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Detection of sarin and soman in a complex airborne matrix by capillary column ammonia chemical ionization gas chromatography–mass spectrometry and gas chromatography–tandem mass spectrometry

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ABSTRACT

The chemical warfare agents, sarin and soman, were detected and confirmed during full scanning capillary column ammonia chemical ionization mass spectrometry at nanogram levels in spiked extracts of a diesel exhaust environment sampled onto the charcoal of a Canadian C2 respirator canister. The selectivity of ammonia chemical ionization enabled the use of selected ion monitoring and resulted in detection limits of 40 pg and just above 500 pg for sarin and soman respectively in this extract. This diesel exhaust environment, typical of what might be encountered under battlefield conditions, was used to evaluate capillary column ammonia chemical ionization tandem mass spectrometry as a possible verification technology. Chemical interferences were reduced and significantly better detection limits, 15 pg and 80 pg for sarin and soman respectively, were obtained during gas chromatographic–tandem mass spectrometric analysis of these agents in the presence of numerous interfering diesel exhaust and charcoal bed components.

INTRODUCTION

Chemical weapon use, although prohibited by the 1925 Geneva Protocol, has been documented in several armed conflicts, including the Iran/Iraq war [1]. Verification of chemical agent use has often been difficult, due in part to inadequate battlefield sampling and identification procedures. Capillary column gas chromatography (GC)–flame ionization detection may be used for the routine screening of samples for the presence of chemical warfare agents [2,3]. However, it is generally agreed that confirmation of the chemical warfare agents or their degradation products requires identification by mass spectrometry (MS). Electron impact (EI), the traditional MS method of ionization, has gained wide acceptance for the verification of organophosphorus chemical warfare agents, as the EI mass spectra of numerous

chemical warfare agents, their decomposition products and related compounds have been published [4–9].

EI mass spectra generally provide excellent structural information [10], but the presence of little or no molecular ion information often hinders the identification of organophosphorus compounds. Chemical ionization (CI) MS [11], a milder ionization technique, has been used with increasing frequency to provide molecular ion information for these compounds [12]. CI-MS using methane, isobutane, ethylene or methanol has been applied to the analysis of organophosphorus chemical warfare agents [5,13] and pesticides [14–19]. More recently, the efficacy of ammonia CI-MS [20] has been demonstrated for phosphorus oxyacids [21], several organophosphorus pesticides [14,18,22] and organophosphorus chemical warfare agents, their decomposition products and related impurities [6,8,9,23,24].

During a recent study designed to evaluate MS methods for the verification of chemical warfare agents in airborne samples similar to those collected during battlefield airborne sampling, it was apparent that the major limitation during capillary column GC–EI-MS analysis was the chemical noise associated with the hydrocarbon content [25]. Ionization under ammonia CI-MS conditions should result in better detection limits than under EI conditions, with the benefit of molecular ion information, as hydrocarbons are not sufficiently basic to ionize under ammonia CI conditions. This mode of operation should reduce the chemical noise associated with the airborne extract and enable the trace detection of the organophosphorus chemical warfare agents, sarin and soman. As in the previous study [25], tandem mass spectrometry (MS–MS) was evaluated as a potential technology for the confirmation of trace levels of organophosphorus chemical warfare agents in the presence of this complex airborne matrix.

Tandem mass spectrometers offer a number of highly specific scan functions including; parent ion, daughter ion, constant neutral loss and reaction ion monitoring. During reaction ion monitoring, the method of choice for many trace "target' compound applications, the first mass analyser is tuned to allow a desired mass (*e.g.*, $(M + NH_4)^+$) into the collisional activated dissociation (CAD) cell while the second mass analyser allows only characteristic ion(s) derived from fragmentation(s) of the ion selected by the first analyser to be detected. The two degrees of selectivity offered by the MS–MS instrument are further enhanced by the use of gas chromatographic sample introduction.

MS–MS has been reviewed recently [26–29], and methods have been reported for selected organophosphorus pesticides [19,30,31], organophosphorus chemical warfare agents [24,25] and mustard [25]. Although capillary column ammonia chemical ionization GC–MS–MS has been suggested as a possible means of chemical warfare agent confirmation in complex environmental samples [24], there have been no reported applications of this methodology.

A capillary column GC study using ammonia CI-MS and ammonia CI-MS–MS detection was initiated with the principal objective being the development and evaluation of these methods for the detection and confirmation of sarin (isopropyl methylphosphonofluoridate or GB) and soman (pinacolyl methylphosphonofluoridate or GD) in a complex airborne matrix. The air samples during this study contained the volatile components of diesel exhaust and was very similar in composition to battlefield air sampled onto charcoal during a recent interlaboraroty analytical

exercise [32]. Charcoal from exposed C2 Canadian respirator canisters was solvent extracted and spiked at several levels to allow evaluation of ammonia CI-MS and ammonia CI-MS–MS for the trace detection of the chemical warfare agents, sarin and soman.

EXPERIMENTAL

Standards and sample handling

Sarin and soman were provided by the Defence Research Establishment Suffield Organic Chemistry Laboratory. Distilled-in-glass dichloromethane was purchased from BDH (Edmonton, Canada). All samples and standards were stored in PTFE-lined screw-capped vials at 4°C prior to GC analysis. Anhydrous-grade ammonia (99.99%) was used during CI-MS analyses (Liquid Carbonic).

Air from a diesel exhaust environment was sampled through a Canadian C2 charcoal canister for 4 h at the typical working respiratory rate of 20 l/min. The canister charcoal (108 g) was Soxhlet extracted for 6 h with 250 ml of dichloromethane and concentrated to 10 ml under a gentle stream of nitrogen.

Instrumental

Capillary column ammonia chemical ionization GC–MS full scanning and selected ion monitoring analyses were performed with a VG 70/70E double focusing mass spectrometer (VG Analytical, Wythenshawe, U.K.) interfaced to a Varian 3700 gas chromatograph under the following chromatographic conditions. All injections were on-column [2] at 40°C onto a 15 m × 0.32 mm I.D. J & W DB-5 (0.25 μm) capillary column with a 40°C (2 min) → 10°C/min → 280 °C temperature program. CI-MS operating conditions were as follows: accelerating voltage, 6 kV; emission, 500 μA; electron energy, 50 eV; source temperature, 120°C and source pressure, $9 \cdot 10^{-5}$ Torr. Full scanning CI data were collected over the 400 to 35 u mass range at 1 s/decade. Both the $(M + NH_4)^+$ and $(M + H)^+$ ions for sarin (m/z 158 and m/z 141) and soman (m/z 200 and m/z 183) were acquired with a 80 ms dwell time and 20 ms delay per ion during selected ion monitoring CI-MS analysis.

Capillary column ammonia chemical ionization GC–MS–MS analyses were performed with a VG 70SQ hybrid tandem mass spectrometer equipped with a Hewlett-Packard 5890 gas chromatograph. All injections were on-column at 40°C using a Hewlett-Packard on-column injector. The 15 m × 0.32 mm I.D. J&W DB-5 (0.25 μm) capillary column was held at this temperature for 2 min and then programmed at either 8°C or 20°C/min to a maximum of 280°C. Ammonia CI source conditions were identical to those employed during GC–MS analysis with the following exceptions: accelerating voltage, 8 kV and emission, 1000 μA. The daughter mass spectra of m/z 158 for sarin and m/z 200 for soman were obtained under the following conditions: CAD cell, 20 eV (laboratory scale)/air ($6 \cdot 10^{-7}$ Torr) and a quadrupole scan function of 300 to 20 u at 0.5 s/decade. Reaction ion monitoring for sarin was carried out using the CAD conditions listed above on the m/z 158 to m/z 141 and m/z 158 to m/z 99 transitions with a 80 ms dwell time and 20 ms delay. Soman reaction ion monitoring was carried out in an identical manner on the m/z 200 to m/z 183 and m/z 200 to m/z 99 transitions.

RESULTS AND DISCUSSION

The diesel exhaust environment sampled onto the charcoal of Canadian C2 canisters contained primarily hydrocarbon compounds [25] and was similar in composition to the volatile battlefield components extracted from a respirator canister circulated as part of a recent interlaboratory analytical exercise [32]. Charcoal extracts used in this study were further complicated by the presence of silicon-containing compounds adsorbed onto the charcoal bed of the Canadian C2 canisters. The development of suitable mass spectrometric confirmation methods for chemical warfare agents adsorbed onto charcoal under realistic conditions would be valuable in a Chemical Weapons Convention verification role as charcoal mask canisters represent a possible retrospective sampling device.

Capillary column ammonia chemical ionization GC–MS

An interpretable full scanning ammonia CI mass spectrum was obtained for sarin during capillary column GC–MS analysis of the charcoal extract spiked at the 5 ng level. The acquired ammonia CI mass spectrum contained both $(M + NH_4)^+$ and $(M + H)^+$ ions with relative intensities of 100 and 20 respectively. Soman, which elutes in a more complex region of the extract chromatogram, could only be tentatively identified at the retention time of the first chromatographic peak (two chromatographic peaks due to diastereoisomeric pairs), due to the co-elution of an interference(s). Characteristic ions due to $(M + NH_4)^+$ and $(M + NH_4\text{-}C_6H_{12})^+$ at m/z 200 and 116 respectively were observed with relative intensities of 100 and 80 respectively. The $(M + H)^+$ ion (typically about 5% of the base ion) was not detectable. The second chromatographic peak for soman was effectively masked by the matrix with only the m/z 200 ion being discernable above the chemical background.

A reduction in chemical background during ammonia CI-MS, as compared to previous EI-MS analysis [25], enabled the use of selected ion monitoring for the trace detection of sarin and soman. Both the $(M + H)^+$ and $(M + NH_4)^+$ pseudo-molecular ions of sarin and soman were monitored during analysis of the unspiked extract and the same extract spiked with sarin and soman at the 500 pg and 50 pg levels. The pseudo-molecular ions for sarin at m/z 158 and m/z 141 were observed without interference at both spiked levels in the same area ratio as observed for a sarin standard. A detection limit of about 40 pg (signal-to-noise, S/N ratio of 5:1) in the presence of this complex matrix was estimated, based on the detection of both sarin pseudo-molecular ions. Fig. 1 illustrates the m/z 158 selected ion monitoring chromatograms obtained for the unspiked extract and the same extract spiked with sarin at the 500 pg and 50 pg levels.

In the case of soman, only the m/z 200 ion was detected above the background chemical noise during capillary column ammonia CI-MS selected ion monitoring analysis of the charcoal extracts spiked at the 500 and 50 pg levels (Fig. 2). This ion, due to $(M + NH_4)^+$, was detected with a S/N ratio of about 8:1 during analysis of the 50 pg spiked extract. The $(M + H)^+$ ion for soman, at m/z 183, was detected with a S/N ratio of approximately 4:1, which suggested a method detection limit of just over 500 pg, based on the detection of both pseudo-molecular ions. Monitoring of the two most intense soman ions, at m/z 200 and m/z 116 (instead of m/z 200 and m/z 183), was not considered viable under voltage scanning selected ion monitoring due to the

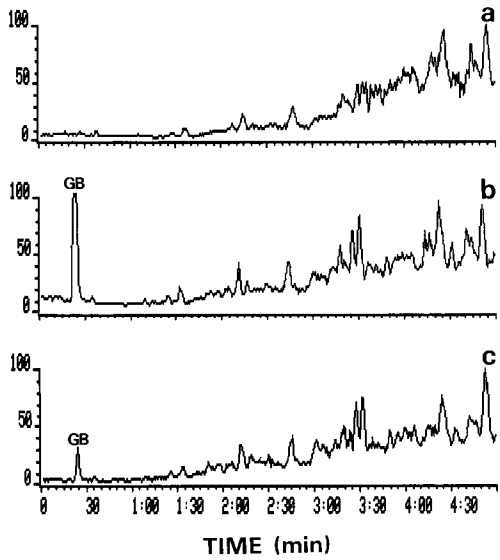

Fig. 1. Capillary column ammonia chemical ionization GC–MS selected ion monitoring chromatograms obtained for m/z 158 [$(M + NH_4)^+$ ion for sarin] during analysis of (a) dichloromethane extract of the equivalent of $4.8 \cdot 10^{-4}$ m^3 of air sampled onto the charcoal of a C2 canister and the previous sample spiked with sarin (GB) at the (b) 500 pg and (c) 50 pg levels. Column 15 m × 0.32 mm I.D. J&W DB-5; temperature, 40°C (2 min) → 10°C/min → 280°C.

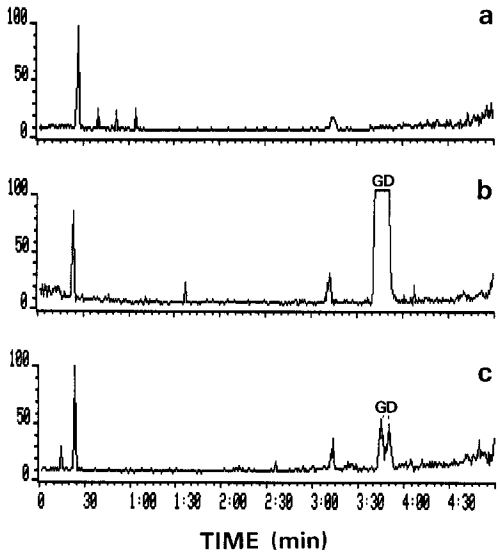

Fig. 2. Capillary column ammonia chemical ionization GC–MS selected ion monitoring chromatograms obtained for m/z 200 [$(M + NH_4)^+$ ion for soman] during analysis of (a) dichloromethane extract of the equivalent of $4.8 \cdot 10^{-4}$ m^3 of air sampled onto the charcoal of a C2 canister and the previous sample spiked with soman (GD) at the (b) 500 pg and (c) 50 pg levels. Conditions as in Fig. 1.

large mass range, but should be considered for quadrupole or magnetic scanning selected ion monitoring.

Capillary column ammonia chemical ionization GC–MS–MS

Hesso and Kostiainen [24] reported the first daughter spectra for the pseudo-molecular ions formed during ammonia chemical ionization of sarin, soman, tabun and VX. The utility of reaction ion monitoring (RIM) for the detection of chemical warfare agents in a complex or environmental matrix, while mentioned, was not demonstrated. Use of GC–MS–MS under ammonia CI conditions, for the trace detection of these chemical warfare agents was investigated in this study, as this technique could prove to be a more sensitive and specific approach for the trace confirmation of sarin and soman in a complex matrix.

The daugher spectra of the $(M + NH_4)^+$ pseudo-molecular ions of sarin and soman were acquired under CAD conditions, which, while perhaps not optimal, provided lower mass ions suitable for use in a RIM experiment. Fig. 3 illustrates the daughter spectra acquired during analysis of a standard. Daughter ions at *m/z* 99 and *m/z* 141 and, at *m/z* 85, *m/z* 99 and *m/z* 183 were observed for sarin and soman respectively. Relative daughter ion intensities were different than those observed by Hesso and Kostiainen [24], which may be due to the use of different CAD gases, pressures and instruments. The data from these experiments suggested the use of the $(M + NH_4)^+$ to $(M + H)^+$ and $(M + NH_4)^+$ to $[(CH_3)(F)P(OH)_2]^+$ RIM transitions for the confirmation of sarin and soman in the airborne sample extracts.

Figs. 4 and 5 illustrate the RIM chromatograms for the unspiked extract and, 500 pg and 50 pg spiked extracts obtained during monitoring of the $(M + NH_4)^+$ to $(M + H)^+$ (*m/z* 158 to *m/z* 141) and $(M + NH_4)^+$ to $[(CH_3)(F)P(OH)_2]^+$ (*m/z* 158 to *m/z* 99) transitions respectively. Sarin was readily detected, with no interferences, at both levels during capillary column ammonia chemical ionization GC–MS–MS analysis of the spiked extracts under these conditions. Chemical noise due to the extract components was particularly low for the *m/z* 158 to *m/z* 99 transition, as this loss is more diagnostic than simply loss of NH_3 from the $(M + NH_4)^+$ ion. Conservative

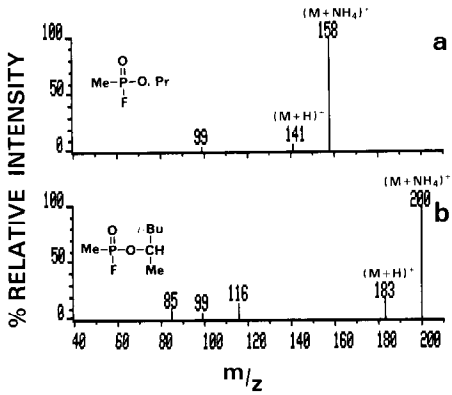

Fig. 3. Daughter spectra obtained for $(M + NH_4)^+$ ions of (a) sarin and (b) soman during capillary column ammonia chemical ionization GC–MS analysis of a standard.

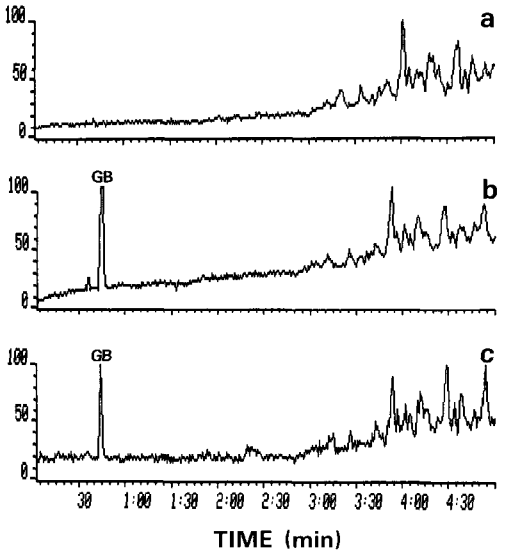

Fig. 4. Reaction ion monitoring chromatogram for m/z 158 to m/z 141 obtained during capillary column ammonia chemical ionization GC–MS–MS analysis of (a) dichloromethane extract of the equivalent of 4.8 $\cdot 10^{-4}$ m^3 of air sampled onto the charcoal of a C2 canister and the previous sample spiked with (b) 500 pg and (c) 50 pg of sarin (GB). Column, 15 m × 0.32 mm I.D. J&W DB-5; temperature, 40°C (2 min) → 20°C/min → 280°C.

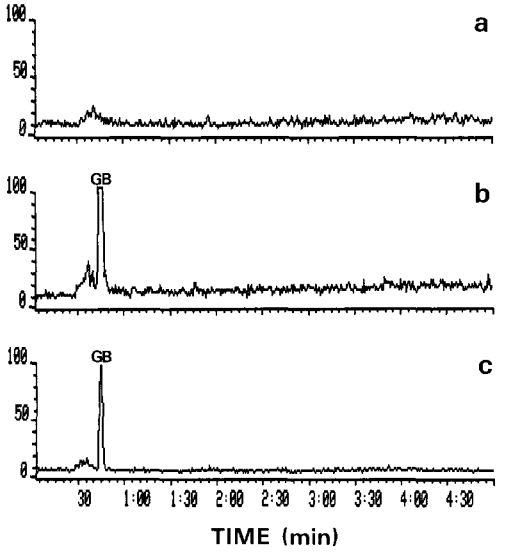

Fig. 5. Reaction ion monitoring chromatogram for m/z 158 to m/z 99 obtained during capillary column ammonia chemical ionization GC–MS–MS analysis of (a) dichloromethane extract of the equivalent of 4.8 $\cdot 10^{-4}$ m^3 of air sampled onto the charcoal of a C2 canister and the previous sample spiked with (b) 500 pg and (c) 50 pg of sarin (GB). Conditions as in Fig. 4.

CI-MS–MS sample detection limits for sarin, based on a S/N ratio of 5:1, were better than under CI-MS conditions and were estimated to be 20 pg for the $(M + NH_4)^+$ to $(M + H)^+$ (m/z 158 to m/z 141) transition and 15 pg for the $(M + NH_4)^+$ to $[(CH_3)(F)P(OH)_2]^+$ (m/z 158 to m/z 99) transition.

Soman, as was the case during capillary column ammonia CI-MS analysis, was not as readily confirmed in the presence of this complex matrix. It was confirmed at both the 500 pg and 50 pg (S/N = 3:1) level during RIM of the $(M + NH_4)^+$ to $(M + H)^+$ (m/z 200 to m/z 183) transition, but was only confirmed at the 500 pg level during monitoring of the $(M + NH_4)^+$ to $[(CH_3)(F)P(OH)_2]^+$ (m/z 200 to m/z 99) transition. The inability to detect soman for the latter transition at the 50 pg level was likely due to the reduced relative ion intensity of the m/z 99 ion in the daughter spectrum of soman. Conservative CI-MS–MS sample detection limits for soman, based on a S/N ratio of 5:1, were much better than obtained under CI-MS conditions and were estimated to be 80 pg for the $(M + NH_4)^+$ to $(M + H)^+$ (m/z 200 to m/z 183) transition and 350 pg for the $(M + NH_4)^+$ to $[(CH_3)(F)P(OH)_2]^+$ (m/z 200 to m/z 99) transition.

Detection limit comparison

The charcoal extract spiked during this study was used in a prior capillary column GC–MS and GC–MS–MS study under EI ionization conditions [25]. Table I compares the ammonia CI-MS detection limits with those obtained under EI-MS conditions for three chemical warfare agents spiked into the same airborne sample extract. Ammonia CI-MS holds a decided advantage over EI-MS during full scanning and selected ion monitoring. This was due to a reduction of chemical noise, as hydrocarbons are not sufficiently basic to form pseudo-molecular ions under ammo-

TABLE I

COMPARISON OF MASS SPECTROMETRIC METHODS FOR THE ANALYSIS OF CHEMICAL WARFARE AGENTS IN A COMPLEX AIRBORNE MATRIX

N/A = Not applicable for this compound; SIM = selected ion monitoring; RIM = reaction ion monitoring.

Method	Detection limit[a]		
	Sarin	Soman	Mustard
GC–MS (EI)[b] (Full scanning)	20 ng	20 ng	20 ng
GC–MS–MS(EI)[b] (RIM on 1 transition)	70 pg	60 pg	30 pg
GC–MS (NH_3-CI) (Full scanning)	5 ng	> 5 ng	N/A
GC–MS (NH_3-CI) [SIM of $(M + H)^+$ and $(M + NH_4)^+$]	40 pg	> 500 pg	N/A
GC–MS–MS (NH_3CI) (RIM on 1 transition)	15 pg	80 pg	N/A

[a] Interpretable mass spectrum for full scanning methods and S/N ratio of 5:1 for SIM and RIM methods.

[b] Data from ref. 25.

nia CI conditions. The major disadvantage of this selectivity was the inability of this method to detect other compounds of chemical defense interest such as the sulfur vesicant, mustard. Mustard, like the hydrocarbons, was not sufficiently basic to form significant pseudo-molecular ions during ammonia CI-MS. Mustard and related compounds do however form abundant $(M + H)^+$ pseudo-molecular ions under isobutane CI conditions [33–35]. However, use of this reagent gas would also lead to hydrocarbon ionization and likely lead to little, if any, gain in sensitivity. GC–MS–MS, under EI conditions, remains the most practical approach for the verification of mustard in this complex matrix.

CONCLUSIONS

The chemical warfare agents, sarin and soman, were detected and confirmed during full scanning capillary column ammonia CI-MS at nanogram levels in spiked dichloromethane extracts of a diesel exhaust environment sampled onto the charcoal of a Canadian C2 gas mask canister. The selectivity of this ionization method enabled the use of selected ion monitoring and resulted in detection limits of 40 pg and just above 500 pg for sarin and soman respectively in the presence of this airborne extract.

This matrix, typical of what might be encountered under battlefield conditions, was used to evaluate capillary column ammonia chemical ionization GC–MS–MS as a possible verification technology. Daughter spectra, obtained during capillary column ammonia chemical ionization GC–MS–MS analysis of sarin and soman, suggested use of both the $(M + NH_4)^+$ to $(M + H)^+$ and $(M + NH_4)^+$ to $[(CH_3)(F)P(OH_2]^+$ transitions for reaction ion monitoring. Reaction ion monitoring of these collisional activated processes proved to be the most sensitive of the methods evaluated for the verification of sarin and soman. Chemical interferences were significantly reduced and detection limits of 15 pg and 80 pg for sarin and soman respectively were obtained during capillary column ammonia CI-MS–MS analysis of these agents in the presence of matrix component concentrations two to three orders of magnitude greater than the spiked agents.

Application of tandem mass spectrometry, under ammonia CI conditions, for the detection of organophosphorus chemical warfare agents appears to be an attractive approach for the verification of "target" compounds in complex environmental matrices such as those that may be encountered during airborne sampling of battlefield emissions.

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