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# METHOD 529 DETERMINATION OF EXPLOSIVES AND RELATED COMPOUNDS IN DRINKING WATER BY SOLID PHASE EXTRACTION AND CAPILLARY COLUMN GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS)

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# METHOD 529

# DETERMINATION OF EXPLOSIVES AND RELATED COMPOUNDS IN DRINKING WATER BY SOLID PHASE EXTRACTION AND CAPILLARY COLUMN GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS)

## 1. SCOPE AND APPLICATION

1.1 This method provides procedures for the determination of explosives and related compounds in finished drinking water. The method may be applicable to untreated source waters and other types of water samples, but it has not been evaluated for these uses. The method is applicable to a variety of explosives that are efficiently partitioned from the water sample onto a solid phase extraction (SPE) sorbent, and sufficiently volatile and thermally stable for gas chromatography. The method includes the following compounds:

| ANALYTE | CAS NUMBER |
|---|---|
| 2-amino-4,6-dinitrotoluene | 35572-78-2 |
| 4-amino-2,6-dinitrotoluene | 19406-51-0 |
| 3,5-dinitroanaline | 618-87-1 |
| 1,3-dinitrobenzene | 99-65-0 |
| 2,4-dinitrotoluene | 121-14-2 |
| 2,6-dinitrotoluene | 606-20-2 |
| hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) | 121-82-4 |
| nitrobenzene | 98-95-3 |
| 2-nitrotoluene | 88-72-2 |
| 3-nitrotoluene | 99-08-1 |
| 4-nitrotoluene | 99-99-0 |
| 1,3,5-trinitrobenzene | 99-35-4 |
| 2,4,6-trinitrophenylmethylnitramine (Tetryl) | 479-45-8 |
| 2,4,6-trinitrotoluene (TNT) | 118-96-7 |

1.2 Detection limit (DL) is defined as the statistically calculated minimum concentration that can be measured with 99% confidence that the reported value is greater than zero (1). The DL is compound dependent and is particularly dependent on extraction efficiency, sample matrix, and instrument performance. DLs for method analytes are listed in Tables 3, 9, and 15.

1.3 This method should be performed only by analysts with experience in solid phase extractions and GC/MS analyses.

## 2. SUMMARY OF METHOD

Analytes and surrogates are extracted by passing a 1 L water sample through a solid phase extraction (SPE) cartridge containing 500 mg of a divinylbenzene/vinylpyrrolidone copolymer or a 47 mm disk containing a reverse phase sulfonated polystyrene divinyl-benzene phase. The organic compounds are eluted from the solid phase with a small quantity of ethyl acetate. The sample components are separated, identified, and measured by injecting an aliquot of the concentrated extract into a high resolution fused silica capillary column of a GC/MS system with a programmed temperature vaporizing (PTV) injector. Compounds eluting from the GC column are identified by comparing their measured mass spectra and retention times to reference spectra and retention times in a data base. Analysis may be performed using either full scan or selected ion monitoring (SIM) mass spectrometry. Reference spectra and retention times for analytes are obtained by the measurement of calibration standards under the same conditions used for samples. The concentration of each identified component is measured by relating the MS response of the quantitation ion(s) produced by that compound to the MS response of the quantitation ion(s) produced by a compound that is used as an internal standard. Surrogate analytes, whose concentrations are known in every sample, are measured with the same internal standard calibration procedure.

The method provides instructions and demonstration data for both the SPE disk and cartridge extraction techniques and for three different GC/MS techniques: PTV splitless injection with full scan mass spectrometry, cold on-column injection with full scan mass spectrometry, and PTV splitless injection with SIM mass spectrometry.

## 3. DEFINITIONS

3.1 ANALYSIS BATCH -- A set of samples analyzed on the same instrument during a 24 hour period that begins and ends with the analysis of the appropriate Continuing Calibration Check (CCC) standards. Additional CCCs may be required depending on the length of the analysis batch and/or the number of Field Samples.

3.2 CALIBRATION STANDARD (CAL) -- A solution prepared from the primary dilution standard solution or stock standard solutions and the internal standards and

surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.3 CONTINUING CALIBRATION CHECK (CCC) -- A calibration standard containing one or more method analytes, which is analyzed periodically to verify the accuracy of the existing calibration for those analytes.

3.4 DETECTION LIMIT (DL) -- The minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero. This is a statistical determination (Sect. 9.2.4), and accurate quantitation is not expected at this level (1).

3.5 EXTRACTION BATCH -- A set of up to 20 field samples (not including QC samples) extracted together by the same person(s) during a work day using the same lot of solid phase extraction devices and solvents, surrogate solution, and fortifying solutions. Required QC samples for each extraction batch include: Laboratory Reagent Blank, Laboratory Fortified Blank, Laboratory Fortified Matrix, and either a Field Duplicate or Laboratory Fortified Matrix Duplicate.

3.6 FIELD DUPLICATES (FD1 and FD2) -- Two separate samples collected at the same time and place under identical circumstances, and treated exactly the same throughout field and laboratory procedures. Analyses of FD1 and FD2 give a measure of the precision associated with sample collection, preservation, and storage, as well as with laboratory procedures.

3.7 INTERNAL STANDARD (IS) -- A pure analyte(s) added to a sample, extract, or standard solution in known amount(s) and used to measure the relative responses of other method analytes and surrogates that are components of the same solution. The internal standard must be an analyte that is not a sample component.

3.8 LABORATORY FORTIFIED BLANK (LFB) -- An aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, including the use of sample preservatives, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.

3.9 LABORATORY FORTIFIED SAMPLE MATRIX (LFM) -- An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

3.10 LABORATORY FORTIFIED SAMPLE MATRIX DUPLICATE (LFMD) -- A second aliquot of the Field Sample, or duplicate Field Sample, that is used to prepare the LFM. The LFMD is fortified, extracted and analyzed identically to the LFM. The LFMD is used instead of the Laboratory Duplicate to assess method precision when the occurrence of target analytes are low.

3.11 LABORATORY REAGENT BLANK (LRB) -- An aliquot of reagent water or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, surrogates, and sample preservatives that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

3.12 MATERIAL SAFETY DATA SHEET (MSDS) -- Written information provided by vendors concerning a chemical's toxicity, health hazards, physical properties, fire, and reactivity data including storage, spill, and handling precautions.

3.13 MINIMUM REPORTING LEVEL (MRL) -- The minimum concentration that can be reported as a quantitated value for a target analyte in a sample following analysis. This defined concentration can be no lower than the concentration of the lowest calibration standard for that analyte, and can only be used if acceptable quality control criteria for the analyte at this concentration are met.

3.14 PRIMARY DILUTION STANDARD SOLUTION (PDS) -- A solution of several analytes prepared in the laboratory from stock standard solutions and diluted as needed to prepare calibration solutions and other needed analyte solutions.

3.15 PROGRAMMED TEMPERATURE VAPORIZING INJECTOR (PTV) -- A GC injector capable of rapid heating. Typical use of a PTV injector involves introducing the sample with the injector cool, then rapidly heating it at 100-200 degrees per minute to volatilize the analytes onto the GC column. One advantage of this type of injection is that thermally labile analytes in a mixture can be transferred to the GC column at a lower temperature than in conventional hot injections.

3.16 QUALITY CONTROL SAMPLE (QCS) -- A solution of method analytes of known concentrations that is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials.

3.17 SELECTED ION MONITORING (SIM) -- A chromatographic/mass spectrometric technique where only one or a few ions are monitored. When used with gas chromatography, the set of ions monitored is usually changed periodically

throughout the chromatographic run, to correlate with the characteristic ions of each analyte or group of analytes as they elute from the chromatographic column.

3.18 STOCK STANDARD SOLUTION (SSS) -- A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

3.19 SURROGATE ANALYTE (SUR) -- A pure analyte, which is extremely unlikely to be found in any sample, and which is added to a sample aliquot in a known amount before extraction or other processing, and is measured with the same procedures used to measure other sample components. The purpose of the SUR is to monitor method performance with each sample.

## 4. INTERFERENCES

4.1 During analysis, major contaminant sources are reagents and SPE devices. Analyses of laboratory reagent blanks provide information about the presence of contaminants. Solid phase extraction devices described in this method have two potential sources of contamination, both the solid phase sorbent and for cartridge extractions, the polypropylene cartridge that it is packed in. Manufacturers' brands and lot numbers of these devices should be monitored and tracked to ensure that contamination will not preclude analyte identification and quantitation.

4.2 Interfering contamination may occur when a sample containing low concentrations of compounds is analyzed immediately after a sample containing relatively high concentrations of compounds. Injection port liners must be replaced as needed (cleaning and deactivation by the analyst is not recommended). After analysis of a sample containing high concentrations of compounds, a laboratory reagent blank should be analyzed to ensure that accurate values are obtained for the next sample. In the case of automated analysis, the analyst may not be aware of high concentration samples until after an entire batch is analyzed. In this situation, the analyst should carefully review data from samples analyzed immediately after high concentration samples, and reanalyze them if necessary.

## 5. SAFETY

5.1 The toxicity or carcinogenicity of many of the chemicals used in this method has not been precisely defined; each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining awareness of OSHA regulations regarding safe handling of chemicals used in this method. Each laboratory should maintain a file of applicable MSDSs.

5.2 Some method analytes including 2,4- and 2,6-dinitrotoluene, RDX, and TNT have been classified as known or suspected human or mammalian carcinogens. Pure standard materials and stock standard solutions of these compounds should be handled with suitable protection to skin, eyes, etc. (2-5).

5.3 RDX, Tetryl and TNT are **explosives** and the neat materials require special handling to be used safely. **It is highly recommended that only dilute solutions of these materials, available as standards from commercial suppliers be used for this method (6).**

**6. EQUIPMENT AND SUPPLIES** (References to specific brands or catalog numbers are included for illustration only, and do not imply endorsement of the product.)

6.1 GLASSWARE -- All glassware must be meticulously cleaned. This may be accomplished by washing with detergent and water, rinsing with water, distilled water, and solvent rinsing or heating (where appropriate) at 400° C for 2 h in a muffle furnace. Volumetric glassware should never be heated to the temperatures obtained in a muffle furnace.

6.2 SAMPLE CONTAINERS -- 1 L or 1 qt amber glass bottles fitted with polytetrafluoroethylene (PTFE) lined polypropylene screw caps. Amber bottles are highly recommended since some of the method analytes are sensitive to light and may degrade upon exposure. Clear glass bottles may be used if they are wrapped in foil, or samples are stored in boxes that prevent exposure to light.

6.3 VOLUMETRIC FLASKS -- various sizes.

6.4 LABORATORY OR ASPIRATOR VACUUM SYSTEM -- Sufficient capacity to maintain a vacuum of approximately 25 cm (10 in.) of mercury.

6.5 MICRO SYRINGES -- various sizes.

6.6 VIALS -- Various sizes of amber vials with PTFE lined screw caps for storing standard solutions and extracts.

6.7 DRYING COLUMN -- The drying tube should contain about 5 to 7 grams of anhydrous sodium sulfate to remove residual water from the extract. Any small tube may be used, such as a syringe barrel, a glass dropper, etc. as long as no particulate sodium sulfate passes through the column into the extract.

6.8 ANALYTICAL BALANCE -- Capable of weighing 0.0001 g accurately.

6.9 FUSED SILICA CAPILLARY GAS CHROMATOGRAPHY COLUMN -- Any capillary column that provides adequate resolution, capacity, accuracy, and precision can be used. Medium polarity, low bleed columns are recommended for use with this method to provide adequate chromatography and minimize column bleed. Deactivated injection port liners are highly recommended. Example retention times are presented in Table 2.

6.9.1. Column - 15 m × 0.25 mm i.d. fused silica capillary column coated with a 0.25 µm bonded film of polyphenylmethylsilicone, (Agilent DB-5ms or equivalent).

NOTE: Although other columns may be used, longer or thicker film columns are not recommended because increased residence time in the column has been shown to contribute to analyte degradation (7).

6.10 GAS CHROMATOGRAPH/MASS SPECTROMETER/DATA SYSTEM (GC/MS/DS)--

6.10.1 The GC must be capable of temperature programming and should be equipped for PTV splitless or cold on-column injection. The injection system should not allow the analytes to contact hot stainless steel or other metal surfaces that promote decomposition. Satisfactory data could not be demonstrated for this method using hot splitless injections.

A large volume injector may be used to increase method sensitivity, or to avoid extract evaporation, if all criteria in Sections 9 and 10 are met.

6.10.2 Deactivated injection port liners should be used, and it is highly recommended that they be replaced when necessary with a new deactivated liner. Cleaning and deactivation of injection port liners by the analyst is not recommended. The injection port liner should be replaced as necessary to meet all QC requirements. The frequency will vary by the type of instrument used and the type and number of samples analyzed.

In general, packed injection port liners should not be used with this method. The use of liner packings such as glass wool and fused silica wool during development of this method caused significant breakdown of some method analytes, particularly RDX. Carbofrits (Restek) did show acceptable performance and may be used with PTV splitless injection. (The data shown in this method in Tables 3-8 were generated using a Carbofrit.)

6.10.3 The mass spectrometer must be capable of electron ionization at a nominal electron energy of 70 eV to produce positive ions. The spectrometer must

be capable of scanning at a minimum from 45 to 250 amu with a complete scan cycle time (including scan overhead) of 0.7 sec or less. (Scan cycle time = total MS data acquisition time in sec divided by number of scans in the chromatogram). The spectrometer must produce a mass spectrum that meets all criteria in Table 1 when an injection of approximately 5 ng of BFB is introduced into the GC. A single spectrum at the apex of the chromatographic peak, or an average of the three spectra at the apex of the peak, or an average spectrum across the entire GC peak may be used to evaluate the performance of the system. Background subtraction is permitted. The scan time must be set so that all analytes have a minimum of 5 scans across the chromatographic peak. Seven to ten scans across chromatographic peaks are strongly recommended.

NOTE: Although BFB is most commonly used as the tune check for volatile compound analysis, it was selected for use in this method for semivolatile analytes because the ions used for the BFB tune check are similar to the analyte quantitation ions in this method.

6.10.4 If the SIM option is selected for use with this method, the mass spectrometer must be capable of this technique. Some ion trap mass spectrometers have an option similar to SIM known as Selected Ion Storage (SIS). Selected ion storage may be used with this method, however a preliminary assessment during method development showed little if any increase in method sensitivity using SIS.

6.10.5 An interfaced data system is required to acquire, store, reduce, and output mass spectral data. The computer software should have the capability of processing stored GC/MS data by recognizing a GC peak within any given retention time window. The software must also allow integration of the ion abundance of any specific ion between specified time or scan number limits, calculation of response factors as defined in Sect. 10.2.5 or construction of a linear regression calibration curve, and calculation of analyte concentrations.

6.11 VACUUM MANIFOLD -- A vacuum manifold (Supelco # 57030 and #57275 for extraction cartridges or Varian #12146001 for disks, or equivalent) is required for processing samples through the extraction/elution procedure. An automatic or robotic sample preparation system designed for use with solid phase extraction cartridges/disks may be utilized in this method if all quality control requirements discussed in Sect. 9 are met. Automated systems may use either vacuum or positive pressure to process samples and solvents through the disk or cartridge. <u>All extraction and elution steps must be the same as in the manual procedure.</u>

Extraction and/or elution steps may not be changed or omitted to accommodate the use of an automated system.

## 7. REAGENTS AND STANDARDS

7.1 HELIUM -- carrier gas, purity as recommended by the GC/MS manufacturer.

7.2 SOLID PHASE EXTRACTION CARTRIDGES -- Waters Porapak RDX. Cartridges are inert non-leaching plastic, for example polypropylene, or glass, and must not contain plasticizers that leach into the ethyl acetate eluant and prevent the identification and quantitation of method analytes. The polypropylene cartridges (6 mL volume) are packed with 500 mg of a divinylbenzene/vinylpyrrolidone copolymer. The packing must have a narrow size distribution and must not leach interfering organic compounds into the eluting solvent.

7.3 SOLID PHASE EXTRACTION DISKS – 3M Empore SDB-RPS, 47mm. NOTE: This SPE material is a chemically modified polystyrene divinyl benzene material. Use of conventional polystyrene divinyl benzene materials will not result in acceptable data.

7.4. COPPER SULFATE -- ACS grade. Used as a sample preservative for inhibiting microbial activity in stored samples.

7.5 TRIZMA PRE-SET CRYSTALS (pH 7.0 BUFFER) -- Tris (hydroxymethyl) aminomethane and Tris hydrochloride (Sigma Chemical Co.). Used as a binding agent for free chlorine, and to keep the copper in solution. Alternatively, a two component buffer of tris(hydroxymethyl)aminomethane [CAS# 77-86-1] and tris(hydroxymethyl)aminomethane hydrochloride [CAS# 1185-53-1] may be used. Proportions of each to be used are listed in Sect. 8.2.1.

7.6 SOLVENTS --

7.6.1 ETHYL ACETATE AND METHANOL -- High purity pesticide quality or equivalent.

7.6.2 REAGENT WATER -- Water in which an interference is not observed at >1/3 the MRL of any of the compounds of interest. Prepare reagent water by passing tap water through a filter bed containing about 0.5 kg of activated carbon or by using a water purification system. Store in clean, narrow-mouth bottles with PTFE lined septa and screw caps.

7.7 SODIUM SULFATE, ANHYDROUS -- ACS grade. Material should be Soxhlet extracted with methylene chloride for a minimum of 4 h or heated to 400° C for 2 h in a muffle furnace.

7.8 ANALYTE STOCK STANDARD SOLUTIONS -- It is recommended that individual solutions of analytes, or mixtures of analytes, be purchased from commercial suppliers. All work done during development of this method was done with commercial mixtures. RDX, Tetryl and TNT are explosives and require special handling to be used safely (6). They are not readily available as neat materials. Stock standard solutions of explosives are frequently provided in acetonitrile. This is acceptable because the acetonitrile will be sufficiently diluted in calibration standards and spiking solutions. Store the amber vials at 0° C or less, or according to the supplier's recommendations.

Stock standards of method analytes that are not explosive may be prepared from neat materials. Typical concentrations of stock standards that can be used conveniently are 1-10 mg/mL.

7.9 ANALYTE PRIMARY DILUTION STANDARD SOLUTION(S) -- The stock standard solutions may be used to prepare a primary dilution standard (PDS) solution that contains multiple method analytes in ethyl acetate. Aliquots of each of the stock standard solutions are combined to produce the primary dilution in which the concentration of the analytes is at least equal to the concentration of the most concentrated calibration solution, typically, 10 ng/µL. Store the primary dilution standard solution in an amber vial at 0° C or less, and check regularly for signs of degradation or evaporation, especially just before preparing calibration solutions.

Alternatively, mixtures of method analytes to be used as primary dilution standards may also be purchased from commercial suppliers. Typically these will be in acetonitrile. This is acceptable because the acetonitrile will be sufficiently diluted in calibration standards and spiking solutions. Store the primary dilution standard solution in an amber vial at 0° C or less, or according to the supplier's recommendations.

7.10 CALIBRATION SOLUTIONS -- These standards are prepared by combining appropriate aliquots of a primary dilution standard solution (Sect. 7.9) and the fortification solution of internal standards and surrogates (Sect. 7.11). All calibration solutions should contain at least 80% ethyl acetate to avoid gas chromatographic problems due to mixed solvents. The following calibration ranges are suggested, but the range may be modified depending on instrument sensitivity. For full scan mass spectral analysis, prepare a series of six calibration solutions in ethyl acetate which contain analytes of interest at suggested concentrations of 10, 5.0, 2.0, 1.0, 0.50, and 0.10 ng/µL. For SIM analysis, prepare a series of seven calibration solutions in ethyl acetate which contain analytes of interest at suggested concentrations of 2.0, 1.0, 0.50, 0.25, 0.10, 0.050, and 0.025 ng/µL. Add the internal standard to each CAL standard at a constant concentration (5-7 ng/µL is recommended). Surrogate analytes are also added to each CAL solution, and may be

added at a constant concentration or varied concentrations (similar to those for method analytes), at the discretion of the analyst. If the surrogate analytes are added at a constant concentration, 1-5 ng/µL is recommended for full scan analysis and 1ng/µL is recommended for SIM analysis. Store these solutions in amber vials at 0° C or less. Check these solutions regularly for signs of evaporation and/or degradation. During method development these solutions were stable for at least 60 days.

7.11 INTERNAL STANDARD SOLUTION AND SURROGATE STOCK SOLUTIONS --

7.11.1 INTERNAL STANDARD STOCK - Prepare a stock standard of the internal standard, 3,4-dinitrotoluene [CAS# 610-39-9], at approximately 2.0 mg/mL in ethyl acetate. Store at 0° C or less. During method development, this solution was stable for at least 1 year.

7.11.2. SURROGATE STANDARD STOCK SOLUTIONS - Prepare or purchase individual stock standards of the following surrogate analytes: 1,3,5-trimethyl-2-nitrobenzene commonly known as 2-nitromesitylene [CAS# 603-71-4], 1,2,4-trimethyl-5-nitrobenzene commonly known as 2-nitropseudocumene [CAS# 610-91-3], and nitrobenzene-$d_5$ [CAS# 4165-60-0]. Standards of 2-nitromesitylene and 2-nitropseudocumene should be prepared in methanol at concentrations of 1-2 mg/mL. Nitrobenzene-$d_5$ should be prepared in methylene chloride at a concentration of 1-2 mg/mL. Store at 0° C or less. During method development, these solutions were stable for at least 1 year.

7.12 SAMPLE FORTIFICATION SOLUTIONS --

7.12.1 INTERNAL STANDARD FORTIFICATION SOLUTION - Prepare a dilution of the stock standard in ethyl acetate such that the final concentration is 0.20 mg/mL. This solution is used to add the internal standard to each sample, LRB, LFB, and LFM extract. Add 5-25 µL of this solution to each 1 mL extract to obtain the recommended final concentration of 1-5 ng/µL. Check these solutions regularly for signs of evaporation and/or degradation. During method development these solutions were stable for at least 60 days.

7.12.2 ANALYTE FORTIFICATION SOLUTION(S) - This solution contains all method analytes of interest in methanol. These solutions are used to fortify LFBs and LFMs with method analytes. It is recommended that more than one concentration of this solution be prepared. During the method development, two solutions were used. One containing 100 µg/mL of each analyte, was used for higher concentration fortifications, and the other containing 10 µg/mL of each analyte in methanol was used for lower level

fortifications. Check these solutions regularly for signs of evaporation and/or degradation. During method development these solutions were stable for at least 60 days.

7.12.3 SURROGATE ANALYTE FORTIFICATION SOLUTION - Prepare a solution of the three surrogate standards listed in Sect. 7.11.2 in methanol. If a single concentration of each was used to prepare calibration standards, then prepare this solution such that a convenient fortification volume will correspond to an equivalent concentration in the extracts. If the surrogates have been calibrated over a concentration range, add surrogate to the samples, LRBs, LFBs, LFMs at a single concentration in the range of 1-5 µg/L. Check these solutions regularly for signs of evaporation and/or degradation. During method development these solutions were stable for at least 60 days.

7.13 GC/MS TUNE CHECK SOLUTION -- Bromofluorobenzene (BFB) [CAS# 460-00-4] in ethyl acetate; suggested concentration, 5 µg/mL. Store this solution in an amber vial at 0° C or less.

## 8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 SAMPLE COLLECTION -- When sampling from a water tap, open the tap and allow the system to flush until the water temperature has stabilized (usually about 2 min). Adjust the flow to about 500 mL/min and collect samples from the flowing stream. The sample should nearly fill the 1 L or 1 qt bottle, but does not need to be headspace free. If preservatives have been added to the bottle prior to sampling, be careful not to rinse them out during sample collection. Keep samples sealed from collection time until analysis. When sampling from an open body of water, fill the sample container with water from a representative area. Sampling equipment, including automatic samplers, must be free of plastic tubing, gaskets, and other parts that may leach interfering analytes into the water sample.

8.2 SAMPLE DECHLORINATION AND PRESERVATION -- All samples must be dechlorinated and preserved with a microbial inhibitor at the time of collection. Jenkins, et al. (8) have clearly shown the need for microbial preservation of several of the method analytes. Copper sulfate pentahydrate is added as a microbial inhibitor at a concentration of 0.5 g/L of water (9). The Trizma Pre-Set Crystals pH7 buffer (Sect. 7.5) is added at a concentration of 5.0 g/L. The buffer acts to tie up free chlorine, and also keeps the copper in solution (9). The buffer should be added to all samples, even those that are unchlorinated. The copper sulfate and Trizma may be added to the sample bottles as dry salts prior to transporting the sample bottles to the sampling site.

8.2.1 As an alternative to the Trizma Pre-Set Crystals pH7 buffer, the following may be used : 0.3 g of tris(hydroxymethyl)aminomethane plus 4.7 g of tris(hydroxymethyl)aminomethane hydrochloride for each 1 L sample.

8.3 SAMPLE TRANSPORT AND STORAGE -- All samples should be iced during shipment and must not exceed 10° C during the first 48 hours. Samples should be confirmed to be at or below 10° C when they are received at the laboratory. Samples stored in the lab must be held at or below 6° C until extraction, but should not be frozen.

Samples that are significantly above 10° C at the time of collection, may need to be iced or refrigerated for a period of time, in order to chill them prior to shipping. This will allow them to be shipped with sufficient ice to meet the above requirements.

8.4 HOLDING TIME -- Samples must be extracted within 14 days of collection. Sample extracts may be stored for up to 30 days after sample extraction, when stored in amber vials at 0° C or less.

## 9. QUALITY CONTROL

9.1 Quality control (QC) requirements include: the initial demonstration of laboratory capability (summarized in Table 23) followed by regular analyses of continuing calibration checks, laboratory performance check standards, laboratory reagent blanks, laboratory fortified blanks, and laboratory fortified matrix samples. In addition, a DL must be determined for each analyte of interest. These criteria are considered the minimum acceptable QC criteria, and laboratories are encouraged to institute additional QC practices to meet their specific needs. The laboratory must maintain records to document the quality of the data generated. A complete summary of QC requirements is summarized in Table 24.

9.2 INITIAL DEMONSTRATION OF CAPABILITY (IDC) -- Requirements for the initial demonstration of laboratory capability are described in the following sections and summarized in Table 23.

9.2.1 INITIAL DEMONSTRATION OF LOW CARTRIDGE/DISK EXTRACTION BACKGROUND AND SYSTEM BACKGROUND -- Before any samples are analyzed, or any time a new lot or brand of solid phase extraction disks or cartridges is received from a supplier, it must be demonstrated that a laboratory reagent blank (LRB) is reasonably free of any contamination that would prevent the determination of any analyte of concern (Sect. 9.2.1.2 and 9.4).

9.2.1.1 A source of potential contamination is the solid phase extraction media which may contain phthalate esters, silicon compounds,

and other contaminants that could interfere with the determination of method analytes. Although extraction media are generally made of inert materials, they may still contain extractable organic material. If the background contamination is sufficient to prevent accurate and precise measurements, the condition must be corrected before proceeding with the initial demonstration.

9.2.1.2 Other sources of background contamination are solvents, reagents, and glassware. Background contamination must be reduced to an acceptable level before proceeding with the next section. Background from method analytes and interferences should be $\leq$ 1/3 the MRL.

9.2.2 INITIAL DEMONSTRATION OF PRECISION (IDP) -- Prepare 4-7 replicate LFBs fortified at 2-5 µg/L, or other mid-range concentration, using solutions described in Sect. 7.12.2 and 7.12.3. This concentration may be lower if SIM is being used. Sample preservatives described in Sect. 8.2 must be added to these samples. Extract and analyze these replicates according to the procedure described in Sect. 11. The relative standard deviation (RSD) of the results of the replicate analyses must be less than or equal to 20% for all method analytes and surrogates.

9.2.3 INITIAL DEMONSTRATION OF ACCURACY (IDA) -- Using the same set of replicate data generated for Sect. 9.2.2, calculate average recovery. The average recovery of the replicate values for all analytes and surrogates must be within 70-130% of the true value.

9.2.4 DL DETERMINATION -- Replicate analyses for this procedure should be done over at least 3 days (both the sample extraction and the GC analyses should be done over at least 3 days). Prepare at least 7 replicate LFBs using solutions described in Sect. 7.12.2 and 7.12.3, at a concentration estimated to be near the DL. This concentration may be estimated by selecting a concentration at 2-5 times the noise level. Concentrations shown in the example data in Tables 3, 9, and 15 may be used as a guide, however the appropriate concentration will be dependent upon the injection technique and the sensitivity of the GC/MS system used. Sample preservatives described in Sect. 8.2 must be added to these samples. Analyze the seven replicates through all steps of Sect. 11. Calculate the DL using the following equation:

$$DL = St_{(n - 1,\ 1 - alpha\ =\ 0.99)}$$

where:

$t_{(n - 1,1 - alpha = 0.99)}$ = Student's t value for the 99% confidence level with n-1 degrees of freedom
n = number of replicates
S = standard deviation of replicate analyses.

NOTE**:** Do not subtract blank values when performing DL calculations.

9.2.5 The analyst is permitted to modify GC columns or GC conditions. Each time such method modifications are made, the analyst must repeat the procedures in Sect. 9.2.1 through 9.2.4.

9.3 MINIMUM REPORTING LEVEL (MRL) -- The MRL is the threshold concentration of an analyte that a laboratory can expect to accurately quantitate in an unknown sample. The MRL should be established at an analyte concentration either greater than three times the DL or at a concentration which would yield a response greater than a signal-to-noise ratio of five. **Although the lowest calibration standard for an analyte may be below the MRL, the MRL for an analyte must never be established at a concentration lower than the lowest calibration standard for that analyte.**

9.4 LABORATORY REAGENT BLANKS (LRB) -- With each extraction batch, analyze a laboratory reagent blank to determine the background system contamination. If, within the retention time window of any analyte, the LRB produces a peak that would prevent the determination of that analyte, determine the source of contamination and eliminate the interference before processing samples. Background contamination must be reduced to an acceptable level before proceeding. Background from method analytes or contaminants that interfere with the measurement of method analyses should be $\leq$ 1/3 the MRL. Any time a new batch of SPE cartridges is received, or new supplies of other reagents are used, repeat the demonstration of low background described in Sect. 9.2.1.

9.5 CONTINUING CALIBRATION CHECK (CCC) -- This calibration check is required at the beginning of each day that samples are analyzed, after every ten field samples, and at the end of any group of sample analyses. See Sect. 10.3 for concentration requirements and acceptance criteria.

9.6 MS TUNE CHECK -- This performance check consists of verifying the MS tune using the mass spectrum of BFB. A complete description of the check is in Sect. 10.2.1. This check must be performed each time a major change is made to the mass spectrometer, and each time analyte calibration is performed (i.e., average RFs are calculated, or first or second order calibration curves are developed).

9.7 LABORATORY FORTIFIED BLANK (LFB) -- With each extraction batch, extract and analyze an LFB containing each analyte of concern. If more than 20 field samples are included in a batch, analyze an LFB for every 20 samples. The fortified concentration of the LFB should be rotated between low, medium, and high concentrations from day to day. The low concentration LFB must be as near as practical to the MRL. Results of LFB analyses corresponding to the low fortification concentration for an analyte must be within 50-150% of the true value. Results of LFB analysis from medium and high level concentrations must be 70-130% of the true value for all analytes.

9.8 INTERNAL STANDARD (IS) --The analyst must monitor the peak area of the IS in all injections during each analysis day. The IS response (peak area) in any chromatographic run should not deviate from the response in the most recent CCC by more than 30%, and must not deviate by more than 50% from the area measured during initial analyte calibration. If the IS area in a chromatographic run does not meet these criteria inject a second aliquot of that extract.

9.8.1 If the reinjected aliquot produces an acceptable internal standard response, report results for that aliquot.

9.8.2 If the reinjected extract fails again, the analyst should check the calibration by reanalyzing the most recently acceptable calibration standard. If the calibration standard fails the criteria of Sect. 10.3.3, recalibration is in order per Sect. 10.2. If the calibration standard is acceptable, extraction of the sample may need to be repeated provided the sample is still within the holding time. Otherwise, report results obtained from the reinjected extract, but annotate as suspect. Alternatively, collect a new sample and re-analyze.

9.9 SURROGATE RECOVERY -- The surrogate standards are fortified into all calibration standards, samples, LFBs, LFMs, FDs, FRBs and LRBs. The surrogate is a means of assessing method performance from extraction to final chromatographic measurement.

9.9.1 Surrogate recovery criteria are 70-130% of the fortified amount for all method surrogates. When surrogate recovery from a sample, blank, or CCC does not meet these criteria, check : (1) calculations to locate possible errors, (2) standard solutions for degradation, (3) contamination, and (4) instrument performance. Correct any problems that are identified. If these steps do not reveal the cause of the problem, reanalyze the extract.

9.9.2 If the extract reanalysis meets the surrogate recovery criterion, report only data for the reanalyzed extract.

9.9.3 If the extract reanalysis fails the recovery criterion, the analyst should check the calibration by reanalyzing the most recently acceptable calibration standard. If the calibration standard fails the criteria of Sect. 10.3.3, recalibration is in order per Sect. 10.2. If the calibration standard is acceptable, it may be necessary to extract another aliquot of sample if sample holding time has not been exceeded. If the sample re-extract also fails the recovery criterion, report all data for that sample as suspect, or analyze a duplicate sample.

9.10 LABORATORY FORTIFIED SAMPLE MATRIX (LFM) -- Determine that the sample matrix does not contain materials that adversely affect method performance. This is accomplished by analyzing replicates of laboratory fortified matrix samples and ascertaining that the precision, accuracy, and method detection limits of analytes are in the same range as obtained with laboratory fortified blanks. If a variety of different sample matrices are analyzed regularly, for example, drinking water from groundwater and surface water sources, LFM data should be collected for each matrix. Over time, LFM data should be documented for all routine sample sources for the laboratory. A laboratory fortified sample matrix should be extracted and analyzed for each extraction batch. If more than 20 samples are processed in a batch, extract and analyze an LFM for every 20 samples. If the recovery data for an LFM does not meet the recovery criteria in Sect. 9.7, and LFBs show the laboratory to be in control, then the samples from that matrix (sample location) are documented as suspect due to matrix effects.

9.10.1 Within each extraction batch, a minimum of one field sample is fortified as an LFM for every 20 samples analyzed. The LFM is prepared by spiking a sample with an appropriate amount of the fortification solutions described in Sect. 7.12.2 and 7.12.3. Select the spiking concentration that is at least twice the matrix background concentration. Selecting a duplicate bottle of a sample that has already been analyzed, aids in the selection of appropriate spiking levels. If this is not possible, use historical data or rotate through low, medium and high calibration concentrations to select a fortifying concentration.

9.10.2 Calculate the percent recovery (R) for each analyte, after correcting the measured fortified sample concentration, A, for the background concentration, B, measured in the unfortified sample, i.e.,

$$R = \frac{(A - B)}{C} * 100$$

where C is the fortified concentration. Compare these values to control limits for LFBs (Sect. 9.7).

9.10.3 Recoveries may exhibit a matrix dependence. For samples fortified at or above their native concentration, recoveries should range between 70 and 130% for all method analytes. If the accuracy (percent recovery) of any analyte falls outside the designated range, and the laboratory performance for that analyte is shown to be in control, the accuracy problem encountered with the fortified sample is judged to be matrix related, not system related. The result for that analyte in the unfortified sample is labeled suspect/matrix to inform the data user that the results are suspect due to matrix effects.

9.11 FIELD DUPLICATES (FD) -- Within each extraction batch, a minimum of one field sample should be analyzed in duplicate. If more than 20 samples are extracted in a batch, analyze a FD for each 20 samples. Duplicate sample analyses serve as a check on sampling and laboratory precision. If analytes are not routinely observed in field samples, duplicate LFMs should be analyzed to substitute for this requirement. Refer to Sect. 9.10.1 for guidance on spiking concentrations.

9.11.1 Calculate the relative percent difference (RPD) for duplicate measurements (FD1 and FD2) as shown below.

$$RPD = \frac{FD1 - FD2}{(FD1 + FD2)/2} * (100)$$

9.11.2 Relative percent differences for laboratory duplicates and duplicate LFMs should fall in the range of ± 30 %.

NOTE: Greater variability may be observed for target analytes with concentrations at the low end of the calibration range.

9.12 QUALITY CONTROL SAMPLE (QCS) -- Each time that new PDSs are prepared, analyze a QCS from an external source. If standards are prepared infrequently, analyze a QCS at least quarterly. The QCS may be injected as a calibration standard, or fortified into reagent water and analyzed as an LFB. If the QCS is analyzed as a calibration check standard, then the acceptance criteria are the same as for the CCC (Sect. 10.3.3). If the QCS is analyzed as an LFB, then the acceptance criteria are the same as for an LFB (Sect. 9.7). If measured analyte concentrations are not of acceptable accuracy, check the entire analytical procedure to locate and correct the problem.

## 10. CALIBRATION AND STANDARDIZATION

10.1 Demonstration and documentation of acceptable mass spectrometer tune and initial calibration is required before any samples are analyzed. After initial calibration is

successful, a continuing calibration check is required at the beginning and end of each period in which analyses are performed, and after every tenth sample. Verification of mass spectrometer tune must be repeated each time a major instrument modification or maintenance is performed, and prior to analyte recalibration.

10.2 INITIAL CALIBRATION

10.2.1 MS TUNE -- Calibrate the mass and abundance scales of the MS with calibration compounds and procedures prescribed by the manufacturer with any modifications necessary to meet tuning requirements. Inject 5 ng or less of BFB into the GC/MS system. Acquire a mass spectrum that includes data for m/z 45-250. If the BFB mass spectrum does not meet all criteria in Table 1, the MS must be retuned and adjusted to meet all criteria before proceeding with calibration. A single spectrum at the apex of the chromatographic peak, or an average of the three spectra at the apex of the peak, or an average spectrum across the entire GC peak may be used to evaluate the performance of the system. Background subtraction is permitted.

NOTE: Although BFB is most commonly used as the tune check for volatile compound analysis, it was selected for use in this method for semivolatile analytes because the ions used for the BFB tune check are similar to the analyte quantitation ions in this method.

10.2.2 ANALYTE CALIBRATION FOR FULL SCAN MASS SPECTROMETRY -- Inject an aliquot, usually 1-2 µL (unless a large volume injector is used), of a medium to high concentration calibration solution. For example, 2-10 µg/mL, and acquire and store data from m/z 45-250 with a total cycle time (including scan overhead time) of 0.7 sec or less. Cycle time must be adjusted to measure at least five or more scans during the elution of each GC peak. Seven to ten scans across each GC peak are recommended.

NOTE: On some instruments that cannot scan quickly, e.g. ion traps, the scan time and the chromatographic peak width may need to be carefully evaluated to make sure that this requirement is met.

Chromatographic conditions used during method development are outlined below. These conditions were found to work well on the instrumentation used. Since some of the method analytes are vulnerable to active sites and thermal decomposition, optimum chromatographic conditions may vary with individual instrument design. Although the following conditions are

recommended, GC conditions may be modified, if all performance criteria in Sections 9 and 10 are met.

10.2.2.1 PTV Splitless Injection, Full Scan Mass Spectrometry - Inject with the injector temperature at 60° C, program the injector at 200° C per min to 250° C. Hold in the splitless mode for 1.0 min. Use an initial GC oven temperature of 45° C for 3.3 minutes. Program the oven temperature at 7° C per min to 210° C. Then program at 20° C per min to 250° C. An example chromatogram obtained under these conditions is shown in Figure 1.

10.2.2.2 Cold On-Column Injection, Full Scan Mass Spectrometry – Inject with the injector temperature at 50° C, program the injector at 150° C per min to 220° C. Hold in the splitless mode for 2.0 min. Use an initial GC oven temperature of 50° C for 3 minutes. Program the oven temperature at 7° C per min to 210° C. Then program at 20° C per min to 250° C.

10.2.3 Performance criteria for the calibration standards. Examine the stored GC/MS data with the data system software. The GC/MS/DS peak identification software should be able to recognize a GC peak in the appropriate retention time window for each of the compounds in the calibration solution, and make correct identifications (Sect. 11.8, 11.9).

10.2.4 If all performance criteria are met, inject an appropriate volume (usually 1-2 µL unless a large volume injector is used) of each of the other CAL solutions using the same GC/MS conditions.

10.2.4.1 Some GC/MS systems may not be sensitive enough to detect some of the analytes in the two lowest concentration CAL solutions. If this is the case, it is acceptable to calibrate using the remaining higher concentration points, as long as a minimum of 5 calibration points are used to generate the calibration curve or average response factor (RF) for each analyte. In addition, some GC/MS systems might reach signal saturation at the highest calibration concentration. If this is the case, it is acceptable to drop the highest point and calibrate on the remaining points, as long as at least 5 calibration concentrations are used to generate the calibration curve or average RF for each analyte. Points in the middle of the calibration range may not be dropped. Use a minimum of 3 standards for a calibration range of 1 order of magnitude, and at least 5 standards for 2 orders of

magnitude. Data outside of the established calibration range should never be reported.

10.2.5 Concentrations may be calculated through the use of average response factor (RF) or through the use of a calibration curve. Average RF calibrations may only be used if the RF values over the calibration range are relatively constant (<30% RSD).

Average RF is determined by calculating the mean RF of each calibration point.

$$RF = \frac{(A_x)(Q_{is})}{(A_{is})(Q_x)}$$

where:

$A_x$ = integrated abundance (peak area) of the quantitation ion of the analyte.

$A_{is}$ = integrated abundance (peak area) of the quantitation ion internal standard.

$Q_x$ = quantity of analyte injected in ng or concentration units.

$Q_{is}$ = quantity of internal standard injected in ng or concentration units.

10.2.6 As an alternative to calculating average RFs and applying the RSD test, use the GC/MS data system software to generate a linear regression or quadratic calibration curve. The analyst may choose whether or not to force zero, to obtain a curve that best fits the data. Examples of common GC/MS system calibration curve options are: 1) $A_x / A_{is}$ vs $Q_x / Q_{is}$ and 2) RF vs $A_x / A_{is}$.

10.2.7 Acceptance criteria for the calibration of each analyte is determined by calculating the concentration of each analyte and surrogate in each of the analyses used to generate the calibration curve or average RF. Each calibration standard, except the lowest point, for each analyte must calculate to be 70-130% of its true value. The lowest point must calculate to be 50-150% of its true value. If this criteria cannot be met, reanalyze the calibration standards, or select an alternate method of calibration. The data in this method were generated using both linear and quadratic fits, depending upon the analyte. Quadratic fit calibrations should be used with caution, because the non-linear area of the curve may not be reproducible.

10.2.8 ANALYTE CALIBRATION FOR SIM MASS SPECTROMETRY – Collect data for a mid to high level standard in the full scan mode as directed in Sect. 10.2.2 above.

Chromatographic conditions used during method development are outlined below. These conditions were found to work well on the instrumentation used. Since some of the method analytes are vulnerable to active sites and thermal decomposition, optimum chromatographic conditions may vary with individual instrument design. Although the following conditions are recommended, GC conditions may be modified, if all performance criteria in Sections 9 and 10 are met.

10.2.8.1 PTV Splitless Injection, SIM Mass Spectrometry - Inject with the injector temperature at 60° C, program the injector at 150° C per min to 220° C. Hold in the splitless mode for 2.0 min. Use an initial GC oven temperature of 45° C for 3 minutes. Program the oven temperature at 7° C per min to 210° C. Then program at 20° C per min to 250° C.

10.2.9 Divide the chromatogram into retention time windows, each of which contains one or more chromatographic peaks. During SIM analysis a small number of selected masses corresponding to dominant ions for the analytes in that window will be scanned within each window. The number of windows used and the selection of the retention times for each window will depend upon the type of instrumentation used. Highest sensitivity can be expected when a minimum number of ions are scanned in a window, i.e. one analyte per window. However, if analytes are closely eluting, it may be necessary to include more than one analyte per window.

CAUTION: When acquiring SIM data, GC operating conditions must be carefully reproduced for each analysis to provide reproducible retention times. If this is not done, the correct ions will not be monitored at the appropriate times. As a precautionary measure, the chromatographic peaks in each window must not elute too close to the edge of the time window. As a minimum, there should be at least 5 sec between the edge of the time window and the beginning or end of an analyte peak.

10.2.10 Using the GC/MS software, create an acquisition method such that 2 or 3 identifying ions are scanned for each chromatographic peak. Three ions are recommended, but in some cases, only 2 ions may be used if only 2 abundant ions are present in the mass spectrum, e.g. RDX. Suggested quantitation ions and secondary confirmation ions are listed in Table 2. Re-analyze the calibration standard using the SIM acquisition method. Continue with calibration as described in Sect. 10.2.3 through 10.2.7.

10.3 CONTINUING CALIBRATION CHECK (CCC) -- The minimum daily calibration verification is as follows. Verify the initial calibration at the beginning and end of each group of analyses, and after every tenth sample during analyses. (In this

context, a “sample” is considered to be a field sample. LRBs, LFMs, LFBs and CCCs are not counted as samples.) The beginning CCC each day should be at or near the MRL in order to verify instrument sensitivity prior to any analyses. If standards have been prepared such that all low CAL points are not in the same CAL solution, it may be necessary to analyze two CAL solutions to meet this requirement. Alternatively, it may be cost effective to obtain a customized standard to meet this criteria. Subsequent CCCs can alternate between a medium and high concentration standard.

10.3.1 Inject an aliquot of the appropriate concentration calibration solution and analyze with the same conditions used during the initial calibration.

10.3.2 Determine that the absolute areas of the quantitation ions of the internal standard have not changed by more than 30% from the areas measured in the most recent continuing calibration check, or by more than 50% from the areas measured during initial calibration. If this area has changed by more than these amounts, adjustments must be made to restore system sensitivity. These adjustments may include cleaning of the MS ion source, or other maintenance as indicated in Sect. 10.3.4. Major instrument maintenance requires recalibration. Control charts are useful aids in documenting system sensitivity changes.

10.3.3 Calculate the concentration of each analyte and surrogate in the check standard. The calculated amount for each analyte for medium and high level CCCs must be within 70-130% of the true value. The calculated amount for the lowest calibration point for each analyte must be within 50-150% of the true value. If these conditions do not exist, remedial action should be taken which may require recalibration. Any field sample extracts that have been analyzed since the last acceptable calibration verification should be reanalyzed after adequate calibration has been restored, with the following exception. **If the continuing calibration check in the middle or at the end of an analysis batch fails because the calculated concentration is >130% of the true value, and field sample extracts showed no detection of method analytes, non-detects may be reported without re-analysis.**

10.3.4 Some possible remedial actions are listed below. This list is not meant to be all inclusive. Major maintenance such as cleaning an ion source, cleaning quadrupole rods, replacing filament assemblies, replacing the electron multiplier, changing the GC column, etc. require returning to the initial calibration step (Sect. 10.2).

10.3.4.1 Check and adjust GC and/or MS operating conditions; check the MS resolution, and calibrate the mass scale.

10.3.4.2 Replace the GC injection port liner; cleaning and deactivating used liners is not recommended.

10.3.4.3 Flush the GC column with solvent according to manufacturer's instructions.

10.3.4.4 Break off a short portion (about 1 meter) of the column from the end near the injector, or replace GC column. This action will cause a change in retention times. A change in retention times may require a change in the SIM scan time windows.

10.3.4.5 Prepare fresh CAL solutions, and repeat the initial calibration step.

10.3.4.6 Clean the MS ion source and rods (if a quadrupole).

10.3.4.7 Replace any components that allow analytes to come into contact with hot metal surfaces.

10.3.4.8 Replace the MS electron multiplier, or any other faulty components.

## 11. PROCEDURE

### 11.1 SOLID PHASE EXTRACTION

11.1.1 This procedure may be performed manually or in an automated mode (Sect. 6.11) using a robotic or automatic sample preparation device. If an automatic system is used to prepare samples, follow the manufacturer's operating instructions, but all extraction and elution steps must be the same as in the manual procedure. Extraction and/or elution steps may not be changed or omitted to accommodate the use of an automated system.

11.1.2 Mark the level of the sample on the outside of the sample bottle for later sample volume determination (Sect. 11.5). Verify that the sample is between pH 5 and 7, and is free of residual chlorine. If the sample is an LRB or LFB, add sample preservatives specified in Sect. 8.2. Add an aliquot of the surrogate fortification solution(s), and mix immediately until homogeneous. The resulting concentration of these compounds in the water should be 1-5µg/L. Generally, SIM analyses should be performed with surrogate concentrations at the low end of this range. If the sample is an LFB or LFM, add the desired amount of analyte fortification solution.

11.2. CARTRIDGE EXTRACTION

11.2.1. CARTRIDGE CLEAN-UP AND CONDITIONING -- Rinse each cartridge with three, 5 mL aliquots of ethyl acetate. Let the cartridge drain dry after each flush. Then rinse the cartridge with three, 5 mL aliquots of methanol, but DO NOT allow the methanol to elute below the top of the cartridge packing. From this point, do not allow the cartridge packing to go dry. Rinse the cartridge with two, 10 mL aliquots of reagent water, stopping the flow when there is approximately 4 cm of reagent water in the column. Attach the transfer tube, and turn on the vacuum, and begin adding sample to the cartridge.

11.2.2. Adjust the vacuum so that the approximate flow rate is 10-15 mL/min. After all of the sample has passed through the SPE cartridge, draw air or nitrogen through the cartridge for 10-15 min at high vacuum (10-15 in. Hg). The drying time may vary, depending upon the strength of the vacuum source, and the number of cartridges being processed simultaneously. Do not dry the cartridge for more than 10-15 min. Additional time is not likely to increase dryness, and excess drying times have been shown to decrease recoveries of nitrobenzene (10).

NOTE: Samples with a high level of hardness and/or high TOC may exhibit a lower flow rate than “cleaner” samples at the same vacuum setting. This may be due to partial plugging of the solid phase. Fortified sample matrices of these types showed no loss of method performance.

11.2.3. Place a collection tube in the vacuum chamber underneath each extraction cartridge. Rinse the inside of each sample bottle with 5 mL ethyl acetate and use vacuum to pull the rinse solvent through the transfer tube and through the cartridge, collecting the solvent in a collection tube. Remove the transfer tubing from the top of the cartridge. Add another 5 mL of ethyl acetate to the top of the cartridge with a disposable pipette. Pull this solvent through the cartridge at low vacuum, such that the solvent exits the cartridge in a dropwise fashion. Combine this second eluate with the first one. Dry and concentrate the combined eluate as directed in Sect. 11.4.

11.3. DISK EXTRACTION

11.3.1 DISK CLEAN-UP AND CONDITIONING -- Rinse each disk with three, 5 mL aliquots of ethyl acetate. Let the disk dry after each rinse. Then rinse the disk with three, 5 mL aliquots of methanol, but DO NOT allow the methanol to elute below the top of the disk. From this point, do not allow the disk to go dry. Rinse the disk with two, 10 mL aliquots of reagent water, stopping the flow when there is approximately 3-4mm of reagent

water on top of the disk. Turn on the vacuum, and begin adding sample to the disk.

11.3.2. The sample can be passed through the disk at high vacuum (10-15 in. Hg). After the entire sample has been extracted, dry the disk at full vacuum for 5-10 min. Do not dry the disk for more than 10 min. Additional time is not likely to increase dryness, and excess drying times have been shown to decrease recoveries of nitrobenzene (10).

11.3.3. Place a collection tube in the vacuum manifold beneath the filtration glassware setup for each extraction disk. Rinse the inside of each sample bottle with 5 mL ethyl acetate and use this rinse solvent to elute each disk, collecting the solvent in a collection tube. Add another 5 mL of ethyl acetate to the top of the disk with a disposable pipette, using the solvent to wash down the sides of the filtration glassware. Pull this solvent through the disk. Add another 3 mL of ethyl acetate to the top of the disk with a disposable pipette, using the solvent to wash down the sides of the filtration glassware. Pull this solvent through the disk. Dry and concentrate the combined eluates as directed in Sect. 11.4.

11.4. Small amounts of residual water from the sample container and the SPE cartridge may form an immiscible layer with the eluate. To eliminate residual water, pass the eluate through the drying column (Sect. 6.7). The drying column is packed with approximately 5 to 7 grams of anhydrous sodium sulfate, and is pre-wetted with a small volume of ethyl acetate prior to passing the eluate through it. Collect the dried eluate in a clean collection tube. After passing the eluate through the drying tube, wash the sodium sulfate with at least 3 mL ethyl acetate and collect it in the same tube. Concentrate the extract to approximately 0.9 mL in a warm (40° C) water bath under a gentle stream of nitrogen. Do not concentrate the extract to less than 0.5 mL, as this will result in loss of analytes. Add the internal standard (Sect. 7.12.1). Adjust final volume to 1 mL. Make any volume adjustments with ethyl acetate.

11.5 Fill the sample bottle to the volume mark noted in Sect.11.1.2. with tap water. Transfer the tap water to a 1000 mL graduated cylinder, and measure the sample volume to the nearest 10 mL. Record this volume for later analyte concentration calculations. As an alternative to this process, the sample volume may be determined by the difference in weight between the full bottle (before extraction) and the empty bottle (after extraction). Assume a sample density of 1.0 g/mL.

11.6 Analyze an aliquot of the sample extract with the GC/MS system under the same conditions used for the initial and continuing calibrations.

11.7 At the conclusion of data acquisition, use the same software that was used in the calibration procedure to identify peaks in predetermined retention time windows of

interest. Use the data system software to examine the ion abundances of components of the chromatogram.

11.8 IDENTIFICATION OF ANALYTES FOR FULL SCAN MASS SPECTROMETRY -- Identify a sample component by comparison of its mass spectrum (after background subtraction) to a reference spectrum in the user-created data base. The GC retention time of the sample component should be within 1-2 sec of the retention time observed for that same compound in the most recently analyzed continuing calibration check standard. Ideally, the width of the retention time window should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time can be used to calculate a suggested window size for a compound. However, the experience of the analyst should weigh heavily in the interpretation of the chromatogram.

11.8.1 In general, all ions that are present above 10% relative abundance in the mass spectrum of the standard should be present in the mass spectrum of the sample component and should agree within absolute 20%. For example, if an ion has a relative abundance of 30% in the standard spectrum, its abundance in the sample spectrum should be in the range of 10 to 50%.

11.9 IDENTIFICATION OF ANALYTES FOR SIM MASS SPECTROMETRY -- Identify a sample component by comparison of its selected ions to a reference spectrum in the user-created data base. The GC retention time of the sample component should be within 1-2 sec of the retention time observed for that same compound in the most recently analyzed continuing calibration check standard. Ideally, the width of the retention time window should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time can be used to calculate a suggested identification window size for a compound. However, the experience of the analyst should weigh heavily in the interpretation of the chromatogram.

NOTE: Because less spectral information is being acquired for analyte identification when SIM is used, retention times of the analyte peaks are an even more important factor in analyte identification than in full scan data analysis.

11.9.1 The apex of the chromatographic peak for the quantiation ion and confirmation ions for each analyte must be within ± 1 scan of one another.

11.9.2 The integrated ion current for each quantitation and confirmation ion must be at least three times background noise, and must not have saturated the detector.

11.9.3 All ions monitored in the standard should be present in the SIM mass spectrum of the sample component and should agree within absolute 20%.

For example, if an ion has a relative abundance of 30% in the standard spectrum, its abundance in the sample spectrum should be in the range of 10 to 50%.

## 12. DATA ANALYSIS AND CALCULATIONS

12.1 Complete chromatographic resolution is not necessary for accurate and precise measurements of analyte concentrations if unique ions with adequate intensities are available for quantitation. Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing the same ions contributed by more than one analyte. When GC peaks obviously represent more than one sample component (i.e., broadened peak with shoulder(s) or valley between two or more maxima), appropriate analyte spectra and background spectra can be selected by examining plots of characteristic ions for each tentatively identified component. When analytes coelute (i.e., only one GC peak is apparent), the identification criteria can be met but each analyte spectrum will contain extraneous ions contributed by the coeluting compound. In validating this method, concentrations were calculated by measuring the quantitation ions listed in Table 2. Other ions may be selected at the discretion of the analyst. If the response of any analyte exceeds the calibration range established in Sect. 10, dilute the extract, add additional internal standard, and reanalyze. The resulting data should be documented as a dilution, with an increased MRL.

12.1.1 Calculate analyte and surrogate concentrations, using the multipoint calibration established in Sect. 10. Do not use daily calibration verification data to quantitate analytes in samples. Adjust final analyte concentrations to reflect the actual sample volume determined in Sect. 11.5.

12.1.2 Calculations should utilize all available digits of precision, but final reported concentrations should be rounded to an appropriate number of significant figures (one digit of uncertainty).

## 13. METHOD PERFORMANCE

13.1 PRECISION, ACCURACY AND DLs-- Single laboratory accuracy and precision data from both fortified reagent water and fortified matrices are presented in Tables 3-20. Detection limits (DLs) are presented in Tables 3, 9 and 15 for the three techniques demonstrated.

13.1.1 Data presented in Tables 3-8 and 21-22 were obtained on a Varian Saturn 4 GC/MS (ion trap) system, using PTV splitless injection and full scan mass spectrometry. Gas chromatographic conditions are given in Sect. 10.2.2.1.

NOTE: Selected ion storage was evaluated on this instrument. Sensitivity was not significantly improved relative to full scan monitoring.

13.1.2 Data presented in Tables 9-14 were obtained on a Schimadzu QP5050A GC/MS (quadrupole) system, using PTV splitless injection and SIM mass spectrometry. A high pressure injection (14.5 psi) was employed on this instrument. Other gas chromatographic conditions are given in Sect. 10.2.8.1.

13.1.3 Data presented in Tables 15-20 were obtained on a Varian Saturn 4 GC/MS (ion trap) system, using cold on-column injection and full scan mass spectrometry. Gas chromatographic conditions are given in Sect. 10.2.2.2.

13.2 EVALUATION OF ADDITIONAL EXPLOSIVES – Nitroglycerin (NG), octahdro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX ) and pentaerythritoltetra-nitrate (PETN) were evaluated for inclusion into this method. HMX was never observed in any of the chromatograms. Precision and accuracy for NG and PETN were not sufficient to reliably meet the QC criteria in the method. The method may be suitable for qualitative identification of these two compounds.

13.3 Data were not obtained for 2,4-dinitrotoluene with the on-column technique. The mass spectrum of this compound was observed to change with concentration. At low concentrations, an unusual spectrum was observed. It was determined that this resulted from reactions of 2,4-dinitrotoluene with residual solvent in the ion trap. This is more likely to happen with on-column techniques than splitless techniques because more solvent is transferred to the column. Although the on-column technique was not demonstrated with a quadrupole instrument, it is suspected that this observation was an ion trap phenomenon.

13.4 Data were not obtained for 3,5-dinitroanaline with the on-column technique. Because a commercial standard mixture was used, where the concentration of this analyte was five times lower than the other analytes, many of the demonstration samples contained it at a concentration too low to be accurately quantified.

13.5 Some matrix effects may be observed. Some method analytes extracted from some water matrices may exhibit “matrix induced chromatographic response enhancement” (11-13). This phenomenon has been widely reported for the analysis of thermally labile pesticides in water matrices, and may be applicable to some of these method analytes as well. Compounds that exhibit this phenomenon may give analytical results that exceed 100% recovery in fortified matrix samples, especially at low concentrations. It has been proposed that thermally labile compounds are susceptible to decomposition in the GC injection port and/or while in the GC column. Co-extracted matrix components help shield and protect these compounds through the GC system, thus resulting in a higher response than when clean

standards are analyzed. This effect can usually be minimized by reducing the residence time of method analytes in the GC system by using a relatively high linear velocity and a short column. The use of clean, deactivated injection port liners is also advised.

13.6 ANALYTE STABILITY STUDIES --

13.6.1 SAMPLES - Chlorinated surface water samples, fortified with method analytes at 5.0 µg/L, were preserved and stored as required in Sect. 8. The average of replicate analyses (n=5) conducted on days 0, 7, 11, 14, and 19 are presented in Table 21. These data document the 14 day holding time.

13.6.2 EXTRACTS - Extracts from the day 0 holding time study described above were stored at 0 °C, and analyzed in replicate (n=5) on days 0, 17, 15, 21, 28, and 35. The results of these analyses are presented in Table 22, and document the 30 day holding time.

## 14. POLLUTION PREVENTION

14.1 This method utilizes SPE technology to remove the analytes from water. It requires the use of very small volumes of organic solvent and very small quantities of pure analytes, thereby minimizing the potential hazards to both the analyst and the environment when compared with the use of large volumes of organic solvents in conventional liquid-liquid extractions.

14.2 For information about pollution prevention that may be applicable to laboratory operations, 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 Street N.W., Washington, D.C., 20036, or on-line at http://membership.acs.org/c/ccs/pub_9.htm.

## 15. WASTE MANAGEMENT

15.1 The analytical procedures described in this method generate relatively small amounts of waste since only small amounts of reagents and solvents are used. The matrices of concern are finished drinking water or source water. However, the Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations, and that laboratories protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Also, compliance is required with any sewage discharge permits and 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 on-line from the American Chemical

Society at http://chemistry.org/portal/Chemistry?PID=acsdisplay.html&DOC=government%5Cpublications%5Ceip_hazwaste.html.

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## 17. TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

**Table 1. Ion Abundance Criteria for BFB**

| Mass (m/z) | Relative Abundance Criteria | Purpose of Checkpoint [a] |
|---|---|---|
| 50 | 15-40% of mass 95 | Low-mass sensitivity |
| 75 | 30-80% of mass 95 | Low-mass sensitivity |
| 95 | Base peak, 100% relative abundance | Low-mass resolution and sensitivity |
| 96 | 5-9% of mass 95 | Low-mass resolution and isotope ratio |
| 173 | < 2% of mass 174 | Mid-mass resolution |
| 174 | > 50% of mass 95 | Mid mass resolution and sensitivity |
| 175 | 5-9% of mass 174 | Mid-mass resolution |
| 176 | > 95% but < 101% of mass 174 | Mid-mass resolution and isotope ratio |
| 177 | 5-9% of mass 176 | Mid-mass resolution |

[a] All ions are used primarily to check the mass measuring accuracy of the mass spectrometer and data system, and this is the most important part of the performance test. The resolution checks, which include natural abundance isotope ratios, constitute the next most important part of the performance test. Finally, the ion abundance ranges are designed to encourage some standardization to fragmentation patterns.

**Table 2. Retention Times and Suggested Quantitation and Confirmation Ions for Explosive Analytes** [a,b]

| Analyte | Retention Time (min) | Quantitation Ion (m/z) | Confirmation Ions (m/z) |
|---|---|---|---|
| nitrobenzene (NB) | 7.72 | 51 or 77 | 51, 77, 123 |
| 2-nitrotoluene (2NT) | 9.40 | 65 | 91, 120 |
| 3-nitrotoluene (3NT) | 10.18 | 91 | 65, 137 |
| 4-nitrotoluene (4NT) | 10.57 | 65 or 91 | 65, 91, 137 |
| 1,3-dinitrobenzene (DNB) | 15.13 | 50 or 75 | 50, 75, 76 |
| 2,6-dinitrotoluene (2,6DNT) | 15.32 | 165 | 63, 89 |
| 2,4-dinitrotoluene (2,4DNT) | 16.60 | 165 | 63, 78 |
| 1,3,5-trinitrobenzene (TNB) | 19.35 | 75 or 213 | 74, 75, 213 |
| 2,4,6-trinitrotoluene (TNT) | 19.43 | 210 | 63, 89 |
| RDX | 21.97 | 46 | 75, 128 |
| 4-amino-2,6-dinitrotoluene (4AmDNT) | 22.81 | 180 | 78, 104 |
| 3,5-dinitroanaline (DNA) | 23.00 | 183 or 64 | 63, 64, 183 |
| 2-amino-4,6-dinitrotoluene (2AmDNT) | 23.47 | 180 or 78 | 52, 78, 180 |
| Tetryl | 24.77 | 194 or 77 | 51, 77, 194 |
| 3,4-dinitrotoluene (IS) | 17.42 | 63 or 182 | 63, 78, 182 |
| nitrobenzene-$d_5$ (SUR) | 7.66 | 82 | 54, 128 |
| 1,3,5-trimethyl-2-nitrobenzene (SUR) | 12.33 | 148 or 91 | 91, 93, 148 |
| 1,2,4-trimethyl-5-nitrobenzene (SUR) | 14.72 | 148 or 91 | 77, 91, 148 |

[a] Even when instruments are tuned to BFB criteria, differences in instrumentation can cause slight variations in mass spectra, e.g. quadrupole vs. ion trap. The ions listed here are suggested ions because they were successfully used during method development.

[b] Two or three ions from the Quantitation Ion and Confirmation Ion columns were used for SIM monitoring.

**Table 3. Detection Limits Obtained Using Programmed Temperature Vaporizing (PTV) Splitless Injection and Full Scan Mass Spectrometry**

| Analyte | DL (μg/L) [a] [fortified conc. for DL determination] | DL (μg/L) [b] [fortified conc. for DL determination] |
|---|---|---|
| nitrobenzene | 0.039 [0.10] | 0.18 [0.50] |
| 2-nitrotoluene | 0.11 [0.50] | 0.041 [0.10] |
| 3-nitrotoluene | 0.083 [0.50] | 0.091 [0.50] |
| 4-nitrotoluene | 0.13 [0.50] | 0.029 [0.10] |
| 1,3-dinitrobenzene | 0.021 [0.10] | 0.076 [0.50] |
| 2,6-dinitrotoluene | 0.029 [0.10] | 0.059 [0.50] |
| 2,4-dinitrotoluene | 0.11 [0.50] | 0.11 [0.50] |
| 1,3,5-trinitrobenzene | 0.037 [0.50] | 0.042 [0.50] |
| 2,4,6-trinitrotoluene (TNT) | 0.084 [0.50] | 0.046 [0.50] |
| RDX | 0.082 [0.50] | 0.12 [0.50] |
| 4-amino-2,6-dinitrotoluene | 0.065 [0.50] | 0.072 [0.50] |
| 3,5-dinitroanaline | 0.052 [0.20] | 0.011 [0.10] |
| 2-amino-4,6-dinitrotoluene | 0.075 [0.50] | 0.053 [0.50] |
| Tetryl | 0.18 [1.0] | 0.058 [1.0] |

[a] Data from replicate disk extractions, n=8.

[b] Data from replicate cartridge extractions, n=8.

**Table 4. Precision and Accuracy Data Obtained from Reagent Water Samples Fortified with Method Analytes at Low Concentrations, Using SPE Disk Extraction, PTV Splitless Injection and Full Scan Mass Spectrometry (n=8)**

| Analyte | Fortified Concentration (μg/L) | Accuracy (% recovery) | Precision (%RSD) |
|---|---|---|---|
| nitrobenzene | 0.10 | 70.6 | 18 |
| 2-nitrotoluene | 0.50 | 102 | 7.1 |
| 3-nitrotoluene | 0.50 | 114 | 4.9 |
| 4-nitrotoluene | 0.50 | 81.4 | 11 |
| 1,3-dinitrobenzene | 0.10 | 126 | 5.4 |
| 2,6-dinitrotoluene | 0.10 | 83.6 | 12 |
| 2,4-dinitrotoluene | 0.50 | 101 | 7.5 |
| 1,3,5-trinitrobenzene | 1.0 | 111 | 4.5 |
| 2,4,6-trinitrotoluene | 1.0 | 136 | 4.5 |
| RDX | 0.50 | 103 | 5.3 |
| 4-amino-2,6-dinitrotoluene | 0.50 | 130 | 3.4 |
| 3,5-dinitroanaline | 0.20 | 130 | 6.3 |
| 2-amino-4,6-dinitrotoluene | 0.50 | 127 | 3.9 |
| Tetryl | 1.0 | 134 | 4.2 |

**Table 5. Precision and Accuracy Data Obtained from Reagent Water Samples Fortified with Method Analytes at Low Concentrations, Using SPE Cartridge Extraction, PTV Splitless Injection and Full Scan Mass Spectrometry (n=8)**

| Analyte | Fortified Concentration (μg/L) | Accuracy (% recovery) | Precision (%RSD) |
|---|---|---|---|
| nitrobenzene | 0.5 | 79.2 | 16 |
| 2-nitrotoluene | 0.5 | 82.4 | 15 |
| 3-nitrotoluene | 0.5 | 82.0 | 7.4 |
| 4-nitrotoluene | 0.1 | 110 | 9.0 |
| 1,3-dinitrobenzene | 0.5 | 99.1 | 5.1 |
| 2,6-dinitrotoluene | 0.5 | 109 | 3.6 |
| 2,4-dinitrotoluene | 0.5 | 99.3 | 7.1 |
| 1,3,5-trinitrobenzene | 0.5 | 122 | 2.3 |
| 2,4,6-trinitrotoluene | 0.5 | 85.2 | 3.6 |
| RDX | 0.5 | 131 | 6.3 |
| 4-amino-2,6-dinitrotoluene | 0.5 | 108 | 4.4 |
| 3,5-dinitroanaline | 0.1 | 133 | 2.6 |
| 2-amino-4,6-dinitrotoluene | 0.5 | 108 | 3.3 |
| Tetryl | 1.0 | 124 | 1.6 |

**Table 6. Precision and Accuracy Data Obtained from Reagent Water Samples Fortified with Method Analytes at 5.0 μg/L, Using PTV Splitless Injection and Full Scan Mass Spectrometry**

| Analyte | Disk Extraction (n=5) | | Cartridge Extraction (n=5) | |
|---|---|---|---|---|
| | Accuracy (% recovery) | Precision (%RSD) | Accuracy (% recovery) | Precision (%RSD) |
| nitrobenzene | 87.8 | 7.8 | 97.3 | 9.3 |
| 2-nitrotoluene | 87.0 | 5.6 | 95.0 | 12 |
| 3-nitrotoluene | 85.9 | 7.9 | 95.8 | 5.9 |
| 4-nitrotoluene | 90.4 | 1.4 | 99.6 | 5.0 |
| 1,3-dinitrobenzene | 99.7 | 8.5 | 92.3 | 6.3 |
| 2,6-dinitrotoluene | 92.2 | 7.5 | 88.1 | 5.1 |
| 2,4-dinitrotoluene | 93.8 | 3.7 | 97.5 | 4.8 |
| 1,3,5-trinitrobenzene | 102 | 4.4 | 98.5 | 4.9 |
| 2,4,6-trinitrotoluene | 111 | 3.2 | 101 | 6.0 |
| RDX | 97.1 | 2.5 | 102 | 8.1 |
| 4-amino-2,6-dinitrotoluene | 100 | 7.5 | 101 | 4.8 |
| 3,5-dinitroanaline | 105 | 2.8 | 97.5 | 4.4 |
| 2-amino-4,6-dinitrotoluene | 109 | 3.5 | 102 | 3.1 |
| Tetryl | 104 | 5.4 | 82.7 | 5.4 |
| nitrobenzene-$d_5$ (SUR) | ND [a] | ND | 90.2 | 8.3 |
| 1,3,5-trimethyl-2-nitrobenzene (SUR) | 94.7 | 3.8 | 96.0 | 2.7 |
| 1,2,4-trimethyl-5-nitrobenzene (SUR) | 106 | 9.3 | 102 | 6.0 |

[a] ND- Not determined; These data were collected before this surrogate was added to the method.

**Table 7. Precision and Accuracy Data Obtained from Tap Water (Chlorinated Water from a Surface Source) Fortified with Method Analytes at 5.0 μg/L, Using PTV Splitless Injection and Full Scan Mass Spectrometry [a]**

| Analyte | Disk Extraction (n=5) | | Cartridge Extraction (n=5) | |
|---|---|---|---|---|
| | Accuracy (% recovery) | Precision (%RSD) | Accuracy (% recovery) | Precision (%RSD) |
| nitrobenzene | 96.3 | 5.1 | 88.0 | 11 |
| 2-nitrotoluene | 84.5 | 6.0 | 85.6 | 11 |
| 3-nitrotoluene | 81.2 | 8.3 | 91.1 | 3.8 |
| 4-nitrotoluene | 98.1 | 6.3 | 87.5 | 7.1 |
| 1,3-dinitrobenzene | 103 | 8.7 | 87.1 | 11 |
| 2,6-dinitrotoluene | 96.1 | 2.3 | 82.8 | 7.1 |
| 2,4-dinitrotoluene | 101 | 5.8 | 94.3 | 11 |
| 1,3,5-trinitrobenzene | 111 | 5.5 | 101 | 9.0 |
| 2,4,6-trinitrotoluene | 109 | 8.2 | 97.9 | 7.1 |
| RDX | 111 | 4.8 | 107 | 6.2 |
| 4-amino-2,6-dinitrotoluene | 108 | 4.8 | 100 | 6.0 |
| 3,5-dinitroanaline | 114 | 1.3 | 97 | 6.1 |
| 2-amino-4,6-dinitrotoluene | 115 | 1.7 | 101 | 6.2 |
| Tetryl | 116 | 4.5 | 87.6 | 8.9 |
| nitrobenzene-$d_5$ (SUR) | ND [b] | ND | 87.5 | 2.2 |
| 1,3,5-trimethyl-2-nitrobenzene (SUR) | 109 | 9.9 | 90.6 | 10 |
| 1,2,4-trimethyl-5-nitrobenzene (SUR) | 112 | 4.0 | 86.6 | 5.0 |

[a] The sample matrix was dechlorinated and preserved as described in Section 8 prior to fortification with method analytes.

[b] ND- Not determined; These data were collected before this surrogate was added to the method.

**Table 8. Precision and Accuracy Data Obtained from Tap Water (Chlorinated Water from a Ground Source with a High Hardness Level [a]) Fortified with method Analytes at 5.0 µg/L, Using PTV Splitless Injection and Full Scan Mass Spectrometry**

| Analyte | Disk Extraction (n=5) | | Cartridge Extraction (n=5) | |
|---|---|---|---|---|
| | Accuracy (% recovery) | Precision (%RSD) | Accuracy (% recovery) | Precision (%RSD) |
| nitrobenzene | 92.1 | 17 | 92.5 | 12 |
| 2-nitrotoluene | 85.9 | 12 | 88.4 | 4.1 |
| 3-nitrotoluene | 87.8 | 5.4 | 93.7 | 7.7 |
| 4-nitrotoluene | 95.1 | 9.7 | 91.8 | 7.7 |
| 1,3-dinitrobenzene | 102 | 3.4 | 90.3 | 9.0 |
| 2,6-dinitrotoluene | 96.3 | 4.3 | 89.2 | 4.3 |
| 2,4-dinitrotoluene | 103 | 6.9 | 97.7 | 4.7 |
| 1,3,5-trinitrobenzene | 106 | 8.2 | 105 | 6.6 |
| 2,4,6-trinitrotoluene | 118 | 8.0 | 106 | 4.8 |
| RDX | 93.1 | 9.7 | 114 | 11 |
| 4-amino-2,6-dinitrotoluene | 106 | 6.8 | 103 | 4.1 |
| 3,5-dinitroanaline [b] | 115 | 8.3 | 103 | 4.5 |
| 2-amino-4,6-dinitrotoluene | 112 | 7.4 | 110 | 6.4 |
| Tetryl | 107 | 16 | 92.9 | 7.9 |
| nitrobenzene-$d_5$ (SUR) | ND [c] | ND | 84.7 | 15 |
| 1,3,5-trimethyl-2-nitrobenzene (SUR) | 96.0 | 8.4 | 95.0 | 10 |
| 1,2,4-trimethyl-5-nitrobenzene (SUR) | 107 | 7.8 | 96.8 | 6.2 |

[a] Hardness level measured at 310 and 360 mg/L as calcium carbonate, for disk and cartridge samples, respectively. The sample matrix was dechlorinated and preserved as described in Section 8 prior to fortification with method analytes.

[b] 3,5-Dinitroanaline was fortified at 0.2 µg/L.

[c] ND - Not determined; These data were collected before this surrogate was added to the method.

**Table 9. Detection Limits Obtained Using Programmed Temperature Vaporizing (PTV) Splitless Injection and Selected Ion Monitoring Mass Spectrometry**

| Analyte | DL (μg/L) [a] [fortified conc. for DL determination] | DL (μg/L) [b] [fortified conc. for DL determination] |
|---|---|---|
| nitrobenzene | 0.009 [0.05] | 0.010 [0.05] |
| 2-nitrotoluene | 0.008 [0.05] | 0.003 [0.05] |
| 3-nitrotoluene | 0.005 [0.05] | 0.004 [0.05] |
| 4-nitrotoluene | 0.005 [0.05] | 0.006 [0.05] |
| 1,3-dinitrobenzene | 0.006 [0.05] | 0.003 [0.05] |
| 2,6-dinitrotoluene | 0.004 [0.05] | 0.004 [0.05] |
| 2,4-dinitrotoluene | 0.004 [0.05] | 0.008 [0.05] |
| 1,3,5-trinitrobenzene | 0.018 [0.05] | 0.012 [0.05] |
| 2,4,6-trinitrotoluene (TNT) | 0.004 [0.05] | 0.008 [0.05] |
| RDX | 0.006 [0.05] | 0.010 [0.05] |
| 4-amino-2,6-dinitrotoluene | 0.005 [0.05] | 0.019 [0.05] |
| 3,5-dinitroanaline | 0.008 [0.01] | 0.029 [0.01] |
| 2-amino-4,6-dinitrotoluene | 0.020 [0.05] | 0.030 [0.05] |
| Tetryl | 0.090 [0.10] | 0.14 [0.25] |

[a] Data from replicate disk extractions, n=8.

[b] Data from replicate cartridge extractions, n=7.

**Table 10. Precision and Accuracy Data Obtained from Reagent Water Samples Fortified with Method Analytes at Low Concentrations, Using SPE Disk Extraction, PTV Splitless Injection and Selected Ion Monitoring Mass Spectrometry (n=8)**

| Analyte | Fortified Concentration (μg/L) | Accuracy (% recovery) | Precision (%RSD) |
|---|---|---|---|
| nitrobenzene | 0.05 | 87.1 | 6.5 |
| 2-nitrotoluene | 0.05 | 79.7 | 6.6 |
| 3-nitrotoluene | 0.05 | 112 | 2.8 |
| 4-nitrotoluene | 0.05 | 123 | 2.5 |
| 1,3-dinitrobenzene | 0.05 | 124 | 3.3 |
| 2,6-dinitrotoluene | 0.10 | 89.2 | 2.2 |
| 2,4-dinitrotoluene | 0.10 | 95.7 | 3.2 |
| 1,3,5-trinitrobenzene | 0.05 | 120 | 9.4 |
| 2,4,6-trinitrotoluene | 0.10 | 104 | 1.9 |
| RDX | 0.10 | 133 | 3.2 |
| 4-amino-2,6-dinitrotoluene | 0.25 | 98.4 | 3.2 |
| 3,5-dinitroanaline | 0.02 | 107 | 10 |
| 2-amino-4,6-dinitrotoluene | 0.10 | 119 | 3.1 |
| Tetryl | 0.25 | 113 | 10 |

**Table 11. Precision and Accuracy Data Obtained from Reagent Water Samples Fortified with Method Analytes at Low Concentrations, Using SPE Cartridge Extraction, PTV Splitless Injection and Selected Ion Monitoring Mass Spectrometry (n=7)**

| Analyte | Fortified Concentration (μg/L) | Accuracy (% recovery) | Precision (%RSD) |
|---|---|---|---|
| nitrobenzene | 0.05 | 107 | 5.7 |
| 2-nitrotoluene | 0.05 | 110 | 1.8 |
| 3-nitrotoluene | 0.05 | 114 | 2.0 |
| 4-nitrotoluene | 0.05 | 119 | 3.2 |
| 1,3-dinitrobenzene | 0.05 | 128 | 1.6 |
| 2,6-dinitrotoluene | 0.10 | 102 | 3.1 |
| 2,4-dinitrotoluene | 0.10 | 109 | 5.4 |
| 1,3,5-trinitrobenzene | 0.10 | 108 | 8.9 |
| 2,4,6-trinitrotoluene | 0.10 | 110 | 4.3 |
| RDX | 0.10 | 114 | 8.9 |
| 4-amino-2,6-dinitrotoluene | 0.25 | 103 | 3.7 |
| 3,5-dinitroanaline | 0.05 | 95.6 | 9.4 |
| 2-amino-4,6-dinitrotoluene | 0.10 | 134 | 5.6 |
| Tetryl | 0.25 | 102 | 17 |

**Table 12. Precision and Accuracy Data Obtained from Reagent Water Samples Fortified with Method Analytes at 1.0 µg/L, Using PTV Splitless Injection and Selected Ion Monitoring Mass Spectrometry**

| Analyte | Disk Extraction (n=4) | | Cartridge Extraction (n=4) | |
|---|---|---|---|---|
| | Accuracy (% recovery) | Precision (%RSD) | Accuracy (% recovery) | Precision (%RSD) |
| nitrobenzene | 91.3 | 5.8 | 86.5 | 3.4 |
| 2-nitrotoluene | 89.7 | 1.8 | 91.9 | 3.0 |
| 3-nitrotoluene | 91.3 | 1.7 | 89.7 | 4.8 |
| 4-nitrotoluene | 90.5 | 2.0 | 89.8 | 4.1 |
| 1,3-dinitrobenzene | 99.0 | 2.8 | 96.2 | 5.9 |
| 2,6-dinitrotoluene | 98.1 | 2.7 | 98.8 | 5.1 |
| 2,4-dinitrotoluene | 102 | 3.3 | 100 | 4.9 |
| 1,3,5-trinitrobenzene | 106 | 2.3 | 96.9 | 6.2 |
| 2,4,6-trinitrotoluene | 110 | 2.6 | 104 | 5.1 |
| RDX | 100 | 2.8 | 108 | 6.4 |
| 4-amino-2,6-dinitrotoluene | 116 | 2.8 | 117 | 4.7 |
| 3,5-dinitroanaline [a] | 104 | 2.6 | 107 | 8.6 |
| 2-amino-4,6-dinitrotoluene | 113 | 1.9 | 111 | 5.7 |
| Tetryl | 122 | 3.2 | 111 | 8.9 |
| nitrobenzene-$d_5$ (SUR) | 88.5 | 2.3 | 86.5 | 2.2 |
| 1,3,5-trimethyl-2-nitrobenzene (SUR) | 84.9 | 2.3 | 84.4 | 1.6 |
| 1,2,4-trimethyl-5-nitrobenzene (SUR) | 87.4 | 3.3 | 88.2 | 2.4 |

[a] 3,5-Dinitroanaline was fortified at 0.2 µg/L.

**Table 13. Precision and Accuracy Data Obtained from Tap Water (Chlorinated Water from a Surface Source) Fortified with Method Analytes at 1.0 µg/L, Using PTV Splitless Injection and Selected Ion Monitoring Mass Spectrometry [a]**

| Analyte | Disk Extraction (n=4) | | Cartridge Extraction (n=4) | |
|---|---|---|---|---|
| | Accuracy (% recovery) | Precision (%RSD) | Accuracy (% recovery) | Precision (%RSD) |
| nitrobenzene | 71.5 | 3.4 | 85.8 | 4.8 |
| 2-nitrotoluene | 79.8 | 2.7 | 93.2 | 4.2 |
| 3-nitrotoluene | 78.9 | 2.6 | 91.2 | 3.6 |
| 4-nitrotoluene | 74.9 | 2.6 | 89.8 | 4.1 |
| 1,3-dinitrobenzene | 80.7 | 2.1 | 102 | 2.4 |
| 2,6-dinitrotoluene | 81.2 | 2.3 | 101 | 2.2 |
| 2,4-dinitrotoluene | 88.7 | 2.6 | 108 | 2.4 |
| 1,3,5-trinitrobenzene | 82.3 | 1.6 | 104 | 3.3 |
| 2,4,6-trinitrotoluene | 91.1 | 2.5 | 116 | 3.8 |
| RDX | 85.2 | 1.3 | 111 | 3.8 |
| 4-amino-2,6-dinitrotoluene | 103 | 2.0 | 127 | 2.5 |
| 3,5-dinitroanaline [b] | 96.5 | 2.3 | 119 | 1.8 |
| 2-amino-4,6-dinitrotoluene | 97.4 | 0.8 | 123 | 2.5 |
| Tetryl | 99.5 | 3.2 | 137 | 3.8 |
| nitrobenzene-$d_5$ (SUR) | 87.4 | 3.4 | 88.4 | 5.1 |
| 1,3,5-trimethyl-2-nitrobenzene (SUR) | 93.3 | 2.8 | 83.2 | 4.6 |
| 1,2,4-trimethyl-5-nitrobenzene (SUR) | 100 | 3.1 | 89.7 | 4.1 |

[a] The sample matrix was dechlorinated and preserved as described in Section 8 prior to fortification with method analytes.

[b] 3,5-Dinitroanaline was fortified at 0.2 µg/L.

**Table 14. Precision and Accuracy Data Obtained from Tap Water (Chlorinated Water from a Ground Source with a High Hardness Level [a] ) Fortified with Method Analytes at 1.0 µg/L, Using PTV Splitless Injection and Selected Ion Monitoring Mass Spectrometry**

| Analyte | Disk Extraction (n=4) | | Cartridge Extraction (n=4) | |
|---|---|---|---|---|
| | Accuracy (% recovery) | Precision (%RSD) | Accuracy (% recovery) | Precision (%RSD) |
| nitrobenzene | 95.6 | 8.6 | 84.2 | 2.4 |
| 2-nitrotoluene | 102 | 4.6 | 85.1 | 3.8 |
| 3-nitrotoluene | 94.6 | 3.3 | 85.0 | 2.4 |
| 4-nitrotoluene | 94.6 | 5.1 | 85.5 | 3.6 |
| 1,3-dinitrobenzene | 86.1 | 5.1 | 104 | 1.0 |
| 2,6-dinitrotoluene | 91.7 | 2.4 | 104 | 0.8 |
| 2,4-dinitrotoluene | 90.1 | 5.9 | 109 | 1.5 |
| 1,3,5-trinitrobenzene | 88.1 | 4.2 | 109 | 2.1 |
| 2,4,6-trinitrotoluene | 94.1 | 9.4 | 113 | 1.2 |
| RDX | 102 | 3.4 | 124 | 6.9 |
| 4-amino-2,6-dinitrotoluene | 105 | 7.1 | 117 | 1.2 |
| 3,5-dinitroanaline [b] | 106 | 5.6 | 98.5 | 3.3 |
| 2-amino-4,6-dinitrotoluene | 106 | 4.6 | 113 | 2.8 |
| Tetryl | 121 | 4.1 | 120 | 5.9 |
| nitrobenzene-$d_5$ (SUR) | 97.1 | 5.5 | 87.6 | 4.5 |
| 1,3,5-trimethyl-2-nitrobenzene (SUR) | 89.2 | 6.5 | 84.7 | 4.3 |
| 1,2,4-trimethyl-5-nitrobenzene (SUR) | 86.0 | 3.1 | 92.2 | 4.5 |

[a] Hardness level measured at 380 and 390 mg/L as calcium carbonate, for disk and cartridge samples, respectively. The sample matrix was dechlorinated and preserved as described in Section 8 prior to fortification with method analytes.

[b] 3,5-Dinitroanaline was fortified at 0.2 µg/L.

**Table 15. Detection Limits Obtained Using On-Column Programmed Temperature Vaporizing (PTV) Injection and Full Scan Mass Spectrometry**

| Analyte | DL (μg/L) [a] [fortified conc. for DL determination] | DL (μg/L) [b] [fortified conc. for DL determination] |
|---|---|---|
| nitrobenzene | 0.031 [0.10] | 0.024 [0.05] |
| 2-nitrotoluene | 0.013 [0.10] | 0.010 [0.05] |
| 3-nitrotoluene | 0.019 [0.05] | 0.007 [0.05] |
| 4-nitrotoluene | 0.010 [0.05] | 0.012 [0.05] |
| 1,3-dinitrobenzene | 0.012 [0.05] | 0.016 [0.05] |
| 2,6-dinitrotoluene | 0.005 [0.05] | 0.005 [0.05] |
| 2,4-dinitrotoluene | ND [c] | ND |
| 1,3,5-trinitrobenzene | 0.026 [0.05] | 0.050 [0.05] |
| 2,4,6-trinitrotoluene (TNT) | 0.010 [0.05] | 0.007 [0.05] |
| Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) | 0.040 [0.10] | 0.024 [0.05] |
| 4-amino-2,6-dinitrotoluene | 0.027 [0.10] | 0.007 [0.05] |
| 3,5-dinitroanaline | ND | ND |
| 2-amino-4,6-dinitrotoluene | 0.05 [0.25] | 0.039 [0.25] |
| 2,4,6-trinitrophenylmethylnitramine (Tetryl) | 0.28 [1.0] [d] | ND |

[a] Data from replicate disk extractions, n=8.

[b] Data from replicate cartridge extractions, n=7.

[c] ND - Not determined; see Sect. 13.3 and 13.4.

[d] n=6

**Table 16. Precision and Accuracy Data Obtained from Reagent Water Samples Fortified with Method Analytes at Low Concentrations, Using SPE Disk Extraction, On Column PTV Injection and Full Scan Mass Spectrometry (n=8)**

| Analyte | Fortified Concentration (μg/L) | Accuracy (% recovery) | Precision (%RSD) |
|---|---|---|---|
| nitrobenzene | 0.25 | 68.5 | 12 |
| 2-nitrotoluene | 0.25 | 64.4 | 5.9 |
| 3-nitrotoluene | 0.10 | 85.1 | 6.7 |
| 4-nitrotoluene | 0.10 | 81.0 | 5.5 |
| 1,3-dinitrobenzene | 0.10 | 77.6 | 5.6 |
| 2,6-dinitrotoluene | 0.10 | 104 | 3.8 |
| 2,4-dinitrotoluene | ND [a] | | |
| 1,3,5-trinitrobenzene | 0.10 | 114 | 16 |
| 2,4,6-trinitrotoluene | 0.25 | 88.6 | 4.3 |
| RDX | 0.10 | 102 | 13 |
| 4-amino-2,6-dinitrotoluene | 0.25 | 92.8 | 5.8 |
| 3,5-dinitroanaline | ND | | |
| 2-amino-4,6-dinitrotoluene | 1.0 | 107 | 7.1 |
| Tetryl | 1.0 | 111 | 5.2 |

[a] ND - Not determined; See Sect. 13.3 and 13.4.

**Table 17. Precision and Accuracy Data Obtained from Reagent Water Samples Fortified with Method Analytes at Low Concentrations, Using SPE Cartridge Extraction, On-Column PTV Injection and Full Scan Mass Spectrometry (n=8)**

| Analyte | Fortified Concentration (μg/L) | Accuracy (% recovery) | Precision (%RSD) |
|---|---|---|---|
| nitrobenzene | 0.10 | 77.0 | 11 |
| 2-nitrotoluene | 0.10 | 74.9 | 10 |
| 3-nitrotoluene | 0.05 | 114 | 4.0 |
| 4-nitrotoluene | 0.05 | 116 | 6.6 |
| 1,3-dinitrobenzene | 0.25 | 92.1 | 2.8 |
| 2,6-dinitrotoluene | 0.10 | 114 | 3.7 |
| 2,4-dinitrotoluene | ND [a] | | |
| 1,3,5-trinitrobenzene | 0.25 | 126 | 11.5 |
| 2,4,6-trinitrotoluene | 0.25 | 116 | 19 |
| RDX | 0.10 | 117 | 10 |
| 4-amino-2,6-dinitrotoluene | 0.25 | 101 | 7.4 |
| 3,5-dinitroanaline | ND | | |
| 2-amino-4,6-dinitrotoluene | 1.0 | 106 | 9.6 |
| Tetryl | 1.0 | 108 | 7.1 |

[a] ND - Not determined; see Sect. 13.3 and 13.4.

**Table 18. Precision and Accuracy Data Obtained from Reagent Water Samples Fortified with Method Analytes at 1.0 μg/L, Using On-Column PTV Splitless Injection and Full Scan Mass Spectrometry**

| Analyte | Disk Extraction (n=4) | | Cartridge Extraction (n=4) | |
|---|---|---|---|---|
| | Accuracy (% recovery) | Precision (%RSD) | Accuracy (% recovery) | Precision (%RSD) |
| nitrobenzene | 95.3 | 2.6 | 95.0 | 1.7 |
| 2-nitrotoluene | 92.3 | 2.5 | 91.5 | 3.4 |
| 3-nitrotoluene | 93.3 | 1.8 | 91.1 | 1.3 |
| 4-nitrotoluene | 91.2 | 3.6 | 88.7 | 1.7 |
| 1,3-dinitrobenzene | 92.8 | 4.0 | 98.7 | 8.0 |
| 2,6-dinitrotoluene | 101 | 2.8 | 104 | 4.1 |
| 2,4-dinitrotoluene | ND [a] | | ND | |
| 1,3,5-trinitrobenzene | 110 | 6.5 | 105 | 14 |
| 2,4,6-trinitrotoluene | 123 | 2.0 | 117 | 6.3 |
| RDX | 112 | 1.6 | 122 | 5.9 |
| 4-amino-2,6-dinitrotoluene | 125 | 4.0 | 123 | 6.8 |
| 3,5-dinitroanaline | ND | | ND | |
| 2-amino-4,6-dinitrotoluene | 107 | 7.1 | 106 | 9.6 |
| Tetryl | 111 | 5.2 | 108 | 7.1 |
| nitrobenzene-$d_5$ (SUR) | 90.4 | 3.1 | 90.7 | 2.6 |
| 1,3,5-trimethyl-2-nitrobenzene (SUR) | 92.8 | 1.4 | 88.5 | 2.2 |
| 1,2,4-trimethyl-5-nitrobenzene (SUR) | 96.8 | 1.5 | 98.0 | 3.0 |

[a] ND - Not determined; See Sect. 13.3 and 13.4.

**Table 19. Precision and Accuracy Data Obtained from Tap Water (Chlorinated Water from a Surface Source) Fortified with Method Analytes at 1.0 μg/L, Using On-Column PTV Injection and Full Scan Mass Spectrometry [a]**

| Analyte | Disk Extraction (n=4) | | Cartridge Extraction (n=4) | |
|---|---|---|---|---|
| | Accuracy (% recovery) | Precision (%RSD) | Accuracy (% recovery) | Precision (%RSD) |
| nitrobenzene | 78.6 | 4.1 | 95.1 | 2.8 |
| 2-nitrotoluene | 77.1 | 3.2 | 90.0 | 2.2 |
| 3-nitrotoluene | 78.8 | 2.8 | 91.7 | 2.5 |
| 4-nitrotoluene | 76.9 | 3.3 | 88.5 | 3.1 |
| 1,3-dinitrobenzene | 83.6 | 2.8 | 95.9 | 1.8 |
| 2,6-dinitrotoluene | 86.7 | 2.8 | 105 | 2.1 |
| 2,4-dinitrotoluene | ND [b] | | | |
| 1,3,5-trinitrobenzene | 107 | 6.7 | 110 | 2.2 |
| 2,4,6-trinitrotoluene | 112 | 2.8 | 131 | 1.8 |
| RDX | 99.3 | 11 | 127 | 7.8 |
| 4-amino-2,6-dinitrotoluene | 107 | 2.7 | 128 | 3.8 |
| 3,5-dinitroanaline | ND | | | |
| 2-amino-4,6-dinitrotoluene | 95.4 | 5.5 | 107 | 3.1 |
| Tetryl | 103 | 2.7 | 123 | 6.5 |
| nitrobenzene-$d_5$ (SUR) | 90.0 | 5.0 | 93.8 | 2.8 |
| 1,3,5-trimethyl-2-nitrobenzene (SUR) | 97.2 | 3.8 | 86.2 | 3.3 |
| 1,2,4-trimethyl-5-nitrobenzene (SUR) | 104 | 3.6 | 96.7 | 1.8 |

[a] The sample matrix was dechlorinated and preserved as described in Section 8 prior to fortification with method analytes.

[b] ND - Not determined; see Sect. 13.3 and 13.4.

**Table 20. Precision and Accuracy Data Obtained from Tap Water (Chlorinated Water from a Ground Source with a High Hardness Level [a]) Fortified with Method Analytes at 1.0 μg/L, Using On-Column PTV Injection and Full Scan Mass Spectrometry**

| Analyte | Disk Extraction (n=4) | | Cartridge Extraction (n=4) | |
|---|---|---|---|---|
| | Accuracy (% recovery) | Precision (%RSD) | Accuracy (% recovery) | Precision (%RSD) |
| nitrobenzene | 94.1 | 2.4 | 91.4 | 3.5 |
| 2-nitrotoluene | 88.5 | 2.7 | 90.0 | 2.4 |
| 3-nitrotoluene | 92.2 | 3.0 | 89.9 | 2.6 |
| 4-nitrotoluene | 89.0 | 2.5 | 89.6 | 2.6 |
| 1,3-dinitrobenzene | 96.4 | 4.0 | 107 | 6.3 |
| 2,6-dinitrotoluene | 101 | 2.4 | 105 | 1.2 |
| 2,4-dinitrotoluene | ND [b] | | | |
| 1,3,5-trinitrobenzene | 129 | 5.3 | 123 | 8.8 |
| 2,4,6-trinitrotoluene | 133 | 3.0 | 136 | 1.7 |
| RDX | 126 | 5.6 | 150 | 3.7 |
| 4-amino-2,6-dinitrotoluene | 128 | 4.4 | 140 | 3.9 |
| 3,5-dinitroanaline | ND | | | |
| 2-amino-4,6-dinitrotoluene | 110 | 2.4 | 121 | 6.5 |
| Tetryl | 132 | 5.6 | 135 | 5.3 |
| nitrobenzene-$d_5$ (SUR) | 89.1 | 4.4 | 88.2 | 3.2 |
| 1,3,5-trimethyl-2-nitrobenzene (SUR) | 91.4 | 4.3 | 92.1 | 6.0 |
| 1,2,4-trimethyl-5-nitrobenzene (SUR) | 96.8 | 4.6 | 97.3 | 5.3 |

[a] Hardness level measured at 380 and 390 mg/L as calcium carbonate, for disk and cartridge samples respectively. The sample matrix was dechlorinated and preserved as described in Section 8 prior to fortification with method analytes.

[b] ND - Not determined; See Sect. 13.3 and 13.4.

**Table 21. Aqueous Holding Time Data for Surface Water Samples Fortified with Method Analytes at 5 µg/L and Preserved and Stored as Directed in Section 8.**

| Analyte | Day 0 Amount [a] (µg/L) | Day 7 Amount (µg/L) | Day 11 Amount (µg/L) | Day 14 Amount (µg/L) | Day 19 Amount (µg/L) |
|---|---|---|---|---|---|
| nitrobenzene | 4.2 | 4.4 | 4.3 | 4.1 | 4.2 |
| 2-nitrotoluene | 3.9 | 4.1 | 4.0 | 3.8 | 3.6 |
| 3-nitrotoluene | 3.8 | 3.9 | 3.7 | 3.6 | 3.6 |
| 4-nitrotoluene | 4.0 | 4.1 | 4.0 | 3.9 | 3.6 |
| 1,3-dinitrobenzene | 4.1 | 4.3 | 4.2 | 4.1 | 4.0 |
| 2,6-dinitrotoluene | 3.8 | 3.7 | 3.6 | 3.6 | 3.5 |
| 2,4-dinitrotoluene | 3.9 | 4.0 | 3.9 | 3.6 | 3.6 |
| 1,3,5-trinitrobenzene | 4.8 | 5.4 | 5.3 | 5.2 | 5.1 |
| 2,4,6-trinitrotoluene | 4.4 | 4.5 | 4.2 | 3.9 | 4.0 |
| RDX | 4.7 | 4.8 | 4.4 | 4.4 | 4.4 |
| 4-amino-2,6-dinitrotoluene | 4.8 | 5.1 | 4.9 | 4.7 | 4.8 |
| 3,5-dinitroanaline [b] | 1.0 | 1.1 | 1.1 | 1.1 | 1.1 |
| 2-amino-4,6-dinitrotoluene | 4.6 | 4.8 | 4.5 | 4.5 | 4.6 |
| Tetryl | 4.5 | 4.9 | 4.9 | 4.4 | 5.1 |

[a] Each concentration represents the mean of 5 replicate measurements. The RSD of each set of replicates is less than 5.2%.

[b] 3,5-Dinitroanaline was fortified at 1µg/L.

**Table 22. Extract Holding Time Data for Surface Water Samples Fortified with Method Analytes at 5 µg/L, Preserved and Stored as Directed in Section 8.**

| Analyte | Day 0 Amount [a] (µg/L) | Day 7 Amount (µg/L) | Day 15 Amount (µg/L) | Day 21 Amount (µg/L) | Day 28 Amount (µg/L) | Day 35 Amount (µg/L) |
|---|---|---|---|---|---|---|
| nitrobenzene | 4.4 | 4.6 | 4.4 | 4.2 | 4.2 | 4.3 |
| 2-nitrotoluene | 4.1 | 4.2 | 4.1 | 3.8 | 3.9 | 4.2 |
| 3-nitrotoluene | 4.0 | 4.0 | 3.8 | 3.6 | 3.8 | 4.0 |
| 4-nitrotoluene | 4.2 | 4.2 | 4.1 | 3.7 | 3.7 | 3.9 |
| 1,3-dinitrobenzene | 4.2 | 4.2 | 4.2 | 4.0 | 4.9 | 4.3 |
| 2,6-dinitrotoluene | 3.9 | 4.0 | 3.8 | 3.5 | 3.6 | 3.7 |
| 2,4-dinitrotoluene | 4.0 | 4.2 | 3.7 | 3.6 | 3.7 | 3.8 |
| 1,3,5-trinitrobenzene | 4.7 | 5.2 | 5.0 | 5.0 | 5.2 | 5.2 |
| 2,4,6-trinitrotoluene | 4.4 | 4.6 | 4.2 | 4.0 | 4.1 | 4.2 |
| RDX | 4.6 | 5.1 | 4.6 | 4.5 | 4.5 | 4.4 |
| 4-amino-2,6-dinitrotoluene | 4.7 | 5.1 | 4.8 | 4.7 | 4.9 | 4.9 |
| 3,5-dinitroanaline [b] | 1.0 | 1.1 | 1.1 | 1.1 | 1.1 | 1.1 |
| 2-amino-4,6-dinitrotoluene | 4.6 | 4.8 | 4.4 | 4.5 | 4.5 | 4.7 |
| Tetryl | 4.4 | 4.7 | 4.7 | 4.6 | 4.7 | 4.7 |

[a] Each concentration represents the mean of 5 replicate measurements. The RSD of each set of replicates is less than 15% except for 2-nitrotoluene on day 15 which was 23%.

[b] 3,5-Dinitroanaline was fortified at 1µg/L.

**Table 23. Initial Demonstration of Capability (IDC) Requirements (Summary)**

| Method Ref. | Requirement | Specification and Frequency | Acceptance Criteria |
|---|---|---|---|
| Sect. 9.2.1 | Initial Demonstration of Low Method Background | Analyze LRB prior to any other IDC steps. | Demonstrate that all target analytes are ≤ 1/3 the MRL, and that possible interferences from extraction media do not prevent the identification and quantification of method analytes. |
| Sect. 9.2.2 | Initial Demonstration of Precision (IDP) | Analyze 4-7 replicate LFBs fortified at 2-5 µg/L | RSD must be ≤20% for all analytes. |
| Sect. 9.2.3 | Initial Demonstration of Accuracy (IDA) | Calculate average recovery for replicates used in IDP | Mean recovery 70-130% of true value. |
| Sect. 9.2.4 | Detection Limit (DL) Determination | Over a period of three days, prepare a minimum of 7 replicate LFBs fortified at a concentration estimated to be near the DL. Analyze the replicates through all steps of the analysis. Calculate the DL using the equation in Section 9.2.4. | **NOTE:** Data from DL replicates are not required to meet method precision and accuracy criteria. If the DL replicates are fortified at a low enough concentration, it is likely that they will not meet precision and accuracy criteria. |

**Table 24. Quality Control Requirements (Summary)**

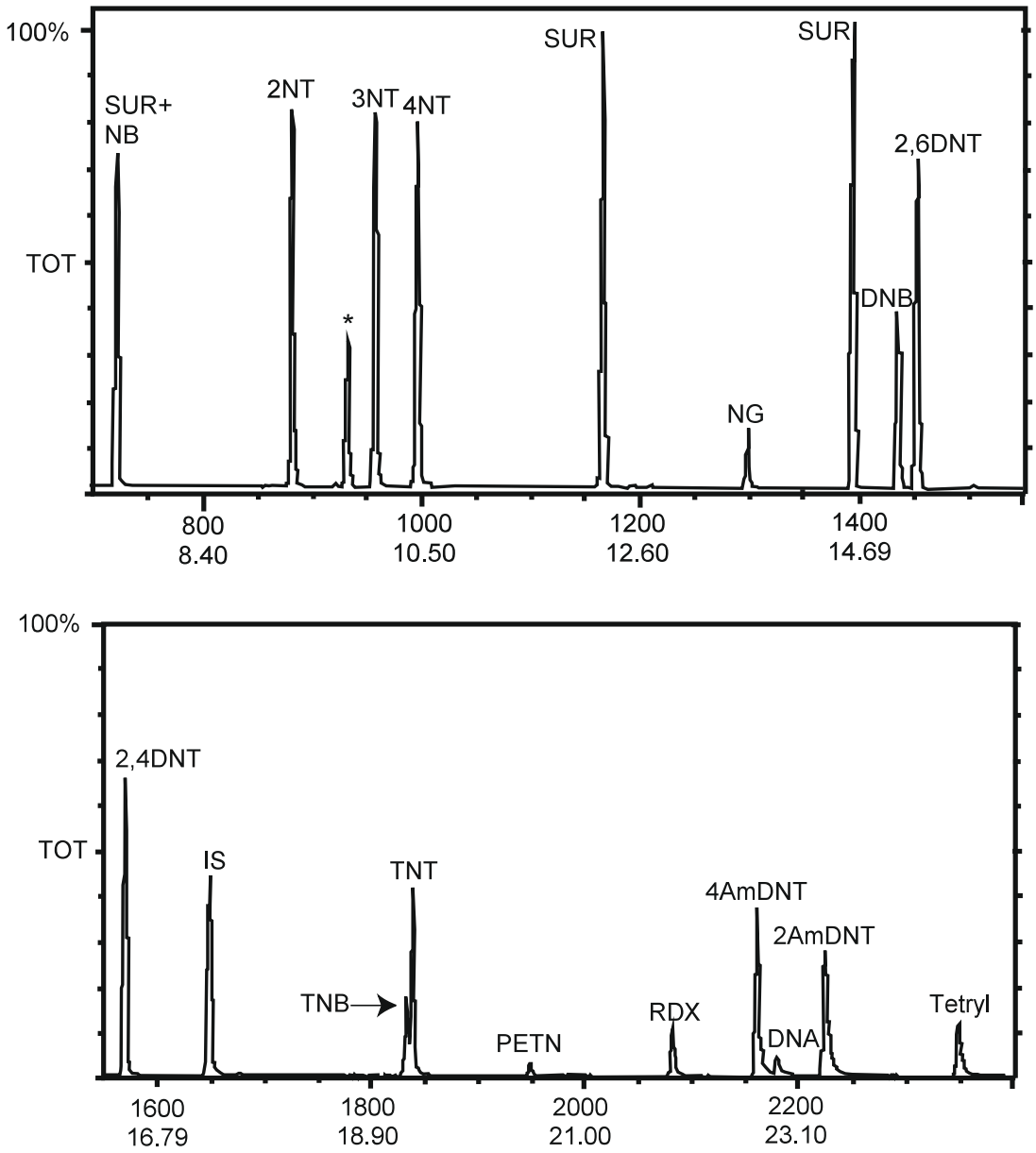
| Method Ref. | Requirement | Specification and Frequency | Acceptance Criteria |
|---|---|---|---|
| Sect. 8.1 - Sect 8.4 | Sample Collection, Preservation, and Holding Time | 14 days, with addition of Trizma buffer and copper sulfate | Iced or refrigerated at 10° C or less for up to 48 hours to allow time for shipping; refrigerated at 6° C or less after arrival at the laboratory. |
| Sect. 8.4 | Extract Holding Time | 30 days | Stored at 0° C or less in amber vials. |
| Sect. 9.10 | Laboratory Fortified Sample Matrix (LFM) | Analyze one LFM per extraction batch (20 samples or less) fortified with method analytes at approximately 2 times the native concentration. | Recoveries not within 70-130% of the fortified amount may indicate a matrix effect. |
| Sect. 9.11 | Field Duplicates | Analyze 1 FD for each 20 samples, or 1 per extraction batch, whichever is greater. | Suggested RPD±30%. |
| Sect. 9.12 | Quality Control Sample (QCS) | Analyze QCS whenever new standards are prepared, or at least quarterly. | If analyzed as a calibration sample, CCC criteria apply. If analyzed as an LFB, those criteria apply. |
| Sect 9.4 | Laboratory Reagent Blank (LRB) | One with each extraction batch of up to 20 samples. | Demonstrate that all target analytes are ≤ 1/3 the MRL, and that possible interference from extraction media do not prevent the identification and quantification of method analytes. |

| Method Ref. | Requirement | Specification and Frequency | Acceptance Criteria |
|---|---|---|---|
| Sect. 9.7 | Laboratory Fortified Blanks (LFB) | Analyze at least one LFB daily or one for each extraction batch of up to 20 field samples. Rotate the fortified concentration between low, medium and high amounts. | Results of LFB analyses must be 70-130% of the true value for each analyte and surrogate for all fortified concentrations greater than the lowest CAL point. Results of LFBs corresponding to the lowest CAL point must be 50-150% of the true value. |
| Sect. 9.8 | Internal Standard | The internal standard, 3,4-dinitrotoluene, is added to all calibration standards and extracts. | Peak area counts for the IS in LFBs, LRBs and sample extracts must be within 70-130% of the peak area in the most recent CCC, and 50-150% of average area in the initial calibration. |
| Sect. 9.9 | Surrogate Standards | Surrogate standards (nitrobenzene-$d_5$; 1,3,5-trimethyl-2-nitro-benzene; and 1,2,4-trimethyl-5-nitro-benzene) are added to all calibration standards, samples, LFBs, LFMs, FDs, and LRBs. | Recovery for all surrogates in all calibration standards, LRB, LFB, LFM, FD and sample extracts must be 70-130% of the true value. |
| Sect. 10.2.1 | MS Tune Check | Analyze BFB to verify MS tune before initial calibration and before every recalibration. | Criteria are given in Table 1. |

| Method Ref. | Requirement | Specification and Frequency | Acceptance Criteria |
|---|---|---|---|
| Sect. 10.2.2-<br>Sect. 10.2.10 | Initial Calibration | Use internal standard calibration technique to generate an average RF or first or second order calibration curve. Use a minimum of 3 standards for a calibration range of 1 order of magnitude, and at least 5 standards for 2 orders of magnitude. | When each calibration standard is calculated as an unknown using the calibration curve, the result must be 70-130% of the true value for all but the lowest standard. The lowest standard must be 50-150% of the true value. |
| Sect. 10.3 | Continuing Calibration Check | Verify initial calibration by analyzing a calibration standard prior to analyzing samples, after every 10 samples, and after the last sample. Always analyze a low concentration (near the MRL) CCC at the beginning of the analysis period. Rotate through low, medium, and high concentration calibration standards to meet every 10 sample requirement. | The result for each analyte and surrogate must be 70-130% of the true value for all concentrations except the lowest CAL point for each analyte. The lowest CAL point for each analyte must be 50-150% of the true value.<br>The peak area of the IS must be within 70-130% of the peak area in the most recent CCC, and 50-150% of the average peak area calculated during initial calibration. |

**Figure 1**

**Chromatogram of Explosives and Related Compounds**




Total ion chromatogram of 16 explosives and related compounds, using a J&W DB5-MS column and the conditions described in Sect. 10.2.2.1; 5ng each analyte, surrogate and internal standard, except DNA which is 1ng. See Table 2 and Sect. 13.2 for compound abbreviations used to label peaks.

* Candidate internal standard that was eventually dropped from the method.