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Determination of hydrogen cyanide in residential ambient air using SPME coupled with GC–MS

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ABSTRACT

Hydrogen cyanide (HCN) is commonly released into the atmosphere from vehicle emissions, biomass burning and industrial processes such as gold mining, pesticide production, and chemical manufacturing. The aim of this study was to quantify the ambient HCN concentration in a residential area close to a gold mine using solid-phase micro extraction (SPME) coupled with gas chromatography–mass spectrometry (GC–MS) and calculate it's potential health risks. Air samples were collected at a distance of 0.1, 1.0 and 2.0 km away from the gold mine. All cyanide compounds were extracted using 75 μm carbowax/polydimethylsiloxane-coated SPME fibre and analysed using GC–MS. Calibration curve was constructed using standard concentrations ranged between 5 and 500 μg L^{-1}. This method showed good linearity (r^2 = 0.999) and accuracy (recoveries = 84–119%), reproducibility (relative standard deviation < 11.5%) and the LOD was 0.16 ppbv. HCN was detected in 68% of samples ranging between 0.16 and 8.56 ppbv. HCN concentration was significantly higher ($p < 0.05$) for samples taken at 0.1 km away from the gold mine compared to concentrations at 1.0 and 2.0 km. The non-carcinogenic risk of HCN from air inhalation was negligible as the calculated hazard quotient was less than 1. The method used in this study was sensitive enough to detect ambient HCN concentrations at levels which were below the reference concentration for long term inhalation exposure by the U.S. Environmental Protection Agency (0.72 ppbv) and it used simpler and less time consuming method compared to the conventional sample preparation method, enabling rapid community exposure assessment.

1. Introduction

Cyanide is present mainly as gaseous hydrogen cyanide (HCN) in air. HCN is a colourless gas with a faint bitter almond-like odour. It is miscible with water and soluble in alcohol (USEPA, 2010). HCN can be released into air from both natural processes and human activities. The natural sources of HCN are from biomass burning, volcanoes and natural biogenic processes from higher plants, bacteria, algae and fungi. Cyanide is released from natural substances in some plants such as coffee, seeds and pits of apple, cashew nuts, cassava and young bamboo (ATSDR, 2006). The man-made sources of hydrogen cyanide include exhaust from vehicle emissions, cigarette smoke and industrial activities such as gold mining, pesticide production, electroplating and chemical manufacturing (Simeonova and Fishbein, 2004). The half-life of HCN in the atmosphere is about 1–3 years (ATSDR, 2006).

Hydrogen cyanide has the potential to be transported over long distances from their respective emission sources and exposing general population to adverse health effects. Acute exposure to low levels of HCN may cause headache, nausea and dizziness, chest tightness, eye irritation and throat discomfort. Whilst at high concentrations, it may cause loss of consciousness, cardia arrhythmias, coma and death. Long term exposure to low levels of cyanide may lead to neurological effects (Pritchard, 2007) but it is not classified as a carcinogenic substance. Reference concentration (RfC) for chronic inhalation exposure established by the U.S. Environmental Protection Agency (EPA) is 0.0008 mg m^{-3} or 0.72 ppbv. The RfC is an estimate of a daily inhalation exposure to which people who are exposed (at this concentration or below) will

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unlikely have deleterious health effects during their lifetime.

There are many analytical methods presented in literature for the detection of cyanides in different matrices ranging from water (Isaad et al., 2013; Kang and Shin, 2014; Rosentreter et al., 2015), air (Greenawald et al., 2015; Magnusson et al., 2012; Musshoff et al., 2011; Orloff et al., 2006), human breath (Lauridsen et al., 2015) and smoking cigarette (Pre and Vassy, 1991). Cyanide can also be detected in biological fluids such as blood (Boadas-Vaello et al., 2008; Calafat and Stanfill, 2002; Desharnais et al., 2012; Ferrari and Giannuzzi, 2015; Frison et al., 2006; Kage et al., 1996; Lindsay et al., 2004; Youso et al., 2010), urine (Liu et al., 2009; Logue et al., 2005; Minakata et al., 2009; Zhang et al., 2015) and saliva (Paul and Smith, 2006).

Previously, determination of a component by analytical technique such as gas chromatography requires extensive and time consuming sample preparation. Solid phase microextraction (SPME) is a simple, fast and solvent-free extraction technique which is an alternative to the conventional extraction method such as liquid-liquid extraction and solid-phase extraction methods. Initial concepts of SPME application was first introduced and published in 1989 by Belardi and Pawliszyn. Rapid development in this technique leads to the first SPME device in 1990, which was commercialised in 1993 by Supelco. Since its introduction, SPME has developed further more because of its many advantages in terms of sample preparation (Kataoka and Saito, 2011). Although a large number of SPME applications have been reported for biomedical analysis (Souza-Silva et al., 2015), it also has great potential in analysing environmental samples (Popiel and Sankowska, 2011; Saraji and Ghani, 2015; Yegemova et al., 2015; Zygmunt et al., 2007) as is the case for HCN analysis. To date, we found only 1 study on analysis of ambient HCN (Smith et al., 2002) as compared to studies for determining cyanide in blood samples (Boadas-Vaello et al., 2008; Calafat and Stanfill, 2002; Frison et al., 2006; Takekawa et al., 1998) using SPME technique.

This paper described the approach of HCN analysis using headspace SPME coupled with GC–MS to determine HCN concentrations in ambient air at a residential area close to a gold mine industry at different distances from 25 January until 21 December 2013. The health risk of exposed community to inhaled HCN was also estimated.

2. Materials and methods

2.1. Sampling site

The study area was a village located in Pahang, one of the districts in Peninsular Malaysia which had a population of approximately 3500 individuals residing in 424 houses. The site map of the sampling area (longitude and latitude) is as in Fig. 1. The economic activities in the studied area consisted of industries ranging from manufacturing bean curd to palm oil industry and gold mining. Gold mining was one of the major economic activities in this village and had operated since 2009, 24 h a day, all year through. The company had been using cyanide since 2009 for extracting gold from tailings using carbon-in-leach (CIL) method. Gold mining activities using CIL method could contaminate the environment and its surrounding area through evaporation of HCN from the tailing ponds. The company had implemented measures to control exposure by using direct reading equipment above the tanks which would trigger an alarm when the HCN level exceeded the action level as well as control measures to prevent seepage of the tailing ponds. However, as the climate in Malaysia can be quite dry and windy at times, potential exposure to contaminated air containing HCN may still occur.

The village in this study was situated very close to the gold mine, whereby the nearest residence was located <100 m from the main entrance of the gold mine. Ambient air samples were collected between 25 January and 21 December 2013. Three sampling points were taken at a distance of 0.1, 1.0 and 2.0 km away from the gold mine. Samples were taken once a month as described in Table 1. On each sampling day; three (3) samples were taken, over a period of 3 h, in the morning (09:00), afternoon (15:00) and evening (21:00) with a total of 108 samples. Sampling was conducted only during non-raining condition.

2.2. Chemicals and supplies

For sampling of ambient HCN, the apparatus used included personal sampling pump, sampling pump calibrator SKC AirCheck 2000, flexible tygon tubing, 37-mm diameter, 1.0 μm pore size PTFE membrane filter (SKC 225-2705), two-piece filter cassette holder (SKC 225-1), 25 mL glass midget bubbler impinger (SKC 225-36-2) and glass trap impinger (SKC 225-22) were made by SKC Inc., USA. The apparatus used for storing collected ambient HCN samples were 20 mL amber bottles (part 5188-6537), 10 mL headspace screw top amber vial (part 5188-6538) and ultra-clean 18 mm screw cap with septa (part 5188-2759) purchased from Agilent Technologies, U.S.

Potassium hydroxide pellets (KOH), 85% phosphoric acid (H_3PO_4), 99% L-ascorbic acid ($C_6H_8O_6$) and potassium cyanide ($K^{13}C^{15}N$) were purchased from R&M Marketing (Essex, U.K.). An amount of 5.6 g KOH was dissolved in deionized water and diluted

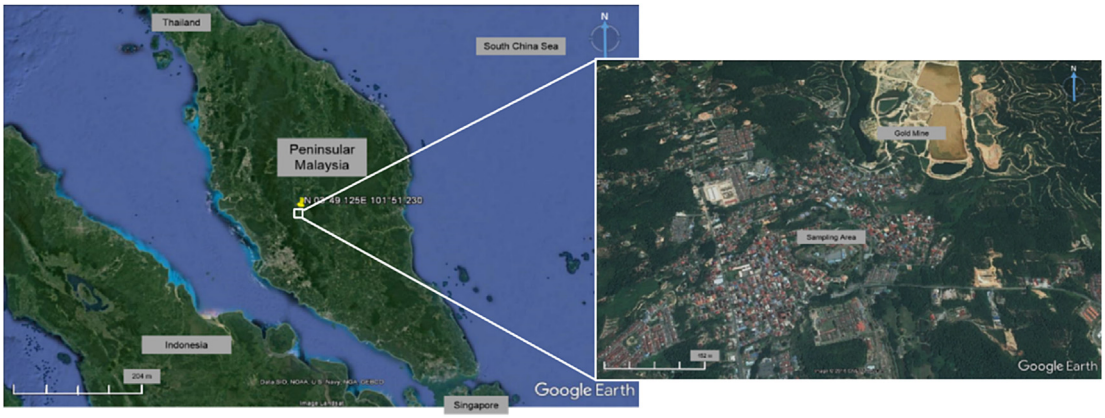

Fig. 1. Site map showing the sampling area in Pahang, Peninsular Malaysia.

Table 1
Sampling dates, distance and geographical coordinates of each sampling site.

Distance	0.1 km	1.0 km	2.0 km
Latitude	N 03°49.125	N 03°49.055′	N 03°48.722′
Longitude	E 101°51.230	E 101°51.125′	E 101°50.811′
1	25th January 2013	21st January 2013	21st January 2013
2	14th February 2013	15th February 2013	16th February 2013
3	25th March 2013	26th March 2013	26th March 2013
4	24th April 2013	23rd April 2013	23rd April 2013
5	17th May 2013	16th May 2013	16th May 2013
6	13th June 2013	13th June 2013	12th June 2013
7	3rd July 2013	3rd July 2013	2nd July 2013
8	20th August 2013	20th August 2013	20th August 2013
9	24th September 2013	23rd September 2013	23rd September 2013
10	21st October 2013	22nd October 2013	22nd October 2013
11	21st November 2013	22nd November 2013	22nd November 2013
12	21st December 2013	22nd December 2013	22nd December 2013

to 1000 mL to obtain 0.1 N of KOH solutions. An amount of 59 mL of phosphoric acid was added to 41 mL of distilled water for a total volume of 100 mL to produce 50% concentration. A weight of 5 g of ascorbic acid was added to 100 mL of distilled water for final solution. Isotopically labelled internal standard, potassium cyanide ($K^{13}C^{15}N$) was weighted for 0.250 g and dissolved in 100 mL of 0.1 N KOH to yield 1000 μg mL^{-1} of $[^{13}C^{15}N]^-$ standard solution. The solution was stable for at least 6 months.

2.3. Sampling procedure

Sampling procedure and preparation was based on National Institute for Occupational Safety and Health Method 7904 (NIOSH, 1994) with modification. The sampling apparatus set-up is as shown in Fig. 2. PTFE membrane filter was taken using a tweezer, placed in a two-piece filter cassette holder and fixed in a cassette holder. The cassette holder was clipped to a tripod during sampling and connected with a flexible tygon tubing to a 25 mL glass midget bubbler impinger containing 15 mL 0.1 N KOH followed by a glass trap impinger containing silica gel. The impingers were connected to a sampling pump with tygon tubing and placed in a cool box full with ice packs where the temperature was maintained at 4 ± 2 °C. Placement of impingers in the cool box was the modification step of

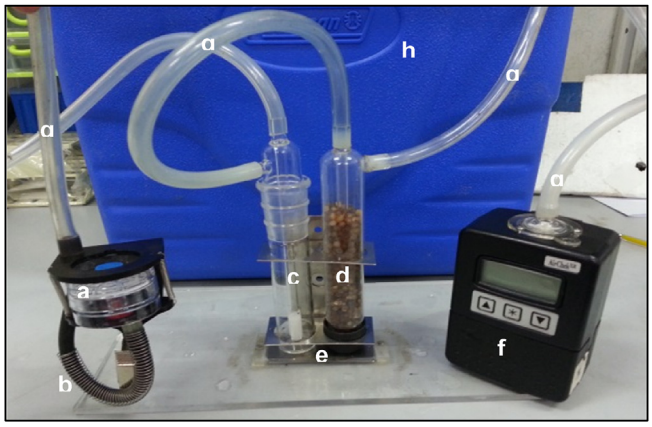

Fig. 2. Sampling apparatus set-up. (a) PTFE membrane filter was placed in the 2-piece filter cassette; (b) Cassette holder was clipped on a tripod; (c) Glass midget bubbler containing 15 mL 0.1 N KOH; (d) Trap impinger containing silica gel; (e) Midget bubbler and trap impinger holder; (f) Personal sampling pump; (g) Flexible tygon tubing to connect membrane filter, glass midget bubbler, trap impinger and sampling pump and (h) Cool box where glass midget bubbler and trap impinger were placed in with ice packs and thermometer for temperature monitoring.

NIOSH 7904 method. It was done to minimize sample loss during sampling. The impingers were fixed to an impinger holder to maintain a vertical position during sampling and the KOH level was ensured not to fall below 10 mL. The sampling pump was calibrated each time before sampling using the SKC AirCheck 2000 pump calibrator. The pre-sample and post-sample flow rates were recorded and ensured that the two rates did not differ more than 5%.

Air samples were drawn through PTFE membrane filter into midget bubbler impinger at a flow rate of 1 L min^{-1} for a total of 180 min with the total sample volume of 180 L. After sampling, the bubbler stem from the midget bubbler impinger was tapped gently against the inside walls of the impinger prior to rinsing with 1–2 mL of unused 0.1 N KOH. The rinse was poured into the bubbler impinger and all contents of the impinger was then transferred to a 20 mL amber vial, screw capped tightly and wrapped with parafilm to avoid sample loss during transit. Samples were transported at 4 ± 2 °C. In the laboratory, they were stored at 4 °C to minimize cyanide losses due to volatilization of HCN and analysed within 14 days of collection.

2.4. Analytical procedure

2.4.1. Sample preparation

Samples were allowed to warm to ambient temperature before analysis. 1 mL of each sample was pipetted into a 10 mL headspace amber vial for analysis. 200 μl of ascorbic acid and phosphoric acid each were added to the sample. The vial was capped, vortexed for ±10 s and placed in vial tray holder, ready to be analysed (Eaton, 2009).

2.4.2. Instrumentation and SPME device

Solid phase-microextraction (SPME) fiber used was carboxen/polydimethylsiloxane (CAR/PDMS) 75 μm thickness purchased from Supelco (Bellefonte, PA, USA) (part 57343-U). Inlet liner used was 0.75 mm ID obtained from Supelco (Bellefonte, PA, USA). A GC SPME liner 0.7 mm (product 5188-6471, Agilent) and GC Long life septa, 11 mm (product 5183-4761, Agilent) were used. The SPME CAR/PDMS fibers were conditioned and thermally cleaned in the injection port of GC equipment prior to use. The conditioning temperature and time for CAR/PDMS fiber followed the manufacturer's conditioning guidelines for SPME fiber coatings. Appropriate inlet liner designed for SPME use, with narrow I.D 0.75 mm was used in the injection port of the GC. Care was taken to ensure that the SPME fiber was not inserted into a liner containing glass wool as that could damage the SPME fiber coating. Before conditioning, the column was installed into GC and carrier gas was adjusted to the

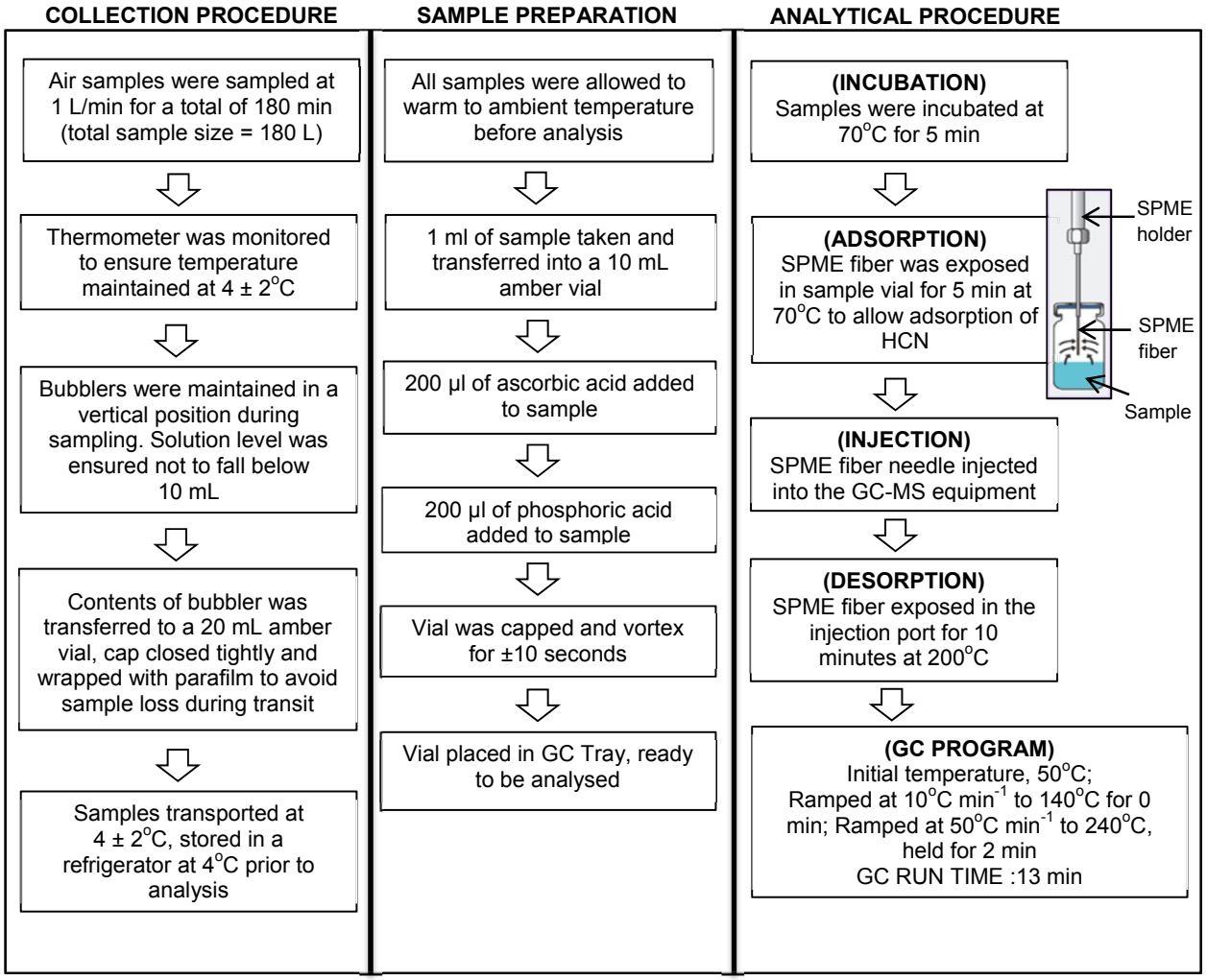

Fig. 3. Sample collection procedure, sample preparation steps and analytical procedure.

desired flow rate. Splitter vent was opened to reduce amount of impurities entering the column and oven temperature was ramped after fiber conditioning to remove any contaminants that may have entered the column. Whenever the fiber was contaminated after repeated use, the same cleaning steps were repeated, as necessary.

The analysis was conducted using Gas Chromatography (Agilent Technologies, Wilmington, DE, USA) Model 7890A equipped with 5975 MSD and CTC PAL auto sampler. The autosampler, mounted on top of the GC system, included a vial tray holder; a sample heater block and one movable head housed with one syringe holder. The movable head was programmed using 7890A ChemStation software to perform motions in *x*, *y* and *z* axes and to actuate the syringe plungers. It was used to transfer sample vials from the vial tray holder to heater block for the incubation process and to inject sample vapour into GC inlet. The separation was accomplished on an Agilent GS-GASPRO (30 m length, 0.32 mm ID, 0.25 µm film thickness) capillary column (part 113-4332) made by Agilent Technologies U.K. Capillary column was heated at 280 °C for 30 min prior to use and CTC auto sampler was used to move the 10 mL sample vial from the vial tray holder to the sampler heater, where the vial was heated at 70 °C for 5 min.

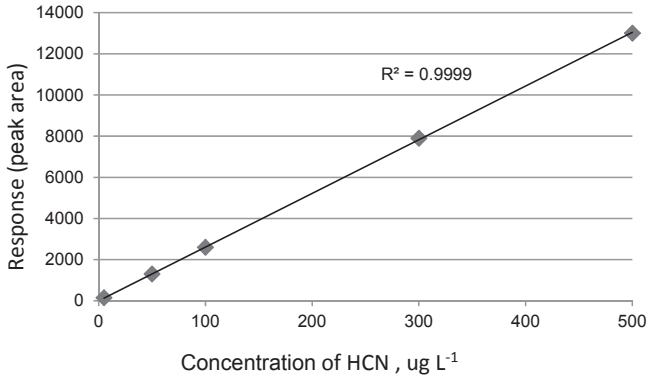

Fig. 4. Calibration curve of HCN at range of concentration from 5 to 500 µg L^{-1}.

SPME fiber was then exposed to the sample headspace for 5 min for extraction of cyanide compound from the sample prior to injection. Injections were made in splitless mode. The injector was held at 200 °C and at a pressure of 5.7 psi. Helium carrier gas (99% purity) flow to the column was set to 2.3 mL min^{-1} with the total gas flow of 14.54 mL min^{-1} and 10 mL min^{-1} purge flow with split vent at 0.5 min. The MS source and MS quadropole temperature was 230 °C and 150 °C, respectively. The initial column temperature was set at 50 °C then ramped at 10 °C min^{-1} to 140 °C for 0 min then 50 °C min^{-1} to 240 °C and held for 2 min with a total run time

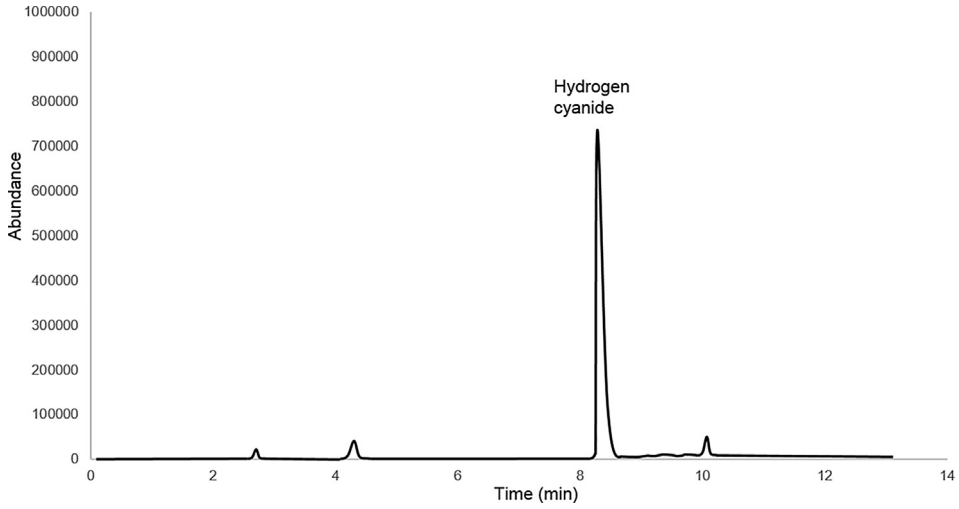

Fig. 5. The chromatogram and retention time of HCN.

of 13 min. Fig. 3 showed the flow of collection procedure, sample preparation steps and analytical procedure.

2.4.3. Data analysis

All of the samples, blanks, standards and QC samples were processed in the same manner. Data were manually integrated when necessary where the HCN response factor was used for quantification. Calibration samples were prepared by spiking 0.1 N KOH with appropriate amounts of $^{13}C^{15}N$ as internal standard. Calibration curve was constructed by plotting the response factor (peak area ratio) versus standard concentration which encompassed the entire linear range of the method at concentrations of 5, 50, 100, 300 and 500 μg L^{-1} as shown in Fig. 4. Within-day precision was calculated as the percentage of relative standard deviation at 200 ppb repeated for five replicates at each concentrations (intra-day precision, n = 5). The accuracy was evaluated by calculating the percent recovery of 200 μg L^{-1} spiked concentration repeated every 30 samples (accepted value of ±20%). The equipment limit of detection (LOD) which was the lowest amount of analyte that can be detected was determined by the 3 times standard deviation of seven replicates blank samples (σ_{blank}) spiked at 5 μg L^{-1} concentration. Limit of quantification was calculated by 10 times the σ_{blank}. Data were automatically processed using the quantitation Chemstation software of the 7890A for the analysis.

Chromatographic conditions were optimized to get a baseline separation of the target analyte of HCN. Selected Ion Monitoring (SIM) was used where ion 29 was selected as the internal standard, ion 27 as the target compound quantitation and ion 26 as the target compound confirmation, based on Method 355.01 by Eaton (2009). Confirmation of HCN analyte was done using full scan mode prior to SIM mode where the analyte retention time for HCN was at 8.680 min as the chromatogram shown in Fig. 5. In order to confirm that no components had interfered with the target analyte, a matrix sample (0.1 N KOH), a procedural blank (0.1 N KOH + internal standard), a blank (ultra-pure water + internal standard) and an empty vial (used for analysis) were also analysed. The chromatogram showed no HCN peak identified for the matrix sample and empty vial. This confirmed that there were no interferences, which occurred with the target analyte determination throughout analysis. A small peak with retention time of HCN was found for both the procedural blank (0.1 N KOH + internal standard) and blank (ultra-pure water + internal standard). The chromatogram peak of HCN for ultra-pure water was slightly higher than the peak of 0.1 N KOH spiked with same amount of internal standard. The background HCN concentration was too small and should not significantly interfere with HCN quantification in the samples.

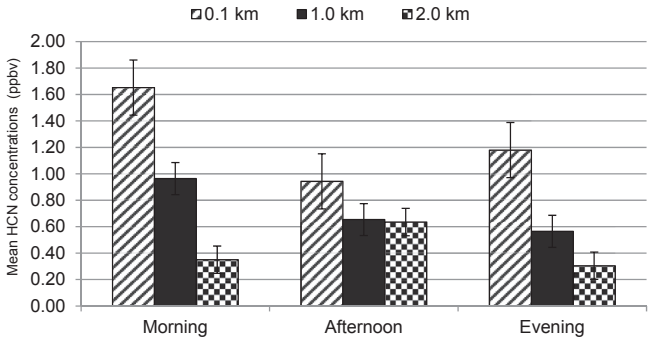

Fig. 6. Mean concentrations of HCN (ppbv) in a year measured at different times at distance of 0.1 km, 1.0 km and 2.0 km from the gold mine.

The cyanide concentrations in the air were reported as parts per billion (ppbv) HCN. Equation (1) was used to calculate the HCN concentration in μg m^{-3} which was later converted to ppbv using conversion factor for HCN in air; 1 ppb = 1.10 μg m^{-3} (ACGIH, 1996). From the sampling method, the B value was 15 mL of 0.1 N KOH solution used and the total air sampled for each sampling, C value was 180 L (0.18 m^3).

$$\text{HCN concentration, } \mu\text{gm}^{-3} = \frac{A\ (\mu g\ mL^{-1}) \times B(mL)}{C(m^3)} \quad (1)$$

where:

A = Concentration of HCN from GC–MS results, μg mL^{-1}
B = Volume of 0.1 N KOH solution used during sampling, mL
C = Total of air volume sampled, m^3

Table 2
Concentrations of HCN (ppbv) measured at different distances.

Distance	N	Min	Max	Mean	SD	Median
0.1 km	36	0.21	8.56	0.56	1.96	0.44
1.0 km	36	0.16	4.62	0.29	1.31	0.25
2.0 km	36	0.26	2.22	0.27	0.51	0.29

N, number; Min, minimum; Max, maximum; SD, standard deviation.

Table 3
Comparison between the concentrations of hydrogen cyanide (HCN) in air recorded in this study and several other studies.

Source and references	Measurement site	Sampling/Analysis method	HCN concentration range
This study	Residential area (100–2000 m from gold mine)	NIOSH Method 7904/SPME with GC–MS	0.16–8.56 ppbv (detected in 76 of 108 samples)
Apel et al. (2015)	Biomass burning from High Park fire, Colorado	Trace organic gas analyser/GC–MS	0.2 ppbv
Le Breton et al. (2013)	Biomass burning events in the troposphere in Canada	Chemical ionization mass spectrometer	1.09 ± 0.85 ppbv
Magnusson et al. (2012)	Inside a car (attempted hydrogen cyanide poisoning)	FTIR spectroscopy gas analyser and colorimetric gas detection tubes/GC–MS	14–20 ppm
Ambrose et al. (2012)	Ambient atmosphere (University of New Hampshire)	PFA Teflon-lined/Gas chromatographic-flame thermionic detector (GC-FTD)	0.15–1.0 ppbv
Crounse et al. (2009)	Biomass burning event in the atmosphere above Mexico City	Nylon wool coated with $NaHCO_3$ filter/Chemical Ionization Mass Spectrometry (CIMS)	0.30–0.53 ppbv
Knighton et al. (2009)	Ambient atmosphere (technical park)	PFA Teflon tubing/Proton Transfer Reaction Mass Spectrometry (PTR-MS)	0.2 ppbv
Orloff et al. (2006)	Residential area (335–460 m from gold mine)	NIOSH Method 7904/visible spectrophotometry	0.26–1.86 ppb (detected in 6 of 18 samples)
Okafor and Maduagwu (2000)	Near large scale cassava processing facilities, Nigeria	Colorimetric determination	18–42 ppm

2.5. Non-parametric statistical analysis

Statistical analysis for the HCN measurement was performed using SPSS version 20. Normality test was conducted and observed from frequency distribution (histogram) and Shapiro-Wilk test. Kruskal Wallis test was used to determine differences between the concentration of HCN with distance, months and sampling times. Mann–Whitney *U* Test was used to compare differences between two groups of independent variables. All statistical tests were carried out at 95% confidence interval. A p-value of <0.05 was considered significant.

2.6. Exposure and risk assessment

Theoretically, potential routes of exposure to cyanide and HCN among the residents in this study were via inhalation of air, incidental ingestion and dermal contact with contaminated soil, ground water and surface water. However, through observation in this study, the possible primary exposure route for HCN among the residents was through inhalation. This was because, the surface water flowing through the sampling area was quite shallow and not used as drinking water, recreational, gardening or fishing activities. Therefore, these routes of exposure were not considered in this study. The estimation of Average Daily Dose (ADD) from inhalation of HCN was estimated based on the exposure point concentration and in this study, the geometric mean concentrations were used as the concentrations changed over time (chronic exposure). The ADD of HCN was calculated by the following equation:

$$\mathrm{ADD} = \frac{\mathrm{C} \times \mathrm{ET} \times \mathrm{EF} \times \mathrm{ED}}{\mathrm{AT}} \quad (2)$$

where:

ADD = average daily dose (mg m^{-3} or ppbv)
C = concentrations of HCN in ambient air (mg m^{-3} or ppbv)
ET = resident air exposure time for whole day, 24 h day^{-1} (USEPA, 2014)
EF = resident exposure frequency, 350 days $year^{-1}$ (USEPA, 1991)
ED = resident exposure duration, 26 years (USEPA, 2011)
AT = average time for residents, ED × 365 days $year^{-1}$ × 24 h day^{-1} (USEPA, 1989)

$$\mathrm{HQ} = \frac{\mathrm{ADD}}{\mathrm{RfC}} \quad (3)$$

As HCN is not classified as a carcinogen, the potential health risk was calculated only for non-cancer human health risks using Hazard Quotient (HQ) as in Equation (3). HQ is the ratio of the calculated average daily dose (ADD) of the chemicals to the reference concentration (RfC): 0.0008 mg m^{-3} or 0.72 ppbv (USEPA, 2010) where the conversion factor for HCN in air was 1 ppm = 1.10 mg m^{-3} (ACGIH, 1996). If the calculated HQ exceeds one (>1), it is interpreted as evidence of potential non-carcinogenic effects; by contrast, a HQ of less than one (<1) indicates a negligible risk of adverse health effects.

3. Results and discussion

3.1. Establishment of HCN analysis

The calibration curve was constructed with 5 concentrations of potassium cyanide standard in the range of 5–500 μg L^{-1} in addition of a blank sample (0 μg L^{-1}). The data showed good linearity, $r^2 = 0.999$. Quality control (QC) samples showed an average accuracy of 94.5% at 200 μg L^{-1} concentration (n = 8) where the recoveries ranged between 84 and 119%. The LOD and LOQ were obtained from standard deviation (σ) of seven blank samples and the calculated $3\sigma_{blank}$ LOD was 3 μg L^{-1} and the $10\sigma_{blank}$ LOQ was 10 μg L^{-1}, corresponding to HCN air concentration of 0.20 ppbv and 0.77 ppbv, respectively. The precision calculated was 5.3–11.5% relative standard deviation (RSD). The performance of the CAR/PDMS fiber fell below the desired recovery range after more than 100 injections. The CAR/PDMS fiber showed an average (n = 7) of 111 ± 31 injections with recovery within 80–120%. The average time consumed for sample preparation of each samples prior to analysis was about 1 min. The sample preparation was very simple, straightforward, uncomplicated and fast where training the untrained staff was undemanding.

3.2. Hydrogen cyanide in ambient air

Fig. 6 showed the mean concentrations of HCN sampled for a year. HCN was detected in 25 out of 36 morning samples (ranging from 0.24 to 6.49 ppbv), 26 out of 36 afternoon samples (ranging from 0.16 to 4.96 ppbv) and 23 out of 36 evening samples (ranging from 0.23 to 8.56 ppbv). Out of the 108 samples, 32% were below

the detection of limit (<LOD) value, 40% were below the RfC value of 0.72 ppbv (8×10^{-4} mg m^{-3}) set by the Unites States Environmental Protection Agency, 2010 and 28% exceeded the RfC value. Fig. 6 showed a similar trend of HCN concentrations where the level was highest at 0.1 km measured in the morning, afternoon and evening. It also showed that HCN was higher in the morning compared to afternoon and evening.

Table 2 showed the mean concentrations of HCN in a year at different distances. Highest mean concentration of HCN was at sampling site 0.1 km away from the gold mine (0.56 ± 1.96 ppbv), followed by 1.0 km away (0.29 ± 1.31 ppbv) and 2.0 km away (0.27 ± 0.51 ppbv). The highest concentration of HCN was detected at 0.1 km sampling point (8.56 ppbv) and the lowest was measured at 1.0 km away from the gold mine (0.16 ppbv). The various concentrations of HCN at different times showed that the level might have been influenced by other surrounding activities as well. In the morning, the nearby road at the main gate of the mine (0.1 km sampling point) was noted to be busy with vehicles entering and passing by that might also have contributed to the HCN concentrations measured.

Mann–Whitney *U* Test was used to compare the differences of HCN concentration between the three distances (0.1, 1.0 & 2.0 km). The results showed that there was a statistically significant difference in the median of HCN concentration between distances. The distributions in the groups differed significantly (Mann–Whitney $U = 457.500$, $n_1 = n_2 = 36$, $z = -2.169$, $p < 0.05$ two-tailed) where the mean rank of 0.1 km and 1.0 km were 41.79 and 31.21, respectively. Comparing the distance at 0.1 km and 2.0 km, the results were significant (Mann–Whitney $U = 444.500$, $n_1 = n_2 = 36$, $z = -2.313$, $p < 0.05$ two-tailed) with the mean rank of 0.1 km and 2.0 km were 42.15 and 30.85, respectively. There were no statistical difference concentrations of HCN at 1.0 km and 2.0 km distance. The HCN concentration was significantly higher at 0.1 km as compared to HCN measured at 1.0 km and 2.0 km.

To determine the association between HCN concentrations at different distances (0.1 km, 1.0 km & 2.0 km) with sampling time (morning, afternoon and evening) and months sampled (January–December), Kruskal Wallis test was performed as the HCN concentrations were not normally distributed. There were significant difference between the medians of HCN concentration for distance ($X^2_{(2)} = 6.788$, p = 0.034) and months ($X^2_{(2)} = 35.244$, p = <0.001). However there was no difference among sampling time on the HCN concentration.

3.3. Comparison with other studies

Table 3 shows the comparison between HCN concentrations recorded in this study with several other studies that measured ambient HCN concentrations. There were not many studies found which measured ambient HCN concentrations close to gold mining area in the literature. Quite a similar study to our study was conducted by Orloff et al. (2006), whereby they also measured HCN concentrations at a residential area, 335–460 m away from the centre of a gold mine. Sampling method for HCN collection from the air used by Orloff et al. was similar with this study. However, it differed in the analysis of HCN as Orloff et al. used visible spectrophotometry (NIOSH Method 6010) and air modelling was used to predict the concentrations. The range of HCN in the study by Orloff et al. (0.26–1.86 ppbv), were within the range of our study and they detected HCN in 6 out of their 18 samples. Ambrose et al. (2012) and Knighton et al. (2009) measured ambient HCN in the atmosphere using gas chromatographic-flame thermionic detector (GC-FTD) and proton transfer reaction-mass spectrometry (PTR-MS) method, respectively where the HCN concentrations ranged between 0.15 and 1.0 ppbv. Some studies measured HCN concentrations during biomass burning events (Apel et al., 2015; Crounse et al., 2009; Le Breton et al., 2013). The HCN concentrations were reported to be between 0.2 and 1.09 ppbv. Okafor and Maduagwu (2000) and Magnusson et al. (2012) reported very high HCN concentrations using colorimetric determination in their studies from 14 to 42 ppm. Comparison from different studies showed that HCN concentration in the air varied depending on nature of activities in the local environment, method of sampling as well as analytical method used.

3.4. Risk assessment

In this study, potential non cancer risk assessments were calculated to evaluate the human health risk of HCN exposure via inhalation at the sampling sites. The Average Daily Dose (ADD) of HCN in the studied community at different distances was calculated using Equation (3). The mean value of ADD in the sampling area was highest at 0.1 km (0.53 ppbv), followed by 1.0 km (0.27 ppbv) and lowest at 2.0 km (0.25 ppbv). The values of HQs associated with inhalation of HCN for the community were then calculated using Equation (3). The calculated HQ values were in the range of 0.35–0.74. Therefore, it would be safe to conclude that the non-carcinogenic risk of HCN exposure through inhalation may be negligible because the calculated HQ values were all less than 1. However, there were limitations and uncertainties in the health risk assessment of HCN in our study in which, the potential non cancer risk assessments did not include all possible exposure pathways that may have occurred, possibly causing some underestimation of risk. We only estimated the risk from intake of exposure through inhalation.

4. Conclusions

In this study, the analytical method used for quantifying ambient HCN by SPME-GCMS method was found to be simple and less time consuming. This method appears promising for monitoring ambient HCN concentrations, studying long term HCN inhalation exposure and its chronic health effects as it could detect low levels of HCN in the air (even below the RfC level). Minimizing the sample preparation step was effective, not only in reducing sources of error but also in reducing time and cost. Although approximately more than a quarter of the samples recorded HCN concentrations above the RfC value, the potential non cancer risk assessment for HCN from air inhalation was negligible, suggesting no or minimal health risks to the local community.

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References

ACGIH (American Conference of Governmental Industrial Hygienists), 1996. Documentation of the Threshold Limit Values and Biological Exposure Indices: Hydrogen Cyanide, seventh ed. ACGIH, Cincinnati, OH.

Ambrose, J.L., Zhou, Y., Haase, K., Mayne, H.R., Talbot, R., Sive, B.C., 2012. A gas chromatographic instrument for measurement of hydrogen cyanide in the lower atmosphere. Atmos. Meas. Tech. 5, 1229–1240. http://dx.doi.org/10.5194/amt-5-1229-2012.

Apel, E.C., Hornbrook, R.S., Hills, A.J., Blake, N.J., Barth, M.C., Weinheimer, A., Cantrell, C., Rutledge, S.A., Basarab, B., Crawford, J., et al., 2015. Upper tropospheric ozone production from lightning NO_x-impacted convection: smoke

ingestion case study from the DC3 campaign. J. Geophys. Res. Atmos. 120, 2505–2523. http://dx.doi.org/10.1002/2014JD022121.
ATSDR (Agency for Toxic Substances and Disease Registry), 2006. Toxicological Profile for Cyanide. Public Health Service, U.S. Department of Health and Human Services, Atlanta, GA. http://www.atsdr.cdc.gov/toxprofiles/tp8.pdf.
Belardi, R.P., Pawliszyn, J.B., 1989. The application of chemically modified fused silica fibers in the extraction of organics from water matrix samples and their rapid transfer to capillary columns. Water Pollut. Res. J. Can. 24 (1), 179–191.
Boadas-Vaello, P., Jover, E., Llorens, J., Bayona, J.M., 2008. Determination of cyanide and volatile alkylnitriles in whole blood by headspace solid-phase microextraction and gas chromatography with nitrogen phosphorus detection. J. Chromatogr. B – Anal. Technol. Biomed. Life Sci. 870, 17–21. http://dx.doi.org/10.1016/j.jchromb.2008.05.031.
Calafat, A.M., Stanfill, S.B., 2002. Rapid quantitation of cyanide in whole blood by automated headspace gas chromatography. J. Chromatogr. B – Anal. Technol. Biomed. Life Sci. 772, 131–137. http://dx.doi.org/10.1016/S1570-0232(02)00067-3.
Crounse, J.D., DeCarlo, P.F., Blake, D.R., Emmons, L.K., Campos, T.L., Apel, E.C., Clarke, A.D., Weinheimer, A.J., McCabe, D.C., Yokelson, R.J., Jimenez, J.L., Wenberg, P.O., 2009. Biomass burning and urban air pollution over the Central Mexican Plateu. Atmos. Chem. Phys. 9, 4929–4944.
Cyanides, aerosol and gas. Method 7904, Issue 2, NIOSH Manual of Analytical Methods (NMAM), Fourth Edition, 15 August 1994.
Desharnais, B., Huppé, G., Lamarche, M., Mireault, P., Skinner, C.D., 2012. Cyanide quantification in post-mortem biological matrices by headspace GC–MS. Forensic Sci. Int. 222, 346–351. http://dx.doi.org/10.1016/j.forsciint.2012.06.017.
Eaton, J., 2009. Determination of Cyanide in Drinking Water by GC/MS Headspace. Method 355.01. Augusta, Maine.
Ferrari, L.A., Giannuzzi, L., 2015. Assessment of carboxyhemoglobin, hydrogen cyanide and methemoglobin in fire victims: a novel approach. Forensic Sci. Int. 256, 46–52. http://dx.doi.org/10.1016/j.forsciint.2015.08.010.
Frison, G., Zancanaro, F., Favretto, D., Ferrara, S.D., 2006. An improved method for cyanide determination in blood using solid-phase microextraction and gas chromatography/mass spectrometry. Rapid Commun. Mass Spectrom. 20, 2932–2938. http://dx.doi.org/10.1002/rcm.2689.
Greenawald, L.A., Snyder, J.L., Fry, N.L., Sailor, M.J., Boss, G.R., Finklea, H.O., Bell, S., 2015. Development of a cobinamide-based end-of-service-life indicator for detection of hydrogen cyanide gas. Sens. Actuators. B. Chem. 221, 379–385. http://dx.doi.org/10.1016/j.snb.2015.06.085.
Isaad, J., El Achari, A., Malek, F., 2013. Bio-polymer starch thin film sensors for low concentration detection of cyanide anions in water. Dyes Pigments 97, 134–140. http://dx.doi.org/10.1016/j.dyepig.2012.12.010.
Kage, S., Nagata, T., Kudo, K., 1996. Determination of cyanide and thiocyanate in blood by gas chromatography and gas chromatography–mass spectrometry. J. Chromatogr. B – Biomed. Appl. 675, 27–32. http://dx.doi.org/10.1016/0378-4347(95)00344-4.
Kang, H.I., Shin, H.S., 2014. Ultra-sensitive determination of cyanide in surface water by gas chromatography-tandem mass spectrometry after derivatization with 2-(dimethylamino)ethanethiol. Anal. Chim. Acta 852, 168–173. http://dx.doi.org/10.1016/j.aca.2014.09.036.
Kataoka, H., Saito, K., 2011. Recent advances in SPME techniques in biomedical analysis. J. Pharm. Biomed. Anal. http://dx.doi.org/10.1016/j.jpba.2010.12.010.
Knighton, W.B., Fortner, E.C., Midey, A.J., Viggiano, A.A., Herndon, S.C., Wood, E.C., Kolb, C.E., 2009. HCN detection with a proton transfer mass spectrometer. Int. J. Mass Spectrom. 283, 112–121. http://dx.doi.org/10.1016/j.jms.2009.02.013.
Lauridsen, R.K., Rindzevicius, T., Molin, S., Johansen, H.K., Berg, R.W., Alstrm, T.S., Almdal, K., Larsen, F., Schmidt, M.S., Boisen, A., 2015. Towards quantitative SERS detection of hydrogen cyanide at ppb level for human breath analysis. Sens. Bio-Sens. 5, 84–89.
Le Breton, M., Bacak, A., Muller, J.B.A., O'Shea, S.J., Xiao, P., Ashfold, M.N.R., Cooke, M.C., Batt, R., Shallcross, D.E., Oram, D.E., Forster, G., Bauguitte, S.J.B., Percival, C.J., 2013. Airborne hydrogen cyanide measurements using a chemical ionisation mass spectrometer for the plume identification of biomass burning forest fires. Atmos. Chem. Phys. 13, 9217–9232. http://dx.doi.org/10.5194/acp-13-9217-2013.
Lindsay, A.E., Greenbaum, A.R., O'Hare, D., 2004. Analytical techniques for cyanide in blood and published blood cyanide concentrations from healthy subjects and fire victims. Anal. Chim. Acta 511, 185–195. http://dx.doi.org/10.1016/j.aca.2004.02.006.
Liu, G., Liu, J., Hara, K., Wang, Y., Yu, Y., Gao, L., Li, L., 2009. Rapid determination of cyanide in human plasma and urine by gas chromatography–mass spectrometry with two-step derivatization. J. Chromatogr. B – Anal. Technol. Biomed. Life Sci. 877, 3054–3058. http://dx.doi.org/10.1016/j.jchromb.2009.07.029.
Logue, B.A., Kirschten, N.P., Petrikovics, I., Moser, M.A., Rockwood, G.A., Baskin, S.I., 2005. Determination of the cyanide metabolite 2-aminothiazoline-4-carboxylic acid in urine and plasma by gas chromatography–mass spectrometry. J. Chromatogr. B – Anal. Technol. Biomed. Life Sci. 819, 237–244. http://dx.doi.org/10.1016/j.jchromb.2005.01.045.
Magnusson, R., Nyholm, S., Åstot, C., 2012. Analysis of hydrogen cyanide in air in a case of attempted cyanide poisoning. Forensic Sci. Int. 222 http://dx.doi.org/10.1016/j.forsciint.2012.05.014.
Minakata, K., Nozawa, H., Gonmori, K., Suzuki, M., Suzuki, O., 2009. Determination of cyanide, in urine and gastric content, by electrospray ionization tandem mass spectrometry after direct flow injection of dicyanogold. Anal. Chim. Acta 651, 81–84. http://dx.doi.org/10.1016/j.aca.2009.08.001.
Musshoff, F., Kirschbaum, K.M., Madea, B., 2011. An uncommon case of a suicide with inhalation of hydrogen cyanide. Forensic Sci. Int. 204 http://dx.doi.org/10.1016/j.forsciint.2010.05.012.
Orloff, K.G., Kaplan, B., Kowalski, P., 2006. Hydrogen cyanide in ambient air near a gold heap leach field: measured vs. modeled concentrations. Atmos. Environ. 40, 3022–3029. http://dx.doi.org/10.1016/j.atmosenv.2005.09.089.
Okafor, P.N., Maduagwu, E.N., 2000. Cyanide contamination of atmospheric air during large scale "gari" processing and the toxicity effects of such cyanide equivalent on rat. Afr. J. Biomed. Res. 3–9.
Paul, B.D., Smith, M.L., 2006. Cyanide and thiocyanate in human saliva by gas chromatography–mass spectrometry. J. Anal. Toxicol. 30, 511–515.
Popiel, S., Sankowska, M., 2011. Determination of chemical warfare agents and related compounds in environmental samples by solid-phase microextraction with gas chromatography. J. Chromatogr. A. http://dx.doi.org/10.1016/j.chroma.2011.09.066.
Pre, J., Vassy, R., 1991. Urine thiocyanate: creatinine ratio as a reliable indicator of cigarette smoking, 204, 87–94.
Pritchard, J.D., 2007. Hydrogen cyanide: toxicological overview. Heal. Prot. Agency 2, 11.
Rosentreter, J.J., Timofeyenko, Y.G., Moreno, M., 2015. Safe routine cyanide detection methodology for aqueous solutions of varied pH. Microchem. J. 119, 17–21. http://dx.doi.org/10.1016/j.microc.2014.10.005.
Saraji, M., Ghani, M., 2015. Hollow fiber liquid-liquid-liquid microextraction followed by solid-phase microextraction and in situ derivatization for the determination of chlorophenols by gas chromatography-electron capture detection. J. Chromatogr. A 1418, 45–53. http://dx.doi.org/10.1016/j.chroma.2015.09.062.
Simeonova F., Fishbein L., 2004. Concise International Chemical Assessment Document 61 hydrogen cyanide and cyanides : Human health aspects. Proc. 6.
Smith, P.A., Sheely, M.V., Kluchinsky, T.A., 2002. Solid phase microextraction with analysis by gas chromatography to determine short term hydrogen cyanide concentrations in a field setting. J. Sep. Sci. 2002 (25), 917–921. http://dx.doi.org/10.1002/1615-9314(20021001)25.
Souza-Silva, É.A., Reyes-Garcés, N., Gómez-Ríos, G.A., Boyaci, E., Bojko, B., Pawliszyn, J., 2015. A critical review of the state of the art of solid-phase microextraction of complex matrices III. Bioanalytical and clinical applications. TrAC – Trends Anal. Chem. http://dx.doi.org/10.1016/j.trac.2015.04.017.
Takekawa, K., Oya, M., Kido, A., Suzuki, O., 1998. Analysis of cyanide in blood by headspace solid-phase microextraction (SPME) and capillary gas chromatography. Chromatographia 47, 209–214. http://dx.doi.org/10.1007/BF02466583.
U.S. EPA, 1989. Risk Assessment Guidance for Superfund. In: Human health evaluation manual (Part A). Interim Final, vol. I. U.S. Environmental Protection Agency, Washington, DC. EPA/540/1-89/002.
U.S. EPA, 1991. Risk Assessment Guidance for Superfund. In: Human health evaluation Manual (Part B), vol. I. U.S. Environmental Protection Agency, Washington, DC. EPA/540/R-92/003.
U.S. EPA, 2010. IRIS Toxicological Review of Hydrogen Cyanide and Cyanide Salts (2010 Final). U.S. Environmental Protection Agency, Washington, DC. EPA/635/R-08/016F.
U.S. EPA, 2011. Exposure Factors Handbook 2011 Edition (Final). U.S. Environmental Protection Agency, Washington, DC. EPA/600/R-09/052F.
U.S. EPA, 2014. Human Health Evaluation Manual, Supplemental Guidance: Update of Standard Default Exposure Factors. U.S. Environmental Protection Agency, Washington, DC. OSWER Directive 9200.1–120.
Yegemova, S., Bakaikina, N., Kenessov, B., Koziel, J., Nauryzbayev, M., 2015. Determination of 1-methyl-1H-1,2,4-triazole in soils contaminated by rocket fuel using solid-phase microextraction, isotope dilution and gas chromatography–mass spectrometry. Talanta 143, 226–233. http://dx.doi.org/10.1016/j.talanta.2015.05.045.
Youso, S.L., Rockwood, G.A., Lee, J.P., Logue, B.A., 2010. Determination of cyanide exposure by gas chromatography–mass spectrometry analysis of cyanide-exposed plasma proteins. Anal. Chim. Acta 677, 24–28. http://dx.doi.org/10.1016/j.aca.2010.01.028.
Zhang, Q., Maddukuri, N., Gong, M., 2015. A direct and rapid method to determine cyanide in urine by capillary electrophoresis. J. Chromatogr. A. http://dx.doi.org/10.1016/j.chroma.2015.08.050.
Zygmunt, B., Zaborowska, A., Swiat Owska, J., Namiesnik, J., 2007. Solid phase microextraction combined with gas chromatography – a powerful tool for the determination of chemical warfare agents and related compounds. Curr. Org. Chem. 11, 241–253. http://dx.doi.org/10.2174/138527207779940847.