Assessment of Cartridges for assaying Toxic Semi-Volatile Organic Contaminants in Solid-Liquid Extraction Technique

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ABSTRACT

The investigation of toxic materials for human health particularly in the form of herbicide, pesticide, and insecticides dissolved in **drinking water** are the subject of this study. Analyzing large number of water samples from various sources would require large volume of hazardous chemicals to be used as solvents. In order to avoid further polluting by these chemicals, this portion of investigation requires to be carried out by solid phase extraction, SPE, instead of concentrating the water samples. In SPE method one liter of drinking water sample would pass through a cartridge, 6-cm tube containing 100-mg of silica gel coated with c-18 to adsorb organic contaminants. The adsorbed materials would be extracted by 5-mL of methylene chloride and 5-mL of ethyl-acetate.

This work primarily concerns investigation on container tube material used for solid-phase extraction (SPE) cartridges for assaying semi-volatile organic compounds (SVOCs) in drinking water. Five different brands of cartridges each with 1000-mg silicate particles coated with C-18 organic adsorbents with polypropylene tubes have been tested. Two of those cartridges were from Burdick & Jackson, two from Alltech Associates, Inc., and one from Agilent Technologies. During sample collection, to each sample 40-50 mg of solid sodium sulfite was added for dechlorination purpose; the pH of the samples were adjusted to < 2 at the sampling site with 6 N hydrochloric acid to retard microbiological degradation. Samples were collected in amber glasses, iced, kept in the dark and refrigerated at 4°C before use. Ethyl acetate, methylene chloride, and methanol were used to pre-wash the cartridges; ethyl acetate and methylene chloride were used to elute the cartridges after passing 1.0 L of water during two hours under 5-in vacuum as described by EPA-Method 525.2. Our studies indicates that the above mentioned cartridges are not quite suitable to be used for SPE because of leaching various types of phthalate esters, silicon compound and other plasticizers from the barrel materials that make analysis unreliable.

However, we have also tested water samples with cartridges with the same C-18 organic adsorbents prepared using 6-mL glass, instead of polymer, tubes with Teflon frits. This kind of cartridges also produced chromatogram for separating semi volatile organic compounds essentially similar to those of polymer type. Consequently, we might conclude that those extraneous peaks are produced mainly from C-18 materials not from the barrel and all the cartridges should be treaded before use.

Introduction

The source of household water for the most rural areas of South Carolina, especially, Orangeburg County is the local wells. This investigation has concentrated on semi-volatile organic compounds, SVOC, which constitute a major series of pollutants in rural areas of South Carolina.

The main source of these types of pollutants is petroleum products from nearby service stations, herbicides, insecticides, septic tanks, and chemical spills. In rural areas the number of service stations, and chemical spills are very much limited and rare which primarily eliminates this category of pollutants from our list.

Semi-volatile organics including, pesticides, insecticides, and herbicides are used locally and abundantly, therefore the drinking groundwater pollution could be extensive resulting form the seeping of these chemicals in water sources. Toxic herbicides that are quite hazardous to human health are used extensively in agriculture. The study of semi-volatile organics seems to have urgency and importance because of the abundance and proximity of the toxic material with the drinking water sources.

Responsibility (PSR) states that more than 14 million people in the US routinely drink water that is contaminated with carcinogenic herbicides. The report, entitled *Tap Water Blues*, investigates the Midwest, Louisiana, and the Chesapeake Bay regions for contamination by five of the most commonly used herbicides in the United States — alachlor, metolachlor, atrazine, cyanazine and simazine. The study finds contamination, often by two or more of the herbicides, in the drinking water of all three regions. In addition, at least 90% of all US municipal water treatment facilities lack the proper equipment to remove these chemicals. In fact, there is no enforceable standard at all for cyanazine, the most toxic of the five herbicides. Sometimes herbicides seep into the ground water system; causing contamination of which the long term effects are not known.

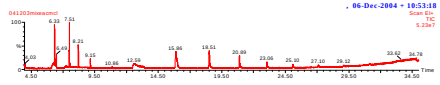
According to the EPA report, all of the surface streams and nearly half of the wells in the US were contaminated by agricultural pollutants in 1990. At some time during 1993 and 1994 one of every five Americans turned on their taps and drank water that was contaminated with feces, radiation, lead, or dangerous parasites. One hundred million Americans live in areas that fail to meet standards set by the Clean Water Act.

Herbicides also cause trouble for wildlife and humans, and cause massive fish kills. Every spring, 150 million pounds of atrazine, cyanazine, simaxine, alachlor, and metoalachlor are applied to soybeans and corn growing in the Corn Belt. Rains and irrigation carry a significant portion of these chemicals into the drinking water of residents. The manufacturers of these chemicals admit that these five chemicals cause nine different types of cancer, myriad birth defects, and genetic mutations. Despite this knowledge, legally allowable levels of contamination have been set only for atrazine, alachlor, and simazine. Any level of contamination by either metoalachlor or cyanazine, no matter how high, is legal.

Experimental Summary for Solid Phase Extraction Method

In the SPE method one liter of drinking water sample would pass through a cartridge, 6-cm tube containing 1000-mg of silica gel coated with C-18 that adsorbs organic contaminants. During this operation the system is brought to a relative vacuum (about 5 inches of mercury) to enable the passage of the water from cartridge to be done in two hours. The adsorbed materials would be extracted by 5-mL of methylene chloride, 5-mL of ethyl-acetate, and 10-mL of methanol. Then the extracted sample would be concentrated to about 0.50-mL which is then injected to GC column to be seoerated and detected by mass spectrometer. The procedure allows for qualitative detection only.

Results and Discussion



Chromatogram for the extracts produced using pure water from Allteck Cartridge. These peaks are the result of triply distilled water with the cartridge. The following is the identified substances all of which are silicates leached from packing material.

Cyclotrisiloxane, hexamethyl-
Formula: C6H18O3Si3
MW: 222 CAS#: 541-05-9
NIST#: 52163 ID#: 18595

Cyclotetrasiloxane, octamethyl-
Formula: C8H24O4Si4
MW: 296 CAS#: 556-67-2
NIST#: 52164 ID#: 20255

Cyclopentasiloxane, decamethyl-
Formula: C10H30O5Si5
MW: 370 CAS#: 541-02-6
NIST#: 163612 ID#: 20952

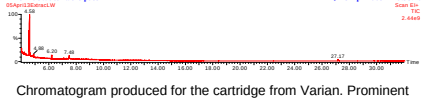
Cyclohexasiloxane, dodecamethyl-
Formula: C12H36O6Si6
MW: 444 CAS#: 540-97-6
NIST#: 52166 ID#: 27931

Cyclooctasiloxane, hexadecamethyl-
Formula: C16H48O8Si8
MW: 592 CAS#: 556-68-3
NIST#: 144324 ID#: 7428

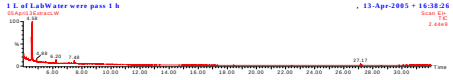
Cyclononasiloxane, octadecamethyl-
Formula: C18H54O9Si9
MW: 666 CAS#: 556-71-8
NIST#: 144326 ID#: 7272

Tetracosamethyl-cyclododecasiloxane
Formula: C24H72O12Si12
MW: 888 CAS#: NA
NIST#: 146517 ID#: 66337

Heptasiloxane, 1,1,3,3,5,5,7,7,9,9,11,11,13,13-tetradecamethyl-
Formula: C14H44O6Si7
MW: 504 CAS#: 19095-23-9
NIST#: 153847 ID#: 27374



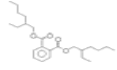
Chromatogram produced for the cartridge from Varian. Prominent substances that are encountered are silicon compounds. These impurities are also of silicate types, the results of analysis are omitted for the sake of brevity.

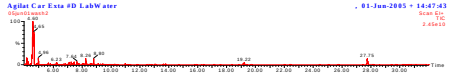


Chromatogram for the extract materials using another type of Cartridge batch called high-rate from Alltech. Other types of substances found are represented bellow:

Tris(trimethylsilyl)borate
Formula: C9H27BO3Si3
MW: 278 CAS#: 4325-85-3
NIST#: 79575 ID#: 27488

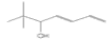
Bis(2-ethylhexyl) phthalate
Formula: C24H38O4
MW: 390 CAS#: 117-81-7
NIST#: 43511 ID#: 66784



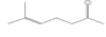


Chromatogram of the extract materials from the Cartridge acquired from Agilent.

6,6-Dimethyl-1,3-heptadien-5-ol (7.23 min)
Formula: C9H16O
MW: 140 CAS#: NA
NIST#: 197370 ID#: 17263



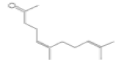
5-Hepten-2-one, 6-methyl- (7.64 min)
Formula: C8H14O
MW: 126 CAS#: 110-93-0
NIST#: 230027 ID#: 1426



Nonanal (8.26 min)
Formula: C9H18O
MW: 142 CAS#: 124-19-6
NIST#: 159565 ID#: 823

Decanal (8.80 min)
Formula: C10H20O
MW: 156 CAS#: 112-31-2
NIST#: 108131 ID#: 4347

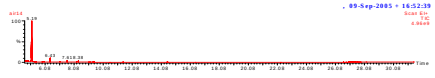
5,9-Undecadien-2-one, 6,10-dimethyl-, (Z)-
Formula: C13H22O
MW: 194 CAS#: 3879-26-3
NIST#: 141210 ID#: 1427



1,3,5-Cycloheptatriene, 2,4-di-t-butyl-7,7-dimethyl- (13.77 min)
Formula: C17H28
MW: 232 CAS#: NA
NIST#: 160925 ID#: 17895

Dodecyl acrylate (14.70 min)
Formula: C15H28O2
MW: 240 CAS#: 2156-97-0
NIST#: 221502 ID#: 3382

4,8,12-Tetradecatrienal, 5,9,13-trimethyl- (17.13 min)
Formula: C17H28O
MW: 248 CAS#: 66408-55-7
NIST#: 163016 ID#: 22387

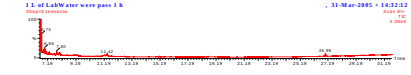


Chromatogram produced from the extracts of Burdick & Jackson cartridge with pure water. Beyond silicates, it contains the following:

Propanoic acid, ethyl ester
Formula: C5H10O2
MW: 102 CAS#: 105-37-3
NIST#: 107280 ID#: 467

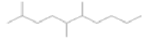
n-Propyl acetate
Formula: C5H10O2
MW: 102 CAS#: 109-60-4
NIST#: 230707 ID#: 5952

1,2-Benzenedicarboxylic acid, butyl octyl ester
Formula: C20H30O4
MW: 334 CAS#: 84-78-6
NIST#: 70709 ID#: 15542



Chromatogram for the extract materials of cartridge purchased from Varian after passage of one liter of pure water.

Decane, 2,5,6-trimethyl-
Formula: C13H28
MW: 184 CAS#: 62108-23-0
NIST#: 61640 ID#: 16364

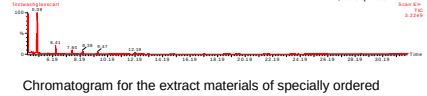


Butylated Hydroxytoluene
Formula: C15H24O
MW: 220 CAS#: 128-37-0
NIST#: 249081 ID#: 18504

1,3-Dioxolane-2-heptanenitrile, .alpha.-methyl-.delta.-oxo-2-phenyl-
Formula: C17H21NO3
MW: 287 CAS#: 58422-90-5
NIST#: 66371 ID#: 66897

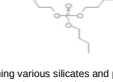
Heptadecane, 2-methyl-Formula: C18H38MW: 254 CAS#: 1560-89-0
NIST#: 68905 ID#: 1679

Decane, 2,4,6-trimethyl-
Formula: C13H28
MW: 184 CAS#: 62108-27-4
NIST#: 61644 ID#: 5615



Chromatogram for the extract materials of specially ordered cartridge with glass tube with one liter of water, purchased from Supelco. A new substance appeared among these peaks.

Tributyl phosphate
Formula: C12H27O4P
MW: 266 CAS#: 126-73-8
NIST#: 125110 ID#: 10723



CONCLUSIONS

All kind of cartridges are producing unwanted contaminants by leaching various silicates and phthalate esters making the analysis very difficult if not impossible. In order to use SPE Method, one has to deal with this problem before using these cartridges, otherwise the results of analysis would be doubtful. Also, the results show that the cartridge with a glass barrel produce somewhat less organic contaminates than those of others, this could be an indication that source of some of this kind of contaminates could be the barrel itself.