ASTM D8193 vs. ASTM D7678

A comparison between two IR based oil-in-water test methods

Introduction

The measurement of oil-in-water (OIW) is a major analytical task in modern oil production throughout the whole distribution chain. Typical applications include upstream oil recovery monitoring and the measurement of reinjection and discharge water, as well as environmental monitoring of water and soil in general.

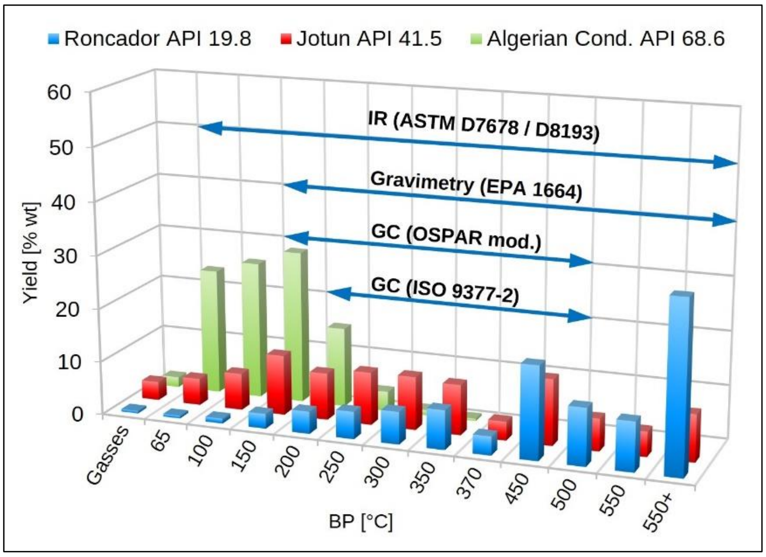

Figure 1: Crude oil mass distribution relative to OIW methods.

The most commonly used OIW test methods are gas chromatography (ISO 9377-2, OSPAR mod.), gravimetric methods (EPA 1664, ASTM D4281) and infrared spectroscopy based methods, such as ASTM D7066, ASTM D7678 and ASTM D8193 – the latest IR method developed by eralytics in 2019. Most OIW test methods utilize a liquid / liquid extraction step as part of the sample preparation, either using n-Hexane or Cyclohexane. Various methods previously using HCFCs or other halogenated solvents are phased out due to their environmental impact of the extraction solvents.

The measurement results for OIW samples can vary as they cover different ranges in the chemical (molecular mass) distribution of crude oils, as visible in figure 1. Especially for crude oils featuring a significant proportion of volatile components in the < C10-fraction, an infrared test method gives a much more representative OIW result compared to a gravimetric or gas chromatography method.

Therefore, “Oil-in-Water” must be considered as a <u>method defined parameter</u>. Even for IR based oil in water test methods – such as ASTM D7678 or D8193 – results can vary in dependance of the chemical composition of the sample.

The aim of this study is:

- To compare the accuracy of ASTM D7678 and D8193 by determining both the TOG (*total oil and grease*) and TPH content (*total petroleum hydrocarbons*; polar compounds are removed by a Florisil cartridge) of several different crude oils and petroleum based products.
- To investigate whether a correlation formula between ASTM D7678 and D8193 can be established.

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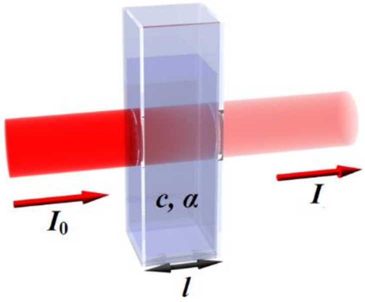
Measuring Principle

Practically all hydrocarbons contain a "CH_3" functional group which absorbs IR light at a wavelength of approximately 1375 cm^{-1}. Both test methods – ASTM D7678 and D8193 – determine the OIW concentration by measuring the IR absorption intensity of hydrocarbons at this wavelength.

Displayed in scheme 1, the initial intensity I_0 of the IR beam is weakened due to absorption by the sample, the resulting intensity I is then quantified at the detector and correlates to the OIW concentration.



Scheme 1: IR measuring principle

The aqueous sample cannot be measured directly, it is first subdued to a sample preparation. An organic solvent is used to extract and therefore concentrate the dissolved oil and/or dispersed oil droplets. This sample preparation is depicted in scheme 2 and consists of the following steps:

Scheme 2: Liquid / liquid extraction procedure for ASTM D7678 and D8193.

(1) The water sample is collected at a sampling point, typically 900 mL.

(2) The solvent (50 mL) is added to the sample bottle.

(3) The bottle is vigorously shaken.

(4) After waiting for a couple of minutes phase separation has set in.

(5) Distilled water is added to lift up the solvent phase for a convenient extraction by syringe.

(6) An aliquot is extracted and used for the measurement.

Cyclohexane serves as the extraction solvent for both methods due to:

- It is no HCFC or other halogenated solvent and therefore ecologically harmless, inexpensive and easily obtainable.
- Its excellent solubility of hydrocarbons (oil, grease, fat, etc.)
- It does not contain a CH_3-groups and can therefore be used for this kind of measurement technique (otherwise it would interfere with the sample).

Nonetheless, Cyclohexane has a low but noticeable IR absorption at 1375 cm^{-1} and needs to be compensated by a *background* measurement. This background absorption level is subtracted from the sample measurement, which is then converted to a OIW concentration.

Calibration

Defined by the standard test method, the reference analytes used for the calibration of the analyzers are tetradecane for ASTM D7678, and a mixture of n-Octane / *iso*-Octane for ASTM D8193, respectively. These reference materials have peak maximums at 1375 cm^{-1} very similar to other hydrocarbons and therefore can be used to calculate the concentration, utilizing the absorption intensity obtained by the measurement.

For this calculation the *enrichment factor* needs to be considered. It resembles the increased concentration from the OIW (oil-in-water) to the OIS (oil-in-solvent) phase due to the extraction step. The enrichment factor is determined by the actual ratio of the aqueous and solvent phase volumes, typically 18 for 900 mL water and 50 mL Cyclohexane.

Even though the two test methods share many similarities, the major differences are the reference materials used for the calibration of the analyzer, and the IR light source type, visualized in figure 2:

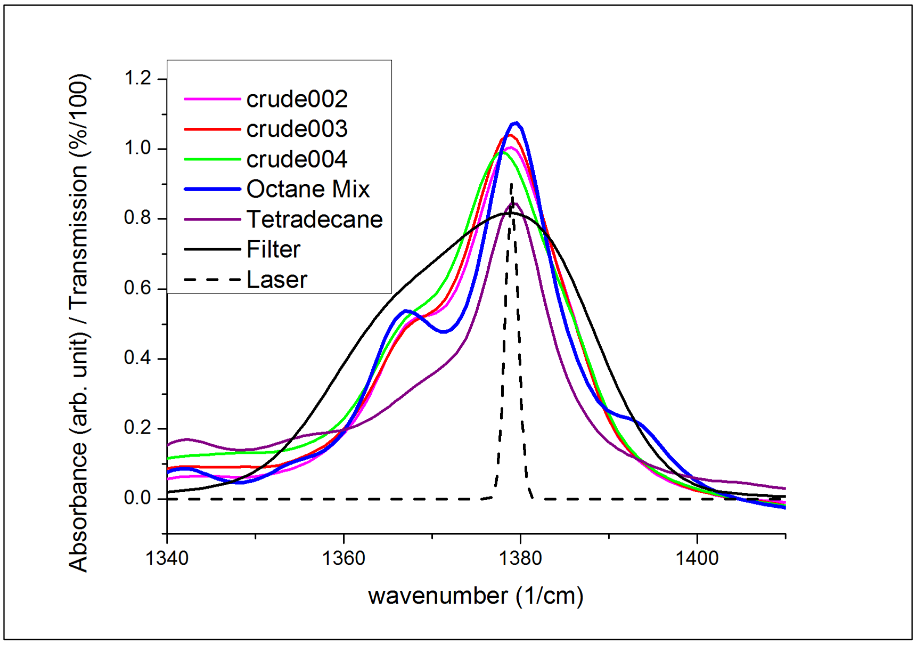


Figure 2: IR absorption peaks (CH3-deformation) of various materials, compared to the optical filter (D8193) and the quantum cascade laser (D7678).

While D7678 uses a quantum cascade laser with a very narrow bandwidth. Tetradecane has been chosen as the reference materials for ASTM D7678 due to its distinct and rather narrow peak, similar to the laser.

In contrast to that ASTM D8193 features a conventional IR source and an optical IR filter at the observed wavelength. An octane mixture, consisting of 90 mass% n-Octane and 10 mass% iso-Octane is used not only to resemble the broader observed bandwidth of the optical filter on the detector, but also to mimic the peak shape of real samples such as crude oil.

As a consequence these two OIW test methods – ASTM D7678 and D8193 – work very similar, but nevertheless may not produce identical results.

Measurements

To determine the accuracy and to establish a correlation between ASTM D7678 and D8193, 12 crude oil samples and 5 petroleum based products were investigated, amongst those:

- "BAM" (BAM-K010) is a 1:1 mixture of diesel fuel and a base lube oil, provided by the German *"Bundesanstalt für Materialforschung und -prüfung"*. It is widely used as a certified reference material for oil-in-water and oil-in-soil contamination measurements.
- "Ondina 919" and "Viscogen KL9" are commercially available lube oils.

In contrast to the usual sample preparation as described before, the extraction step was omitted to eliminate any possible impact on the measurements. Instead, all 17 samples were directly prepared in 250 mL volumetric flasks with nominal concentrations of 1800 mg/L OIS, or 100 mg/L OIW, respectively, applying the typical enrichment factor of 18.

TOG and TPH were then measured for all samples according to ASTM D7678 and D8193. The results – normalized to 100 mg/L OIW – are shown in detailly in table 1, figure 3 and 4:

Sample	ASTM D7678 TOG [mg/L]	ASTM D7678 TPH [mg/L]	ASTM D7678 TPH [%]	ASTM D8193 TOG [mg/L]	ASTM D8193 TPH [mg/L]	ASTM D8193 TPH [%]
PL (47.8°)	138.7	133.1	96.0	108.1	105.6	97.7
PL (46.3°)	137.3	131.2	95.6	107.7	102.1	94.8
OMV (43.1°)	138.2	128.1	92.7	107.1	98.9	92.4
PL (41.8°)	129.0	119.0	92.3	100.8	92.7	92.0
PL (37.9°)	125.5	106.2	84.6	101.4	85.7	84.5
OMV (37.1°)	121.0	103.6	85.6	95.1	79.8	83.9
PL (35.5°)	124.9	105.0	84.1	101.8	82.5	81.0
OMV (30.2°)	132.6	103.5	78.0	114.0	85.7	75.2
AP (26.2°)	120.3	97.7	81.2	96.6	76.1	78.7
OMV (26.4°)	128.5	92.7	72.1	109.2	77.5	71.0
RAG (26°)	119.1	98.8	83.0	95.7	80.1	83.7
OMV (21.9°)	120.6	73.1	60.6	101.1	56.6	56.0
JET A1	145.8	141.6	97.1	108.8	108.1	99.4
Petroleum	137.7	135.5	98.4	102.6	102.4	99.8
BAM	135.1	131.5	97.3	98.5	95.0	96.5
Ondina 919	144.5	143.0	99.0	103.7	103.6	100.0
Viscogen KL 9	143.2	125.3	87.5	113.8	96.2	84.5
Average	**131.9 (± 8.7)**	**-**	**-**	**103.9 (± 5.7)**	**-**	**-**

Table 1: TOG results and TPH content for 12 crude oils and 5 finished petroleum based products. The API density of the individual crude oils is shown in brackets.

Discussion – Accuracy

Visible in the table 1 above, the TOG and TPH results measured according to ASTM D7678 are systematically higher throughout all samples compared to ASTM D8193. The normalized TOG concentration of 100 mg/L is marked with a dashed green line in figure 3.

The average TOG recovery of ASTM D7678 (131.9 mg/L) is significantly higher than the values of ASTM D8193 (103.9 mg/L). This is even more obvious when plotting and comparing the two methods in figure 3.

Independent from the sample type ASTM D7678 clearly shows an average accuracy bias of 32%, in extreme cases (Jet A1) this can be as high as 45%. In contrast to that, the TOG results obtained according to ASTM D8193 have a negligibly small average bias of 3.9%, the highest value reaching 14%:

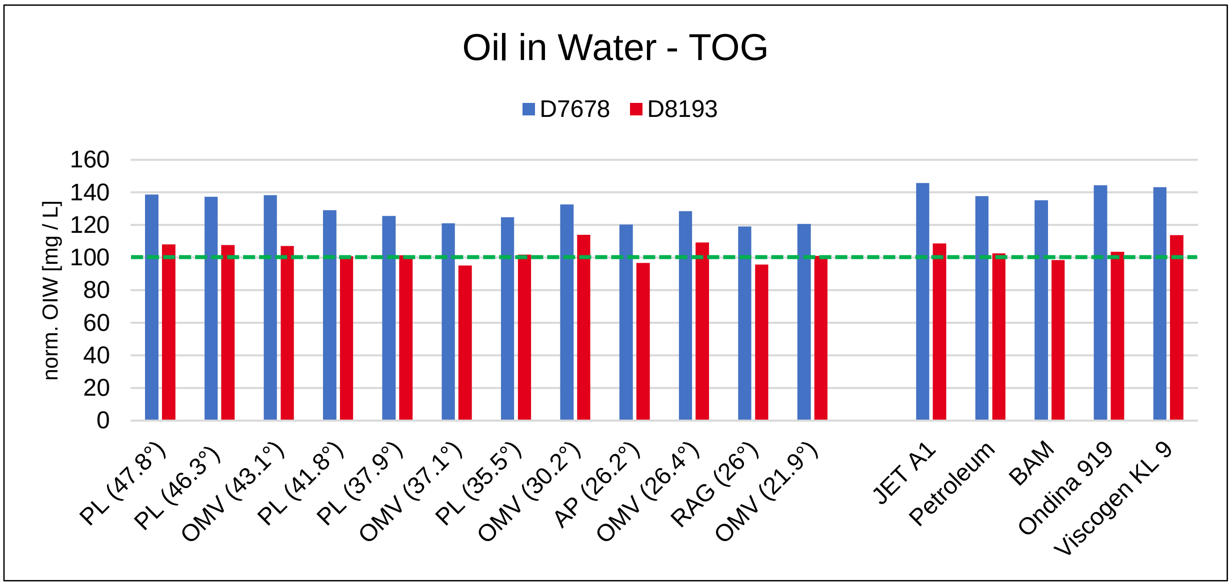


Figure 3: TOG results of ASTM D7678 (blue) and D8193 (red). The normalized concentration of 100 mg/L OIW is marked with a green line.

The TPH results do show a similar behavior for ASTM D7678 and D8193, though an average bias in terms of accuracy is not applicable for different sample types with different chemical compositions. The relative TPH content obtained by the two test methods remains practically identical, no systematic bias can be observed:

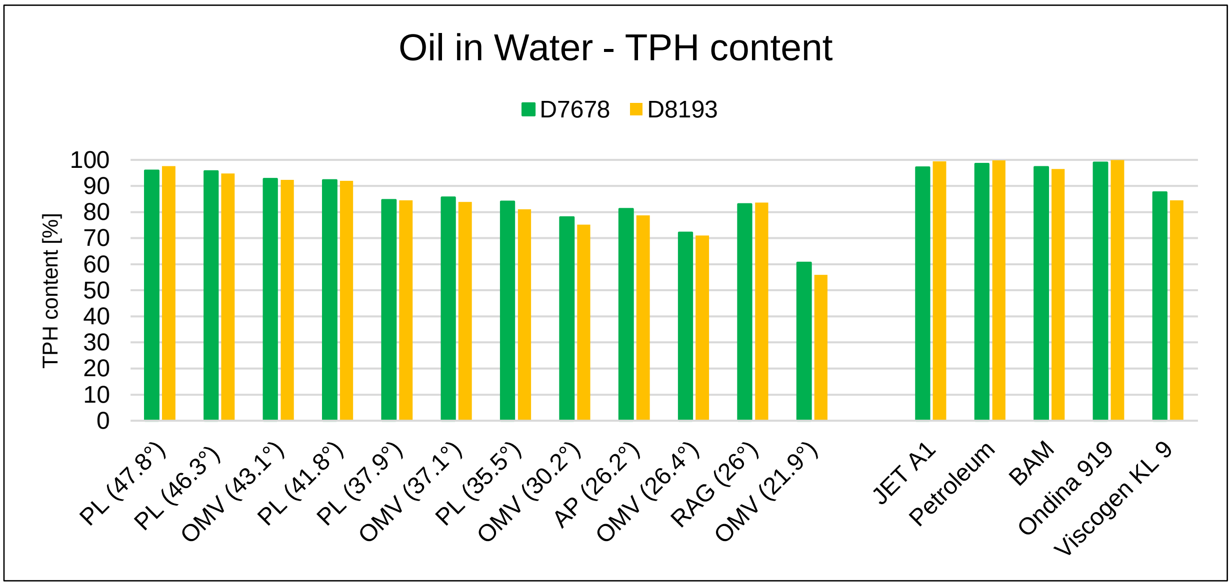


Figure 4: TPH content of TOG in [%]

Discussion – Correlation

Based on the obtained data a general trend can be observed: the TOG results of ASTM D7678 exhibit an average bias (higher) of 126.9% relative to ASTM D8193. For typical oil-in-water applications in the petroleum industry an approximate correlation formula can be estimated:

$$OIW_{(D7678)} = OIW_{(D8193)} \times 1.269$$

It has to be noted, though, that this correlation formula describes the trend between the two methods when applying the default calibrations with the limitation of an observed OIW concentration level at 100 mg/L. To establish a general correlation formula, additional concentration levels have to be measured.

Due to the fact that oil-in-water is a method defined parameter, the relative bias between ASTM D7678 and D8193 can be minimized by creating customized calibrations, individually for each sample (type).

Conclusions

- ASTM D8193 offers a significantly higher TOG accuracy compared to ASTM D7678 for all measured samples of the petroleum industry.
- The accuracy bias of ASTM D7678 is as high as 45% with an average value of 32%, whereas for ASTM D8193 an average bias of only 3.9% to max. 14% was observed.
- The relative bias for ASTM D7678 compared to D8193 was found to be +27% for the measured samples
- Correlation ASTM D7678 vs. D8193: at 100 mg/L OIW a factor of 1.269 was determined for oil-in-water applications in the petroleum industry.

The general pros and cons of the test methods can be considered as listed in table 2 below:

ASTM D7678	**ASTM D8193**
✓ Limit of detection = 0.1 mg/L OIW *	✓ Highest accuracy of all OIW methods
X Average accuracy bias for TOG of 32%	✓ Highly rugged spectrometer design
X Expensive quantum cascade laser technology	✓ Low cost of ownership
X Serviceability difficult due to sensitive equipment	X Limit of detection = 0.5 mg/L OIW **

Table 2: Comparison of ASTM D7678 and D8193 analyzers.
*: determined without extraction (D7678)
** : determined including extraction (D8193)

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