UV Quality Assurance

This document presents the Quality Assurance protocol used for the measurement of broad spectrum UV spectra according to the guidelines given by the United States Environmental Protection Agency and other agencies that certify the calibration, operation and maintenance of broadband spectroscopy related to the sampling of the atmosphere. Currently there are no EPA guidance documents for available that specifically address Quality Assurance (QA) for broadband UV spectroscopy. But because these systems operate in a similar manner as infrared air monitoring systems, we can borrow from the vast array of QA documentation that has been established for the air monitors. Specifically this document uses the EPA's TO-16 Guidance Document for Op-FTIR Air Monitoring as its primary source for QA procedures. The following items are recommended as part of the standard operations document for the UV Sentry product line:

Dark current correction check

Determination of root mean square (RMS) noise

Spectral feature match check

Field QA with a UV lollipop

Each of these items is discussed below. In addition, the field sheets for the March 2005 calibration of the North and South Fenceline Systems are presented.

Dark Current Correction

Charged diode array spectrometers will build up a charge over time that is independent the actual light being detected. This charge buildup is defined as dark current and must be subtracted from each single beam spectra, before data analysis can occur. Although the system can be setup in a manner where the dark current is measured and then manually subtracted out of each individual spectra, the CEREX UVS software performs this task automatically. To determine if the CEREX UVS software is performing this function adequately, the user needs to examine the first 15 pixels of a single beam spectra. The average for these pixels should fall with ± 20 counts. Dark current is shown in the bracketed rows of Figure 1.

Figure 1

Dark Current

	A	B	C
1	UVS File F	2	
2	Site	South Park #1a	
3	Pathlength	72	
4	File Count	9935	
5	Integration	600	
6	Averages	100	
7	Date	11/24/2004 8:37:51 AM	
8	Operator	Walter	
9	Reference	South Park #1a-9933	
10	Signal Stre	2476.594248	
11	Reference	11/24/2004 8:29:00 AM	
12			
13			
14	176.11	0	
15	176.1851	0	
16	176.2603	-4.595752869	
17	176.3354	-6.910064392	
18	176.4106	-2.425752869	
19	176.4857	-4.460064392	
20	176.5608	-0.145752869	
21	176.636	2.379935608	
22	176.7111	3.834247131	
23	176.7862	14.09993561	
24	176.8613	5.064247131	
25	176.9364	2.259935608	
26	177.0116	5.364247131	
27	177.0867	6.019935608	
28	177.1618	5.274247131	

Root Mean Square (RMS) Noise

RMS noise is used to determine the inherent noise of the system. This is an important QA element as it determines the detection limits for the gases of interest. The procedure to measure RMS noise is to collect two successive single beam spectra. The spectra should simulate the standard field setup including the following:

- A typical path length for the equipment (100m, 200 m etc.)

- A typical integration time for the data collection

- A typical sample time for each spectra

Three sample regions should be selected that incorporate the regions where spectral absorption occurs. Each of these regions should include 100 data points. The following procedure should then be followed:

- Open both spectral files in Microsoft Excel™.

- Copy data from one of the files into the other file.

- In Microsoft Excel™, run the regression function, make sure that the software has the Residual Function enabled.

- Run the regression analysis

Results similar to those at right will appear:

	A	B	C
22	RESIDUAL OUTPUT		
23			
24	*Observation*	*Predicted Y*	*Residuals*
25	1	200.5070065	0.415793521
26	2	204.737158	-0.479357984
27	3	207.942696	0.421604046
28	4	211.5949426	-0.134442574
29	5	210.9224241	0.549975944
30	6	214.7462581	0.164741887
31	7	214.2362064	0.637093562
32	8	219.3287051	-0.088905087
33	9	218.0421	0.642000014
34	10	218.5747026	0.034497419
35	11	217.8614922	-0.078292181
36	12	222.6243466	0.155953493
37	13	229.3559462	0.202053822
38	14	229.7937347	-0.396234686
39	15	230.7509961	-1.044396142
40	16	235.6086646	-0.535564554
41	17	238.2589488	-0.354148785
42	18	246.8186763	-0.227476292
43	19	243.3560578	-0.153957844
44	20	245.811903	-0.32440304
45	21	244.6968854	0.266414623
46	22	248.3085403	0.791659658
47	23	248.5795523	0.343247724
48	24	251.3649416	-0.035041568
49	25	253.1484687	-1.104068698

Once the residuals have been generated, they should be copied into the cell next to the actual values. To calculate the RMS values use the following formula

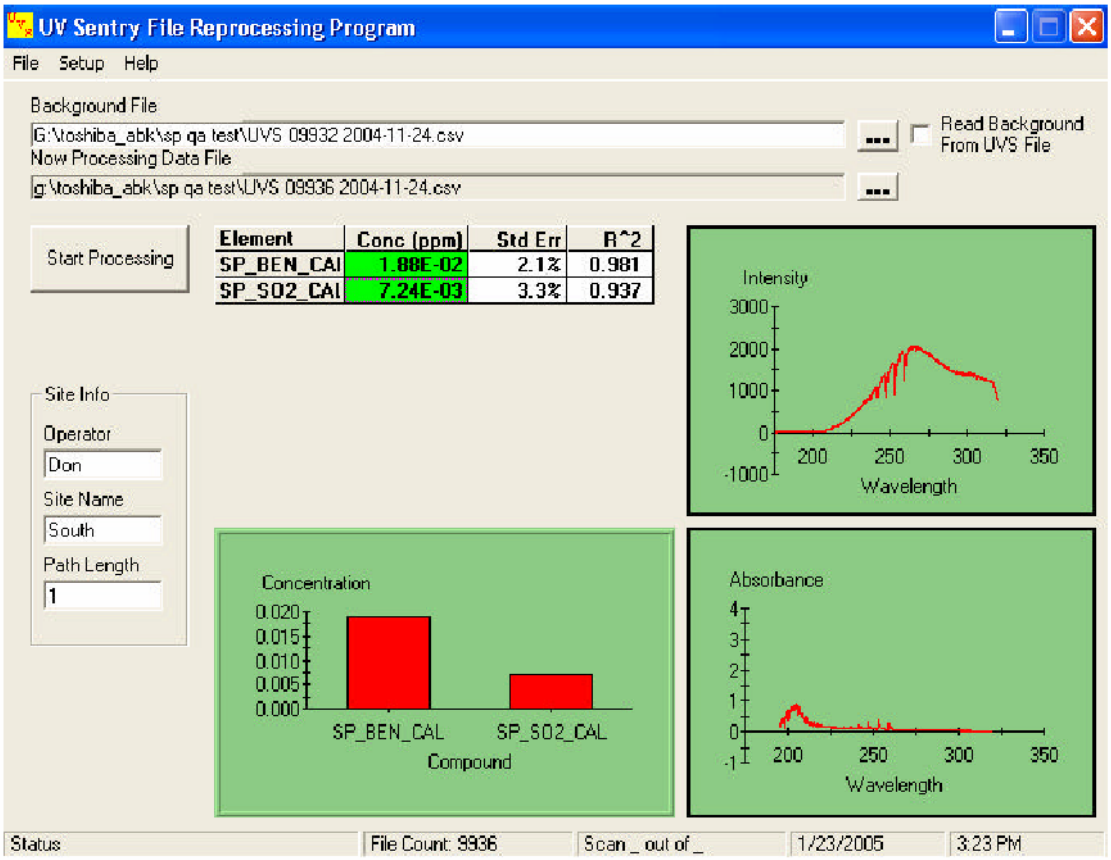
$$\{\text{sum}[(X_{actual} - X_{predicted})^2]\}^{.5}/(N-2)$$

with N being the number of points being sampled.

This analysis should be perform in three regions of the UV spectra. For a system with a xenon source, the regions should be near 240, 270, and 300 nanometers.

Match Spectral Features

Typically a CEREX UV Air monitoring systems comes with a QA standard that contains benzene and SO2 gas. There is also a set of special QA reference spectra that are matched to the spectrometer. When loaded into the continuous monitoring software the results should include a quantity of .90 to 1.1 for each of these gases with a correlation coefficient greater than 0.90. The QA reference spectra are denoted by the letters QA in their name. For example the file Benzene_Ref_QA.txt, is the QA reference check for Benzene gas.



Perform Field Calibration with UV Lollipop

The UV lollipops can be either filled with a known quantity of gas, or the Benzene/SO2 QA cells can be used a field check. TO-16 suggests that field QA be performed for at least one compound of interest. The second gas can be a gas that is a good UV absorber (does not necessarily need to be a target analyte. In the event that the monitoring program is going to involve the measurement of ambient gases, CEREX suggests that SO2 be included in the target analyte list. The reason for this is there are an abundant number of sources of SO2 in the ambient air and the system will pick up the sources easily. The second reason SO2 is a recommended target analyte is the CEREX QA lollipop can then be used to QA check that meets the TO-16 criteria of having one target analyte in the QA sample. In addition CEREX provides refillable QA cells that can be used for site specific gas analysis.

QA Field Sheet

Unit # Conoco South

Dark Current Correction

Dark Current Correction: Enabled

Sample Spectra Name: QA_March_1

Collection Time and Date: 03/16/2005 10:15 am

Average of first 15 cells: 1.22 (Range of Average between –10 and 10)

RMS Noise:

Collection Time and Date: 03/16/2005 10:15 am

Sample Spectra Name #1: QA_March_1

Sample Spectra Name #2: QA_March_2

Absorbance Spectra Name: ABS_March_2

		RMS Noise
Region of Interest	240-247 nm	0.000243
	270 – 277 nm	0.000189
	300-307 nm	0.000326

Spectra Matching:

Calibration Cell # Conoco UVS #1

Collection Time and Date: 03/16/2005 10:15 am

Background Spectra: Back_qa_1

Data Spectra: Data_qa_1

Target Gas: SO2

R-Square: 0.93 (<.90)

Target Gas: Benzene

R-Square: 0.96 (<.90)

Calibration Check:

Calibration Cell # Conoco UVS #1

Collection Time and Date: 03/16/2005 10:15 am

Background Spectra: Back_qa_1

Data Spectra: Data_qa_1

Target Gas: SO2

R-Square: 0.94 (Target Range 1.10 to 0.90)

Target Gas: Benzene

R-Square: 01.01 (Target Range 1.10 to 0.90)

QA Field Sheet

Unit # Conoco North

Dark Current Correction

Dark Current Correction: Enabled

Sample Spectra Name: QA_March_1

Collection Time and Date: 03/16/2005 2:15 pm

Average of first 15 cells: 2.586867 (Range of Average between –10 and 10)

RMS Noise:

Collection Time and Date: 03/16/2005 2:15 pm

Sample Spectra Name #1: QA_March_1

Sample Spectra Name #2: QA_March_2

Absorbance Spectra Name: ABS_March_2

		RMS Noise
Region of Interest	240-247 nm	0.004145
	270 – 277 nm	0.001499
	300-307 nm	0.000936

Spectra Matching:

Calibration Cell # Conoco UVS #1

Collection Time and Date: 03/16/2005 2:15 pm

Background Spectra: Back_qa_1

Data Spectra: Data_qa_1

Target Gas: SO2

R-Square: 0.64 (<.90)

Target Gas: Benzene

R-Square: 0.98 (<.90)

Calibration Check:

Calibration Cell # Conoco UVS #1

Collection Time and Date: 03/16/2005 10:15 am

Background Spectra: Back_qa_1

Data Spectra: Data_qa_1

Target Gas: SO2

R-Square: 0.927 Target Range (1.10 to 0.90)

Target Gas: Benzene

R-Square: 0.98 Target Range (1.1 to 0.90)