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Determination of Benzene and Toluene in Soils and Plant Material by Azeotropic Distillation

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Contamination of soil and ground water by gasoline has resulted from underground storage tanks which have corroded and from spillage and improper disposal. The presence of about 0.8 to 1.4 per cent benzene in typical gasolines (Sanders and Maynard 1968) presents a problem of particular concern in groundwater contamination since benzene is a recognized leukemogen (Sax 1979). Furthermore, aromatics have relatively high solubility in water compared to alkanes (McAuliffe 1966), which can result in the preferred migration in groundwater of the aromatics. The relatively high vapor pressure of dissolved alkanes compared to that of dissolved aromatics (McAuliffe 1971) enhances their loss to interstitial air spaces. These two mechanisms result in a preferential migration of aromatics in groundwater.

The analysis of aromatics in water has advanced considerably in the last several years with the use of both headspace and purge and trap (PAT) techniques (Mieure 1980). The commercial development of PAT equipment enables routine monitoring of volatile trace pollutants at the parts per trillion level (EPA 82). Even the problem of background interference from other volatiles which may be present in the water has been dealt with in headspace (McAuliffe 1971) and PAT (Kozloski and Sawhney 1982) by multiple purging.

The analysis of trace quantities of volatile aromatics in other matrices such as soils and plant matter has been less thoroughly developed. Simple solvent extraction followed by gas chromatography (GC) with flame ionization detection (FID) is relatively insensitive. The presence in the extract of non-volatile material and components with long retention times (RTs) can limit column life and result in excessive waiting periods between injections. Modified purge and trap (PAT) techniques can increase sensitivity, avoid the problem of GC column contamination and the presence of a solvent front (Tore and Mestrick 1981). A disadvantage of the modified PAT techniques is the need for specialized equipment. Another drawback is that samples which require grinding, such as plant material, cannot be handled

readily by PAT techniques since loss of volatiles may result during the milling process.

The suspected dumping of gasoline near a garden resulted in the need for a method that would measure trace amounts of benzene and toluene in both soil and plant samples. In this report we show that a method involving methanolic extraction and azeotropic distillation is a highly sensitive technique that eliminated the contamination of the GC column by non-volatile material.

MATERIALS AND METHODS

Soil and plant samples [tomatoes (Lycopersicon esculentum), broccoli (Brassica oleracea var. italica), marigold (Tagetes sp.), acorn and butternut squash (Cucurbita pepo and C. Muschata)] obtained from the garden under study were refrigerated at -12° C until analyzed. The soil samples were stored in jars with foil-lined lids and the plant samples in sealed plastic bags. Cutting the plant material while frozen avoided the loss of juices and minimized the loss of volatiles.

To achieve optimum reproducible results, the azeotropic distillation was carried out with a fixed ratio of two parts methanol to one part water. In analyzing plant material, the water content of the sample supplies the water necessary to achieve the two to one methanol to water ratio.

For vegetable matter, an amount of sample containing 50 ml of water was added to 100 ml of methanol. For example, acorn squash which has a water content of 85.1% required a sample size of 58.7 grams. The amount of water in the sample may be approximated by using the values found in Composition of Foods (Watt and Merrill 1963). The plant-methanol-water mixture was blended to a puree using either a Waring Laboratory Blendor (Waring Prod. Corp., New York, NY) or Lourdes blender (Model MM-1), (Lourdes Instrument Corp., Brooklyn, NY). For the Waring blender a one-pint blender jar on a high speed setting for three minutes was used. The Lourdes blender, operated at moderate speed for one minute, and then for two minutes at high speed, was also tested. The 425 ml container was sealed with a polytetrafluoroethylene gasket and was cooled by an ice bath during blending. The blended mixture was then filtered through a rapid filtering paper (VWR, No. 615). For the azeotropic distillation, a 60 ml aliquot and boiling chips were then placed in a 100 ml flask equipped with a Vigreaux distillation head (Kontes K-287200, Kontes, Vineland, NJ). Ten ml of distillate was collected. An alcohol lamp that provided a distillation rate of about one and a half ml/min. was found to be a convenient source of heat. The distillation equipment was dried under vacuum before the next distillation. The ten ml of distillate was then redistilled at about the same rate as the first distillation and the first one ml of distillate collected.

Soil samples were prepared by adding 20 g of soil, 40 ml of methanol and 20 ml of water to the 100 ml distilling flask. If the soil is wet the amount of water added should be adjusted to correct for the amount of water in the soil. The mixture was then treated in the same way as that described for the vegetables.

One liter of methanol ('Baker Analyzed' reagent, low in acetone, or Burdick and Jackson) was passed through a 1.9 cm I.D. x 30 cm column packed to a length of 25 cm with activated carbon (F-100, Calgon Corp., Pittsburg, PA) to remove interfering impurities. The methanol was filtered through a slow filter paper (Whatman No. 42) to remove any traces of carbon which could strongly absorb the aromatics being analyzed. Sodium borohydride (2 g/L) was added and the methanol stored until hydrogen evolution ceased.

Distilled water was boiled to remove volatiles, and after cooling, was passed through activated carbon and filtered in the same manner as the methanol.

One µl of air and 7 µl of the final distillate, in that order, were drawn into a 10 µl microsyringe, to insure quantitative transfer when injected. A Hewlett-Packard 5840A GC with a 6' x 2 mm glass column packed with 1% SP-1000 on 60/80 mesh carbopack B (Supelco, Bellefonte, PA) was used for the analysis. The initial column temperature of 100° C was held for one minute and then programmed to 210° C at a rate of 10° C/min. The helium flow rate was 30 ml/min. The injection port and flame ionization detector were kept at 175° C.

RESULTS AND DISCUSSION

The detection of trace levels of benzene in the distillates places limits on the choice of GC packing material. Carbopack B coated with 1% SP-1000 easily separates the solvent front from the benzene peak by 6.3 minutes. In contrast a 6' x 2 mm column packed with 10% SP-2100 on 100/200 mesh Supelcoport separates the two by 0.8 minutes when operated at 80° C with a 20 ml/min helium flow.

The azeotropic distillation was found to concentrate impurities which were not noticeable before the distillation. The filtration through activated carbon reduced the level of many of the less polar impurities. Further treatment with sodium borohydride destroyed the more polar ketones and aldehydes not removed by the activated carbon. Baker methanol and Burdick and Jackson methanol were compared in ability to provide low blank values. The lowest blanks achieved in the benzene GC region were with Baker methanol, equivalent to 4 ppb of benzene, while the equivalent of 11 ppb was the lowest obtained with Burdick and Jackson methanol. However, in the toluene GC region

Burdick and Jackson methanol gave a zero blank while the blanks with Baker methanol were the equivalent of from 4 to 19 ppb of toluene.

The effect of varying the concentration of water in the azeotropic mixture was tested. Three mixtures containing 28.6%, 33.3% and 38.5% water in methanol were spiked at the 100 ppb level with benzene, toluene and 2,3-dimethylpentane (DMP). All tests were performed in triplicate and the 33.3% water mixture was used as the reference point. The data show that for the benzene and DMP the greater the methanol content of the distillation mixture the higher the recovery of the hydrocarbons (Table 1). The scatter in the toluene data is too wide to draw a valid conclusion. The two successive distillations concentrate the benzene, toluene and DMP 32, 23 and 31 fold respectively with 33.3% water in methanol.

Two different blenders were tested in analyzing spiked samples of uncontaminated butternut squash. A one-pint jar was used with the Waring blender and operated at high speed for three minutes. The jar became noticeably warm, contributing to the loss of volatiles. A Lourdes blender operated at moderate speed for one minute and then at high speed for two minutes was also tested. The Lourdes container was kept cool in an ice bath during blending which could not be accomplished with the Waring blender. The higher recoveries with the Lourdes blender were particularly noticeable (Table 1) with the DMP which proved to be the most readily lost of the spiked components. The disproportionate losses of the DMP demonstrate the impracticality of using alkanes as internal standards.

The possible poor recovery of aromatics from soils because of adsorption by clays and organic matter was investigated by spiking a Buxton silty loam (18% clay and 8.8% organic matter) at the 100 ppb level with benzene, toluene and DMP. The recoveries of benzene and toluene were excellent, 101 and 107% respectively (Table 1). Even the 75% recovery of DMP was reasonable given inaccuracies contributed by problems in sampling and handling that would be expected in the field and laboratories (Ramstad and Nestrick 1981).

On analyzing soil samples not known to be contaminated with aromatics, an increase in the size of interfering peaks over that seen for the methanol alone was observed in the region of the benzene and toluene peaks (Figure 1). These peaks, which correspond to about 5 to 10 ppb of aromatics, are believed to arise either from simple organics already present in the soil or from the oxidizing effects of the soil on the impurities in the methanol. These peaks, along with the normal background peaks, set the lower limit of detection for the method. In the tests conducted on the vegetable and soil samples obtained from the garden suspected of contamination, no aromatics were found. Improvements in the

Table 1. Recoveries of benzene, toluene and DMP from butternut squash, Buxton loam and variations of distillation mixtures

	Per Cent Mean Recoveries[1]		
	Benzene	Toluene	DMP
Distillation Mixtures[2]			
28.6% Water	103.6 (3)[4] ± 1.5	105.7 (3) ± 12.7	107.9 (3) ± 1.5
33.3% "	100.0 (3) ± 2.6	100.0 (3) ± 1.2	100.0 (3) ± 6.6
38.5% "	99.4 (3) ± 0.9	109.0 (3) ± 8.9	91.5 (3) ± 4.3
Squash (Waring Blendor)[3]	84.2 (3) ± 5.2	66.2 (3) ± 7.6	19.5 (3) ± 3.4
" (Lourdes Blender)	96.1 (3) ± 3.3	80.6 (3) ± 6.2	38.2 (3) ± 5.5
Buxton Soil[3]	101.1 (3) ± 5.5	106.9 (3) ± 1.2	74.6 (3) ± 3.1

[1] Relative to 33.3% water distillation mixture.
[2] Containing 0.1 µg/ml of each compound.
[3] Containing 0.1 µg/g of each compound.
[4] Number in parenthesis indicates number of determinations.

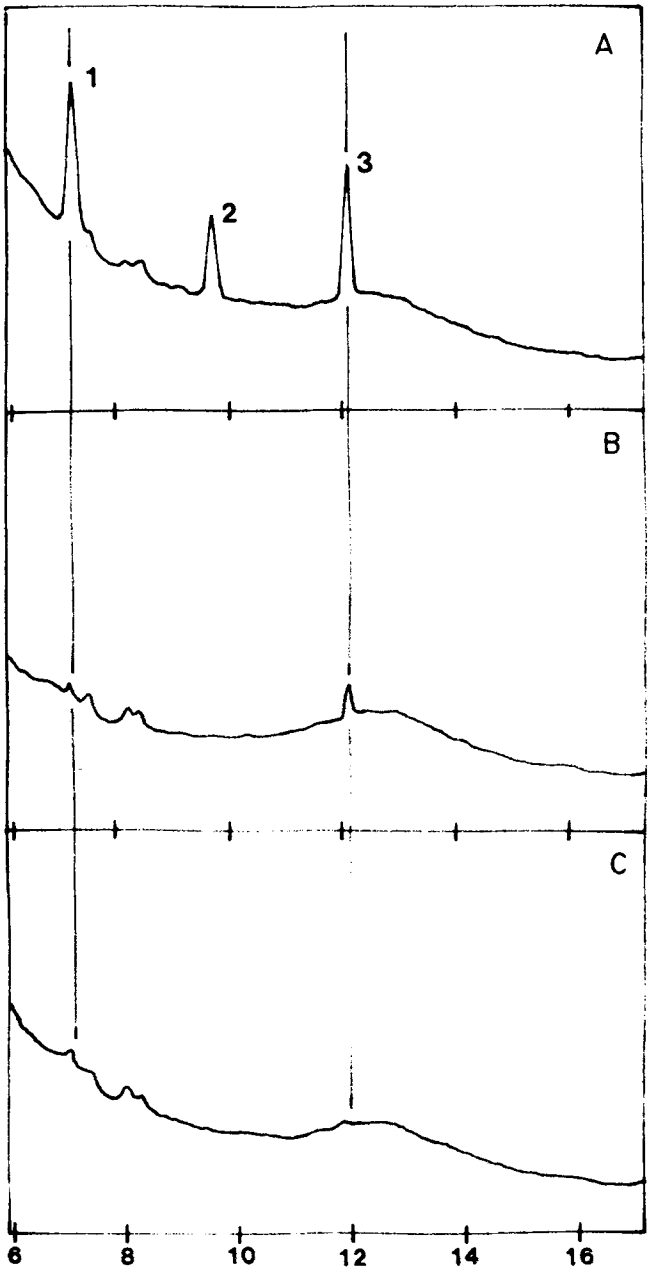

Figure 1. Gas chromatograms of (A) spiked Buxton loam, (B) Buxton loam and (C) solvent blank. 1% SP-1000 on 60/80 mesh, carbopack B, 6' x 2 mm glass column. Col. Temp.: 1 min. at 100° C temperature programmed to 210° C at 10° C/min. Helium flow 30 ml/min. Benzene (1), 2,3-dimethylpentane (2), toluene (3).

method, such as a single distillation with a spinning band column under total reflux, and the use of a photoionization detector for greater detector selectivity should increase the sensitivity of the method.

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