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Title:

Tandem extraction/liquid chromatography-mass spectrometry protocol for the analysis of acrylamide and surfactant-related compounds in complex matrix environmental water samples

Introduction:

Ethoxylated alcohols, alkylphenols, and acrylamide are emerging contaminants with many different routes into the environment. Ethoxylated alcohols are used ubiquitously as surfactants in both industrial and household products. The use of ethoxylated alcohols and alkylphenols as surfactants raises the possibility of toxicity to aquatic life through their degradation byproducts, including nonylphenol, an endocrine disruptor. Acrylamide, a probable carcinogen, is used as a coagulant aid, a grouting agent, and is formed during the heating of starch-rich foods. Currently, standard methods are not established for these classes of compounds. Described here is the application of a tandem solid-phase extraction (SPE) protocol combined with liquid chromatography-mass spectrometry (LC-MS) to analyze environmental samples for multiple classes of compounds, including ethoxylated compounds, alkylphenols, and acrylamide.

Methods:

Analytes of interest were extracted from water samples using an Autotrace SPE workstation. Ethoxylated alcohols, alkylphenols, and alkylphenol ethoxylates were extracted using polystyrene-divinylbenzene SPE cartridges. Acrylamide was extracted using activated carbon cartridges. Because the highly polar acrylamide is not retained at all by the polystyrene-divinylbenzene cartridges, the flowthrough solution from the polystyrene-divinylbenzene cartridge sample loading was collected for the acrylamide extraction. The eluates were concentrated and then filtered using 0.2 micron syringe filters. The extracted samples were analyzed by LC-MS, using either full scan or multiple reaction monitoring (MRM) mode for the various analytes, and analytes were quantified using isotope dilution or external calibration curves.

Preliminary data:

Various SPE cartridges were analyzed for their extraction efficiencies for the various compounds, including polystyrene-divinylbenzene (Waters Oasis HLB), C18, Isolute ENV+, graphitized carbon, and activated carbon. Acceptable recoveries of ethoxylated compounds and alkylphenols were obtained using the polystyrene-divinylbenzene SPE cartridges. Acrylamide is a highly polar compound that remains in the aqueous phase and so was not retained on any SPE cartridge except for the activated carbon cartridges from Biotage. As a result of this finding, and to minimize the necessary sample volume to analyze both the surfactant-based compounds following polystyrene-divinylbenzene extraction and the acrylamide following activated carbon extraction, a tandem SPE protocol was performed. This tandem system resulted in a reduction of sample and solvent volumes that were required to extract the various classes of compounds and acceptable recoveries.

Different HPLC columns were investigated for use with acrylamide, including reversed-phase C18, ion exclusion, and porous graphitic carbon. The only column that retained the acrylamide was the

ion exclusion chromatography column using an isocratic elution profile. In all other columns tested, acrylamide eluted with the dead volume and was not retained. However, because the retention time of the acrylamide using the ion exclusion column was >25 minutes and the reversed-phase C18 column provided accurate quantification, the reversed-phase C18 column was used for the acrylamide analyses for higher throughput. Additionally, the other surfactant-related compounds were also separated using the reversed-phase C18 column.

Acceptable quantitation was found using external calibration curves for the ethoxylated compounds. Isotope dilution was utilized to quantify the amounts of acrylamide and alkylphenols in the samples because deuterated standards were commercially available. Work is in progress to validate the methods and to analyze real-world samples.

Novel aspect:

Tandem SPE extraction approach allows for the extraction of both surfactants and acrylamide using lower sample volumes.