

VOLATILE ORGANIC COMPOUNDS IN WATER, SOIL, SOIL GAS, AND AIR  
BY DIRECT SAMPLING ION TRAP MASS SPECTROMETRY (DSITMS)

## 1.0 SCOPE AND APPLICATION

1.1 This method uses direct sampling ion trap mass spectrometry (DSITMS) for the rapid quantitative measurement, continuous real-time monitoring, and qualitative and quantitative preliminary screening of volatile organic compounds (VOCs) in water, soil, soil gas, and air. DSITMS introduces sample materials directly into an ion trap mass spectrometer by means of a simple interface (such as a capillary restrictor). There is little if any sample preparation and no chromatographic separation. The response of the instrument to analytes in a sample is nearly instantaneous. In addition, the instrument is field transportable, rugged, and relatively easy to operate and maintain.

1.2 This method is applicable to the determination of VOCs in discrete samples taken to the laboratory and to on-site measurement and monitoring. It is best suited for semiquantitative screening, for repetitive quantitative analysis of previously characterized samples for pre-selected analytes, and for establishing the absence/presence of VOCs at the limit of detection of the operating conditions employed. Specialty applications include on-line deployment with direct-push technologies, *in situ* sampling, and continuous real-time monitoring of VOCs.

1.3 The method is not suited to identifying or quantitating a large number of constituents in highly complex mixtures nor to quantitating constituents at the isomeric level. Identifying unknown or unusual constituents in complex multi-component mixtures is better achieved using standard gas chromatography/mass spectrometry methods. This procedure is usually not applicable if results are required for individual positional isomers (e.g.; *o*-, *m*-, or *p*-xylenes) or individual geometric isomers (e.g., *cis*- or *trans*-1,2-dichloroethenes) unless unique operating conditions are developed and demonstrated. The principal limitation of the method is the need to demonstrate the absence of interfering analytes at the levels of concern before quantitative analysis can be performed.

1.4 This method is especially useful for the analysis of large numbers of samples, for screening samples, for on-site analyses, and for applications benefitting from its special sampling probes. Examples include surveys with high spatial and/or temporal resolution, plume mapping where results determine the next sampling point, monitoring a remedial action, *in situ* sampling of VOCs, and depth-profiling a groundwater well.

1.5 VOCs in air can be monitored continuously in real-time (~1 mass spectrum/second) at concentrations down to 50 ppbv, or lower, depending on the analyte. The method is applicable to ambient air, soil gas, headspace, process streams, and stack emissions, as well as to VOCs continuously purged from groundwater, surface water, and aqueous process streams.

1.6 This method is applicable to VOCs such as those listed below and to volatile mixtures such as hydrocarbon fuels, provided that one or more ions are identified which are unique to the analyte at the level of concern.

Compound	CAS Registry No.
Acetone	67-64-1
Benzene	71-43-2
Bromodichloromethane	75-27-4
Bromoform	75-25-2
Bromomethane	74-83-9
Carbon disulfide	75-15-0
Carbon tetrachloride	56-23-5
Chlorobenzene	108-90-7
Chloroethane	75-00-3
Chloroform	67-66-3
Chloromethane	74-87-3
Dibromochloromethane	124-48-1
1,1-Dichloroethane	75-34-3
1,2-Dichloroethane	107-06-2
1,1-Dichloroethene	75-35-4
<i>cis</i> -1,2-Dichloroethene	156-59-2
<i>trans</i> -1,2-Dichloroethene	156-60-5
Dichloromethane	75-09-2
1,2-Dichloropropane	78-87-5
<i>cis</i> -1,3-Dichloropropene	10061-01-5
<i>trans</i> -1,3-Dichloropropene	10061-02-6
Ethylbenzene	100-41-4
2-Hexanone	591-78-6
Methyl ethyl ketone (MEK)	78-93-3
Methyl isobutyl ketone (MIBK)	108-10-1
Methyl- <i>tert</i> -butyl ether (MTBE)	1634-04-4
Styrene	100-42-5
1,1,2,2-Tetrachloroethane	79-34-5
Tetrachloroethene	127-18-4
Toluene	108-88-3
1,1,1-Trichloroethane	71-55-6
1,1,2-Trichloroethane	79-00-5
Trichloroethene	79-01-6
Vinyl acetate	108-05-4
Vinyl chloride	75-01-4
Xylenes	1330-20-7

In addition, by monitoring common hydrocarbon fragment ions, this method can be used to monitor the presence of the generalized class of "petroleum hydrocarbons."

1.7 Multiple component full scan (masses from 15 to 250 amu) analysis for VOCs in discrete samples can be performed in three minutes or less, with quantitation limits of at least 5 µg/L in water and 20 µg/kg in soil. Quantitation limits for air samples collected on sorbent traps equal or exceed those for water and soil, depending on the volume of air sampled. Operating conditions optimized to measure a single VOC can provide a ten-fold improvement in quantitation limit.

1.8 This method is applicable to the initial investigation of sites suspected to have VOC contamination, as well as to sites with previously known VOC contamination. When applied to sites with previously known contamination, the DSITMS is initially calibrated only for the known analytes of interest at the site, instead of the entire list of applicable analytes. If unexpected compounds are detected at any time during the investigation, a new calibration curve may be generated to include the additional analytes of interest. When the method is applied to sites with suspected VOC contamination, but the specific analytes of interest are unknown, site samples are screened to obtain mass spectra to identify analytes of interest present at the site. Once the site-specific analyte list has been established, the DSITMS can be calibrated for quantitative analysis of subsequent samples. One of the advantages derived from the rapid analysis time and high throughput of this method (3 to 4 minutes/sample) is that initial calibration or recalibration generally can be achieved in one hour. This allows for very rapid recalibration when unexpected analytes are encountered after initial calibration, or for recalibration after routine instrument maintenance.

1.9 Another advantage of the rapid analysis capability of this method is that it allows more time to be devoted to the analysis of quality control samples. Since most field sampling methods do not exceed the daily analytical capabilities of a single DSITMS deployed at a site, significant time is available to continuously monitor system performance. It is practical, for example, to run blanks before and after samples and check standards, and to run check standards more frequently to document performance, if desired. It is also practical to analyze samples in replicate, if desired.

1.10 It is recommended that a certain percentage (determined on a project-specific basis and specified in a properly executed QAPP, SAP, or other appropriate planning document) of the samples analyzed by DSITMS be also analyzed by a traditional fixed-laboratory method (e.g., Method 5021 for solid samples or 5030 for aqueous samples/Method 8260) as a quality control measure. An additional quality control option is to install a solid sorbent trap on the exit of the split vent of the direct sampling interface. Material collected on the solid sorbent trap may be analyzed by thermal desorption GC/MS to confirm the identities of the analytes, if needed.

1.11 Prior to employing this method, analysts are advised to consult the base method for each type of procedure that may be employed in the overall analysis (e.g., Method 8000). Analysts should consult the disclaimer statement at the front of the manual and the information in Chapter Two, for guidance on the intended flexibility in the choice of methods, apparatus, materials, reagents, and supplies, and on the responsibilities of the analyst for demonstrating that the techniques employed are appropriate for the analytes of interest, in the matrix of interest, and at the levels of concern.

In addition, analysts and data users are advised that, except where explicitly specified in a regulation, the use of SW-846 methods is *not* mandatory in response to Federal testing requirements. The information contained in this method is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to generate results that meet the data quality objectives for the intended application.

1.12 Use of this method is restricted to use by, or under supervision of, trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

## 2.0 SUMMARY OF THE METHOD

2.1 Volatile organic compounds (VOCs) are purged or desorbed from liquid or solid samples, and conveyed directly into the mass spectrometer ion source by means of a stream of helium (or air and/or other gas for suitable mass spectrometers), where the compounds are ionized by electron impact (EI) and/or chemical ionization (CI). Full-scan mass spectra are acquired continuously and are used to identify the VOCs. Characteristic ions unique to the target analytes are monitored for a selected period of time to establish an accumulated (integrated or averaged) response and the response is compared to that from a comparably generated calibration factor for quantitation. Selective ionization, multiple stage/mass spectrometry (MS/MS), and spectral subtraction may be employed in cases where additional selectivity is required.

2.2 Discrete samples of water or soil may be analyzed for VOCs by purging the sample with a stream of helium (or air and/or other gas) in a manner comparable to that performed in standard purge-and-trap GC/MS methods. However, the VOCs are monitored continuously, rather than being collected for subsequent analysis. Discrete samples of VOCs collected from air on sorbent traps are thermally-desorbed in a stream of helium (or air and/or other gas) and monitored similarly during the desorption process.

2.3 *In situ* continuous real-time measurement of VOCs may be performed using sampling probes that transfer the VOCs from their matrix into the vapor phase. An air-monitoring module employs a pump to deliver the VOCs to the mass spectrometer. Sampling probes are available which allow the *in situ* measurement of VOCs in groundwater, surface water, and soil, and the continuous monitoring of air, gaseous process streams, and aqueous process streams. The probes may be deployed with site characterization tools such as cone penetrometry and hydropunch or may be used at existing sampling wells and sites.

2.4 This procedure permits data to be acquired in both EI and CI modes, if desired, alternating between one and the other under computer control. In the EI mode, structural information is obtained from the fragmentation pattern produced, while complementary molecular ion information is obtained in the CI mode. The CI mode also provides enhanced sensitivity and improved selectivity for certain compounds, including alkyl-aromatics, ketones, and aldehydes.

## 3.0 DEFINITIONS

Refer to Chapter One for a listing of applicable quality assurance/quality control (QA/QC) definitions.

## 4.0 INTERFERENCES

4.1 VOCs which yield molecular ions or fragment ions with the same  $m/z$  values as the characteristic ions of the targeted VOCs will give a false positive response or a positive-biased result if present in sufficient quantities. This is detected by abnormal isotope distribution patterns, where applicable, and/or the presence of other ions from the interferent in the mass spectrum.

4.2 Major differences in the purge profiles for any given analyte between the calibration standard and the sample may indicate an unexpected matrix effect.

4.3 Positional and geometric isomers cannot usually be distinguished from one another using this method (unless suitable operating conditions are developed and demonstrated) because the isomers yield identical mass spectra.

## 5.0 SAFETY

This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals mentioned in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

## 6.0 EQUIPMENT AND SUPPLIES

This section lists the equipment for DSITMS measurements in water (Sec. 6.1), soil (Sec. 6.2), and soil gas and air (Sec. 6.3).

Except where otherwise noted, instrumentation described in this method is available from Tri-Corders Environmental, Inc., 1800 Old Meadow Rd., Suite 102, McLean, VA, 22107; 703-442-9866, or Oak Ridge National Laboratory (ORNL), Chemical and Analytical Sciences Division, P.O. Box 2008, Oak Ridge, TN 37831-6130; 865-574-4862.

### 6.1 Equipment for the analysis of water

6.1.1 Ion trap mass spectrometer - capable of operation in alternating EI and CI modes (Finnigan MAT ITMS, San Jose, CA, or Varian Saturn 2000, Palo Alto, CA).

NOTE: Other mass spectrometers may be used if they have capabilities and performance specifications appropriate for the intended application.

6.1.2 Heated, deactivated fused-silica capillary restrictor direct sampling interface - with built-in gas flow splitter and a fitting for quick connection of sampling modules and probes (see Figure 1). Capillary restrictor is commonly 24 cm long and 100 microns ID and can be heated to a maximum temperature of 300 °C.

#### 6.1.3 Direct sampling modules and probes for analyzing water

6.1.3.1 A direct sparging device is used for the analysis of water in 40-mL VOA vials.

6.1.3.2 An *in situ* sparging probe is used for *in situ* monitoring of groundwater or surface water.

6.1.4 Precalibrated variable volume pipets that are compatible with methanol or other organic solvents (Polymerase chain reaction (PCR) pipet, Tri-Continent Scientific, Inc., Gross Valley, CA, or equivalent).

6.1.5 Syringe, 10- $\mu$ L capacity (Precision Sampling, Baton Rouge, LA, or equivalent).

6.1.6 Screw-cap vials, 5-mL capacity - pre-cleaned, with solid caps containing fixed polytetrafluoroethylene (PTFE) liners.

- 6.1.7 Screw-cap VOA vials, 40-mL - pre-cleaned.
- 6.1.8 Volumetric flask, 10-mL (Pyrex®, or equivalent).
- 6.1.9 Flow meter - capable of measuring 100 mL/min. (A.P. Buck Calibration Meter, Model M-5, Orlando, FL, or equivalent).
- 6.1.10 Stopwatch, laboratory timer, or wristwatch with alarm - capable of timing to 3 minutes.
- 6.1.11 Disposable 2-mL pipets.
- 6.2 Equipment for the analysis of soil
  - 6.2.1 Ion trap mass spectrometer as described in Sec. 6.1.1.
  - 6.2.2 Capillary restrictor inlet as described in Sec. 6.1.2.
  - 6.2.3 Sampling module as described in Sec. 6.1.3.1.
  - 6.2.4 Heated injector module for soil extracts.
  - 6.2.5 Electronic balance - capable of weighing to the nearest 0.1 gram (Allied Fisher Scientific balance, Model 8301A, Denver, CO, or equivalent).
  - 6.2.6 Portable heater (for 40-mL VOA sample vials) - capable of reaching a temperature range between 140 - 200 °F (Omega Engineering heater, Model CN9000A, Stamford, CT, or equivalent). For heated purge.
  - 6.2.7 Aluminum sleeve - 0.5-cm in thickness, 5.5-cm in length, and 2.8-cm ID. Used as a heating jacket for 40-mL VOA vials. For heated purge.
  - 6.2.8 Thermocouple - attached to aluminum sleeve for monitoring vial temperature (Omega Engineering, Stamford, CT, or equivalent). For heated purge.
  - 6.2.9 Digital thermometer - Model HH81 (Omega Engineering, Stamford, CT), or equivalent. Used to monitor vial temperature. For heated purge.
  - 6.2.10 Magnetic stirrer - Model 15 (Arthur H. Thomas Co., Philadelphia, PA), or equivalent.
  - 6.2.11 Stirring bar - approximately 0.8-cm in thickness and 2-cm in length.
- 6.3 Equipment for the analysis of soil gas and air
  - 6.3.1 Ion trap mass spectrometer as described in Sec. 6.1.1.
  - 6.3.2 Real-time air sampling module.
  - 6.3.3 Tedlar® gas sample bags, 10- and 20-L capacity (SKC, Inc, Eighty Four, PA, or equivalent).
  - 6.3.4 Syringe, 2000-mL capacity (Hamilton Co., Reno, NV, or equivalent).

- 6.3.5 Sample lock, 1-, 5-, 25-, and 50-mL capacity (Hamilton Co., Reno, NV, or equivalent).
- 6.3.6 Thermal desorber - capable of accepting 0.25-in diameter by 3-in length sorbent tubes.
- 6.3.7 Variable power transformer or timer-type heater controller - for thermal desorber.
- 6.3.8 Digital thermometer as described in Sec. 6.2.9.
- 6.3.9 Stopwatch, laboratory timer, or wristwatch with alarm - must be capable of timing to 3 minutes.

## 7.0 REAGENTS AND STANDARDS

Reagent grade (or better) chemicals of known purity must be used in all tests. Unless otherwise indicated, all reagents must conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

References to water (other than water samples) in this method refer to organic-free reagent water, as defined in Chapter One.

7.1 Simulated groundwater - prepared by adding 148 mg/L of sodium sulfate and 165 mg/L of sodium chloride (100 mg/L each of  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  ions) to organic-free reagent water.

NOTE: Commercially-available water may be substituted for the simulated groundwater provided that it has been shown to be free of any detectable VOCs. Waters marketed under the names of "artesian" or "spring" are generally acceptable. Waters whose source is municipal in origin generally contain trace VOCs and are unacceptable. These are marketed under names such as "distilled" or "drinking".

7.2 Methanol, purge-and-trap grade, or equivalent, demonstrated to be free of analytes. Store apart from other solvents.

7.3 Helium, 99.996% minimum purity and free of detectable VOCs.

7.4 Neat standard chemicals, 99% purity or better.

NOTE: Chemicals may also be purchased as dilute solutions of known concentrations in methanol, shipped and stored in ampules, and substituted for neat target chemicals.

7.5 Compressed breathing air, or higher purity air if required.

7.6 Soil for preparing blanks and standards.

NOTE: Soil for preparing blanks and standards may be obtained from any suitable source, provided that the soil can be demonstrated to be VOC-free. If practical, the soil used for this purpose should be of a type and composition similar to that of the unknown soil samples. This will help to minimize differences in soil matrix effects between the standards and the unknowns.

7.7 Sorbent traps for preparing standards (3 in x 0.25 in diameter).

NOTE: The choice of the specific sorbent material used will depend on the sampling method employed and the VOCs that must be collected.

CAUTION: Sorbent material must be verified to be VOC-free before the preparation of standards.

7.8 Solution standards of individual target analytes.

NOTE: For fixed-laboratory applications, or in cases where available, store solutions in a freezer maintained between -10 °C and -20 °C. In field applications, or in cases where a freezer is not available, maintain all standards as cool as practical. Also, minimize the duration and number of times that the cap is removed. Freezer storage maintains integrity for 3 months. Cool storage maintains integrity for up to one week.

7.8.1 Analyte master stock solution from neat liquids

7.8.1.1 Dilute required volume of analyte in a 10-mL volumetric flask with methanol to yield 5000 mg analyte/L solution (5000 ng/μL). Add the analyte liquid to a partially filled flask then dilute to the mark. This is the analyte master stock solution from neat liquids. The volumes of neat liquid analyte for example target analytes are given in Table 2.

7.8.1.2 Transfer the solution prepared in Sec. 7.8.1.1 to two appropriately labeled 5-mL capacity screw-cap vials. Store as described in Sec. 7.8.

7.8.2 Analyte working solution from analyte master stock solution (see Sec. 7.8.1)

7.8.2.1 Dilute exactly 200 μL of the analyte master stock solution (see Sec. 7.8.1.1) to 10 mL in a volumetric flask with methanol. This is the analyte working solution from the analyte master stock solution. The final solution concentration is 100 mg/L or 100 ng/μL.

7.8.2.2 Transfer the solution prepared in Sec. 7.8.2.1 to two appropriately labeled 5-mL vials. Store as described in Sec. 7.8.

7.8.3 Analyte working solution from individual analytes available in 1-mL ampules containing 1 mL of 1000 mg analyte/L methanol solution

7.8.3.1 Dilute the contents of the ampule with methanol to exactly 10 mL final volume in a volumetric flask. This is the analyte working solution from individual analytes available in 1-mL ampules. The final concentration is 100 mg/L.

7.8.3.2 Transfer the solution prepared in Sec. 7.8.3.1 to two appropriately labeled 5-mL capacity screw-cap vials. Store this solution according to Sec. 7.8.

7.9 Performance evaluation standard (PES)

The following describes a mixture of VOCs that is suggested for the preparation of the performance evaluation standard (PES). This mixture contains acetone, methylene chloride, benzene, and bromobenzene, and will result in a response in both the EI and CI modes of the DSITMS. Other VOCs may be substituted for those listed above, if they are more representative of the VOCs present in the unknown samples. This is left to the professional judgment of the operator.



#### 7.9.1 Performance evaluation master stock solution

7.9.1.1 Dilute 101  $\mu\text{L}$  of acetone, 121  $\mu\text{L}$  of methylene chloride, 46  $\mu\text{L}$  of benzene, and 27  $\mu\text{L}$  of bromobenzene to exactly 10 mL in methanol using a volumetric flask. This is the performance evaluation master stock solution.

7.9.1.2 Transfer the performance evaluation master stock solution to a 20-mL screw-cap vial with a solid PTFE-lined cap. Store as described in Sec. 7.8.

7.9.1.3 Replace the performance evaluation master stock solution every three months, or more frequently, as necessary.

#### 7.9.2 Performance evaluation working solution

7.9.2.1 Dilute 500  $\mu\text{L}$  of the performance evaluation master stock solution (see Sec. 7.9.1.1) to exactly 10 mL with methanol in a volumetric flask. This is the performance evaluation working solution.

7.9.2.2 Transfer the performance evaluation working solution to a 5-mL screw-cap vial with a solid PTFE-lined cap. Store as described in Sec. 7.8.

7.9.2.3 Replace the performance evaluation working solution every two to three weeks, or more frequently, as necessary.

#### 7.10 Internal standard

##### 7.10.1 Internal standard master stock solution

7.10.1.1 Dilute 45  $\mu\text{L}$  of 1,4-difluorobenzene to exactly 10 mL with methanol in a volumetric flask. This is the internal standard master stock solution. The solution concentration is 5000 mg/L.

7.10.1.2 Transfer the internal standard master stock solution to two appropriately labeled 5-mL capacity screw-cap vials with a PTFE-lined cap. Store as described in Sec. 7.8.

##### 7.10.2 Internal standard working solution

7.10.2.1 Dilute 400  $\mu\text{L}$  of the internal standard master stock solution to exactly 10 mL with methanol in a volumetric flask. This is the internal standard working solution. The final solution concentration is 200 mg/L.

7.10.2.2 Transfer the internal standard working solution to two appropriately labeled 5-mL capacity screw-cap vials with a PTFE-lined cap. Store as described in Sec. 7.8.

#### 7.11 Air and soil gas standards

##### 7.11.1 Analyte master standard

7.11.1.1 Fill an empty 20-L Tedlar® bag approximately half-full with pure breathing air.

NOTE: Pure helium or dry nitrogen can be substituted for air, if necessary.

7.11.1.2 Using a vacuum line, completely evacuate the air from the Tedlar® bag.

7.11.1.3 Repeat the steps in Secs. 7.11.1.1 and 7.11.1.2 at least two more times, to remove residual VOC contamination.

7.11.1.4 Fill the Tedlar® Bag with 20 L of pure breathing air.

NOTE: Pure helium, nitrogen, or other gases can be substituted for air if necessary for special applications.

7.11.1.5 Using the following formula, calculate the volume of neat compound to make a 1000 ppmv standard for the analyte of interest. "R" is the universal gas constant with a value of 82.1 (atm mL/g mole °K). The result of the calculation gives the number of mL of neat liquid needed to produce a 1,000 ppmv stock standard in air.

$$\frac{[\text{mw} \times \text{barometric press. (atm)}] \times [\text{final conc. desired (ppm)}] \times [\text{final vol. (L)}]}{\text{liquid density (g/mL)} \times 82.1 \text{ (R)} \times \text{temp. (}^\circ\text{K)}}$$

7.11.1.6 Using a syringe, inject the required amount of neat liquid into the Tedlar® bag through the septum port.

7.11.1.7 Manually agitate the Tedlar® bag to help disperse the analyte.

7.11.1.8 Allow at least 5 minutes for the standard in Tedlar® bag to equilibrate after all of the liquid has evaporated. This is the analyte master standard.

7.11.1.9 The storage life of the analyte master standard is approximately 2 days.

#### 7.11.2 Analyte working standard

7.11.2.1 Fill a 10-L Tedlar® bag with pure breathing air.

NOTE: Pure helium or dry nitrogen can be substituted for air, if necessary.

7.11.2.2 Using a vacuum line, completely evacuate the air from the Tedlar® bag.

7.11.2.3 Repeat the steps in Secs. 7.11.2.1, and 7.11.2.2 at least two more times to remove residual VOC contamination.

7.11.2.4 Fill the Tedlar® bag with 10 L of pure breathing air.

NOTE: Pure helium, nitrogen, or other gases can be substituted for air, if necessary for special applications.

7.11.2.5 Use a gas-tight syringe to inject a quantity of the analyte master standard into the 10-L Tedlar® bag of air to make analyte working standards ranging from 10 to 1000 ppbv. See Table 3 for the exact amount of analyte master standard to inject.

7.11.2.6 The analyte working standard should be prepared daily.

## 8.0 SAMPLE HANDLING, PRESERVATION, AND STORAGE

8.1 Samples collected for analysis in the field should be stored in an ice chest at 4 °C unless they will be analyzed within one hour of collection.

8.2 Storage of water samples for 24 hours or more should include refrigerated (4 °C) storage and the addition of sodium bisulfate (approximately 1 g/40-mL VOA vial) as a preservative, if necessary.

8.3 Samples are analyzed without further preparation.

8.4 Also, sampling procedures should follow the guidelines in Chapter Nine or other appropriate guidance, if not contrary to the method-specific guidelines described in this method.

## 9.0 QUALITY CONTROL

9.1 For analyses in the field or as a supplement to quality control practices in the laboratory, it is recommended that blanks be run before and after performance check standards and samples are run. Replicate samples should be analyzed when sufficient sample is available to provide multiple identical aliquots, or as required on a project-specific basis.

9.2 When the method is used for quantitative analysis, a certain percentage (determined on a project-specific basis, and specified in a properly executed QAPP, SAP or other appropriate planning document) of the samples should be analyzed by a traditional fixed-laboratory method (e.g., Method 5021 for solid samples or 5030 for aqueous samples/Method 8260). An additional quality control option is to install a solid sorbent trap on the exit of the split vent of the direct sampling interface. Material collected on the solid sorbent trap may be analyzed by thermal desorption GC/MS to confirm the identities of the analytes, if needed.

9.3 Refer to Chapter One for additional guidance on quality assurance protocols. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated. All data sheets and quality control data should be maintained for reference or inspection.

## 10.0 CALIBRATION AND STANDARDIZATION

Instrument operating parameters are examined daily and adjusted if necessary. The mass axis of the mass spectrometer is calibrated daily and the sampling module to be used is examined for contamination and cleaned before use if found to be contaminated. Quantitation calibration may be performed before or after a sample is analyzed, provided that the same operating conditions are used for both the samples and standards.

### 10.1 Daily instrument operational checks

10.1.1 Check and adjust, as needed, the following aspects of the DSITMS system:

- Mass spectrometer RF tune (dip) and linearity according to the appropriate instrument operating manual.

- Mass spectrometer integrator offset (zero) according to the appropriate instrument operating manual.
- Rotational speed of the mass spectrometer vacuum pump (turbo pump) for normal operation according to the appropriate instrument manual.
- Mass spectrometer internal power supplies using built-in instrument diagnostics, if available.

10.1.2 Install the appropriate sample inlet module and/or probe and check the background mass spectrum for excessive air and water according to the criteria in the instrument operator's manual. Check for excessive organic contamination that may cause interferences in the same mass range as the analytes of interest. Clean probes and/or mass spectrometer as necessary according to the instructions in the appropriate operators manual.

10.1.3 Calibrate the mass spectrometer's mass axis using an appropriate calibration compound such as perfluorotributylamine (PFTBA). Record the results of the calibration for future reference.

## 10.2 Quantitative calibration

Follow the quantitative calibration steps described in the method procedure (Sec. 11.0).

## 11.0 PROCEDURE

The DSITMS system may be used for the measurement of volatile organic compounds (VOCs) in water, soil, soil gas, or air. This section describes procedures for the measurement of VOCs in:

- water by direct purge from a 40-mL VOA vial (Sec. 11.1)
- water by *in situ* sparging (Sec. 11.2)
- soil by heated purge (Sec. 11.3)
- methanol extracts of higher concentration (>10 mg/kg of any analyte) soil by purge (Sec. 11.4)
- soil gas and air by real-time monitoring (Sec. 11.5)
- soil gas and air on sorbent traps by thermal desorption (Sec. 11.6)

While the sample introduction method for these procedures will vary, most of the procedures employ similar measurement strategies and similar analytical sequences. The typical analytical sequence includes:

- instrument set up
- analysis of a spiked blank to ensure no background interference
- analysis of a performance evaluation standard (PES) to test system performance
- quantitative calibration when required
- analysis of samples

VOC-free blanks, spiked blanks, and performance evaluation standards may be analyzed more frequently if desired. As noted above and in Sec. 10.2, instructions for quantitative calibration are included in this section, and may be performed daily or as dictated by the results of the performance evaluation standard analysis. In addition to the steps described in this method, analysts should consult the instrument manufacturer's instructions and/or operating manuals.

## 11.1 Direct purging of water in 40-mL VOA vials

This procedure is subject to carryover when changing from one sample or standard to another. Therefore, it is good practice to remove the septum gasket, wipe dry the inside of the sparging head, and replace the septum gasket after running a mid-level to high-level sample or standard. It is also prudent to install a blank water vial between runs and use the real time monitoring capabilities of the direct sampling ion trap to check for carryover contamination before continuing to the next sample or standard. Contaminated septum gaskets may be reused after baking at 50 °C for 12 hours (suggested bake time), or simply discarded.

The direct sampling ion trap is well suited to prescreening samples. Dilutions of 100-, 400-, and 1,000-fold can be achieved by diluting 400 µL, 100 µL, or 40 µL of a sample respectively in 40 mL of VOC-free water. In this manner, carryover problems may be minimized and the operator may determine the level of calibration standards required for a particular set of samples.

### 11.1.1 Suggested instrument set up

11.1.1.1 See Sec. 10.1 for instructions regarding daily instrument operational checks.

11.1.1.2 Connect the sampling module designed for sparging water samples contained in 40-mL VOA vials to the mass spectrometer. Attach a source of helium (or other purge gas if allowed by the mass spectrometer) to the sparging module for use as the sample purge gas. The suggested operating conditions are as follows:

Helium pressure	20 - 40 psig
Helium flow rate	100 ± 5mL/min
Sample temperature	Ambient temperature
MS operating conditions	See Table 4
Cl reagent gas source	Water from the sparging or other Cl gas from instrument Cl manifold
Ionization times	Refer to the manufacturer's operating instructions
Electron multiplier settings	Refer to the manufacturer's operating instructions
Data acquisition time	3.0 min

11.1.1.3 Use these conditions as guidance to establish operating conditions appropriate for the analysis of the target analytes of interest for the project. Once established, the same operating conditions must be used for the analysis of both samples and standards.

**NOTE:** Shorter data acquisition times may be employed, provided that the same acquisition time is used for all standards and samples and that sufficient data are collected for the purpose of the analysis.

### 11.1.2 Water blank

11.1.2.1 Prepare a water blank. For example, fill a 40-mL VOA vial to within ¼ inch of the lip with VOC-free water and add 10 µL of the internal standard working solution (see Sec. 7.10.2) to make a water blank. This solution contains approximately 0.050 ng/µL internal standard.

11.1.2.2 Attach the 40-mL VOA vial containing the water blank to the sparging head and start the data acquisition program. Turn on the purge gas flow at the beginning of the data acquisition and sparge the vial for the entire data acquisition period.

11.1.2.3 At the end of the data acquisition period, turn off the purge gas flow. Remove the water blank and follow the cleaning procedure described in Sec. 11.1.

11.1.2.4 Evaluate the results for the water blank. If there is a significant EI/CI response for the characteristic ions corresponding to an analyte of interest, reanalyze the same blank or prepare a new blank. If evidence of significant instrument contamination remains, then take corrective action to remove the contamination. Run a new blank after cleaning or other corrective action to demonstrate freedom from contamination.

### 11.1.3 Performance evaluation standard (PES)

The PES is used to determine if the response of the DSITMS instrument (sample inlet and mass spectrometer) has changed significantly over a period of time. An unacceptable PES result could indicate an instrument malfunction and/or the need to perform a new quantitative calibration. It is not necessary to run PES samples if quantitative calibration is repeated more than once during a working day.

11.1.3.1 Prepare an aliquot of the performance evaluation standard (PES) by adding 10  $\mu$ L of the performance evaluation working solution (see Sec. 7.9.2) to a 40-mL aliquot of VOC-free water in a VOA vial. Add 10  $\mu$ L of the internal standard working solution (see Sec. 7.10.2).

11.1.3.2 Attach the vial to the sparging head and start the data acquisition program. Turn on the purge gas flow at the beginning of the data acquisition and sparge the vial for the entire acquisition period.

11.1.3.3 At the end of the data acquisition period, turn off the purge gas flow. Remove the PES and clean the sparging head.

11.1.3.4 Evaluate the PES results. The integrated response for each VOC in the PES should fall within  $\pm 50\%$  of the established mean response for the corresponding VOCs in the PES. Refer to Sec. 12.7.2 for this determination.

11.1.3.5 If the response for the PES is outside of the acceptable range, it may indicate a malfunction of the sample inlet or degradation of the mass spectrometer tuning conditions. Refer to the appropriate instrument manufacturer's manual for diagnosing and correcting problems.

11.1.3.6 If the reason for an unacceptable PES response has been corrected, repeat Secs. 11.1.3.1 through 11.1.3.5 and verify that the PES response has returned to an acceptable value.

11.1.3.7 If the mass spectrometer tuning parameters or other instrument operating parameters have been significantly altered, the mean response of the PES should be re-determined. Refer to Sec. 12.7.2 for calculating the mean response of the PES.

11.1.3.8 The PES should be evaluated at the beginning of the working day. An additional PES may be run at any point during the working day, as needed for QA purposes.

#### 11.1.4 Quantitative calibration

**NOTE:** Quantitative calibration may be postponed until after prescreening a sample, if extra samples are available, in order to choose an optimal calibration range.

11.1.4.1 Fill a 40-mL VOA-vial with VOC-free water leaving approximately  $\frac{1}{4}$  inch of headspace. Add a sufficient aliquot of the analyte working solution (see Sec. 7.8.2) to obtain a solution of the desired concentration (see Table 5 for examples). Add 10  $\mu$ L of the internal standard working solution (see Sec. 7.10.2) to the vial. Three or more concentration levels are typically used.

11.1.4.2 Attach the VOA-vial containing the standard to the sparging head and start the data acquisition program.

11.1.4.3 Turn on the purge gas flow at the beginning of the data acquisition and continue to sparge the standard for the entire acquisition period.

11.1.4.4 At the end of the data acquisition period, turn off the purge gas flow. Remove the water standard vial, clean the sparging head, and install an empty vial.

11.1.4.5 Repeat the process for replicate standards.

11.1.4.6 Repeat the process for the desired additional concentration levels to be included in the calibration curve.

11.1.4.7 Refer to Sec. 12.0 for the appropriate data analysis and calculation procedures.

#### 11.1.5 Sample analysis

11.1.5.1 Run a blank as described in Sec. 11.1.2. This blank can be used to establish a background for spectral subtraction and will also enable carryover of analytes from the calibration procedure to be identified.

11.1.5.2 Obtain a 40-mL VOA vial containing the sample. Pour off enough sample to provide  $\frac{1}{4}$  inch of headspace at the top of the vial. Add 10  $\mu$ L of the internal standard working solution to the vial and attach the vial to the sparging head.

**NOTE:** A pipet may be used to remove enough sample to provide  $\frac{1}{4}$  inch of headspace in the vial. To avoid cross-contamination between samples, the pipet is should be carefully cleaned and rinsed between samples.

11.1.5.3 Start data acquisition. Turn on the purge gas flow at the beginning of the data acquisition and continue to sparge the sample for the entire acquisition period.

11.1.5.4 At the end of the data acquisition period, turn off the purge gas flow. Remove the water sample vial, clean the sparging head, and install an empty vial.

11.1.5.5 Refer to Sec. 12.0 for the appropriate data analysis and calculation procedures.

11.1.5.6 Repeat these steps if replicate samples are being analyzed.

## 11.2 *In situ* sparging of water

This procedure uses an *in situ* probe for the measurement of VOCs in groundwater without retrieving a discrete sample of water from a well. The *in situ* probe can be placed with a cone penetrometer-driven groundwater sampler, such as the Hydropunch II<sup>®</sup>. The probe may also be used alone to monitor VOCs in existing groundwater wells.

### 11.2.1 Suggested instrument set up

11.2.1.1 See Sec. 10.1 for instructions regarding daily instrument operational checks.

11.2.1.2 Ensure that the *in situ* sparging probe and associated equipment are properly connected to the mass spectrometer. The suggested operating conditions are as follows:

Helium pressure	20 - 40 psig
Helium flow rate	30 - 200 mL/min
Sample temperature	Ambient temperature
MS operating conditions	See Table 4
CI reagent gas source	Water from the sparging or other CI gas from instrument CI manifold
Ionization times	Refer to the manufacturer's operating instructions
Electron multiplier settings	Refer to the manufacturer's operating instructions
Data acquisition time	Estimated run time x 2

11.2.1.3 Use these conditions as guidance to establish operating conditions appropriate for the analysis of the target analytes of interest for the project. Once established, the same operating conditions must be used for the analysis of both samples and standards.

**NOTE:** Shorter data acquisition times may be employed, provided that the same acquisition time is used for all standards and samples and that sufficient data are collected for the purpose of the analysis.

11.2.1.4 Optimize the helium flow to the *in situ* sparger. The optimal flow rate will depend on the design of the *in situ* sparger and the return line composition, diameter, and length, and should be in the range of 30 - 200 mL/min. Too little flow can result in poor analytical sensitivity and excessive analysis times. Too much flow can result in the rapid depletion of available analytes and moisture carryover into the return line. Secs. 11.2.1.5 through 11.2.1.8 describe the optimization of the helium flow.

11.2.1.5 Verify that the return line metering valve is fully off and energize the vacuum source.



11.2.1.6 Insert the *in situ* sparger into a VOC-free water blank. A constant helium bubble stream should be evident.

11.2.1.7 Slowly open the return line metering valve until a noticeable reduction in the bubble stream rate is apparent. From this point forward, very fine valve adjustments should be initiated so as to not draw water into the return line.

11.2.1.8 Adjust the metering valve so that a bubble of helium exits the probe approximately once every 1 to 5 seconds. Pause 30 to 60 seconds between each adjustment to allow for the system to return to equilibrium. A larger return line internal volume (i.e., longer line) will result in a dampening effect which must be taken into consideration when making metering valve adjustments.

**CAUTION:** It is critical that the flow of helium through the return line is always maintained at slightly less than the flow from the helium source to the sparging head to ensure that water is not drawn into the return line and up into the mass spectrometer interface. Although drawing water into the interface will not permanently damage the mass spectrometer, it will, at the very least, result in the need to back flush and dry the system. A worst case scenario would require cleaning of the mass spectrometer.

11.2.1.9 Once the proper flow conditions have been set, remove the *in situ* sparging probe from the water blank and allow air to be drawn through the line to remove any residual moisture. Do not change the helium pressure or flow rates without repeating the flow optimization steps in Secs. 11.2.1.5 through 11.2.1.8.

## 11.2.2 *In situ* sample analysis

11.2.2.1 Set the acquisition time such that it is in excess of that required for analysis of all samples and calibrants. Generally, a time of 120 minutes is sufficient.

11.2.2.2 Carefully lower the *in situ* sparger into a VOC-free blank. Monitor the signal using the real time monitoring capabilities of the direct sampling ion trap mass spectrometer and verify that there is an acceptable level of characteristic ions corresponding to the analytes of interest.

**NOTE:** The sample transfer line is the primary source of contamination that will give rise to an unacceptable background signal level. If the background signal is unacceptable, the transfer line will need to be cleaned or replaced as specified in the *in situ* probe operator's manual.

11.2.2.3 Confirm that the water level has stabilized in the well or wells to be analyzed. Note and record the depth to water in each well.

11.2.2.4 Start the data acquisition program and collect several minutes of blank signal. The delay time for the vapor front to travel through the transfer line may be included in the collection time for the blank signal. Therefore, it is acceptable to begin Sec. 11.2.2.5 before the complete blank collection time has expired.

11.2.2.5 Remove the *in situ* sparger from the blank and lower it into the well to be analyzed. When the sparger is within approximately one foot of the water surface, reduce the descent rate to between ½ and 1 inch per second and slowly

lower the sparger beneath the water surface. If the probe is equipped with a conductivity water sensor, it will be evident when the probe reaches the water. If not, rely on the depth to water reading recorded earlier.

**CAUTION:** Exercise due care in handling the sample transfer line such that the *in situ* sparging probe is always held in the upright vertical position, to prevent water droplets from being drawn into the helium return line.

11.2.2.6 Once the water level has been reached, slowly lower the probe until it is approximately 6 to 12 inches below the water surface and leave the probe in this position to acquire several minutes of data while in the well.

11.2.2.7 At the end of the data acquisition, withdraw the probe from the well. Visually verify that the probe was inserted below the water surface by inspecting it for residual water droplets. Restore the probe and the sample transfer line to their respective storage positions. Ensure that the probe stays in the upright and vertical position.

11.2.2.8 Decontaminate the probe by rinsing it with VOC-free water.

11.2.2.9 Slowly insert the probe into a VOC-free blank and continue to acquire data until the background signal is reduced to an acceptable level.

### 11.2.3 Instrument calibration

11.2.3.1 Beginning with the lowest concentration standard, sequentially acquire several minutes of data for each as necessary. Use the response profile from the well that produced the greatest signal response to determine the highest standard concentration that needs to be acquired. Continue to run successively higher standards until the highest well concentration has been bracketed by two standard concentrations. Decontaminate the probe between each standard by rinsing it with VOC-free water.

11.2.3.2 Manually terminate the data acquisition according to the manufacturer's directions upon completing the series of standards.

11.2.3.3 Remove the *in situ* sparging probe from any water that it may be in, rinse, and leave it open to the air between runs so as to allow any entrained moisture in the sampling transfer line to dissipate as much as possible.

11.2.4 Refer to Sec. 12.0 for the appropriate data analysis and calculation procedures.

### 11.3 Heated purge of soil slurries in 40-mL VOA vials

This procedure is preferred for samples which contain target analyte concentrations in the range of 1 µg/kg to 10 mg/kg. Detection limits will be comparable to those for VOCs in water provided that the soil matrix does not strongly retain the targeted compounds. Heating of the soil slurry helps to reduce the soil matrix effects. Ambient temperature purge may be used if it provides the required detection limit. Also see the text under Sec. 11.1 for additional guidance.

### 11.3.1 Suggested instrument set up

11.3.1.1 See Sec. 10.1 for instructions regarding daily instrument operational checks.

11.3.1.2 Connect to the mass spectrometer the sampling module designed for sparging soil slurry samples contained in 40-mL VOA vials. Attach a source of helium (or other purge gas if allowed by the mass spectrometer) to the sparging module for use as the sample purge gas. Follow manufacturer's instructions for attachment of the heating sleeve, thermocouple (attach to digital thermometer), and 40-mL VOA vial. The suggested operating conditions are as follows:

Helium pressure	20 - 40 psig
Helium flow rate	100 ± 5mL/min
Sample temperature	Set heating sleeve to 50 °C
MS operating conditions	See Table 4
CI reagent gas source	Water from the sparging or other CI gas from instrument CI manifold
Ionization times	Refer to the manufacturer's operating instructions
Electron multiplier settings	Refer to the manufacturer's operating instructions
Data acquisition time	3.0 min

11.3.1.3 Use these conditions as guidance to establish operating conditions appropriate for the analysis of the target analytes of interest for the project. Once established, the same operating conditions must be used for the analysis of both samples and standards.

**NOTE:** Shorter data acquisition times may be employed, provided that the same acquisition time is used for all standards and samples and that sufficient data are collected for the purpose of the analysis.

11.3.1.4 Water vapor from the sample sparging process is normally used as the CI reagent gas. If an alternate source of CI reagent is employed, turn on and adjust the CI reagent pressure according to the directions in the appropriate mass spectrometer operating manual.

### 11.3.2 Soil blank

11.3.2.1 Prepare a soil blank. For example, weigh a 5-g aliquot of a clean soil to the nearest 0.1 g using an electronic balance. Place the weighed soil in a 40-mL VOA vial. Place a stirring bar in the 40-mL vial. Add enough VOC-free water to bring the water level in the 40-mL VOA vial to within ¼ inch of the top. Add 10 µL of internal standard working solution to make a blank. This solution contains 0.050 ng/µL of internal standard.

11.3.2.2 Quickly attach the 40-mL VOA vial to the sparging head.

11.3.2.3 Place the aluminum heating sleeve around the 40-mL VOA vial and support it with a ring stand and heat resistant clamp.

11.3.2.4 Place a magnetic stirrer under the 40-mL VOA vial and begin stirring.

11.3.2.5 Start the data acquisition program. Turn on the purge gas flow at the beginning of the data acquisition and sparge the sample vial for the entire data acquisition period.

11.3.2.6 At the end of the data acquisition period, turn off the purge gas flow. Remove the soil blank, clean the sparging head, and install an empty 40-mL VOA vial.

11.3.2.7 Evaluate the results for the soil blank. If there is a significant EI/CI response for the characteristic ions corresponding to an analyte of interest, reanalyze the same blank or prepare a new blank. If evidence of significant instrument contamination remains, then take corrective action to remove the contamination. Run a new blank after cleaning or other corrective action to demonstrate freedom from contamination.

### 11.3.3 Performance evaluation standard (PES)

The PES is used to determine if the response of the DSITMS instrument (sample inlet and mass spectrometer) has changed significantly over a period of time. An unacceptable PES result could indicate an instrument malfunction and/or the need to perform a new quantitative calibration. It is not necessary to run PES samples if quantitative calibration is repeated more than once during a working day.

11.3.3.1 Prepare an aliquot of the performance evaluation standard (PES) by, for example, adding 10  $\mu$ L of the performance evaluation working solution (see Sec. 7.9.2) to a 40-mL soil blank.

11.3.3.2 Quickly attach the 40-mL VOA vial to the sparging head.

11.3.3.3 Place the aluminum heating sleeve around the 40-mL VOA vial and support with a ring stand and heat resistant clamp.

11.3.3.4 Place a magnetic stirrer under the 40-mL VOA vial and begin stirring.

11.3.3.5 Start the data acquisition program. Turn on the purge gas flow at the beginning of the data acquisition and sparge the vial for the entire acquisition period.

11.3.3.6 At the end of the data acquisition period, turn off the purge gas flow. Remove the PES, clean the sparging head, and install a clean 40-mL VOA vial.

11.3.3.7 Evaluate the PES results. The integrated response for each VOC in the PES should fall within  $\pm 50\%$  of the established mean response for the corresponding VOCs in the PES. Refer to Sec. 12.7.2 for this determination.

11.3.3.8 If the response for the PES is outside of the acceptable range, it may indicate a malfunction of the sample inlet or degradation of the mass spectrometer tuning conditions. Refer to the appropriate instrument manufacturer's manual for diagnosing and correcting problems.

11.3.3.9 If the reason for an unacceptable PES response has been corrected, repeat Secs. 11.3.3.1 through 11.3.3.7 and verify that the PES response has returned to an acceptable value.

11.3.3.10 If the mass spectrometer tuning parameters or other instrument operating parameters have been significantly altered, the mean response of the PES should be re-determined. Refer to Sec. 12.7.2 for calculating the mean response of the PES.

11.3.3.11 The PES should be evaluated at the beginning of the working day. An additional PES may be run at any point during the working day, as needed for QA purposes.

#### 11.3.4 Quantitative calibration

NOTE: Quantitative calibration may be postponed until after prescreening a sample, if extra samples are available, in order to choose an optimal calibration range.

Prepare a soil slurry standard of known concentration for the analytes of interest. Example approaches follow in Secs. 11.3.4.1 through 11.3.4.3. After standard preparation, proceed with the instructions beginning at Sec. 11.3.4.4.

##### 11.3.4.1 Standard from pre-spiked dry soil standards

Weigh a 5-g aliquot of the spiked soil to the nearest 0.1 g using an electronic balance. Place the weighed soil in a 40-mL VOA vial. Place a stirring bar in the 40-mL VOA vial. Add enough VOC-free water to bring the water level in the 40-mL VOA vial to within ¼ inch of the top. Add 10 µL of internal standard working solution to the soil slurry to effect a 0.050 ng/µL internal standard concentration.

##### 11.3.4.2 Standard from vapor-fortified soil standards in sealed ampules

Place a clean 40-mL VOA vial on an electronic balance and zero the reading. Open the ampule containing the soil and transfer entire contents to the 40-mL VOA vial on the balance. Record the weight of the soil to the nearest 0.1 g. Place a stirring bar in the 40-mL VOA vial. Add enough VOC-free water to leave approximately ¼ inch of headspace. Add 10 µL of internal standard working solution to the soil slurry to effect a 0.050 ng/µL internal standard concentration.

##### 11.3.4.3 Standard from dry soil and analyte working solution

Weigh a 5-g aliquot of a clean standard soil to the nearest 0.1 g using an electronic balance. Place the weighed soil in a 40-mL VOA vial. Place a stirring bar in the 40-mL vial. Add enough VOC-free water to leave approximately ¼ inch of headspace. Add 10 µL of internal standard working solution to the soil slurry to effect a 0.050 ng/µL internal standard concentration. Add a sufficient aliquot of the analyte working solution of the analyte (or analytes) below the water surface to obtain the desired concentration in the soil.

11.3.4.4 Quickly attach the 40-mL VOA vial containing the standard to the sparging head.

11.3.4.5 Place the aluminum heating sleeve around the 40-mL VOA vial and support with a ring stand and heat resistant clamp.

11.3.4.6 Place a magnetic stirrer under the 40-mL VOA vial and begin stirring.

11.3.4.7 Start the data acquisition program and simultaneously turn on the purge gas flow. Sparge the vial until data acquisition is complete.

11.3.4.8 Repeat the process for replicate standards.

11.3.4.9 Repeat the process for the desired additional concentration levels to be included in the calibration curve.

11.3.4.10 Analyze results for each sample and generate calibration curves for each analyte. Refer to Sec. 12.0 for the appropriate data analysis and calculation procedures.

#### 11.3.5 Sample analysis

11.3.5.1 Run a soil blank as described in Sec. 11.3.2. This blank can be used to establish a background for spectral subtraction and will also enable carryover of analytes from the calibration procedure to be identified.

11.3.5.2 Weigh a 5-g aliquot of the unknown soil sample to the nearest 0.1 g using an electronic balance. Place the weighed soil in a 40-mL VOA vial. Place a stirring bar in the 40-mL vial. Add enough VOC-free water to leave approximately ¼ inch of headspace. Add 10 µL of internal standard working solution to the soil slurry to effect a 0.050 ng/µL internal standard concentration.

11.3.5.3 Quickly attach the VOA vial containing the sample to the sparging head.

11.3.5.4 Place the aluminum heating sleeve around the 40-mL VOA vial and support it with a ring stand and heat resistant clamp.

11.3.5.5 Place a magnetic stirrer under the 40-mL VOA vial and begin stirring.

11.3.5.6 Start the data acquisition program. Turn on the purge gas flow at the beginning of the data acquisition period and sparge the sample vial for the entire acquisition period.

11.3.5.7 At the end of the data acquisition period, turn off the sparge gas flow. Remove the soil sample vial, clean the sparging head, and install an empty vial.

11.3.5.8 Refer to Sec. 12.0 for the appropriate data analysis and calculation procedures.

11.3.5.9 Repeat these steps if replicate samples are being analyzed.

#### 11.4 Purge of soil methanol extracts (40-mL VOA vial)

This procedure is preferred for soil samples that are known or suspected to be contaminated with more than 10 mg/kg of any VOC analyte. This procedure may reduce the risk of saturating the sample inlet and mass spectrometer. Because of the dilution factors involved, the detection limits for VOCs in soil will generally be in the range of 1 mg/kg.

#### 11.4.1 Suggested instrument set up

11.4.1.1 See Sec. 10.1 for instructions regarding daily instrument operational checks.

11.4.1.2 Connect to the mass spectrometer the sampling module designed for sparging soil slurry samples contained in 40-mL VOA vials. Attach a source of helium (or other gas as allowed by mass spectrometer) to the sparging module for use as the sample purge gas. The suggested operating conditions are as follows:

Helium pressure	20 - 40 psig
Helium flow rate	100 ± 5 mL/min
Purge temperature	Ambient temperature
MS operating conditions	See Table 4
CI reagent gas source	Water from the sparging or other CI gas from instrument CI manifold
Ionization times	Refer to the manufacturer's operating instructions
Electron multiplier settings	Refer to the manufacturer's operating instructions
Data acquisition time	3.0 min

11.4.1.3 Use these conditions as guidance to establish operating conditions appropriate for the analysis of the target analytes of interest for the project. Once established, the same operating conditions must be used for the analysis of both samples and standards.

**NOTE:** Shorter data acquisition times may be employed, provided that the same acquisition time is used for all standards and samples and that sufficient data are collected for the purpose of the analysis.

11.4.1.4 Water vapor from the sample sparging process is normally used as the CI reagent gas. If an alternate source of CI reagent is employed, turn on and adjust the CI reagent pressure according to the directions in the appropriate mass spectrometer operating manual.

#### 11.4.2 Soil bank

11.4.2.1 Prepare a soil blank. For example, weigh a 5-g aliquot of a clean soil to the nearest 0.1 g using an electronic balance. Place the weighed soil in a 40-mL VOA vial. Add 10 mL of methanol to the soil and seal the 40-mL VOA vial with a PTFE-lined screw cap.

11.4.2.2 Extract the VOCs from the soil by vigorously shaking the 40-mL VOA vial by hand for 60 seconds.

11.4.2.3 Using a syringe, remove a 100- $\mu$ L aliquot of the methanol extract.

11.4.2.4 Inject the methanol extract into a 40-mL VOA vial containing 40-mL of VOC-free water.

11.4.2.5 Using a syringe, add exactly 10  $\mu$ L of the internal standard working solution (see Sec. 7.10.2) to the 40-mL VOA vial containing the methanol extract/water mixture.

11.4.2.6 Quickly attach the 40-mL VOA vial containing the methanol extract/water mixture to the sparge head.

11.4.2.7 Start the data acquisition program. Turn on the purge gas flow at the beginning of the data acquisition and sparge the vial for the entire data acquisition period.

11.4.2.8 At the end of the data acquisition period, turn off the purge gas flow. Remove the soil blank, clean the sparging head, and install an empty 40-mL VOA vial.

11.4.2.9 Evaluate the results for the soil blank. If there is a significant EI/CI response for the characteristic ions corresponding to an analyte of interest, reanalyze the same blank or prepare a new blank. If evidence of significant instrument contamination remains, then take corrective action to remove the contamination. Run a new blank after cleaning or other corrective action to demonstrate freedom from contamination.

#### 11.4.3 Performance evaluation standard (PES)

The PES is used to determine if the response of the DSITMS instrument (sample inlet and mass spectrometer) has changed significantly over a period of time. An unacceptable PES result could indicate an instrument malfunction and/or the need to perform a new quantitative calibration. It is not necessary to run PES samples if quantitative calibration is repeated more than once during a working day.

11.4.3.1 Prepare the performance evaluation standard (PES) by, for example, spiking a 40-mL soil blank (see Sec. 11.4.2) with 10  $\mu$ L of the performance evaluation working solution (see Sec. 7.9.2).

11.4.3.2 Quickly attach the 40-mL VOA vial to the sparging head.

11.4.3.3 Start the data acquisition program. Turn on the purge gas flow at the beginning of the data acquisition and sparge the vial for the entire acquisition period.

11.4.3.4 At the end of the data acquisition period, turn off the purge gas flow. Remove the PES, clean the sparging head, and install a clean 40-mL VOA vial.

11.4.3.5 Evaluate the PES results. The integrated response for each VOC in the PES should fall within  $\pm 50\%$  of the established mean response for the corresponding VOCs in the PES. Refer to Sec. 12.7.2 for this determination.

11.4.3.6 If the response for the PES is outside of the acceptable range, it may indicate a malfunction of the sample inlet or degradation of the mass spectrometer tuning conditions. Refer to the appropriate instrument manufacturer's manual for diagnosing and correcting problems.

11.4.3.7 If the reason for an unacceptable PES response has been corrected, repeat Secs. 11.4.3.1 through 11.4.3.5 and verify that the PES response has returned to an acceptable value.

11.4.3.8 If the mass spectrometer tuning parameters or other instrument operating parameters have been significantly altered, the mean response of the PES



should be re-determined. Refer to Sec. 12.7.2 for calculating the mean response of the PES.

11.4.3.9 The PES should be evaluated at the beginning of the working day. An additional PES may be run at any point during the working day, as needed for QA purposes.

#### 11.4.4 Quantitative calibration

NOTE: Quantitative calibration may be postponed until after prescreening a sample, if extra samples are available, in order to choose an optimal calibration range.

Prepare a soil extract standard of known concentration in 40 mL of VOC-free water for the analytes of interest. Example procedures follow in Secs. 11.4.4.1 through 11.4.4.2. After standard preparation, proceed with the instructions beginning at Sec. 11.4.4.4

##### 11.4.4.1 Standard from pre-spiked dry soil standards

Weigh a 5-g aliquot of the spiked soil to the nearest 0.1 g using an electronic balance. Place the weighed soil in a 40-mL VOA vial. Add 10 mL of methanol to the soil and seal the 40-mL VOA vial with a PTFE-lined screw cap. Extract the VOCs from the soil by vigorously shaking the 40-mL VOA vial by hand for 60 seconds. Using a syringe, remove a sufficient aliquot of the methanol extract to produce the desired final concentration of analytes in 40 mL of water. Inject the methanol extract into a 40-mL VOA vial containing 40 mL of VOC-free water. Using a syringe, add exactly 10  $\mu$ L of the internal standard working solution to the 40-mL VOA vial containing the methanol extract/water mixture.

##### 11.4.4.2 Standard from vapor-fortified soil standards in sealed ampules

Place a clean 40-mL VOA vial on an electronic balance and zero the reading. Open the ampule containing the soil and transfer the entire contents of the ampule to the 40-mL VOA vial on the balance. Record the weight of the soil to the nearest 0.1 g. Add 10 mL of methanol to the soil and seal the 40-mL VOA vial with a PTFE-lined screw cap. Extract the VOCs from the soil by vigorously shaking the 40-mL VOA vial by hand for 60 seconds. Using a syringe, remove a sufficient aliquot of the methanol extract to produce the desired final concentration of analytes in 40 mL of water. Inject the methanol extract into a 40-mL VOA vial containing 40 mL of VOC-free water. Using a syringe, add exactly 10  $\mu$ L of the internal standard working solution to the 40-mL VOA vial containing the methanol extract/water mixture.

11.4.4.3 Quickly attach the 40-mL VOA vial containing the standard to the sparging head.

11.4.4.4 Start the data acquisition program and simultaneously turn on the purge gas flow. Sparge the vial until data acquisition is complete.

11.4.4.5 Repeat the process for replicate standards.

11.4.4.6 Repeat the process for the desired additional concentration levels to be included in the calibration curve.

11.4.4.7 Analyze results for each sample and generate calibration curves for each analyte. Refer to Sec. 12.0 for the appropriate data analysis and calculation procedures.

#### 11.4.5 Sample analysis

11.4.5.1 Run a soil blank as described in Sec. 11.4.2. This blank can be used to establish a background for spectral subtraction and will also enable carryover of analytes from the calibration procedure to be identified.

11.4.5.2 Weigh a 5-g aliquot of the soil sample to the nearest 0.1 g using an electronic balance. Place the weighed soil in a 40-mL VOA vial. Add 10 mL of methanol to the soil and seal the 40-mL VOA vial with a PTFE-lined screw cap.

11.4.5.3 Extract the VOCs from the soil by vigorously shaking the 40-mL VOA vial by hand for 60 seconds.

11.4.5.4 Using a syringe, remove a 100- $\mu$ L aliquot of the methanol extract.

11.4.5.5 Inject the methanol extract into a 40-mL VOA vial containing 40 mL of VOC-free water.

11.4.5.6 Using a syringe, add exactly 10  $\mu$ L of the internal standard working solution (see Sec. 7.10.2) to the 40-mL VOA vial containing the methanol extract/water mixture.

11.4.5.7 Quickly attach the 40-mL VOA vial to the sparging head.

11.4.5.8 Start the data acquisition program. Turn on the purge gas flow at the beginning of the data acquisition and sparge the vial for the entire acquisition period.

11.4.5.9 At the end of the data acquisition period, turn off the sparge gas flow. Remove the VOA vial, clean the sparging head, and install a clean 40-mL VOA vial.

11.4.5.10 Refer to Sec. 12.0 for the appropriate data analysis and calculation procedures.

11.4.5.11 Repeat these steps if replicate samples are being analyzed.

#### 11.5 Real-time monitoring of VOCs in soil gas and air

This procedure is used for real-time direct monitoring of VOCs in soil gas or air and can be used to detect most target analytes at a level of approximately 50 ppbv with a temporal resolution of less than 1 second per data point. For improved sensitivity, the procedure described in Sec. 11.6 (thermal desorption of VOCs collected on sorbent traps) can be used instead, provided that real-time results are not required.

##### 11.5.1 Suggested instrument set up

11.5.1.1 See Sec. 10.1 for instructions regarding daily instrument operational checks.

11.5.1.2 Connect the real-time air sampling module to the capillary restrictor inlet of the mass spectrometer. Connect a source of pressurized helium to the air sampling module. Connect a flow meter to the air inlet port of the air sampling module. The suggested operating conditions are as follows:

Helium pressure	20 ± 5 psig
Helium flow rate	Control valve on air module completely off
MS operating conditions	See Table 4
CI reagent gas source	Appropriate CI gas from instrument CI manifold
Ionization times	Refer to the manufacturer's operating instructions
Electron multiplier settings	Refer to the manufacturer's operating instructions
Data acquisition time	Estimated run time x 2

11.5.1.3 Use these conditions as guidance to establish operating conditions appropriate for the analysis of the target analytes of interest for the project. Once established, the same operating conditions must be used for the analysis of both samples and standards.

**NOTE:** Shorter data acquisition times may be employed, provided that the same acquisition time is used for all standards and samples and that sufficient data are collected for the purpose of the analysis. Also see Sec. 11.5.1.8.

11.5.1.4 Turn on the internal air sampling pump of the air sampling module. Using the flow control valve on the air sampling module, adjust the flow rate of air to that required for a specific application.

**NOTE:** The internal air pump of the sampling module will permit a flow rate of up to 2 L/min. For higher flow rates, an external sampling pump can be connected to the air sampling module. Refer to the operating instructions provided with the air inlet for details.

11.5.1.5 Set the mass spectrometer operating conditions to permit the acquisition of alternating EI/CI data.

**NOTE:** If the DSITMS instrument being used does not have the capability of acquiring alternating EI/CI scans, then two replicate samples must be analyzed, one in EI mode and one in CI mode.

11.5.1.6 Using background peaks in the mass spectrum as a guide, slowly increase the flow of helium into the air sampling module until the maximum mass resolution is achieved.

**CAUTION:** Once the maximum mass resolution is achieved, increasing the helium flow further will result in sensitivity loss.

11.5.1.7 Prepare a sample of VOCs in a 10-L Tedlar® bag at a VOC concentration approximately equal to the expected VOC concentration of the unknown samples. Connect the Tedlar® bag to the sample inlet and adjust the mass spectrometer tuning conditions as necessary to achieve the desired instrument response.

11.5.1.8 The data acquisition time should be set to twice the expected length of time that measurements will be taken. This will prevent premature termination of a data file.

#### 11.5.2 Air blank

11.5.2.1 Prepare an air blank. For example, fill a clean 10-L Tedlar® bag with 10 L of pure breathing air using a 2-L gas syringe. Using a 10- $\mu$ L syringe, add 7  $\mu$ L of the internal standard master stock solution (see Sec. 7.10.1) to the 10-L Tedlar® bag through the septum port. Agitate the Tedlar® bag by hand until the liquid has completely evaporated.

11.5.2.2 Attach a 6-inch length of ¼-inch OD PTFE tubing to the valve nipple of the Tedlar® bag.

11.5.2.3 Connect the other end of the ¼-inch OD PTFE tubing to the sample inlet port of the air sampling module.

11.5.2.4 Open the valve on the Tedlar® bag.

11.5.2.5 Start the data acquisition program.

11.5.2.6 At the end of the data acquisition period, close the valve on the Tedlar® bag. Disconnect the Tedlar® bag by removing it from the ¼-inch OD PTFE tubing. Leave the tubing attached to the air sampling module.

11.5.2.7 Evaluate the results of the air blank. If there is a significant EI/CI response for the characteristic ions corresponding to an analyte of interest, reanalyze the same blank or prepare a new blank. If contamination is present in the air sampling module, connect a source of clean breathing air to the inlet and purge for at least 5 min. Repeat blank analysis until the background is acceptable.

#### 11.5.3 Performance evaluation standard (PES)

The PES is used to determine if the response of the DSITMS instrument (sample inlet and mass spectrometer) has changed significantly over a period of time. An unacceptable PES result could indicate an instrument malfunction and/or the need to perform a new quantitative calibration. It is not necessary to run PES samples if quantitative calibration is repeated more than once during a working day.

11.5.3.1 Prepare a performance evaluation standard (PES). For example, fill a 10-L Tedlar® bag with 10 L of pure breathing air using a 2-L gas syringe. Using a 10- $\mu$ L syringe, add 7  $\mu$ L of the performance evaluation master stock solution (see Sec. 7.9.1) to the 10-L Tedlar® bag through the septum port. Agitate the Tedlar® bag by hand until the liquid has completely evaporated.

11.5.3.2 Connect the valve nipple of the Tedlar® bag to the ¼-inch OD PTFE tubing attached to the inlet of the air sampling module.

11.5.3.3 Open the valve on the Tedlar® bag.

11.5.3.4 Start the data acquisition program.

11.5.3.5 At the end of the data acquisition period, close the valve on the Tedlar® bag. Disconnect the Tedlar® bag by removing it from the ¼-inch OD PTFE tubing. Leave the tubing attached to the air sampling module.

11.5.3.6 Evaluate the PES results. The integrated response for each VOC in the PES should fall within  $\pm 50\%$  of the established mean response for the corresponding VOCs in the PES. Refer to Sec. 12.7.2 for this determination.

11.5.3.7 If the response for the PES is outside of the acceptable range, it may indicate a malfunction of the sample inlet or degradation of the mass spectrometer tuning conditions. Refer to the appropriate instrument manufacturer's manual for diagnosing and correcting problems.

11.5.3.8 If the reason for an unacceptable PES response has been corrected, repeat Secs. 11.5.3.1 through 11.5.3.6 and verify that the PES response has returned to an acceptable value.

11.5.3.9 If the mass spectrometer tuning parameters or other instrument operating parameters have been significantly altered, the mean response of the PES should be re-determined. Refer to Sec. 12.7.2 for calculating the mean response of the PES.

11.5.3.10 The PES should be evaluated at the beginning of the working day. An additional PES may be run at any point during the working day, as needed for QA purposes.

#### 11.5.4 Quantitative calibration

NOTE: Quantitative calibration may be postponed until after prescreening a sample, if extra samples are available, in order to choose an optimal calibration range.

11.5.4.1 Prepare an air standard (see Sec. 7.11) containing the analytes of interest. Start with the lowest concentration that will be incorporated in the calibration curve.

11.5.4.2 Connect the valve nipple of the Tedlar® bag to the ¼-inch OD PTFE tubing attached to the inlet of the air sampling module.

11.5.4.3 Open the valve on the Tedlar® bag.

11.5.4.4 Start the data acquisition program.

11.5.4.5 At the end of the data acquisition period, close the valve on the Tedlar® bag. Disconnect the Tedlar® bag by removing it from the ¼-inch OD PTFE tubing. Leave the tubing attached to the air sampling module.

11.5.4.6 Repeat the process for replicate standards.

11.5.4.7 Repeat the process for the desired additional concentration levels to be included in the calibration curve.

11.5.4.8 Analyze results for each sample and generate calibration curves for each analyte. Refer to Sec. 12.0 for the appropriate data analysis and calculation procedures.

### 11.5.5 Sample analysis

11.5.5.1 Run an air blank as described in Sec. 11.5.2. This blank can be used to establish a background for spectral subtraction and will also enable carryover of analytes from the calibration procedure to be identified.

11.5.5.2 Obtain a Tedlar® Bag containing the unknown air sample.

NOTE: Other containers suitable for air sampling may be substituted for Tedlar® bags.

11.5.5.3 Connect the valve nipple of the Tedlar® bag to the ¼-inch OD PTFE tubing attached to the inlet of the air sampling module.

11.5.5.4 Open the valve on the Tedlar® bag.

11.5.5.5 Start the data acquisition program.

11.5.5.6 At the end of the data acquisition period, close the valve on the Tedlar® bag. Disconnect the Tedlar® bag by removing it from the ¼-inch OD PTFE tubing. Leave the tubing attached to the air sampling module.

11.5.5.7 Refer to Sec. 12.0 for the appropriate data analysis and calculation procedures.

11.5.5.8 Repeat Secs. 11.5.5.1 - 11.5.5.7 if replicate samples are being analyzed.

NOTE: Air sample blanks should be run frequently to ensure that analyte carryover does not interfere with or bias the results of subsequent samples. In general, for samples that contain >50 ppmv of total VOC contamination, blanks should be run between each sample. For those samples that contain lesser concentrations of VOCs, blanks should be run any time carryover is suspected or at least between the analysis of samples from a different source.

### 11.6 Thermal desorption of VOCs in air and soil gas collected on sorbent traps

This procedure is used for the measurement of VOCs which have been collected and preconcentrated on a sorbent trap.

#### 11.6.1 Suggested instrument set up

11.6.1.1 See Sec. 10.1 for instructions regarding daily instrument operational checks.

11.6.1.2 Connect the thermal desorption module to the mass spectrometer. Refer to the thermal desorption module operator's manual for details. Connect a source of pressurized helium to the thermal desorption module. The suggested operating conditions are as follows:

Helium pressure	20 ± 5 psig
Helium flow rate	40 ± 5 mL/min

MS operating conditions	See Table 4
CI reagent gas source	Appropriate CI gas from instrument CI manifold
Ionization times	Refer to the manufacturer's operating instructions
Electron multiplier settings	Refer to the manufacturer's operating instructions
Data acquisition time	3.0 min

11.6.1.3 Use these conditions as guidance to establish operating conditions appropriate for the analysis of the target analytes of interest for the project. Once established, the same operating conditions must be used for the analysis of both samples and standards.

**NOTE:** Shorter data acquisition times may be employed, provided that the same acquisition time is used for all standards and samples and that sufficient data are collected for the purpose of the analysis.

#### 11.6.2 Sorbent trap blank

11.6.2.1 Replace the old sorbent trap with a sealed and clean, preconditioned sorbent trap, according to the manufacturer's instructions. The new sorbent trap inside the thermal desorber should fit snugly against the bottom of the desorber chamber.

**NOTE:** The sorbent trap must be installed in the thermal desorption module such that the direction of helium flow is opposite to the direction which was used to load analytes or sample onto the trap.

11.6.2.2 Install the "O"-ring compression sleeve over the sorbent trap.

11.6.2.3 Install the septum cap.

11.6.2.4 Wait 20 seconds for the air to be purged from the sorbent tube by the helium.

11.6.2.5 Start the mass spectrometer data acquisition program. Immediately turn on the thermal desorber heater for the length of time described in the thermal desorber operator's manual.

**CAUTION:** Make certain that the thermal desorber heater is not left on for an extended period of time. This can destroy the sorbent trap, the thermal desorber, and can contaminate the mass spectrometer.

11.6.2.6 At the end of the data acquisition period, turn on the cooling fan located on the thermal desorption module. Allow to cool to ambient temperature.

11.6.2.7 Evaluate the blank results. If there is a significant EI/CI response for the characteristic ions corresponding to an analyte of interest, reanalyze the same blank or prepare a new blank. If contamination is present in the thermal desorption module, remove the sorbent trap and heat the module to 250 °C for 5 minutes while purging with clean helium.

### 11.6.3 Performance evaluation standard (PES)

The PES is used to determine if the response of the DSITMS instrument (sample inlet and mass spectrometer) has changed significantly over a period of time. An unacceptable PES result could indicate an instrument malfunction and/or the need to perform a new quantitative calibration. It is not necessary to run PES samples if quantitative calibration is repeated more than once during a working day.

11.6.3.1 Obtain a clean, preconditioned sorbent trap, that has been sealed. Remove the old sorbent trap from the thermal desorption module according to the manufacturer's instructions.

11.6.3.2 Dilute 100  $\mu\text{L}$  of the performance evaluation working solution (see Sec. 7.9.2) to exactly 10 mL with methanol.

11.6.3.3 Remove the caps from the new sorbent trap.

11.6.3.4 Using a 10- $\mu\text{L}$  syringe, inject 5  $\mu\text{L}$  of the diluted performance evaluation working solution onto the sorbent material.

11.6.3.5 Transfer the "O"-ring from the old sorbent trap to the new sorbent trap. Install the new sorbent trap inside the thermal desorber according to the manufacturer's instructions. The new sorbent trap should fit snugly against the bottom of the desorber chamber.

11.6.3.6 Install the "O"-ring compression sleeve over the sorbent trap.

11.6.3.7 Install the septum cap.

11.6.3.8 Wait 20 seconds for the air to be purged from the sorbent tube by the helium.

11.6.3.9 Start the data acquisition program. Immediately turn on the thermal desorber heater for the length of time described in the thermal desorber operator's manual.

**CAUTION:** Make certain that the thermal desorber heater is not left on for an extended period of time. This can destroy the sorbent trap and the thermal desorber, and can contaminate the mass spectrometer.

11.6.3.10 At the end of the data acquisition period, turn on the cooling fan located on the thermal desorption module. Allow to cool to ambient temperature.

11.6.3.11 Evaluate the PES results. The integrated response for each VOC in the PES should fall within  $\pm 50\%$  of the established mean response for the corresponding VOCs in the PES. Refer to Sec. 12.7.2 for this determination.

11.6.3.12 If the response for the PES is outside of the acceptable range, it may indicate a malfunction of the sample inlet or degradation of the mass spectrometer tuning conditions. Refer to the appropriate instrument manufacturer's manual for diagnosing and correcting problems.



11.6.3.13 If the reason for an unacceptable PES response has been corrected, repeat Secs. 11.6.3.1 through 11.6.3.11 and verify the PES response has returned to an acceptable value.

11.6.3.14 If the mass spectrometer tuning parameters or other instrument operating parameters have been significantly altered, the mean response of the PES should be re-determined. Refer to Sec. 12.7.2 for calculating the mean response of the PES.

11.6.3.15 The PES should be evaluated at the beginning of the working day. An additional PES may be run at any point during the working day, as needed for QA purposes.

#### 11.6.4 Quantitative calibration

**NOTE:** Quantitative calibration may be postponed until after a prescreening, if extra samples are available, in order to choose an optimal calibration range.

11.6.4.1 Prepare a sorbent tube standard containing the analytes of interest by using a syringe to inject a known quantity of analyte solution onto the sorbent material. Vapor phase loading is also acceptable. Start with the lowest concentration that will be incorporated in the calibration curve. Seal the sorbent trap until ready to be used.

11.6.4.2 Replace the old sorbent trap with a sealed and clean, preconditioned sorbent trap, according to the manufacturer's instructions. The new sorbent trap inside the thermal desorber should fit snugly against the bottom of the desorber chamber.

11.6.4.3 Install the "O"-ring compression sleeve over the sorbent trap.

11.6.4.4 Install the septum cap.

11.6.4.5 Wait 20 seconds for the air to be purged from the sorbent tube by the helium.

11.6.4.6 Start the data acquisition program. Immediately turn on the thermal desorption heater for the length of time described in the thermal desorber operator's manual.

**CAUTION:** Make certain that the thermal desorber heater is not left on for an extended period of time. This can destroy the sorbent trap and the thermal desorber, and can contaminate the mass spectrometer.

11.6.4.7 At the end of the data acquisition period, turn on the cooling fan located on the thermal desorption module. Allow to cool to ambient temperature.

11.6.4.8 Repeat the process for replicate standards.

11.6.4.9 Repeat the process for the desired additional concentration levels to be included in the calibration curve.

11.6.4.10 Analyze results for each sample and generate calibration curves for each analyte. Refer to Sec. 12.0 for the appropriate data analysis and calculation procedures.

#### 11.6.5 Sample analysis

11.6.5.1 Replace the old sorbent trap with a sealed and clean, preconditioned sorbent trap, according to the manufacturer's instructions. The new sorbent trap inside the thermal desorber should fit snugly against the bottom of the desorber chamber.

11.6.5.2 Install the "O"-ring compression sleeve over the sorbent trap.

11.6.5.3 Install the septum cap.

11.6.5.4 Wait 20 seconds for the air to be purged from the sorbent tube by the helium.

11.6.5.5 Start the data acquisition program. Immediately turn on the thermal desorption heater for the length of time described in the thermal desorber operator's manual.

**CAUTION:** Make certain that the thermal desorber heater is not left on for an extended period of time. This can destroy the sorbent trap, the thermal desorber, and can contaminate the mass spectrometer.

11.6.5.6 At the end of the data acquisition period, turn on the cooling fan located on the thermal desorption module. Allow to cool to ambient temperature.

11.6.5.7 Refer to Sec. 12.0 for the appropriate data analysis and calculation procedures.

11.6.5.8 Repeat Secs. 11.6.5.1 through 11.6.5.7 if replicate samples are being analyzed.

## 12.0 DATA ANALYSIS AND CALCULATIONS

This section describes the procedure for data analysis and calculations for the measurement of volatile organic compounds (VOCs) in:

- water by direct purge from a 40-mL VOA vial (Sec. 12.1)
- water by *in situ* sparging (Sec. 12.2)
- soil by heated purge (Sec. 12.3)
- methanol extracts of higher concentration (>10 mg/kg of any analyte) soil by purge (Sec. 12.4)
- soil gas and air by real-time monitoring (Sec. 12.5)
- soil gas and air on sorbent traps, by thermal desorption (Sec. 12.6)

Also included in this section are the procedures for:

- determination of performance evaluation standard (PES) response (Sec. 12.7)
- qualitative examination of DSITMS mass spectra (Sec. 12.8)

Most of the procedures employ a similar sequence of data handling events regardless of whether the data were generated from a blank sample, calibration standard, PES, or an unknown sample. The typical data handling sequence includes:

- retrieval of stored data files
- deconvolution of combined EI/CI data (when necessary)
- background subtraction of selected mass profiles (optional)
- extraction of selected mass profiles
- selection of data integration windows
- integration of selected mass profile data
- generation of calibration curves
- calculation of VOC concentrations in unknown samples

The procedures described in this section are typically performed using software specifically designed for the purpose of mass spectral data analysis. General purpose software for data analysis is typically provided by the manufacturer of the mass spectrometer hardware and is included with the instrument when it is sold to the customer. Software programs specifically designed for handling DSITMS data may also be available from third-party sources.

**NOTE:** Data file formats differ from one instrument manufacturer to another. Make certain that the data analysis software is compatible with the specific data file format used.

## 12.1 VOCs in water by purging of water in 40-mL VOA vials

### 12.1.1 Retrieval of data files

12.1.1.1 Start the data analysis program.

12.1.1.2 Open the file containing the raw data for the desired 40-mL VOA vial water sample. Refer to the instrument manufacturer's software manual for specific instructions.

### 12.1.2 Deconvolution of combined EI/CI data (when necessary)

12.1.2.1 If the raw data files for both the EI and CI spectra were stored as a combined data file, it will be necessary to deconvolute the file into separate EI and CI data files before proceeding further with data handling. Refer to the instrument manufacturer's software manual for specific instructions.

12.1.2.2 Save the data files for the deconvoluted EI and CI spectra. It is suggested that data filenames reflect original file name and type of ionization.

12.1.2.3 Data files for both EI and CI spectra are handled in the same manner for the remaining steps of Sec. 12.1.

### 12.1.3 Background subtraction of DSITMS data files (optional)

Subtraction of background data from calibration data or sample data may be performed, if desired, to remove contributions to the instrument response that actually originate from background contamination of the DSITMS instrument or sample inlets. This will help to reduce a positive intercept on the calibration curve and may help improve qualitative analysis of mass spectra. Background responses (blank samples) for VOCs purged from water in 40-mL VOA vials are typically recorded in data files that are separate from the data files for the calibration samples and the unknown samples.

NOTE: If background subtraction is used, it must be performed in an identical manner for all calibration files and unknown sample data files in order to produce accurate quantitative results.

NOTE: Background subtraction of data files is a feature that may not be available with all data analysis programs.

This section contains a suggested sequence of events for background subtraction of DSITMS data files. Other variations are possible that will produce satisfactory results. Refer to the instrument manufacturer's software manual for specific instructions related to the background subtraction of data files.

12.1.3.1 Open a data file containing raw spectral data for a background sample. This file will typically be a blank sample that was analyzed in an identical manner as the calibration and unknown samples.

12.1.3.2 Save this data file as the "background" data file.

12.1.3.3 Open the data file containing the raw spectral data for a calibration sample or an unknown sample.

12.1.3.4 Save this data file as the "analysis" data file.

CAUTION: Make certain that the "background" data file and the "analysis" data file contain the same type of ionization data (EI or CI).

12.1.3.5 Execute the BACKGROUND SUBTRACTION routine to generate the background subtracted data file.

12.1.3.6 Save the background subtracted data file for subsequent data analysis operations.

12.1.4 Extraction of selected mass profiles

12.1.4.1 Refer to the instrument manufacturer's software manual for specific instructions related to the extraction of selected mass profiles.

12.1.4.2 Start the SELECTED MASS PROFILE routine of the data analysis software.

12.1.4.3 Open the desired deconvoluted and/or background subtracted data file.

12.1.4.4 Refer to Table 1 for a list of characteristic masses used for the quantitation of specific VOCs.

NOTE: Be sure to use the proper masses for EI and CI mass spectra.

12.1.4.5 Enter the masses for which selected mass profiles are desired.

12.1.4.6 Execute the SELECTED MASS PROFILE routine to generate plots.

12.1.4.7 Save the profile plots so that they can be later retrieved for data integration.

12.1.4.8 Export the plots to a printer or PLOT SPOOLER program for printing at a later time.

12.1.4.9 There is typically a maximum number of plots that can be generated each time the SELECTED MASS PROFILE routine is executed. If necessary, repeat Secs. 12.1.4.5 through 12.1.4.8 until plots have been generated for all of the desired masses.

#### 12.1.5 Integration of selected mass profile data

Refer to the instrument manufacturer's software manual for specific instructions regarding integration of selected mass profile data. The following is a suggested sequence of events for manual integration of data. Alternative approaches may be available for automated integration of data files that will also produce satisfactory results.

12.1.5.1 Open the data file containing the desired selected mass plot.

12.1.5.2 The selected mass profiles for VOCs purged from water samples in 40-mL VOA vials will typically be very broad. VOCs that are slightly soluble in water (chloroform) will exhibit a rapid increase in signal intensity during the first seconds of the purge process followed by a gradually decreasing signal intensity over the remainder of the 3-minute data acquisition period. VOCs that are highly soluble in water (acetone) may exhibit a rapid increase in signal intensity followed by a nearly steady signal over the remainder of the 3-minute data acquisition time.

12.1.5.3 Manually select the scan for the beginning of the integration window.

NOTE: It is suggested that the first scan for integration be at least 5 scans after the start of the purge profile in order to eliminate artifacts that may be caused by residual air in the headspace of the 40-mL VOA vial and water purge module during the first few seconds of the purging process. Scan numbers are typically displayed at the location of a cursor that can be scrolled across the selected mass profile.

12.1.5.4 Manually select the scan for the ending of the integration window.

NOTE: It is suggested that the width of the integration window include at least 2 minutes of data acquisition. This will help improve the precision of the quantitative measurements by averaging electronic noise and minor perturbations in the purge process.

12.1.5.5 Execute the MANUAL INTEGRATION routine in the data analysis software to calculate the area in the window of the selected mass DSITMS purge profile.

NOTE: Due to the width of DSITMS purge profiles, it is generally best to integrate from an assumed zero baseline if given the option in the software.

12.1.5.6 The value of integrated data will typically appear on the selected ion plot near the apex of the selected integration window of the selected mass response curve.

12.1.5.7 Save this plot as a data file that can be recalled later for further data processing. The values of the integrated selected mass profile should also be stored in a text file along with a description of the sample including sample identification, the compound names, selected masses, and the concentrations of calibrant compounds, if applicable. This text file will be used for generation of calibration curves (Sec. 12.1.6) or the quantitation of unknowns (Sec. 12.1.7).

12.1.5.8 Repeat Secs. 12.1.5.1 through 12.1.5.7 until all selected mass profiles have been processed and the data have been saved.

**CAUTION:** All data files including blanks, performance evaluation standards (PES), calibration standards, and unknown samples must be integrated using the same integration window (scan limits).

#### 12.1.6 Generation of calibration curves

Refer to the instrument manufacturer's software operation manual for generating calibration curves. The following is a general sequence of events that will work with most data analysis programs and most third-party spreadsheet software.

12.1.6.1 Start the CALIBRATION routine.

12.1.6.2 Recall the text file generated in Sec. 12.1.5.7 that contains the compound names, selected masses, integrated areas of selected mass profiles, and analyte concentrations for a water purge calibration sample.

12.1.6.3 Enter the data as prompted by the CALIBRATION routine of the data analysis program. Alternatively, the data may be manually entered into a spreadsheet program using a different column for sample identification, compound names, selected masses, integrated area of the selected mass plots, and known concentration of each of the analytes in the sample.

12.1.6.4 Enter all of the data for all of the VOCs present in the calibration sample. Repeat Secs. 12.1.6.2 and 12.1.6.3 for all calibration samples including replicates.

12.1.6.5 Execute the software command to generate a calibration curve for each VOC that is to be quantitated.

**NOTE:** It is generally best to generate calibration curves for DSITMS using a linear least-squares curve-fitting routine. Other curve fitting options may be available for data that exhibit non-linear behavior. This is left to the professional judgment of the operator.

**CAUTION:** Calibration curves that exhibit significant departure from a linear fit over a concentration range of approximately 10 µg/L to 1,000 µg/L may indicate a problem with data acquisition or data reduction. Re-check all prior steps in Sec. 12.1 before proceeding further.

12.1.6.6 Export the calibration curve plots to a printer or to a PLOT SPOOLER for later printing.

12.1.6.7 Save the linear regression parameters for calculation of VOC concentrations in the unknown samples. This linear regression parameters provide the relationship between the concentration of a VOC in a sample and the measured integrated area of a selected mass plot (instrument response).

#### 12.1.7 Calculation of VOC concentrations in unknown samples

Refer to the instrument manufacturer's software manual for specific details regarding the quantitation of analytes in unknown sample. The following is a suggested sequence of events that will work with most data analysis programs.

12.1.7.1 Start the QUANTITATION routine of the data analysis program.

12.1.7.2 Recall the text file generated in Sec. 12.1.5.7 that contains the compound names, selected masses, and integrated areas of the selected mass profiles for an unknown water purge sample.

12.1.7.3 Enter the data as prompted by the QUANTITATION routine of the data analysis program. Alternatively, the data may be manually entered into a spreadsheet program using a different column for sample identification, compound names, selected masses, and integrated areas of the selected mass profiles.

12.1.7.4 Recall the file containing the linear regression parameters generated in Sec. 12.1.6.7.

12.1.7.5 Execute the software command to calculate the concentration of the analytes in the unknown sample.

12.1.7.6 Save the results of Sec. 12.1.7.5 as a text file including the compound identification, the compound names, and the calculated concentrations. This file will be used to generate an analysis report for the sample.

12.1.7.8 Repeat Secs. 12.1.7.2 through 12.1.7.6 until all data files for the unknown samples have been processed.

## 12.2 *In situ* sparging of water

12.2.1 Retrieve and deconvolute data files for *in situ* sparge samples in the same manner as described in Secs. 12.1.1 through 12.1.2.

**NOTE:** Data files for *in situ* sparge samples often contain instrument response profiles for blanks, calibration samples, and unknown samples all in the same file. Be certain to properly identify the response profiles and associate them with the proper sample before proceeding further with data handling.

#### 12.2.2 Background subtraction of DSITMS data files (optional)

Subtraction of background data from calibration data or sample data may be performed if desired to remove contributions to the instrument response that actually originate from background contamination of the DSITMS instrument or sample inlets. This will help to reduce a positive intercept on the calibration curve and may help with qualitative

analysis of mass spectra. For *in situ* sparge samples, a background response (blank sample) may be included in the same data file as the response for calibration samples and unknown samples.

NOTE: If background subtraction is used, it must be performed in an identical manner for all calibration files and unknown sample data files in order to produce accurate quantitative results.

NOTE: Background subtraction of data files is a feature that may not be available with all data analysis programs.

This section contains a suggested sequence of events for background subtraction of DSITMS data files. Other variations are possible that will produce satisfactory results. Refer to the instrument manufacturer's software manual for specific instructions related to the background subtraction of data files.

12.2.2.1 Open a data file containing raw spectral data for an *in-situ* sparge sample. This file will typically include a series of response profiles including a blank sample, one or more calibration standards, and an unknown sample produced using identical experimental conditions.

12.2.2.2 Select the scans for the background response (blank sample).

12.2.2.3 Save the average of these scans as the "background" data file.

12.2.2.4 Select the scans for either a calibration sample or the unknown sample.

12.2.2.5 Save the average of these scans as the "analysis" data file.

CAUTION: Make certain that the "background" data file and the "analysis" data file contain the same type of ionization data (EI or CI).

12.2.2.6 Execute the BACKGROUND SUBTRACTION routine to generate the background subtracted data file.

12.2.2.7 Save the background subtracted data file for subsequent data analysis operations.

12.2.3 Generate selected mass profiles using the procedure described in Sec. 12.1.4.

12.2.4 Integration of selected mass profile data

Refer to the instrument manufacturer's software manual for specific instructions regarding integration of selected mass profile data. The following is a suggested sequence of events for manual integration of data. Alternative approaches may be available for automated integration of data files that will also produce satisfactory results.

12.2.4.1 Open the data file containing the desired selected mass plot. This file will typically include more than one response profile including the responses for a blank sample, one or more calibration standards, and an unknown sample.



12.2.4.2 The selected mass profiles for VOCs by *in situ* sparge of water samples will typically exhibit a nearly steady response because the sample is constantly being replenished during the sparging process. VOCs that are slightly soluble in water (chloroform) will exhibit a rapid increase in signal intensity during the first seconds of the sparging process followed by a nearly-constant signal intensity over the remainder of the 1-minute (or longer) data acquisition period. VOCs that are highly soluble in water (acetone) may exhibit a slower increase in signal intensity followed by a nearly steady (or slowly increasing) signal over the remainder of the 1-minute (or longer) data acquisition time.

NOTE: The selected mass profiles for VOCs by *in situ* sparge of small volumes of water, such as encountered with 3/4-inch diameter wells, may exhibit a slowly decreasing response over a period of a few minutes instead of a steady response.

12.2.4.3 Manually select the scan for the beginning of the integration window for the desired response profile.

12.2.4.4 Manually select the scan for the ending of the integration window for the same response profile.

NOTE: It is suggested that the integration window include at least 1 minute of data acquisition for each sample response. This will help improve the precision of the quantitative measurements by averaging electronic noise and minor perturbations in the *in-situ* sparging process.

12.2.4.5 Execute the MANUAL INTEGRATION routine in the data analysis software to calculate the area beneath the curve of the selected DSITMS *in-situ* sparge profile.

NOTE: Due to the width of DSITMS *in-situ* sparge response profiles, it is generally best to integrate from an assumed zero baseline if given the option in the software.

12.2.4.6 The value of integrated data will typically appear on the selected ion plot near the apex of the response curve.

12.2.4.7 Save this plot as a data file that can be later recalled for further data processing. The values of the integrated selected mass data should also be stored in a text file along with a description of the sample including sample identification, the compound names, selected masses, the concentrations of calibrant compounds, if applicable. This text file will be used for generation of calibration curves (Sec. 12.2.5) or the quantitation of unknowns (Sec. 12.2.6).

12.2.4.8 Repeat Secs. 12.2.4.1 through 12.2.4.7 until all selected mass profiles have been processed and the data have been saved.

CAUTION: All response profiles in all *in-situ sparge* data files including blanks, performance evaluation standards (PES), calibration standards, and unknown samples must be integrated using an integration window of the same width (number of scans).

12.2.5 Generate calibration curves using the procedure described in Sec. 12.1.6.

**CAUTION:** Calibration curves that exhibit significant departure from a linear fit over a concentration range of approximately 10 µg/L to 1,000 µg/L may indicate a problem with data acquisition or reduction. Re-check all prior steps in Sec. 12.2 before proceeding further.

12.2.6 Calculate the concentration of VOCs for an unknown *in-situ* sparge sample using the procedure described in Sec. 12.1.7.

### 12.3 VOCs by heated purge of soil slurries in 40-mL VOA vials

12.3.1 Retrieve and deconvolute data files for heated purge of soil slurry samples using the procedure described in Secs. 12.1.1 through 12.1.2.

12.3.2 Perform background subtraction on the data files using the procedure described in Sec. 12.1.3. (Optional)

12.3.3 Generate selected mass profile plots using the procedure described in Sec. 12.1.4.

12.3.4 Integrate the selected mass profile data using the procedure described in Sec. 12.1.5.

**NOTE:** Some types of soil may interact strongly with volatile organic compounds, greatly reducing the rate at which they can be purged from a sample. Response profiles VOCs in soil may therefore be less intense and exhibit a slower rate of decay than the response profiles for the same VOCs purged from a water sample.

12.3.5 Generate calibration curves using the procedure described in Sec. 12.1.6.

**CAUTION:** Calibration curves that exhibit significant departure from a linear fit over a concentration range of approximately 10 µg/L to 1,000 µg/L in the soil slurry may indicate a problem with data acquisition or reduction. Re-check all prior steps in Sec. 12.3 before proceeding further.

12.3.6 Calculate the concentration of VOCs for an unknown soil slurry sample using the procedure described in Sec. 12.1.7.

12.3.7 Once the values in Sec. 12.3.6 have been obtained, they may be correlated to the concentration of VOCs in the soil by the following equation.

$$\text{soil concentration } (\mu\text{g/kg}) = \frac{[\text{Sec. 12.3.6 result } (\mu\text{g/L})] \times [0.04 \text{ L}]}{[\text{soil mass (kg)}]}$$

### 12.4 VOCs by purge of soil methanol extracts (40-mL VOA vial)

12.4.1 Retrieve and deconvolute data files for purge of soil methanol extract samples using the procedure described in Secs. 12.1.1 through 12.1.2.

12.4.2 Perform background subtraction on the data files using the procedure described in Sec. 12.1.3. (Optional)

12.4.3 Generate selected mass profile plots using the procedure described in Sec. 12.1.4.

12.4.4 Integrate the selected mass profile data using the procedure described in Sec. 12.1.5.

12.4.5 Generate calibration curves using the procedure described in Sec. 12.1.6.

**CAUTION:** Calibration curves that exhibit significant departure from a linear fit over a concentration range of approximately 10 µg/L to 1,000 µg/L (in the 40-mL water surrogate) indicate a problem with data acquisition or reduction. Re-check all prior steps in Sec. 12.4 before proceeding further.

12.4.6 Calculate the concentration of VOCs for an unknown soil methanol extract sample using the procedure described in Sec. 12.1.7.

12.4.7 Once the values in Sec. 12.4.6 have been obtained, they may be correlated to the concentration of VOCs in soil by the following equation.

$$\text{soil concentration } (\mu\text{g/kg}) = \frac{[\text{Sec. 12.4.6 result } (\mu\text{g/L})] \times [\text{methanol extract vol (L)}]}{[\text{soil mass (kg)}]}$$

## 12.5 Real-time monitoring of VOCs in soil-gas and air

12.5.1 Retrieve and deconvolute data files for real-time monitoring samples using the procedure described in Secs. 12.1.1 through 12.1.2.

**NOTE:** Data files for real-time monitoring of VOCs in soil gas and air samples often contain instrument response profiles for blanks, calibration samples, and unknown samples all in the same file. Be certain to properly identify the response profiles and associate them with the proper sample before proceeding further with data handling.

12.5.2 Background subtract data using the procedure described in Sec. 12.1.3.

12.5.3 Generate selected mass profiles using the procedure described in Sec. 12.1.4.

12.5.4 Integrate the selected mass profile data using the procedure described in Sec. 12.2.4.

12.5.5 Generate calibration curves using the procedure described in Sec. 12.1.6.

**CAUTION:** Calibration curves that exhibit significant departure from a linear fit over a concentration range of approximately 60 ppbv to 10 ppmv may indicate a problem with data acquisition or reduction. Re-check all prior steps in Sec. 12.5 before proceeding further.

12.5.6 Calculate the concentration of VOCs for an unknown soil-gas or air sample using the procedure described in Sec. 12.1.7.

## 12.6 Thermal desorption of VOCs in air and soil gas collected on sorbent traps

12.6.1 Retrieve and deconvolute data files for thermal desorption of sorbent trap samples using the procedure described in Secs. 12.1.1 through 12.1.2.

12.6.2 Perform background subtraction on the data using the procedure described in Sec. 12.1.3. (Optional)

12.6.3 Generate selected mass profile plots using the procedure described in Sec. 12.1.4.

### 12.6.4 Integration of selected mass profile data

Refer to the instrument manufacturer's software manual for specific instructions regarding integration of selected mass profile data. The following is a suggested sequence of events for manual integration of data. Alternative approaches may be available for automated integration of data files that will also produce satisfactory results.

12.6.4.1 Open the data file containing the desired selected mass plot. This file will typically include the response profile for only one sample (a blank, a calibration sample, a PES sample, or an unknown sample).

12.6.4.2 The selected mass profiles for VOCs in thermal desorption samples will typically exhibit a response that is relatively narrow (10 to 30 seconds wide) compared with other types of DSITMS samples.

12.6.4.3 Manually select the scan for the beginning of the integration window for the desired response profile. This should typically be at a point at which the profile begins to show an increase in intensity.

12.6.4.4 Manually select the scan for the ending of the integration window for the same response profile. This should be a point at which the profile has nearly returned to the baseline.

**NOTE:** It is suggested that the integration window for thermal desorption samples be individually selected for each sample based on the criteria in Secs. 12.6.4.3 and 12.6.4.4. This may produce better quantitative precision than using a fixed integration window due to variability in sorbent tube characteristics that may affect the width of a thermal desorption profile.

12.6.4.5 Execute the MANUAL INTEGRATION routine in the data analysis software to calculate the area beneath the curve of the selected DSITMS thermal desorption profile.

**NOTE:** Due to the comparatively narrow width of most DSITMS thermal desorption response profiles, it may be better to integrate from the true baseline if given the option in the software.

12.6.4.6 The value of integrated data will typically appear on the selected ion plot near the apex of the response curve.

12.6.4.7 Save this plot as a data file that can be later recalled for further data processing. The values of the integrated selected mass data should also be stored in a text file along with a description of the sample including sample

identification, the compound names, selected masses, and the concentrations of calibrant compounds, if applicable. This text file will be used for generation of calibration curves (Sec. 12.6.5) or the quantitation of unknowns (Sec. 12.6.6.).

12.6.4.8 Repeat steps in Secs. 12.6.4.1 through 12.6.4.7 until all selected mass profiles have been processed and the data have been saved.

12.6.5 Generate calibration curves using the procedure described in Sec. 12.1.6.

**CAUTION:** Calibration curves that exhibit significant departure from a linear fit over a concentration range of approximately 50 pg to 5 ng of an adsorbed VOC on a sorbent tube may indicate a problem with data acquisition or reduction. Re-check all prior steps in Sec. 12.6 before proceeding further.

12.6.6 Calculate the amount (ng) of each target VOC for the unknown thermal desorption samples using the procedure described in Sec. 12.1.7.

12.6.7 Once the amounts of each of the target VOCs have been determined using the procedure described in Sec. 12.6.6, they may be correlated with the actual concentration in the soil-gas or air sample by the following equation.

$$\text{air concentration (ng/L)} = \frac{[\text{Sec. 12.6.6 result (ng)}]}{[\text{total vol of air collected on sorbent trap (L)}]}$$

12.6.8 The results of Sec. 12.6.7 may be express in units of parts-per-billion-volume (ppbv) using the following equation.

**NOTE:** This calculation assumes a standard volume of 22.4 L for 1 mole of air.

$$\text{air concentration (ppbv)} = \frac{[22.4 \text{ L/mol} \times \text{air concentration VOC (ng/L)}]}{[\text{mol wt VOC (g/mol)}]}$$

## 12.7 Determination of the PES response

This section describes the suggested procedure for determining the mean response of VOCs in a PES and calculating the response of VOCs for an individual PES sample relative to the established mean values. This procedure applies to all types of PES samples, regardless of the sample introduction method used. For speed, it is recommended that a spreadsheet program be used for calculations. If necessary, a calculator may be used and will provide satisfactory results.

12.7.1 Refer to Secs. 12.1 through 12.6 for handling data files and the integration of data for specific types of sample introduction.

12.7.2 Determination of mean response for VOCs in a PES

12.7.2.1 Data files must be available for 3 replicate PES samples acquired using the most recent instrument operating conditions and spanning a total time period of not more than 4 consecutive hours.

12.7.2.2 Reduce the data files for each sample and integrate the appropriate selected mass profiles for each VOC in the PES.

12.7.2.3 Save the values of the integrated data for each replicate sample in a single text file.

12.7.2.4 Export the text file to an appropriate spreadsheet program. It is suggested that the format of the spreadsheet include a different column name for each VOC in the PES. The values for the integrated responses of the VOCs in the replicate samples should be entered into rows beneath the appropriate compound name.

12.7.2.5 For each compound in the PES sample, sum the values of the integrated responses. Calculate the mean response by dividing the summed responses by 3.

$$\text{mean response of PES} = \frac{[(\text{response}_1) + (\text{response}_2) + (\text{response}_3)]}{3}$$

12.7.2.6 Save the established mean response for the PES in a text file or record the results in an appropriate manner so that they may be used to evaluate the response of subsequently run PES samples.

12.7.3 Determination of PES sample response relative to the established mean response

12.7.3.1 Reduce the data files for each sample and integrate the appropriate selected mass profiles for each VOC in the PES in a manner identical to that in Sec. 12.7.2.2.

12.7.3.2 Save the values of the integrated data in a text file.

12.7.3.3 Export the text file to an appropriate spreadsheet program. It is suggested that the format of the spreadsheet include a different column name for each VOC in the PES. The values for the integrated responses of the VOCs in the PES should be entered into rows beneath the appropriate compound name.

12.7.3.4 Open the text file containing the established mean response of the PES generated in Sec. 12.7.2.6.

12.7.3.5 Export the established mean responses into the spreadsheet program containing the responses of the individual PES sample.

12.7.3.6 Divide the integrated response for each VOC in the individual PES sample by the corresponding established mean response for the PES. This is the response relative to the established mean.

$$\text{relative response of PES} = \frac{(\text{response of individual PES})}{(\text{mean response of PES})}$$

12.7.3.7 The response of each VOC in the individual PES sample should be within  $\pm 50\%$  of the established mean response. The acceptable range of values is between 0.51 and 1.50.

## 12.8 Qualitative examination of DSITMS mass spectra

The following procedure is used to plot DSITMS mass spectra and visually inspect them for the presence of appropriate ion signals for the VOCs of interest. The same procedure is used for both EI or CI mass spectra. This is a suggested sequence of events that will function with most mass spectrometry data analysis software. Alternative sequences are possible depending on the specific features of the software that is used.

### 12.8.1 Reduction of data files

12.8.1.1 Refer to Secs. 12.1 through 12.6 for opening raw data files, deconvolution of EI/CI spectra, and background subtraction of data for the appropriate types of samples.

### 12.8.2 Plotting of mass spectra

12.8.2.1 Open a data file containing deconvoluted EI or CI spectral data. This may be a background-subtracted data file, if desired, and is left up to the professional judgment of the operator.

12.8.2.2 Select the TOTAL ION PLOT feature of the data analysis software. Refer to the instrument manufacturer's software manual for specific details.

12.8.2.3 Execute the TOTAL ION PLOT command to generate an instrument response profile for the combined ion signal of all ions in the scan range used for the mass spectrometer data acquisition file.

12.8.2.4 Visually inspect the resulting total ion profile plot and identify a scan near the apex of the profile.

12.8.2.5 Select the MASS SPECTRUM feature of the data analysis software. Refer to the instrument manufacturer's software manual for specific details.

12.8.2.6 Select the scan that was identified in Sec. 12.8.2.4. Execute the MASS SPECTRUM command to generate a plot of the mass spectrum at this scan.

12.8.2.7 Export the mass spectrum plot to a printer or a PLOT SPOOLER program for later printing.

### 12.8.3 Visual inspection of the DSITMS mass spectrum

12.8.3.1 The following are suggested qualitative checks of DSITMS mass spectra. All steps may not apply to every sample.

12.8.3.2 Retrieve the plot of a DSITMS mass spectrum as described in Sec. 12.8.2.

12.8.3.3 Visually inspect the plot of the mass spectrum for obvious problems (such as no peaks in a spectrum of a sample known to contain VOCs).

12.8.3.4 Keep in mind that a DSITMS mass spectrum represents the combined ion signals for all VOCs present in a sample.

12.8.3.5 Keep in mind that CI mass spectra are typically less complicated than EI mass spectra. The EI mass spectra will exhibit a response for all compounds in a sample while CI mass spectra produce a selective response for only those compounds that will be ionized by the specific chemical ionization reagent used. The EI mass spectrum for a typical VOC will also contain more peaks (due to fragmentation) than the CI mass spectrum of the same VOC.

12.8.3.6 Verify that ion intensity is present at the characteristic masses of the internal standards, if they are used. Refer to Table 1 for a list of these masses.

12.8.3.7 Verify that ion intensity is present at the characteristic masses of the target VOCs of interest. Refer to Table 1 for a list of these masses.

12.8.3.8 Verify that the mass spectrum does not contain an excessive number of ions that may indicate the presence of compounds that could interfere with the quantitation of the desired VOCs.

12.8.3.9 Verify that the mass spectra for samples suspected of containing chlorinated or brominated VOCs exhibit ion intensities at the appropriate masses corresponding to the distribution of the chlorine and/or bromine isotopes for those VOCs. Reference spectra are available from many sources for this purpose.

12.8.3.10 Inspect the mass spectrum for excessive noise that could indicate a malfunction of the mass spectrometer and result in false positive results for targeted VOCs.

NOTE: Excessive noise in a DSITMS mass spectrum will typically be characterized by the presence of significant intensity at all masses. Electronic noise will usually exhibit a random distribution of intensity vs. mass.

Samples containing a large number of VOCs, such as water contaminated with gasoline, may also exhibit significant intensity at most masses. However, the mass spectra of these samples will usually be characterized by periodic maxima and minima that are spaced 14 mass units apart.

12.8.3.11 Mass spectra of samples believed to contain only one VOC may be compared with a mass spectral library spectrum to verify the correct identity of the VOC. Suitable library search routines and compilations of mass spectra are available from several sources. This is left to the professional judgment of the operator.

12.8.3.12 Software may be available from third-party vendors that can be used to deconvolute DSITMS mass spectra into the individual mass spectra of the targeted VOCs in a sample. Results may vary depending on the capabilities of the specific software and the number of compounds in the sample. Use of such software is left to the professional judgment of the operator.

## 13.0 METHOD PERFORMANCE

Method performance is illustrated in Tables 6 through 13. Additional data may be found in some of the references to this method.



13.1 Table 6 lists method quantitation limits for example volatile organic compounds in water and in air under electron impact (EI) and/or chemical ionization (CI) conditions when calibrated over the ranges of 2.5 to 15 ppb for water and 50 to 500 ppbv for air. These limits are provided for illustrative purposes only.

13.2 Table 7 gives accuracy and precision parameters for the quantitative measurement of carbon tetrachloride, tetrachloroethene, and trichloroethene in water by 40-mL purge at concentrations of 5, 10, and 40 ppb. These data are provided for illustrative purposes only.

13.3 Table 8 compares the concentrations of trichloroethene, tetrachloroethene, and carbon tetrachloride in groundwater samples taken from the Department of Energy Oak Ridge Tennessee Reservation as measured by this method and by GC/MS. These data are provided for illustrative purposes only.

13.4 Table 9 compares results on gasoline range organics (GROs) in groundwater samples taken from the Department of Energy Oak Ridge Tennessee Reservation as measured by this method and by a gas chromatography with flame ionization detection (GC/FID). These data are provided for illustrative purposes only.

13.5 Table 10 compares results from analyses of groundwater samples for trichloroethene and tetrachloroethene performed in the field by *in situ* sparge with those from sampling followed by analysis in the laboratory. The data are provided for illustrative purposes only.

13.6 Table 11 lists results for dichloroethene and trichloroethene in water performance evaluation check standards as measured by *in situ* sparge. These data are provided for illustrative purposes only.

13.7 Table 12 gives results on the recovery of benzene, toluene, and ethylbenzene plus xylenes from soils taken from the Department of Energy Oak Ridge Tennessee Reservation. Quantities found by purging water slurries of spiked soil samples are compared to those from a purge of water containing no soil. These data are provided for illustrative purposes only.

13.8 Table 13 compares results obtained using the thermal desorption mode of this method with those obtained using a reference method for the measurement of nicotine on solid sorbent traps used to collect environmental tobacco smoke from experimentally contaminated air. These data are provided for illustrative purposes only.

## 14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better: Laboratory Chemical Management for Waste Reduction* available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036.

## 15.0 WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* available from the American Chemical Society at the address listed in Sec. 14.2.

## 16.0 REFERENCES

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## 17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

The pages to follow contain Tables 1 through 13 and Figure 1.

TABLE 1

CHARACTERISTIC<sup>a</sup> IONS FOR DSITMS MEASUREMENT OF REPRESENTATIVE VOCs

Compound	Ionization Mode	
	Electron Impact (EI)	Chemical Ionization (CI) <sup>b</sup>
Acetone	- <sup>c</sup>	59
Benzene	78	79
Bromodichloromethane	83+85	-
Bromoform	171+173	-
Bromomethane	94+96	-
Carbon disulfide	76	-
Carbon tetrachloride	117+119+121	-
Chlorobenzene	112	113
Chloroethane	64+66	-
Chloroform	83+85	-
Chloromethane	50+52	-
Dibromochloromethane	127+129+131	-
1,1-Dichloroethane	63+65	-
1,2-Dichloroethane	62+64	-
1,1-Dichloroethene	96+98	97
<i>cis</i> -1,2-Dichloroethene	96+98	-
<i>trans</i> -1,2-Dichloroethene	96+98	-
Dichloromethane	84+86	-
1,2-Dichloropropane	63+65	-
<i>cis</i> -1,3-Dichloropropene	75+77	75
<i>trans</i> -1,3-Dichloropropene	75+77	75
Ethylbenzene	91+106	107
2-Hexanone	100	101
Methyl ethyl ketone (MEK)	72	73
Methyl isobutyl ketone (MIBK)	100	101
Methyl- <i>tert</i> -butyl ether (MTBE)	73	57

(continued)

TABLE 1  
(Continued)

Compound	Ionization Mode	
	Electron Impact (EI)	Chemical Ionization (CI) <sup>b</sup>
Styrene	104	105
1,1,2,2-Tetrachloroethane	83+85	-
Tetrachloroethene	164+166	-
Toluene	91	93
1,1,1-Trichloroethane	97+99	-
1,1,2-Trichloroethane	97+99	-
Trichloroethene	130+132	-
Vinyl acetate	-	75
Vinyl chloride	62+64	-
Xylenes	91+106	107
Petroleum hydrocarbons	56+57	-

<sup>a</sup> Major ions. Minor ions, different groups of ions, or MS/MS may be used to avoid interfering analytes in some cases.

<sup>b</sup> Water chemical ionization.

<sup>c</sup> Not determined.

TABLE 2

VOLUMES OF NEAT LIQUID REQUIRED TO PREPARE MASTER STOCK SOLUTIONS  
AT 5000 mg/L IN 10 mL VOLUME OF EXAMPLE VOLATILE ORGANIC COMPOUNDS

Compound	Density (mg/ $\mu$ L)	$\mu$ L Required
Acetone	0.7880	63.4
Methyl isobutyl ketone (MIBK)	0.8010	62.4
Methyl ethyl ketone (MEK)	0.8050	62.1
2-Hexanone	0.8120	61.6
Total xylenes	0.8600	58.1
Toluene	0.8623	57.1
Ethylbenzene	0.8660	57.7
Benzene	0.8737	57.2
Styrene	0.9059	55.2
Vinyl acetate	0.9320	53.7
Chlorobenzene	1.1004	45.4
1,2-Dichloropropane	1.1590	43.1
1,1 -Dichloroethane	1.1680	42.8
1,1 -Dichloroethene	1.2129	41.2
<i>trans</i> -1,3-Dichloropropene	1.2200	41.0
<i>cis</i> -1,3-Dichloropropene	1.2200	41.0
1,2-Dichloroethane	1.2569	39.8
Carbon disulfide	1.2632	39.6
1,2-Dichloroethene (total)	1.2650	39.5
Dichloromethane	1.3170	38.0
1,1,1-Trichloroethane	1.3376	37.4
1,1,2-Trichloroethane	1.4416	34.7
Trichloroethene	1.4640	34.2
Chloroform	1.4798	33.8
1,1,2,2-Tetrachloroethane	1.5866	31.5
Carbon tetrachloride	1.5890	31.5
Dibromochloromethane	2.4330	20.6
Bromoform	2.9035	17.2

TABLE 3

VOLUME OF ANALYTE MASTER STANDARD INJECTED INTO A 10-L TEDLAR BAG TO PRODUCE ANALYTE WORKING STANDARDS FOR MEASUREMENT OF VOCs IN AIR

Target VOC Concentration (ppbv)	Volume (mL) of Analyte Master Standard Required for 10 L of Air
0	0.0
10	0.1
50	0.5
250	2.5
500	5.0
1,000	10.0

TABLE 4

BASIC ION TRAP SCAN FUNCTION FOR GENERATING ALTERNATING EI/CI MASS SPECTRA

Acquire electron ionization (EI) mass spectrum	
Event	Instrument Function
1	Reset and zero the scan parameters
2	Electron ionization (store all ions >40 Daltons)
3	Turn on the electron multiplier
4	Scan the mass spectrum and acquire data to the computer
Acquire chemical Ionization (CI) mass spectrum	
5	Reset and zero the scan parameters
6	Ionize CI reagent by electron ionization (Store all ions >15 Daltons)
7	Eject ions >25 Daltons
8	Allow CI reagent to react with analytes for 10-200 msec
9	Turn on the multiplier
10	Scan the mass spectrum and acquire data to the computer
11	Reset all scan parameters and return to event #1

\*Note: The scan function listed above depicts the basic operations that occur within an ion trap mass spectrometer during the acquisition of alternating scans generated using electron ionization (EI) and chemical ionization (CI). It is assumed in the above a case that the CI reagent used is water vapor. This scan function is generic for most ion trap mass spectrometers although the software and hardware means of implementing these scans is dependent on the manufacturer and specific model of the instrument. Refer to the instrument operating manual for specific information regarding setup and operation.

Source: References 1 and 10.

TABLE 5

VOLUME OF ANALYTE WORKING SOLUTION INJECTED INTO 40 mL OF WATER TO  
OBTAIN A SOLUTION CONCENTRATION IN THE RANGE OF 0 TO 1,000 µg/L

Final Solution Concentration (µg/L)	Volume (µL) of Analyte Working Solution Injected into 40 mL of Water
0	0.0
2	0.8
5	2.0
15	6.0
25	10.0
50	20.0
100	40.0
250	100.0
500	200.0
1,000	400.0



TABLE 6

EXAMPLE METHOD QUANTITATION LIMITS<sup>a</sup> FOR EXAMPLE VOCs IN WATER AND AIR

Compound	Water (ppb) <sup>b</sup>		Air (ppbv) <sup>b</sup>	
	EI <sup>c</sup>	CI <sup>c</sup>	EI <sup>c</sup>	CI <sup>c</sup>
Acetone	- <sup>d</sup>	2.3	-	12
Benzene	1.3	1.7	21	42
Bromodichloromethane	2.5	-	3	-
Bromoform	2.0	-	58	-
Bromomethane	2.4	-	53	-
Carbon disulfide	1.5	-	3	-
Carbon tetrachloride	1.3	-	5	-
Chlorobenzene	0.5	1.4	16	12
Chloroethane	3.2	-	17	-
Chloroform	1.5	-	17	-
Chloromethane	4.7	-	-	-
Dibromochloromethane	4.4	-	4	-
1,1-Dichloroethane	3.0	-	8	-
1,2-Dichloroethane	1.5	-	12	-
1,1-Dichloroethene	2.0	2.6	14	-
<i>cis</i> -1,2-Dichloroethene	2.5	-	11	-
<i>trans</i> -1,2-Dichloroethene	1.7	-	12	-
Dichloromethane	3.0	-	17	-
1,2-Dichloropropane	3.2	-	10	-
<i>cis</i> -1,3-Dichloropropene	2.2	2.0	2	-
<i>trans</i> -1,3-Dichloropropene	1.9	1.5	3	-
Ethylbenzene	1.3	1.4	21	14
2-Hexanone	-	2.1	104	35
Methyl ethyl ketone (MEK)	-	3.2	37	46
Methyl isobutyl ketone (MIBK)	-	2.6	33	16
Styrene	0.5	0.9	13	12

(continued)

TABLE 6  
(Continued)

Compound	Water (ppb) <sup>b</sup>		Air (ppbv) <sup>b</sup>	
	EI <sup>c</sup>	CI <sup>c</sup>	EI <sup>c</sup>	CI <sup>c</sup>
1,1,2,2-Tetrachloroethane	2.1	-	27	-
Tetrachloroethene	1.3	-	12	-
Toluene	0.5	0.5	4	6
1,1,1-Trichloroethane	0.6	-	15	-
1,1,2-Trichloroethane	3.3	-	5	-
Trichloroethene	2.7	-	6	-
Vinyl acetate	-	3.3	61	-
Vinyl chloride	1.0	-	-	-
Xylenes	0.8	1.9	9	8

<sup>a</sup> Calculated using the detection limit algorithm based on the linear regression line from experimentally determined calibration curves (4 points 2.5 to 15 ppb for water, 50 to 500 ppbv for air for the data presented) under a single set of operating conditions. Conditions may be optimized to provide improved limits for any given analyte.

<sup>b</sup> Water by 40-mL vial purge. Air by real-time sampling from Tedlar bag.

<sup>c</sup> EI: Electron impact ionization. CI: Water chemical ionization.

<sup>d</sup> Not determined.

Source: References 3 and 9.

TABLE 7

EXAMPLE DSITMS PERFORMANCE EVALUATION (40-mL PURGE/WATER)<sup>a</sup>

VOC	Target Conc. (ppb)	N	Found Mean Conc. (ppb)	Accuracy		Precision	
				Bias <sup>b</sup>	Percent Bias	Standard Deviation	% Coefficient of Variation <sup>c</sup>
Carbon tetrachloride	5	5	5.00	0.00 ± 0.34	0.0	0.275	5.5
	10	6	9.42	-0.58 ± 0.39	-5.8	0.373	4.0
	40	6	39.18	-0.82 ± 1.32	-2.0	1.259	3.2
Tetrachloroethene	5	5	5.20	0.20 ± 0.89	4.0	0.719	13.8
	10	6	8.72	-1.28 ± 0.49	-12.8	0.466	5.3
	40	6	35.92	-4.08 ± 1.25	-10.2	1.189	3.3
Trichloroethene	5	5	4.97	-0.03 ± 0.18	-0.6	0.148	3.0
	10	6	9.45	-0.55 ± 0.42	-5.5	0.402	4.3
	40	6	39.17	-0.83 ± 1.11	-2.1	1.061	2.7

N = Number of samples

<sup>a</sup> 40-mL purge of spiked ASTM groundwater over three week period.

<sup>b</sup> Bias = (Mean - Target Conc.) ± (t)(S)/√N

Where S = Standard Deviation; t = Students t-Value for 95% Confidence; √N = square root of number of samples

<sup>c</sup> % Coefficient of Variation = (S/Mean)(100%)

Source: Reference 11.

TABLE 8

EXAMPLE COMPARISON OF DSITMS AND GC/MS RESULTS FOR VOCs IN  
GROUNDWATER<sup>a</sup>

Sample	Trichloroethene (ppb)		Tetrachloroethene (ppb)		Carbon Tetrachloride (ppb)	
	DSITMS	GC/MS <sup>b</sup>	DSITMS	GC/MS <sup>b</sup>	DSITMS	GC/MS <sup>b</sup>
1	3	3	0	0	0	0
2	89	81	0	0	1	0
3	5	3	32	27	634	370
4	11	8	57	38	592	430
5	90	56	0	0	0	0
6	5	2	9	8	100	93
7	40	49	256	210	32	5

<sup>a</sup> Local groundwater wells. 40-mL vial purge.

<sup>b</sup> Similar to Method 8260

Source: Reference 11.

TABLE 9

EXAMPLE COMPARISON OF RESULTS FOR  
GASOLINE RANGE ORGANICS (GRO) IN WATER

Sample ID	GRO Concentration (ppb)	
	DSITMS <sup>a</sup>	GC/FID
193	2598	2400
708	8828	6400
657	< 5	< 100
707	< 5	< 100
808	< 5	< 100
810	13	< 100
204	172	150
656 <sup>b</sup>	368 <sup>b</sup>	2300 <sup>b</sup>
806	24	160
632	7538	8200
508	35933	58000

<sup>a</sup> Measured using m/z 56 plus 57.

<sup>b</sup> Contaminated with carbon tetrachloride and trichloroethene.

Source: Reference 9.

TABLE 10

EXAMPLE COMPARISON OF DSITMS RESULTS WITH LABORATORY RESULTS FOR  
SOLVENTS IN GROUNDWATER BY IN-SITU SPARGE

Sample	Trichloroethene (µg/L)			Tetrachloroethene (µg/L)		
	Lab 1 <sup>a</sup>	Lab 2 <sup>a</sup>	DSITMS <sup>b</sup>	Lab 1 <sup>a</sup>	Lab 2 <sup>a</sup>	DSITMS <sup>b</sup>
1	56	74	88	34	43	49
2	18	19	15	22	23	20
3	40	50	60	70	383	298

<sup>a</sup>EPA Method 5030/8260

<sup>b</sup>In-situ hydrosparge

Source: Reference 4.

TABLE 11

## EXAMPLE PERFORMANCE EVALUATION CHECK STANDARDS BY IN-SITU SPARGE

Day	EPA VOA nominal ( $\mu\text{g/L}$ )	Hydrosparge ( $\mu\text{g/L}$ )	
		DCE	TCE
1	40	38	29
2	16	18	14
3	100	83	112
3	16	16	15
4	72	87	75
5	100	134	109
5	350	302	343
6	40	67	44
7	20	36	20
8	20	29	19

Source: Reference 12.

TABLE 12

EXAMPLE SPIKE RECOVERIES OF BTEX<sup>a</sup> FROM SOIL<sup>b</sup> USING DSITMS

Sample	Spike Recovery (%)		
	Benzene	Toluene	EtBz + Xyl
1	64	74	64
2	70	82	54
3	60	52	48
4	50	62	58
5	78	64	56
Mean	64.4	66.8	56
Std Dev	10.5	11.5	5.8

<sup>a</sup>Benzene, toluene, ethylbenzene, plus xylenes

<sup>b</sup>Room temperature purge of local soil spiked at 400 ng/g versus purge of pH 7 water.

Source: Reference 9.

TABLE 13

## EXAMPLE OF THERMAL DESORPTION DSITMS RESULTS FOR NICOTINE IN AIR

Sample <sup>a</sup>	Nicotine ( $\mu\text{g}/\text{m}^3$ )	
	DSITMS	Reference Method
1	0.82	0.45
2	27	18
3	122	123
4	141	178
5	361	260

<sup>a</sup>Collected on solid sorbent trap

Source: Reference 9.

FIGURE 1

CAPILLARY RESTRICTOR INTERFACE WITH OPEN-SPLIT INLET AND QUICK-CONNECT FITTING FOR THE ATTACHMENT OF SAMPLE INTRODUCTION MODULES AND SAMPLE ARCHIVAL SORBENT TRAPS

