Real time monitoring of hazardous airborne chemicals: A styrene investigation

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Abstract

The low level detection of air pollutants requires reliable sampling and calibration techniques, as well as using sophisticated analytical instrumentation. Incorporating these requirements into a mobile platform allows for accurate, curb side measurement of airborne ambient chemicals in real time. In this case study, air emissions from two manufacturing facilities in close proximity to each other were monitored with a mobile unit to chemically characterize and differentiate the emissions from each facility. Based upon the downwind fingerprinting and concentration levels, the mobile unit was able to isolate the source of the emissions to the responsible facility. A few chemicals which were detected by the TAGA had never been reported by the companies. Real time proximity monitoring was accomplished by using a triple quadrupole mass spectrometer (TAGA IIe). The TAGA IIe interfaces with a low pressure chemical ionization source that operates at 3 Torr and 100 μA. By monitoring the response of specific parent/daughter ion pairs, the TAGA IIe unit was able to determine the point-of-impingement concentrations of styrene and other ambient airborne chemicals. Positive identification and quantitation of styrene was accomplished by multiple measurements of the following ion pairs: 104/78, 104/77, 104/65 and 104/52. By optimizing various parameters of the TAGA IIe a method detection limit of 1.1 μg/m^3 was achieved for styrene. A daily multi-point calibration was performed using a liquid standard. The maximum half-hour average concentration of styrene measured downwind of the two facilities was 2300 μg/m^3 and the maximum instantaneous level was measured at 15,000 μg/m^3. The mobile capability of the unit was also utilized in determining the ambient airborne concentration of styrene at various distances from the companies with the maximum levels measured at close proximity to the emission sources.
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1. Introduction

Styrene (C$_8$H$_8$) is a clear, colourless liquid hydrocarbon which is easily polymerized and therefore widely used in the manufacturing of plastics, synthetic rubber, resins, insulators and in the production of protective surface coatings. Industrial workers are exposed potentially to styrene emissions during the manufacturer or production of boats, tubs and showers enclosures. The acute health effects attributed to styrene exposure is irritation of the skin, eyes, upper respiratory tract and gastrointestinal effects [1–3]. Chronic exposure to styrene emissions can affect the central nervous system with symptoms such as depression, headache, fatigue and weakness shown and can cause minor effects on kidney function and blood [1–3]. Styrene is classified as a possible human carcinogen by the United States Environmental Protection Agency (US EPA) and by the International Agency for Research on Cancer (IARC) [2,3]. The environmental and human health impacts of styrene are quite severe hence the need for ongoing monitoring of sources that release this substance is critical.

The ambient airborne levels of styrene in urban areas range between 0.29 and 3.8 μg/m^3 [1]. Styrene has a penetrating, distinctive smell with an odour threshold in the range of 200–640 μg/m^3 [4]. In 1987, the World Health Organization (WHO) presented a 30-min average guideline for styrene expo-

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sure, based upon odour annoyance at 70 μg/m^3 [5]. The Ontario Ministry of the Environment (OMOE) also uses a half-hour point of impingement (POI) standard based upon odour of 400 μg/m^3 [6]. To date, the US EPA does not provide an ambient air exposure limit [7].

The purpose of this study was to chemically characterize and differentiate emissions from two styrene-emitting companies located in close proximity of each other and to confirm if the applicable Province of Ontario environmental standard for styrene was being exceeded.

2. Experimental

2.1. TAGA IIe mass spectrometer

The Trace Atmospheric Gas Analyzer IIe (TAGA IIe) mass spectrometer (Fig. 1) is a real time, direct-air sampling analytical instrument mounted in a 10-m "Orion" coach [8] as shown in Fig. 2. The mobile TAGA technology has been used extensively by the OMOE since the early 1980s in a variety of air compliance monitoring studies [9] as well as for environmental emergencies [10]. Ambient airborne levels of several hundreds of unknown chemicals can be identified and quantified using this type of technology.

The coach also accommodates a computer for automated control of the TAGA IIe including data acquisition and analysis and a meteorological tower. A telescopic 10-m meteorological tower equipped with a combination anemometer/wind vane, used for recording ambient air temperature, wind direction and wind speed. The mobile TAGA IIe can be fully functional in 30 min from a complete shut-down mode.

A TAGA IIe is a triplet quadrupole mass spectrometer (MS) consisting of an air inlet system, an ionization source, a mass analyzer with a series of mass filters and focusing elements, an ion detector and operating computer. Under ambient monitoring conditions, air is sampled continuously at a flow rate of 90 l/min directly into the ion source. This high flow rate and a direct link to a heated ionization chamber assured that sample adsorption or degradation is negligible.

Upon arrival at an investigation site, the TAGA IIe is used to determine background levels and calibration for the target chemicals (if they are known) are performed upwind of the emission source. Following upwind measurements, "plume tracking" is conducted by driving the mobile unit downwind of the source while monitoring for selected target compounds to determine the location of the maximum instantaneous levels. Monitoring includes "chemically fingerprinting" the air to identify as many chemicals as possible and determine the airborne levels. Depending on wind direction shifts, monitoring is performed at several downwind locations. During surveys, weather forecasts for the region being monitored are used to assist with the air monitoring. The monitoring information is collected by the computer which includes minute-by-minute meteorological data and instantaneous levels of target compounds.

Fig. 1. External view of the mobile TAGA IIe, "Explorer" and retractable meteorological tower.
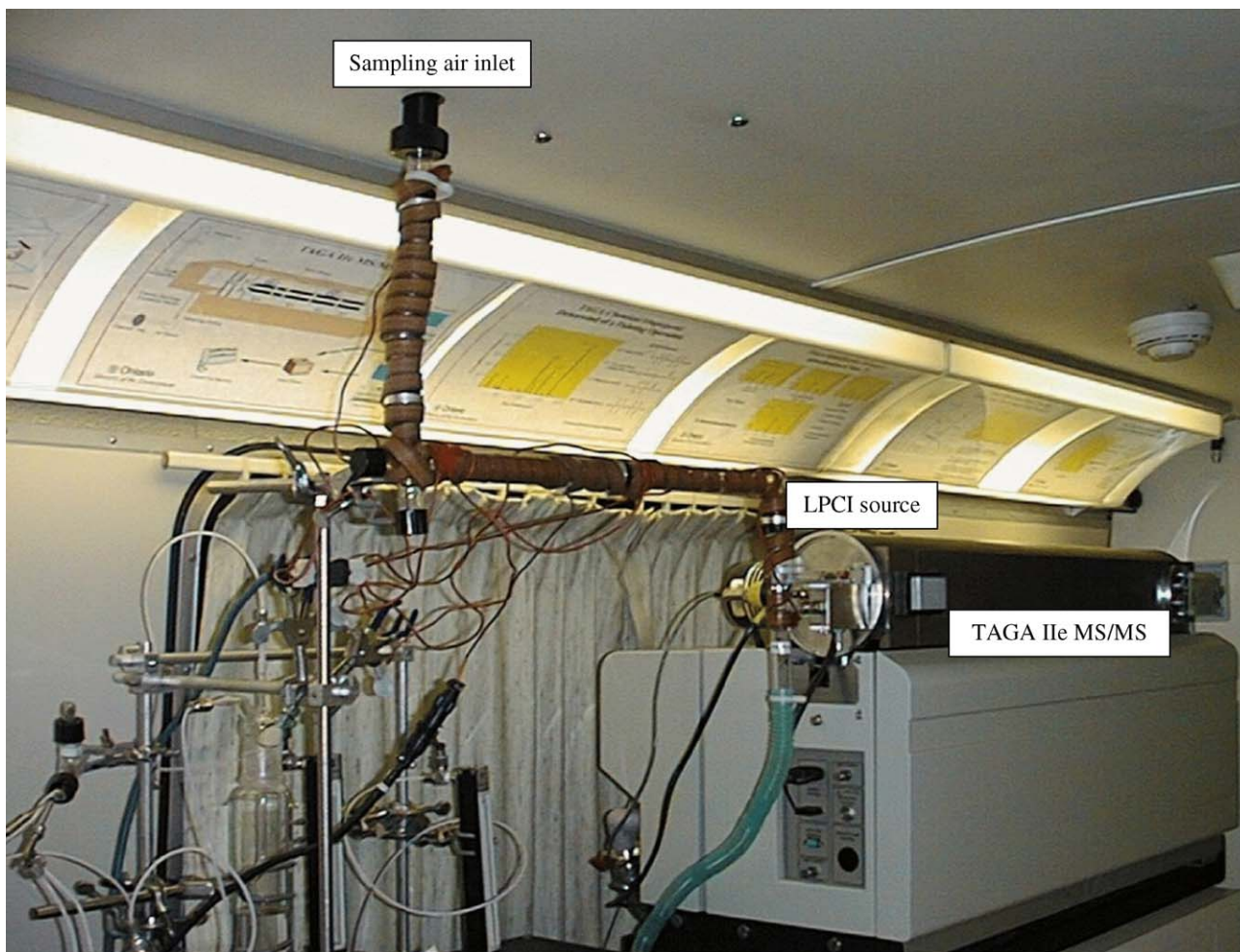
Fig. 2. The TAGA IIe mass spectrometer housed inside the mobile analytical laboratory, known as the "Explorer".

2.2. Low pressure chemical ionization source

For several years, the most common method for sampling volatile organic pollutants (VOC) involved cartridge sampling and analysis at a later time using gas chromatography/tandem mass spectrometry (GC/MS/MS); this method is particularly useful for low levels (μg/m^3) [11,12]. However, when ambient VOC concentrations are higher than approximately 300 μg/m^3, adsorbent cartridges become overloaded, breakthrough can occur and consequently ambient pollutant levels cannot be reliably quantified. A low pressure chemical ionization (LPCI) source was developed for the TAGA IIe to measure in real time aromatic compounds in the ambient air yielding quantitative results with low detection limits (i.e. 0–800 μg/m^3).

The ionization of airborne chemicals is accomplished through a series of gas-kinetic, chemical ionization reactions, initiated in the LPCI source. The LPCI source consists of a stainless steel rod to which a current is applied to produce a glow discharge in a small volume of ambient air. This discharge allows for the formation of positive and negative reagent ions by donating or removing an electron. The LPCI source is normally operated at a pressure of 3 Torr and 100 μA. Airborne chemicals undergo charge transfer reactions with reagent ions (typically NO$^+$, N$_2$$^+$

and O$_2$$^+$) to yield parent ions which are mass analyzed in the first quadrupole, Q1.

2.3. Identification

The single MS spectrums obtained downwind of two companies (Companies A and B) in Cornwall, Ontario is shown in Fig. 3. The major parent ions observed downwind of Company A were at 58, 60, 73, 88, 92, 100, 104 and 106 atomic mass units (amu). The major parent ions observed while downwind of Company B were at 58, 92 and 104 amu. These selected Q1 parent ions were then subjected to collision activated dissociation (CAD) with an inert gas, nitrogen, to produce fragment ions "daughter" in the second quadrupole region (Q2). By comparing the parent/daughter (P/D) ion fragmentation pattern with the TAGA IIe's library of known chemicals it was possible to positively identify the unknown.

A standard CAD library containing several hundred air contaminants has been created using 20 eV of collisional ion energy and nitrogen as the collision gas. The CAD fragmentation pattern of the "unknown" parent ion at 104 amu obtained while downwind of Company B, as shown in Fig. 4 (bottom left) is dominated by the daughter ions at 52, 65, 77, 78, 95 and 103 amu.
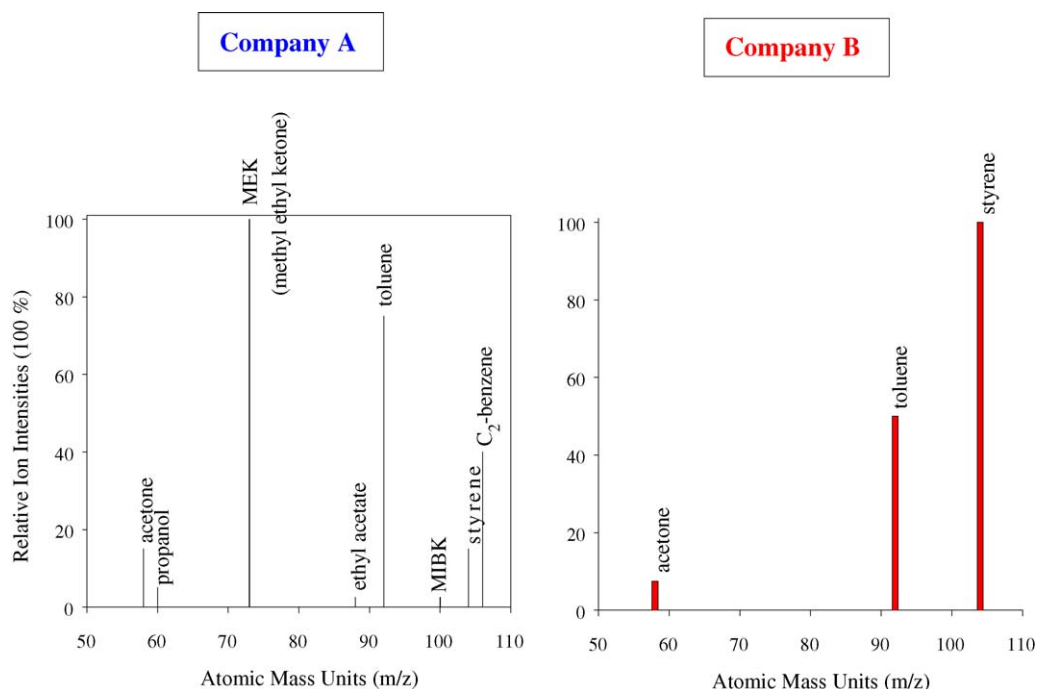
Fig. 3. TAGA IIe single MS spectrum obtained downwind of Company A (left) and Company B (right).

Fig. 4 (bottom right) also shows the standard CAD library spectra for $m/z = 104$ amu for styrene. The spectrum of the "unknown" is compared with the standard CAD library spectra; agreement between the "reverse" and "forward" library search results and their closeness to unity indicates the degree of certainty for compound identification. In this case, the best search results matched with styrene. The daughter ion fragment at 95 amu is a resulting

artifact from the ion chemistry occurring within the LPCI source region and thus is not used to monitor styrene levels.

A similar analysis was undertaken to identify the other prominent parent ions seen from the single MS spectrums. The major parent ions from Company A correspond to the following contaminants: acetone (58 amu), propanol (60 amu), methyl ethyl ketone (72 amu), ethyl acetate (88 amu), toluene (92 amu),

Library Search Results (TAGA IIe LPCI)
Parent Ion = 104

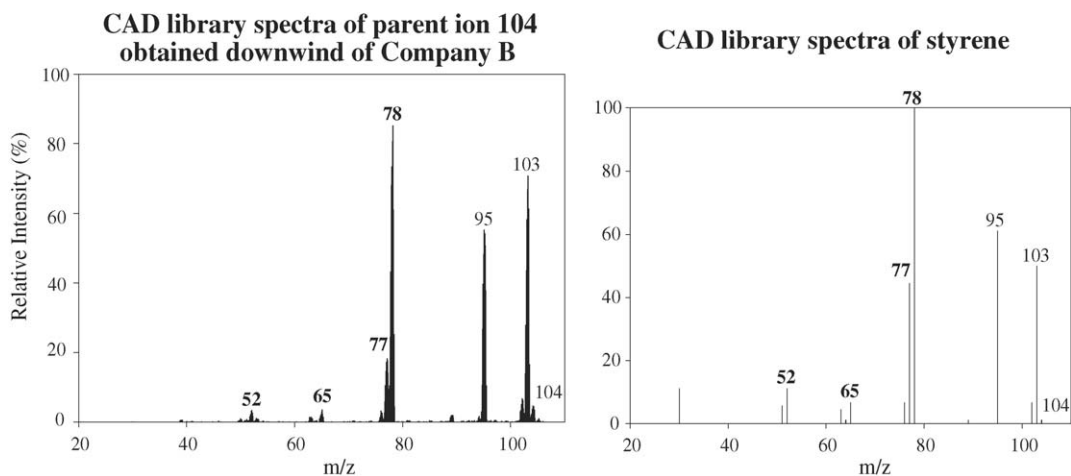| Name	Formula	Molecular Weight (amu)	Purity (%)	Forward Fit (%)	Reverse Fit (%)
Styrene	C_8H_8	104	90.13	94.54	93.58

Fig. 4. TAGA IIe library search of molecular ion at 104 amu. The CAD spectrum of the parent of the parent ion at 104 amu obtained downwind of Company B is shown in the lower left and the CAD library match of the parent ion at 104 amu is shown on the lower right.
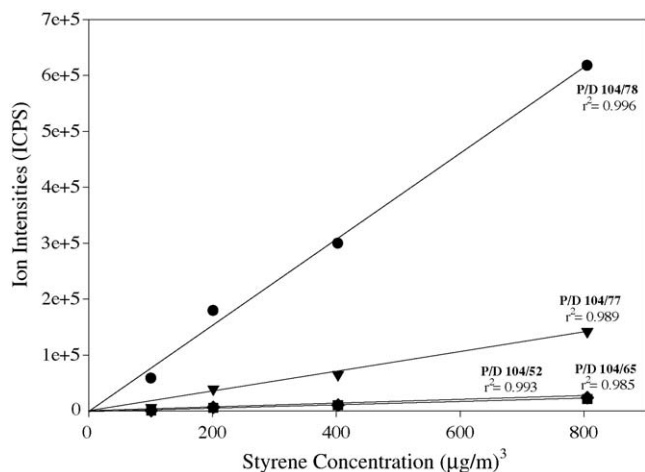
Fig. 5. TAGA IIe calibration plot of styrene using four *P/D* ion pairs: 104/78, 104/77, 104/65 and 104/52.

methyl isobutyl ketone (100 amu), styrene (104 amu) and C_2-benzene (106 amu). In contrast, the major parent ions detected downwind of Company B correspond to acetone (58 amu), toluene (92 amu) and styrene (104 amu).

2.4. Quantitation

The quantitation of airborne contaminants is accomplished by multiple reaction monitoring (MRM) of selected *P/D* ion pairs, e.g. the 104/78, 104/77, 104/65 and 104/52 ion pairs are used to monitor ambient styrene levels. In order to quantitate levels of ambient air toxics, the response of the TAGA IIe is calibrated using a known chemical standard (liquid or gas). A liquid based calibration method developed by the OMOE [13] involves injecting an aqueous standard into the inlet air flow via a heated nebulizer. The nebulizer system used with the TAGA IIe consists of a capillary tube for liquid sample injection and two outer concentric stainless steel tubes for nebulizing and purging gases. This configuration ensures uniform sample atomization providing for the addition of controlled amounts of standards into the TAGA IIe LPCI ion source. The standard solution is injected into the nebulizer with a 1 mL, 22 s gauge Hamilton Gastight syringe mounted in a Harvard (model 22) syringe infusion pump. The flow rates of the liquid standard are controlled by the speed of the syringe pump. For example, flow rates between 0 and 20 μL/min result in styrene concentrations in the range of 0–800 μg/m^3 being generated in the LPCI source. Daily five-point calibration curves for styrene were developed by simultaneously recording the responses of the four *P/D* ion pairs. An example of a styrene calibration over the range of 0–800 μg/m^3 is shown in Fig. 5. Calibrations are performed in-situ, where, ambient air is used as the carrier gas to automatically account for any matrix effects. The slopes of the response curves are a measure of the sensitivity of the LPCI/MS/MS system to styrene. A linear response for styrene was observed up to 800 μg/m^3.

The TAGA IIe real time method for styrene used in this survey had been compared with the US EPA TO-17 method involving cartridge air sampling and thermal desorption GC/MS/MS anal-

ysis. The two methods had been utilized from 1998 to 2002 in concurrent measurements of various chemicals, including styrene. Satisfactory results (±15%) were obtained from inter-comparison measurements of styrene emissions from industries in Sarnia, Ontario. Detection limits for styrene were <0.1 μg/m^3 for the cartridge method and approximately 1 μg/m^3 for the TAGA IIe real time method.

During this survey, the calibration response factors and detection limits were determined at least twice daily at various upwind locations for each of the airborne compounds monitored. Each of these compounds have an unique detection limit which is defined as three times the standard deviation of the background signal (upwind of the site) divided by the slope of the calibration curve. Detection limits vary day to day due to variations in the air matrix which can affect the sensitivity as well as the background levels. The average detection limit for styrene during this monitoring period was 1.1 μg/m^3.

3. Results and discussion

The locations of the two styrene sources in Cornwall, Ontario are shown in Fig. 6. The two companies are situated within 300 m of each other in a densely populated residential area located in a nearby development to the northeast of these facilities.

3.1. Contaminants detected

The chemical fingerprints obtained while downwind of each of these companies were unique and permitted the mobile TAGA unit to isolate each of the company's air emissions. While downwind of Company A the TAGA identified eight airborne chemicals: acetone, propanol, methyl ethyl ketone methyl acetate, toluene, methyl isobutyl ketone, styrene and C_2-benzene. While downwind of Company B only acetone, toluene and styrene were detected and identified. Company A was characterized by sweet odours while Company B could be characterized by burning odours.

When comparing the on-site TAGA results with the reported 2000 National Pollution Release Inventory (NPRI) data, [14] there were similarities. Company A which manufactures resins and paints for furniture and re-enforced plastics, lists 10 major air releases (the volume amount is shown in brackets in yearly quantities): acetone (1.4 tonnes), propanol (4.0 tonnes), methyl ethyl ketone (2.9 tonnes), methyl isobutyl ketone (0.7 tonnes), toluene (15.6 tonnes), mixed isomers of xylene or C_2-benzene (9.9 tonnes), styrene (7.4 tonnes), methanol (4.2 tonnes) and *n*- and *i*-butyl alcohol (5.7 tonnes). The TAGA IIe detected and identified all of these compounds with the exception of methanol and *n*- and *i*-butyl alcohol. The largest relative component observed in the TAGA fingerprint was methyl ethyl ketone, but the NPRI data lists this emission as less than 6% of the total yearly release. Company B which is a manufacturer for acrylic bathtubs, showers and whirlpools only lists a single chemical airborne release in the 2000 NPRI data: styrene (19 tonnes). The TAGA identified styrene as the largest contributor, but also found major contributions from acetone and toluene from the site.
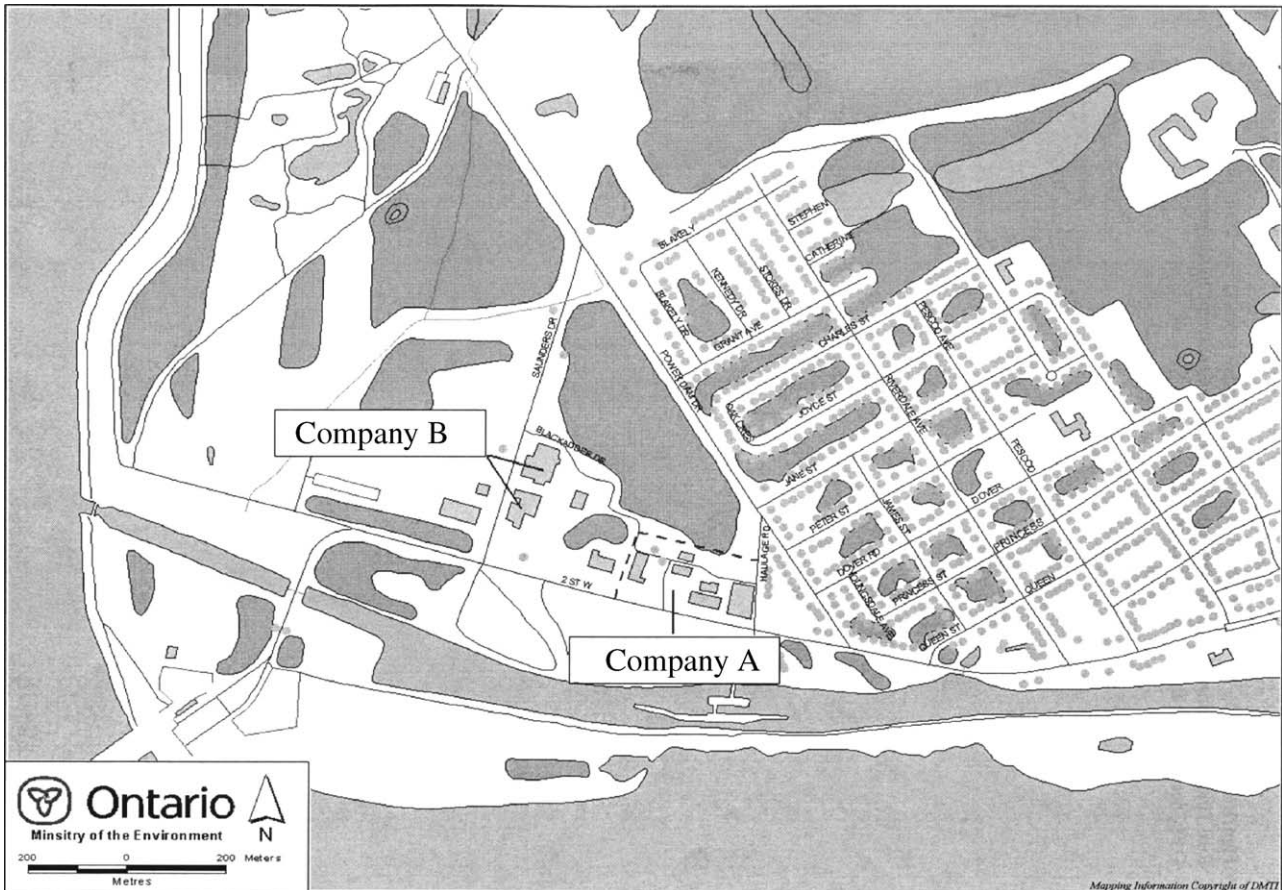
Fig. 6. The location of two possible styrene sources in Cornwall, Ontario.

While several other airborne chemicals were detected, the primary focus of this study was to identify and differentiate the styrene levels being emitted from each source (Companies A and B). This was achieved by plume tracking (driving upwind and downwind of each company) and by fingerprinting particularly at times when the wind was from the north so that the TAGA bus could be located precisely downwind of one company thus avoiding any impact of emissions from the other company.

An example of plume tracking for styrene is shown in Fig. 7. With the wind from the east the mobile unit began tracking from an upwind site at the corner of Haulage Road and Second Street West. As the mobile unit proceeded eastward along Second Street West the levels of styrene rise indicating being downwind of Company A. As the unit turned north along Saunders Drive the styrene level dropped back down to ground level. When the mobile unit was positioned downwind of Company B the levels spike dramatically upward in the range of 5000–10,000 µg/m^3. The mobile unit then started to sample the plume from Company B at this location and took measurements for comparison to the OMOE POI standard.

An example of a real time 30 min measurement for styrene taken while downwind of Company B in August 2000 is shown in Fig. 8. Readings were recorded every five seconds for a period of thirty minutes at a fixed location to obtain a half-hour average concentration. During this monitoring period for styrene the half-hour average concentration was 2200 µg/m^3 and the

highest instantaneous level was 15,000 µg/m^3. This half-hour average concentration is more than 5 times above the OMOE POI for styrene and an instantaneous reading of more than 75 times higher the odour threshold. Background levels of styrene measured upwind of the companies were below 1.1 µg/m^3.

The highest recorded concentrations of airborne styrene were measured while downwind and at very close proximity to the two
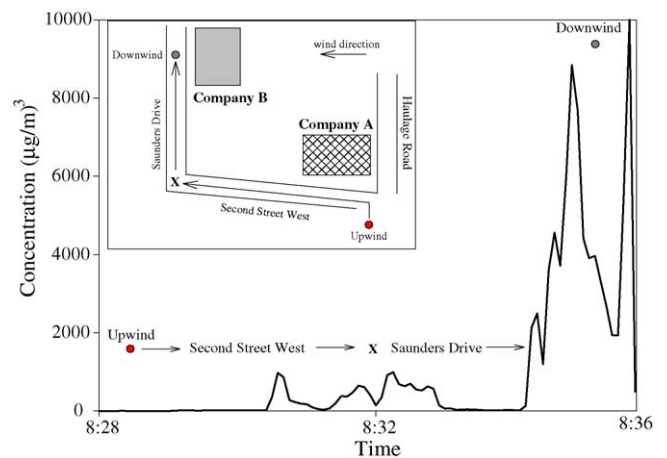

Fig. 7. Real time plume tracking for styrene from upwind to downwind by the TAGA IIe in the vicinity of Companies A and B in Cornwall, Ontario in August 2000.
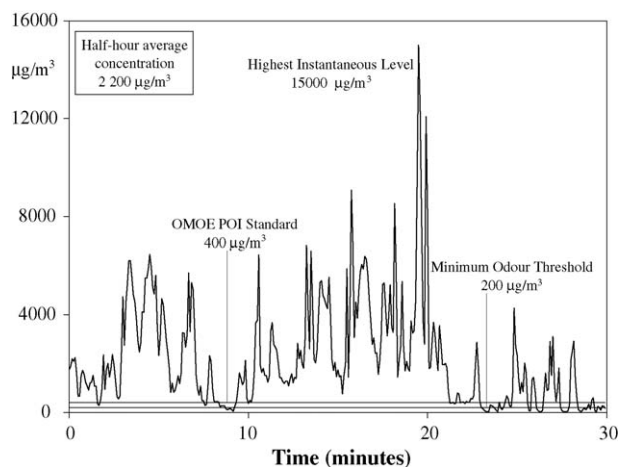
Fig. 8. A real time measurement at a fixed location for 30 min of styrene using the *P/D* ion pair of 104/78 obtained by the TAGA IIe downwind of Company B in Cornwall, Ontario in August 2000.

facilities. The residential area located to the northeast was only impacted slightly by the facilities' styrene emissions and only when the winds were from the southwest.

A summary of the half-hour average concentrations measured by the TAGA IIe during August 2000 and 2001, while downwind of Companies A and B are shown in Figs. 9 and 10, respectively. Fig. 9 indicates that 7 of 100 downwind samples (7%) measuring emissions from Company A exceeded the OMOE POI standard for styrene with the highest half-hour average concentration being 1100 µg/m³. Fig. 10 indicates that 37 of 69 downwind samples (54%) measuring emissions from Company B exceeded the OMOE POI standard for styrene, with 7% of the total samples exceeding the POI standard by more than five times. The highest half-hour average concentration recorded while downwind of Company B was 2300 µg/m³. The total concentration of chemicals detected while downwind of Company A is in the mg/m³ range, representing the highest total concentration of airborne contaminants measured by the mobile unit in the past twenty years.
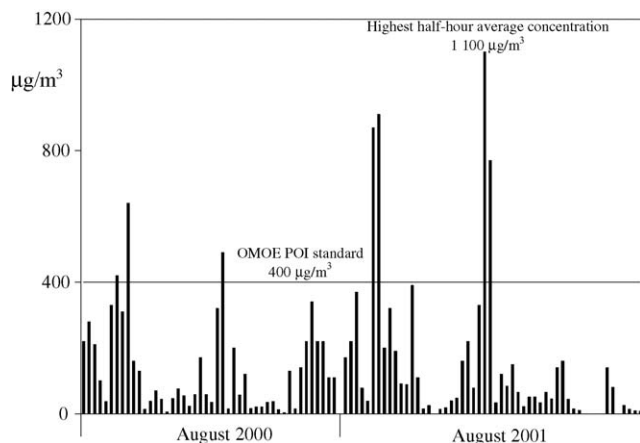

Fig. 9. A survey summary of the styrene half-hour average concentrations measured by the TAGA IIe at several sites downwind of Company A in Cornwall, Ontario in August 2000 and August 2001.
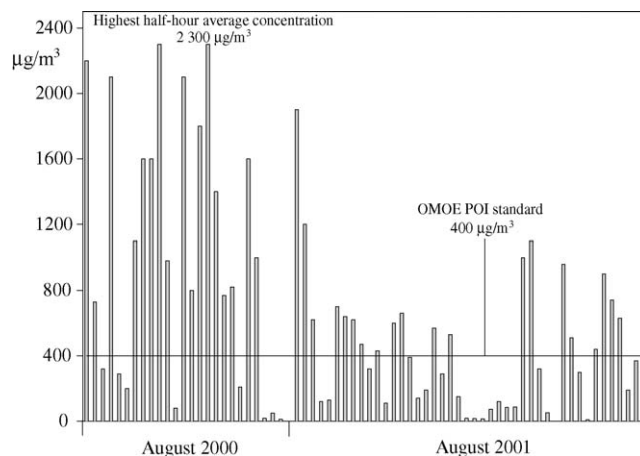

Fig. 10. A survey summary of the styrene half-hour average concentrations measured by the TAGA IIe at several sites downwind of Company B in Cornwall, Ontario in August 2000 and August 2001.

Following the 2001 survey, Company B was fined and in 2002 it modified its emissions controls. A follow-up TAGA survey in August 2003 indicated a tremendous reduction in styrene emissions. The highest half-hour concentration for styrene from Company B in 2003 was 75 µg/m³, which was in compliance with the Ministry air standard.

4. Summary

The TAGA IIe is an effective tool to identify and quantify the chemical nature of airborne emissions. It was able to definitely characterize and differentiate the airborne emissions from Companies A and B based upon their chemical fingerprints and concentration levels. The TAGA fingerprinting results also indicate that the 2000 NPRI data supplied by the Company B is incomplete and does not account for fugitive emissions which are a large contributor to its air releases. The TAGA IIe results from the surveys are consistent and accurately represent the air emissions from these two facilities.

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