Combined GPC and On-Line Carbon Column for Automation of Extract Cleanups in Isotopic Dilution High Resolution PCDD/PCDF Determinations

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Introduction

Extract purification is critical to picogram or nanogram scale GC/MS determinations of chlorinated aromatic hydrocarbons. Such time-consuming, laborious techniques are costly and also suffer from variations in performance of manual gravity and low-pressure chromatography. These issues are continually faced by laboratories performing analyses of chlorinated dioxins, furans and biphenyls. Size exclusion chromatography (GPC) followed by adsorptive chromatography provides useful cleanup of many biota, soil, and sediment extracts for these types of analyses. GPC cleanup of sample extracts is allowed or encouraged in several EPA dioxin methods, such as EPA Office of Water Method 1613. Combining these two types of chromatography into a robust, automated method is of great value to laboratories practicing these analyses.

Sample extract cleanups for PCDD/PCDF always involve a carbon column stage. Sample concentrate, typically following other cleanups, is passed onto a carbon column and forward elution drives out various interferences. Elution with reverse flow utilizes a solvent mixture containing a component (e.g. benzene or toluene) that has great affinity for carbon. This treatment disgorges PCDD/PCDF congeners into an eluate that is ready for evaporation and analysis. In this study GPC eluate was forward eluted through a carbon cartridge containing a bed comprised of carbon powder mixed with granular substrate, packed between two frits. The cartridge was placed in line after the GPC column. During forward elution (with GPC mobile phase), target compounds collect at or near the carbon column head while interferences were flushed forward. Valve switching enabled reverse elution with toluene for collection of target analytes. Thus PCDD/PCDF sample cleanup was simplified by combining GPC with on-line post-GPC carbon cleanup. The entire sample cleanup can be conducted in highly automated manner with minimal operator contact relative to other cleanup regimes.

Materials and Methods

Prototype graphitized carbon cartridges (Restek) in a polypropylene barrel with HDPE frit and Luer tips were used. Purity of blanks recovered from elution of the carbon column exceeded all method specifications.

GPC was perfomed using an automated system (J2 Scientific, AccuPrep) equipped with 2.5 cm i.d. by 50 cm glass-barreled column, packed with 3% cross-linked styrene divinylbenzene copolymer gel. Elution was with 100% methylene chloride, at 5 mL/min. Flow characteristics of the GPC system (as evidenced by on-line UV calibration of GPC column) were unchanged by installation of the carbon column. No breakthrough of target compounds was observed following forward elution of GPC and carbon columns with GPC mobile phase during the normal PCDD/PCDF GPC collection window.

Reverse elution of the carbon column with 25 mL toluene was used to recover adsorbed target analytes. The reverse eluate was evaporated and analyzed (high resolution GC/MS, Agilent 6890 GC with 2 uL injection, Thermo MAT 95-S mass spectrometer, electron impact MID mode at 10000 resolving power) according to conditions and specifications contained in EPA Method 1613.

Results and Discussion

Four spiked extracts containing corn oil were processed through GPC and carbon. Precision of native and 13-C PCDD/PCDF recoveries met all Method 1613 specifications. Recoveries of all analytes except 13C-OCDD met the method specifications. It is believed 13C-OCDD recovery can be improved by optimizing back-elution volume. Overall, the system is functional and considered capable of meeting all EPA isotope dilution method requirements.

Operating it requires less labor and repetitive motion than classic gravity columns. Also presented are results from samples previously analyzed using other, more complicated cleanup techniques.

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