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Analysis of volatiles and semivolatiles in drinking water by microextraction and thermal desorption

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Abstract

A new technique to analyze aqueous samples for nanograms per liter levels of volatile and semivolatile compounds using microextraction and thermal desorption into a gas chromatograph/ion trap mass spectrometer (GC/MS) is described. This method is inherently sensitive (50 mL of aqueous sample is extracted prior to each desorption), uses no solvents, and detects volatiles and semivolatiles in the same analysis. Aqueous standards and environmental samples are pumped through a length of porous-layer open-tubular capillary column, which is then thermally desorbed onto a 30 m × 0.25 mm i.d. analytical column interfaced to an ion trap mass spectrometer for subsequent separation and detection. Sharp chromatographic peaks and reproducible retention times (RT) were observed. Replicate injections of surrogates ($n = 6$) averaged 32.6% R.S.D. Analysis of domestic tap water detected 55 analytes, some at the low-nanograms per liter level, and detected 3 halogenated ethenes, not previously reported in drinking water. Analysis of an aqueous sample from a municipal ground water source detected the presence of numerous semivolatile compounds at trace-levels.
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Keywords: Microextraction; Thermal desorption; Drinking water

1. Introduction

The development of simpler, faster, and less costly methodologies for the analysis of pollutants is a part of the mission for the U.S. Environmental Protection Agency (EPA) and especially the Office of Research and Development (ORD) [1–3]. For example, more sensitive methods for quantifying pharmaceuticals and personal care products (PPCPs) [4] are needed. Method development is an ongoing process within ORD and is a vital element to maintain confidence in EPA's ability to assess risk or formulate effective remedial strategies if needed for newly recognized pollutants.

This manuscript describes a new technique, large-volume-extraction thermal-desorption gas chromatograph/ion trap mass spectrometer (LVE-TD-GC/MS). This technique has evolved from solid phase microextraction (SPME) [5]. SPME uses a coated fiber to extract organics from aqueous solutions (generally 10–20 mL). The fiber is then desorbed directly for analysis by gas chromatography coupled with mass spectrometry. The polarity of the SPME fiber can be varied depending on the analytes of interest. SPME can be automated. This is a mature technique for qualitative and quantitative analysis. In contrast, microextraction with thermal desorption typically extracts 50 mL of sample prior to desorption. The thermally desorbed tubular trap, depicted in Fig. 1, contains a styrene–divinyl benzene polymer to effect extraction.

GC/MS has been an EPA stalwart technology for over three decades. Recent innovations in ion trap technology have increased GC/MS sensitivity and utility. Ion traps can now perform tandem mass spectrometry to make sample "clean-up" possible by preferentially trapping target analyte ions and expelling background or matrix ions from the manifold [6,7]. The added sensitivity has made analysis of samples without pre-concentration possible [8,9]. Typically, ion trap mass spectrometers can identify picogram quantities in the full scan mode. With this technique it is now possible to analyze at the parts-per-trillion (ppt) level.

This technique is amenable to the analysis of volatile components in water such as disinfection by-products (DBPs) found in drinking water. The first analysis of volatiles in drinking

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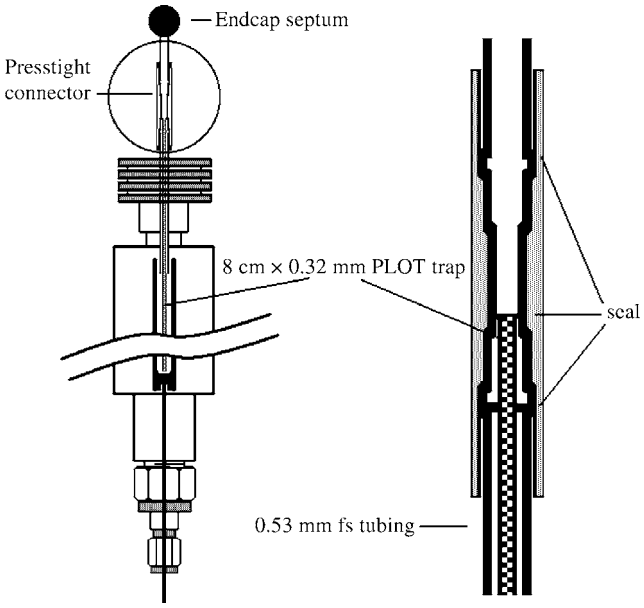

Fig. 1. Schematic of modified split/splitless injector.

water was performed by Bellar and Lichtenberg [10] using purge and trap technology. They found four major components, being the trihalomethanes: chloroform, dichlorobromomethane, dibromochloromethane, and bromoform. These DBPs represent the highest levels of contaminants found in drinking water.

One other EPA method involved using vacuum distillation (VD) [11]. The sample is analyzed by vacuum distilling it for volatile analysis. One attribute of VD is its ability to analyze other difficult matrices besides drinking water such as fish tissue, milk, sediment, bark, leaves, and soil.

More recently, EPA researchers [12–15] have found lower levels of these type of volatile halogenated compounds in drinking water. These include halogenated ethanes, ethenes, and propanes. Chlorination and ozonation are used to treat water to remove bacterial contamination. In the Las Vegas area, ozonation [16] has been instituted to lower the level of toxic trihalomethanes produced by chlorination. Some chlorinated DBPs remain in potable water because a residual amount of oxidant is maintained in the water distribution system. Other DBPs are produced by ozonation, such as carboxylic acids, aldehydes, and aldoketoacids [17]. The purpose of the research described here was to increase the ease, number, and type of analytes that can be detected and quantified in a workday.

2. Experimental

2.1. GC/MS instrumentation

A Finnigan (Sunnyvale, CA) GCQ gas chromatograph was interfaced to an ion trap mass spectrometer, which had been modified with turbo-molecular pump and high temperature source upgrades. Instrument control and data acquisition was accomplished using Navigator© software. The separation column was a Phenomenex (Torrance, CA) Zebron 30 m × 0.25 mm ZB-5 fused silica capillary column coated with a 0.25 μm film of bonded 5% phenyl polysiloxane liquid phase. The end of the analytical column was inserted directly into the vacuum manifold. These capillary column dimensions maintained helium flow into the manifold to the manufacturer recommended 1.0 mL/min. The ion trap detector was scanned from 48 to 400 Da at 0.6 scan/s (each scan is an average of 4 μscans) with the source temperature at 220 °C, no solvent delay, and a −50 mmu/100 amu mass defect. A Windows NT™ personal computer controlled the autosampler, GC, and MS acquisition. After a 1-min hold, at 40 °C, the GC oven temperature was programmed from 40 to 280 °C at 10 °C/min with a final hold of 1.0 min (total run time 26 min). The initial helium flow was set to zero so that the analytes were not forced out of the injector. Helium flow was resumed after trap insertion. The linear velocity was set to 50 cm/s in the constant flow mode using the GC's electronic pressure control. The transfer line was held at 280 °C. The modified split/splitless injector (see Fig. 1) with a Restek direct injection insert (catalog number 21390-214.1) was held at 280 °C with a split rate of 40 mL/min. The injector was run in the splitless mode from 0 to 0.2 min.

2.2. Aqueous extraction

Aqueous duplicate extractions were performed using a dual position Harvard (Cambridge, MA) Model 22 syringe pump. A 50-mL Hamilton (Reno, NV) gastight syringe was filled with the water sample to be extracted and run at 1000 μL/min (50 min run time) through a trap consisting of an 8 cm × 0.32 mm i.d. × 10 μm film thickness Chrompack (Varian, Walnut Creek, CA) porous-layer open-tubular capillary column (CP-PoraPLOT Q-HT). This trap solid phase consisted of styrene–divinyl benzene and this was chosen because it worked well on the volatiles and semivolatiles standards. There was more surface area for contact of the analytes with the column bed aiding extraction. This gave adequate results and no further investigation was done.

The syringe was fitted with a stainless steel Hamilton needle (catalog number 90020) inserted into a 5-cm length of 2 mm o.d. Teflon tubing. The trap was connected to the needle and sealed to the sample flow using stainless steel Swagelok fittings. The trap was dried by pulling 5 mL of air back through the trap with the syringe plunger immediately after extraction. The trap was then removed, wiped with a Kimwipe, and inserted into the injector prior to thermal desorption. A 5-μL methanolic solution containing surrogate compounds at 10 ng/μL (aqueous concentration of 1 ppb) was injected directly into the syringe containing the water sample prior to extraction.

Reagent water (18 MΩ cm resistivity) was obtained from a Barnstead NANOpure ultrapure water filtration system (Barnstead International, Dubuque, WI).

2.3. Injector modification and trap desorption

The injector, as seen in Fig. 1, was modified by inserting an 8-cm length of megabore fused silica tubing through the inlet septum. The tubing was inserted through the septum using a

syringe with the fused silica encased over 5-cm, 26 gauge needle. The top of the tubing was sealed with an endcap fabricated by coupling a Restek (Bellefonte, PA) Universal Presstight Connector (catalog number 20400) to a piece of megabore column plugged with a septum.

The PLOT trap containing the extracted analytes and surrogates was inserted into the modified injector by placing the endcap over the distal end of the trap thereby introducing the trap into the heated injector for desorption. Care was taken to avoid contaminating the exterior of the trap before injection by handling the trap with disposable gloves. The trap was removed at the end of the analysis and discarded. Used traps have been redesorbed and have shown no significant levels of contamination. Inverted redesorbed traps showed that approximately 30% of material remained since only 6 cm of the 8 cm trap were actually in the heated zone.

2.4. Preparation of standard solutions

Standards of the surrogate compounds were Supelco-certified: pentafluorobenzene (catalog number 4-8945) and acenaphthene-d10 (catalog number 4-8093). Standards were Supelco-certified: 8270 A and B base-neutrals mix (catalog numbers 4-8470 and 4-8195), 8260 volatiles calibration mix (catalog number 5-00607), and EPA 8270A phthalate esters mix (catalog number 48805-U). All purities were certified to be 97.6% pure or greater. The stock solutions were diluted to 10 ng/μL in methanol within 1.8 mL on autosampler vials using a syringe and stored at 4 °C until needed.

3. Results and discussion

Analysis of drinking water detected 122 compounds, of which 55 were found only in the sample and not in the distilled water blank. The vast majority of the compounds comprised volatile disinfection by-products, halogenated methanes, ethenes, and ethanes. Only three of the compounds were semivolatiles, defined as compounds that eluted after 2-methyl naphthalene. Many tentative identifications were made in both the sample and the blank using the NIST library provided as part of the data system. Dirty blanks made identification of sample analytes more difficult (see Fig. 2). The contaminating compounds were associated with the process of trap injection (either compounds that adhered to the outside of the trap or injector contamination) or with lab air contamination. Trap insertion caused the reintroduction of previously observed analytes that had been cold trapped on the Helium inlet and outlet lines when the trap was desorbed. These compounds were resolvated when the wet trap was placed into the injector. A needle injection does not introduce these compounds into the analyses. These compounds included low levels of phthlates, free fatty acids, polychlorinated biphenyls (PCBs), pesticides, and other semivolatile compounds. This made it necessary to run numerous blanks. When trap controls were run, it was determined that the trap also introduced its own compounds from its liquid phase, including alkylated benzaldehydes, alkylated benzenes, and styrene.

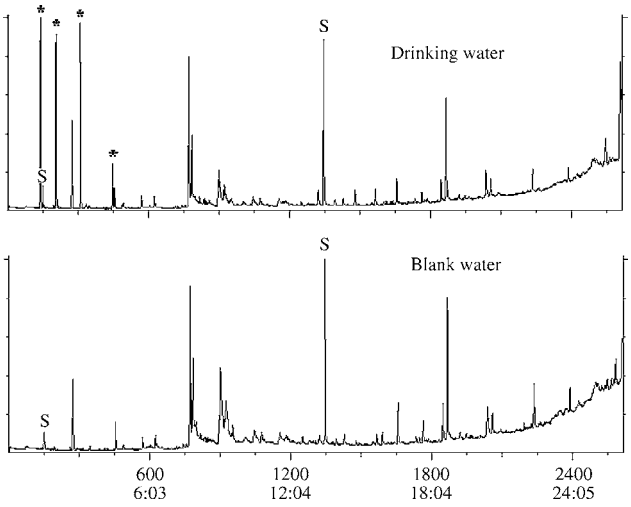

Fig. 2. Dual gas chromatograms of drinking water and blank water (surrogates (S) and 4-trihalomethanes (*)).

The advantages of LV-TD-GC/MS are: the traps were made from 8 cm lengths of a 30 m PLOT column (inexpensive, costing less than a dollar) and in this study were used once and discarded; the sensitivity was better since 50 mL of water was extracted compared to 20 mL of sample per SPME analysis. One feature of the apparatus for this method is that the parts are found in most chemistry laboratories, making it easy for chemists to construct their own LV-TD-GC/MS. The trap was chosen because it worked well on the volatiles and semivolatiles standards. There was more surface area for contact of the analytes with column bed aiding extraction. This gave adequate results and no further investigation was done. The injector could only accommodate 8 cm traps. If a shorter trap were used, the chemist would not be able to easily retrieve the desorbed trap. Also the trap can be inverted and desorbed as a replicate run.

3.1. Criteria of identification of analytes

In Table 1 are listed 55 analytes found in drinking water. It was not possible to obtain certified standards for all of the compounds listed. As noted, many of these are tentatively identified using mass spectral library searches, boiling points (BP), and mass spectral interpretation. Boiling points are a useful indicator because they correlate well with retention times (RT, see Fig. 3). Often, this is a good way to ascertain whether a compound's identification is reasonable. In the figure, the outliers (×) indicate implausible identifications based on boiling point. These were not included in the 55 analytes. The polar compounds (◯), such as halogenated acetonitriles, benzoic acid, and nitriles, elute before non-polar compounds, with the exception of bromodichloroacetonitrile, because the column has low polarity and therefore the polar compounds are not retained as long. The retention times of the certified standards (●) and the compounds identified by library searches or mass spectral interpretation (△) fall near the BP versus RT curve. Three compounds that were identified by mass spectral interpretation, tribro-

Table 1
List of 55 chemicals found in tap water using microextraction and thermal desorption

No.	Compound name	Note[a]	*m/z*	Retention time (min:s)	Boiling point (°C)	Average response ($n = 6$)	% R.S.D.	Conc.[b] (ng/L)
1	Pentafluorobenzene (surr)	1	168,99	01:28	85	468114	22.7	1000
2	Acenaphthene-d10 (surr)	1	164,162	13:31	279	1375978	42.6	1000
3	Bromomethane	2	96,94	00:43	4	1136	116.4	1
4	Methylene chloride	1	49,47	00:46	40	8474	148.1	9
5	*trans*-1,2-Dichloroethene	1	96,61	00:58	48	1927	106.7	2
6	Carbon disulfide	2	78,76	01:02	46	605	128.5	1
7	Chlorobromoethene	4	142,140	01:16		617	75.4	1
8	Bromochloromethane	1	130,128	01:20	68	553	70.4	1
9	Chloroform	1	85,83	01:20	61	1777848	34.8	1928
10	Benzene	1	78,77	01:38	80.2	3156	46.9	3
11	Carbon tetrachloride	1	119,117	01:38	76.5	4879	30.9	5
12	Trichloroacetonitrile	2	110,108	01:45	85.7	791	127.1	1
13	Dibromomethane	1	174,93	02:00	97	922	51.5	1
14	Bromodichloromethane	1	85,83	02:01	90.1	1540601	36.5	1671
15	Dichloroacetonitrile	2	82,74	02:06	112	11518	44.2	12
16	Propanenitrile	2	55,54	02:12	97	4578	41.4	5
17	Dichloronitromethane	2	85,83	02:27		4898	118.9	5
18	Toluene	1,3	92,91	02:42	109	48383	63.5	52
19	Trichloronitromethane	2	119,117	02:53	112.4	6743	133.5	7
20	1,1-Dichloro-1-nitroethane	2	97,61	02:58	125	936	57.4	1
21	Dibromochloromethane	1	129,127	03:00	120	1611462	72.6	1748
22	Tetrachloroethene	1,3	166,164	03:17	121.1	2515	47.5	3
23	Bromochloroacetonitrile	2	155,74	03:20	138	13208	75.1	14
24	Dichloroiodomethane	2	127,83	03:30	132	9128	60.3	10
25	1,1,1-Trichloro-2-propanone	2	97,83	03:47	135.7	1580	80.3	2
26	2-Chloro-2-nitropropane	2	97,77	03:57	132	2584	132.7	3
27	Ethylbenzene	1,3	106,91	04:05	136	10125	42.8	11
28	*p*-Xylene	1,3	106,91	04:12	138.5	13886	87.9	15
29	*m*-Xylene	1,3	106,91	04:12	138	13886	87.9	15
30	1,2-Dibromo-1-chloroethane	2	143,141	04:20	158.8	739	105.7	1
31	*o*-Xylene	1,3	106,91	04:27	144	11220	26.3	12
32	Bromoform	1	173,171	04:27	145.5	356327	33.6	386
33	2,3-Dibromopropanenitrile	2	134,132	04:30	173	921	41.7	1
34	Dibromodichloromethane	2	163,161	04:31	150.2	1218	133.2	1
35	Styrene	1,3	104,78	04:33	145.2	100610	21.2	109
36	Dibromochloroacetonitrile	2	154,152	04:41	118.2	1509	117.5	2
37	Bromotrichloroethene	2	210,208	04:48	133.2	1828	35.6	2
38	Dibromoacetonitrile	2	120,118	04:54	163.1	13126	37.1	14
39	Bromochloroiodomethane	2	129,127	04:57	157.4	14861	37.7	16
40	1,2-Dibromo-2-methylpropane	2	136,134	05:29	150	1691	35.6	2
41	1,3,5-Trimethylbenzene	1,3	120,105	05:44	162	117503	37.1	127
42	1,1,1-Tribromoethane	2	187,185	05:51	152.5	624	141.9	1
43	Benzonitrile	2	103,76	06:08	190.7	5517	29.6	6
44	Tribromochloromethane	2	209,207	06:16	158.5	225	129.0	0
45	Dibromodichloroethene	4	254,252	06:28		1596	24.5	2
46	Dibromoiodomethane	2	198,173	06:29	185.9	6259	37.1	7
47	1,4-Dichlorobenzene	1,3	148,146	06:35	174	2686	34.5	3
48	Hexachloroethane	2	201,166	07:36	189	3577	42.3	4
49	Carbon tetrabromide	2	253,251	08:03	190	886	141.9	1
50	Tribromochloroethene	4	300,298	08:08		704	26.4	1
51	Benzeneacetonitrile	2	117,90	08:38	234	78511	21.1	85
52	1,2,4-Trichlorobenzene	1	182,180	09:15	214.4	235	133.2	0
53	Naphthalene	1,3	128,102	09:22	217.9	12474	84.1	14
54	2-Methylnaphthalene	1,3	142,141	11:00	241	6575	41.3	7
55	Hexachlorocyclopentadiene	2	272,237	11:34	239	6926	69.5	8
56	Pentachlorobromocyclopentadiene	2	237,235	12:55	256.6	4601	63.4	5
57	4-Ethoxy benzoic acid ethyl ester	2	191,124	13:59	275	2319	38.7	3

[a] *Notes*: 1, certified standard available; 2, plausible identification based on library search and boiling point; 3, air contaminants (see References); 4, plausible identification based on mass spectral interpretation.
[b] Estimated concentration (see Section 3).

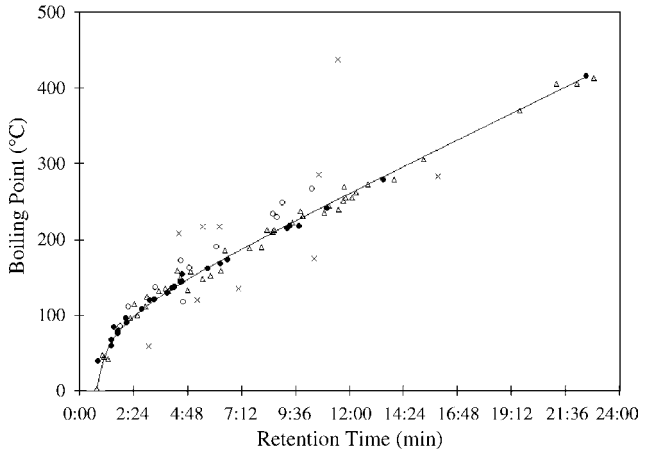

Fig. 3. Graph of 122 potential water contaminants, boiling point (°C) vs. retention time (min). (●) Certified standards; (◯) polar compounds; (△) plausible identifications based on library searches; and (×) implausible identifications (see Section 3).

mochloroethene, *cis*- or *trans*-dibromodichloroethene, and an isomer of chlorobromoethene have not been previously reported in drinking water. The spectrum of the tentatively identified tribromochloroethene (monoisotopic ion at *m*/*z* 296) contained a characteristic tribromochloro cluster at *m*/*z* 296, 298, 300, 302, and 304 and the tentatively identified spectrum of the dibromodichloroethene (monoisotopic ion at *m*/*z* 252) contained a characteristic dibromodichloro cluster at *m*/*z* 252, 254, 256, and 258. The spectrum of chlorobromoethene (monoisotopic ion at *m*/*z* 140) is shown in Fig. 4.

In Table 1 are listed retention times, quantitation ions (*m*/*z*), average response ($n = 6$), % relative standard deviation (%R.S.D.), estimated concentration based on average response factor of two surrogates, and boiling points. The four trihalomethanes gave the highest response (see Table 1), while the other disinfection by-products were much lower in concentration, demonstrating the wide concentration range that is quantifiable using this method. The %R.S.D. of the surrogates was 22.7% for pentafluorobenzene and 42.6% for acenaphthene-d10.

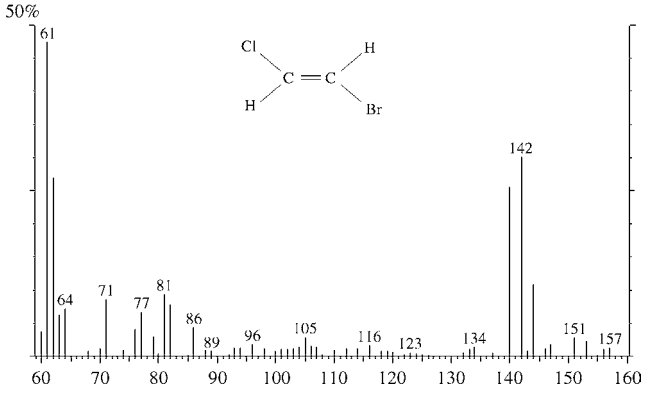

Fig. 4. Tentative identification of novel disinfection by-product found in drinking water. This analyte, *trans*-chlorobromoethene, has not previously been reported in drinking water.

A distilled water blank was run concurrently with each sample. A statistically significant difference in recoveries between surrogates in the sample versus the blank was apparent and makes quantitation problematic. This may be due to the difference in ionic strength between the drinking water and the distilled water blank, affecting the extraction of the surrogates from water. Attempts to equalize the ionic strength using sodium chloride were not successful.

An analysis of a municipal groundwater source detected several halogenated compounds at trace-levels. These included an isomer of 3-bromo-4-methoxyphenylacetonitrile, chloroalkyl phosphates (both flame retardants) [17], and three structurally similar tribrominated compounds: a phenol, an aniline, and an anisole.

The method is rapid, inexpensive, easily applied, and inherently sensitive. It can concurrently detect and semiquantitate both volatile and semivolatile components. These characteristics make it a useful screening tool for drinking water pollutants. Performing a slower extraction (overnight) did not significantly improve recoveries. The 8-cm, porous-layer open-tubular trap has a large surface area, a 10-μm film thickness, and can therefore accommodate analytes from a large amount of sample (although recoveries are not quantitative).

The method has several weaknesses. The blanks are dirty. Reproducibility was difficult. The technique's irreproducibility stemmed from the inability to quantitatively desorb the extracted material onto the analytical column. When the trap was placed in the injector, the analytes are heated rapidly and a portion of the sample escapes before the trap was sealed to the atmosphere. An on-column programmable injector would solve this problem since the injector could heat and elute the analytes after it is placed and sealed in the injector.

Memory effects can be a problem. Low concentrations of standards can appear in subsequent analyses unless the syringes are adequately cleaned. Recoveries are low. In the future, design changes may improve the method.

4. Summary

- A new analytical technique was developed and used to identify 55 compounds in a domestic drinking water supply.
- Literature searches indicated that three of the volatile organic compounds were not previously found in drinking water, and were tentatively identified.
- Boiling point data were used to eliminate several erroneous identifications.
- The analysis of a ground water source revealed the presence of trace-levels of several halogenated semivolatile components.
- This apparatus can be easily cobbled from parts found in most labs and is inexpensive.

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