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Project Summary

Capillary Column GC-MS Determination of 77 Purgeable Organic Compounds in Two Simulated Liquid Wastes

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The suitability of purge-trap-desorb (PTD) procedures for determination of 84 volatile organic compounds with capillary column gas chromatography (GC) and mass spectrometry (MS) was evaluated. After collecting GC-MS data not previously available for some analytes, 7 of the 84 compounds were eliminated from further consideration because of poor purging efficiency or analyte stability problems.

For each of the remaining 77 compounds, the linear concentration range and detection limit were determined with data obtained by PTD GC-MS analysis of spiked reagent water. A relative standard deviation (RSD) of ≤25% for the average response factor (RF) was chosen as the acceptance criterion for determining the linear range. This criterion was met over a concentration range of at least two orders of magnitude for 56 of the 77 analytes, 1.5 orders of magnitude for 12 analytes, and 1 order of magnitude for 6 analytes. The criterion was not met for acetone, trichlorofluoromethane, and 2-chloro-1,3-butadiene.

Method performance was assessed by analyzing eight replicate aliquots of each of two simulated liquid waste samples (a municipal sewage sludge leachate and reagent water containing fulvic acid) containing analytes spiked at two concentrations. For >80% of the analytes, bias of measured concentrations was ≤30%. For most other analytes accuracy was >+30%. The observed high positive bias was attributed to enhanced sensitivity caused by high concentrations of ions in the MS source. Calibration data showed that short term (daily) and long term (two weeks) precision was very good.

This Project Summary was developed by EPA's Environmental Monitoring and Support 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

The Resource Conservation and Recovery Act (RCRA) specifies over 200 toxic organic compounds (in Appendix IX to 40 CFR, Parts 264 and 270) to be used to screen for suspected ground water contamination at land-based hazardous waste treatment, storage, and disposal facilities (Federal Register *52*, July 9, 1987, pp. 25942-25953). Analytical methods for most of these analytes are published in SW-846, "Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods," Third Ed., November, 1986).

The SW-846 method recommended for determining volatile, relatively water insoluble, organic analytes is Method 8240, which involves purge-trap-desorb (PTD) analyte extraction followed by packed column GC separation and MS detection and measurement. Advances in GC column technology now permit determination of a wider range of compounds in a shorter time with greater sensitivity using a fused silica or glass capillary column. In this study, a 0.75 mm i.d. glass capillary column was used to

evaluate Method 8240 procedures for 84 analytes. The compounds considered for inclusion in this study include all USEPA Method 524.2 analytes and all compounds on the Appendix IX list (Federal Register, 51, 26639, July 24, 1986) that might be amenable to determination by room temperature PTD extraction followed by GC-MS analysis using a 0.75 mm i.d. glass capillary column.

Experimental

PTD-GC-MS Analyses

Analyses were performed with Method 8240 procedures using a Tekmar Model LSC-2 PTD system, a Carlo Erba Model 4160 GC, a Finnigan Model 3200 MS fitted with a glass jet separator, and an Incos data system with Revision 5.5 software. The PTD system was fitted with a 5-mL fritted glass purge tube and a 305 mm x 4 mm i.d. stainless steel trap containing 10 mm of 3% SP-2100 on Supelcoport, 77 mm of Tenax, 77 mm of silica gel, and 77 mm of coconut charcoal. The system was operated with a helium purge for 11 min at 26 mL/min at room temperature (23-25°C), desorption for 4 min at 15 mL/min at 180°C, and a trap bake for 7 min at 26 mL/min at 180°C. The GC was fitted with a 60 m x 0.75 mm i.d. Supelco VOCOL column coated with a 1.5 μm film and operated with helium carrier gas flow of 15 mL/min. The column temperature was maintained at 10°C during the desorb cycle, programmed to 200°C at 10°C/min at the end of the desorb cycle, and maintained at 200°C for 10 min. The MS was tuned daily to meet bromofluorobenzene (BFB) criteria daily and was operated with a scan time of 1 sec over a mass range of 35-325 amu. The emission current was selected to achieve acceptable tuning and to stay within the emission current range recommended by the manufacturer. For maximum dynamic range, the electron multiplier voltage was set to permit analytes to be detected without saturation of the multiplier at concentrations up to four times the internal standard (IS) concentration of 50 μg/L specified by Method 8240.

The system met all daily performance criteria specified by Method 8240. In addition to BFB tuning criteria, these criteria include (1) minimum RF of 0.30 for each of the five system performance check compounds (chlorobenzene, chloromethane, 1,1-dichloroethane, 1,1,2,2-tetrachloroethane, and tribromomethane); (2) RF difference of $\leq$25% for the six calibration check compounds (chloroform, 1,1-dichloroethene, 1,2-dichloropropane, ethylbenzene, toluene, and vinyl chloride); (3) IS retention time changes of $\leq$30 sec; and (4) IS peak area changes of $\leq$50%.

Method Range Studies

In method range studies, 5-mL aliquots of reagent water were spiked with composite spiking solutions to achieve 13 concentrations ranging from 0.1 to 550 lg/L for most analytes, but 15 analytes expected to be poorly purged were spiked at 10-fold higher concentrations. Eight replicate samples were analyzed for each of the 13 spike levels.

A reverse library search of the data was performed using a project-specific mass spectral library containing the retention time and quantitation ion of each analyte and IS. The quantitation ion was chosen for maximum sensitivity while attempting to avoid interferences from coeluting materials. For the majority of analytes, the quantitation ion selected was the base peak. For Method 8240 analytes, the primary ion specified in Method 8240 was used as the quantitation ion. When the quantitation ion was detected above the background, an RF was calculated for each analyte using the area responses and concentrations of the analyte and the appropriate IS.

To determine an estimated detection limit (EDL) for each analyte, a trained analyst inspected the mass spectrum from one of the replicate samples at the lowest concentration at which the computer detected the quantitation ion in at least four replicates. The analyst examined extracted ion current profiles of 2-5 major ions, including the quantitation ion, selected from the reference mass spectrum. The analyte was considered to be present if the major ions comaximized and had relative intensities within 20% of those in the reference mass spectrum (as specified in Method 8240), and if the quantitation ion gave an area response greater than 1000 or a signal-to-noise ratio of at least 3:1. If, in the opinion of the analyst, the mass spectrum indicated the presence of the analyte in question, that concentration was considered the estimated detection limit. If the mass spectrum did not indicate the presence of the analyte, the inspection process was repeated at the next higher concentration.

Mean RFs and RSDs of measured RFs were calculated at each concentration as the first step in determining the linear range of the method for a given analyte. The high concentration data were evaluated for system saturation by plotting and visually evaluating the RF as a function of analyte concentration. When an RF obviously decreased with increasing concentration, appropriate concentrations were eliminatec from the linear range. For each analyte ar overall average RF was calculated usinç RFs from all concentrations other than re jected high concentrations. If the RSD fo an overall average RF was >25% (an ac ceptable threshold value selected with USEPA personnel concurrence), the con centration range was narrowed in ar attempt to achieve $\leq$25% RSDA. A concen tration range was, however, never reducec to less than one order of magnitude.

The lowest concentration at which the analyte was identified and measured in a least four of eight replicates was considerec the EDL. Data obtained at the EDL were used to calculate the method detectior limits (MDLs) using the USEPA procedure described in Appendix B to 40 CFR Par 136 (Federal Register 49 198, October 26 1984).

Matrix Validation Studies

Two simulated liquid waste samples were prepared for further method evaluation One sample was a municipal sludge leachate prepared using a modification o the USEPA toxicity characteristic leachinç procedure (Federal Register 51, 21685 June 13, 1986). The other sample was ar artificial ground water prepared by spikinç reagent water with fulvic acid (Suwannee Stream Reference, U.S. Geological Survey International Humic Substance Society) a a concentration of 1 mg/L.

Eight replicates at each of two analyte spike concentrations (20 and 200 μg/L fo most analytes; 200 and 2000 μg/L for the poorly purged analytes) and eight unspiked replicates were analyzed for each of the tw samples. Calibration standards prepared b spiking reagent water with each analyte a a concentration of 50 μg/L for most analytes and 500 μg/L for the poorly purged analytes were analyzed at the beginning, middle and end of each day. Measured analyte concentrations were calculated using dai ly average RFs. Precision (RSD) and ac curacy (bias) of measured concentrations were calculated for each analyte at eacl spiking concentration in each sample.

Results and Discussion

Method Range Studies

For three compounds (acetone, 2-chloro 1,3-butadiene, and trichlorofluoromethane) RSDs of measured RFs were >25%, evei with a concentration range of one order c magnitude. Acetone might yield mor reliable data using m/z 58 as the quantita tion ion rather than m/z 43, which i specified by Method 8240. A decreasing RI

with increasing concentration was evident for 2-chloro-1,3-butadiene, which is known to polymerize readily. The degree of polymerization, which would result in loss the monomer, would be expected to be higher at higher concentrations and could account for lower observed RFs at higher concentrations. Trichlorofluoromethane was particularly sensitive to the effects of methanol and water on GC peak shape. Other early eluting compounds such as dichlorodifluoromethane (20% RSD), chloromethane (23% RSD), and vinyl chloride (20% RSD) also produced average RFs that were less precise than those of most other analytes. The range for a fourth compound (hexachloropropene) that produced an average RF with >25% RSD was not narrowed because the greatest deviation from the average RF occurred at 300 μg/L, near the middle of the concentration range.

Of the 74 analytes having a satisfactory method range and average RF precision, the linear range for 56 was at least two orders of magnitude and for 12 others was at least 1.5 orders of magnitude. For the remaining six analytes, the linear range was only one order of magnitude. Three of those analytes (dichlorodifluoromethane, chloromethane, and chloroethane) were highly volatile and two (trans-1,4-dichloro-2-butene and hexachloropropene) were poorly purged.

The linear range, EDL, and MDL for each analyte are given in Table 1. For all but 10 analytes, the EDL (the lowest concentration at which the analyte was detected and quantified in at least four of eight replicates) was the same as the lowest concentration in the linear range. Lower EDLs could undoubtedly have been achieved for most analytes if MS operating conditions had been selected to achieve maximum sensitivity instead of a wide dynamic range and measurement of high analyte concentrations.

For all analytes except acetone, calculated MDLs were considerably lower than EDLs. For all but seven analytes each calculated MDL was even lower, usually by a factor of two to five, than a concentration at which the analyte could be detected experimentally. In all cases, the highest concentration at which an analyte was not detected in any of eight replicates (Table 1) was within a factor of three of the associated EDL. Low calculated MDLs reflect excellent measurement precision at the EDL rather than excessively high signal-to-noise ratios. The data indicate that calculated MDLs may be misleading.

Matrix Validation Studies

The 74 analytes studied included 29 of the 30 compounds listed in Method 8240 Table 6, which specifies acceptance criteria for data obtained from analysis of a quality control check sample. For 28 of those 29 compounds, Method 8240 acceptance criteria were achieved in both matrices at both high and low concentrations. The one exception was ethylbenzene spiked at the high concentration into reagent water containing fulvic acid; a bias of +77% was observed while +62% is acceptable.

The acceptability of measured concentrations for all 74 analytes was evaluated by selecting a bias of ±30% as an acceptance limit. (This limit is much more stringent that Method 8240 analyte-specific criteria, which are generally ±50% or greater.) With a ±30% bias limit, measured concentrations were acceptable for 61 of the 74 analytes spiked into the POTW sludge leachate at the high concentration and for 63 analytes at the low concentration. Acceptable concentrations were measured for 50 analytes added to the fulvic acid spiked water at the high concentration and for 70 at the low concentration.

In nearly 90% of the cases in which the bias of measured concentrations was >30%, the bias was positive rather than negative. A possible explanation of the high positive biases is an increased MS sensitivity when ion concentrations are unusually high. This effect would be expected to be much more noticeable when a capillary column is used rather than a packed column, because a capillary column produces much sharper peaks and higher momentary analyte concentrations than a packed column. The high positive bias was more prevalent at the high spike concentration than at the low spike concentration, especially for the fulvic acid spiked water. The high spike concentration of 200 μg/L provides 1000 ng of analyte in the 5 mL of sample purged. The increased sensitivity at high concentrations was not as apparent in the method range study as in the matrix validation study, possibly because the ion source had been cleaned immediately before beginning the method range study. Decreased source cleanliness may enhance the effect.

For all but two of the cases in which the bias was > −30%, the low spike concentration was involved and the analyte was one of the 14 poorly purged analytes spiked at a 10-fold higher concentration than other analytes. For those analytes, the calibration standard provided 2500 ng, which could have produced a high ion concentration and high RF; that could account for a negative bias at the low spike concentration. Thus, an increased sensitivity resulting from high ion concentrations can account for essentially all biases, high and low. No evidence for a matrix effect, which would be expected to give a negative bias, was observed.

Conclusions and Recommendations

The following conclusions and recommendations are based on the results of this study:

- The use of methanol as a solvent interferes with the chromatographic performance of a nonpolar capillary column for the determination of polar volatile compounds such as acetonitrile, isobutyl alcohol, and propargyl alcohol.
- Methanol and water desorbed from a trap containing Tenax, silica gel, and charcoal, interfere with the chromatographic performance of a nonpolar capillary column for the determination of gaseous and very low boiling nonpolar compounds by a PTD procedure.
- Of the 84 volatile compounds studied, 74 can be determined satisfactorily by SW-846 Method 8240 using a VOCOL capillary column.
- With MS conditions that permit Method 8240 performance criteria to be met using a capillary column and 250 ng of IS, an increased sensitivity may be observed at high ion concentrations in the mass spectrometer source. The effect of MS source tuning parameters and cleanliness on changes in RF with concentration should be evaluated.
- Calculated MDLs cn be considerably lower than the lowest concentrations at which analytes can be detected experimentally.
- Cryofocusing or other means to focus early eluting compounds to minimize peak broading and improve quantiation, especially at low concentrations, should be investigated.
- A non-volatile, water soluble solvent should be used for spiking solutions to avoid deleterious chromatographic effects of methanol on early eluting analytes.
- Differences between calculated and observed detection limits should be investigated to establish a protocol for obtaining more meaningful MDLs.

TABLE 1. *Linear Range and Detection Limits Obtained From Method Range Study*

Analyte	Applicable Linear Range, µg/L	Experimentally Determined EDL, µg/L[a]	Calculated MDL, µg/L[b]	Nondetection Limit, µg/L[c]
1. *Acetone*	5500-170	170	200	100
2. Acrolein	5500-100	55	10	30
3. Acrylonitrile	5500-170	170	40	100
4. Allyl chloride	550-10	5.5	2	3.0
5. Benzene	550-3.0	3.0	0.2	1 0
6. Bis-(2-chloroethyl) ether	5500-55	55	10	30
7. Bromobenzene	170-3.0	3.0	0.7	1.0
8. Bromodichloromethane	550-3.0	3.0	0 2	1.0
9. Bromomethane	550-5.5	5.5	2	3.0
10. 2-Butanone	5500-100	30	10	10
11. n-Butylbenzene	170-1.0	1.0	0.4	0.3
12. sec-Butylbenzene	170-1.0	1.0	0.4	0.3
13. tert-Butylbenzene	170-1.0	1.0	0.8	0.3
14. Carbon disulfide	550-3 0	3 0	0.3	1.0
15. Carbon tetrachloride	550-3.0	3 0	0.2	1.0
16. Chlorobenzene	300-3.0	3 0	0.3	1.0
17. 2-Chloro-1,3-butadiene	550-5.5	5.5	2	3.0
18. Chlorodibromomethane	550-3.0	3.0	0.2	1.0
19. Chloroethane	550-30	17	5	10
20. 2-Chloroethyl ethyl ether	5500-30	30	9	10
21. Chloroform	550-3.0	3.0	0 1	1.0
22. 1-Chlorohexane	550-3.0	3.0	0.1	1 0
23. Chloromethane	550-30	17	10	10
24. 2-Chlorotoluene	550-3 0	3 0	0.3	1 0
25. 4-Chlorotoluene	550-3.0	3 0	0 3	1.0
26. 1,2-Dibromo-3-chloropropane	550-10	10	2	5.5
27. 1,2-Dibromoethane	550-3.0	3.0	0.2	1.0
28. Dibromomethane	550-3 0	3 0	0.2	1 0
29. 1,2-Dichlorobenzene	300-3 0	3 0	0.5	1 0
30. 1,3-Dichlorobenzene	300-3 0	3 0	0.4	1 0
31. 1,4-Dichlorobenzene	300-3.0	3 0	0.5	1.0
32. trans-1,4-Dichloro-2-butene	550-170	55	30	30
33. Dichlorodifluoromethane	55-5.5	5 5	1	3 0
34. 1,1-Dichloroethane	550-5 5	5.5	0.7	3.0
35. 1,2-Dichloroethane	550-5.5	5 5	0.4	3.0
36. 1,1-Dichloroethene	550-5.5	5.5	1	3.0
37. cis-1,2-Dichloroethene	550-5.5	5.5	1	3.0
38. trans-1,2-Dichloroethene	550-5.5	5 5	0.7	3 0
39. Dichloromethane	550-5 5	5.5	0.8	3 0
40. 1,2-Dichloropropane	550-5.5	5.5	0.7	3.0
41. 1,3-Dichloropropane	550-3 0	3 0	0.3	1 0
42. 1,1-Dichloropropene	550-5.5	5 5	0.5	3 0
43. cis-1,3-Dichloropropene	550-5.5	5 5	0.9	3 0
44. trans-1,3-Dichloropropene	550-5.5	5.5	1	3.0
45. 1,2-Dimethylbenzene	550-1.0	1.0	0.2	0 3
46. 1,4-Dimethylbenzene	550-10	1.0	0.6	0.3
47. Ethyl methacrylate	1000-10	10	7	3 0
48. Ethylbenzene	550-1.0	1.0	0 4	0.3
49. Hexachlorobutadiene	300-3.0	3.0	0.7	1.0
50. Hexachloroethane	550-5.5	5.5	2	3.0
51. Hexachloropropene	3000-170	170	50	100
52. 2-Hexanone	5500-30	30	6	17
53. Iodomethane	550-5.5	5.5	2	3.0
54. Isopropylbenzene	300-3.0	3.0	0.4	0.3
55. p-Isopropyltoluene	300-10	10	0.7	5.5
56. Methacrylonitrile	5500-30	30	9	17
57. Methyl methacrylate	3000-30	30	5	3.0
58. 4-Methyl-2-pentanone	1700-30	30	6	17
59. Naphthalene	300-3.0	3.0	0.5	1.0
60. Propionitrile	5500-170	170	40	100
61. n-Propylbenzene	170-1.0	1.0	0.2	0.3
62. Styrene	300-3.0	3.0	0.4	1 0
63. 1,1,1,2-Tetrachloroethane	300-3.0	3.0	0.2	1.0
64. 1,1,2,2-Tetrachloroethane	550-5.5	5.5	1	3.0
65. Tetrachloroethene	300-3.0	3.0	0.2	1.0

TABLE 1. *Continued*

Analyte	Applicable Linear Range, µg/L	Experimentally Determined EDL, µg/L[a]	Calculated MDL, µg/L[b]	Nondetection Limit, µg/L[c]
66. Toluene	550-3.0	3.0	0.2	0.3
67. Tribromomethane	300-3.0	3.0	0.3	1.0
68. 1,2,4-Trichlorobenzene	300-3.0	3.0	0.3	1.0
69. 1,1,1-Trichloroethane	550-3.0	3.0	0.2	1.0
70. 1,1,2-Trichloroethane	550-5.5	5.5	0.3	3.0
71. Trichloroethene	550-3.0	3.0	0.1	0.3
72. Trichlorofluoromethane	300-30	30	10	17
73. 1,2,3-Trichloropropane	550-17	17	2	10
74. 1,2,4-Trimethylbenzene	300-3.0	3.0	1	1.0
75. 1,3,5-Trimethylbenzene	300-3.0	3.0	0.3	1.0
76. Vinyl acetate	3000-55	55	4	30
77. Vinyl chloride	550-5.5	5.5	0.6	3.0

[a]Experimentally determined estimated detection limit.
[b]Calculated method detection limit.
[c]Nondetection limit is the highest concentration studied at which the analyte was not detected.

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***Thomas Pressley** is the EPA Project Officer (see below).*
The complete report, entitled "Capillary Column GC-MS Determination of 77 Purgeable Organic Compounds in Two Simulated Liquid Wastes," (Order No. PB 88-245 881/AS; Cost: $14.95, subject to change) will be available only from:
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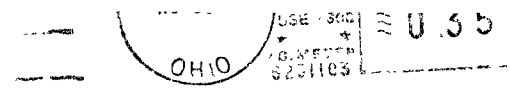

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