



Project Summary

Determination of Volatile Organic Compounds in Soils Using Equilibrium Headspace Analysis and Capillary Column Gas Chromatography/Mass Spectrometry—Evaluation of the Tekmar 7000 HA Analyzer

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Existing methods for determination of volatile organic compounds (VOCs) in soil matrices using the purge and trap technique with gas chromatography/mass spectrometry (GC/MS) have several problems, which include preserving sample integrity from collection to analysis and efficiently extracting a broad spectrum of VOCs from the soil matrix. This investigation was undertaken using the Tekmar 7000 headspace autosampler to evaluate its ability to resolve these problems. The objective of this study was to optimize analytical conditions and then to study the efficiency of the headspace technique to extract VOCs from soils. Variations of sample preparation procedures were studied, and method analytes were identified and measured using internal standard calibration GC/MS. Using these data, relative standard deviations and percent recoveries are reported for 59 analytes in four different types of soil matrices: sand, clay, garden soil, and hazardous waste landfill soil. The most accurate and precise results are obtained with sand. Method detection limits (MDLs), ranging from 0.2 to 7.9 $\mu\text{g}/\text{kg}$, were calculated for all analytes, using results of replicate analyses of sand, the matrix that had the least matrix effect. It is concluded that the 7000-HA headspace analyzer can be used to determine VOCs in soils.

This Project Summary was developed by EPA's Environmental Monitoring Systems Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project report ordering information at back).

Introduction

An accurate and precise procedure is needed to effectively remove volatile organic compounds (VOCs) from soils for identification and measurement using gas chromatography/mass spectrometry (GC/MS). Ten years ago, the number of VOCs that could be determined by GC/MS was limited by packed column GC technology. The least volatile compounds included toluene and ethyl benzene. Currently, with capillary column capabilities, the scope of VOCs in aqueous samples has been expanded for a single column analysis to include non-polar compounds with boiling points ranging from -30°C to $>220^{\circ}\text{C}$. Heated purge and trap methodology has also been applied to soil samples using capillary column technology.¹ The results illustrated that many compounds currently determined in water matrices can be included in the list of compounds determined in soil matrices. However, the method was subjected to matrix effects, particularly for those compounds with high boiling points.



In this work, we evaluated the capability of the Tekmar 7000 Headspace Autosampler (7000-HA) to effectively introduce VOCs partitioned from soil matrices into a fused silica capillary column using the static headspace technique. The integral features of the procedure evaluated include sample fortification, different 7000-HA extraction parameters for a wide variety of volatile compounds, and the quantitative capabilities of the method using different soil matrices and different internal standards.

The 7000-HA was chosen for evaluation because of its potential to include the VOCs contained in the headspace of the sample collection vials and extract VOCs from a soil into the gas volume above the sample, as well as its ability to permit analysis with a minimal amount of sample preparation. The analytes used for the evaluation and their characteristic ions are listed in Table 1. The results of this evaluation are discussed in the following sections of this report.

Experimental Approach

Each sample was prepared by adding 5.0 g of a soil matrix to a 20-mL 7000-HA crimp-seal glass headspace vial. In rapid succession, each soil sample was fortified with the target analytes in methanol, the matrix modifier solution (MMS) was added, and the vial was sealed. The purpose of the matrix modifier solution was to increase the efficiency of the headspace analysis by providing a salting-out effect and to minimize dehydrohalogenation reactions through pH adjustment.² The vials were placed in the autosampler carousel and maintained at room temperature. Approximately 1 h prior to analysis, the individual vials were moved to a heating zone and allowed to equilibrate for 50 min at 85°C. The sample was then mixed by mechanical vibration for 8 min while the temperature was maintained at 85°C. The autosampler then raised the vial causing a stationary needle to puncture the septum and pressurize the vial with helium at 7.5 psi. The vial was allowed to pressure equilibrate for a 0.10 min to ensure complete mixing of the pressurization gas with the vial headspace. The pressurized headspace was then vented through a 2-mL sample loop to the atmosphere for 15 sec. In this manner, a representative volume of headspace was isolated within the loop. Finally the carrier gas, at a flow rate of 9.5 mL/min, backflushed the sample loop, sweeping the sample through the heated transfer line into the GC/MS system for separation, identification, and measurement of the method analytes.

Parameters studied were

1. Precision of the Tekmar 7000 Headspace Autosampler
2. Selection of the Matrix-Modified Solution
3. Verification of the Fortifying Procedure
4. Assessment of Analyte Recoveries Using the Matrix Modifying Solution
5. Analyte Recoveries From Various Soil Matrices
6. Analyte Recoveries From Various Soil Matrices Using Internal Standard Calibration
7. Different Headspace Volume Recovery

Results and Discussion

Replicate analyses of fortified samples showed the headspace analyzer to be reproducible for all 59 analytes tested in aqueous matrices. Only one relative standard deviation (RSD) was in excess of 13 percent. The RSDs were comparable to those obtained using standard purge and trap technology. Results from experiments to evaluate the use of a matrix-modified solution to increase the recovery of the analytes from a solid matrix showed that a saturated solution of sodium sulfate was the most suitable. Replicate analytes of fortified soils showed this solution produced the highest recoveries of most compounds and the lowest relative standard deviations.

Analyte recoveries from various types of soils were studied using both the external standard and the internal standard calibration approaches. Four soils were selected: sand, clay, garden soil, and a subsurface soil sample collected near a hazardous waste landfill. Table 1 summarizes the results showing the relative percent recovery obtained from each matrix. These relative percent recoveries were obtained by dividing the peak areas from each analyte by the respective peak areas in a control sample, and multiplying by 100. High ratios are indicative of high recoveries. These data indicate that matrix effects are evident when analyzing certain types of soils.

Figure 1 illustrates recoveries obtained for representative compounds from the analyte list when the headspace volume in the sample vials was varied. Errors are introduced into the analytical results if the headspace volume is not held constant in every vial. This is especially true for the less volatile compounds.

Conclusions and Recommendations

The following conclusions were made from evaluation of study results.

1. The accuracy and precision of the 7000-HA were acceptable when used to determine VOCs in water, the matrix-modifying solution (MMS), and sand. The 7000-HA produced somewhat lower recoveries from other tested soil matrices. However, these lower recoveries were not due to inefficient headspace analysis, but to stronger adsorption capacity of soil. This is the matrix effect. The results obtained with the 7000-HA are equivalent or better than current methodology for volatiles in soil.
2. The matrix fortifying procedure was found to be reproducible for all the compounds evaluated.
3. Comparing recoveries obtained in the different experiments for different matrices, indicated a definite matrix effect.
4. In an attempt to correct for the matrix effect, seven internal standards were evaluated. Results suggest that the use of one internal standard improved data quality but did not completely overcome the matrix effect problem. Adding additional internal standards with chemical and physical properties similar to those of the problem compounds helped resolve this problem.
5. The less volatile compounds, such as trichlorobenzenes, did not appear to be good candidates for accurate measurement using the headspace technique with a single internal standard.
6. Headspace volume had a definite effect on the sensitivity of the method. When headspace volume is decreased, sensitivity increases. This effect is greater as the volatility of the compound decreases.
7. The amount of the matrix-modifying solution added to the matrix had little effect on analyte recovery. The percent difference between experiments was within the experimental error.
8. This work pointed out the definite need to develop a mechanism to collect an exact predetermined sample size and establish the hermetic seal in the field. Until this is done, this method cannot be used to its fullest potential.

Table 1. Relative Analyte Recoveries for Four Matrices

Analyte	MMS/Sand			MMS/Garden			MMS/Horizon-C			MMS/Clay		
	Avg Area	Rsd (%)	Recovery (%)	Avg Area	Rsd (%)	Recovery (%)	Avg Area	Rsd (%)	Recovery (%)	Avg Area	Rsd (%)	Recovery (%)
Dichlorodifluoromethane	164	44	33	161	20	33	94	33	19	753	18	39
Chloromethane	775	10	65	402	37	34	454	22	38	885	4	35
Vinyl chloride	1656	9	67	479	7	19	1330	8	54	1693	3	44
Bromomethane	148	42	89	69	74	42	53	12	32	81	35	43
Chloroethane	600	6	65	103	73	11	476	34	52	410	8	48
Trichlorofluoromethane	3761	6	71	2195	1	42	2969	3	56	2310	4	42
1,1-Dichloroethene	6259	7	78	2840	4	35	5027	2	62	4377	9	47
Methylene chloride	7569	1	85	4330	2	49	6107	5	67	5151	9	65
trans-1,2-Dichloroethene	6001	6	81	1718	9	23	5188	6	70	3703	9	48
1,1-Dichloroethane	9273	5	87	3058	13	37	7318	4	69	5390	13	54
2,2-Dichloropropane	4237	12	73	2749	24	48	4298	4	74	1863	18	40
cis-1,2-Dichloroethene	7051	1	77	1193	63	13	5978	3	66	4208	13	54
Bromochloromethane	5472	3	94	1175	15	20	4421	4	76	3373	14	67
Chloroform	8387	3	88	3235	18	34	6960	2	73	4462	18	55
1,1,1-Trichloroethane	6531	3	89	3387	14	46	5515	5	75	2957	21	47
1,1-Dichloropropene	5909	3	84	2052	12	29	4805	5	68	2853	21	46
Carbon tetrachloride	5549	3	87	2795	19	44	4572	5	71	2424	20	43
Benzene	14743	3	87	5308	7	31	10710	3	63	6658	16	59
1,2-Dichloroethane	9184	3	89	1739	20	17	6381	3	62	5236	16	82
Trichloroethylene	6296	4	81	1885	14	24	5046	4	65	2664	22	47
1,2-Dichloropropane	4802	8	90	1740	15	33	4000	5	75	2629	24	57
Dibromomethane	3533	1	98	745	23	21	2741	1	76	1920	17	68
Bromodichloromethane	7310	3	87	2272	21	27	5891	2	70	3782	23	59
Toluene	19477	4	164	6488	13	16	12893	5	119	6737	31	48
1,1,2-Trichloroethane	3983	4	100	1107	27	28	3145	4	79	2025	24	64
Tetrachloroethylene	3833	11	90	1053	16	25	2604	9	91	946	37	32
1,3-Dichloropropane	6476	7	89	1098	31	15	4793	6	66	3527	23	69
Dibromochloromethane	5574	4	98	1141	31	20	4236	6	74	2263	30	61
1,2-Dibromoethane	4726	3	91	717	24	14	3904	1	75	2058	24	69
Chlorobenzene	11075	4	83	1208	28	9	8006	11	60	3460	38	43
1,1,1,2-Tetrachloroethane	5317	1	92	1043	23	18	3796	4	66	1665	34	51
Ethyl benzene	26235	2	85	4042	20	13	19240	8	62	5726	39	40
p-Xylene	17955	5	103	2634	18	15	11383	19	65	3102	30	33
o-Xylene	22680	3	80	4004	18	14	19003	13	67	4774	38	39
Styrene	8348	7	48	602	79	3	8362	19	48	2006	33	24
Bromoform	3362	8	89	516	24	14	2737	7	72	1192	31	63
Isopropylbenzene	9334	6	87	2118	18	20	6437	11	60	1801	36	27
p-Bromofluorobenzene	NI	-	-	NI	-	-	NI	-	-	NI	-	-
Bromobenzene	17581	6	93	1515	47	8	12394	2	65	4719	37	42
1,1,2,2-Tetrachloroethane	8022	3	95	1902	22	22	6126	4	72	3583	32	57
1,2,3-Trichloropropane	7490	16	80	1377	53	15	642	126	59	4142	29	67
n-Propyl benzene	27107	6	87	3577	21	9	20731	18	53	5033	44	25
2-Chlorotoluene	24763	7	87	1894	64	7	16840	15	59	4145	44	29
4-Chlorotoluene	20877	1	95	1270	30	6	12792	11	5448	3508	44	25
tert-Butylbenzene	20987	7	95	2887	24	13	12863	22	58	2811	43	21
1,3,5-Trimethylbenzene	26847	9	90	3231	13	11	155410	16	52	3494	42	20
sec-Butyl benzene	31773	5	94	3434	18	10	16769	22	48	3188	43	17
1,2-Dibromo-3-chloropropane	4276	6	92	554	64	12	3231	6	70	1684	40	62
1,2,4-Trimethylbenzene	26210		95	4795	10	17	16259	23	59	4222	38	25
1,3-Dichlorobenzene	8182	6	80	422	22	4	5165	15	50	1266	44	23
p-Isopropyl toluene	22003	5	86	2163	21	8	11430	18	45	2287	41	18
1,4-Dichlorobenzene	9024	4	91	564	22	6	5430	15	55	1325	47	23
1,2-Dichlorobenzene-d4	NI	-	-	NI	-	-	NI	-	-	NI	-	-
1,2-Dichlorobenzene	8181	16	86	400	4	4	5459	16	57	1302	47	25
n-Butyl benzene	27107	6	87	2073	24	7	12660	23	41	2667	42	16
1,2,4-Trichlorobenzene	5253	5	75	75	47	1	2687	24	38	473	48	13
Hexachlorobutadiene	3885	6	87	92	27	2	1617	22	36	176	59	9
Naphthalene	16109	7	77	1399	27	7	8811	20	42	2637	44	24
1,2,3-Trichlorobenzene	4641	3	70	88	53	1	2653	24	40	461	50	13

NI = not included

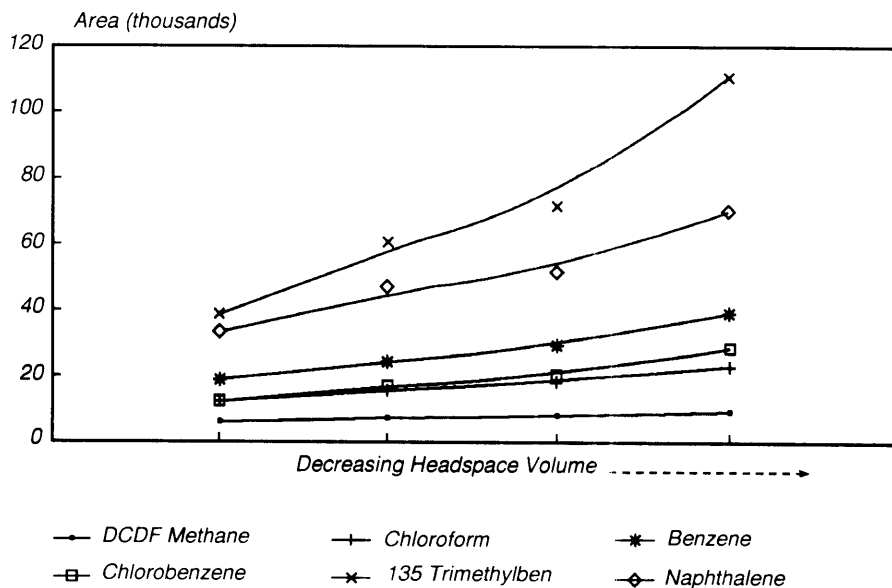


Figure 1. Effect of different headspace volumes on analyte recovery.

The linear dynamic range of this method extends from the MDL of each analyte to approximately 1000 x the MDL. Because vial contents cannot be diluted or subsampled after the vial is sealed without losing headspace, for high concentration samples multiple static headspace analysis techniques² should be investigated to complement the single headspace evaluations reported here. The 7000-HA has the capacity to perform this type of analysis, and further investigation is encouraged. Moreover, work must continue on developing multiple internal standard methods to correct for matrix effects in soil.

References

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2. B.V. Ioffe and A.G. Vitenberg, Headspace Analysis and Related Methods in Gas Chromatography, John Wiley and Sons, 1984.
3. J.W. Eichelberger and W.L. Budde, U.S. EPA Method 524.2, Office of Research and Development, Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry. Revision 3.0, 1989.

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The complete report, entitled "Determination of Volatile Organic Compounds in Soils Using Equilibrium Headspace Analysis and Capillary Column Gas Chromatography/Mass Spectrometry," (Order No. PB93-155992; Cost: \$19.50; subject to change) will be available only from

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