Methodology for gas chromatographic–mass spectral analysis of volatile organic compounds emerging from a low-pressure, flow-through reaction cell

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Abstract

A methodology has been developed for the analysis of volatile organic compounds (VOCs) emerging from a plasma discharge cell operating at a constant flow-rate under subatmospheric pressure (0.266 to 2.66 kPa). The analytical system consisted of a gas reservoir for trapping a portion of the VOC–rare gas mixture, a sampling loop for cryogenically concentrating the VOC products, and either gas chromatography–mass spectrometry (GC–MS) or gas chromatography–flame ionization detection (GC–FID). The methodology was evaluated for the analysis of methylene chloride, benzene and tetrachloroethylene, using *n*-octane as the internal standard. Calibration curves were constructed by plotting the pressure ratios of the gas standard relative to the internal standard versus the corresponding peak area ratios. Over a pressure range of 1.133 to 5.32 kPa, the linearity of the calibration curve for each gas standard was determined with correlation coefficients ranging from 0.96 to 0.98. The relative standard deviation for a minimum of triplicate analyses varied from 1.1 to 18.3% for most VOCs. The calibration curves were used to measure the concentration of premixed VOC–rare gas mixtures as a function of energy input of the plasma reactor. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Instrumentation; Sample handling; Volatile organic compounds; Benzene; Methylene chloride

1. Introduction

In gas phase analysis, techniques for collecting, concentrating and transferring gas samples to the analytical instruments are critical to the efficiency of the process [1–8]. In general, gas samples are first collected either onto solid sorbent traps or into stainless steel canisters. The gas samples collected on the traps are then thermally desorbed [1,9–13] and transferred onto a gas chromatographic (GC) column for subsequent analysis. Gas samples collected in the canisters are normally transferred and cryogenically concentrated in a sampling loop, followed by heating the sampling loop and injecting gas samples onto the GC column for analysis [2,14,15]. Gas sampling techniques are generally developed for collecting gas from a static source at atmospheric pressure [1–15].

In this paper, we report a methodology to determine the destruction efficiency of volatile organic compounds (VOCs) emerging from a plasma discharge cell. We have developed a glow-discharge-

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based process for the destruction of low concentrations of VOCs. Such low concentrations of VOCs are of environmental concern because of their presence in the effluent from the treatment of highly concentrated wastes and in the off-gases generated from the extraction of dense non-aqueous phase liquids. It is the goal of these to maximize the destruction efficiency (concentration of VOC destroyed/initial VOC concentration) per energy input into the process. Nonthermal plasma processing techniques have been shown to be efficient in removing dilute mixtures of such hazardous gases [16]. Because the plasma discharge experiments were performed with gas mixtures flowing through the discharge cell at a constant flow-rate [250 to 1000 sccm (standard cc/min)] under less than atmospheric pressure, conventional gas analysis techniques could not be used to measure the destruction efficiency [17,18]. We have developed a system for sampling and pre-concentrating VOCs for subsequent GC–MS or GC–flame ionization detection (FID) analysis.

In order to determine the destruction efficiency of VOCs in our plasma reactor, we had to measure the concentration of the VOCs for a known energy input into the plasma. Calibration curves were constructed by plotting the response from GC–MS and GC–FID as a function of the concentration of a NIST (National Institute of Standards and Technology)-traceable standard mixture. The methodology was evaluated in terms of precision, linearity of the calibration curve and limits of detection, by analyzing a NIST-traceable gas standard mixture that contained 400 ppmv (parts per million by volume) of methylene chloride, benzene, carbon tetrachloride and tetrachloroethylene (in argon), using 400 ppmv *n*-octane (in argon) as the internal standard (I.S.). Currently, the validated methodology is being used to determine the destruction efficiency of target VOCs by plasma discharge processes operating either in the pulsed or in the direct current mode.

2. Experimental

2.1. Plasma discharge reactor

A schematic diagram of the apparatus that was used for these studies is shown in Fig. 1. A Varian Vacuum Products scroll pump and an MKS Baratron Type 1298B mass flow controller were used to maintain a constant flow of the target VOC mixture through the plasma reactor (discharge cell). The pressure in the plasma reactor was varied by the valve at the inlet to the scroll pump. A glow discharge was produced in the discharge cell by either a d.c. or pulsed power supply and could be maintained over a pressure range of 0.266 to 2.66 kPa. After a stable discharge was achieved, a portion of the flowing gas was diverted into the 300 ml reservoir for analysis. The instrumentation and procedure for analysis is described in the following sections.

2.2. Instrumentation for analysis

2.2.1. Gas sample collection

The sample reservoir was evacuated to 10^{-7} kPa prior to sample collection by the turbomolecular pump. The 300 ml reservoir and associated tubing was used to mix the remaining VOC target gas and VOC products emerging from the plasma discharge cell with an I.S. emerging from a Summa canister (Grasbey Andersen, Symrna, GA, USA) and balance gas emerging from a gas cylinder. The internal standard used in this study was a 400 ppmv mixture of *n*-octane in argon. The gas mixture at 10.64 kPa pressure was then transferred (via a sampling loop and valve) either to a GC–FID system or to a GC–MS system for subsequent analysis. MKS Baratron Type 222BA absolute pressure transducers were used to monitor the pressure of the gas mixture.

2.3. Sampling loop

A sampling loop (0.442 ml capacity) was constructed from a piece of 1.6 mm O.D. stainless steel tubing that was 54.6 cm in length. One end of the sampling loop was connected to the sampling reservoir and the other end was connected to a low-dead-volume, two-position six-port switching valve (Valco Instruments, model C6UW). All transfer lines were constructed from 1.6 mm stainless steel tubing and were heated to 34°C during analysis. The gas mixture was delivered from the sampling reservoir by switching the valve to the 'load' position. The
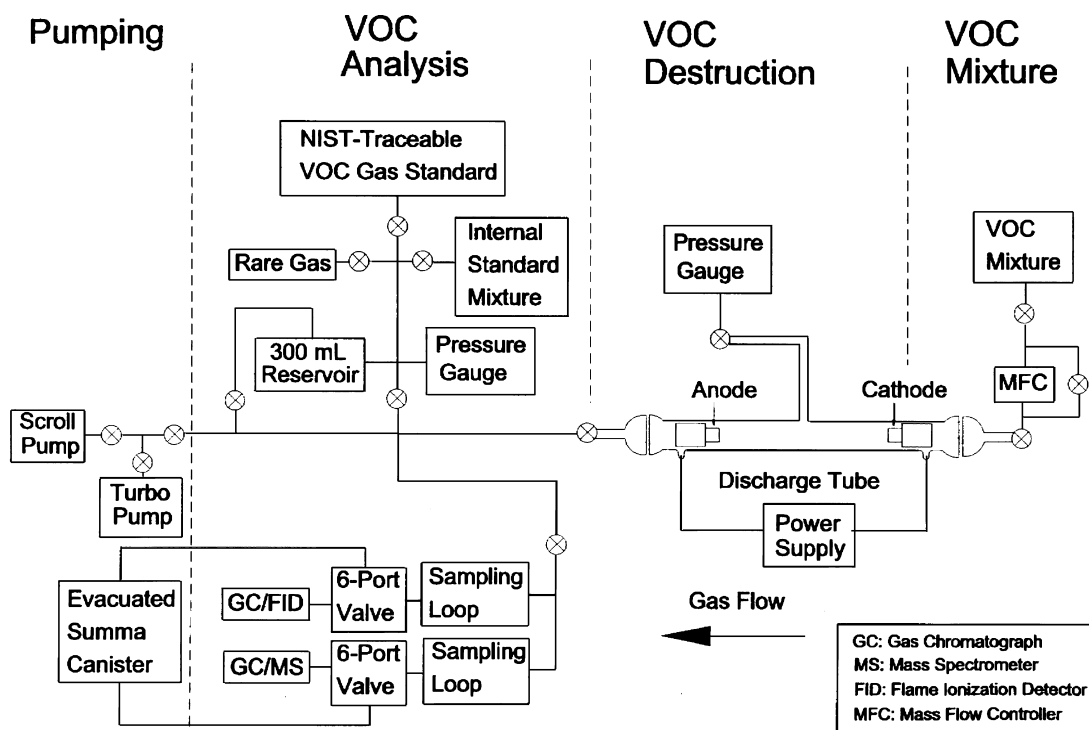
Fig. 1. Schematic diagram of the apparatus used for VOC destruction and sampling.

analyte was cryogenically concentrated in the sampling loop by immersing the loop in a liquid nitrogen bath. The trapped sample was transferred from the sampling loop to the GC injection port by switching the valve to the 'injection' position and by simultaneously immersing the sampling loop in a hot water bath (37°C).

2.4. Procedure

2.4.1. Gas standards

The NIST-traceable gas standard mixture (in argon) containing 400 ppmv each of methylene chloride, benzene, carbon tetrachloride and tetrachloroethylene, was purchased from Scott Specialty Gases. The internal standard (400 ppmv n-octane in argon) was prepared by mixing 0.053 kPa of n-octane vapor with 133 kPa of argon. The gas mixture was equilibrated at ambient temperature for at least seven days prior to utilizing it as an I.S.

2.5. Analysis procedure

The procedure to analyze the target VOC mixture and the NIST traceable standard were the same. In a typical analysis, the following procedures were performed: (1) The sampling valve was switched to the 'load' position; (2) The sampling reservoir, sampling loop (including transfer lines) and the Summa canister were evacuated to 10^{-7} kPa; (3) A continuously flowing gas sample was initiated in the discharge tube. Destruction of benzene occurred in the tube as a function of energy delivered to the plasma; (4) A portion of the flowing gas was diverted into the sampling loop and then isolated from the flowing stream; (5) The I.S. (1.33 kPa) was added to the gas sample and then pressurized with argon to a final pressure of 10.64 kPa; (6) With the sampling loop immersed in a liquid nitrogen bath, 1.33 kPa of the gas mixture was withdrawn from the sampling reservoir to the Summa canister. The vacuum in the Summa canister downstream of the sample loop was used to pull the 1.33 kPa sample aliquot through the

sampling loop. The VOC gases were cryogenically trapped in the sampling loop; (7) The GC oven temperature program was initiated immediately after the six-port valve was switched to the 'injection' position, and the sampling loop was placed in a hot water bath.

2.6. Instrument conditions

GC–MS analysis was performed on a Hewlett-Packard 5970 B GC–MS system equipped with an Rtx-5 column (30 m×0.25 mm I.D., 1.0 μm film thickness; Restek, Bellefonte, PA, USA). The oven temperature was held at 10°C for 10 min, then programmed to 200°C at a rate of 10°C/min. The flow-rate of carrier gas (helium) was held at 1.00 ml/min throughout the GC detector run by an electronic pressure controller with vacuum compensation. The injector temperature was held at 200°C and the GC–MS detector transfer line temperature was held at 280°C. Electron impact spectra were obtained with an electron energy of 70 eV and a source temperature of 180°C. Mass spectral data were acquired with a scan rate of 0.625 s/scan over a mass range of 29–300 u. The integrated area of a selected ion for each of the five VOCs was obtained using a validated software package (Hewlett-Packard EnviroQuant, Version C.00.02).

GC–FID analysis was carried out on a Hewlett-Packard GC–FID system equipped with an Rtx-5 column (60 m×0.53 mm I.D., 3.0 μm film thickness; Restek). The oven temperature was held at an initial temperature of 50°C for 10 min, then programmed to 200°C at a rate of 20°C/min. The injector and detector temperatures were both maintained at 230°C. The carrier gas (helium) flow was set at 5 ml/min. Integrated areas for each chromatographic peak were obtained with a Hewlett-Packard 3396A integrator.

3. Results and discussion

3.1. Calibration of VOC concentration:

3.1.1. Reproducibility

Replicate gas samples, including three NIST-traceable standards and I.S. (1.33 kPa) were analyzed at each of eight pressure levels, ranging from 0.133 to 5.32 kPa. The area ratio was defined as (integrated area of a selected ion for an analyte)/(integrated area of I.S.). The selected ions used were: m/z 49 for methylene chloride, m/z 78 for benzene, m/z 166 for tetrachloroethylene and m/z 43 for n-octane. Table 1 summarizes the relative standard deviations (RSD) of the area ratios that were measured at the eight pressure levels. The majority of the RSDs for the entire procedure (including gas mixing, sampling and analysis) are less than 18%. Carbon tetrachloride was also present in the NIST-traceable standard and

Table 1
Reproducibility (RSD) and number of determinations versus pressure ratio for the calibration of volatile organic compounds

Pressure ratio[a]	RSD, % (n)				
	Benzene[b]	Tetrachloro-ethylene[b]	Methylene chloride[b]	Methylene chloride[c]	Tetrachloro-ethylene[c]
4.00	9.17 (5)	9.3 (5)	11.98 (5)	13.56 (7)	3.13 (7)
3.00	10.88 (8)	9.69 (8)	18.34 (8)	3.49 (3)	4.13 (3)
2	8.65 (7)	8.84 (7)	15.38 (7)	13.12 (6)	11.1 (6)
1.5	7.06 (3)	3.01 (3)	26.46 (3)	12.58 (3)	13.42 (3)
1	7.29 (4)	15.15 (4)	17.57 (4)	11.66 (3)	12.64 (3)
0.5	7.88 (5)	5.45 (5)	17.76 (5)	16.02 (4)	2.37 (4)
0.25	5.84 (5)	11.17 (5)	17.87 (5)	6.96 (3)	6.04 (3)
0.1	7.24 (3)	3.89 (3)	8.19 (3)	25.14 (3)	2.02 (3)

[a] Pressure of I.S. was 0.67 to 2.66 kPa.
[b] Analyzed by GC–MS.
[c] Analyzed by GC–FID.

co-elutes with benzene on the Rtx-5 column. Since carbon tetrachloride is not one of the target compounds in the plasma discharge destruction experiments, no attempt was made to resolve these two gases by optimizing GC conditions. Therefore, benzene was not analyzed by GC–FID. Additionally, because a column 30 m long with a film thickness of 1.0 μm was used in the GC–MS analysis, methylene chloride exhibits a very short retention time (5.8 min) even at an initial oven temperature of 10°C (Fig. 2), resulting in large RSDs for this compound (8–26%). As expected, the abnormally large RSD (25.14%) observed for methylene chloride, as analyzed by GC–FID, was because the pressure level

(0.133 kPa) was near its limit of detection (0.122 kPa).

3.2. Linearity and limit of detection

Over a pressure range of 0.133 to 5.32 kPa, an eight-point calibration curve with replicate measurements at each point was constructed for each analyte by plotting the pressure ratios of the gas analytes relative to the I.S. versus their corresponding area ratios. Slopes were determined by linear regression with and without intercept computation for all of the experimental data (a minimum of 32 data points for each compound). The *t*-tests for all linear regressions
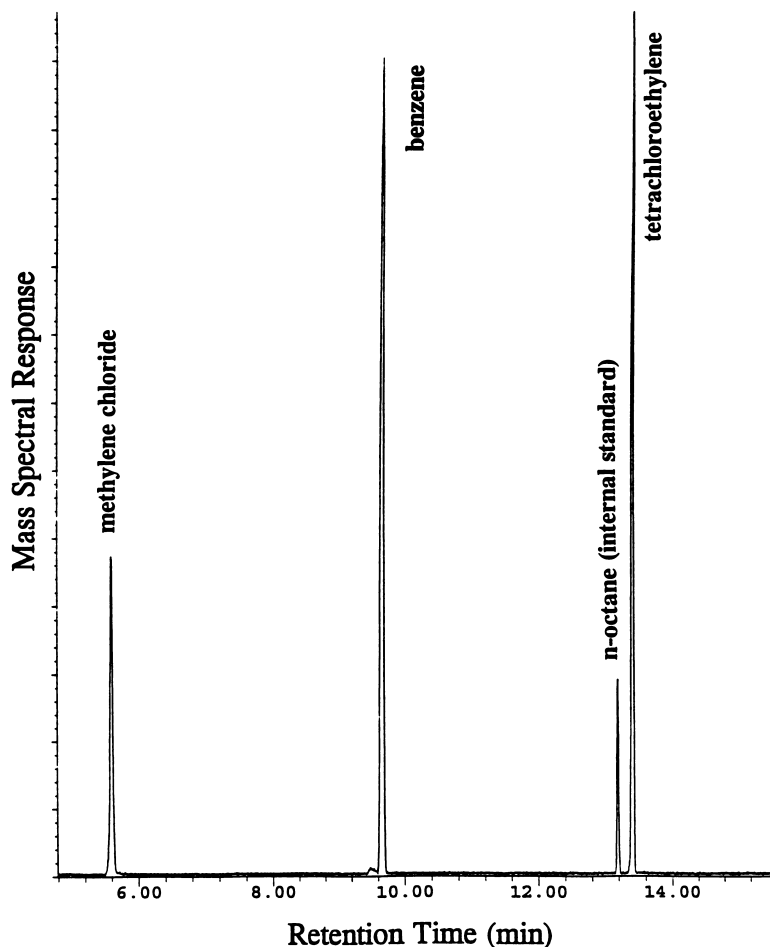

Fig. 2. Total ion mass chromatogram for four analytes and I.S.

Table 2
Linearity of the calibration and detection limit for volatile organic compounds

Linearity/ detection limit	Benzene[a]	Tetrachloro- ethylene[a]	Methylene chloride[a]	Methylene chloride[b]	Tetrachloro- ethylene[b]
Slope	1.12	0.98	1.12	0.29	0.49
Correlation coefficient	0.98	0.97	0.96	0.98	0.97
Detection limit (nmol)	0.83	0.96	0.9	5.26	0.35

[a] Analyzed by GC–MS.
[b] Analyzed by GC–FID.

found that the intercepts given in Table 2 were not significant at the 5% significance level. Thus, it was concluded that the intercepts were not different from zero. Also shown in Table 2, the correlation coefficients for all of the analytes fell in a range of 0.96–0.98, and the slopes ranged from 0.98 to 1.35 for GC–MS analysis and from 0.29 to 0.49 for GC–FID analysis. The limit of detection is defined [19,20] as:

$$\text{limit of detection} = 3.3 \, (\text{SD}/\text{slope})$$

where SD is the standard deviation of the area ratio at the lowest detectable pressure ratio, and slope is the slope determined from linear regression analysis for each analyte. This definition implies a risk of 0.05% for false positive based on the normal probability distribution. The limits of detection for all of the analytes evaluated in this methodology are listed in Table 2, ranging from 0.66 to 5.32 nmole, which are much higher than the detection limits obtained with thermal desorption–GC–MS methodology [1,8,9]. This is because the GC–MS detection limits were based on a gas sampling size of 1.33 kPa, which is equivalent to a volumetric sample of 3.9 ml, a considerably smaller volume than the conventional air sample (>1 l) [1,8,9].

3.3. Destruction efficiency of VOCs

Calibration curves were constructed as described in the preceding section to determine the concentrations of VOC mixtures in rare gases. Methylene chloride was mixed with argon, neon and helium, and benzene was mixed with argon and neon to approximately 400 ppmv in 44 l pressurized gas cylinders to produce target gas mixtures. The mixed gases were allowed to come to equilibrium for at

least a week before sampling. The concentrations measured for the five gas mixtures using GC–MS are shown in Table 3. The measured concentrations of the VOC mixtures were significantly less than the concentrations based on the ratio of the partial pressures, probably because of absorption and/or reaction of the VOCs with the cylinder walls.

We have used this procedure to analyze the VOC concentration in the plasma reactor as a function of energy input to the plasma. A DC glow discharge was produced in the plasma reactor for a continuous flow of the methylene chloride–neon mixture. The concentration of methylene chloride is shown in Fig. 3 for a 1000-sccm (standard cm³/min) flow-rate as a function of energy density, defined as the energy input applied to the plasma divided by the flow-rate. The concentration of methylene chloride decreases exponentially with energy density and the destruction efficiency increases with increasing pressure [18]. We have investigated the destruction efficiency for the mixtures in Table 3. The results of this study and a discussion of the destruction mechanism will be published separately [18].

4. Conclusion

The goal of this study was to provide a validated

Table 3
Concentration of VOC mixtures

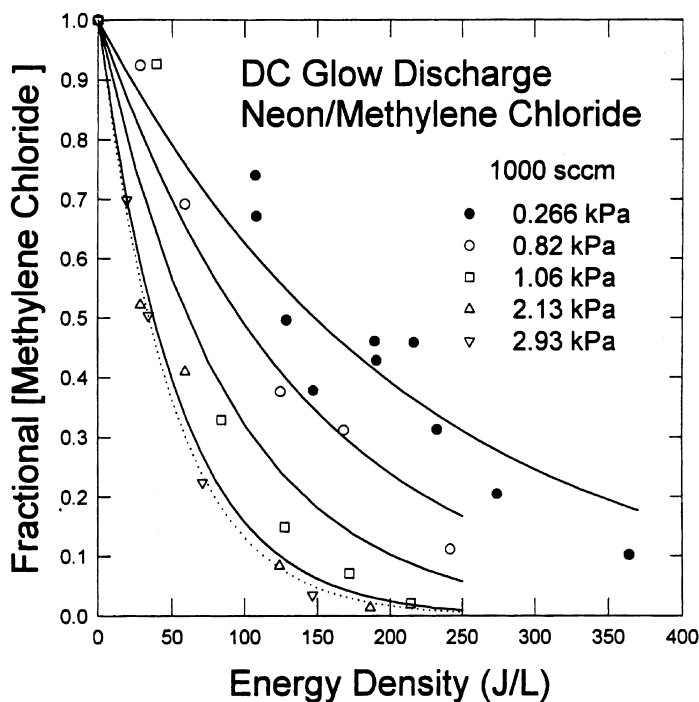| VOC mixtures	Concentration (ppmv)
Methylene chloride–argon	304
Methylene chloride–neon	314
Methylene chloride–helium	312
Benzene–argon	320
Benzene–neon	280

Fig. 3. Methylene chloride concentration as a function of input energy density at different pressures for a methylene chloride–neon mixture. The flow-rate was 1000 sccm.

analytical methodology for monitoring the destruction efficiency of VOCs emerging from a low pressure, flow-through plasma discharge cell. The results presented here revealed that both precision and linearity for sampling and analysis were sufficient to meet this goal. In addition, because the limits of detection were below the operating pressure range normally employed in the plasma discharge experiments [18], and the calibration curves were constructed to include the discharge pressure ranges, the validated methodology is currently being used on a routine basis in the plasma discharge experiments. Identification of the plasma discharge products, as well as the destruction efficiency and mechanism, will be the scope of future manuscripts.

Acknowledgements

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