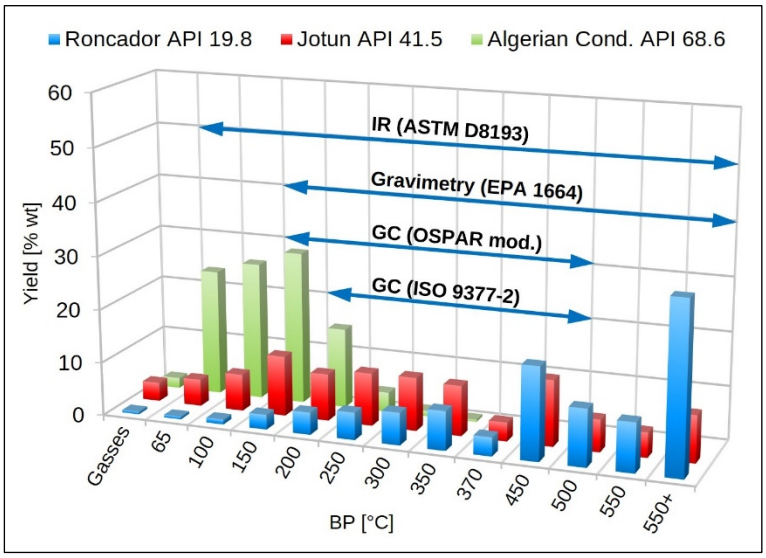
ASTM D8193 Oil-in-Water testing

Accuracy & Correlation to EPA 1664 – A case study

Background

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.



Graph 1: Crude oil mass distribution relative to OIW test 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 D3921, 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 graph 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.

As a consequence “Oil-in-Water” must be considered as a method dependent parameter.

The aim of this study is:

- To compare the accuracy of the infrared test method ASTM D8193 applied by eralytics on era**check X** to the gravimetric test method EPA 1664.
- To investigate how to define a possible correlation between these two methods for two typical crude oil samples.

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Measurements

In total 24 spiked water samples with a volume of 1000 mL each at three different target concentrations of two different crude oils were prepared and measured according to both methods ASTM D8193 and EPA 1664 (3 x 2 x 2 x 2 = 24):

- 3 nominal concentrations (20 mg/L, 50 mg/L & 100 mg/L)
- 2 methods (ASTM D8193 & EPA 1664)
- 2 crude oils (“API 27.3” & “API 35.8”, source: Gulf of Mexico)
- 2x prepared for each nominal concentration

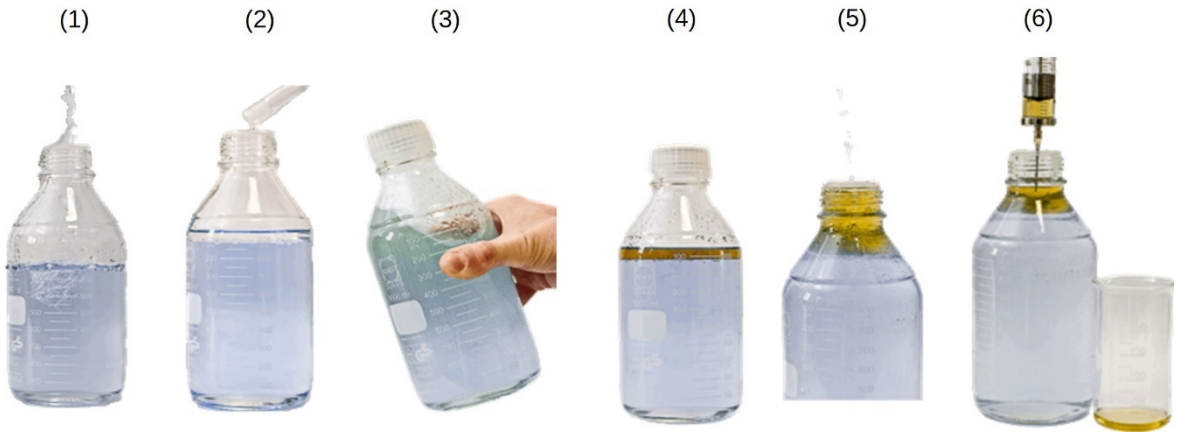
EPA 1664

For EPA 1664 the water samples were quantitatively extracted with 100 mL n-Hexane in total. The combined organic phases were dried over sodium sulfate and the solvent was then removed by evaporation at 70°C.

ASTM D8193

A measurement according to ASTM D8193 consist of a background determination (fresh Cyclohexane) and the actual sample measurement of the extracted Cyclohexane. The water samples were extracted with 100 mL Cyclohexane of which an aliquot of appr. 5 mL was then used for the sample measurement. Before as well as after the sample measurements the era**check X** OIW analyzer was verified with 2 blank Cyclohexane measurements (results: < 1 mg/L OIW).

The extraction procedure with Cyclohexane for ASTM D8193 is depicted in scheme 1:



Scheme 1: Liquid / liquid extraction procedure for ASTM D8193

(1) The water sample is collected at a sampling point; for the study distilled water was spiked with crude oil.

(2) Cyclohexane is added to the sample bottle.

(3) The bottle is vigorously shaken.

(4) 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 of 5 mL is extracted and used for the measurement.

Discussion – Accuracy

The OIW results are shown in the tables and graphs below. The measured values were normalized referring to the nominal concentrations of 20 mg/L, 50 mg/L and 100 mg/L (tables 1 & 2), respectively, and then displayed together with the nominal concentrations for comparison in the graphs 2-5. The columns in the tables contain the following data:

"Nominal": Nominal concentration (20, 50 or 100 mg/L)

"Actual": Weight of the crude oil quantum used for spiking the samples

"Measured": Measurement results of the corresponding test method

"Normalized": Results normalized referring to the nominal concentrations

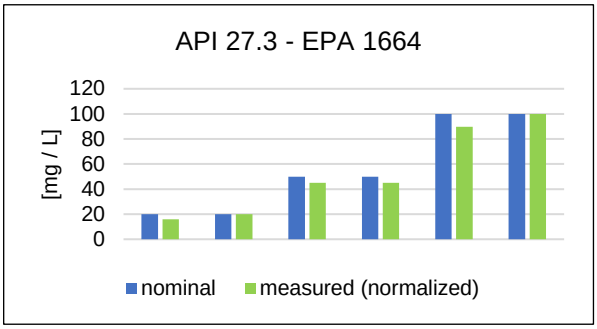
The corresponding individual measurements marked in the tables feature the highest bias of each measurement series. These were considered to be outliers and were therefore ignored for the bias estimation.

Sample "API 27.3"

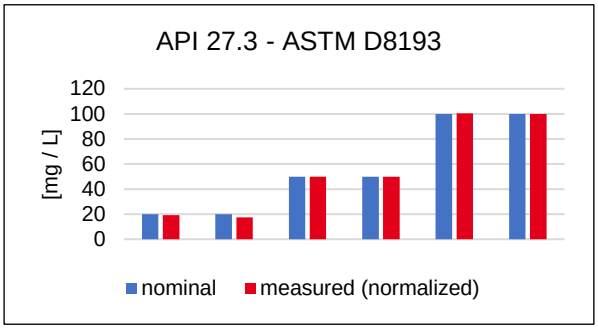
For crude oil "API 27.3" the recovery was found to be within 10% for the gravimetric method EPA 1664. A small bias can be observed due to loss of volatiles by evaporation, but it remains relatively small. The IR method ASTM D8193 could successfully measure these samples with a maximum bias of 4% by using the standard calibration.

API 27.3 [mg / L]	EPA 1664 [mg / L]			ASTM D8193 [mg / L]		
Nominal	Actual	Measured	Normalized	Actual	Measured	Normalized
20	20	16	16.0	19	18.3	19.3
20	21	21	20.0	20	17.5	17.5
50	50	45	45.0	48	47.8	49.8
50	51	46	45.1	50	49.9	49.9
100	98	88	89.8	95	95.5	100.5
100	105	105	100.0	99	98.8	99.8

Table 1: OIW test results of crude oil "API 27.3", outliers are marked.



Graph 2: EPA 1664 OIW test results for sample "API 27.3"



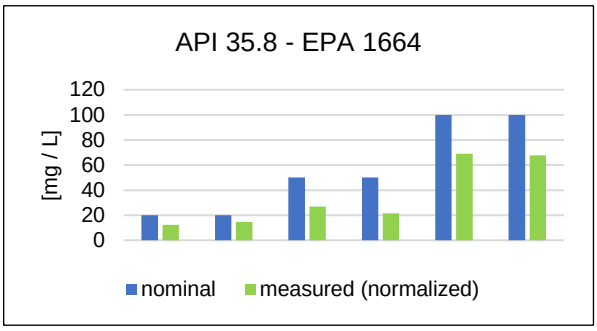
Graph 3: ASTM D8193 OIW test results for sample "API 27.3"

Sample "API 35.8"

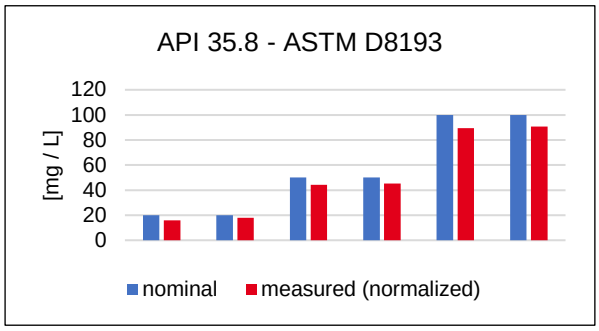
For the lighter crude oil "API 35.8" the recovery dropped to < 50% for EPA 1664. This indicates a significant amount of volatiles in this crude oil. For ASTM D8193 a maximum bias of 20% could be observed.

API 35.8 [mg / L]	EPA 1664 [mg / L]			ASTM D8193 [mg / L]		
Nominal	Actual	Measured	Normalized	Actual	Measured	Normalized
20	21	13	12.4	19	15.1	15.9
20	22	16	14.5	19	17.0	17.9
50	41	22	26.8	47	41.5	44.1
50	44	19	21.6	55	49.8	45.3
100	97	67	69.1	96	85.9	89.5
100	99	67	67.7	98	88.9	90.7

Table 2: OIW test results of crude oil “API 35.8”, outliers are marked.



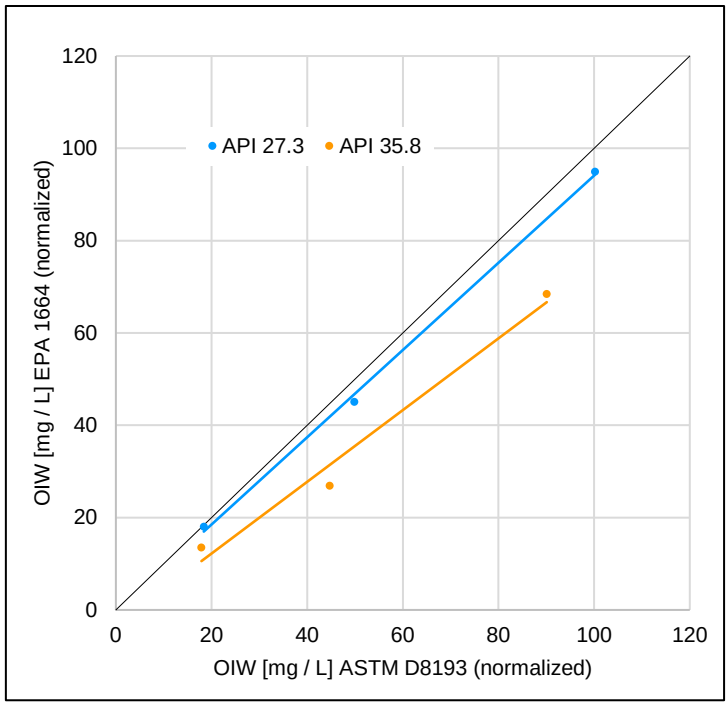
Graph 4: EPA 1664 OIW test results for sample “API 35.8”



Graph 5: ASTM D8193 OIW test results for sample “API 35.8”

Discussion – Correlation

The normalized result values for both sample types are plotted in graph 6. The arithmetic mean values of each nominal concentration level were used to establish the correlation formulas, and the outliers were ignored. The black line resembles an ideal 1:1 correlation:



Graph 6: Correlation of ASTM D8193 to EPA 1664

Sample "API 27.3"

For crude oil "API 27.3" a correlation close to 1:1 between ASTM D8193 and EPA 1664 can be observed. Given the repeatability of r = 0.3 mg /L for the test method ASTM D8193 in general and 8.7% for EPA 1664 the minor offset -0.3926 can be ignored and this formula can be approximated to:

API 27.3: $OIW_{EPA\ 1664} \approx OIW_{ASTM\ D8193} \times 0.9450$

Sample "API 35.8"

As for the lighter crude oil "API 35.8" the loss of volatiles shifts the gain of the correlation formula significantly, and additionally an offset of -3.3201 has been determined:

API 35.8: $OIW_{EPA\ 1664} = OIW_{ASTM\ D8193} \times 0.7769 - 3.3201$

Even though the recovery for sample "API 35.8" is distinctively low for the gravimetric method EPA 1664, the results are consistent throughout the investigated concentration range. This allows for a correlation between the IR method ASTM D8193 and the gravimetric method EPA 1664. Clearly visible in graph 6 and the calculated correlation formulas above, a general correlation formula cannot be assumed for all sample types, but it can be empirically determined.

Conclusions

- ASTM D8193 exhibits a superior accuracy compared to EPA 1664 for both investigated crude oil samples "API 27.3" and "API 35.8".
- The OIW results according to ASTM D8193 remain well within +/- 20% accuracy by using the standard calibration. To achieve an improved accuracy on era**check X** a customized, crude oil specific calibration can be applied.
- Heavier crude oils (API 27.3 in this study) will give similar OIW results for gravimetric (EPA 1664) and IR methods (ASTM D8193) with a high recovery rate close to 100%.
- Especially for lighter crudes (API 35.8) the recovery rate significantly decreases (up to 100% bias) for EPA 1664 while only a minor bias is found for ASTM D8193.
- Correlating ASTM D8193 to EPA 1664 is possible, and the correlation formula can easily be determined for all kinds of crude oils.