

Determination of Phenols in Drinking and Bottled Mineral Waters Using Online Solid-Phase Extraction Followed by HPLC with UV Detection

INTRODUCTION

Phenolic compounds are subject to regulation as water pollutants due to their toxicity. The European Community (EC) Directive specifies a legal tolerance level of 0.5 µg/L for each phenol in water intended for human consumption¹ and Japan's Ministry of Health, Labour, and Welfare specifies a maximum contaminant level (MCL) of 5 µg/L for phenols in drinking water.² The U.S. EPA specifies a MCL of 1 µg/L for pentachlorophenol,³ and eleven common phenols are on the U.S. EPA priority pollutants list.⁴ The structures for these common phenols are shown in Figure 1. The method typically used for determining phenols is gas chromatography (GC) combined with flame ionization detection (FID)^{5,6} or mass spectrometric detection (GC-MS).⁷⁻⁹ However, liquid chromatography (LC) methods combined with UV/DAD,¹⁰ electrochemical,¹¹ and fluorescence¹² detections are finding increased application, particularly due to nonvolatiles in many samples that can poison GC columns.

Method detection limits (MDLs) of LC techniques employing direct injection of samples are too high for the detection of the low levels allowed in natural waters. Therefore, water samples require preconcentration before analysis. Solid-phase extraction (SPE) is one of the most important techniques for sample enrichment, because it overcomes many of the disadvantages of liquid-liquid extraction. Unfortunately, preparing individual samples is time consuming, and a new SPE cartridge must be used for each sample.

The expense of using multiple SPE cartridges and the associated manual labor can be eliminated with online SPE combined with HPLC. This technique delivers a simple, rapid, and accurate means for determining phenols at low concentrations in real samples.^{13,14} The UltiMate® 3000 was designed to easily execute more

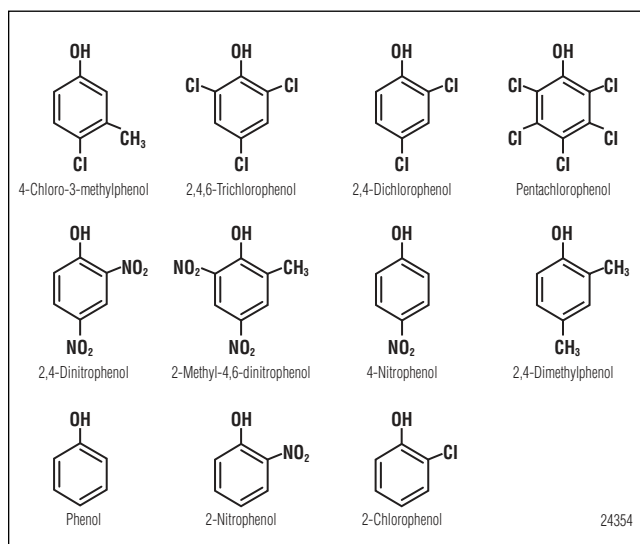


Figure 1. Structures of the 11 phenols specified in the U.S. EPA priority pollutants list.

advanced HPLC methods, such as parallel LC, 2-D LC, and online SPE/HPLC. An UltiMate 3000 together with an autosampler capable of injecting large volumes can be used to execute an online SPE method to determine phenols in drinking and bottled waters. A method using one pump channel of a dual pump system instead of the large volume injector can also be used to achieve online SPE, as described in the Appendix.

This application note details an online SPE method followed by HPLC with UV detection for determining the 11 phenols specified in U.S. EPA Priority Pollutants List at the concentrations required by world regulatory agencies. Phenols from drinking and bottled waters are trapped on an IonPac® NG1, a small polymeric reversed-phase column, then separated on a polar-embedded reversed-phase column, the Acclaim® PA. This automated method is a cost-effective way to determine phenols in drinking and bottled water samples.

EQUIPMENT

Dionex UltiMate 3000 HPLC system consisting of:
DGP 3600M dual gradient pump
SRD 3600 solvent rack with integrated vacuum degasser
TCC-3200 Thermostatted Column Compartment with two two-port, six-position (2P-6P) valves
VWD-3400 Variable Wavelength Detector
AS-HV High-Volume Autosampler*
Chromeleon® Chromatography Management Software, version 6.80
*See Precautions.

REAGENTS AND STANDARDS

Use only ACS reagent grade chemicals for all reagents and standards.

Deionized (DI) water from a Milli-Q® Gradient A10 water purification system

Methanol (CH₃OH), HPLC grade (Fisher)

Acetonitrile (CH₃CN), HPLC grade (Fisher)

Glacial acetic acid (HAc), analytical reagent-grade (Shanghai Chemical Reagent Company)

Ammonium acetate (NH₄Ac), analytical reagent-grade (Shanghai Chemical Reagent Company)

Methanesulfonic acid (MSA), > 99.5% (Aldrich)

Trifluoroacetic acid (TFA), > 99% (Aldrich)

604 Phenols Calibration Mix (Restec) 2000 µg/mL in methanol, consisting of:

4-chloro-3-methylphenol, 2-chlorophenol, 2,4-dichlorophenol, 2,4-dimethylphenol, 2,4-dinitrophenol, 2-methyl-4,6-dinitrophenol, 2-nitrophenol, 4-nitrophenol, pentachlorophenol, phenol, and 2,4,6-trichlorophenol

CONDITIONS

Solid-Phase Extraction

Column: IonPac NG1, 5 µm, 4 × 35 mm (P/N 039567)
Mobile Phases for SPE
(Left Pump): A. 0.2 mM MSA
B. CH₃CN
Flow Rates: Rinse: 1 mL/min with 100% B
Loading: 2 mL/min with 100% A
Phenol Elution: 1 mL/min with 15% B
Inj. Volume: 10 mL
Column Temperature: 40 °C

The total time for on-line SPE is 14 min. For the detailed program see Table 1A.

Analytical

Column: Acclaim PA, 5 µm, 4.6 × 150 mm (P/N 061320)
Mobile Phases for Analysis (Right Pump): A. 25 mM HAc / 25 mM NH₄Ac (1.45 : 1, v/v)
B. CH₃CN
Gradient: 25 to 70% B in 17.5 min
Flow Rate: 1 mL/min
Inj. Volume: 10 mL
Temperature: 40 °C
Detection: UV, 280 nm

Total analysis time is 18 min. During SPE, the column is equilibrated for the next separation prior to injection while online SPE is occurring. For the detailed program see Table 1B.

Table 1A. Left Pump Program (Loading Pump Used for SPE) A = 0.2 mM MSA, B = Acetonitrile		
Time (min)	Commands	Comments
Preparation	ValveLeft = 6_1, ValveRight = 6_1	
-14.0	Flow = 1000 [µL/min] %B = 100.0, %C = 0.0, Curve = 5	Rinse the SPE column (NG1) using 100% CH ₃ CN, about 3 min.
-11.5	Flow = 1000 [µL/min] %B = 100.0, %C = 0.0, Curve = 5	
-11.0	Flow = 1000 [µL/min] %B = 1.0, %C = 0.0, Curve = 5	Equilibrate the SPE column.
-8.5	Flow = 2000 [µL/min] %B = 1.0, %C = 0.0, Curve = 5	Load sample from the loop to SPE column at 2 mL/min, about 5 min.
-3.5	Flow = 2000 [µL/min] %B = 1.0, %C = 0.0, Curve = 5	
-3.0	Flow = 1000 [µL/min] %B = 15.0, %C = 0.0, Curve = 5	Wash the SPE column.
0.2	Flow = 0 [µL/min] %B = 0.0, %C = 0.0, Curve = 5	
3.5	Flow = 200 [µL/min] %B = 100.0, %C = 0.0, Curve = 5	SPE column switches back to the system. Begin to wash the SPE column to prepare for loading the next sample.

Table 1B. Right Pump Program (Analytical Pump) A = 25 mM HAc/NH₄Ac, B = Acetonitrile		
Time (min)	Commands	Comments
Preparation	ValveLeft = 6_1, ValveRight = 6_1	
-14.0	Flow = 200 [µL/min] %B = 100.0, %C = 0.0, Curve = 5	Wash the analytical column.
-13.0	Flow = 200 [µL/min] %B = 25.0, %C = 0.0, Curve = 5	
-7.0	Flow = 200 [µL/min] %B = 25.0, %C = 0.0, Curve = 5	
-5.0	Flow = 1000 [µL/min] %B = 25.0, %C = 0.0, Curve = 5	Begin to equilibrate the analytical column using initial conditions for 5 min. Injections at 0 min.
17.5	Flow = 1000 [µL/min] %B = 70.0, %C = 0.0, Curve = 5	17.5 min gradient
18.0	Flow = 1000 [µL/min] %B = 100.0, %C = 0.0, Curve = 5	Begin the column wash.

PREPARATION OF STANDARDS

The preparation of standards for calibration is based on the requirements of EPA Method 604.⁶

Stock Standard Solution 1

Add 9.95 mL methanol using a graduated 5-mL pipette (two times) to a 10-mL vial, and add 50 µL of the 604 Phenols Calibration Mix (2000 µg/mL) using a 250-µL syringe. The concentration of stock standard solution 1 is 10 µg/mL.

Stock Standard Solution 2

Add 900 µL methanol to a 10-mL vial using a 5-mL graduated pipette, and add 100 µL of stock standard solution 1 using a 250-µL syringe. The concentration of stock standard solution 2 is 1 µg/mL.

Working Standard Solutions

Add 50, 100 and 200 µL of stock standard solution 2 into three separate 100-mL volumetric flasks, using a 250-µL syringe. Bring each to volume with a 0.2 mM MSA solution containing 1% methanol. The concentrations of these solutions are 0.5, 1.0 and 2.0 µg/L.

Add 50, 100 and 200 µL of stock standard solution 1 into three separate 100-mL volumetric flasks, using a 250-µL syringe. Bring each to volume with a 0.2 mM MSA solution containing 1% methanol. The concentrations of these solutions are 5, 10 and 20 µg/L.

SYSTEM SETUP

Figure 2A is a schematic of the devices used for the determination of phenols using online solid-phase extraction (SPE) followed by HPLC with UV detection. The AS-HV has a peristaltic pump that can draw samples from sample bottles through a movable needle. This needle can sample from 15 different 100 mL sample bottles in the sample tray. The movement of the AS-HV is controlled by Chromeleon software. The AS-HV uses the left valve of the TCC-3200 as a sample valve and the right valve as an online SPE switching valve. Figure 2B shows the diagram for programming the large volume injection using the AS-HV. The program for the AS-HV is listed in Table 2. Tables 1A and 1B list the programs for the left (SPE) and right (analytical) UltiMate pumps.

SAMPLE PREPARATION

For the present analysis, tap water was collected at the Dionex Shanghai Applications Lab located in the Pudong District, Shanghai, China. One bottle of pure distilled drinking water and two brands of bottled mineral drinking water (named mineral drinking water 1 and 2, respectively) were purchased from a local supermarket.

Bottled pure distilled drinking water, bottled mineral drinking waters 1 and 2, and tap water samples were prepared by filtering 495 mL of each through 0.45 μm filters into four 500-mL bottles and adding 5 mL methanol and 56 μL MSA to each. The final concentration of MSA in the samples was approximately 2 mM.

Spiked samples were prepared from the above solutions. The procedures for preparation of spiked water samples are shown in Table 3.



Figure 2. A) Schematic of devices for determination of phenols using online solid-phase extraction (SPE) followed by HPLC with UV detection. B) Time line diagram for programming the high-volume injection using the AS-HV.

Table 2. AS-HV Program		
Time (min)	Commands	Comments
Preparation	Y_Axis = AIM_sampl.er.posi-tion X_Axis = AIM_sampl.er.posi-tion Needle = 157, Go To Position	Find position from CM sequence. Set the needle's height and enter the sample bottle.
-14.0	Pump On	Begin to load sample from the bottle. The flow rate of the peristaltic pump is about 3.3 mL/min.
-10.0	Pump Off Needle Home	End sample loading. After sample loading, sample loop switches inline with the SPE column.
-2.8	AIM Sampler, Wash = On, Pump On	Wash the sampling needle and the sample loop in preparation for the next injection.
3.0	Pump Off, Needle Home	End of AS-HV wash.

Table 3. Preparation of Spiked Water Samples

Samples prepared with 1% methanol and 2 mM MSA	Amount of added stock standard solution 1 (μL)	Phenol concentration ($\mu\text{g/L}$)
Distilled drinking water	50	5
Mineral drinking water 1	100	10
Mineral drinking water 2	100	10
Tap water	150	15

RESULTS AND DISCUSSION

Optimization of the Online SPE Method

Different concentrations of acids (HAc or MSA) mixed with methanol or acetonitrile were investigated as wash solutions to elute phenols concentrated on the SPE column. Experiments demonstrated that compared to the acid/methanol solutions, acid/acetonitrile solutions yielded higher peak efficiency, and 0.2 mM MSA/acetonitrile yielded the lowest background.

Figure 3 shows an overlay of chromatograms of phenols spiked into tap water samples, eluted from the SPE column using acetonitrile solutions with different concentrations, and then separated on an Acclaim PA column. More impurities and a high background (poor baseline) were obtained when using acidified water only (Chromatogram A). Although fewer impurities and a lower background were found when using a 20% acetonitrile solution, the recovery of early eluting phenols was reduced (Chromatogram D). Therefore, a 15% acetonitrile solution was selected to ensure recovery of all phenols (Chromatogram C).

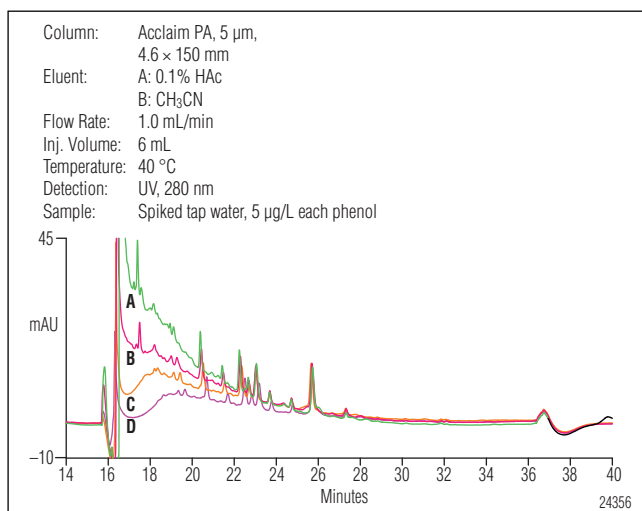


Figure 3. Overlay of chromatograms of tap water samples spiked with 5 $\mu\text{g/L}$ of each phenol, and washed from the IonPac NG1 SPE column using acetonitrile solutions with different concentrations: A) 0% CH_3CN , B) 10% CH_3CN , C) 15% CH_3CN , D) 20% CH_3CN .

Effect of Acidic Solution and Its Concentration in the Mobile Phase on Retention of Phenols

Several acid solutions¹⁵⁻¹⁷ can be used as mobile phases to separate phenols. As shown in Figure 4, good separation of the phenols can be obtained when using methanesulfonic acid (MSA), trifluoroacetic acid (TFA), acetic acid (HAc), or an acetic acid-ammonium acetate buffer (HAc- NH_4Ac).

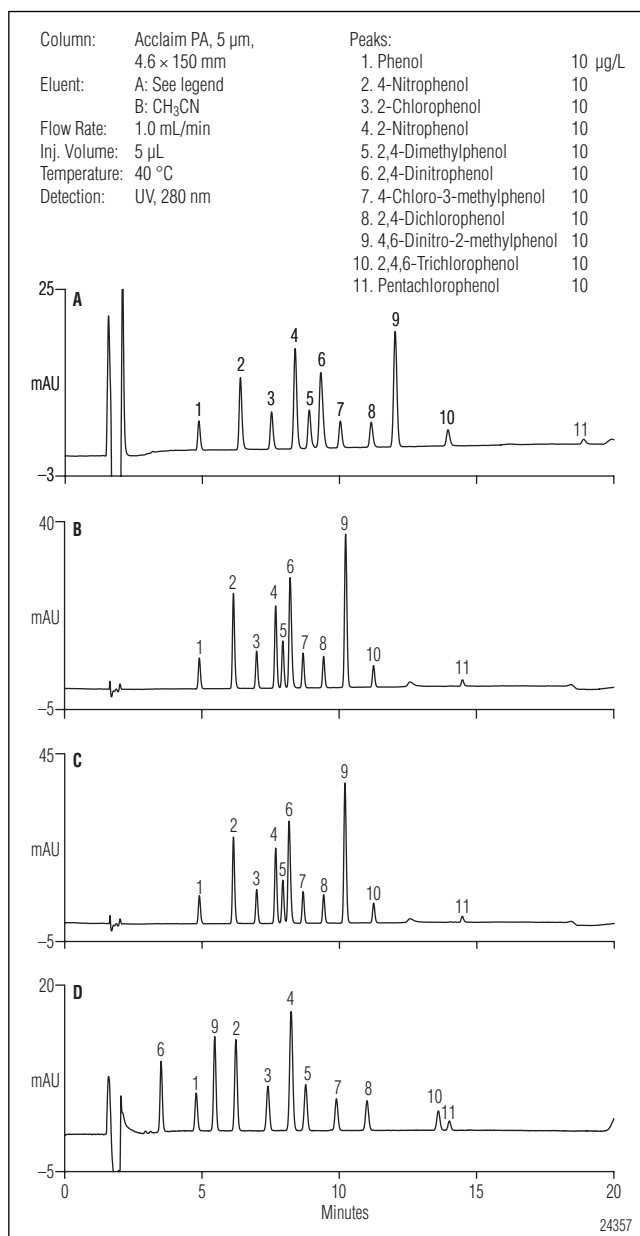


Figure 4. Chromatograms of 10 $\mu\text{g/L}$ phenol working standard separated using acetonitrile as mobile phase B and different acid solutions as mobile phase A: A) 0.1 mM MSA, B) 0.1% TFA, C) 0.1% HAc, D) 25 mM HAc/ NH_4Ac .

The effect of changing the mobile phase acid concentration on retention of phenols was investigated. As shown in Figure 5, the retention time of most phenols changed slightly, but that of a few phenols changed significantly with mobile phases and concentrations. When MSA concentration was increased from 0.1 mM to 3.0 mM, the retention time of 2,4-dinitrophenol shifted considerably. The retention time of 4,6-dinitro-2-methylphenol also decreased slightly (Figure 5A). When HAc concentration was increased from 0.03% to 2.0%, the same pattern of retention change was observed (Figure 5B). Substituting TFA for HAc yielded similar results, therefore those data have been omitted.

Changing the proportions of the 25 mM HAc/ NH_4Ac buffer had a stronger effect on the retention times of 2,4-dinitrophenol and 4,6-dinitro-2-methylphenol than changing the concentrations of the acid solutions. The retention times of 2,4,6-trichlorophenol and pentachlorophenol also shifted more with changes in the buffer than with changes in the acid concentration (Figure 5C).

Selection of Mobile Phase

HAc, MSA, and TFA solutions all yielded good separation of the eleven phenols specified in U.S. EPA Method 604. When the concentration of acid in the mobile phase was lower, the separation was much better, but the retention times of a few phenols were sensitive to small changes in acid concentration, resulting in unsatisfactory method reproducibility. Therefore, HAc/ NH_4Ac buffer was selected as the mobile phase for separating phenols, because it delivered good separation and reproducibility. From Figure 5C, we can predict all eleven phenols will be well resolved using the buffer at about a 1.5:1 (v/v) ratio of the two 25 mM components.

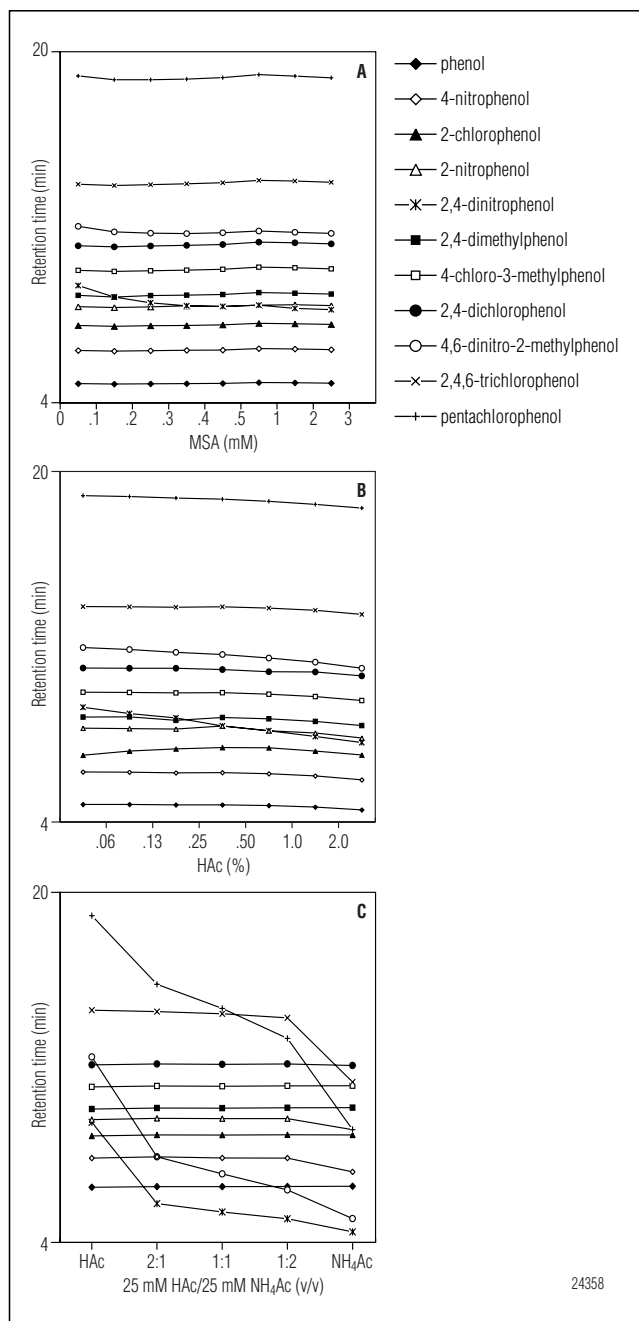


Figure 5. Effect of changing acid concentration in the mobile phase on retention time. A) MSA from 0.1 to 3.0 mM, B) HAc from 0.03 to 2.0%, C) 25 mM HAc- NH_4Ac buffer from 100% HAc to 100% NH_4Ac (v/v).

Table 4. Retention Time Reproducibility, Peak Area Reproducibility, and Comparison of Detection Limits for the 11 Phenols on the U. S. EPA Priority Pollutants List

Phenol	RT RSD ^a (%)	Area RSD ^a (%)	MDL ^b (µg/L)	MDL (µg/L) obtained by GC-FID in EPA 604	MDL (µg/L) obtained by GC-ECD in EPA 604
2,4-Dinitrophenol	0.292	1.358	0.46	13.0	0.63
Phenol	0.240	5.584	0.87	0.14	2.2
4,6-Dinitro-2-methylphenol	0.164	0.647	0.40	16.0	not detected
4-Nitrophenol	0.155	0.432	0.42	2.8	0.70
2-Chlorophenol	0.122	1.659	0.41	0.31	0.58
2-Nitrophenol	0.092	1.487	0.41	0.45	0.77
2,4-Dimethylphenol	0.089	0.462	0.30	0.32	0.68
4-Chloro-3-methylphenol	0.085	0.477	0.31	0.36	1.8
2,4-Dichlorophenol	0.072	0.731	0.08	0.39	not detected
2,4,6-Trichlorophenol	0.056	0.717	0.20	0.64	0.58
Pentachlorophenol	0.064	8.599	0.93	7.40	0.59

^aSeven injections of the 2 µg/L working standard solution.

^bThe single-sided Student's *t* test method (at the 99% confidence limit) was used for estimating MDL, where the standard deviation (SD) of the peak area of seven injections is multiplied by 3.14 (at *n* = 7) to yield the MDL.

Reproducibility, Detection Limits, and Linearity

The reproducibility was estimated by making seven replicate injections of the 2 µg/L calibration standard. Table 4 summarizes the retention time and peak area precision data. The method detection limits (MDLs) of the phenols are also listed in Table 4, as are the MDLs reported for the GC method in U.S. EPA Method 604. The MDLs of the on-line SPE-HPLC method are similar to and in most cases better than those achieved using GC, without the labor and cost of liquid/liquid extraction or manual SPE.

Calibration linearity for the determination of phenols was investigated by making replicate injections of a mixed standard of phenols prepared at six different concentrations. The external standard method is used in EPA Method 604. Therefore, we used it to calculate the calibration curve and for sample analysis. Table 5 lists the data from the calibration as reported by Chromeleon.

Table 5. Calibration Data and Linearity of the 11 Phenols

Phenol	r	RSD (%)
2,4-Dinitrophenol	0.9998	1.73
Phenol	0.9984	4.29
4,6-Dinitro-2-methylphenol	0.9998	1.69
4-Nitrophenol	0.9997	1.79
2-Chlorophenol	0.9996	2.22
2-Nitrophenol	0.9992	3.03
2,4-Dimethylphenol	0.9999	1.33
4-Chloro-3-methylphenol	0.9998	1.42
2,4-Dichlorophenol	0.9998	1.33
2,4,6-Trichlorophenol	0.9999	1.28
Pentachlorophenol	0.9965	6.07

Sample Analysis

To achieve satisfactory chromatography of phenols in the tap and mineral water samples, these samples should be acidified to approximately pH 3.5 prior to analysis. Figure 6 shows the chromatograms of spiked mineral water sample acidified to pH 7 and pH 3 with MSA, respectively. The peak shapes of 2,4-dinitrophenol, 4,6-dinitro-2-methylphenol, and 4-nitrophenol are superior at pH 3.

For different water samples, the amount of acid required to achieve a pH < 4.5 varies. For example, 6 μL MSA (about 0.2 mM final concentration) was added to the 500 mL pure distilled water sample solution (495 mL distilled water + 5 mL methanol) to yield a pH of approximately 3.9. For the tap water and mineral water samples, much more MSA was needed because these samples contain ions that are capable of buffering the MSA, most notably bicarbonate (Table 6). Therefore, approximately 56 μL MSA (about 2 mM final concentration) was added to the tap and mineral water samples to achieve pH values ranging from 2.5 to 4.5.

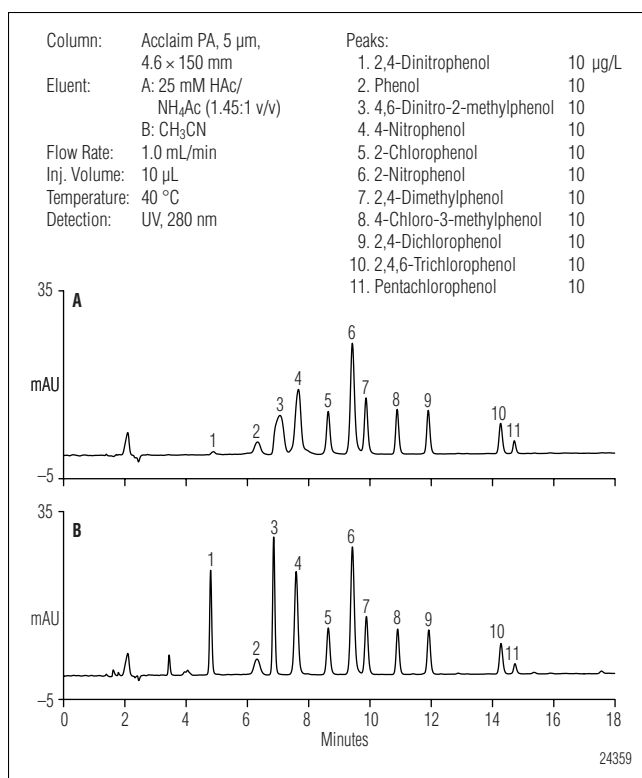


Figure 6. Chromatograms of bottled mineral drinking water 1 spiked with 10 $\mu\text{g/L}$ phenols and acidified with MSA to A) pH 7, and B) pH 3.

Table 6. Listed Amounts of Ions in Bottled Mineral Drinking Waters

Labeled contents	Bottled mineral drinking water 1 (mg/L)	Bottled mineral drinking water 2 (mg/L)
Na ⁺	≥0.8	4–12
K ⁺	≥0.35	0.3–1.0
Ca ²⁺	≥4	not reported
Mg ²⁺	≥0.5	0.3–0.5
Zn ²⁺	not reported	0.25
Sr ²⁺	not reported	0.14
HSiO ₂	≥1.8	71.6
HCO ₃ ⁻	not reported	14
pH (25 $^{\circ}\text{C}$)	7.35 ± 0.5	7.0–8.0

Table 7. Bottled Mineral Drinking Water Analytical Results

Phenol	Bottled mineral drinking water 1 ^a				Bottled mineral drinking water 2 ^b			
	Unspiked (µM)	Added (µM)	Found (µM)	Recovery (%)	Unspiked (µM)	Added (µM)	Found (µM)	Recovery (%)
2,4-Dinitrophenol	ND ^c	10	9.44	94.4	ND	10	9.57	95.7
Phenol	ND	10	11.9	119	0.37	10	10.0	100
4,6-Dinitro-2-methylphenol	ND	10	9.56	95.6	ND	10	9.57	95.7
4-Nitrophenol	ND	10	10.2	102	ND	10	10.0	100
2-Chlorophenol	ND	10	10.4	104	ND	10	9.02	90.2
2-Nitrophenol	ND	10	11.9	119	ND	10	10.9	109
2,4-Dimethylphenol	ND	10	10.5	105	ND	10	9.97	99.7
4-Chloro-3-methylphenol	ND	10	9.56	95.6	ND	10	9.40	94.0
2,4-Dichlorophenol	ND	10	9.75	97.5	ND	10	9.05	90.5
2,4,6-Trichlorophenol	ND	10	10.1	101	0.75	10	9.55	95.5
Pentachlorophenol	0.73	10	9.67	96.7	ND	10	9.60	96.0

^aOne unspiked sample of mineral drinking water 1 was prepared and two injections were made. One spiked sample was prepared and four injections were made.

^bOne unspiked sample of mineral drinking water 2 was prepared and three injections were made. One spiked sample was prepared and five injections were made.

^cND = not detected.

Bottled Mineral Drinking Water

Two brands of bottled mineral drinking water were analyzed. Table 6 shows the contents listed on the labels of each. Figures 7 and 8 show chromatograms of the bottled mineral water samples and the same samples spiked with phenols. The results are summarized in

Table 7. Low concentrations of two phenols were detected in the unspiked mineral water 2 sample and a low concentration of one phenol in the unspiked mineral water 1. Good recoveries were obtained for all eleven phenols.

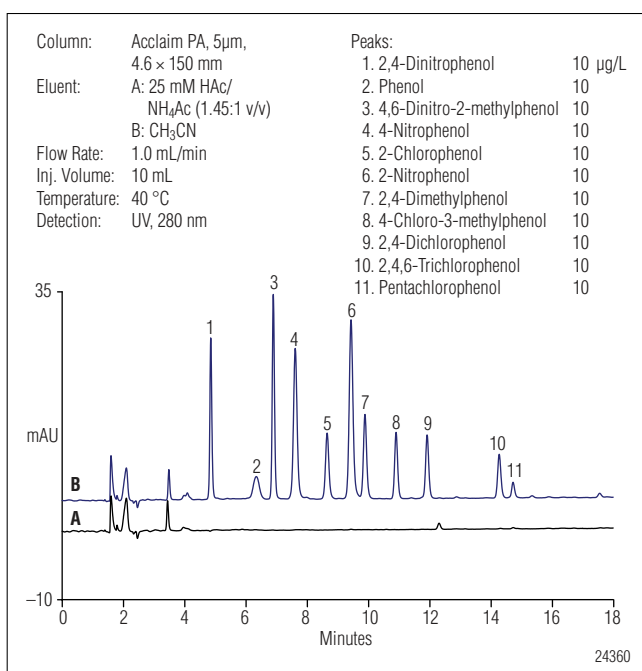


Figure 7. Overlay of chromatograms of bottled mineral drinking water 1, A) unspiked, and B) spiked with 10 µg/L phenols.

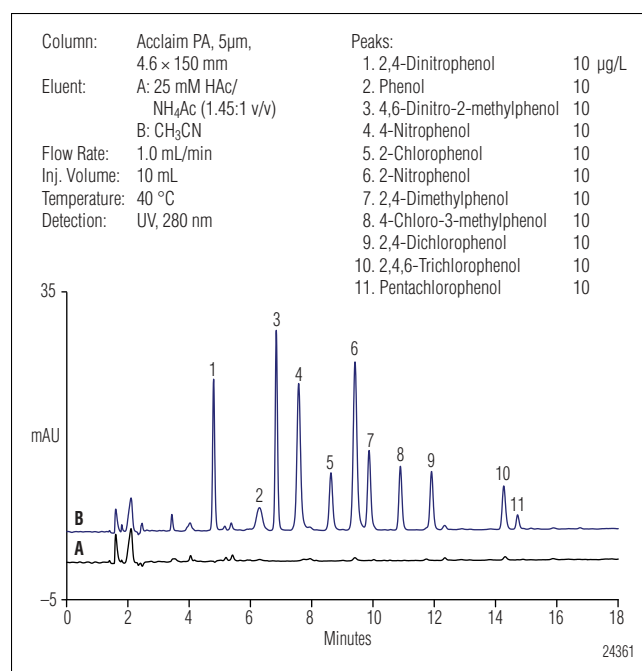


Figure 8. Overlay of chromatograms of bottled mineral drinking water 2, A) unspiked, and B) spiked with 10 µg/L phenols.

Table 8. Bottled Pure Distilled Drinking Water and Tap Water Analytical Results

Phenol	Pure distilled water ^a				Tap water ^b			
	Unspiked (µM)	Added (µM)	Found (µM)	Recovery (%)	Unspiked (µM)	Added (µM)	Found (µM)	Recovery (%)
2,4-Dinitrophenol	ND ^c	5	4.95	99.0	2.11	15	10.4	70.0
Phenol	ND	5	4.84	96.8	0.41	15	14.2	94.7
4,6-Dinitro-2-methylphenol	ND	5	5.02	100	ND	15	15.1	101
4-Nitrophenol	ND	5	5.09	102	0.80	15	15.2	101
2-Chlorophenol	ND	5	5.22	104	<MDL ^d	15	11.50	76.7
2-Nitrophenol	ND	5	5.30	106	ND	15	14.0	93.3
2,4-Dimethylphenol	ND	5	5.19	104	1.63	15	15.0	100
4-Chloro-3-methylphenol	ND	5	5.07	101	<MDL	15	14.5	96.4
2,4-Dichlorophenol	ND	5	4.98	99.6	ND	15	14.1	94.0
2,4,6-Trichlorophenol	ND	5	5.20	104	0.65	15	14.6	97.0
Pentachlorophenol	ND	5	4.99	99.8	1.13	15	14.2	94.5

^aOne unspiked sample of pure distilled drinking water was prepared and five injections were made. One spiked sample was prepared and four injections were made.

^bOne unspiked sample of tap water was prepared and two injections were made. One spiked sample was prepared and five injections were made.

^cND = not detected.

^d<MDL = lower than method detection limit.

Bottled Pure Distilled Drinking Water

Figure 9 shows chromatograms of pure distilled drinking water and the same water spiked with phenols. The results are summarized in Table 8. No phenols were found in the unspiked sample, and recovery of all phenols in the spiked sample was excellent.

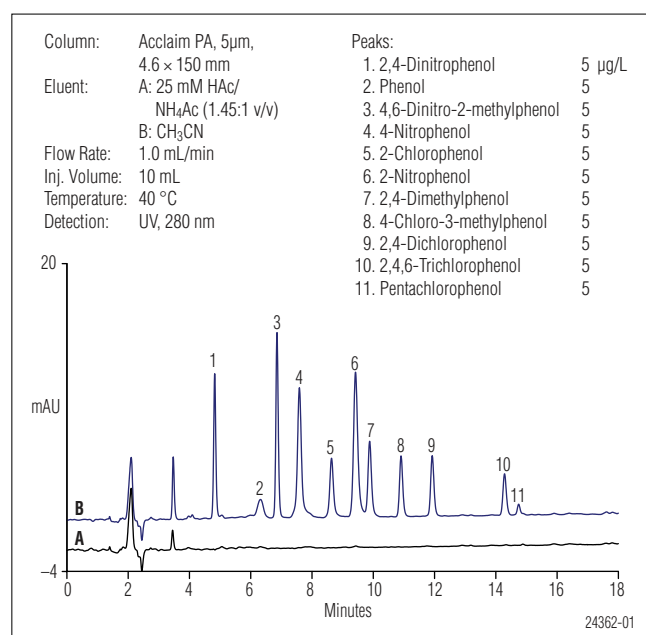


Figure 9. Overlay of chromatograms of pure distilled drinking water, A) unspiked, and B) spiked with 5 µg/L phenols.

Tap Water

Figure 10 shows chromatograms of tap water and the tap water spiked with phenols. The results are summarized in Table 8. Low concentrations of several phenols were detected and some peaks were detected with peak areas that yielded concentrations below the estimated MDL.

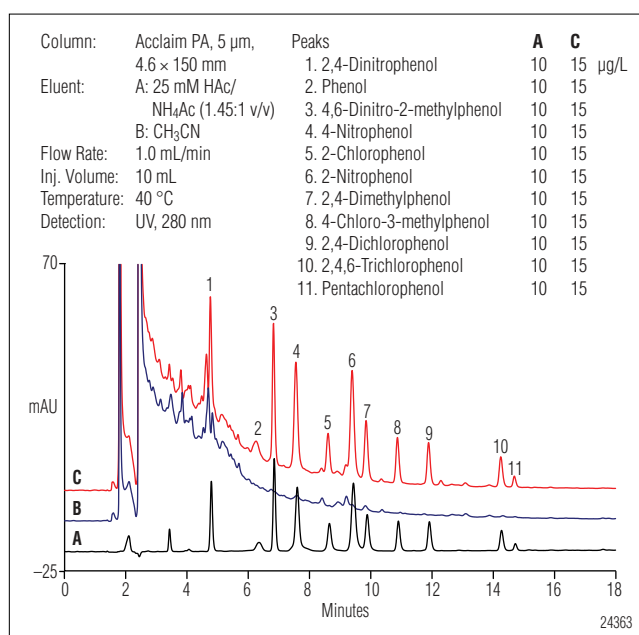


Figure 10. Overlay of chromatograms of A) the 10 µg/L phenol standard, B) unspiked tap water, and C) tap water spiked with 15 µg/L phenols.

CONCLUSION

The successful analysis of all the water samples above demonstrates that online SPE with a dual UltiMate system can determine the 11 phenols designated on the EPA Priority Pollutants List without laborious offline sample preparation. The online SPE method with UV detection has very good reproducibility, with detection limits similar to and in many cases superior to the GC methods described in EPA Method 604.

PRECAUTIONS

Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware. Clean all glassware scrupulously and use high purity reagents and solvents to minimize interference problems.

Samples must be acidified to about pH 3.5 with MSA before large volume injections, especially for the mineral drinking water and tap water samples. If not, the determination of 2,4-dinitrophenol, 4,6-dinitro-2-methylphenol and 4-nitrophenol can be affected.

The tubing and sample loop of the AS-HV are not compatible with high concentration organic solvents. Change the sample loop and the tubing used to connect the loop to the sample valve to either stainless steel or PEEK™.

APPENDIX

Using One Pump Channel of a Dual Pump System Instead of the High-Volume Autosampler

If only a few samples need to be analyzed for phenols, it is possible to use one pump channel of a dual pump system instead of the AS-HV autosampler for sample injection. This configuration is shown in Figure 11. Figure 11A shows the system schematic and Figure 11B shows the program.

Place the sample in an eluent bottle and use one pump of the dual pump system to deliver the sample to the SPE column at a defined flow rate for a set amount of time. Bypass the degasser with the eluent lines used to deliver sample to minimize carryover between injections. Clean eluent lines thoroughly with 100% organic solvent and pure water prior to using this pump channel for other applications.

Use the left pump as the SPE pump and channel C of the left pump as an injector. Pump the sample for 6 min at 1 mL/min to deliver 6 mL of sample to the SPE column. Use channels A (0.2mM MSA) and B (acetonitrile) of

the left pump to rinse the SPE column and elute the captured phenols. Use the second (right) pump to deliver the gradient to separate the phenols on the Acclaim PA column. Figure 12 shows a chromatogram of the separation of phenols in a spiked tap water sample using this setup.

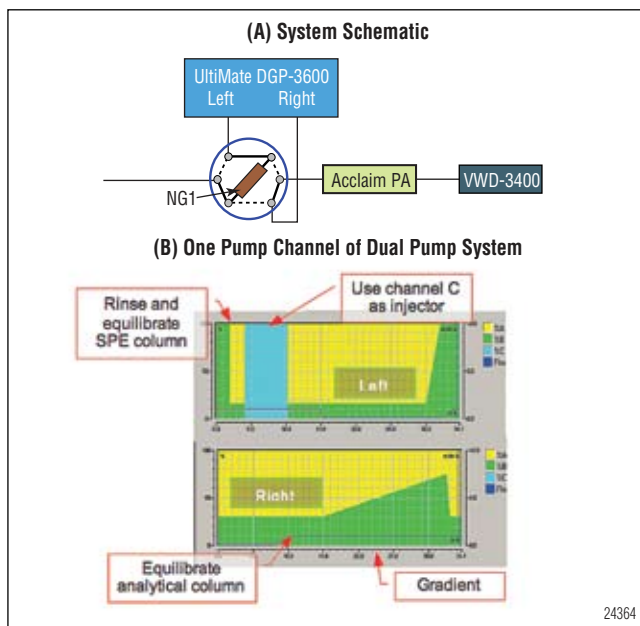


Figure 11. A) System schematic and B) program for using one pump channel of a dual pump system in place of the AS-HV Autosampler.

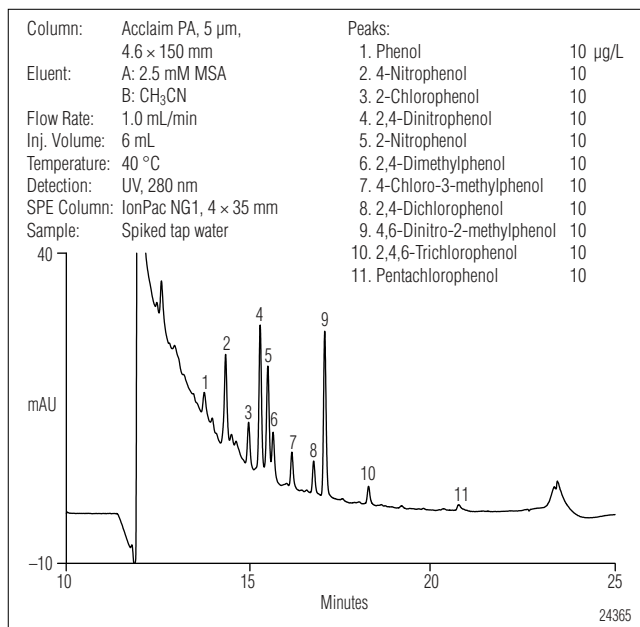


Figure 12. Chromatogram of a tap water sample spiked with 10 μ g/L phenols, using one pump channel of a dual pump system instead of the AS-HV Autosampler.

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