METHOD 554

DETERMINATION OF CARBONYL COMPOUNDS IN DRINKING WATER BY DINITROPHENYLHYDRAZINE DERIVATIZATION AND HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

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METHOD 554

DETERMINATION OF CARBONYL COMPOUNDS IN DRINKING WATER BY DINITROPHENYLHYDRAZINE DERIVATIZATION AND HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)

1.0 SCOPE AND APPLICATION

1.1 This is a high performance liquid chromatographic (HPLC) method optimized for the determination of selected carbonyl compounds in finished drinking water and raw source water. The analytes applicable to this method are partitioned from the water onto a reverse phase C_{18} bonded silica packed cartridge, then eluted with ethanol. Liquid-solid extraction disks may also be used for this purpose. Single-laboratory accuracy and precision data have been generated for the following compounds:

Analyte	Chemical Abstract Services Registry Number
Formaldehyde	50-00-0
Acetaldehyde	75-07-0
Propanal	123-38-6
Butanal	123-72-8
Pentanal	110-62-3
Hexanal	66-25-1
Heptanal	111-71-7
Octanal	124-13-0
Nonanal	124-19-6
Decanal	112-31-2
Cyclohexanone	108-94-1
Crotonaldehyde	123-73-9

1.2 The method detection limits (MDLs) for the analytes are listed in Tables 1 and 2. The MDL is defined as the statistically calculated minimum amount that can be measured with 99% confidence that the reported value is greater than zero[1]. The MDLs for a specific sample may differ from that of the standard matrix and by the volume of sample used in the procedure. For the listed analytes, MDLs range from 3.0-69.0 µg/L.

1.3 This method is restricted to use by or under the supervision of analysts experienced in the use of HPLC and in the interpretation of chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method, using the procedure described in Section 11.0.

2.0 SUMMARY OF METHOD

2.1 A measured volume of aqueous sample, approximately 100 mL, is buffered to pH 3 and the analytes are derivatized at 40°C for one hour with 2,4-dinitrophenylhydrazine (DNPH). The derivatives are extracted from the water by passing the sample through a series of three cartridges each of which contains 500 mg of a chemically bonded C_{18} organic phase (liquid-solid extraction, LSE). The solid sorbent cartridges are then eluted with 10 mL of ethanol. LSE disks may also be used as long as all the (QC) criteria specified in Section 9.0 of this method are met. Liquid chromatographic conditions are described which permit the separation and measurement of the carbonyl compounds in the extract by absorbance detection at 360 nm.

3.0 DEFINITIONS

3.1 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 and reagents, internal standards, and surrogates 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.

3.2 Field Reagent Blank (FRB) -- An aliquot of reagent water or other blank matrix that is placed in a sample container in the laboratory and treated as a sample in all respects, including shipment to the sampling site, exposure to sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the FRB is to determine if method analytes or other interferences are present in the field environment.

3.3 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, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.

3.4 Laboratory Fortified Matrix Sample (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.

3.5 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.

3.6 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.

3.7 Calibration Standard (CAL) -- A solution prepared from the primary dilution standard solution and 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.

3.8 Quality Control Sample (QCS) -- A solution of method analytes of known concentrations which is used to fortify an aliquot of LRB or sample matrix. The QCS 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.

4.0 INTERFERENCES

4.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in the chromatograms. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by analyzing laboratory reagent blanks as described in Section 9.2.

4.1.1 Glassware must be scrupulously cleaned as soon as possible after use by rinsing with the last solvent used. This should be followed by detergent washing with hot water, and rinses with tap water and distilled water. Glassware should then be drained, dried, and heated in a laboratory oven at 130°C for several hours before use. Solvent rinses with methanol may be substituted for the oven heating. After drying and cooling, glassware should be stored in a clean environment to prevent any accumulation of dust or other contaminants.

4.1.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

4.2 Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the matrix being sampled. If interferences occur, cleanup may be necessary.

4.3 The extent of interferences that may be encountered using liquid chromatographic techniques has not been fully assessed. Although the HPLC conditions described allow for resolution of the specific compounds covered by this method, other matrix components may interfere.

4.4 Acetaldehyde is generated during the derivatization step due to the use of ethanol as the solvent for the DNPH. This background will impair the measurement of acetaldehyde at levels below 250 µg/L. Accordingly, if acetaldehyde is a compound of interest, use of another solvent, such as acetonitrile, for the DNPH solution is suggested.

5.0 SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method[2]. A reference file of material safety data sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available.

5.2 Formaldehyde and acetaldehyde have been tentatively classified as known or suspected human or mammalian carcinogens.

6.0 EQUIPMENT AND SUPPLIES

6.1 Sample Containers

6.1.1 Grab sample bottle (aqueous samples) -- 8 oz. (237 mL) amber glass, screw cap bottles and caps equipped with Teflon-faced silicone septa. Prior to use, wash bottles and septa.

6.1.2 Grab sample bottle (solids) -- 8 oz., amber glass, wide mouth, screw cap bottles and caps equipped with Teflon-lined closures. Prior to use wash bottles and septa.

6.2 Reaction Vessel -- 250 mL Florence flask.

6.3 Vials -- 10 mL and 25 mL, glass with Teflon-lined screw-caps.

6.4 Volumetric Flasks -- 10 mL, with ground glass stopper.

6.5 Balance -- Analytical, capable of accurately weighing to the nearest 0.0001 g.

6.6 pH Meter -- Capable of measuring to the nearest 0.01 units.

6.7 High Performance Liquid Chromatographic Apparatus (Modular)

6.7.1 Pumping system -- Gradient, with constant flow control capable of 1.50 mL/min.

6.7.2 High pressure injection valve with 20 µL loop.

6.7.3 Column -- 250 mm x 4.6 mm i.d., 5 µm particle size, C18 (Zorbax or equivalent).

6.7.4 Absorbance detector -- 360 nm.

6.7.5 Strip-chart recorder compatible with detector -- Use of a data system for measuring peak area and retention times is recommended.

6.8 LSE Cartridges -- Packed with about 500 mg silica whose surface is modified by chemically bonded octadecyl (C-18) groups. These cartridges are available from several commercial suppliers. LSE disks may also be used as long as all the QC criteria specified in Section 9.0 of this method are met.

6.9 Vacuum Manifold -- Capable of simultaneous extraction of 10 samples

6.10 Sample Reservoirs -- 60 mL capacity.

6.11 Pipet -- Capable of accurately delivering 0.10 mL solution.

6.12 Syringes -- Luer-Lok, 5 mL, 500 µL, and 100 µL.

6.13 Environmental Shaker -- Controlled temperature incubator (±2°C) with orbital shaking (Lab-Line Orbit Environ-Shaker Model 3527 or equivalent).

7.0 REAGENTS AND STANDARDS

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

7.2 Reagent Water -- All references to reagent water in this method refer to water in which an interference is not observed at the MDL of the compound of interest. Reagent water can be generated by passing tap water through a carbon filter bed containing about 1 lb. of activated carbon. Subsequently, while maintaining the temperature at 90°C, bubble a contaminant-free inert gas through the water for one hour. A water purification system may be used to generate organic-free deionized water.

7.3 Methanol -- HPLC grade or equivalent.

7.4 Ethanol -- Reagent grade.

7.5 2,4-Dinitrophenylhydrazine (DNPH) -- 70% (W/W) in water.

7.6 Citric Acid -- $C_6H_8O_7$.

7.7 Sodium Citrate -- Trisodium salt dihydrate.

7.8 Sodium Hydroxide -- Concentrated.

7.9 Sodium Chloride

7.10 Sodium Sulfite -- Na_2SO_3.

7.11 Sodium Sulfate -- Na_2SO_4, granular, anhydrous.

7.12 Hydrochloric Acid -- 0.1 N.

7.13 Acetic Acid -- Glacial.

7.14 Ammonium Chloride -- NH_4Cl.

7.15 Extraction Fluid -- Dilute 64.3 mL of 1.0 N NaOH and 5.7 mL of glacial acetic acid to 900 mL with water. The pH should be 4.93 ±0.02. Dilute to 1 L with water.

7.16 Stock Standard Solutions

7.16.1 Stock standard formaldehyde solution approximately 1 mg/mL -- Prepare by diluting 265 µL of formalin to 100 mL with water.

7.16.2 Standardization of formaldehyde stock solution -- Transfer a 25 mL aliquot of a 0.1 M Na_2SO_3 solution to a beaker and record the pH. Add a 25.0 mL aliquot of the formaldehyde stock solution (Section 7.16.1) and record the pH. Titrate this mixture back to the original pH using 0.1 N HCl. The formaldehyde concentration is calculated using the following equation:

$$\text{Concentration (mg/mL)} = 30.03 \times (\text{N HCl}) \times (\text{mL HCl}) / 25.0$$

where: N HCl = Normality of HCl solution used.
mL HCl = mL of standardized HCl solution used.
30.03 = MW of formaldehyde.

NOTE: The pH value of the 0.1 Na_2SO_3 should be 10.5 ±0.2. When the stock formaldehyde solution and the 0.1 M Na_2SO_3 solution are mixed together as in Section 7.16.2, the pH should be 11.5 ±0.2. It is recommended that new solutions be prepared if the pH deviates from this value.

7.16.3 Stock aldehyde(s) and ketone(s) -- Prepare by adding an appropriate

amount of the analyte to 90 mL of methanol, then dilute to 100 mL to give a final concentration of 1.0 mg/mL.

7.16.4 Stock standard solutions must be replaced after six weeks, or sooner, if comparison with check standards indicates a problem.

7.17 Reaction Solutions

7.17.1 DNPH (3.00 g/L) -- Dissolve 428.7 mg of 70% (w/w) reagent in 100 mL absolute ethanol. Slight heating or sonication may be necessary to effect dissolution.

NOTE: If the DHPH does not complete by dissolve, filter the solution to remove the undissolved compound.

7.17.2 pH 3 Citrate buffer (1 M) -- Prepare by adding 80 mL of 1 M citric acid solution to 20 mL 1 M sodium citrate solution. Mix thoroughly. Adjust pH with 6N NaOH or 6N HCl as needed.

7.17.3 Sodium chloride solution (saturated) -- Prepare by mixing an excess of the reagent grade solid with water.

7.17.4 Reducing agent, ammonium chloride (100 mg/L) -- Added to all samples containing residual chlorine. Sodium thiosulfate is not recommended because it may produce a residue of elemental sulfur that can interfere with some analytes. The ammonium chloride may be added as a solid with stirring until dissolved, to each volume of water.

7.18 Syringe Filters -- 0.45 µm filtration disks (Gelman Acrodisc No. 4438, or equivalent).

8.0 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 two to five minutes). Adjust the flow to about 500 mL/min and collect samples from the flowing stream. 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 must be free of plastic and other parts that may leach analytes into water. Follow other conventional sampling procedures[3] as needed.

8.2 Sample Dechlorination and Preservation -- All samples should be iced or refrigerated at 4°C from the time of collection until extraction. Residual chlorine should be reduced at the sampling site by addition of a reducing agent (Section 7.17.4).

8.2.1 The use of HCL as a sample preservative has not been implemented in

this method. Method 554 has been designed to measure "free" aldehydes and cyclohexanone by employing mild reaction conditions. The evolution of aldehydes can occur in samples whose pH is low (less than or equal to 2[4,5].

8.3 Holding Time -- Samples must be derivatized and extracted within three days of sample collection. In reagent water, the analyte concentrations remained constant over a seven-day period. In ground water, hexanal, octanal and decanal experienced losses after the first day. The other analytes degraded after the third day. Matrices, such as groundwater, which are biologically active, should be extracted upon receipt. All samples should be extracted within three days of collection.

8.4 Field Reagent Blanks (FRB) -- Processing of a FRB is recommended along with each sample set, which is composed of the samples collected from the same general sampling site at approximately the same time. At the laboratory, fill a sample container with reagent water, seal and ship to the sampling site along with the empty sample containers. Return the FRB to the laboratory with filled sample bottles.

9.0 QUALITY CONTROL

9.1 Each laboratory that uses this method is required to operate a formal QC program. Minimum QC requirements are initial demonstration of laboratory capability, analysis of laboratory reagent blanks, laboratory fortified blanks, laboratory fortified sample matrices, and QC samples. Additional QC practices are encouraged.

9.2 Laboratory Reagents Blanks (LRB) -- Before processing any samples, the analyst must analyze at least one LRB to demonstrate the absence of contaminants that would prevent the determination of any method analyte. In addition, each time a set of samples is extracted or reagents are changed, a LRB must be analyzed. 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.

9.3 Initial Demonstration of Capability

9.3.1 Select a representative fortified concentration for each of the target analytes at approximately 250 µg/L. Prepare a primary dilution standard (PDS) in methanol 1000 times more concentrated than the selected concentration. This primary dilution standard must be prepared independently from the standards used to prepare the calibration curve. With a syringe, add 100 µL of the PDS to each of four to seven 100 mL aliquots of reagent water. Analyze the aliquots according to the method beginning in Section 11.0.

9.3.2 Calculate the measured concentration of each analyte in each replicate, the mean concentration of each analyte in all replicates, the mean accuracy (as mean percentage of true value), the precision (RSD), and the MDL[1]. Determine accuracy based upon extracted standards as called for in Section 10.0. For each analyte, the mean accuracy must fall in the range of R ±30% using the values for reagent water listed in Table 3 at the lower concentration level. The calculated standard deviation should be less than ±30% or 3 Sr (value listed in Table 3), whichever is larger. For those compounds that meet these criteria, performance is considered acceptable and sample analysis may begin. For those compounds that fail these criteria, the procedures in Section 9.3.1 must be repeated using a minimum of four fresh samples until satisfactory performance has been demonstrated.

9.3.3 The initial demonstration of capability is used primarily to preclude a laboratory from analyzing unknown samples using a new, unfamiliar method prior to obtaining some experience with it. As laboratory personnel gain experience with this method, the quality of data should improve beyond those required here.

9.3.4 The analyst is permitted to modify HPLC conditions. Each time a method modification is made, the analyst must repeat the procedures in Section 9.3.1.

9.4 Laboratory Fortified Blank (LFB)

9.4.1 The laboratory must analyze at least one LFB sample with every 20 samples or one per sample set (all samples extracted within a 24-hour period), whichever frequency is greater. A fortified concentration near the lower value in Table 3 is recommended. The LFB sample must be prepared from a primary dilution standard which is prepared separately and independently from the standards used to prepare the calibration curve. Calculate the mean recovery (R). If the accuracy for any analyte falls outside the control limits (See Section 9.4.2), that analyte is judged out of control, and the source of the problem should be identified and resolved before continuing analyses.

9.4.2 Prepare control charts based on mean upper and lower control limits R ±3 S_r. The initial demonstration of capability (Section 9.3) establishes the initial limits. After each four to six new accuracy measurements, recalculate R and S_r using all the data, and construct new control limits. When the total number of data points reach 20, update the control limits by calculating R and S_r using only the most recent 20 data points. At least quarterly, replicates of LFBs should be analyzed to determine the precision of the laboratory measurements. Add these results to the ongoing control charts to document data quality.

9.5 Laboratory Fortified Sample Matrix

9.5.1 The analyst must add known concentrations of analytes to a minimum of 10% of the routine samples or one concentration per sample set, whichever frequency is greater. The concentrations should be equal to or greater than the background concentrations in the sample selected for fortification. Ideally, the concentration should be the same as that used for the laboratory fortified blank (Section 9.4). Over time, samples from all routine sample sources should be fortified.

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

$$R = 100 (A - B) / C,$$

where C is the fortified concentration. Compare these values to control limits appropriate for reagent water data collected in the same fashion (Section 9.4).

9.5.3 If the accuracy of any analyte falls outside the designated range, and the laboratory performance for that analyte is shown to be in control (Section 9.4), the accuracy problem encountered with the fortified sample is judged to be matrix related, not system related. The result for that analyte in the unfortified sample is labeled suspect/matrix to inform the data user that the results are suspect due to matrix effects.

9.6 Quality Control Sample (QCS) -- At least quarterly, analyze a QCS from an external source. If measured analyte concentrations are not of acceptable accuracy, check the entire analytical procedure to locate and correct the problem source.

9.7 The laboratory may adopt additional QC practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. For example, field or laboratory duplicates may be analyzed to assess the precision of the environmental measurements, or field reagent blanks may be used to assess contamination of samples under site, transportation and storage conditions.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Establish HPLC operating parameters to completely separate the peaks. Table 1 lists some retention times produced using the following conditions:

HPLC Column:	C18, 250 mm x 4.6 mm i.d., 5 µm particle size
Mobile Phase:	70%/30% methanol/water (v/v) for 20 min, up to 100% methanol in 15 minutes, hold at 100% methanol for 10 minutes
Flow Rate:	1.5 mL/min
UV Detector:	360 nm
Injection Size:	20 µL

10.2 Prepare procedural calibration standards according to the procedure in Section 10.2.1. Calibrate the chromatographic system using the external standard technique (Section 10.2.2).

10.2.1 Preparation of calibration standards

10.2.1.1 Prepare calibration solutions at a minimum of five concentration levels for each analyte of interest by adding volumes of stock standard solutions (Section 7.16) to reagent water and diluting to 100 mL. The lowest concentration level of each analyte should be near to, but above, the MDLs listed in Table 1 or 2, while the other concentration levels should correspond to the expected range of concentrations found in real samples.

10.2.1.2 Process each calibration standard solution through derivatization and extraction using the same extraction option employed for sample processing (Section 11.1.3).

10.2.2 External standard calibration procedure

10.2.2.1 Analyze each processed calibration standard (some suggested chromatographic conditions are listed in Section 10.1) and tabulate peak area (y axis) versus calibration solution concentration (x axis) in µg/L. The results may be used to prepare calibration curves for the analytes. By linear regression, determine the slope, m, of the calibration curve.

10.2.2.2 The working calibration curve must be verified on each working day by the measurement of one or more fresh calibration standards. If the response for any analyte varies from the previously established responses by more than 10%, the test must be repeated after it is verified that the analytical system is in control. Alternatively, a

new calibration curve may be prepared for that compound. If an autosampler is available, it may be convenient to prepare a calibration curve daily by analyzing standards along with test samples.

11.0 PROCEDURE

11.1 Derivatization and Extraction

11.1.1 Measure a 100 mL aliquot of the sample. Other sample volumes, from 50-100 mL, may be used to accommodate the anticipated analyte concentration range. Quantitatively transfer the sample aliquot to a 250 mL Florence flask.

NOTE: In cases where the selected sample or extract volume is less than 100 mL, the total volume of the aqueous phase should be adjusted to 100 mL with reagent water.

11.1.2 Derivatization and extraction of the derivatives can be accomplished using the liquid-solid extraction (Section 11.1.3).

11.1.3 Liquid-solid extraction -- Either LSE cartridges or disks may be used.

11.1.3.1 Add 4 mL of citrate buffer to the sample and adjust the pH to 3.0 ±0.1 with 6 M HCl or 6 M NaOH. Add 6 mL of DNPH reagent, seal the container, and place in a heated, orbital shaker (Section 6.13), set at 40°C, for one hour. Adjust the agitation to gently swirl the reaction solution.

11.1.3.2 Assemble the vacuum manifold and connect it to a water aspirator or vacuum pump. Entrain three solid sorbent cartridges and attach the nested cartridges to the vacuum manifold. Condition the cartridges by passing 10 mL of dilute citrate buffer (10 mL of 1 M citrate buffer dissolved in 250 mL of water) through the cartridge train.

11.1.3.3 Remove the reaction vessel from the shaker and add 10 mL of saturated NaCl solution to the vessel.

11.1.3.4 Add the reaction solution to the cartridge train and apply a vacuum to draw the solution through the cartridges at a rate of 3-5 mL/min. Continue applying the vacuum for about 10 minutes after the liquid sample has passed through the cartridges.

11.1.3.5 While maintaining vacuum conditions, elute the cartridges with approximately 9 mL of absolute ethanol, directly into a 10 mL volumetric flask. Dilute the eluate to volume with absolute ethanol, mix thoroughly, and place in a tightly sealed vial until analysis.

NOTE: Because this method uses an excess of DNPH, the cartridges will retain a yellow color after this step. This color is not indicative of incomplete recovery of the analyte derivatives from the cartridges.

11.2 Analyze samples by HPLC, using recommended conditions provided in Section 10.1. Tables 1 and 2 list the retention times and MDLs that were obtained under these conditions. Other HPLC columns, chromatographic conditions, or detectors may be used provided the requirements of Section 9.3 are met.

11.3 The width of the retention time window used to make identifications 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 for a compound can be used to calculate a suggested window size; however, the experience of the analyst should weigh heavily in the interpretation of the chromatograms.

11.4 If an analyte peak area exceeds the linear range of the calibration curve, a smaller sample volume should be used. Alternatively, the final solution may be diluted with ethanol and reanalyzed.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Identify the method analytes in the sample chromatogram by comparing the retention time of the suspect peak to the retention time of an analyte peak in a calibration standard or the laboratory fortified blank. Computerized linear regression analysis is recommended for assessment of the linearity of the calibration and for slope calculation. Linearity is achieved when the coefficient of correlation (R) for the linear regression is ≥0.99. Alternatively, the slope, m, may be determined by calculating the average peak area to concentration ratio for each calibration standard. The percent relative standard deviation (% RSD) of the slope must be less than 10% if the latter procedure is to be employed.

12.2 Calculate the analyte concentrations as follows:

$$C_s = \frac{A}{m} \times \frac{100\ (mL)}{V_s}$$

where: m = slope of calibration curve, L/µg.
C_s = sample concentration in µg/L.
A = area of signal.
V_s = volume of sample in mL.

13.0 METHOD PERFORMANCE

13.1 The MDL concentrations listed in Tables 1 and 2 were obtained in reagent water and dechlorinated tap water using LSE. Results reported in both tables were achieved using fortified 100 mL samples.

13.2 This method has been tested for linearity of recovery from fortified reagent water and has been demonstrated to be applicable over the range from 10 x MDL to 1000 x MDL.

13.3 Single operator precision and accuracy data are provided in Tables 3, 4, 5, and 6. The tables report data at two fortification levels for reagent water, ground water and dechlorinated tap water. Data for ozone treated water are reported at a single fortification level (500 µg/L).

13.4 To generate the MDL and precision and accuracy data reported in this section, analytes were segregated into two fortification groups (A and B) and analyzed separately. Representative chromatograms using LSE for both Groups A and B are presented in Figures 1 and 2, respectively.

14.0 POLLUTION PREVENTION

14.1 This method utilizes the new liquid-solid extraction (LSE) technology to remove the analytes from water. It requires the use of very little organic solvent, thereby eliminating the hazards involved with the use of large volumes of organic solvents in conventional liquid-liquid extractions. A 10 mL aliquot of ethanol, a nontoxic solvent, is used per sample to elute the derivatized aldehydes and ketone from the LSE cartridge. This method is safe for the laboratory analyst to use and will not harm the environment.

15.0 WASTE MANAGEMENT

15.1 Due to the nature of this method and the reagents employed, there is no need for waste management in disposing of the used or unused samples. No toxic solvents or hazardous chemicals are used. The matrices are drinking water or

source water and can be discarded in the sink drain.

16.0 REFERENCES

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17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

TABLE 1. METHOD DETECTION LIMITS[a] USING LIQUID-SOLID EXTRACTION IN REAGENT WATER

Analyte	Retention Time (min)	MDL (µg/L)
Formaldehyde	5.3	6.2
Acetaldehyde	7.5	43.7[b]
Propanal	11.7	11.0
Butanal	18.1	6.3
Pentanal	26.9	15.3
Hexanal	32.5	10.7
Heptanal	36.6	10.0
Octanal	40.4	6.9
Nonanal	43.0	13.6
Decanal	45.5	4.4
Cyclohexanone	27.9	5.8
Crotonaldehyde	16.7	7.7

[a]MDL was computed as follows:

$$MDL = t\ (N\text{-}1,\ 0.01) \times S.D.$$

where: t (n-1, 0.01) = the upper first percentile point of the t-distribution with n-1 degrees of freedom.
S.D. = the standard deviation in µg/L.

With the exception of acetaldehyde all reported MDLs are based upon analyses of six to eight replicate, fortified blanks (25 µg/L) (See Reference 1).

[b]Reported MDL based upon analyses of three replicate, fortified blanks at 250 µg/L.

TABLE 2. METHOD DETECTION LIMITS[a] USING LIQUID-SOLID EXTRACTION IN DECHLORINATED TAP WATER

Analyte	Retention Time (min)	MDL (µg/L)
Formaldehyde	5.3	8.1
Acetaldehyde	7.5	69.0[b]
Propanal	11.7	3.4
Butanal	18.1	8.6
Pentanal	26.9	3.3
Hexanal	32.5	9.6
Heptanal	36.6	7.3
Octanal	40.4	6.0
Nonanal	43.0	24.3
Decanal	45.5	12.9
Cyclohexanone	27.9	9.5
Crotonaldehyde	16.7	6.3

[a]MDL was computed as follows:

$$MDL = t\ (N\text{-}1,\ 0.01) \times S.D.$$

where: t (n-1, 0.01) = the upper first percentile point of the t-distribution with n-1 degrees of freedom
S.D. = the standard deviation in µg/L.

With the exception of acetaldehyde all reported MDLs are based upon analyses of six to eight replicate, fortified blanks (25 µg/L) (See Reference 1).

[b]Reported MDL based upon analyses of three replicate, fortified blanks at 250 µg/L.

TABLE 3. SINGLE OPERATOR ACCURACY AND PRECISION USING LIQUID-SOLID EXTRACTION IN REAGENT WATER

Analyte	FL[a]	R[b]	Sr[c]	Number of Analyses
Formaldehyde	250	96.3	7.6	7
	2500	109.8	1.5	3
Acetaldehyde	250	40.2	1.0	3
	2500	112.2	21.3	3
Propanal	250	93.8	2.3	7
	2500	110.8	2.4	3
Butanal	250	91.1	2.9	7
	2500	108.2	2.6	3
Pentanal	250	91.6	.20	7
	2500	100.5	2.0	3
Hexanal	250	87.0	4.7	7
	2500	94.6	5.4	3
Heptanal	250	90.1	2.4	7
	2500	104.9	1.7	3
Octanal	250	89.2	.09	7
	2500	97.1	1.0	3
Nonanal	250	90.2	3.0	7
	2500	105.3	2.2	3
Decanal	250	85.0	1.1	7
	2500	98.9	1.6	3
Crotonaldehyde	250	87.6	7.3	7
	2500	104.3	1.5	3
Cyclohexanone	250	94.8	4.1	7
	2500	116.7	4.7	3

[a]FL = Fortification Level in µg/L.
[b]R = Average Percent Recovery.
[c]Sr = Standard Deviation of Percent Recovery.

TABLE 4. SINGLE OPERATOR ACCURACY AND PRECISION USING LIQUID-SOLID EXTRACTION IN GROUND WATER

Analyte	FL[a]	R[b]	Sr[c]	Number of Analyses
Formaldehyde	250	103.2	10.3	7
	2500	118.4	9.2	3
Acetaldehyde	250	50.2	3.9	3
	2500	109.2	6.5	3
Propanal	250	99.1	1.3	7
	2500	105.4	9.4	3
Butanal	250	94.7	3.9	7
	2500	95.9	8.7	3
Pentanal	250	90.0	12.7	3
	2500	96.7	1.6	3
Hexanal	250	89.0	4.7	6
	2500	95.9	1.9	3
Heptanal	250	96.4	6.3	7
	2500	98.0	9.6	3
Octanal	250	94.1	1.8	7
	2500	96.9	1.5	3
Nonanal	250	93.1	5.1	7
	2500	97.9	11.6	3
Decanal	250	86.0	4.3	7
	2500	98.5	2.2	3
Crotonaldehyde	250	93.6	3.0	7
	2500	100.2	2.6	3
Cyclohexanone	250	107.6	4.0	7
	2500	111.1	10.8	3

[a]FL = Fortification Level in µg/L.
[b]R = Average Percent Recovery.
[c]Sr = Standard Deviation of Percent Recovery.

TABLE 5. SINGLE OPERATOR ACCURACY AND PRECISION USING LIQUID-SOLID EXTRACTION IN DECHLORINATED TAP WATER

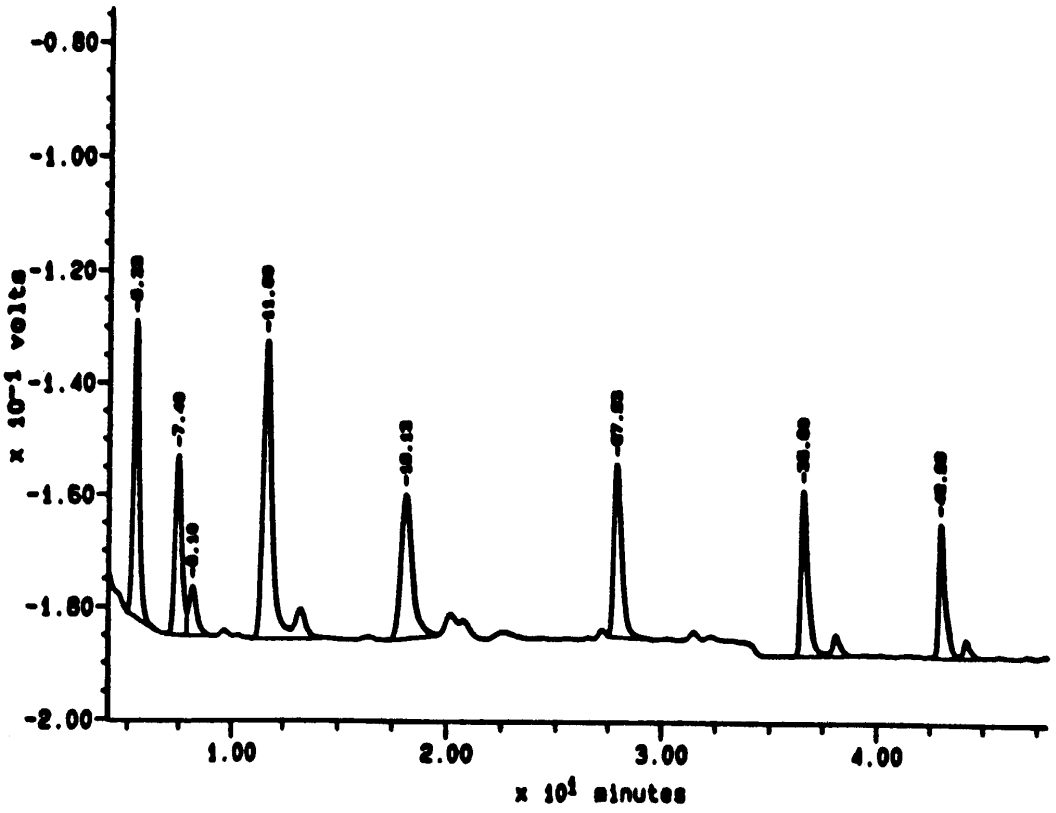
Analyte	FL[a]	R[b]	Sr[c]	Number of Analyses
Formaldehyde	25	90.0	1.1	3
	250	90.8	11.6	8
Acetaldehyde	250[d]	52.0	9.7	8
Propanal	25	120.2	17.9	8
	250	83.4	6.3	8
Butanal	25	91.6	11.4	8
	250	79.4	.81	3
Pentanal	25	106.1	1.1	8
	250	72.3	3.9	3
Hexanal	25	99.2	3.2	8
	250	70.4	4.0	3
Heptanal	25	97.2	9.8	8
	250	79.2	5.4	8
Octanal	25	60.5	2.0	8
	250	75.6	14.8	3
Nonanal	25	120.6	32.4	8
	250	69.9	12.7	3
Decanal	25	109.8	23.9	8
	250	91.5	34.2	3
Crotonaldehyde	25	86.8	2.1	8
	250	97.7	5.5	8
Cyclohexanone	25	94.8	12.7	8
	250	104.5	10.8	8

[a]FL = Fortification Level in µg/L.
[b]R = Average Percent Recovery.
[c]Sr = Standard Deviation of Percent Recovery.
[d]Background levels of this analyte will impair measurement if the fortification level is below 250 µg/L.

TABLE 6. SINGLE OPERATOR ACCURACY AND PRECISION USING LIQUID-SOLID EXTRACTION IN OZONE TREATED WATER

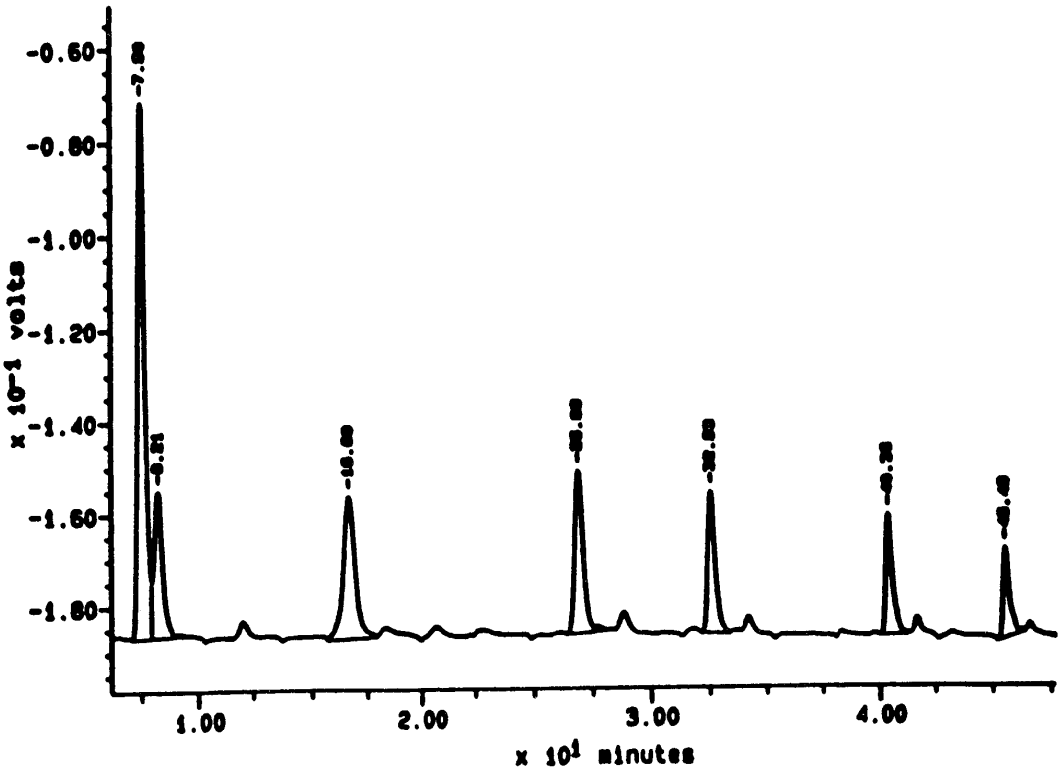
Analyte	FL[a]	R[b]	Sr[c]	Number of Analyses
Formaldehyde	500	78.8	1.1	8
Acetaldehyde	500	99.4	2.3	8
Propanal	500	93.7	1.8	8
Butanal	500	97.6	1.2	8
Pentanal	500	89.6	1.7	8
Hexanal	500	91.8	1.7	8
Heptanal	500	99.0	3.2	8
Octanal	500	93.9	2.5	8
Nonanal	500	100.0	3.8	8
Decanal	500	93.4	6.9	8
Crotonaldehyde	500	89.5	2.5	8
Cyclohexanone	500	97.2	.83	8

[a]FL = Fortification Level in µg/L.
[b]R = Average Percent Recovery.
[c]Sr = Standard Deviation of Percent Recovery.



RT (min)	Analyte
5.33	Formaldehyde
11.68	Propanal
18.13	Butanal
27.93	Cyclohexanone
36.60	Heptanal
42.99	Nonanal

Figure 1 Liquid-solid Procedural Standard of Group A Analytes at 625 µg/L.



RT (min)	Analyte
7.50	Acetaldehyde
16.68	Crotonaldehyde
26.88	Pentanal
32.53	Hexanal
40.36	Octanal
45.49	Decanal

Figure 2 Liquid-solid Procedural Standard of Group B Analytes at 625 µg/L.