haze rating 2 to Haze rating 3.

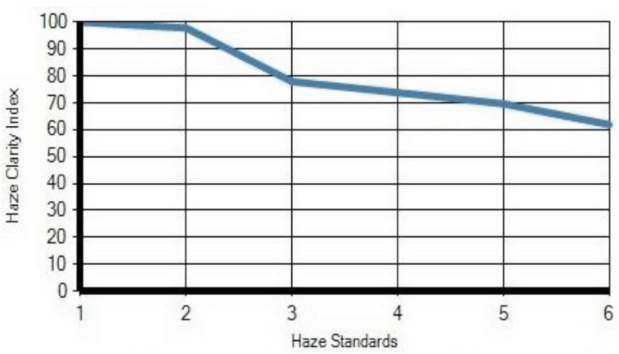


Fig. 2 Typical Haze Calibration Curve for ASTM D8148-17

Lab Equivalency Study

Two labs provided data for a repeatability study pursuant to ASTM Practice D6300 guidelines where each lab used separate instrumentation and operators. Each lab received a total of 40 samples consisting of five randomized replicates taken from 8 bulk samples that included 4 fuel grades in duplicate. The bulk samples were from multiple sources and had attributed Test Method D4176 haze levels (1 to 6). Each lab reported 5 replicate analysis for both IHR and HCI for each of the 8 fuels and the results obtained are summarized in Figure 3 for the Instrument Haze Rating and Figure 4 for the Haze Clarity Index

Since D4176 and IHR are non-quantitative, no information about the precision of IHR in the fuels tested could be estimated. However, an assessment of the within-operator consistency for the apparatus determination of IHR was determined:

- For Haze ratings repeated 5 times by the same operator within a short interval of time using the same apparatus at the same location, the probability of no disagreement amongst the 5 ratings (i.e.: unanimous ratings for all 5 IHR) is approximately 80%
- The probability of no more than 1 disagreement amongst the 5 repeats is approximately 20%.
- For the two labs, the probability that IHR values will agree with D4176 attribute ratings is approximately 90 %.

When the above IHR findings are compared to the quantitative HCI measurements the differentiating power of HCI data is illustrated. Repeatability (r) for HCI in accordance with ASTM Practice D6300 at two laboratories, with statistically significant findings as listed below:

- Lab A: r = 2.0 HCI
- Lab B: r = 3.3 HCI

Where (r) = The difference between repetitive results obtained by the same operator in a given laboratory applying the same test method with the same apparatus under constant operating conditions on identical test material within short intervals of time would in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in 20:

Case Study – Water-Induced Haze in Jet & Diesel Fuels

It is generally understood that water contamination is a primary cause of haze in fuels but to study this it is important to understand that water in fuel can be present in different forms defined as one of the following:-

Dissolved water - water that is in solution in the fuel. This water is not free water and cannot be removed by conventional means or measured by field equipment.

Suspended water - Undissolved free water that is so finely dispersed as to be invisible to the naked eye.

Entrained water - Small droplets of free water in suspension that may make fuel appear hazy

Free water. water in a fuel other than dissolved water. Free water may be in the form of droplets or haze suspended in the fuel (entrained H2O), a H2O layer at the bottom of the container holding the fuel, or both.

HCI case study on Jet Fuels: - Identical jet fuel samples were prepared in clear one-litre containers. The weight of jet fuel added to each jar was recorded and each container was measured for baseline H2O content by ASTM D6304 (4) and found to contain from 31.8 to 33.2 mg/kg H2O. All materials were then analysed by D8148 and found to have an HCI of 100 and a IHR of 1. D4176 Procedure 1 attribute was "Clear and Bright", while Procedure 2 attribute was "1". All testing for this study was conducted in the lighting range of 750-775 Lumens One jar, labelled Jet 1, was designated as a control. Another jar was selected and was labelled Jet 2. The amount of H2O needed to add 25 mg/kg to Jet 2 was calculated and then added with a certified micro-syringe and the contents were mixed vigorously for 1 minute with a high-shear blender.

Actual H2O present was calculated and determined by D6304 and the sample was then analysed by D8148 and D4176. This procedure was repeated with increasing quantities of water and the results obtained are documented in Table 2.

HCI study on Diesel Fuels:- The H2O -Induced Haze experiment for jet fuel was repeated for pure diesel (B0) and the results are listed in Table 3. As in the previous jet fuel experiment, limited H2O solubility caused D6304 to under report showing an average 80 % recovery for diesel.

One result of note was that the 250 mg/kg of H2O produced a strong D4176 Haze rating of 3, well below the current D975 maximum H2O specification for many pipelines of 500 mg/kg.

Table 2 – Data Summary: - H2O Induced Haze in Jet Fuel

Water Added (mg)	Total Water (mg)	Water by KF (mg)	% Recovery by KF	D4186	HCI
0	33	33	100	1	100.00
25	58	48	85	1	100.00
50	83	47	57	1	100.00
75	108	55	51	1	98.68
100	133	58	44	2	96.20
125	157	65	41	2	94.54
150	183	78	43	2	95.06
175	208	79	38	2	91.58
200	233	87	37	2	89.74
225	258	140	49	3	80.61

Table 3- Data Summary - H2O Induced Haze in Diesel Fuel

Water Added (mg)	Total Water (mg)	Water by KF (mg)	% Recovery by KF	D4186	HCI
0	50	50	100	1	100.00
50	100	80	80	1	99.36
75	125	97	78	2	92.82
100	150	125	83	2	88.95
150	200	160	80	2	81.80
200	250	191	75	3/4	72.76

Case Study Results Summary

1. Testing confirms that KF D6304 might do a reasonable job of measuring water while it remains completely soluble, these results clearly show significant under reporting of actual water content once it is in a Free, Suspended or Emulsion state
2. In a subjective way D4176 (procedure 2) can track H2O induced Haze but entrained H2O complicates the issue.
3. The transition from Clear and Bright (D4176 Haze rating 1) to all lines on the D4176 card turning a light grey (D4176 Haze rating 2), is subjective primarily due to a combination of lighting conditions, operator skill and experience and potential bias.
4. The ability to describe/report quantitatively an increasing D4176 Haze Rating 2 (lines on the D4176 card become increasingly lighter) to the point where the bottom line on the card is obscured (D4176 haze rating 3) is extremely difficult in practice.
5. D8148 is well suited for Diesel & Jet Fuel testing and would provide more precise objective determinations of a fuels Haziness or Clarity.
6. While HCI and IHR is not a direct measure of water, the results track extremely well to the actual addition of water and operators should have confidence that any HCI reading in Jet above 97.5 or an IHR reading of "1" indicates no issues with water or other causes of haze

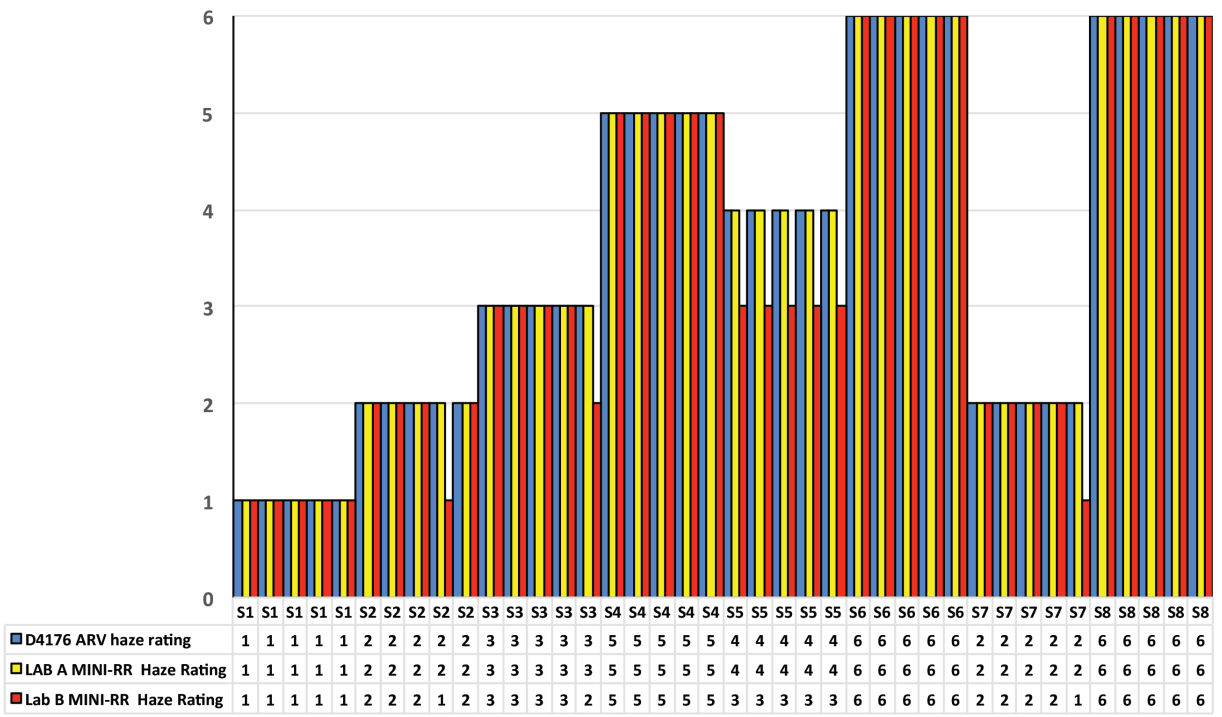
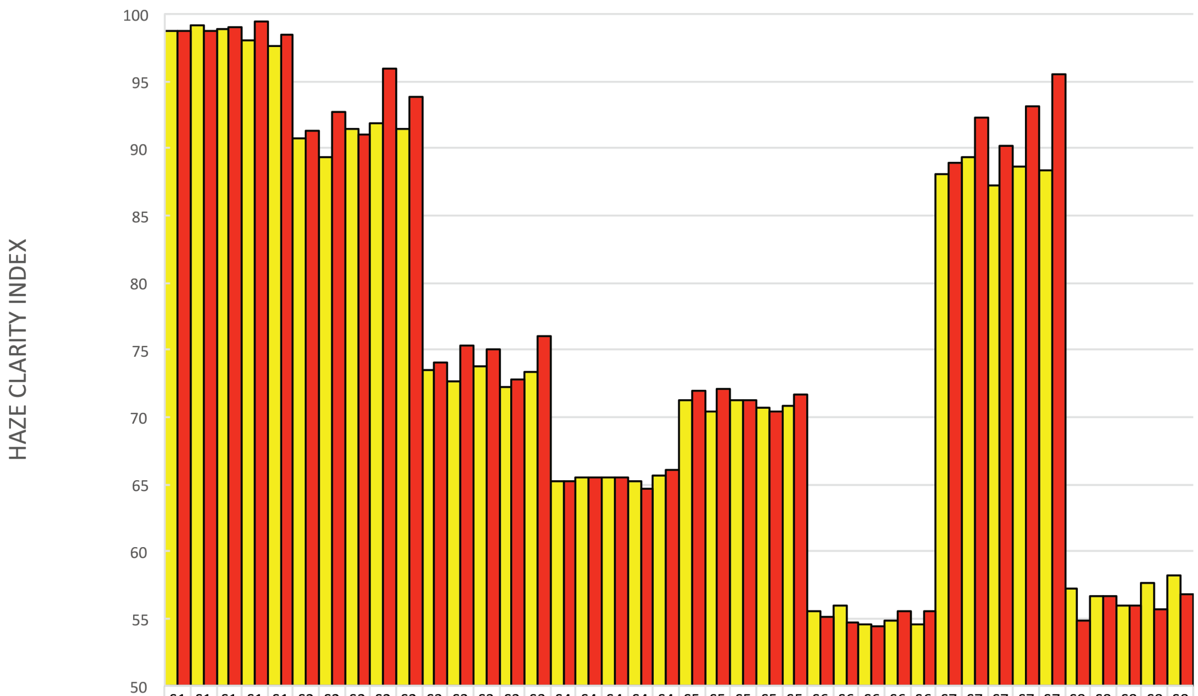


Figure 3 Results Summary from the Lab Equivalency Study for the Instrument Haze Rating, D4176 rating in blue, , Lab A results in Yellow, Lab B in Red



	S1	S1	S1	S1	S1	S2	S2	S2	S2	S2	S3	S3	S3	S3	S3	S4	S4	S4	S4	S4
Lab A MINI-RR HCI	99	99	99	98	98	91	89	92	92	91	74	73	74	72	73	65	66	66	65	66
Lab B MINI-RR HCI	99	99	99	100	98	91	93	91	96	94	74	75	75	73	76	65	66	66	65	66

	S5	S5	S5	S5	S5	S6	S6	S6	S6	S6	S7	S7	S7	S7	S7	S8	S8	S8	S8	S8
Lab A MINI-RR HCI	71	70	71	71	71	56	56	55	55	55	88	89	87	89	88	57	57	56	58	58
Lab B MINI-RR HCI	72	72	71	70	72	55	55	54	56	56	89	92	90	93	96	55	57	56	56	57

Figure 4 Results Summary from the Lab Equivalency Study for Haze Clarity Index, Lab A results in Yellow, Lab B in Red

Closing Comments

The potential for HCI to provide statistically significant Haze rating results opens an opportunity for much improved documentation and communication regarding important fuel appearance specifications and the introduction of D8148 is an important step in this journey. Furthermore, the desire to move away from the highly subjective visual methods has prompted the ASTM Diesel Fuel Sub Committee to add D8148 as an alternative method in the workmanship section.

Robust highly specified instrumentation is available which provides a high level of precision and accuracy for the measurement and tracking of both Instrument Haze Rating (IHR) from 1 to 6 and a Haze Clarity Index (HCI) value from 50.0 to 100.0 as per D8148. The instrumentation also offers significant benefits in terms of health and safety, and sample handling and storage, over conventional methods.

In terms of future initiatives, ASTM D02.J – Aviation Fuels Committee have assigned a Work Group (work item number is WK69723) with the goal of producing a ballot which would add D8148 to D1655 as a possible addition to the non-mandatory appendix on workmanship and ASTM D02.E0 - Burner, Diesel, Non- Aviation Gas Turbine, and Marine Fuels is exploring the possibility that HCI values used in D8148 might improve on the current visual methods.

References

(1) ASTM D4176-04(2014), Standard Test Method for Free Water and Particulate Contamination in Distillate Fuels (Visual Inspection Procedures), ASTM International, West Conshohocken, PA, 2014, www.astm.org

(2) ASTM D6986-03(2016), Standard Test Method for Free Water, Particulate and Other Contamination in Aviation Fuels (Visual Inspection Procedures), ASTM International, West Conshohocken, PA, 2016, www.astm.org

(3) ASTM D8148-17, Standard Test Method for Spectroscopic Determination of Haze in Fuels, ASTM International, West Conshohocken, PA, 2017, www.astm.org

(4) ASTM D6304-16e1, Standard Test Method for Determination of Water in Petroleum Products, Lubricating Oils, and Additives by Coulometric Karl Fischer Titration, ASTM International, West Conshohocken, PA, 2016, www.astm.org

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