

CORRELATING FIELD MONITORS TO EPA METHOD 1664

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INTRODUCTION

The American Petroleum Institute (API) recently completed a study of oil and grease monitors for produced water. The goal of this project was to understand the reliability, practicality, sensitivity, and performance limitations of the various portable instrument methods currently used in the field as alternatives to Method 1664 for the routine analysis of produced water oil & grease. While conducting this study, it became obvious that a major problem concerning these monitors was correlating them to EPA Method 1664, which defines oil and grease. This paper uses material from the API project report to illustrate this problem.

Oil and grease is defined by EPA regulations as that material which is extractable in N-hexane from water at pH 2 or less and remains after the hexane is removed using the procedures described in the method. In effect this means that oil and grease is a mixture of organic materials. Some of it is from droplets of crude oil in the produced water. Some is from dissolved components of the water including soluble oils (carboxylic acids, phenols, dissolved aromatics) or residual treatment and workover chemicals. Method 1664 makes no attempt to identify any of the constituents of oil and grease but simply weighs them.

The field monitors all measure some property of oil and grease that can be related to its weight. In order to make these measurements useful, one must be able to correlate them to the total weight of oil and grease present as measured by EPA 1664. To develop the necessary correlation, one must find a suitable set of duplicate samples, analyze one of each set using EPA 1664, analyze each of the other samples in the sets using the field instrument and plot the resulting values against each other. This relationship must be a straight line (or else it is not useable) and a mathematical equation relating the values can be determined by a least squares fit of the data. Once a correlation is developed an operator can use the field monitor to measure oil and grease around his treatment system and using the correlation then determine if the system is meeting discharge requirements.

Two factors affecting correlations can cause operators trouble:

- The variability in the predicted results, and
- The validity of the correlation over time.

For example, if a predicted value of oil and grease is 27 mg/L and the uncertainty in the number is +/- 10 mg/L it will not be very useful. The true value might be as high as 37 mg/L and the system would be out of compliance. In addition, if one develops a new correlation every week and the predicted values of a single analyses were 25 mg/L for one correlation, 35 mg/L for another and 15 mg/L for another it would not be useful. This paper uses the data and findings from the API report to examine the properties and some of the problems with correlations.

WHAT MONITORS MEASURE

To understand what affects correlations one must know what they are measuring and how they work. Three monitors were studied, each measuring a different property:

- An infra red (IR) absorption device which measured the absorption of IR by a layer of oil deposited by evaporation of a plate,
- An IR device which measured the IR absorption of a Freon extract of produced water, and
- An ultra violet fluorescence (UVF) device which measured the fluorescence from a hexane extract of produced water.

Infra Red Monitors

Infra red energy is adsorbed by the carbon-hydrogen (C-H) bonds in organic compounds. Since all organic compounds contain these bonds, a measurement proportional to the number of bonds in a sample should be proportional to the weight of oil and grease in the sample. Using IR methods you are essentially counting the number of carbon hydrogen bonds and equating the measurement to a measured weight of oil and grease. This weight will vary from compound to compound because of the presence of other atoms such as oxygen and nitrogen in some of the compounds extracted as "oil and grease". Therefore the particular composition of the oil at a particular site is very important and its tendency to change with time is also vitally important.

Ultra Violet Fluorescence Monitors

Ultra violet energy is adsorbed by certain aromatic compounds in produced water. When this energy is lost by the molecules that adsorbed it, the energy is released as another wave length of ultra violet energy (called fluorescence). Most produced waters contain aromatic compounds which will measure as oil and grease using Method 1664. As long as the ratio of aromatic compounds measured has the same ratio to total oil as used in the correlation, UVF measurements can be correlated to Method 1664. However, one must be careful because some field operations and some analytical procedures can alter this ratio and introduce errors.

Calibrating Monitors

The measurements made using a field monitor are converted to oil and grease concentrations by calibrating the monitor with a standard solution of known concentration. One prepares a series of standard solutions of known concentration using the oil in the solvent which is used to extract the produced water samples. The oil is usually measured by volume but can also be weighed. Concentrations commonly used for calibration are: 25 ppm, 50 ppm, 100 ppm and 200 ppm. Readings of instrument response are made with each solution. IR monitors usually return absorbance numbers or percent transmission values. Then the pairs of numbers: concentrations and absorbance numbers, are entered into the monitor's internal computer. Most monitors are equipped with internal circuitry which performs a least squares analyses of these numbers and set the instrument to read oil concentration directly when the monitor is used in future analyses. UVF instruments use a similar procedure where fluorescence is measured and fitted to the known concentrations.

A calibration is not a correlation and the number the instrument returns is not oil and grease concentration as measured using Method 1664. A correlation is used to predict the Method 1664 value of oil and grease concentration from concentrations determined by instrument readings. It should be noted that for IR monitors, **it is not important what oil is used for calibration**. Any oil will do. Since the concentrations must be correlated to Method 1664, the magnitude of the measured values are irrelevant as it is only their relative values that matter. The oil used to calibrate a UVF monitor is important. UVF monitors are much more sensitive than IR monitors and the calibration solutions must be in the same UV intensity range as the oil and grease in the water being analyzed.

PROBLEMS WITH CORRELATIONS

To be reliable and useful correlations must meet several criteria:

- They must have a relatively low variability. A high standard deviation will not reliably predict compliance with the discharge limits.
- They must remain valid over time. If the correlation relationship is continuously changing, it can't predict Method 1664 values.
- The concentration range they cover must be wider than the concentration range being measured. Some operators take duplicate samples with every Method 1664 sample, analyze the duplicates using the field monitor and plot the results against the 1664 results and use this as a correlation. If the treatment system is in compliance most of the time, the concentration range will not be broad enough to be meaningful.
- The correlation must be developed to meet the needs of a particular sample point. Most operators use oil and grease analyses to ensure that their treatment systems are operating in compliance with discharge regulations and to trouble shoot the treatment system. The point in the system that is of most interest is the discharge from the treatment system. The oil and grease composition at this point is the one that should be correlated to Method 1664.

Variability of Oil and Grease Measurements

Table 1.0 shows average standard deviations for effluent triplicate samples from the correlations developed for the API project. For each set of data an average and a standard deviation was calculated both on the instrument results and the predicted concentrations for EPA 1664 calculated using the correlations developed. Only effluent samples were used in determining standard deviations. The values for the field monitors are worst cases because a large number of samples were gathered at the same time for this study and the water stream varied during the sampling interval.

Table 1.0 Standard Deviations of Oil and Grease Measurements

	EPA 1664	IR(HATR)		IR(ABS)		UVF	
		Measured	Correlated	Measured	Correlated	Measured	Correlated
Site A	2.92	7.03	5.47	3.37	9.05	3.37	5.41
Site B	4.67	7.62	6.89	2.99	9.92	10.94	16.80
Site C	3.71	0.99	3.31	1.50	4.98	4.54	5.21
Site D	4.03	0.94	24.86	3.36	1.45	2.63	13.39

These numbers are important because they illustrate possibilities for being out of compliance as measured by EPA Method 1664 even though your field monitor indicates that you are in compliance. For example, if the oil and grease concentration at Site A was measured to be 27 mg/L using the IR(HATR) instrument and its correlation, there is an 87.5% probability that the true value is between 21.5 and 32.5 mg/L A good bit of this concentration range is outside of the compliance limit. When the variability of the EPA Method 1664 results are included, the likelihood of being out of compliance is even greater. In effect, if you want to be sure you are operating your water treatment equipment within discharge limits, you should try to keep the effluent concentration below $(29 - SD)$. In this example, $29 - 5.5 = 23.5$ mg/L. This example

shows the value of closely controlling the variability of your field measurements. Some of the reasons for high variability are discussed below.

Figures 1.0 and 2.0 show examples of correlation plots for the IR(HATR) monitor at two test sites. Casual observation of these two figures might lead you to the conclusion that the Figure 2.0 correlation is a lot better than that shown in Figure 1.0. However, the standard deviations for Figure 1.0 replicates was 5.47 compared to 3.31 for Figure 2.0 replicates. This is not a big difference but it is significant. The site where the Figure 1.0 data was gathered had very unstable flow during the sampling period for the correlation samples. This flow variability resulted in an overly variable correlation. Differences in flow result in differences in oil concentration and rapidly changing oil concentrations during gathering of correlation samples (or replicate effluent samples) decreases the probability that the samples are truly replicates.

For the API study, correlation samples were gathered around water treatment systems and included influent samples and effluent samples. Some of the samples were diluted with water. These measures were taken in order to obtain a range of concentrations. However, the choice of this approach to correlation samples introduced problems. Even though all the organic components in produced water are not included in oil and grease as defined by EPA Method 1664, some of them are measured by the field monitors. If some correlation samples do not contain all the components measured by the instrument and some do, the correlation will be affected. Two examples are shown in Figures 3.0 and 4.0. Only the UVF and IR(ABS) monitors are affected by dilution of samples. Figure 3.0 shows an example for the UVF monitor and Figure 4.0 shows an example for an IR(ABS) monitor. These two figures illustrate the need to ensure that all samples are compatible and share a common composition. The problem encountered in Figure 3.0 was not found at all test sites

Another factor that adds to the variability of oil and grease measurements and therefore affects correlations is changing oil composition in the water stream. These changes occur because oil and grease in produced water is made up of several types of components including dispersed droplets of oil and dissolved organic acids that measure as oil using EPA Method 1664. The treatment system removes dispersed oil but little, if any, of the dissolved oil. For example, consider a produced water influent stream containing 60 mg/L dispersed crude oil droplets and 20 mg/L dissolved organic acids that measure as oil using Method 1664. This results in a total oil and grease concentration of 80 mg/L (75% crude oil and 25% organic acids). A potential effluent concentration for this mixture is 5 mg/L crude oil and 20 mg/L of dissolved organic acids (20% crude oil and 80% acids). IR monitors measure the

Table 2.0 Impact of Oil Composition Through the Treatment Process On Measured Oil and Grease Concentration

Acid Content of OIL, %		Calibrant for IR Instrument	
		100% Hydrocarbon	80% Acid - 20% Hydrocarbon
Oil Concentrations, mg/L			
	EPA 1664	IR	IR
25	80.0	74.6	95.1
31	65.0	59.6	76.1
40	50.0	44.6	57.2
57	35.0	29.6	38.3
80	25.0	19.6	25.7

concentration of carbon-hydrogen (C-H) bonds. Table 2.0 summarizes the oil concentrations through the treatment process as measured by EPA 1664 and an IR unit calibrated with two different standards. This table is a simulation assuming that the EPA 1664 concentrations would be the same as the actual concentrations. The IR concentrations are estimated from weights per molecular bond. As the water moves through the treatment system, the dispersed oil is removed and the fraction of soluble oil in the remaining oil increases. This is illustrated in the first column. If an IR unit was calibrated with a 100% hydrocarbon oil (pure octane, for example), measurement of the concentration at various points in the system using this unit would yield the concentrations in the third column. However, if the calibration oil used was the residue from an EPA 1664 sample, the IR unit would yield the concentration in the third column. As long as the composition of the oil in the water stream does not change this difference would not matter since the correlation would preserve the relationship. However, if the composition of the oil in the produced water changes, one might be faced with using a correlation like the hydrocarbon example when one should be using one like the acid calibrant example. A related problem is that the correlation is only valid at the point in the system it was developed to represent. In the API project we chose to use correlation samples taken at various points in the system. Therefore they do not exactly represent any specific point in the system such as the effluent. Note two things about this illustration. It demonstrates the need for correlations and it shows why variations in oil composition due to such operations as turning wells on and off, which may result in oil composition changes can lessen the validity of a correlation. Imagine that wells from various formations are turned on and off during operations and each source of produced water has a different ratio of oil droplets and organic acids. This could cause the data points on the correlation line to move up and down in response to changes in composition and this could add significant variability to the correlation. The impact of concentration change is a very complex issue and it is hard to determine the magnitude of the problems it might cause. It is an issue that needs more consideration and study.

Simulated correlation curves are shown in Figure 5.0 for calibration of the IR using a pure hydrocarbon oil and one containing 80% organic acids (a likely effluent composition for several Gulf of Mexico discharge points). Correlation curves with lesser concentrations of organic acids in the calibrant oil would fall between these two.

It should also be noted that in real field samples the presence of treating chemicals and other added materials can further complicate the measurement of oil and grease. The intermittent nature of the use of these materials is a variable that can add confusion to a study of the oil and grease measurement dilemma.

Validity of Correlations Over Time

Another important criteria for correlations is validity over time. Figures 1.0 and 2.0 show correlations as they were developed during the first phase of the study. Later the test sites were visited again and effluent samples only were taken over four periods. These samples were analyzed using the monitors and the results of these analyses were correlated using the correlations developed earlier. Then plots were made of predicted Method 1664 oil and grease concentrations versus measured oil and grease concentrations. Both correlation sample results and comparison sample results are plotted. At three of the test sites the correlations were still reasonably valid over the study interval, but were affected by some problems. However, at one site the correlation for all three monitors were no longer valid. The most striking thing about the correlations was that the quality of the predictions made using the correlations was much more site specific than monitor specific. That is, if one of the monitors gave good predictions then all of them did. This indicates that the conditions at the site and

the mechanics of correlation development had much more impact on the quality of the correlation than the particular monitor used.

Three of these plots are shown in Figures 6.0, 7.0 and 8.0. Figure 6.0 shows the correlation test for the IR(HATR) monitor at Site A. Site A produced from a number of wells which provided the opportunity for changes in oil composition as wells were started up and shut down. There were also more chances that field operations could affect the produced water quality. Here the comparison data was spread over a much wider range than the correlation data. The concentration range for the correlation samples was very short. The comparison samples were taken in two sets. The first set overlays the correlation samples almost exactly, but the second set was in a higher concentration range and were widely scattered around the correlation line. Obviously some change in the character or composition of the oil occurred which added variability to the predicted concentrations. Note also that several of the samples were over the discharge limit for oil and grease. This behavior was mirrored in the results for the other two monitors.

Figure 7.0 shows the correlation test for the IR(ABS) monitor at Site C. At this site the concentration range for the correlation was much broader than the effluent concentrations measured. For both effluent sample sets, the predicted values of oil and grease closely matched the measured values. This behavior was duplicated for the other two monitors as well.

Figure 8.0 shows the correlation test for the UVF monitor at Site D. Here all the predicted concentrations were effectively constant. This was also true for the other two monitors but the concentration was different for each monitor. The measured values of oil and grease covered a wide concentration range. At this site some change in the oil and grease composition occurred that changed the correlations. Whatever component caused the measured oil and grease concentration to vary was NOT detected by either IR absorption or UV fluorescence. This component was soluble in hexane or it would not have been detected by EPA Method 1664. The average IR(HATR) concentration was 47.5 mg/L, the IR(ABS) average was 110.3 mg/L and the UVF average was 81.8 mg/L. What was this material?

The data presented in these figures indicates that changes in oil and grease composition do occur in the field and these changes can damage or invalidate the correlation. The differences observed at Site D are dramatic and it is easy to recognize that something is wrong. Was there a similar problem at Site A that was just not as obvious? Standards are needed for validating correlations.

Concentration Range for Correlations

If one plots the measured EPA 1664 values of oil and grease against the measured values using a field monitor the data points should fall on a straight line. This is essential for a correlation to be useful. Fitting the data to a straight line provides an equation that is used to calculate a predicted EPA Method 1664 oil and grease concentration from a field instrument measurement. This equation is of the form:

$$C_{1664} = \text{slope} * C_{\text{Monitor}} + \text{Intercept}$$

If a very narrow concentration range is used to develop the correlation, then the standard deviations of the analyses of the samples will be large compared to difference and minimum concentrations used. To illustrate the problem, consider Figure 9.0 which shows a plot of EPA Method 1664 values and IR(HATR) values for diluted samples and undiluted samples at Site

A. The concentration range for each data subset is less than 10 ppm for the IR(HATR) data. Three correlations are indicated on this figure: the total data (solid line), the diluted data only (dotted light line), and the undiluted data only (dotted dark line). At this site the standard deviation for the IR(HATR) measurement was 7.03 ppm and the standard deviation for the EPA 1664 measurements was 2.92 mg/L. Therefore it is possible that the highest concentration for the diluted samples is 20 ppm, not the approximate 24 ppm shown. This would put the point on the solid line and the slope of the diluted sample correlation would be the same as the solid line.

To see the significance of this, extend the plotted light dotted line to 35 ppm. If one uses this diluted correlation line a IR(HATR) measured value of 35 would predict an EPA 1664 value of about 18 mg/L. Using the correlation line developed using all the data the predicted EPA 1664 value would be about 26 mg/L, a difference of 8 mg/L. This illustrates how a small error in concentration can make a huge difference in the correlation slope. The broader the concentration range of the correlation, the more reliable the slope of the correlation.

THE CHALLENGE – HOW TO CORRELATE A FIELD MONITOR

We have seen that to develop a good, reliable correlation of a field monitor to EPA Method 1664 we must have:

- True replicate samples;
- Samples over a wide concentration range;
- The oil and grease composition in the water should be constant over the test time interval; and
- The correlation should be developed for the sample point of interest to the operator.

The questions that need to be answered are:

1. Where do you get samples for use in developing the correlation?
2. How do you minimize differences between replicates?
3. How do you know the correlation is still valid? How do you test it?
4. Is it possible to develop a general correlation that applies to all sample points in a produced water treatment system?
5. If a universal correlation is not theoretically possible, can one be developed that gives estimates that are useful?

Although the study cannot be definitive about the reasons behind the behavior observed because of the very limited amount of data gathered, it indicates that a universal correlation at any given site is not possible. An averaged correlation as many have used in the past may give estimates that are useful, they will not be exact.

In the API study we chose to use samples around the water treatment system. We know that samples at various points in the system cannot have the same oil and grease composition. Therefore, we will get an "average" correlation. Is this good enough? In the study a large number of replicates were taken at each sample point. This was necessary because multiple replicates were needed for four instruments (One was subsequently dropped from the study.). Therefore, the sampling period for each replicate set was relatively long and this was

heightened by the fact that triplicate samples were taken for each instrument. For sites with a highly variable oil concentration in the water, this introduced errors.

In the past many operators simply collected duplicates when they took compliance samples from the permitted outfall and plotted them on a graph. The result was that the correlation was not good for concentrations that were not very near the average values measured. Is it good enough to take a large number of duplicate samples, have them analyzed and average the results? One could simply multiply the monitor value by the ratio of EPA 1664 results to the original monitor results and get an estimate of the EPA 1664 oil and grease concentration. This ratio would not be good at any other point in the system. For example, if one wanted to know the influent concentration to the water treatment system for diagnostic purposes this simple correlation probably would not give an accurate concentration. But do you care. In this situation it may be enough just to know the inlet concentration is a lot higher than it was before and the absolute value is not necessary. If one adopted this approach then the correlation could be checked at intervals by gathering several replicates and repeating the process. If the new EPA 1664 to monitor ratio was significantly different from the old one, just substitute the new one.

AN IDEA TO CONSIDER

The effluent from the water treatment system is the only place where a very precise and accurate measurement of oil and grease is needed. So develop a correlation for that point only to get the best field determination of oil and grease determination at that point.

Since correlation samples with the same composition are needed, use the residue from EPA Method 1664 analyses and make up "extracts" that mimic the concentration of a range of oil and grease concentrations as measured by EPA Method 1664. Then measure the oil and grease concentration of these extracts using the field monitor and develop a correlation using the results. The concentration range of the correlation could be made as large as you wanted. Then the difference between future measured oil and grease concentrations determined using EPA Method 1664 and the predicted concentration obtained by analyzing with the field monitor and applying the correlation could be plotted against time. When the trend of this difference becomes too large (or larger and larger) a new calibration can be made.

This idea has not been tested but experience so far indicates that it should work. It has the advantage that all the analyses and technical manipulation would be done in laboratories by experienced analysts and the only analysis needed in the field is the sample analysis. Then the operator need only enter the results of this analysis and its corresponding EPA 1664 value and enter them on a plot. The IR(HATR) could be calibrated with the EPA Method 1664 residue and would then read the EPA Method 1664 value directly. A correlation would be needed for the IR(ABS) instrument.

Whether or not this approach would work with the UV instruments would have to be investigated. However, there must be some equivalent to this approach for these instruments.

It would help if some technical body were to take up this problem, determine what operational needs are and then design and test a correlation method specifically to meet offshore needs.

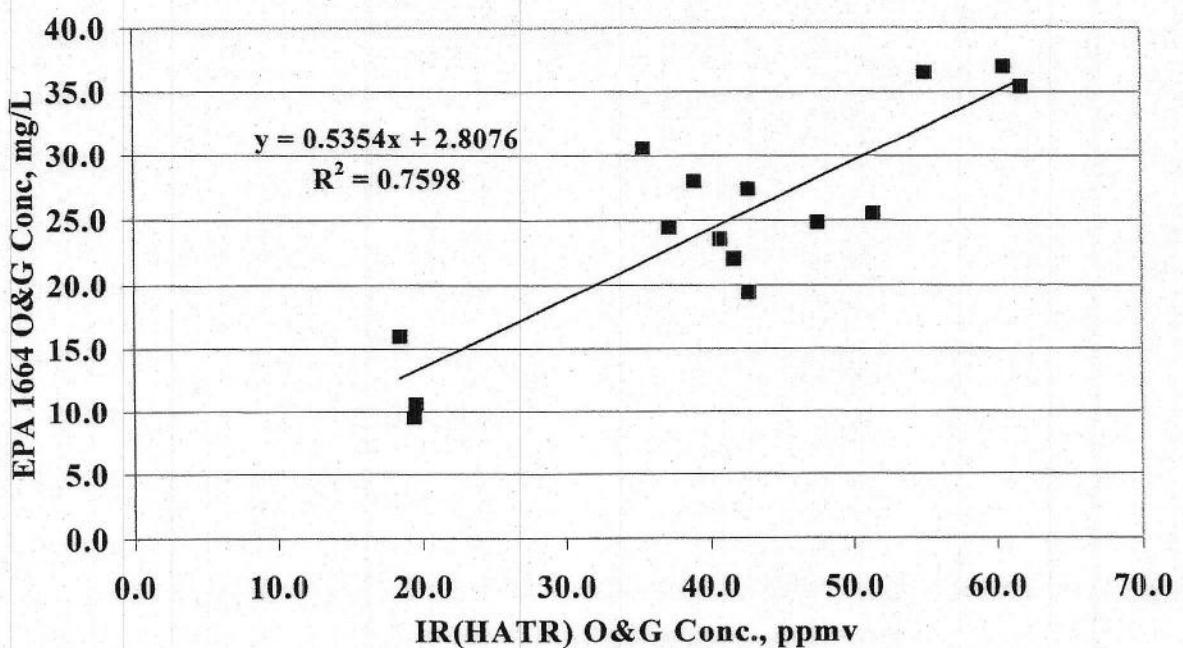


Figure 1.0 A Correlation Example from a Large Central Facility

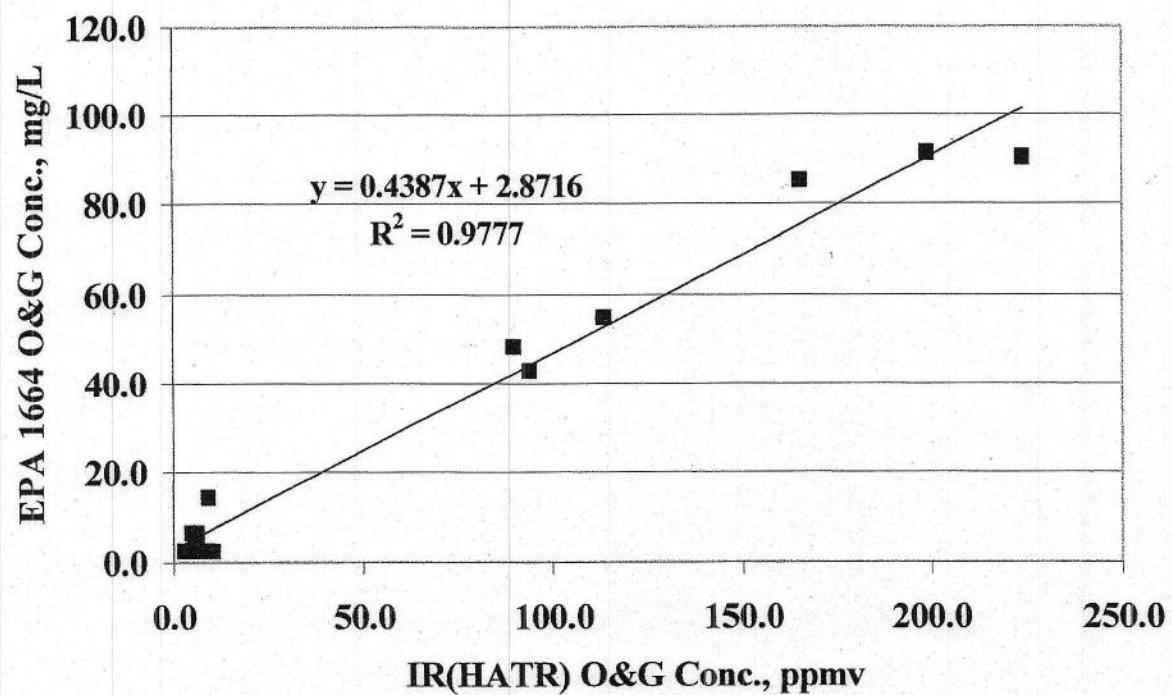


Figure 2.0 A Correlation from a Single Platform with Few Wells

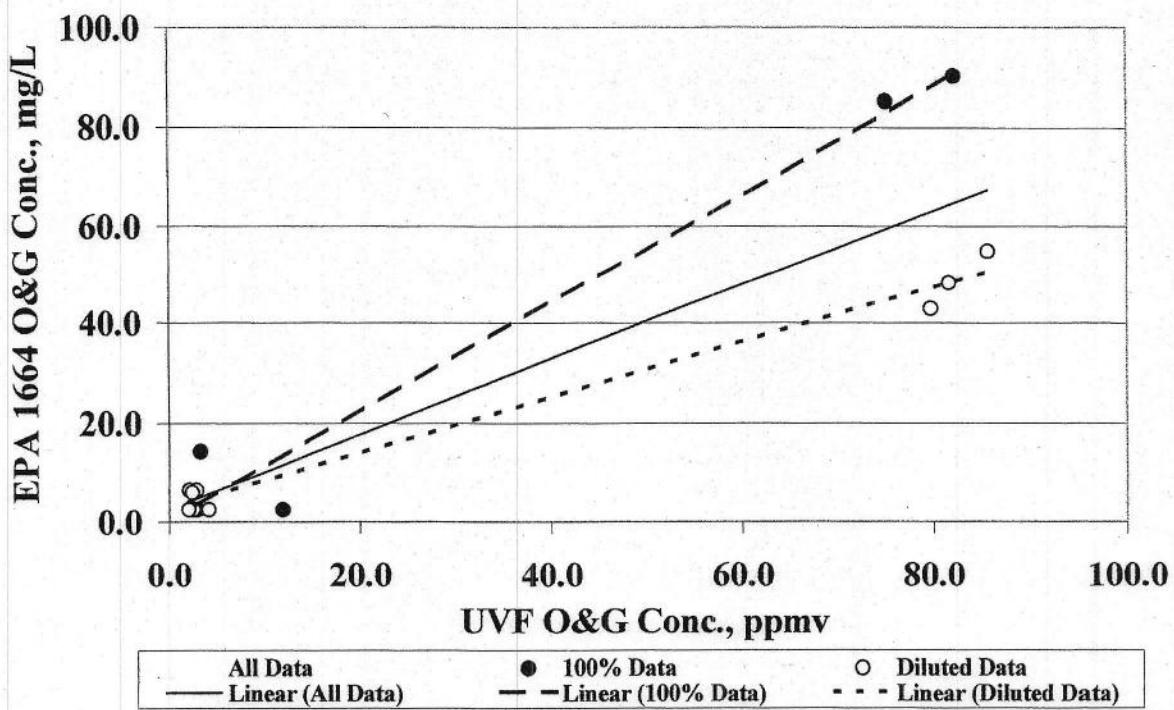


Figure 3.0 Example of UVF Correlation Problems Caused by Diluting Samples

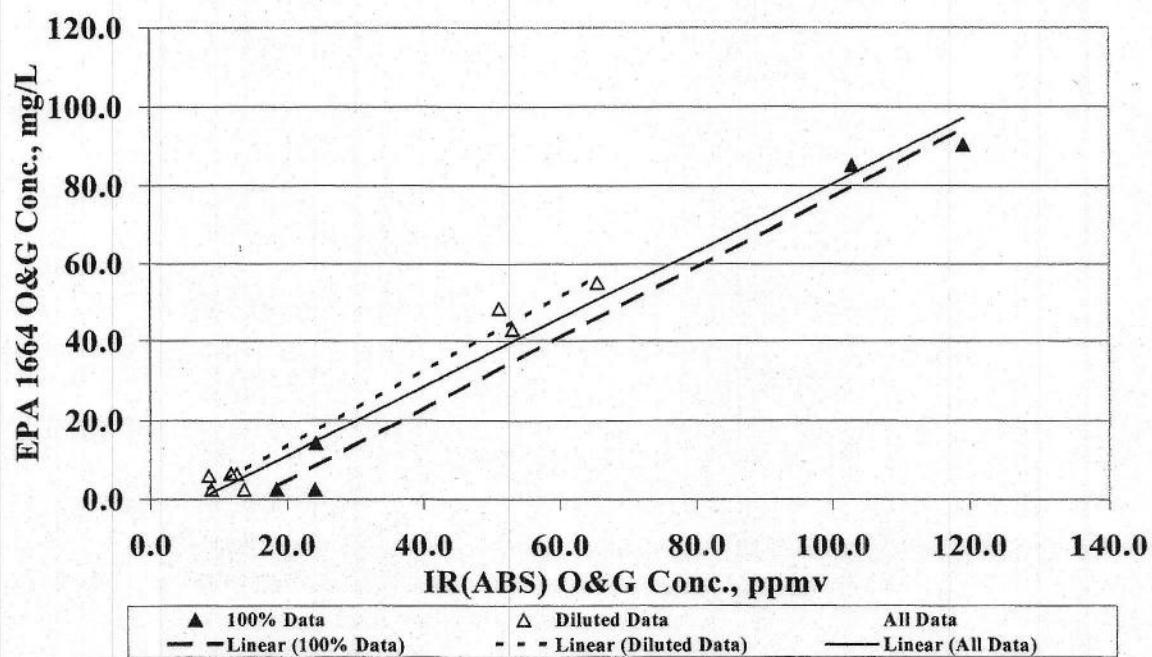


Figure 4.0 Example of IR(ABS) Correlation Problems Caused by Diluting Samples

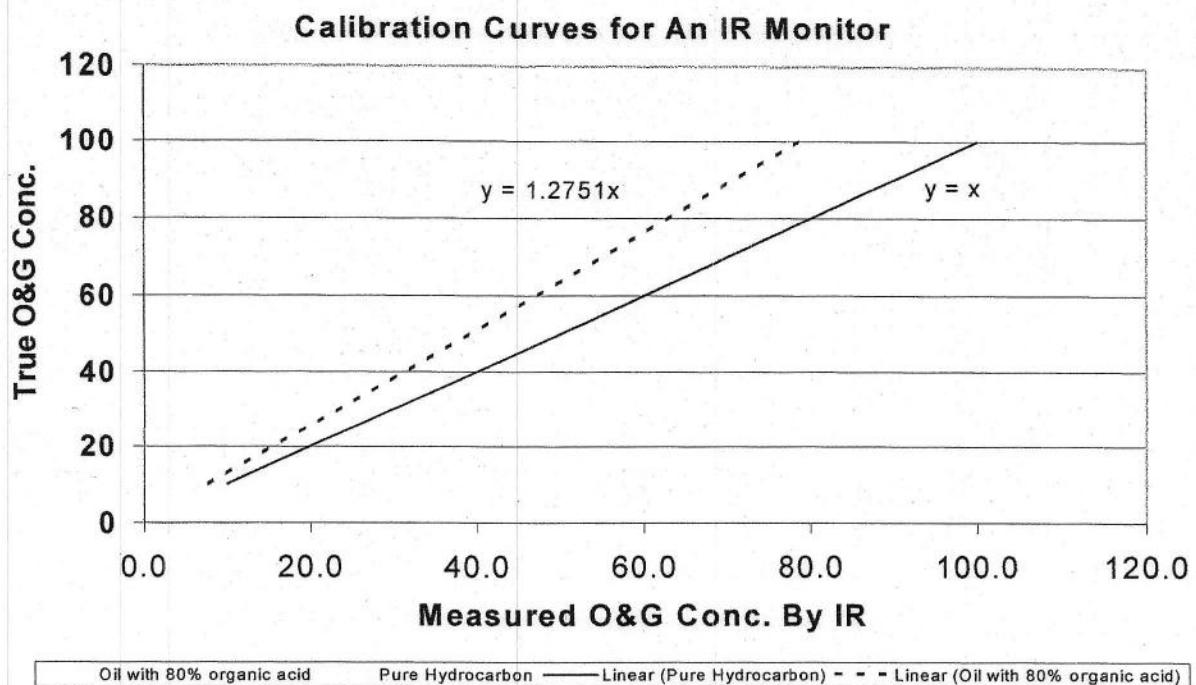


Figure 5.0 Comparison of Calibration Curves for Two Organic Acid Concentrations

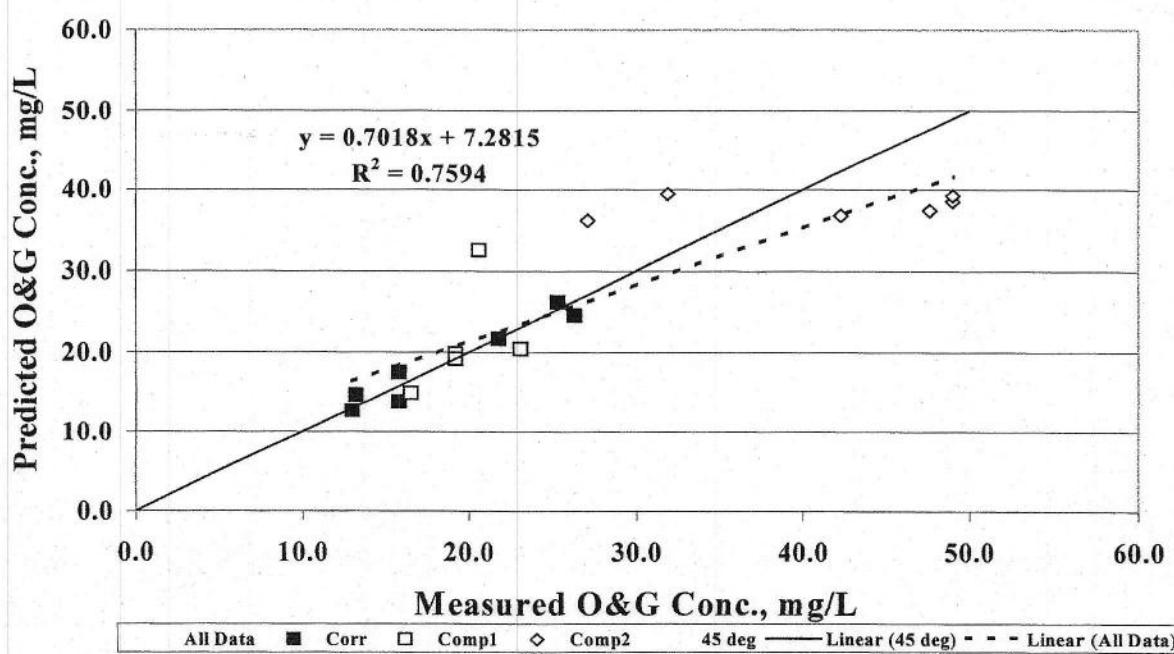


Figure 6.0 Test of Correlation for IR-HATR at Site A

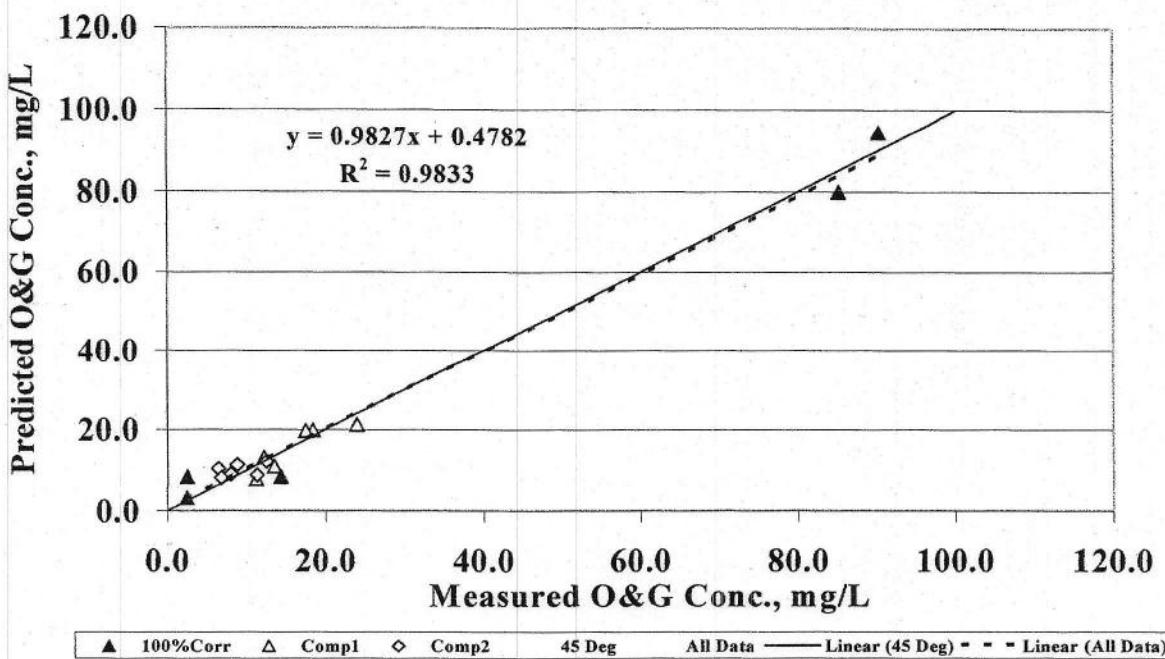


Figure 7.0 Test of Correlation for IR-ABS at Site C (100% Data)

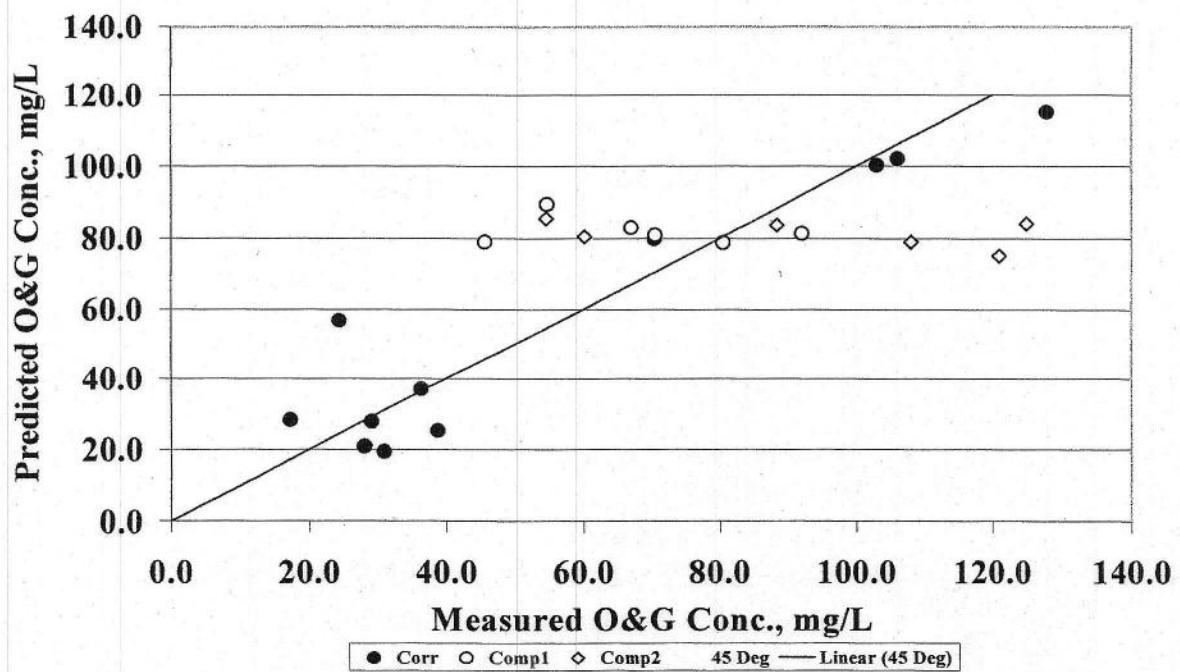


Figure 8.0 Test of Correlation for UVF at Site D

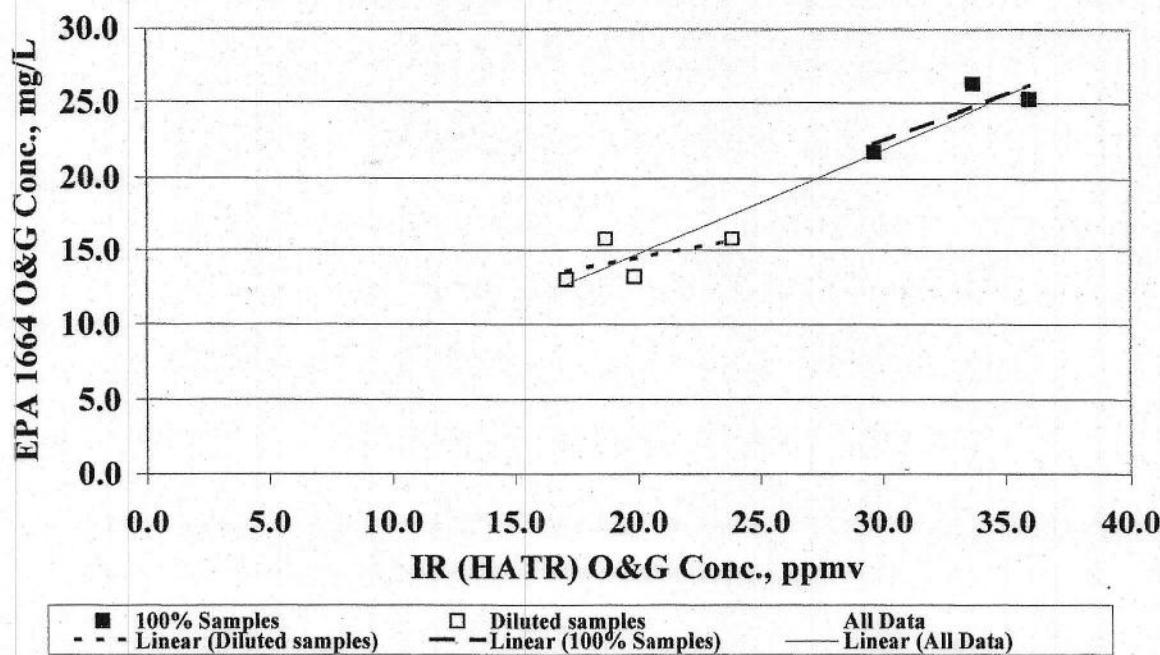


Figure 9.0 Comparison Correlations Using Diluted and 100% Samples For the IR-HATR for Site A