METHOD 528 DETERMINATION OF PHENOLS IN DRINKING WATER BY SOLID PHASE EXTRACTION AND CAPILLARY COLUMN GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS)

Revision 1.0

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METHOD 528

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1. SCOPE AND APPLICATION

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

ANALYTE	CAS NUMBER
phenol	108-95-2
2-chlorophenol	95-57-8
2-methylphenol (o-cresol)	95-48-7
2-nitrophenol	88-75-5
2,4-dimethylphenol	105-67-9
2,4-dichlorophenol	120-83-2
4-chloro-3-methylphenol	59-50-7
2,4,6-trichlorophenol	88-06-2
2,4-dinitrophenol	51-28-5
4-nitrophenol	93951-79-2
2-methyl-4,6-dinitrophenol	534-52-1
pentachlorophenol	87-86-5

1.2 Method detection limit (MDL) is defined as the statistically calculated minimum concentration that can be measured with 99% confidence that the reported value is greater than zero (1). The MDL is compound dependent and is particularly dependent on extraction efficiency, sample matrix, and instrument performance. MDLs for method analytes range from 0.02-0.58 :g/L, and are listed in Table 1. The concentration calibration range demonstrated by this method is 0.1 :g/L to 15 :g/L for most analytes, and approximately 1.0 :g/L to 15 :g/L for 2,4-dinitrophenol, 4-nitrophenol, 2-methyl-4,6-dinitrophenol, and pentachlorophenol.

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

2. SUMMARY OF METHOD

Analytes and surrogates are extracted by passing a 1 L water sample through a solid phase extraction (SPE) cartridge containing 0.5 g of a modified polystyrene divinyl benzene copolymer. The organic compounds are eluted from the solid phase with a small quantity of methylene chloride. The sample components are separated, identified, and measured by injecting an aliquot of the concentrated extract into a high resolution fused silica capillary column of a GC/MS system. Compounds eluting from the GC column are identified by comparing their measured mass spectra and retention times to reference spectra and retention times in a data base. Reference spectra and retention times for analytes are obtained by the measurement of calibration standards under the same conditions used for samples. The concentration of each identified component is measured by relating the MS response of the quantitation ion(s) produced by that compound to the MS response of the quantitation ion(s) produced by a compound that is used as an internal standard. Surrogate analytes, whose concentrations are known in every sample, are measured with the same internal standard calibration procedure.

3. DEFINITIONS

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

3.2 CALIBRATION STANDARD (CAL) -- A solution prepared from the primary dilution standard solution or stock standard solutions and the internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

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

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

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

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

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

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

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

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

3.11 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.

3.12 METHOD DETECTION LIMIT (MDL) -- 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 (Section 9.2.4), and accurate quantitation is not expected at this level. [1]

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

3.14 PEAK TAILING FACTOR (PTF) -- A calculated value that indicates the amount of peak tailing exhibited by a chromatographic peak. The value is calculated by dividing the peak width of the back half of the peak (at 10% peak height), by the peak width of the front half of the peak (at 10% peak height). The calculation is demonstrated in Figure 4.

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

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

3.17 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.

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

4. INTERFERENCES

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

4.2 Interfering contamination may occur when a sample containing low concentrations of compounds is analyzed immediately after a sample containing relatively high concentrations of compounds. Syringes and splitless injection port liners must be cleaned carefully or replaced as needed. After analysis of a sample containing high concentrations of compounds, a laboratory reagent blank should be analyzed to ensure that accurate values are obtained for the next sample.

4.3 Silicone compounds may be leached from autosampler vial septa by methylene chloride. This contamination of the extract will be enhanced if particles of the septa are introduced into standards and sample extracts by the needle used for injection. These silicone compounds should, in most cases, have no effect on the analysis. However, the analyst should be aware of this potential problem.

4.4 Airborne phenol may be a source of phenol contamination in samples and sample extracts. Samples should not be stored or extracted in areas where phenol is used for other laboratory operations.

4.5 2,3,4,5-Tetrachlorophenol is used as one of the internal standards for the quantitation of reactive and thermally labile phenols. Tetrachlorophenol isomers may be present at low levels (less than 4% total tetrachlorophenol) in pentachlorophenol used as a pesticide and wood preservative. However, occurrence of pentachlorophenol in U.S. drinking waters is rare, and measured concentrations are typically 1 :g/L or less. If a matrix interference with the internal standard is suspected, an alternate internal standard may be selected.

5. SAFETY

5.1 The toxicity or carcinogenicity of chemicals used in this method has not been precisely defined; each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining awareness of OSHA regulations regarding safe handling of chemicals used in this method. Each laboratory should maintain a file of applicable MSDSs. Additional references to laboratory safety are cited (2-4).

5.2 Some method analytes and solvents, including 2,4,6-trichlorophenol, pentachloro- phenol, and methylene chloride have been classified as known or suspected human or mammalian carcinogens. Pure standard materials and stock standard solutions of these compounds should be handled with suitable protection to skin, eyes, etc.

6. EQUIPMENT AND SUPPLIES (All specifications are suggested. References to specific brands or catalog numbers are included for illustration only.)

6.1 GLASSWARE -- All glassware must be meticulously cleaned. This may be accomplished by washing with detergent and water, rinsing with water, distilled water, or solvents, air-drying, and heating (where appropriate) in a muffle furnace. Volumetric glassware should never be heated to the temperatures obtained in a muffle furnace.

6.2 SAMPLE CONTAINERS -- 1 L or 1 qt amber glass bottles fitted with polytetrafluoroethylene (PTFE) lined polypropylene screw caps. Amber bottles are highly recommended since some of the method analytes are sensitive to light and may degrade upon exposure. Clear glass bottles may be used if they are wrapped in foil, or samples are stored in boxes that prevent exposure to light. Although specific contamination problems from bottle caps were not observed during method development, phenolic resin bottle caps should be avoided.

6.3 VOLUMETRIC FLASKS -- various sizes.

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

6.5 MICRO SYRINGES -- various sizes.

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

6.7 DRYING COLUMN -- The drying tube should contain about 5 to 7 grams of anhydrous sodium sulfate to remove residual water from the extract. Any small tube may be used,

such as a syringe barrel, a glass dropper, etc. as long as no particulate sodium sulfate passes through the column into the extract.

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

6.9 FUSED SILICA CAPILLARY GAS CHROMATOGRAPHY COLUMN -- Any capillary column that provides adequate resolution, capacity, accuracy, and precision can be used. Medium polarity, low bleed columns are recommended for use with this method to provide adequate chromatography and minimize column bleed. Deactivated injection port liners are highly recommended. During the course of the development of this method, two columns were used. Although these are both polyphenylmethylsilicone columns, the exact phase is slightly different. Information on the exact composition of each phase is available from the manufacturers. Most of the work was performed with column 1. Any column which provides analyte separations equivalent to or better than these columns may be used. Example chromatograms are shown in Figs 1-3. Retention times are presented in Table 2.

6.9.1. Column 1- 30 m × 0.25 mm id fused silica capillary column coated with a 0.25 :m bonded film of polyphenylmethylsilicone, (J&W DB-5ms).

6.9.2 Column 2- 30 m × 0.25 mm id fused silica capillary column coated with a 0.25 :m bonded film of polyphenylmethylsilicone, (SGE BPX5).

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

6.10.1 The GC must be capable of temperature programming and should be equipped for split/splitless injection. The injection system must not allow the analytes to contact hot stainless steel or other metal surfaces that promote decomposition. Other injection techniques such as temperature programmed injections, cold on-column injections and large volume injections may be used if QC criteria in Section 9 and 10 are met. If an alternate injection technique is performed, the analyst will need to select an instrument configuration which has been specifically designed for that application. Performance data in Section 17 include data obtained both by hot, splitless injection and temperature programmed splitless injection.

6.10.2 The GC/MS interface should allow the capillary column or transfer line exit to be placed within a few mm of the ion source. Other interfaces, for example the open split interface, are acceptable if the system has adequate sensitivity.

6.10.3 The mass spectrometer must be capable of electron ionization at a nominal electron energy of 70 eV to produce positive ions. The spectrometer must be capable of scanning at a minimum from 45 to 450 amu with a complete scan cycle time (including scan overhead) of 1.0 sec or less. (Scan cycle time = total MS data acquisition time in sec divided by number of scans in the chromatogram). The spectrometer must produce a mass spectrum that meets all criteria in Table 3 when an injection of approximately 5 ng of DFTPP is introduced into the GC. A single spectrum at the apex of the chromatographic peak, or an average of the three spectra at the apex of the peak, or an average spectrum across the entire GC peak may be used to evaluate the performance of the system. Background subtraction is permitted. The scan time must be set so that all analytes have a minimum of 5 scans across the chromatographic peak. Seven to ten scans across chromatographic peaks are recommended.

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

6.11 VACUUM MANIFOLD -- A vacuum manifold (Supelco # 57030 and #57275) is required for processing samples through the extraction/elution procedure. An automatic or robotic sample preparation system designed for use with solid phase extraction cartridges may be utilized in this method if all quality control requirements discussed in Sect. 9 are met. Automated systems may use either vacuum or positive pressure to process samples and solvents through the cartridge. All extraction and elution steps must be the same as in the manual procedure. Extraction and/or elution steps may not be changed or omitted to accommodate the use of an automated system.

7. REAGENTS AND STANDARDS

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

7.2 SOLID PHASE EXTRACTION CARTRIDGES -- Varian Bond Elut PPL or equivalent. Cartridges are inert non-leaching plastic, for example polypropylene, or glass, and must not contain plasticizers that leach into the methylene chloride eluant and prevent the identification and quantitation of method analytes. The polypropylene cartridges (6 mL volume) are packed with 0.5 g highly cross-linked, and chemically modified styrene divinyl

benzene copolymer. The packing must have a narrow size distribution and must not leach interfering organic compounds into the eluting solvent.

7.3 SOLVENTS --

7.3.1 Methylene chloride, acetone, and methanol. High purity pesticide quality or equivalent.

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

7.4 HYDROCHLORIC ACID -- 6 N and 0.05 N.

7.5 SODIUM SULFATE, ANHYDROUS -- (Soxhlet extracted with methylene chloride for a minimum of 4 h or heated to 400°C for 2 h in a muffle furnace.)

7.6 STOCK STANDARD SOLUTIONS -- Individual solutions of surrogates, internal standards, and analytes, or mixtures of analytes, may be purchased from commercial suppliers or prepared from pure materials. To prepare stocks from neat materials, add 10 mg (weighed on an analytical balance to within 0.1 mg) of the pure material to 1.9 mL of methanol, methylene chloride, or acetone in a 2 mL volumetric flask, dilute to the mark, and transfer the solution to an amber glass vial. The solvent to be used is dependent upon the final use of the standard. In general, calibration standards and internal standards are prepared in methylene chloride, sample fortification solutions are prepared in methanol or acetone. Follow any specific instructions for each standard or standard mixture. If compound purity is confirmed by the supplier at >96%, the weighed amount can be used without correction to calculate the concentration of the solution (5 :g/:L). Store the amber vials at 0°C or less.

7.7 PRIMARY DILUTION STANDARD SOLUTION -- The stock standard solutions are used to prepare a primary dilution standard solution that contains multiple method analytes in methylene chloride. Aliquots of each of the stock standard solutions are combined to produce the primary dilution in which the concentration of the analytes is at least equal to the concentration of the most concentrated calibration solution, that is, 15 ng/:L. Store the primary dilution standard solution in an amber vial at 0°C or less, and check regularly for signs of degradation or evaporation, especially just before preparing calibration solutions. Mixtures of method analytes to be used as primary dilution standards may also be purchased from commercial suppliers.

7.8 CALIBRATION SOLUTIONS (CAL1 through CAL7) -- Prepare a series of seven calibration solutions in methylene chloride which contain analytes of interest at suggested concentrations of 15,10, 5, 2, 1, 0.5, and 0.1 ng/:L, with a constant concentration of each internal standard in each CAL solution (2-5 ng/:L is recommended). Surrogate analytes are also added to each CAL solution, and may be added at a constant concentration or varied concentrations (similar to those for method analytes), at the discretion of the analyst. CAL1 through CAL7 are prepared by combining appropriate aliquots of a primary dilution standard solution (Sect. 7.7) and the fortification solution of internal standards and surrogates (Sect. 7.10). All calibration solutions should contain at least 80% methylene chloride to avoid gas chromatographic problems due to mixed solvents. Store these solutions in amber vials at 0°C or less. Check these solutions regularly for signs of evaporation and/or degradation.

NOTE: Because the MS sensitivity to analytes 9-12 (Table 2) is significantly less than compounds 1-8, it may be more convenient to prepare calibration solutions in which the concentrations of analytes 9-12 (Table 2) are higher than the concentrations of analytes 1-8. Use of this option is at the discretion of the analyst. Calibration requirements are specified in Sect. 10.

7.9 INTERNAL STANDARD SOLUTION(S) -- This method uses two internal standards: 1,2-dimethyl-3-nitrobenzene (IS#1) and 2,3,4,5-tetrachlorophenol (IS#2). The first internal standard, 1,2-dimethyl-3-nitrobenzene is used to monitor instrument sensitivity and is used to quantify analytes 1-8 in Table 2. The second internal standard, 2,3,4,5-tetrachlorophenol is used to quantify analytes 9-12 (Table 2). IS#2 was selected for its chemical similarity to these compounds which are susceptible to adsorption and/or thermal decomposition in the GC inlet. A full explanation of the use of 2,3,4,5-tetrachlorophenol to quantify these compounds is given in Section 13. If cold, on-column or temperature programmed injection techniques are used, acceptable performance may be obtained using only one internal standard (IS#1).

7.9.1 1,2-Dimethyl-3-nitrobenzene (Aldrich) -- 100 :g/mL in methylene chloride. Use 25 :L of this solution per 1 mL of sample extract for a final concentration of 2.5 :g/mL.

7.9.2 2,3,4,5-Tetrachlorophenol (Chem Service Inc.) -- 200 :g/mL in methylene chloride. Use 25 :L of this solution per 1 mL of sample extract for a final concentration of 5 :g/mL.

7.9.3 The internal standard solutions listed above can be made individually or together in one solution.

7.10 SAMPLE FORTIFICATION SOLUTIONS --

7.10.1 Surrogate fortification solutions --

7.10.1.1. 2-Chlorophenol-3,4,5,6-d_4 (Chem Service Inc.) -- 100 :g/mL in methanol. Use 20 :L of this solution per 1 L of water sample for a final concentration of 2 :g/L.

7.10.1.2 2,4-Dimethylphenol-3,5,6-d_3 (CDN Isotopes) -- 100 :g/mL in acetone. Use 20 :L of this solution per 1 L of water sample for a final concentration of 2 :g/L.

7.10.1.3 2,4,6-Tribromophenol -- 200 :g/mL in methanol. Use 25 :L of this solution per 1 L water sample for a final concentration of 5 :g/L.

7.10.2 Analyte fortification solution(s). This solution contains all method analytes of interest in methanol. These solutions are used to fortify LFBs and LFMs with method analytes. It is recommended that more than one concentration of this solution be prepared. During the method development, two solutions were used. One containing 100 :g/mL of each analyte, was used for higher concentration fortifications, and the other containing10 :g/mL of each analyte in methanol was used for lower level fortifications.

NOTE: Because the MS sensitivity to analytes 9-12 (Table 2) is significantly less than analytes 1-8, it may be more convenient to prepare analyte fortification solutions in which the concentrations of analytes 9-12 are higher than the concentrations of analytes 1-8. Use of this option is at the discretion of the analyst.

7.11 GC/MS TUNE CHECK SOLUTION -- Decafluorotriphenylphosphine (DFTPP), 5 :g/mL in methylene chloride. Store this solution in an amber vial at 0°C or less.

7.12 SODIUM SULFITE, ANHYDROUS -- Reducing agent used to reduce residual chlorine at the time of sample collection.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 SAMPLE COLLECTION -- When sampling from a water tap, open the tap and allow the system to flush until the water temperature has stabilized (usually about 2 min). Adjust the flow to about 500 mL/min and collect samples from the flowing stream. The sample

should nearly fill the 1 L or 1 qt bottle, but does not need to be headspace free. Keep samples sealed from collection time until analysis. When sampling from an open body of water, fill the sample container with water from a representative area. Sampling equipment, including automatic samplers, must be free of plastic tubing, gaskets, and other parts that may leach interfering analytes into the water sample.

8.2 SAMPLE DECHLORINATION AND PRESERVATION -- All samples must be dechlorinated and acidified at the time of collection. Residual chlorine is reduced by addition of 40-50 mg of sodium sulfite. It may be added as a solid to the sample bottles before the bottles are transported to the field. It is **very important** that the sample be dechlorinated prior to acidification. Wait until sodium sulfite is dissolved before acidification. Adding sodium sulfite and HCl (together) to the sample bottles prior to shipping bottles to the sampling site is not permitted. After dechlorination, samples are acidified to less than pH 2 with 6 N hydrochloric acid. The acid serves as a chemical and biological preservative. This pH is the same that is used in the sample extraction, and is required to support the recovery of several method analytes.

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

8.4 HOLDING TIME -- Results of holding time studies of all method analytes showed that all compounds are stable for 14 days in water samples when the samples are dechlorinated, preserved, and stored as described in Sect. 8.2 and 8.3. Therefore, samples must be extracted within 14 days of collection. Sample extracts may be stored at 0°C or less for up to 30 days after sample extraction. Data from holding time studies are shown in Tables 7 and 8.

9. QUALITY CONTROL

9.1 Quality control (QC) requirements include: the initial demonstration of laboratory capability (summarized in Table 9) followed by regular analyses of continuing calibration checks, laboratory performance check standards, laboratory reagent blanks, laboratory fortified blanks, and laboratory fortified matrix samples. An MDL must be determined for each analyte of interest. These criteria are considered the minimum acceptable QC criteria, and laboratories are encouraged to institute additional QC practices to meet their specific needs. The laboratory must maintain records to document the quality of the data generated. A complete summary of QC requirements is summarized in Table 10.

9.2 INITIAL DEMONSTRATION OF CAPABILITY (IDC) -- Requirements for the initial demonstration of laboratory capability are described in the following sections and summarized in Table 9.

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

9.2.1.1 A source of potential contamination is the solid phase extraction cartridge which may contain phthalate esters, silicon compounds, and other contaminants that could interfere with the determination of method analytes. Although extraction cartridges are generally made of inert materials, they may still contain extractable organic material. If the background contamination is sufficient to prevent accurate and precise measurements, the condition must be corrected before proceeding with the initial demonstration.

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

9.2.2 INITIAL DEMONSTRATION OF PRECISION (IDP) -- Prepare 4-7 replicate LFBs fortified at 5-10 :g/L, or other mid-range concentration. Sample preservatives described in Sect. 8.2 must be added to these samples. Extract and analyze these replicates according to the procedure described in Section 11. The relative standard deviation (RSD) of the results of the replicate analyses must be less than or equal to 20% for all method analytes with the exception of phenol. The RSD for replicate analyses for phenol must be less than or equal to 30%.

9.2.3 INITIAL DEMONSTRATION OF ACCURACY (IDA) -- Using the same set of replicate data generated for Section 9.2.2, calculate average recovery. The average recovery of the replicate values must be within 70-130% of the true value, except for phenol. Phenol will typically be recovered less effectively than other method analytes. Because of its higher water solubility some breakthrough

from the extraction cartridge does occur. The recovery limits for phenol are 50-150%.

9.2.4 MDL DETERMINATION -- Replicate analyses for this procedure should be done over at least 3 days (both the sample extraction and the GC analyses should be done over at least 3 days). Prepare at least 7 replicate LFBs at a concentration estimated to be near the MDL. This concentration may be estimated by selecting a concentration at 2-5 times the noise level. Concentrations shown in the example data in Table 1 may be used as a guide, however the appropriate concentration will be dependent upon the injection technique and the sensitivity of the GC/MS system used. Sample preservatives described in Sect. 8.2 must be added to these samples. Analyze the seven replicates through all steps of Section 11. Calculate the MDL using the following equation:

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

where:

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

NOTE: Do not subtract blank values when performing MDL calculations.

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

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

9.4 LABORATORY REAGENT BLANKS (LRB) -- With each extraction batch, analyze a laboratory reagent blank to determine the background system contamination. If, within the retention time window of any analyte, the LRB produces a peak that would prevent the

determination of that analyte, determine the source of contamination and eliminate the interference before processing samples. Background contamination must be reduced to an acceptable level before proceeding. Background from method analytes or contaminants that interfere with the measurement of method analyses should be # 1/3 the MRL. Any time a new batch of SPE cartridges is received, or new supplies of other reagents are used, repeat the demonstration of low background described in Sect. 9.2.1.

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

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

9.7 PEAK TAILING FACTOR (PTF) -- This check consists of calculating the PTF as described in Sect. 10.2.3.1. and in Figure 4. This check must be performed once every 24 hr of instrument operation.

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

9.9 INTERNAL STANDARD (IS) --The analyst must monitor the peak area of the 1,2-dimethyl-3-nitrobenzene (IS#1) in all injections during each analysis day. The IS#1 response (peak area) in any chromatographic run should not deviate from the response in the most recent CCC by more than 30%, and must not deviate by more than 50% from the area measured during initial analyte calibration. If the IS#1 area in a chromatographic run does not meet these criteria inject a second aliquot of that extract.

NOTE: The peak area of 2,3,4,5-tetrachlorophenol may not be consistent. It may vary depending upon the composition of the extract or standard being analyzed. See Section 13.2.1 for a detailed explanation.

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

9.9.2 If a deviation of greater than 30% is obtained for the reinjected extract, when compared to the most recent CCC, the analyst should check the calibration by reanalyzing the most recently acceptable calibration standard. If the calibration standard fails the criteria of Section 10.3.3, recalibration is in order per Section 10. If the calibration standard is acceptable, extraction of the sample may need to be repeated provided the sample is still within the holding time. Otherwise, report results obtained from the reinjected extract, but annotate as suspect.

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

9.10.1 Surrogate recovery criteria are 70-130% of the fortified amount for 2-chlorophenol-3,4,5,6-d_4 and 2,4-dimethylphenol-3,5,6-d_3. The criteria for 2,4,6-tribromophenol is 60-130% of the fortified amount. When surrogate recovery from a sample, blank, or CCC does not meet these criteria, check (1) calculations to locate possible errors, (2) standard solutions for degradation, (3) contamination, and (4) instrument performance. Correct any problems that are identified. If these steps do not reveal the cause of the problem, reanalyze the extract.

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

9.10.3 If the extract reanalysis fails the recovery criterion, the analyst should check the calibration by reanalyzing the most recently acceptable calibration standard. If the calibration standard fails the criteria of Section 10.3.3, recalibration is in order per Section 10. If the calibration standard is acceptable, it may be necessary to extract another aliquot of sample if sample holding time has not been exceeded. If the sample reextract also fails the recovery criterion, report all data for that sample as suspect.

9.11 LABORATORY FORTIFIED SAMPLE MATRIX (LFM) -- Determine that the sample matrix does not contain materials that adversely affect method performance. This is

accomplished by analyzing replicates of laboratory fortified matrix samples and ascertaining that the precision, accuracy, and method detection limits of analytes are in the same range as obtained with laboratory fortified blanks. If a variety of different sample matrices are analyzed regularly, for example, drinking water from groundwater and surface water sources, matrix independence should be established for each. Over time, LFM data should be documented for all routine sample sources for the laboratory. A laboratory fortified sample matrix should be extracted and analyzed for each extraction batch. If more than 20 samples are processed in a batch, extract and analyze a LFM for every 20 samples. If the recovery data for an LFM does not meet the recovery criteria in Sect. 9.8, and LFBs show the laboratory to be in control , then the samples from that matrix (sample location) are documented as suspect due to matrix effects.

9.11.1 Within each extraction batch, a minimum of one field sample is fortified as a LFM for every 20 samples analyzed. The LFM is prepared by spiking a sample with an appropriate amount of the fortification solution. The concentrations 5, 10, and 15 :g/L are suggested spiking concentrations. Select the spiking concentration that is closest to, and at least twice the matrix background concentration. Use historical data or rotate through the designated concentrations to select a fortifying concentration. Selecting a duplicate bottle of a sample that has already been analyzed, aids in the selection of appropriate spiking levels.

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

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

where C is the fortified concentration. Compare these values to control limits for LFBs (Sect. 9.8).

9.11.3 Recoveries may exhibit a matrix dependence. For samples fortified at or above their native concentration, recoveries should range between 70 and 130%, for all method analytes except phenol which should be recovered at 50-150%. If the accuracy of any analyte falls outside the designated range, and the laboratory performance for that analyte is shown to be in control, the accuracy problem encountered with the fortified sample is judged to be matrix related, not system related. The result for that analyte in the unfortified sample is labeled

suspect/matrix to inform the data user that the results are suspect due to matrix effects.

NOTE: Matrix effects are expected to be more likely with compounds 9-12 (Table 2) than other method analytes.

9.12 FIELD DUPLICATES (FD) -- Within each extraction batch, a minimum of one field sample should be analyzed in duplicate. Duplicate sample analyses serve as a check on sampling and laboratory precision. If analytes are not routinely observed in field samples, duplicate LFMDs should be analyzed to substitute for this requirement.

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

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

9.12.2 Relative percent differences for laboratory duplicates and LFMDs should fall in the range of ± 30 %.

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

9.13 QUALITY CONTROL SAMPLE (QCS) -- Each time that new standards are prepared, analyze a QCS from an external source. If standards are prepared infrequently, analyze a QCS at least quarterly. The QCS may be injected as a calibration standard, or fortified into reagent water and analyzed as an LFB. If the QCS is analyzed as a calibration check standard, then the acceptance criteria are the same as for the CCC (Sect. 10.3.3). If the QCS is analyzed as a LFB, then the acceptance criteria are the same as for an LFB (Sect. 9.8). If measured analyte concentrations are not of acceptable accuracy, check the entire analytical procedure to locate and correct the problem.

10. CALIBRATION AND STANDARDIZATION

10.1 Demonstration and documentation of acceptable mass spectrometer tune and initial calibration is required before any samples are analyzed. After initial calibration is successful, a continuing calibration check is required at the beginning and end of each period in which analyses are performed, and after every tenth sample. Verification of mass spectrometer tune must be repeated each time a major instrument modification or maintenance is performed, and prior to analyte calibration. A peak tailing factor check is

required every day that samples are analyzed. In periods of continuous operation, the peak tailing factor must be performed every 24 hr.

10.2 Initial calibration

10.2.1 MS TUNE -- Calibrate the mass and abundance scales of the MS with calibration compounds and procedures prescribed by the manufacturer with any modifications necessary to meet tuning requirements. Inject 5 ng or less of DFTPP solution into the GC/MS system. Acquire a mass spectrum that includes data for m/z 45-450. If the DFTPP mass spectrum does not meet all criteria in Table 3, the MS must be retuned and adjusted to meet all criteria before proceeding with calibration. A single spectrum at the apex of the chromatographic peak, or an average of the three spectra at the apex of the peak, or an average spectrum across the entire GC peak may be used to evaluate the performance of the system. Background subtraction is permitted. The tune check may be performed as a separate analysis, or for routine MS tune verification, DFTPP may be added to one or more of the CAL standards used for calibration verification, so that the tune check and calibration verification can be performed in a single analysis. DFTPP elutes shortly after pentachlorophenol on both of the columns cited in Sect.6.9.

10.2.2 ANALYTE CALIBRATION -- Inject an aliquot of a medium concentration calibration solution. For example, 2-10 : g/mL, and acquire and store data from m/z 45-350 with a total cycle time (including scan overhead time) of 1.0 sec or less. Cycle time must be adjusted to measure at least five or more scans during the elution of each GC peak. Seven to ten scans across each GC peak are recommended.

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

10.2.2.1 The following parameters are suggested GC conditions for hot, splitless injection: injector temperature 200° C, carrier gas head pressure 12-15 psi. Inject at an oven temperature of 35° C and hold in splitless mode for 0.2 min. After 6 min, temperature program the GC oven at 8° C per min to 250° C. Start data acquisition at

approximately 10 min. Example chromatograms are shown in Figures 1 and 2.

10.2.2.2 The following parameters are suggested injection conditions for temperature programmed splitless injection. Inject with the injector temperature at 25° C, program the injector at 200° C per min to 200° C. Hold in the splitless mode for 1.0 min. Use the same column temperature program as listed in Sect. 10.2.2.1. An example chromatogram is shown in Figure 3.

10.2.3 Performance criteria for the calibration standards. Examine the stored GC/MS data with the data system software.

10.2.3.1 PEAK TAILING FACTOR (PTF) -- Peak tailing can be a problem associated with phenols. The phenols most likely to tail are those with low acidity constants: 2,4-dinitrophenol, 4-nitro-phenol, pentachlorophenol and 2-methyl-4,6-dinitrophenol. These compounds must exhibit a peak tailing factor of 5 or less at a concentration equivalent to 5-10 :g/L in a water sample (5-10 :g/mL in an extract or calibration standard). For example peak tailing factor calculations, see Fig.4. Peak tailing factors must be evaluated for the four analytes listed above each day that samples are analyzed. In periods of continuous instrument operation, verify acceptable PTFs every 24 hr. Peak tailing factors may be evaluated in either a CAL standard, LFB or LFM.

10.2.3.2 The GC/MS/DS peak identification software should be able to recognize a GC peak in the appropriate retention time window for each of the compounds in the calibration solution, and make correct identifications (Sect. 11.5).

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

10.2.4.1 Some GC/MS systems may not be sensitive enough to detect some of the analytes in the two lowest concentration CAL solutions (0.1 and 0.5 :g/mL). If this is the case, it is acceptable to calibrate using the remaining (higher concentration) points, as long as a minimum of 5 calibration points are used to generate the calibration curve or average response factor (RF) for each analyte. In addition, some

GC/MS systems might reach signal saturation at the highest calibration concentration. If this is the case, it is acceptable to drop the highest point and calibrate on the remaining points, as long as at least 5 calibration concentrations are used to generate the calibration curve or average RF for each analyte. Points in the middle of the calibration range may not be dropped. Data outside of the established calibration range should never be reported.

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

Average RF is determined by calculating the mean RF of each calibration point, with a minimum of five calibration concentrations.

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

where:

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

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

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

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

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

10.2.7 Acceptance criteria for the calibration of each analyte is determined by calculating the concentration of each analyte and surrogate in each of the analyses used to generate the calibration curve or average RF. Each calibration point, except the lowest point, for each analyte must calculate to be 70-130 % of its true value. The lowest point must calculate to be 50-150% of its true value. If this criteria cannot be met, reanalyze the calibration standards, or select an alternate method of calibration. The data presented in this method were

obtained using linear regression (RF vs A_x / A_{is}). 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) -- The minimum daily calibration verification is as follows. Verify the initial calibration at the beginning and end of each group of analyses, and after every tenth sample during analyses. (In this context, a "sample" is considered to be a field sample. LRBs, LFMs, LFBs and CCCs are not counted as samples.) The beginning CCC each day should be at or near the MRL in order to verify instrument sensitivity prior to any analyses. If standards have been prepared such that all low CAL points are not in the same CAL solution, it may be necessary to analyze two CAL solutions to meet this requirement. Subsequent CCCs can alternate between a medium and high concentration standard.

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

10.3.2 Determine that the absolute areas of the quantitation ions of the internal standard 1,3-dimethyl-2-nitrobenzene has not changed by more than 30% from the areas measured in the most recent continuing calibration check, or by more than 50% from the areas measured during initial calibration. If this area has changed by more than these amounts, adjustments must be made to restore system sensitivity. These adjustments may include cleaning of the MS ion source, or other maintenance as indicated in Sect. 10.3.4. Major instrument maintenance requires recalibration. Control charts are useful aids in documenting system sensitivity changes.

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

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

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

10.3.4.2 Clean or replace the splitless injection liner; silanize a new injection liner.

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

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

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

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

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

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

11. PROCEDURE

11.1 CARTRIDGE EXTRACTION

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

11.1.2 Mark the level of the sample on the outside of the sample bottle for later sample volume determination (Sect. 11.2). Verify that the sample is at pH 2 or less and is free of residual chlorine. If the sample is a LRB or LFB, add sodium sulfite

and acidify following procedures in Sect.8.2. Add an aliquot of the surrogate fortification solution(s), and mix immediately until homogeneous. The resulting concentration of these compounds in the water should be 2-5 :g/L. If the sample is a LFB or LFM, add the desired amount of analyte fortification solution.

11.1.3 CARTRIDGE CLEAN-UP AND CONDITIONING -- Rinse each cartridge with three, 3 mL aliquots of methylene chloride. Let the cartridge drain dry after each flush. Then rinse the cartridge with three, 3mL aliquots of methanol, but DO NOT allow the methanol to elute below the top of the cartridge packing. From this point, do not allow the cartridge packing to go dry. Rinse with three, 3mL aliquots of 0.05 N hydrochloric acid, but before the dilute acid level drops below the top edge of the packing, turn off the vacuum. Add approximately 3 mL additional 0.05 N hydrochloric acid to the cartridge, attach the transfer tube, and turn on the vacuum, and begin adding sample to the cartridge.

11.1.4 Adjust the vacuum so that the approximate flow rate is 20 mL/min (50 min for a 1 L sample). After all of the sample has passed through the SPE cartridge, draw air or nitrogen through the cartridge for 15-30 min at high vacuum (10-15 in Hg). The cartridge packing should appear dry (light tan color) before continuing with the elution steps. It is important that the cartridge packing be dry, in order to obtain good recoveries. The drying time may vary, depending upon the strength of the vacuum source, and the number of cartridges being processed simultaneously. The color and appearance of the packing is the most reliable indicator of dryness. During the method development, drying for more than 60 minutes was not observed to have any negative effect upon the sample data.

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

11.1.5 Rinse the inside of each sample bottle with 8-10 mL methylene chloride and use vacuum to pull the solvent through the transfer tube and through the cartridge, collecting the solvent in a collection tube. Remove the transfer tubing from the top of the cartridge. Add 2-3 mL methylene chloride to the top of the cartridge with a disposable pipette. Pull this solvent through the cartridge at low vacuum, such that the solvent exits the cartridge in a dropwise fashion. Small amounts of residual water from the sample container and the SPE cartridge may form an immiscible layer with the eluate. Pass the eluate through the drying column (Sect. 6.7), which is packed with approximately 5 to 7 grams of anhydrous sodium

sulfate, and collect in a clean collection tube. Wash the sodium sulfate with at least 2 mL methylene chloride and collect in the same tube. Concentrate the extract to approximately 0.9 mL in a warm (40°C) water bath under a gentle stream of nitrogen. Do not concentrate the extract to less than 0.5 mL, as this will result in losses of analytes. Add the internal standards (Sect 7.9). Adjust final volume to 1 mL. Make any volume adjustments with methylene chloride.

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

11.3 Analyze an aliquot of the sample extract with the GC/MS system under the same conditions used for the initial and continuing calibrations (Sect. 10.2.2 and 10.3).

11.4 At the conclusion of data acquisition, use the same software that was used in the calibration procedure to identify peaks in predetermined retention time windows of interest. Use the data system software to examine the ion abundances of components of the chromatogram.

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

11.5.1 In general, all ions that are present above 10% relative abundance in the mass spectrum of the standard should be present in the mass spectrum of the sample component and should agree within absolute 20%. For example, if an ion has a relative abundance of 30% in the standard spectrum, its abundance in the sample spectrum should be in the range of 10 to 50%. Some ions, particularly the molecular ion, are of special importance, and should be evaluated even if they are below 10% relative abundance.

12. DATA ANALYSIS AND CALCULATIONS

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

12.1.1 Calculate analyte and surrogate concentrations, using the multipoint calibration established in Sect. 10. Do not use daily calibration verification data to quantitate analytes in samples. Adjust final analyte concentrations to reflect the actual sample volume determined in Section 11.2.

12.1.2 Calculations should utilize all available digits of precision, but final reported concentrations should be rounded to an appropriate number of significant figures (one digit of uncertainty). Experience indicates that three significant figures may be used for concentrations above 99 :g/L, two significant figures for concentrations between 1.0-99 :g/L, and one significant figure for lower concentrations.

13. METHOD PERFORMANCE

13.1 PRECISION, ACCURACY AND MDLs-- Single laboratory accuracy and precision data from both fortified reagent water and fortified matrices using hot, splitless injection are presented in Tables 4 and 5. Table 6 includes data from 2 matrices using temperature programmed splitless injection. Method detection limits (MDLs) are presented in Table 1 for both types of injectors used. MDLs were calculated using the formula in Section 9.2.4. Although the calculated MDLs using the two different types are not dramatically different, for compounds 9-12 (Table 2) the peak shapes are significantly better using temperature programmed injection, and the peak heights and areas are greater.

13.2 POTENTIAL PROBLEM COMPOUNDS –

13.2.1 2,4-Dinitrophenol, 4-nitrophenol, 2-methyl-4,6-dinitrophenol, pentachlorophenol and 2,4,6-tribromophenol have a tendency to exhibit a chromatographic phenomenon known as "matrix-induced chromatographic response enhancement" (5-8). Compounds that exhibit this phenomenon often give analytical results that exceed 100% recovery. The theory behind this phenomenon is that these compounds are susceptible to adsorption and/or thermal degradation in the GC inlet. The "cleaner" the matrix they are injected in, e.g. clean solvent, the more they degrade. When they are injected in a sample extract, matrix components in the sample extract "protect" these compounds from decomposition and a relatively greater response is observed. While most of the literature references to this phenomenon refer to organophosphate pesticides in river water and food samples, the effect seen during development of this method suggests the same type of problem occurs with these acidic phenols.

This method uses 2,3,4,5-tetrachlorophenol as the internal standard for quantifying these analytes. The chromatographic behavior of 2,3,4,5-tetrachlorophenol mimics these particular method analytes. Therefore its use as an internal standard helps maintain accurate measurement of these analytes. It should be noted however that these particular analytes will probably not be measured with the same level of precision and accuracy as other method analytes, but the precision and accuracy requirements should still be achievable.

13.2.2 The same compounds listed in sect. 13.2.1. also have a tendency to tail. QC criteria for peak tailing factors have been given in Sect. 10.2.3.1. During method development, significantly less peak tailing was observed using temperature programmed injection. Other measures shown to minimize peak tailing and improve peak shape are pressure pulsed injection, and increasing the GC oven temperature program rate. Pulsed injection is recommended on GCs which have that option available. A faster GC oven temperature program is recommended if there are no interferences, and if the minimum number of scans across all chromatographic peaks can be obtained. This is a function of how fast the MS can scan.

13.2.3 Phenol is very water soluble compared to other method analytes. Breakthrough experiments performed during method development indicate that some breakthrough from the SPE cartridge can be expected. Breakthrough can be minimized by monitoring the flow of the sample through the cartridge. In general, slower flow rates will minimize breakthrough. Precision and accuracy requirements in Sect. 10 should be achievable.

13.3 HOLDING TIME STUDY RESULTS –

13.3.1 Holding time studies for aqueous samples were conducted for a period of 35 days. Chlorinated surface water samples fortified with method analytes and preserved and stored according to requirements in Section 8, were analyzed on days 0, 7, 10, 15, 23, 28, and 35. Small, but statistically significant losses of 2-chlorophenol, o-cresol, and 2,4-dimethylphenol were observed beginning between day 15 and 23. Therefore the aqueous holding time was determined to be 14 days. Data from these studies are in Table 7.

13.3.2 Holding time studies for sample extracts were conducted for a period of 35 days. A single set of extracts were stored at 0°C, and analyzed on days 0, 14, 23, and 35. No significant losses were observed within this time frame. Therefore the extract holding time was established at 30 days. Data from these studies are in Table 8.

14. POLLUTION PREVENTION

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

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

15. WASTE MANAGEMENT

15.1 The analytical procedures described in this method generate relatively small amounts of waste since only small amounts of reagents and solvents are used. The matrices of concern are finished drinking water or source water. However, the Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations, and that laboratories protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Also, compliance is required with any sewage discharge permits and regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult “The Waste Management Manual for Laboratory Personnel” also available from the American Chemical Society at the address in Section 14.2.

16. REFERENCES

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17. TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

TABLE 1. METHOD DETECTION LIMITS [a]

Analyte	Hot Splitless Injection [b]		Temperature Programmed Splitless Injection [c]	
	Spiking Conc. (:g/L)	MDL (:g/L)	Spiking Conc. (:g/L)	MDL (:g/L)
phenol	1.0	0.58	0.1	0.025
2-chlorophenol	0.1	0.020	0.1	0.041
2-methylphenol (o-cresol)	0.1	0.026	0.1	0.028
2-nitrophenol	0.1	0.026	0.1	0.044
2,4-dimethylphenol	0.1	0.026	0.1	0.034
2,4-dichlorophenol	0.1	0.027	0.1	0.046
4-chloro-3-methylphenol	0.1	0.036	0.1	0.042
2,4,6-trichlorophenol	0.1	0.046	0.1	0.024
2,4-dinitrophenol	1.0	0.31	0.5	0.22
4-nitrophenol	1.0	0.42	0.5	0.18
2-methyl-4,6-dinitrophenol	1.0	0.26	0.5	0.092
pentachlorophenol	1.0	0.25	0.5	0.081

a- data obtained using Column 1
b- n=7
c- n=8

TABLE 2. RETENTION TIMES (RTs) AND SUGGESTED QUANTITATION IONS (QIs)

Cmpd # [a]	Analyte	RTs (min) column 1 [b]	RTs (min) column 2 [c]	QIs (m/z)	IS Ref
1	phenol	11:00	12:38	94	1
2	2-chlorophenol	11:07	12:50	128	1
3	2-methylphenol (o-cresol)	12:52	14:27	107	1
4	2-nitrophenol	14:36	16:22	139	1
5	2,4-dimethylphenol	15:00	16:35	107	1
6	2,4-dichlorophenol	15:22	17:04	162	1
7	4-chloro-3-methylphenol	17:46	19:27	142	1
8	2,4,6-trichlorophenol	18:56	20:42	97	1
9	2,4-dinitrophenol	21:30	23:30	154,184[d]	2
10	4-nitrophenol	21:53	23:44	139	2
11	2-methyl-4,6-dinitrophenol	23:09	25:09	121,198[d]	2
12	pentachlorophenol	25:14	27:12	266	2
13	1,2-dimethyl-3-nitrobenzene (IS#1)	17:43	19:29	134	
14	2,3,4,5-tetrachlorophenol (IS#2)	22:09	24:02	232	
15	2-chlorophenol-3,4,5,6-d_4 (SURR)	11:04	12:47	132	1
16	2,4-dimethylphenol-3,5,6-d_3 (SURR)	14:59	16:34	110	1
17	2,4,6-tribromophenol (SURR)	23:37	25:37	330	2

a- Number refers to peak number in Figures 1-3.
b- Column 1- 30 m × 0.25 mm id DB-5ms (J&W), 0.25 :m film thickness.
c- Column 2- 30 m × 0.25mm id BPX5 (SGE), 0.25 :m film thickness.
d- Because the MS response to these compounds is low, and both the listed ions are near 100% ion abundance, the signal from both ions may be added together to increase sensitivity.

TABLE 3. ION ABUNDANCE CRITERIA FOR DECAFLUOROTRIPHENYLPHOSPHINE (DFTPP)

Mass (m/z)	Relative Abundance Criteria	Purpose of Checkpoint [a]
51	10-80% of the base peak	low mass sensitivity
68	<2% of mass 69	low mass resolution
70	<2% of mass 69	low mass resolution
127	10-80% of the base peak	low-mid mass sensitivity
197	<2% of mass 198	mid-mass resolution
198	base peak or >50% of 442	mid-mass resolution and sensitivity
199	5-9% of mass 198	mid-mass resolution and isotope ratio
275	10-60% of the base peak	mid-high mass sensitivity
365	>1% of the base peak	baseline threshold
441	Present and < mass 443	high mass resolution
442	base peak or >50% of 198	high mass resolution and sensitivity
443	15-24% of mass 442	high mass resolution and isotope ratio

a- All ions are used primarily to check the mass measuring accuracy of the mass spectrometer and data system, and this is the most important part of the performance test. The three resolution checks, which include natural abundance isotope ratios, constitute the next most important part of the performance test. The correct setting of the baseline threshold, as indicated by the presence of low intensity ions, is the next most important part of the performance test. Finally, the ion abundance ranges are designed to encourage some standardization to fragmentation patterns.

TABLE 4. RESULTS FROM REPLICATE ANALYSES OF REAGENT WATER FORTIFIED WITH METHOD ANALYTES AT 1-10 :g/L [a] USING HOT SPLITLESS INJECTION

Analyte	Concentration= 10 :g/L [b], n=4		Concentration= 5 :g/L [c], n=4		Concentration= 1 :g/L [b], n=7	
	Mean % Recovery	RSD (%)	Mean % Recovery	RSD (%)	Mean % Recovery	RSD (%)
phenol	75.9	4.3	103	18	90.8	20
2-chlorophenol	91.3	2.6	86.7	4.3	89.7	7.9
2-methylphenol (o-cresol)	93.3	2.2	86.1	3.6	84.9	7.3
2-nitrophenol	97.4	3.6	97.8	4.8	75.0	11
2,4-dimethylphenol	91.0	1.7	74.7	8.5	76.3	8.0
2,4-dichlorophenol	94.3	2.9	94.4	1.8	88.2	4.8
4-chloro-3-methylphenol	96.5	1.9	92.3	4.2	90.8	8.4
2,4,6-trichlorophenol	89.9	3.4	91.5	4.7	92.9	11
2,4-dinitrophenol	107	3.6	104	6.0	61.8	16
4-nitrophenol	107	3.0	90.5	11	96.3	14
2-methyl-4,6-dinitrophenol	105	3.2	83.0	1.6	91.5	8.9
pentachlorophenol	103	1.9	86.2	9.8	103	7.6
2-chlorophenol-3,4,5,6-d4 (SURR)	93.4	1.8	84.9	6.6	95.9	11
2,4-dimethylphenol-3,5,6-d3 (SURR)	94.0	2.0	82.0	7.2	95.1	13
2,4,6-tribromophenol (SURR)	82.2	1.8	77.1	6.1	98.0	8.6

a- Surrogate concentrations in all sample are 5 :g/L for tribromophenol and 2 :g/L for the deuterated phenols.
b- Data obtained using Column 1.
c- Data obtained using Column 2

TABLE 5. ACCURACY [a] AND PRECISION DATA FOR METHOD ANALYTES FORTIFIED AT 10 :g/L IN THREE MATRICES HOT SPLITLESS INJECTION

ANALYTE	HARD GROUND WATER [b, c] n=4		CHLORINATED SURFACE WATER [c] n=4		SIMULATED HIGH TOC WATER [c, d] n=4	
	% Rec	RSD (%)	%Rec	RSD (%)	%Rec	RSD (%)
phenol	77.6	5.1	73.9	4.5	73.7	5.1
2-chlorophenol	91.2	2.6	88.6	3.0	85.8	5.2
2-methylphenol (o-cresol)	93.2	3.4	91.3	2.3	89.2	4.3
2-nitrophenol	102	2.5	99.4	2.1	99.0	2.8
2,4-dimethylphenol	86.3	2.0	86.6	1.9	83.2	5.3
2,4-dichlorophenol	94.8	1.2	93.3	1.4	90.0	5.1
4-chloro-3-methylphenol	98.5	1.6	97.5	1.4	94.6	3.9
2,4,6-trichlorophenol	95.5	3.9	92.7	3.1	89.1	4.1
2,4-dinitrophenol	117	4.2	118	2.3	121	1.0
4-nitrophenol	102	2.4	102	3.8	95.9	2.3
2-methyl-4,6-dinitrophenol	115	2.2	113	1.5	115	0.71
pentachlorophenol	110	4.0	108	5.1	105	1.8
2-chlorophenol-3,4,5,6-d4 (SURR)	93.0	2.4	91.5	1.6	89.1	5.3
2,4-dimethylphenol-3,5,6-d3 (SURR)	88.9	3.0	87.2	2.4	85.4	4.8
2,4,6-tribromophenol (SURR)	74.7	2.6	76.3	5.1	71.0	4.5

a- Accuracy is presented as % recovery

b- Hard municipal chlorinated ground water, 450mg/L hardness measured as calcium carbonate.

c- Data obtained using Column 1.

d- Simulated high organic content (high Total Organic Carbon) sample prepared by adding 10 mg/L humic acid (Fluka Chemical Corp., Milwaukee, WI) to reagent water.

TABLE 6. RESULTS OF REPLICATE ANALYSES IN TWO MATRICES USING TEMPERATURE PROGRAMMABLE INJECTION [a]

ANALYTE	Reagent Water Concentration= 0.5 :g/L, n=7		Reagent Water Concentration= 5 :g/L, n=4		Chlorinated Surface Water Concentration= 10 :g/L, n=5	
	% Recovery	RSD (%)	% Recovery	RSD (%)	% Recovery	RSD (%)
phenol	74.5	13	107	21	74.1	7.5
2-chlorophenol	88.3	11	95.5	7.7	94.8	4.3
2-methylphenol (o-cresol)	96.2	9.4	93.0	4.5	103	8.1
2-nitrophenol	89.1	8.9	102	6.8	94.5	7.4
2,4-dimethylphenol	82.0	8.2	85.5	8.8	93.8	9.8
2,4-dichlorophenol	83.0	8.3	100	7.3	93.7	2.9
4-chloro-3-methylphenol	79.0	6.6	101	7.5	96.6	2.9
2,4,6-trichlorophenol	78.9	8.1	102	10	90.7	3.3
2,4-dinitrophenol	63.8	22	95.4	6.6	113	4.7
4-nitrophenol	84.1	14	103	8.1	102	6.8
2-methyl-4,6-dinitrophenol	62.4	9.4	103	5.1	107	4.9
pentachlorophenol	72.0	7.2	88.0	7.2	93.8	6.8
2-chlorophenol-3,4,5,6-d4 (SURR)	79.1	7.6	87.6	3.9	84.7	10
2,4-dimethylphenol-3,5,6-d3 (SURR)	79.9	8.5	91.9	7.8	97.0	8.3
2,4,6-tribromophenol (SURR)	79.6	7.8	86.1	7.8	79.5	12

a- Data obtained using Column 1.

TABLE 7. RESULTS OF AQUEOUS HOLDING TIME STUDIES FOR METHOD 528 ANALYTES [a]

ANALYTE	DAY 0		DAY 7		DAY 10		DAY 15	
	% Rec	RSD (%)	% Rec	RSD (%)	% Rec	RSD (%)	% Rec	RSD (%)
phenol	74.5	1.9	77.0	3.8	74.3	3.4	74.3	3.5
2-chlorophenol	91.5	1.9	88.8	1.3	88.0	2.9	85.8	4.1
2-methylphenol (o-cresol)	99.9	2.8	96.0	1.2	94.3	2.6	93.0	2.8
2-nitrophenol	99.1	4.3	100	4.0	98.8	3.9	101	3.1
2,4-dimethylphenol	85.5	4.2	80.7	3.9	79.1	8.1	75.2	4.7
2,4-dichlorophenol	94.2	2.2	93.0	2.5	92.3	1.0	91.8	3.3
4-chloro-3-methylphenol	96.5	2.1	95.5	3.5	96.5	2.3	96.5	3.9
2,4,6-trichlorophenol	94.8	3.3	97.1	2.9	96.0	2.8	95.0	3.3
2,4-dinitrophenol	102.8	5.1	102	3.4	107	8.0	112	2.9
4-nitrophenol	100.1	3.2	100	4.2	101	4.9	96.2	3.3
2-methyl-4,6-dinitrophenol	96.1	5.1	109	8.7	113	5.8	115	5.0
pentachlorophenol	94.5	4.1	102	2.1	103	3.5	102	2.3

a- All analytes fortified into a chlorinated surface water at a concentration of 10 :g/L, dechlorinated and acidified according to Section 8, stored for 48 hr at 10° C, followed by storage at 6° C. For each time point, n=5.

TABLE 8. RESULTS OF EXTRACT HOLDING TIME STUDIES FOR METHOD 528 ANALYTES [a]

ANALYTE	DAY 0		DAY 14		DAY 23		DAY 35	
	% Rec	RSD (%)	% Rec	RSD (%)	% Rec	RSD (%)	% Rec	RSD (%)
phenol	74.5	1.9	74.2	3.8	72.7	3.4	74.9	3.5
2-chlorophenol	91.5	1.9	89.8	1.3	88.6	2.9	89.1	4.1
2-methylphenol (o-cresol)	99.9	2.8	97.5	1.2	98.4	2.6	96.6	2.8
2-nitrophenol	99.1	4.3	100	4.0	96.4	3.9	101	3.1
2,4-dimethylphenol	85.5	4.2	86.9	3.9	88.0	8.1	88.7	4.7
2,4-dichlorophenol	94.2	2.2	95.4	2.5	96.1	1.0	98.6	3.3
4-chloro-3-methylphenol	96.5	2.1	98.9	3.5	98.1	2.3	102	3.9
2,4,6-trichlorophenol	94.8	3.3	97.1	2.9	97.6	2.8	102	3.3
2,4-dinitrophenol	102.8	5.1	104	3.4	90.9	8.0	99.1	2.9
4-nitrophenol	100.1	3.2	91.1	4.2	89.3	4.9	96.3	3.3
2-methyl-4,6-dinitrophenol	96.1	5.1	108	8.7	98.2	5.8	110	5.0
pentachlorophenol	94.5	4.1	99.1	2.1	100	3.5	105	2.3

a- All extracts were from the Day 0 aqueous holding time samples, and were stored in amber vials at 0° C. For each time point, n=5.

TABLE 9. INITIAL DEMONSTRATION OF CAPABILITY (IDC) REQUIREMENTS

Method Reference	Requirement	Specification and Frequency	Acceptance Criteria
Sect. 9.2.1	Initial Demonstration of Low Method Background	Analyze LRB prior to any other IDC steps.	Demonstrate that all target analytes are below 1/3 the MRL, and that possible interferences from extraction media do not prevent the identification and quantification of method analytes.
Sect. 9.2.2	Initial Demonstration of Precision (IDP)	Analyze 4-7 replicate LFBs fortified at 5-10 : g/L	RSD must be #20% for all analytes except phenol which must be # 30%.
Sect. 9.2.3	Initial Demonstration of Accuracy (IDA)	Calculate average recovery for replicates used in IDP	Mean recovery 70-130% of true value, except phenol which is 50-150%
Sect. 9.2.4	Method Detection Limit (MDL) Determination	Over a period of three days, prepare a minimum of 7 replicate LFBs fortified at a concentration estimated to be near the MDL. Analyze the replicates through all steps of the analysis. Calculate the MDL using the equation in Section 9.2.4.	**Note:** Data from MDL replicates are not required to meet method precision and accuracy criteria. If the MDL replicates are fortified at a low enough concentration, it is likely that they will not meet precision and accuracy criteria.

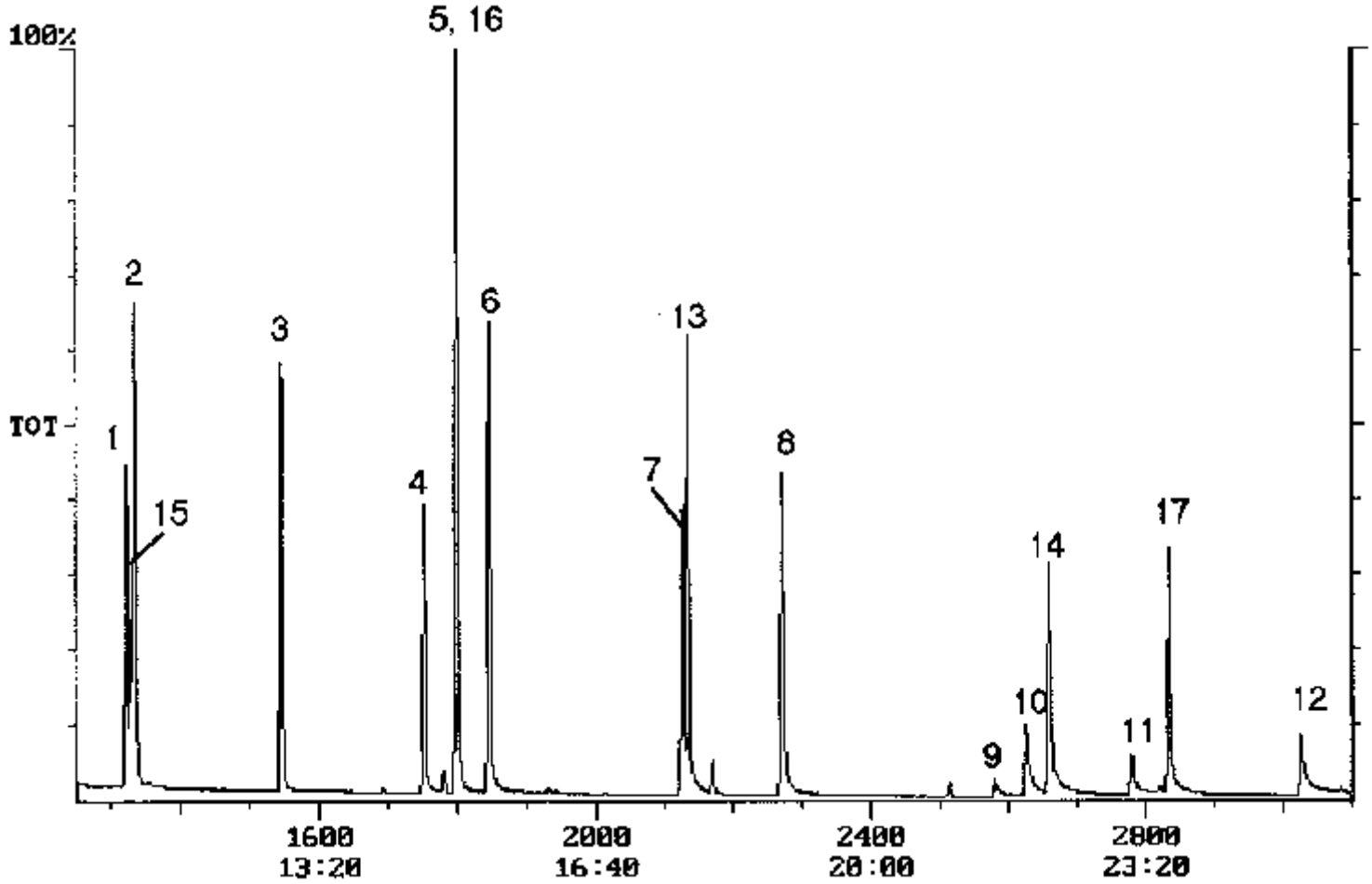
TABLE 10. QUALITY CONTROL REQUIREMENTS (SUMMARY)

Method Reference	Requirement	Specification and Frequency	Acceptance Criteria
Sect. 8.4	Sample Holding Time	14 days, dechlorinated and acidified to pH#2	Iced or refrigerated at 10°C or less for up to 48 hours, 6°C thereafter.
Sect. 8.4	Extract Holding Time	30 days	Stored at 0°C or less in amber vials.
Sect.9.11	Laboratory Fortified Sample Matrix (LFM)	Analyze one LFM per extraction batch (20 samples or less) fortified with method analytes at a concentration close to the native concentration.	Recoveries not within 70-130% of the fortified amount may indicate a matrix effect.
Sect. 9.12	Field Duplicates	Analyze 1 FD for each 20 samples, or 1 per extraction batch, whichever is greater.	Suggested RPD±30%.
Sect. 9.13	Quality Control Sample (QCS)	Analyze QCS whenever new standards are prepared, or at least quarterly.	If analyzed as a calibration sample, CCC criteria apply. If analyzed as a LFB, those criteria apply.
Sect 9.2.1	Laboratory Reagent Blank (LRB)	Daily, or with each extraction batch of up to 20 samples, whichever is more frequent.	Demonstrate that all target analytes are below 1/3 the MRL, and that possible interference from extraction media do not prevent the identification and quantification of method analytes.
Sect. 9.8	Laboratory Fortified Blanks (LFB)	Analyze at least one LFB daily or for each extraction batch of up to 20 field samples. Rotate the fortified concentration between low, medium and high amounts.	Results of LFB analyses must be 70-130% of the true value (except phenol) for each analyte and surrogate for all fortified concentrations greater than the lowest CAL point. Results of LFBs corresponding to the lowest CAL point must be 50-150% of the true value.

Sect. 9.9	Internal Standard	1,2-dimethyl-3-nitrobenzene (IS#1) and 2,3,4,5-tetrachloro-phenol (IS#2) are added to all standards and sample extracts.	Peak area counts for IS#1 in LFBs, LRBs and sample extracts must be within 70-130% of the peak area in the most recent CCC, and 50-150% of average area in the initial calibration.
Sect 9.10	Surrogate Standards	Surrogate standards are added to all standards, samples, LFBs, LFMs, FDs, LRBs, and LFBs.	Recovery for 2-chlorophenol-3,4,5,6-d_4 and 2,4-dimethylphenol-3,5,6-d_3 in all standards, LRB, LFB, LFM, FD and sample extracts must be 70-130% of the true value. Recovery for 2,4,6-tribromophenol must be 60-130%.
Sect. 10.2.1	MS Tune Check	Analyze DFTPP to verify MS tune before initial calibration and before every recalibration.	Criteria are given in Table 3.
Sect.10.2.2	Initial Calibration	Use internal standard calibration technique to generate an average RF or first or second order calibration curve. Use at least 5 standard concentrations that span the approximate range of 0.1- 15 :g/L.	When each calibration standard is calculated as an unknown using the calibration curve, the result must be 70-130% of the true value for all but the lowest standard. The lowest standard must be 50-150% of the true value.
Sect. 10.2.3.1	GC Performance-Peak Tailing Check	Calculate the peak tailing factor for compounds listed in the referenced section, at the beginning of each day during which samples are analyzed. In cases of continuous instrument operation, check peak tailing factors every 24 hr.	Peak tailing factor of 5 or less. (See Fig.4 for calculation of PTF.)

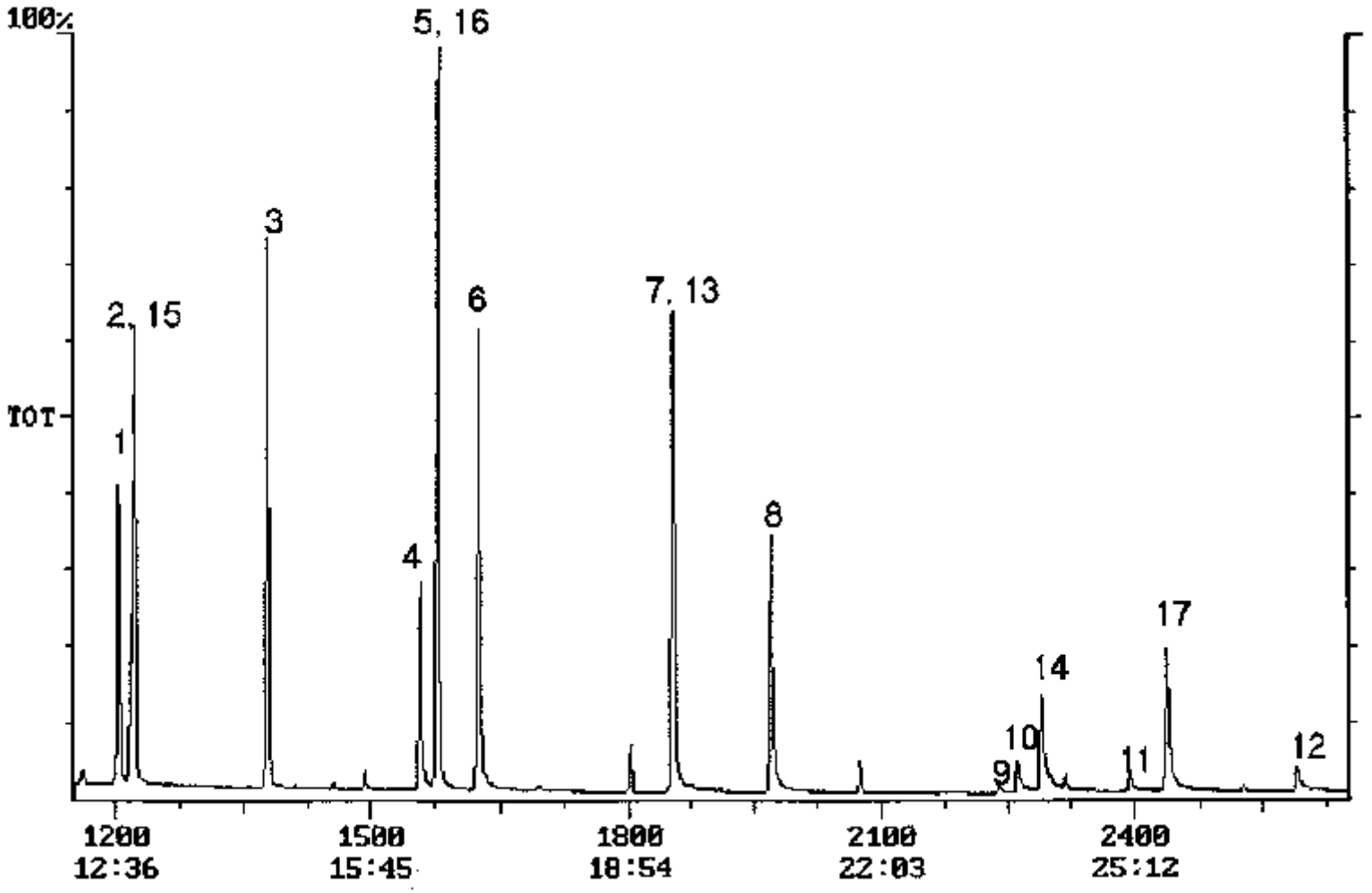
Sect. 10.3	Continuing Calibration Check	Verify initial calibration by analyzing a calibration standard prior to analyzing samples, after every 10 samples, and after the last sample. Always analyze a low concentration (near the MRL) CCC at the beginning of the analysis period.	The result for each analyte and surrogate must be 70-130% of the true value for all concentrations except the lowest CAL point for each analyte. The lowest CAL point for each analyte must be 50-150% of the true value. The peak area of IS#1 must be within 70-130% of the peak area in the most recent CCC, and 50-150% of the average peak area calculated during initial calibration.

FIGURE 1.CHROMATOGRAM OF PHENOL STANDARD MIX (5 ng/ :L EACH ANALYTE) ON A DB-5ms COLUMN WITH HOT SPLITLESS INJECTION [a].



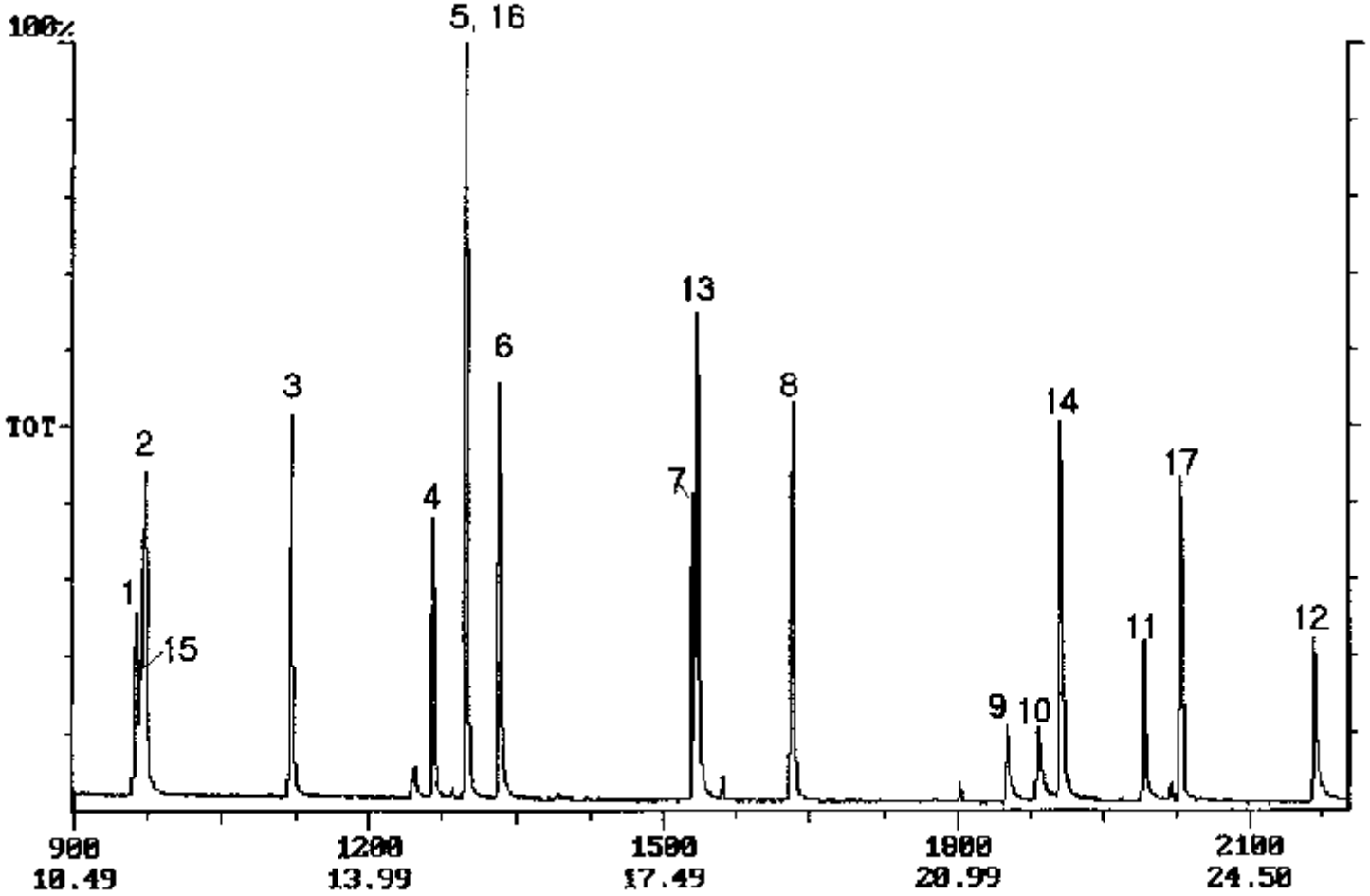
a- peak numbers refer to compounds as listed in Table 2.

FIGURE 2.CHROMATOGRAM OF PHENOL STANDARD MIX (5 ng/ :L EACH ANALYTE) ON A BPX5 COLUMN WITH HOT SPLITLESS INJECTION. [a]



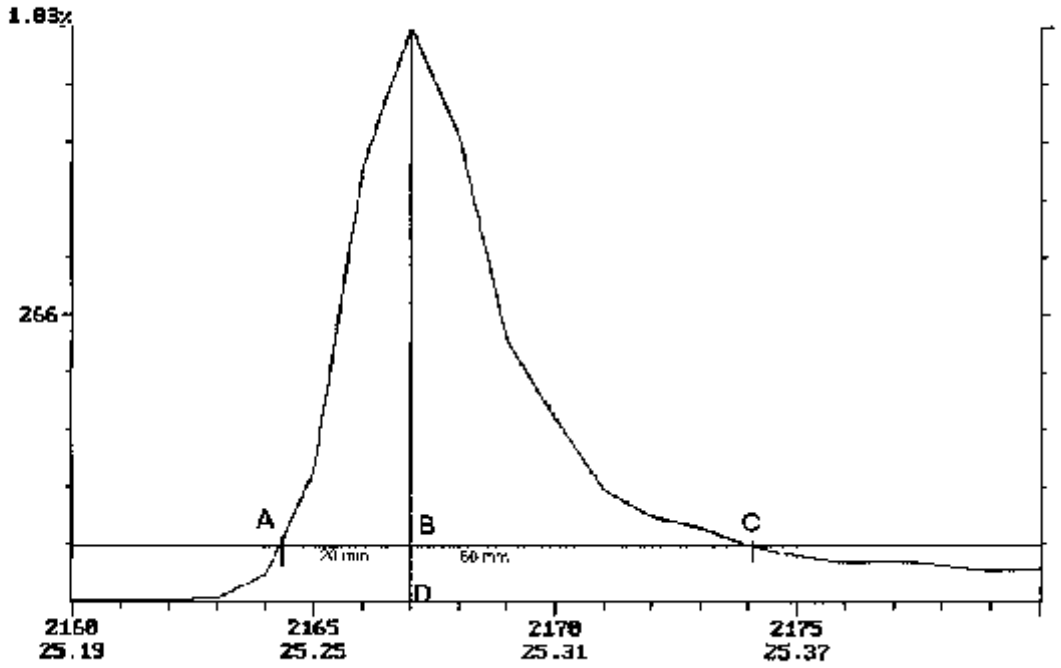
a- peak numbers refer to compounds as listed in Table 2..

FIGURE 3. CHROMATOGRAM OF PHENOL STANDARD MIX (5 ng/ :L EACH ANALYTE) ON A DB-5ms COLUMN WITH TEMPERATURE PROGRAMMED SPLITLESS INJECTION. [a]



a- peak numbers refer to compounds as listed in Table 2.

FIGURE 4. PEAK TAILING FACTOR (PTF) CALCULATION.



$$\text{Peak Tailing Factor} = \frac{BC}{AB}$$

BD = 10 % peak height

Note: the PTF should be calculated from the single ion chromatogram of the quantitation ion. This example is for the pentachlorophenol peak. The PTF = 2.5.