VIII. Organic Solvents in Air: Charcoal Tube and Badge Sampling with GC Analysis

Objectives

In the workplace, exposure to volatile organic chemicals including solvents may occur from a variety of sources. Examples include components of engine exhaust, spillage/leakage of engine fuel, evaporation of solvent from cleaning agents, paints or laquers, evaporation of solvent from new building materials , carpeting, plastics, leakage of solvents stored on-site, etc.

Sampling for volatile organic chemicals typically involves the use of sorbent tubes or badges. In this experiment Charcoal tube and badge samples will be taken from the dynamic generator that is used to simulate an exposed workplace. The samples will be analyzed by gas chromatography. As with many industrial exposures and formulations, the sample contains a mixture of several volatile chemicals. Please see the Appendix for Theory & Instrumentation of sampling & analysis.

I. Purpose

To become familiar with:

a. Charcoal adsorbent tube and diffusive (passive) badge sampling.
b. The use of a Dynamic Generator with a syringe drive to produce a continuous air concentration.
c. The desorption of analytes and the determination of their efficiencies/recoveries.
d. Gas Chromatographic analysis of organic vapor samples:
   1. Selection of operating parameters.
   2. Column separation techniques.
   3. Detector applications.
   4. Interpretation of chromatograms.
   5. Incorporation of adequate quality control measures.
e. The preparation of calibration solutions, and the analyzing and quantifying the average concentrations of the unknown samples.

II. Readings:

NIOSH NMAM 1500 & 4000

McDermott, Air Monitoring for toxic exposures
Gas and vapor sampling Chapter 6

Harris, Quantitative Chemical Analysis, 6th or 7th edition
Gas Chromatography Chapter 24

III. Outline (See page 2 for the Lab Schedule)

The experiment has five parts that are to be completed in two lab periods. Please read the NIOSH methods 1500 & 4000 and this lab guide before coming to class.

A. Tasks and Schedule

Day 1:

Part 1. Set up the GC and identify the compounds from the dynamic air generation system by their retention times.

Part 2. Collect samples from the dynamic generation system with charcoal tubes and badges for quantification of the system contaminants (as if from a contaminated workplace).

Part 3. Prepare 'known' samples by spiking the charcoal tubes and badges with known amounts of the analytes you identified in part 1 for the determination of desorption efficiency (DE).

Day 2:

Part 4. Prepare quantitative standards with which to calibrate the GC; analyze and generate calibration curves.

Part 5. Desorb & analyze sample tubes and badges: Plan a schedule for the replicate injection of all standards, samples, spikes and blanks. Load systematically into the auto-sampler and analyze.

IV. Equipment

A. 600 mg charcoal sampling tubes (~10/group), and passive charcoal badges (6)
B. 10 pure solvent solutions
C. bulk unknown mixture solution
D. file, funnel and desorption kit
E. 4 ml vials, with solid or septum caps and 2 ml auto-sampler vials
F. 10 microliter syringes
G. sampling pumps and rotameter
H. Syringe Drive Dynamic Generator
I. assorted glassware (pipettes, 25 ml volumetric flasks, desorbing vials)
J. carbon disulfide (CS_2) and desorbing solution with internal standard.
K. Shaker table
L. gas chromatograph with auto-sampler

V. Experimental Procedure -- (Reference NIOSH Procedure 1500 or 1501)

Day One

NOTE: This lab will use 600 mg charcoal tubes; whereas, the NIOSH method uses 150 mg.

Keep in mind that this experiment represents a sample collection phase using sorbent tube & badge sampling for a time weighted average evaluation of the work place concentrations in the field and secondly, analysis of these contaminants in the laboratory. First, the identification experiments would be somewhat similar to the application of a field gas chromatograph or detector tubes to find what organic vapors were in the workplace.

1. Identification –
   Determination of compound retention times: The instructor will provide you with ten pure solvents. Prepare a 1:1000 dilution of each compound in carbon disulfide (work in the fume hood!) in a GC vial, label the vial and place in the GC autosampler. Note that the dilution only has to be approximate, these solutions will be used in a qualitative manner only, to determine the retention time of each chemical. You will also be given a vial containing a mixture representative of the paint solvent compounds. This mixture is used in the dynamic air generation system, representing the spray painting atmosphere from which you will collect air samples. Make a 1:1000 dilution of the mixture in CS_2, as described above, and analyze by GC. Inject and identify the composition of the unknown mixture by comparing its retention times with the pure compounds. Be sure to make multiple injections (n=3) for two of the analytes so that you can determine the precision of the retention times for this GC.

2. Guideline for Determining Charcoal Sampling Volume:
   In practice you would need to determine the identity of the unknown compounds prior to deciding the appropriate sample media, collection time and flow rate. However, for the purposes of this experiment, you will collect samples on the charcoal badges for 1 hr, and on the charcoal tubes for 8 minutes at a flow rate of 0.75 L/minute and 15 min at a flow rate of 1 L/minute.

3. Sample collection:
   A: Passive Charcoal Dosimeters: Sample the dynamic generator exhaust stream with two passive charcoal dosimeter badges for 1 hr. Record the sampling times.
   B: Charcoal tubes: Use a rotometer to calibrate your sampling pumps to the desired flow rate, with a charcoal tube in-line. Collect two samples for 8 minutes at a flow rate of 0.75 L/minute and two samples for 15 min at a flow rate of 1 L/minute.

4. Desorption of Samples: Because injection techniques introduce a large variability into the gas chromatographic technique, the method of internal standards (IS) is

used to minimize this effect. The 'desorbing solution' (2 mL/sample) is prepared to contain a prescribed amount of a compound not found in the samples, but similar to the analytes and in an average expected amount. This additional compound is the internal standard. All samples, standards, blanks, and desorption efficiency solutions will be desorbed with equal portions of solvent and have the same quantity of the IS compound; thus, the injection volumes can be normalized to the IS compound peak area (usually by making a ratio of all analyte peaks to the IS compound peak). See the instructor about the choice of internal standard compound and its application to the final quantitation.

5. Desorption Efficiency: Spike known amounts of analytes into charcoal tubes and badges and take them through the entire procedure to determine their recovery.

The amount of material you spike onto the tubes and badges should be similar to the amount of analyte that would be collected on the tubes or badges in the dynamic generator. The 'collected mass of analyte' will depend on the analyte concentration in the dynamic generator, and the total air volume sampled. For the purposes of calculating how much analyte to spike for the desorption efficiency samples, assume a sampled volume of 5 L, and that the analyte concentrations in the dynamic generator are at their TLVs.

Make one spike solution, containing equal amounts of each analyte. **Spike 20 µL of the mix onto each of two charcoal tubes, and one charcoal badge**. To rule out mechanical technique errors, **20 µL of each mix** should also be spiked into the "extraction solution" (carbon disulfide + IS) in GC autosampler vials. The amount recovered from the two kinds of spikes are compared. The ratio becomes the desorption efficiency (DE).

$$\text{desorption efficiency} = \frac{\text{amount recovered}}{\text{amount spiked}}$$

$$= \frac{\text{sample mass - lab blank mass}}{\text{mass injected}}$$

Since the DE can vary with the amount of tube loading, good lab practice would require that at least two levels of amount are spiked (a high concentration and a low concentration). For this lab a single spike concentration will be sufficient.

**** Desorption efficiency is determined by applying liquid solvent directly on the charcoal. How realistic is this compared to vapor adsorption****

Day Two

Before class, complete a written dilution scheme for the preparation of the calibration standards. Knowing the compounds, their TLVs and the air volume collected, will define levels for the standards that will be needed to cover the sampling range (0.4 to 4 times the TLV for each compound based upon the air volume sampled).

The worksheet attached to the back of this lab guide can be used to help you figure out what range of concentrations the calibrants should cover. Check your scheme with the instructor before starting. It is suggested each group divide activities such that the preparation of the standards and preparation of the samples for analysis proceeds simultaneously.

1. Standards: Prepare 6 calibration solutions (standards) representing 0.2 to 4 times the TLV for each compound based upon your calculations above. HINT: It is easiest and more accurate to make a three compound mixed solution and then prepare the dilute standards from this solution. Use the internal standard solution to prepare all dilutions. Round off the calculated volumes, to easy (whole number) multiples for more accurate pipetting.

2. Chromatography: Set up the GC for optimum resolution vs. run time. Record all chromatography conditions. Aliquot samples into autosampler vials, cap, load into tray and start sampler. Use the autosampler to systematically inject 2 μL aliquots of standards, samples, spikes and blanks into the GC under identical conditions.

Repeat injection of a benchmark standard, and several of your field samples, at intervals during the sample queue to help characterize any drift of response by the chromatograph, and to assess precision of the instrument.

3. Sample Preparation: Desorb, analyze and quantify all samples. Remember to desorb and analyze separately the front and back portions of the charcoal tubes. If pressed for time, analyze the back portions of the tubes last. If significant amount of analytes carry into the backup charcoal, breakthrough has occurred and accurate quantitation of the samples cannot be made. Resampling with a smaller sampling volume would then be necessary to properly evaluate concentrations.

VI. Write up

Begin with a short introductory paragraph describing the objectives of this experiment.

1. Identification of unknowns:

State the instrument conditions (Column, Carrier, Temperatures, & Flow Split). Prepare a data table and record the retention times for each pure compound and for each component of the mixture: Compare unknown analytes retention times with those of the knowns. Identify and list the unknown compounds by their retention times. Indicate the precision of the retention time data.

Were there any compounds for which the retention times were too similar to allow you to confidently identify these compounds in an unknown mixture?

B. Quantitative Results of the sample collection and analysis:
Remember to include one worked examples for each type of calculation.

1. Describe the collection of samples from the exposure generating system, including procedures used to calibrate pump flow rates. Include a table listing: sample identifiers, start times, end times and elapsed times for sample collection; initial flows, final flows and sample volumes for each sample.

2. Show the calculations for the preparation of the calibration standards and the desorption efficiency spiking solution.

3. Prepare data tables of the standards and all samples including desorption efficiency samples, replicate samples, spiked solvent and extraction blanks. Enter the raw data into an Excel Spread Sheet. Calculate the ratios (analyte peak area to internal standard peak area for each injection) and enter into a table. Plot calibration curves for each compound (analyte concentration (x-axis) vs response ration (y-axis) and determine the linear regression equation for these curves.

Linearity: If the highest standards are beyond the linear region, omit them from the regression. *Note: if the sample areas exceed this limit of linearity, dilute them until they are within the linear range for further injections.*

4. Calculate and show the desorption efficiencies from the recoveries of the charcoal spikes vs. the carbon disulfide spikes (show worked examples!).

5. The regression coefficients *together with the compound densities* can then be applied to the Excel Spread Sheet formulas to calculate the mg per sample from the peak area ratios per sample. Calculate the mass quantities (show worked examples!) of the components per sample and their air concentrations for the sample tubes and the dosimeter badges taken from the dynamic generating system (consider blanks and desorption efficiency). Air concentrations for the passive badges should be determined using the theoretical sampling rates taken from the manufacturers booklet.

6. How well do the results compare for the charcoal tubes collected at different flow rates? How well do the data from the charcoal tubes compare to the passive badges?

7. Determine your analytical precision from the replicate injections (instrumental precision) and replicate vials (assay precision).

8. Application of Results: Assume these detected air concentrations (from the dynamic generator air stream) were equivalent to those found in a workplace, compare them to the TLVs and briefly state the extent of hazard.

Appendix 1:

Determining calibration range for the assay

The following set of calculations are worked using MEK as an example. Note that MEK is NOT one of the analytes you are measuring. You'll have to rework these calculations for the three analytes that you are measuring.

Calibration range required = 0.4 - 4 TLV.
GC limit of detection = 0.02 μg.

Density MEK: 0.81 g/mL
TLV MEK: 200ppm (590mg/m^3 = 0.590 mg/L)

The sample volumes you will collect are:

Passive badges ~14 ml/min * 60 min =	0.84L
Tube 1: 0.75 L/min * 8 min =	6 L
Tube 2: 1 L/min * 15 min =	15 L

Your lowest concentration calibrant should have a concentration similar to the lowest expect sample that you collect. From the above data, the lowest expected sample would be 0.4 TLV collected on the passive tubes:

0.4 * 0.590 mg/L * 0.84L = 0.198 mg MEK

the tubes and badges are extracted into 2 ml desorbing solution, so this represents:
0.198 mg/2mL CS_2 = 0.099 mg/mL MEK in the sample extract.

Since the density of MEK = 0.81g/mL (~mg/μL):
0.099 mg MEK/mL CS_2/ 0.81 mg/μL = 0.12 μL MEK/mL CS_2

So, your lowest calibrant should contain 0.12 μL MEK/mL CS_2.

Similarly, for the highest calibrant, use 4 TLV and the highest sample volume (15 L):
4 * 0.590 mg/L * 15L = 35.4 mg MEK
35.4 mg MEK/2 mL CS_2 = 17.7 mg/mL MEK in the sample extract.

Since the density of MEK = 0.81g/mL (~mg/μL):
17.7 mg MEK/mL CS_2/ 0.81 mg/μL = 21.9 μL MEK/mL CS_2.

So, your highest calibrant should contain 22 μL MEK/mL CS_2.

Appendix 2:

The Theory and Instrumentation of Gas Chromatography and the Analysis of Charcoal Tubes

A. Charcoal Sampling

Charcoal media is the recommended method for organic sample collection especially for aliphatic, aromatic and halogenated hydrocarbons. The NIOSH 1500 method recommends 150 mg coconut charcoal, however larger tubes are available and will be used in this experiment. All commercially available sample tubes are divided into two portions, front and back. The front portion contains two thirds of the sampling media followed by a urethane foam plug, the back section has the remaining one third. The front portion is used to collect solvents while the back portion is intended to determine solvent breakthrough (when front is saturated).

The sample tube is opened by scoring with a file and breaking off the tip ends. Place the tube in a holder attached to a calibrated pump. Sample at the calculated flow rate for a designated period of time. After sampling, cap the tubes, store appropriately and record the sampling information.

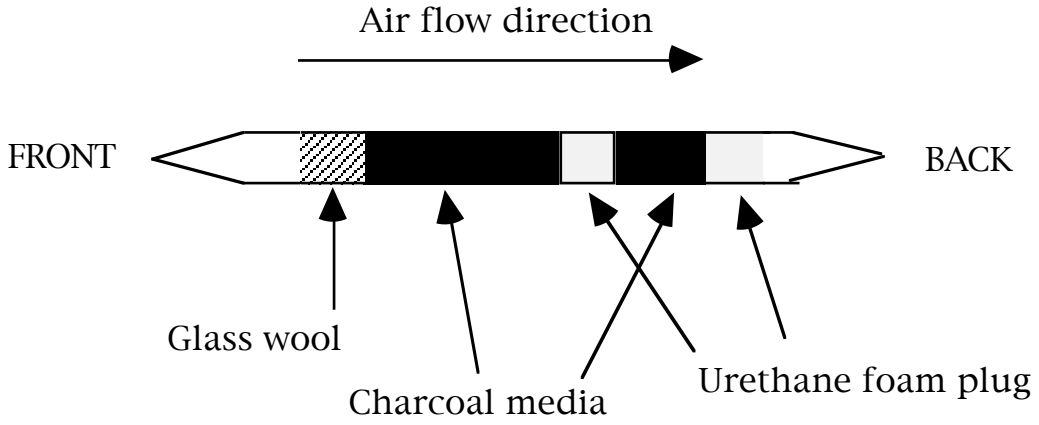

Figure 1: *Air Sampling Tube*

Removal of the collected sample from the charcoal tube is accomplished by desorption in carbon disulfide (CS_2) or other solvents. A capped tube end is scored with a file and broken off. Each charcoal section is removed and placed in separate sample vials. The glass wool and urethane foam used as separators are discarded. To each sealed vial, 2 mL of CS_2 'desorbing solution' is added and is quickly capped. (one mL CS_2 is used if the small 150 mg charcoal tubes are used). All work with CS_2 should be performed in a hood due to its highly toxic nature and obnoxious odor. For complete desorption the sample suspension should be agitated and allowed to desorb for a minimum of 30 minutes. If the desorbed sample is not analyzed that day it may be refrigerated, but if kept longer than a few days, losses may occur.

After desorption the sample is ready for Gas Chromatographic (GC) analysis. 2 μL of the desorbing solution are injected into the GC. Both front and back charcoal portions are analyzed in the same manner. If back section contaminant concentration is greater than 10% of the front contaminant concentration, the possibility of sample loss exists and sample should be voided.

Not all compounds are 100% desorbed by the CS_2, therefore desorption efficiency (DE) must be determined for each compound. Desorption efficiency can be determined by injecting a known solvent mass onto the charcoal tube or badge with a microliter syringe. A mixed solvent can be used to check the DE of all compounds simultaneously. At least five separate unused charcoal tubes are needed for this determination. Several solvent concentrations should be checked to determine desorption efficiency and variation with solvent concentration. Desorption efficiency analysis procedure is the same as sample analysis. Desorption efficiency is determined as:

$$\text{desorption efficiency} = \frac{\text{sample mass - lab blank mass}}{\text{mass injected}}$$

Certain limitations must be considered in adsorption media sampling:

a. Sample media have saturation limits for each solvent sampled. When this limit is exceeded, breakthrough occurs.

b. Charcoal is not always the most efficient collection material due to sample stability, adsorption, or desorption properties. Other media (silica gel, molecular sieve, coated filters or etc.) should be considered to improve collection efficiency and recovery.

c. A collected solvent could be displaced by another solvent that is more strongly adsorbed by the charcoal.

d. High humidity severely decreases the breakthrough volume of charcoal.

e. CS_2 does not readily displace all organic solvents from carbon and other desorption solvents could be necessary to obtain acceptable dissolution efficiency.

f. Reactive gases may be converted to another species on the carbon surface and would not be properly identified.

A.2. Passive Badge Sampling---See SKC product Brochure

B. Gas Chromatography.

Gas chromatography is the physical separation of two or more compounds, based on their differential distribution between two phases, one of which is stationary and the other fluid or mobile. In the case of gas chromatography the fluid is an inert gas.

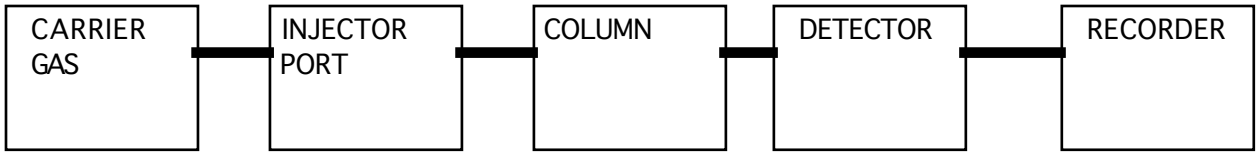

Figure 3: *Components of a Gas Chromatograph*

The chromatograph employs a carrier gas (mobile phase) under pressure to move a vapor sample from the injection port through a stationary phase (column) where separation takes place, to a detector where the vapor is converted to an electrical signal that is then measured by an integrator or computerized data acquisition system. The record of detector response vs. time is called a chromatogram. Retention time (RT) is measured from the point of injection to the apex of the peak (minutes are most common) and is a qualitative fingerprint for each component under the experimental conditions.

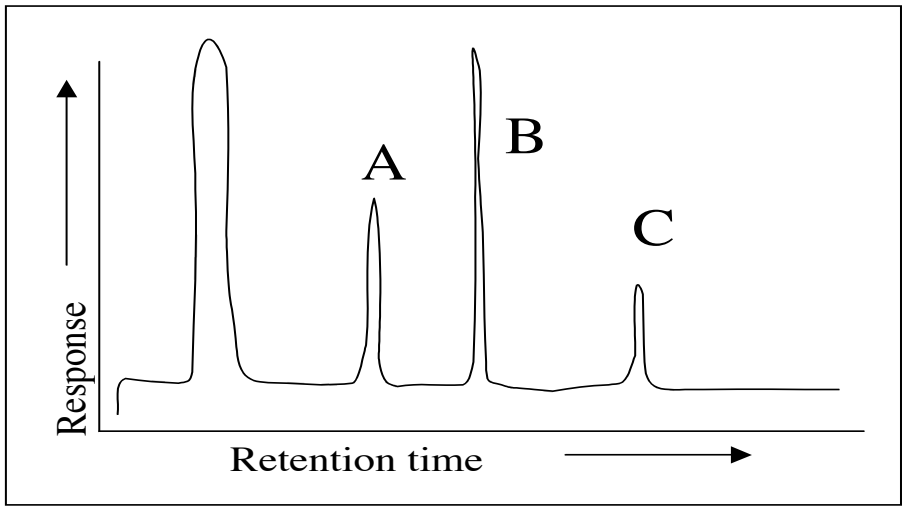

Figure 4*: Example Chromatogram*

Several general observations can be made about this chromatogram:

1) In addition to solvent, this is at least a three component mixture.

2) The peak with the shortest retention time probably has the lowest molecular weight and the peak with the longest retention time probably has the highest molecular weight.

3) Assuming similar response factors for each analyte, Compound B is present in the largest concentration, while Compound A and C are successively less than B.

These are generalizations and should be regarded as "probably true". There are conditions, in which any of these, or even all three, may be wrong; however this gives us a beginning in understanding chromatography.

C. Parts of a Gas Chromatograph System

1. Carrier gas

The carrier gas must be inert, dry and pure. Common carrier gases are helium, hydrogen, nitrogen and argon. Carrier gas choice depends upon the detector and sometimes the column. The carrier gas must be regulated to provide constant pressure and constant mass flow.

2. Injection Port

The injection port provides a means of introducing the sample into the flowing carrier gas stream and subsequently to the column. The injector is heated to quickly vaporize the injected solution. The sample is introduced by piercing a self sealing polymer septum at the injector port with a μL syringe needle. The narrower the sample band injected, the narrower the resulting peak widths. Narrow peaks are desirable to permit complete separation of closely eluting compounds. Sample injection volume depends on the column type: capillary column, 1 uL; packed columns, 2-5 uL.

3. Column

The column is the most important single part of a gas chromatograph. It is composed of three elements: 1) the container for the packing - metal or glass tubing or capillary glass tubing 2) the solid support and 3) the stationary phase. (Note that for most modern capillary columns, the stationary phase is bonded directly to the inner surface of the glass capillary). The tubing usually does not interfere with chromatographic separations, but it can become easily broken. The solid support provides an inert surface area to hold the liquid phase. There are a variety of materials that can be used. The stationary phase should be the only active portion of the column; separation takes place between the carrier gas and this material. This process may be visualized as a series of partitions where the sample goes into solution (or is adsorbed) in the stationary phase and is subsequently revaporized many times. The affinity of the sample for the stationary phase determines the length of time individual sample components will remain on the column. Compounds with the least affinity emerge first and compounds with the greatest affinity emerge last.

Stationary phases are roughly classed as polar or non-polar in nature. Maximum temperature of a stationary phase is an important consideration when selecting one over another, as is the affinity of the sample for that material.

The column length can vary depending upon application. Column diameter can also vary. Generally, packed columns are 1/8 inch diameter and less than six feet in length. Capillary columns are less than 1 mm in diameter and frequently 30-60 meters long.

4. Detectors

As the sample is separated and emerges from the column, components must be detected. There are five common detectors.

1) Thermal conductivity detectors (**TCD**) employ a resistor or element that is electrically heated. Carrier gas dissipates heat from the element at some constant rate, but when a sample component passes through the detector, this rate is altered and the temperature of the resistor changes. This change is transmitted to the recorder, appearing as a peak. This detector is used for gases such as CO, CO_2, N_2, H_2, He, and methanol or any vapors with different TC. TC detectors are not as sensitive as the ionization types.

2) The flame ionization detector (**FID**) employs a hydrogen flame to combust the sample and produce positive ions. A DC potential applied between collector and the flame jet traps the ions as a current that is then converted to a voltage, amplified, and displayed on a recorder as a peak. This detector is the workhorse of gas chromatography and is one of the most sensitive. It detects hydrogen and carbon ions or compounds containing these atoms. This is the detector you will be using in the laboratory.

3) The electron capture detector (**ECD**)is one of the most sensitive detectors in use today, but it is limited to monitoring halogen containing compounds, such as some pesticides and PCBs. The operating principle is that certain radioactive isotopes release beta particles during the decay process. On colliding with carrier gas molecules, these relatively high energy particles produce a large number of secondary, low energy electrons. By placing electrodes with the proper voltage in the detector cavity, these secondary electrons can be collected and become a small but measurable current, usually called the "standing current" of the detector. Sample molecules, particularly those containing halogen atoms, are capable of capturing low energy electrons to form negatively charged ions. This capture process reduces the number of electrons that can be collected and therefore reduces the cell current below the standing current value. The result is a negative peak that corresponds to the loss of current. The ‘peak’ is inverted during amplification to give a positive response on the chart recorder or integrator.

4) The photoionization detector (**PID**) is one of the more recent detectors on the market. It consists of a UV light with a specific ionization potential in electron volts and an electrode. If an eluting compound has an ion potential less than the electron volt potential in the lamp it becomes ionized, the ions are drawn towards the electrode creating a current measured that is then converted to a voltage, amplified, and displayed on a recorder as a peak. This detector's advantage is that it is non-destructive to the sample and allows it to be analyzed by another detector if they are connected serially.

5) The Mass selective detector (**MS or MSD**) is one of the most sensirive, specific and versatile detectors for GC. MSDs come in a variety of formats (e.g. quadrupole, ion-trap, time-of-flight). The basic operating principle is that the analyte molecules are ionized (typical via an electron beam) as they exit the GC column, and the ions are then separated on the basis of their mass to charge ratio as they pass through electric and/or magnetic fields. After mass separation, the ions impinge on an electon multiplier tube (detector0which generates a burst of current as each ion hits the detector

HYDROCARBONS, BP 36°-216 °C 1500

FORMULA: Table 1 MW: Table 1 CAS: Table 1 RTECS: Table 1

METHOD: 1500, Issue 3	EVALUATION: PARTIAL	Issue 1: 15 August 1990 Issue 3: 15 March 2003

OSHA : Table 2
NIOSH: Table 2
ACGIH: Table 2

PROPERTIES: Table 1

COMPOUNDS: (Synonyms in Table 1)

cyclohexane
cyclohexene
n-decane
n-dodecane
n-heptane
n-hexane
methylcyclohexane
n-nonane
n-octane
n-pentane
n-undecane

SAMPLING

SAMPLER: SOLID SORBENT TUBE [1]
(coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: Table 3

VOL-MIN: Table 3
-MAX: Table 3

SHIPMENT: Routine

SAMPLE STABILITY: 30 days @ 5 °C

BLANKS: 10% of samples

ACCURACY

RANGE STUDIED: Table 3

BIAS: Table 3

OVERALL PRECISION ($\hat{S}_{rT}$): Table 3

ACCURACY: Table 3

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID [1]

ANALYTE: Hydrocarbons listed above

DESORPTION: 1 mL CS_2; stand 30 min

INJECTION VOLUME: 1 µL

TEMPERATURES
-INJECTION: 250 °C
-DETECTOR: 300 °C
-COLUMN: 35 °C (8 min) - 230 °C (1 min)
ramp (7.5 °C /min)

CARRIER GAS: Helium, 1 mL/min

COLUMN: Capillary, fused silica, 30 m x 0.32-mm ID; 3.00-µm film 100% dimethyl polysiloxane

CALIBRATION: Solutions of analytes in CS_2

RANGE: Table 4

ESTIMATED LOD: Table 4

PRECISION ($\hat{S}_r$): Table 4

APPLICABILITY: This method may be used for simultaneous measurements; however, interactions between analytes may reduce breakthrough volumes and alter analyte recovery.

INTERFERENCES: At high humidity, the breakthrough volumes may be reduced. Other volatile organic solvents such as alcohols, ketones, ethers, and halogenated hydrocarbons are potential interferences.

OTHER METHODS: This method is an update for NMAM 1500 issued on August 15, 1994 [2] which was based on methods from the 2nd edition of the NIOSH Manual of Analytical Methods: S28, cyclohexane [3]; S82, cyclohexene [3]; S89, heptane [3]; S90, hexane [3]; S94, methylcyclohexane [3]; S378, octane [4]; and S379, pentane [4].

REAGENTS:

1. Eluent: Carbon disulfide *, low benzene, chromatographic quality.
2. Analytes, reagent grade.*
3. Helium, prepurified and filtered.
4. Hydrogen, prepurified and filtered.
5. Air, prepurified and filtered.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends, containing two sections of activated coconut shell charcoal (front = 100 mg, back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section, and a 3-mm urethane foam plug follows the back section. Tubes are commercially available.
2. Personal sampling pumps (0.01 to 1.0 L/min, Table 3) with flexible tubing.
3. Gas chromatograph, FID, integrator, and a Rtx-1 or equivalent capillary column (page 1500-1).
4. Glass autosampler vials (2-mL) with PTFE-lined caps.
5. Pipettes (1-mL) and pipette bulb.
6. Syringes (10, 25, 100, and 250 µL).
7. Volumetric flasks (10-mL).

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and extremely flammable (flash point = -30°C). Prepare samples and standards in a well-ventilated hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach the sampler to a personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min (0.01 to 0.05 L/min for n-pentane) for a total sample size as shown in Table 3.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Include the glass wool plug in the vial with the front sorbent section. Discard the foam plugs.
6. Add 1.0 mL carbon disulfide to each vial. Attach crimp cap to each vial immediately.
7. Allow to stand at least 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards from below the LOD to 10 times the LOQ. Additional standards may be added to extend the calibration curve if necessary.
   a. Add known amounts of analytes to carbon disulfide in 10-mL volumetric flasks and dilute to the mark. Prepare additional standards by serial dilution in 10-mL volumetric flasks.
   b. Analyze with samples and blanks (steps 11 and 12).
   c. Prepare a calibration graph (peak area of analyte vs. µg of analyte per sample).
9. Determine the desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8).
   a. Prepare three tubes at each of five levels plus three media blanks.
   b. Remove and discard the back sorbent section of a media blank sampler.

c. Inject a known amount of stock solution (5 to 25 µL) directly onto the front sorbent section with a microliter syringe.
d. Allow the tubes to air equilibrate for several minutes, then cap the tubes and allow to stand overnight.
e. Desorb (steps 5 through 7) and analyze with standards and blanks (steps 11and 12).
f. Prepare a graph of DE vs. µg analyte recovered.

10. Analyze at least three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set the gas chromatograph according to the manufacturer's recommendations and to the conditions given on page 1500-1. Inject a 1-µL aliquot manually using a solvent flushing technique or with an autosampler.
NOTE: If the peak area is above the linear range of the working standards, dilute with solvent, reanalyze and apply the appropriate dilution factor in the calculations.

Analyte	Approximate Retention Time (min)
n-pentane	7.5
solvent (CS_2)	9.6
n-hexane	13.0
cyclohexane	16.1
cyclohexene	16.8
n-heptane	17.7
methylcyclohexane	18.9
n-octane	21.6
n-nonane	24.9
n-decane	27.8
n-undecane	30.5
n-dodecane	32.9

NOTE: Retention times may vary slightly due to column manufacturer and age of column, and be influenced by other GC instrumental parameters.

12. Measure the peak area.

CALCULATIONS:

13. Determine the mass, µg (corrected for DE), of analyte found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
NOTE: If $W_b > W_f / 10$, report breakthrough and possible sample loss.
14. Calculate the concentration, C, of analyte in the air volume, V(L), sampled:

$$C = \frac{(W_f + W_b - B_f - B_b)}{V}, mg / m^3$$

NOTE: µg/L = mg/m^3

EVALUATION OF METHOD:

Issues 1 and 2:

Precisions and biases (Table 3) were determined by analyzing generated atmospheres containing one-half, one, and two times the OSHA standard. Table 3 does not contain data for n-decane, n-dodecane and n-heptane since they were not evaluated previously. Generated concentrations were independently verified. Breakthrough capacities were determined in dry air. Storage stability was assessed at 7, 14, and 30 days. Measurement precisions (Table 4) were determined by spiking sampling media with amounts corresponding to one-half, one, and two times the OSHA standard for nominal air volumes. Desorption efficiencies for spiked samplers containing only one compound exceeded 75% [2,3,4,8].

Issue 3:

The desorption efficiency, at levels ranging from 10 times the LOQ to 0.1 times the REL, was determined by spiking known amounts of analytes (in CS_2) on coconut shell charcoal tubes. All analytes exhibited acceptable desorption efficiency recovery results at six levels evaluated.

Each analyte was evaluated for its storage stability. Sorbent tubes were spiked at approximately 100 µg and stored in a drawer for 7 days, then transferred to a refrigerator at 5° C. Samples were analyzed after 7, 14, and 30 days. All analytes had acceptable recoveries (>90%), except cyclohexene, which had a 30 day recovery of 85% [1].

REFERENCES:

[1] Pendergrass SM and May L, Backup Data Report, ACS/CEMB/DART/NIOSH (1999).
[2] NIOSH[1994]. Hydrocarbons, BP 36-136°C. In: Eller PM, ed. NIOSH Manual of Analytical Methods, 4th rev. ed. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 94-113.
[3] NIOSH Manual of Analytical Methods, 2nd. ed., V. 2, S28, S82, S89, S90, S94, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
[4] NIOSH Manual of Analytical Methods, 2nd. ed., V. 3., S378, S379, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
[5] Code of Federal Regulations; Title 29 (Labor), Parts 1900 to 1910; U.S. Government Printing Office, Washington, (1989); 29 CFR 1910.1000.
[6] NIOSH Recommendations for Occupational Safety and Health. U.S. Department of Health and Human Services, DHHS (NIOSH) Publication No. 92-100 (1992).
[7] 1993 Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices. ACGIH, Cincinnati, OH (1993).
[8] Documentation of the NIOSH Validation Tests, S28, S82, S89, S90, S94, S378, S379, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).

AUTHORS:

Issues 1 and 2:

R. Alan Lunsford, Ph.D., NIOSH/DPSE

Issue 3:

Stephanie M. Pendergrass, NIOSH/DART and Leroy R. May, NIOSH/PRL

TABLE 1. SYNONYMS, FORMULA, MOLECULAR WEIGHT, PROPERTIES

Name/ Synonyms	Empirical Formula	Molecular Weight	Boiling Point (°C)	Vapor Pressure @ 25°C (mm Hg)	(kPa)	Density @ 25°C (g/mL)
cyclohexane hexahydrobenzene CAS # 110-82-7 RTECS GU6300000	C_6H_{12}	84.16	80.7	97.6	13.0	0.779
cyclohexene tetrahydrobenzene CAS # 110-83-8 RTECS GW2500000	C_6H_{10}	82.15	83.0	88.8	11.8	0.811
n-decane CAS # 124-18-5 RTECS HD6550000	$C_{10}H_{22}$	142.28	174	NA	NA	0.730
n-dodecane CAS # 112-40-3 RTECS JR2125000	$C_{12}H_{26}$	170.34	216.2	NA	NA	0.750
n-heptane CAS # 142-82-5 RTECS MI7700000	C_7H_{16}	100.21	98.4	45.8	6.1	0.684
n-hexane CAS # 110-54-3 RTECS MN9275000	C_6H_{14}	86.18	68.7	151.3	20.2	0.659
methylcyclohexane CAS # 108-87-2 RTECS GV6125000	C_7H_{14}	98.19	100.9	46.3	6.2	0.769
n-nonane CAS # 111-84-2 RTECS RA6115000	C_9H_{20}	128.26	151	NA	NA	0.718
n-octane CAS # 111-65-9 RTECS RG8400000	C_8H_{18}	114.23	125.7	14.0	1.9	0.703
n-pentane CAS # 109-66-0 RTECS RZ9450000	C_5H_{12}	72.15	36.1	512.5	68.3	0.626
n-undecane hendecane CAS # 1120-21-4 RTECS YQ1525000	$C_{11}H_{24}$	156.31	196	NA	NA	0.740

TABLE 2. EXPOSURE LIMITS, PPM [5-7]

	OSHA		NIOSH		ACGIH		mg/m^3
Substance	TWA	PEAK	TWA	C	TLV	STEL	per ppm
cyclohexane	300		300		300		3.44
cyclohexene	300		300		300		3.36
n-decane	none		none		none		5.82
n-dodecane	none		none		none		6.97
n-heptane	500		85	440	400	500	4.10
n-hexane [a]	500		50		50		3.52
methylcyclohexane	500		400		400		4.01
n-nonane	none		200		200		5.25
n-octane	500		75	385	300	375	4.67
n-pentane	1000		120	610	600	750	2.95
n-undecane	none		none		none		6.39

[a] The ACGIH recommendation for other hexane isomers is: TLV 500, STEL 1000.

TABLE 3. SAMPLING FLOWRATE [a], VOLUME, CAPACITY, RANGE, OVERALL BIAS AND PRECISION [3, 4, 8]

	Sampling			Breakthrough Volume		Range of	Overall		
	Flowrate	Volume (L)		Vol	Concentration	Generated Samples	Bias	Precision	Accuracy
Substance	(L/min)	MIN	MAX [b]	(L)	(mg/m^3)	(mg/m^3)	(%)	($\hat{S}_{rT}$)	(%)
cyclohexane	0.01- 0.2	2.5	5	7.6	1650	510-2010	1.1	0.060[c]	±11.5
cyclohexene	0.01- 0.2	5	7	10.4	2002	510-2030	10.6	0.073	±20.7
n-hexane	0.01- 0.2	not	studied	-	-	-	-	-	-
methylcyclohexane	0.01- 0.2	4	4	6.1	4060	968-4060	-6.5	0.056	±15.0
n-nonane	0.01- 0.2	4	4	5.9	3679	877-3679	-1.8	0.062	±12.5
n-octane	0.01- 0.2	4	4	6.1	3941	940-3941	6.1	0.052	±15.2
n-pentane	0.01-0.2	4	4	6.5	4612	1050-4403	-2.0	0.060	±12.1
n-undecane	0.01-0.05	2	2	3.1	5640	1476-6190	-8.4	0.055	±16.6

[a] Minimum recommended flow is 0.01 L/min.
[b] Approximately two-thirds the breakthrough volume.
[c] Corrected value calculated from data in Ref. 3

TABLE 4. MEASUREMENT RANGE AND PRECISION [1, 3, 4, 8]

		Measurement	
Substance	LOD (µg/sample)	Range (µg)	Precision ($\bar{S}_r$)
cyclohexane [a]	0.1	4 - 5300	0.012
cyclohexene [a]	0.08	3 - 9700	0.014
n-decane	0.06	2 - 584	0.020
n-dodecane	0.05	2 - 600	0.027
n-heptane	0.06	2 - 16300	0.014
n-hexane	0.4	10 - 14500	0.011
methylcyclohexane	0.1	4 - 16100	0.013
n-nonane	0.04	1 - 574	0.018
n-octane	0.3	11 - 18900	0.022
n-pentane	0.6	19 - 11800	0.012
n-undecane	0.05	2 - 592	0.024

[a] Corrected value, calculated from the data in [1,8].

HYDROCARBONS, AROMATIC 1501

FORMULA: Table 1 MW: Table 1 CAS: Table 1 RTECS: Table 1

METHOD: 1501, Issue 3 **EVALUATION: Full** **Issue 1: 15 August 1990**
Issue 3: 15 March 2003

OSHA : Table 2
NIOSH: Table 2
ACGIH: Table 2

PROPERTIES: Table 1

SYNONYMS: (Synonyms in Table 1)
Group A: benzene; toluene; ethylbenzene; o-xylene; m-xylene; p-xylene
Group B: cumene; p-tert-butyltoluene; α-methylstyrene; β-methylstyrene; styrene

SAMPLING

SAMPLER: SOLID SORBENT TUBE (coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: Table 3

VOL-MIN: Table 3
-MAX: Table 3

SHIPMENT: Routine

SAMPLE STABILITY: 30 days @ 5°C

BLANKS: 10% of samples

ACCURACY

RANGE STUDIED: Table 3

BIAS: Table 3

OVERALL PRECISION ($\hat{S}_{rT}$): Table 3

ACCURACY: Table 3

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: Hydrocarbons listed above

DESORPTION: 1 mL CS_2, stand 30 min with agitation

INJECTION VOLUME: 1 µL (Group A: split 5:1; Group B: split 1:1)

TEMPERATURE
-INJECTION: 250 °C
-DETECTOR: 300 °C
-COLUMN: Group A: 40 °C (10 min) to 230°C (10 °C/min)
Group B: 35°C (8 min) to 225°C (10°C/min)

CARRIER GAS: He @ 2.6 mL/min

COLUMN: Capillary, fused silica
Group A: 30m x 0.32-mm ID; 1-µm film 100% PEG or equivalent
Group B: 30m x 0.53-mm ID; 3-µm film crossbonded® 35% diphenyl 65% dimethyl polysiloxane or equivalent

CALIBRATION: Solutions of analytes in CS_2

RANGE: Table 4

ESTIMATED LOD: Table 4

PRECISION ($\tilde{S}_r$): Table 4

APPLICABILITY: This method is for peak, ceiling, and TWA determinations of aromatic hydrocarbons. Interactions between analytes may reduce breakthrough volumes and affect desorption efficiencies. Naphthalene, originally validated in S292 [4], failed to meet acceptable desorption efficiency recovery and storage stability criteria at the levels evaluated in this study. However, the application of this method to naphthalene levels at or near the REL/PEL continues to meet acceptable recovery criteria. Styrene failed to meet acceptable recovery criteria at the two lowest levels evaluated in this study (highest level to meet the criteria was 181 µg/sample).

INTERFERENCES: Under conditions of high humidity, the breakthrough volumes may be reduced. Other volatile organic compounds such as alcohols, ketones, ethers, and halogenated hydrocarbons are potential analytical interferences.

OTHER METHODS: This method updates NMAM 1501 issued on August 15, 1994 [1] which was based upon P&CAM 127 (benzene, styrene, toluene, and xylene) [2]; S22 (p-tert-butyltoluene) [3]; S23 (cumene) [3]; S29 (ethylbenzene) [3] ; S26 (α-methylstyrene) [3]; S30 (styrene); S311 (benzene) [4]; S343 (toluene) [4]; and S318 (xylenes) [4].

REAGENTS:

1. Carbon disulfide*, low benzene, chromatographic quality.
2. Analytes, reagent grade.
3. Helium, prepurified and filtered.
4. Hydrogen, prepurified and filtered.
5. Air, prepurified and filtered.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends, containing two sections of activated coconut shell charcoal (front = 100 mg, back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 1.0 L/min (Table 3), with flexible connecting tubing.
3. Gas chromatograph, FID, integrator, and columns (page 1501-1).
4. Autosampler vials, glass, 1.8 mL, with PTFE-lined caps.
5. Pipets, 1-mL, and pipet bulb.
6. Syringes, 10-µL, 25-µL, and 250-µL.
7. Volumetric flasks, 10-mL.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and extremely flammable (flash point = -30°C), benzene is a suspect carcinogen. Prepare standards and samples in a well ventilated hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size as shown in Table 3.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Include the glass wool plug in the vial along with the front sorbent section.
6. Add 1.0 mL eluent to each vial. Attach crimp cap to each vial immediately.
7. Allow to stand at least 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards from below the LOD to 10 times the LOQ. If necessary, additional standards may be added to extend the calibration curve.
   a. Add known amounts of analytes to carbon disulfide solvent in 10-mL volumetric flasks and dilute to the mark. Prepare additional standards by serial dilution in 10-mL volumetric flasks.
   b. Analyze together with samples and blanks (steps 11 through 12).
   c. Prepare calibration graph (peak area of analyte vs. µg analyte per sample).

9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8).
   a. Prepare three tubes at each of five levels plus three media blanks.
   b. Inject a known amount of DE stock solution (5 to 25 µL) directly onto front sorbent section of each charcoal tube with a microliter syringe.
   c. Allow the tubes to air equilibrate for several minutes, then cap the ends of each tube and allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze together with standards and blanks (steps 11 and 12).
   e. Prepare a graph of DE vs. µg analyte recovered.
10. Analyze a minimum of three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1501-1. Inject a 1-µL sample aliquot manually using the solvent flush technique or with an autosampler.
    Note: If peak area is above the linear range of the working standards, dilute with solvent, reanalyze, and apply the appropriate dilution factor in the calculations.

Analyte	Approximate Retention Time (min)
benzene[a]	3.52
toluene[a]	6.13
ethylbenzene[a]	10.65
o-xylene[a]	12.92
m-xylene[a]	11.33
p-xylene[a]	11.04
cumene[b]	18.61
p-tert-butyltoluene[b]	21.45
α-methylstyrene[b]	19.99
β-methylstyrene[b]	20.82
styrene[b]	18.33

[a] Separation achieved using a 30-m Stabilwax fused silica capillary colum.
[b] Separation achieved using a 30-m Rtx-35 fused silica capillary column.

12. Measure peak areas.

CALCULATIONS:

13. Determine the mass, µg (corrected for DE) of analyte found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of analyte in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b)}{V}, mg/m^3$$

NOTE: µg/L = mg/m^3

EVALUATION OF METHOD:

The desorption efficiency, at levels ranging from 5 times the LOQ to 0.1x the REL, was determined for each analyte by spiking known amounts (in CS_2) on coconut shell charcoal tubes. Both groups of analytes (A and B) were spiked together on the charcoal sorbent tubes. All analytes, with the exception of styrene and naphthalene, exhibited acceptable desorption efficiency recovery results at all five levels evaluated. Styrene failed to meet the 75% recovery criteria at the 18.1 µg and 90.6 µg levels. Naphthalene failed to meet the 75% criteria at all levels evaluated ranging from 48.8 µg to 976.0 µg.

Each analyte, at a level approximately 0.05x REL/PEL, was evaluated for its storage stability @ 5°C after 7, 14, and 30 days. All analytes, with the exception of naphthalene, had acceptable recoveries after 30 days storage.

REFERENCES:

[1] NIOSH [1984]. Hydrocarbons, Aromatic: Method 1501. In: Eller PM, ed. NIOSH Manual of Analytical Methods. 4th rev. ed. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 94-113.

[2] NIOSH [1977]. NIOSH Manual of Analytical Methods, 2nd. ed., V. 1, P&CAM 127, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A.

[3] Ibid, V. 2, S22, S23, S25, S26, S29, S30, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).

[4] Ibid, V. 3, S292, S311, S318, S343, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).

[5] NIOSH [1977]. Documentation of the NIOSH Validation Tests, S22, S23, S25, S26, S29, S30, S292, S311, S318, S343, U.S. Department of Health, Education, and Welfare; Publ. (NIOSH) 77-185.

METHOD WRITTEN BY:

Stephanie M. Pendergrass, NIOSH/DART

TABLE 1. SYNONYMS, FORMULA, MOLECULAR WEIGHT, PROPERTIES

Name/Synonyms	Empirical Formula	Molecular Weight	Boiling Point (°C)	Vapor Pressure @ 25 °C (mm Hg)	(kPa)	Density @ 20 °C (g/mL)
benzene CAS #71-43-2 RTECS CY1400000	C_6H_6	78.11	80.1	95.2	12.7	0.879
p-tert-butyltoluene CAS #98-51-1 RTECS XS8400000 1-tert-butyl-4-methylbenzene	$C_{11}H_{16}$	148.25	192.8	0.7	0.09	0.861
cumene CAS #98-82-8 RTECS GR8575000 isopropylbenzene	C_9H_{12}	120.20	152.4	4.7	0.63	0.862
ethylbenzene CAS #100-41-4 RTECS DA0700000	C_8H_{10}	106.17	136.2	9.6	1.28	0.867
α-methylstyrene CAS #98-83-9 RTECS WL5075300 isopropenylbenzene (1-methylethenyl)-benzene	C_9H_{10}	118.18	165.4	2.5	0.33	0.909
β-methylstyrene CAS #873-66-5 RTECS DA8400500	C_9H_{10}	118.18	175.0	—	—	0.911
toluene CAS #108-88-3 RTECS XS5250000 methylbenzene	C_7H_8	92.14	110.6	28.4	3.79	0.867
xylene[c]	C_8H_{10}	106.17				
CAS #1330-20-7	(ortho)		144.4	6.7	0.89	0.880
RTECS ZE2100000	(meta)		139.1	8.4	1.12	0.864
dimethylbenzene (p-xylene)	(para)		138.4	8.8	1.18	0.861
styrene CAS #100-42-5 RTECS WL3675000 vinylbenzene	C_8H_8	104.15	145.2	6.1	0.81	0.906

TABLE 2. PERMISSIBLE EXPOSURE LIMITS, PPM

		NIOSH			ACGIH		
Substance	OSHA TWA	TWA	C	STEL	TLV	STEL	mg/m³ per ppm
benzene	1	0.1[a]	1		10[b]		3.19
p-tert-butyltoluene	10	10		20	1		6.06
cumene	50 (skin)	50 (skin)			50 (skin)		4.91
ethylbenzene	100	100		125	100	125	4.34
α-methylstyrene	100	50		100	50	100	4.83
β-methylstyrene	100	50		100	50	100	4.83
toluene	200	100		150	50 (skin)		3.77
o-xylene	100	100[c]		150	100	150	4.34
m-xylene	100	100			100	150	4.34
p-xylene	100	100			100	150	4.34
styrene	100	50		100	50	100 (skin)	4.26

[a] Potential carcinogen
[b] Suspect carcinogen
[c] Group I Pesticide

TABLE 3. SAMPLING FLOWRATE[a], VOLUME, CAPACITY, RANGE, OVERALL BIAS AND PRECISION

	Sampling			Breakthrough		Range at	Overall		
	Flowrate	Volume[b] (L)		Volume @ Concentration		VOL-MIN	Bias	Precision	Accuracy
Substance	(L/min)	MIN	MAX	(L)	(mg/m³)	(mg/m³)	(%)	($\hat{S}_{r_T}$)	(±%)
benzene	≤0.20	5	30	>45	149	42 - 165	-0.4	0.059	11.4
p-tert-butyltoluene	≤0.20	1	29	44	112	29 - 119	-10.3	0.071[c]	20.7
cumene	≤0.20	1	30	>45	480	120 - 480	5.6	0.059	15.2
ethylbenzene	≤0.20	1	24	35	917	222 - 884	-7.6	0.089[c]	17.1
α-methylstyrene	≤0.20	1	30	>45	940	236 - 943	-7.6	0.061[c]	16.9
β-methylstyrene	≤0.20	1	30	>45	940	236 - 943	-7.6	0.061	16.9
toluene	≤0.20	1	8	12	2294	548 - 2190	1.6	0.052	10.9
xylene (o-,m-,p-)	≤0.20	2	23	35	870	218 - 870	-1.2	0.060	12.2
styrene	≤1.00	1	14	21	1710	426 - 1710	-7.9	0.058[c]	16.7

[a] Minimum recommended flow is 0.01 L/min.
[b] V_{Min} = minimum sample volume @ OSHA TWA;
V_{Max} = maximum sample volume @ OSHA TWA
[c] Corrected value, calculated from data in Reference 5.

TABLE 4. MEASUREMENT RANGE AND PRECISION[a]

Substance	LOD (µg/sample)	Measurement	
		Range (mg)	Precision ($\hat{S}_r$)
benzene	0.5	0.004-0.35	0.013
p-tert-butyltoluene	1.1	0.013-1.09	0.017[a]
cumene	0.6	0.039-3.46	0.017
ethylbenzene	0.5	0.045-8.67	0.015
α-methylstyrene	0.6	0.036-3.57	0.014
β-methylstyrene	0.6	0.036-0.728	0.014
toluene	0.7	0.024-4.51	0.022
o-xylene	0.8	0.044-10.4	0.014
m-xylene	0.8	0.043-0.864	0.013
p-xylene	0.7	0.043-0.861	0.015
styrene	0.4	0.181-8.49	0.014

[a] Corrected value, calculated from data in [5].