

Standard Operating Procedures for

BETX Analysis in Single Charcoal Organic Vapor Monitors

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Objective

This method is designed to determine the relative amounts of benzene, toluene, Ethylbenzene, and the xylenes adsorbed on to single charcoal organic vapor monitors

Scope and Application

This method is for peak, ceiling and Time Weighted Average (TWA) determinations of Volatile Petroleum Hydrocarbons (VPH), specifically benzene, toluene, ethylbenzene, p&m-xylene, and o-xylene. There is the possibility that interactions between analytes may reduce the breakthrough volumes and change desorption efficiencies. Samples are analyzed using a Varian 3800 Gas Chromatograph equipped with a 2200 ion trap mass selective detector (MSD) and an 8400 auto injector. Helium is used as the carrier gas and a compatible high resolution capillary column. Results are compared to a calibration curve. A separate computer program is used to convert concentrations to ppbv. This procedure assumes working knowledge of the software analysis packages currently in use.

Responsibilities

The Quality Assurance Manager maintains a master file of this SOP to insure review on a timely basis. The filing system serves as an accounting of SOP distribution and insures that distributed SOPs are current and complete. The accounting includes destruction of controlled copies of expired and retired SOPs. The QA Manager also maintains a historical file of all original and electronic versions of this SOP for a minimum of five years.

An electronic copy of this SOP and any prior versions of this SOP are maintained on the computer network in a "read only" file. It is the responsibility of all personnel to follow this SOP as written, document deviations to the SOP and submit needed SOP revisions to the Quality Assurance Manager.

This SOP is scheduled for review on an annual basis. Any required revisions will be incorporated into the SOP. The new revision of the SOP will be distributed to appropriate personnel and the superseded version returned to the QA Manager. If no revisions are required, the SOP cover page is signed and dated to document the review, and the updated cover page will be distributed.

Interferences

No interferences have been observed with this analysis. Unknown compounds can typically be identified by mass spectral characterization.

Sample Handling

Organic vapors in air are collected with Organic Vapor Monitors (OVM) containing a single charcoal adsorbent pad. To quantitatively confirm the presence and concentration of a contaminant in the atmosphere, most analysts require a minimum of 10 micrograms for gas chromatographic analysis. A sampling period of at least 15 minutes is recommended even when 10 micrograms of the contaminant could be collected in a shorter period. OVM are simple to use, but they do have limitations just like all types of sampling devices. Prior to using the monitor, the user must understand the limitations of this sampling device. Accurate results can be obtained if the OVM is used within its performance limitations and if the analytical laboratory conducting the analysis provides correct information. Some of the more common sampling errors are overloading the sorbent pad, sampling for contaminants that cannot be captured and retained by carbon, and the laboratory using incorrect recovery coefficients.

Apparatus

A Varian 3800 gas chromatograph equipped with an 8400 auto injector and a 2200 ion trap mass selective detector capable of scanning from 10 - 600 amu every second or less.

A J&W Scientific DB-23 (122-2362) or equivalent 60m x 0.25 mm x 0.25 μm column are used in the analysis of the extracts.

The instrument analysis conditions are as follows: Injector – 250 °C; Interface – 250 °C; Split vent flow - 5 mL/min; Initial Temperature 50 °C, rate 3 °C, Final Temperature 95 °C.

Reagents and Standards

All standards should be prepared using CLASS A volumetric flasks ONLY!!

Benzene free carbon disulfide (CAS 75-15-0) suitable for industrial hygiene analysis is available from Aldrich (42,464-1).

Internal Standard Stock Solution, 10,000 $\mu\text{g}/\text{mL}$: Add 10.0 mg p-Cymene to carbon disulfide and diluting to 1 mL.

Internal Standard Working Solution, 100 $\mu\text{g}/\text{mL}$: Dilute 250 μL Internal Standard Stock Solution in 25 mL carbon disulfide.

Stock BETX Mix Standard prepared from high purity compounds: Gravimetrically weight out 100.0 mg each of pure standard in gastight syringes. The compounds are added to a 2 mL Autosampler vial and capped.

Standard Calibration Stock Solution, 10,000 $\mu\text{g}/\text{mL}$ each: Gravimetrically weight out 60.0 mg of Stock BETX Mix Standard in a gastight syringe and add to 1 mL Internal Standard Working Solution.

Working Calibration Stock Solution, 1,000 $\mu\text{g}/\text{mL}$ each: Add 100 μL Standard Calibration Stock Solution to 1 mL Internal Standard Working Solution.

Initial Calibration Verification (ICV) and Continuing Calibration Verification (CCV) Standard Solution, 5 $\text{ng}/\mu\text{L}$: Dilute 25 μL of Working Calibration Stock Solution to 5 mL with carbon disulfide containing 100 $\text{ng}/\mu\text{L}$ p-cymene.

Quality Control Standard (QCS) Stock Solution: Restek (30213) BTEX Standard (or equivalent) at 2,000 $\mu\text{g}/\text{mL}$ each in P&T methanol.

QCS Working Standard Solution, 10 $\mu\text{g}/\text{mL}$ each: Add 5 μL QCS Stock Solution to 1 mL Internal Standard Working Solution.

Calibration

All standards should be prepared using CLASS A volumetric flasks ONLY!

Calibration Levels

The instrument is calibrated using a minimum of 5 points. The compounds are calibrated using the external standard technique. Once the oven parameters have been verified and the computer system has been set to acquire, the GC is ready for the first calibration standard. Using the BTEX stock solution five solutions are made at the following concentrations: 1 $\text{ng}/\mu\text{L}$, 5 $\text{ng}/\mu\text{L}$, 10 $\text{ng}/\mu\text{L}$, 25 $\text{ng}/\mu\text{L}$ and 50 $\text{ng}/\mu\text{L}$. Due to co-elution p&m-Xylene is the sum of the analytes p-Xylene and m-Xylene. Calibration is established if $R^2 \geq 0.999$.

Calibration level solutions are prepared in Internal Standard Working Solution at 5 concentration levels from the Working Calibration Stock Solution (the total final volume of each calibration solution is 1.0 mL).

Table 1. Concentration of analyte and Internal Standard:

Compound Type	Compound	Concentration (ng/ μ L) at Level:				
		1	2	3	4	5
Analyte	Benzene	1.0	5.0	10.0	25.0	50.0
	Ethylbenzene	1.0	5.0	10.0	25.0	50.0
	Toluene	1.0	5.0	10.0	25.0	50.0
	o-Xylene	1.0	5.0	10.0	25.0	50.0
	p-Xylene	1.0	5.0	10.0	25.0	50.0
	m-Xylene	1.0	5.0	10.0	25.0	50.0
Internal Standard	p-Cymene	100.0	100.0	100.0	100.0	100.0

Extraction Procedure

Place the sorbent section of the sampler into separate 2 mL autosampler glass vials. Add 1.0 mL carbon disulfide containing the internal standard into each vial and cap immediately. Sonicate at least 30 minutes prior to analysis. Remove the sorbent and place the sample vial containing the extract on to the auto sampler for analysis.

Analysis

The instrument calibration is checked prior to processing the samples for analysis. Once the calibration check is complete, samples are run.

Calculations

The following equation is used to convert from ng/ μ L as given to mg/sorbent pad for reporting: ng/ μ L \times 1000 μ L \times 1mg/10⁶ ng = mg/sorbent pad. A spread sheet containing this calculation is available in Microsoft EXCEL. Results for the primary and secondary sections are summed for the reported result. If the secondary result is greater than 10% of the primary result then report breakthrough and possible sample loss.

$$mg / sorbent pad = \frac{ng}{\mu L} \times 1000 \mu L \times \frac{1}{10^6} mg/ng$$

Recoveries for standard solutions are calculated by dividing the observed value by the expected value. The result is multiplied by 100 to give a percent recovery.

$$\% \text{ recovery} = \frac{V_0}{V_e} \times 100\%$$

$V_0 = \text{Observed Value}$

$V_e = \text{Expected Value}$

The relative percent difference between duplicate samples is calculated as the absolute difference between the sample and the duplicate, divided by the average of the sample and the duplicate, all multiplied by 100.

$$\%RPD = \frac{|S_c - D_c|}{[(S_c + D_c)/2]} \times 100\%$$

$S_c = \text{Observed Sample Concentration}$

$D_c = \text{Observed Duplicate Sample Concentration}$

Quality Control

Laboratory Method Blank (MB)

At least one MB sample is extracted and analyzed with every 20 samples or sample set (all samples extracted within a 24-hour period), whichever is greater. The MB is to be extracted and analyzed as an unknown sample using an unused OVM as the blank sample. The MB value of each analyte must be less than the calculated limit of detection. If recovered values are greater than the limit of detection, the MB is to be reanalyzed once; if the values are found to be outside this range the values are reported and the samples are flagged.

Calibration Verification and Qualification

The calibration curves must have an R^2 greater than or equal to 0.999. The calibration curves are verified by the analysis of an Initial Calibration Blank (ICB), and Initial Calibration Verification (ICV) sample and a second source Quality Control Sample (QCS). The acceptance criteria for ICV and QCS are $\pm 10\%$ and $\pm 15\%$ of true values respectively. The ICB value of each compound must be less than the calculated limit of detection.

For each group of no more than ten samples analyzed, a Continuing Calibration Verification (CCV) and Calibration Blank (CB) are analyzed. In order to validate each bracketed group of analysis results, each compound in the CCV must be determined with a tolerance of no greater than $\pm 15.0\%$ of actual value. Should any CCV fail, the CCV is to be reanalyzed once. In the event of multiple CCV failures, instrument recalibration is indicated. The CB value of each compound must be less than the calculated limit of detection. If recovered values for the CB are greater than the limit of detection, the CB is to be reanalyzed once. If the values are found to be outside this range analysis must be halted until contamination problem has been fixed. Samples bracketed by failed QC's must be reanalyzed after problems have been corrected.

Determination of Limit of Detection (LOD)

Prior to the analysis of unknown samples, the LOD must be determined for each analyte. The LOD is calculated from the calibration curves using the equation $3.3 \cdot S_{xy}/m$, where (S_{xy}) is the standard deviation of the x-intercept and (m) is the slope. For all compounds where a peak is detected but below the limit of detection are reported as $<LOD$. If no peak is detected in the chromatogram, data is reported as non-detect (ND).

Table 2. Typical limits of detections:

Analyte	(mg/sorbent pad)
Benzene	0.0004
Toluene	0.0022
Ethylbenzene	0.0008
p&m-Xylene	0.0013
o-Xylene	0.0016

Calibration Range

Should any analysis results be found to exceed the range of instrument calibration, the sample must be diluted according to the judgment of the analyst and reanalyzed.

Laboratory Control Sample/Duplicate (LCS/LCSD)

For each group of samples extraction batch in a 24 hour period, a Laboratory Control Sample (LCS) and a Laboratory Control Sample Duplicate (LCSD) must be extracted and analyzed. For each LCS/D, a blank OVM charcoal wafer will be placed in 2 mL vials, 1.0 mL carbon disulfide containing the internal standard and 10 ng/ μ L BETX is added into each vial and cap immediately. The LCS/D is to be extracted and analyzed as an unknown sample.

Recoveries for the LCS and LCSD must be within $\pm 20\%$ of the true value. The %RPD must be less than 10%. If percent recoveries or %RPD are outside accepted range, LCS and LCSD must be reanalyzed; if the criteria are still not met, the values are reported and samples are flagged.

Data Review

Collected data are evaluated by BS Chemist Benjamin Applegate, including baseline and stability of peak-time relation, regression quality of calibration, recovery of internal standard, limits of detection.

The data are plotted in an excel spreadsheet and handed for further review to Dr. B. Hagedorn (lab manager) and Prof. Dr. J. Kennish (Department of Chemistry). Data are released if all values and calculations are in agreement with quality standard.

Chain of Custody

Chain of custody form is in place in the ASET laboratory. All samples handed to ASET have to be announced in advances. Ideally an electronic sample list with running number and sample name which is unique for each sample is send to ASET lab manager (or analyst in absence). A hardcopy of this sample list is required with each sample batch handed to ASET personnel. PI, date, number and kind of samples and the required storage environment are listed in *Chain of Custody Document*. This document is signed by the person who delivers the samples and person who receives the sample (only ASET personnel is allowed to accept samples).

Health and Safety

Carbon disulfide is toxic and extremely flammable (flash point = -30°C, ignition point= 100°C). Benzene is a suspected carcinogen. Prepare samples in a well-ventilated hood.

References

1. NIOSH Manual of Analytical Methods, Fourth Edition, August 15, 1994, 2.
2. SW846 Method 8000B, Revision 2, December 1996, section 7.5.2
3. 3M Technical Data Bulletin 1028.
4. Laboratory generated limits based on instrument performance.

Chromatogram Plot

File: c:\saturday\s\kennish-data\btex data 062506\std 25.s.ms
 Sample: STD 25
 Scan Range: 1 - 1358 Time Range: 0.00 - 13.31 min.

Operator: kennish
 Date: 6/25/2006 1:43 P M

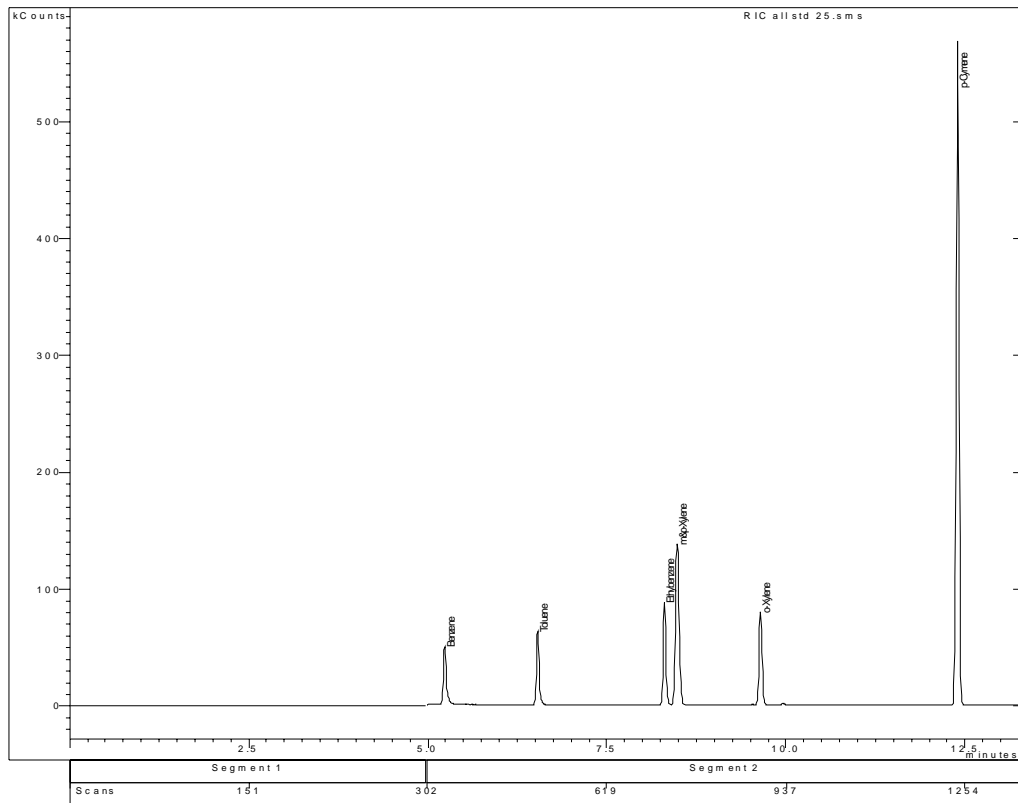


Figure 1. Typical chromatogram of standard solution.