

Headspace Measurement of BTEX Constituents in Water with Dielectric Discharge Argon Ionization Detector

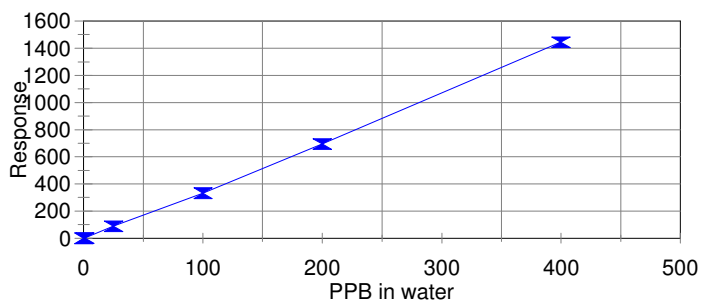
Introduction: To obtain part per billion detection limits for benzene, toluene, ethyl benzene, and the xylenes, analytical laboratories have traditionally used concentration techniques such as purge-and-trap or solid phase microextraction. While able to obtain p.p.b. sensitivity, these methods often require over 20 minutes of preparation per sample and they require expensive or delicate hardware systems.

Headspace analysis offers an attractive alternative for analyzing samples due to its potential simplicity and speed. Headspace analysis relies on the partitioning of the analytes of interest from the sample matrices into the headspace of a container, a volume of gaseous space (typically air) above the sample. Once partitioned, an aliquot of the headspace is then used for analysis by G.C. However, headspace is not a concentration technique and, as such, it has been limited to applications where the detector is highly sensitive or reserved for screening applications.

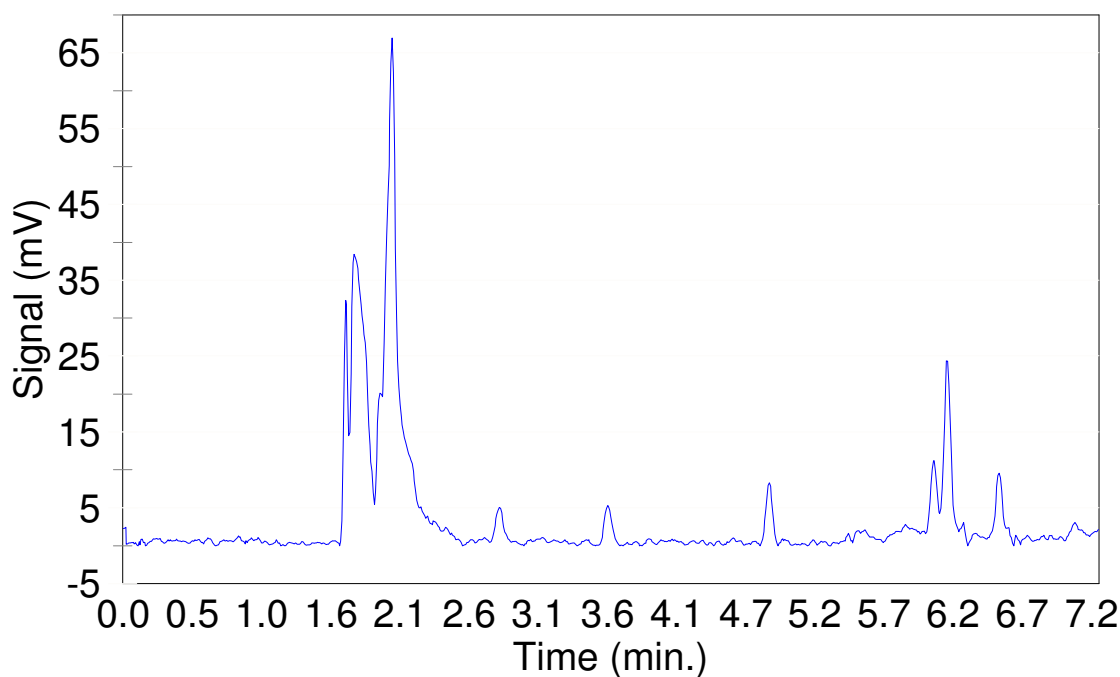
AIC Corporation has developed a detector that is sufficiently sensitive to perform BTEX analysis at regulatory levels using headspace. The detector, the Dielectric Barrier Discharge Argon Ionization Detector, is a windowless detector that is capable of measuring the sub-nanogram quantities of BTEX required by headspace analysis at regulatory limits.

Experimental: Samples were ten mL. aliquots placed in 20 mL. VOA vials and 1 microliter (μL .) of internal standard (1,2,4-trimethylbenzene) added. The sample was shaken vigorously by hand for one minute and allowed to settle. A 500 μL . aliquot of the sample headspace was then injected into the GC. The G.C. was a Varian 3400 equipped with a splitless/split injector operated in the splitless mode for the first 30 seconds. The column, a 75 meter DB-624 (0.53 m.m. i.d. X 3 μm . film), was held at 80 $^{\circ}\text{C}$ for 1 minute and ramped at 15 $^{\circ}\text{C}/\text{minute}$ to a final temperature of 160 $^{\circ}\text{C}$ where it was held for 5 minutes. The detector was an Advanced Industrial Chemistry Corporation developed dielectric barrier discharge argon ionization detector. Injector temperature was 200 $^{\circ}\text{C}$ and the detector was held at 220 $^{\circ}\text{C}$.

Results: A five point calibration curve was generated for each component. Linear range for the components was from 1 p.p.b. to 400 p.p.b. for all components except m,p-xylene which ranged from 2 p.p.b. to 800 p.p.b.. Analytes had correlation coefficients greater than 0.990. A calibration curve for toluene can be seen to the right.



The dielectric barrier discharge argon ionization detector is a windowless detector. For this reason, it is a very sensitive detector. Below is a chromatogram of a 1 p.p.b. water sample analyzed using the headspace method. If 100 % of the analytes transfer to the 10 mL headspace then a $\frac{1}{2}$ mL injection of the headspace means that the detector is detecting 500 picograms of each analyte on column. The peak for toluene, retention time 4.8 minutes, is 9 seconds wide. Given this peak width, this yields a detected quantity of 55 picograms per second with at least a 10:1 signal to noise ratio.



Chromatogram of 1p.p.b. water sample analyzed by headspace with the Dielectric Barrier Discharge Argon Ionization Detector.

A method detection limit study was run according to EPA methodology. Seven replicate samples were analyzed at 2.5 p.p.b.. This data is shown below. Calculated method detection limit values are all below 0.5 p.p.b.

Method Detection Limit for B.T.E.X. in Water

Compound	Benzene	Toluene	Ethyl benzene	MP xylene	O xylene
% Relative Standard Deviation.	8.4	5.1	7.9	10.8	4.9
Calculated M.D.L. (p.p.b., n=7)	0.40	0.21	0.34	0.29	0.33

Conclusion: The sensitivity of the dielectric barrier discharge detector in argon ionization mode allows for rapid screening of samples for BTEX. By simply shaking an aliquot of the sample in a vial and injecting an aliquot of the headspace, an analyst can determine the presence or absence of B.T.E.X. compounds at a detection limit of one part-per-billion. As an alternative to more lengthy analytical techniques, this technique offers a rapid method for the analysis of samples at regulatory levels.