



Real time air monitoring of hydrogen chloride and chlorine gas during a chemical fire

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Abstract

On 9 August 2000 a fire started at a facility that manufactures pool chemicals in Guelph, Ontario. A mobile trace atmospheric gas analyzer (TAGA) unit was summoned to provide on-site air monitoring operated by the Ontario Ministry of the Environment (OMOE). The responsibility of the TAGA unit was to monitor in real time the airborne contaminants released through the combustion of pool chemicals. This was accomplished by using an atmospheric pressure chemical ionization (APCI) source with the newest TAGA (model IIe): a triple quadrupole mass spectrometer which allows for the direct sampling and real time analysis of air for a wide range of toxics at low parts-per-billion (ppb) levels. The ionization mechanism under negative APCI conditions is dominated by charge transfer reactions, yielding parent ions which are selected in Q1, dissociated in Q2 and the resultant daughter ions are identified in Q3. By monitoring specific parent/daughter (P/D) ion pairs, the TAGA IIe was able to simultaneously measure, in real time, levels of hydrogen chloride (HCl) and chlorine (Cl_2) present in the air. The response of the TAGA IIe was characterized by multi-point calibration curves which were linear up to $250 \mu\text{g}/\text{m}^3$ for HCl and up to $600 \mu\text{g}/\text{m}^3$ for Cl_2 . The average detection limit (DL) for this application was $0.50 \mu\text{g}/\text{m}^3$ for both HCl and Cl_2 . On-site measurements of HCl and Cl_2 were made at several locations upwind and downwind of the fire site over a period of 3 days. The data collected by the TAGA unit was used by the local officials for a real time assessment of the airborne levels of HCl and Cl_2 .

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1. Introduction

The ability to rapidly perform on-site chemical analysis is very important in the evaluation of airborne volatile hazardous chemicals [1]. Situations where air quality assessment is

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critical include fires involving chemicals and accidental chemical spills especially when the public could be at risk due to exposure to toxics. Accurate and timely information on the types and levels of airborne toxic chemicals is required by medical officers of health, fire and police department personnel as well as public officials. This on-site information can then be used for immediate assessment of the air quality and, if necessary, plan for remedial action to limit the release of chemicals into the environment and to limit the exposure of the public to airborne contaminants. In such cases, the best approach is to bring a mobile air monitoring unit to the areas of concern and conduct real time air quality analysis and monitoring. The conventional method of sample collection and analysis at an analytical laboratory usually takes several hours or days and are not practical for the minute-by-minute decisions that are required at an emergency site.

The mobile trace atmospheric gas analyzer (TAGA) technology has been used since 1980 by the Ontario Ministry of the Environment (OMOE) for on-site analysis of airborne contaminants from a variety of industrial sources and environmental emergencies. The first generation TAGA (model 3000), a single quadrupole mass spectrometer, was used from 1980 to 1988 and the second generation TAGA (model 6000), a triple quadrupole mass spectrometer, from 1988 to 1998. The earlier TAGA's were equipped with a robust and extremely effective cryogenic vacuum pumping system which permitted continuous monitoring for 12 h before the cryogenic traps had to be re-generated. Since 1998, the mobile TAGA units have been using a TAGA IIe system which is a state-of-the-art triple quadrupole mass spectrometer coupled with turbo molecular vacuum pumps, which allow for around the clock monitoring.

In this paper, we describe how a mobile TAGA unit was used to monitor two toxic contaminants during a fire at a pool chemical manufacturer in August 2000. Hydrogen chloride (HCl) and chlorine gas (Cl₂) were identified and quantitated at sub parts-per-billion (ppb) levels. Hydrogen chloride is a colourless, corrosive gas with a pungent, irritating odour [2]. Chlorine is a greenish-yellow gas with a suffocating, bleach odour that has been used as a military poison gas in the past [3]. These two chemicals are largely used in the process of fabric and paper bleaching, purifying water, disinfecting, detinning and dezincing iron and in the manufacturing of synthetic rubbers and plastics. The OMOE has set the half-hour point of impingement (POI) air standards for HCl and Cl₂ at 100 and 300 µg/m³, respectively [4].

2. The mobile TAGA unit

The TAGA IIe is a real time, direct-air sampling, analytical instrument [5] which is mounted in a 10 m "Orion" coach shown in Fig. 1. It is a completely self-contained mobile air monitoring unit, capable of detecting thousands of different air contaminants *on the fly*. The coach accommodates the TAGA IIe (Fig. 2) and other essential pieces of equipment: two computer stations for automated control of the TAGA IIe including data acquisition and analysis, a fume hood, a refrigerator, meteorological tower and work benches. The 10 m telescopic meteorological tower equipped with a combination anemometer/wind vane, is used for recording on-site ambient air temperature, wind direction and speed. Meteorological data is recorded every minute and displayed on real time basis. A communication link



Fig. 1. External view of the mobile laboratory, Explorer IIe.

to other vehicles and the home base office is facilitated by two-way radios, cellular and digital phones and a portable computer. Four roof-mounted air conditioners provide the necessary environmental control to the interior of the mobile unit. All power requirements of the mobile are supplied by an on-board 17.5 kW generator, interfaced with a four-cylinder water-cooled diesel engine. The mobile TAGA IIe can be fully functional in less than 20 min from a complete shut-down mode.

3. Experimental

3.1. TAGA IIe mass spectrometer

The TAGA IIe is a triple quadrupole mass spectrometer which is used to differentiate and quantitate thousands of different chemicals [5]. The main components of the TAGA IIe include an air inlet system, an APCI source housing a corona discharge needle, a triple quadrupole mass analyzer consisting of a series of mass filters and focusing elements, an ion detector, two turbo molecular and rotary backing pumps and a MAC-based computer system (Fig. 3). Ambient air is sampled continuously at a flow rate of 90 l/m directly into the ion source region which is maintained at atmospheric pressure (760 Torr). The quadrupole region (Q1 and Q3) is maintained at a pressure of 10^{-5} Torr by the two turbo molecular pumps. The high sampling rate and the large volume of the APCI source assures that sample adsorption or degradation is negligible.



Fig. 2. The TAGA IIe mass spectrometer housed inside the mobile analytical laboratory, known as the “Explorer”.

The operation of the TAGA IIe is based on the principles of tandem mass spectrometry (MS/MS). The parents ions are focused in the Q0 region, mass selected in the first quadrupole (Q1) region and then subjected to collision activation dissociation (CAD) in the Q2 region with an inert gas (nitrogen) to produce fragment daughter ions. The daughter ions are then identified in the third quadrupole region (Q3) and a Channeltron multiplier is used to detect the ions exiting from the Q3 region. The Q1 and Q3 regions function as mass filters while the Q0 and Q2 regions operate in a non-resolving, radio-frequency only mode. Under these conditions the MS/MS process can occur in a fraction of a second.

3.2. Atmospheric pressure chemical ionization (APCI)

Early mass spectrometric (MS) methods for the real time detection of air pollutants used a well established APCI technique involving a corona discharge needle for ionizing chemicals [6]. Chemical reagents such as water vapour was used to highlight alcohols and ketones, while ammonia was used to highlight amines through proton transfer reactions and benzene was used to focus on some aromatics through charge transfer reactions. To target halogens and the organic acidic family of chemicals, the APCI source is operated in negative mode [7].

The ion chemistry under negative APCI conditions is dominated by dissociative attachment reactions. For example when monitoring chlorine gas the ion chemistry occurring in

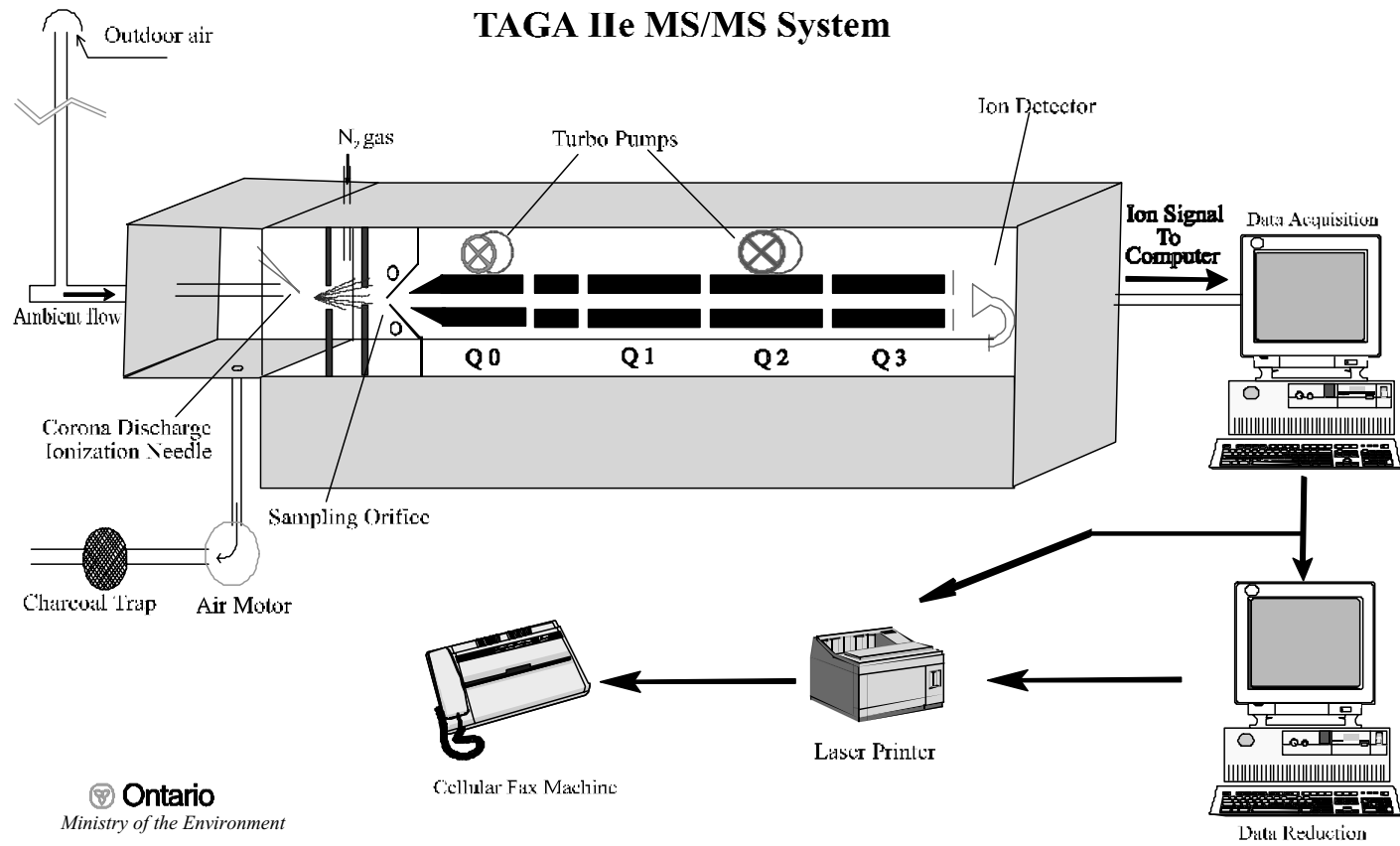


Fig. 3. Schematic of the TAGA IIe tandem quadrupole mass spectrometer.

the APCI region is described in reaction (1):



where Y refers to OH or O₂.

Reaction (1) results in the parent ions at 70 atomic mass units (amu) and the isotopic ions at 72 and 74 amu. The MS of Cl₂ is shown in Fig. 4 (bottom). These parent ions (70, 72 and 74) are mass selected in the Q1 region subjected to CAD in Q2 and produce daughter fragment ions of 35 and 37 amu which are then identified in the Q3 region. Multiple reaction monitoring (MRM) of the following parent/daughter (P/D) pairs 70/35, 72/37, 72/35 and 74/37 are used to positively identify and monitor Cl₂ in real time (see Section 3.3 for more details).

Monitoring for HCl in real time is more complicated than Cl₂ monitoring. The ion chemistry of HCl in the ion source is governed by deprotonation reactions, shown in reaction (2):



where Y refers to OH or O₂ and by the formation of adduct ions via a clustering reaction shown in reaction (3):



where Z being OH, O₂ or HCO₃.

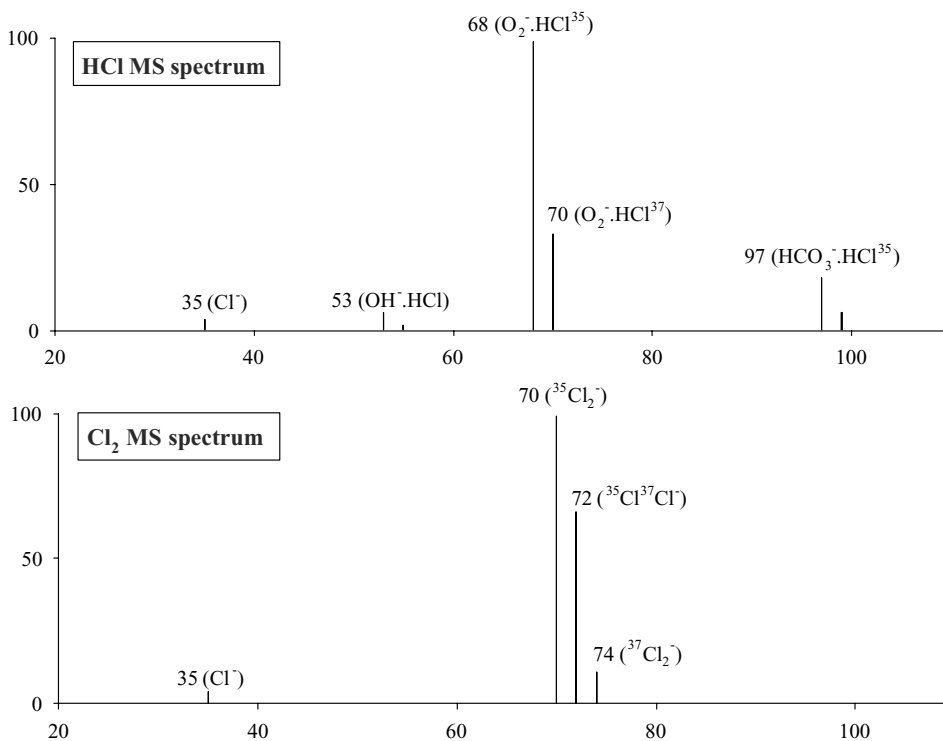


Fig. 4. TAGA IIe single MS spectrum of HCl (top) and Cl₂ (bottom) obtained downwind of the fire scene.

Fig. 4 (top) is an example of a MS of HCl obtained downwind of the fire site. A background subtracted MS of HCl is obtained by admitting trace amounts of HCl gas into the APCI source. Anions are produced at masses ($M - 1$) at 35 amu, ($M + 17$) at 53 amu, ($M + 32$) at 68 amu and the isotopic ion at 70 amu and ($M + 61$) at 97 amu. These ions are produced by HCl deprotonation and clustering with OH^- , O_2^- and HCO_3^- . The Cl^- ion may arise from a variety of chlorinated species so that Cl^- is only a valid identifier of HCl in the absence of any other chlorine-containing compounds. It was found that selective monitoring of $\text{O}_2^- \cdot \text{HCl}$ and to a lesser extent $\text{OH}^- \cdot \text{HCl}$, together with the ^{35}Cl isotope provides a reliable mechanism for identifying and monitoring HCl in a complex matrix even when other chlorinated compounds are present.

3.3. Identification

A collisionally activated dissociation or MS/MS library of HCl and Cl_2 was created using 20 eV ion energy and nitrogen as the inert collision gas. Air pollutants are identified by comparing the CAD spectrum of the parent ions from the on-site pollutant source with those of known chemicals contained in a CAD library. The CAD fragmentation pattern of the unknown parent ions at 68 and 70 amu obtained downwind of the fire site are shown in the bottom left corners of Figs. 5 and 6.

Library Search Results (TAGA IIe APCI)

Library File: Parent ion = 68

<u>Name</u>	<u>Formula</u>	<u>M.W.</u> (amu)	<u>Purity</u> (%)	<u>Forward Fit</u> (%)	<u>Reverse Fit</u> (%)
Hydrogen Chloride Oxygen adduct	O_2HCl	68	99.4	99.4	100

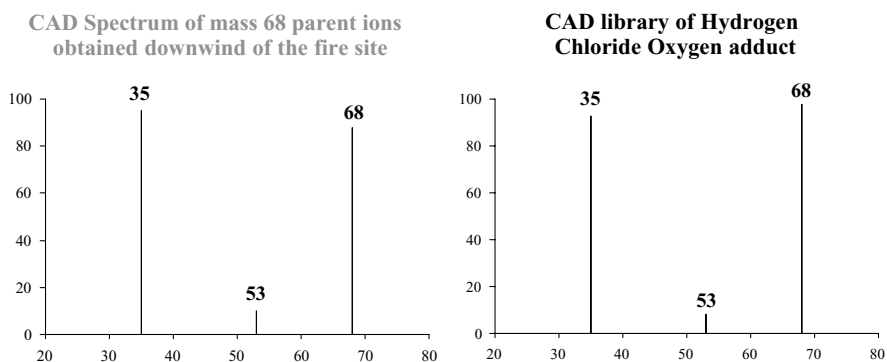


Fig. 5. TAGA IIe MS/MS library search of molecular ion at 68 amu.

Library Search Results (TAGA IIe APCI)

Library File: Parent ion = 70

<u>Name</u>	<u>Formula</u>	<u>M.W.</u> (amu)	<u>Purity</u> (%)	<u>Forward Fit</u> (%)	<u>Reverse Fit</u> (%)
Chlorine	Cl ₂	70	99.9	99.9	100

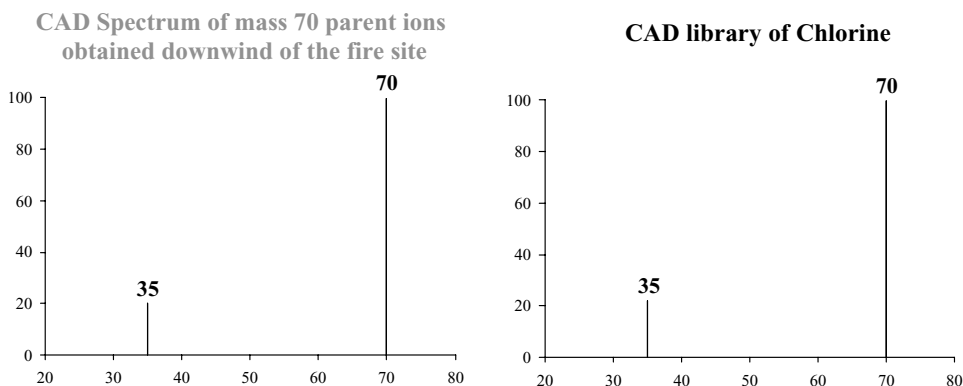


Fig. 6. TAGA IIe MS/MS library search of molecular ion at 70 amu.

The CAD spectrum of the “unknown” parent ion at mass 68 (Fig. 5, bottom left) is dominated by the parent ion at 68 amu and the two daughter ions at 53 and 35 amu. Fig. 5 (bottom right) also shows the CAD library for m/z at 68 amu; hydrogen chloride oxygen adduct. The CAD spectrum of the “unknown” is compared with the CAD library; agreement between the “reverse” and “forward” library search results, indicate the degree of certainty for compound identification. In this case the “best” search results matched with the hydrogen chloride oxygen ($O_2^- \cdot HCl$) adduct.

In comparison, the CAD spectrum of the “unknown” parent ion at 70 amu (Fig. 6, bottom left) is dominated by only two daughter ions; 70 and 35 amu. The CAD library for the chlorine ion at $m/z = 70$ amu is also shown in Fig. 6 (bottom right). The spectrum of the “unknown” is compared with the CAD library; agreement between the “reverse” and “forward” library search results indicated that in this case the “best” search results matched with chlorine.

3.4. Quantitation

Quantitation of contaminants in the ambient air is based on the response of the TAGA IIe to a known set of chemical standards. A known gaseous standard is metered at various

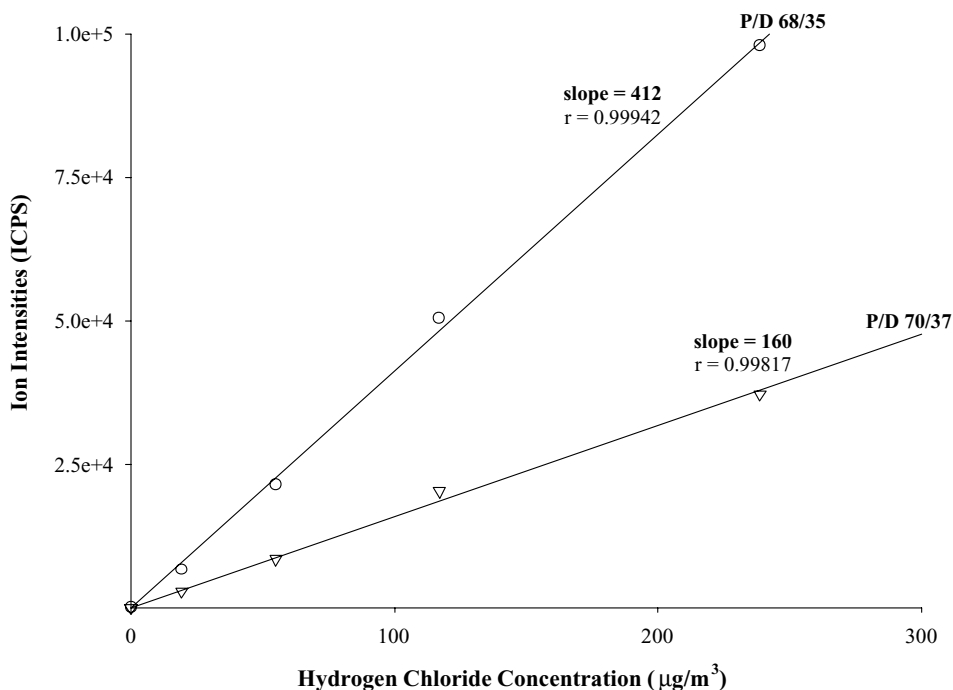


Fig. 7. TAGA IIe calibration plot of hydrogen chloride using two parent/daughter ion pairs: 68/35 and 70/37.

concentrations [7] into the air flow pathway to generate the calibration curve. A daily five-point calibration of HCl was performed by simultaneously recording the responses of two P/D ion pairs (68/35 and 70/37). An example of a daily calibration using a certified gas cylinder of 50 ppm HCl in N_2 in the concentration range of 0–250 $\mu\text{g}/\text{m}^3$ is shown in Fig. 7. Due to potential losses of HCl to cylinder walls a titration method was also developed for standardizing the concentration of HCl contained in the gas cylinder, prior to its use. The HCl/ N_2 mixture was bubbled through distilled water and then the acidic solution produced was titrated to neutralization end point with 0.1 M NaOH. The slope of the daily calibration graph is a measure of the response of the TAGA IIe to HCl. The y-intercept of this graph represents the signal of the P/D ion pairs associated with HCl when no calibration standard has been introduced into the air flow pathway. The calibration plots of $\text{OH}^- \cdot \text{HCl}$ (P/D = 53/35) were also linear, however the intensities in ion counts per second (ICPS) were about an order of one magnitude lower. Daily variations in the ion signal response were as high as 30% for all ions. These variations can be attributed primarily to change in atmospheric humidity. High humidity for example enhanced the sensitivities of $\text{OH}^- \cdot \text{HCl}$ but suppressed the signal of $\text{O}_2^- \cdot \text{HCl}$ significantly.

The daily calibration curve for Cl_2 (Fig. 8) was generated by a similar method, but using a certified cylinder of 50 ppm Cl_2 in N_2 . Five-point calibrations of Cl_2 were obtained by simultaneously recording the responses for four P/D ion pairs: 70/35, 72/37, 72/35 and 74/37. The response for these four pairs was observed to be linear up to 600 $\mu\text{g}/\text{m}^3$.

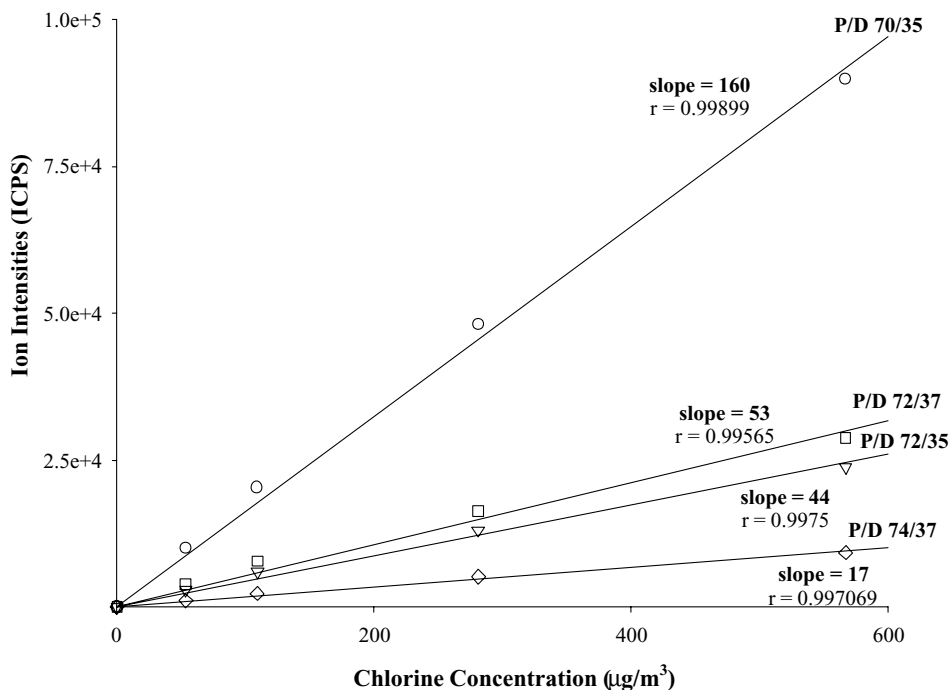


Fig. 8. TAGA IIe calibration plot of chlorine gas using four parent/daughter ion pairs: 70/35, 72/37, 72/35 and 74/37.

The detection limit (DL) is defined as three times the standard deviation of the y-intercept obtained from the calibration curve divided by the slope of the curve. Small variations in the DL from day-to-day is normal. The average DL achieved during this monitoring activity was $0.50 \mu\text{g}/\text{m}^3$ for both HCl and Cl₂.

3.5. Strategy of mobile TAGA air monitoring

Upon arrival at a site to be investigated, the TAGA IIe proceeds to a location of the emission source and determines the background levels of the target chemicals (if they are known). Following upwind measurements, plume tracking is conducted by driving the mobile unit downwind of the source while monitoring the air for the target compounds. Monitoring also includes, “chemically fingerprinting” the air to identify as many chemicals as possible and determining the levels of the predominant chemicals and/or those known to be the most toxic. Depending on wind direction shifts, plume tracking and stationary monitoring is performed at several downwind locations. The TAGA crew records monitoring locations, on-site activities and the local weather conditions. The information collected includes minute-by-minute meteorological data and instantaneous levels of target compounds over pre-selected monitoring periods. Should target compounds levels exceed provincial standards, the TAGA crew immediately notifies the on-site environmental staff or city officials.

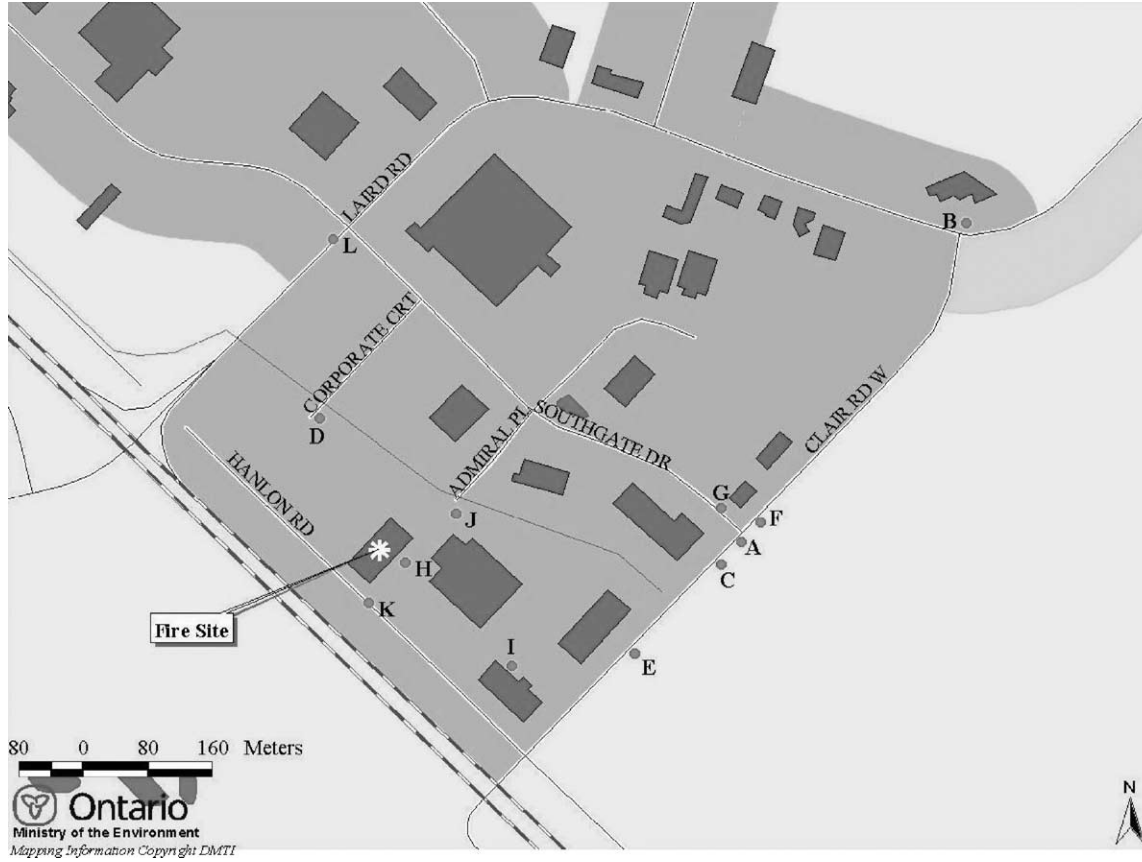


Fig. 9. The upwind and downwind monitoring locations of the TAGA IIe in the vicinity of the fire site in Guelph, Ontario in August 2000.

4. Results and discussion

This method was applied successfully on 9 August 2000, during a chemical fire at a company which manufactured industrial water-treatment and pool chemicals in Guelph, Ontario. An explosion tore open this plant shortly before 7 p.m. on 8 August sending fireballs 30–40 m into the sky and spilling a thick cloud of smoke over the south end of the city of Guelph. At the height of the emergency, Guelph city officials evacuated a neighbouring subdivision and all roads surrounding the plant were closed. People living as far away as 20 km from the fire were warned to stay indoors, close windows and turn off air conditioners. During the course of this emergency five people from the surrounding area visited the local hospital complaining of minor respiratory problems due to smoke inhalation. The fire burned in total for over 60 h, it was brought under control in the early hours of 9 August, but the last hot spots were put out on 11 August.

Upon arrival at the fire site a vast amount of malodorous smoke was drifting towards a nearby residential area. A map of monitoring sites in the vicinity of the fire scene is shown in Fig. 9. The mobile unit immediately performed a series of chemical fingerprints upwind and downwind of the fire. Chemical fingerprints indicated that HCl and Cl₂ were the most abundant airborne chemicals detected downwind of the fire site.

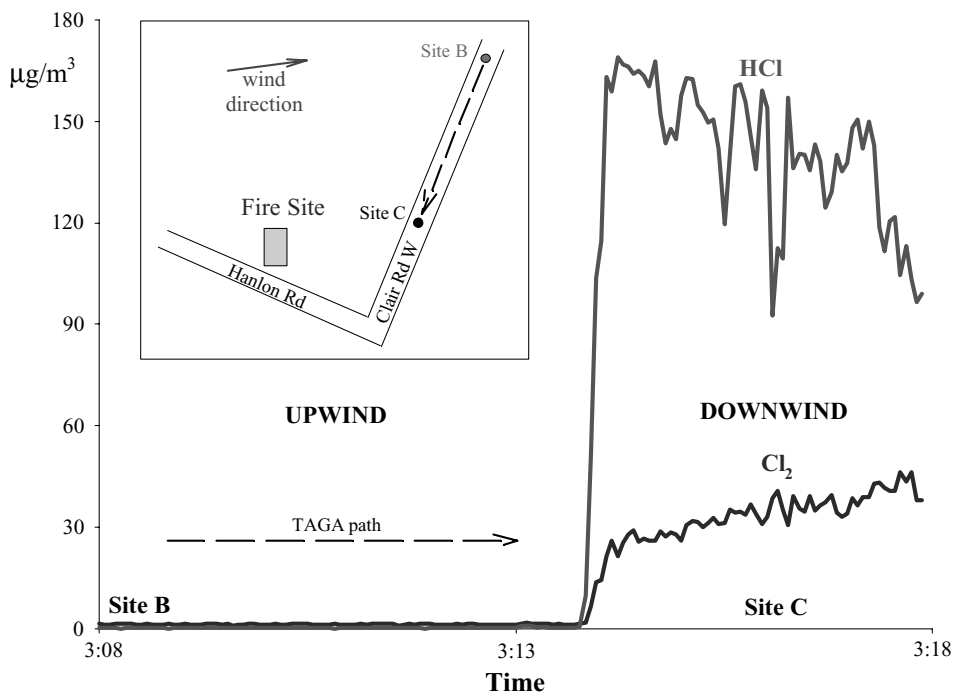


Fig. 10. Real time plume tracking for HCl and Cl₂ from Site B (upwind) to Site C (downwind) by the TAGA IIe in the vicinity of the fire scene in Guelph, Ontario on 9 August 2000.

Information from the mobile TAGA unit was used by the local environment officials, police and fire fighters on a daily basis to assess the effectiveness of the fire extinguishing activities. Following discussions with the municipal officials, the mobile unit then began stationary monitoring to determine the half-hour average concentrations of HCl and Cl₂ at locations downwind of the fire site. Downwind monitoring locations were selected according to wind direction and speed and plume tracking results. To determine the highest concentrations the mobile TAGA performed plume tracking by continuously monitoring in real time, the levels of HCl and Cl₂ while in motion. An example of plume tracking is shown in Fig. 10. With the wind predominantly from a westerly direction, the mobile unit was driven from Site B, along Clair Rd. W. to Site C directly downwind of the fire. The highest levels of HCl and Cl₂ were found to be on Clair Rd. W. near Hanlon Rd (Site C).

Fig. 11 is a real time measurement of HCl (top) and Cl₂ (bottom) as recorded downwind of the fire site (Site C) over a half-hour period. The half-hour average concentration is determined by averaging 360 readings recorded every 5 s over a 30 min period at a fixed location. Rapid changes in the airborne chemical concentrations are mainly due to local air eddies, changes in the wind directions, levels of chemicals emitted and secondary reactions occurring in the atmosphere. For HCl, the half-hour average concentration during this time period was 88 μg/m³ and the maximum instantaneous level was 210 μg/m³. During the same monitoring period and at the same location the half-hour concentration for Cl₂ was 31 μg/m³ and the maximum instantaneous level was 86 μg/m³. Over the 3 days that the

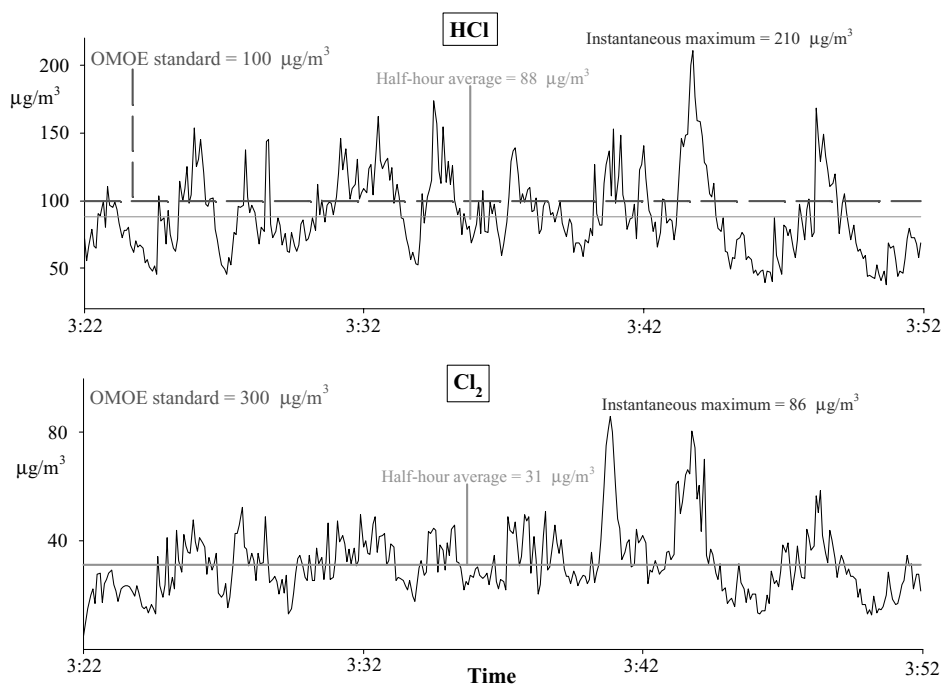


Fig. 11. Mobile TAGA IIe real time monitoring of HCl (top) and Cl₂ (bottom) downwind (Site C) of the fire scene, Guelph, Ontario on 9 August 2000.

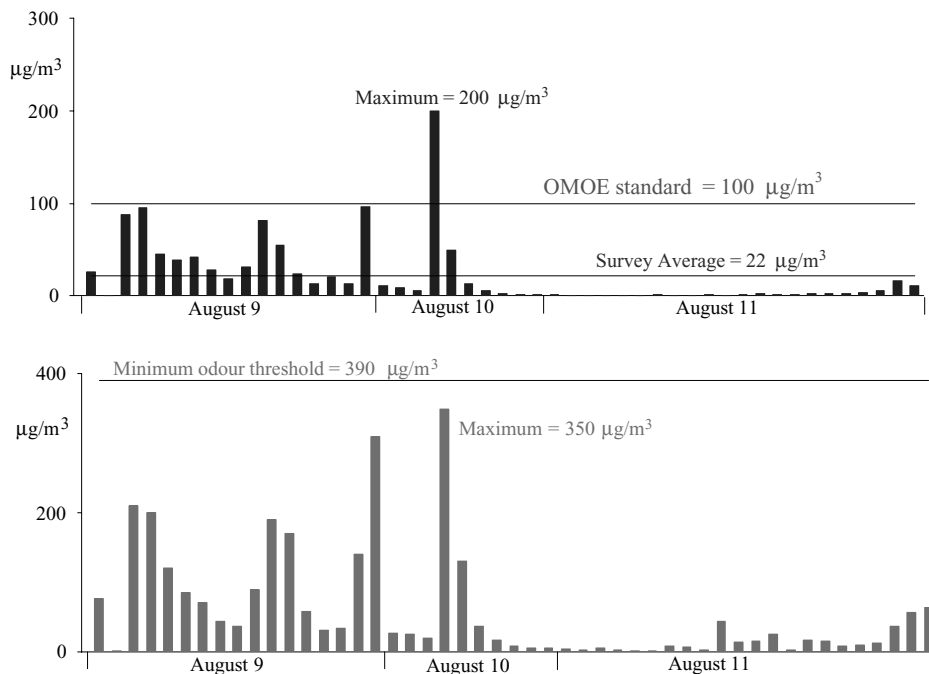


Fig. 12. HCl half-hour concentrations (top) and maximum instantaneous levels (bottom) measured by the TAGA Ite in the vicinity of the fire site in Guelph, Ontario in Augusts 2000.

mobile unit was on-site, 49 half-hour average concentrations were determined for these two chemicals.

4.1. Hydrogen chloride

A summary of the half-hour average concentrations (top) and maximum instantaneous levels (bottom) of HCl recorded during this emergency are shown in Fig. 12. The OMOE POI standard for HCl is $100 \mu\text{g}/\text{m}^3$ for a half-hour period, which is based on corrosion effects [3]. On 10 August, the highest half-hour concentration was $200 \mu\text{g}/\text{m}^3$, which is twice the OMOE POI standard. The highest maximum instantaneous level for HCl was $350 \mu\text{g}/\text{m}^3$, which is about 90% of the minimum odour threshold of $390 \mu\text{g}/\text{m}^3$ [8]. The elevated measurements were taken at Site H, while the fire debris was being pulled apart and only 20 m downwind of the fire site.

4.2. Chlorine gas

A summary of the half-hour average concentrations (top) and maximum instantaneous levels (bottom) of Cl_2 recorded during this emergency are shown in Fig. 13. The highest half-hour concentration of Cl_2 was $170 \mu\text{g}/\text{m}^3$, which is about half of the OMOE POI

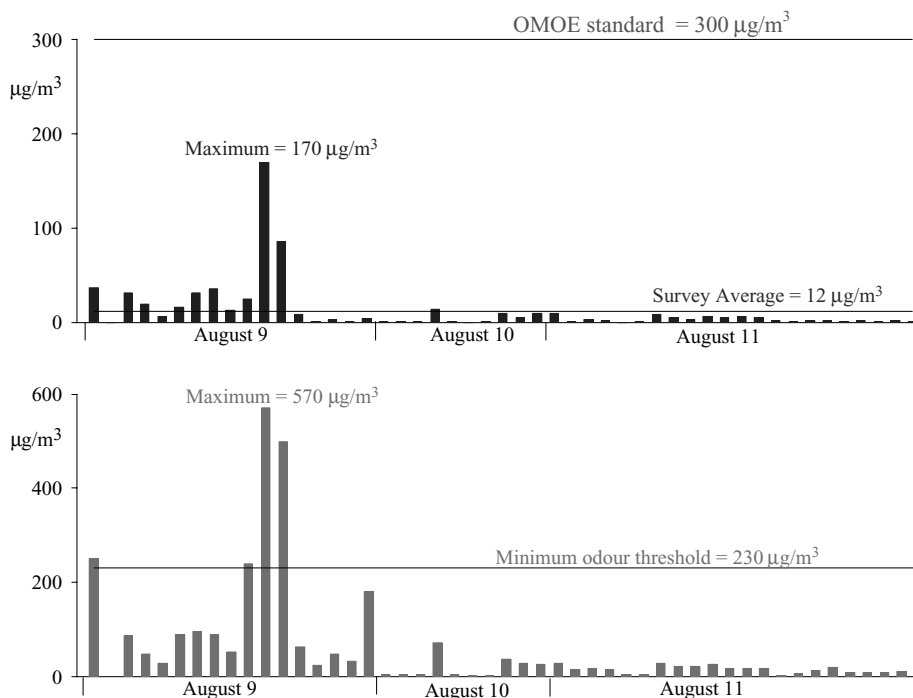


Fig. 13. Cl₂ half-hour concentrations (top) and maximum instantaneous levels (bottom) measured by the TAGA IIe in the vicinity of the fire site in Guelph, Ontario in August 2000.

standard of 300 µg/m³ for a half-hour period [4]. On 9 August 2000 the maximum instantaneous level of Cl₂ was 570 µg/m³ or more than twice the minimum odour threshold of 230 µg/m³ [3]. This measurement was recorded at Site F, about 500 m downwind of the fire site. Four of the half-hour average concentrations for Cl₂ contained maximum instantaneous levels that exceeded the minimum odour threshold.

5. Summary

The development of a new method to monitor, in real time, trace amounts (sub ppb levels) of HCl and Cl₂ in ambient air using a mobile TAGA IIe unit was applied successfully in August 2000, during a fire in Guelph, Ontario. This method used a tandem mass spectrometer, TAGA IIe, operated in the negative APCI mode. This mode of operation provided a direct method to quantitate for HCl and Cl₂ levels in the ambient air in real time with sub µg/m³ levels and detection limits. Calibration curves were produced using certified gas standards which resulted in reliable and reproducible curves up to 250 µg/m³ for HCl and 600 µg/m³ for Cl₂. Real time instantaneous HCl levels as high as 350 µg/m³ and Cl₂ levels as high as 570 µg/m³ were recorded during this fire. This information was given to the local

environmental and health officials as well as the on-site police and fire personnel to alter remediation activities in order to minimize exposure to the public.

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