Application Note: 10136

30X Increased Sensitivity in the Determination of PCBs in Water and Soil by GC-ECD using Large Volume Splitless Technique

Thermo Fisher Scientific Inc., Milan, Italy

Key Words

- TRACE GC Ultra
- Environmental Analyses
- Large Volume Injection
- PCBs

Figure 1: TRACE GC Ultra™ with TriPlus™ AS Autosampler

Introduction

Environmental legislations approved by federal agencies like US EPA, or by European Commission Directives [1,2], aim at the most severe reduction of the PCB levels in water and soils (≤ 1 ng/kg in the original sample). This implies, for a PCB analytical method to be validated, the achievement of very low detection limits (≤ 0.5 ng/kg in the extract).

The identification and quantitation of PCBs is most often accomplished by gas chromatographic techniques coupled with Electron Capture Detector (ECD), which has selective sensitivity to chlorinated compounds. Method sensitivity can be further amplified using large sample volume injection into the GC [3]. Among the different techniques used for large volume injection, the recently introduced LV-SL [4] has the following advantages: (1) It is simpler because it allows injections, up to 50 µL, in a conventional split/splitless injector without any special tuning of operating parameters, and (2) it is robust when analyzing sample by-products or contaminants, such as those found in food matrices or soil extracts. It is also suitable for the analysis of labile pesticides, and it is compatible with any GC detector [5].

In this method, the application of Large Volume Splitless (LV-SL) to GC-ECD is validated for the determination of polychlorinated biphenyls (PCBs) in soil and water samples. GC-ECD analyses of 20-30 µL of (1) standard Aroclor mixtures and (2) Liquid/Liquid or Accelerated Solvent Extraction (ASE) extracts of spiked water/soil matrices are reported. Injections were performed with the Thermo Scientific TriPlus Autosampler. A Thermo Scientific TRACE GC Ultra™ GC oven, and conventional SSL injector conditions were set-up with dedicated software. The analytical method was validated through determination of detection limits, linearity, extraction recoveries, and repeatability.

As an outcome, PCBs were detected at ppt levels in water and soil matrices. A 20-30 fold increase of sensitivity with respect to traditional GC-ECD was obtained. A large number of injections of complex matrices can be performed without a significant decrease in chromatographic performance.

Principles of Large Volume Splitless injection technique

LV-SL injection overcomes the limitation of the maximum sample volume to 1-2 µL of classical splitless injection by exploiting the Concurrent Solvent Recondensation (CSR) technique [4]. This technique is based on the control of the evaporation rate in the vaporizing chamber, involves the use of a strong pressure increase in the injector resulting from solvent evaporation (auto pressure surge), and provides a strongly accelerated transfer of the sample vapors from the injector into the inlet of an uncoated precolumn by recondensation of the solvent.

Concurrent Solvent Recondensation: Steps of the Process

Five crucial steps denote the LV-SL process (Figure 2):
(1) Introduction of the needle syringe a few millimeters inside the injection port and fast injection, minimizing contact between syringe and injector exploiting liquid band formation;
(2) auto pressure surge strongly accelerating transfer of vapors in the precolumn;

(3) recondensation of the solvent vapors in the precolumn;
(4) completion of the evaporation and transfer into the precolumn of high boiling point solutes;
(5) purge of the vaporizing chamber and solvent evaporation in the precolumn.

Once the proper parameters have been set-up using a dedicated software (Figure 4), the described mechanism is self-regulated and takes place automatically into a conventional Split/Splitless injector hardware.

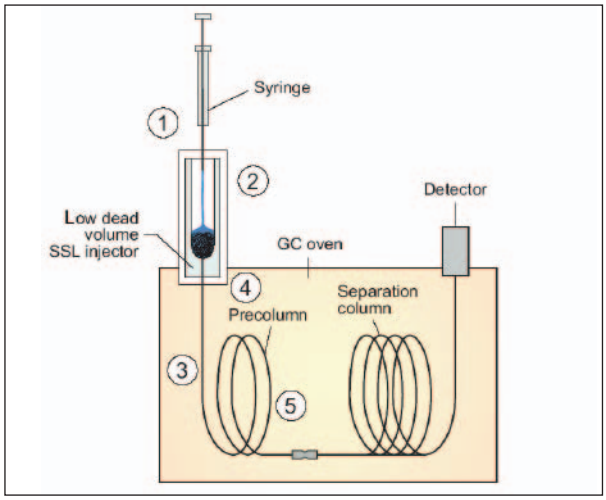

Figure 2: CSR Large Volume Splitless Injection schematic diagram (Numbers correspond to the steps of the process as noted in the text)

Experimental

Reagents: A series of Aroclor mixtures in *n*-hexane were prepared at 2-20 ng/mL values as standard solutions. Standard LV-SL solutions were prepared at different levels of concentration from 1.6 to 36 ppb. Test samples were prepared by spiking (level from 10 ng/L in water to 10 µg/kg in soil) negative-to-PCBs environmental samples, purified and re-concentrated at about 2-40 µg/L according to US EPA 8082 (see Figure 3 and text below).

Materials: Splitless and Large Volume Splitless injections were performed with a TriPlus Autosampler on a TRACE GC Ultra equipped with ECD detector (Figure 1).

GC Methods: LV-SL oven method was determined with LV-SL Assistant software. (See Figure 4 and text below). GC parameters are reported in box chromatograms.

Autosampler Method: 1.0 µL in SL, 30 µL with LV-SL. Minimum injection depth in the injector and 100 µL/sec injection speed (cold needle mode).

PCBs analysis (US EPA 8082) procedure using the LV-SL technique (Figure 3)

Waters extraction: 1 L of sample is extracted twice with methylene chloride, 100 mL in a separation funnel.

Soils extraction: 20 g of sample is first air-dried then uniformly mashed and mixed with hydromatrix to remove moisture and increase surface for the extraction with solvent. A methylene chloride/acetone 1:1 mixture, 120 mL, is used to extract PCBs with Accelerated Solvent Extraction (ASE® 300, Dionex Corporation) equipment according to US EPA 3545.

Sample Preparation: The extract is dried on anhydrous sodium sulfate and purified first with concentrated sulfuric acid and then through a Florisil® column. After the clean-up, the sample is evaporated to dryness under nitrogen-flow and recuperated with 0.25-0.5 mL of *n*-hexane (from 400 to 4,000 times sensitivity increase with respect to initial sample).

GC-ECD analysis: Injection of 20 µL in LV-SL mode allows an additional 20-fold sensitivity increase.

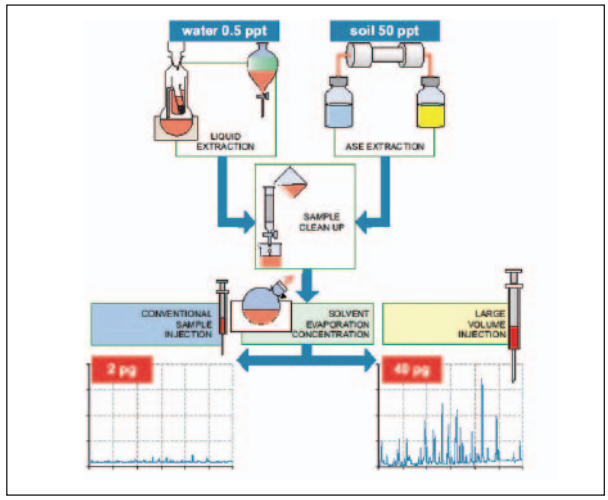

Figure 3: PCBs analysis (EPA 8082) procedure using the LV-SL technique

Large Volume Splitless Software

GC oven method for LV injections was created with the aid of the Large Volume Splitless Assistant software. Depending on the analytical parameters (like solvent type and volume to inject) the Assistant allows for the prediction of how long the initial isotherm of the temperature program should last to achieve the best LV-SL performance. Figure 4 shows the estimated time (about 2 minutes) when injecting 20 µL of *n*-hexane in a GC equipped with a 60 m column, 0.25 mm ID.

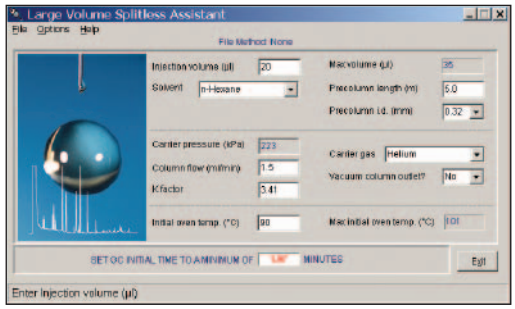

Figure 4: Front-page of the LV-SL Assistant with determination of oven method parameters suitable for the injection of a 20 µL *n*-hexane solution. This software provides the maximum initial oven temperature for a solvent at given conditions of carrier gas pressure and calculates the minimum oven initial time. Setting of these parameters ensures that the pressure surge is automatically generated, thus granting a quick transfer of the vapors into the pre-column, while the calculated minimum oven time enables a proper solvent trapping effect to occur into the pre-column.

Results and discussion

Validation (step 1): LV-SL analysis of aroclor standards

Figure 5 reports the chromatogram of 30 µL injection of a 2 ppb solution of Aroclor 1242/1254/1260 1:1:1 in *n*-hexane. Congeners 30 (2,4,6-Trichlorobiphenyl) and 209 (Decachlorobiphenyl), added at a concentration of 3 ppb, were used as markers for the identification of 5 congeners for each Aroclor mixture.

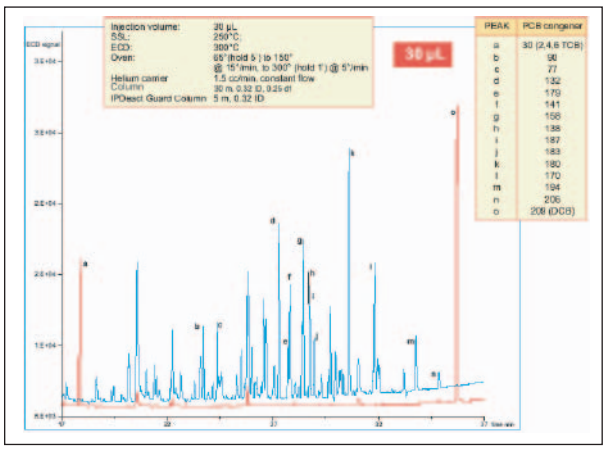

Figure 5: LV-SL analysis of Aroclor standards.

Validation (step 2): detection limits, recoveries and linearity

Four Aroclor 1260 solutions, 20 µL injection volume, concentration ranging between 1.6 and 32 µg/L, were injected to verify the calibration curve linearity (Figure 6). The MDL (Method Detection Limit) was estimated according to CFR regulation [6] using the formula: MDL = Student's t value x Standard Deviation. The standard deviation was evaluated on a sequence of seven injections at the lower level of concentration. The Student's t value is referred to 6 degrees of freedom (3.143). The EQL (Estimated Quantification Limit) is defined as 3 times the MDL. Recoveries were evaluated on (1) extract of 1 L of surface water spiked with Aroclor 1260 mixture, 10 ppt; (2) extract of 20 g of soil sample spiked with Aroclor 1260 mixture, 20 ppb. Recoveries were respectively 105 % and 110 % for the water and soil samples.

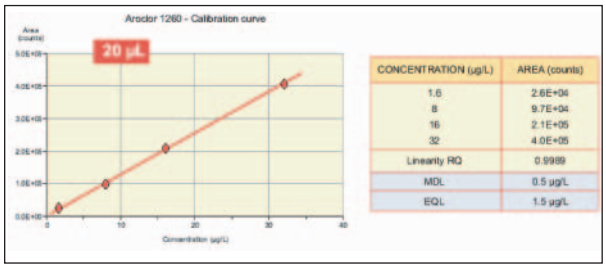

Figure 6: Method Linearity and Detection Limits

Validation (step 3): standards repeatability

LV-SL performance was evaluated by seven consecutive 30 µL injections (see example in Figure 5) of 2 ppb solution of Aroclor 1242/1254/1260 1:1:1 in *n*-hexane, added with congeners 30 and 209 (3 ppb) for identification of at least 5 typical congeners for each Aroclor mixture. ECD absolute peak areas show deviations between 1 and 3 % (Table 1). Standard deviations of retention times were, on average, around 0.002 minutes.

Congener	RETENTION TIMES		ABSOLUTE PEAK AREAS	
IUPAC number	Mean (min)	SD (min)	Mean (counts)	RSD%
90	23.695	0.002	1.9E+05	1.3%
77	24.359	0.001	1.8E+05	2.0%
132	27.288	0.002	4.0E+05	1.1%
179	27.732	0.002	1.1E+05	1.9%
141	27.828	0.002	2.9E+05	1.0%
158	28.399	0.002	1.7E+05	1.3%
138	28.475	0.002	4.3E+05	1.2%
187	28.790	0.002	2.6E+05	1.3%
183	28.969	0.002	1.3E+05	2.1%
180	30.636	0.002	5.7E+05	1.8%
170	31.852	0.002	3.4E+05	0.8%
194	33.815	0.003	1.2E+05	0.9%
206	34.904	0.002	3.7E+04	2.9%

Table 1: Retention Times and Peak Areas repeatability of 7 consecutive standard analyses

LV-SL analysis of real samples

Analyses of real water and soil samples at unknown PCB concentration were performed according to the method thus far (for method details see Figure 3). Figure 7 shows a 20 µL injection of a 0.5 mL *n*-hexane solution obtained after extraction of 20 g of soil coming from a contaminated area of Northern Italy. Overlapping of the real sample with the analysis of 20 µL standard Aroclor 1260 20 ppb shows an impressive match. The overall concentration evaluated on the initial dry soil is 2.5 µg/kg.

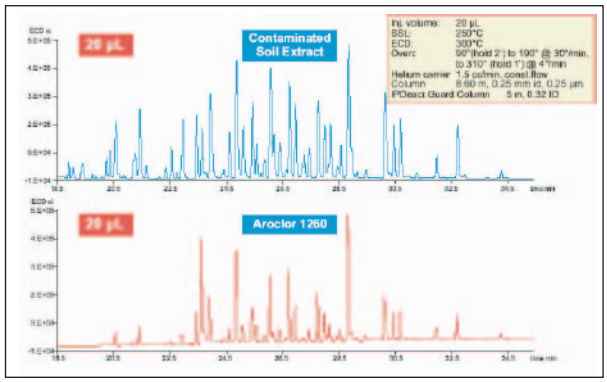

Figure 7: Real soil sample analysis compared with standard Aroclor 1260

Conclusions

A 20-30 times more sensitive method than traditional GC-ECD has been developed and validated for the determination of PCBs in soil and water. Methods of analysis were evaluated through determination of detection limits (down to sub ppb level), quantification limits (down to few ppb), linearity and repeatability. Validation was completed by the determination of PCBs extraction recoveries obtained using Liquid/Liquid and ASE extraction.

LV-SL has proven to be a reliable tool for trace analysis in environmental applications, being robust against "very dirty" samples like soil extracts. LV-SL is the easiest large volume injection GC technique, since it does not require any special hardware or tedious tuning of operating parameters. Full automation is provided through the dedicated LV-SL Assistant software.

References

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6. CFR Title 40, Part 136, Appendix B.

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Authors: Thomas Porzano and Andrea Cadoppi

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+61 2 8844 9500
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