

Determination of Total Recoverable Phenolics in Waters at sub-ppb Levels by In-Line Distillation and Injection Segmented Flow Analysis (iSFA)

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INTRODUCTION

Phenolic compounds are naturally occurring and man-made chemicals found in natural waters, domestic and industrial wastewater effluents, and drinking water. Phenols are high toxicity persistent pollutants, many of which have low taste and odor thresholds. Chlorination of water for disinfection purposes is known to produce chlorophenols as byproducts of the process.

The 4-aminoantipyrine (4-AAP) colorimetric reaction method is the primary testing method used for phenolic compounds in water samples. United States Environmental Protection Agency (USEPA) Methods 420.1¹ and 420.4² employ an initial distillation step followed by reaction of the distillate with alkaline ferricyanide (FeCN) and 4-AAP for detection of total recoverable phenolics over a range of 2 – 500 ppb. Attaining a lower method detection limit (MDL) would increase confidence in data reliability when reporting levels of 2 ppb or less.

Activated carbon treatment is an effective process for removal of phenolic compounds capable of reducing levels to less than 1.0 µg/L³. Lowering the MDL of the 4-AAP test method below 2 µg/L would also improve phenol monitoring capabilities in critical applications such as drinking water and aquaculture.

This poster describes a fully automated method for the determination of total recoverable phenolics using in-line distillation and injection segmented flow analysis. This method eliminates manual distillation and lowers the detection limit 10-fold. A two-column comparison with USEPA Method 420.4 is provided to demonstrate equivalency, and report results of interference and matrix spike studies.

EXPERIMENTAL

Instrumentation

Instrumentation used for this study was an OI Analytical Flow Solution FS IV[®], automated chemistry analyzer equipped with an in-line distillation module, and Expanded Range[™] photometric detector (see Figure 1).

A general flow diagram of the FS IV system for in-line distillation of phenol and colorimetric reaction with 4-AAP and alkaline ferricyanide is shown in Figure 2.

Methodology

Phenol is distilled in-line from an acidic solution at 190 °C set on the distillation module. Phenol reacts with 4-AAP and alkaline ferricyanide to form a red complex. Absorbance is measured at 505 nm². This method is used for the determination of phenolic compounds in drinking water, surface and saline water, and domestic or industrial waste waters according to USEPA Method 420.4. The MDL is <0.5 µg/L phenol with an applicable range of 1–50 µg/L phenol.



Figure 1: FS IV[®] Automated Chemistry Analyzer

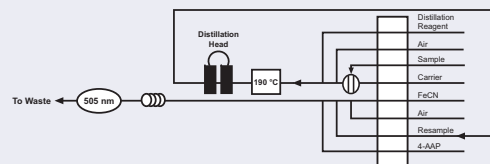


Figure 2. Flow Diagram of System with In-Line Distillation Module

RESULTS & DISCUSSION

To demonstrate performance of the in-line distillation, iSFA phenol analysis method, a 5-point calibration curve (1-50 ppb), repeatability and MDL study were conducted. Peak traces from the 5-point calibration are shown in Figure 3. The method achieves a linear response over the 1-50 ppb measurement range.

To measure repeatability (precision) ten replicates of the 10-ppb phenol standard were analyzed. The resulting peak traces are shown in Figure 4. The average RSD at the 10-ppb level was 1.14%.

Method detection limit was determined in accordance with USEPA methodology defined in Appendix B to Part 136 in the Federal Register. Peak traces for the MDL determination are shown in Figure 5. A summary of precision and MDL results are presented in Table 1.

Matrix effects were tested by spiking 10-ppb phenol into effluent and sea water samples. The interference of sulfide and nitrate/nitrite (NO₂/NO₃) were studied by spiking 10-ppb phenol into a 200-ppb sulfide solution and a 10,000-ppm NO₂/NO₃ solution. Phenol recovery from the spiked samples ranged from 93 to 111% as shown in Table 2.

A two-column comparison between USEPA Method 420.4 and the OI in-line distillation iSFA phenol analysis method is presented in Table 3.

Table 1. Results Summary

Parameter	Calibrant 1 µg/L	Calibrant 10 ppb
Average	1.22	10.46
Standard Deviation	0.024	0.12
%RSD	1.93	1.14
MDL	0.07	—

Table 2. Results of Sample Matrix and Interference Study

Sample Matrix	Spiked Phenol	Phenol Results	%Recovery
10,000-ppm NO ₂ /NO ₃ Solution	10 ppb	11.01ppb	107%
200-ppb Sulfide Solution	10 ppb	9.62 ppb	93%
Effluent Sample	10 ppb	11.08 ppb	107%
Sea Water	10 ppb	11.46 ppb	111%
DI Water	10 ppb	10.30 ppb	100%

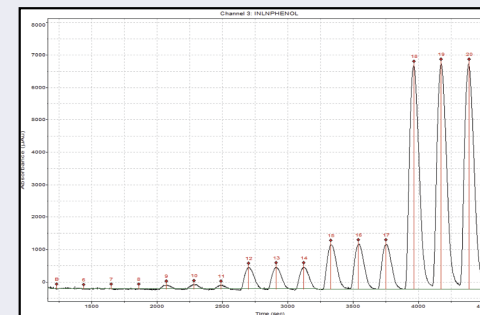


Figure 3. In-Line Distillation Phenol Calibration (1–50 ppb)

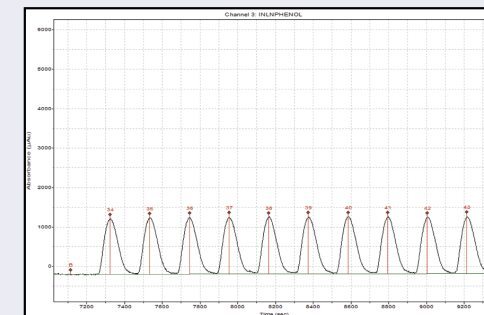


Figure 4. Peak traces demonstrating precision of in-line distillation, iSFA Phenol Analysis Method (%RSD=1.14 at 10-ppb standard)

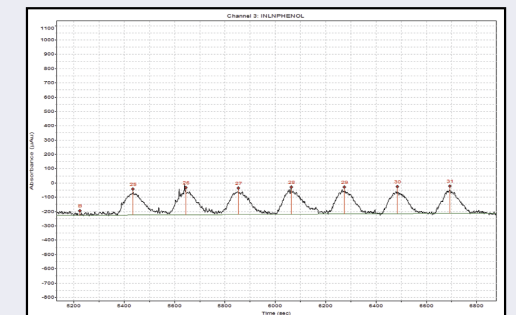


Figure 5. Peak traces from MDL determination of in-line distillation iSFA Phenol Analysis Method using a 1-ppb standard. (MDL=0.07 µg/L)

Table 3. Two-Column Comparison with USEPA Method 420.4

	USEPA Method 420.4	OI Method Cartridge #324648 and A002606
Scope and Application	Refer to EPA method 420.4 with range 2–200 µg/L and 10 –500 µg/L	Same as EPA method 420.4 with range 1–50µg/L and 5–500 µg/L
Summary of Method	Semi-automated based on manual distillation of phenol and subsequent reaction of distillation with alkaline ferricyanide and 4-AAP to form a red complex measured at 505 nm.	Automated method based on in-line distillation of phenol, reaction of distillation of phenol/reaction of distillation with alkaline ferricyanide, and 4-AAP to form a red complex measured at 505 nm.
Interference	Interference from sulfur compounds are eliminated by acidifying the sample to a pH of 4.0 and aerating briefly by stirring.	Eliminate interferences from sulfur compounds by acidifying the sample to a pH <2 and aerating briefly by stirring. The method is able to tolerate 200-ppb sulfide.
Equipment	Manual distillation apparatus and automated continuous flow analysis equipment	In-line distillation module and automated continuous flow analysis equipment.
Final Concentration of Reagent (g/L)	Range 2–500 µg/L: 4-AAP: 0.082 Potassium ferricyanide: 0.277 boric acid: 0.430 potassium chloride: 0.520	Range 1–50 µg/L: 4-AAP: 0.063 Potassium ferricyanide: 0.096 Boric acid: 0.154 Potassium chloride: 0.183 Range 5 –500 µg/L: A-AAP: 0.100 Potassium ferricyanide: 0.309 Boric acid: 0.494 Potassium chloride: 0.586
Data Performance	X = 0.0149 at 0.02 ppm S = 0.0074 RSD = 49%	X = 0.0105 at 0.01 ppm S = 0.000119 RSD = 1.1% X = 1.22 ppb at 1.00 ppb S = 0.024 RSD = 1.93% MDL = 0.07

SUMMARY & CONCLUSIONS

Test results indicate that in-line distillation and injection segmented flow analysis (iSFA) allows the MDL of the 4-AAP Total Recoverable Phenolics method to be lowered to 0.07 µg/L. This ensures more reliable data is available for samples with low concentrations of phenolics. The method also eliminates preliminary manual distillation and extraction steps reducing analysis time by more than 4 hours.

REFERENCES

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