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AGILENT WATER ANALYSIS SOLUTIONS
TABLE OF CONTENTS

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Determination of 24 PAHs in Drinking Water

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Introduction

Polycyclic aromatic hydrocarbons (PAHs) are environmental pollutants formed at high temperature and under pyrolytic conditions during the incomplete combustion of organic matter. They are found throughout the environment in air, water, soil, and food. Due to carcinogenic and mutagenic properties shown for certain PAHs, systematic monitoring is applied in most countries worldwide. Several U.S. and EU guidelines document or report recommended analytical procedures. The number of PAHs and the maximum levels for PAHs documented in these guidelines were increased in the past and will be extended again in the future. Today most laboratories determine up to 16 PAHs in water. Discussions continue and more PAHs may be identified. Our goal was to develop an analytical method to detect a range of PAHs.

We present a validation method for the determination of 24 PAHs. The method uses automated solid phase extraction (SPE) to concentrate the analyte in an 800-mL water sample, with further analysis by high-performance liquid chromatography (HPLC) with fluorescence detector (FLD) and diode-array detector (DAD).

Method and Results
HPLC analysis

The first step was to optimize a chromatographic separation for PAHs, using fast high-performance liquid chromatography (HPLC). Tables 1 and 2 summarize the chromatographic conditions and FLD parameters.

Chromatographic conditions and FLD parameters

Table 1. Time program for fluorescence detection

RT	λ exc	λ em	PMT-gain	PAHs
0.0	269	327	12	Naphthalene
9.5	250	328	12	Acenaphthene, fluorene
11.6	250	375	12	Phenanthrene, anthracene
13.8	237	440	12	Fluoranthene
14.6	270	376	12	Pyrene, benzo[c]fluorene
17.2	265	380	12	Benzo[a]anthracene, chrysene, methylchrysene
19.3	240	505	12	Benzo[j]fluoranthene
19.9	290	440	12	Benzo[b]fluoranthene, Benzo[k]fluoranthene, benzo[a]pyrene
22.5	293	485	15	Dibenzo[a,h]anthracene dibenzo[a,l]pyrene, benzo[g,h,i]perylene, indeno[1,2,3-c,d]pyrene
24.5	280	404	15	Dibenzo[a,e]pyrene
26.0	292	440	15	Dibenzo[a,i]pyrene
27.5	260	456	15	Dibenzo[a,h]pyrene

HPLC column	Agilent Pursuit PAH, 100 × 4.6 mm, 3 μm (p/n A7001100X046)
Column temperature	30 ºC
Injection volume	5 μL

Table 2. HPLC gradient profile

RT(min)	H$_2$O (%)	ACN (%)	Flow (mL/min)
0	60	40	1.8
4	60	40	1.8
23	10	90	1.8
23.5	10	90	2.0
24	5	95	2.0
24.5	0	100	3.0
25	0	100	3.5
29	0	100	3.5
29.5	60	40	1.8
34	60	40	1.8

The optimized chromatogram on an Agilent Pursuit 3 PAH column led to a separation of 24 PAHs in 27 minutes. This is a definite improvement as traditional HPLC methods need around 45 minutes per run to separate a similar amount of analytes. Figure 1 shows the FLD chromatogram of the 22 fluorescent analytes spiked at the quantification limit of 0.02 μg/L.
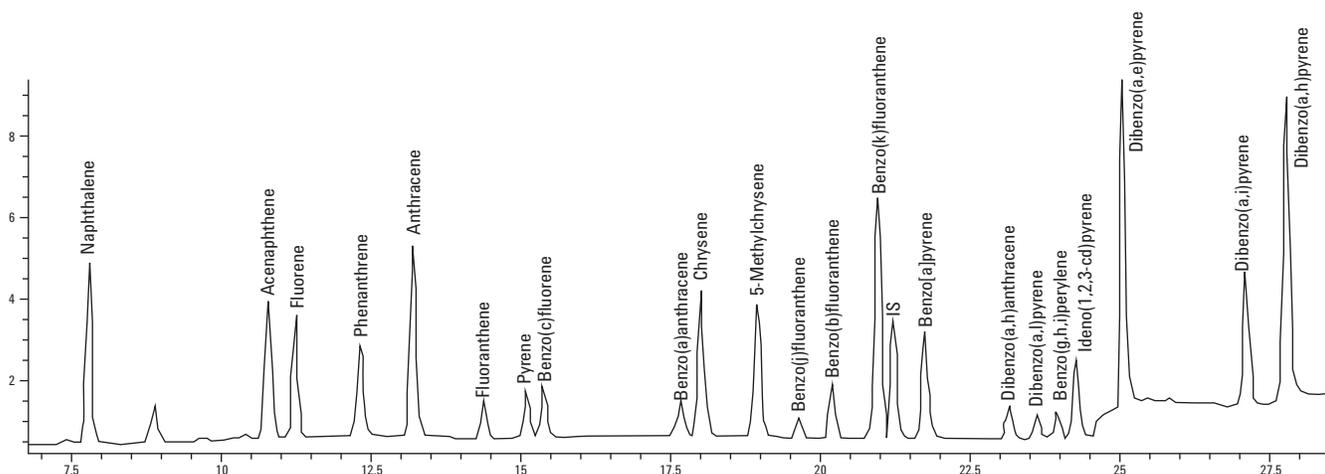
Figure 1. HPLC/FLD chromatogram of a 5 µL injection of the 20 ppt PAH standard solution on the Agilent Pursuit 3 PAH column

The two PAHs, acenaphthylene and cyclopentapyrene, that are not revealed by FLD are detected by UV at 254 nm. Figure 2 shows the UV chromatograms of acenaphthylene and cyclopentapyrene, both at a concentration of 50 ppt.
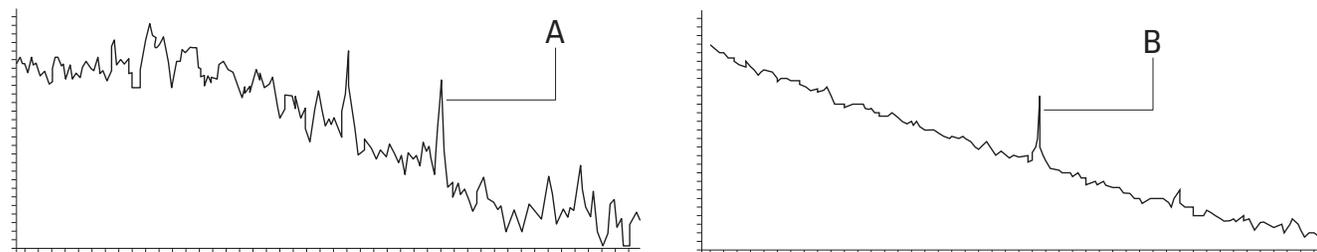

Figure 2. HPLC/DAD chromatogram of acenaphtylene (A) and cyclopentapyrene (B), both at a concentration of 50 ppt, separated on the Agilent Pursuit 3 PAH column

Sample Preparation

The second step was the optimization of the SPE method. We tested different polymer- and silica-based sorbents, drying time, and pH adjustment, and optimized the recoveries by adding isopropanol to provide a final concentration of 5% in the water sample. The internal standard benzo[a]pyrene-d[12] was added to the 800 mL sample prior to the SPE step.

Best results and the most robust application were achieved on the polymer-based sorbent Bond Elut Plexa. Bond Elut Plexa is a polymeric SPE product, designed for improved analytical performance and ease of use. Its uniqueness lies in the novel hydroxylated exterior and advanced polymeric architecture. Due to this structure, analytes from a large polarity scale are extracted with high recoveries and very good standard deviation.

SPE method

The optimized SPE conditions are:

800 mL water sample + 5% isopropanol + internal standard (BaP-d[12])

SPE sorbent, Bond Elut Plexa 200 mg (p/n 12109610)

Condition with 4 mL ethyl acetate/4 mL dichloromethane/
4 mL methanol/4 mL water

Load sample

Dry for 30 minutes

Elute with 4 mL ethyl acetate/4 mL dichloromethane

Take to 10 mL with ethyl acetate/dichloromethane (1:1)

Evaporation of 4 mL with N_2 (avoid dryness)

Redissolve in 500 µL acetonitrile

The process for the 800 mL water sample was automated on the Auto Trace Workstation (Zymark). The method has been fully validated and results are presented in Table 3. Linearity was excellent across the range studied, giving values of 0.99 or greater in all cases with very high precision.

Table 3. Results of SPE method

PAH Name	RT	Signal	LOQ (ng/mL)	Precision (% RSD)	Accuracy	Linearity
Naphthalene	7.8	FLD	0.20	7.97	73.88	0.9999
Acenaphthylene	9.2	DAD	0.50	5.39	78.09	0.9749
Acenaphthene	10.8	FLD	0.20	6.57	75.54	0.9980
Fluorene	11.3	FLD	0.02	5.82	76.71	0.9972
Phenanthrene	12.3	FLD	0.02	6.34	87.17	0.9944
Anthracene	13.2	FLD	0.02	4.78	79.19	0.9961
Fluoranthene	14.4	FLD	0.02	7.81	91.55	0.9961
Pyrene	15.1	FLD	0.02	16.69	95.85	0.9948
Benzo[c]fluorene	15.4	FLD	0.02	6.76	92.22	0.9985
Cyclopentapyrene	17.0	DAD	2.50	2.72	88.88	0.9874
Benzo[a]anthracene	17.7	FLD	0.02	8.37	90.01	0.9979
Chrysene	18.0	FLD	0.02	8.32	91.38	0.9977
Methylchrysene	18.9	FLD	0.02	8.34	90.52	0.9980
Benzo[j]fluorene	19.6	FLD	1.00	5.23	93.36	0.9974
Benzo[b]fluorene	20.2	FLD	0.02	8.85	90.60	0.9974
Benzo[k]fluorene	20.9	FLD	0.02	9.18	88.67	0.9977
Benzo[a]pyrene	21.7	FLD	0.01	3.06	61.20	0.9964
Dibenzo[a,h]anthracene	23.1	FLD	0.02	9.91	80.30	0.9985
Dibenzo[a,l]pyrene	23.6	FLD	0.02	3.87	64.17	0.9974
Benzo[g,h,i]perylene	23.9	FLD	0.02	12.84	82.25	0.9918
Indeno(1,2,3-cd)pyrene	24.2	FLD	0.02	11.37	79.18	0.9956
Dibenzo[a,e]pyrene	25.0	FLD	0.02	10.02	63.22	0.9922
Dibenzo[a,i]pyrene	27.1	FLD	0.02	13.36	48.18	0.9902
Dibenzo[a,h]pyrene	27.7	FLD	0.02	14.36	45.28	0.9910

Conclusion

The combination of the Agilent Pursuit PAH 3 HPLC column and automated SPE on Bond Elut Plexa provides a perfect and fast solution for the analysis of 24 PAHs from a large volume of water. The HPLC analysis time of 28 minutes was a definite improvement as traditional HPLC methods need around 45 minutes per run to separate a similar number of analytes. The method showed excellent reproducibility and led to high recoveries for all 24 PAHs under investigation.

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EPA Method 538: Determination of Selected Organic Contaminants in Drinking Water by Direct Aqueous Injection with the Agilent 6460 Triple Quadrupole LC/MS System

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Abstract

A new method from the U.S. EPA (538) on 11 selected organic contaminants in drinking water by direct aqueous injection liquid chromatography/mass spectrometry/mass spectrometry (LC/MS/MS) has been developed using ultra-high-performance liquid chromatography (UHPLC) and the Agilent Model 6460 triple quadrupole LC/MS System. One advantage of the EPA method is that solid phase extraction (SPE) is no longer needed for sample preparation. This means that the analysis time is reduced by at least half. Furthermore, run time was cut by almost two-thirds by the use of UHPLC. The method provided excellent linearity ($R^2 \geq 0.9999$) for all analytes, with limits of detection from 1 to 500 ng/L.

Introduction

Pesticides and other organic contaminants in drinking water pose potential human health risks. Agricultural and industrial uses of these chemicals are major sources of such contamination. To ensure the quality of drinking water in the United States, the Environmental Protection Agency (EPA) has a number of monitoring requirements. EPA Method 538 has been developed and implemented for the determination of selected organic contaminants in drinking water, most of which are organophosphate pesticides.

EPA Method 538 involves analysis of water by direct aqueous injection and LC/MS/MS. The method measures the presence of 11 target analytes, using five deuterated internal standards. The analytes are separated and identified by comparing the acquired transition ions and retention times to calibration standards obtained under identical LC/MS/MS conditions. The concentration of each analyte is determined by internal standard calibration following standard procedures. Because the method requires no sample extraction, it is rapid and inexpensive compared to other LC/MS/MS methods.

This application note describes an Agilent implementation of EPA Method 538, which is demonstrated with the Agilent 1290 Infinity LC system and an Agilent 6460 triple quadrupole LC/MS system using Jet Stream technology. The 10-minute UHPLC chromatographic analysis is more than twice as fast as the original EPA Method 538, saving time and solvent costs. The method was modified by adding a second transition for all analyte ions for confirmation, which satisfies the European Union (EU) specifications for unequivocal identification by mass spectrometry. This gives an even greater assurance of correct identification than prescribed by the EPA. The utility of the method was demonstrated using local water samples.

Experimental

Reagents and standards

All standard solutions (100 µg/mL) were purchased from Accustandards (New Haven, CT, USA). The deuterated standards were obtained from Cambridge Isotopes (Cambridge, MA, USA). HPLC-grade acetonitrile and methanol were obtained from Burdick and Jackson (Muskegon, MI, USA). Formic acid was obtained from Sigma-Aldrich (St. Louis, MO, USA). Individual stock solutions (1 µg/mL) were prepared in pure methanol and stored at -18 °C. From these solutions, working standard solutions were prepared by dilution with acetonitrile and water.

Instruments

The method was run on the 1290 Infinity LC system with a 100 µL sample loop, coupled to the 6460 triple quadrupole LC/MS System with Jet Stream Technology. Table 1 lists the instrument conditions.

Table 1. LC and MS instrument conditions

LC conditions	
Column	Agilent ZORBAX C-18 Eclipse Plus, 2.1 x 50 mm, 1.8 µm (p/n 959757-902)
Column temperature	25 °C
Injection volume	100 µL
Mobile phase	A = Acetonitrile B = 0.1% acetic acid in water
Run time	10 min
Flow rate	0.4 mL/min
Gradient	90% B at time 0, and hold for 1.7 min. Gradient to 100% B at 10 min.

MS conditions	
Sheath gas temperature	350 °C
Sheath gas flow	11 L/min
Gas temperature	250 °C
Desolvation gas flow rate	10 L/min
Nebulizer pressure	45 psi
Capillary voltage	4000 V
Nozzle voltage	0 V
Delta EMV	200 V

Sample preparation

Method 538 calls for a 40 mL water sample, preserved with sodium omadine and ammonium acetate. Remove a 950 µL aliquot and place it in a vial, along with a 50 µL aliquot of five deuterium-labeled internal standards. The organic solvent content of the sample should not exceed 5%. Collect the samples in baked amber glass bottles and store at 4 °C until analyzed. Pass the water sample through a polytetrafluoroethylene (PFTE) filter (0.2 µm), before addition of internal standards, to prevent plugging of the analytical column. The sample is then ready for direct injection into the LC/MS/MS system. Blanks should also be passed through the filter to check for interferences.

Results and Discussion
Method 538

Table 2 shows the 10 organophosphate analytes included in EPA Method 538 along with the polynuclear aromatic heterocycle, quinoline. These 11 analytes represent important possible drinking water contaminants [1]. Five deuterated standards are also part of the method and are shown in

Table 3. One advantage of the EPA method is that solid phase extraction (SPE) is no longer needed for sample preparation, which means that total analysis time is cut at least in half. In addition, suppression from the sample matrix is reduced, because the matrix is not concentrated as may occur with SPE. Although concentration of the sample may enable lower detection limits, this advantage will be mitigated by suppression effects. In addition, the sensitivity of the instrument negates the need for concentration of the sample. The method is quite simple, requiring only the addition of the internal standard mixture to the water sample.

Table 2. Ten organophosphate pesticides and quinoline are the 11 compounds measured in EPA Method 538 as drinking water contaminants

Analyte	Chemical Abstract Services Registry Number (CASRN)
Acephate	30560-19-1
Aldicarb	116-06-3
Aldicarb sulfoxide	1646-87-3
Dicrotophos	141-66-2
Diisopropyl methylphosphonate (DIMP)	1445-75-6
Fenamiphos sulfone	31972-44-8
Fenamiphos sulfoxide	31972-43-7
Methamidophos	10265-92-6
Oxydemeton-methyl	301-12-2
Quinoline	91-22-5
Thiofanox	39196-18-4

Table 3. The five deuterated internal standards used in EPA Method 538[1]

Internal standards
Acephate-d_6
Diisopropyl methylphosphonate-d_{14} (DIMP-d_{14})
Metamidophos-d_6
Oxydemeton-methyl-d_6
Quinoline-d_7

Limits of detection and linearity

EPA Method 538 calls for one multiple reaction monitoring (MRM) transition per compound [1]. The adaptation of the method described includes a second transition to provide a confirmation ion for each detected compound. This change also conforms to standard analytical procedures that call for a second confirming transition for analysis by LC/MS/MS using triple quadrupole methods, as well as ion-ratio percentages. Table 4 shows the transitions for each of the 11 compounds, along with the fragmentation and collision energies. Table 5 shows the transition used for each of the deuterated labeled standards used for quantitation, as well as their fragmentation and collision energies.

Table 5. Transitions, fragmentation energies and collision energies for each of the five labeled standards for EPA method 538

Compound	Transition	Fragmentation energy	Collision energy
Acephate-d_6	190→149	50	0
DIMP-d_{14}	195→99	70	5
Methamidophos-d_6	148→97	70	10
Oxydemeton-methyl-d_6	253→175	70	10
Quinoline-d_7	137→81	110	35

Table 4. Transitions, fragmentation energies, and collision energies used for each of the 11 standards for EPA Method 538

Compound name	Precursor ion	Product ion	Dwell	Fragmentation energy (V)	Collision energy (V)	Polarity
Acephate	206	165	10	90	5	Positive
Acephate	184	143	10	50	0	Positive
Aldicarb	213	116	10	90	5	Positive
Aldicarb	213	89	10	90	15	Positive
Aldicarb-sulfoxide	229	166	10	70	5	Positive
Aldicarb-sulfoxide	229	109	10	70	10	Positive
Dicrotophos	238	193	10	70	0	Positive
Dicrotophos	238	112	10	70	5	Positive
DIMP	181	139	10	70	0	Positive
DIMP	181	97	10	70	5	Positive
Fenamiphos-sulfone	336	308	10	110	10	Positive
Fenamiphos-sulfone	336	266	10	110	15	Positive
Fenamiphos-sulfoxide	320	292	10	110	10	Positive
Fenamiphos-sulfoxide	320	233	10	110	20	Positive
Methamidophos	142	125	10	70	10	Positive
Methamidophos	142	94	10	70	10	Positive
Oxydemeton-methyl	269	191	10	110	5	Positive
Oxydemeton-methyl	247	169	10	70	10	Positive
Quinoline	130	103	10	110	25	Positive
Quinoline	130	77	10	110	35	Positive
Thiofanox	241	184	10	90	5	Positive
Thiofanox	241	57	10	90	15	Positive

Figure 1 shows the extracted ion chromatogram (EIC) for the 11 compounds of EPA Method 538, using a 10-minute rapid gradient with UHPLC. The 11 compounds elute in approximately 6 minutes. The more polar compounds, such as methamidophos, acephate, and aldicarb sulfoxide, elute in the first minute of the chromatogram. The more hydrophobic compounds, such as diisopropyl methylphosphonate (DIMP), aldicarb, fenamiphos sulfoxide, and sulfone, along with thiofanox, elute at the end of the chromatographic run. Good peak shape, which improves sensitivity and increases the limit of detection, was accomplished with this gradient.

The limits of detection (LODs) for the 11 analytes varied from 1 ng/L for aldicarb sulfoxide, which was the most sensitive compound, to 500 ng/L for acephate, which was the least sensitive compound (Table 6). The wide variation in LODs reflects the ability of each analyte to form ions in electrospray. The most polar analytes, such as acephate and methamidophos were the least sensitive, while fenamiphos sulfone and thiofanox were some of the most sensitive compounds and also the most hydrophobic. The LODs for nine of the 11 compounds were lower than those posted in Table 5 of Method 538. The method reporting limits (MRLs) for the same nine compounds were also equal to or lower than those listed in Table 5. Quinoline in particular is much more sensitive using the Agilent 6460 triple quadrupole LC/MS system with Jet Stream Technology because it is a stable compound (PNA) with a nitrogen heteroatom. Therefore this adaptation of Method 538 meets the criteria for a sensitive method for organophosphate pesticides in drinking water.

The extra MRM transition used in this adaptation of Method 538 is an important component of a valid method for water quality analysis of pesticides in water samples. The European Union (EU) specifications for unequivocal identification by mass spectrometry require two transitions. This procedure has become an unofficial standard worldwide.

Table 6. Limits of detection for EPA Method 538

Compound	Fortified conc. (ng/L)[a]	LOD (ng/L)[b]	MRL (ng/L)[c]
Acephate	500	500	1000
Aldicarb	5	2	5
Aldicarb sulfoxide	5	1	2
DIMP	10	10	20
Dicrotophos	10	10	20
Fenamiphos sulfone	5	5	10
Fenamiphos sulfoxide	5	5	10
Methamidophos	50	50	100
Oxydemeton-methyl	5	5	10
Quinoline	10	10	20
Thiofanox	5	2	5

a. Spiking concentration used to determine LOD
b. LOD (determined as three times signal-to-noise)
c. MRL (determined as six times signal-to-noise with two transitions per compound taken into account)

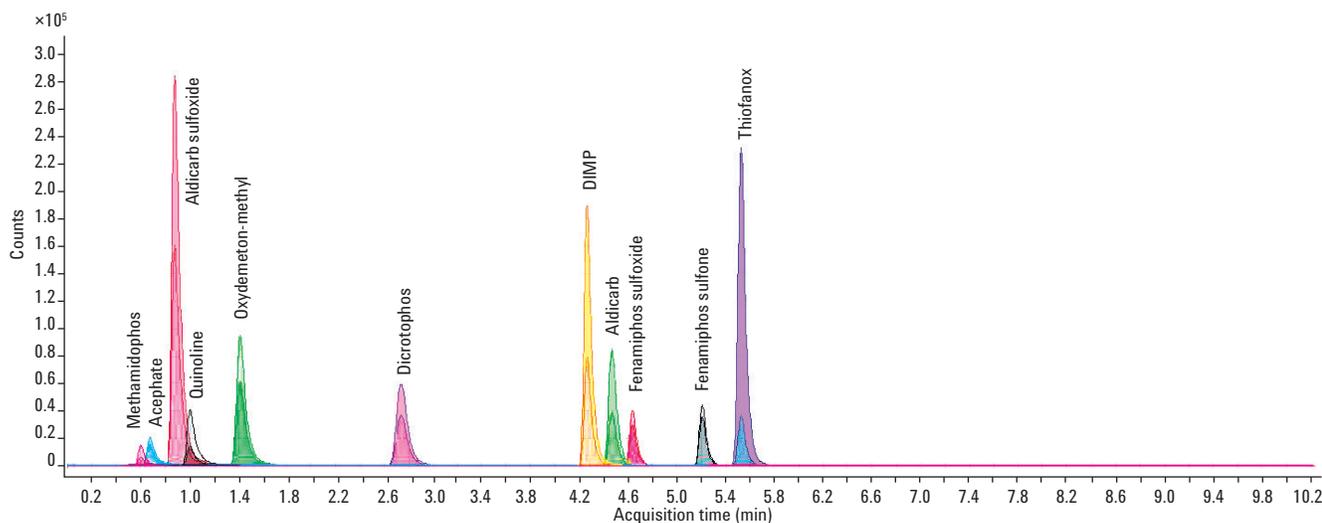**Figure 1.** UHPLC extracted ion chromatogram (EIC) with the Agilent 1290 Infinity LC System, for the 11 analytes of EPA Method 538

Figure 2 shows the excellent linearity that was achieved with the direct-injection method for two of the analytes, quinoline and fenamiphos sulfone. In fact, the R^2 values are ≥0.9999 for all compounds in this method.
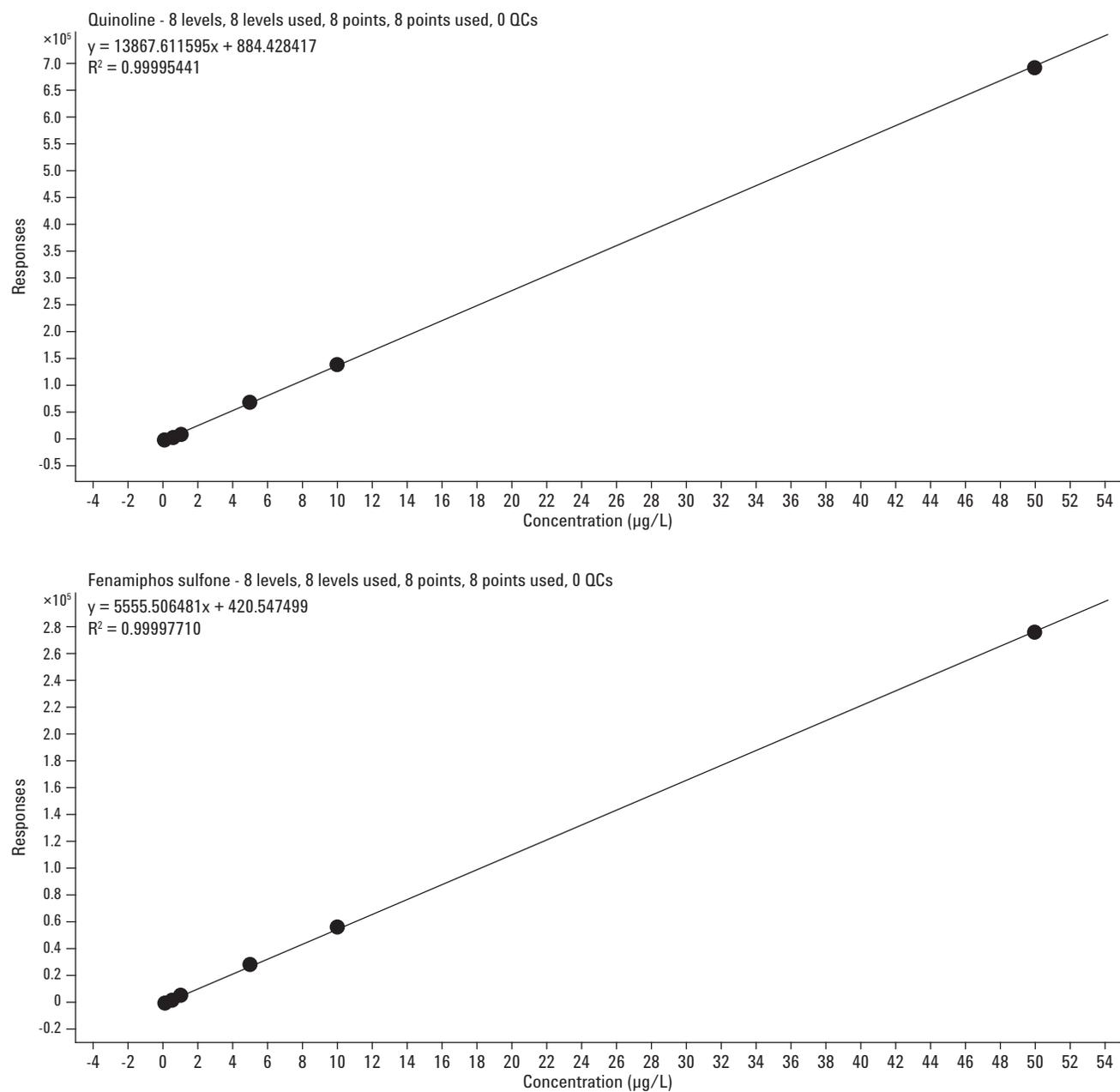

Figure 2. Calibration curves for quinoline and fenamiphos sulfone

Testing of drinking water samples

EPA Method 538 was tested on several samples from river, reservoir, and drinking water sources. The method detected only DIMP in one of the samples taken from a reservoir prior to drinking water treatment (Figure 3). The treated drinking water contained no detectable organophosphate pesticides. Therefore the method was found to be reliable and useful for the analysis of drinking water contaminants, as well as rapid and sensitive.
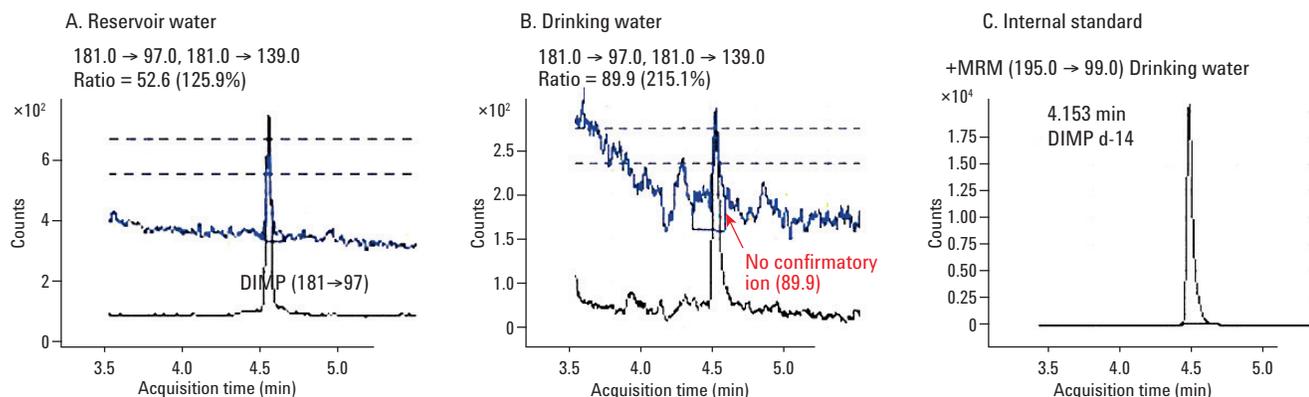

A. Reservoir water
$181.0 \rightarrow 97.0, 181.0 \rightarrow 139.0$
Ratio = 52.6 (125.9%)

B. Drinking water
$181.0 \rightarrow 97.0, 181.0 \rightarrow 139.0$
Ratio = 89.9 (215.1%)

C. Internal standard
+MRM ($195.0 \rightarrow 99.0$) Drinking water

Figure 3. Analysis of the reservoir water prior to treatment (A) and treated water (B) for the pesticide DIMP using the modified Method 538. DIMP is detected using the 181→97 transition as the quantifier ion, and the 181→139 transition as the qualifier ion. In the case of the drinking water, the qualifier (confirmatory) ion is not present, resulting in a quantifier-to-qualifier ion ratio that is much too high, indicating the absence of DIMP in the drinking water. The deuterated DIMP internal standard is shown in C.

Conclusions

Running EPA Method 538 on the Agilent 1290 Infinity LC system and the Agilent 6460 triple quadrupole LC/MS System with Jet Stream Technology shortens time to results by almost a factor of three and increases reliability of the method by adding a second transition. In addition, the detection limits and adaptations conform to the requirements of this method [1].

Reference

[1]   J.A. Shoemaker, 2009, EPA Method 538: Determination of selected organic constituents in drinking water by direct aqueous injection-liquid chromatography/tandem mass spectrometry, EPA/600/R-09/149, 40p.

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Analyzing Wastewater Effluents for PAHs and PBDEs Using the Agilent 7000 Triple Quadrupole GC/MS

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Abstract

An analytical method has been developed on the Agilent 7000 Series triple quadrupole gas chromatograph/mass spectrometer (GC/MS) for the analysis of polyaromatic hydrocarbons (PAHs) and polybrominated diphenyl ethers (PBDEs) in wastewater. With a single extraction and no cleanup, this method meets the detection limit requirements of the United Kingdom Chemical Investigations Programme.

Introduction

The European Union Water Framework Directive (2000/60/EC) [1] promotes sustainable water use, including the long-term reduction of wastewater contaminant discharges to the aquatic environment. It is supplemented by the Priority Substances Daughter Directive (PSDD), which establishes Environmental Quality Standards (EQSs) for priority substances. The EQSs define concentrations of chemical contaminants that are consistent with good chemical status in EU water bodies. To address the PSDD obligations, a clearer understanding of the occurrence and concentration of these substances and their behavior in wastewater treatment is required.

To meet this challenge, UK Water Industry Research (UKWIR), in collaboration with the UK Environment Agency, has created the Chemical Investigations Programme (CIP) for the management and control of concentrations of priority substances. This program includes the quantification of risk and assessment of treatment options through the analysis of crude sewage, process streams, final effluents, and sludge.

The CIP focuses on several categories of priority substances, including PAHs and PBDEs. This application note describes the development of a single extraction and sensitive method for the detection of these two classes of priority substances on the Agilent 7890 Series GC system coupled to the 7000 Series quadrupole gas chromatography/mass spectrometer (GC/MS) to meet the requirements of the CIP. It provides a single method for all 14 analytes, using only one extraction step and minimal or no cleanup, in both µg/L and ng/L concentrations. The reporting limits of the method are all below 3.0 ng/L and well below the CIP analytical quality control (AQC) requirements.

Experimental
Reagents and standards

Reagent or Standard	Source
Hexane	HPLC grade, Rathburn Chemicals Ltd, UK
Ammonia solution	35% aqueous solution
PAHs	QMX Thaxted, UK
PBDEs	Accustandard, Kinesis, UK
^{13}C internal standards (ISTD)	Sigma Aldrich, UK

Calibration standard solutions were prepared by accurately weighing each analyte into a volumetric flask and diluting with hexane to generate a mixed stock solution. Subsequent calibration and fortification solutions were created by dilution from this stock using hexane. These calibration standards also contained a deuterated and ^{13}C-labeled internal standard cocktail.

Instruments

This method was developed on the Agilent 7890A GC with a multimode inlet (MMI) in solvent vent mode and a 4-mm liner packed with glass beads. The GC was coupled to the Agilent 7000B triple quadrupole GC/MS. Table 1 shows the instrument conditions.

Table 1. GC and MS instrument conditions

GC run conditions	
Analytical column	Agilent J&W HP-5, 30 m × 0.25 mm, 0.25 µm 5% phenyl methyl siloxane (p/n 19091J-233)
Injection volume	25 µL
Injection mode	MMI in solvent mode, 4-mm liner packed with glass beads
Inlet temperature	60 °C
Vent flow	100 mL/min for 0.09 minutes
Oven temperatures	60 °C for 2 minutes 25 °C/min to 300 °C; hold for 8.4 minutes
Carrier gas	Helium velocity 30 cm/s constant flow mode
Transfer line temp	300 °C
Run time	20 minutes

MS conditions	
Acquisition parameters	Extracted ion (EI) mode; multiple reaction monitoring (MRM)
Collision gas	Nitrogen, constant flow, 1.5 mL/min
Quench gas	Helium, constant flow, 2.25 mL/min
MS temperatures	Source 300 °C; quadrupoles 230 °C

Sample collection, preparation, and cleanup

Samples were collected in 500-mL amber glass bottles. A 100-mL aliquot of the sample was taken and placed in a 250-mL amber screw cap bottle. A 50-µL amount of 35% aqueous ammonia solution was added by pipette and the sample diluted with ultrapure water to approximately 200 mL. The internal standard solution was then added, followed by 10 mL of hexane. The vessel was then placed on a bottle roller overnight (a minimum of 12 hours) to extract the analytes into the organic phase. The bottle was topped with ultrapure water.

A pipette was used to take a 5-mL aliquot of the upper, organic hexane phase. This was then concentrated under a flow of nitrogen to 250 µL and transferred to a 2-mL autosampler vial for analysis by GC/MS/MS. The sample extracts were shown to be stable if stored refrigerated and analyzed within 28 days of extraction.

Analysis parameters

Tables 2 and 3 show the 7000 triple quadrupole GC MS analysis parameters for the analytes and their internal standards.

Results and Discussion
Chromatographic separation

This method resolves eight PAHs and six PBDEs in less than 20 minutes, with the exception of benzo(b)fluoranthene and benzo(k)fluoranthene, which are partially resolved (Figure 1). Combined with the MRM MS detection, this chromatographic approach provides low interference and sensitive detection.

Accuracy of quantitation

Calibration curves for all of the PAHs and PBDEs spiked into final effluent provide excellent correlation coefficients (>.999) that assure accurate estimations of quantitation for all of the analytes. Figures 2 and 3 show representative quantifier ion traces and calibration curves.

Table 2. MS/MS analysis parameters

Compound	Retention time (min)	Precursor ion	Product ion	Collision energy (V)
Naphthalene	6.8	128	127	20
		128	102	22
Anthracene	10.1	178	176	34
Fluoranthene	11.3	202	201	30
		202	200	50
PBDE 28	11.8	408	248	22
		406	246	20
		406	167	25
PBDE 47	12.9	486	326	28
		484	324	32
PBDE 100	13.9	566	406	28
		404	297	35
PBDE 99	14.3	566	406	28
		404	297	35
Benzo(b)Fluoranthene	14.4	252	250	42
		252	248	40
Benzo(k)Fluoranthene	14.4	252	250	42
		252	248	40
Benzo(a)Pyrene	15.0	252	250	42
		252	248	40
PBDE 154	15.4	644	484	20
		484	375	40
		484	324	35
PBDE 153	16.2	644	484	20
		484	324	35
		484	375	40
Indeno(123cd)Pyrene	17.8	276	274	38
Benzo(Ghi)Perylene	18.6	276	274	42

Table 3. Internal standard analysis parameters

Compound	Retention time (min)	Precursor ion	Product ion	Collision energy (V)
Naphthalene-d8	6.6	136	108	25
Anthracene-d10	8.1	188	160	34
Fluoranthene-d10	11.28	212	210	30
PBDE 28-C13	11.79	420	260	22
		418	258	20
PBDE 47-C13	12.9	498	338	28
		496	336	32
PBDE 100-C13	13.9	578	418	28
		416	308	35
PBDE 99-C13	14.3	416	308	35
		578	418	28
Benzo(K)Fluoranthene-d12	14.37	264	260	42
Benzo(A)Pyrene-d12	15.0	264	260	42
PBDE 154-C13	15.4	496	388	38
		496	336	33
PBDE 153-C13	16.2	496	336	33
		496	388	38
Indeno(123cd)Pyrene-d12	17.05	288	284	42
Benzo(Ghi)Perylene-d12	18.6	288	284	42
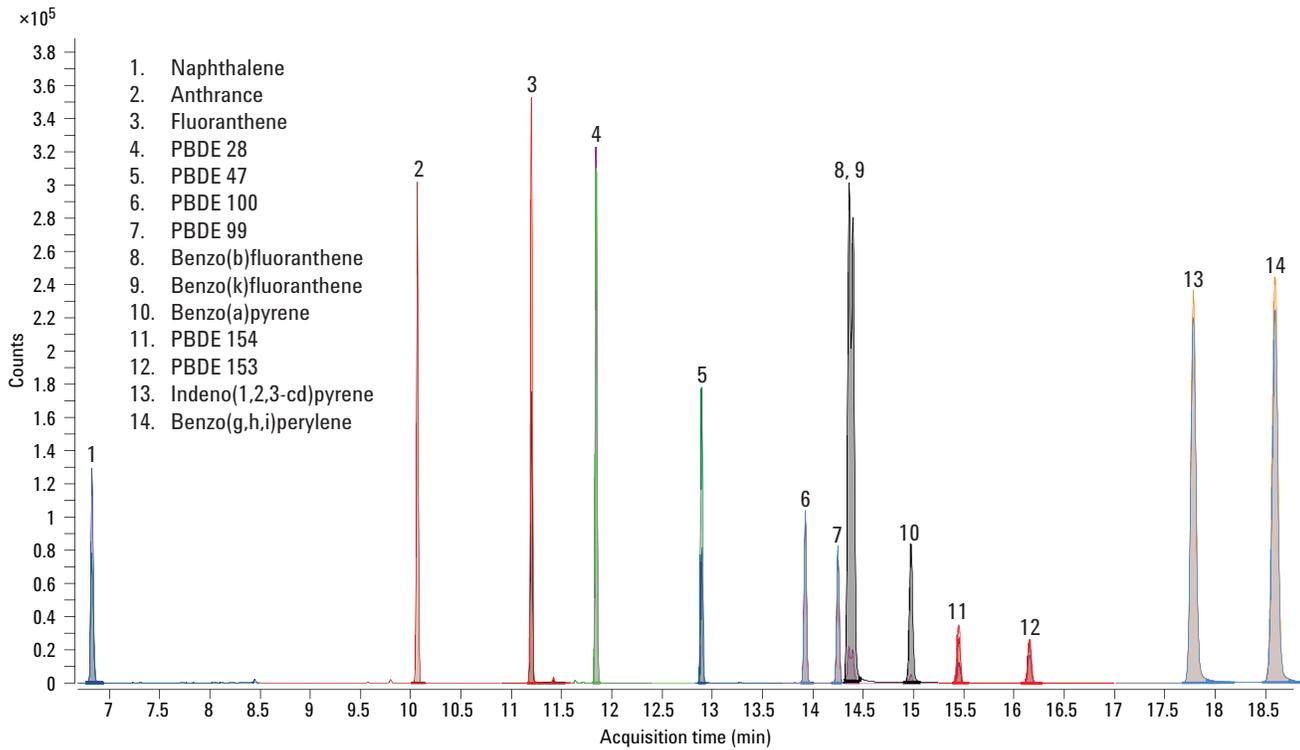
Figure 1. Extracted ion current chromatogram of mid-level calibration standard

1. Naphthalene
2. Anthrance
3. Fluoranthene
4. PBDE 28
5. PBDE 47
6. PBDE 100
7. PBDE 99
8. Benzo(b)fluoranthene
9. Benzo(k)fluoranthene
10. Benzo(a)pyrene
11. PBDE 154
12. PBDE 153
13. Indeno(1,2,3-cd)pyrene
14. Benzo(g,h,i)perylene

Naphthalene

+ MRM 128.0 -> 127.0

*RT = 6.426 minutes
Naphthalene

Naphthalene - 4 levels, 4 levels used, 4 points, 4 points used, 0 QCs

$y = 0.424375x^2 + 8.987272x$
$R^2 = 0.99996281$
Type: Quadratic, Origin: Force, Weight: None

Anthracene

+ MRM 178.0 -> 176.0

*RT = 9.668 minutes
Anthracene

Anthracene - 4 levels, 4 levels used, 4 points, 4 points used, 0 QCs

$y = 1.017257x^2 + 16.763251x$
$R^2 = 0.99999988$
Type: Quadratic, Origin: Force, Weight: None

Figure 2. Representative quantifier ion traces and calibration curves for the first seven analytes eluting from the column (Continued)

Fluoranthene

PBDE 28

PBDE 47

PBDE 100

Figure 2. Representative quantifier ion traces and calibration curves for the first seven analytes eluting from the column (Continued)

PBDE 99

Figure 2. Representative quantifier ion traces and calibration curves for the first seven analytes eluting from the column.

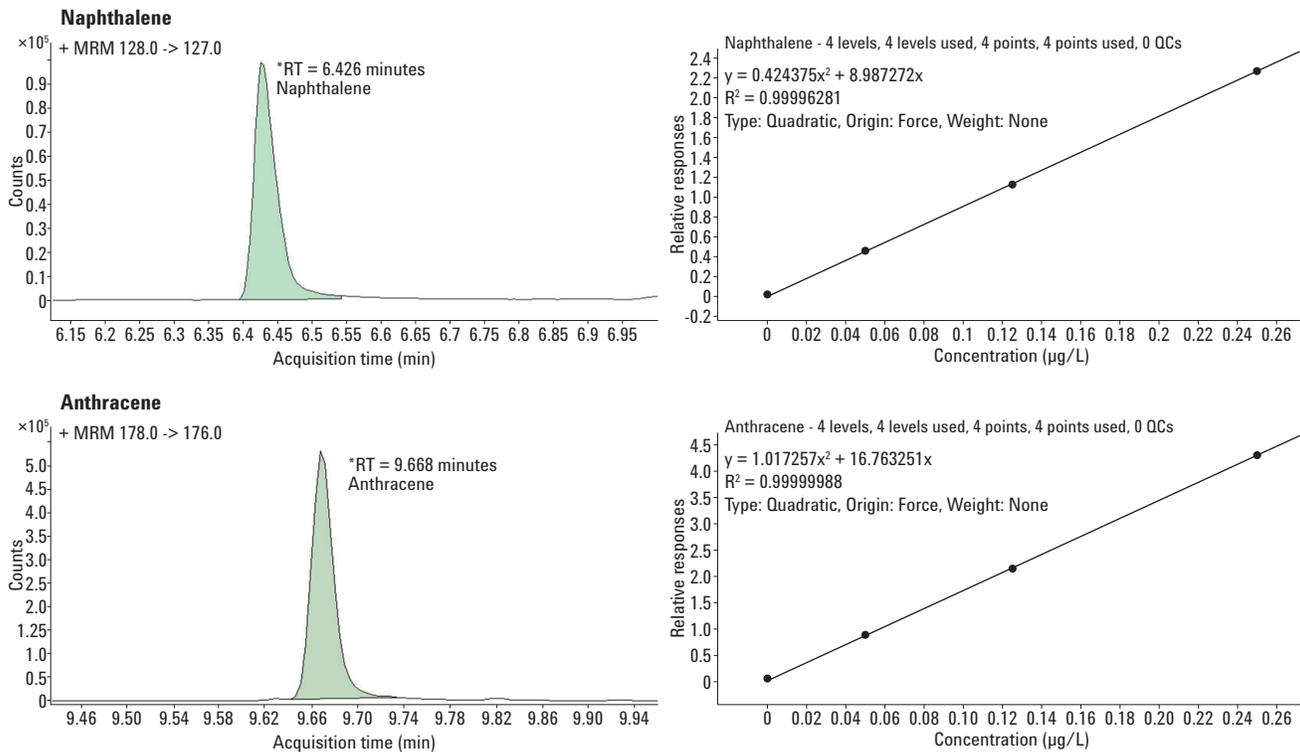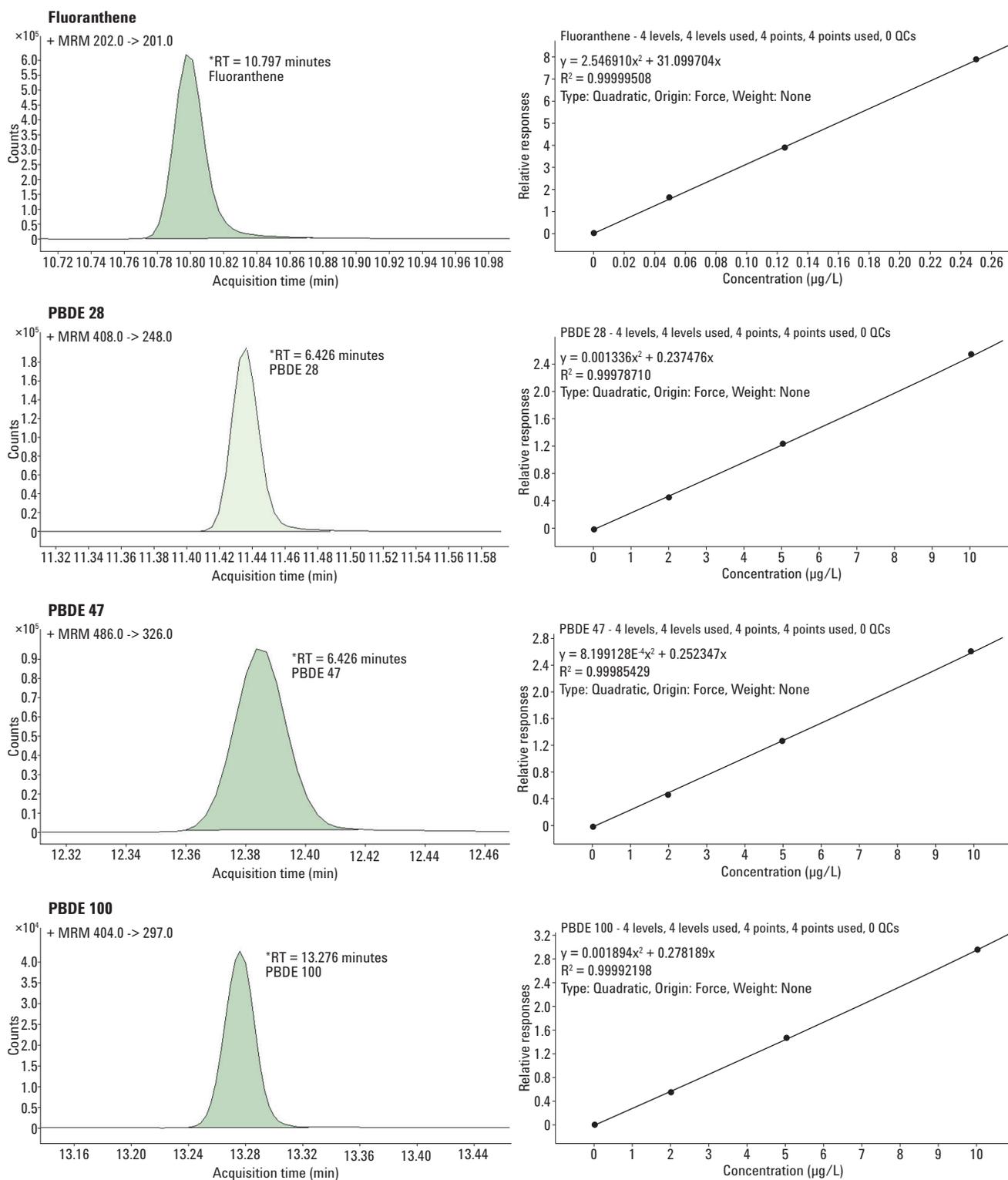**Benzo(b)Fluoranthene**

Benzo(k)Fluoranthene

Benzo(a)pyrene

Figure 3. Representative quantifier ion traces and calibration curves for the last seven analytes eluting from the column (Continued)
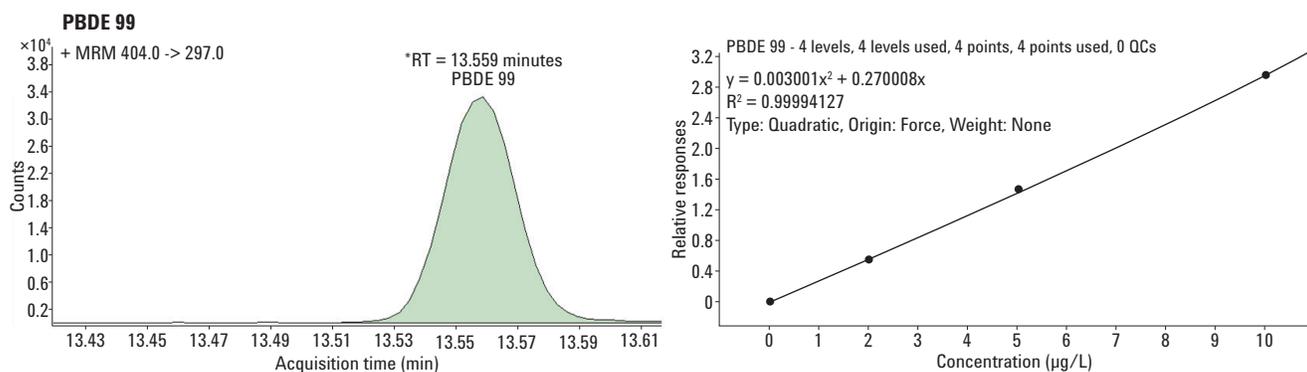
PBDE 154

$\times 10^3$
Counts

*RT = 14.577 minutes
PBDE 154

Acquisition time (min)

PBDE-154 - 4 levels, 4 levels used, 4 points, 4 points used, 0 QCs

$y = 0.001533x^2 + 0.269264x$
$R^2 = 0.99986121$
Type: Quadratic, Origin: Force, Weight: None

Relative responses

Concentration (µg/L)

PBDE 153

+ MRM 484.0 -> 375.0

$\times 10^3$
Counts

*RT = 15.171 minutes
PBDE 153

Acquisition time (min)

PBDE-153 - 4 levels, 4 levels used, 4 points, 4 points used, 0 QCs

$y = 0.003190x^2 + 0.264487x$
$R^2 = 0.99992960$
Type: Quadratic, Origin: Force, Weight: None

Relative rresponses

Concentration (µg/L)

Indeno(123cd)pyrene

+ MRM 276.0 -> 274.0

$\times 10^5$
Counts

*RT = 16.625 minutes
indeno(123cd)pyrene

Acquisition time (min)

i(123cd)pyrene - 4 levels, 4 levels used, 4 points, 4 points used, 0 QCs

$y = 9.578095x^2 + 34.731592x + 0.004451$
$R^2 = 0.99999027$
Type: Quadratic, Origin: Force, Weight: None

Relative responses

Concentration (µg/L)

Benzo(ghi)perylene

+ MRM 276.0 -> 274.0

$\times 10^5$
Counts

*RT = 17.320 minutes
benzo(ghi)perylene

Acquisition time (min)

b(ghi)perylene - 4 levels, 4 levels used, 4 points, 4 points used, 0 QCs

$y = 12.660597x^2 + 37.608506x + 0.003699$
$R^2 = 0.99999605$
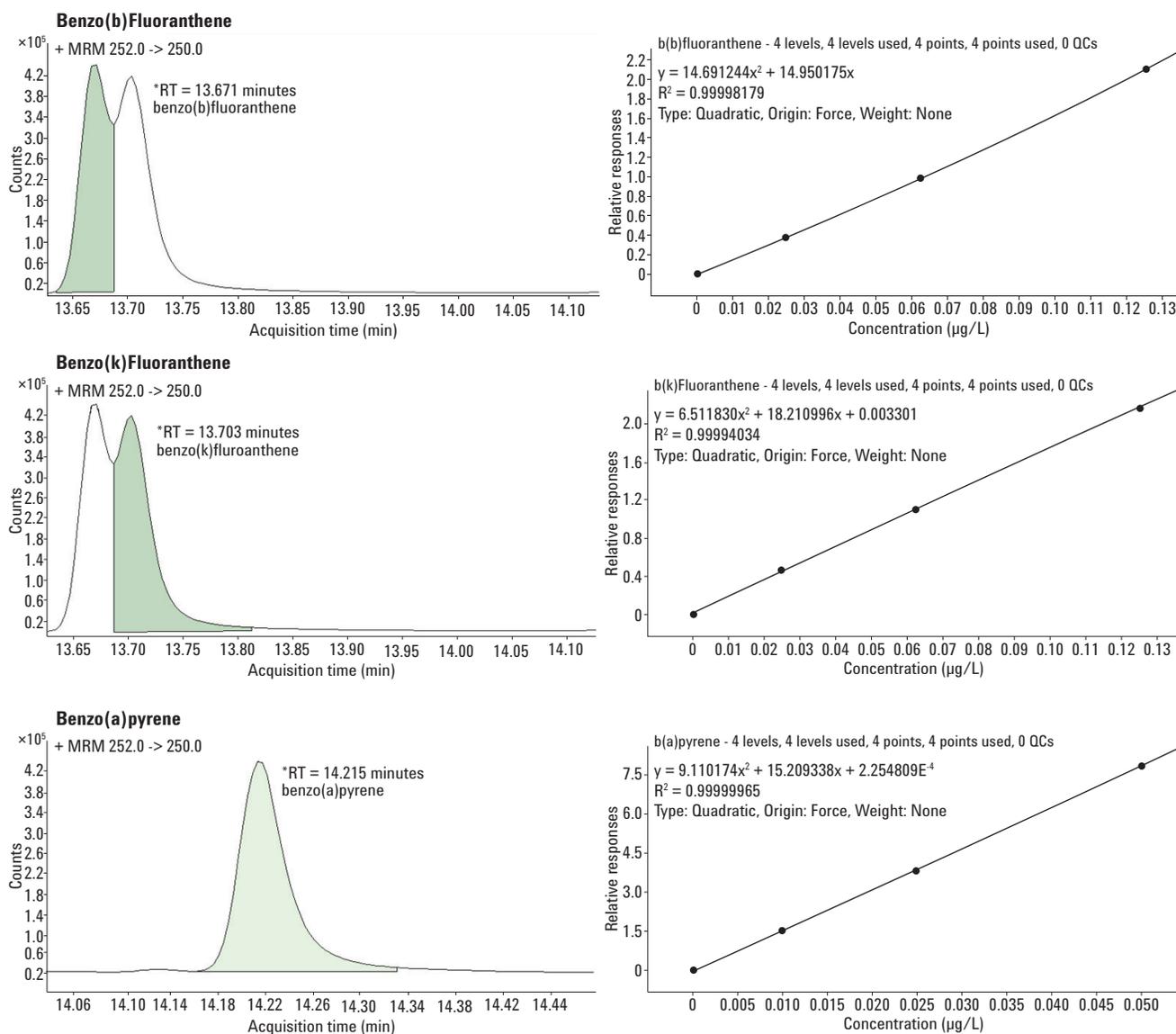Type: Quadratic, Origin: Force, Weight: None
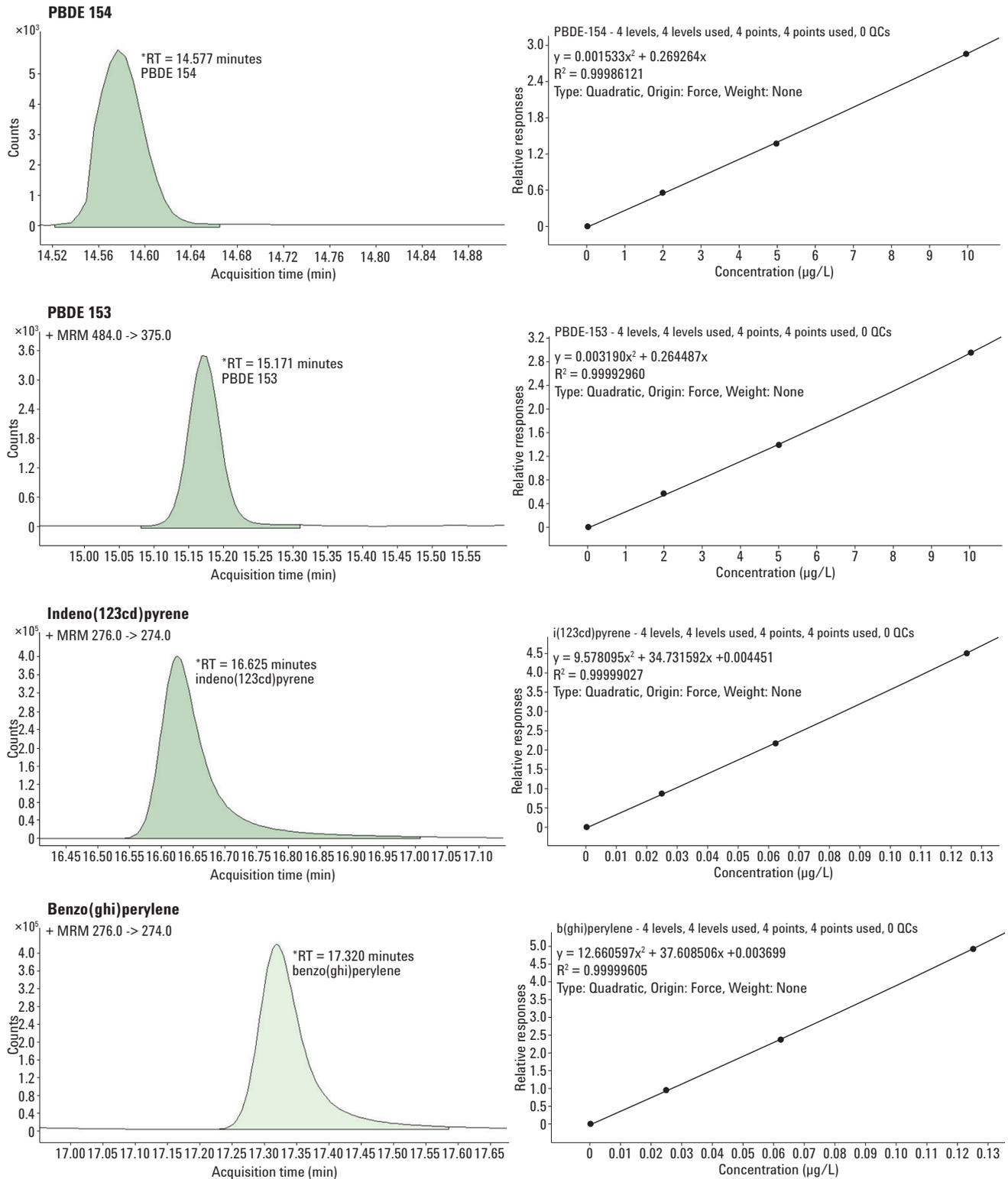
Relative responses

Concentration (µg/L)

Figure 3. Representative quantifier ion traces and calibration curves for the last seven analytes eluting from the column

Table 4. CIP analytical quality control (AQC) limits

Compound	Lowest calibration level	+3s	+2s	−2s	−3s	Limit of detection[1]
Naphthalene	0.05 µg/L	0.0550	0.0533	0.0467	0.0451	0.001 µg/L
Anthracene	0.05 µg/L	0.0644	0.0596	0.0404	0.0356	0.002 µg/L
Fluoranthene	0.05 µg/L	0.0590	0.0560	0.0440	0.0410	0.002 µg/L
PBDE 28	2 ng/L	2.4318	2.2887	1.7163	1.5732	0.057 ng/L
PBDE 47	2 ng/L	2.8056	2.5811	1.6831	1.4586	0.185 ng/L
PBDE 100	2 ng/L	2.4544	2.3166	1.7654	1.6276	0.112 ng/L
PBDE 99	2 ng/L	2.5365	2.3865	1.7865	1.6365	0.074 ng/L
Benzo(b)Fluoranthene	0.025 µg/L	0.0323	0.0299	0.0201	0.0177	0.003 µg/L
Benzo(k)Fluoranthene	0.025 µg/L	0.0316	0.0294	0.0206	0.0184	0.002 µg/L
Benzo(a)Pyrene	0.010 µg/L	0.0114	0.0109	0.0091	0.0087	0.001 µg/L
PBDE 154	2 ng/L	2.7789	2.5521	1.6449	1.4181	0.121 ng/L
PBDE 153	2 ng/L	2.8585	2.6103	1.6175	1.3693	0.152 ng/L
Indeno(123cd)Pyrene	0.025 µg/L	0.0289	0.0276	0.0224	0.0211	0.001 µg/L
Benzo(ghi)Perylene	0.025 µg/L	0.0276	0.0267	0.0233	0.0224	0.001 µg/L

1. Limit of detection (LOD), same as reporting limit in this instance

LOD and/or reporting limit

Table 4 lists the AQC limits for each of the analytes. The Limit of Detection or reporting limit in this case varied from 3.0 ng/L for benzo(b) fluoranthene down to 0.06 ng/L for PBDE 28.

Conclusions

The 7000 triple quadrupole GC/MS System provided reproducible and sensitive detection of PAHs and PBDEs in wastewater down to levels of less than 3.0 ng/L. This single extraction method with no cleanup and no solvent exchange enables the laboratory to exceed the minimum reporting requirements of the United Kingdom Chemical Investigation Programme.

References

[1] Pollutants in Urban Waste Water and Sewage Sludge, http://ec.europa.eu/ environment/waste/sludge/pdf/sludge_pollutants_xsum.pdf

For More Information

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The Measure of Confidence

Agilent Technologies

Ultra-Fast ICP-OES Determination of Trace Elements in Water, Conforming to U.S. EPA 200.7 and Using Next-Generation Sample Introduction Technology

D. Hoobin, Agilent Technologies, Melbourne, Australia

Introduction

This work describes an implementation of the U.S. EPA 200.7 guidelines for the analysis of trace elements in water using the Agilent switching valve system (SVS) 2, a new and innovative sample-introduction system for the Agilent 720/730 Series inductively coupled plasma-optical emission spectrometer (ICP-OES), to improve sample throughput.

A typical sample analysis cycle using an ICP-OES involves sample uptake at high pump rates from the autosampler to the plasma, followed by a stabilization delay to allow the plasma to return to equilibrium. The sample is then measured and rinsed from the system. A high-throughput contract laboratory using a conventional sample introduction system would typically measure a solution in approximately 2 minutes, 30 seconds.

The SVS 2 improves sample-introduction efficiency by greatly reducing sample uptake and washout times. This can more than double sample throughput and significantly reduce operating costs. In addition, the constant flow of solution to the plasma improves plasma stability and reduces stabilization times.

Instrumentation

An Agilent 720 Series simultaneous ICP-OES with axially viewed plasma and sample preparation system (SPS) 3 was used for this work.

The Agilent 720 features a custom designed charged-couple device (CCD) detector, which provides true simultaneous measurement and full wavelength coverage from 167 to 785 nm. The CCD detector contains continuous angled arrays that are matched exactly to the two-dimensional image from the echelle optics. The thermally stabilized optical system contains no moving parts, ensuring excellent long-term stability.

The SVS 2 has two software-triggered valve positions. The first position allows the sample to be quickly loaded into a sample loop using a positive displacement pump operating at up to 500 rpm. The sample is loaded and ready to be aspirated into the plasma for measurement. The controlling software triggers the valves to switch and inject the sample into the ICP-OES. In a typical ICP-OES analysis without the SVS 2, sample is fast-pumped into the plasma, and the pump speed is then reduced to normal speed for the duration of the measurement. The change from high to low sample flow destabilizes the plasma and may result in an unstable signal. To allow the plasma to re-equilibrate at the normal pump speed, a stabilization time of 10–15 s is required to enable the signal to stabilize prior to measurement. Using the SVS 2, the flow of solution into the plasma remains constant. High pump speeds are used to fill the sample loop, but the sample loop is disconnected from the plasma during this step. The continuous flow of solution through the nebulizer ensures better plasma stability and allows use of much shorter stabilization delays. In addition, an uptake delay is not required and a stabilization of <10 s is sufficient to load the sample loop and inject the sample into the plasma to attain a stable signal. Conventional ICP-OES systems operating without the SVS 2 would typically require an additional 25 seconds to perform the same function.
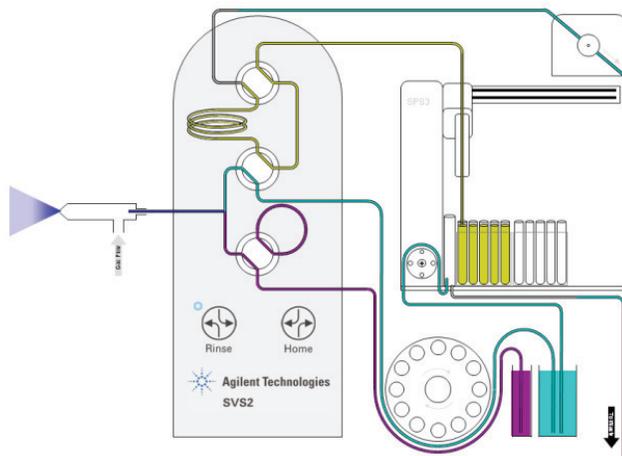

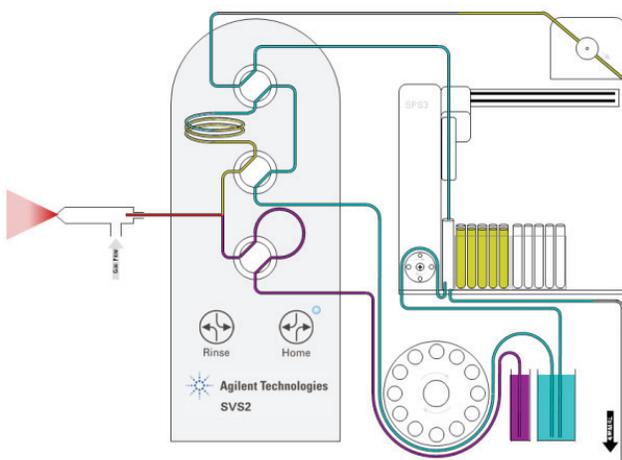**Figure 1.** Agilent SVS 2 in sample load position

Figure 2. Agilent SVS 2 in sample inject position

For a complete description of the SVS 2 throughput advantages, hardware, and modes of operation, see Reference 1.

Tables 1 and 2 list the operating conditions used for the ICP-OES and the SVS 2 during this analysis.

Table 1. ICP OES instrument operating parameters
Note: All-glass sample-introduction system used

Condition	Setting
Power	1.4 kW
Plasma gas flow	15 L/min
Auxiliary gas flow	1.5 L/min
Spray chamber type	Glass cyclonic (single-pass)
Torch	Standard one-piece quartz axial
Nebulizer type	SeaSpray
Nebulizer flow	0.7 L/min
Pump tubing	Rinse/instrument pump Ionization buffer/internal standard
Pump speed	12 rpm
Total sample usage	1 mL
Replicate read time	20 s
Number of replicates	2
Sample uptake delay time	12 s
Stabilization time	0 s
Rinse time	0 s
Fast pump	Off
Background correction	Fitted

Table 2. Agilent SVS 2 operating parameters

Condition	Setting
Sample uptake delay time	12 s
Stabilization time	0 s
Rinse time	0 s
Fast pump	Off
Background correction	Fitted
Nebulizer type	SeaSpray

Preparation of calibration solutions

Calibration and quality control solutions were prepared from Inorganic Ventures, Inc multi-element solutions designed for U.S. EPA 200.7 methodology. Table 3 summarizes the calibration scheme.

Method 200.7 standards — prepared 1:100 from:

- WW-Cal-1 A: Ag, As, B, Ba, Ca, Cd, Mn, Se, Sr
- WW-Cal-1 B: Sb
- WW-Cal- 2: K, Li, Mo, Na, Ti
- WW-Cal-3: Ce, Co, P, V
- WW-Cal-4 A: Al, Cr, Hg, Zn
- WW-Cal-4B: SiO_2, Sn
- WW-Cal-5: Be, Fe, Mg, Ni, Pb, Tl

200.7 Quality control (QC) solutions — prepared 1:100 from:

- QCP-QCS-1: Ag, Al, As, B, Ba, Be, Ca, Cd, Ce, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Na, Ni, P, Pb, Se, Sr, Tl, V, Zn
- QCP-QCS-2: Mo, Sb, SiO_2, Sn, Ti

200.7 Interference check solutions — prepared 1:100 from:

- 2007ICS-1: B, Mo, Si, Ti
- 2007ICS-2: Sb
- 2007ICS-3: Ag, As, Ba, Be, Cd, Co, Cr, Cu, K, Mn, Ni, Pb, Se, Tl, V, Zn
- 2007ICS-4: Al, Ca, Fe, Mg, Na

Laboratory-fortified blanks — prepared 1:100 from:

- WW-LFS-1: Ag, Al, As, B, Ba, Be, Ca, Cd, Ce, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Na, Ni, P, Pb, Se, Sr, Tl, V, Zn
- WW-LFS-2: Mo, Sb, SiO2, Sn, Ti

Laboratory-fortified matrix spikes were also prepared from WW-LFS-1 and 2.

The calibration and quality-control (QC) solutions were diluted with >18 MW/cm^3 deionized water and stabilized in 5% v/v HNO_3 (Merck Ultrapur). The calibration blank was prepared from >18 MW/cm^3 deionized water in 5% v/v HNO_3. An ionization buffer/internal standard solution of composition 1% $CsNO_3$/10 ppm scandium was prepared from Merck Tracepur $CsNO_3$ and 1000 ppm scandium stock.

Table 3. Calibration scheme

Elt	(nm)	Std 1A	Std 1B	Std 2	Std 3	Std 4A	Std 4B	Std 5
Ag	328.068	0.5						
Al	308.215					10		
As	188.980	10						
B	249.772	1						
Ba	493.408	1						
Be	313.042							1
Ca	315.887	10						
Cd	226.502	2						
Ce	418.659				2			
Co	228.615				2			
Cr	205.56					5		
Cu	324.754	2						
Fe	259.94							10
K	766.491			20				
Li	610.365			5				
Mg	279.078							10
Mn	261.02	2						
Mo	203.846			10				
Na	589.592			10				
Ni	231.604							2
P	214.914				10			
Pb	220.353							10
Sb	206.834		5					
Se	196.026	5						
Si	251.611					10		
Sn	189.925						4	
Sr	421.552	1						
Ti	334.941			10				
Tl	190.794							5
V	292.401				2			
Zn	213.857					5		

U.S. EPA 200.7 guidelines summary

This method is a performance-based set of guidelines for the analysis of 32 elements in drinking waters and waste waters. Preferred wavelengths, quality control, and calibration procedures are defined. Method performance criteria, such as method-detection limits, spectral interference check procedures and linear range determination, are also outlined. The minimum QC requirements described in section 9.0 Quality Assurance/Quality Control of Method 200.7 Rev 5.0 are as follows:

Demonstration of laboratory capability

Periodic analysis of:

- laboratory reagent blanks
- fortified blanks
- other laboratory solutions as a continuing check of performance
- performance records of data quality

Initial demonstration of performance

- establish linear dynamic range (LDR)
- measure QC solution to $\pm$ 5% recovery
- determine method detection limits
- conduct spectral interference check (SIC)

Monitor laboratory performance

Periodic analysis of:

- laboratory reagent blank (LRB)
- laboratory fortified blank (LFB)
- instrument performance check solution (IPC)
- interference check solutions (ICS)

Assess analyte recovery and data quality

- laboratory fortified matrix spikes (LFM)
- standard reference materials (if available)

Table 4 shows the mnemonics used in the description of the 200.7 QC scheme.

Table 4. Mnemonics used in the description of the 200.7 QC scheme

Mnemonic	Description	Sample rate	Limit or %R
QCS	QC solution: second-source calibration check	After initial calibration	95–105%
ICS	Interference check solution: Verifies effectiveness of correction processes	3 months	-
IPC	Instrument performance check: Continuing drift and accuracy verification	1 in 10 and end of run	90–110%
Blank	Measure blank as sample	1 in 10	< IDL

For a full description of the US EPA 200.7 Guidelines including the appropriate standard and sample sequence, see Reference 2.

Initial demonstration of performance
Linear range analysis (LRA)
The LRA represents the upper concentration limit for each analyte of the ICP-OES linear range beyond which results cannot be reported without dilution of the sample. The maximum error for each calibration standard within the linear range cannot exceed 10%. Table 5 shows the LDR for each element.

Table 5. LDR for each element

Element	LDR (ppm)	Element	LDR (ppm)	Element	LDR (ppm)
Ag 328.068	50	Cu 324.754	100	Sb 206.834	500
Al 308.215	1000	Fe 259.940	100	Se 196.026	500
As 188.980	200	K 766.491	50	Si 251.611	200
B 249.772	100	Li 670.784	100	Sn 189.925	70
Ba 493.409	10	Mg 279.079	1000	Sr 421.552	10
Be 313.042	2	Mn 261.020	200	Ti 334.941	20
Ca 315.887	100	Mo 203.846	100	Tl 190.794	100
Cd 226.502	20	Na 259.592	100	V 292.401	30
Ce 413.765	100	Ni 231.604	50	Zn 213.857	20
Co 228.616	100	P 214.914	1000		
Cr 205.552	40	Pb 220.353	100		

Method detection limits (MDL)
The MDL of each element was determined following the procedure defined in 40 CFR, part 136 Appendix B, as specified in Section 9.2.1 Method 200.7 revision 5. A standard solution containing analytes at a concentration of three to five times the instrument manufacturer's suggested instrument detection limit (IDL) was measured on three non-consecutive days. Table 6 shows the MDL for each element.

Table 6. MDL for each element

Element	MDL (ppb)	Element	MDL (ppb)	Element	MDL (ppb)
Ag 328.068	0.1	Cu 324.754	2	Sb 206.834	2.7
Al 308.215	2.6	Fe 259.940	3	Se 196.026	4
As 188.980	3.3	K 766.491	15.8	Si 251.611	13.0
B 249.772	1.2	Li 670.784	1.5	Sn 189.925	1.3
Ba 493.409	2.0	Mg 279.079	2.8	Sr 421.552	0.2
Be 313.042	0.3	Mn 261.020	0.2	Ti 334.941	0.4
Ca 315.887	8.4	Mo 203.846	1.6	Tl 190.794	1.9
Cd 226.502	0.2	Na 259.592	5.4	V 292.401	2.1
Ce 413.765	1.3	Ni 231.604	1.4	Zn 213.857	0.6
Co 228.616	0.4	P 214.914	16.1		
Cr 205.552	1.1	Pb 220.353	1.8		

Initial QCS performance

As part of the initial demonstration of lab performance, it is necessary to analyze a QC solution and achieve a recovery of ±5% of the true values for each element. Table 7 shows the recovery for each element.

Table 7. Recovery for each element

Element	%R	Pass/fail	Element	%R	Pass/fail
Ag 328.068	99.2	Pass	Mn 261.020	103.2	Pass
Al 308.215	99.2	Pass	Mo 203.846	99.6	Pass
As 188.98	101	Pass	Na 259.592	98.1	Pass
B 249.772	101	Pass	Ni 231.604	101.2	Pass
Ba 493.409	99.4	Pass	P 214.914	98.6	Pass
Be 313.042	102	Pass	Pb 220.353	101.5	Pass
Ca 315.887	102	Pass	Sb 206.834	92.7	Pass
Cd 226.502	101	Pass	Se 196.026	100.3	Pass
Ce 413.765	99	Pass	Si 251.611	99	Pass
Co 228.616	99.8	Pass	Sn 189.925	100.6	Pass
Cr 205.552	104	Pass	Sr 421.552	100.6	Pass
Cu 324.754	101.5	Pass	Ti 334.941	99.8	Pass
Fe 259.94	99.3	Pass	Tl 190.794	99.6	Pass
K 766.491	97.2	Pass	V 292.401	100.7	Pass
Li 670.784	97.5	Pass	Zn 213.857	98.5	Pass
Mg 279.079	96.9	Pass			

Spectral interference check

From Method 200.7 Revision 4.4 Section 7.15:

SIC solutions (containing similar concentrations of the major components in the samples, for example, ≥10 mg/L) can serve to verify the absence of effects at the wavelengths selected. These data must be kept on file with the sample analysis data. If the SIC solution confirms an operative interference that is ≥10% of the analyte concentration, the analyte must be determined using a wavelength and background correction location free of the interference or by another approved test procedure. The analysis of solutions 2007ICS-1 through -4 at the utilized wavelengths shows no significant spectral interferences when using the default ICP 720 background correction technique.

Analytical results

Reference materials were analyzed using the instrument and accessory conditions defined in Tables 1 and 2. Tables 8 through 10 show the reported results.

Instrument stability

The IPC solution was analyzed every 10 samples over a period of six hours. The measured concentration of each element in the IPC must be within ±10% of the true value. The IPC results trends are a measure of the stability of the instrument. Figure 3 shows that conditions remain stable over the six-hour period. The precision for all 32 elements was better than 2%.
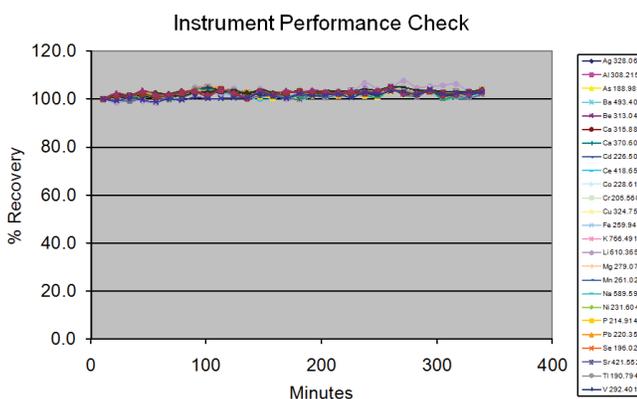

Figure 3. Long-term stability of instrument performance check (IPC) was better than 2% over six hours

Speed of analysis

An analysis sequence that conforms to U.S. EPA protocols can be time-consuming, because a large number of QC solutions are required for conformance to the protocol. In this study, the use of the SVS 2 sample-introduction system dramatically reduced analysis time, with a resulting tube-to-tube analysis time of 68 s.

Table 8. NIST SRM 1643e results

Trace elements in water: sample source NIST U.S. Dept of Commerce

Element	Spec µg/L	Found	Dup	QC spike	Spike level	% rec LCS	RPD dup %	% spike rec
Ag 328.068	1.062	1.123	1.042	0.061	0.075	105.7	7.5	79.8
Al 308.215	141.8	151.936	150.101	2.172	2	107.1	1.2	101.0
As 188.980	60.45	57.051	59.461	0.862	0.8	94.4	4.1	100.6
B 249.772	157.9	159.720	161.242	0.473	0.3	101.2	0.9	104.4
Ba 493.408	544.2	534.966	537.325	0.728	0.2	98.3	0.4	96.5
Be 313.042	13.98	13.843	13.867	0.212	0.2	99	0.2	99.1
Ca 315.887	32300	30995.4	30966.2	31.982	1	96	0.1	98.7
Cd 226.502	6.568	6.565	6.586	0.209	0.2	100	0.3	101.2
Co 228.615	27.06	26.775	27.176	0.227	0.2	98.9	1.5	100.1
Cr 205.560	20.4	20.271	20.423	0.423	0.4	99.4	0.7	100.7
Cu 324.754	22.76	23.729	23.126	0.334	0.3	104.3	2.6	103.4
Fe 259.940	98.1	98.036	99.205	3.076	3	99.9	1.2	99.3
K 766.491	2034	2017.45	2026.59	12.149	10	99.2	0.5	101.3
Mg 279.078	8037	7901.66	7913.59	9.792	2	98.3	0.2	94.5
Mn 257.610	38.97	39.725	39.569	0.244	0.2	101.9	0.4	102.1
Mo 203.846	121.4	119.736	120.517			98.6	0.7	
Na 589.592	20740	19061.6	19007.1	21.896	3	91.9	0.3	94.5
Ni 231.604	62.41	61.763	60.219	0.557	0.5	99	2.5	99
P 214.914		41.893	56.332	6.178	6		29.4	102.3
Pb 220.353	19.63	21.138	20.422	1.028	1	107.7	3.4	100.7
Sb 206.834	58.3	55.64	54.15			95.4	2.7	
Se 196.026	11.97	14.118	13.377	1.973	2	117.9	5.4	97.9
Si 251.611		27.676	26.563	0.193			4.1	
Sr 421.552	323.1	320.029	324.499	0.517	0.2	99	1.4	98.5
Tl 190.794	7.445	8.162	7.773	2.008	2	109.6	4.9	100
V 292.401	37.86	36.671	36.843	0.339	0.3	96.9	0.5	100.8
Zn 213.857	78.5	79.832	79.133	0.284	0.2	101.7	0.9	102.1

Table 9. NIST SRM 1640a results
Trace elements in natural water: sample source NIST U.S. Dept of Commerce

Element	Spec µg /L	Found	Dup	QC spike	Spike level	% rec LCS	RPD dup %	% spike rec
Ag 328.068	8.081	8.07	8.192	0.071	0.1	99.9	1.5	83.9
Al 308.215	53	53.305	52.266	2.012	2	100.6	2	97.9
As 188.980	8.075	6.677	8.427	0.777	0.8	82.7	23.2	96.3
B 249.772	303.1	321.542	305.727	0.596	0.3	106.1	5	91.5
Ba 493.408	151.8	151.023	147.974	0.337	0.2	99.5	2	93
Be 313.042	3.026	3.038	2.915	0.197	0.2	100.4	4.1	97
Cd 226.502	3.992	3.924	3.789	0.200	0.2	98.3	3.5	98
Co 228.615	20.24	20.064	19.738	0.216	0.2	99.1	1.6	98
Cr 205.560	40.54	39.52	38.749	0.429	0.4	97.5	2	97.4
Cu 324.754	85.75	84.949	83.357	0.378	0.3	99.1	1.9	97.7
Fe 259.940	36.8	37.472	35.993	2.938	3	101.8	4	96.7
K 766.491	579.9	573.916	563.117	10.598	10	99	1.9	100.2
Mg 279.078	1058.6	1042.15	1022.54	2.974	2	98.4	1.9	96.6
Mn 257.610	40.39	40.955	40.316	0.238	0.2	101.4	1.6	98.5
Mo 203.846	45.6	45.991	43.85	0.044		100.9	4.8	
Na 589.592	3137	2911.38	2859.63	5.829	3	92.8	1.8	97.3
Ni 231.604	25.32	24.24	24.058	0.510	0.5	95.7	0.8	97.2
P 214.914		47.423	58.729	5.933	5			117.7
Pb 220.353	12.101	13.404	13.04	1.010	1	110.8	2.8	99.7
Sb 206.834	5.105	5.71	5.237	0.004		111.9	8.6	
Se 196.026	20.13	23.159	20.121	1.912	2	115	14	94.4
Sr 421.552	126.03	127.037	124.371	0.315	0.2	100.8	2.1	94
Tl 190.794	1.619	1.839	1.846	1.977		113.6	0.4	
V 292.401	15.05	15.101	14.542	0.309	0.3	100.3	3.8	98
Zn 213.857	55.64	56.157	55.004	0.256	0.2	100.9	2.1	99.9

Table 10. Trace elements in certified waste water results
Sample source: High Purity Standards, PO Box 41727, Charleston, SC 29423 USA
Cat # CWW-TM-C

Element	Spec μg /L	Found	Dup	QC spike	Spike level	% rec LCS	RPD dup %	% spike rec
Al	0.50	0.535	0.545	2.553	2.000	107.0	1.9	100.9
Sb	0.15	0.137	0.141	0.136	0.000	91.3	2.9	n/a
As	0.15	0.143	0.146	0.914	0.800	95.3	2.1	96.4
Ba	0.50	0.480	0.492	0.673	0.200	96.0	2.5	96.5
Be	0.15	0.140	0.144	0.331	0.200	93.3	2.8	95.5
B	0.50	0.513	0.520	0.840	0.300	102.6	1.4	109.0
Cd	0.15	0.146	0.149	0.341	0.200	97.3	2.0	97.5
Cr	0.50	0.476	0.485	0.860	0.400	95.2	1.9	96.0
Co	0.50	0.478	0.487	0.668	0.200	95.6	1.9	95.0
Cu	0.50	0.494	0.502	0.789	0.300	98.8	1.6	98.3
Fe	0.50	0.486	0.495	3.374	3.000	97.2	1.8	96.3
Pb	0.50	0.487	0.496	1.443	1.000	97.4	1.8	95.6
Mn	0.50	0.490	0.492	0.674	0.200	98.0	0.4	92.0
Mo	0.50	0.469	0.481	0.471	0.000	93.8	2.5	n/a
Ni	0.50	0.477	0.490	0.952	0.500	95.4	2.7	95.0
Se	0.15	0.151	0.149	2.051	2.000	100.7	1.3	95.0
Ag	0.15	0.144	0.148	0.211	0.075	96.0	2.7	89.3
Sr	0.50	0.481	0.492	0.673	0.200	96.2	2.3	96.0
Tl	0.15	0.145	0.149	2.101	2.000	96.7	2.7	97.8
V	0.50	0.480	0.490	0.770	0.300	96.0	2.1	96.7
Zn	0.50	0.498	0.509	0.696	0.2	99.6	2.2	99.0

Conclusion

Using the Agilent SVS 2 with an Agilent 720 Series axially viewed ICP-OES resulted in more than a doubling of sample throughput—from approximately 210 seconds[2] per sample without the SVS 2 to 68 seconds per sample using the SVS 2. Even with the improvement in productivity, analytical performance was maintained. Stability during a six-hour period was better than 2% for all elements. Detection limits exceeded the requirements of the U.S. EPA.

As the tubing does not make contact with peristaltic pump tubing prior to being aspirated into the plasma, the inert sample path results in reduced sample carry-over.

References

[1]   D. Hoobin and E. Vanclay, Ultra-fast ICP OES determinations of soil and plant material using next generation sample introduction technology.

[2]   S. Bridger and M. Knowles, A complete method for environmental samples by simultaneous axially viewed ICP-OES following U.S. EPA guidelines.

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