Forensic Science International 222 (2012) e7–e12

Contents lists available at SciVerse ScienceDirect

Forensic Science International

journal homepage: www.elsevier.com/locate/forsciint

Case Report

Analysis of hydrogen cyanide in air in a case of attempted cyanide poisoning

R. Magnusson, S. Nyholm, C. Åstot *

The Swedish Defence Research Agency (FOI), CBRN Defence and Security, SE-901 82 Umeå, Sweden

ARTICLE INFO

Article history:
Received 20 December 2011
Received in revised form 14 May 2012
Accepted 19 May 2012
Available online 15 June 2012

Keywords:
Hydrogen cyanide poisoning
Air sampling
On-site detection
Chemical analysis
Gas chromatography–mass spectrometry (GC–MS)
Fourier transform infrared (FTIR) spectroscopy

ABSTRACT

A 32-year-old man attempted to poison his ex-girlfriend with hydrogen cyanide by hiding the pesticide Uragan D2 in her car. During the police investigation, chemical analysis of the air inside the car was performed. Hydrogen cyanide was detected through on-site air analysis using a portable Fourier transform infrared (FTIR) spectroscopy gas analyzer and colorimetric gas detection tubes. Furthermore, impinger air-sampling was performed for off-site sample preparation and analysis by gas chromatography–mass spectrometry (GC–MS). All three independent techniques demonstrated the presence of hydrogen cyanide, at concentrations of 14–20 ppm. Owing to the high volatility of hydrogen cyanide, the temperature and the time since exposure have a substantial effect on the likelihood of detecting hydrogen cyanide at a crime scene. The prevailing conditions (closed space, low temperature) must have supported the preservation of HCN in the car thus enabling the identification even though the analysis was performed several days after the hydrogen cyanide source was removed. This paper demonstrates the applicability of combining on-site FTIR measurements and off-site GC–MS analysis of a crime scene in order to ensure fast detection as well as unambiguous identification for forensic purposes of hydrogen cyanide in air.

1. Introduction

Cyanide has been used as a poison for thousands of years. The effects of high-dose cyanide are quick, and death occurs within minutes [1]. Cyanide exists in several forms, including hydrogen cyanide (HCN), cyanogen (NCCN), cyanogen halides, soluble potassium and sodium cyanide salts, and insoluble mercury, copper, gold, and silver cyanide salts. Although there are many chemical forms of cyanide, HCN (or the cyanide anion CN^-) is the primary toxic agent, regardless of its origin [1]. Hydrogen cyanide is a colorless or pale blue liquid, or a gas (with a boiling point of 26 °C), the gas is lighter than air and may be perceived by some to have a bitter almond-like odor. HCN is highly poisonous by all routes of administration and the toxic effect involves inhibition of several metal-containing enzymes. The critical interaction appears to be the inactivation of cytochrome C oxidase, an end-chain enzyme of cellular respiration, consequently causing cellular anoxia. The cardiovascular, respiratory, and central nervous systems are primarily affected [2]. Estimates of lethal dose vary, but exposures to gaseous HCN at concentrations above 300 ppm will likely result in death within a few minutes [2,3]. Cyanide salts (for example, potassium cyanide) are the most frequently associated with criminal poisoning in modern society [4] whereas inhalation of volatile HCN is rather rare, comprising 4–5% of all cases [5]. Cyanide salts react readily with acid or water to form HCN [4].

A great number of methods are available for the analysis of cyanides in different matrices including water, soil, air, exhaled breath, food, and biological fluids (blood, urine, saliva, etc.). The dramatic increase in the number of publications on cyanide measurements in such different applications as analytical chemistry, environmental science, medicine, and forensic science [6] indicates the great interest in this chemical threat. A major advantage of HCN on-site detection methods is the ability to immediately obtain a result. However, GC–MS after appropriate derivatization serves as a preferred confirmation and quantification method for forensic purposes owing to its ability to provide unambiguous qualitative identification and excellent quantitative sensitivity. Available standard analytical methods for HCN in air include sampling using midget impingers filled with potassium or sodium hydroxide solution [7,8], solid sorbent tubes [9] or passive samplers [10] with soda lime adsorbent, and analysis with ion chromatography or ion-specific electrodes. Because of the high volatility of HCN, air concentrations of HCN will decline rather fast after the source of exposure has been removed. Thus, to achieve identification of HCN, measurements generally have to be made soon after exposure. This paper reports a case of attempted cyanide poisoning where HCN in air was detected on-site followed by air sampling for subsequent extraction, derivatization, and GC–MS analysis at the laboratory.

---

* Corresponding author. Tel.: +46 90106808; fax: +46 90106800.
E-mail addresses: roger.magnusson@foi.se (R. Magnusson), sune.nyholm@foi.se (S. Nyholm), astot@foi.se (C. Åstot).

0379-0738/$ – see front matter © 2012 Elsevier Ireland Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.forsciint.2012.05.014

2. Case report

On February 1, 2009, a 32-year-old man attempted to poison his ex-girlfriend with HCN by placing two paper reels of the HCN-based pesticide Uragan D2, behind the driving-seat in her car. When the woman opened the car door a strong odor and vapor faced her, causing her to jump away and almost made her vomit. She opened the doors and vented the car for about 45 min. After the ventilation she rolled down the car window and drove home with her head outside the car. Two weeks after the incident the Swedish Defence Research Agency was asked to support the Swedish police by performing air measurements for forensic purposes. The aim was to determine if any detectable amounts of HCN still remained in the car and, if so, unambiguously prove the presence of HCN. In addition, the task was to assist in the search for caches of Uragan D2 at other locations. This was the third of a total of four attempts over a period of six weeks by the 32-year-old man to poison his former girlfriend. Fortunately, on each occasion she escaped without injury. Ultimately, the man was sentenced to nine years in prison on one count of attempted murder. According to the court, the remaining three poisoning attempts (including the one reported here) were cases of attempted assault and aggravated assault.

3. Sampling and chemical analysis

On behalf of the Swedish police, on-site air measurements were performed in the car and at a number of other locations where storage of Uragan D2 was suspected, including his house, garage, and hunting cabin, and the woman's apartment. In the car, measurements and sampling were performed by the front passenger seat. Care was taken to minimize ventilation of the car during the measurements. Uragan D2 is a pesticide consisting of stabilized liquid HCN (a mixture of approximately 98% HCN with phosphoric acid and sulfur dioxide as stabilizing additives) fully soaked in porous cardboard paper reels with a diameter of 145 mm, a central opening of 30 mm and a thickness of 4 mm, packaged in gastight tins. Uragan D2 is intended for an authorized professional use as fumigant for wood conservation, control of insects and rodents in buildings and other closed spaces. The product is analogous with Zyklon B, which was used by the Nazis during the Holocaust in World War II. The two Uragan D2 paper reels, which were the assumed source of HCN, were removed during the initial forensic investigation. The air measurements inside the car were taken on February 24, 23 days after the event. The car was then located at a fenced, supervised training area of the emergency services where it was placed directly after the incident. During this period, the car remained totally closed and was deliberately covered with snow, which was removed the day before the air measurements; thus, no one accessed the car until then. During the period February 1 to February 24, the weather remained cold (with a daily average temperature between -4 °C and -23 °C, the average over the whole period being -13 °C) and the ground was constantly covered with a layer of snow. The temperature inside the car at the time of sampling (during daytime) was 2.2 °C. On-site measurements were performed using a portable Fourier transform infrared (FTIR) spectroscopy gas analyzer (Gasmet DX-4030 FTIR Gas Analyser, Gasmet Technologies Oy, Helsinki, Finland) and colorimetric gas detection tubes (Dräger Tube CH 25701, Drägerwerk AG & Co. KGaA, Lübeck, Germany). In addition air was sampled for off-site chemical analysis. Gasmet DX-4030 is a multi-component FTIR gas analyzer which can detect up to 25 organic and/or inorganic gases simultaneously. The instrument was pre-calibrated for HCN by the manufacturer at two concentration levels; 20 ppm and 50 ppm. An instrumental application library was created adapted to HCN and a number of possible background gases on the measuring site, such as water, carbon dioxide and carbon monoxide, enabling measurement of and correction for chemical background. The wave number range of 3180–3400 cm^{-1} was used for HCN analysis. Due to the FTIR technology, the calibrations remain very stable and the only correction required is a zero calibration, which was performed before starting the measurements. The FTIR method enabled on-site identification and quantification of HCN with a detection limit of 0.35 ppm. The Dräger detection tubes served as a quick pass/fail method giving a concentration estimate in the range 2–150 ppm. The air sampling for off-site chemical analysis was performed by pumping a known volume (14 l) of air at a flow of 1.16 l/min through a midget impinger filled with 20 ml sodium hydroxide solution (0.1 M), capturing HCN as the sodium salt. Subsequently, the sample was extracted, derivatized, and analyzed with gas chromatography–mass spectrometry (GC–MS) at the laboratory. The cyanide sample was extracted and derivatized according to the procedure established by Miki et al. [11] using extractive pentafluorobenzylation by means of a polymeric phase-transfer catalyst. Cyanide ions captured in the impinger solution were transferred from the impinger sample (500 μl) into dichloromethane (400 μl) using polymer-bound tri-*n*-butylmethylphosphonium bromide (1.4 mmol Br^-/g polymer), and simultaneously derivatized by 2,3,4,5,6-pentafluorobenzyl bromide (PFB-Br) to 2-(2,3,4,5,6-pentafluorophenyl)acetonitril (PFB-CN) which is soluble in dichloromethane and suitable for subsequent analysis using GC–MS. 15 μg tetraline was added as internal standard before the triphasal derivatization procedure. A 1.0-μl aliquot of the dichloromethane phase was injected into an Agilent 6890 gas chromatograph equipped with a DB-5MS capillary column (J&W Scientifics, 30 m × 0.25 mm i.d., 0.25 μm film thickness) under the following conditions: helium as carrier gas, an injection temperature of 250 °C, a constant flow of 0.9 ml/min, split 1:10, an oven temperature from 60 °C to 280 °C at 10 °C/min, and an interface temperature of 280 °C. Detection was accomplished using an Agilent 5973N Mass Selective Detector in electron ionization (EI) mode operating both in full scan and selected-ion monitoring (SIM) measurement modes, using m/z of 207, 188, and 157 as the SIM ion channels for PFB-CN. Three 500 μl aliquots of the impinger solution were extracted, derivatized, and analyzed for the presence of cyanide ions. For calibration, standard solutions of cyanide ions were prepared, by dissolving potassium cyanide in 0.1 M NaOH, at three cyanide concentrations: 1.6 μg/ml, 16 μg/ml, and 32 μg/ml; corresponding to HCN air concentrations of 2 ppm, 20 ppm, and 40 ppm, respectively, assuming quantitative impinger collection efficiency [8]. The calibration samples (three replicates at each concentration) as well as three procedural blanks (of 0.1 M NaOH) were extracted, derivatized, and analyzed in the same manner as described above. In addition, a number of solvent blanks were analyzed. The GC–MS quantitative analysis was validated in terms of linearity, accuracy, precision, limit of detection (LOD), and limit of quantification (LOQ) for a number of 0.1 M NaOH samples spiked with potassium cyanide. The calibration graph ($y = 0.0195x - 0.00017$) for peak areas ratios of m/z 207 for PFB-CN against m/z 104 for the internal standard gave good linearity ($r^2 = 0.996$) over the cyanide ion concentration range 1.6–32 μg/ml. Within this concentration range the precision was 2.6–3.0% RSD and the accuracy 92–109%. The limit of detection (S/N = 3) was 0.02 μg/ml and the limit of quantification 0.1 μg/ml, corresponding to HCN air concentrations of 30 ppb and 130 ppb, respectively.

4. Results

Air analysis was performed in the woman's car and in other locations suspected as storage sites for the pesticide Uragan D2.