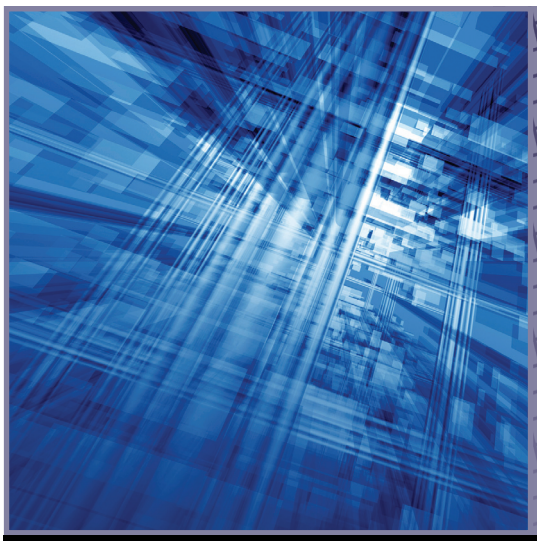

ASTM Standard D7678-11 Brings Back CFC-free IR Measurement for Oil-in-water

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The new standard method ASTM D7678 published by ASTM International enables an alternative and accurate way of measuring total petroleum hydrocarbons in water. It uses environmentally-friendly cycloalkanes for the extraction rather than CFCs. This method and the availability of new infrared lasers allow the transition from old CFC-based methods while maintaining the advantages of infrared spectroscopy. By the invention of mid-infrared quantum cascade lasers a new form of liquid spectroscopy became possible. The Austrian company QuantaRed Technologies GmbH (www.quantared.com) develops the quantum cascade laser based core technology within the portable and field-proven ERACHECK instrument of Eralytics (www.eralytics.com). ERACHECK enables fast, easy and reliable measurements in harsh environments. Moreover this instrument is complying with the new standard method ASTM D7678.

New infrared technology research

Intensive research work through the last years led to the implementation of mid-infrared quantum cascade lasers (QCL) in the chemical analysis of gases and liquids. The new technology benefits from the distinct wavelength of the laser source and the increased spectral power density, which inherently leads to enhanced detection capabilities. ERACHECK oil-in-water analyser was the first device to show these unique capabilities. The improvements in the development of better QCLs and chemical analysis methods led to a new standard method for the infrared spectroscopy based oil in water measurement.

Figure 1: ERACHECK measures oil-in-water down to a limit of detection of 0.25 mg/l according to ASTM D7678

A new standard for measuring oil-in-water

Recently, ASTM International has published method D7678-11. It is the first infrared standard method, which does not rely on CFC solvents for precise quantification of hydrocarbons in water.

Since 1980 the infrared based method ASTM D3921 was the standard method for measuring total petroleum hydrocarbon (TPH) concentrations in water. This method requires the use of the extraction solvent 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113, Freon®). In 1989 the phasing out of ozone-depleting substances such as CFCs and HCFCs was decided by the Montreal Protocol. The infrared test methods continuously started to become replaced by gravimetry (e.g. EPA 1664A) or gas chromatography (e.g. ISO 9377-2). However, these other methods require more laborious and careful operation in a laboratory environment. The infrared test method ASTM D3921 still found use in spectroscopic applications at many industrial sites and remote places. Its unique advantages like accuracy, short measurement time and ease of use maintained its role as an important test method. In 2001 the related Freon-based standard method DIN 38409-H18 was withdrawn. Finally in 2012 the ASTM 3921 standard now comes into discussion for withdrawal, marking the end of a long history of using CFCs for infrared spectroscopy.

The alternative is standard method D7678-11, which is a test method for the determination of total petroleum hydrocarbons (TPH) in water and waste water. It uses environmentally-friendly cycloalkanes (cyclohexane or cyclopentane) for the extraction rather than CFCs. The sample is then analysed by infrared spectroscopy in the spectral range from 1370 to 1380 cm^{-1}. The method was shown to be applicable for TPH concentrations down to 0.5 mg/L and up to 1000 mg/L. On the lower side of this range laser-based infrared absorption spectroscopy is the key to measure sub-ppm hydrocarbon concentrations in the hydrocarbon extraction solvent.

Method	**ERACHECK ASTM D7678**	ASTM D 3921 EPA 413.2 EPA 418.1 DIN 38 409	ASTM D 7066	EPA 1664	OSPAR 2005-15 ISO 9377-2
Technology	Laser-based IR with cyclohexane	Conventional IR with CFC/CHC	Conventional IR with S-316	Gravimetry with hexane	Gas chromatography
Solvent **free of handicaps** (e.g. CFC, ban by Montreal protocol, carcinogen, critical availability, etc.)	✓			✓	✓
Portable instrumentation, push button simplicity, result **on-site** within 10 min.	✓	✓	✓		
Reproducible measurements **below 2ppm** (high precision and sample homogeneity)	✓	✓	✓		✓
Full coverage of oil compounds (e.g. light-end, long-chain; free, dispersed, dissolved)	✓	✓	✓		
Solvent **price** < 25 $ per liter	✓	✓		✓	✓

Table 1: Overview of test methods for the oil-in-water detection.

In comparison to alternative methods for oil-in-water detection, ASTM D7678 offers significant benefits. The most relevant methods used worldwide are listed in Table 1.

Further methods for oil-in-water analysis rely on attenuated total reflection (ATR), fluorescence and solid phase extraction by means of a membrane. None of these techniques are able to provide accurate and reproducible results for total petroleum hydrocarbons (TPH) concentrations in the low ppm range. The values are jeopardised by slight changes in sample preparation or sample composition. This is crucial whenever oils from several wells with varying oil compositions have to be monitored.

D7678 and its ultimate tool

ERACHECK by Eralytics fully and exclusively complies with method ASTM D7678-11. Based on quantum cascade laser technology, it is a portable and rugged oil-in-water analyser, which brings back the benefits of the infrared detection principle. ERACHECK provides fast and reliable on-site results in the range from 0 to 2000 mg/L. Continuous development of ERACHECK enables the availability of state-of-the-art technology with detection capabilities down to a lower limit of detection of around 0.25 mg/L. The comparison to the CFC based method DIN 38409 (evaluated by OMV AG) shows good accordance with the measurement results obtained with ERACHECK. Figure 2 shows the record of different measurements obtained by the two competing infrared

methods. Further a comparison to the GC based method ISO 9377-2 by the Norwegian oil company Statoil ASA confirmed the good correlation between the methods.

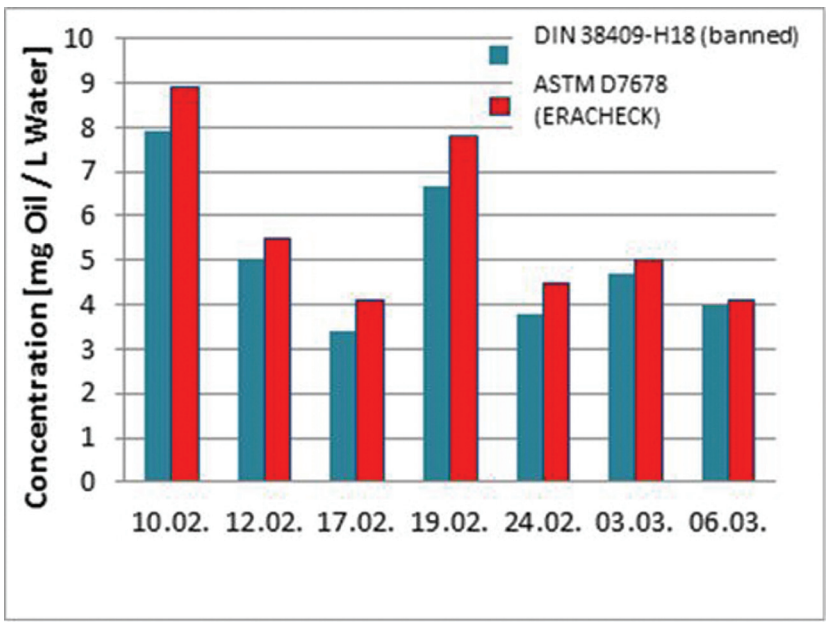

Figure 2: Method comparison using sewage water after purification (OMV flood facilities, Austria).

ERACHECK is designed for use in the petrochemical industry to evaluate and address water treatment issues, which results in significant operational and capital cost savings and relevant improvements in terms of process flow and regulatory compliance. Examples of considerable customer benefits include optimisation of process chemical usage, reduction of the reinjection pressure and in-time corrective action for scaling and corrosion.

Figure 3: ERACHECK – a portable and rugged oil-in-water analyzer

The reliable and easy-to-use ERACHECK method helps customers to establish benchmark process control in various fields of application. An overview is given in Table II.

upstream oil recovery	downstream process water monitoring
step-by-step optimisation of the water separation process (onshore/offshore)	analysis of oil contaminants
efficiency enhancement of process chemicals (e.g. emulsifier/demulsifier)	water reuse testing
evaluation of equipment (filters, hydrocyclones, flotation, etc.)	
testing of novel separation techniques	
reinjection water control (injectivity analysis)	

Table II: ERACHECK fields of application

Easy Clean-Up

Depending on the method applied, clean-up procedures have to be performed after extraction and before the measurement due to polar substances, which are often referred to as "grease". This time-consuming sample preparation step involves the preparation and cleaning of equipment (e.g. columns, separating funnels, etc.) and might lack of reproducibility.

To circumvent these difficulties a simple, automated cleanup procedure has been developed by QuantaRed Technologies for the use with ERACHECK. Ready-made solid-phase extraction (SPE) cartridges are directly plugged to the instrument's sample inlet port and connected with the inlet tubing. With an embedded pump, ERACHECK automatically primes the cartridge, performs the solid phase extraction, rinses the measurement cell and starts the measurement. Afterwards the cartridge is unplugged and disposed. Clear instructions are given on the large colour touch-screen during the whole measurement procedure. The use of cartridges with ERACHECK is optional. The cartridges simplify and speed-up the clean-up procedure while maximising reproducibility and applicability of oil-in-water analysis. The use of TPH cartridges is in full compliance with ASTM D7678-11.

Figure 4: Na_2SO_4/Florisil cartridge for ERACHECK.

Conclusion

Being of highest applicability, speed and ease of use, the launch of ASTM D7678-11 paves the way for bringing the infrared method back to CFC-free oil-in-water analysis. The method is fast, accurate and can be performed on-site by using the ERACHECK oil-in-water analyser from Eralytics. Ready-made SPE cartridges in full compliance with standard ASTM D7678 simplify and speed-up the clean-up procedure while maximising reproducibility. The excellent correlation to reference methods DIN 38409-H18 (Freon®-based infrared) and ISO 9377-2 (gas chromatography) has been verified by OMV and Statoil ASA.