

## **An Update of Infrared Methods as applied to Produced Water Analysis**

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### ***New ASTM Method D7066-04***

With the manufacture of Freon 113 banned by the Montreal Protocol in 1995, the old ASTM method (D 3921) that used infrared analysis and Freon 113 had to be replaced. Numerous oil and grease applications including EPA Methods 413.2 and 418.1 and ASTM Method D 3921 used Freon as the extraction solvent. Freon-113 has two key characteristics that made it ideal for use as the solvent in Method 418.1: Hydrocarbons have a high solubility in Freon-113 and it is infrared transparent in the spectral region where hydrocarbons absorb. In addition, it is non-toxic and relatively non-volatile. Finding a comparable solvent to Freon was the most difficult task faced by the ASTM committee when asked by the EPA to develop a new method with a new solvent.

A number of different solvents have been studied as replacements. The British DTI has permitted the temporary use of tetrachloroethylene (TTCE) or perchloroethylene (perc) as a replacement solvent. This material is infrared transparent although there is some concern about its potential toxicity. The US EPA has selected n-hexane for its gravimetric procedure, EPA Method 1664 A. Since hexane is not infrared transparent, it must be evaporated away before its residue can be examined by infrared to determine hydrocarbon concentration. Because of the evaporation stage for both the gravimetric and infrared, hexane extraction does not measure the volatile hydrocarbons. The Scandinavian countries have accepted pentane, which has similar characteristics as hexane, as their solvent of choice.

The US EPA wanted a method that would measure volatile constituents and would be portable enough for platform and field analysis. They requested the ASTM to create a new method using an alternate solvent suitable for an infrared transmission measurement. Accordingly, subcommittee D19-06 was formed in 2002 to replace ASTM D3921 Standard Test Method for Oil and Grease and Petroleum Hydrocarbons in Water with a method to accommodate an alternate solvent to Freon-113. After evaluating potential candidates, the committee tested two solvents for the round robin: Dichloro-pentafluoropropane (Asahiklin AK-225) and dimer/trimer of chlorotrifluoroethylene (Horiba S-316). Perchloroethylene was not even considered as it is on the Montreal Protocol list to be banned in 2030. As there was not enough data for the precision and bias statement for the AK-225, the method submitted for approval used S-316 as the extraction solvent. The data for AK-225 is included in an appendix to encourage other interested organizations to perform their own round robin if they would like to use AK-

225. ASTM Method D7066-04 Test Method for dimer/trimer of chlorotrifluoroethylene (S-316) Recoverable Oil and Grease and Nonpolar Material by Infrared Determination was passed and published in July 2004. The US EPA's intent was to expand on the ASTM round robin testing and adopt D7066-04 as an EPA Method. Unfortunately, since 9-11 all of the funding has been diverted to testing and protecting potable water so the funds were not (and probably won't be) available for wastewater testing.

As the International Maritime Organization (IMO) and the ISO (International Standards Organization) are currently looking at proposing this method, other organizations with existing infrared methods, such as OSPAR and the DTI could possibly modify their methods for the new solvent.

#### ***New ASTM Method Comparable to Earlier Freon/IR Methods***

ASTM Method D 7066-04 is comparable to the earlier Freon/infrared procedures in sampling methodology and extraction procedure. No direct testing was done between the two solvents as the head of the Office of Water at the EPA was adamant that the new method should be a stand alone method for measurement of volatile constituents. The extraction efficiencies for Freon and S-316 are both in the 90% range and the % usable infrared energy at the C-H Band is 89% for Freon and 80% for S-316. The boiling points are quite different (Freon is 48C and S-316 is 134C). This gives S-316 the advantage of better reclamation as less is lost to volatilization. Unfortunately, the cost per liter is about the same for each solvent.

#### ***Measuring Aromatic/Aliphatic Ratios with a Spectral Range Infrared Analyzer***

There is increasing interest in being able to report aromatic content separately from the aliphatic content. Total Petroleum Hydrocarbons (TPH) can be determined by IR measurements at 2930cm<sup>-1</sup> (3.4 micrometers). When an IR transmitting solvent such as Freon-113, TTCE (perc), S-316 or AK-225 is used, both aromatics and aliphatics will be included in the analysis at this wavelength.

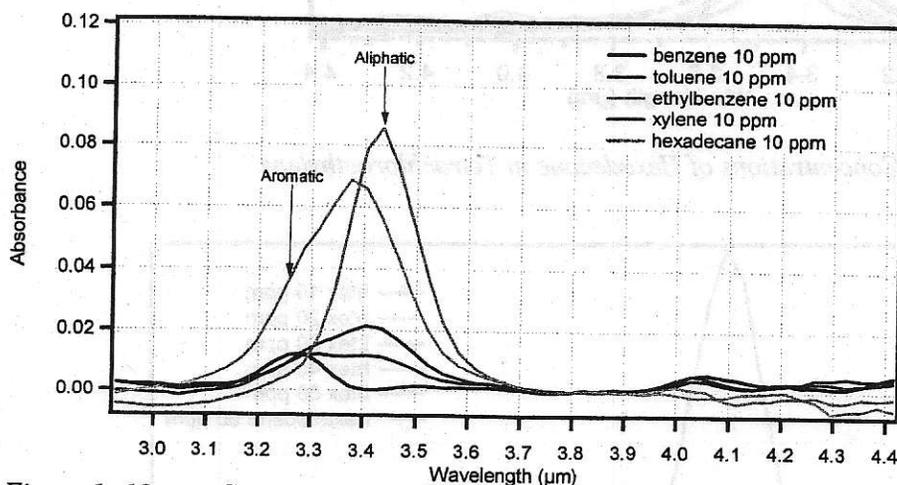
When FT-IR instruments are used with IR transmitting solvents, it is possible to obtain aromatic and aliphatic values independently from IR absorptive data by scanning through the IR range from 3400 cm<sup>-1</sup> (2.74 microns) to 2600cm<sup>-1</sup> (3.85 microns) as described in the Institute of Petroleum test procedure "IP 426/98 Determination of Oil Content of Effluent Water Extraction and Infrared Spectrographic Method". Because it is impractical to position FT-IR instruments on platforms or in a field environment, samples are generally delivered to the laboratory causing an inevitable delay.

A new concept portable infrared spectrometer, the InfraSpec™ VFA-IR Spectrometer, enables the user to obtain infrared information for a spectral range much like an FTIR but with no moving parts and no exposed air path. It is compact, rugged and insensitive to environmental changes making it ideal for onsite or platform applications. It is also easy for non technical personnel to operate. The InfraSpec VFA-IR Spectrometer utilizes a detector

array and a linear variable filter in order to produce a spectrum. The spectral information can be used to distinguish aromatics from aliphatic hydrocarbon.

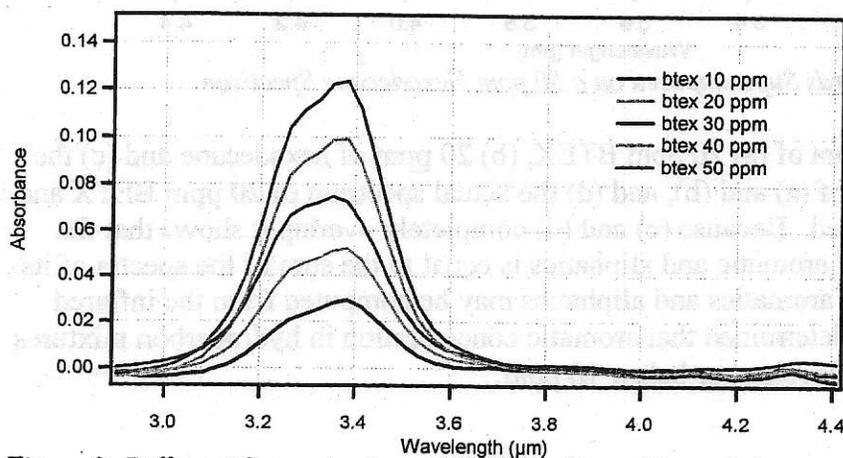
### *Analysis of Aromatic and Aliphatic Hydrocarbons*

To test InfraSpec VFA-IR Spectrometer for aromatic/aliphatic measurements, independent solutions of benzene, ethyl benzene, toluene, and xylene were made in 100 ppm, 200 ppm, 300 ppm, 400 ppm and 500 ppm concentrations in the solvent tetrachloroethylene. Assuming a 10:1 extraction ratio these values compare to 10, 20, 30, 40, and 50 ppm. In the remainder of this paper, concentrations will be referenced to the extraction ratio values. BTEX was chosen for these tests because these components are not seen with solvent evaporation techniques. Spectra showing 10 ppm of each in tetrachloroethylene are shown in figure 1.



*Figure 1: 10 ppm Concentrations of Benzene, Toluene, Ethylbenzene, Xylene and Hexadecane*

Next a mixture of equal parts of benzene, ethyl benzene, toluene, and xylene (BTEX) was used for a representative sample of the aromatic components in produced water again at equivalent extract concentrations of 10, 20, 30, 40, and 50 ppm. (Figure 3).



*Figure 2: Different Concentrations of BTEX in Tetrachloroethylene*

Similar mixtures of hexadecane to represent the aliphatic components in produced water were also tested (Figure 4). Spectra of the 5 BTEX standards superimposed on the 50 ppm hexadecane spectrum are shown in Figure 5.

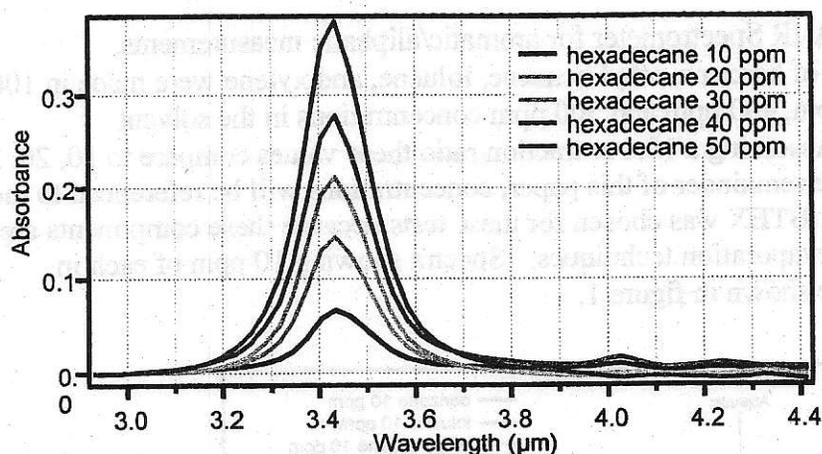


Figure 3: Different Concentrations of Hexadecane in Tetrachloroethylene

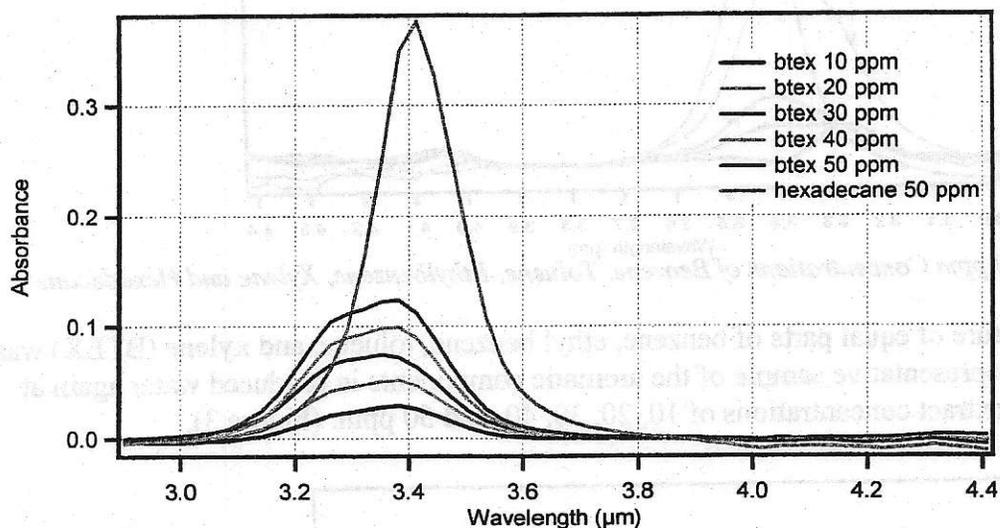
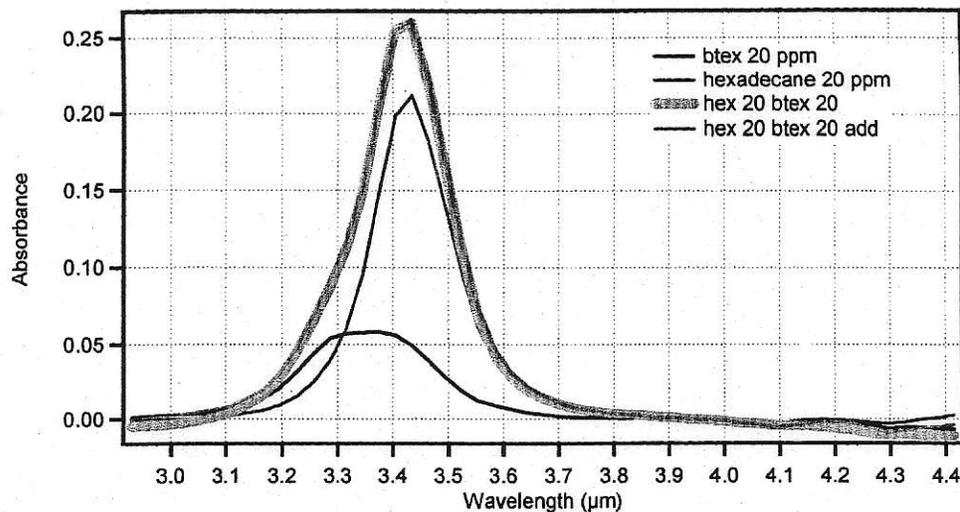


Figure 4: 5 BTEX Standards Superimposed on a 50 ppm Hexadecane Spectrum

Figure 7 shows the spectra of (a) 20 ppm BTEX, (b) 20 ppm of hexadecane and (c) the mathematical summary of (a) and (b), and (d) the actual spectrum of 20 ppm BTEX and 20 ppm hexadecane mixed. Because (c) and (d) completely overlap it shows that the spectrum of a mixture of aromatic and aliphatics is equal to the sum of the spectra of its parts and hence ratios of aromatics and aliphatics may be computed from the infrared spectral data. We have determined that aromatic concentration in hydrocarbon mixtures can be detected down to levels at or below 10 ppm.



*Figure 6: Spectra of 20 ppm BTEX, 20 ppm of Hexadecane, the Mathematical Summary of the Two, and the Actual Spectrum of 20 ppm BETX and 20 ppm Hexadecane Mixed*

Further work is required to develop the necessary computational algorithms to determine the aromatic and aliphatic relationships. The InfraSpec VFA-IR Spectrometer is not intended to replace a gas chromatograph and the detailed hydrocarbon information it can give. The benefit of the InfraSpec is that it is relatively simple to use, portable and has a small footprint--all necessary features for instrumentation on oil platforms. With the tests performed to date, it is apparent that the information from InfraSpec is adequate to provide spectral data to break down the hydrocarbon components in produced water into total aromatic content and total aliphatic content.

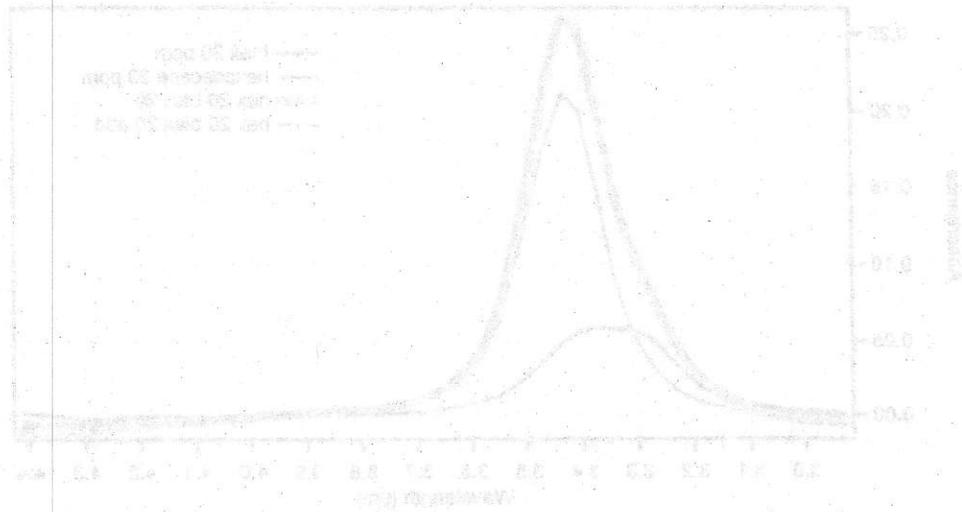


Figure 2: Spectra of 20 ppm RTX, 30 ppm RTX, and 40 ppm RTX. The absorbance increases with concentration. The peak absorbance for 20 ppm is approximately 0.05, for 30 ppm is approximately 0.12, and for 40 ppm is approximately 0.18.

Further work is required to develop the necessary computational algorithms to determine the accurate and reliable results. The infrared VFA-IR spectrometer is not intended to replace a gas chromatograph and the detailed hydrocarbon information it can give. The benefit of the infrared is that it is relatively simple to use, portable and has a much footprint - all necessary features for environmental monitoring. With the gas chromatograph, it is apparent that the information from infrared is adequate to provide spectral data to break down the hydrocarbon components in produced water into total aromatic content and total aliphatic content.