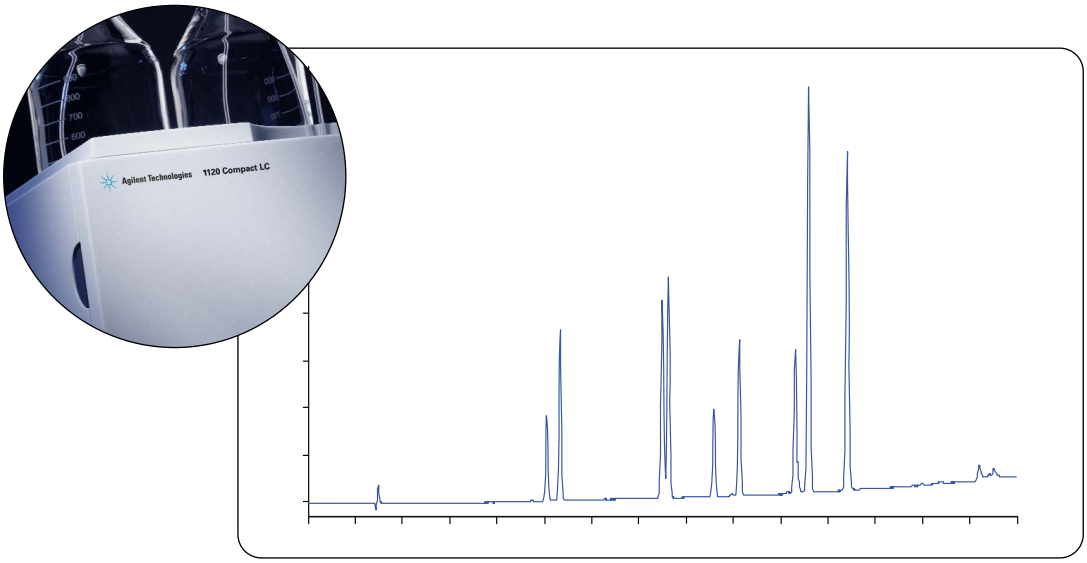
Analysis of herbicides in drinking water using the Agilent 1120 Compact LC

Application Note

Angelika Gratzfeld-Huesgen



Abstract

The Agilent 1120 Compact LC is the system of choice for conventional, analytical scale liquid chromatography. It is an intergrated LC designed for ease of use, performance and reliability. It is ideally suited for the analysis of herbicides on account of its capability to achieve highly precise retention times and peak areas, and low detection limits for the analyzed compounds. In this Application Note, data is presented that demonstrates:

- Excellent retention time precision of less than 0.1 % RSD
- Excellent peak area precision of less than 0.5 % RSD
- Limit of detection (LOD) less than 150 pg for all herbicides analyzed

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Introduction

The analysis of herbicides in various environmental and biological matrices is highly important in the protection of nature and the environment. In most countries, regulations limit the concentration of herbicides that are allowed in drinking water and other foodstuffs. Several analytical techniques are used in the control these limits. For compounds that are thermally unstable, high performance liquid chromatography (HPLC) is the recommended analysis technique.

In this study, nine herbicides were analyzed and the precision of retention times and peak areas was measured. Further, the limit of detection (LOD) of the compounds was determined. Drinking water spiked with trace amounts of the nine herbicides was used as sample.

Experimental

Equipment

- Agilent 1120 Compact LC comprising gradient pump with integrated degasser, autosampler with vial tray, column oven and variable wavelength detector, see figure 1
- Agilent HC-C18(2), high carbon load, 150 x 4.6 mm, 5 µm particle size column
- Agilent EZChrom Elite Compact software
- Nine herbicides were selected for the experiments and purchased from Sigma/Aldrich, see table 1.

Figure 1
Agilent 1120 Compact LC

Chromatographic conditions

- Mobile phase: A: Water, B: ACN
- Gradient: 10 to 90 %B in 15 min
- Flow rate: 1.5 mL/min
- Injection volume:
  5 µL for 1:100 dilution
  20 µL for 1:1000 dilution
  20 µL for 1:10,000 dilution
- Column temperature: 40 °C
- Detection wavelength: 225 nm
  Peakwidth: > 0.0025 min
  Response time: 0.06 s

Results and discussion

Analyzing herbicides with UV detection means that precision of retention times is of utmost importance. In addition, precision of peak areas must be less than 1 % in the low ng range. According to the United States Environmental Protection Agency the tolerance level for diuron in different food commodities is about 0.1–2.0 ppm. This corresponds to about 1–20 ng per 10 µL. For simazine, the tolerance level in different commodities is 0.02–0.25 ppm, corresponding to 200–2500 pg per 10 µL.

As a consequence the demands on this application can be summarized as follows.

- Relative standard deviation of retention times less than 0.1 %
- Relative standard deviation of peak areas (in low ng range) less than 1 %
- Limit of detection (LOD) less than 150 pg for a 20 µL injection

Compound	Stock Solution mg/10 mL	1:100 dilution 5 µL inj. vol. (ng per inj.)	1:1000 dilution 20 µL inj. vol. (ng per inj.)	1:10,000 dilution 20 µL inj. vol. (ng per inj.)
Metamitron	3.3	16.5	6.6	0.66
Chloridazone	2.5	12.5	5	0.5
Simazine	2.5	12.5	5	0.5
Cyanazine	3.7	18.5	7.4	0.74
Prometryn	4.8	24	9.6	0.96
Chlortoluron	9.6	48	19.2	1.920
Diuron	2	10	4	0.4
Propazine	4.6	23	9.2	0.92
Terbuthylazine	5.8	29	11.6	1.160

Table 1
Analyzed Herbicides and used concentrations.

The 1:100 dilution of the stock solution was used to evaluate the chromatographic conditions and the resulting chromatogram is shown in figure 2.

To evaluate the relative standard deviation six runs were performed using the 1:1000 dilution of the stock solution and the results are shown in table 2.

The limits of detection were determined using 20 µL injections of the 1:10,000 dilution of the stock solution. The results are shown in figure 3 and table 3.

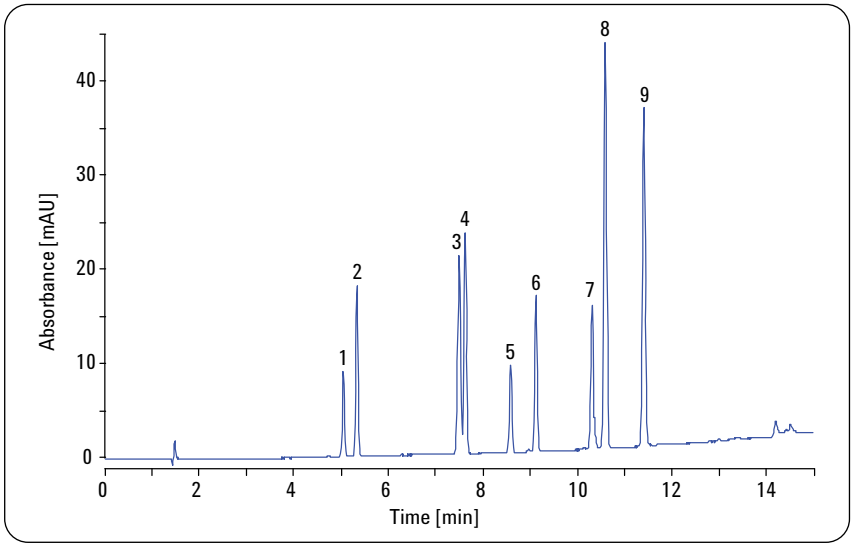

Figure 2
Chromatogram from analysis of the 1:100 dilution for evaluation of chromatographic conditions.

Peak	Compound	% RSD Ret. Times	% RSD Areas
1	Metamitron	0.07	0.19
2	Chloridazone	0.07	0.17
3	Cyanazine	0.05	0.10
4	Simazine	0.05	0.12
5	Prometryn	0.06	0.39
6	Diuron	0.02	0.34
7	Propazine	0.02	0.16
8	Terbuthylazine	0.02	0.33
9	Chlortoluron	0-04	0.26

Table 2
Relative standard deviations of retention times and peak areas in the low ng range.

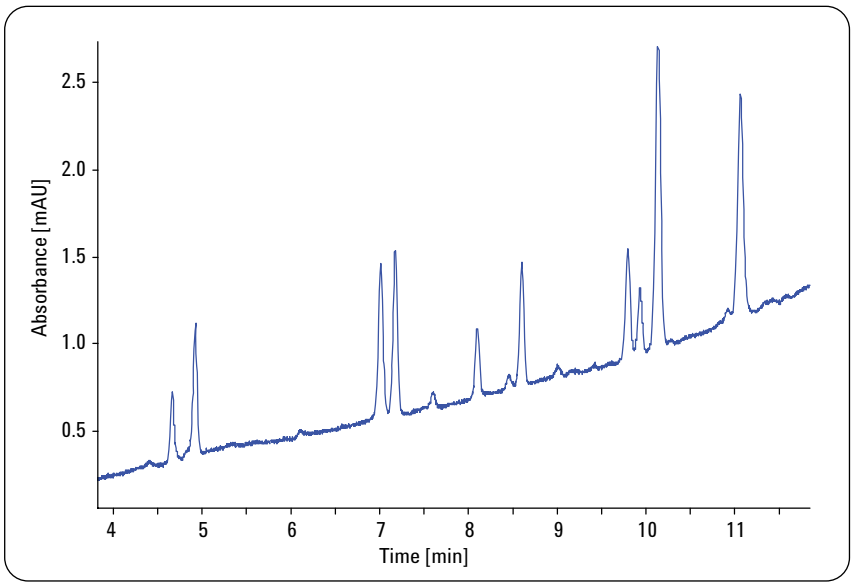

Figure 3
Chromatogram from analysis of the 1.10,000 dilution with an injection volume of 20 µL.

Peak	Compound	LOD with S/N = 3 P-to-P noise 0.02 mAU (pg)
1	Metamitron	132
2	Chloridazone	50
3	Cyanazine	49
4	Simazine	50
5	Prometryn	144
6	Diuron	34
7	Propazine	34
8	Terbuthylazine	37
9	Chlortoluron	128

Table 3
Limits of detection for the analyzed herbices.

Analysis of herbicides in drinking water

600 µL of drinking water was spiked with 100 µL of the 1:1000 dilution and 300 µL of acetonitrile. Acetonitrile was added to avoid adhesion of the trace amounts of the herbicides on the glass surface of the vial. The resulting concentration was equivalent to the 1:10,000 dilution of the stock solution. Figure 4 shows the chromatograms of the analyses of the blank drinking water sample (lower trace), spiked drinking water sample (center trace) and the 1:10,000 dilution of the stock solution. The chromatographic conditions were the same as for the analysis shown in figure 1.

The chromatograms showed that these herbicides can be analyzed in the low pg range using the described chromatographic conditions.

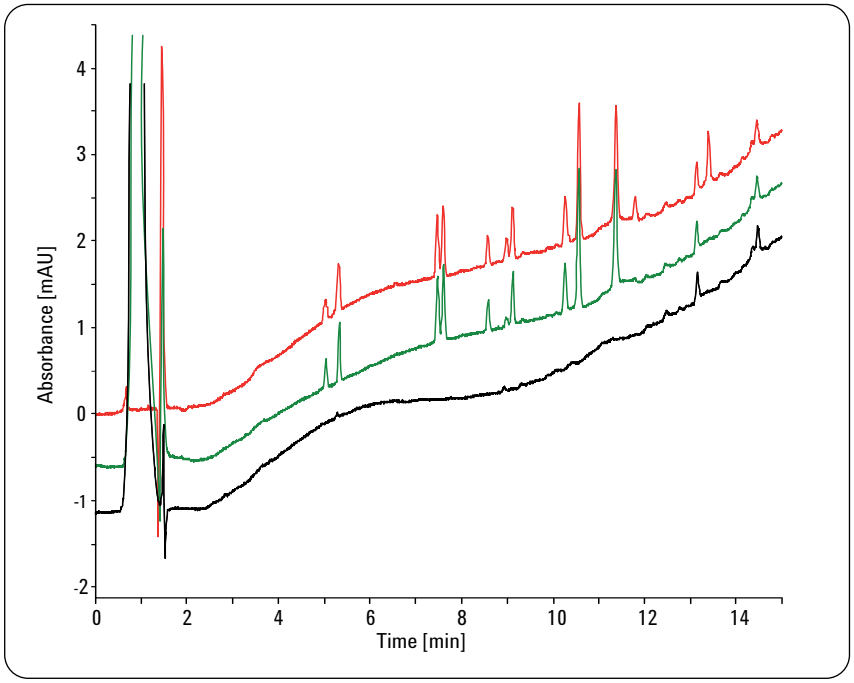

Figure 4
Chromatogram of analysis of spiked drinking water:
Upper trace – 1:10,000 diluted stock solution
Center trace – spiked drinking water sample
Lower trace – blank drinking water sample

Conclusion

The Agilent 1120 Compact LC was used for the analysis of herbicides in drinking water. This instrument was able to analyze these compounds at levels as low as 0.02 ppm, for example, for simazine. The identification of these compounds using retention times was based on the excellent retention time precision of less than 0.08 %. The quantification in the low nanogram range yielded relative standard deviations less than 0.4 % for the peak areas and allowed accurate determination of the compounds.

Angelika Gratzfeld-Huegen is an Application Chemist at Agilent Technologies, Waldbronn, Germany.

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