THE USE OF COMBINED HIGH VOLUME INJECTION/DUAL DATA ACQUISITION TO REDUCE THE ANALYSIS TIME OF POLYCHLORINATED DIBENZO-P-DIOXINS AND POLYCHLORINATED DIBENZOFURANS

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Abstract

Laboratories are constantly looking for ways to improve efficiency and reduce turnaround times. The use of large volume injection (PTV/LVI) and dual data acquisition each contributes to a reduction in the time needed to process samples being analyzed for PCDDs and PCDFs. Large volume injections reduce the time requirements associated with the final concentration and solvent switching processes while the use of dual GC/single MS configuration with staggered injections (dual data acquisition) increases the number of sample extracts that can be analyzed during a typical 12-hour analytical sequence. The combination of these procedures offers a unique approach to PCDD/PCDF analysis and a time savings that can offer laboratory analytical productivity improvements of over 50% compared to standard methodology.

Introduction

The analysis of PCDDs/PCDFs is a time consuming process and analytical laboratories are always looking for ways to improve the throughput of samples. The use of PTV/LVI techniques allows the time needed for the final concentration step of the sample preparation procedure to be reduced. The use of dual data acquisition[1] with dual GC/single MS configuration allows sample data to be collected from a second GC during the "dead time" at the beginning and end of the primary PCDD/PCDF analysis on the first GC. The combination of these procedures offers a significant improvement in laboratory productivity.

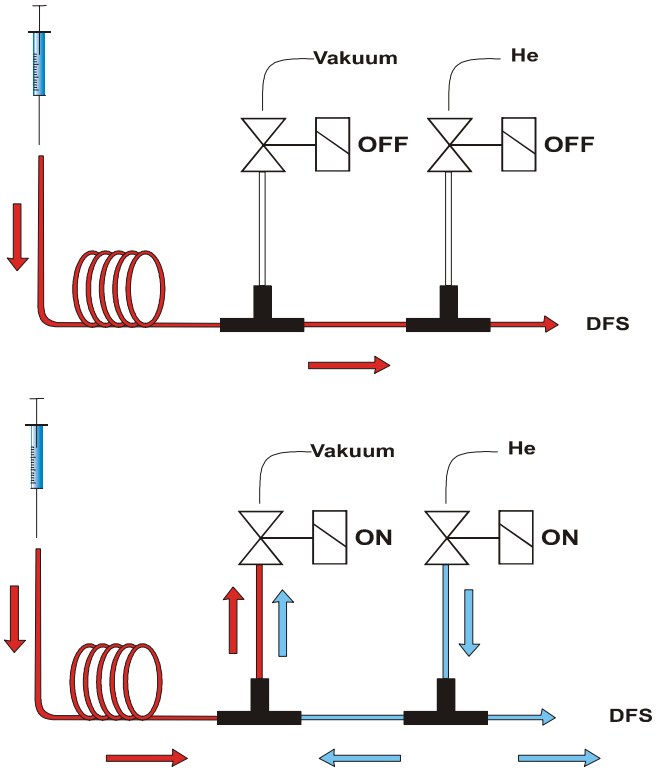
Materials and Methods

Sample extraction and enrichment were performed according to USEPA Method 1613B[2]. These tests followed the same procedures typically used at the laboratory for extract preparation except that the final concentration step was stopped at a volume of 1 mL of toluene. This corresponded to an injection volume of 50 µL instead of the more typical 1 µL injection. This change allowed the additional concentration and solvent exchange steps needed to reach the final volume of 20 µL to be omitted.

The extracts were analyzed using a Thermo Scientific DFS high-resolution mass spectrometer system. The DFS was configured with two Trace GC Ultra gas chromatographs each containing a PTV injector coupled to a 60 m x 0.25 mm x 0.25µm DB-5MS capillary column. The GCs were served by a single TriPlus XT autosampler with an extended rail. The mass spectrometer was operated following the typical Method 1613 parameters (>10,000 resolution, EI-MID, etc.), except in the dual data acquisition mode.

In addition to the time savings derived from the dual data acquisition, another benefit was that the solvent was not allowed to enter the ion source chamber. The dual data acquisition system used a vacuum attachment to prevent unwanted materials from passing into the ion source. This was supplemented with an additional helium supply that both ensured that the column effluent was forced into the vacuum line and also maintained a constant helium flow to

the source. The dual data acquisition layout is shown in the diagram below. After removing the solvent, the analytes were transferred onto the column by rapidly heating the injector and were eluted through the column using the standard temperature program for this analysis.



Dual Data Acquisition Flow Diagram

After the extract on GC 1 was partially eluted, a second injection was made in the same manner using GC 2. The dual data acquisition valves on GC 2 were immediately activated and kept on while the initial analysis was completed. After that time the valves on GC 1 were activated to prevent analytes from reaching the source and those on GC 2 were closed to allow the analytes from the GC 2 to be collected. This alternating process was continued for each sample in the analytical sequence.

Results and Discussion

The time savings associated with sample preparation averaged approximately one hour per analytical batch. However, in some cases automated procedures that allow the unattended concentration of extracts to 1 mL or less could be used to increase this time savings. In these cases, the improvement in savings was greater since the extract was transferred directly to the GC vial. This allowed the entire process of further concentration/solvent exchange to be removed from the process. There may also be additional benefits in minimizing the loss of analytes during the concentration process, especially for other analyte sets, such as PCBs.

The use of dual data acquisition provided a more significant improvement in the efficiency of analysis. Using this procedure, assuming an approximate run time of 45 minutes per sample and a dead time of 18 minutes before the first analyte elutes, the effective run time changes from 45 minutes for a single sample to 54 minutes per pair of samples. This increased the number of injections in a 12-hour sequence from sixteen to twenty-six. Even taking into account the doubling of QC analyses, the number of field samples analyzed in a 12-hour sequence increases from eleven to nineteen or more.

Typical 12-Hour Run Sequence

Sequential Analysis	Dual Data Acquisition Analysis
Calibration Standard	Calibration Standard GC1
Laboratory Control Standard	Calibration Standard GC2
Laboratory Control Standard Duplicate	Laboratory Control Standard GC1
System Blank	Laboratory Control Standard Duplicate GC2
Method Blank	System Blank GC1
Samples 1…11	System Blank GC2
	Method Blank GC1
	Samples 1-19 GC1 + GC2

Acknowledgements

Pace Analytical Services, Inc.
Thermo Scientific

References

1. Heinz Mehlmann, Jens Griep-Raming, Dirk Krumwiede, Helmut Munster *Application Note 30174* 2009

2. USEPA Method 1613: Tetra- through Octa- Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS (September 1997, Revision B)