

Central Lancashire Online Knowledge (CLoK)

Title	Quantification of Hydrogen Cyanide in Fire Effluent
Type	Article
URL	https://clock.uclan.ac.uk/48151/
DOI	##doi##
Date	2023
Citation	Hansen-Bruhn, Iben, Mckenna, Sean Thomas and Hull, T Richard orcid iconORCID: 0000-0002-7970-4208 (2023) Quantification of Hydrogen Cyanide in Fire Effluent. Journal of Fire Science . ISSN 0734-9041
Creators	Hansen-Bruhn, Iben, Mckenna, Sean Thomas and Hull, T Richard

It is advisable to refer to the publisher's version if you intend to cite from the work. ##doi##

For information about Research at UCLan please go to <http://www.uclan.ac.uk/research/>

All outputs in CLoK are protected by Intellectual Property Rights law, including Copyright law. Copyright, IPR and Moral Rights for the works on this site are retained by the individual authors and/or other copyright owners. Terms and conditions for use of this material are defined in the <http://clock.uclan.ac.uk/policies/>

Quantification of hydrogen cyanide in fire effluent

Journal of Fire Sciences

1–14

© The Author(s) 2023




Article reuse guidelines:

sagepub.com/journals-permissions

DOI: 10.1177/07349041231193756

journals.sagepub.com/home/jfs

Iben Hansen-Bruhn^{1,2}, Sean T McKenna¹ and
T Richard Hull¹ 

Date received: 30 May 2023; accepted: 25 July 2023

Abstract

Hydrogen cyanide is often the most toxicologically significant component in fire effluents from nitrogen-containing materials. Unlike the other major asphyxiant, carbon monoxide, sensors for continuous hydrogen cyanide quantification, at and above dangerous concentrations, are not commercially available. This article investigates the analysis of fire effluent captured in bubbler solutions, by colorimetric quantification of hydrogen cyanide using chloramine-T/isonicotinic acid. The bubbler samples were mixed with colorimetric reagents to give a blue dye in response to cyanide ions. A novel reaction scheme accounting for the formation of the blue dye from cyanide ions is presented. Dilute, standard cyanide solutions were found to be stable after storage for up to 1 year. Alkaline bubbler solutions, through which the fire effluent has passed, showed consistent cyanide concentrations, for samples stored between 5°C and 21°C, for up to 31 days after sampling. The effect of other common ions likely to be present in fire effluent solution samples (CO_3^{2-} , SO_3^{2-} , SO_4^{2-} , NO_2^- and NO_3^-) was investigated for their potential interference. The most significant interference was sulphite which reduced the apparent cyanide concentration by 13% at 10 mg L⁻¹ SO_3^{2-} concentration.

Keywords

Hydrogen cyanide, HCN, analysis, toxicity, hazard, fire chemistry

Introduction

Exposure to combustion products from fires in modern residential structures results in multiple hazards. Besides heat and visual obscuration by smoke, the toxic effect of fire smoke

¹Centre for Fire and Hazards Sciences, University of Central Lancashire, Preston, UK

²Plastic and Polymer Engineering, Department of Biological and Chemical Engineering, Aarhus University, Aarhus, Denmark

Corresponding author:

T Richard Hull, Centre for Fire and Hazards Sciences, University of Central Lancashire, Preston PR1 2HE, UK.

Email: trhull@uclan.ac.uk

leads to incapacitation, due to respiratory tract and eye irritation, followed by asphyxiation as the major cause of death and injury.^{1–4} The main asphyxiants in fire effluent are carbon monoxide (CO) and hydrogen cyanide (HCN). CO binds to the active site in haemoglobin preventing oxygen transport by red blood cells. HCN stops the body's cells from utilising oxygen, by binding to the trivalent iron atom of cytochrome oxidase, the reducing component of mitochondrial electron transport, resulting in histotoxic hypoxia.^{5,6} The resulting oxygen deprivation stimulates respiration leading to hyperventilation, increasing the uptake of HCN. This leads to rapid incapacitation.^{7–10} This pattern of incapacitation, leading to loss of consciousness, followed by further toxic gas inhalation, is the normal sequence of events leading to fire fatalities. It is, therefore, very important to predict HCN emissions from unwanted fires.

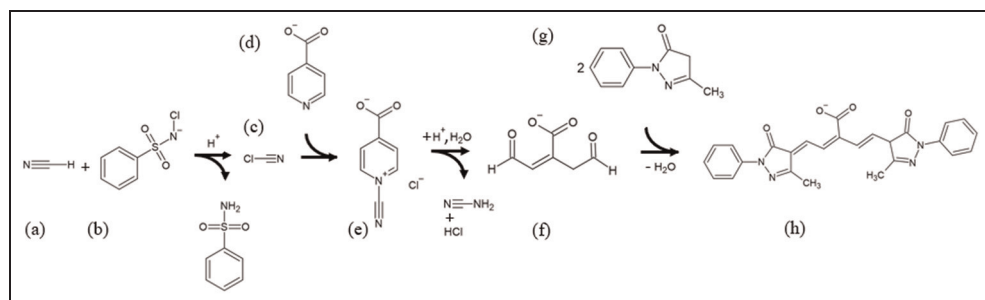
In common with CO, HCN is formed near the base of the flame during combustion of nitrogen-containing materials,^{11–13} but is then decomposed in a well-ventilated flame, partly to molecular nitrogen.¹⁴ However, it persists in under-ventilated flames or in the presence of gas phase inhibitors (such as halogenated or organophosphorus flame retardants).¹⁵ It has been detected following burning of fibres,¹⁶ polymers,^{17,18} building insulation foams¹⁹ and flexible polyurethane foams.^{20,21} Due to its high toxicity, and the prevalence of large amounts of nitrogen-containing materials in modern enclosed environments, it is necessary to quantify HCN released from fires robustly, to ensure life safety.

During fire tests, HCN can be collected by bubbling fire effluent through an aqueous sodium hydroxide (NaOH) solution (0.1 mol L^{-1}) trapping HCN as cyanide (CN^-) ions.²²

Methods for the determination of cyanide ions in solution have generally been designed for use in the analysis of soil, water, food, and biological fluids.^{23–26} Fire effluent analysis is somewhat different, in that higher HCN concentrations are often encountered, and they occur in a complex mixture of water, organic vapours, and soot particles.

ISO 19701²⁷ includes the description of methods for quantification of HCN: high performance ion chromatography (HPIC), and two methods that utilise colourimetry (chloramine-T/pyrazolone, and picric acid-based analysis). HPIC normally requires a specialised instrument dedicated to HCN analysis with a special column and amperometric detector. The columns are sensitive to particulates in fire effluent solutions, so extra care in sample preparation is needed to avoid blocking the active sites on the column;²⁸ filtration is essential. Picric acid has a similar structure to trinitrotoluene (TNT). When dry, picric acid is liable to explode spontaneously, so ensuring safe storage presents problems. ISO 19702²⁹ describes the use of Fourier transform infrared spectroscopy (FTIR) for gas phase quantification of HCN. Though FTIR is a powerful gas analysis technique, data from complex gas mixtures contain overlapping peaks and require detailed interpretation with the risk of increased variability in quantification. In particular, water overlaps one of the main absorption bands and is difficult to subtract quantitatively from the spectrum. Recently, a robust and versatile portable tunable diode laser-based measurement system for measuring high concentrations of HCN in a time-resolved manner, from two locations simultaneously, has been reported for application in the fire environment.³⁰ However, this is currently at the stage of a completed PhD project. This leaves colorimetric quantification with chloramine-T/pyrazolone as an attractive method.

The use of pyridine and pyrazolone reagents for the quantification of cyanide has been reported in literature without a detailed explanation of the chemistry.^{31–33} A definitive summary of the sequence of the chloramine-T/isonicotinic acid/pyrazolone colour development reaction is outlined in Scheme 1, based on literature reports.^{34,35} The sequence starts with



Scheme 1. (a) Hydrogen cyanide. (b) Chloramine-T. (c) Cyanogen chloride. (d) Isonicotinic acid. (e) 4-carboxy-1-cyano-pyridinium chloride. (f) Glutacondialdehyde. (g) 1-phenyl-3-methyl-5-pyrazolone. (h) Polymethine dye product (blue). Reaction buffered to pH = 7.2.

cyanide (a), collected in the bubbler, being oxidised by chloramine-T (b). The resulting cyanogen chloride (c) reacts with isonicotinic acid (d) to form 4-carboxy-1-cyano-pyridinium chloride (e) which undergoes a Zincke reaction.^{36,37} The resulting glutacondialdehyde (f) condenses with two molar equivalents 1-phenyl-3-methyl-5-pyrazolone (g) to form a blue polymethine dye (h) that can be quantitatively analysed at $\lambda = 638$ nm.^{32,38} The key benefits of the method are the selectivity (few other compounds produce such a blue colour) and the sensitivity (concentrations as low as 1 ppm are readily quantified).

ISO 19701 provides a brief outline of the method, specifying various procedures which must be followed, including the lifetime of standard solutions, the time interval between sampling and analysis, and the stability of the blue dye produced. These requirements have been investigated experimentally in this work.

This study presents an optimised method for analysis of fire gas samples, collected using 0.1 M NaOH as an absorbing solution and subsequent spectrophotometric quantification of cyanide. Even though colorimetric quantification of cyanide with chloramine-T/pyrazolone is considered a promising method due to its simplicity, low toxicity, and availability of visible region spectrophotometers in many analytical laboratories, no systematic investigation on method repeatability and robustness has been reported.

An investigation of potential interferences on the cyanide quantification (from carbonate, sulphite, sulphate, nitrite, nitrate) is also presented. This includes demonstration of the specificity of the chloramine-T/pyrazolone reaction to cyanide. The work further reports storage stability and repeatability data and investigates the time/temperature dependence of the blue dye formation reaction to provide the correct analytical window for robust quantification of HCN in fire effluent.

Material and methods

Sample preparation

Cyanide standard solutions. A 500 mg L⁻¹ stock cyanide solution as CN⁻ was prepared (0.3225 g KCN, Sigma Aldrich 97%, made up to 250 mL with 0.1 M NaOH). Five standard cyanide solutions were prepared: 0.3 mg L⁻¹, 0.8 mg L⁻¹, 2.0 mg L⁻¹, 5.0 mg L⁻¹ and 8.0 mg L⁻¹ by dilution of an intermediate cyanide solution of 20 mg L⁻¹ (10 mL of

stock cyanide solution made up to 250 mL with 0.1 mol L⁻¹ NaOH). All samples were stored in a refrigerator at 5°C until further testing.

Cross-sensitivity solutions. All cross-sensitivity solutions contained 2.0 mg L⁻¹ cyanide and one of five potentially interfering ions. To simulate fire gases containing CO₂, SO₂, SO₃, NO, and NO₂, respectively, sodium salts of CO₃²⁻, SO₃²⁻, SO₄²⁻, NO₂⁻ and NO₃⁻ (Sigma Aldrich, analytical grades) were added to obtain ion concentrations of 1.0 and 10 mg L⁻¹ as the ion in solution. A total of 20 cross-sensitivity solutions were prepared as two sets of the 1 and 10 mg L⁻¹ solutions. All cross-sensitivity solutions were tested immediately (day 0): half of the solutions were stored at 5°C; the other half of the solutions were stored at 21°C. The solutions were analysed again after 1 day and after 7 days.

Fire effluent solution. HCN was generated by burning pellets of polyamide 6.6 in the steady state tube furnace (ISO/TS 19700)³⁹ under controlled conditions, representing under-ventilated flaming at 650°C. These conditions have been reported to produce HCN and other products of incomplete combustion in high yield.¹⁵ A proportion of diluted fire effluent was bubbled through a train of 250 mL Drechsel bottles (with perforated glass bulb to maximise absorption, but avoid blockage by soot), containing 150 mL of 0.1 mol L⁻¹ NaOH at an effluent sampling volume rate of 1 L min⁻¹ (flow verified using a PFM71-F01F flow sensor, SMC, Japan) for 3–5 min, and the total volume of sampled effluent was recorded. After immediate testing, approximately 4 h after sampling, aliquots of the bubbler solution were transferred into two airtight polypropylene bottles and stored at 5°C and 21°C, respectively, and kept for further testing after 31 days.

Reagent preparation

The following reagents were prepared: **Reagent A** (0.1 g chloramine-T in 100 mL distilled water); **Reagent B** (0.75 g 1-phenyl-3-methyl-5-pyrazolone dissolved in 50 mL dimethylformamide (DMF) mixed with buffered isonicotinic acid solution (3.75 g isonicotinic acid in 50 mL 1 mol L⁻¹ NaOH adjusted to pH = 7.0 by 1 mol L⁻¹ hydrochloric acid (HCl)) and made up to 250 mL with distilled water); phosphate buffer, 19.8 g sodium hydrogen phosphate (Na₂HPO₄) to 300 mL distilled water, adjusted to pH = 7.2 with potassium dihydrogen phosphate (KH₂PO₄ 200 g L⁻¹), and made up to 500 mL with distilled water). **Reagents A and B** were prepared freshly on each test day.

Colorimetric quantification of HCN with ultraviolet-visible spectroscopy

To a test tube, the following were added sequentially: 1.00 mL of cyanide test sample (cyanide standard solution or bubbler solution), 9.00 mL distilled water, 4.50 mL phosphate buffer, 2.00 mL **reagent A**. After 5 min, 4.50 mL **reagent B** was added. After a further 30 min, the absorbance of the solution was simultaneously measured in both 10 and 40 mm cuvettes (QS, Hellma, DE) with two equivalent UV-visible wavelength spectrophotometers (WPA lightwave II, Biochrom Ltd, UK) at $\lambda = 638$ nm. 0.1 mol L⁻¹ NaOH was employed as a blank, and standards were included in all analyses. Subsequently, the gas phase HCN concentration of fire atmosphere can be calculated in g L⁻¹ of effluent according to §5.4.1.9 of ISO 19701.

Absorbance ($\lambda = 638 \text{ nm}$), in 10 and 40 mm cuvettes of five standard cyanide solutions (0.3, 0.8, 2.0, 5.0 and 8.0 mg L^{-1}), was determined regularly during the storage period of 1 year. Within the first 10 min of all tests, the colour was observed to shift from red, to purple, to blue. Absorbance versus time for an 8.0 mg L^{-1} cyanide standard was collected on five separate occasions at two wavelengths corresponding to the red and blue colours (543 and 638 nm, using 10 mm cuvette) for 90 min in total. Temperature dependence was tested by reacting an 8.0 mg L^{-1} cyanide standard with reagents, water, and buffer (taken from water baths at 18°C , 21°C and 35°C). The absorbance was followed at 543 and 638 nm for 90 min.

Results

Repeatability

Table 1 lists average absorbance, absolute, and relative (%) standard deviations (SD) from repeatability tests in two different cuvettes (10 and 40 mm) on the same UV-visible spectrophotometers for the five stored standard cyanide solutions, determined over a period of 1 year. The data show that there was no increase in standard deviation over this period. They also show low relative SD ($<5\%$) for all standard cyanide solutions, except 0.3 mg L^{-1} measured in a 10 mm cuvette (9%). However, changing to a 40 mm cuvette reduces the relative SD below 4%.

Figure 1 shows the resulting colour for cyanide standards of different $[\text{CN}^-]$ concentrations (28 min after addition of **reagent B**).

Figure 2 shows the linearity of the absorbance of the polymethine dye product as a function of cyanide concentration over the range $0.3\text{--}8 \text{ mg L}^{-1}$, using the repeatability data presented in Table 1.

Time/temperature dependence of colorimetric reaction

Figure 3 depicts the fraction of maximum absorbance as function of time for three reaction temperatures (18°C , 21°C (5 repeats) and 35°C) of a 8.0 mg L^{-1} standard cyanide solution measured at two wavelengths (543 and 638 nm) expressed as a fraction of maximum value.

Table 1. Repeatability test over 12 months (reaction temperature 21°C)

$[\text{CN}^-] / \text{mg L}^{-1}$	Absorbance \pm SD (%)	
	40 mm cuvette	10 mm cuvette
0.3	0.219 ± 0.008 (4%)	0.055 ± 0.005 (9%)
0.8	0.545 ± 0.013 (2%)	0.143 ± 0.006 (4%)
2.0	1.168 ± 0.015 (1%)	0.355 ± 0.007 (2%)
5.0	NA ^a	0.806 ± 0.024 (3%)
8.0	NA ^a	1.207 ± 0.060 (5%)

CN: cyanide; SD: standard deviation; NA: not applicable.

Absorbance (A) of the standard cyanide solutions for 40 and 10 mm cuvettes with standard deviation (SD).

^aThe 40 mm cuvette does not give linear absorbance above 2.0 mg L^{-1} $[\text{CN}^-]$ but provides greater sensitivity at $[\text{CN}^-] < 2.0 \text{ mg L}^{-1}$.

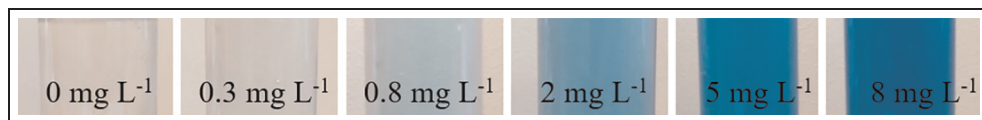


Figure 1. Photographs of test tubes showing the colour appearance developed 28 min (reaction temperature 21°C) after addition of **reagent B** for blank ($0.1 \text{ mol L}^{-1} \text{ NaOH}$), and standard cyanide solutions.

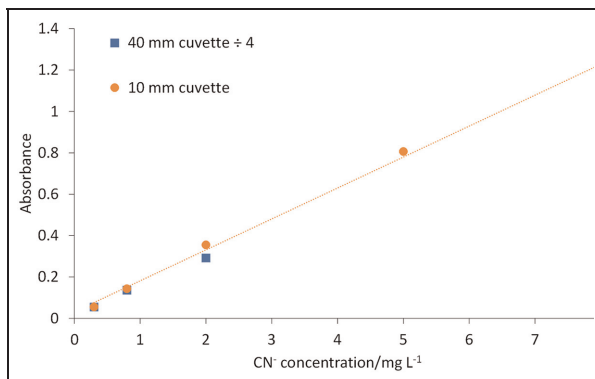


Figure 2. Variation of absorbance with CN^- concentration.

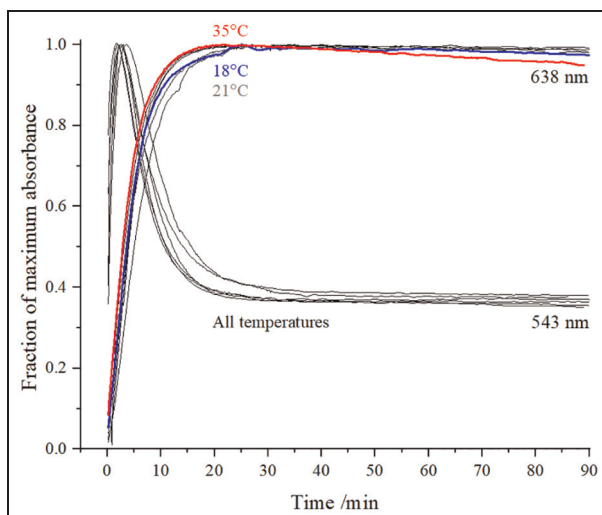


Figure 3. Temperature dependence of colorimetric reaction plotted as absorbance at 543 and 638 nm versus time after addition of **reagent B** (18°C, 21°C and 35°C), as a function of maximum absorbance. Line colours for 638 nm curves show reagent storage temperature.

Table 2. Storage stability of fire effluent solution (measured in 10 mm cuvettes)

Sample	Absorbance		Rel. diff./ %
	Day 0	Day 31	
5°C	0.418 ± 0.005	0.410 ± 0.001	-1.91
21°C	0.424 ± 0.008	0.409 ± 0.001	-3.42

Regardless of the reagent temperature, Figure 3 shows that the initial red colour, developed after addition of **reagent B** (measured at 543 nm), reaches a maximum absorbance after less than 5 min, and then the absorbances decrease to a constant level, 40% of maximum absorbance, after approximately 20 min. The absolute value of maximum absorbance for 543 nm is around 0.65. At the same time, a rapid increase in absorbance measured at 638 nm is seen (blue curves) with maximum absorbance after 20 min (absolute value around 1.20). However, a slight drop in fraction of maximum absorbance (-5% at 90 min) is observed for one blue curve after 50 min; this curve corresponds to reagent temperature 35°C.

Storage stability of fire effluent solution

Table 2 shows absorbance measurements 30 min after addition of **reagent B** measured on fire effluent solutions. The day 0 samples were analysed approximately 4 h after collection and the day 31 samples were stored for 31 days (5°C and 21°C) before analysis. Table 2 shows that absorbance data acquired on the same day coincide (within the experimental variability). After 31 days of storage, both refrigerated (5°C) and room temperature (21°C) samples showed a decrease in absorbance, corresponding to less than a 3.5% relative decrease.

Cross-sensitivity

Figure 4 summarises the effects of analysing a 2.0 mg L⁻¹ cyanide solution when CO₃²⁻, SO₃²⁻, SO₄²⁻, NO₂⁻, or NO₃⁻ were added at concentrations of 1 mg L⁻¹ or 10 mg L⁻¹ (Figure 4(a) and (b), respectively) to assess potential cross-sensitivity of the analysis. In each case, the analyses were undertaken on day 0, day 1, and day 7. At concentrations of 1 mg L⁻¹, Figure 4(a) shows that carbonate and sulphate have negligible effect on the quantification of cyanide (2.0 mg L⁻¹). At 1 mg L⁻¹, sulphite reduced the apparent concentration of cyanide by approximately 0.25 mg L⁻¹ (9.5%–12.5%), and both nitrite and nitrate reduced the apparent concentration of cyanide by approximately 0.20 mg L⁻¹ (7%–8%). Increasing the interfering ion concentrations to 10 mg L⁻¹, Figure 4(b), shows that carbonate does not significantly affect the quantification of cyanide, whereas sulphate is observed to interfere with cyanide quantification (about -0.25 mg L⁻¹, 7.5%–13%). Surprisingly, sulphite displays the largest reduction in the apparent concentration of cyanide on the day of measurement (about -0.50 mg L⁻¹, 26%–28%), which came closer to the actual concentration after 24 h (about -0.25 mg L⁻¹, 13%). On no occasion did the addition of these ions result in an increase in the measured cyanide concentration.

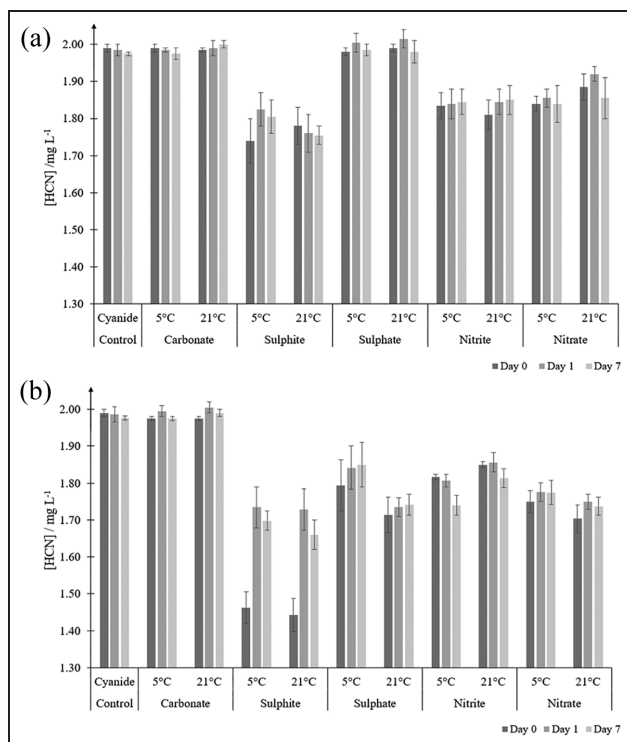


Figure 4. Cross-sensitivity tests on a 2.0 mg L^{-1} cyanide concentration. Potentially interfering ion concentrations of 1 mg L^{-1} (a) and 10 mg L^{-1} (b) after 0, 1 and 7 days for samples stored at 5°C and 21°C , respectively. Note that the Y axis has been expanded to emphasise the small difference in the results.

Discussion

Analytical window for the colour development reaction

The progress of the colorimetric cyanide detection reaction was monitored as a function of time at different reagent temperatures. The ISO 19701 standard specifies a 10 min window (from 25 to 35 min), for taking absorbent measurements. The data in Figure 3 indicate that over the range of ambient temperatures, a stable blue colour is formed within 20 min and remains stable until at least 90 min after addition of **reagent B** at both 18°C and 21°C and with slight drop in absorbance after 90 min for 35°C (-5%). This suggests that the narrow requirements for compliance with ISO 19701 do not correspond with the wider window of stability found in practice. Previous reports, mainly on barbiturate/isonicotinic acid combinations, report similar polymethine dye stability regimes.^{25,33,35} Interestingly, Figure 3 also reveals new insights on the kinetics of the colour forming reaction; it takes around 20 min for a possible rearrangement of the conjugated double bond system of the polymethine dye (Scheme 1, compound (h)) from the red to the blue colour. The colours arise as the dye exists as both ketone and enol tautomers ('keto-enol tautomerism'). Such a rearrangement between tautomeric forms has previously been reported, but not monitored as a function of time, such as the zolon red/zolon blue system.^{38,40}

Within the chosen analytical window, Table 1 summarises the repeatability of quantifying standard cyanide solutions. For cyanide concentrations above 2 mg L^{-1} , uncertainty is around 3% if a 10 mm cuvette is used. For concentrations less than 2 mg L^{-1} , a 40 mm cuvette will result in similar uncertainty (below 4%). Hence, below 2 mg L^{-1} , a 40 mm cuvette is preferable, but in practice both cuvettes are used during data collection. Furthermore, it has been shown in 'Repeatability' section that standard cyanide solutions are stable after storage in a refrigerator over a period of 1 year. This is in contrast to the requirements to prepare fresh standards daily in ISO 19701²⁷ and elsewhere.⁴¹ From the results in Figures 2 and 3 and Table 1, the colour development in Figure 1 appears to be a reliable indicator of cyanide concentration. Consequently, the 70 min analytical window allows for batch analysis of samples.

HCN sampling conditions

Collecting HCN from samples of fire atmosphere by trapping in an absorbing solution is a critical part of its quantification and must suit the fire experiment and material under test. By bubbling fire atmospheres through an alkaline solution, HCN, a weak acid ($\text{pK}_a = 9.31$),⁴² is trapped in its anionic form.²² ISO 19701 states that the effluent shall be drawn through a fritted bubbler tube containing 20 mL 0.01 mol L^{-1} NaOH solution at a flow rate of 0.4 L min^{-1} for 4–5 min.²⁷ While these conditions will trap HCN, the small volume of low concentration NaOH may be neutralised by the much greater volume of CO_2 or other acidic gases present in the effluent. For the optimised method described here, the effluent is bubbled into a Drechsel bottle containing 150 mL of 0.1 mol L^{-1} NaOH at 1 L min^{-1} over 3–5 min. Furthermore, the bubbler tube head is perforated to reduce the bubble size but avoids the potential blocking by soot particles of a fritted (sintered glass) head. The rationale for using the more concentrated alkaline solution is best explained using an example. Under the conditions described above, using 20 mL of 0.01 mol L^{-1} of NaOH, the absorbing solution contains 0.0002 mol OH^- . Sampling effluent containing 100 ppm HCN for 5 min at 0.4 L min^{-1} results in 2 L of effluent being sampled into solution, thus containing 0.0002 L HCN in total. Since 1 mol occupies 24 L, the sampled solution contains $8.33 \times 10^{-6} \text{ mol HCN}$ and therefore uses 0.02% of the available NaOH. However, if the sampled 5 L fire effluent also contained 5% CO_2 , this results in 0.25 L CO_2 , or approximately 0.01 mol, which would neutralise all the OH^- ions in the bubbler. (In aqueous solution, CO_2 exists in equilibrium with carbonic acid (H_2CO_3) for which $\text{pK}_{a1} = 6.37$ and $\text{pK}_{a2} = 10.32$. As the first pK_a is significantly lower than that of HCN, dissociation of carbonic acid would reprotonate the HCN, allowing trapped CN^- to escape from the bubbler solution, or neutralise the alkalinity so the slightly soluble HCN gas was not trapped.) Therefore, using 0.1 mol L^{-1} NaOH ensures sufficient alkalinity for trapping HCN gas and allows greater effluent volumes to be collected, minimising dead volumes in tubes and so on. Hence, to ensure that HCN is not lost, a higher NaOH concentration should be used. ISO 19701 specifies that a second bubbler should be placed in series to ensure that any carry-over can be quantified.

Another potential advantage of using the 0.1 mol L^{-1} NaOH bubbler solution is that its greater alkalinity will stabilise the CN^- in solution, helping to increase the stability of the solution and increase safe sample storage times. The difference in storage stability between the ISO 19701 specified 0.01 mol L^{-1} NaOH and 0.1 mol L^{-1} NaOH was not investigated directly in the current work.

Fire effluent storage stability

Once HCN has been captured, ISO 19701 stipulates that quantification should be carried out on the same day, as the fire effluent solution is unstable over time. Table 2 shows minor (less than 2%) absorbance reductions for more alkaline 0.1 mol L^{-1} NaOH fire effluent bubbler solutions tested immediately and stored for 31 days at both 5°C or 21°C . The absorbance reduction (less than 3.5%) is considered negligible when converted to HCN concentration in fire atmosphere. For example, at a concentration of 190 ppm of HCN, the fire atmosphere is predicted to lead to incapacitation of 50% of the exposed population within 5 min, according to ISO 13571.⁴³ In addition, Figure 4 shows that the measured apparent concentration of cyanide is independent of storage temperatures (5°C , 21°C) and storage over 0–7 days. Hence, fire effluent solutions collected in 0.1 mol L^{-1} NaOH are considered stable, even when not cooled, reducing concerns of sample losses, for example, when transporting samples from external testing locations or when samples cannot be immediately refrigerated prior to analysis.

Interferences from other fire gas ions

A review of literature showed that different interferences can change the apparent HCN concentration. Cyanide could be partially oxidised to cyanate in the presence of oxidants such as SO_2 , O_2 , NO , or NO_2 in alkaline solution.^{42,44} The resultant cyanate may slowly decompose to form carbonate ions (negative interference).⁴⁵ However, Table 2 shows that fire effluent solutions have high storage stability, so cyanate formation appears negligibly small and does not affect cyanide quantification, as reported elsewhere.³²

Reports in the literature show that cyanide reacts with polysulphide S_xS^{2-} (with formation of thiocyanate, SCN^-), elemental sulphur S_8 (second order ring opening reaction resulting in formation of thiocyanate) and thiosulphate $\text{S}_2\text{O}_3^{2-}$ (with formation of sulphite (SO_3^{2-}) and thiocyanate).^{42,46,47} The resulting thiocyanate gives a positive interference as the slow reaction with chloramine-T forms cyanogen chloride and subsequently produces blue dye.^{22,32,33} Sulphide is mentioned in ISO 19701 as a small negative interference. In this work, a negative interference was also observed for sulphite. A possible explanation is that even though sulphide, on reaction with cyanide, forms thiocyanate (positive interference), sulphide is also reported to promote the hydrolysis reaction of cyanogen chloride.⁴⁸ However, in fire atmospheres these sulphur compounds (i.e. S_xS^{2-} , S_8 , $\text{S}_2\text{O}_3^{2-}$, SCN^-) are rarely found even when burning sulphur-containing materials, as the released SO_2 and SO_3 gases dissolve in alkaline aqueous solution to form sulphite (SO_3^{2-}) and sulphate (SO_4^{2-}) ions.⁴⁹

Early interference studies from Epstein showed no interferences from carbonates, borates, chlorides, ammonium/sodium salts, cyanate, oxalate, ferri/ferrocyanides and sulphates. Furthermore, it was reported that reducing agents (i.e. nitrite and sulphite in this work) are likely to be oxidised by the excess of chloramine-T.³² Cyanide analysis of cigarette smoke has been reported to show no interference from other gases present.⁵⁰

However, in this work cross-sensitivity mainly arises from the presence of sulphite (1 mg L^{-1} , Figure 4(a)). At 10 mg L^{-1} , the losses increase to 26%–28% when tested immediately but decreased to 13% after 24 h (Figure 4(b)). Even though sulphite ions are reported to react with cyanogen chloride,^{51,52} no satisfactory explanation for this observation has been found. Materials that may be of concern due to their sulphur content could include rubbers, coal, and phenolic foams/resins.

Interference from CO_2 in fire gas could acidify the absorbing solution sufficiently to prevent trapping of HCN. The combination of optimised sampling conditions and the data in Figure 4 indicate that, apart from the effect on trapping by the absorbing solution, carbonate (and bicarbonate) has negligible effect on the analysis.

Well-ventilated fire conditions, where high concentrations of NO_x are formed, generally produce low HCN concentrations.^{53,54} Figure 4 shows losses in cyanide quantification range from about 7% at 1 mg L^{-1} to about 13% at 10 mg L^{-1} , possibly due to oxidation of cyanide.⁵⁵ Hence, interferences from NO_x products could result in 7%–13% underestimation of HCN in the least toxic, well-ventilated fire condition, but in situations where HCN levels are at their highest (during under-ventilated flaming), the NO_x is unlikely to be present in high concentrations.

ISO 19701 states that small negative interferences arise from nitriles, oxides of nitrogen, and sulphide. This work suggests that interferences from S_xS^{2-} , S_8 , $\text{S}_2\text{O}_3^{2-}$, and SCN^- which have been reported to overestimate cyanide concentration (as described in the introductory literature section), actually showed experimental underestimation of cyanide. A relative reduction of 7%–13% was observed from SO_3^{2-} , NO_2^- , and NO_3^- present at 1 mg L^{-1} and SO_4^{2-} at 10 mg L^{-1} , but negligible effect of CO_3^{2-} even if present at 10 mg L^{-1} in the fire effluent solution.

Conclusions

An optimised colorimetric quantification method for HCN in fire effluent, based on chloramine-T/isonicotinic acid, has been demonstrated to be a robust analytical method. In contrast to the outline description and rigid requirements specified in ISO 19701, the optimised method is more effective at trapping HCN, and more flexibility is permitted in the analysis, without affecting the results. It is possible that the higher alkalinity of the bubbler solution also improves the stability of the cyanide solutions. It has been shown that fire effluent solutions can be stored for up to 31 days at 21°C before analysis. Time/temperature dependence of the colour reaction was shown to give constant absorbance from 20 to 90 min after addition of reagents in the temperature range 18°C – 35°C which allows for efficient testing of multiple samples in a sequence. The repeatability is within 4% if absorbance is measured on a UV-visible spectrophotometer with appropriate cuvette (10 or 40 mm, the latter preferred for quantifying 2 mg L^{-1} cyanide or less).

Small interferences (around -12%) from commonly expected, dissolved fire gases were found, always reducing the apparent cyanide concentration. Cross sensitivity was investigated by adding 10 mg L^{-1} of CO_3^{2-} , SO_3^{2-} , SO_4^{2-} , NO_2^- , and NO_3^- ions to 2 mg L^{-1} cyanide solutions, storing at 21°C for a week and analysing.

The work demonstrates the enhanced stability and repeatability of the analysis. An optimised method for quantification of HCN in fire effluent has been reported. The method is robust for fire effluent sample transport and storage, and offers quick, repeatable batch analysis in an analytical laboratory.

Acknowledgment

The authors would like to thank Katarina Handlovicova for help in the laboratory, and Dr. Malthe Hansen-Bruhn for discussions on reaction schemes.

Author contributions

Iben Hansen-Bruhn: Formal analysis, Investigation, Methodology, Validation, Visualisation, Writing–Review & Editing. Sean T McKenna: Conceptualisation, Formal analysis, Investigation, Methodology, Writing–Original Draft. T Richard Hull: Conceptualisation, Funding, Resources, Project administration, Supervision, Writing–Review & Editing.

Declaration of conflicting interests

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

Funding

The author(s) disclosed receipt of the following financial support for the research, authorship, and/or publication of this article: This work is partly funded by Innovation Fund Denmark under File No 9065-00233B.

ORCID iD

T Richard Hull  <https://orcid.org/0000-0002-7970-4208>

References

- ISO. Estimation of lethal toxic potency from fire effluents (ISO 13344:2015). Geneva: ISO.
- Stefanidou M, Athanaselis S and Spiliopoulou C. Health impacts of fire smoke inhalation. *Inhal Toxicol* 2008; 20(8): 761–766.
- Anseeuw K, Delvau N, Burillo-Putze G, et al. Cyanide poisoning by fire smoke inhalation: a European expert consensus. *Eur J Emerg Med* 2013; 20(1): 2–9.
- Public Health England. Hydrogen cyanide – general Information. *PHE Publications Gateway Number 2014790*, 2016, https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment_data/file/500821/Hydrogen_Cyanide_PHE_TO_120216.pdf
- Pierik AJ, Roseboom W, Happe RP, et al. Carbon monoxide and cyanide as intrinsic ligands to iron in the active site of [NiFe]-hydrogenases: NiFe(CN)₂CO, biology's way to activate H₂. *J Biol Chem* 1999; 274(6): 3331–3337.
- Cooper CE and Brown GC. The inhibition of mitochondrial cytochrome oxidase by the gases carbon monoxide, nitric oxide, hydrogen cyanide and hydrogen sulfide: chemical mechanism and physiological significance. *J Bioenerg Biomembr* 2008; 40(5): 533–539.
- Navarro KM, Clark KA, Hardt DJ, et al. Wildland firefighter exposure to smoke and COVID-19: a new risk on the fire line. *Sci Total Environ* 2021; 760: 144296.
- Hartzell GE, Priest DN and Switzer WG. Modelling of toxicological effects of fire gases: II. Mathematical modelling of intoxication of rats by carbon monoxide and hydrogen cyanide. *J Fire Sci* 1985; 3(2): 115–128.
- Purser DA. Chapter 3, asphyxiant components of fire effluents. In: Stec AA and Hull TR (eds) *Fire toxicity*. Amsterdam: Woodhead Publishing Limited/Elsevier, 2010, pp. 118–198.
- Subcommittee on Acute Exposure Guideline Levels. *Acute exposure guideline levels for selected airborne chemicals volume 2 appendix 5 hydrogen cyanide*. Washington, DC: The National Academies Press, <https://www.epa.gov/aegl/hydrogen-cyanide-results-aegl-program>
- Simonson M, Tuovinen H and Emanuelsson V. Formation of hydrogen cyanide in fires. A literature and experimental investigation. *Brandforsk project 510-991.2000*, <https://www.diva-portal.org/smash/get/diva2:962156/FULLTEXT02>
- Purser DA and Purser JA. HCN yields and fate of fuel nitrogen for materials under different combustion conditions in the ISO 19700 tube furnace and large-scale fires. *Fire Saf Sci* 2008; 9: 1117–1128.
- Tuovinen H, Blomqvist P and Saric F. Modelling of hydrogen cyanide formation in room fires. *Fire Saf J* 2004; 39(8): 737–755.
- Sun Z, Försth M, Li Z, et al. In situ measurements of HCN in a tube furnace with infrared polarization spectroscopy. *Fire Saf Sci* 2011; 10: 279–291.
- Glarborg P, Jensen AD and Johnsson JE. Fuel nitrogen conversion in solid fuel fired systems. *Prog Energy Combust Sci* 2003; 29(2): 89–113.
- Bertol E, Mari F, Orzalesi G, et al. Combustion products from various kinds of fibers: toxicological hazards from smoke exposure. *Forensic Sci Int* 1983; 22(2–3): 111–116.
- Bott BJG, Firth JG and Jones TA. Evolution of toxic gases from heated plastics. *Br Polym J* 1969; 1(5): 203–204.
- Stec AA, Hull TR, Lebek K, et al. The effect of temperature and ventilation condition on the toxic product yields from burning polymers. *Fire Mater* 2008; 32(1): 49–60.
- Stec AA and Hull TR. Assessment of the fire toxicity of building insulation materials. *Energy Build* 2011; 43(2–3): 498–506.
- Jellinek HHG and Takada K. Toxic gas evolution from polymers: evolution of hydrogen cyanide from polyurethanes. *J Polym Sci* 1977; 15(9): 2269–2288.
- McKenna ST and Hull TR. The fire toxicity of polyurethane foams. *Fire Sci Rev* 2016; 5(1): 1–27.

22. Williams WJ. *Handbook of anion determination*. Amsterdam: Butterworth Heinemann Books, 1979, pp. 70–87.
23. Fisher FB and Brown JS. Colorimetric determination of cyanide in stack gas and waste water. *Anal Chem* 1952; 24(9): 1440–1444.
24. Ma J and Dasgupta PK. Recent developments in cyanide detection: a review. *Anal Chim Acta* 2010; 673(2): 117–125.
25. Essers SA, Bosveld M, Van Grift RMD, et al. Studies on the quantification of specific cyanogens in cassava products and introduction of a new chromogen. *J Sci Food Agric* 1993; 63(3): 287–296.
26. Logue BA, Hinkens DM, Baskin SI, et al. The analysis of cyanide and its breakdown products in biological samples. *Crit Rev Anal Chem* 2010; 40(2): 122–147.
27. ISO. *Methods for sampling and analysis of fire effluents (ISO 19701:2013)*. Geneva: ISO.
28. Fardell P and Guillaume E. Chapter 11, sampling and measurement of toxic fire effluent. In: Stec A and Hull R (eds) *Fire toxicity*. Amsterdam: Woodhead Publishing Limited/Elsevier, 2010, pp. 385–423.
29. ISO. *Guidance for sampling and analysis of toxic gases and vapours in fire effluents using Fourier transformed infrared (FTIR) spectroscopy (ISO 19702:2015)*. Geneva: ISO.
30. Ghanekar S, Horn GP, Kesler RM, et al. Quantification of Elevated Hydrogen Cyanide (HCN) concentration typical in a residential fire environment using Mid-IR tunable diode laser applied spectroscopy. *Appl Spectrosc* 2023; 77(4): 382–392.
31. König W. Über eine neue, vom pyridin derivierende klasse von farbstoffen. *J Prakt Chem* 1904; 69(1): 105–137.
32. Epstein J. Estimation of microquantities of cyanide. *Anal Chem* 1947; 19(4): 272–274.
33. Nagashima S. Spectrophotometric determination of cyanide with sodium isonicotinate and sodium barbiturate. *Anal Chim Acta* 1978; 99(1): 197–201.
34. Eicher T, Hauptmann S and Speicher A. *The chemistry of heterocycles: structures, reactions, synthesis, and applications*. Hoboken, NJ: John Wiley & Sons, 2012, pp. 356–357, 378–379.
35. Lambert JL, Ramasamy J and Paukstelis JV. Stable reagents for the colorimetric determination of cyanide by modified Koenig reactions. *Anal Chem* 1975; 47(6): 916–918.
36. Cheng WC and Kurth MJ. The Zincke reaction. A review. *Org Prep Proced Int* 2002; 34(6): 585–608.
37. Zincke T, Heuser G and Möller W. Ueber dinitrophenylpyridiniumchlorid und dessen umwandlungsprodukte. *Justus Liebigs Ann Chem* 1904; 333(2–3): 296–345.
38. Qureshi AM and Patel AN. The nature of zolon red. *Z Naturforsch B* 1978; 33(4): 450–453.
39. ISO. *Controlled equivalence ratio method for the determination of hazardous components of fire effluents – steady-state tube furnace (ISO/TS. 19700:2016)*. Geneva: ISO.
40. Svatos G and Goldenson J. Zolon red and the zolon red-silver complex. *J Org Chem* 1956; 21(10): 1171–1173.
41. Labsert. Storage and usage of cyanide reference solution, <https://www.labsertchemical.com/Latest-News/Storage-Stability-Cyanide-Standard-Reference-Solution> (accessed 30 March 2023).
42. Housecroft CE and Sharpe AG. *Inorganic chemistry*. Vol. 1. London: Pearson Education, 2008, pp. 279–380.
43. ISO. *Life-threatening components of fire – guidelines for the estimation of time to compromised tenability in fires (ISO 13571:2012)*. Geneva: ISO.
44. Wilmot JC. The chemistry of cyanide in the presence of reduced sulfur sources. PhD thesis. The University of Nebraska-Lincoln, Lincoln, NE, 1997.
45. Lister MW. Some observations on cyanic acid and cyanates. *Can J Chem* 1955; 33(2): 426–440.
46. Bartlett PD and Davis RE. Reactions of elemental sulfur. II. The reaction of alkali cyanides with sulfur, and some single-sulfur transfer reactions. *J Am Chem Soc* 1958; 80(10): 2513–2516.
47. Luthy RG and Bruce SG. Kinetics of reaction of cyanide and reduced sulfur species in aqueous solution. *Environ Sci Technol* 1979; 13(12): 1481–1487.
48. Price CC, Larson TE, Beck KM, et al. Hydrolysis and chlorinolysis of cyanogen chloride. *J Am Chem Soc* 1947; 69(7): 1640–1644.
49. Fardell P and Guillaume E. Sampling and measurement of toxic fire effluent – chapter 11. In: Stec A and Hull R (eds) *Fire toxicity*, pp. 385–423. Amsterdam: Woodhead Publishing Limited/Elsevier, 2010.
50. Jiang Y, Lu N, Yu F, et al. Sampling and determination of hydrogen cyanide in cigarette smoke. *Fresenius J Anal Chem* 1999; 364(8): 786–787.
51. Bailey PL and Bishop E. Reaction of sulphite ions with cyanogen chloride. *J Chem Soc Dalton Trans* 1973; 9: 17–21.
52. Shang C, Qi Y, Xie L, et al. Kinetics of cyanogen chloride destruction by chemical reduction methods. *Water Res* 2005; 39(10): 2114–2124.
53. Purser DA, Stec AA and Hull TR. Chapter 2 – fire scenarios and combustion conditions. In: Stec A and Hull R (eds) *Fire Toxicity*. Amsterdam: Woodhead Publishing Limited/Elsevier, 2010, pp. 26–47.
54. Dagaut P, Glarborg P and Alzueta MU. The oxidation of hydrogen cyanide and related chemistry. *Prog Energy Combust Sci* 2008; 34(1): 1–46.
55. Liu X, Ma L, Zhou J, et al. The influence of nitrogen dioxide on the determination of hydrogen cyanide in mainstream and sidestream cigarette smoke and the improvement of the determination method by continuous flow analyzer. *Anal Methods* 2014; 6(24): 9841–9849.

Author biographies

Iben Hansen-Bruhn obtained her PhD in 2023 from Aarhus University, Denmark, in materials chemistry. She is an active researcher in fire chemistry with special focus on fire protection of timber, from mechanisms to flammability and smoke toxicity. Currently her research is focused on the complex chemistry of fire retardant coating systems.

Sean T McKenna completed an integrated master's in chemistry (MChem) in 2015 and a PhD in fire chemistry in 2019, both at the University of Central Lancashire. Since 2020, he has run his business, Mckenna Editing, offering academic and technical editing services to academics and businesses worldwide.

T Richard Hull is the Professor of Chemistry and Fire Science at the University of Central Lancashire. He has been actively researching fire retardants for the last 40 years. His current interests revolve around fire retardancy, fire toxicity and fire science.