Detection of BPA in Water Using Gas Chromatography Mass Spectrometry: Solid Phase Microextraction and Solvent Partitioning

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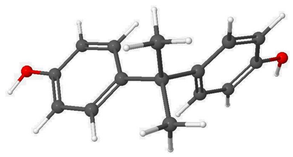
Abstract

Gas chromatography mass spectrometry (GC/MS) is a common method used to detect and quantitate nanogram-scale amounts of chemical species in solution. Not all liquids make suitable GC/MS solvents; in particular, GC/MS cannot be directly used to analyze aqueous solutions. Various techniques exist to facilitate the study of aqueous solutions by GC/MS methods. In the present study, two such methods were used to analyze the suspect environmental endocrine disruptor bisphenol A (BPA). In solid phase microextraction (SPME), polydimethylsiloxane (PDMS) fibers are exposed to the headspace gas above a heated aqueous solution for a set period of time in order to adsorb volatile solute molecules; these adsorbed molecules desorb on exposure to the heated inlet chamber of the GC/MS. In solvent partitioning, a mode of liquid-liquid extraction, BPA in aqueous solution is mixed with a solvent that is immiscible in water and dissolves some fraction of the solute (characterized by the *partition coefficient*). Advantages and disadvantages of the two methods were compared.

Introduction

BPA, an estrogen-like chemical[1,2], is used in the production of polycarbonate materials, epoxy resins, and cash register receipts. Due to its prevalence in industrial processes, residual BPA has become pervasive in the environment, and in a recent study was found to be present in the urine of 93% of Americans tested[3]. The detection of BPA in the environment has become increasingly important in recent years due to scientific concern that the chemical may be linked to harmful effects in humans and wildlife[2,3]. Studies have shown some success in the quantitation of BPA in water through various liquid-solid, liquid-liquid, and solid phase microextraction techniques[4-7]. A recent study compared PDMS fibers and carbon nanotube fibers for efficiency of SPME detection of derivatized BPA, and determined the optimal conditions for each fiber type[4]. This information was used in the present study to maximize the sensitivity of BPA detection in the PDMS fibers. The other approach presented here used liquid/liquid extraction into dichloromethane, which was then used directly as a GC/MS solvent.



Rendering of a bisphenol A molecule using the program WebMO.

Gas Chromatography Mass Spectrometry

GC/MS is used to analyze the chemical composition of small liquid or gaseous samples. The sample is inserted into the inlet chamber, where liquids are evaporated at high temperatures. The sample is carried by the eluent gas (helium in this case) through a long, coiled capillary tube called the column, which is heated according to a set temperature program which optimizes separation of molecules due to different interactions with the column stationary phase. As molecules exit the GC at their different retention times, they enter the mass spectrometer, become ionized, and fragment. The mass/charge ratio of fragment ions is detected through electromagnetic deflection.

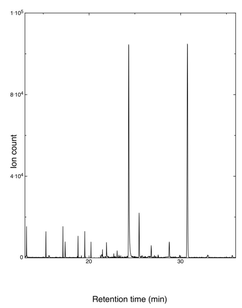
Samples

Several samples labeled in parts per million (ppm) and parts per billion (ppb) were used in the SPME procedure. These samples were made by weighing BPA on an analytical balance and dissolving the measured sample into a small portion of methanol. The initial concentration was obtained by adding 0.0100 grams of BPA in 10.0 mL methanol. Distilled water was added to this solution in a 100 mL volumetric flask, and the resulting solution was defined as 100 ppm. This sample was diluted by a factor of ten several times, and the lowest concentration made was 10 ppb.

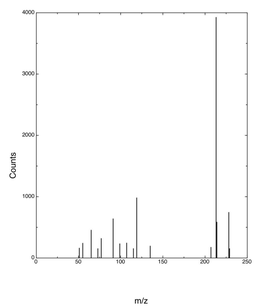
Solid Phase Microextraction

For each concentration measured, the following procedure was performed: A 50 mL beaker full of distilled water was heated on a hot plate set at 270 degrees Celsius. 15 mL of the aqueous BPA sample was pipetted into a 20 mL vial. 0.3 g sodium chloride and 0.2 g potassium bicarbonate were measured on an analytical balance and added to the vial containing the sample. 0.3 mL acetic anhydride was pipetted into the vial, and the vial was sealed with a crimped septum cap. The acetic anhydride was added in order to derivatize the BPA to form BPA-diacetyl, which is less polar than BPA and thus likely to be more volatile. In the acetylation process, the two hydroxyl protons are removed and replaced by a pair of acetyl groups. The vial was placed in the heated water bath, and the SPME fiber was inserted through the septum and then exposed to the headspace above the sample for 20 minutes. The fiber was retracted, inserted into the GC/MS inlet chamber, and exposed for 5 minutes. The inlet temperature was set at 250 degrees Celsius, sufficient to desorb the BPA-diacetyl but not to decompose it.

SPME Results



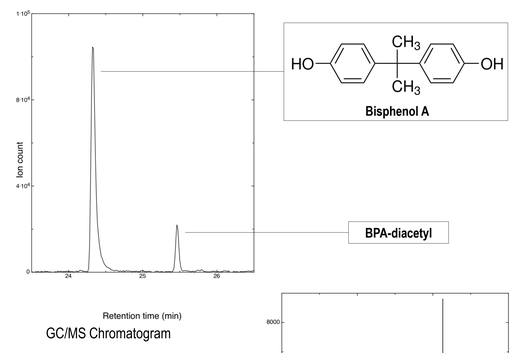
Chromatogram from SPME BPA sample (67 ppm). The BPA peak occurs near 24 minutes. The small peak at 25 minutes is due to BPA diacetyl derivative.The peak at 31 minutes diisooctyl phthalate from the vial septum.



Mass Spectrum from SPME BPA sample at BPA peak. The base peak at m/z 213 corresponds to loss of a methyl group.

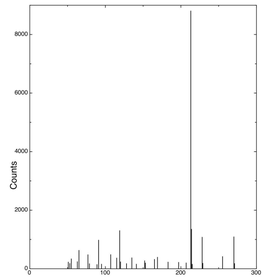
In each of the aqueous samples, the GC/MS was able to detect BPA after SPME. Some noise was present in the chromatograms, but did not interfere with BPA detection. (In addition to column bleed, chromatograms contained small noise peaks probably due to inlet contamination.) Although detection of BPA was achieved in each sample, quantitation was problematic due to the lack of a suitable internal standard for SPME. (Rastkari et al.[4] used d14-BPA in their study, but expense precluded the use of this material in the present study.)

Results



GC/MS Chromatogram

One unexpected aspect of the collected data was the amount of unacetylated BPA that was detected. (The purpose of the acetylation was to form a more volatile derivative of BPA in order to increase detection sensitivity.)

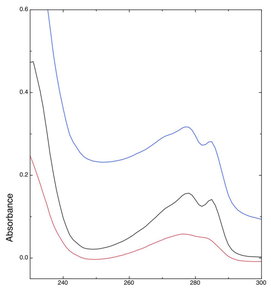


MS data for BPA-diacetyl

One possibility is that the BPA was not sufficiently acetylated to a level that would have caused it to be more present in the headspace than the unacetylated BPA. Perhaps a more complete acetylation would result in higher volatilization of BPA, and therefore increase detection sensitivity. It is also possible that BPA is sufficiently volatile as it exists in the samples, and the acetylation process would not aid in the detection of BPA at any level of completion.

Solvent Partitioning

In solvent partitioning, the sample solution is mixed with another solvent that is immiscible with the first solvent and that dissolves some of the solute sample into itself. The fraction of the sample that is dissolved into the second solvent is characterized by the partition coefficient. The partition coefficient of BPA between dichloromethane and water was not found in the literature, so an attempt was made to measure its value using UV/Visible spectrophotometry. The results suggested that BPA is quantitatively transferred into the dichloromethane.



UV/Visible spectra of BPA: 5 ppm in CH_2Cl_2 (black line), in CH_2Cl_2 after liquid/liquid transfer from 5 ppm in H_2O (blue line), and 5 ppm in H_2O (red line). Note that 5 ppm in H_2O corresponds to a molar concentration about 1.33 x that corresponding to 5 ppm in CH_2Cl_2.

Solvent Partitioning Results

This quantitativeness of the solvent transfer was tested by comparing a dichloromethane solution with a known concentration to a solution that had been partitioned with an aqueous solution of equal molarity. Benzophenone was added to the two solutions to act as an internal standard.

The GC/MS did not detect BPA or benzophenone, however, and column bleed was detected at a higher level than had previously been observed. This could mean that no BPA was dissolved into the dichloromethane and that the benzophenone was not dissolved or not detected. Based on the earlier data collected from the UV/Vis spectrophotometer, however, it appears that a more likely answer may stem from some other error that occurred during the procedure. Solvent partitioning may still be a viable option for BPA detection, but further work is needed to optimize the procedure.

Conclusions and Future Work

SPME was able to detect BPA in all aqueous samples tested, the lowest concentration being 10 ppb by mass. Quantification of BPA, however, proved to be more difficult because of the lack of linearity between detector response and sample concentration.

Based on the higher abundance of BPA molecules relative to the BPA-diacetyl peaks in the chromatogram, it was unclear whether the acetylation of BPA was a necessary step. Further studies may need to be done to determine if the acetylation process can be made more complete or to decide if the procedure is necessary for SPME detection of BPA in aqueous samples.

Dichloromethane appeared to be a suitable solvent for solvent partitioning because of its apparent ability to quantitatively extract BPA from water. However, further studies may need to be done to optimize the liquid/liquid solvent extraction procedure using dichloromethane for quantitative GC/MS detection of BPA.

References

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