Screening Environmental Samples Using UV-Vis Spectroscopy

Application

Gas Chromatogrphy
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Authors

Chin-Kai Meng
Agilent Technologies, Inc.
Wilmington, DE 19808

Lisa Stafford
Quanterra Environmental Services
Sacramento, CA 95605

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Abstract

Instrument contamination is a continuing problem for laboratories analyzing environmental samples. Many environmental samples have complex matrices that require extensive cleanup to remove background contaminants embedded with the target analytes. Without considerable cleanup, which is time-consuming and costly, laboratories risk contaminating analytical instruments and potentially closing down an instrument for hours or days-reducing productivity. This paper describes initial results in using UV-Visible spectroscopy to identify environmental samples that are likely to cause problems during analysis. This fast (45 seconds per sample), non-interfering technology successfully identified harmful levels of hydrocarbon in samples even when gas chromatograph results showed no significant hydrocarbon present. Moreover, UV-Vis reliably predicted surrogate recovery problems for reasons other than hydrocarbon contamination. Similarly successful results were achieved for samples containing PCBs. UV-Vis is not a universal screening tool, but may be valuable for screening samples with a hydrocarbon matrix.

Introduction

Environmental regulations call for routine analysis of field samples. These samples, such as samples of soil and sludge, typically have complex matrices, with target analytes embedded in the matrix. During routine preparation steps, background contaminants may be extracted along with the target analytes. When this happens, analytical instruments can become contaminated, invalidating subsequent analyses and potentially causing instrument shutdown—for hours or even days.

To avoid such contamination, most laboratories introduce a cleanup step before sample analysis. Samples that have particularly complex matrices, however, may require additional, more exhaustive cleanup, which greatly increases the cost of analysis per sample. Without a way to identify which samples need additional cleanup, laboratories must either perform time-consuming and costly extensive cleanup of all samples or run the risk of contaminating their analytical instruments.

Screening samples before analysis to identify the particular samples that are likely to need additional cleanup can prevent several problems, including:

- **Low surrogate recovery.** Hydrocarbon, prevalent in environmental samples, interferes with GC inlets and columns and causes low detectable surrogate recovery. This occurs at both low and high hydrocarbon levels. When surrogate recovery is below the minimum specified in environmental regulations, the sample must be rerun after additional cleanup.
- **Instrument contamination.** High levels of either target analytes or undesirable matrix components can contaminate analytical instruments. This contamination can be difficult to remove, and often results in instrument shutdown. Severe instrument contamination can cause days of lost productivity.
- **Out-of-calibration results.** Environmental regulations specify the calibration range required to measure levels of target analytes accurately. If the levels of target analytes are too high, they will be above the calibration range and the sample must be diluted and rerun; if too low, the sample must be concentrated and rerun, or a larger sample run. These steps involve time, impeding laboratory productivity.

Currently, most laboratories do not perform any screening. Those that do generally use a dedicated gas chromatograph (GC). This GC does not need calibration because its task merely is to identify samples with target analytes outside of the calibration range or with low surrogate recovery[1,2].

When dedicated GCs are used for screening, the sample flow through the analytical laboratory is not interrupted by instrument contamination problems, but high levels of target analytes or other matrix components may decrease productivity by slowing down the

screening process. Even fast GC methods take several minutes per sample. And dedicated GCs still require inlet maintenance and GC cycle time. Moreover, GCs dedicated to sample screening are themselves susceptible to contamination.

Spectroscopy, which identifies elements by measuring the radiant energy absorbed or emitted by a substance in response to excitation by an external energy source, is nondestructive, avoids the chance of contamination, and is inherently fast. These characteristics make spectroscopy a promising option for screening environmental samples.

Our initial study used UV-Visible spectroscopy, which is more selective than other spectroscopy techniques, to screen environmental samples. This study compares UV-Vis results with dedicated GC results for the same samples. The study:

- Compares UV-Vis analyses of samples with and without matrix contamination effects to determine the reliability of UV-Vis in identifying contaminated samples.
- Examines UV-Vis screening to ascertain if it can identify high matrix levels of hydrocarbon differentially.
- Studies the effectiveness of UV-Vis data in identifying samples with PCBs.

Experimental

The UV-Vis spectroscopy instrument used for this study is an Agilent 8453 system controlled with Agilent's G1116AA Advanced UV-Visible ChemStation software. The 8453 system is automated with an 89068C/D sipper/sampler and an 89072A automatic liquid sampler (ALS).

The typical procedure was as follows. Put 1 to 2 mL of raw sample in a 10-cm culture tube on the ALS. After loading all the samples and wash solvents, enter the sequence into the ChemStation for automation. The sipper draws each sample into the flowcell. After light is passed through the flowcell for a few seconds, the absorbance spectrum is displayed. If desired, the sample in the flowcell can be recovered (80 to 90 percent). Then 4 to 6 mL of solvent is used to flush the sample path to minimize carryover. The whole cycle for each sample takes only 45 seconds to complete.

At the end of the run sequence, a macro (contained in the appendix) makes it easy for the operator to interpret the data or set pass/fail criteria. The macro can also print out a report that states whether the sample passes the screening and the amount of dilution or concentration required to bring the target analytes within the calibration range.

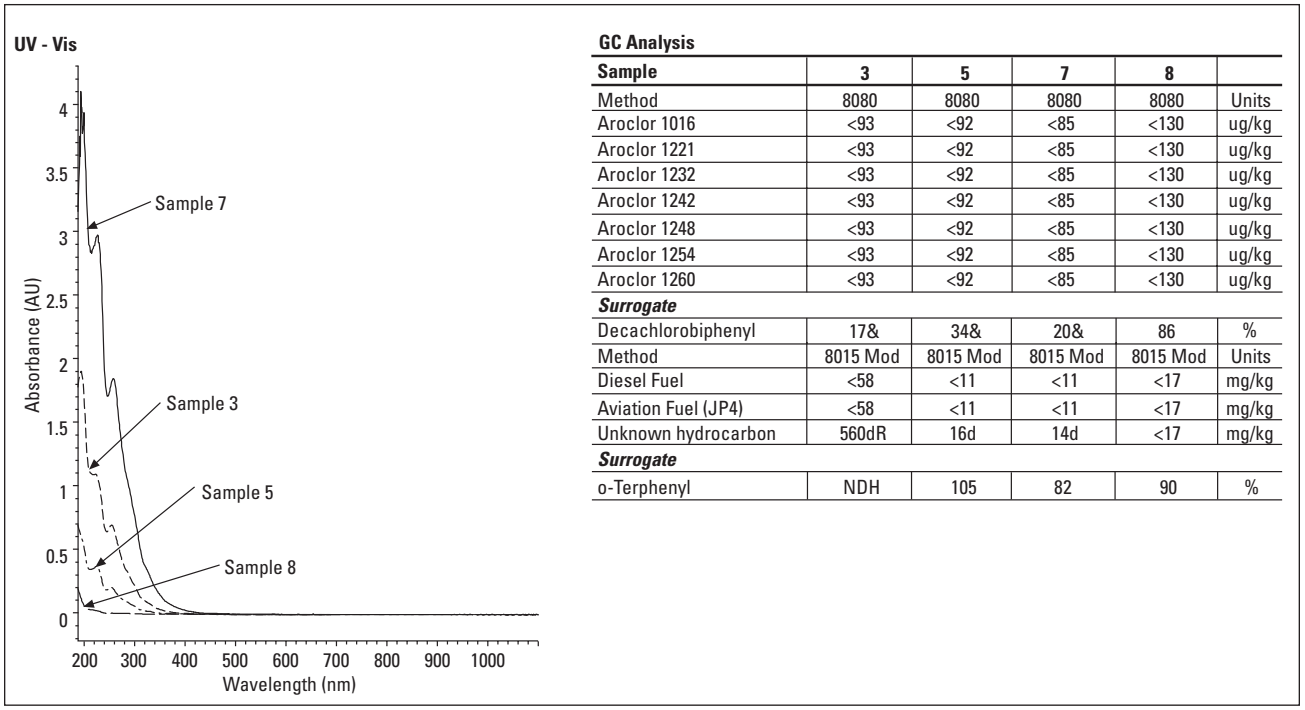
Samples were obtained from Quanterra Environmental Services (Sacramento, CA).

Results and Discussion

UV-Vis spectroscopy is not appropriate as a universal screening tool, but it has potential as a suitable screening tool for environmental samples with complex hydrocarbon matrices.

1. Reliability of UV-Vis in Identifying Contaminated Samples

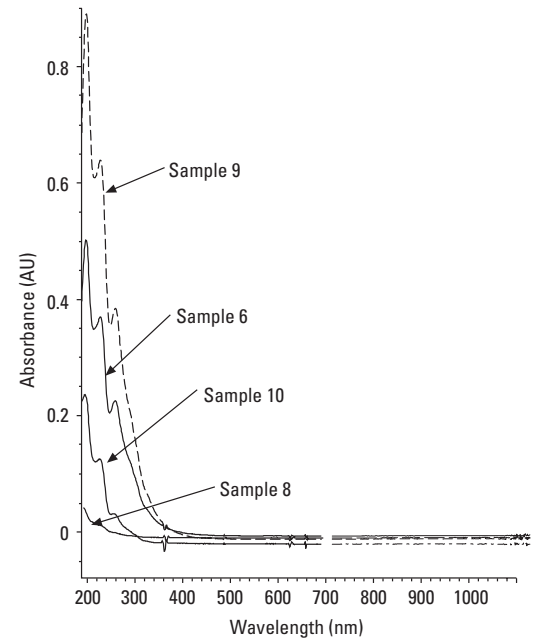
Hydrocarbon extracted with the sample interferes with GC analysis by creating a high level of background noise. The result is low detectable surrogate recovery. Figure 1 shows the UV-Vis screening spectra (on the left) and the GC analysis data for four samples using EPA methods 8080 and 8015. The GC data indicate that only sample 8 shows recovery of Decachlorobi-phenyl, the surrogate, within the limits specified by Method 8080. Method 8015 results



GC Analysis

Sample	3	5	7	8	
Method	8080	8080	8080	8080	Units
Aroclor 1016	<93	<92	<85	<130	ug/kg
Aroclor 1221	<93	<92	<85	<130	ug/kg
Aroclor 1232	<93	<92	<85	<130	ug/kg
Aroclor 1242	<93	<92	<85	<130	ug/kg
Aroclor 1248	<93	<92	<85	<130	ug/kg
Aroclor 1254	<93	<92	<85	<130	ug/kg
Aroclor 1260	<93	<92	<85	<130	ug/kg
Surrogate					
Decachlorobiphenyl	17&	34&	20&	86	%
Method	8015 Mod	8015 Mod	8015 Mod	8015 Mod	Units
Diesel Fuel	<58	<11	<11	<17	mg/kg
Aviation Fuel (JP4)	<58	<11	<11	<17	mg/kg
Unknown hydrocarbon	560dR	16d	14d	<17	mg/kg
Surrogate					
o-Terphenyl	NDH	105	82	90	%

Figure 1. Comparison of GC and UV-Vis Screening Data on Environmental Samples. The UV-Vis spectroscopy results show harmful levels of hydrocarbons while GC results show no significant hydrocarbon present.



GC Analysis

Sample	6	8	9	10	
Method	8080	8080	8080	8080	Units
Aroclor 1016	<92	<140	<87	<92	ug/kg
Aroclor 1221	<92	<140	<87	<92	ug/kg
Aroclor 1232	<92	<140	<87	<92	ug/kg
Aroclor 1242	<92	<140	<87	<92	ug/kg
Aroclor 1248	<92	<140	<87	<92	ug/kg
Aroclor 1254	<92	<140	<87	<92	ug/kg
Aroclor 1260	<92	<140	<87	<92	ug/kg
Surrogate					
Decachlorobiphenyl	23&	78	29&	84	%
Method	8015 Mod	8015 Mod	8015 Mod	8015 Mod	Units
Gasoline	<1.2	<1.7	<1.1	<1.2	mg/kg
Unknown hydrocarbon	<1.2	<1.7	<1.1	<1.2	mg/kg
Surrogate					
4-Bromofluorobenzene	95	84	101	106	%

Figure 2. Comparison of GC and UV-Vis Screening Data with Low Levels of Hydrocarbon. Even low levels of hydrocarbons are detectable with UV-Vis screening.

show unknown hydrocarbon present in the problematic samples. Similarly, the UV-Vis spectra reveal that only sample 8 has a low baseline (revealing high surrogate recovery); the other three samples exhibit various peaks in the wavelength range of 200 to 400 nm, signifying the presence of hydrocarbons. These results indicate that UV-Vis screening can reliably identify the presence of contaminants before the samples are run.

Even extremely low levels of hydrocarbon can interfere with surrogate recovery, as demonstrated in figure 2. Method 8015 results show good surrogate recovery and no significant hydrocarbon present for all four samples. However, in the UV-Vis spectra, there is noticeable absorbance of contaminants from about 0.1 to 0.9 AU in the wavelength range of 200 to 400 nm. This reveals, before analysis, that three samples of the four will cause problems. Only sample 8, with a relatively flat baseline, has an acceptable recovery of the surrogate Decachlorobiphenyl—78 percent—within the limits of Method 8080.

2. Correlations of UV-Vis Screening Data to Hydrocarbon Contamination

A calibration curve of the UV-Vis screening of hydrocarbons, shown in figure 3, was prepared by diluting a sample that contained hydrocarbon (confirmed by Method 8015) from

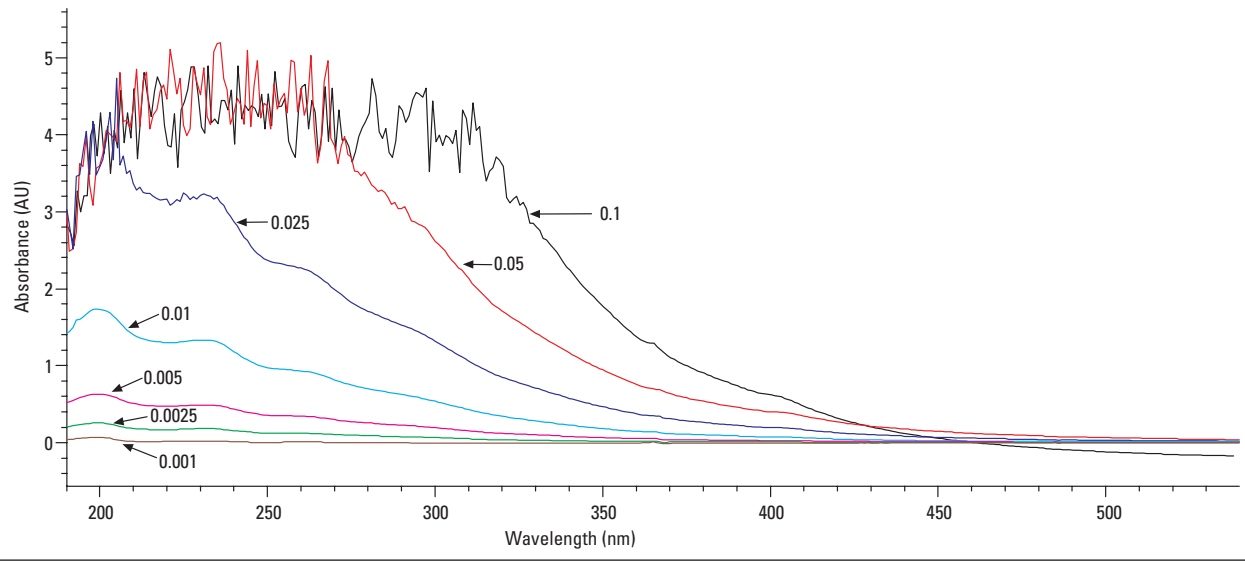


Figure 3. A Dilution Series of a Sample with High Hydrocarbon Content

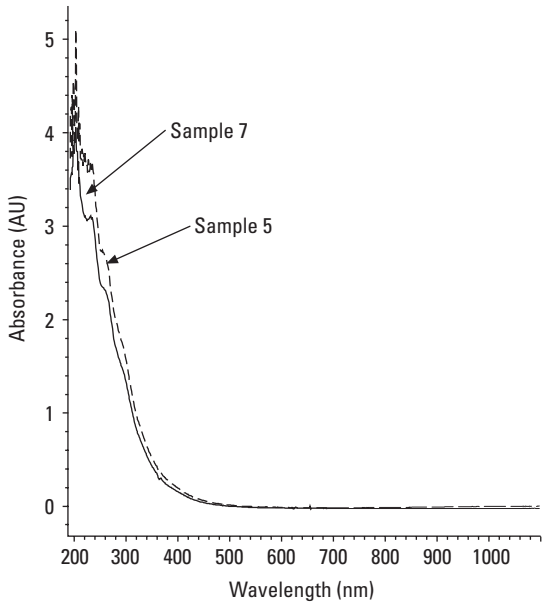
0.001 (a 1,000-to-1 dilution) to 0.1 (a 10-to-1 dilution). Surrogate (Decachlorobiphenyl) recovery was only 24 percent, suggesting hydrocarbon interference. The absorbance decreases with increasing dilution of the sample, demonstrating the close correlation between interference level and absorbance, particularly in the wavelength region from 200 to 500 nm. This result indicates that UV-Vis screening can differentially identify high matrix levels of hydrocarbons.

3. Identification of Samples with PCBs Using UV-Vis Screening

Low surrogate recovery is not always caused by hydrocarbon contamination. Figure 4 does not indicate high hydrocarbon levels, yet the UV-Vis screening data still show high absorbance in the wavelength range of 200 to 400 nm. Similarly, the GC data show that surrogate recovery is very low in the two test samples, even while hydrocarbon levels are low. This indicates that UV-Vis screening can reliably predict surrogate recovery problems for reasons other than hydrocarbon contamination.

If further testing confirms these results, as expected, UV-Vis spectro-scopy may be ideal for field screening. The instrument is small, lightweight, and requires only electricity to operate. It is easier to use in the field than a portable GC. In addition, screening time is only about 45 seconds per sample compared with the minutes required for GC. Moreover, UV-Vis is much faster than immunoassay tests, which typically take about 30 minutes to get results when field screening for PCBs. Also, the reagent set for immunoassay tests is relatively expensive.

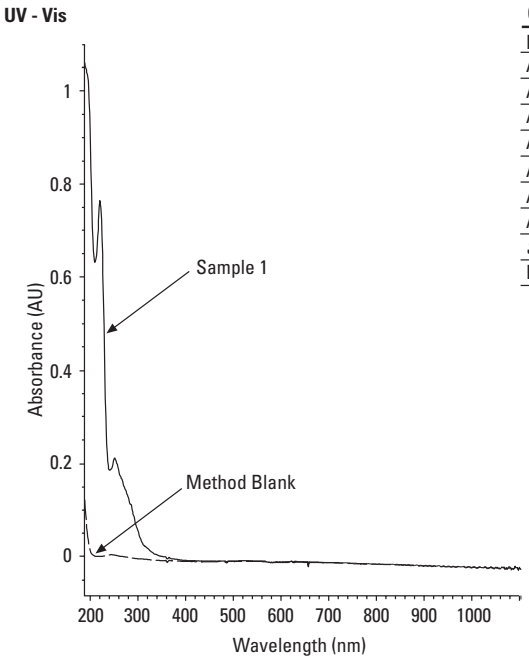
UV - Vis



GC Analysis

Sample	5	7	
Method	8080	8080	Units
Aroclor 1016	<100	<96	ug/kg
Aroclor 1221	<100	<96	ug/kg
Aroclor 1232	<100	<96	ug/kg
Aroclor 1242	<100	<96	ug/kg
Aroclor 1248	<100	<96	ug/kg
Aroclor 1254	<100	<96	ug/kg
Aroclor 1260	<100	<96	ug/kg
Surrogate			
Decachlorobiphenyl	17&	20&	%
Method	8015 Mod	8015 Mod	Units
Gasoline	<1.2	<1.2	mg/kg
Unknown hydrocarbon	<1.2	<1.2	mg/kg
Surrogate			
4-Bromofluorobenzene	54&	58&	%

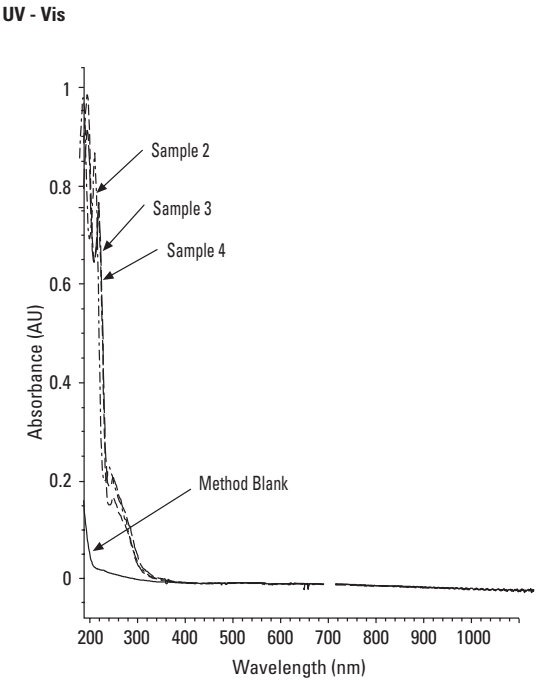
Figure 4. Problematic Samples with Low Surrogate Recovery



GC Analysis

Method	TO-4/SW	Units
Aroclor 1016	2,200	ng/Sample
Aroclor 1221	<300R	ng/Sample
Aroclor 1232	<300R	ng/Sample
Aroclor 1242	<750	ng/Sample
Aroclor 1248	<1,500	ng/Sample
Aroclor 1254	940	ng/Sample
Aroclor 1260	1,700	ng/Sample
Surrogate		
Decachlorobiphenyl	43&	%

Figure 5. Comparison of UV-Vis and GC Screening Data for One Aroclor Sample. PCB Aroclors have a unique UV-Vis spectra, making it easy to identify PCBs using UV-Vis spectroscopy.



GC Analysis

Sample	**2**	**3**	**4**	**Method Blank**	
Method	TO-4/SW	TO-4/SW	TO-4/SW	TO-4/SW	Units
Aroclor 1016	3,000	14,000R	4,400	<750	ng/Sample
Aroclor 1221	<3,000R	<15,000	<4,500R	<750	ng/Sample
Aroclor 1232	<3,000R	<23,000	<4,500R	<750	ng/Sample
Aroclor 1242	<750	<7,600	<750	<750	ng/Sample
Aroclor 1248	<1,000R	<3,800	<3,000R	<750	ng/Sample
Aroclor 1254	1,300	4,700	2,100	<750	ng/Sample
Aroclor 1260	2,200	3,400J	2,900	<750	ng/Sample
Surrogate					
Decachlorobiphenyl	41&	91	41&	93&	%

Figure 6. Comparison of UV-Vis and GC Screening Data Using Three Aroclor Samples and a Method Blank.

To establish the suitability of UV-Vis screening for PCBs, we compared the UV-Vis data to GC data for a group of samples that contains Aroclors. Figure 5 shows the UV-Vis spectrum of one of these samples and a method blank; figure 6 shows results for three of these samples, plus a method blank. The GC data for all samples indicate which Aroclors are present. The UV-Vis results in figure 5 clearly show the presence of each Aroclor in sample 1. The UV-Vis results in figure 6, showing a close overlay of three samples, still reveal the presence of each Aroclor.

Conclusions

Initial results indicate that a UV-Vis spectrometer can be a reliable, easily portable tool for screening environmental samples quickly and accurately. Fast identification of samples that are likely to cause problems during analysis can save laboratories from costly rework, increase laboratory productivity, and avoid instrument contamination. Identification of contamination before analysis enables the chemist to treat these samples with a dilution or cleanup step, or at least to rearrange samples in the sample queue to minimize the impact of contamination.

The extremely fast turnaround time (less than 1 minute per sample, including sample path solvent washing) and ease of data interpretation using the macro described in the appendix further recommend UV-Vis as a screening tool for environmental samples, either in the laboratory or in the field.

References

1. Stafford, Lisa, "Screening Environmental Compounds of Interest to Eliminate Contamination and Rework," American Environmental Laboratory, May 1997, issue cover.

2. Meng, Chin-Kai, and Stafford, Lisa, "Improving Environmental Laboratory Efficiency by Screening Extractables," Hewlett-Packard Application Note 228-360, publication number (23) 5965-1437E, 1996.

Appendix

```
PASSFAIL. MAC
Name PASSFAIL
Local i, value1, value2, name$, endoftable
opendevice “printer” as #5
endoftable = regsize (Eval_results_1)          ! number of samples
for i = 1 to endoftable                        ! info of each sample
        name$ = ObjhdrText$ (Eval_results_1 [i], Samplename)
! value1, 2, and 3 are the absorbencies at three specified
! wavelengths in the ChemStation method.
        value1 = TabVal (Eval_Results_1 [i], AnalyteTable, 1, Value)
        value2 = TabVal (Eval_Results_1 [i], AnalyteTable, 2, Value)
        value3 = TabVal (Eval_Results_1 [i], AnalyteTable, 3, Value)
! specify the pass/fail criteria in the next Boolean statement
                IF (value < 20) AND (ABS (value3) < 0.05) then
                        P_F$ = “PASS”
                ELSE
                        P_F$ = “FAIL”
                ENDIF
        Print #5, name$, value1, value2, value3, P_F$
next I
close #5 Endmacro
```

Example: a sequence using the ratio of two wavelengths as the pass/fail criteria.

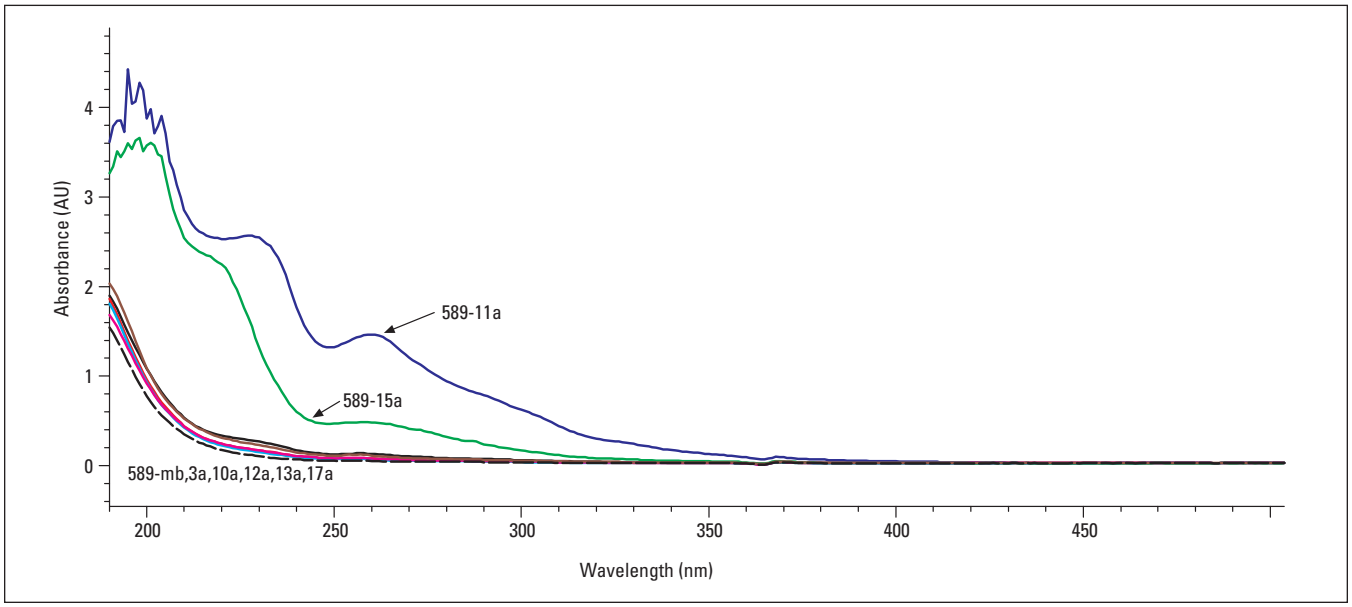
The pass/fail criteria in the above macro would be:
ratio = (ABS (value1) / ABS (value2))
IF ratio < 50 then
where value1 is absorbence at 200 nm and value2 is the absorbence at 400 nm. Other wavelengths can also be selected.

Using print #5, name$, value1, value2, ratio, P_F$, the report would look like this, reformatted for clarity.

589-mb	0.77545	0.0028047	27.649	PASS
589-11a	3.8744	0.0047077	82.299	FAIL
589-15a	3.5748	0.003048	117.28	FAIL
589-3a	1.0819	0.0028686	37.717	PASS
589-10a	0.96139	0.0029754	32.312	PASS
589-12a	0.92955	0.0027837	33.393	PASS
589-13a	0.91638	0.0030437	30.107	PASS
589-17a	1.0913	0.0033216	32.853	PASS

The overlaid spectra of the above samples are in the following figure. For this set of samples, it is clear that, without looking at the final report, samples 11 and 15 are “out of spec” (showing high hydrocarbon content). The pass/fail criterion and the macro report can help to minimize human error and to make solid decisions about which samples to preclean.

UV-Vis Spectra for the Macro Example



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