North Carolina Division of Air Quality

Quality Assurance Project Plan

2.51 Volatile Organic Compounds (VOCs) by TO-15

Section 4.1

Raleigh Central Office Responsibilities

Standard Operating Procedure for Performing a QA Review of a VOC Data Batch

Version 2015

Submitted by:
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Approval Sign-Off Sheet

I certify that I have read and approve of the contents of this revision of this SOP with an effective date of 7/31/15.

John Holland 7/23/15
John Holland, UAT Quality Assurance Coordinator Date

Joette Steger 8/11/2015
Joette Steger, PPB Supervisor Date

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Jim Bowyer for Donald Redmond 8/12/15
Donald D. Redmond, Jr., Ambient Monitoring Section Chief Date

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2.51.4.1 Standard Operating Procedure for Performing a QA Review of a VOC Data Run

2.51.4.1.1 Purpose: The purpose of this SOP is to describe the steps needed to review the VOC analysis data from the GC/MS laboratory before it is transferred to the master VOC spreadsheet.

2.51.4.1.2 Equipment Description: PC connected to the network drive group on 'air.ncdenr.net\dfs' – usually mapped to drive letter P.

2.51.4.1.3 Directions for reviewing the VOC data from the GC/MS laboratory:

2.51.4.1.3.1 Open the file folder and check that all the documents on the list below are there. The check list (VOC Data QA Checklist) at the end of this SOP may be used to document this step.

- QA/QC spreadsheet print out and file(s) e-mailed from the VOC Laboratory Analyst
- Leak Check Report
- Sample List Printout
- BFB 524.2 Report
- Calibration Curves Report, may be in a different folder
- Calibration Block Report, may be in a different folder
- VOC Sample Reports in chronological order

2.51.4.1.3.2 Check the dates (the "Acquisition Date" on the VOC Sample Reports) and make sure that all the reports are in chronological order. If there are any missing time periods, check the Sample List Printout and ask the VOC Laboratory Analyst. Each VOC Sample Report (one chromatographic run) should take about 50 minutes and be on 3 pages. The third page may be in a separate group of pages.

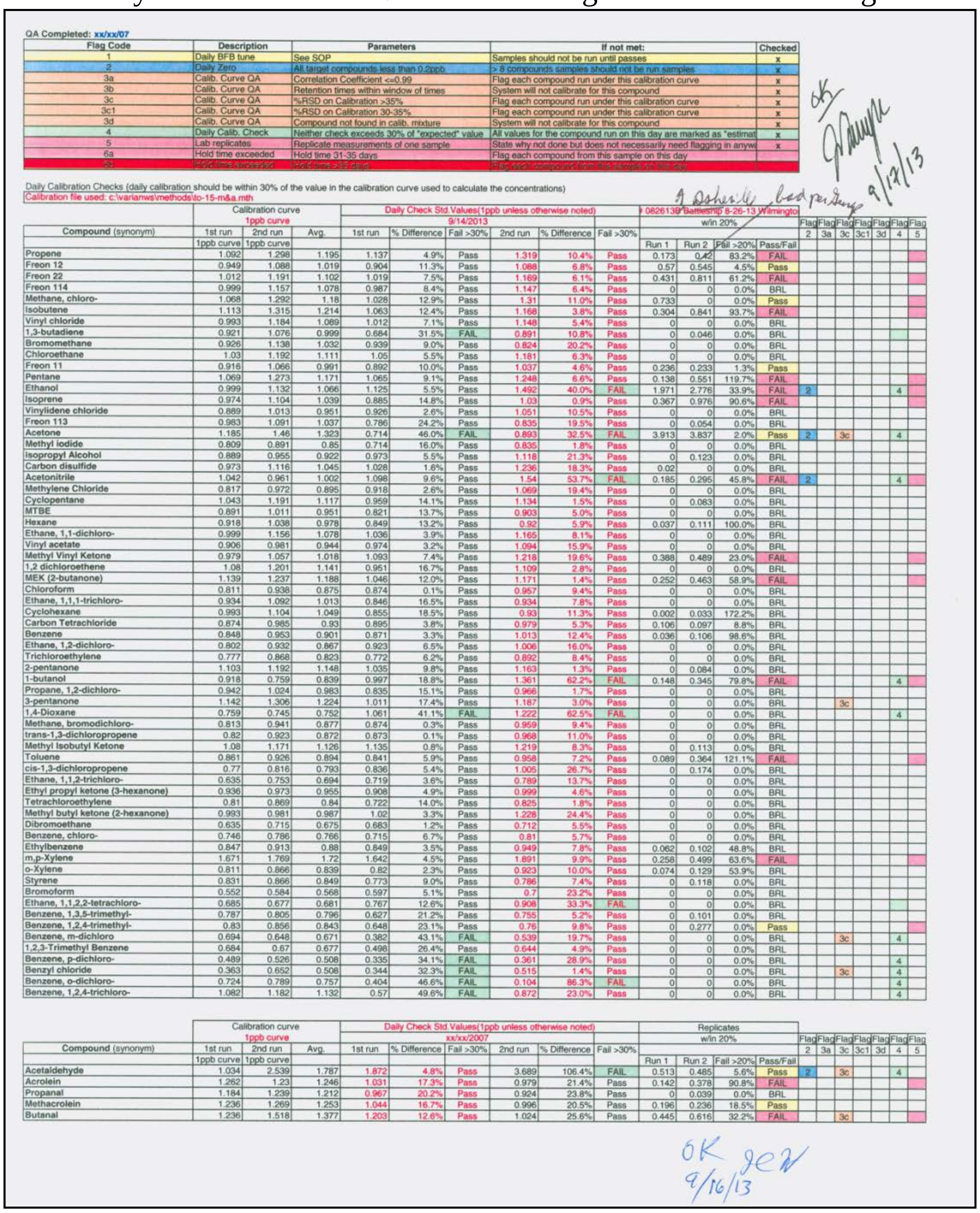
2.51.4.1.3.3 Check that the BFB 524.2 Report shows all values "PASS" and that the Leak Check Report shows all inlets end with 0.2 or less for the Entech-Varian system or no fail comments for the Markes-Agilent system. If one or more inlets fail, there may be a subsequent report showing that those leaking have passed.

2.51.4.1.3.4 If there are two QA/QC spreadsheets, combine them into one (see Figure 1). On the QA/QC spreadsheet (see Figure 1) note all the flagged compounds. If a compound of interest like benzene or toluene is flagged, check the details of that flag and void it if possible. For example, if benzene has a flag 3c1 and in checking the calibration data, which may be in a different folder, the r^2 value is 0.9985 and the %RSD is 30.1%, void the 3c1 flag (delete the flag from the QA/QC spreadsheet).

2.51.4.1.3.5 Match the Daily Check Std. Values for the 1st and 2nd runs with the actual VOC Sample Reports and write the date and time of each run on the VOC Data QA Checklist. The first run should be before any samples are run and the second run should be after all samples have been run. These VOC Sample Reports will

be labeled in the “Inj. Notes:” as “1 ppb TO-15 check standard.” There should be two such VOC Sample Reports at the beginning of the batch and two at the end. Mark the specific VOC Sample Reports that were used to perform the QA/QC check as 1st and 2nd. If there are many flag 4’s or a flag 4 for a compound of interest like benzene or toluene, see if using a different 1ppb check standard would improve the results so that we can remove one or more flags. Also, you can try comparing the 1st and 2nd runs with each other; if that produces a good result, you may consider removing a flag 4.

2.51.4.1.3.6 Following (or just before) the initial check standards there should be at least one blank or zero air sample run. There may be other zero air samples run at the end or anywhere in the batch. Check it for agreement with the Flag 2 criteria.



QA Completed: xx/xx/07

Flag Code	Description	Parameters	If not met:	Checked
1	Daily BFB tune	See SOP	Samples should not be run until passes	x
2	Daily Zero	All target compounds less than 0.2ppb	> 8 compounds samples should not be run samples	x
3a	Calib. Curve QA	Correlation Coefficient <=0.99	Flag each compound run under this calibration curve	x
3b	Calib. Curve QA	Retention times within window of times	System will not calibrate for this compound	x
3c	Calib. Curve QA	%RSD on Calibration >35%	Flag each compound run under this calibration curve	x
3c1	Calib. Curve QA	%RSD on Calibration 30-35%	Flag each compound run under this calibration curve	x
3d	Calib. Curve QA	Compound not found in calib. mixture	System will not calibrate for this compound	x
4	Daily Calib. Check	Neither check exceeds 30% of "expected" value	All values for the compound run on this day are marked as "estimat	x
5	Lab replicates	Replicate measurements of one sample	State why not done but does not necessarily need flagging in anyw	x
6a	Hold time exceeded	Hold time 31-35 days	Flag each compound from this sample on this day	
6b	Hold time exceeded	Hold time >35 days	Flag each compound from this sample on this day	

ok
9/17/13

Daily Calibration Checks (daily calibration should be within 30% of the value in the calibration curve used to calculate the concentrations)
Calibration file used: c:\varianws\methods\to-15-m&a.mth

Compound (synonym)	Calibration curve 1ppb curve: 1st run 1ppb curve	2nd run 1ppb curve	Avg.	Daily Check Std.Values(1ppb unless otherwise noted) 9/14/2013: 1st run	% Difference	Fail >30%	2nd run	% Difference	Fail >30%	# 082613B Battleship 8-26-13 Wilmingto w/in 20%: Run 1	Run 2	Fail >20%	Pass/Fail	Flag 2	Flag 3a	Flag 3c	Flag 3c1	Flag 3d	Flag 4	Flag 5
Propene	1.092	1.298	1.195	1.137	4.9%	Pass	1.319	10.4%	Pass	0.173	0.42	83.2%	FAIL							
Freon 12	0.949	1.088	1.019	0.904	11.3%	Pass	1.088	6.8%	Pass	0.57	0.545	4.5%	Pass							
Freon 22	1.012	1.191	1.102	1.019	7.5%	Pass	1.169	6.1%	Pass	0.431	0.811	61.2%	FAIL							
Freon 114	0.999	1.157	1.078	0.987	8.4%	Pass	1.147	6.4%	Pass	0	0	0.0%	BRL							
Methane, chloro-	1.068	1.292	1.18	1.028	12.9%	Pass	1.31	11.0%	Pass	0.733	0	0.0%	Pass							
Isobutene	1.113	1.315	1.214	1.063	12.4%	Pass	1.168	3.8%	Pass	0.304	0.841	93.7%	FAIL							
Vinyl chloride	0.993	1.184	1.089	1.012	7.1%	Pass	1.148	5.4%	Pass	0	0	0.0%	BRL							
1,3-butadiene	0.921	1.076	0.999	0.684	31.5%	FAIL	0.891	10.8%	Pass	0	0.046	0.0%	BRL							
Bromomethane	0.926	1.138	1.032	0.939	9.0%	Pass	0.824	20.2%	Pass	0	0	0.0%	BRL							
Chloroethane	1.03	1.192	1.111	1.05	5.5%	Pass	1.181	6.3%	Pass	0	0	0.0%	BRL							
Freon 11	0.916	1.066	0.991	0.892	10.0%	Pass	1.037	4.6%	Pass	0.236	0.233	1.3%	Pass							
Pentane	1.069	1.273	1.171	1.065	9.1%	Pass	1.248	6.6%	Pass	0.138	0.551	119.7%	FAIL							
Ethanol	0.999	1.132	1.066	1.125	5.5%	Pass	1.492	40.0%	FAIL	1.971	2.776	33.9%	FAIL	2					4	
Isoprene	0.974	1.104	1.039	0.885	14.8%	Pass	1.03	0.9%	Pass	0.367	0.976	90.6%	FAIL							
Vinylidene chloride	0.889	1.013	0.951	0.926	2.6%	Pass	1.051	10.5%	Pass	0	0	0.0%	BRL							
Freon 113	0.983	1.091	1.037	0.786	24.2%	Pass	0.835	19.5%	Pass	0	0.054	0.0%	BRL							
Acetone	1.185	1.46	1.323	0.714	46.0%	FAIL	0.893	32.5%	FAIL	3.913	3.837	2.0%	Pass	2		3c			4	
Methyl iodide	0.809	0.891	0.85	0.714	16.0%	Pass	0.835	1.8%	Pass	0	0	0.0%	BRL							
Isopropyl Alcohol	0.889	0.955	0.922	0.973	5.5%	Pass	1.118	21.3%	Pass	0	0.123	0.0%	BRL							
Carbon disulfide	0.973	1.116	1.045	1.028	1.6%	Pass	1.236	18.3%	Pass	0.02	0	0.0%	BRL							
Acetonitrile	1.042	0.961	1.002	1.098	9.6%	Pass	1.54	53.7%	FAIL	0.185	0.295	45.8%	FAIL	2					4	
Methylene Chloride	0.817	0.972	0.895	0.918	2.6%	Pass	1.069	19.4%	Pass	0	0	0.0%	BRL							
Cyclopentane	1.043	1.191	1.117	0.959	14.1%	Pass	1.134	1.5%	Pass	0	0.083	0.0%	BRL							
MTBE	0.891	1.011	0.951	0.821	13.7%	Pass	0.903	5.0%	Pass	0	0	0.0%	BRL							
Hexane	0.918	1.038	0.978	0.849	13.2%	Pass	0.92	5.9%	Pass	0.037	0.111	100.0%	BRL							
Ethane, 1,1-dichloro-	0.999	1.156	1.078	1.036	3.9%	Pass	1.165	8.1%	Pass	0	0	0.0%	BRL							
Vinyl acetate	0.906	0.981	0.944	0.974	3.2%	Pass	1.094	15.9%	Pass	0	0	0.0%	BRL							
Methyl Vinyl Ketone	0.979	1.057	1.018	1.093	7.4%	Pass	1.218	19.6%	Pass	0.388	0.489	23.0%	FAIL							
1,2 dichloroethene	1.08	1.201	1.141	0.951	16.7%	Pass	1.109	2.8%	Pass	0	0	0.0%	BRL							
MEK (2-butanone)	1.139	1.237	1.188	1.046	12.0%	Pass	1.171	1.4%	Pass	0.252	0.463	58.9%	FAIL							
Chloroform	0.811	0.938	0.875	0.874	0.1%	Pass	0.957	9.4%	Pass	0	0	0.0%	BRL							
Ethane, 1,1,1-trichloro-	0.934	1.092	1.013	0.846	16.5%	Pass	0.934	7.8%	Pass	0	0	0.0%	BRL							
Cyclohexane	0.993	1.104	1.049	0.855	18.5%	Pass	0.93	11.3%	Pass	0.002	0.033	172.2%	BRL							
Carbon Tetrachloride	0.874	0.985	0.93	0.895	3.8%	Pass	0.979	5.3%	Pass	0.106	0.097	8.8%	BRL							
Benzene	0.848	0.953	0.901	0.871	3.3%	Pass	1.013	12.4%	Pass	0.036	0.106	98.6%	BRL							
Ethane, 1,2-dichloro-	0.802	0.932	0.867	0.923	6.5%	Pass	1.006	16.0%	Pass	0	0	0.0%	BRL							
Trichloroethylene	0.777	0.868	0.823	0.772	6.2%	Pass	0.892	8.4%	Pass	0	0	0.0%	BRL							
2-pentanone	1.103	1.192	1.148	1.035	9.8%	Pass	1.163	1.3%	Pass	0	0.084	0.0%	BRL							
1-butanol	0.918	0.759	0.839	0.997	18.8%	Pass	1.361	62.2%	FAIL	0.148	0.345	79.8%	FAIL						4	
Propane, 1,2-dichloro-	0.942	1.024	0.983	0.835	15.1%	Pass	0.966	1.7%	Pass	0	0	0.0%	BRL							
3-pentanone	1.142	1.306	1.224	1.011	17.4%	Pass	1.187	3.0%	Pass	0	0	0.0%	BRL			3c				
1,4-Dioxane	0.759	0.745	0.752	1.061	41.1%	FAIL	1.222	62.5%	FAIL	0	0	0.0%	BRL						4	
Methane, bromodichloro-	0.813	0.941	0.877	0.874	0.3%	Pass	0.959	9.4%	Pass	0	0	0.0%	BRL							
trans-1,3-dichloropropene	0.82	0.923	0.872	0.873	0.1%	Pass	0.968	11.0%	Pass	0	0	0.0%	BRL							
Methyl Isobutyl Ketone	1.08	1.171	1.126	1.135	0.8%	Pass	1.219	8.3%	Pass	0	0.113	0.0%	BRL							
Toluene	0.861	0.926	0.894	0.841	5.9%	Pass	0.958	7.2%	Pass	0.089	0.364	121.1%	FAIL							
cis-1,3-dichloropropene	0.77	0.816	0.793	0.836	5.4%	Pass	1.005	26.7%	Pass	0	0.174	0.0%	BRL							
Ethane, 1,1,2-trichloro-	0.635	0.753	0.694	0.719	3.6%	Pass	0.789	13.7%	Pass	0	0	0.0%	BRL							
Ethyl propyl ketone (3-hexanone)	0.936	0.973	0.955	0.908	4.9%	Pass	0.999	4.6%	Pass	0	0	0.0%	BRL							
Tetrachloroethylene	0.81	0.869	0.84	0.722	14.0%	Pass	0.825	1.8%	Pass	0	0	0.0%	BRL							
Methyl butyl ketone (2-hexanone)	0.993	0.981	0.987	1.02	3.3%	Pass	1.228	24.4%	Pass	0	0	0.0%	BRL							
Dibromoethane	0.635	0.715	0.675	0.683	1.2%	Pass	0.712	5.5%	Pass	0	0	0.0%	BRL							
Benzene, chloro-	0.746	0.786	0.766	0.715	6.7%	Pass	0.81	5.7%	Pass	0	0	0.0%	BRL							
Ethylbenzene	0.847	0.913	0.88	0.849	3.5%	Pass	0.949	7.8%	Pass	0.062	0.102	48.8%	BRL							
m,p-Xylene	1.671	1.769	1.72	1.642	4.5%	Pass	1.891	9.9%	Pass	0.258	0.499	63.6%	FAIL							
o-Xylene	0.811	0.866	0.839	0.82	2.3%	Pass	0.923	10.0%	Pass	0.074	0.129	53.9%	BRL							
Styrene	0.831	0.866	0.849	0.773	9.0%	Pass	0.786	7.4%	Pass	0	0.118	0.0%	BRL							
Bromoform	0.552	0.584	0.568	0.597	5.1%	Pass	0.7	23.2%	Pass	0	0	0.0%	BRL							
Ethane, 1,1,2,2-tetrachloro-	0.685	0.677	0.681	0.767	12.6%	Pass	0.908	33.3%	FAIL	0	0	0.0%	BRL							
Benzene, 1,3,5-trimethyl-	0.787	0.805	0.796	0.627	21.2%	Pass	0.755	5.2%	Pass	0	0.101	0.0%	BRL							
Benzene, 1,2,4-trimethyl-	0.83	0.856	0.843	0.648	23.1%	Pass	0.76	9.8%	Pass	0	0.277	0.0%	Pass							
Benzene, m-dichloro	0.694	0.648	0.671	0.382	43.1%	FAIL	0.539	19.7%	Pass	0	0	0.0%	BRL			3c			4	
1,2,3-Trimethyl Benzene	0.684	0.67	0.677	0.498	26.4%	Pass	0.644	4.9%	Pass	0	0	0.0%	BRL							
Benzene, p-dichloro-	0.489	0.526	0.508	0.335	34.1%	FAIL	0.361	28.9%	Pass	0	0	0.0%	BRL						4	
Benzyl chloride	0.363	0.652	0.508	0.344	32.3%	FAIL	0.515	1.4%	Pass	0	0	0.0%	BRL			3c			4	
Benzene, o-dichloro-	0.724	0.789	0.757	0.404	46.6%	FAIL	0.104	86.3%	FAIL	0	0	0.0%	BRL						4	
Benzene, 1,2,4-trichloro-	1.082	1.182	1.132	0.57	49.6%	FAIL	0.872	23.0%	Pass	0	0	0.0%	BRL						4	

Compound (synonym)	Calibration curve 1ppb curve: 1st run 1ppb curve	2nd run 1ppb curve	Avg.	Daily Check Std.Values(1ppb unless otherwise noted) xx/xx/2007: 1st run	% Difference	Fail >30%	2nd run	% Difference	Fail >30%	Replicates w/in 20%: Run 1	Run 2	Fail >20%	Pass/Fail	Flag 2	Flag 3a	Flag 3c	Flag 3c1	Flag 3d	Flag 4	Flag 5
Acetaldehyde	1.034	2.539	1.787	1.872	4.8%	Pass	3.689	106.4%	FAIL	0.513	0.485	5.6%	Pass	2		3c			4	
Acrolein	1.262	1.23	1.246	1.031	17.3%	Pass	0.979	21.4%	Pass	0.142	0.378	90.8%	FAIL							
Propanal	1.184	1.239	1.212	0.967	20.2%	Pass	0.924	23.8%	Pass	0	0.039	0.0%	BRL							
Methacrolein	1.236	1.269	1.253	1.044	16.7%	Pass	0.996	20.5%	Pass	0.196	0.236	18.5%	Pass							
Butanal	1.236	1.518	1.377	1.203	12.6%	Pass	1.024	25.6%	Pass	0.445	0.616	32.2%	FAIL			3c				

OK
9/16/13

Figure 1. QA/QC Spreadsheet

2.51.4.1.3.7 Review the duplicate sample analyses (Run1 and Run2) in the columns just to the left of the flags columns. Correct the flag 5's if needed.

2.51.4.1.3.8 Now review each VOC Sample Report.

- Make sure the system identified at the top is the same system as the calibration data.
- Make sure there is a correct Sample ID in the "Inj. Notes:" space. This will be matched up to the "VOC Sample Log No." in the master spreadsheet.
- Does the GC graph look OK, are there strange peaks or lumps? If so, mark it as a bad GC run.
- Mark out with a single line the data for any compound that has a flag.
- Circle any value ≥ 0.1 ppb that has not been flagged.
- Mark with an arrow any value ≥ 1 ppb that has not been flagged.
- Note how much the CCl_4 value is different from 0.090 ppb.
- Compare collocated data with primary data and mark any significant differences.
- Do the concentrations seem reasonable for ambient air at that site; this could indicate that the IDs have been inadvertently switched.
- Compare the patterns. If two Sample Reports appear very similar, they may have been the same canister but are mislabeled.

2.51.4.1.3.9 Send any questions that arose during the review to the VOC Laboratory Analyst. His or her initials should be in the "Operator Name:" space on each VOC Sample Report.

2.51.4.1.3.10 When all questions have been resolved, begin recording QA data in the appropriate spreadsheets, for example RepeatsCV2012.xls, DuplicatesCV2012.xls, and CollocatedCV2012.xls. These spreadsheets are located on the P:\ drive in the P:\Toxics\Urban Air Toxics\VOC's Current Year Data\ folder. Record acrolein and benzene precision data. Other compounds may be added.

Type of Data (at least benzene and acrolein)	**File to record the data in**
Data from collocated and primary samplers run on the same day at the same site (the collocated sample ID will match the primary ID but end in "D")	CollocatedCV201x.xls
Data from two analyses of the same sample in the same batch (the second analysis should have an ID ending with "S")	DuplicatesCV201x.xls
Data from samples that were analyzed in a previous batch (the ID will end in "R")	RepeatsCV201x.xls

2.51.4.1.3.11 Once all the data have been recorded in the precision spreadsheets, add lines to the master VOC spreadsheet for these repeat sample analyses and for the duplicate sample analysis (see step 2.51.4.1.3.10 above). A line is added by placing the cursor on the line below the sample ID (VOC Sample Log No.) that

is being repeated, right click, select “Insert,” copy the cells from the line with the sample ID that is being repeated up through the Hold Time Flag column and paste them in the inserted line, then change the sample ID in the inserted line by adding “S” or “R” to the end of the sample ID to indicate the expected type of data.

2.51.4.1.3.12 This completes the review. Initial and date the QA/QC Spreadsheet at the bottom and give it to the Laboratory Supervisor for review.

2.51.4.1.3.13 When the Laboratory Supervisor has approved the analytical run and returns the folder, notify the VOC Laboratory Analyst to transfer the data to the P:\ drive for subsequent transfer to the master spreadsheet. (See SOPs for VOCdataFromGCMS_lab and VOCdata2spreadsheetMacroVxx).

VOC Data QA Checklist

For batch run on _____

Before beginning the VOC data review verify that all these documents are present in the data packet:

___ QA/QC spreadsheet print out, see Figure 1 in the "SOP for Performing a QA Review of a VOC Data Run" (and electronic copy of the spreadsheet file e-mailed from the VOC Laboratory Analyst)

___ Leak Check Report

___ "SampleList Printout"

___ BFB 524.2 Report

For a calibration run:

___ Calibration Block Report

___ Calibration Curves Report

For all data batches:

___ VOC Sample Reports matching the "SampleList Printout" and in chronological order

___ Zero air: _____

___ Initial 1 ppb calibration check _____

___ Final 1 ppb calibration check _____

Update Tracking Chart _____ _____

Date of Review: _____ Reviewer: _____