Application Note 113

Rapid Separation of 2,3,7,8-TCDD from Other TCDD Isomers

Partially crosslinked SP-2331 fused silica capillary columns are more stable than the nonbonded SP-2330 phases specified in US EPA methodology for separating TCDD isomers. SP-2331 columns are slightly more polar, but provide similar resolution and analysis times for the dioxins.

Key words:
- tetrachlorodibenzo-p-dioxin • TCDD
- cyanosilicone phase • capillary GC

In current versions of US Environmental Protection Agency (EPA) methods for analyzing tetrachlorodibenzo-p-dioxin (TCDD) isomers (1,2), a highly polar, nonbonded cyanosilicone capillary column is used to resolve 2,3,7,8-TCDD◆ from the other isomers. The high operating temperature and the splitless or cold on-column injection techniques specified in these methods can stress this nonbonded phase.

To elute the isomers in a reasonable analysis time, the oven temperature is raised to 250°C. This is the limit of thermal stability for a nonbonded cyanosilicone phase. Repeated operation of a nonbonded cyanosilicone capillary column at its maximum temperature causes high phase bleed that decreases column life. The conditions used also can create thermal shock, causing the phase to puddle. Likewise, the splitless or cold on-column injections used can displace or dissolve the phase at the column inlet.

To overcome these problems, we developed a more stable cyanosilicone phase capillary column specifically for analyses of TCDD isomers (Figures A and B). In contrast to the nonbonded SP™-2330 columns we previously recommended for these analyses (and which are listed in EPA Method 613), SP-2331 columns have a partially crosslinked phase. Because of their higher thermal limit (275°C vs. 250°C), you can use them at the 250°C temperature specified in the EPA analyses, with less chance of phase decomposition.

SP-2331 columns are slightly more polar than SP-2330 columns, but provide similar resolution and analysis times for the dioxin isomers. To ensure compliance with EPA specifications, we test each SP-2331 column for TCDD isomer separation. We use the performance evaluation mix recommended by the EPA. Column variables for analyzing dioxins are therefore minimized. Although SP-2330 columns usually provide satisfactory separation of 2,3,7,8-TCDD from other TCDD isomers, they are not tested for this purpose.

Figure A. Separation of TCDD Isomers Using a 0.25mm ID SP-2331 Column

Column: **SP-2331, 60m x 0.25mm ID, 0.2µm film**
Cat. No.: **24104-U**
Oven: 200°C (1 min) to 250°C at 8°C/min
Carrier: helium, 30cm/sec (set at 200°C)
Det.: ECD, 270°C
Inj.: 2µL n-dodecane containing 0.25ng each isomer, splitless, 250°C (splitless hold time — 45 sec; splitless vent flow — 70mL/min)

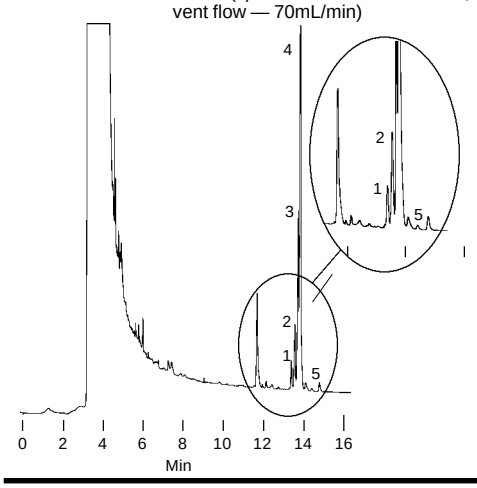

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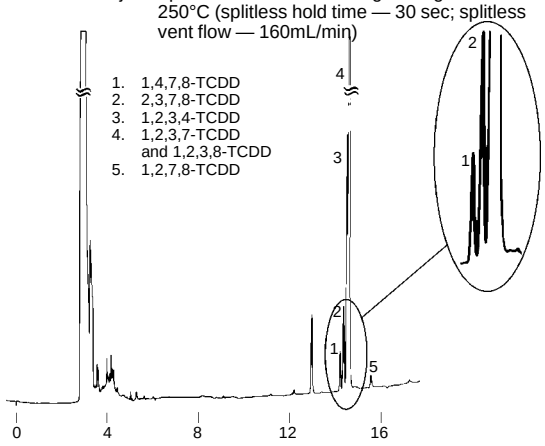
Figure B. Separation of TCDD Isomers Using a 0.32mm ID SP-2331 Column

Column: **SP-2331, 60m x 0.32mm ID, 0.2µm film**
Cat. No.: **24105**
Oven: 200°C (1 min) to 250°C at 3°C/min
Carrier: helium, 30cm/sec (set at 200°C)
Det.: ECD, 270°C
Inj.: 2µL n-dodecane containing 0.25ng each isomer, splitless, 250°C (splitless hold time — 30 sec; splitless vent flow — 160mL/min)



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EPA Method 613 calls for splitless or cold on-column sample injection, because TCDD isomers are usually present in low ng/µL concentrations. With either mode, the sample is focused at the column inlet. This tends to displace or dissolve the phase at the inlet of a nonbonded column, eventually decreasing resolution of sample components. The stabilized phase in an SP-2331 column resists displacement.

Sample focusing also can cause thermal shock in a capillary column. To properly focus a sample, the oven temperature must initially be well below the boiling point of the sample solvent. Then it must be increased rapidly. In the EPA methods (1,2), the sample solvent, hexane, boils at 69°C, so an initial oven temperature of 55°C is specified. Subsequently, the temperature is raised by 25-30°C/min to 200°C. Repeated use in this manner can cause a nonbonded cyanosilicone phase to puddle from thermal shock. In contrast, the SP-2331 stabilized phase resists thermal shock.

The EPA also allows n-dodecane, which boils at 215°C, to be used as the sample solvent. This minimizes the difference between the initial oven temperature and the temperature at which TCDD isomers are eluted (1,2). Whether you use a nonbonded SP-2330 column or a stabilized SP-2331 column, you can prolong column life (and shorten analysis time) by using n-dodecane as the focusing solvent.

Although an SP-2331 column resists damage from solvent focusing, it cannot be rinsed to eliminate nonvolatiles and high boiling residue (present in many dioxin samples) that accumulate in the column inlet. We recommend connecting a one-meter, 0.25mm or 0.32mm ID fused silica guard column to the column inlet. You can easily change a contaminated guard column to maintain column performance at acceptable levels.

Trace amounts of oxygen and water will also damage any cyanosilicone capillary column. You should, therefore, use a carrier gas purifier to make certain the carrier gas contains less than 5ppm of oxygen and water. After installing a column, purge it with carrier gas for about 30 min to eliminate trapped air. Only then is it safe to heat the column.

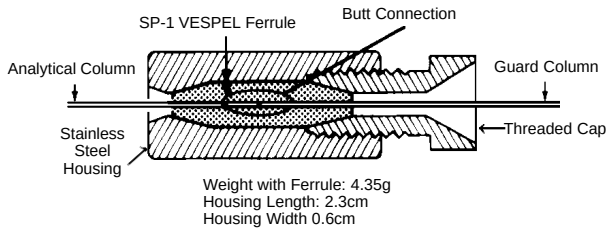
We offer both 0.25mm and 0.32mm ID SP-2331 columns for dioxin analyses (Figures A and B). In most cases, we recommend 0.32mm ID columns. They accept a higher flow rate than 0.25mm ID columns (1.8mL/min vs. 0.8mL/min), allowing more efficient solvent focusing in splitless or cold on-column injection.

During cold on-column injection, a 0.32mm ID column minimizes sample flashback in the column inlet (3). This eliminates a source of peak broadening and poor sample resolution. The larger capacity of a 0.32mm ID column (500ng vs. 50-100ng) expands the analytical range without significantly reducing sample resolution or increasing analysis time.

SP-2331 columns were field tested in several laboratories where dioxin analyses are conducted. Their performance was praised. These tested columns ensure consistent separation of TCDD isomers, column to column. And they last far longer than columns previously used, especially when protected by a guard column.

Figure C. Capillary Column Butt Connector■

Cross-Sectional View of a Butt Connector Joining an Analytical Column to a Guard Column



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Ordering Information:

Description	Cat. No.
SP-2331 Fused Silica Capillary Columns	
60m x 0.25mm ID, 0.2µm film	**24104-U**
60m x 0.32mm ID, 0.2µm film	**24105**
Capillary Column Butt Connector (see Figure C)	
Butt connector body (housing and threaded cap only – select appropriate ferrule below)	**23804**
Supeltex™ M-2B* Ferrules, pk. of 2	
0.4mm ID (connect 0.25mm ID fused silica tubing)	**22453**
0.5mm ID (connect 0.32mm ID fused silica tubing)	**22454**
Deactivated Fused Silica Guard Columns/ Mass Spec Transfer Lines (three 1-meter pieces)	
0.25mm ID	**24025**
0.32mm ID	**24058**
Qualitative TCDD Standard	
2,3,7,8-TCDD, approximately 10µg/mL in 1mL toluene	**48599**

◆Because 2,3,7,8-TCDD is extremely toxic, samples believed to contain dioxins (and all dioxin standards) should be handled only be analysts familiar with safe handling procedures for toxic substances. Safe handling of dioxins is discussed in EPA Method 613 (1).

■Supelco US Pat. No. 4,529,230.

*Du Pont VESPEL® SP-211 part (10% Teflon® fluorocarbon resin/15% graphite/ 75% polyimide), max. temp.: 350°C.

Fused silica columns manufactured under HP US Pat. No. 4,293,415.

References

1. *Analysis of 2,3,7,8-Tetrachlorodibenzo-p-dioxin from Wastewater*, EPA Method 613, Federal Register, Vol. 49, No. 209, October 1984.
2. EPA Region VII Procedure for Analyzing Dioxin Isomers in Soil, 25 Funston Rd., Kansas City, Kansas 66115 USA.
3. Grob, K. Jr., *Chromatogr.* **282:** 21-35 (1984).

References not available from Supelco.

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