Application Brief

Water Analysis

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Endrin and DDT Stability Study for Drinking Water Methods with an Agilent 8890 GC/5977B GC/MSD Combined System

Author

Angela Smith Henry, Ph.D.
Agilent Technologies, Inc.

Introduction

Endrin and 4,4'-DDT, organochlorine pesticides, can be used to determine flowpath inertness and cleanliness of a gas chromatography (GC) system. Active sites, matrix, or septum particles, and high temperatures, especially in the inlet, can cause the degradation of 4,4'-DDT to 4,4'-DDE and 4,4'-DDD. The isomerization of endrin to endrin ketone and endrin aldehyde can also occur in those conditions[1,2,3]. Decomposition of 4,4'-DDT typically occurs when the compound is exposed to active surfaces, such as matrix, debris, or nondeactivated metal[4]. Endrin is more temperature-sensitive, and can isomerize with or without a catalyst[5,6].

To verify the instrument inertness before quantitative analysis, the United States Environmental Protection Agency (US EPA) has written methods that incorporate endrin and 4,4'-DDT testing. The US EPA Method 525.2 requires a degradation limit of no greater than 20 % breakdown for endrin or 4,4'-DDT[7]. US EPA method 525.3 has the same limit of breakdown for 4,4'-DDT[8]. The standards enacted by the People's Republic of China, Method HJ 699-2014[9], have the same limits for endrin and 4,4'-DDT. If the limit is exceeded, corrective maintenance must be performed before the system can be used for analysis. Previous application briefs have used this method to verify performance of other Agilent GC systems[10].

This Application Brief demonstrates that the Agilent 8890 GC can meet the instrument performance check criteria established by US EPA Method 525.2 and Method 525.3 as well as other internal standards for drinking water quality.

Experimental

Instrumentation and consumables

- Agilent 8890 GC
- Agilent 5977B MSD with an Inert EI source
- Agilent 7650A automatic liquid sampler
- Agilent J&W DB-8270D 30 m × 0.25 mm × 0.25 µm column (p/n 122-9732)
- Agilent Ultra Inert inlet liner, single taper, splitless (p/n 5190-2292)
- Agilent inlet septum, Advanced Green, nonstick, 11 mm (p/n 5183-4759 for 50 pack)
- Agilent ALS syringe, Blue Line, 10 µL, PTFE-tip plunger (p/n G4513-80203)
- Agilent A-Line screw top vials, certified, amber; 100/pk (p/n 5190-9590)
- Agilent deactivated vial inserts, 5.6 × 30 mm, 250 µL; 100/pk (p/n 5181-8872)
- Agilent screw caps, PTFE/silicone/PTFE septa, cap size: 12 mm; 500/pk (p/n 5185-5862)

Table 1 shows the parameter details. GC and mass spectrometer (MS) parameters are compatible with EPA Method 525.2 guidelines as well as HJ 699-2014 and the European Union Water Framework Directive[11].

Sample preparation

The instrument performance check (IPC) solution was prepared by diluting a standard solution of DFTPP, 4,4'-DDT, and endrin (GCM-160A, Agilent, formerly ULTRA Scientific) to a concentration of 5 ng/µL in methylene chloride.

Table 1. GC and MSD instrument conditions.

Parameter	Value
Injection volume	1 µL
Inlet	Split/splitless 200 °C, Pulsed splitless 50 psi for 1 minute, Purge 50 mL/min at 1 minute, Standard septum purge
Column temperature program	40 °C (hold for 1 minute), 25 °C/min to 160 °C (hold 3 minutes), 6 °C/min to 312 °C
Carrier gas and flow rate	Helium at 1.2 mL/min, constant flow
Transfer line temperature	270 °C
Ion source temperature	300 °C
Quadrupole temperature	180 °C

Results and discussion

A series of injections was made with a repeating section. After a blank injection of ethyl acetate, five injections of the IPC solution were run. This was followed by a repetitive set of blanks and IPC samples: 10 blank ethyl acetate injections and three IPC injections were repeated until 310 blank injections were made. The sequence ended with five injections of the IPC solution, for a total of 412 injections. For each injection of the IPC solution, the percent degradation was calculated for 4,4'-DDT and endrin, as specified in Method 525.2. Tuning stability was also evaluated for every injection of the IPC solution, based on the ion ratio criteria of EPA Method 525.2. The DFTPP tuning criteria was achieved for each injection.

Figure 1 shows the average percent degradation per injection number with error bars representing the calculated standard deviation. The calculated degradation for each measurement is significantly below the 20 % limit for both compounds. The average percent degradations, across all the measurements, were 5.95 and 0.54 % for endrin and 4,4'-DDT, respectively, and an average total degradation of 6.50 %.

Figure 2 illustrates the comparison of the first and last IPC solution injections. The two chromatograms are similar. The peak at 19.1 minutes was tentatively identified as an oxidation by-product of DFTPP. DFTPP is more stable in DCM than ethyl acetate[8]; the oxidation product of DFTPP could occur from interactions with residual wash solvent (ethyl acetate). Alternatively, this could occur by exposure to light and air at ambient temperature during queuing of samples in the autosampler.

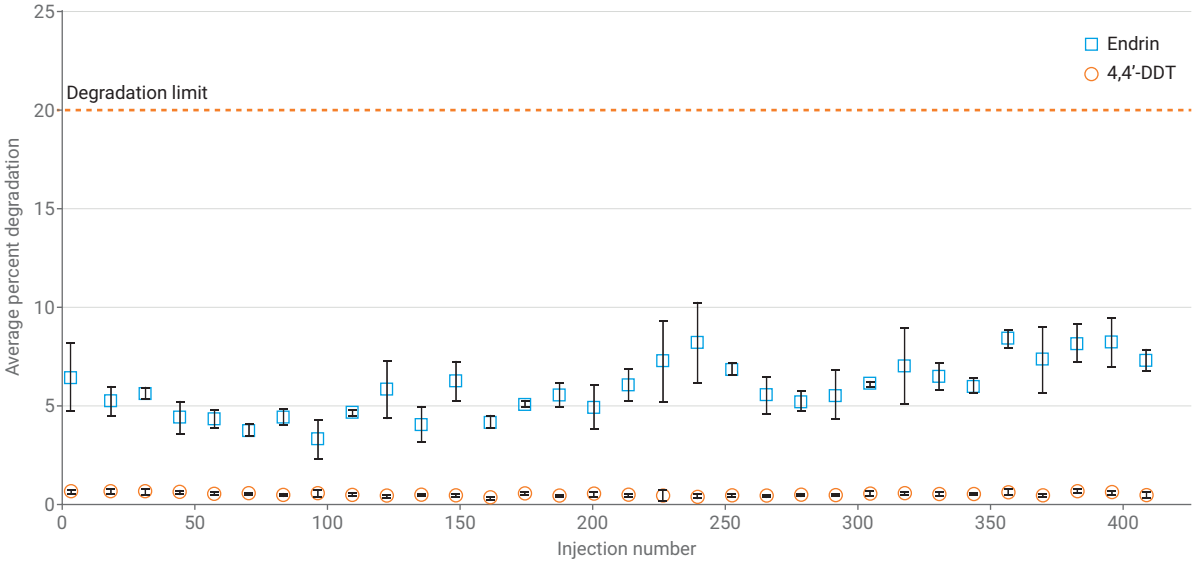

Figure 1. Degradation measurements for 4,4'-DDT and endrin.

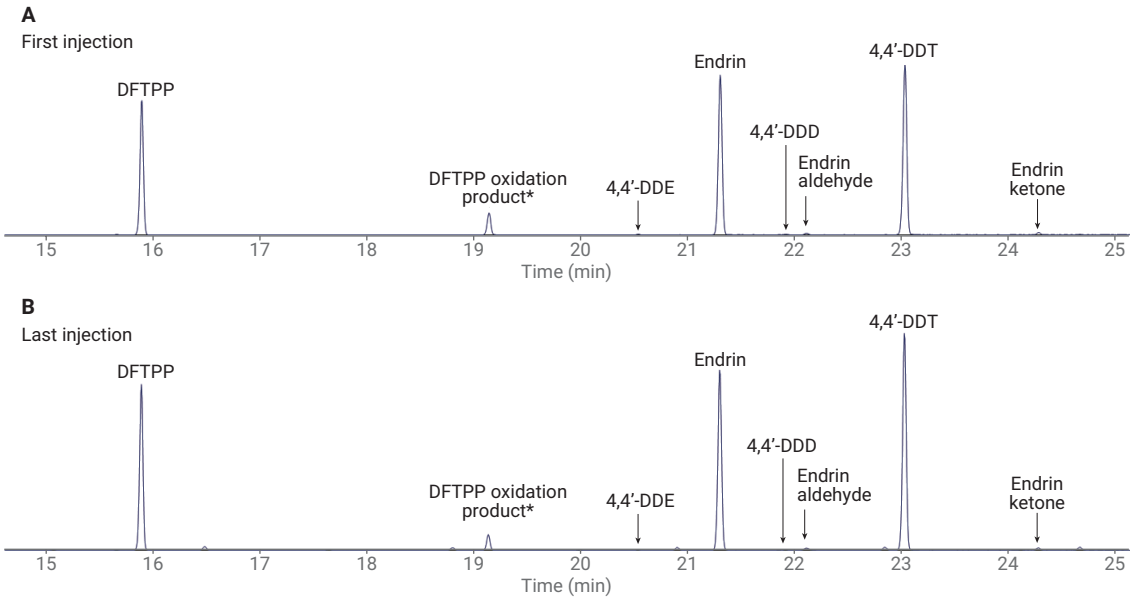

Figure 2. Total ion chromatograms from the first and last injections of the IPC solution.

Conclusion

The 8890 GC demonstrates excellent flowpath inertness from inlet to detector, based on the endrin and 4,4'-DDT testing. The system easily achieves the system inertness criteria specified in:

- US EPA Method 525.2
- US EPA Method 525.3
- National Environmental Protection Standards of the People's Republic of China HJ 699-2014
- The European Union Water Framework Directive

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