

Selecting a Solvent for TOG/TPH Determinations in Produced Water by Means of Infrared Analysis

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Ever since the Montreal Protocol established rules for phasing out the manufacture and use of Freon-113, a variety of other solvents have been evaluated as replacements for use in the infrared analysis of produced water for total oil and grease (TOG) and total petroleum hydrocarbon (TPH).

The replacement solvents fall into two categories: Those that transmit infrared radiation in the C-H region where hydrocarbons absorb and thus may be used directly without an evaporation step and those that contain hydrocarbon bonds and hence absorb in the C-H region and must be evaporated before the residual TOG or TPH can be determined.

In the first category are carbon tetrachloride, chloroform, tetrachloroethylene (also known as perchloroethylene or "perk"), Asahiklin AK225T (AK225), Horiba S-136 and Freon-113 (The EPA has recently extended the use of Freon-113 until 2005, however, the price has increased substantially making its continued use questionable). Because of toxicity and other considerations carbon tetrachloride and chloroform have been eliminated from consideration. (A newly available solvent is described in Appendix 1).

In the second category are n-hexane, which is used in the newly promulgated EPA procedure 1664, and Vertrel, a compound similar to Freon but with hydrocarbon replacing flourene. (See Appendix 2).

Transmission vs. Evaporation (HATR)

The TOG/TPH values indicated by the transmission methods EPA 413.2 and 418.1 include all of the hydrocarbons extracted into the solvents whether volatile or non-volatile. Evaporation procedures such as EPA method 1664 and the infrared HATR method will lose the volatile materials that boil below hexane or Vertrel. Thus the IR hexane evaporation procedure should have the best agreement with the 1664 gravimetric procedure while Vertrel values should be slightly higher due to its lower boiling point. An example of the variation in results obtained from two different crude oil samples carried out by both transmission and evaporation is shown in figure 1. where one is a gas oil concentrate (VR267) with a large percentage of volatiles and the other a heavy crude (VR256). From an EPA standpoint, the legal TOG concentration is that material left after 1664 evaporation.

Solvent Characteristics

Table 1 compares the most important physical values of the six solvents in current use. This is followed by the infrared spectrum in the C-H region of each of the solvents with that of the band pass filter superimposed plus the spectrum of crude oil. Finally, a comprehensive chart is included covering key features of each solvent including sensitivity, method of use and cost.

Solvent	Boiling Point (0°)	% Transmission at 2930 ^{cm-1}	Toxicity	Explosion Hazard
Freon	49	88	Low	No
Perk	121	81	Moderate	Low
AK-225	54	28	Low	No
Horiba S-136	134	80	Low	No
Hexane	69	0	Moderate	Yes
Vertrel	39	0	Low	No

Table 1. Key characteristics of the six evaluated solvents

Choosing a Solvent

The choice of solvent will depend on the principle uses to be made of the analysis and also, to a certain extent by company rules on safety. Infrared transmitting solvents generally are somewhat easier to use and may be the method of choice for screening purposes and equipment performance evaluation. Solvents requiring evaporation will ordinarily give results closer to on-shore laboratory gravimetric tests. Evaporation procedures may require more operator care for best results. Hexane, of all the solvents, has the advantage of being the easiest to dispose of after use – up stream of the oil/water separator. All the others must be collected and disposed of on-shore according to established procedures.

Instrument Calibration

Infrared absorption is different from UV fluorescence in that it can determine concentrations of individual hydrocarbon classes or the sum of all hydrocarbons while UV fluorescence responds only to the aromatic components. For this reason UV fluorescence equipment must be calibrated for each different cude while IR filter instruments can analyze a wide variety of cudes with a single calibration.

The calibration curves that accompany each of the solvent spectra show that the ratio of IR absorption to concentrations is quite linear up to about 500 ppm (50 ppm hydrocarbon in water using a 1 to 10 extraction ratio of solvent to water).

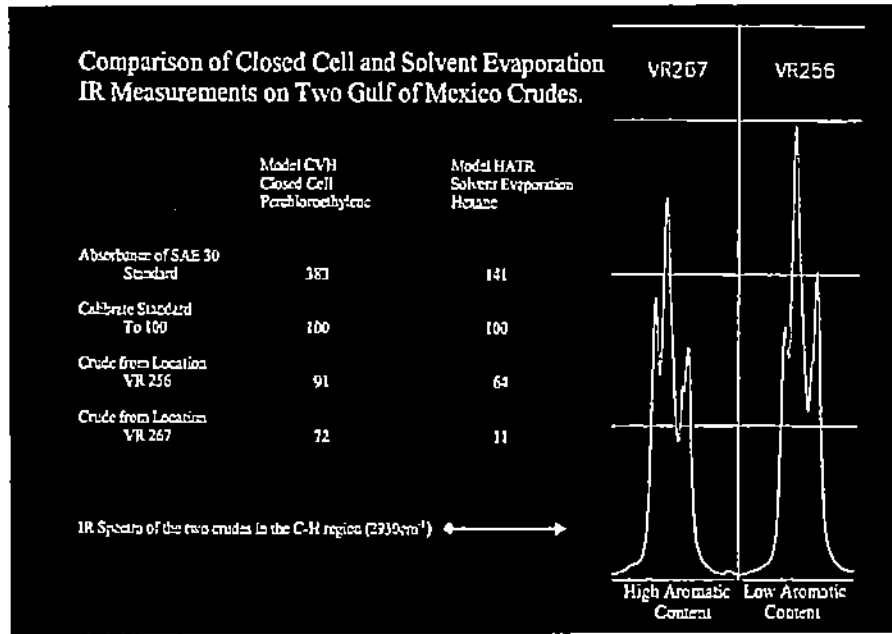


Figure 1. Comparative results from a heavy and light crude by transmission and evaporation.

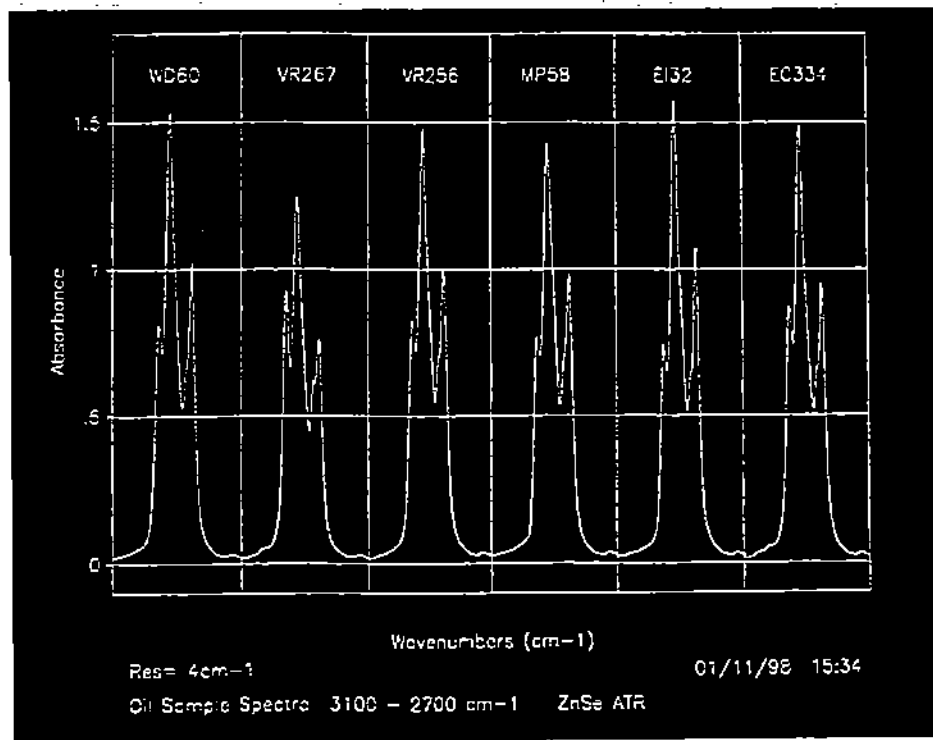
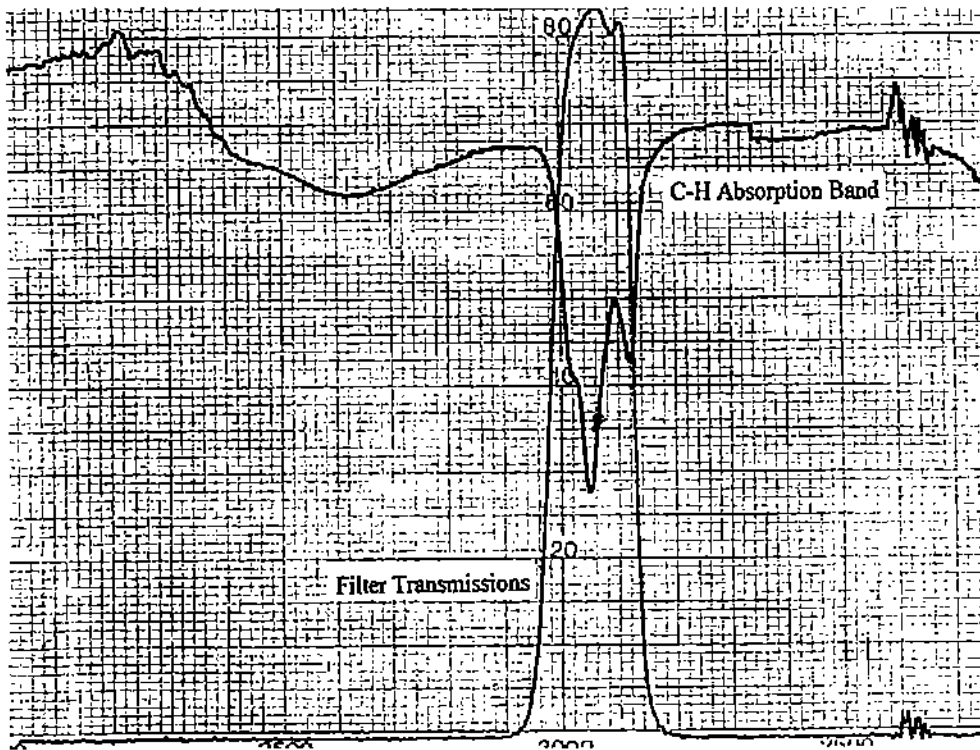
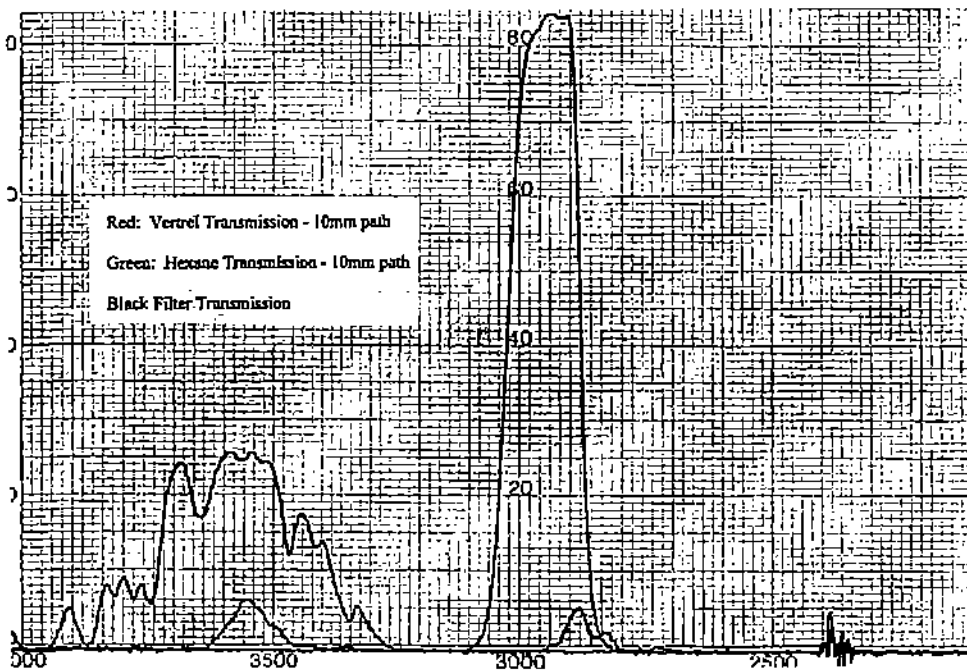


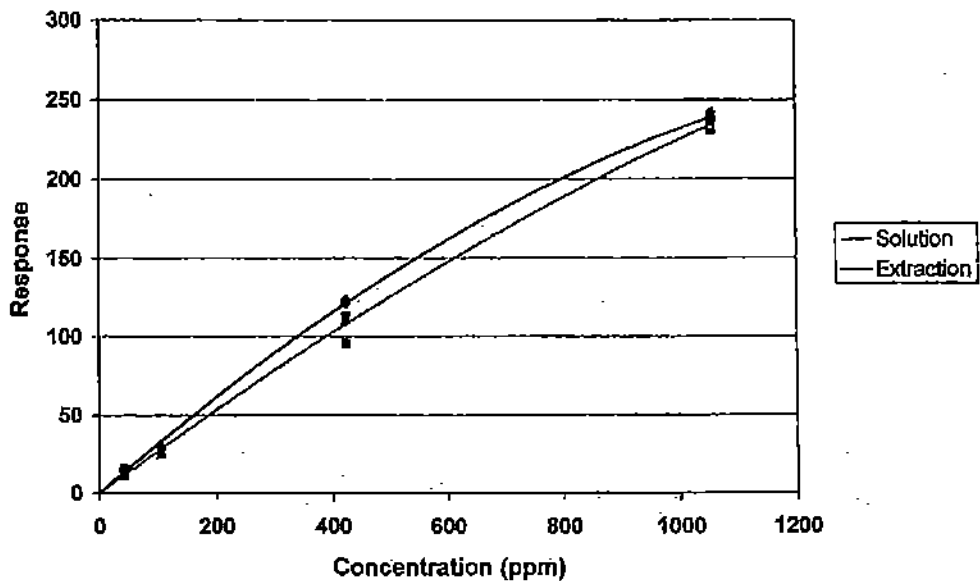
Figure 2. IR Spectra, such as the above, show different aromatic/aliphatic ratios and can be used to compute the ratio.



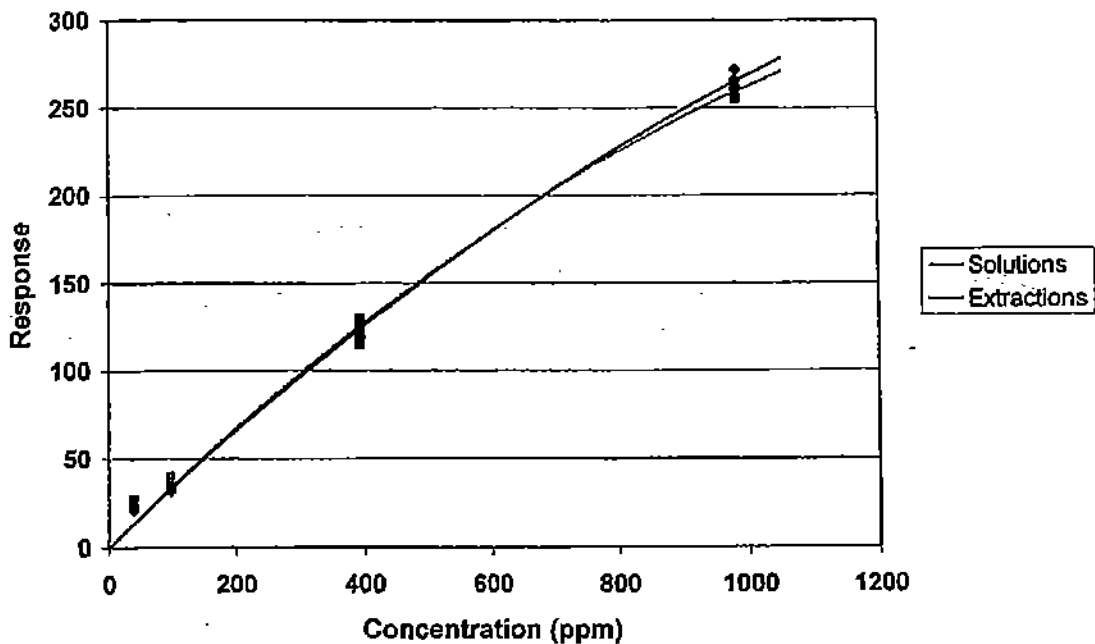
Hexane and Vertrel have 0 transmission in C-H region.

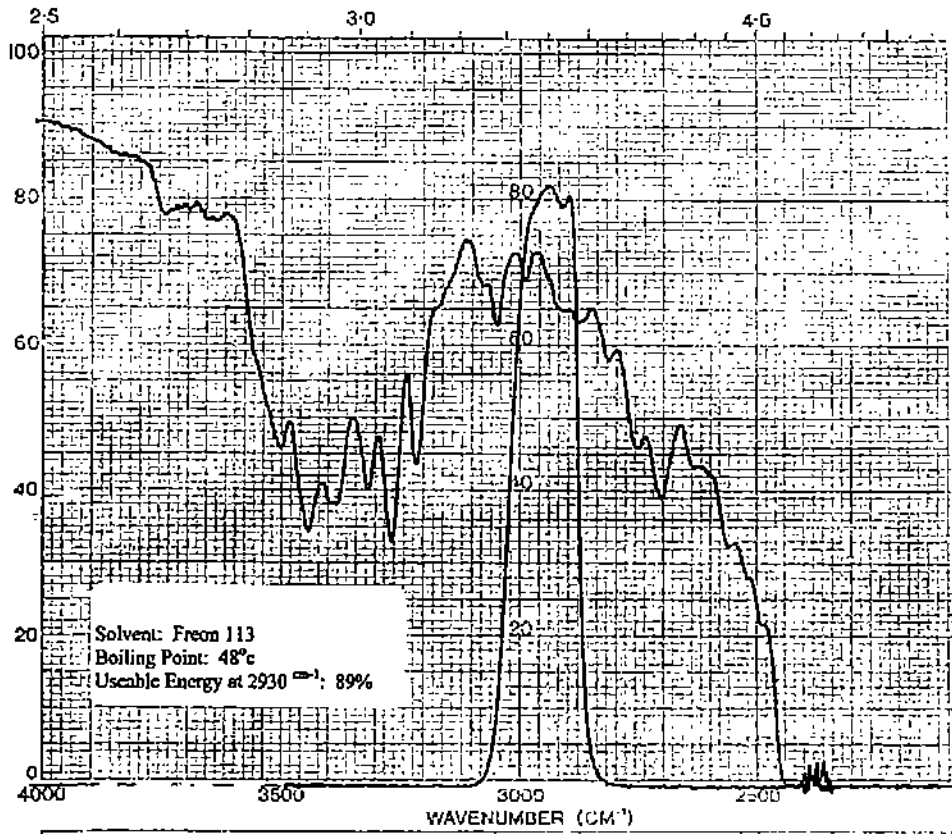


Infracal Model HATR-T Response with Hexane

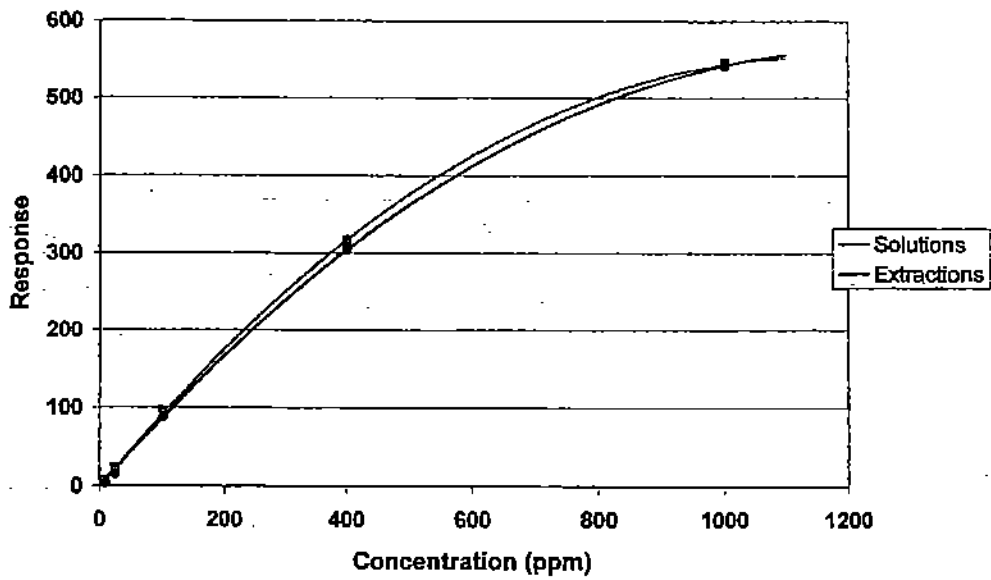


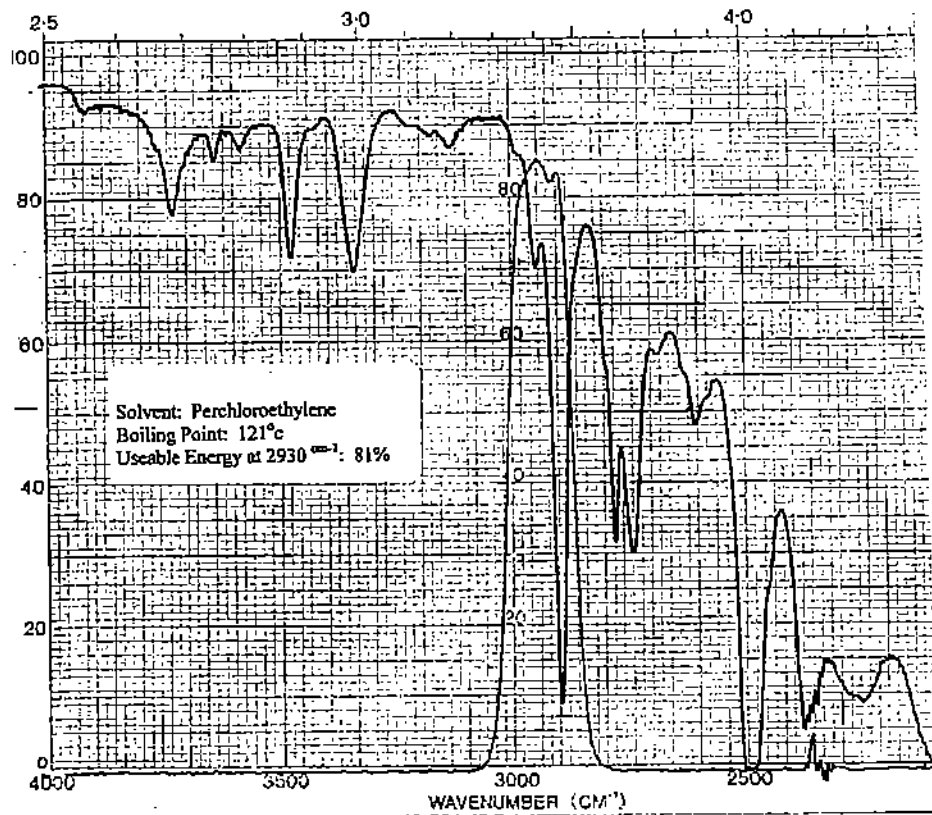
Infracal Model HATR-T Response with Vertrel-MCA



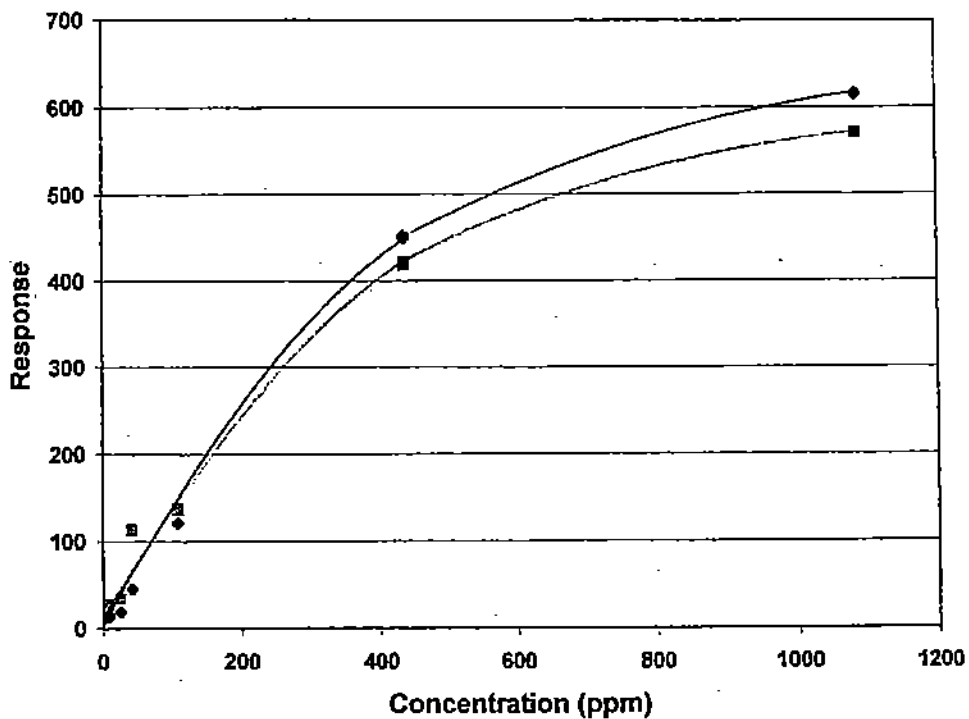


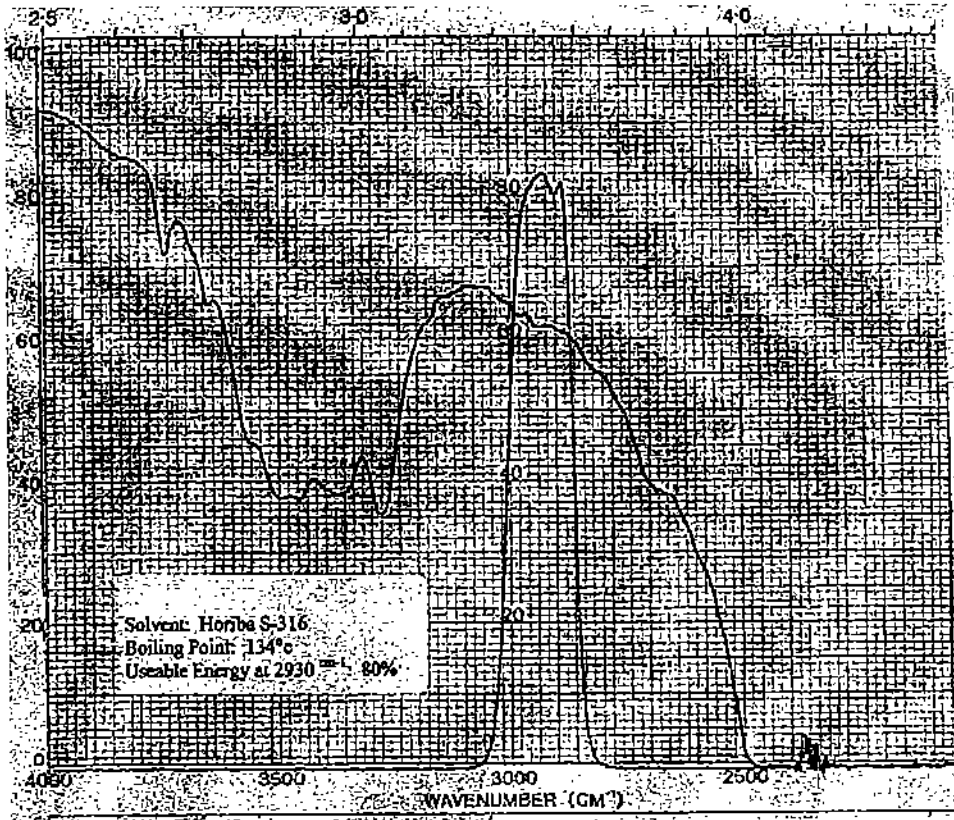
Infracal Model CVH Response with Freon-113



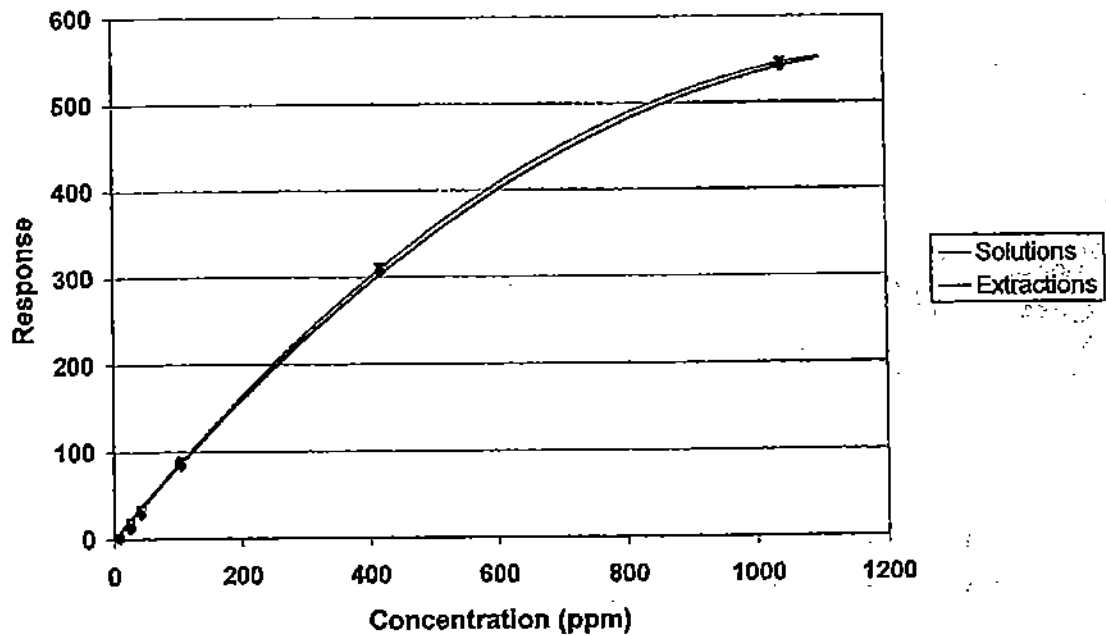


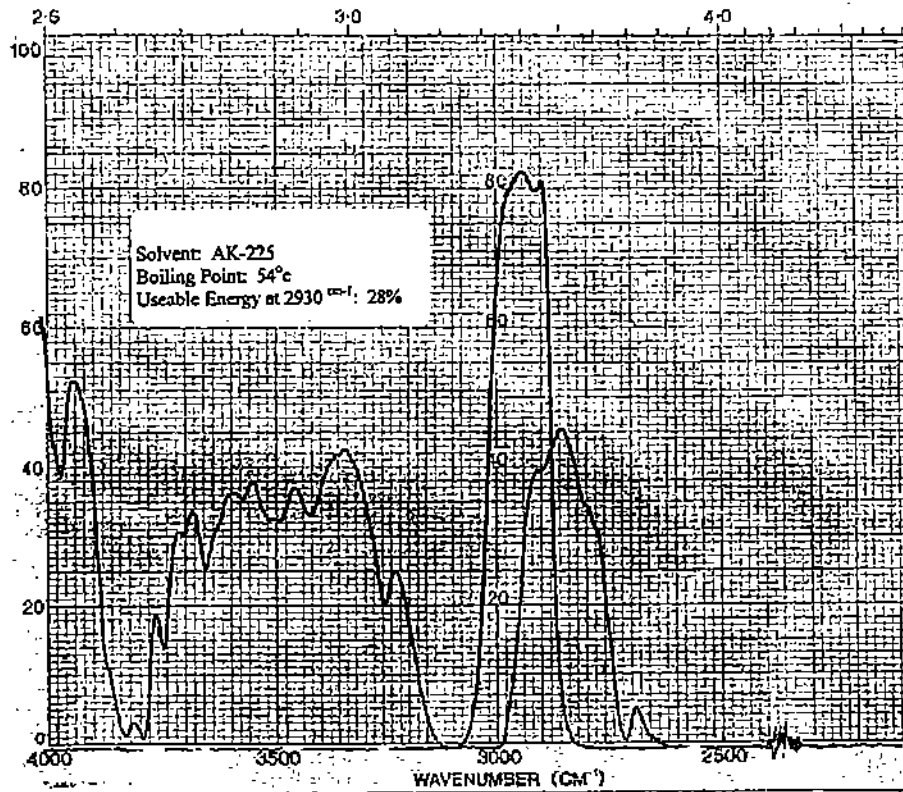
Infracal Model CVH Response with Perchloroethylene



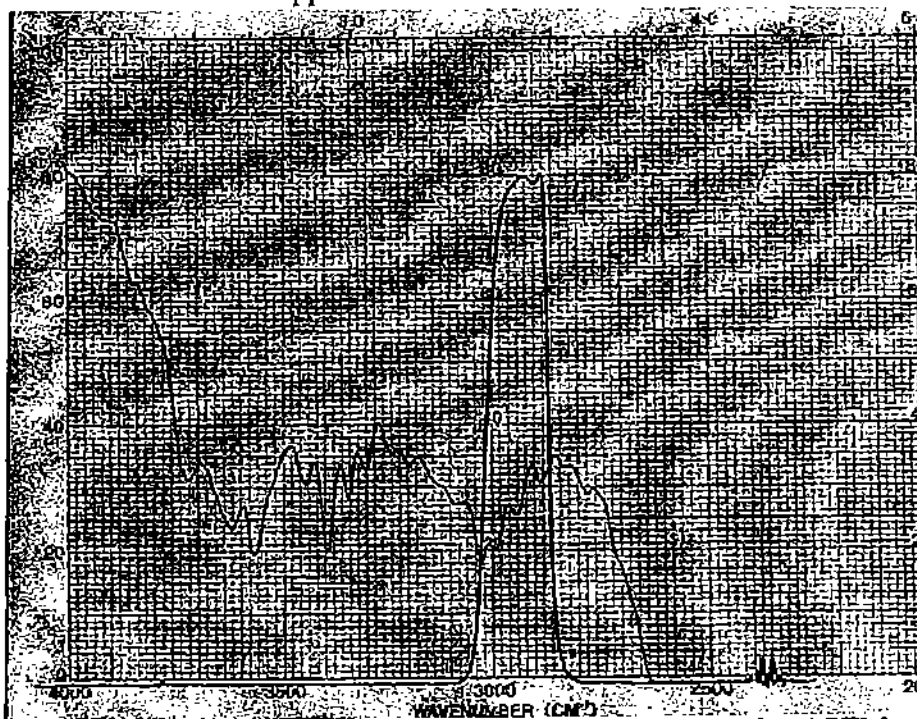


Infracal Model CVH Response with S-316





Appendix 1. IKON Solvent P



A new EPA approved iodine fluorocarbon compound under test by ASTM as a TOG solvent. Manufactured by ETEC, Albuquerque, NM. For more information visit their web site – www.etec-nm.com.

EPA Method 1664

Comparison of Extraction Solvents in the Analysis of Oil in Produced Water

By Jeff Keathley and Ken Konrad

A new solvent is proposed as a replacement for n-hexane.

The 1990 Montreal Protocol called for the elimination of chlorofluorocarbons (CFCs). The subsequent 1995 ban on production of CFCs meant that Freon 113 was no longer a viable solvent for use with U.S. Environmental Protection Agency (EPA) Method 413.1 for the analysis of total oil and grease. EPA then introduced Method 1664, N-Hexane Extractable Material (HEM; Oil and Grease) and Silica Gel Treated N-Hexane Extractable Material (SGT-HEM; Nonpolar Material) by Extraction and Gravimetry.

Many laboratories soon began complaining about a variety of issues concerning this method. Complaints included items such as the length of the title, the length of the method, and particularly about the solvent n-hexane, which is a lighter-than-water solvent and floats on top of the aqueous sample. This is the antithesis of Freon 113, a heavier-than-water solvent used in Method 413.1. EPA Method 1664 dictates that the aqueous sample has to be removed from the separatory funnel after each extraction prior to collecting the n-hexane extract and replaced prior to beginning the next extraction of the three extraction series. The additional sample handling can lead to mistakes, sample loss and poor quality control. In addition, n-hexane has a higher boiling point, and the method dictates that the solvent should be evaporated within 30 minutes at a temperature of at least 85°C. Hexane is seldom completely evaporated under these conditions. Thus, the additional extraction steps, combined with the prolonged evaporation, result in a significant increase in analysis time and costs. However, Vertrel MCA,* a mixture of a fluorinated solvent and a chlorinated solvent, does not fall within the purview of the Montreal Protocol. Vertrel MCA, which is characteristically similar to Freon 113, has a low boiling point, is heavier than water, nonflammable and slightly polar. Thus, replacing n-hexane with Vertrel MCA could solve two of the problems with EPA Method 1664.

In situations where oil and grease (O&G) removal systems are being operated and it is not feasible to use EPA's defining method for routine monitoring, accurate and reliable results can

be obtained by correlating the infrared (IR) analysis results with those of the gravimetric lab analysis by using the residue from the gravimetric analysis to calibrate a field portable IR analyzer. This is an indirect measurement where a property of the residue is related to the gravimetric analysis. Of the various measurement techniques, IR absorption has gained popularity. This indirect technique measures the number of C-H bonds in the O&G, which is proportional to the weight of the O&G. Since the partition coefficient of O&G is high for both n-hexane and Vertrel MCA, a single extraction can be used instead of the three serial extractions used in EPA Method 1664. Evaporation of the solvent and the light volatile components of the residue mimic the EPA Method 1664 analysis. This article presents a comparison of extraction solvents, including the suitability of each for O&G analysis on a field portable IR analyzer.

MATERIALS, METHODS AND PROCEDURE

Materials. Approximately 20 L of produced water, acidified at collection to pH < 2 with sulfuric acid, from an offshore platform, was obtained and used as the sample in this examination. Commercial grade Vertrel MCA (DuPont) and capillary gas chromatography/mass spectrometry grade hexane (Burdick & Jackson) were used as the extraction solvents. A field portable IR analyzer, Model HATR-T Infracal Analyzer (Wilks Enterprise), which combines the solvent removal of the gravimetric analysis and IR analysis through horizontal attenuated total reflection (HATR), was used in the solvent comparison. In using the HATR technique, 50 µL of the O&G extract is placed on a cubic zirconia sample stage and the solvent allowed to evaporate. The infrared energy is introduced at a 45-degree angle and is reflected several times from the inner surfaces of the crystal as it traverses the length. At the reflection points, the IR energy penetrates slightly beyond the surface of the crystal into the residue that is in contact with the crystal surface and is absorbed by compounds in the residue at various frequencies. The IR absorption is measured by the detec-

*Vertrel MCA is a registered trademark of DuPont.

Extraction Number	Vertrel MCA O&G (mg/L)	Hexane O&G (mg/L)
1	38.4	31.9
2	38.0	21.8
3	40.1	33.8
4	35.5	22.2
5	46.2	27.7
6	35.8	14.9
Average	39.0	23.1
Standard Deviation	3.6	9.1
Deviation %RSD	9.2	39.4

The difference between average concentration of Vertrel MCA and hexane extracts is 25.6%.

Table 1. Solvent comparison for EPA Method 1664 oil and grease analysis.

tor, related to the calibration curve and displayed as a concentration on the digital LED.

EPA Method 1664 extraction and analysis. The produced water sample was well-mixed and 1-L aliquots were removed to 2-L separatory funnels. Half of the samples were serially extracted three times with 30 mL of hexane and the other half were extracted likewise with the Vertrel MCA. The extracts were collected in 125-mL Erlenmeyer flasks and dried by passing them through a column of anhydrous sodium sulfate and the extracts collected in tared 250-mL Erlenmeyer flasks. The solvent was evaporated to dryness at 85°C in a water-bath. The moisture was removed from the surface of the flask by placing it in a drying oven at 82°C. The flasks were cooled in a desiccator, then weighed to the nearest 0.1 mg. The weight of the residue was calculated for each sample (Table 1).

Extraction and analysis using the field portable IR analyzer. Six graduated, 6-ounce (177 mL) prescription bottles were filled to the 140-mL mark with produced water. Fourteen mL of hexane were added to half of the samples. The bottles were capped and shaken vigorously for two minutes, after which time the solvent was allowed to separate from the water. The remaining half of the samples were extracted with Vertrel MCA, but instead of the phenolic cap, a Teflon-faced silicone septum cap was placed on the bottle to facilitate collection for analysis.

The field portable IR analyzer was calibrated at 25 mg/L and 50 mg/L prior to analysis using standards prepared from the EPA Method 1664 extract residues from each extraction solvent by dissolving in that extraction solvent and diluting to the working concentrations. The calibration was checked prior to each analysis using the 50 mg/L standard.

Each sample in the two extraction sets was analyzed in duplicate. A 50- μ L portion of the hexane extract was pipetted into the trough of the HATR platform and the solvent allowed to evaporate for five minutes at ambient conditions prior to analysis. The HATR platform was cleaned with extraction solvent between measurements. The Vertrel extract, on the other hand, was drawn off through the silicone septum of the inverted bottle using a 50- μ L gas-tight syringe and deposited in the trough of the HATR plate. Since Vertrel MCA is much heavier than hexane, the pipette will not retain it, and therefore, the syringe is required to maintain precision. For consistency this solvent was also allowed to evaporate for five minutes prior to analysis. The concentration is read directly from the calibrated instrument. The results of these analyses are shown in Table 2.

RESULTS

The EPA Method 1664 extraction using hexane, a lighter-than-water solvent, has the additional extraction steps of removing the water sample from the separatory funnel and replacing it after each extraction. This additional sample handling increases the extraction time and could result in the loss of sample or extract. Removal of the hexane solvent at 85°C is time-intensive, usually taking more than the 30 minutes indicated in the method. Prolonged solvent distillation can result in the azeotropic loss of analyte. Both factors contributed to an artificially

depressed average concentration (23.1 mg/L) and decreased precision as exhibited by a relative standard deviation (RSD) of 39.4%. Vertrel MCA, a heavier-than-water solvent, allows removal of the extract without removing the water sample during extraction. Solvent removal is significantly faster, generally taking about 10 minutes, due to the lower boiling point (39°C compared to 69°C for hexane). As a result, the Vertrel MCA extractions were completed in half the time and the precision increased significantly, with an RSD of 9.2%.

The field portable IR analyzer uses a single solvent extraction for analysis. Elimination of the serial extractions and the heated volatilization of the solvent dramatically increased the analytical precision, the %RSD for hexane and Vertrel MCA was very close at 4.0 and 4.7, respectively. This is most likely attributed to volume measurement. In this light, the difference (3.6%) in the average O&G concentration, 32.8 ppm for Vertrel MCA and 30.5 ppm for hexane, could be the result of the extraction efficiency, and/or the difference in the boiling points of the two solvents. Vertrel MCA, being a somewhat more polar solvent, could dissolve polar constituents of the produced water that hexane cannot. Qualitative GC analysis of the Vertrel MCA and hexane extracts for petroleum hydrocarbons were virtually identical. The Vertrel MCA showed no propensity for dissolving significant numbers or amounts of compounds with respect to the hexane under

Vertrel MCA Extraction	Analysis 1 O&G (mg/L)	Analysis 2 O&G (mg/L)	Average O&G (mg/L)
1	35.0	35.0	35.00
2	31.0	32.0	31.50
3	32.0	32.0	32.00
Average	32.5	33.0	32.60
Standard Deviation	1.7	1.4	1.55
Deviation %RSD	5.2	4.2	4.70

Hexane Extraction	Analysis 1 O&G (mg/L)	Analysis 2 O&G (mg/L)	Average O&G (mg/L)
1	29.00	29.00	29.00
2	30.00	31.00	30.50
3	32.00	32.00	32.00
Average	30.33	30.70	30.50
Standard Deviation	1.24	1.24	1.22
Deviation %RSD	4.10	4.00	4.00

The difference between average concentration of Vertrel MCA and hexane extracts is 3.6%.

The difference between EPA Method 1664 and field portable IR analysis concentration for Vertrel MCA extracts is 0.6%.

The difference between EPA Method 1664 and field portable IR analysis concentration for hexane extracts is 13.6%.

Table 2. Solvent comparison for field portable IR analysis.

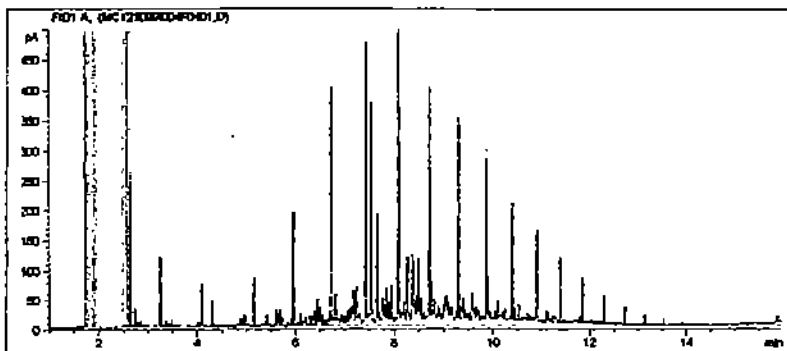


Figure 1. Gas chromatogram of hexane extract of petroleum hydrocarbons.

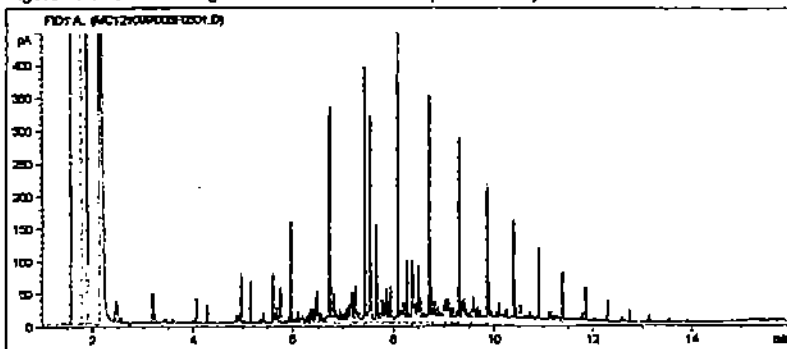


Figure 2. Gas chromatogram of Vertrel MCA extract of petroleum hydrocarbons.

the GC conditions used (Figures 1, 2).

The 25.6% difference in the average concentration obtained for each solvent is not likely to be a completely fair comparison (Table 1). It has been previously noted that the EPA Method 1664 hexane extraction requires knowledge and practice to obtain consistent results. The analyst performing these tests is knowledgeable in the mechanics of Method 1664, but he or she is not practiced. Therefore, it can be argued that the 25.6% difference in the average concentration obtained for each solvent is not representative. The noticeable difference in the RSD between the Method 1664 hexane (39.4%) and the Vertrel MCA (9.2%) sets illustrate that the hexane extraction is more challenging for both the novice and experienced analyst, and the quality control for hexane is not likely to equal that for Vertrel MCA for either analyst.

The more important comparison is the differences between the EPA 1664 analysis (Table 1) and the IR analysis (Table 2) for use in monitoring produced water quality. The average concentrations obtained for hexane for each procedure were 23.1 ppm and 30.5 ppm, respectively, yielding 13.8% difference. The respective values of 39.0 ppm and 32.8 ppm were obtained for Vertrel MCA, for a difference of 8.6%. Even with considerations for the lack of experience, the values ob-

tained for each type of analysis for each solvent are comparable.

CONCLUSION

This preliminary investigation indicates that this technique should be examined as a replacement for the EPA Method 1664 oil and grease analysis utilizing a suitable calibration standard.

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