Increased Sample Throughput and Capacity for Online SPE Enrichment

Agilent 1200 Infinity Series Online SPE Solution with Agilent 1260 Infinity Multisampler

Technical Overview

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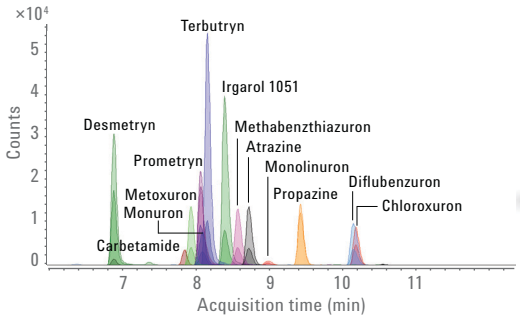
Abstract

This Technical Overview describes how the combination of the Agilent 1200 Infinity Series online SPE solution and the Agilent 1260 Infinity Multisampler achieves maximum sample throughput and highest efficiency. The 1260 Infinity Multisampler can be fitted with a 900-µL sample loop to enable injection of large sample volumes, making it ideally suited for online solid-phase extraction (SPE). The 1260 Infinity Multisampler increases the efficiency and flexibility of the online SPE system by maximizing sample capacity. With this sample hotel, more samples can be run within one work-list. Up to sixty 6-mL vials and one hundred-eight 2-mL vials can be inserted. In contrast, the 1260 Infinity standard autosampler can hold thirty 6-mL vials. This Technical Overview demonstrates the performance of the 1260 Infinity Multisampler with the 1200 Infinity Series online SPE solution. Validation parameters such as linearity, area precision, and recovery for environmental water samples are shown and discussed.



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Introduction

The Agilent 1260 Infinity Multisampler has a completely new design, and provides high flexibility in choice of configuration of the sample hotel[1]. The sample hotel offers the possibility to equip the system with different drawers, and vial- or microtiter plates. In combination with the Agilent 1200 Infinity Series online SPE solution, three drawers are recommended. This configuration enables four vial plates for fifteen 6-mL vials (60 samples), and two vial plates for fifty-four 2-mL vials (108 samples) to be loaded into the sample hotel for standards or samples for direct injection methods. The 1260 Infinity Multisampler can be configured according to needs and applications. For online SPE, it can be equipped optionally with a 900-µL metering device and loop for large volume injections up to a pressure limit of 400 bar. When more sample volume is required, a multidraw option with up to 1,800 µL is available. The 1260 Infinity Multisampler can also be equipped a multiwash option for ultralow carryover.

This Technical Overview shows the combination of the 1200 Infinity Series online SPE solution and the 1260 Infinity Multisampler for enhanced sample throughput and large volume injection with a 900-µL loop. Different water samples (river, ground, and tap water) were spiked with a low concentration of pesticides and analyzed with direct injection and online SPE. Performance parameters such as linearity, area precision, and recovery for these water samples are shown and discussed.

Design of the Agilent 1260 Infinity Multisampler

The 1260 Infinity Multisampler provides high flexibility in sample logistics through high capacity, even with different vial sizes. Lowest carryover is achieved using the multiwash feature, which gives the choice of three different solvents for washing the injection needle and backflushing the needle seat. The flush pump cleans the outside surfaces of the needle with three solvents and backflushes the seat to reduce carryover.

The 1260 Infinity Multisampler used in this study was equipped with different options:

- Option #100: sample cooler
- Option #112: multiwash option
- Option #133: triple-height drawer (quantity 2) for the 6-mL vials
- Option #163: analytical head 900 µL
- Option #156: sample loop-flex 900 µL right (standard position)

One dual-height drawer (for 2-mL vials) is already included in the standard configuration of the 1260 Infinity Multisampler.

Experimental

Instrumentation

All experiments were carried out on an Agilent 1200 Infinity Series online SPE system comprising:

- Agilent 1290 Infinity Flexible Cube (G4227A), equipped with:
  - Agilent Online SPE starter kit (G4742A), including one 2-position/10-port valve, 600 bar, capillaries, cartridge holder, and cartridges
  - Additional capillaries required to connect valve A to Multisampler (p/n 5067-4670), and from Multisampler to valve A (p/n 5065-9932)
  - Agilent Online SPE direct injection kit (G4744A), including one 2-position/10-port valve, 600 bar, and capillaries
- Agilent 1260 Infinity Binary Pump (G1312B) with LAN card (G1369C)
- Agilent 1260 Infinity Multisampler with 900-µL head and metering device (G7167A)
- Agilent 1260 Infinity Thermostatted Column Compartment (G1316A)
- Agilent 6490 Triple Quadrupole LC/MS System (G6490A) with Agilent Jet Stream technology

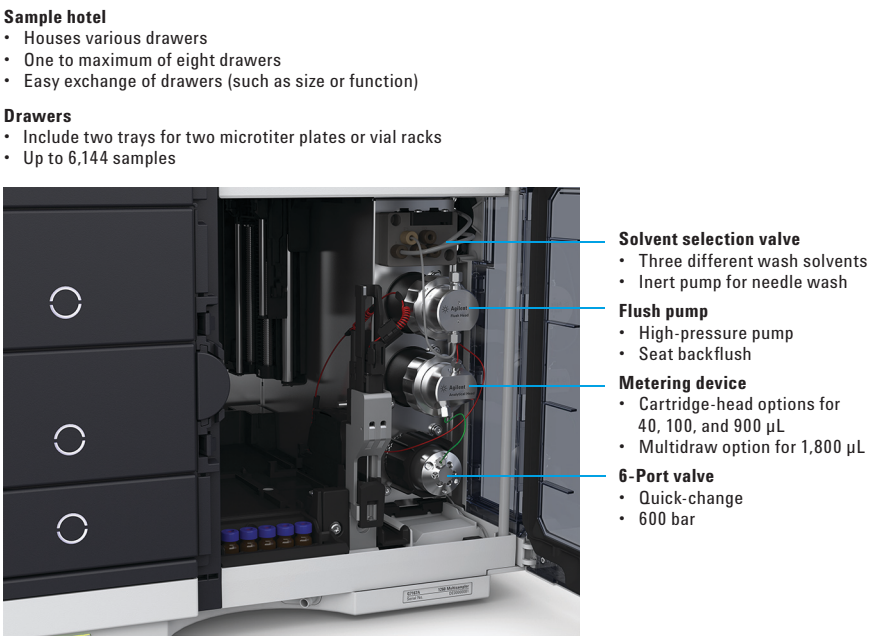

Figure 1. Agilent 1260 Infinity Multisampler with four dual-height drawers, a 900-µL metering device, and a multiwash option.

For more information about the general online SPE setup for direct injection and online SPE, see an earlier Agilent Application Note[2].

Software

- Agilent MassHunter data acquisition for triple quadruple mass spectrometer, version 07.00, SP1
- Agilent MassHunter Optimizer Software, version 06.00
- Agilent MassHunter source and iFunnel Optimizer Software, version 06.00
- Agilent MassHunter Qualitative Software, version 06.00
- Agilent MassHunter Quantitative Software, version 07.00

Samples

Tap water was taken from Waldbronn, Germany, surface water from a river near Waldbronn, and ground water from Karlsruhe, Germany. The samples and standards were stored at 5 °C, and were centrifuged for 5 minutes at 5,000 rpm before injection. The water samples were spiked with different concentrations of pesticides by diluting a stock solution of 100 µg/L. A seven-level calibration curve (0.1, 0.5, 1, 5, 10, 25, and 50 ng/L) was prepared in ultrapure water. Tap, ground, and river water were spiked at a concentration of 5 ng/L.

Chemicals

All solvents used were LC/MS grade. Acetonitrile was purchased from Merck, Germany. Fresh ultrapure water was obtained from a Milli-Q Integral system equipped with LC-Pak Polisher and a 0.22-µm membrane point-of-use cartridge (Millipak). Formic acid (p/n G2453-85060) was from Agilent. Pesticide standards were purchased from Dr. Ehrenstorfer GmbH, Germany.

Online SPE method

Table 1. Online SPE method.

Parameter	Value
Mobile phase	A) Water + 0.1 % formic acid B) Acetonitrile + 0.1 % formic acid
Gradient	0–2.5 minutes, 2 %B 2.5–15 minutes, 2–98 %B 15–20 minutes, 98 %B
Post time	5 minutes
Flow rate	0.4 mL/min
Injection volume	900 µL
Cooler	10 °C
Multiwash washing procedure	15 seconds with acetonitrile 15 seconds with water
LC column	Agilent ZORBAX SB-Aq 2.1 × 100 mm, 3.5 µm (861753-914)
Column temperature	35 °C
Flexible cube	
0 minutes	Pump 3 mL, flow 1.5 mL/min Solvent A1 (water)
2 minutes	Right valve increase valve position
2.1 minutes	Pump 4 mL, flow 2 mL/min Solvent A2 (ACN)
5.5 minutes	Pump 6 mL, flow 2 mL/min Solvent A1

The MS method was developed and optimized as described in an earlier Agilent Application Note[3].

Results and Discussion

For the determination of herbicides in water samples, the tap, river, and ground water were spiked. Calibration curves were obtained for every compound with the developed online SPE method. All samples were quantified using linear calibration curves at seven concentration levels between 0.1 and 50 ng/L, with each calibration level injected four times.

The recovery of the SPE trapping process was determined by comparing the peak areas of an injection of spiked tap water onto the SPE column to a direct injection of the same concentration level and volume (500 µL of 50-ng/L standard, n = 7) onto the analytical column. Table 2 shows good values for the recovery data (80 to 105 %). The relative standard deviation (RSD) of these areas was

Table 2. Performance data for all herbicides of the online SPE method such as recovery (%), linearity, area (RSD %), LOD, and LOQ (ng/L).

Compound	Recovery (%)	Area (RSD %)	Linearity (R^2)	LOD (ng/L) (S/N = 3)	LOQ (ng/L) (S/N = 10)
Desmetryn	94.1	1.50	0.9992	0.03	0.1
Carbetamide	82.5	3.15	0.9982	0.15	0.5
Metoxuron	90.5	3.99	0.9990	0.03	0.1
Monuron	89.0	3.56	0.9915	0.015	0.05
Prometryn	105.7	2.28	0.9990	0.03	0.1
Terbutryn	100.5	4.17	0.9973	0.03	0.1
Irgarol 1051	99.9	1.71	0.9985	0.03	0.1
Methabenzthiazuron	90.6	3.15	0.9987	0.006	0.02
Atrazine	92.2	3.77	0.9990	0.03	0.1
Monolinuron	81.4	2.35	0.9955	0.1	0.5
Propazine	93.9	2.60	0.9950	0.003	0.01
Trietazine	95.7	4.01	0.9990	0.1	0.5
Chloroxuron	103.0	5.09	0.9980	0.03	0.1
Diflubenzuron	87.5	4.30	0.9950	0.5	1

also determined and was found to be less than 5 % for two alternatively used SPE cartridges.

Performance parameters (Table 2) such as linear coefficients, were found to be good for all compounds with values typically greater than 0.997. For determination of the limit of detection (LOD), a signal-to-noise (S/N) ratio of 3 was used. The LODs for all compounds were in the range of 0.003 to 0.5 ng/L, with an injection volume of 900 µL. A S/N ratio of 10 was used for the calculation of the limit of quantification (LOQ). The values for the LOQ were found to be between 0.01 and 1 ng/L.

To show the removal of matrix and especially matrix effects from environmental water samples, the river and ground water were spiked with a low concentration of herbicides (5 ng/L). Tap water is meant to be free of heavy matrix and analytes, and was taken as a reference for spiked river and ground water. Hence, the apparent recovery of the analytes was calculated in comparison to the area response of 5-ng/L spiked tap water. Some pesticides such as monuron, terbutryn, atrazine, and propazine have been detected at trace levels in river water and atrazine in ground water. These concentrations were subtracted from the measured result.

Figure 2 shows the summary of the apparent recovery test, where a recovery within the range of 70 to 130 % was seen as accepatble[4]. All compounds show similar intensity and response in both environmental waters. This indicates that most of the matrix such as salt and organic contaminants are not enriched onto the cartridge and flushed to the waste. The area RSD of river and ground water was less than 10 %. These results confirm online SPE is a fast and effective approach to analyze compounds sensitively and reliably. Using the multiwash option of the 1260 Infinity Multisampler, no carryover was observed for all standards and samples.

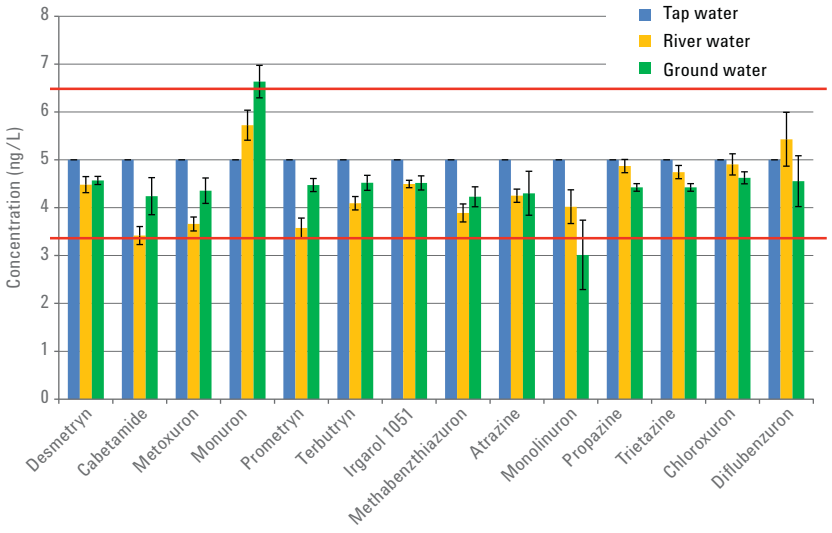

Figure 2. Tap, river, and ground water were spiked at a concentration of 5 ng/L with a suite of herbicides. Apparent recoveries are shown in ng/L (n = 7). The acceptable range was between 70 and 130 % (3.5 to 6.5 ng/L).

Conclusion

The combination of the Agilent 1260 Infinity Multisampler, with 900-µL loop, and the Agilent 1200 Infinity Series online SPE solution is a perfect match to increase sample throughput due to more vial capacity. Up to sixty 6-mL vials and one hundred-eight 2-mL vials can be loaded in the sample hotel. In this Technical Overview, a sensitive and stable online SPE method was developed for the analysis of herbicides in river and ground water. The method was applied for the analysis of 14 herbicides, and good recovery values were found for all compounds. Performance parameters such as linearity and area deviation were excellent and showed high precision (greater than 10 % in environmental water samples). Low concentration levels can be quantified reliably (LOQ 0.01 ng/L) with an injection volume of just 900 µL.

References

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