Fast Analysis of Organochlorine Pesticides Standard Using Conventional GC Instrumentation

Anila I. Khan, Thermo Fisher Scientific, Runcorn, UK

Key Words
Fast GC analysis, organochlorine pesticides, OCP, EPA Method 8081, Fast GC column, TraceGOLD TG-5SilMS

Abstract
This application note compares the performance of a 0.15 mm internal diameter (i.d.) GC column with that of a 0.25 mm i.d. GC column. An increase in the speed of analysis for an organochlorine pesticide (OCP) reference standard mix using EPA Method 8081 is demonstrated with the 0.15 mm column. No compromise in the separation capability of the method was observed and conversion of the conventional method was easily achieved.

Introduction
An important consideration in many laboratories is speed and sample throughput. A GC separation on a 30 m column with a 0.25 mm i.d. at 1.0 mL/min flow rate can take 30 minutes or more of analysis time, depending on the mixture of analytes being separated. There are some parameters that can be adjusted in a GC method to reduce run time, including an increase in column temperature, an increase in temperature ramp rate, or a reduction in column length. However, these changes can be detrimental to the resolution of the analytes.

Shorter columns can be used to reduce analysis time without loss of resolution, as long as the column inner diameter is also reduced, so that faster mass transfer and better efficiency can be achieved.

There are some practical considerations when reducing column length and i.d.:

- The ratio of column length to i.d. should remain the same.
- The column stationary phase should remain the same.
- The phase ratio (β) of the columns should be kept the same where possible.

This application note describes the transfer of a method for an organochlorine pesticide (OCP) standard solution from a standard GC column to a Thermo Scientific™ TraceGOLD™ TG-5SilMS Fast GC column with an equivalent phase.

Consumables		Part Number
Fast GC column:	TraceGOLD TG-5SilMS, 20 m × 0.15 mm × 0.15 µm	26096-2760
Standard GC column:	Equivalent 5% phenyl methylpolysiloxane, 30 m × 0.25 mm × 0.25 µm	
Injection port septum:	Thermo Scientific 17 mm BTO septum	31303211
Liner:	Thermo Scientific™ Split FocusLiner™ for 50 mm needle, 5 × 8 × 105 mm	453T1905
Column ferrules:	100% graphite ferrules for Thermo Scientific™ TRACE™ injector, 0.1–0.25 mm i.d.	29053488
Injection syringe:	50 mm 25s gauge, 10 µL fixed needle syringe for Thermo Scientific™ TriPlus™ Autosampler	36500525
Vials and closures:	Thermo Scientific 9 mm Wide Opening Screw Thread Vials Convenience Kit, 2 mL Clear glass vial with PTFE/Blue Silicone septum	60180-599

Separation Preparation

A pre-prepared stock standard solution of OCP standard mix with a concentration of 200 µg/mL in hexane / toluene (1:1 v/v) was obtained commercially. The stock standard was diluted to 50 µg/mL in hexane and used as a working standard solution.

GC Conditions

Instrumentation:	Thermo Scientific TRACE GC Ultra
Injector type:	Split/Splitless
Injector mode:	Split, constant septum purge
Injector temperature:	280 °C
Detector type:	Flame ionization detector (FID)
Detector temperature:	300 °C
Detector air flow:	350 mL/min
Detector hydrogen flow:	35 mL/min
Detector nitrogen flow:	30 mL/min

Data acquired and processed using Thermo Scientific™ Xcalibur™ software.

Method Transfer Equations

The following calculations were used to determine the system parameters required to optimize performance using a TraceGOLD Fast GC column:

$$t_{g2} = t_{g1} \frac{\nu_2}{\nu_1} \frac{\beta_2}{\beta_1} \frac{l_1}{l_2} \qquad T_2 = T_1 \frac{\nu_1}{\nu_2} \frac{\beta_1}{\beta_2} \frac{l_2}{l_1}$$

Where;

t_{g1}, t_{g2}	- temperature gradient for original and new conditions
ν_1, ν_2	- linear velocity of gas for original and new conditions
T_1, T_2	- hold time for isothermal part of separation for original and new conditions
β_1, β_2	- phase ratio for original and new conditions
l_1, l_2	- length of column for original and new conditions

Standard method (I):	Equivalent to 5% phenylmethyl polysiloxane (silarylene) phased GC column, 30 m × 0.25 mm × 0.25 µm, β = 250
Carrier gas:	1.2 mL/min helium flow rate, linear velocity 30 cm/s, constant flow
Split injection:	30:1, 1.0 µL
Oven:	150 °C (0.5 min), 30 °C/min, 260 °C (3 min), 10 °C/min, 300 °C (4 min), 15.17 min total run time

Fast method (II):	TG-5SilMS 20 m × 0.15 mm × 0.15 µm, β = 250
Carrier gas:	0.6 mL/min helium flow rate, linear velocity 30 cm/s, constant flow
Split injection:	30:1, 0.5 µL
Oven:	150 °C (0.3 min), 45 °C/min, 260 °C (2.5 min), 15 °C/min, 300 °C (3 min), 10.91 min total run time
Faster method (III):	TG-5SilMS 20 m × 0.15 mm × 0.15 µm, β = 250
Carrier gas:	1.0 mL/min helium flow rate, linear velocity 43 cm/s, constant flow
Split injection:	30:1, 0.5 µL
Oven:	150 °C (0.25 min), 60 °C/min, 260 °C (2 min), 20 °C/min, 300 °C (2 min), 8.08 min total run time

Results

Figure 1 illustrates that the analysis time decreased by 30% on the Fast GC column (II) compared to the standard column (I), with a minimal reduction in resolution of approximately 4%. The method (II) was then further modified by increasing the linear velocity by approximately 40–50%. As a result, the speed of separation was further increased as shown in the faster method (III). Overall, the analysis time was reduced by approximately 50% of the original method (I), with a slight increase in resolution of around 7%.

Pressure considerations: The column head pressure on the Fast GC column was 348 kPa (method II) and the standard GC column was 190 kPa (method I) at an oven temperature of 300 °C and linear velocity of 30 cm/s. By increasing the linear velocity to 43 cm/s, the column head pressure increased to 472 kPa on the Fast GC column (method III). The increase in performance was gained with an increase in column head pressure but was still within the operating limits of a conventional GC system with a maximum pressure input of 1000 kPa.

Six replicate injections were carried out on standard and Fast GC columns, the latter at two linear velocities. The data illustrates excellent retention time reproducibility for all OCP standard solution components according to EPA Method 8081 (Table 1).

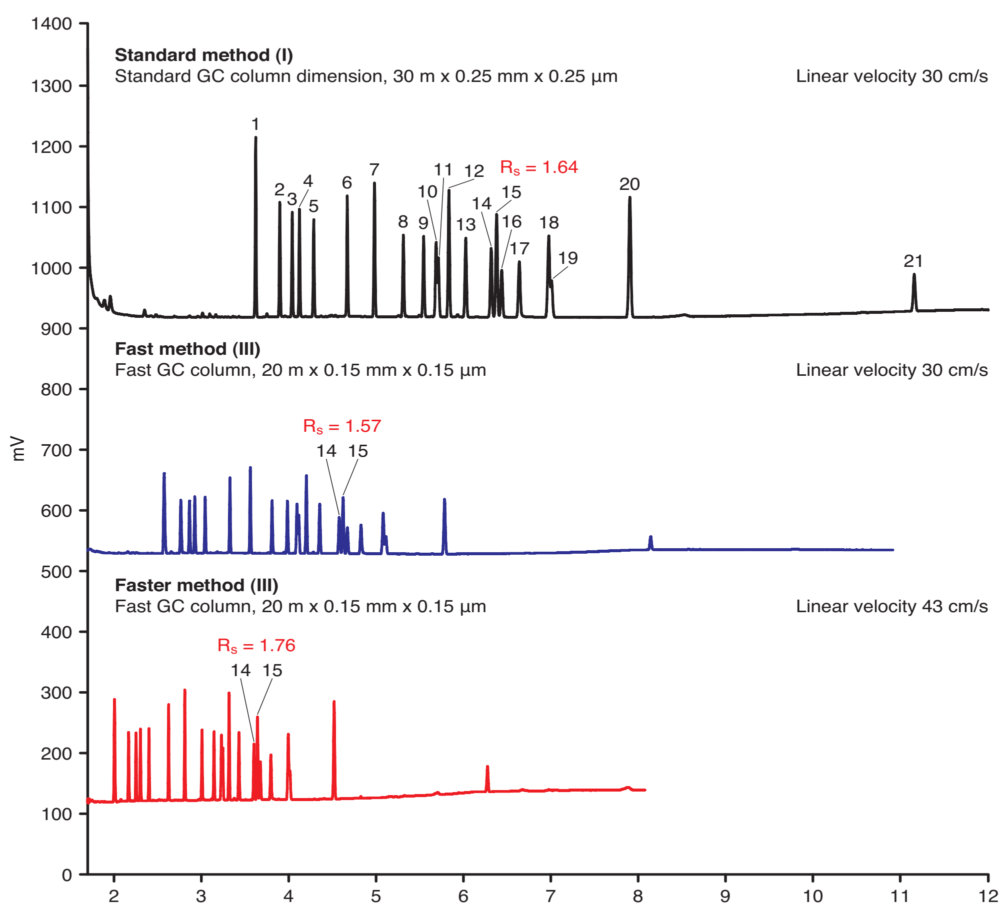

Figure 1: Chromatograms for 20 µg/mL OCP standard solution according to EPA Method 8081 analyzed on a standard GC column and Fast GC column. Resolution values were compared on peaks 14 and 15.

Compound	Linear Velocity 30 cm/s				Linear Velocity 43 cm/s	
	Standard GC Column (I) Mean t_R (min)	%RSD (n=6)	Fast GC Column (II) Mean t_R (min)	%RSD (n=6)	Fast GC Column (III) Mean t_R (min)	%RSD (n=6)
1. 2,4,5,6-Tetrachloro-m-xylene	3.62	0.02	2.57	0.03	2.00	0.12
2. Alpha-BHC	3.90	0.01	2.76	0.06	2.15	0.13
3. Gamma-BHC	4.04	0.03	2.86	0.04	2.24	0.14
4. Beta-BHC	4.12	0.01	2.92	0.06	2.29	0.15
5. Delta-BHC	4.29	0.02	3.04	0.04	2.39	0.14
6. Heptachlor	4.67	0.02	3.33	0.04	2.61	0.15
7. Aldrin	4.98	0.02	3.56	0.05	2.79	0.16
8. Heptachlor epoxide isomer B	5.31	0.02	3.81	0.03	2.99	0.16
9. Gamma-chlordane	5.54	0.01	3.98	0.03	3.13	0.14
10. Alpha-chlordane	5.69	0.01	4.09	0.05	3.21	0.14
11. Endosulfan I (alpha)	5.71	0.00	4.11	0.04	3.22	0.13
12. 4,4'-DDE	5.83	0.01	4.20	0.06	3.30	0.15
13. Dieldrin	6.02	0.02	4.35	0.05	3.41	0.14
14. Endrin	6.32	0.02	4.57	0.05	3.58	0.14
15. 4,4'-DDD* & Endosulfan II (beta)*	6.38	0.01	4.62	0.05	3.62	0.15
16. Endrin aldehyde	6.44	0.02	4.67	0.05	3.65	0.14
17. 4,4'-DDT	6.64	0.01	4.82	0.06	3.77	0.15
18. Endosulfan sulfate	6.97	0.01	5.08	0.04	3.97	0.13
19. Endrin ketone	7.01	0.02	5.11	0.04	3.99	0.12
20. Methoxychlor	7.90	0.02	5.78	0.04	4.50	0.09
21. Decachlorobiphenyl	11.15	0.01	8.14	0.01	6.26	0.04

*These compounds co-elute in FID. Separation can be achieved using GC-MS.

Table 1: Retention time and reproducibility data from six replicate injections

Conclusion

The use of a Fast GC column gave a reduction in the run time of 30% over a standard GC column, following a method transfer with no changes in system configuration. Further reduction in run time was observed when the linear velocity was increased by 50% without loss of resolution compared to the standard method. Data on the Fast GC column showed excellent retention time reproducibility at 30 and 43 cm/s linear velocity.

GC analysis time can be reduced by transferring a method to a Fast GC column, without compromising performance; however, it is necessary to consider:

- Column length
- Column i.d.
- Column film thickness
- Carrier gas linear velocity
- Temperature ramp rate

This approach has been used to transfer an EPA Method 8081 OCP standard solution analysis from a standard 30 m × 0.25 mm × 0.25 µm GC column to a Fast GC column. Up to 50% faster analysis time can be achieved without a compromise in resolution and without changes to the system configuration.

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USA and Canada +1 800 332 3331
France +33 (0)1 60 92 48 34
Germany +49 (0) 2423 9431 20 or 21
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China +86 21 68654588 +86 10 84193588
+86 20 83145199   800 810 5118
India +91 22 6742 9494 +91 27 1766 2352
Australia 1 300 735 292 (free call domestic)
New Zealand 0800 933 966 (free call domestic)
All Other Enquiries +44 (0) 1928 534 050

Technical Support
North America +1 800 332 3331
Outside North America +44 (0) 1928 534 440

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