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VOLATILE ORGANIC ANALYSIS BY DIRECT AQUEOUS INJECTION

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Summary—Gas chromatographic environmental analysis by direct aqueous injection (DAI) was studied
for 24 volatile organic analytes (VOAs). Internal standardization was used to determine the precision of
analyzing these compounds by DAI. Aqueous samples were directly introduced to a gas chromatograph
using fused-silica, mega-bore capillary column separation with subsequent full-scan ion trap mass spectral
detection. Triplicate injections at seven levels of VOA standard solutions over a 10^3 concentration range
were performed using an autosampler set up for on-column injection of 0.2 μl. Comparison of single-ion
response curves to triple-ion response curves showed that triple-ion quantitation was more sensitive and
precise than single-ion quantitation. Of the 24 VOAs determined at the 20 parts per billion (ppb) level,
19 and 20 were detected by the single-ion calibration and triple-ion calibration, respectively. The weighted
and non-weighted regression correlation coefficients, r^2, for the 24 responses curves by the two methods,
ranged from 0.910 to 0.998, with 76 of 96 being greater than 0.990. Precision, as measured by per cent
relative standard deviation, was shown to be best for later eluting compounds and for higher
concentrations. Analysis of an environmental sample by DAI was accomplished in 12 min and indicated
the presence of benzene at 80 ppb and chlorobenzene at 2 ppm. This demonstrated the feasibility of
applying this technique for screening. Several chlorinated benzenes were also detected, establishing the
potential for expanding the method to include higher boiling compounds.

INTRODUCTION

As a result of existing legislation,[1-4] Congress
has charged the U.S. Environmental Protection
Agency (U.S. EPA) with the development of
methods to analyze for pollutants in the en-
vironment. The U.S. EPA's Office of Research
and Development supervises and supports the
development of methods to meet this responsi-
bility. To support new guidelines and incorpor-
ate new innovations and technology, method
development within the U.S. EPA is an on-
going process. As part of this process, we deter-
mined the feasibility of direct aqueous injection
(DAI) for the gas chromatographic analysis of
volatile organic compounds.

Volatile organic compounds (VOAs) have
been shown to occur in most drinking water,
ground water and wastewaters. They may orig-
inate from industrial contamination or as by-
products of water purification such as
chlorination. Purge and trap methodology was
developed to analyze for these compounds.[5]

Subsequent to this earlier work, purge and
trap analysis has undergone many changes and
improvements in response to innovations in
technology.[6-10]

A recent commercial innovation, the ion trap
detector, has made it possible to conduct mass
spectral analysis at the picogram level in the
full-scan mode.[11] Quadrupole ion trap technol-
ogy is an area of active investigation[12-14] and has
been applied to environmental analysis.[15-17]
After electron ionization, the ion trap mass
spectrometer uses an RF voltage to store ions of
various mass-to-charge ratios. Ion ejection oc-
curs by sweeping the trapping RF voltage caus-
ing instability and subsequent ejection of the ion
on a mass-to-charge basis. Detection occurs at
the electron multiplier located behind the aper-
ture at the center of the lower end cap. Ion trap
sensitivity in the full-scan mode is in the low
picogram level. This increased sensitivity has
made it possible to perform parts per billion
(ppb) analysis by direct injection of aqueous
samples into the instrument.

DAI analysis with gas chromatographic sep-
aration has been attempted by several groups of

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investigators. Harris *et al.* investigated the impact of DAI on GC/MS fragmentation patterns, detection limits and background subtraction.[18] To lower DAI detection limits, several papers report using electron capture detection (ECD). Grob separated several halocarbon compounds at the low-ppb level[19] using ECD detection and on-column injection. He surmised that halocarbons had a low enough solubility in water to prevent uneven distribution in the column resulting in poor peak shape. Other work explored the feasibility of on-column DAI analysis of trihalomethanes using ECD detection with capillary column separation.[20-22] Analysis of non-ionic alkyl phosphates,[23] volatile fatty acids[24] and chlorpyrifos[25] have also been accomplished by DAI analysis.

This work has shown that DAI provides faster analyses, lowers laboratory costs by eliminating sample extraction and generation of solvent wastes, and gives more accurate data by eliminating sampling errors and procedural analyte losses.

EXPERIMENTAL

GC/ITS instrumentation

Ion trap studies were carried out on a Finnigan (Sunnyvale, CA) Model ITS 40 upgraded for chemical ionization to the Magnum configuration. The column was a Restek Corp. (Belefonte, PA) 30-m by 0.53-mm XTI-5 megabore fused silica capillary column coated with a 1.5-μm film of bonded 5% phenyl–95% dimethyl polysiloxane liquid phase. The end of the analytical column was connected by a Supelco (Bellefonte, PA) glass butt connector to a 60-cm by 0.18-mm section of capillary column for insertion into the vacuum manifold. This narrower length of fused silica acted as a restrictor and reduced the flow into the manifold to the manufacturer recommended 1.5 ml/min. The ion trap detector was scanned from 46 to 180 amu at 0.6 scans/sec (each scan an average of 5 μscans) with the manifold temperature at 260°C, a 150-sec solvent delay, and a 30 mmu/100 amu mass defect. To facilitate the exclusion of water from the manifold, the first tune segment RF storage potential was set to 204 digital-to-analog conversion units (DACs). The gas chromatograph was a Varian (Walnut Creek, CA) Model 3400 equipped with a septum programmable injector (SPI) and a CTC Model A200S autosampler. A Compaq Model 386/20E Deskpro personal computer controlled the GC

and MS acquisition. After a 3-min hold, the GC was temperature programmed from 40 to 148°C at 12 deg/min (total run time 12 min). For the environmental sample, the temperature ramp was continued to a final temperature of 280°C. The initial linear velocity was 30 cm/sec with a helium head pressure of 5 psig. The transfer line was held at 280°C. The SPI injector was held at 90°C and upon injection was ramped at 200 deg/min to 190°C and held for 5 min.

Preparation of standard solutions

Supelco-certified standards, Purgeable A and Purgeable B, containing 24 volatile compounds (see Table 1) in methanol, and VOA Internal Standard containing three internal standards, also in methanol, were diluted to the appropriate level with distilled water to a final volume of 1.0 ml. All purities were certified to be 97.6% pure or greater at the 200-μg/ml level. The sealed amber ampules were opened when needed and immediately diluted and analyzed within 8 hr. Injection of 0.2 μl of the aqueous samples with 2 μl of air was performed in triplicate with a distilled water blank between each concentration level. Sample concentrations were 20, 50, 200, 500, 2000, 5000 and 20,000 ppb in distilled water for the VOAs. Internal standards were spiked at the 5000-ppb level for each sample level.

Calculation methods

Calibration was performed using the most abundant single-ion area response *vs.* concentration and by triple-ion (sum of three most abundant ions) area response *vs.* concentration. The triple-ion method was a novel approach to quantitation and was calculated for comparison to the more common single-ion approach. Precision was calculated by normalizing area response to the area of the appropriate internal standard. This corrected for any uncertainty in sample injection. The automated, manufacturer-supplied software was used to determine the area for each compound for each replicate injection when possible. At the lowest level, manual integration was used to determine peak area. Per cent relative standard deviations (%RSDs) were calculated with $n - 1$ degrees of freedom for each compound at each concentration level.

Linear regression analysis was performed on the single- and triple-ion areas *vs.* concentration for each replicate analysis at each concentration level to determine the slopes,

y-intercepts and correlation coefficients. Because the standard concentrations spanned a 1000-fold range, the correlation coefficients were also calculated as the log of the response *vs.* the log of the concentration to give a weighted correlation.

Method detection limits (MDLs) were calculated using the slopes (m) from the linear least squares fit of the response curve as compound response and assuming that the minimum detectable area was 100 counts (the 3 N_{rms} noise level for the ions varied greatly). MDLs were calculated for comparison purposes only.

RESULTS AND DISCUSSION

Preliminary studies on the DAI VOA analysis showed that injection volumes greater than 0.2 μl provided imprecise results and did not give correspondingly higher responses or good peak shape, especially for early eluting compounds. Presumably this resulted from residual water that eluted from the column shortly after the majority of water had eluted and after the filament had been turned on. With the smaller injection volumes used in this study and the

ability of the ion trap to specify the RF voltage to exclude water ions from the manifold, adequate peak shape and precision were obtained using a 0.2-μl injection volume. Figure 1 illustrates the ion trap's ability to exclude water, oxygen and nitrogen from the manifold by raising the RF storage potential from 124 to 204 DACS (see Experimental). Higher RF storage potentials will not store lower-mass ions in the manifold.

Table 1 shows the compound number, compound name, retention time, quantitation ions (the ions in bold were used for single ion quantitation), and internal standard reference compound used for quantitation of 24 VOAs and the three internal standards used in this study. Figure 2 shows the reconstructed ion chromatogram (RIC) of the 20-ppm standard. The numbers on the chromatogram correspond to the compound numbers in Table 1. Good peak shape at all concentration levels for all the compounds was obtained throughout the study. An example of peak shape is shown in Fig. 2.

It was more difficult to obtain peak areas for the lowest calibration level, 20 ppb, because this represented the low end of the instrument's

Table 1. Volatile compounds with retention times (RT), quantitation ions, and internal standard reference compound

No.	Compound	RT (*min*)	Quantitation ions	Internal standard
1	Bromochloromethane (IS)	4:56	49, **128**, 130	—
2	1,4-Difluorobenzene (IS)	6:10	63, 88, **114**	—
3	Chlorobenzene-d_5 (IS)	9:38	82, **117**, 119	—
4	Trichlorofluoromethane	2:59	47, **101**, 103	1
5	1,1-Dichloroethene	3:22	61, **96**, 98	1
6	Dichloromethane	3:33	49, 51, **84**	1
7	*trans*-1,2-Dichloroethene	3:59	61, **96**, 98	1
8	1,1-Dichloroethane	4:13	**63**, 65, 83	1
9	Trichloromethane*	4:56	47, **83**, 85	1
10	1,1,1-Trichloroethane	5:30	**97**, 99, 119	2
11	1,2-Dichloroethane	5:35	49, **62**, 63	2
12	Tetrachloromethane	5:51	**117**, 119, 121	2
13	Benzene	5:51	51, 77, **78**	2
14	1,2-Dichloropropane	6:37	**62**, 63, 75	2
15	Trichloroethene	6:37	**95**, 130, 131	2
16	Bromodichloromethane	6:47	**83**, 85, 129	2
17	2-Chloroethyl vinyl ether	7:14	62, 63, **65**	2
18	*trans*-1,3-Dichloropropene	7:28	**75**, 77, 109	2
19	*cis*-1,3-Dichloropropene	7:59	**75**, 77, 109	3
20	Methyl benzene	8:04	65, 91, **92**	3
21	1,1,2-Trichloroethane	8:08	**83**, 85, 97	3
22	Dibromochloromethane	8:41	79, 127, **129**	3
23	Perchloroethylene	8:56	164, **166**, 168	3
24	Chlorobenzene*	9:40	77, **112**, 114	3
25	Ethyl benzene	9:55	**91**, 105, 106	3
26	Bromoform	10:28	171, **173**, 175	3
27	1,1,2,2-Tetrachloroethane	10:58	**83**, 85, 133	3

*Denotes difficulty with quantitation at low-ppb level (see Results and Discussion).

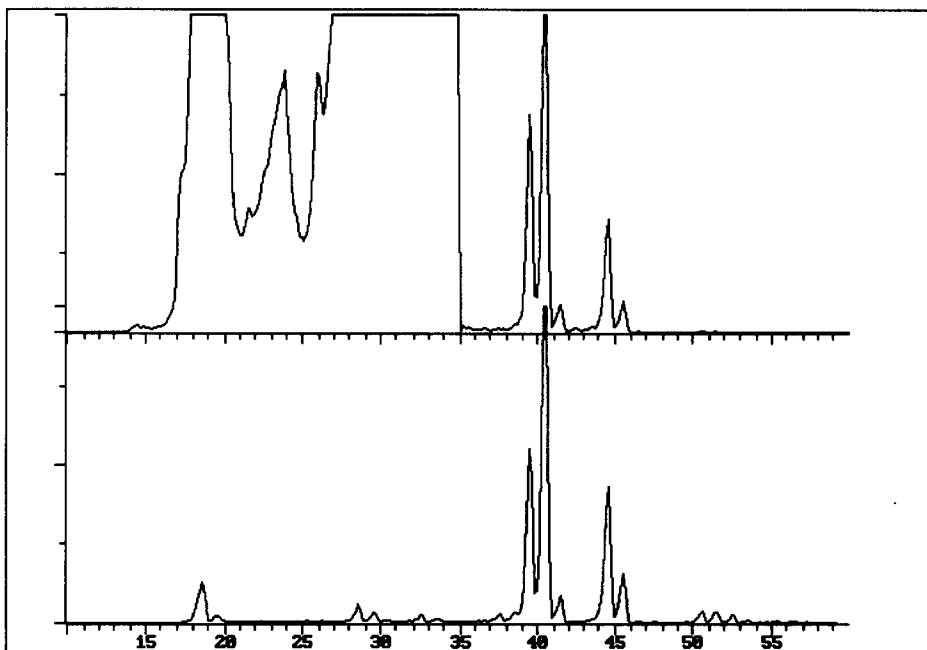Bold type indicates single-ion quantitation.

Fig. 1. Effect of RF storage potential on water retention. Top portion shows RF storage potential = 124 DACS. Bottom shows RF storage potential = 204 DACS.

ability to detect the components. For example, Fig. 3(a) shows the response of the 20-ppb standard (4 pg on-column) of *trans*-1,3-dichloropropene. The middle and lower portions of Fig. 3(a) are the single-ion RIC and the sum of the three most abundant ions RIC, respectively. The integrated peak occurs within one scan of the retention time. While the response is low, it can be seen that it represents real signal and not random noise [compared with the blank shown in Fig. 3(b)], and it was consistent for the triplicate injections.

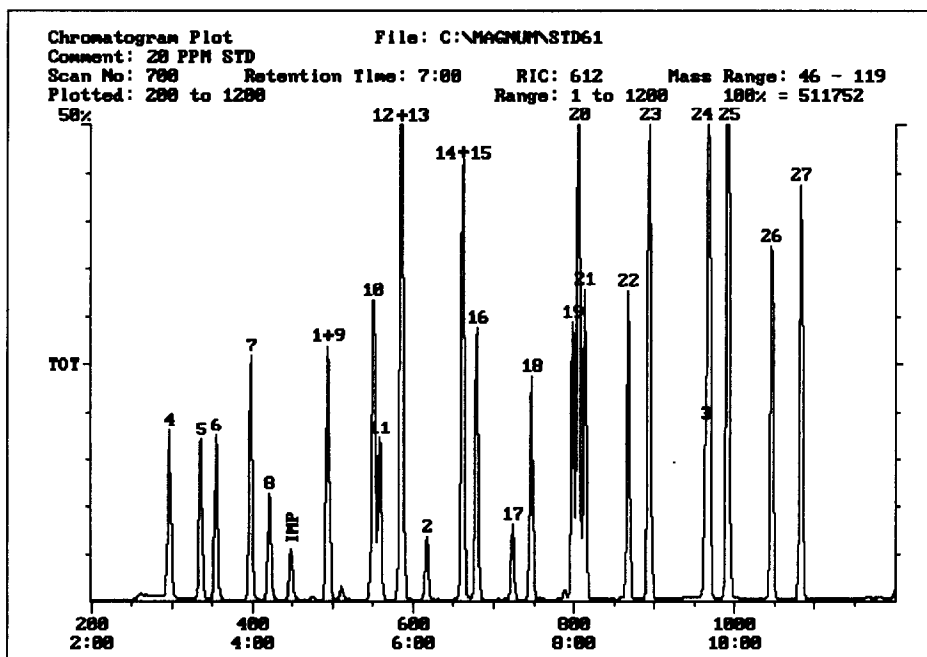The low-level quantitation of two compounds, chlorobenzene and chloroform, pre-

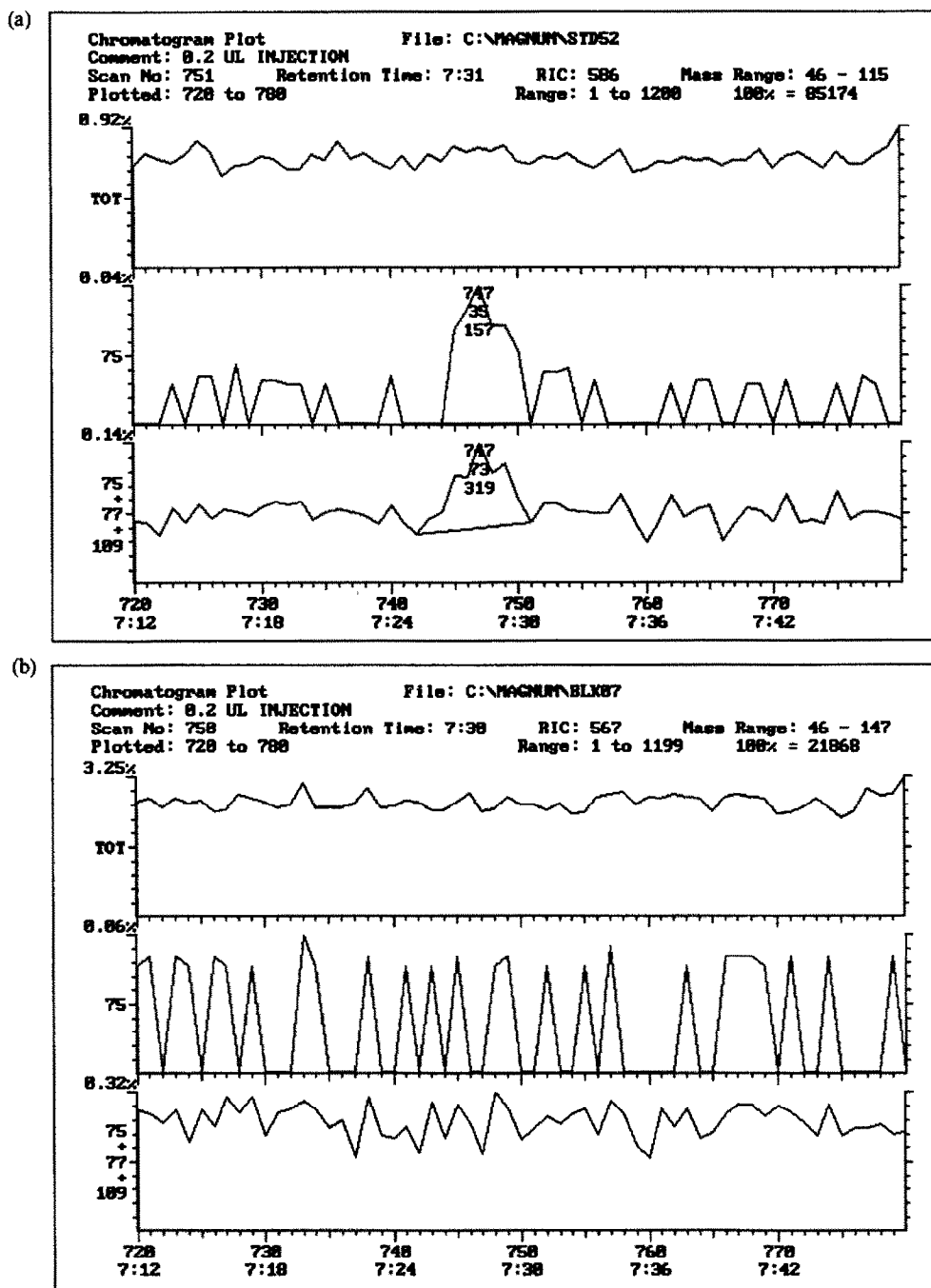Fig. 2. RIC of 20 ppm VOA standard solution.

(a)

(b)

Fig. 3. (a) RIC and selected ion chromatograms of 20 ppb *trans*-1,2-dichloropropene. (b) RIC and selected ion chromatograms of blank.

sented a problem because each co-eluted with an internal standard. At the 20-ppb level, the contribution to the quantitation ion from the internal standard (at 5000 ppb), even though it may be a minor ion in the spectrum, became significant and obscured the contribution of the quantitation ion of the co-eluting compound making quantitation at the 20-ppb level impractical. Note that benzene and tetra-

chloromethane, as well as the 1,2-dichloropropane and trichloroethene, also co-eluted (Table 1). Low-level quantitation was not a problem for these two pairs because quantitation ions had been selected for each compound and the co-eluting pairs were always at the same levels, making any contribution to the quantitation ion from the other compound insignificant. With ion trap detection, low-level

Table 2. Linear regression analysis of single-ion and triple-ion (sum of three most abundant ions) quantitation

| No. | Compound | Single ion | | | | | Triple ion | | | | |
		m	b	r^2	r_w^2	MDL (ppb)	m	b	r^2	r_w^2	MDL (ppb)
4	Trichlorofluoromethane	8.99	8514	0.927	0.981	11.13	14.78	15,469	0.910	0.980	6.77
5	1,1-Dichloroethene	3.44	726	0.994	0.975	29.04	12.37	2907	0.993	0.990	8.08
6	Dichloromethane	10.44	−2540	0.993	0.990	9.58	14.21	−3584	0.993	0.990	7.04
7	trans-1,1-Dichloroethene	5.10	−681	0.997	0.977	19.60	17.34	−2172	0.997	0.996	5.77
8	1,1-Dichloroethane	6.21	−882	0.997	0.992	16.10	9.02	−889	0.997	0.993	11.08
9	Trichloromethane	10.18	−1987	0.995	0.992	9.82	20.72	−85	0.994	0.916	4.83
10	1,1,1-Trichloroethane	13.38	629	0.998	0.995	7.48	23.58	1254	0.998	0.995	4.24
11	1,2-Dichloroethane	8.96	−2818	0.991	0.991	11.16	13.50	−1451	0.981	0.952	7.41
12	Tetrachloromethane	10.78	5174	0.986	0.985	9.27	24.00	11,889	0.986	0.990	4.17
13	Benzene	20.43	−2702	0.995	0.996	4.90	31.37	−3183	0.996	0.996	3.19
14	1,2-Dichloropropane	4.10	−15	0.997	0.991	24.37	7.72	−210	0.998	0.991	12.95
15	Trichloroethene	5.73	1448	0.995	0.991	17.47	18.53	3944	0.996	0.993	5.40
16	Bromodichloromethane	10.56	−2822	0.993	0.992	9.47	18.57	−4851	0.993	0.994	5.39
17	2-Chloroethyl vinyl ether	0.89	−267	0.995	0.988	112.50	4.91	−1241	0.994	0.980	20.37
18	trans-1,3-Dichloropropene	9.49	−1900	0.995	0.981	10.54	14.05	−3236	0.994	0.993	7.12
19	cis-1,3-Dichloropropene	11.75	−2176	0.994	0.995	8.51	17.74	−3767	0.994	0.992	5.64
20	Methyl benzene	12.16	538	0.997	0.995	8.22	50.26	3345	0.996	0.995	1.99
21	1,1,2-Trichloroethane	5.27	−1057	0.995	0.992	18.96	13.93	−2924	0.995	0.994	7.18
22	Dibromochloromethane	10.03	−1459	0.995	0.994	9.97	21.49	−3006	0.995	0.994	4.65
23	Perchloroethylene	9.71	6804	0.977	0.987	10.30	18.57	15,225	0.977	0.988	4.66
24	Chlorobenzene	22.49	3335	0.996	0.993	4.45	42.50	8545	0.996	0.989	2.35
25	Ethyl benzene	44.27	17,668	0.990	0.990	2.26	64.05	24,256	0.990	0.991	1.56
26	Bromoform	11.51	−694	0.996	0.995	8.69	22.94	−1535	0.997	0.996	4.36
27	1,1,2,2-Tetrachloroethane	13.53	710	0.997	0.996	7.39	24.02	1475	0.997	0.996	4.16

m = slope, b = y intercept, r^2 = correlation coefficient, r_w^2 = weighted correlation coefficient (see Calculation Methods).

identification is possible only when co-elution does not occur with compounds at higher concentrations.

Due to the increased flexibility of manufacturer supplied software and the need to optimize sensitivity for DAI analyses, quantitation using the sum of the three most abundant ions was investigated. The goal of this investigation was to determine the usefulness of this approach as opposed to the usual single-ion quantitation. The response of the standards solutions at the various levels was determined for both methods

Table 3. Precision data (%RSDs) for triplicate injections using single-ion calibration

Compound	20 ppm	5 ppm	2 ppm	500 ppb	200 ppb	50 ppb	20 ppb
Trichlorofluoromethane	20.68	59.17	56.81	27.75	7.83	81.06	7.15
1,1-Dichloroethene	19.55	42.51	37.75	26.00	4.54	72.35	86.53
Dichloromethane	18.48	5.73	30.81	15.94	1.43	14.58	10.56
trans-1,2-Dichloroethene	18.85	28.34	33.82	22.77	10.26	45.54	109.26
1,1-Dichloroethane	18.89	18.76	33.83	20.49	5.37	16.40	ND
Trichloromethane	19.14	11.96	32.63	17.49	6.96	16.00	30.66
1,1,1-Trichloroethane	1.52	11.52	1.03	1.94	2.95	19.43	19.94
1,2-Dichloroethane	1.28	13.02	8.77	12.69	7.99	43.58	3.03
Tetrachloromethane	1.87	16.75	5.36	7.42	4.97	36.21	22.15
Benzene	1.64	2.94	2.02	2.32	5.64	5.84	7.19
1,2-Dichloropropane	0.55	4.01	1.67	4.83	2.88	23.12	33.67
Trichloroethene	0.99	6.10	3.90	2.96	3.10	2.67	28.56
Bromodichloromethane	0.40	8.78	5.59	6.98	6.06	20.84	16.02
2-Chloroethyl vinyl ether	1.67	11.45	8.70	16.15	21.70	ND	ND
trans-1,3-Dichloropropene	1.48	9.35	5.65	5.72	1.59	77.75	9.08
cis-1,3-Dichloropropene	1.79	8.60	13.13	13.56	7.46	20.86	4.07
Methyl benzene	1.04	2.25	3.47	2.33	5.08	10.00	8.90
1,1,2-Trichloroethane	0.96	9.24	11.87	10.58	9.34	31.55	38.83
Dibromochloromethane	1.67	7.04	11.12	9.96	6.76	16.57	2.52
Perchloroethylene	2.06	11.38	2.90	4.49	1.54	7.23	8.89
Chlorobenzene	0.54	1.14	1.22	0.52	1.49	2.88	6.71
Ethyl benzene	1.96	5.52	3.62	5.77	5.17	11.43	7.34
Bromoform	1.77	5.97	10.34	6.71	4.58	15.67	7.66
1,1,2,2-Tetrachloroethane	0.31	4.82	8.96	6.20	3.96	3.21	14.81
Average	5.80	12.76	13.96	10.48	5.78	25.86	21.98

ND = not detected.

Table 4. Precision data (%RSDs) for triplicate injections using triple-ion calibration

Compound	20 ppm	5 ppm	2 ppm	500 ppb	200 ppb	50 ppb	20 ppb
Trichlorofluoromethane	6.59	51.56	34.29	22.20	6.40	78.01	31.33
1,1-Dichloroethene	5.40	34.95	11.43	14.66	2.41	61.68	39.28
Dichloromethane	3.84	2.74	3.75	5.41	1.94	19.44	2.54
trans-1,2-Dichloroethene	3.83	20.14	7.18	12.41	3.62	39.51	27.48
1,1-Dichloroethane	4.13	11.74	6.39	9.68	4.88	27.13	ND
Trichloromethane	4.48	5.27	5.32	7.66	0.62	6.76	2.42
1,1,1-Trichloroethane	1.16	11.74	0.92	2.44	4.00	17.34	23.11
1,2-Dichloroethane	1.59	14.16	6.86	10.10	7.70	41.49	12.72
Tetrachloromethane	2.20	16.70	5.73	7.28	4.03	23.10	12.97
Benzene	1.14	2.39	1.56	2.09	5.80	13.06	6.72
1,2-Dichloropropane	0.71	11.67	2.13	3.86	4.36	13.78	27.15
Trichloroethene	1.01	5.17	2.87	3.66	3.64	5.39	11.14
Bromodichloromethane	0.35	8.62	5.19	6.19	5.24	22.09	20.67
2-Chloroethyl vinyl ether	0.96	11.87	9.50	4.84	9.18	ND	ND
trans-1,3-Dichloropropene	2.52	8.77	5.81	6.36	3.53	27.87	31.68
cis-1,3-Dichloropropene	1.53	8.55	14.33	11.78	5.69	22.79	4.05
Methyl benzene	0.97	1.91	3.11	2.34	4.08	4.70	3.69
1,1,2-Trichloroethane	0.51	9.39	11.22	9.53	7.65	21.07	20.12
Dibromochloromethane	1.26	7.96	11.13	7.54	6.24	19.41	2.78
Perchloroethylene	2.04	11.52	2.11	5.41	2.80	5.97	11.53
Chlorobenzene	0.51	1.12	1.21	1.24	1.53	1.49	5.68
Ethyl benzene	1.86	5.22	2.77	5.30	5.00	11.87	5.92
Bromoform	2.14	5.73	10.03	6.15	5.08	10.10	9.42
1,1,2,2-Tetrachloroethane	0.20	4.80	9.39	6.17	3.48	10.02	14.30
Average	2.12	11.40	7.26	7.26	4.54	21.92	14.85

ND = not detected.

and statistically analyzed to determine the relative precision and MDLs. The calibration results of the two quantitation methods are shown in Table 2. As expected, the slopes (m) were all larger for the triple-ion method. Higher slopes correlate to greater component sensitivity. There were no large differences in the correlation coefficients between the single-ion or triple-ion methods or between the weighted and non-weighted r^2 values.

Tables 3 and 4 show the precision data for the single-ion and triple-ion methods, respectively. In general, the %RSDs are better for the later eluting compounds and for the higher concentrations. At the triple-ion, %RSDs are consistently lower than those calculated from the single-ion data.

To demonstrate the applicability of this technique, a field sample known to contain volatile and semi-volatile components was collected. DAI target analysis for VOAs quantified benzene at 80 ppb and chlorobenzene at 2 ppm. Also, by extending the GC temperature ramp to 280°C, two isomers of dichlorobenzene and two isomers of tetrachlorobenzene were identified.

CONCLUSIONS

The feasibility of analyzing for volatile organic compounds by direct aqueous injection was demonstrated in the 20-ppm–20-ppb range.

Precision and method detection limits were determined for single- and triple-ion quantitation methods and were judged adequate for screening environmental samples for volatile organic components. The method of triple-ion calibration was shown to be more sensitive and precise than using just a single ion for calibration. Consideration should be given to using multiple-ion calibrations in method development in the future. When this method was applied to an environmental sample, the level of target analytes as well as the identification of non-target semi-volatile compounds in the sample was determined in 20 min.

While DAI analysis of volatile compounds has not yet replaced purge-and-trap analysis (MDLs for U.S. EPA Method 624 range from 1.6 to 6.0 μg/l), it is faster (12 $vs.$ 50 min per sample), does not discriminate on the basis of compound volatility, has a larger dynamic range, and is simpler to apply. Also, DAI shows potential for analysis of higher boiling semi-volatile compounds and as a field screening method.

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