NOVEL SILICA ADSORBENTS FOR THE ISOLATION OF POLYCHLORINATED DIBENZO-P-DIOXINS AND POLYCHLORINATED DIBENZOFURANS

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The determination of low levels of polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) has advanced rapidly over the past years with the more widespread availability of high resolution gas chromatograph - high resolution mass spectrometer (HRGC-HRMS). As lower levels are approached, other organic contaminants interfere with the analysis of PCDD and PCDF. For example, chlorinated diphenyl ethers cause interfences in the analysis of PCDF. A great deal of research has focused on the detection of PCDD/PCDF using HRMS, but as lower and lower levels of PCDD and PCDF are being detected, the effectiveness of the clean-up, prior to analysis, must also be examined in greater detail.

The separation/clean-up of the sample is an important part of the overall analysis. The separation must remove all irrelevant co-extracted material prior to final analysis. For example, large amounts of lipids and polychlorinated biphenyls are detrimental to the final determination. Most clean-up methods involve a gross separation using acid and/or base modified silica and alumina, followed by a carbon column clean-up. The carbon column is effective in trapping the PCDD and PCDF but there are a number of drawbacks with this adsorbent. The problems associated with carbon include: irreversible adsorption of the PCDD/PCDF, excessive tailing of the analytes, and batch-to-batch variation of the carbon because of its non-homogeneous nature.

To overcome the shortcomings of the carbon, an alternative material is required that will retain the PCDD/PCDF selectively, but will be more reproducible from batch-to-batch. A proposed solution to this dilemma is to attach certain organic functional group derivatives to silica gel such that the separation capabilities would rely on the unique planarity of the PCDD/PCDF, especially the 2378-substituted PCDD/PCDF.

New modified silica adsorbents have been synthesized using a number of organic derivatives, a coupling agent and fine mesh silica. The modified silicas have been tested for PCDD/PCDF recovery efficiency using standards and environmental samples.

The compounds chosen for the silica gel modification were selected so as to use π-π interactions between benzoid rings and dipole-dipole interactions of bonded oxygen atoms. These interactions will allow separation of the PCDD and PCDF from PCBs, polychlorinated diphenyl ethers and other chlorinated aromatic compounds. The modified substrate is also expected to retain, to a lesser degree, the non-ortho PCBs that exhibit dioxin-like activity.

Results of the synthesis of these novel silica-based adsorbents and the efficacy of the adsorbents as suitable agents for the isolation of PCDD and PCDF from standard mixtures and environmental samples will be presented. Simulated molecular orbital calculations will also be presented showing the interactions of the substrate and PCDD/PCDF.