INTRODUCTION

The brominated flame retardant hexabromocyclododecane (HBCDD) is commonly monitored for its presence in the human population as well as the environment. HBCDD shows a complex stereochemistry, with six stereogenic centers. The three most commonly detected forms of HBCDD are the +,− and diastereomers, each comprised of a + and − enantiomer pair (Figure 1). Here we describe a rapid method using supercritical CO2 with an organic co-solvent to separate the three most abundant HBCDD enantiomer pairs on a chiral cellulose column. The presented method offers an advantage over existing LC methodologies by increasing throughput and decreasing solvent usage whilst maintaining the resolution required for quantification.

METHOD DEVELOPMENT

Method development was performed on three chiral stationary phases with 2.5µm particle diameters. Table 1 highlights the screening approach and resulting optimum conditions. Table 2a shows the HS/MS MRM method and 2b the final chromatographic method.

Table 1: Optimization parameters for supercritical fluid CO2 method, implemented on all three column chemistries. Mobile phase and column temperature had the most significant impact on HBCDD enantiomer separations.

Table 2a: MRM optimized in previously developed achiral method.

RESULTS AND DISCUSSION

The final method was developed first using commercially available +,− and HBCDD diastereomers (Figure 3a). Individual enantiomer standards, isolated using a permutated (-)-cycloextrim stationary phase by liquid chromatography, were injected in order to establish enantiomer elution order (Figure 3b). RSDs of peak areas were measured across 9 injections of mixed standard (Table 3).

Table 3: RSDs across 9 injections of a 100 pg/µL standard for all enantiomers.

A rapid and efficient method for separating HBCDD enantiomers is achieved using supercritical fluid CO2 chromatography.

REFERENCES

4. P. C. Wallaert et al., Chemosphere, 2006, 63, 979-988.

CONCLUSIONS

A rapid and efficient method for separating HBCDD enantiomers is achieved using supercritical fluid CO2 chromatography.

Sample analysis throughput could be greatly increased using this method.

Supercritical CO2 chromatography requires the use of significantly less solvent than lengthy chiral LC methods, reducing costs and laboratory waste.