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METHOD 530 DETERMINATION OF SELECT SEMIVOLATILE ORGANIC CHEMICALS IN DRINKING WATER BY SOLID PHASE EXTRACTION AND GAS CHROMATOGRAPHY/ MASS SPECTROMETRY (GC/MS)

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METHOD 530

DETERMINATION OF SELECT SEMIVOLATILE ORGANIC CHEMICALS IN DRINKING WATER BY SOLID PHASE EXTRACTION AND GAS CHROMATOGRAPHY/ MASS SPECTROMETRY (GC/MS)

1. SCOPE AND APPLICATION

1.1. This is a gas chromatography/mass spectrometry (GC/MS) method for the determination of selected semivolatile organic compounds in drinking waters. Accuracy and precision data have been generated in reagent water, and in finished ground and surface waters for the compounds listed in the table below. This method was initially developed with full scan GC/MS, but performance has also been demonstrated in the selected ion monitoring (SIM) mode for all analytes. SIM is useful when enhanced sensitivity is desirable. An example chromatogram which includes the entire analyte list is shown in Fig. 1.

Analyte	Chemical Abstract Services Registry Number (CASRN)
o-toluidine	95-53-4
quinoline	91-22-5
butylated hydroxyanisole (BHA)	25013-16-5
dimethipin	55290-64-7

1.2. The Minimum Reporting Level (MRL) is the lowest analyte concentration that meets Data Quality Objectives (DQOs) that are developed based on the intended use of this method. The single laboratory lowest concentration MRL (LCMRL) (Sect. 3.12) is the lowest true concentration for which the future recovery is predicted to fall, with high confidence (99 percent), between 50 and 150 percent recovery. The LCMRL is compound dependent and is also dependent on extraction efficiency, sample matrix, fortification concentration, and instrument performance. The procedure used to determine the LCMRL is described elsewhere.[1,2] During method development, LCMRLs were determined from the results of laboratory fortified blanks (LFBs) in full scan mode and in the SIM mode for all method analytes. These LCMRLs are provided in Tables 5 and 9 for full scan and SIM modes, respectively.

1.3. Laboratories using this method are not required to determine the LCMRL for this method, but will need to demonstrate that their laboratory MRL for this method meets the requirements described in Sect. 9.2.4.

1.4. Determining the Detection Limit (DL) for analytes in this method is optional (Sect. 9.2.6). Detection limit is defined as the statistically calculated minimum concentration that can be measured with 99% confidence that the reported value is greater than zero.[3] The DL is compound dependent and is also dependent on extraction efficiency, sample matrix, fortification concentration, and instrument performance. DLs have been determined for all analytes in full scan mode (Table 5) and in SIM mode (Table 9).

1.5. This method is intended for use by analysts skilled in solid phase extractions, the operation of GC/MS instruments, and the interpretation of the associated data.

1.6. METHOD FLEXIBILITY – In recognition of technological advances in analytical systems and techniques, the laboratory is permitted to modify the GC inlet, inlet conditions, column, injection parameters, and all other GC and MS conditions. Changes may not be made to sample collection and preservation (Sect. 8), sample extraction (Sect. 11) or to the Quality Control (QC) requirements (Sect. 9). Method modifications should be considered only to improve method performance. Modifications that are introduced in the interest of reducing cost or sample processing time, but result in poorer method performance, should not be used. In all cases where method modifications are proposed, the analyst must perform the procedures outlined in the initial demonstration of capability (IDC, Sect. 9.2), verify that all QC acceptance criteria in this method (Sect. 9) are met, and that method performance in real sample matrices is equivalent to that demonstrated for Laboratory Fortified Sample Matrices (LFSMs) in Sect. 17.

Note: The above method flexibility section is intended as an abbreviated summation of method flexibility. Sects. 4-12 provide detailed information of specific portions of the method that may be modified. If there is any perceived conflict between the general method flexibility statement in Sect. 1.6 and specific information in Sects. 4-12, Sects. 4-12 supersede Sect.1.6.

2. SUMMARY OF METHOD

2.1. A 1-liter water sample is fortified with surrogate analytes and passed through a solid phase extraction (SPE) device (Sects. 6.9-6.11) to extract the target analytes and surrogates. The compounds are eluted from the solid phase with a small amount of organic solvents. The solvent extract is dried by passing it through a column of anhydrous sodium sulfate, concentrated by evaporation with nitrogen gas, and then adjusted to a 1-mL volume with dichloromethane after adding the internal standards. A splitless injection is made into a GC equipped with a high-resolution fused silica capillary column that is interfaced to an MS. The analytes are separated and identified by comparing the acquired mass spectra and retention times to reference spectra and retention times for calibration standards acquired under identical GC/MS conditions. The GC/MS may be operated in the full scan, SIM, or selected ion storage (SIS) mode (Sects 3.19 and 3.20). The GC/MS may be calibrated using standards prepared in solvent or using matrix-matched standards (Sects. 3.15 and

7.2.4). The concentration of each analyte is calculated by using its integrated peak area and the internal standard technique. Surrogate analytes are added to all Field and Quality Control (QC) Samples to monitor the performance of each extraction and overall method performance.

2.2 Butylated hydroxyanisole (BHA) can be affected by matrix induced chromatographic response enhancement (Sect. 3.14), when analyzed at low concentrations. Refer to Sect. 13 for information regarding method performance.

3. DEFINITIONS

3.1. ANALYSIS BATCH - A set of samples that is 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 solution(s) and the internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration. In this method, traditional CAL standards prepared in dichloromethane (DCM) may be used or matrix-matched standards (Sect. 3.15) prepared in a concentrated laboratory reagent water (LRW) extract may be used. This procedure is described in Sect. 7.2.4.2.

3.3. CONTINUING CALIBRATION CHECK (CCC) STANDARD - 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. 9.2.6), and accurate quantitation is not expected at this level.[3]

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, solvents, surrogate solution, and fortifying solutions. Required QC samples include Laboratory Reagent Blank, Laboratory Fortified Blank, Laboratory Fortified Sample Matrix, and either a Field Duplicate or Laboratory Fortified Sample 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 provide an estimate of the precision associated with sample collection, preservation, and storage, as well as with laboratory procedures.

3.7. INTERNAL STANDARD (IS) - A pure compound added to an extract or standard solution in a known amount and used to measure the relative responses of the method analytes and surrogates.

3.8. LABORATORY FORTIFIED BLANK (LFB) - An aliquot of reagent water or other blank matrix to which known quantities of the method analytes and all the preservation compounds are added. The LFB is processed and analyzed exactly like a sample, 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 (LFSM) - An aliquot of a Field Sample to which known quantities of the method analytes and all the preservation compounds are added. The LFSM is processed and 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 LFSM corrected for background concentrations.

3.10. LABORATORY FORTIFIED SAMPLE MATRIX DUPLICATE (LFSMD) - A duplicate Field Sample used to prepare the LFSM, which is fortified, extracted and analyzed identically to the LFSM. The LFSMD is used instead of the Field Duplicate to assess method precision and accuracy when the occurrence of a method analyte is infrequent.

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

3.12. LOWEST CONCENTRATION MINIMUM REPORTING LEVEL (LCMRL) - The single-laboratory LCMRL is the lowest true concentration for which the future recovery is predicted to fall, with high confidence (99 percent), between 50 and 150 percent recovery.[1,2]

3.13. 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.

3.14. MATRIX-INDUCED CHROMATOGRAPHIC RESPONSE ENHANCEMENT (MICRE) - This phenomenon occurs when, in the absence of matrix components, method analytes in calibration solutions are degraded or absorbed in the GC injector or column, resulting in poor peak shapes and low response. When subsequent sample extracts containing the analytes and components from a complex sample matrix are injected, peak shape and response improve. In this situation, quantitative data for

field samples may exhibit a high bias.[4-11] Generally, overestimation of results is more pronounced at low analyte concentrations.

3.15. MATRIX-MATCHED CALIBRATION STANDARD - A calibration standard that is prepared by adding method analytes to a concentrated extract of a matrix (reagent water is used for this method) that has been prepared following all the extraction and sample preparation steps of the analytical method. The material extracted from the matrix reduces matrix-induced response enhancement effects and improves the quantitative accuracy of sample results.[10,11]

3.16. MINIMUM REPORTING LEVEL (MRL) - The minimum concentration that can be reported by a laboratory as a quantitated value for a method analyte in a sample following analysis. This concentration must meet the criteria defined in Sect. 9.2.4 and must not be any lower than the concentration of the lowest continuing calibration check standard for that analyte. The MRL may be determined by the laboratory based upon project objectives, or may be set by a regulatory body as part of a compliance monitoring program.

3.17. PRIMARY DILUTION STANDARD SOLUTION (PDS) - A solution containing method analytes, internal standards, or surrogate analytes prepared in the laboratory from stock standard solutions and diluted as needed to prepare calibration solutions and other analyte solutions.

3.18. QUALITY CONTROL SAMPLE (QCS) - A solution prepared using a PDS of method analytes obtained from a source external to the laboratory and different from the source of calibration standards. The second source PDS and the surrogate PDS are used to fortify the QCS at a known concentration. The QCS is used to verify the accuracy of the primary calibration standards.

3.19. SELECTED ION MONITORING (SIM) - An MS technique where only one or a few ions are monitored for each target analyte. 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 the analytes, SURs and ISs as they elute from the chromatographic column. The technique is often used to increase sensitivity. Throughout this document, the term “SIM” will be used to include both SIM as described here and SIS as described in Sect. 3.20.

3.20. SELECTED ION STORAGE (SIS) - An MS technique typically associated with ion trap mass spectrometers in which only one or a few ions are stored at any given time point. When used with gas chromatography, the set of ions stored is usually changed periodically throughout the chromatographic run, to correlate with the characteristic ions of the analytes, SURs and ISs as they elute from the chromatographic column. SIS can be used to enhance sensitivity. Throughout this document the term “SIM” will be used to include both SIM (Sect. 3.19) and SIS.

3.21. 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.

3.22. 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. In this method, the SURs are isotopically labeled analogues of selected method analytes.

4. INTERFERENCES

4.1. All glassware must be meticulously cleaned. Wash glassware with detergent and tap water, rinse with tap water, followed by reagent water. Rinse with methanol and/or acetone. Non-volumetric glassware may be heated in a muffle furnace at 400 °C for two hours as a substitute for solvent rinsing. Volumetric glassware should not be heated in an oven above 120 °C.

4.2. Method interferences may be caused by contaminants in solvents, reagents (including reagent water), sample bottles and caps, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in the chromatograms. All items such as these must be routinely demonstrated to be free from interferences (less than $^1/_3$ the MRL for each target analyte) under the conditions of the analysis by analyzing laboratory reagent blanks as described in Sect. 9.3.1. **Subtracting blank values from sample results is not permitted.**

4.3. Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature of the water. Water samples high in total organic carbon (TOC) may have elevated baselines or interfering peaks. Matrix components may directly interfere by producing a signal at or near the retention time of an analyte peak. They can also enhance the signal of method analytes (Sect. 3.14). Analyses of LFSMs are useful in identifying matrix interferences.

4.4. Relatively large quantities of the buffer and preservatives (Sect. 8.1.2) are added to sample bottles. The potential exists for trace-level organic contaminants in these reagents. Interferences from these sources should be monitored by analysis of laboratory reagent blanks, particularly when new lots of reagents are acquired.

4.5. Solid phase extraction media have been observed to be a source of interferences.[12] The analysis of laboratory reagent blanks can provide important information regarding the presence or absence of such interferences. Brands and lots of solid phase extraction devices should be tested to ensure that contamination does not preclude analyte identification and quantitation.

4.6. Analyte carryover may occur when a relatively "clean" sample is analyzed immediately after a sample (or standard) that contains relatively high concentrations of compounds. Syringes and GC injection port liners must be cleaned carefully or replaced as needed. After analysis of a sample (or standard) that contains high concentrations of compounds, a laboratory reagent blank should be analyzed to ensure that accurate values are obtained for the next sample.

4.7. Silicone compounds may be leached from punctured autosampler vial septa, particularly when particles of the septa are present in the vial for an extended time. This can occur after repeated injections from the same autosampler vial. These silicone compounds, which appear as regularly spaced chromatographic peaks with similar MS fragmentation patterns, can unnecessarily complicate the total ion chromatograms and may cause interferences at high levels.

4.8. In cases where the SPE disks or cartridges are dried by pulling room air through the media using vacuum, it may be possible for the media to become contaminated by components in room air. This was not observed during method development, but if laboratories encounter contamination problems associated with room air, compressed gas cylinders of high purity nitrogen may be used for drying SPE media during sample processing.

5. SAFETY

5.1. The toxicity or carcinogenicity of each reagent 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 an awareness of OSHA regulations regarding safe handling of chemicals used in this method. A reference file of MSDSs should be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available.[13-15]

5.2. Pure standard materials and stock standard solutions of these compounds should be handled with suitable protection to skin and eyes, and care should be taken not to breathe the vapors or ingest the materials.

6. EQUIPMENT AND SUPPLIES

References to specific brands or catalog numbers are included for illustration only, and do not imply endorsement of the product. Other brands of equivalent quality may be used. The SPE sorbents described in Sect. 6.9 are proprietary products that have been fully evaluated for use in this method. Due to their proprietary status, some chemistry aspects of the sorbents are unknown, making equivalency difficult to determine. The EPA document "Technical Notes on Drinking Water Methods"[16] provides criteria for judging equivalency of SPE products (pg. 47). Before analyses are performed for compliance under the Safe Drinking Water Act, questions regarding equivalency of alternate sorbent materials must be addressed to the Office of Ground Water and Drinking Water Alternate Test Procedure Coordinator.[17]

6.1. SAMPLE CONTAINERS - 1-L or 1-qt amber glass bottles fitted with polytetrafluoroethylene (PTFE)-lined screw caps are preferred. Clear glass bottles with PTFE-lined screw caps may be substituted if sample bottles are wrapped with foil, stored in boxes, or otherwise protected from light during sample shipping and storage.

6.2. VIALS - Various sizes of amber glass vials with PTFE-lined screw caps for storing standard solutions and extracts. Amber glass 2-mL autosampler vials with PTFE-faced septa.

6.3. VOLUMETRIC FLASKS - Class A, suggested sizes include 1, 5, and 10 mL for preparation of standards and dilution of extract to final volume.

6.4. GRADUATED CYLINDERS - Suggested sizes include 5, 10, 250 and 1000 mL.

6.5. MICRO SYRINGES - Suggested sizes include 10, 25, 50, 100, 250, 500, and 1000 µL.

6.6. DRYING COLUMN - The drying column must be able to contain 7-8 g of anhydrous sodium sulfate (Na_2SO_4). The drying column should not leach interfering compounds or irreversibly adsorb method analytes. Any small glass or polypropylene column may be used, such as Supelco #57176.

6.7. COLLECTION TUBES - 15 mL, conical tubes (Fisher #05-569-3) or other glassware suitable for collection of the eluent from the solid phase sorbent after extraction and for collecting extract from drying tube.

6.8. ANALYTICAL BALANCE - Capable of weighing to the nearest 0.0001 g.

6.9. SPE APPARATUS USING SPE CARTRIDGES (6-mL COLUMNS); MANUAL EXTRACTION

6.9.1. SPE CARTRIDGES - Modified DVB or PS/DVB polymer

6.9.1.1. Waters Oasis HLB, 500 mg (Waters #186000115) – divinylbenzene N-vinylpyrrolidone copolymer

6.9.1.2. Phenomenex Strata-X, 500 mg (Phenomenex #8B-S100-HCH) – polystyrene divinylbenzene N-vinylpyrrolidone copolymer

6.9.1.3. Agilent Mega Bond Elut Plexa, 500 mg (Agilent #12259506) – hydrophilic polystyrene divinylbenzene polymer

6.9.2. VACUUM EXTRACTION MANIFOLD - Equipped with flow/vacuum control (Supelco #57030-U or equivalent).

6.9.3. SAMPLE DELIVERY SYSTEM - Use of a transfer tube system (Supelco "Visiprep", #57275 or equivalent), which transfers the sample directly from the sample container to the SPE cartridge is recommended.

6.9.4. An automatic or robotic system designed for use with SPE cartridges may be used 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 cartridge. All sorbent washing, conditioning, sample loading, rinsing, drying and elution steps must be performed as closely as possible to the manual procedure. The solvents used for washing, conditioning, and sample elution must be the same as those used in the manual procedure; however, the amount used may be increased as necessary to achieve the required data quality. Solvent amounts may not be decreased. Sorbent drying times prior to elution may be modified to achieve the required data quality. Caution should be exercised when increasing solvent volumes. Increased extract volume will likely necessitate the need for additional sodium sulfate drying, and extended evaporation times which may compromise data quality. Caution should also be exercised when modifying sorbent drying times. Excessive drying may cause losses due to analyte volatility, and excessive contact with room air may oxidize some method analytes. Insufficient drying may leave excessive water trapped in the disk and lead to poor recoveries.

6.10. EXTRACT CONCENTRATION SYSTEM - Extracts are concentrated by evaporation with nitrogen gas using a water bath set at 40 °C (N-Evap, Model 11155, Organomation Associates, Inc., or equivalent).

6.11. LABORATORY OR ASPIRATOR VACUUM SYSTEM - Sufficient capacity to maintain a vacuum of approximately 15 to 25 inches of mercury.

6.12. GAS CHROMATOGRAPH/MASS SPECTROMETER (GC/MS) SYSTEM

6.12.1. FUSED SILICA CAPILLARY GC COLUMN - 30 m x 0.25-mm inside diameter (i.d.) fused silica capillary column coated with a 0.25 μm bonded film of cyanopropyl phenyl and dimethylpolysiloxane (Restek Rtx-1701 or equivalent). Any capillary column that provides adequate capacity, resolution, accuracy, and precision may be used. A mid-polar, low-bleed column is recommended for use with this method to provide adequate resolution and minimize column bleed.

6.12.2. GC INJECTOR AND OVEN - Some of the target compounds included in this method are subject to thermal breakdown in the GC injection port. This problem is exacerbated when the injector and/or the injection port liner is

not properly deactivated or is operated at excessive temperatures. The injection system must not allow analytes to contact hot stainless steel or other metal surfaces that promote decomposition. The performance data in Sect. 17 were obtained using hot, splitless injection using a 4 or 5-mm i.d. glass deactivated liner. Other injection techniques such as temperature programmed injections, cold on-column injections and large volume injections may be used if the QC criteria in Sect. 9 are met. Equipment designed appropriately for these alternate types of injections must be used if these options are employed.

6.12.3. GC/MS INTERFACE - The interface should allow the capillary column or transfer line exit to be placed within a few millimeters of the ion source. Other interfaces are acceptable as long as the system has adequate sensitivity and QC performance criteria are met.

6.12.4. MASS SPECTROMETER (MS) - Any type of MS may be used (i.e., quadrupole, ion trap, time of flight, etc.) with electron ionization. The instrument may be operated in full scan mode or in SIM mode for enhanced sensitivity. The minimum scan range capability of the MS must be 45 to 450 *m/z*, and it must produce a full scan mass spectrum that meets all criteria in Table 2 when a solution containing 5 ng (or less) of decafluorotriphenylphosphine (DFTPP) is injected into the GC/MS (Sect. 10.2.1).

6.12.5. DATA SYSTEM - An interfaced data system is required to acquire, store, and output MS data. The computer software should have the capability of processing stored GC/MS data by recognizing a GC peak within a given retention time window. The software must allow integration of the ion abundance of any specific ion between specified time or scan number limits. The software must be able to construct linear regressions and quadratic calibration curves, and calculate analyte concentrations.

7. <u>REAGENTS AND STANDARDS SUPPLIES</u> (References to specific brands or catalog numbers are included for illustration only, and do not imply endorsement of the product.)

7.1. REAGENTS AND SOLVENTS - Reagent grade or better chemicals should be used in all tests. Unless otherwise indicated, it is intended that all reagents will conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society (ACS), where such specifications are available. Other grades may be used, if the reagents are demonstrated free of analytes and interferences, and all method requirements in the Initial Demonstration of Capability (IDC) are met.

7.1.1. HELIUM - 99.999 % or better, GC carrier gas. Alternate carrier gases, such as hydrogen (99.999 % or better) may be used if the QC criteria in Sect. 9 are met. Instrument manufacturers should be consulted prior to any GC carrier gas conversion.

7.1.2. LABORATORY REAGENT WATER (LRW) - Purified water which does not contain any measurable quantities of any target analytes or interfering compounds at or above $^1/_3$ the MRL for each compound of interest.

7.1.3. METHANOL (MeOH) (CASRN 67-56-1) - High purity, demonstrated to be free of analytes and interferences (Fisher Optima or equivalent).

7.1.4. DICHLOROMETHANE (DCM) (CASRN 75-09-02) - High purity, demonstrated to be free of analytes and interferences (Fisher GC Resolv or equivalent).

7.1.5. ACETONE (CASRN 67-64-1) - High purity, demonstrated to be free of analytes and interferences (Tedia Absolv or equivalent).

7.1.6. SODIUM SULFATE (Na_2SO_4), ANHYDROUS (CASRN 7757-82-6) - Soxhlet extracted with DCM for a minimum of four hours or heated to 400 °C for two hours in a muffle furnace. An "ACS grade, suitable for pesticide residue analysis," is recommended.

7.1.7. SAMPLE PRESERVATION REAGENTS – The following preservatives are solids at room temperature and may be added to the sample bottle before shipment to the field.

7.1.7.1. BUFFER SALT MIX, pH 7 – The sample must be buffered to pH 7 with two components: 1) tris(hydroxymethyl)aminomethane, also called Tris, 0.47 g (CASRN 77-86-1, ACS Reagent Grade or equivalent); and 2) tris(hydroxymethyl)aminomethane hydrochloride, also called Tris HCl, 7.28 g (CASRN 1185-53-1, ACS Reagent Grade or equivalent). Alternately, 7.75 g of a commercial buffer crystal mixture, that is blended in proportion to the amounts given above (Sigma-Aldrich #T7193 or equivalent), can be used.

7.1.7.2. L-ASCORBIC ACID (CASRN 50-81-7) - Ascorbic acid reduces free chlorine at the time of sample collection (ACS Reagent Grade or equivalent).

7.1.7.3. ETHYLENEDIAMINE TETRAACETIC ACID (EDTA), TRISODIUM SALT (CASRN 10378-22-0) - Trisodium EDTA is added to inhibit metal-catalyzed hydrolysis of analytes.

7.1.7.4. DIAZOLIDINYL UREA (DZU) (CAS# 78491-02-8) – DZU is added to inhibit microbial growth.

7.2. STANDARD SOLUTIONS - Standard solutions of internal standards, surrogates and method analytes may be prepared gravimetrically or from commercially available stock solutions. When a compound purity is assayed to be 96% or greater, the weight can be used without correction to calculate the concentration of a gravimetrically prepared stock standard. Solution concentrations listed in this section were those used to develop this method and are included as an example only. Solution preparation steps may be modified as needed to meet the needs of the laboratory. Often, standard mixes appropriate to the method become commercially available subsequent to method publication. **Even though stability times for standard solutions are suggested in the following sections, laboratories should use standard QC practices to determine when their standards need to be replaced. In addition, signs of evaporation and/or discoloration are indicators that a standard should be replaced.**

7.2.1. INTERNAL STANDARD (IS) SOLUTIONS - This method uses two IS compounds listed in the table below. A commercial mixture of ISs was used for method development, and it is highly recommended that other analysts use a commercial mix as well. However, if an analyst chooses to prepare a gravimetric stock solution, it should be prepared in acetone using a procedure similar to the preparation of analyte stocks as outlined in Sect. 7.2.3.1. The PDS mix for ISs has been shown to be stable for at least one year when stored in amber glass screw cap vials at -5 °C or less. Using 10 µL of the IS to fortify the final 1-mL extracts (Sect. 11.5) will yield a concentration of 5 µg/mL each for ISs for full scan analysis. Lower concentrations of ISs should be used for SIM analysis. For SIM analysis during method development, ISs were added to extracts such that their final concentration was 500 ng/mL.

Note: Stock standard solutions and PDSs should be brought to room temperature and sonicated for a few minutes prior to use. This ensures that components are dissolved and the solution is homogeneous.

Internal Standards	CASRN	Solvent	PDS conc.
acenaphthene-d_{10} (IS 1)	15067-26-2	acetone	500 µg/mL
phenanthrene-d_{10} (IS 2)	1517-22-2	acetone	500 µg/mL

7.2.2. SURROGATE ANALYTE STANDARD SOLUTIONS - The surrogate analytes used in this method are listed in the table below. All SUR PDSs were used at the same concentration and were prepared in methanol. The SURs may be prepared from neat material or purchased (if available from commercial suppliers) as individual PDSs or a single PDS. For method development, neat material was purchased from CDN Isotopes (*o*-toluidine-d_9, #D-3571) and Cambridge Isotopes (quinoline-d_7, #DLM-1158-0.1). The SUR PDSs have been shown to be stable for at least

one year when stored in amber glass screw cap vials at -5 ºC or less. For full scan analysis, 10 µL of each of these solutions was added to each 1L aqueous QC and Field Sample prior to extraction, for an expected final extract concentration of 5 µg/L of each SUR. For SIM analysis, the QC and Field Samples were fortified such that the expected final extract concentration was 500 ng/L for each SUR.

Surrogates	CASRN	Solvent	PDS conc.
o-toluidine-d_9 (SUR 1)	194423-47-7	methanol	500 µg/mL
quinoline-d_7 (SUR 2)	34071-94-8	methanol	500 µg/mL

Notes:

- Stock standard solutions and PDSs should be brought to room temperature and sonicated for a few minutes prior to use. This ensures that components are dissolved and the solution is homogeneous.
- Stock standard solutions that will be used for aqueous sample fortification generally should be prepared at a concentration such that only a small volume (e.g., 5-100 µL) needs to be added to achieve the desired final concentration. This will minimize the quantity of organic solvent added to aqueous samples.

7.2.3. ANALYTE STOCK SOLUTIONS

7.2.3.1. ANALYTE STOCK STANDARD SOLUTIONS (SSS) (5.0 mg/mL) - Analyte standards may be purchased commercially as ampulized solutions prepared from neat materials. Commercially prepared SSSs are widely available for most method analytes. To prepare gravimetric stock standard solutions, add 10 mg (weighed on analytical balance to 0.1 mg) of the pure material to 1.9 mL of methanol in a 2-mL volumetric flask, dilute to the mark, and transfer the solution to an amber glass vial. If the neat material is only available in quantities less than 10 mg, reduce the volume of solvent accordingly. If compound purity is confirmed by the supplier to be ≥ 96%, the weighed amount can be used without correction to calculate the concentration of the solution. Store at 4 ºC or less to guard against degradation and evaporation.

Note: Stock standard solutions and PDSs should be brought to room temperature and sonicated for a few minutes prior to use. This ensures that components are dissolved and the solution is homogeneous.

7.2.3.2. ANALYTE PRIMARY DILUTION STANDARD (100 µg/mL) - Prepare the 100-µg/mL Analyte PDS by volumetric dilution of the Analyte Stock Standard Solutions (Sect. 7.2.3.1) in methanol to make a 100-µg/mL solution. The PDS can be used to fortify the LFBs and LFSMs with method analytes and to prepare calibration solutions. Care should be taken during storage to prevent evaporation. The Analyte PDS Solutions used during method development were stable for 6 months stored in an amber glass screw cap vials at -5 °C or less.

Notes:

- Two separate Analyte PDS mixtures should be prepared: one PDS for *o*-toluidine and quinoline, and one PDS for BHA and dimethipin. Method development work exhibited degradation of *o*-toluidine in PDS mixtures with multiple analytes at high concentrations.
- Fortification generally should be prepared at a concentration such that only a small volume (e.g., 5-100 µL) needs to be added to achieve the desired final concentration. This will minimize the quantity of organic solvent added to aqueous samples.
- Stock standard solutions and PDSs should be brought to room temperature and sonicated for a few minutes prior to use. This ensures that components are dissolved and the solution is homogeneous.

7.2.4. CALIBRATION SOLUTIONS - Calibration standards may be prepared in DCM or as matrix-matched calibration standards (Sect. 3.15). This option is provided so that the analyst has the flexibility to prepare calibration curves that will be appropriate for the various types of analytes and the calibration range of interest. If the analyses to be performed include only those analytes that are not susceptible to matrix induced response enhancement, and/or the concentrations to be measured are relatively high (e.g., ≥ 5µg/L), it is likely that accurate data can be obtained with the use of traditional CAL standards prepared in DCM. If low concentrations of analytes susceptible to matrix induced response enhancement need to be measured, it is likely that matrix-matched standards will be required to obtain accurate quantitative data. Whichever type of CAL solutions are selected, those CAL solutions should be used for all calibration and QC procedures described in the method.

Note: Analytes observed to be susceptible to matrix induced response enhancement during method development are indicated in the "comments" portion of Table 1. However, the occurrence and degree of enhancement will depend upon the GC injector design, and the history of the injector, injector liner and GC column. It is highly recommended that prior to the initial demonstration of capability, separate calibration curves be generated

using DCM CALs and matrix-matched CALs for each analyte to be measured. A careful evaluation of the relative peak areas using each type of CAL, especially low concentration CALs, can serve as a guide to the possible occurrence and extent of matrix enhancement, and thus an indicator of which type of standards should be used.

7.2.4.1. CALIBRATION SOLUTIONS PREPARED IN SOLVENT - Prepare a series of six concentrations of calibration solutions in DCM, which contain the analytes of interest. The suggested concentrations in this paragraph are a description of the concentrations used during method development, and may be modified to conform with instrument sensitivity. For full scan analyses, concentrations ranging from 0.10-5.0 ng/µL are suggested for each analyte, with IS and SUR concentrations as described in Sect. 7.2.1 and 7.2.2. For SIM analysis, six concentrations in the range of 0.005-0.5 ng/µL are suggested, with reduced concentrations of the ISs and SURs (Sect. 7.2.1 and 7.2.2). The six CAL standards (CAL1 through CAL6) are prepared by combining appropriate aliquots of the Analyte PDS solution (Sect. 7.2.3.2) and the IS and SUR PDSs (Sects. 7.2.1. and 7.2.2). All calibration solutions should contain at least 60% DCM to avoid gas chromatographic anomalies such as poor peak shape, split peaks, etc. During method development, all analytes were prepared in a single set of calibration solutions. Calibration solutions were stable for six months when stored at -5 ºC in amber screw top vials.

7.2.4.2. MATRIX-MATCHED CALIBRATION SOLUTIONS - Prepare a series of six calibration solutions in the same manner as in Sect. 7.2.4.1, but instead of preparation in DCM, calibration solutions are prepared in final solvent extracts derived from laboratory reagent water. One-liter aliquots of reagent water with sample preservatives added, are extracted using the sorbent selected for sample analysis, dried with sodium sulfate, and evaporated to <1 mL following the same procedure used for samples (Sects. 11.3-11.5). **However, the ISs, SURs, and analyte PDSs are added to the extract at appropriate concentrations immediately before the adjustment of the extract to 1 mL, i.e., they are <u>not</u> extracted.**

7.2.5. GC/MS TUNE CHECK SOLUTION (5 µg/mL or less) (CASRN 5074-71-5) - Prepare a DFTPP solution in DCM. Store this solution in an amber glass screw cap vial at 4 °C or less.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1. SAMPLE BOTTLE PREPARATION

8.1.1. Grab samples must be collected using 1-liter or 1-quart sample bottles that meet the requirements in Sect. 6.1.

8.1.2. Preservation reagents, listed in the table below, are added to each sample bottle as dry solids prior to shipment to the field (or prior to sample collection).

Compound	Amount	Purpose
L-Ascorbic acid	0.10 g/L	Dechlorination
Ethylenediaminetetraacetic acid, trisodium salt	0.35 g/L	Inhibit metal-catalyzed hydrolysis of targets
Diazolidinyl Urea	1.0 g/L	Microbial inhibitor
***Tris(hydroxymethyl)aminomethane**	0.47 g/L	First component of pH 7 buffer mixture
***Tris(hydroxymethyl)aminomethane hydrochloride**	7.28 g/L	Second component of pH 7 buffer mixture

*Alternately, 7.75 g of a commercial buffer crystal mixture, that is blended in the proportions given in the table, can be used (Sect. 7.1.7.1).

8.1.2.1. Residual chlorine must be reduced at the time of sample collection with 100 mg of ascorbic acid per liter.

8.1.2.2. Trisodium EDTA must be added to inhibit potential metal-catalyzed hydrolysis of method analytes.

8.1.2.3. Diazolidinyl urea (1.0 g) is added to inhibit microbial degradation of analytes.

8.1.2.4. The sample must be buffered to pH 7 to reduce the acid and base catalyzed hydrolysis of target analytes. The pH buffer has two components: tris(hydroxymethyl)aminomethane (0.47 g) and tris(hydroxymethyl)aminomethane hydrochloride (7.28 g). A commercially prepared combination of these two compounds can be purchased as pre-mixed crystals. When using the pH 7 pre-mixed crystals, add 7.75 g per liter of water sample.

8.2. SAMPLE COLLECTION

8.2.1. Open the tap and allow the system to flush until the water temperature has stabilized (usually 3-5 min). Collect samples from the flowing system.

8.2.2. Fill sample bottles, taking care not to flush out the sample preservation reagents. Samples do not need to be collected headspace free.

8.2.3. After collecting the sample, cap the bottle and agitate by hand until preservatives are dissolved. Immediately place in ice or refrigerate.

8.3. SHIPMENT AND STORAGE - Samples must be chilled during shipment and must not exceed 10 °C during the first 48 hours after collection. Sample temperature must be confirmed to be at or below 10 °C when they are received at the laboratory, with the following exception. Samples arriving at the laboratory on the day of sampling may not have had time to achieve a temperature of less than 10 °C. This is acceptable as long as the cooling process has begun. Samples stored in the lab must be held at or below 6 °C until extraction, but should not be frozen. Sample holding time data are discussed in Sect. 13.3.

Note: Samples that are significantly above 10 ºC 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. SAMPLE AND EXTRACT HOLDING TIMES - Water samples should be extracted as soon as possible after collection but must be extracted within 14 days of collection. All extracts must be stored at -5 °C or less, protected from light and analyzed within 14 days after extraction (Sect. 13.4).

9. QUALITY CONTROL

9.1. QC requirements include the Initial Demonstration of Capability (IDC) and ongoing QC requirements that must be met when preparing and analyzing Field Samples. This section describes QC parameters, their required frequency, and the performance criteria that must be met in order to meet EPA quality objectives. The QC criteria discussed in the following sections are summarized in Tables 10 and 11. These QC requirements are considered the minimum acceptable QC criteria. Laboratories are encouraged to institute additional QC practices to meet their specific needs.

9.2. INITIAL DEMONSTRATION OF CAPABILITY - The IDC must be successfully performed prior to analyzing any Field Samples. Prior to conducting the IDC, the analyst must first generate an acceptable Initial Calibration following the procedure

outlined in Sect. 10.2. **The IDC must be repeated if the laboratory changes the type or brand of SPE sorbent being used.**

9.2.1. INITIAL DEMONSTRATION OF LOW SYSTEM BACKGROUND - Any time a new lot of SPE cartridges or disks is used, it must be demonstrated that a Laboratory Reagent Blank is reasonably free of contamination and that the criteria in Sect. 9.3.1 are met.

9.2.2. INITIAL DEMONSTRATION OF PRECISION (IDP) - Prepare, extract, and analyze four to seven replicate LFBs fortified near the midrange of the initial calibration curve according to the procedure described in Sect. 11. Sample preservatives as described in Sect. 8.1.2 must be added to these samples. The relative standard deviation (RSD) of the results of the replicate analyses must be ≤ 20%.

9.2.3. INITIAL DEMONSTRATION OF ACCURACY - Using the same set of replicate data generated for Sect. 9.2.2, calculate average recovery. The average recovery expressed as the mean of the replicate values must be within 70-130 % of the true value for all analytes except *o*-toluidine, which must be within 50-130% of the true value.

9.2.4. MINIMUM REPORTING LEVEL (MRL) CONFIRMATION - Establish a target concentration for the MRL based on the intended use of the method. The MRL may be established by a laboratory for their specific purpose or may be set by a regulatory agency. Establish an Initial Calibration following the procedure outlined in Sect. 10.2. The lowest calibration standard used to establish the Initial Calibration (as well as the low-level Continuing Calibration Check standard) must be at or below the concentration of the MRL. Establishing the MRL concentration too low may cause repeated failure of ongoing QC requirements. Confirm the MRL following the procedure outlined below.

9.2.4.1. Fortify, extract, and analyze seven replicate Laboratory Fortified Blanks (LFBs) at the proposed MRL concentration. These LFBs must contain all method preservatives described in Sect. 8.1.2. Calculate the mean and standard deviation for these replicates. Determine the Half Range for the Prediction Interval of Results (HR_{PIR}) using the equation below

$$HR_{PIR} = 3.963S$$

where:

S = the standard deviation, and 3.963 is a constant value for seven replicates.[1]

9.2.4.2. Confirm that the upper and lower limits for the Prediction Interval of Result (PIR = Mean + HR_{PIR}) meet the upper and lower recovery limits as shown below:

The Upper PIR Limit must be ≤150 percent recovery.

$$\frac{Mean + HR_{PIR}}{Fortified\ Concentration} \times 100\% \leq 150\%$$

The Lower PIR Limit must be ≥ 50 percent recovery.

$$\frac{Mean - HR_{PIR}}{Fortified\ Concentration} \times 100\% \geq 50\%$$

9.2.4.3. The MRL is validated if both the Upper and Lower PIR Limits meet the criteria described above (Sect. 9.2.4.2). If these criteria are not met, the MRL has been set too low by the laboratory and must be demonstrated again at a higher concentration. If a required MRL set by a regulatory body has not been met, the analyst should evaluate possible problems in the execution of the extraction steps, and/or possible problems with instrument sensitivity. Reattempt MRL validation at the required MRL after problems have been addressed.

9.2.4.4. Confirmation of the MRL Using Fortified Matrix Samples *(optional)- This validation procedure may be used in addition to the reagent water confirmation described above. It may be useful in assessing any matrix induced quantitative bias at the MRL.*

Obtain replicate 1 L aliquots of a water sample similar in nature to the ones planned for analysis. If tap waters from both ground and surface water sources are to be analyzed, it is recommended that a surface water sample be selected for verification. Analyze one aliquot using the procedures in this method to verify the absence of analytes of interest. Fortify seven remaining aliquots with the analytes to be measured near the expected MRL, and verify the MRL as described in Sects. 9.2.4.1 through 9.2.4.3.

9.2.5. CALIBRATION CONFIRMATION - Analyze a Quality Control Sample as described in Sect. 9.3.9 to confirm the accuracy of the standards/calibration curve.

9.2.6. DETECTION LIMIT DETERMINATION *(optional) - While DL determination is not a specific requirement of this method, it may be required by various regulatory bodies associated with compliance*

monitoring. It is the responsibility of the laboratory to determine if DL determination is required based upon the intended use of the data.

Replicate analyses for this procedure should be done over at least three days (both the sample extraction and the GC analyses should be done over at least three days). Prepare at least seven replicate LFBs 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. The DLs in Tables 5 and 9 were calculated from LFBs fortified at various concentrations as indicated in the table. The appropriate fortification concentrations will be dependent upon the sensitivity of the GC/MS system used. All preservation reagents listed in Sect. 8.1.2 must also be added to these samples. Analyze the seven (or more) replicates through all steps of Sects. 11 and 12.

Note: If an MRL confirmation data set meets these requirements, a DL may be calculated from the MRL confirmation data, and no additional analyses are necessary.

Calculate the *DL* using the following equation:

$$DL = s \times t_{(n-1,\,1-\alpha=0.99)}$$

where:

$t_{(n\text{-}1,\ 1\text{-}\alpha=0.99)}$ = 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.

9.3. ONGOING QC REQUIREMENTS - This section summarizes the ongoing QC criteria that must be followed when processing and analyzing Field Samples.

9.3.1. LABORATORY REAGENT BLANK (LRB) - An LRB is required with each extraction batch of up to 20 Field Samples to confirm that potential background contaminants are not interfering with the identification or quantitation of target analytes. If the LRB produces a peak within the retention time window of any analyte that would prevent the determination of that analyte, locate 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 other contaminants that interfere with the measurement of method analytes must be at or below $^1/_3$ of the MRL. Blank contamination may be estimated by extrapolation, if the concentration is below the lowest calibration standard. Although this procedure is not allowed for sample

results as it may not meet data quality objectives, it can be useful in estimating background concentrations. If any of the method analytes are detected in the LRB at concentrations greater than $^1/_3$ of the MRL, then all data for the problem analyte(s) must be considered invalid for all samples in the extraction batch.

Note: It is extremely important to evaluate background values of analytes that commonly occur in LRBs. The MRL must be set at a value greater than three times the mean concentration observed in replicate LRBs. If LRB values are highly variable, setting the MRL to a value greater than the mean LRB concentration plus three times the standard deviation may provide a more realistic MRL.

9.3.2. CONTINUING CALIBRATION CHECK (CCC) - CCC Standards are analyzed at the beginning of each analysis batch, after every ten Field Samples, and at the end of the analysis batch. See Sect. 10.3 for concentration requirements and acceptance criteria.

9.3.3. LABORATORY FORTIFIED BLANK (LFB) - An LFB is required with each extraction batch of up to 20 Field Samples. The fortified concentration of the LFB must be rotated between low, medium, and high concentrations from batch to batch. The low concentration LFB must be as near as practical to, but no more than two times the MRL. Similarly, the high concentration LFB should be near the high end of the calibration range established during the initial calibration (Sect. 10.2). Results of the low-level LFB analyses must be 50-150% of the true value. Results of the medium and high-level LFB analyses must be 70-130% of the true value for all analytes except *o*-toluidine, which may be between 50-130% of the true value. If the LFB results do not meet these criteria for target analytes, then all data for the problem analyte(s) must be considered invalid for all samples in the extraction batch.

9.3.4. MS TUNE CHECK - A complete description of the MS Tune Check is found in Sect. 10.2.1. The acceptance criteria for the MS Tune Check are summarized in Table 2. The MS Tune Check must be performed each time a major change is made to the mass spectrometer, and prior to establishing and/or re-establishing an initial calibration (Sect. 10.2). Daily DFTPP analysis is not required.

Note: The tune check is performed in full scan mode, even if samples will be analyzed in SIM mode.

9.3.5. INTERNAL STANDARDS (IS) - The analyst must monitor the peak areas of the ISs in all injections during each analysis day. The peak area for each IS in any chromatographic run must not deviate by more than ±50% from the mean response in the CAL solutions analyzed for the initial analyte

calibration. In addition, the peak areas of ISs must not deviate by more than ± 30% from the most recent CCC. If the IS areas in a chromatographic run do not meet these criteria, inject a second aliquot of that standard or extract.

9.3.5.1. If the reinjected aliquot produces acceptable internal standard responses, report results for that aliquot.

9.3.5.2. If the reinjected aliquot is a sample extract and fails again, the analyst should check the calibration by evaluating the CCCs within the analysis batch. If the CCCs are acceptable, extraction of the sample may need to be repeated provided the sample is still available and within the holding time. Otherwise, report results obtained from the reinjected extract, but annotate as "suspect/IS area." Alternatively, collect a new sample and reanalyze.

9.3.5.3. If the reinjected aliquot is a CAL standard, take remedial action (Sect. 10.3.3).

9.3.6. SURROGATE RECOVERY - Surrogate standards are fortified into the aqueous portion of all samples, LRBs, LFBs, CCCs, LFSMs, and LFSMDs prior to extraction. They are also added to the calibration standards. The surrogates are a means of assessing method performance from extraction to final chromatographic measurement. Calculate the recovery (%R) for each surrogate using the equation

$$\%R = \left(\frac{A}{B}\right) \times 100$$

where:

A = measured surrogate concentration for the QC or Field Sample, and
B = fortified concentration of the surrogate.

9.3.6.1. Surrogate recovery must be within 70-130% of the true value for quinoline-d_7 and within 50-130% for *o*-toluidine-d_9. When surrogate recovery from a sample, blank, or CCC is outside the acceptable range, check 1) calculations to locate possible errors, 2) the integrity of the surrogate analyte solution, 3) contamination, and 4) instrument calibration. Correct the problem and reanalyze the extract.

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

9.3.6.3. If the extract reanalysis fails the recovery criterion, the analyst should check the calibration by evaluating the CCCs within the

analysis batch. If the CCCs fail the criteria of Sect. 9.3.6.1, recalibration is in order per Sect.10.2. If the calibration standard is acceptable, extraction of the sample should be repeated, provided the sample is still available and within the holding time. If the re-extracted sample also fails the recovery criterion, report all data for that sample as "suspect/surrogate recovery" to inform the data user that the results are suspect due to surrogate recovery.

9.3.7. LABORATORY FORTIFIED SAMPLE MATRIX (LFSM) - Within each analysis batch of up to 20 Field Samples, analyze a minimum of one LFSM. The native concentrations of the analytes in the sample matrix must be determined in a second duplicate sample and subtracted from the measured values in the LFSM. If a variety of different sample matrices are analyzed regularly, for example, drinking water from ground water and surface water sources, performance data must be collected for each source.

9.3.7.1. Prepare the LFSM by fortifying a Field Duplicate with an appropriate amount of analyte PDS (Sect. 7.2.3.2). Select a fortification concentration that is greater than or equal to the matrix background concentration, if known. Selecting a duplicate sample that has already been analyzed aids in the selection of an appropriate fortification concentration. If this is not possible, use historical data. If historical data are unavailable, rotate the fortifying concentrations for LFSMs between low, medium and high concentrations based on the calibration range.

9.3.7.2. Calculate the percent recovery (%*R*) for each analyte using the equation

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

where:

A = measured concentration in the fortified sample
B = measured concentration in the unfortified sample
C = fortification concentration.

Note: LFSMs and LFSMDs fortified at concentrations near the MRL, where the associated Field Sample contains native analyte concentrations above the DL but below the MRL, should be corrected for the native levels in order the obtain meaningful %R values. This example, and the LRB extrapolation (Sect. 9.3.1), are the only permitted uses of analyte results below the MRL.

9.3.7.3. Analyte recoveries may exhibit matrix bias. For samples fortified at or above their native concentration, recoveries should be within 70-130% (50-130% for *o*-toluidine), except for low-level fortification near or at the MRL (within a factor of two times the MRL concentration) where 50-150% recoveries are acceptable. If the accuracy of any analyte falls outside the designated range, and the laboratory performance for that analyte is shown to be in control in the CCCs, the recovery is judged to be matrix biased. The quantitative result for that analyte in the unfortified sample is labeled "suspect/matrix" to inform the data user that the quantitative results may be suspect due to matrix effects.

9.3.8. FIELD DUPLICATE OR LABORATORY FORTIFIED SAMPLE MATRIX DUPLICATE (FD or LFSMD) - Within each extraction batch, analyze a minimum of one Field Duplicate (FD) or Laboratory Fortified Sample Matrix Duplicate (LFSMD). Duplicates check the precision associated with sample collection, preservation, storage, and laboratory procedures. If target analytes are not routinely observed in Field Samples, an LFSMD should be analyzed rather than an FD.

9.3.8.1. Calculate the relative percent difference (*RPD*) for duplicate measurements (*FD1* and *FD2*) using the equation

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

9.3.8.2. RPDs for Field Duplicates should be ≤ 30 %. Greater variability may be observed when Field Duplicates have analyte concentrations that are within two times the MRL. At these concentrations, Field Duplicates should have RPDs that are ≤ 50%. If the RPD of any analyte falls outside the designated range, and the laboratory performance for that analyte is shown to be in control in the CCC, the recovery is judged to be affected by the matrix. The result for that analyte in the unfortified sample is labeled "suspect/matrix" to inform the data user that the quantitative results may be suspect due to matrix effects.

9.3.8.3. If an LFSMD is analyzed instead of a Field Duplicate, calculate the relative percent difference (RPD) for duplicate LFSMs (LFSM and LFSMD) using the equation

$$RPD = \frac{|LFSM - LFSMD|}{(LFSM + LFSMD)/2} \times 100$$

9.3.8.4. RPDs for duplicate LFSMs should be ≤ 30% for samples fortified at or above their native concentration. Greater variability may be observed when LFSMs are fortified at analyte concentrations that are within two times the MRL. LFSMs fortified at these concentrations should have RPDs that are ≤ 50% for samples fortified at or above their native concentration. If the RPD of any analyte falls outside the designated range, and the laboratory performance for that analyte is shown to be in control in the CCC, the recovery is judged to be affected by the matrix. The result for that analyte in the unfortified sample is labeled "suspect/matrix" to inform the data user that the quantitative results may be suspect due to matrix effects.

9.3.9. QUALITY CONTROL SAMPLES (QCS) - As part of the IDC (Sect. 9.2), each time a new Analyte PDS (Sect. 7.2.3.2) or CAL solutions (7.2.4) are prepared, or at least quarterly, analyze a QCS sample from a source different from the source of the calibration standards. If a second vendor is not available then a different lot of the standard should be used. The QCS should be prepared and analyzed just like a CCC. Acceptance criteria for the QCS are identical to the CCCs; the calculated amount for each analyte must be ± 30% of the expected value. If measured analyte concentrations are not of acceptable accuracy, check the entire analytical procedure to locate and correct the problem. If the discrepancy is not resolved, one of the standard materials may be degraded or otherwise compromised and a third standard must be obtained.

9.4. METHOD MODIFICATION QC REQUIREMENTS - The analyst is permitted to modify GC columns, GC conditions, GC injection techniques, extract evaporation techniques, MS conditions and quantitation ions (QIs). However, each time such method modifications are made, the analyst must repeat the procedures of the IDC (Sect. 9.2).

9.4.1. Each time method modifications are made, the analyst must repeat the procedures of the IDC (Sect. 9.2) and verify that all QC criteria can be met in ongoing QC samples (Sect. 9.3).

9.4.2. Each time method modifications are made, the analyst is also required to evaluate and document method performance for the proposed method modifications in real matrices that span the range of waters that the laboratory analyzes. This additional step is required because modifications that perform acceptably in the IDC, which is conducted in reagent water, can fail ongoing method QC requirements in real matrices. This is particularly important for methods subject to matrix effects. If, for example, the laboratory analyzes finished waters from both surface and groundwater municipalities, this requirement can be accomplished by assessing precision and accuracy (Sects. 9.2.2 and 9.2.3) in an analyte fortified surface water

with moderate to high TOC (e.g., 2 mg/L or greater) and an analyte fortified hard groundwater (e.g., 250 mg/L or greater as calcium carbonate).

9.4.3. The results of Sects. 9.4.1 and 9.4.2 must be appropriately documented by the analyst and should be independently assessed by the laboratory's Quality Assurance (QA) officer prior to analyzing Field Samples. When implementing method modifications, it is the responsibility of the laboratory to closely review the results of ongoing QC, and in particular, the results associated with the LFSMs (Sect. 9.3.7), FDs or LFSMDs (Sect. 9.3.8), CCCs (Sect. 9.3.2), and the IS area counts (Sect. 9.3.5). If repeated failures are noted, the modification must be abandoned.

10. CALIBRATION AND STANDARDIZATION

10.1. Demonstration and documentation of acceptable mass spectrometer tune and initial calibration is required before performing the IDC and prior to analyzing Field Samples. The MS tune check and initial calibration must be repeated each time a major instrument modification is made, or maintenance is performed.

10.2. INITIAL CALIBRATION

10.2.1. MS TUNE/MS TUNE CHECK - 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 the DFTPP solution (Sect. 7.2.5) into the GC/MS system. Acquire a mass spectrum that includes data for *m/z* 45 to 450. The scan time should be set so that a minimum of five scans are acquired during the elution of the chromatographic peak. Seven to ten scans per chromatographic peak are recommended. Use a single spectrum at the apex of the DFTPP peak, an average spectrum of the three highest points of the peak, or an average spectrum across the entire peak to evaluate the performance of the system. If the DFTPP mass spectrum does not meet all criteria in Table 2, the MS must be retuned and adjusted to meet all criteria before proceeding with the initial calibration. The tune check should be conducted as described above for both full scan and SIM MS operation.

10.2.2. INSTRUMENT CONDITIONS - Operating conditions used during method development are described below. Conditions different from those described may be used if QC criteria in Sect. 9 are met. Different conditions include alternate GC columns, temperature programs, MS conditions, and injection techniques and volumes, such as cold on-column and large volume injections. Equipment specifically designed for alternate types of injections must be used if these alternate options are selected.

10.2.2.1. GC Conditions - Inject a 1-µL aliquot into a hot, splitless injection port held at 275 ºC with a pressure pulse of 20 psi and a split delay

of 1 min. The temperature program is as follows: initial oven temperature of 60 ºC, hold for 1 min, ramp at 10 ºC/min to a final temperature of 290 ºC and hold for 1 min. The GC is operated at a constant carrier gas flow rate of 1 mL/min. Total run time is approximately 25 min. Begin data acquisition at about seven min.

10.2.2.2. Full Scan MS Acquistion Parameters - Select a scan range that allows the acquisition of a mass spectrum for each of the method analytes, which includes all of the major fragments *m/z* 45 and above. Adjust the cycle time to measure at least five spectra during the elution of each GC peak. Seven to ten scans across each GC peak are recommended. The chromatogram may be divided into time windows, also known as segments or periods, with different scan ranges for each time window. Minimizing the scan range for each time window may enhance sensitivity. If the chromatogram is divided into time windows, the laboratory must ensure that each method analyte elutes entirely within the proper window during each analysis. This can be achieved by carefully monitoring the retention times of all ISs and SURs in each sample, and carefully monitoring the retention times of all method analytes in CCCs, LFBs and LFSMs. This requirement does not preclude continuous operation by sequencing multiple analysis batches; however, the entire analysis batch is invalid if one or more analyte peaks have drifted outside of designated time windows in the CCC at the beginning or end of the analysis batch.

10.2.2.3. SIM MS Acquistion Parameters - Prior to selecting SIM parameters, analyze a mid- to high-concentration CAL in full scan mode. Select one primary QI and at least one secondary ion for confirmation. Suggested QIs and secondary ions for all method analytes are designated in Table 1, but these may be modified. An internal standard for each analyte is also designated in Table 1. Verify that the primary ion is free from interferences due to an identical fragment ion in any overlapping peak(s). Selection of the QI should be based on the best compromise between the intensity of the signal for that ion and the likelihood and intensity of interferences. The most intense ion may not be the best QI. However, the QI and secondary ions must be $\geq$30% relative abundance. Adjust the cycle time to measure at least five spectra during the elution of each GC peak. If the chromatogram is divided into time windows, the laboratory must ensure that each method analyte elutes entirely within the proper window during each analysis. This can be achieved by carefully monitoring the retention times of all ISs and SURs in each sample, and carefully monitoring the retention times of all method analytes in CCCs, LFBs and LFSMs. This requirement does not preclude continuous

operation by sequencing multiple analysis batches; however, the entire analysis batch is invalid if one or more analyte peaks have drifted outside of designated time windows in the CCC at the beginning or end of the analysis batch. The SIM parameters used during method development for selected analytes are provided in Table 6 as an example.

10.2.2.4. Alternating Full and SIM Scan Modes - Alternating full and SIM scan modes during a single sample acquisition is permitted if the minimum number of scans across each GC peak acquired in each mode is maintained (as specified in Sect. 10.2.2.2 and 10.2.2.3), i.e., a minimum of five scans in full scan mode and a minimum of five scans in SIM mode. If the chromatogram is divided into time windows, the laboratory must ensure that each method analyte elutes entirely within the proper window during each analysis. This can be achieved by carefully monitoring the retention times of all ISs and SURs in each sample, and carefully monitoring the retention times of all method analytes in CCCs, LFBs and LFSMs. This requirement does not preclude continuous operation by sequencing multiple analysis batches; however, the entire analysis batch is invalid if one or more analyte peaks have drifted outside of designated time windows in the CCC at the beginning or end of the analysis batch.

10.2.3. CALIBRATION SOLUTIONS - To establish a calibration range extending two orders of magnitude, prepare a set of at least six calibration standards as described in Sect. 7.2.4. The lowest concentration CAL must be at or below the MRL for each method analyte. The MRL must be confirmed using the procedure outlined in Sect. 9.2.4 after establishing the initial calibration.

Note: This method contains analytes that vary with regard to instrument sensitivity. If the analytes of interest differ in response, and the CAL standards have been prepared such that all analytes are at the same concentration, more standards may be needed to obtain the minimum six CAL points for each analyte. Analytes with poor response may not be observed in the low concentration standards, and the most responsive analytes may saturate the detector at the higher concentrations. It is likely that the calibration range for all analytes will not be the same. The use of custom calibration standards with varying analyte concentrations based on their relative instrument response is a possible alternative.

10.2.4. CALIBRATION - Calibrate the GC/MS system using the internal standard technique in either full scan, SIM or alternating full scan/SIM mode. Subsequent sample analysis must be performed in the same calibration mode using identical instrument conditions and parameters. Internal standard designations and suggested QIs for all method analytes are listed in

Table 1. Table 6 contains example scanning parameters for selected analytes in SIM mode. Linear or quadratic calibrations may be used. Weighting may be used at the discretion of the analyst.

10.2.5. CALIBRATION ACCEPTANCE CRITERIA - Validate the initial calibration curves by using the regression equations to calculate the concentration of each analyte as an unknown in each of the analyses used to generate the curves. Calibration points that are ≤ MRL must calculate to be within ± 50% of their true value. All other calibration points must calculate to be within ± 30% of their true value. If these criteria cannot be met, the analyst may eliminate either the highest or lowest point on the curve and reassess the acceptance criteria. If the acceptance criteria still cannot be met, the analyst will have difficulty meeting ongoing QC criteria. **It is highly recommended that corrective action be taken before proceeding.** This may include one or more of the following actions: analyze the calibration standards, further restrict the range of calibration, or select an alternate method of calibration. The data presented in this method were obtained using either linear regression or quadratic fits. Quadratic fit calibrations should be used with caution, because the non-linear area of the curve may not be reproducible.

10.3. CONTINUING CALIBRATION CHECK (CCC) - Analyze a CCC to verify the initial calibration at the beginning of each analysis batch, after every tenth Field Sample, and at the end of each analysis batch. The beginning CCC for each analysis batch must be at or below the MRL. This CCC verifies instrument sensitivity prior to the analysis of samples. Alternate subsequent CCCs between the remaining calibration levels.

Note: If standards have been prepared such that all analytes are not in the same calibration standard (or all low CAL points are not in the same CAL standard), it may be necessary to analyze more than one CCC to meet this requirement. Alternatively, it may be cost effective to prepare or obtain a customized standard to meet this criterion.

10.3.1. Verify that the peak area of the QI of each IS has not changed by more than ± 50% from the mean peak area measured for that IS during initial calibration. In addition, verify that the peak area of the QI of each of the two ISs are within ± 30% from the most recently analyzed CCC. If these limits are exceeded, remedial action must be taken (Sect. 10.3.3). Control charts are useful aids in documenting system sensitivity changes.

10.3.2. Calculate the concentration of each analyte and surrogate in the CCC. The calculated amount for each analyte for medium and high level CCCs must be ± 30% of the true value. The calculated amount for the lowest calibration level for each analyte must be within ± 50% of the true value. If these criteria are not met, then all data for the problem analyte must be considered

invalid, and remedial action (Sect. 10.3.3) must be taken. Recalibration may be required. 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 CCC at the end of an analysis batch fails because the calculated concentration is greater than 130% (150% for the low-level CCC) for a particular target analyte, and Field Sample extracts show no detection for that target compound, non-detects may be reported without reanalysis.

10.3.3. REMEDIAL ACTION - Failure to meet CCC QC performance criteria may require remedial action. Major maintenance such as cleaning an ion source, cleaning the mass analyzer, replacing filament assemblies, or replacing the GC column, etc., will require returning to the initial calibration step (Sect. 10.2).

11. PROCEDURE

11.1. This section describes the procedures for sample preparation, SPE, final extract preparation and storage, and extract analysis. Important aspects of this analytical procedure include proper preparation of laboratory glassware, sample containers (Sect. 4.1), and sample collection and storage (Sect. 8). Procedures for data analysis and calculations are described in Sect. 12.

11.2. SAMPLE PREPARATION

11.2.1. Samples are preserved, collected and stored as described in Sect. 8. All field and QC samples, including LRBs and LFBs, must contain the preservatives listed in Sect. 8.1.2. Mark the level of the sample on the outside of the sample bottle for later sample volume determination. If using weight to determine volume (Sect. 11.6), weigh the bottle and sample contents before extraction.

11.2.2. Add an aliquot of the SUR PDS(s) to each sample to be extracted. For full scan method development work, a 10-µL aliquot of each of the 500-µg/mL SUR PDSs (Sect. 7.2.2) was added to 1 L samples for a final concentration of 5.0 µg/L.

11.2.3. If the sample is an LFB, LFSM, or LFSMD, add the necessary amount of Analyte Fortification Solution(s) (Sect. 7.2.3.2). Swirl each sample to ensure all components are mixed.

11.2.4. Proceed with sample extraction using the SPE procedure described in Sect. 11.3.

11.3. CARTRIDGE SPE (6 mL) PROCEDURE - This cartridge extraction procedure may be carried out in a manual mode or by using a robotic or automatic sample

preparation device. This section describes the SPE procedure using the equipment outlined in Sects. 6.9-6.11 in its simplest, least expensive mode without the use of a robotic system. The manual mode described below was used to collect data presented in Sect. 17. The extraction steps are written for an individual sample, but multiple samples may be extracted simultaneously depending upon the extraction equipment used.

11.3.1. CARTRIDGE CLEANUP - Install the SPE cartridge (Oasis HLB, Phenomenex Strata-X, or Agilent Bond Elut Plexa as described in Sect. 6.9.1) into the vacuum manifold. For alternate sorbents, see Sect. 6 regarding sorbent equivalency. Wash the cartridge with 5 mL of DCM by adding the solvent to the cartridge; draw about half through the sorbent, soak for about one min, then draw the remaining solvent through the cartridge.

11.3.2. CARTRIDGE CONDITIONING - Polymeric SPE sorbents are water wettable (unlike C-18 SPE sorbents). Many manufacturers of polymeric SPE media suggest that their products do not need to be kept wet during conditioning and sample processing. However, little data have been shown to demonstrate performance under those conditions for the wide variety of environmental contaminants using these media. Therefore, in the interest of providing a single procedure for the sorbents and analytes in this method, the authors chose to use procedures similar to those used with C-18 where the sorbent is kept wet.

11.3.2.1. CONDITIONING WITH METHANOL - Add 10 mL MeOH to the cartridge and allow it to soak for about one min. Then draw most of the MeOH through. A layer of MeOH must be left on the surface of the cartridge. Do NOT let the cartridge go dry from this point on until the end of sample extraction.

11.3.2.2. CONDITIONING WITH WATER - Rinse the cartridge by adding 10 mL of reagent water to the cartridge and drawing most through, again leaving a layer on the surface of the cartridge.

11.3.3. SAMPLE EXTRACTION - Attach a PTFE transfer line to the top of the cartridge. Insert the opposite end of the transfer line into the sample to be extracted. Apply vacuum to begin the extraction. Adjust the vacuum so that the sample passes through the cartridge at a rate of about 10 mL/min. Pass the entire sample volume through the cartridge, draining as much water from the sample container as possible. Rinse the bottle with 10 mL LRW and transfer to the cartridge under full vacuum. Rinsing the sorbent with LRW prior to drying helps remove sample preservatives from the sorbent so they are not transferred to the extract. Remove the sample transfer line from the cartridge and dry by maintaining vacuum for about 10 min.

11.3.4. CARTRIDGE ELUTION - Remove the manifold lid (but do not remove the cartridge) and insert a suitable collection tube to contain the eluent (15-mL collection vial). Reassemble the apparatus. Add ~2 mL of acetone to the sample bottle, and rinse the inside walls thoroughly. Allow the solvent to settle to the bottom of the bottle, then transfer it to the cartridge. Draw the solvent through the cartridge by applying vacuum. Add 5 mL of DCM to the sample bottle, and rinse the inside walls thoroughly. Allow the solvent to settle to the bottom of the bottle, and then transfer to the cartridge by applying vacuum. Draw about half of the solvent through the cartridge, cut off vacuum at the cartridge, and allow the cartridge to soak for one min. Draw the remaining solvent through the cartridge. Repeat the above step with another 5 mL of DCM. Shut off vacuum, remove the transfer line, and remove the collection vial. Proceed to Sects. 11.4 and 11.5 to dry and concentrate the extract.

11.4. DRYING THE EXTRACT - Transfer the combined eluent through a drying tube containing about 7 g of anhydrous sodium sulfate. Rinse the collection tube with 3 mL DCM, and then put the DCM through the sodium sulfate. Collect the dried extract and DCM rinse in a clean collection tube.

11.5. EXTRACT CONCENTRATION - Concentrate the extract to about 0.7 mL under a gentle stream of nitrogen gas in a warm water bath (at ~ 40 ºC). Do not blow down samples to less than 0.5 mL, because the more volatile compounds will exhibit diminished recovery. Transfer the extract to a 1-mL volumetric flask and add the internal standards (Sect. 7.2.1). Rinse the collection tube that held the dried extract with small amounts of DCM and add to the volumetric flask to bring the volume up to the 1-mL mark. Transfer to an autosampler vial. Store extracts at -5 ºC or less until analysis.

11.6. SAMPLE VOLUME OR WEIGHT DETERMINATION - Use a graduated cylinder to measure the volume of water required to fill the original sample bottle to the mark made prior to extraction (Sect. 11.2.1). Determine volume to the nearest 10 mL for use in the final calculations of analyte concentration (Sect. 12.2). If using weight to determine volume, reweigh the empty sample bottle. Subtract the empty bottle weight from the weight of the original combined bottle/sample weight measured in Sect. 11.2.1. To calculate the sample volume from its weight , assume a sample density of 1 g/mL. Use the calculated sample volume for analyte concentration calculations in Sect.12.2.

11.7. ANALYSIS OF SAMPLE EXTRACTS

11.7.1. Establish instrument operating conditions as described in Sect. 10.2.2. Confirm that compound separation and resolution are similar to those summarized in Table 1 and Figure 1.

11.7.2. Establish a valid initial calibration following the procedures outlined in Sect. 10.2 or confirm that the calibration is still valid by running a CCC as described in Sect. 10.3. If establishing an initial calibration for the first time, complete the IDC as described in Sect. 9.2.

11.7.3. Analyze aliquots of Field and QC Samples at appropriate frequencies (Sect. 9) with the GC/MS conditions used to acquire the initial calibration and the CCC. At the conclusion of data acquisition, use the same software that was used in the calibration procedure to tentatively identify peaks in predetermined retention time windows of interest. Use the data system software to examine the ion abundances of components of the chromatogram to confirm identity.

12. DATA ANALYSIS AND CALCULATIONS

12.1. COMPOUND IDENTIFICATION - Identify sample components by comparison of their retention times and mass spectra to the reference retention times and spectra in the user-created data base as follows:

12.1.1. Establish an appropriate retention time window for each analyte, internal standard and surrogate analyte to identify them in QC and Field Sample chromatograms. Ideally, the retention time window should be based on measurements of actual retention time variation for each compound in standard solutions collected on each GC/MS over the course of time. The suggested variation is plus or minus three times the standard deviation of the retention time for each compound for a series of injections. The injections from the initial calibration and from the IDC (Sect. 9.2) may be used to calculate a suggested window size. However, the experience of the analyst should weigh heavily on the determination of an appropriate retention window size.

12.1.2. Each compound should be identified from its reference spectrum obtained during the acquisition of the initial calibration curve. The mass spectrum used for identification of each compound is acquired in the full scan or SIM mode.

12.1.2.1. Full Scan MS Identification - In general, all ions that are present at or above 30% relative abundance in the mass spectrum of the reference standard obtained during calibration should be present in the mass spectrum of the sample component and should agree within an absolute 20%. For example, in full scan mode, 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 10-50%.

12.1.2.2. SIM MS Identification - In SIM mode, all ions monitored in the standard should be present in the SIM mass spectrum of the sample component and relative abundance from integrated peak areas 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 10-50%. Secondary ions should have a relative abundance of ≥30% in the standard. **The IS phenanthrene-d_{10} does not have a secondary ion with a relative abundance of ≥30%, therefore no relative abundance calculation for compound confirmation is required.**

12.1.3. Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing 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. Comparing a background subtracted spectrum to the reference spectrum is suggested. If two or more analytes coelute but 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.

12.1.4. BHA exists as two structural isomers, 2-BHA and 3-BHA, which commonly appear as one chromatographic peak. Structural isomers that produce very similar mass spectra can be explicitly identified only if they have sufficiently different GC retention times. Acceptable resolution is achieved if the height of the valley between two isomer peaks is <25% of the average height of the two isomer peaks. Otherwise, combine the peak areas of the isomers and quantify and identify as an isomeric pair.

12.2. QUANTITATION AND CALCULATIONS

12.2.1. Calculate analyte and surrogate concentrations using the multipoint calibration established in Sect. 10.2. In validating this method, concentrations were calculated by measuring the characteristic ions listed in Table 1. Other ions may be selected at the discretion of the analyst. Do not use daily continuing calibration check data to quantitate analytes in samples. Adjust the final analyte concentrations to reflect the actual sample volume determined in Sect. 11.6. Field Sample extracts that require dilution should be treated as described in Sect. 12.2.2.

12.2.2. If the calculated amount of any analyte exceeds the calibration range of the curve, the extract must be diluted with DCM, with the appropriate amount of additional internal standard added to match the original concentration. Analyze the diluted extract. Acceptable surrogate performance (Sect. 9.3.6) should be determined from the undiluted sample extract. Incorporate the

dilution factor into final concentration calculations. The resulting sample should be documented as a dilution, and MRLs should be adjusted accordingly. If matrix-matched calibration standards are being used, the dilution may be made with DCM, but care should be taken to dilute just enough to position the analyte within the calibration range. Excessive dilution and resulting low concentration may affect the accuracy of the final measurement.

12.2.3. Calculations must utilize all available digits of precision, but final reported concentrations should be rounded to an appropriate number of significant figures (one digit of uncertainty), typically two, and not more than three significant figures.

Note: Some data in Sect. 17 of this method are reported with more than two significant figures. This is done to better illustrate the method performance data.

13. METHOD PERFORMANCE

13.1. PRECISION AND ACCURACY DATA

13.1.1. FULL SCAN GC/MS - Precision and accuracy data were collected from LFBs at three concentration levels using sorbents described in Sect. 6.9.1. Precision and accuracy data were also collected at a single fortified concentration using two challenging water matrices. Tap water matrices were selected to be representative of ground water with high mineral content and surface water with a moderate level of TOC. Precision and accuracy data in both fortified reagent water and fortified matrices are presented in Tables 3 and 4.

13.1.2. SIM GC/MS - The SIM GC/MS analysis option may be used for added analyte sensitivity. Precision and accuracy data were collected using LFBs fortified at three concentration levels. Precision and accuracy data were also collected at a single fortified concentration using two challenging water matrices. Tap water matrices were selected to be representative of ground water with high mineral content and surface water with a moderate level of TOC. Precision and accuracy data in both fortified reagent water and fortified matrices are presented in Tables 7 and 8.

13.2. LCMRLs and DLs

13.2.1. FULL SCAN GC/MS - The DL and LCMRL values for all analytes in full scan mode are presented in Table 5.

13.2.2. SIM GC/MS - The DL and LCMRL values for all analytes in SIM are presented in Table 9.

13.3. SAMPLE STORAGE STABILITY STUDIES - Drinking water samples from a chlorinated surface source were used as a representative matrix for an analyte holding time study in aqueous solution. Replicate samples in amber bottles were preserved as described in Sect. 8, fortified with method analytes, then stored for 48 hours at 10 ºC, followed by storage at 4 ºC until analysis. Randomly selected samples were analyzed in replicate (n=4) on day 0 and at several time points up to the 14 day holding time. Data from days 0, 7 and 14 are presented in Fig. 2. These data were used to establish the 14 day aqueous holding time for method analytes (Sect. 8.4).

Notes:

- Surrogate analytes were not stored in this study, but added at the time of extraction. The data in Fig. 2 for SURs are same day data, obtained for QC purposes.
- Holding time studies conducted during method development indicated moderate analyte losses (more than 10% in 14 days, with increasing loss at subsequent time points) for *o*-toluidine using the sample collection, preservation and holding time procedures in this method. *o*-Toluidine exhibited a loss of 11% at 7 days and 14% at 14 days.

13.4. EXTRACT STORAGE STABILITY STUDIES - Replicate sample extracts (n=4) that were stored at -5 ºC and protected from light, were analyzed on days 0, 7 and 14. Data from these analyses validate the 14 day extract holding time and are presented in Fig. 3.

Notes:

- Surrogate analytes were stored in this study, added at the time of extraction.
- Extract holding time studies conducted during method development indicated significant analyte losses (more than 15% in 14 days, with increasing loss at subsequent time points) for *o*-toluidine using the sample collection, preservation and holding time procedures in this method. *o*-Toluidine in extracts exhibited a loss of 13% at 7 days and 16% at 14 days. The SUR *o*-toluidine-d_9 shows similar losses in extracts over time.

13.5. POTENTIAL PROBLEMS/ PROBLEM COMPOUNDS

13.5.1. MATRIX INDUCED CHROMATOGRAPHIC RESPONSE ENHANCEMENT (MICRE) - BHA has the potential to exhibit a high bias. The bias has been attributed to the phenomenon of MICRE. Examples of this are shown in Table 8 for BHA, which show recovery data for fortified tap waters that approach 130% of the fortified amount. Data in Table 4 show that this phenomenon is related to analyte concentration, since the high bias is not observed at the higher fortified concentration. Although the use of matrix-matched standards will improve quantitative accuracy for BHA, a bias may still be observed. In addition to the use of matrix matched

standards, "priming" the GC system by injecting one or more sample extracts at the beginning of each analytical sequence was found to reduce matrix enhancement effects. Literature citations suggest that temperature programmed or cold injections may also reduce matrix enhancement,[12,13,18] although trials of these types of injections during method development showed little or no improvement. The biased data were instrument dependent, and not related to the sorbent used. Similar tap water extracts generated using different sorbent options listed in this method, showed similarly high biased data on the same instrument.

Depending upon the intended use of the data, the analyst should consider performing the MRL verification (Sect. 9.2.4.4) in fortified matrices similar to the samples being analyzed.

13.5.2. OVERDRYING SPE MEDIA PRIOR TO ELUTION – If SPE media is over dried between sample loading and solvent elution by drawing excessive amounts of room air through the media, analytes that can undergo oxidation may be observed to have low recoveries. An example of an analyte that may be affected is *o*-toluidine.

13.6. MULTIPLE LABORATORY DEMONSTRATION - The performance of this method was demonstrated by three independent laboratories. These laboratories produced acceptable results and provided valuable method performance data. The author wishes to acknowledge the assistance of the analysts and managers at the laboratories listed below for their participation in the multi-laboratory study.

13.6.1. Dr. Yongtao Li and Mr. William Davis of Eurofins Eaton Analytical, Inc., South Bend, IN.

13.6.2. Mr. Kevin Durk and Ms. Annmarie Walsh of Suffolk County Water Authority, Hauppauge, NY.

13.6.3. Dr. Andrew Eaton and Mr. Patrick Chapman of Eurofins Eaton Analytical, Inc., Monrovia, CA.

14. POLLUTION PREVENTION

14.1. This method utilizes SPE to extract 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 as compared to 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: Guide to Minimizing Waste in Laboratories" available on-line from the American Chemical Society at http://www.acs.org/content/dam/acsorg/about/governance/committees/chemicalsafety/publications/less-is-better.pdf.

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.

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17. TABLES, FIGURES AND VALIDATION DATA

Table 1. Retention Times (RTs), Suggested Quantitation Ions (QIs), Suggested SIM Secondary Ions, and Suggested Internal Standard Reference

Peak Identification #, Figure 1	RT (min)	Internal Standards, Analytes and Surrogates	IS Ref. #	QI (*m/z*)	SIM Secondary Ion(s) (*m/z*)	Comments
5	12.66	acenaphthene-d_{10} (IS 1)		162	164	a
7	16.39	phenanthrene-d_{10} (IS 2)		188	--*	a
1	7.73	*o*-toluidine-d_9 (SUR)	1	114	112	b
2	7.78	*o*-toluidine	1	106	107	b
3	9.84	quinoline-d_7 (SUR)	1	136	108	b
4	9.86	quinoline	1	129	102	b
6	13.68	BHA	2	180	137	b, c
8	18.36	dimethipin	2	54	118	b

* No secondary ion present at ≥30% relative abundance.

Comment Key

a. PDS solvent, acetone

b. PDS solvent, methanol

c. Potential to exhibit matrix induced chromatographic response enhancement was observed during method development. This assessment was done based on a peak area comparison of a standard prepared in solvent compared to a matrix-matched standard, both at a concentration of 0.1 ng/µL. If the matrix-matched standard area was ≥130% of the solvent prepared standard, the analyte was flagged as having the potential for matrix induced chromatographic response enhancement.

Table 2. Ion Abundance Criteria for Decafluorotriphenyl Phosphine (DFTPP)[a]

Mass (*m/z*)	Relative Abundance Criteria	Purpose of Checkpoint[b]
68	<2% of *m/z* 69	Low-mass resolution
69	present	Low-mass resolution
70	<2% of *m/z* 69	Low-mass resolution
197	<2% of *m/z* 198	Mid-mass resolution
198	present [c]	Mid-mass resolution and sensitivity
199	5-9% of *m/z* 198	Mid-mass resolution and isotope ratio
365	>1% of base peak	Baseline threshold
441	<150% of *m/z* 443	High-mass resolution
442	present [c]	High-mass resolution and sensitivity
443	15-24% of *m/z* 442	High-mass resolution and isotope ratio

a. These ion abundance criteria have been developed specifically for target compound analysis as described in this method. Adherence to these criteria may not produce spectra suitable for identifying unknowns by searching commercial mass spectral libraries. If the analyst intends to use data generated with this method to identify unknowns, adherence to stricter DFTPP criteria as published in previous methods[19] is recommended.
b. All ions are used primarily to check the mass accuracy of the mass spectrometer and data system, and this is the most important part of the performance test. The three sets of resolution checks, which include natural abundance isotope ratios, constitute the next most important part of the performance test, followed by the correct setting of the baseline threshold, as indicated by the presence of *m/z* 365.
c. Either *m/z* 198 or 442 is typically the base peak.

Table 3. Precision and Accuracy Data Obtained for Method Analytes Extracted from Fortified Reagent Water at Three Concentrations; Full Scan GC/MS Analyses

Analytes	Fortified Conc. 0.10 µg/L* n=4		Fortified Conc. 1.0 µg/L* n=4		Fortified Conc. 5.0 µg/L* n=4	
	Mean % Recovery	RSD	Mean % Recovery	RSD	Mean % Recovery	RSD
o-toluidine-d_9 (SUR)	87.2	1.7	90.8	1.9	89.0	3.0
o-toluidine	101	24	94.2	2.9	84.6	2.3
quinoline-d_7 (SUR)	103	0.70	104	3.9	105	1.7
quinoline	123	16	112	2.7	99.2	1.1
BHA	110	13	104	2.8	90.8	2.5
dimethipin	91.5	9.2	105	5.1	99.0	2.3

* Surrogate concentrations are 5.0 µg/L

Table 4. Precision and Accuracy Data Obtained for Method Analytes Extracted from Fortified Finished Drinking Waters from Ground and Surface Water; n=4 for Each Matrix; Full Scan GC/MS Analyses

Analytes	Fortified Conc. (µg/L)	Ground Water[a]		Surface Water[b]	
		Mean % Recovery[c]	RSD	Mean % Recovery[c]	RSD
o-toluidine-d_9 (SUR)	1.0	87.0	1.7	73.1	6.1
o-toluidine	1.0	86.0	2.2	71.3	1.3
quinoline-d_7 (SUR)	1.0	98.5	1.4	89.3	4.2
quinoline	1.0	97.6	1.2	86.6	2.6
BHA	1.0	99.2	7.5	97.9	3.5
dimethipin	1.0	106	3.7	93.4	3.5

a. Tap water from a ground water source with high mineral content. Tap water hardness was 376 mg/L as calcium carbonate.
b. Tap water from a surface water source. TOC of 2.0 mg/L.
c. Recoveries have been corrected to reflect the native amount in the unfortified matrix water.

Table 5. DLs and LCMRLs (µg/L) Calculated from Replicate Analyses of Fortified Reagent Water Samples Analyzed in Full Scan GC/MS Mode

Analytes	DL*	Fortified conc. of DL replicates	LCMRL
o-toluidine	0.007	0.05	0.011
quinoline	0.036	0.05	0.084
BHA	0.044	0.05	0.062
dimethipin	0.037	0.05	0.075

* DL calculated from eight replicates.

Table 6. Example SIM Parameters for Method Analytes

SIM Segment	Compound	RT (min)	QI (*m/z*)	Secondary Ion(s) (*m/z*)	Dwell Time (ms)	Scan Rate (scan/sec)
# 1	*o*-toluidine-d_9 (SUR)	8.84	114	112	75	3.1
	o-toluidine	8.89	106	107		
# 2	quinoline-d_7 (SUR)	11.05	136	108	75	3.1
	quinoline	11.07	129	102		
# 3	acenaphthene-d_{10} (IS 1)	13.91	162	164	75	3.1
	BHA	14.92	180	137		
# 4	phenanthrene-d_{10} (IS 2)	17.77	188	--*	100	8.3
# 5	dimethipin	19.83	54	118	100	4.5

* No secondary ion present at ≥30% relative abundance.

Table 7. Precision and Accuracy Data Obtained for Method Analytes Extracted from Fortified Reagent Water at Three Concentrations; SIM GC/MS Analyses

Analytes	Fortified Conc. 0.01 µg/L* n=4		Fortified Conc. 0.10 µg/L* n=4		Fortified Conc. 0.50 µg/L* n=4	
	Mean % Recovery	RSD	Mean % Recovery	Mean % Recovery	Mean % Recovery	RSD
o-toluidine-d_9 (SUR)	88.9	3.2	85.3	6.8	91.4	9.4
o-toluidine	98.8	22	97.5	6.5	101	8.4
quinoline-d_7 (SUR)	107	1.8	107	3.2	102	4.3
quinoline	112	2.5	93.5	3.3	105	5.3
BHA	137	11	116	9.0	112	8.9
dimethipin	121	15	126	2.9	116	1.2

* Surrogate concentrations are 0.50 µg/L.

Table 8. Precision and Accuracy Data Obtained for Method Analytes Extracted from Fortified Finished Drinking Waters from Ground and Surface Water; n=4 for Each Matrix; SIM GC/MS Analyses

Analytes	Fortified Conc. (µg/L)	Ground Water[a]		Surface Water[b]	
		Mean % Recovery[c]	RSD	Mean % Recovery[c]	RSD
o-toluidine-d_9 (SUR)	0.10	90.4	3.4	75.1	3.4
o-toluidine	0.10	87.7	2.1	71.8	4.5
quinoline-d_7 (SUR)	0.10	103	3.0	125	2.5
quinoline	0.10	108	2.9	116	3.3
BHA	0.10	124	2.6	127	2.2
dimethipin	0.10	106	2.4	102	2.7

a. Tap water from a ground water source with high mineral content. Tap water hardness was 359 mg/L as calcium carbonate.
b. Tap water from a surface water source. TOC of 5.7 mg/L.

Table 9. DLs and LCMRLs (µg/L) Calculated from Replicate Analyses of Fortified Reagent Water Samples Analyzed in SIM GC/MS Mode

Analytes	DL*	Fortified conc. of DL replicates	LCMRL
o-toluidine	0.001	0.005	0.003
quinoline	0.003	0.005	0.005
BHA	0.003	0.005	0.013
dimethipin	0.001	0.005	0.003

* DL calculated from eight replicates.

Table 10. Initial Demonstration of Capability (IDC) and Quality Control (QC) Requirements (Summary)

Method Reference	Requirement	Specification and Frequency	Acceptance Criteria
Sect. 9.2.1 & 9.3.1	Initial Demonstration of Low Background	Analyze LRB prior to any other IDC steps. When a new lot of SPE media is obtained, verify that background is at acceptable limits.	Demonstrate that the method analytes are ≤ 1/3 the MRL, and that possible interferences from extraction media do not prevent the identification and/or quantification of any analytes, SURs or ISs. **Note:** This includes the absence of interferences at both the QIs and secondary ions at the RTs of interest.
Sect. 9.2.2	Initial Demonstration of Precision (IDP)	Analyze four to seven replicate LFBs fortified near the midrange calibration concentration.	%RSD must be ≤ 20%
Sect. 9.2.3	Initial Demonstration of Accuracy (IDA)	Calculate average recovery for replicates used in IDP.	Mean recovery ± 30% of the true value for all analytes except *o*-toluidine, which must be within 50-130% of the true value
Sect. 9.2.4	Minimum Reporting Limit (MRL) Confirmation	Fortify, extract and analyze seven replicate LFBs at the proposed MRL concentration. Calculate the mean, standard deviation and HR_{PIR} for each analyte. Confirm that the upper and lower limits for the Prediction Interval of Result (Upper PIR, and Lower PIR, Sect. 9.2.4.2) meet the recovery criteria.	Upper PIR ≤ 150% Lower PIR ≥ 50%
Sect. 9.2.5 & 9.3.9	Calibration Confirmation, Quality Control Sample (QCS)	Analyze a standard from a second source (QCS) to verify the initial calibration curve.	± 30% of the expected value.

NOTE: Table 10 is intended as an abbreviated summary of QC requirements provided as a convenience to the method user. Because the information has been abbreviated to fit the table format, there may be issues that need additional clarification, or areas where important additional information from the method text is needed. In all cases, the full text of the QC in Sect. 9 supersedes any missing or conflicting information in this table.

Table 11. Ongoing Quality Control (QC) Requirements (Summary)

Method Reference	Requirement	Specification and Frequency	Acceptance Criteria
Sect. 8.4	Sample Holding Time	14 days for analytes with appropriate preservation and storage as described in Sects. 8.1-8.3.	Sample results are valid only if samples are extracted within sample hold time.
Sect. 8.4	Extract Holding Time	14 days stored at -5 °C and protected from light	Sample results are valid only if extracts are analyzed within extract hold time.
Sect. 9.3.1	Laboratory Reagent Blank (LRB)	One LRB with each extraction batch of up to 20 Field Samples.	Demonstrate that the method analyte concentration is $\leq {}^{1}/_{3}$ the MRL, and confirm that possible interferences do not prevent quantification. If the background concentration exceeds $^{1}/_{3}$ the MRL, results for the extraction batch are invalid.
Sect. 9.3.3	Laboratory Fortified Blank (LFB)	One LFB is required for each extraction batch of up to 20 Field Samples. Rotate the fortified concentrations between low, medium, and high amounts.	Results of LFB analyses at medium and high fortifications must be ± 30% of the true value for all analytes except *o*-toluidine which may be 50-130% of the true value. Results of the low-level LFB must be ± 50% of the true value.
Sect. 9.3.5	Internal Standard (IS)	Compare IS area to the mean IS area from the analysis of each CAL in the initial calibration and the area in the most recent CCC.	Peak area counts for all ISs in all injections must be within ± 50% of their mean peak area calculated during the initial calibration. Peak areas of ISs must also be ± 30% from the most recent CCC. If the ISs do not meet these criteria, target analyte results are invalid. Consult Sect. 9.3.5 for further information.
Sect. 9.3.6	Surrogate (SUR) Standards	The SUR standards are added to all calibration standards and samples, including QC samples prior to extraction. Calculate SUR recoveries.	Quinoline-d_7 must be 70-130% of the true value and *o*-toluidine-d_9 must be 50-130% of the true value. If any SUR fails this criterion, report all results for sample as suspect/SUR recovery.
Sect. 9.3.7	Laboratory Fortified Sample Matrix (LFSM)	Analyze one LFSM per extraction batch (of up to 20 Field Samples) fortified with the method analytes at a concentration greater than or equal to the native concentration. Calculate LFSM recoveries.	See Sect. 9.3.7.3 for instructions on the interpretation of LFSM results.

Table 11. Ongoing Quality Control (QC) Requirements (Summary) (Continued)

Sect. 9.3.8	Laboratory Fortified Sample Matrix Duplicate (LFSMD) or Field Duplicates (FD)	Extract and analyze at least one FD or LFSMD with each extraction batch of up to 20 Field Samples. An LFSMD may be substituted for a FD when the frequency of detects for analytes of interest are low. Calculate RPDs.	Method analyte RPDs for the LFSMD or FD should be ≤30% at mid and high levels of fortification and ≤50% at concentrations within two times the MRL. Failure to meet this criterion may indicate a matrix effect.
Sect. 9.3.9	Quality Control Sample (QCS)	Analyze a QCS during the IDC, and each time new CAL solutions or PDSs are prepared. A QCS must be analyzed at least quarterly.	Results must be ±30% of the expected value.
Sect. 10.2	Initial Calibration	Use the IS calibration technique to generate a linear or quadratic calibration curve for each analyte. A minimum of six standards should be used for a calibration range of two orders of magnitude. Suggested concentrations can be found in Sect. 7.2.4. Check the calibration curve against the acceptance criteria in Sect. 10.2.5.	When each calibration standard is calculated as an unknown using the calibration curve, the result should be ± 30% of the true value for all except the lowest standard (<MRL), which should be ± 50% of the true value. If this criterion is not met, reanalyze CALs, select a different method of calibration or recalibrate over a shorter range.
Sects. 10.1 and 10.2.1	MS Tune Check	Analyze DFTPP to verify the MS tune after instrument maintenance and each time the instrument is mass calibrated. The MS tune must also be verified prior to analyzing CAL stds and establishing calibration curves for method analytes.	Acceptance criteria are given in Table 2.
Sect. 10.3	Continuing Calibration Check (CCC)	Verify initial calibration by analyzing a calibration standard at the beginning of each analysis batch prior to analyzing samples, after every10 Field Samples, and after the last sample of each analysis batch. The first CCC daily must be at or below the MRL. Subsequent CCCs alternate between the remaining calibration levels. Low CCC – at or below the MRL concentration Mid CCC – near midpoint in the initial calibration curve High CCC – near the highest calibration standard.	Low: ±50% of true value Mid: ±30% of true value High: ±30% of true value

Note: Table 11 is intended as an abbreviated summary of QC requirements provided as a convenience to the method user. Because the information has been abbreviated to fit the table format, there may be issues that need additional clarification, or areas where important additional information from the method text is needed. In all cases, the full text of Sects. 8-10 in the method supersedes any missing or conflicting information in this table.

Figure 1. Example full scan chromatogram of a calibration standard (concentration of 5 ng/µL injected for all analytes). Peak identification numbers correspond to those in the legend and to those in Table 1.

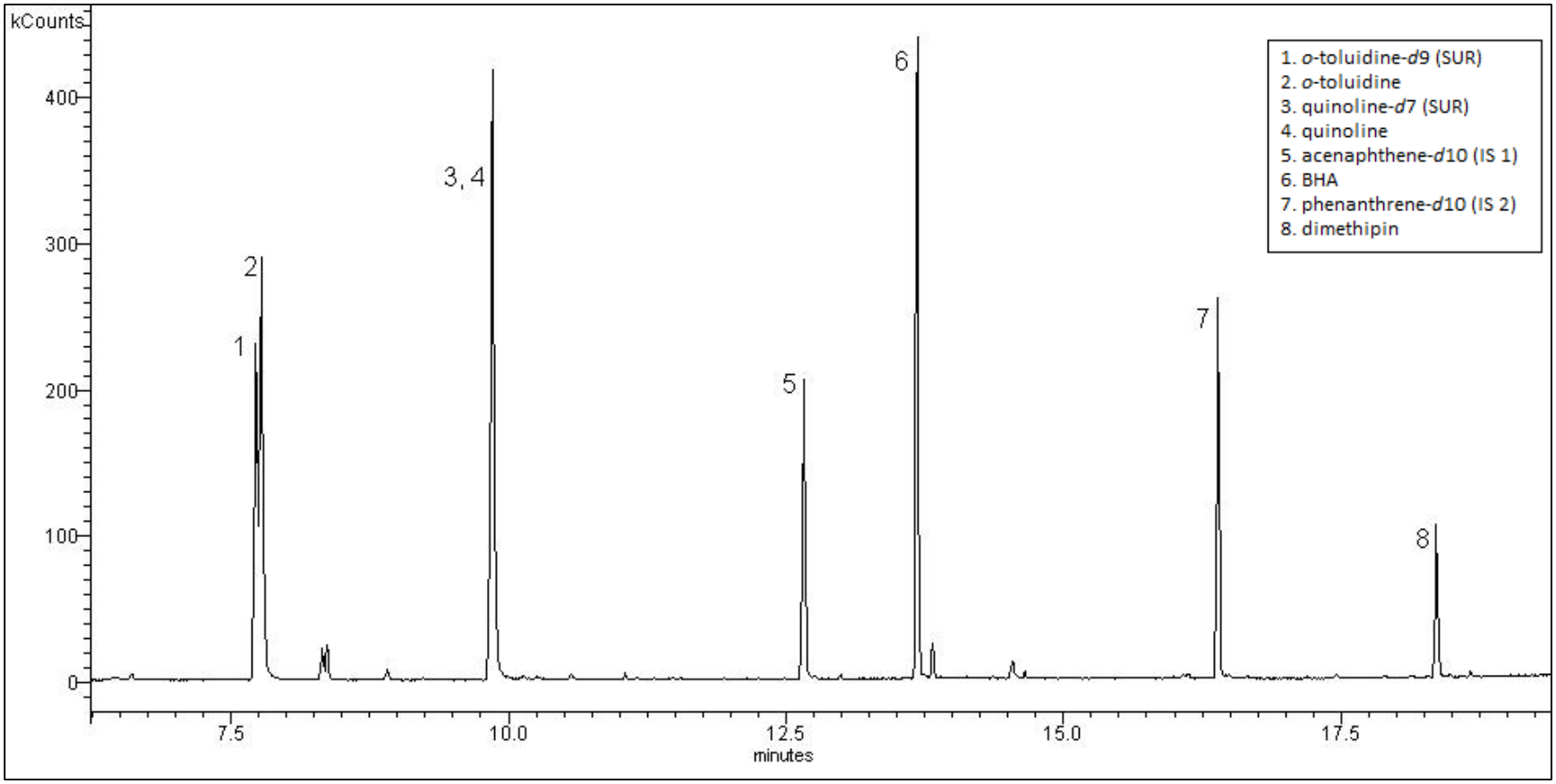

Figure 2. Results of Aqueous Holding Time Study (Sect. 13.3)

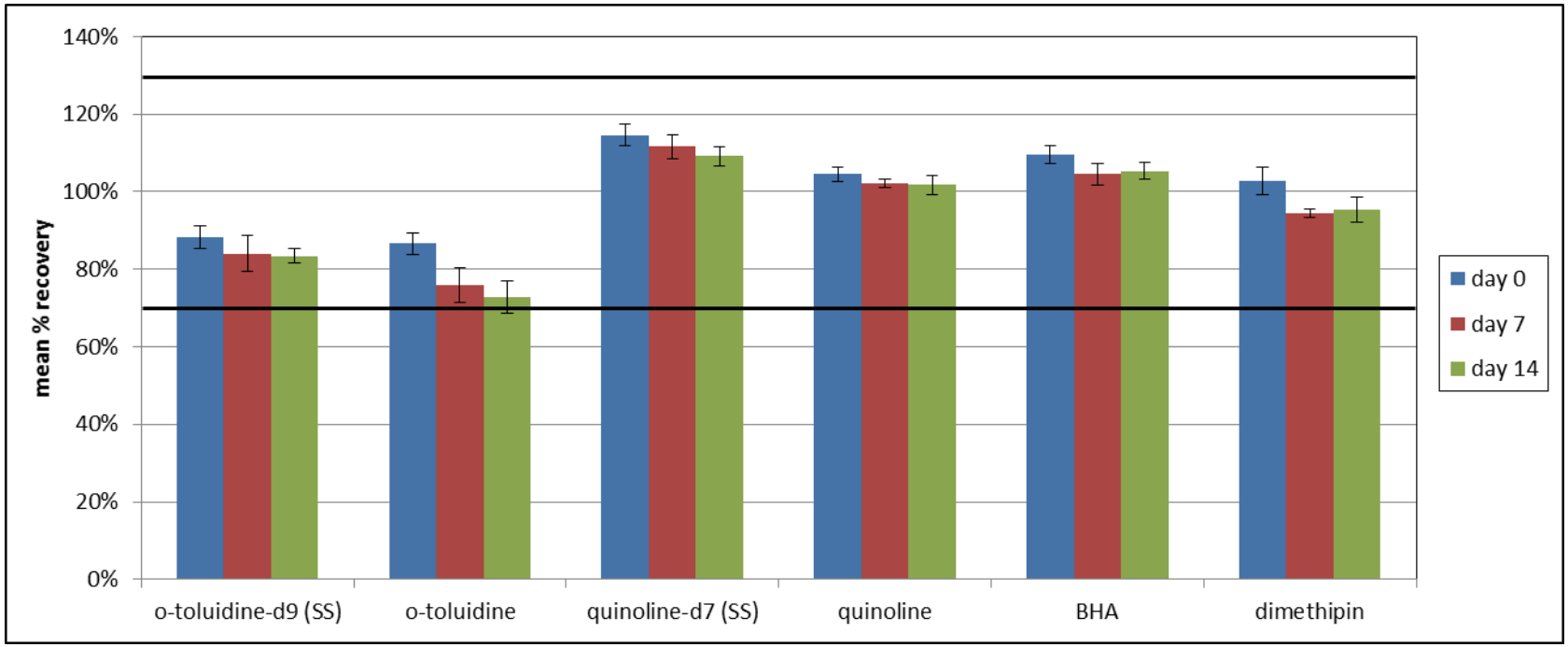

Figure 3. Results of Extract Holding Time Study (Sect. 13.4)