Application Note: 10093

Screening for Dioxin Contamination in Fats and Oils Using Large Volume Injection and Electrolytic Conductivity Detection

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Key Words

- Dioxin Contamination
- Hall Detector
- Large Volume Injection

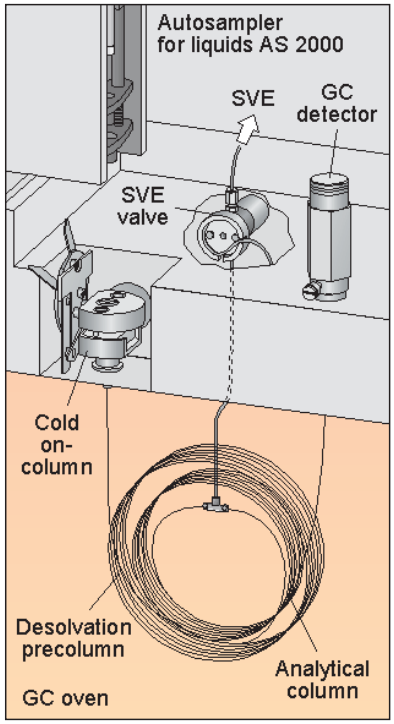
Introduction

The production of poultry and animal feeds consumes large quantities of vegetable oils and recycled fats. The oils and fats which are used must be analyzed for traces of chlorinated compounds such as pesticide and herbicide residues, as well as Chlorinated Dibenzodioxins. The analytical laboratories supporting this industry use AOAC Method 968.23 as a screening method for Dioxins. Samples which show a response on the screening method are analyzed for 2,3,7,8-Tetrachlorodibenzo-dioxin using a High Resolution GC/Mass Spectrometry method.

The screening method calls for the use of an Electron Capture Detector (ECD), which requires substantial cleanup of sample extracts to reduce interferences from the fat or oil matrix. The HALL® Electrolytic Conductivity Detector (HECD) is more selective for Halogenated analytes but not as sensitive as an ECD. The HECD detects Hydrogen Chloride generated from the catalytic Hydrogenation of peaks eluting from the column (Figure 1). This report describes a methodology which yields excellent sensitivity with the HECD while also reducing the laboratory extraction and solvent concentration workload.

Description

The TRACE™ Gas Chromatograph is available with a patented Cold-On-Column injector. This true on-column injector can be configured with an optional Large Volume Injection accessory kit. An On-Column Large Volume Injection (OCLVI) technique using the HECD eliminates much of the sample extract concentration requirement, yet still maintains good method detection limits. The instrumentation used for OCLVI consists of an Auto-sampler with injection parameters calculated and controlled from a unique Large Volume Assistant software program, a Cold-on-Column inlet, a desolvation precolumn, a tee fitting, and a heated Solvent Vapor Exit valve (Figure 1). In OCLVI, 50 to 200 microliters of extract are injected into a desolvation precolumn (Figure 2A). The injection conditions for both the Autosampler and the Gas Chromatograph are under computer control to allow precise evaporation of the solvent without loss of the components of interest (Figure 2B). After most of the solvent has been vented, the remaining liquid containing the analytes of interest is allowed to proceed onto the analytical column very much like a splitless injection



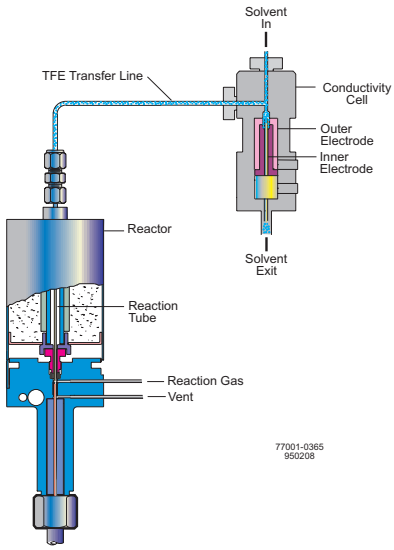


Figure 1: Components of an on-column Large Volume Injection instrument and detail of the HALL Electrolytic Conductivity Detector.

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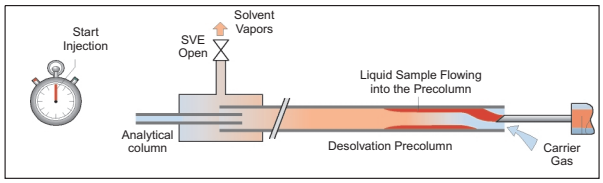

Figure 2A: Sample Injection

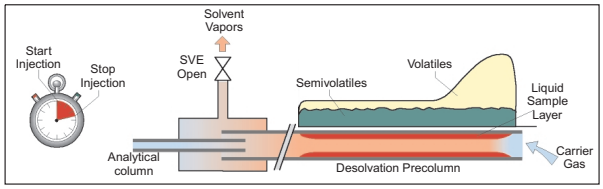

Figure 2B: Solvent Evaporation

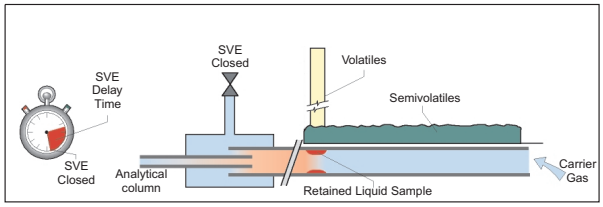

Figure 2C: Component Transfer

(Figure 2C). The OCLVI technique can be used to achieve lower detection limits if the sample is concentrated before injection. It can also be used to increase productivity with standard detection limits by eliminating the need for the time consuming concentration step. In this application, the intent was to adapt an existing method in a way that would allow the use of the higher detection limit of the HECD, yet still maximize productivity.

The analysis of trace compounds such as Dioxins or Pesticides is usually done by extracting the target compounds into a solvent followed by cleanup before analysis. This requires considerable expenditure of labor and materials to carry out the extraction part of the method. The solvent must be concentrated to maintain good detection limits, and large quantities of solvent must be disposed of or reclaimed and tested before reuse. In most trace analytical procedures, the initial solvent extract is concentrated to 1 mL, passed through a cleanup column such as Florisil with several mL of solvent rinses, then reconcentrated to 1 mL before injection. Using OCLVI, the extract can be less concentrated, and after cleanup, diluted to 10 or 20 mL rather than concentrating back to 1 mL. While diluting to the larger volume, the extract can be spiked with an internal standard. To compensate for the dilute extract, 50 to 200 µL are injected into the GC. This eliminates the need to concentrate to 1 mL, which requires close operator attention. To get a final volume of 1 mL, evaporation is continued to 200 or 300 µL so the extract can be transferred to a sample vial with multiple solvent rinses for good recovery. This procedure requires operator diligence to avoid evaporating to dryness with possible loss of volatile components. Since all compounds in the sample extract are concentrated, interference peaks are a major concern. With the ECD, interfering peaks from the matrix can mask target analytes or give a false positive response. Using the Halogen specific HECD reduces the effect of interfering compounds, offering excellent sensitivity for the Chlorinated Dioxins and Pesticides. The chromatogram below of a Dioxins standard shows good peak shapes (Figure 3), illustrating the applicability of the HECD to these difficult compounds.

The HECD can be used for Chlorinated Pesticides as in the TCL mix shown (Figure 4). There is minimal detector response to the solvent, and peak shapes are well defined. The HECD has traditionally been utilized in PCB analytical methods. Note the clean baseline for the PCB chromatogram with virtually no interfering peaks in the region of the target compounds (Figure 5). These illustrations are extracts which were not concentrated. If the extracts were concentrated more before analysis using OCLVI, the detection limits could be further reduced. It is possible that sub-picogram levels could be achieved before solvent and sample background interferences would become significant.

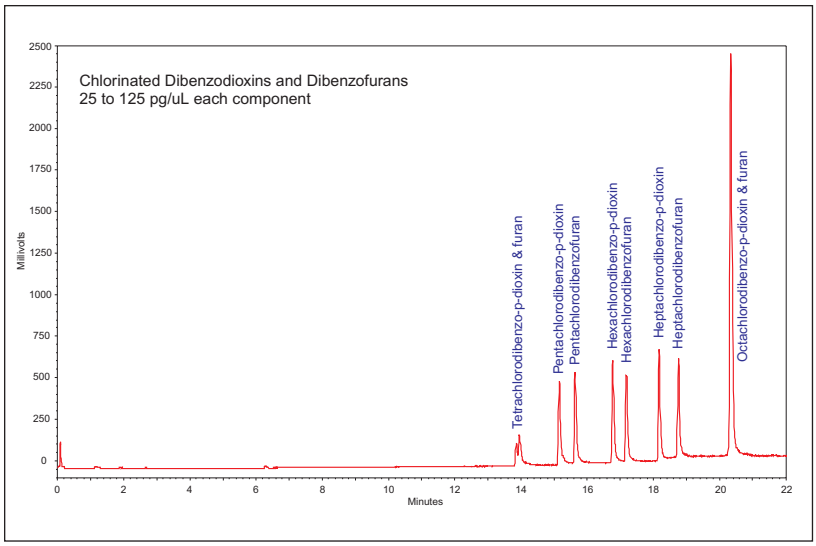

Figure 3: Chromatogram of 100 µL injection of standard mixture of isomers of chlorinated Dibenzo-p-dioxins and Dibenzofurans.

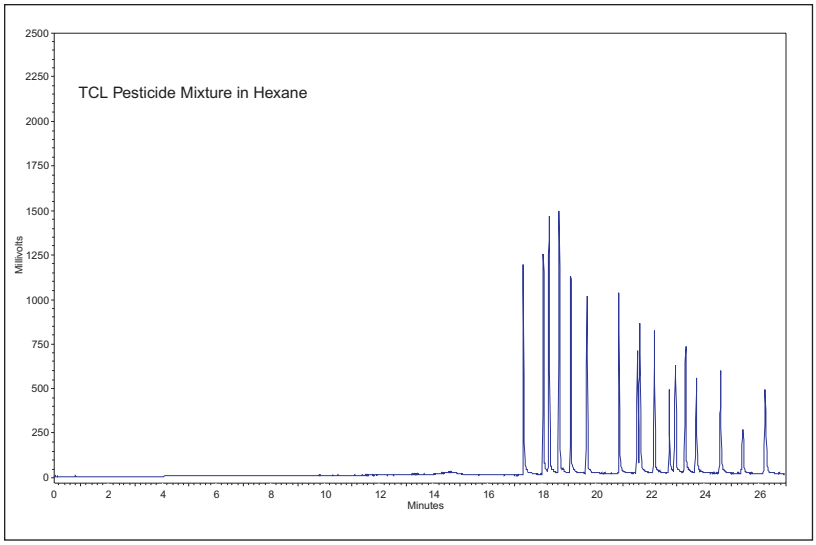

Figure 4: Chromatogram of 100 µL injection of TCL Pesticide Mix.

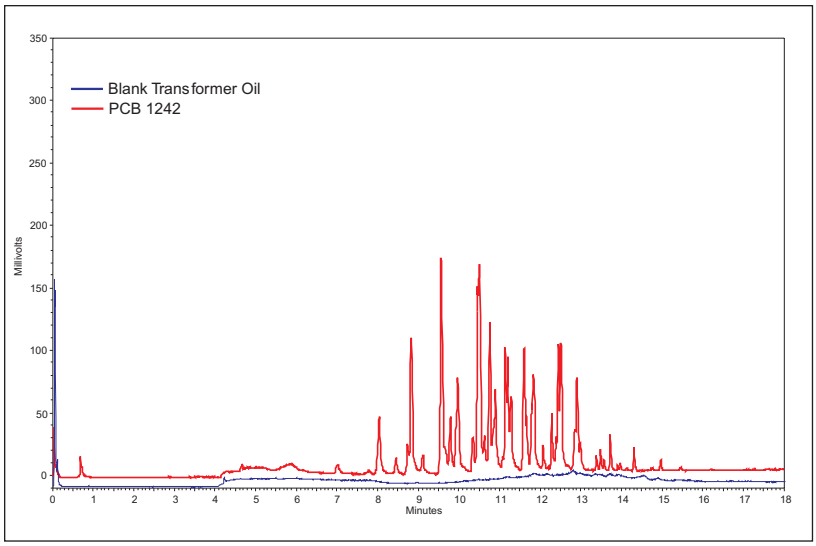

Figure 5: Chromatograms of 50 µL injection of a diluted transformer oil Blank and a Standard of PCB 1242.

Conclusion

With OCLVI, the ability to inject vol-umes up to 100 times larger than conventional splitless injection maintains the sensitivity of the method. OCLVI allows the use of the HECD with its greater selectivity and still achieves method detection limits comparable to the ECD. The combination of selective detection of Chlorinated compounds with the Electrolytic Conductivity Detector and a relatively simple sample cleanup procedure yields a method which is robust and sensitive. This technique is also applicable to many Chlorinated compounds other than Dioxins, such as Pesticides, PCBs, Chlorinated Paraffins, and other Halogenated analytes.

The use of the Large Volume Injection technique allows higher productivity while maintaining method sensitivity. This is an important consideration for an analytical laboratory utilizing methods where sample preparation time is lengthy. Solvent extraction and evaporation is a labor intensive procedure which is not easily automated. The injection of large volumes of solvent extracts can be carried out reproducibly with proper instrumentation, as shown here.

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