

# Determination of Ultra Trace Levels of 1,2-Dichloroethane in Air by Sample Enrichment Micromachined Gas Chromatography–Differential Mobility Detection

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## Abstract

A novel analytical procedure has been developed for the analysis of ultra trace levels of 1,2-dichloroethane (EDC) in air using sample enrichment in combination with micromachined gas chromatography (GC) and differential mobility detection (DMD). When compared to other contemporary GC techniques, such as GC–flame ionization detection, GC–electron capture detection, or GC–electrolytic conductivity detection, the employment of a DMD in combination with a preconcentrator provided better sensitivity and markedly improved selectivity. The increase in sensitivity reduces false-negative results, while the improvement in selectivity decreases the potential for false-positive results. Using the technique described, a complete analysis can be conducted in less than 10 min, with a detection limit of 0.7 ppb (v/v) of EDC and a short term precision of less than 6%. A correlation coefficient of 0.9988 was obtained over an EDC concentration range from 0.7 ppb to 36.4 ppb (v/v). The analytical system also has an on-board microTCD in series with the DMD, allowing both detector outputs to be monitored simultaneously. With the pre-concentration technique, the microTCD can detect EDC as low as 15 ppb (v/v) with a substantially enhanced linear dynamic range in addition to providing a confirmation means for the presence of EDC at the level cited.

## Introduction

The compound 1,2-dichloroethane, commonly known as ethylene dichloride (EDC), is a chemical of industrial significance. It is used mainly to produce vinyl chloride monomer, the major precursor for the manufacture of polyvinyl chloride (PVC) (1). EDC can also be used as an intermediate in the production of other organic compounds, such as vinylidene chloride, 1,1,1-trichloroethane, trichloroethylene, ethylene diamines, and as a

solvent. The production of EDC typically involves reacting ethylene with chlorine via a direct chlorination process (2) or reacting ethylene with hydrogen chloride and oxygen via an oxychlorination process (3).

As a result of recent government studies of volatile organic compounds in ambient air, especially EDC in the Fort Saskatchewan (Alberta region), a need for monitoring of EDC at the part per billion level has been identified. A common approach for the analysis of EDC is the use of gas chromatography (GC) with flame ionization detection (FID) (4,5,6). While this technique is simple and easy to implement, there are two major constraints. GC–FID does not have sufficient sensitivity for the application described, which requires detection limits at the 1 ppb (v/v) level. Furthermore, the possibility of obtaining a false-positive result exists because identification of the solute of interest is strictly based on retention time. Alternative approaches to obtain improved sensitivity such as the employment of selective detectors, for example, electron capture detection (ECD) or electrolytic conductivity detection (ELCD), would be impractical for field and continuous deployment due to the lack of long-term system stability and ease of use (7,8).

Recently, a new GC detector, based on the principle of microelectromechanical radio frequency modulated-ion mobility spectrometry (MEMS-RF-IMS), also known as differential mobility detection (DMD), has been successfully developed and commercialized (9,10). This detector offers both high degrees of sensitivity and selectivity.

This paper describes an analytical method involving the use of a preconcentrator in combination with a micromachined GC equipped with a DMD detector for the measurement of part per billion levels of EDC in ambient air.

## Experimental Details

### Equipment and Supplies

Two portable AIRSENSE EDU GC-3 Sample Enrichment Devices (Schwerin, Germany) were used for solute preconcen-

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tration.

A Varian CP-4900 Micromachined GC (Middelburg, The Netherlands), equipped with a 8 m, 0.25-mm i.d., 0.25 micron CP-Sil 5CB analytical column, and a micro thermal conductivity detector ( $\mu$ TCD) was used for the analytical work. The  $\mu$ TCD was connected in series with a Sionex micromachined differential mobility (DMD) detector (Bedford, MA), allowing both detector outputs to be monitored simultaneously. Figure 1 (See page 5A) shows a photograph of the apparatus used.

For the  $\mu$ GC, purified helium was used as a carrier gas. For the DMD, purified air (free of carbon dioxide and water) was used as transport gas. The data collected were processed with the Sionex Expert version 2.5 and the Varian Elite software.

The 1,2-dichloroethane standard, the carrier gas, and the transport gas were obtained from BOC Gas, of Nisku, Alberta, Canada.

The final conditions used for solute enrichment the gas chromatographic conditions used are as follows. Conditions for AIRSENSE EDU-3 Preconcentrator: (i) Sampling phase: sampling time, 120 s; sampling temperature, 40°C; post sampling time, 0 s; (ii) Desorption phase: desorption time, 120 s; desorption temperature, 200°C; (iii) Injection phase: injection time, 10 s; injection temperature, 200°C; (iv) Cleaning phase: cleaning time, 60 s; cleaning temperature, 250°C; (v) Cooling phase: cooling time, 220 s; (vi) External purge gas pressure: 15 psig; (vii) Pump rate: 150 mL/min.

GC conditions used for  $\mu$ GC- $\mu$ TCD-DMD: (i) Carrier gas: helium, Pressure, 250 kPa; (ii) Column, 50°C; (iii) Injector: temperature, 110°C; injector time, 200 msec; (iv) Sampling time, 3 s; (v) Sampling line temperature, 110°C; (vi) Stabilization time, 5 s; (vii) Continuous flow, Disabled.

## Results and Discussions

### Preconcentrator performance optimization

The preliminary study conducted on the first AIRSENSE EDU GC-3 unit for the analysis of EDC showed the preconcentrator was not suitable for use in this application due to severe carry over. Carry over at a level of 30% following a 100 ppb (v/v) standard was encountered. At least 10 subsequent blank analyses were required to remove the carry-over. The sources were found to be the rubber polymer used in the sampling tip, the polymer O-rings in the flow path of the samples, and untreated solenoid/valve surfaces.

A second AIRSENSE EDU GC-3, which incorporated the latest surface deactivation treatment and the removal of organic polymers such as silicone, Teflon, and Viton from the sample flow path and sampling tip, was employed for the rest of the project.

Tenax TA was selected for use as the trapping medium based on its versatility and hydrophobic properties (11). Figure 2 illustrates the operating principle of the AIRSENSE unit. In order to

obtain the maximum sensitivity for 1,2-dichloroethane, several important parameters associated with the preconcentrator had to be optimized.

### Sampling time

One of the most important parameters is sampling time, the length of time a sample is exposed to the trapping medium. Figure 3 shows a plot of the change in 1,2-dichloroethane signal area as the sampling time varied from 1 to 10 min. Significant sample enrichment is observed initially with increased sampling time; however, a plateau was reached after about 4 min. A sampling time of 2 min was chosen for the EDC analysis, as this would improve the overall sample throughput capability, while still providing adequate sensitivity. If required, a 4 min sampling time can be used to increase the system sensitivity by a further

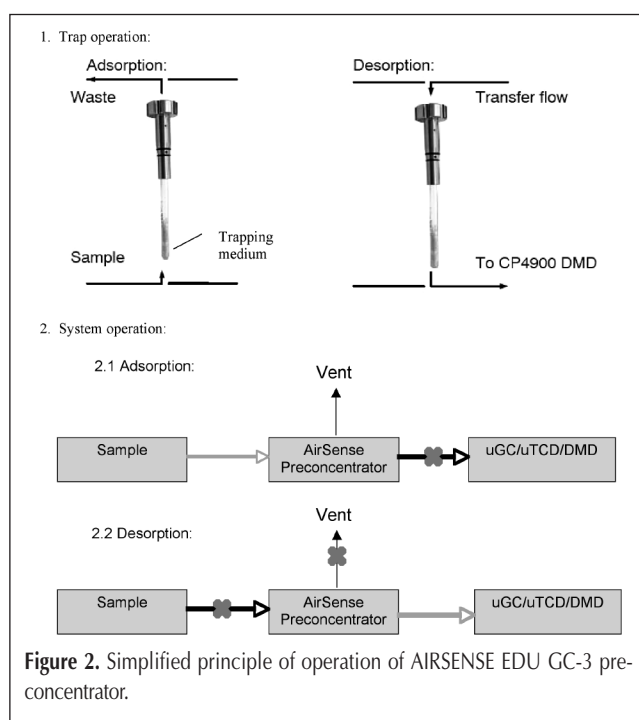


Figure 2. Simplified principle of operation of AIRSENSE EDU GC-3 preconcentrator.

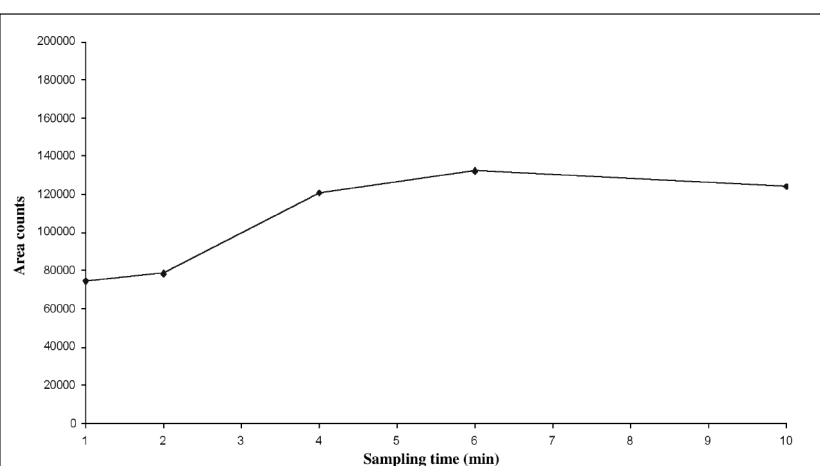


Figure 3. Sample enrichment optimization: 1,2-dichloroethane signal area vs. sampling time for 7.3 ppb (v/v) EDC in nitrogen at ca 150 mL/min sampling rate.

33% as shown in Figure 3.

#### Trapping temperature

Trapping temperature is the temperature used to trap the solute of interest on an adsorbent. In general, a lower temperature improves adsorbent retention for the solute to be trapped, thus, enhancing overall system sensitivity. A trapping temperature of 40°C was chosen for this application to deliver reliable trapping efficiency for up to 4 min sampling time at a sampling flow rate of 150 mL/min. Lower trapping temperatures can be employed at the expense of the analytical cycle time. For example, lowering the trapping temperature from 40°C to 30°C requires an extra 8 min for the preconcentrator to recycle to a ready state. This becomes impractical when a short cycle time is required.

#### Desorption temperature

Desorption temperature is the temperature applied to the adsorbent to remove the trapped analyte. For 1,2-dichloroethane, recovery of the analyte remains constant between 180°C and 250°C. In comparison, an approximately 37% loss of recovery for 1,2-dichloroethane was observed at 150°C. For this application, a desorption temperature of 200°C was chosen to achieve reliable solute recovery.

#### Desorption time

The desorption time is the length of time at which the adsorbent is kept at an elevated temperature to remove trapped analyte. For complete removal of 1,2-dichloroethane under the conditions stated, a minimum of 1.5 min was required. A time of 2 min was chosen for this application.

Other parameters such as injection time, post sampling temperature, and post sampling purge time were selected based on the manufacturer's suggested values.

#### Analytical performance

MEMS-RF-IMS has recently been developed and commercialized (9,10). In contrast to conventional TOF-IMS, which operates in the low field regime where the applied field strength is less than 1000 V/cm and the ion mobility is constant, MEMS-RF-IMS uses the nonlinear mobility dependence in strong radio frequency (RF) electric fields for ion filtering. This enhances system selectivity towards target compounds. Another key advantage of differential mobility is that it does not require ion pulses for operation, and the resolution is not dictated by the width of the ion pulse. Instead, the ions are introduced continuously into the ion filter and almost all of the desired ions are passed through the filter, maintaining the high sensitivity of the device. Also, the simultaneous detection of both positive and neg-

ative ions is feasible using DMD. A detailed discussion of differential mobility spectrometry employed as a GC detector has been previously published by Luong et al (9,10).

In this application, the DMD offers two distinctive advantages when compared to classical GC detectors such as the FID, ECD, and ELCD: (i) high sensitivity; and (ii) high selectivity, derived from four different subcomponents of the detector, namely ionization selectivity, selectivity offered by the voltages chosen for

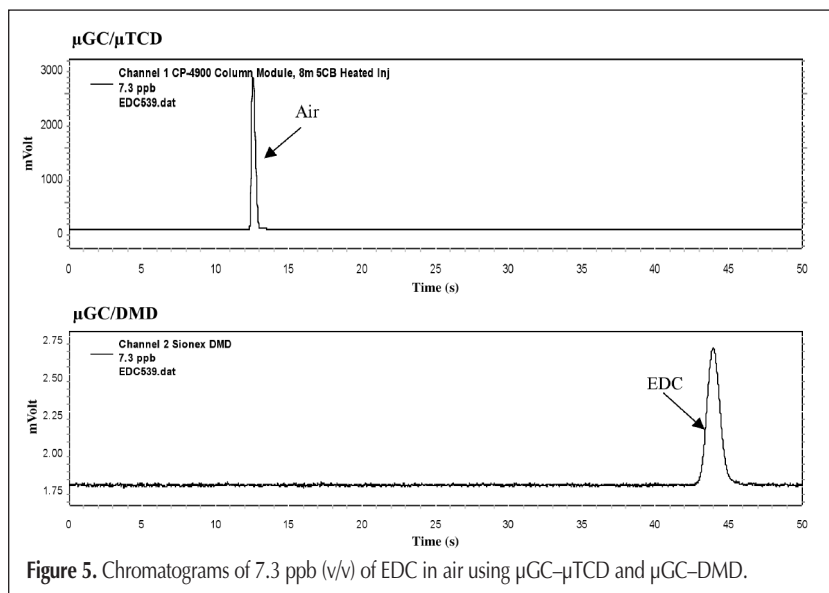


Figure 5. Chromatograms of 7.3 ppb (v/v) of EDC in air using  $\mu$ GC- $\mu$ TCD and  $\mu$ GC-DMD.

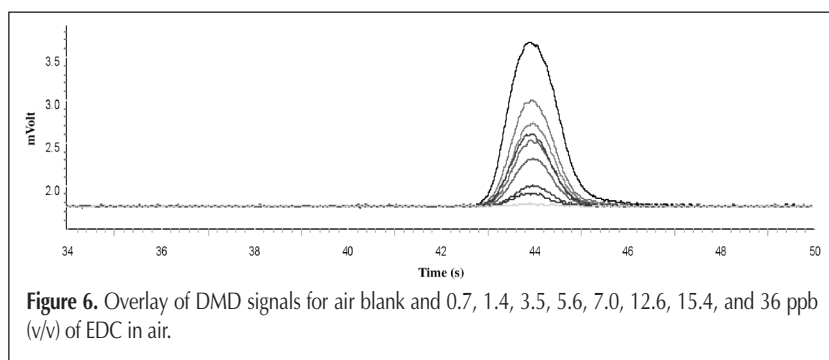


Figure 6. Overlay of DMD signals for air blank and 0.7, 1.4, 3.5, 5.6, 7.0, 12.6, 15.4, and 36 ppb (v/v) of EDC in air.

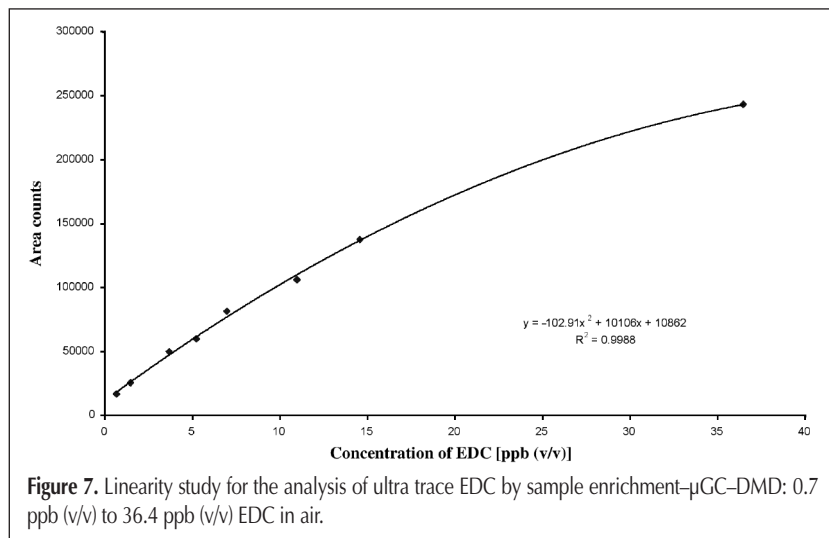


Figure 7. Linearity study for the analysis of ultra trace EDC by sample enrichment- $\mu$ GC-DMD: 0.7 ppb (v/v) to 36.4 ppb (v/v) EDC in air.

the RF, and compensation voltages ( $V_c$ ), and finally detection on either the positive or the negative channel. The high degree of selectivity resulting from these four subcomponents in combination with the selectivity gained from the analytical column used minimizes the possibility of a false-positive result.

An FID can be used for the measurement of EDC with good sensitivity; however, the FID is a universal detector for most organic compounds. The lack of selectivity of the FID can lead to unwanted false positives because the analytical system has to rely solely on retention time to establish the identity of a solute. The potential for chromatographic interferences in this application is high because the presence of ultra trace organic compounds in ambient air, particularly in industrial environments, is a very real possibility (12). In addition, an FID requires compressed hydrogen and air for fuel gases and compressed nitrogen as an auxiliary gas, making it less practical for field deployment and resulting in a higher cost of long term ownership.

An ECD is very sensitive for EDC (4,7,8). While an ECD reduces the possibility of false positives with its selectivity for halogenated compounds, this issue is not completely resolved because an ECD can also be quite responsive to other common airborne organics from vehicle emissions, such as aromatics, light oxygenated compounds, and sulfur-containing compounds.

Additionally, to provide good performance, an ECD requires very clean reaction gas.

The ELCD also offers a very high degree of selectivity for chlorinated compounds. This detector is not very amenable for field use because the reactor constantly operates around 800°C to convert EDC to hydrogen chloride. Also, the level of the solvent used for the electroconductivity measurement must be monitored, and the anion exchange cartridges require frequent replacement (7,8,13).

In contrast, only filtered compressed air is required to operate the DMD. By design, the detector requires no routine maintenance owing to the fact that it has no moving parts. It is also portable, making it the detector of choice for the application described.

Optimization of the system sensitivity and selectivity involved choosing appropriate RF and compensation voltages. Figure 4 (See page 5A) shows a topographic chart obtained for EDC at an RF voltage of 800 V with air as transport gas.

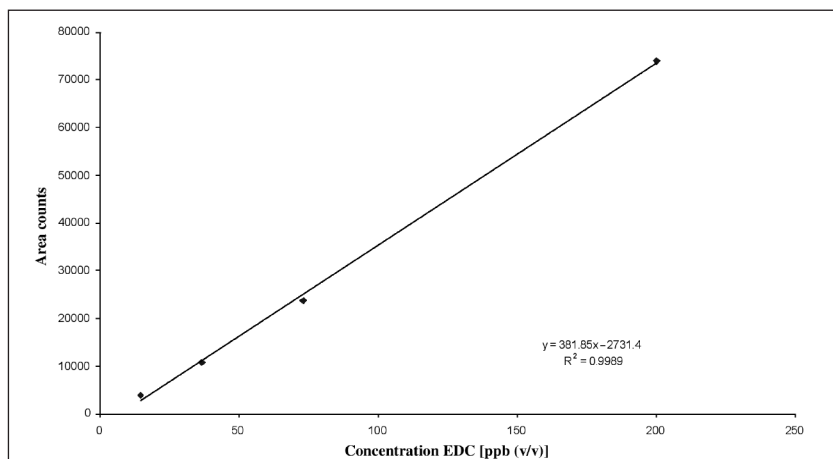
At an RF voltage of 800 V, the cluster representing EDC was found to be at a  $V_c$  of -18.5 V. This cluster is well resolved from the reactant ion product ridge, which is at a  $V_c$  of -13 V and free of any potential chromatographic interferences with no dimer or trimer clusters in the vicinity. For a compound to be identified as

EDC, it must have a retention time of 44 s and a  $V_c$  of -18.5 V under an RF of 800 V on the negative channel. The possibility of falsely identifying EDC is substantially reduced if not completely eliminated due to the multiple filtering parameters stated.

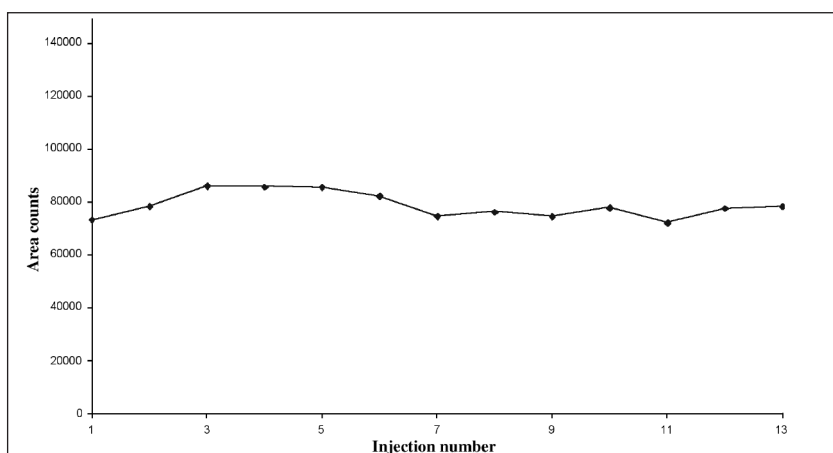
The aspects of the analytical performance of the system that were evaluated are: (i) detection limit, (ii) linear dynamic range, (iii) precision, and (iv) carry-over.

The detection limit of the system was studied by conducting serial dilutions of a standard gas mixture containing 7.3 ppm (v/v) EDC in nitrogen with air. Figure 5 shows chromatograms for 7.3 ppb (v/v) EDC on the  $\mu$ TCD and DMD, respectively. On the  $\mu$ TCD, no EDC was detected, whereas on the DMD, the EDC signal was clearly visible. On the other hand, air was detected on the  $\mu$ TCD but not on the DMD, demonstrating the selectivity of the DMD against the matrix of the sample.

Figure 6 shows an overlay of signals of an air blank and standards containing from 0.7 to 36 ppb (v/v) EDC on the DMD. Figure 7 illustrates the linearity of the results obtained. Using the technique described, a practical detection limit of 0.7 ppb EDC (v/v) can be attained. The analytical system was found to be linear from 0.7 ppb to 15 ppb (v/v), with a correlation coefficient of 0.9921. Using a quadratic fit, the correlation coefficient over the range of 0.7 to 36 ppb was 0.9988. At higher concentrations, EDC can easily be detected by the on-board  $\mu$ TCD. This provides another means for confirmation and also extends the linear dynamic range of the analytical system.



**Figure 8.** Linearity study for the analysis of ultra trace EDC by sample enrichment- $\mu$ GC- $\mu$ TCD: 14.6 ppb (v/v) to 200 ppb (v/v) EDC in Air.



**Figure 9.** Short term precision study: 7.3 ppb (v/v) of EDC in air by sample enrichment- $\mu$ GC-DMD.

Figure 8 illustrates the linearity obtained on the  $\mu$ TCD over the range of 14.6 to 200 ppb (v/v) EDC.

A short term precision study was conducted by analyzing 13 ambient lab air samples containing 7.3 ppb (v/v) of EDC over a period of two days. A respectable relative standard deviation of

Injection Number	Area Counts
1	73276
2	78283
3	86076
4	85854
5	85583
6	82223
7	74725
8	76332
9	74473
10	77883
11	72140
12	77686
13	78369
Ave	78685
SD	4822
%RSD	6.13

6.1% was obtained as shown in Figure 9. Table I lists the results obtained.

Carry over is an important issue that required close examination because it can degrade system readiness and might lead to a false-positive result. Figures 10 and 11 show chromatograms of a system blank after an injection of 7.3 ppb (v/v) of EDC and an overlay of the blank and the 7.3 ppb (v/v) standard, respectively. At a concentration of 7.3 ppb (v/v) of EDC, a very slight baseline elevation at the retention time of EDC was observed as shown in Figure 11. This level of carry over, however, was found to be less than the detection limit of the analytical system (0.7 ppb). The carry over issue was further examined by deliberately using an unusually high concentration of EDC of 200 ppb (v/v) in air. Figure 12 shows an overlay of 200 ppb (v/v) of EDC and two subsequent blank runs. As seen on the chromatogram, a carry over of approximately 7.8% was detected in the first blank run, but in the second blank run, no EDC was detected. The results showed the issue with carry over in the first generation of the preconcentrator has been substantially reduced if not eliminated, making the system acceptable for the application described.

### Constraints and limitations

The  $\mu$ GC–DMD was found to be very highly reliable due to its design. Over the course of a six month evaluation, successful daily start-up was attained with no maintenance or system calibration adjustment required. The system does need transport gas that is free of carbon dioxide and water for optimum and reliable performance. Either a recirculating transport gas system or an air generator is needed for ease of use because the rate of air consumption for the device is high at 0.5 L/min.

The AIRSENSE preconcentrator demonstrated the concept of solute enrichment to improve sensitivity. Rectifiable improvements include a more accurate pump system and software feedback control of the heating that is driven by temperature rather than time.

### Conclusions

A novel analytical procedure has been developed for the analysis of ultra trace levels of 1,2-dichloroethane (EDC) in air by sample enrichment in conjunction with  $\mu$ GC and DMD. This approach affords a detection limit of 0.7 ppb (v/v) for EDC. The on-board microTCD can also detect EDC at levels as low as 15 ppb (v/v) with a substantially enhanced linear dynamic range in addition to providing a means of confirmation for the presence of EDC at the level cited.

The  $\mu$ GC–DMD was found to be highly reliable for the intended application. Despite some rectifiable limitations, the AIRSENSE portable preconcentrator was found to function as described. When compared to other contemporary GC tech-

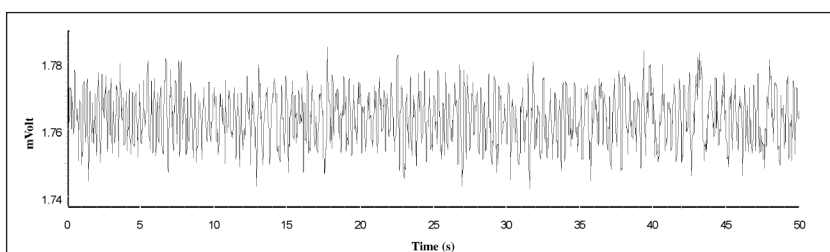


Figure 10. Chromatogram of an injection of air blank after the analysis of a 7.3 ppb (v/v) EDC in air.

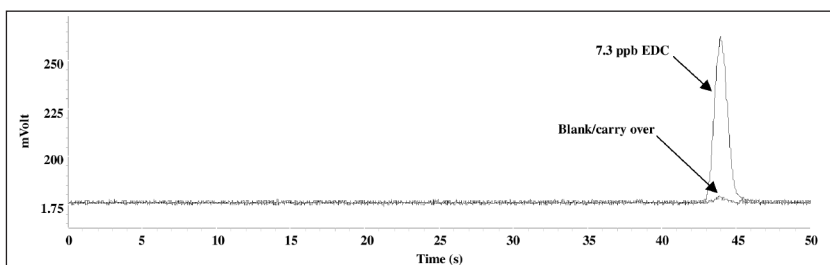


Figure 11. Carry over study: overlay of blank and 7.3 ppb (v/v) of EDC in air.

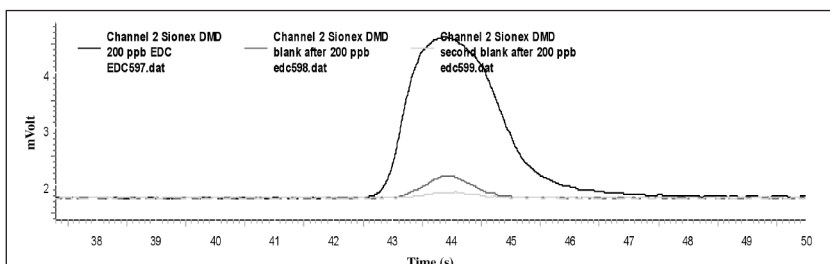


Figure 12. Carry over study: overlay of 200 ppb (v/v) of EDC in air and two subsequent air blanks.

niques such as GC-FID, GC-ECD, or GC-ELCD, the employment of a DMD in combination with a preconcentrator provided better sensitivity, markedly improved selectivity, and lower cost of ownership. The increase in sensitivity reduces false negative results, while the improvement in selectivity decreases the potential for false-positive results.

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