Analysis of 2-Chloroacetophenone in Air by Multi-Fiber Solid-Phase Microextraction and Fast Gas Chromatography–Mass Spectrometry

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Summary. 2-Chloroacetophenone (CA) is widely used as tear gas by law-enforcement agents, and by civilians for personal protection. Crimes involving robbery and rape using tear gas sprays have recently increased. Experimental and in-field evaluations have been performed to validate use of solid-phase microextraction (SPME) with a porous fiber for sampling and analysis of CA in air before analysis by fast gas chromatography–mass spectrometry equipped with a new device called a multi-fiber system. CA vapor was generated by use of a syringe pump in a dynamic system in which temperature, relative humidity, and air velocity were monitored. The theoretical sampling rate for time-weighted average and rapid-SPME were, furthermore, estimated by use of the Fuller–Schettler–Giddings diffusion coefficient and the theory of heat transfer, respectively, and were in accordance with experimental values. Concentrations of CA were analyzed in a military store containing tear gas canisters, to evaluate the risk. The results obtained in this field study showed values ranging from 0.206 to 2.46 mg m⁻³.

Key Words: Multi Fiber SPME, Fast GC-MS, 2-Chloroacetophenone, sampling rate, diffusion coefficient

Introduction

2-Chloroacetophenone (CA) CAS No 532-27-4, which was discovered by a German chemist in 1869, is widely used as “tear gas” by law enforcement and military agencies throughout the world. Use of CA as a riot-control agent has caused several deaths, however; the estimated lethal concentration for humans is 8,500 mg m⁻³ for 10 min [1]. Severe inhalation causes pulmonary edema. The presence of large quantities of CA causes heavy
flows of tears and mucus, nausea, dermatitis, and severe corneal irritation. The threshold limit value (TLV) time weighted average (TWA) of 0.32 mg m\(^{-3}\) (0.05 ppm) is recommended by the American Conference of Governmental Industrial Hygienists (ACGIH). The ACGIH limit is based on the risk or irritation, sensitization and possible systemic effects. CA in small quantities has an apple blossom odor (threshold 0.035 ppm).

CA has been used in personal defense products since the 1920s and was marketed as a personal defense spray in 1965 by the General Ordinance and Equipment Company under the brand name Mace. Some 15,000,000 Americans now carry personal defense sprays. Moreover, crimes involving robbery and rape using tear gas sprays have recently increased [2]. The maximum direct spray range of personal defense products is generally 2 to 5 meters, but irritant effects can be produced up to 30 meters away, depending on factors such as canisters size, bad pressurization, nozzle type, and wind conditions [3]. In June 2002, the United States authorities passed a bill called the “Health Security and Bioterrorism Preparedness and Response Act” (Bioterrorism Act) which aims at preparing for and responding to the threat of bioterrorism and other health emergencies. CA is one of the specified substances which must be carefully assessed.

Although not regarded as a persistent agent, CA can penetrate plaster and rubber-based products, resulting in long-term contamination of vehicles or homes. Residues in furniture, carpets, and other fabrics can be neutralized by treatment with alkaline solutions and steam, but this process may require the services of professionals. Criminal investigation teams should be involved in the identification of CA that has often been used in crimes, by performing on-site detection in air samples. Published methods for the detection of CA in air include ion mobility spectrometry (IMS) and active sampling then analysis by gas or liquid chromatography [4–6]. The sensitivity of IMS is low, however, and the cost high, and active sampling requires extensive preparation of the sample before analysis.

Effective gas chromatographic (GC) methods which enable very rapid analysis are becoming commercially available; these methods are suitable for rapid analysis of the compounds of interest. In this context rapid GC techniques are particularly interesting. They are based on the use of short, narrow-bore, capillary column which enables achievement of high-speed separations while maintaining excellent resolution. The principles and theory of rapid GC analysis were established as early as the 1960s, but it has only been in the last decade that this technique has found routine application by the achievement of adequate specific conditions, for example high inlet pressures, rapid oven heating, and rapid electronics for detection and data collection [7, 8]. High split ratios are necessary when liquids are injected, because otherwise the low sample capacities of narrow-bore capil-
lary columns may affect efficiency. This problem is readily overcome by use of solid-phase microextraction (SPME), a solvent-free technique that incorporates sampling, isolation, and enrichment into one step.

SPME was introduced at the beginning of the 1990s, because of the intuition of Janusz Pawliszyn, Professor at the University of Waterloo, Canada [9]. The fiber is assembled inside a stainless-steel syringe needle used for GC. Absorption characteristic of liquid-phase coatings [for example polydimethylsiloxane (PDMS) and polyacrylate (PA)] or adsorption characteristic of solid, porous phases [e.g. Carboxen (CAR) and divinylbenzene (DVB), when the thick structure of the coating enables the analyte to be fixed in the pores of the solid phase only] occurs on the fiber surface. Since 1998, SPME has been proposed as a passive sampler [10–12] in the field and in personal samplers, both as rapid SPME with a completely exposed fiber for short sampling (Fig. 1a) and as ‘TWA-SPME’ in which the fiber is retracted inside the needle to a defined distance, Z (from 0.1 to 3.5 cm), when the volume sampled is fixed by the depth of the well defined by the needle wall and fiber apex surface (Fig. 1a). SPME is regarded as a major idea that shaped twentieth-century analytical chemistry [13].

To verify theoretically the suitability of SPME for analysis of CA in air, the behavior of both porous and liquid phases was investigated by meas-
urement of linear temperature-programmed retention indexes (LTPRI) and the theory of heat transfer, respectively. The authors applied, and discuss, the gaseous diffusion coefficients in air ($D_g$) proposed by Gilliland, Andrussov, Arnold, Hirschfelder–Bird–Spotz (HBS), Fuller–Schettler–Giddings (FSG), and Brokaw [14–19]. Theoretical data have been compared with experimental data obtained by syringe pump CA injection in a dynamic system.

Finally, we used in-field SPME sampling to evaluate the risk posed by CA in a military store containing tear gas canisters.

On the basis of the results obtained, the authors present a new and effective method combining a sequential mixed-mode SPME multi-fiber system (MFS) with rapid GC–MS for sampling and high-throughput automated analysis of CA in air.

**Experimental**

**Chemicals and Reagents**

2-Chloroacetophenone, acetophenone, $O$-(2,3,4,5,6 pentafluorobenzyl)hydroxylamine (PFBHA), and hexane (Aldrich) were purchased from Sigma–Aldrich (Milan, Italy). The $n$-alkanes decane, dodecane, tetradecane, hexadecane, octadecane, eicosane, docosane, tetracosane, hexacosane, and octacosane (Supelco, Sigma–Aldrich, Italy) were used for evaluation of the LTPRI.

**Sampling**

**SPME Fibers and Holders**

The fibers used were 65 µm polydimethylsiloxane (PDMS)–divinylbenzene (DVB), 85 µm Carboxen (CAR)–PDMS, 100 µm PDMS, 30 µm PDMS, and 85 µm polyacrylate (PA) fibers (Supelco, Sigma–Aldrich). SPME holders were obtained from Chromline, Prato, Italy.

**Theory of TWA-SPME Used for Passive Sampling**

Using Fick’s law of diffusion, it is possible to determine the amount of analyte loaded, at equilibrium, on the fiber coating, and thus to calculate the corresponding sampling rate ($SR$). The $SR$ of the SPME passive sampling system, used with ‘TWA-SPME’ can be expressed as [10]:
Theoretical $SR = D_g \times (A/Z)$ \hfill (1)

where $Z$ is the distance between the needle opening and the fiber upper surface, $A$ is the surface of the needle opening ($0.00086 \text{ cm}^2$), and $D_g$ is the analyte diffusion coefficient in the air ($\text{cm}^2 \text{s}^{-1}$).

**Theory of Porous Coating Fiber Used for ‘Rapid-SPME’**

With the ‘rapid-SPME’ method it is not possible to define $Z$ because the fiber is completely exposed. To calculate theoretical $SR$ using a porous coating, the theory of heat transfer is applied [20, 21], as follows, expressed as a function of the quantity of heat that passes through the walls of the tube during a given time ($t$):

$$Q = \left(2\pi \times l \times K_{TC} \times \frac{(\theta_1 - \theta_2)}{\ln (r_2/r_1)}\right) \times t \hfill (2)$$

where $2\pi \times l$ is the surface area of the tube, $\ln (r_2/r_1)$ is the thickness of the tube, integrated between the limits $r_1$ and $r_2$, in the infinitesimal progression of the heat through the cylindrical wall, $Q$ is the quantity of heat, $K_{TC}$ is the coefficient of thermal conductivity, and $\Delta \theta$ is the temperature difference at the sides of the matrix.

Equation (2) can be used to calculate the mass of analyte extracted by SPME fibers; for this purpose it is necessary to substitute heat $Q$ for the mass $n$ of extracted analyte, the coefficient of heat transfer $K_{TC}$ for $D_g$, the temperature difference $\Delta \theta$ for the concentration difference $\Delta C$, and the thickness of the tube for the thickness of the fiber, expressed by $b$ (radius of the fiber) and $\delta$ (thickness of the boundary layer surrounding the fiber coating).

$$n = \frac{[2\pi \times l \times D_g \times (C_g - C_0)]}{\ln [(b + \delta)/b]} \times t \hfill (3)$$

So this complies with Fick’s law, where $n$ is the mass of analyte adsorbed (ng) in a sampling time $t$ (s), $b$ the radius of the fiber ($65 \mu\text{m}$ PDMS/DVB 0.012 cm), $l$ the length of the fiber (1 cm), $\delta$ the thickness of the boundary layer surrounding the fiber coating (cm), $C_g$ the concentration of the analyte in the bulk air ($\text{ng mL}^{-1}$), $C_0$ the concentration of the analyte on the surface of the fiber. $C_g$ can be regarded as constant when short sampling times are used, because adsorption binding is instantaneous and the $C_0$ is far from saturation. When $\delta < b$, it follows that $\ln [(b + \delta)/b] \approx \delta/2\pi \delta b l = A$, therefore the equation may be simplified as follows:

$$n = [(D_g \times A)/\delta] \times C_g \times t \hfill (4)$$
This equation is similar to that used to calculate the SR in the method used to measure the ‘TWA-SPME’ where Z is replaced by δ. The factors which most affect δ are the linear velocity and temperature of the air, the radius of the SPME fiber, and $D_g$. Transfer is considered to occur according to conventional principles, but as far as the transfer of the analyte inside the film is concerned, it occurs by diffusion. Therefore, the real thickness of δ can be obtained by the laws which rule heat transfer, using the model suggested by Nernst, in which the matrix inside the film is within a coating.

$$\delta = 9.52 \times (Re^{0.62} \times Sc^{0.38})$$  \hspace{1cm} (5)

where $Re$ (the Reynolds number) = $2ub/v$ (where $u$ is the linear air speed (cm s$^{-1}$), $v$ the air viscosity, 0.014607 cm$^2$ s$^{-1}$), and $Sc$ (Schmidt’s number) = $v/D_g$.

Theoretically, linear air speeds higher than 10 cm s$^{-1}$ yield a δ value closer to 0 and invalidate Eq. (4) [20]. Augusto et al. [22] have suggested portable dynamic air sampling (PDAS-SPME) by use of a suction pump or a hairdryer, which enables sampling of air at high speed.

**Theory of Liquid Coating Fiber Used for ‘Rapid-SPME’**

The absorptive liquid coating PDMS was tested for sampling because it is not affected by air flow, as indicated in Eq. (6) [23]:

$$\log K_1 = a/T + b$$  \hspace{1cm} (6)

where $K_1$ (at equilibrium), $= C_{\text{fiber}}/C_{\text{air}}$ (concentration of the analyte in the fiber)/concentration of the analyte), is the SPME fiber liquid polymeric coating/air partition constant, $a = \Delta H_v/2.303R$ and $b = [(\log(RT/\gamma P_{\text{vap}}) - \Delta H_v/2.303RT^*)]$, $\Delta H_v$ (J mol$^{-1}$) is the analyte heat of vaporization, $R$ (8.314 J mol$^{-1}$ K) the gas constant, $T$ (K) the sampling temperature, $\gamma$ the solute activity coefficient, $P_{\text{vap}}$ (Pa) the vapor pressure, and $T^*$ the known temperature coefficient.

Establishing a $K_1$ value with Eq. (6) can be a tedious and time-consuming process. Therefore, a simple yet accurate and universally reproducible means of estimating $K_1$ is based on $LTPRI$ [24] where $LTPRI = 100 \times (T_{R(A)} - T_{R(c)}/T_{R(c+1)} - T_{R(c)}) + 100 \times c$, $T_{R(A)}$ is the analyte retention time, $T_{R(c)}$ is the retention time of the n-alkane eluting immediately before the analyte, $T_{R(c+1)}$ is the retention time of the n-alkane eluting immediately after the analyte, and $c$ is the number of carbon atoms for $T_{R(c)}$. $LTPRI$ are measured experimentally by GC using a PDMS capillary column.
\[
\log K_1 = 0.0042 \times LTPRI - 0.188
\] (7)

So, at equilibrium for a fixed temperature, the mass of extracted analyte \( n \), can be expressed as:

\[
n = \frac{K_1}{C_g}
\] (8)

**Calibration Air Sampling System**

Once evaluated from the above theoretical considerations, experiments were performed to verify their validity. For this the calibration curve for air concentration of CA (\( C_{CA \text{ air}} \)) in a dynamic system was obtained by syringe pump CA injection, described in detail below. The experimental \( SR \) for the ‘rapid-SPME’ and ‘TWA-SPME’ system was obtained by use of Eq. (9):

\[
SR = \frac{\text{Uptake}}{C_{CA \text{ air}}}
\] (9)

The uptake (\( \text{ng s}^{-1} \)) is the slope of the equation of the line obtained by correlating the mass of CA adsorbed on the fiber with the sampling time for known air concentrations. The absolute quantity of CA adsorbed on the fiber was previously calculated by injecting 0.3 \( \mu \text{L} \) standard solutions containing different amounts (0.1–10 ng) in hexane. We evaluated the effects of temperature, relative humidity, and linear velocity on the SPME system by means of CA vapor generated in a dynamic system for 480 min by use of a Harvard Plus 11 syringe-pump (Harvard Apparatus, Holliston, USA) equipped with a 1-mL gas-tight syringe (Hamilton, Bonaduz, Switzerland) set to 2 \( \mu \text{L min}^{-1} \). The CA solutions (0.4 \( \mu \text{g L}^{-1} \) for ‘rapid-SPME’ and 4 \( \mu \text{g L}^{-1} \) for ‘TWA-SPME’) evaporated in the injector (250°C) and were carried by a current of nitrogen (0.1 L min\(^{-1}\)) and blended with a flow of nitrogen (2.5–25 L min\(^{-1}\)), previously moistened, into a glass thermostat exposure chamber provided with plugs for the introduction of SPME fibers in automated mode. The \( C_{CA \text{ air}} \) concentration was calculated from:

\[
C_{CA \text{ air}} = C_{CA \text{ sol}} F_{\text{syringe-pump}} / F_{\text{air}}
\] (10)

where \( C_{CA \text{ air}} \) is the concentration of analyte in air (\( \mu \text{g L}^{-1} \)), \( C_{CA \text{ sol}} \) the concentration of the solution (\( \mu \text{g} \mu \text{L}^{-1} \)), \( F_{\text{syringe-pump}} \) the syringe-pump flow (\( \mu \text{L min}^{-1} \)), and \( F_{\text{air}} \) the air flow (L min\(^{-1}\)).

Every thirty minutes 5 \( \mu \text{L} \) generated CA vapor was injected in automated mode by means of an XYZ axes robotic system and a 10-\( \mu \text{L} \) gas-tight syringe (Hamilton) into the rapid GC–MS system. The effect of air velocity on the SPME system was verified using a glass cylinder connected to the
exposure chamber. The glass cylinder, with four different internal diameters, each provided with a plug for introduction of the fiber, enables 0.2 to 83 cm s\(^{-1}\) air speed to be obtained [20]. The linear velocity was calculated by dividing the air flow (mL s\(^{-1}\)) by the cross-sectional area (cm\(^2\)). Mixtures with known CA concentrations in a known range of relative humidity (10 and 80%) and of temperature (20–35°C) were produced. The relative humidity was calculated by use of the photoacoustic multi-gas monitor which measures the temperature at the dew point (\(T_{\text{dew}}\)).

**Analytical Equipment**

**Rapid GC-MS Conditions**

Rapid GC-MS analysis was performed with a Shimadzu GC 2010 with the system acquisition GC Solution software 2.5 SU3 version, using an SLB5-MS customizer column (5 m × 0.10 mm × 0.4 µm film thickness; Supelco, Sigma–Aldrich) with a Shimadzu QP 2010 series mass-selective detector (Shimadzu Italia, Milano, Italy) operating in EI-scan mode. GC oven temperature was 45°C for 1 min, then ramps of 150° min\(^{-1}\) to 100°C and 50° min\(^{-1}\) up to 300° C. Inlet pressure and average linear velocity were, respectively, 344 kPa and 100 cm s\(^{-1}\). The injector (250°C) was initially set in splitless mode for 1 min and then switched to 20:1 split mode. For conventional GC a 30 m × 0.10 mm internal diameter (i.d.) × 0.25 µm film thickness SPB-5 column (Supelco, Sigma–Aldrich) was used. For LTPRI a PDMS column (Equity-1, 5 m × 0.10 mm × 0.1 µm film thickness) purchase (Supelco, Sigma–Aldrich) was used under the same condition as indicated above.

**XYZ Axes Robotic System**

Full automation of the procedure was achieved by use of an AOC-5000 autosampler (Shimadzu Italia) equipped with SPME/MFS and Fast Kit SPME fiber (Fig. 1b), developed and patented by Chromline [25]. The Fast Kit enables use of fibers for high-throughput processes. It is formed from four adaptors that make the fiber much more robust and is identifiable by its barcode. Because of the Fast Kit it is possible to change SPME fibers in automatic mode by means of the MFS. With SPME/MFS, the multi-fiber analysis sequence works simply – the fibers assembled with the Fast Kit are transported between the 25-position tray and injector by the new holder equipped with a plunger and magnetic system. At the end of the analysis
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the desorbed fiber is moved back to the tray and the cycle is repeated. The autosampler settings complete the analysis cycle by conditioning and sealing the fiber in the Teflon septum inserted into the tray.

Results and Discussion

To achieve the proposed objective, different steps were required:

(i) investigation of the derivatization procedure and yield, and the stability of the derivatized product;
(ii) choice of fiber and rapid GC–MS conditions;
(iii) calculation of the diffusion coefficients of CA in air by use of the equations given above;
(iv) laboratory validation of the SPME passive sampler used in a dynamic system; and
(v) evaluation of the risk in a military store because of the manipulation of CA canisters, which will be discussed in detail below.

Reactivity of 2-Chloroacetophenone

Several authors [26–28] have proposed use of the SPME after derivatization of carbonyl groups with O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA). Experimentally, with the SPME-GC–MS technique, we observed that the reactivity of CA with the nucleophile PFBHA is triggered by the steric hindrance of the aromatic group.

\[
\text{ClO} PFBHA \text{Cl} \quad \text{N} \quad \text{O} \quad \text{F} \quad \text{F} \quad \text{F} \quad \text{F} \quad \text{F} \quad 25^\circ C
\]

(11)

So the corresponding oxime does not form immediately and, by monitoring the reaction with rapid GC–MS (Fig. 2), we observed that complete conversion of CA takes almost 3 h (Fig. 3). Analogous problems have previously been reported with both CA and acetophenone [29]. Consequently no derivatization procedure has been used.
Fig. 2. Chromatogram obtained from CA (1) after reaction with PFBHA and conversion into oxime (2), to monitor the kinetics of the reaction by rapid GC-MS.
With regard to the stability of the CA, it must be stressed that generation of a standard atmosphere by a syringe-pump instead of by use of permeation tubes is necessary because CA is rapidly hydrolyzed and its contact with air leads to the production of hydrogen chloride and hydroxyacetophenone. Radical initiators (impurities, oxygen, etc) enable radical scission of the carbon–chlorine bond with the formation of acetophenone. Thus the decomposition of CA can be easily detected by GC–MS, because of the appearance of the acetophenone peak, as previously described [2]. Generation of static vapors in Tedlar bags was also assessed in this investigation, but poor CA recovery was observed, presumably because of absorption of the analyte on the bag surface. In contrast, no decomposition or CA loss were observed when the syringe-pump was used and the experimental CA concentration data were consistent with the theoretical data calculated by use of Eq. (10). CA must be stored in an anhydrous solvent, so preventing any reaction with water.

### Choice of Fiber and Rapid GC–MS Conditions

The fiber coating was selected for its affinity for CA; better results were obtained with the 100-μm PDMS fiber than with the 30 μm PDMS fiber, in accordance with theoretical considerations which suggest thin films enable more efficient rapid extraction of high-molecular-weight compounds. When liquid coatings are used, limits of detection are, moreover, lower for com-
pounds such as CA with larger $K_1$ ($1.1 \times 10^5$, 298 K). The amount of CA extracted with the absorptive coating was less than with the adsorptive coating (Fig. 4) so solid phases were preferred. Poor resolution chromatograms were obtained when CAR/PDMS was used, so PDMS/DVB was selected for further experiments. The lower chromatographic resolution with CAR/PDMS, because of the presence of peak tailing, was not attributable to chromatographic phenomena, but to a different desorption ratio from the fiber in the chromatographic injector. When storage stability was assessed no significant change of mass adsorbed was observed after storage at $-20^\circ C$ for one week on solid-phase PDMS/DVB.

Rapid GC enabled rapid separation and resulted in analysis of excellent quality (Fig. 5), with sufficient resolving power for the compound of interest. In this investigation, the GC analysis of CA was performed in 2.420 min, almost five times faster than by traditional GC (12.394 min). Moreover, rapid GC–MS with PDMS columns was used for LTPRI determination; a typical chromatogram is shown in Fig. 6.

**Coefficient Diffusion Models**

To calculate the $D_g$ of CA, a variety of models using different predictive variables are suggested in the scientific literature. These methods include the Gilliland, Andrußow, Arnold, HBS, FSG, and Brokaw methods. The
Fig. 5. Rapid GC–MS chromatogram and electron-impact spectrum of the CA (rapid SPME, sampling 1 min, 0.008 mg m$^{-3}$)
Fig. 6. Rapid GC–MS chromatogram of $n$-alkanes for measurement of LTPRI: 1, decane; 2, dodecane; 3, tetradecane; 4, hexadecane; 5, octadecane; 6, eicosane; 7, docosane; 8, tetracosane; 9, hexacosane; 10, octacosane
Gilliland model is a correlation based on the hard sphere model; one obvious fault of this method is that the equation has $3/2$ power temperature dependence and experimental evidence has shown this to be too low [30]. An equation similar to Gilliland, but with improved temperature dependence, was introduced by Andrussow. Arnold extended the simple hard-sphere model to allow for attractive forces between the molecules, and the HBS method uses collision integrals and the collision diameter between the molecules. The Gilliland, Andrussow, Arnold, and HBS methods use 28.967 as the molecular weight of air and the value of 29.9 cm$^3$ mol$^{-1}$ for the molecular volume of air at its boiling point [31]. The molar volume of each compound at its boiling point in these four equations was calculated by the Le Bas method. The FSG equation uses atomic diffusion volumes and the Brokaw correlation method uses the potential energy of polar molecules and, as a result, this method should accurately predict the behavior of polar gas mixtures. We first calculated the $D_g$ of CA as indicated in Table I. The values of $D_g$ calculated with these different methods are very similar and so the FSG equation was chosen because it also has advantages in terms of accuracy, convenience, and general applicability (the program for calculating $D_g$ is available at www.epa.gov/; accessed January 20, 2009). The FSG yields the best agreement between calculated and observed values, with a mean error of 4.2% [32].

Table I. Calculated $D_g$ (cm$^2$ s$^{-1}$) of CA by use of six different equations for binary mixtures (A = air, B = analyte), at a pressure, $P$, of 1 atm and a temperature, $T$, of 298 K, by evaluation of molecular weight ($M_A, M_B$), molar volumes ($V_A, V_B$), Sutherland constant ($S_{AB}$), collision integral ($\sigma_{AB}^2$), collision diameter ($\Omega_{D,AB}$), and atomic diffusion volumes ($\sum V_A, \sum V_B$).

<table>
<thead>
<tr>
<th>Method</th>
<th>Equation</th>
<th>$D_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gilliland</td>
<td>$D_g = 0.0043T^{3/2}(1/M_A + 1/M_B)^{1/2}/P(V_A + V_B)^2$</td>
<td>0.060</td>
</tr>
<tr>
<td>Andrussow</td>
<td>$D_g = 0.606T^{1.78}(1/M_A + 1/M_B)^{1/2} + 1/(M_A M_B)^{1/2}/P(V_A^{1/3} + V_B^{1/3})^2$</td>
<td>0.059</td>
</tr>
<tr>
<td>Arnold</td>
<td>$D_g = 0.00837T^{3/2}(1/M_A + 1/M_B)^{1/2}/P(V_A^{1/3} + V_B^{1/3})^2(1 + S_{AB}/T)$</td>
<td>0.074</td>
</tr>
<tr>
<td>HBS</td>
<td>$D_g = 0.001858T^{1.5/2}(1/M_A + 1/M_B)^{1/2}/P\sigma_{AB}\Omega_{D,AB}$</td>
<td>0.067</td>
</tr>
<tr>
<td>FSG</td>
<td>$D_g = [(0.001T^{1.75})/P\sigma_{AB}^2(\sum V_A^{1/3} + (\sum V_B^{1/3})^2]$</td>
<td>0.063</td>
</tr>
<tr>
<td>Brokaw</td>
<td>$D_g = [(0.001858T^{3/2}M_B^{1/2})]/[P\sigma_{AB}^2\Omega_{D,AB}]$</td>
<td>0.069</td>
</tr>
</tbody>
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Sampling Rate

The suitability of SPME for ‘rapid’ and ‘TWA’ sampling of CA under non-equilibrium conditions was investigated (the details are reported in the Experimental section). For ‘TWA-SPME’ sampling, statistical analysis of labo-
ratory validation revealed that temperature (20 and 35°C), relative humidity (10 and 80%) and air flow (0.5 and 83 cm s$^{-1}$) did not affect adsorption efficiency ($p < 0.05$). The theoretical (0.01086 mL min$^{-1}$, 0.460 mg m$^{-3}$ min) and experimental average $SR$ values (0.00885 mL min$^{-1}$, $n = 5$), at 25°C for $Z = 0.3$ cm were in good agreement. Fig. 7 shows a plot of amount of CA adsorbed (ng) as a function of exposure time (min). The slope of the curve is the uptake (ng min$^{-1}$) of CA on the SPME fiber as indicated in Eq. (9). In ‘rapid-SPME’ sampling (1 min) the theoretical $SR$ results were 7.6, 8.7, 10.2, and 12.2 mL min$^{-1}$ (0.00041 mg m$^{-3}$ min) for air flow of 0.5, 1.0, 2.0, and 4.0 cm s$^{-1}$, respectively. These theoretical values correlate strongly with the experimental average $SR$ values of 6.1, 10.0, 12.0, and 14.4 mL min$^{-1}$, respectively (Fig. 8), for $n = 5$. At air flow higher than 4.0 cm s$^{-1}$ theoretical and experimental $SR$ values differed substantially, however. This implies that the theoretical value of $\delta$ is near to zero and is not valid when sampling at air flows exceeding 4 cm s$^{-1}$. There was no significant difference between the $SR$ experimental values at 4 cm s$^{-1}$ and at 100 cm s$^{-1}$. Method precision ($n = 5$) for ‘TWA-SPME’ sampling ($Z = 0.3$ cm) was established to be 10% (0.032 mg m$^{-3}$) and 8% (3.2 mg m$^{-3}$) relative standard deviation (RSD) and for ‘rapid-SPME’ sampling (1.0 mg m$^{-3}$), 16% (air velocities, 1 cm s$^{-1}$) and 12% RSD (air velocities, 4 cm s$^{-1}$).

Fig. 7. Rate of uptake of CA by TWA-SPME with $Z = 0.3$ cm (0.320 mg m$^{-3}$)
The limit of quantification (LOQ) of the assay for CA was 5 pg (m/z 105). This was calculated by use of the expression [33] LOQ = (3SEq + q)/m, where SEq is the standard error of the intercept, m is the slope, and q is the intercept. To calculate LOQ, calibration curve at low concentration (from 2.5 to 25 pg) was used.

It was found experimentally that more than 150 analyses can be performed with each fiber.

**Field Sampling**

The authors used this method to evaluate the risk in a military store because of manipulation of CA canisters. ‘TWA-SPME’ sampling with rapid GC–MS analysis revealed concentrations of CA ranging from 0.049 to 0.206 mg m$^{-3}$. A 20-min period was monitored using twenty SPME fibers each for ‘rapid-SPME’ (sampling, 1 min), in sequential order. The highest levels of CA were 2.46 mg m$^{-3}$.

It should be emphasized that the conditions used for in-field measurements were different from those used in the previous investigation, because of the occurrence, in greater yield, of the decomposition reac-
tion of CA. The measurement performed under in-field conditions is, however, analytically correct, indicating that CA concentrations inhaled by exposed subjects might lead to health problems.

**Conclusion**

A rapid, sensitive, robust, and practical method has been developed for sampling and analysis of CA in air by SPME/MFS then rapid GC–MS. This paper is the first report of sampling of this tear gas using this methodology. Sampling by SPME does not require pumps or polluting organic solvents, thus reducing analysis time and sampling cost. It is, moreover, of reduced dimension and does not require accessories. This is an important point because SPME may be of value in the rapid sampling of scene-of-crime samples, suspicious spray cans, to institute decontamination and to evaluate the risk of CA. The GC–MS has substantially more discriminating power and sensitivity than other techniques proposed for identification of CA, and GC–MS facilities are usually available in forensic laboratories.

The sampling time ranged from 1 to 480 min, making the SPME device useful for a wide range of exposure assessments and proving it to be a powerful option for forensic applications. For accurate, rapid sampling, the air flow must either be known, or higher than 4 cm s\(^{-1}\), because the boundary layer is almost constant above this speed. Starting from theoretical considerations used to determine the passive adsorption of the analytes in an SPME sampling system, the authors of this work have developed a system suitable for analysis of large quantities of samples in a very short time, in this way reducing the cost of monitoring campaigns. This application can also be used in on-site analysis for immediate assessment of sampled air; increased sample throughput enables hot spot sampling.

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